ORGANIC CHEMISTRY

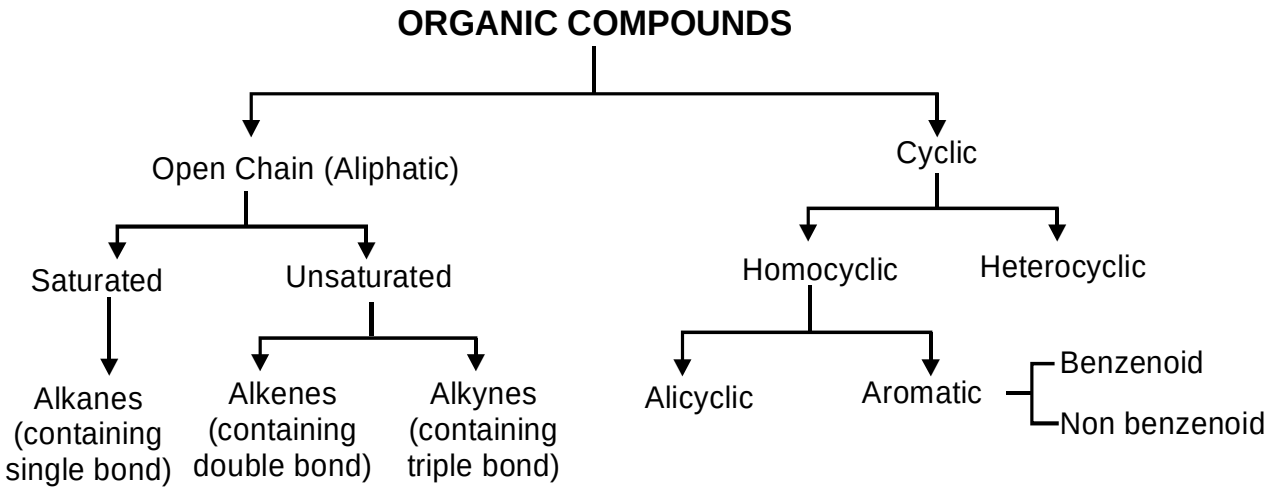
VOLUME – I

(ENGLISH)

CONTENTS

- *NOMENCLATURE* *2*
- *GOC* *39*
- *ISOMERISM* *75*
- *HYDROCARBON* *111*
- *ALKYL HALIDE* *175*

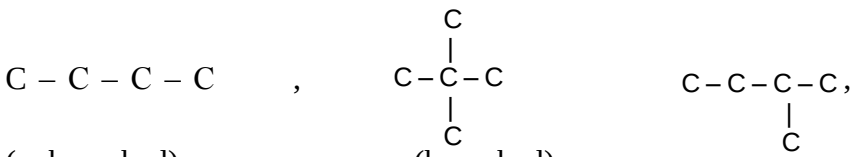
ORGANIC COMPOUNDS - INTRODUCTION AND CLASSIFICATION



ALIPHATIC OR OPEN CHAIN COMPOUNDS :–

Are those compounds in which first & last carbon atoms are not connected with each other. Branched or unbranched chains are possible in these compounds.

For example :-



(unbranched) (branched)

There are two varieties in these compounds -

(1) Saturated Hydrocarbons :–

(a) In such type, adjacent carbons are attached with single bonds.
example - $CH_3 – CH_2 – CH_3$

(b) General formula of these compounds is C_nH_{2n+2}.

(c) These are also called as paraffins (Parum + Affinis i.e. little reactivity) because these are less reactive due to absence of π – bonds.

(2) Unsaturated Hydrocarbons : –

(a) There will be a double bond or a triple bond between any two carbon atoms,
Exmaple: $CH_2 = CH – CH_3$ (Propene), $CH \equiv C – CH_3$ (Propyne)

(b) Gen. formula is C_nH_{2n} or C_nH_{2n-2} .

(c) Alkenes are also called as olefins because they reacts with halogens to form oily substances olefins (Oleum + fines i.e. Oil forming).

(d) Due to presence of π bonds these are more reactive.

CLOSED CHAIN COMPOUNDS :

In these compounds first & last carbons are attached with each other.

Example:- Cyclopropane

These are of two types

(1) Homocyclic compounds :

These are the compounds in which the complete ring is formed by carbon atoms only. These are also of two types

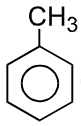
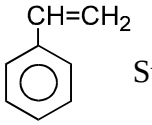
(a) Alicyclic compounds :

These are the compounds having the properties like aliphatic compounds. These may be saturated or unsaturated like aliphatic compounds.

Exmple:- Cyclopropane, Cyclopropene, Cyclobutene

(b) Aromatic compounds :

These compounds consist of at least one benzene ring i.e. a six-membered carbcyclic ring having alternate single and double bonds. These compounds have some fragrant odour and hence, named as aromatic (greek word aroma means sweet smell)

Example:  Benzene  Toluene  Styrene

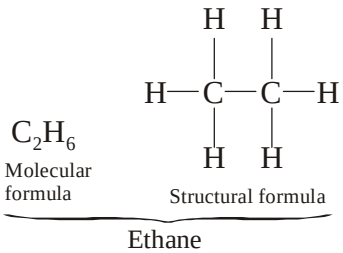
(2) Heterocyclic Compounds : –

These are cyclic compounds having ring or rings built up of more than one kind of atoms.

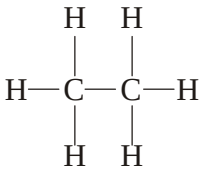
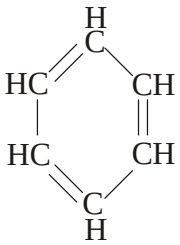
 Furan  Thiophene

WRITING OF ORGANIC COMPOUNDS STRUCTURE

(1) ***Structural formula:*** The structural formula is more informative as it shows the arrangement of various atoms in a molecule. A single covalent bond is shown as a line (–) joining the two atoms. Double line (=) represents a double bond while triple line (≡)a triple bond.



(2) ***Condensed formula:*** Condensed formula is a short hand method of representing the structural formula. In a condensed formula, all atoms bonded to a carbon atom are written after 'C' in the same line but their bonds are not shown. The atoms or groups other than hydrogen are written after the hydrogen atom. in a condensed structural formula double and triple bonds are shown by double line (=) and triple line (≡) respectively.

Compound	Molecular formula	Structural formula	Condensed formula
Ethane	(C_2H_6)		CH_3CH_3
Benzene	(C_6H_6)		

Classification of carbon and hydrogen of an organic compound

Carbon and hydrogen atoms of an organic compound may be classified in two ways:

* **First classification** : First classification depends on the mode of arrangement of carbon atoms in a chain. According to this classification we get four types of carbon atoms and three types of hydrogen atoms. These are:

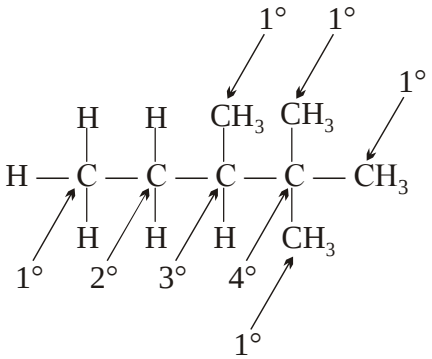
(i) Primary carbon or 1°C : A carbon atom attached to one (or no) other carbon atom then it called as primary carbon.

(ii) Secondary carbon or 2° C : If in a carbon chain a carbon is bonded to two other carbon atoms, then it is known as secondary carbon.

(iii) Tertiary carbon or 3°C : If in a carbon chain a carbon is bonded to three other carbon atoms, then it is known as tertiary carbon.

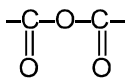
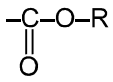
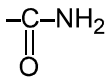
(iv) Quarternary carbon or 4°C : If in a carbon chain a carbon is bonded to four other carbon atoms, then it is known as quaternary carbon.

The hydrogen atoms present on primary, secondary and tertiary carbon atoms are said to be primary, secondary and tertiary hydrogen atoms respectively. Quarternary carbon has no hydrogen.



Functional Group :

A functional group is an atom or group of atoms present in a molecule that gives the molecule its characteristic chemical properties.

S. No.	Name	Functional group Formula
1.	Carboxylic acid	
2.	Suphonic acid	$-SO_3H$
3.	Anhydride	
4.	Ester	
5.	Acyl halide	
6.	Amide	
7.	Cyanide	$C \equiv N$
8.	Iso cyanide	$-N \overset{+}{=} C$
9.	Aldehyde	
10.	Ketone	
11.	Alcohol	– OH
12.	Thio alcohol	– SH
13.	Amine	$-NH_2$
14.	Ether	– O –
15.	Double bond	C = C
	Triple bond	$C \equiv C$
16.	Halo	– X
17.	Nitro	$-NO_2$

HOMOLOGOUS SERIES

A series of organic compounds, in which all the members can be represented by one general formula is termed as Homologous series and the members are termed as Homologues.

Characteristics of Homologous series:

1. All homologues can be represented by one general formula.
2. Two consecutive homologues differ by 1-CH_2 unit.
3. Two consecutive homologues differ by 14 amu.
4. All homologues can be prepared by some common methods.
5. They have different physical properties but almost similar chemical properties.

e.g., Alkanes formula (C_nH_{2n+2})

Methane CH_4

Ethane C_2H_6

Propane C_3H_8

$\updownarrow$ — CH_2 unit/14 amu

NOMENCLATURE

Mainly three systems are adopted for naming an organic compound –

(i) Common Names or Trivial System

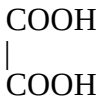
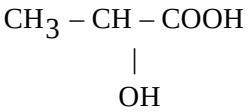
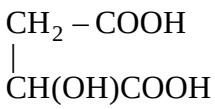
(ii) Derived System

(iii) IUPAC system or Jeneva System

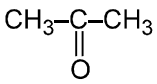
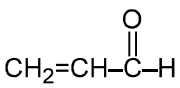
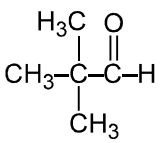
COMMON OR TRIVIAL SYSTEM

Initially organic compounds are named on the basis of source from which they were obtained. eg.

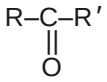
S. N.	Organic Compound	Trivial Name	Source
1.	CH_3OH	Wood spirit or Methyl spirit	Obtained by destructive distillation of wood.
2.	NH_2CONH_2	Urea	Obtained from urine
3.	CH_4	Marsh gas (fire damp)	It was produced in marsh places.
4.	CH_3COOH	Vinegar	Obtained from Acetum - i.e. Vinegar

5.		Oxalic acid	Obtained from oxalis plant.
6.	HCOOH	Formic acid	Obtained from formicus [Red ant]
7.		Lactic acid	
8.		Malic acid	
9	$CH_3CH_2CH_2COOH$	Butyric acid	Obtained from butter.
10.	$CH_3(CH_2)_4COOH$	Caproic acid	Obtained from goats.

Some typical compounds in which common & trivial names are also differ.

S.No	Compounds	Trivial Name	Common name
1.	CH_4	Marsh gas	Methane
2.	CH_3OH	Woodspirit	Methyl alcohol
3.	CH_3COOH	Vinegar	Acetic acid
4.		Acetone	Dimethyl ketone
5.		Acrolein	Acryl Aldehyde
6.		Pivaldehyde	Tertiary valer aldehyde

(Common – Names R is termed as alkyl **-)**

S.N.	Compound	Name
1.	R – X	Alkyl halide
2.	R – OH	Alkyl alcohol
3.	R – SH	Alkyl thio alcohol
4.	R – NH_2	Alkyl amine
5.	R–O–R	Dialkyl ether
6.	R–S–R	Dialkyl thioether
7.		Dialkyl ketone
8.	R–NH–R	Dialkyl amine
9.		Trialkyl amine
10.	R–O–R′	Alkyl alkyl′ ether
11.		Alkyl alkyl′ ketone
12.	R–S–R′	Alkyl alkyl′ thio ether
13.	R–NH–R′	Alkyl alkyl′ amine
14.		Alkyl alkyl′ alkyl″ amine

GROUP

Atom or a group of atoms which possess any 'free valency' are called as **Groups**.

If their are two structure of same molecular formula then some prefix (n, iso, neo) are used to differenciate them.

Normal group : –

(a) It is represented by 'n'.

(b) Groups having no branch (Straight chain).

(c) Free bond will come either on Ist carbon atom or on last carbon atom.

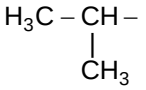
n – butyl $CH_3 - CH_2 - CH_2 - CH_2 -$

n – propyl $CH_3 - CH_2 - CH_2 -$

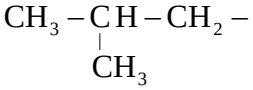
Iso group : –

When one methyl group is attached to the second last carbon of the straight carbon chain is named as iso group.

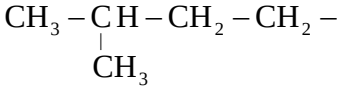
e.g.



Isopropyl

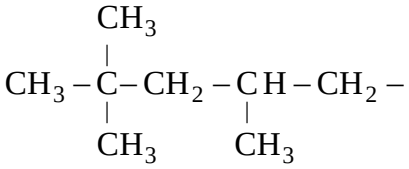


Isobutyl

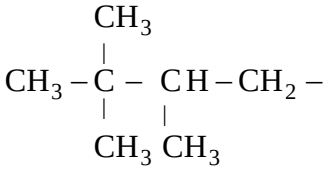


Isopentyl

Exception :



(i) Iso octyl

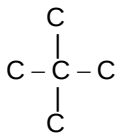


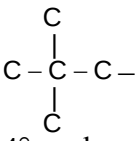
(ii) Iso heptyl

Neo group : –

(a) When two methyl groups are present on second last carbon of a straight carbon chain then group is named as neo group.

(b) It is represeted by following structure -

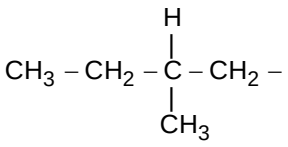


for eg.  Neo pentyl

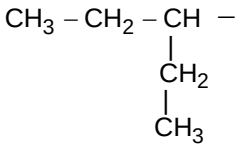
(c) There should be one 4° carbon and atleast three methyl group on 4° carbon.

NOTE : (Optically Active) = If all valency are attached to different atoms.

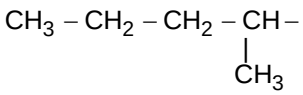
Amyl group : –



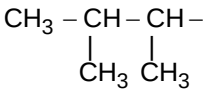
Active amyl



Secondary amyl



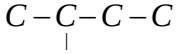
Active secondary amyl

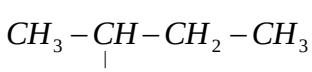
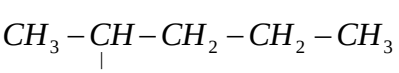


Active iso secondary amyl

Secondary group : –

(a) The carbon having free valency attached to two carbon is called secondary carbon.

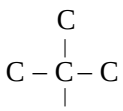
(b) It is represented by following structure. 

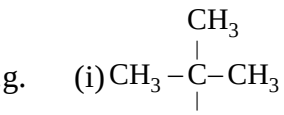
eg. (i)  (ii) 

(secondary butyl) (secondary pentyl)

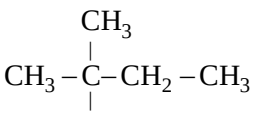
Tertiary group : –

(a) The carbon having free valency attached to three other carbon .

(b) It is represented by following structure - 

e.g. (i) 

(Tertiary butyl)



(Tertiary pentyl)

Alkyl group : –

When a hydrogen is removed from Alkane (saturated hydrocarbon) then alkyl group is formed.

A bond is vacant on alkyl group on which any functional group may come.

$$\textbf{alkane} \xrightarrow[-H]{} \textbf{Alkyl -}$$

$$(C_nH_{2n+2}) \qquad (C_nH_{2n+1})$$

e.g.

(i) $CH_4 \xrightarrow[-H]{} CH_3-$

Methane Methyl

(ii) $CH_3-CH_3 \xrightarrow[-H]{} CH_3-CH_2-$

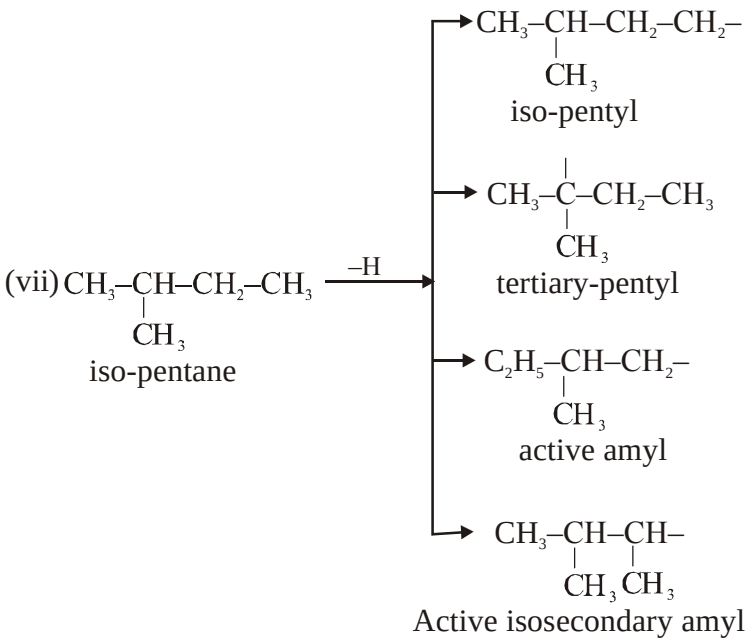
Ethane ethyl

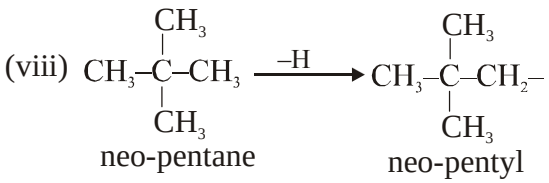
(iii) $CH_3-CH_2-CH_3$ (Propane) $\xrightarrow{-H}$ $CH_3-CH_2-CH_2-$ (n-Propyl), $CH_3-\underset{|}{CH}-CH_3$ (iso-Propyl)

(iv) $CH_3-CH_2-CH_2-CH_3$ (n-Butane) $\xrightarrow{-H}$ $CH_3-CH_2-CH_2-CH_2-$ (n-Butyl), $CH_3-\underset{|}{CH}-CH_2-CH_3$ (Sec. Butyl)

(v) $CH_3-\underset{|}{\underset{CH_3}{CH}}-CH_3$ (iso-butane) $\xrightarrow{-H}$ $CH_3-\underset{|}{\underset{CH_3}{CH}}-CH_2-$ (iso-butyl), $CH_3-\overset{|}{\underset{|}{\underset{CH_3}{C}}}-CH_3$ (tertiary-butyl)

(vi) $CH_3-CH-CH_2-CH_2-CH_3$ (n-pentane) $\xrightarrow{-H}$ $CH_3-CH_2-CH_2-CH_2-CH_2-$ (n-pentyl), $CH_3-\underset{|}{CH}-CH_2-CH_2-CH_3$ (active secondary amyl), $C_2H_5-\underset{|}{CH}-C_2H_5$ (secondary amyl)





Alkenyl group : –

alkene $\xrightarrow[-H]{}$ **Alkenyl -**

(C_nH_{2n}) **(C_nH_{2n-1})**

$CH_2 = CH –$ Vinyl

$CH_2 = CH – CH_2 –$ Allyl

$CH_3 – CH = CH –$ Propenyl(1-propenyl)

$CH_3 – C(=CH_2) –$

Isopropenyl (1-methyl ethenyl)

Alkynyl group –

alkyne $\xrightarrow[-H]{}$ **Alkynyl -**

(C_nH_{2n-2}) **(C_nH_{2n-3})**

$CH \equiv C –$ Ethynyl

$CH \equiv C – CH_2 –$ Propargyl (2-propynyl)

$CH_3 – C \equiv C –$ Propynyl (1-propynyl)

Alkylidene group –

$$\textbf{alkane} \xrightarrow[\text{from same carbon}]{-2H} \textbf{Alkylidene -}$$

Alkylene group

$$\textbf{alkane} \xrightarrow[\text{from different carbon}]{-2H} \textbf{Alkylene -}$$

(1) Types of Ethylene:– (**Symmetrical & Unsymmetrical)**

(a) Symmetrical : –

In the given two alkyl groups one group is attached to the one carbon of ethylene & next on the next carbon.

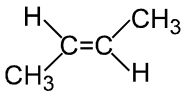
(b) Unsymmetrical : –

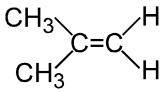
When both the given groups are attached on the same carbon.

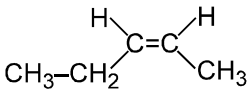
Note : – Symmetrical & Unsymmetrical : –

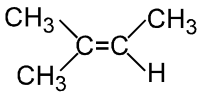
terms are used only when two alkyl groups are given.

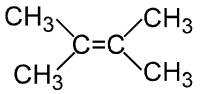
Ex.

(i)  Symmetrical dimethyl ethylene

(ii)  Unsymmetrical dimethyl ethylene

(iii)  Symmetrical ethyl methyl ethylene

(iv)  Tri methyl ethylene

(v)  Tetra methyl ethylene

(vi) $CH_3–C\equiv C–CH_3$ Dimethyl acetylene

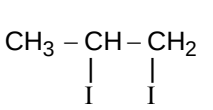
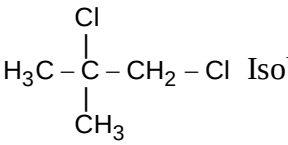
(1) Common – Naming of dihalides :–

(a) When two same halogen atoms are attached to the same carbon such compounds are called **Gemdihalides**.

(b) Common names of such compounds are alkylidene halides
eg. : Ethylidene chloride , Isobutylidene Iodide
Exception : Methylidene halide(wrong)
Methylene halide (right)

(c) When two same halogen atoms are attached to adjacent carbon, these are called as **vicinal dihalides.**

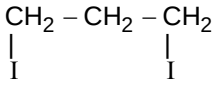
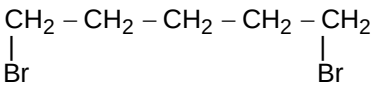
Common names of such compounds are alkylene halide.

Ex.  Propylene Iodide  Isobutylene chloride

(d) When two same halogen atoms are attached at the two ends of a carbon chain its common naming will be polymethylene halide.

'poly' word indicates the number of $-CH_2-$ groups.

$-CH_2-$	2	3	4	5	6
Poly	di	tri	tetra	penta	Hexa

Ex.  

Trimethylene Iodide Pentamethylene Bromide

Exception : –

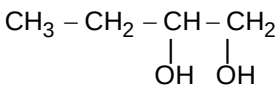
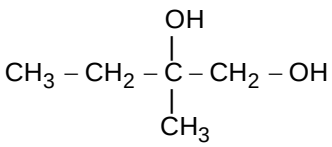
$CH_2 - X$ dimethylene halide (wrong)

|

$CH_2 - X$ ethylene halide (right)

(2) Common - Naming of di-hydroxy compounds:

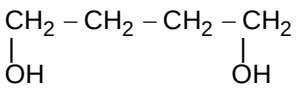
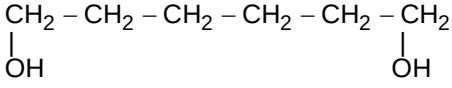
(a) When two –OH groups are attached to adjacent carbon's they are termed as alkylene glycol.

Butylene glycol Active amylene glycol

(b) When two –OH group are attached at the two ends of a carbon chain, these compounds are named as polymethylene glycol.

Poly $\rightarrow$ Number of CH_2 groups.

eg. :  

Tetra methylene glycol Hexamethylene glycol

Exception :

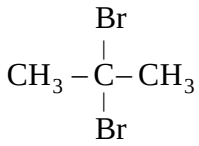
$CH_2 - OH$ Dimethylene glycol (wrong)

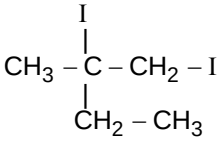
|

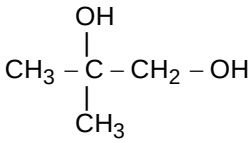
$CH_2 - OH$ Ethylene glycol (right)

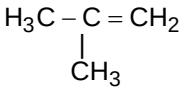
Ex. Make the structure of following organic compounds -

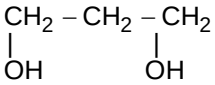
1. Isopropylidene Bromide
2. Active amylene Iodide
3. Isobutylene glycol
4. Isobutylene
5. Trimethylene glycol

Sol. 1. 

2. 

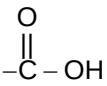
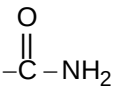
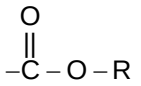
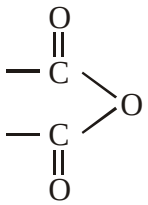
3. 

4. 

5. 

(3) Common - Naming of the functional group having carbon : –

Chart - 1

Functional group	**Suffix**	**Functional group**	**Suffix**
	-aldehyde		-ic Acid
	-yl halide		-amide
– C ≡ N	-o-nitrile		-o-isonitrile
	-ate		-ic anhydride

Prefix : –

1 Carbon → Form-

2 Carbon → Acet-

3 Carbon → Propion-

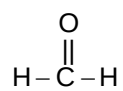
4 Carbon → Butyr | → Normal, → Iso -

5 Carbon →

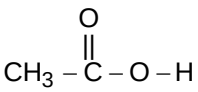
Valer → Normal-, Iso, Secondary-, Tertiary-

3C + (=) double bond = Acryl-

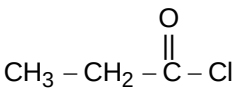
4 C + double bond = Croton-

Ex. 

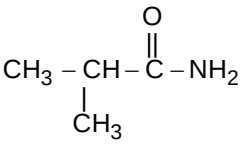
Formaldehyde

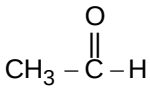


Acetic Acid



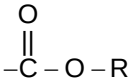
Propionyl chloride



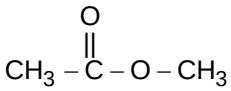


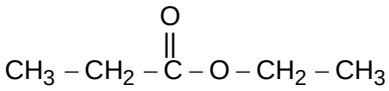
Isobutyr amide Acetaldehyde

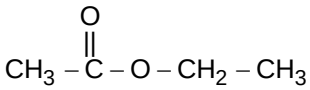
(4) Nomenclature of Ester : –

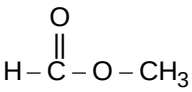


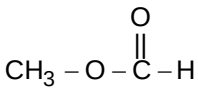
The group which is attached to the oxygen is written as alkyl & the remaining structure is named same as defined in chart-1.

eg.  Methyl acetate

 Ethyl propionate

 Ethyl acetate

 Methyl formate

 Methyl formate

(5) Nomenclature of Anhydride : –

Rule : – Add the total number of carbon atoms & divide it by 2, the substract will give you the number of C - atom. Now name it according to Chart - 1.

$\frac{\text{Total}}{2}$ = Substract $\Rightarrow$ Number of C atom

In Acetic anhydride $\Rightarrow$ $\frac{4}{2} = 2$

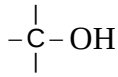
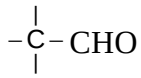
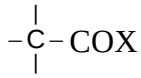
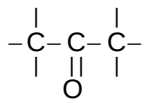
Propionic anhydride $\Rightarrow$ $\frac{6}{2} = 3$

If $R \neq R'$ You need not to find out substract.

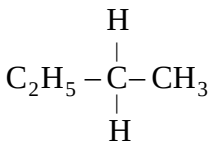
Ex. Acetic propionic anhydride (right)
Propionic Acetic anhydride (wrong)
Divide it in two parts as above & name it by suffixing ic anhydride (alphabatically)
eg. Butyric propionic anhydride
eg. Isobutyric Secondary valeric anhydride
eg. Acrylic anhydride

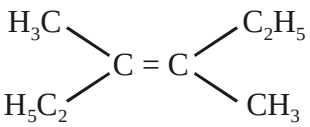
DERIVED SYSTEM

According to this system name to any compound is given according to the parent name of the homologous series. This system is reserved for the following nine homologous series.

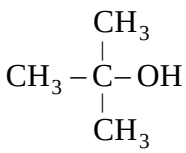
Series	Name of Homologous series	Derived Name	Structure of group
1.	Alkane	Methane	
2.	Alkene	Ethylene	>C=C<
3.	Alkyne	Acetylene	–C ≡ C –
4.	Alkanol	Carbinol	
5.	Alkanal	Acetaldehyde	
6.	Alkanoic acid	Acetic acid	
7.	Alkanoylhalide	Acetyl halide	
8.	Alkanamide	Acetamide	
9.	Alkanone	Acetone	

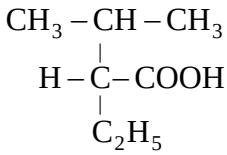
Examples of derived nomenclature system

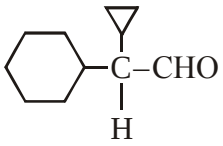
(i)  ethyl methyl methane

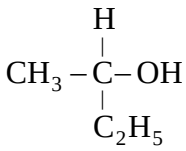
(ii)  diethyl dimethyl ethylene

(iii) $CH_3–CH_2–CH_2–C\equiv C–H$ propyl acetelene

(iv)  Trimethyl carbinol

(v)  ethyl isopropyl acetic acid

(vi)  cyclohexyl cyclopropyl acetaldehyde

(vii)  ethyl methyl carbinol

IUPAC NOMENCLATURE SYSTEM

*** STRAIGHT CHAIN HYDROCARBONS**

Writing Formula : Word Root + Suffix

(1) Word root : The basic unit is a series of root words which indicate linear or continuous chains of carbon atoms. Chains containing one to four carbon atoms are known by special root words while chains from C_5 onwards are known by Greek number roots.

1 C ⟶ meth	2 C ⟶ eth
3 C ⟶ prop	4 C ⟶ but
5 C ⟶ pent	6 C ⟶ hex
7 C ⟶ hept	8 C ⟶ oct
9 C ⟶ non	10 C ⟶ dec
11 C ⟶ undec	12 C ⟶ dodec-
13 C ⟶ tridec-	20 C ⟶ ecos
30 C ⟶ Triacont	40 C ⟶ Tetracont
50 C ⟶ Pentacont	

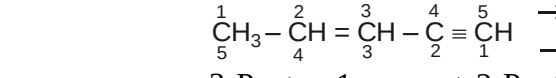
(2) Suffix : Suffixes are added to the root words to show saturation or unsaturation in a carbon chain.

C– C bond	– ane
C = C bond	– ene
C ≡ C bond	– yne
2 C = C bonds	– diene
2 C ≡ C bond	– diyne
C = C + C ≡ C bonds	– enyne

*** UNSATURATED STRAIGHT CHAIN HYDROCARBONS**

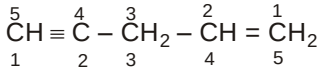
Lowest locant rule of numbering :

1. When more than one double or triple bond is present then
   word root ⇒ Alka
   Ex. $CH_2 = CH–CH = CH_2$
   buta -1,3-diene
2. When double and triple bonds are present, the hydrocarbon is named as alkenyne
3. The numbering of the parent chain should always be done from that end which gives lowest sum for the multiple bonds. For example,



3-Penten-1-yne not 2-Penten-4-yne

4. If, however, there is a choice in numbering, the dobule bond is always given preference over the triple bond. For example



1-Penten-4-yne not 4-Penten-1-yne

IUPAC naming for Groups

(A) $R - H \xrightarrow[-H]{} R -$

(Alkane, C_nH_{2n+2}) (Alkyl, C_nH_{2n+1})

Rule : (i) Longest chain in a branch is selected starting from the same end where it originates from.
(ii) Numbering is started from the originating end of a branch.

Example :				**IUPAC Names**
(1)	CH_4	$-CH_3$		methyl (Me–)
(2)	C_2H_6	$-C_2H_5$		ethyl (Et–)
(3)	C_3H_8	$-C_3H_7$	$-CH_2CH_2CH_3$	propyl (Pr–)

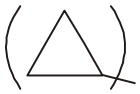
(B) $C_nH_{2n} \xrightarrow{-H} C_nH_{2\,n-1}$ (Alkene) (Alkenyl)

$C_nH_{2\,n-2} \xrightarrow{-H} C_nH_{2\,n-3}$ (Alkyne) (Alkynyl)

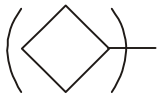
Examples :			**IUPAC Name**
(1)	$H_2C = CH_2$	$H_2C = CH -$ (vinyl)	ethenyl
(2)	$H_2C = CH–CH_3$	(i) $H_2C = CH–CH_2 -$ (alkenyl)	2-propenyl
		(ii) $H_2C = \underset{\vert}{C}–CH_3$	1-methyl ethenyl (isopropenyl)
		(iii) $HC = \underset{\vert}{CH} – CH_3$	1-propenyl
(3)	$HC \equiv CH$	$HC \equiv C -$	ethynyl
(4)	$HC \equiv C – CH_3$	$HC \equiv C – CH_2 -$ (Propargyl)	2-propynyl

(C) Cycloalkane $\xrightarrow{-H}$ Cycloalkyl

Example:

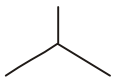
(1)  

Cyclopropyl

(2)  

Cyclobutyl

(D) When 2 Hs are replaced in alkanes



either from the same carbon (i.e.Alkylidene)

or from two different carbons (i.e.Alkylene)

Example :

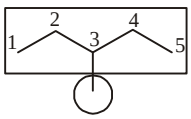
(1) $H_3C - CH =$ (ethylidene) $\quad H_2C - CH_2$ (ethylene)

(2) $H_3C - CH_2 - CH =$ (Propylidene) $\quad H_3C - CH - CH_2$ (1,2-propylene)

$H_2C - CH_2 - CH_2$ (1,3-propylene)

$(H_2C)=$ is called methylene.

BRANCHED CHAIN HYDROCARBONS

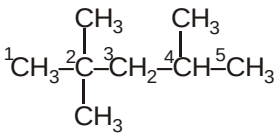


→ Principal/Parent chain

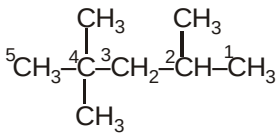
→ Branch / Substituent

3-methyl pentane

The numbering is done in such a way that the substituted carbon atoms have the lowest possible numbers.



2,2,4-Trimethylpentane
(Correct)



2,4,4-Trimethylpentane
(Wrong)

RULES FOR BRANCHED CHAIN HYDROCARBONS.

(1) Saturated Branched chain hydrocarbons.

Rules:

(a) Chain selection :

(i) Longest chain selection with maximum number of branches.

(b) Numbering :

(i) Lowest locant rule

(ii) Numbering in accordance with alphabetical order of names of substituents.

(iii) Lowest sum rule

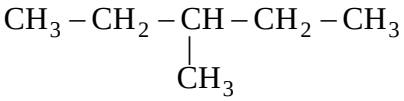
(c) Writing the names :

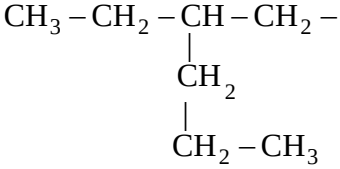
(i) Names of branches are written in alphabetical order of first letter of their names (Note : First letter of di / tri / tetra is not considered)

(ii) Complex alkyl groups:

* Always write in small bracket
* First letter of complex alkyl group is considered to decide alphabetical order even if it is (di, tri, tetra) as it is the part of name.

Example :

(1)  3- methylpentane

(2)  3-ethylhexane

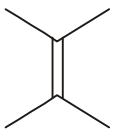
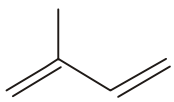
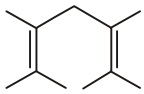
V. UNSATURATED BRANCHED CHAIN HYDROCARBONS :

Rule :

(A) *Chain selection* : Longest chain selection with maximum number of multiple bonds possible.

(= bond is preferred over , ≡ bond in a chain selection if there are same number of carbons in both possible chains).

Example :

(1)  (2)  (3) 

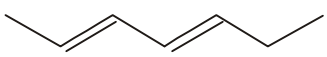
(B) *Numbering* :

(i) Lowest locant rule with respect to multiple bonds.

(ii) (=) bond is preferred over (≡) bond for numbering if both have same locants/ positions.

(iii) Lowest sum rule.

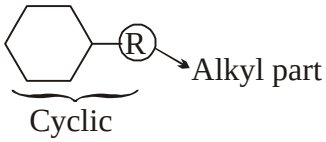
Example:

(1)  (2) $H_2C = CH - C \equiv C - CH_3$

(3) $H_3C - CH = CH - C \equiv CH$ (4) $H_2C = CH - C \equiv CH$

VI. CYCLOALKANES

Cycloalkanes are alkanes in which carbon atoms are arranged in a ring. These are named by adding prefix cyclo to the name of alkane having the same number carbon atoms as in ring.



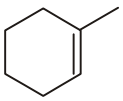
(1)  Cyclohexane

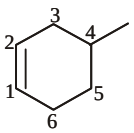
(2)  Cyclopropane

(3)  Cyclobutane

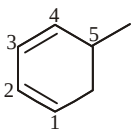
(4)  Cyclohexene

Cycloalkene and Cycloalkyne : In case of cycloalkene & cycloalkyne the numbering of double or triple bond is done as 1 and 2, the direction is so chosen as to give lowest numbers to the substituents.

 1-Methyl cyclohexene



4-methyl cyclohexene

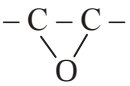


5-methyl cyclohexa-1,3-diene

VII. ORGANIC COMPOUND CONTAINING FUNCTIONAL GROUPS

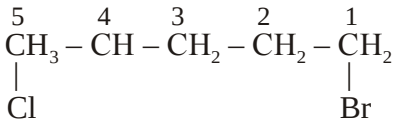
In IUPAC nomenclature functional groups are catagorized into two categories.

Category I : Groups of this category are not considered as functional groups in IUPAC nomenclature. They are considered as substituents & therefore represented by prefix. Category I functional group & their prefix are shown below :

	Prefix
– F	fluoro
– Cl	chloro
– Br	bromo
– I	iodo
$-NO_2$	nitro
– NO	nitroso
– OR	alkoxy
	epoxy

Rules for their nomenclature :

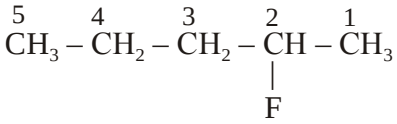
Rule I : If two substituents are present on same position from different ends, then priority is decided on the basis of alphabetical order.

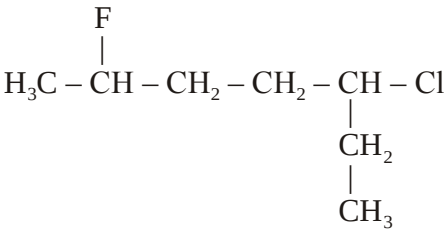


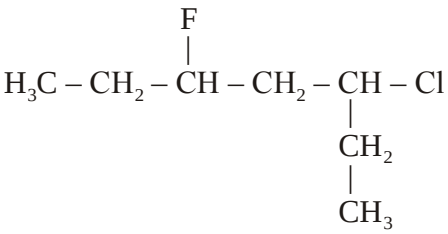
Rule II : In multiple bond and category I functional group both are present, the priority is given to multiple bond.



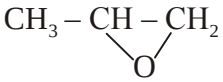
Rule III : These groups are written is alphabatical order in IUPAC name.

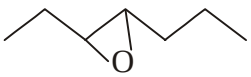
Example : (i)  2-fluoropentane

(ii)  5-chloro-2-fluoroheptane

(iii)  3-chloro-5-fluoroheptane

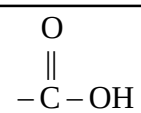
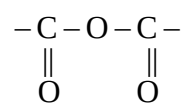
Epoxides :

(1)  1, 2-epoxy propane

(2)  3, 4-epoxy heptane

VIII. Case-II : Groups of this category are treated as functional groups and represented by suffix in IUPAC nomenclature.

Priority table for functional group.

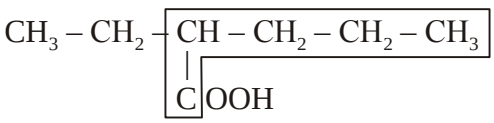
	Functional group	Name	Suffix	Prefix
(1)		Carboxylic acid oic acid	Carboxy	
(2)		Sulphonic acid	sulphonic acid	Sulpho
(3)		Acid anhydride	oic anhydride	–

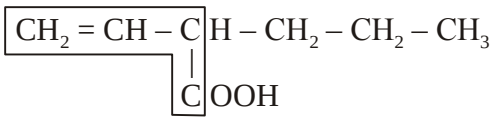
(4)	$-C(=O)-OR$	Ester	oate (alkyl+w.r.+oate)	Alkoxy carbonyl
(5)	$-C(=O)-Cl$	Acid chloride	oyl chloride	Chlorocarbonyl
(6)	$-C(=O)-NH_2$	Amide	amide	Carbamoyl
(7)	$-C \equiv N$	Cyanide	nitrile	Cyano
(8)	$-N \equiv C$	Isocyanide	isonitrile	Isocyano
(9)	$-CHO$	Aldehyde	al	Oxo / formyl
(10)	$-C(=O)-$	Ketone	one	Oxo/Keto
(11)	$-OH$	Alcohol	ol	Hydroxy
(12)	$-SH$	Thio-alcohol	thiol	Mercapto
(13)	$-NH_2$	Amine	amine	Amino
(14)	(=)		ene	
(15)	(≡)		yne	

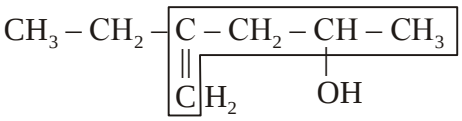
Note : *Double bond & tripple bond are not true functional groups.*

Rule for their nomenclature :

(1) Selection of parent 'C' chain : longest possible 'C' chain with functional group and having maximum number of multiple bonds is selected as parent 'C' chain.





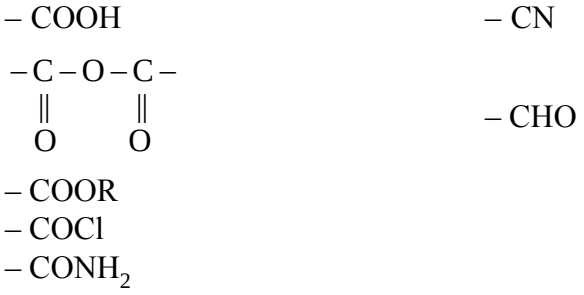


(2) Numbering :

(a) Numbering starts from the side of functional group. For numbering priority order is given below :

Functional group > Multiple bonds > Substituents

(b) If chain ending 'C' containing functional group is present then numbering starts from the 'C' of functional group these functional groups are known as DON category functional groups functional groups of this catagoly are shown below :

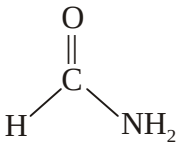


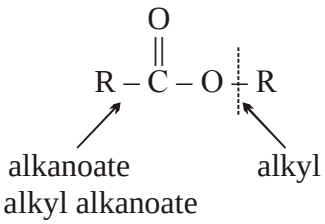
Rule 3 : 'e' of primary suffix is dropped if secondary suffix starts from a vowel.

Example of compounds having don catagory functional groups :

(i) $CH_3 - CH_2 - CH_2 - COOH$ Butanoic acid

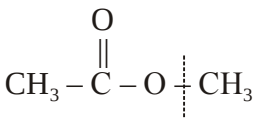
(ii) $CH_3 - CH(COOH) - CH_2 - CH_3$ 2-methyl butanoic acid

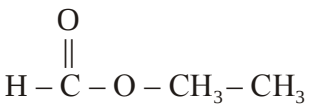
(iii)  methanamide

Ester : 

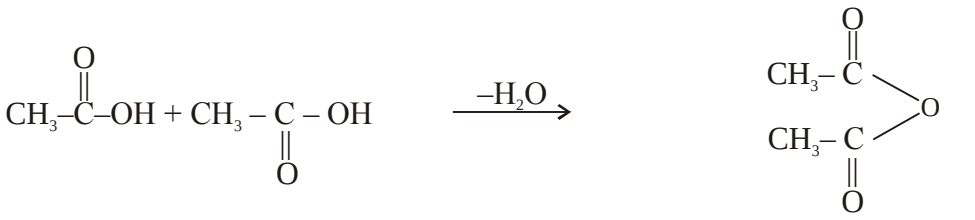
→ alkyl alkanoate

Example :

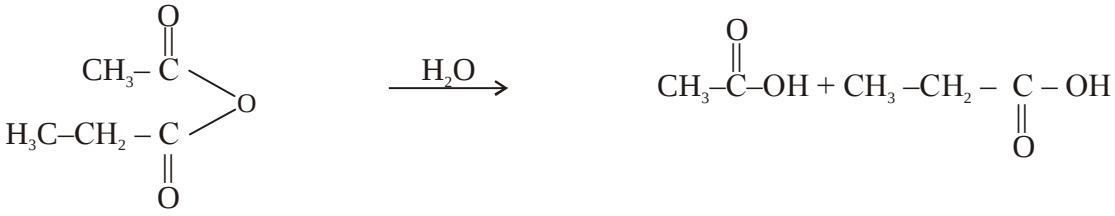
(i)  Methyl ethanoate

(ii)  ethyl methanoate

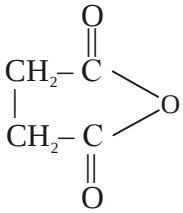
Anhydride : Nomenclature of anhydride is done on basis of the carboxylic acid from which it is obtained.



ethanoic acid ethanoic anhydride



ethanoic propanoic anhydride

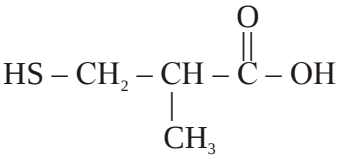


butanedioic anhydride

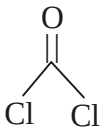
IX. POLYFUNCTIONAL COMPOUNDS :

Rule-I : If more than one functional gps are present then one is selected as principle functional gp. and represented by suffix. Other functional groups are treated as substituents & representated by prefix.

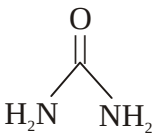
Selection of principle functional gp. is done according to priority table

1. 

3–mercapto-2-methyl propanoic acid

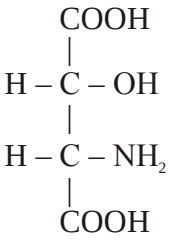
2. 

chloromethanoylchloride

3. 

amino methanamide (Urea)

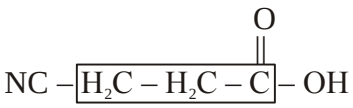
Rule-II : When principle gp. is selected then there is no use of priority table.

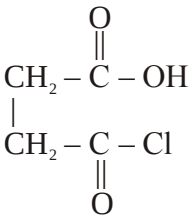
4. 

3–amino–2–hydroxy butane – 1, 4–dioic acid (Incorrect)

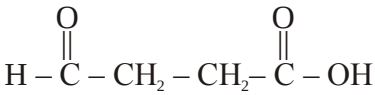
2 – amino – 3– hydroxybutane –1, 4–dioic acid (Correct)

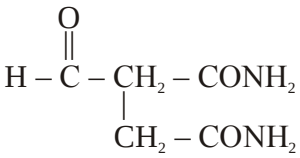
Rule-III : If any carbon containing functional gp. is present as sec. functional gp. then its 'C' is not included in principle 'C' chain except –CHO gp.

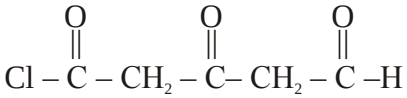
5.  3–cyanopropanoic acid

6.  3-chlorocarbonyl propanoic acid

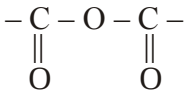
Rule-IV : As sec. functional gp., if 'C' of –CHO gp. is included in parcent 'C' chain then oxo is used as prefix, otherwise we use formyl group as prefix.

7.  4 – oxobutanoic acid

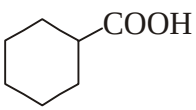
8.  2–formyl butane–1, 4–diamide

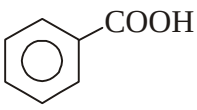
9.  3, 5–dioxopentanoyl chloride

X. IUPAC nomenclature if Carbon containing category functional gp. is present as principle functional gp. & its 'C' is not included in parent 'C' chain →

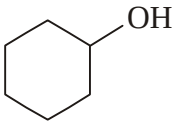
– COOH	Carboxylic acid
	Carboxylic anhydride
– COOR	Carboxylate
– COCl	Carbonyl chloride
– $CONH_2$	Carboxamide
– CN	Carbnitrile
– CHO	Carbaldehyde

Ex-1

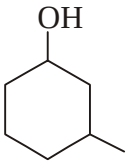
1.  Cyclohexane carboxylic acid

2.  Benzene carboxylic acid

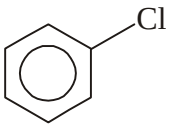
Nomenclature of cyclic compounds with functional groups :

1. 

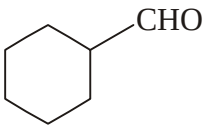
Cyclohexanol

2. 

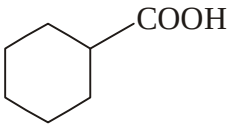
3-Methyl cyclohexanol

3. 

Chlorobenzene

4. 

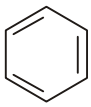
Cyclohexanecarbaldehyde

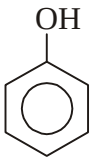
5. 

Cyclohexane carboxylic acid

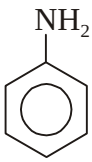
XII. Nomenclature of aromatic compound :

Common name of most of the aromatic compounds are accepted as their IUPAC name.

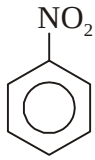

Benzene



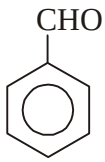
Benzenol
(Phenol)



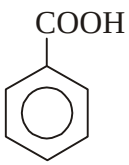
Benzenamine
(Aniline)



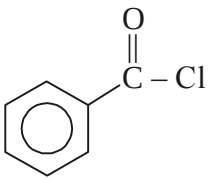
Nitro benzene



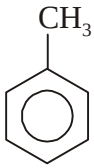
benzene carbaldehyde
(Benzaldehyde)



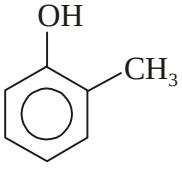
Benzene carboxylic acid
(Benzoic acid)



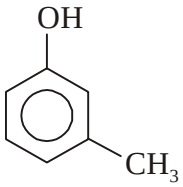
Benzene carbonyl chloride
(Benzoyl chloride)



methyl benzene
(Toluene)



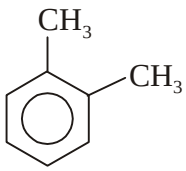
2-methyl phenol
(o-cresol)



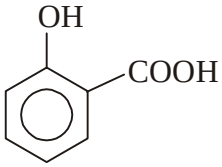
3-methyl phenol
(m-cresol)



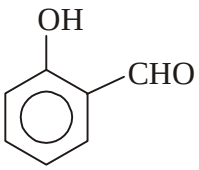
4-methyl phenol
(p-cresol)



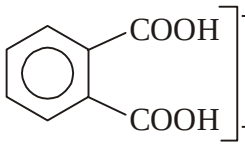
2-methyl toluene
(o-xylene)



2-hydroxy benzoic acid
(Salicylic acid)



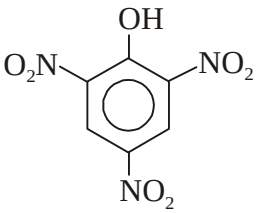
2-hydroxy benzaldehyde or
(Salicyldehyde)



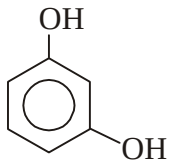
m-Isophthalic

p-Terphthalic acid

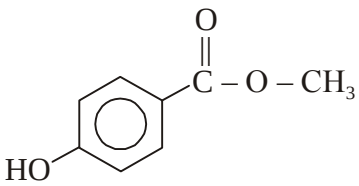
Phthalic acid
Benzene-1,
2-dicarboxylic acid



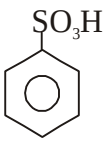
2, 4, 6-trinitro phenol
(Picric acid)



Benzene-1, 3-diol
(Resorcinol)



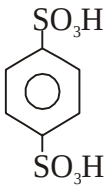
Methyl-4-hydroxy benzoate



Benzene
sulphonic acid



4–sulpho benzoic acid



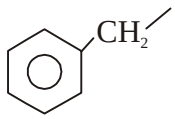
1, 4–benzenedisulphonic
acid

Some Alkyl groups : -

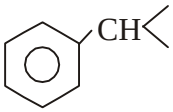
$CH_2 = CH –$ Vinyl

$CH_2 = CH – CH_2 –$ Allyl

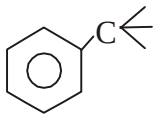
Ph– /  / $C_6H_5 –$ Phenyl



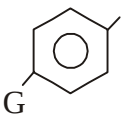
Benzyl



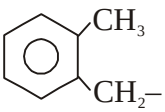
Benzal



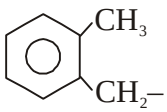
Benzo



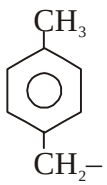
Aryl



o–tolyl



m – tolyl

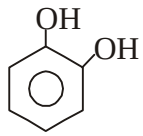


p – tolyl

$CH_3 - CH = CH - CH_2 -$ Crotyl

$Ph - CH = CH - CH_2 -$ Cinnamyl

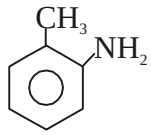
Some other aromatic :-



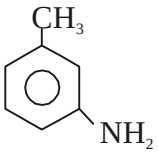
Catechol



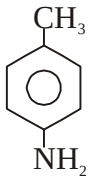
Hydroquinone



o–toludiene



m–toludiene



p–toludiene

EXERCISE-I

Q.1 Which is an acyclic compound :

(A) Methane (B) Benzene (C) Pyrrole (D) Cyclobutane

Q.2 The commercial name of trichloroethene is:

(A) Westron (B) Perclene (C) Westrosol (D) Orlone

Q.3 The group of heterocyclic compounds is ;

(A) Phenol, Furan (B) Furan, Thiophene

(C) Thiophene, Phenol (D) Furan, Aniline

Q.4 C_5H_{12} gives ___ types of alkyl groups.

(A) 5 (B) 8 (C) 6 (D) 4

Q.5 iso-octane contains

(A) 5 prim. one sec. & two ter. C atoms.

(B) 4 prim. 2 sec. & one ter. C atoms.

(C) 5 (1^0C). one (2^0C), one (3^0C) & one (4^0C) atoms.

(D) 4 (1^0C). two (2^0C), one (3^0C) & one (4^0C) atoms.

Q.6 The structure of active sec-amyl is

(A) $(CH_3–CH_2)_2CH–$ (B) $(CH_3)_2CH–CH_2–CH_2–$

(C) $CH_3 - CH_2 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} -$ (D) $(CH_3)_4C–$

Q.7 How many 1°carbon atom will be present in a simplest hydrocarbon having two 3° and one 2° carbon atom?

(A) 3 (B) 4 (C) 5 (D) 6

Q.8 How many carbons are in simplest alkyne having two side chains?

(A) 5 (B) 6 (C) 7 (D) 8

Q.9 Which of the following is the triad of a homologous series -

(A) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3$ N

(B) C_2H_5OH, $(CH_3)_2CHOH$, $(CH_3)_3COH$

(C) Both the above

(D) $CH_2 = CH_2$, $CH_3 – CH = CH_2$, $C_2H_5 – CH = CH_2$

Q.10 What is not true about homologous series ?

(A) All the members have similar chemical properties

(B) They have identical physical properties

(C) They can be represented by a general formula

(D) Adjacent members differ in molecular mass by 14

Q.11 Which of the following compound is wrongly named?

(A) $CH_3CH_2CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH$; 2-Chloro pentanoic acid

(B) $CH_3C \equiv \underset{\displaystyle CH_3}{\underset{|}{C}}CHCOOH$; 2-Methyl hex-3-enoic acid

(C) $CH_3CH_2CH=CHCOCH_3$; Hex-3-en-2-one

(D) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CHO$; 4-Methyl pentanal

Q.12 Which one of the following I.U.P.A.C. name is correct ?

(A) 2-Methyl-3-ethyl pentane (B) 2-Ethyl-3-methyl pentane

(C) 3-Ethyl-2-methyl pentane (D) 3-Methyl-2-ethyl pentane

Q.13 The IUPAC name of $C_6H_5-\underset{\displaystyle C_6H_5}{\underset{|}{C}}H-CH_2-CCl_3$ is ;

(A) 1,1,1-trichloro-3,3-diphenyl propane (B) 1,1-diphenyl-3,3,3-trichloro propane

(C) both (A) and (B) (D) none of these

Q.14 IUPAC name of:

$$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle CH_3}{\underset{|}{C}}H-\overset{\displaystyle O}{\overset{\|}{C}}-O-C_2H_5$$

(A) Ethyl-4-methyl-3-oxo pentanoate (B) 2–Ethoxy carbonyl pentan-3-one

(C) 4-Ethoxy carbonyl pentan-3-one (D) Ethyl 2-methyl 3-oxo-pentanoate

Q.15 I.U.P.A.C. name of $(CH_3)_2CH–CH_2–CH_2Br$ is

(A) 1-bromo pentane (B) 2-methyl-4-bromo pentane

(C) 1-bromo-3-methyl butane (D) 2-methyl-3-bromo propane

Q.16 $$CH_3-\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{\displaystyle F}{\overset{|}{C}}}}-CH_2-\underset{\displaystyle CH_2CH_3}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}-CH_3$$

The IUPAC name of this compound is :

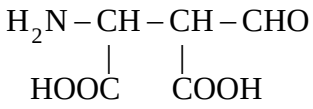
(A) 2-fluoro-4-chloro-2,4-diethyl pentane

(B) 3-fluoro-5-chloro-3-methyl-5-ethyl hexane

(C) 3-chloro-5-fluoro-3,5-dimethyl heptane

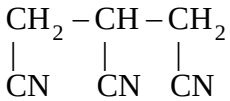
(D) 3,5-dimethyl-5-fluoro-3-chloro heptane

Q.17 The IUPAC name of the structure is:

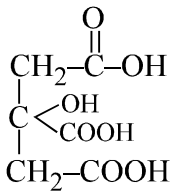


(A) 3-Amino-2-formyl butane-1, 4-dioic acid
(B) 3-Amino-2, 3-dicarboxy propanal
(C) 2-Amino-3-formyl butane-1, 4-dioic acid
(D) 1-Amino-2-formyl succinic acid

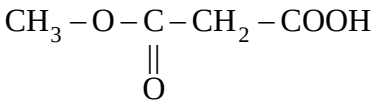
Q.18 The IUPAC name of $C_6H_5CH=CH-COOH$ is:
(A) Cinnamic acid
(B) 1-Phenyl-2-carboxy ethane
(C) 3-Phenyl prop-2-enoic acid
(D) Dihydroxy-3-phenyl propionic acid

Q.19 IUPAC name will be 

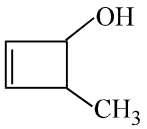
(A) 1,2,3-Tricyano propane
(B) Propane-1,2,3- trinitrile
(C) 1,2,3-Cyano propane
(D) Propane-1,2,3-tricarbonitrile

Q.20 The IUPAC name of compound 

(A) 1,2,3-Tricarboxypropan-2-ol
(B) 2-Hydroxy propane-1,2,3- tricarboxylic acid
(C) 3-Hydroxy-3-carboxypentane-1,5-dioic acid
(D) None

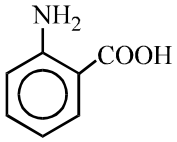
Q.21 

The correct IUPAC systematic name of the above compound is:
(A) 2-Acetoxy ethanoic acid
(B) 2-Methoxy carbonyl ethanoic acid
(C) 3-Methoxy formyl ethanoic acid
(D) 2-Methoxy formyl acetic acid

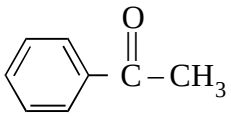
Q.22 The IUPAC name of  is

(A) 3-Methyl cyclobut-1-ene-2-ol
(B) 4-Methyl cyclobut-2-ene-1-ol
(C) 4-Methyl cyclobut-1-ene-3-ol
(D) 2-Methyl cyclobut-3-ene-1-ol

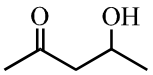
Q.23 The IUPAC name of $CH_2 = CH - C\equiv CH$ is –
(A) 1–Butenyne–3
(B) 1–Butynene–3
(C) Vinyl acetylene
(D) all of them

Q.24 The IUPAC name of  is -

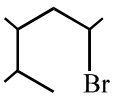
(A) 1-amino-2-carboxybenzene
(B) 2-amino-1-carboxybenzene
(C) 1-amino-2-benzenecaroxylic acid
(D) 2-aminobenzenecarboxylic acid

Q.25 The IUPAC name of  is:

(A)Phenyl ethanone
(B) Methyl phenyl ketone
(C) Acetophenone
(D) Phenyl methyl ketone

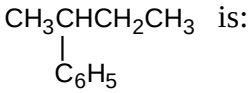
Q.26 The IUPAC name of  is -

(A) 4-oxo-2-pentanol
(B) 4-hydroxy-2-pentanone
(C) pentane-4-ol-2-one
(D) pentane-2-one-4-ol

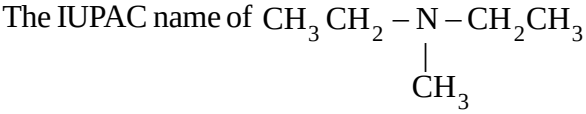
Q.27 The IUPAC name of  is -

(A) 2-bromo-4-isopropylpentane
(B) 2, 3-dimethyl-5-bromohexane
(C) 2-bromo-4, 5-dimethylhexane
(D) 5-bromo-2, 3-dimethylhexane

Q.28 The IUPAC name of the compound

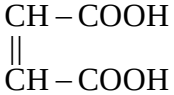
 is:

(A) 2-cyclohexyl butane
(B) 2-phenyl butane
(C) 3-cyclohexyl butane
(D) 3-phenyl butane

Q.29 The IUPAC name of  is:

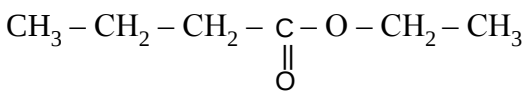
(A) N-Methyl-N-ethyl ethanamine
(B) Diethyl methanamine
(C) N-Ethyl-N-methyl ethanamine
(D) Methyl diethyl ethanamine

Q.30 Which of the following is crotonic acid:

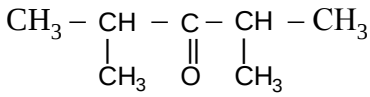
(A) CH_2= CH–COOH
(B) C_6H_5–CH=CH–COOH
(C) CH_3–CH=CH–COOH
(D) 

EXERCISE-II

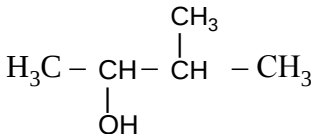
Q.1 Of the following compounds which has a wrong IUPAC name - **[AIEEE-2002]**

I 

ethyl butanoate

II 

2,4- dimethyl -3- pentanone

III 

2-methyl -3- butanol

IV $CH_3 - CH_2 - CH_2 - CHO$

butanal

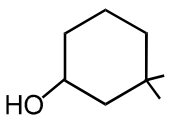
(A) I (B) II (C) III (D) IV

Q.2 The IUPAC name of $CH_3COCH(CH_3)_2$ is – **[AIEEE-2003]**

(A) 4-methylisopropyl ketone (B) 3-methyl-2-butanone

(C) Isopropylmethyl ketone (D) 2-methyl-3-butanone

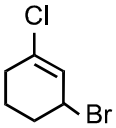
Q.3 The IUPAC name of the compound **[AIEEE-2004]**

 is -

(A) 3,3 -dimethyl-1-hydroxy cyclohexane (B) 1, 1 – dimethyl–3– hydroxy cyclohexane

(C) 3,3-dimethyl-1-cyclohexanol (D) 1,1 - dimethyl - 3- cyclohexanol

Q.4 The IUPAC name of the compound shown below is - **[AIEEE-2006]**



(A) 6-bromo-2-chlorocyclohexene (B) 3-bromo-1-chlorocyclohexene

(C) 1-bromo-3-chlorocylohexene (D) 2-bromo-6-chlorocycohex-1-ene

Q.5 The IUPAC name of **[AIEEE-2007]**

 is –

(A) 1, 1-diethyl-2-dimethylpentane (B) 4, 4-dimethyl-5, 5-diethylpentane

(C) 5, 5-diethyl-4, 4-dimethylpentane (D) 3-ethyl-4, 4 dimethylheptane

Q.6 The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is **[AIEEE 2008]**

(A) $-SO_3H$, $-COOH$, $-CONH_2$, $-CHO$ (B) $-CHO$, $-COOH$, $-SO_3H$, $-CONH_2$

(C) $-CONH_2$, $-CHO$, $-SO_3H$, $-COOH$ (D) $-COOH$, $-SO_3H$, $-CONH_2$, $-CHO$

Q.7 Compound having open chain is -

(A) Pentane (B) Isopentane (C) Neopentane (D) All the above

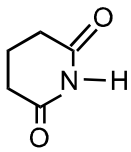
Q.8 In unsaturated compound have –

(A) Carbon - carbon double bond

(B) Carbon - carbon tripel bond

(C) Carbon - carbon double and triple bond

(D) Carbon - oxygen double bond

Q.9 No. of heteroatoms (other than C) present in the following heterocyclic compound 

is –

(A) 3 (B) 2 (C) 1 (D) 0

Q.10 Alicyclic compound is

(A) Aromatic compound (B) Aliphatic compound

(C) Hetero cyclic compound (D) Aliphatic cyclic compound

Q.11 Which of the following radicals are bivalent ?

(a) Ethylidene (b) Vinylidene (c) Benzyl (d) Methylidyne

(A) a , d (B) a , b , d (C) a , b (D) a, b, c

Q.12 Which of the following pairs have absence of carbocyclic ring in both compounds?

(A) Pyridine, Benzene (B) Benzene, Cyclohexane

(C) Cyclohexane, Furane (D) Furane, Pyridine

Q.13 How many secondary carbon atoms does methyl cyclopropane have?

(A) None (B) One (C) Two (D) Three

Q.14 Which of the following is the first member of ester homologous series?

(A) Ethyl ethanoate (B) Methyl ethanoate (C) Methyl methanoate (D) Ethyl methanoate

Q.15 In homologous series :

(A) Molecular formula is same (B) Structural formula is same

(C) Physical properties are same (D) General formula is same

Q.16 Which of the following is the first member of ester homologous series ?

(A) Ethyl ethanoate (B) Methyl ethanoate

(C) Methyl methanoate (D) Ethyl methanoate

Q.17 The correct IUPAC name of $CH_3 - CH_2 - \underset{\underset{CH_2}{\|}}{C} - COOH$ is:

(A) 2-Methyl butanoic acid (B) 2-Ethylprop-2-enoic acid

(C) 2-Carboxybutene (D) None of the above

Q.18 The IUPAC name of compound $CH_3 - \underset{\underset{NH_2}{|}}{\overset{\overset{HO-C=O}{|}}{C}} = \underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}} - H$ is:

(A) 2-Amino-3-chloro-2-methylpent-2-enoic acid

(B) 3-Amino-4-chloro-2-methylpent-2-enoic acid

(C) 4-Amino-3-chloro-2-methylpent-2-enoic acid

(D) All of the above

Q.19 The IUPAC name of $BrCH_2 - \underset{\underset{CONH_2}{|}}{CH} - CO - CH_2 - CH_2CH_3$ is:

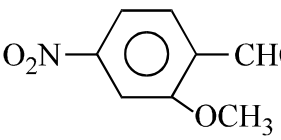
(A) 2-Bromomethyl-3-oxohexanamide (B) 1-Bromo-2-amino-3-oxohexane

(C) 1-Bromo-2-amino-n-propyl ketone (D) 3-Bromo-2-propyl propanamide

Q.20 The IUPAC name of $CH_3 - \underset{\underset{O}{\|}}{C} - O - CH_2 - \underset{\underset{O}{\|}}{C} - OH$ is:

(A) 1-Acetoxy acetic acid (B) 2-Acetoxy ethanoic acid

(C) 2-Ethanoyloxyacetic acid (D) 2-Ethanoyloxyethanoic acid

Q.21 The IUPAC name of  is:

(A) 2-Methoxy-4-nitro benzaldehyde (B) 4-Nitro anisaldehyde

(C) 3-Methoxy-4-formyl nitro benzene (D) 2-Formyl-4-nitro anisole

Q.22 The IUPAC name of compound

$H_3COOC - \underset{\underset{CH_2OH}{|}}{CH} - COOCH_3$

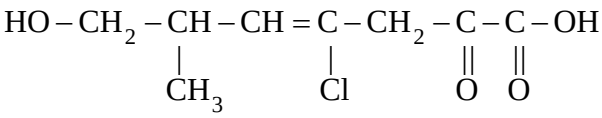
(A) 2-(Hydroxy methyl) methyl propanedioate

(B) Methyl-2-(hydroxy methyl) propanedioate

(C) 2-(Hydroxy methyl) dimethyl propanedioate

(D) None of these

Q.23 The suffix of the principal group, the prefixes for the other groups and the name of the parent in the structure

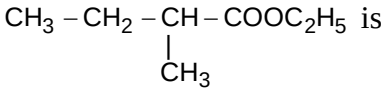


(A) -oic acid, chloro, hydroxy, oxo, methyl, hept-4-ene
(B) -oic acid, chloro, hydroxy, methyl, oxo, hept-4-ene
(C) -one, carboxy, chloro. methyl, hydroxy, hept-4-ene
(D) -one, carboxy, chloro, methyl, hydroxy, hept-4-ene

Q.24 The I.U.P.A.C. name of $(C_2H_5)_2$ CH.CH_2 OH is
(A) 2-ethyl butanol-1
(B) 2-methyl pentanol-1
(C) 2-ethyl pentanol-1
(D) 3-ethyl butanol-1

Q.25 The correct name of 3,3-dimethyl propanamide is
(A) 2-methyl butanamide
(B) 3-methyl butanamide
(C) iso-propyl ethanamide
(D) iso propyl acetamide

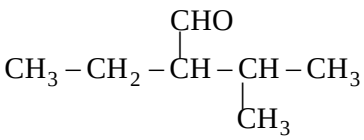
Q.26 The IUPAC name of



(A) 2-ethyl-ethyl acetate
(B) ethyl 3-methyl butanoate
(C) ethyl 2-methyl butanoate
(D) 2-methyl butanoic acid ethyl ester

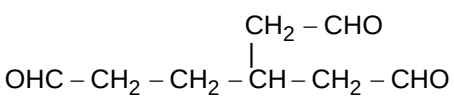
Q.27 The IUPAC name of $N \equiv C - CH_2 - CH_2 - OH$ is;
(A) 1-hydroxy ethanenitrile
(B) 3-hydroxy propanenitrile
(C) 2-hydroxy ethyl cyanide
(D) 1-hydroxy-2-cyanoethane

Q.28



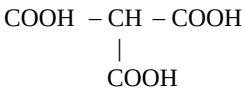
The IUPAC name of this compound is
(A) 2-isopropyl butanal
(B) 2-ethyl-3-methyl butanal
(C) 3-ethyl-2-methyl butanal
(D) 2-methyl pentane-3-aldehyde

Q.29 The IUPAC name of



is :
(A) 4, 4-di(formylmethyl) butanal
(B) 2-(formylmethyl) butane-1, 4-dicarbaldehyde
(C) hexane-3-acetal-1, 6-dial
(D) 3-(formylmethyl) hexane-1, 6-dial

Q.30 The IUPAC name of compound



(A) Tricarboxy methane
(B) Propane trioic acid
(C) Tributanoic acid
(D) 2- carboxy propanedioic acid

ANSWER KEY

EXERCISE-I

Q.1	A	Q.2	C	Q.3	B	Q.4	B	Q.5	C	Q.6	C	Q.7	B
Q.8	B	Q.9	D	Q.10	B	Q.11	B	Q.12	C	Q.13	A	Q.14	D
Q.15	C	Q.16	C	Q.17	C	Q.18	C	Q.19	D	Q.20	B	Q.21	B
Q.22	B	Q.23	A	Q.24	D	Q.25	A	Q.26	B	Q.27	B	Q.28	B
Q.29	C	Q.30	C										

EXERCISE-II

Q.1	C	Q.2	B	Q.3	C	Q.4	B	Q.5	D	Q.6	B	Q.7	D
Q.8	C	Q.9	C	Q.10	D	Q.11	C	Q.12	D	Q.13	C	Q.14	C
Q.15	D	Q.16	C	Q.17	B	Q.18	B	Q.19	A	Q.20	D	Q.21	A
Q.22	B	Q.23	B	Q.24	A	Q.25	B	Q.26	C	Q.27	B	Q.28	B
Q.29	D	Q.30	D										

1. BOND CLEAVAGE

- Organic reaction is a process in which breaking and formation of covalent bonds takes place simultaneously.
- In organic reaction, the organic compound which is converted into a new compound by breaking and formation of covalent bonds is known as the **reactant** or **substrate** and the new compound formed is known as the **product**.
- The chemical species (more reactive) which causes the change is called **reagent**.

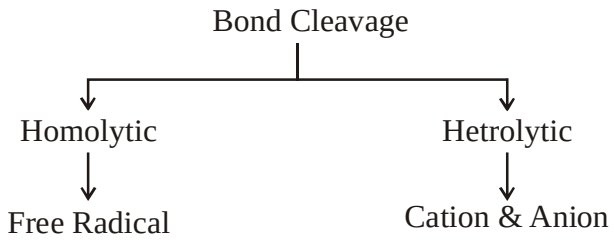
$CH_3— CH_2 — Br + OH^- \longrightarrow CH_3 — CH_2 — OH + Br^-$

substrate Reagent Product

or

Reactant

Breaking of covalent bond is known as **bond cleavage**. A bond can be broken by two ways :



Homolytic Fission or Homolysis

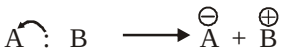
- The covalent bond is broken in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.
- Homolytic bond fission gives free radical as the reaction intermediate.



- The factor which favours homolysis is zero or a small difference in electronegativity between A and B.
- Homolytic bond fission takes place in gaseous phase or in the presence of non polar solvents (CCl_4, CS_2).

Hetrolytic Bond Fission or Heterolysis

- In heterolysis, the covalent bond is broken in such a way that one species (i.e., less electronegative) loss its own electron, while the other species (i.e., more electronegative) gains both the electrons.



- Thus formation of opposite charged species takes place. In case of organic compounds, if positive charge is present on the carbon then cation is tremed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**.
- The factor which favours heterolysis is a greater difference of electronegativity between A and B.

2. REACTION INTERMEDIATES

Reaction intermediates are generated by the breaking of covalent bond of the substrate. They are short -lived species (half life $\geq 10^{-6}$ sec.) and are highly reactive. few important types of reaction-intermediates are as follows.

(1) Carbocation

(2) Carbanion

(3) Free radical

2.1 Carbocations

An organic species which has a carbon atom bearing six electrons in its outermost shell and has a positive charge is called a carbocation.

Characteristics of Carbocation :

(i) Carbocation have a positive charge on carbon.

(ii) Carbocation has only 6 electrons in the outermost shell. It has an incomplete octet. So it behaves like a lewis acid.

(iii) Since all electrons are in paired state so carbocations are diamagnetic.

(iv) Carbocations are sp^2 hybridised.

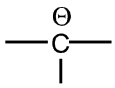
(v) Carbocations are planar with a perpendicular empty p-orbital. Due to planar structure carbocation leads racemization in stereogenic conditions.

(vi) Carbocations are formed in polar solvent.

(vii) It stabilize by presence of e^- donating group (EDG)

2.2 Carbanions

Anion of carbon is known as carbanion. Carbanion carries three bond pairs and one lone pair, thus making the carbon atom negatively charged thus carbanion may be represented as



Characteristic of Carbanions :

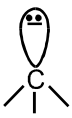
(i) It is formed by heterolytic bond fission.

(ii) There are eight electrons in the outermost orbit of carbanionic carbon hence its octet is complete.

(iii) It behaves as charged nucleophile.

(iv) It is diamagnetic in character because all eight electrons are paired.

(v) Hybridisation and geometry : Alkyl carbanion has three bond pairs and one lone pair. Thus hybridisation is sp^3 and geometry is pryamidal.



Note : Geometry of allyl and benzyl cabanion is almost planar and hybridisation is sp^2.

(vi) It reacts with electrophiles.

(vii) It stabilize by presence of e^- withdrawing group (EWG)

2.3 Carbon Free Radical

(i) Carbon free radicals are odd electron species in which carbon atom bears the odd electron.

(ii) Homolytic bond fission of a covalent single bond gives rise to free radicals.

(iii) There are seven electrons in the outer most shell of carbon free radicals.

(iv) Owing to the presence of an odd electron; a carbon radical is paramagnetic in nature. Due to this reason free radicals are highly reactive.

(v) Hybridization state of free radicals changes from radical to radical depending on the hybridization state of C in its original state.

(vi) Free radicals are neutral electrophiles.

(vii) Free radical generally reacts with free radical.

(viii) It stabilize by presence of e^- releasing group (ERG)

QUESTION BASED ON BOND CLEAVAGE AND INTERMEDIATES

Ex.1 Which one is the characteristic feature of a free radical :
(A) presence of negative or positive charge (B) presence of unpaired electron
(C) presence of even number of electrons (D) assiociated with high stability

Sol. (B) Presence of unpaired electrons

Ex.2 The number of electrons present in the valency shell of carbon of $CH_3\overset{+}{C}H_2$ ion bearing +ve charge :
(A) 8 (B) 7 (C) 6 (D) 4

Sol. (C) Carbocation consist 3 bond pair in outer most orbit and containing 6 electron in valence shell.

Ex.3 Benzoylperoxide, when heated to about 80ºC gives a-
(A) Free radical (B) Carbonium ion (C) Carbenium ion (D) Carbanion

Sol. (A)

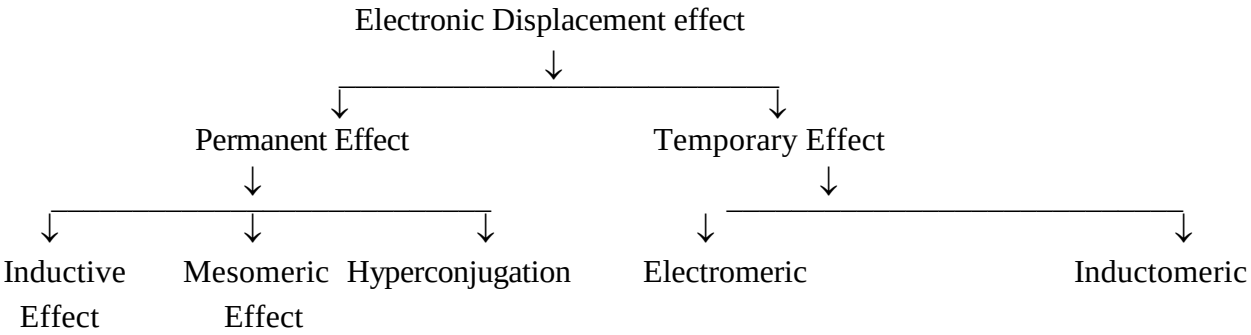
$$C_6H_5-\underset{\underset{O}{||}}{C}-O-O-\underset{\underset{O}{||}}{C}-C_6H_5 \rightarrow 2C_6H_5-\underset{\underset{O}{||}}{C}-O^{\bullet}$$

Ex.4 Which one is a 1° carbocation of the following:

(A) $CH_3\overset{+}{C}H_2$ (B) $CH_3\overset{+}{C}H—C_2H_5$ (C) $(CH_3)_2\overset{+}{C}H$ (D) $(CH_3)_3\overset{+}{C}$

Sol. (A)

3. ELECTRONIC DISPLACEMENT EFFECTS (EDE)



3.1 Inductive Effect (I-effect)

The displacement (shifting) of an electron (shared) pair along the carbon chain due to the diffrence in electron nagativity of the groups present along with carbon chain is known as inductive effect.

$\delta\delta+ \quad \delta+ \quad \delta-$

➢ C--→--C--→-- C --→ G (G : I-effect showing group)

$\delta\delta- \quad \delta- \quad \delta+$

C --←-- C --←-- C --← G

But the effect is insignificant beyond third carbon atom. (distance dependent effect)

➢ This effect is transmitted through the chain of σ bonds and diminishes, with increasing chain length.

Inductive effect is thus

(i) A permanent effect

(ii) The electrons never leave their original atomic orbital.

(iii) Operates through σ bonds

(iv) Polarisation of electrons is always in single direction.

(v) It is generally observed in saturated compounds.

(vi) Its magnitude (i.e., electron withdrawing or donating power) decreases with increase in distance.

On the basis of electron releasing group (ERG) or elctron withdrawing group (EWG) inductive effect, can be of two types.

– *I* effect : The group which withdraws electrons is known as – *I* group and its effect is known as – *I* effect.

– I power of various group & cation.

$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_3H > -CN > -CHO > -CO > -COOH > -COOR >$
$-CONH_2 > -F > -Cl > -Br > I > -OH > -OR > -NH_2 > -C_6H_5 > -CH = CH_2 > -H$

– I power of groups in decreasing order with respect to the reference H

+ *I* effect : The group which donates or gives electron is known as + *I* group and effect is known as + *I* effect.

e.g., Alkyl groups, $\overset{\ominus}{O}$, $COO^{\ominus}$ are + *I* groups. (Generally negative charged atoms or groups)

(a) + *I* power of different type groups and anions :

$-\bar{C}H_2 > -NH^- > -O^- > -COO^- >$ tert. alkyl > sec. alkyl > pri. alkyl > $-CH_3 > -H$

+ *I* power in decreasing order with reference to H

(b) + *I* power of same type of alkyl groups :

+ *I* power ∝ number of C's in same type of alkyl group

For example

$CH_3 - CH_2 -$
$CH_3 - CH_2 - CH_2 -$
$CH_3 - CH_2 - CH_2 - CH_2 -$

↓ + *I* power in increasing order

APPLICATIONS OF INDUCTIVE EFFECT

(A) Stability of reaction intermediates

(i) Stability of carbocation (ii) Stability of free Radical (iii) Stability of carbanion

(i) Stability of carbocation

Stability of carbocation ∝ Presence of electron releasing group ∝ +I group ∝ $\frac{1}{-\text{I group}}$.

eg. : Stability of carbonium ion decrease in the following order

(a) $\underset{3^o}{(CH_3)_3C^+} > \underset{2^o}{(CH_3)_2CH^+} > \underset{1^o}{CH_3CH_2^+} > CH_3^+$

(b) $\overset{\oplus}{C}H_2 - CH_3 > Br - CH_2 - \overset{\oplus}{C}H_2 > Cl - CH_2 - \overset{\oplus}{C}H_2 > F - CH_2 - \overset{\oplus}{C}H_2$

Maximum –I of F

(c) $\overset{\oplus}{C}H_2-\underset{\underset{F}{|}}{C}H-CH_2CH_3 < \overset{\oplus}{C}H_2-CH_2-\underset{\underset{F}{|}}{C}H-CH_3 < \overset{\oplus}{C}H_2-CH_2-CH_2-CH_2-F$

Maximum –I
Minimum distance

Minimum -I
Maximum distance

(d) $\overset{\oplus}{C}H_2-\underset{\underset{F}{|}}{C}H-CH_2CH_3 > \overset{\oplus}{C}H_2-CH_2-\underset{\underset{NO_2}{|}}{C}H-CH_3$ (Distance dominates over power)

(ii) Stability of free Radical

Stability of F.R. $\propto$ Presence of electron releasing group $\propto$ +I group $\propto \frac{1}{-\text{I group}}$.

Stability of F.R. decrease in the following order

(a) $\underset{3^o}{(CH_3)_3C^\bullet} > \underset{2^o}{(CH_3)_2CH^\bullet} > \underset{1^o}{CH_3CH_2^\bullet} > CH_3^\bullet$

(b) $\overset{\bullet}{C}H_2 - CH_3 > Br - CH_2 - \overset{\bullet}{C}H_2 > Cl - CH_2 - \overset{\bullet}{C}H_2 > F - CH_2 - \overset{\bullet}{C}H_2$
Maximum –I of F

(iii) Stability of carbanion

Stability of carbanion $\propto$ Presence of electron withdrowing group $\propto$ –I group $\propto \frac{1}{+\text{I group}}$.

(a) $\underset{3^o}{(CH_3)_3C^-} < \underset{2^o}{(CH_3)_2CH^-} < \underset{1^o}{CH_3CH_2^-} < CH_3^-$

(b) $\overset{\Theta}{C}H_2-CH_2 \rightarrow NO_2 > \overset{\Theta}{C}H_2-CH_2 \rightarrow F > \overset{\Theta}{C}H_2-CH_2 \rightarrow OH > \overset{\Theta}{C}H_2-CH_2 \rightarrow NH_2$

(B) Acidic Strength

Strength of Carboxylic Acid : Acid strength is measured by the position of equilibrium of ionisation in water.

$HA \rightleftharpoons H^+ + A^-$
conjugate base

or $K_a = \frac{[H^+][A^-]}{[HA]}$ (K_a = acid ionisation constant)

or, acid strength $\propto [H^+] \propto K_a \propto \frac{1}{pK_a}$
(here $pK_a = -\log K_a$)

or Acid strength $\propto$ concentration of $[H^+]$

or Acid strength $\propto$ stability of conjugate base

Thus strength of acid is the function of stability of conjugate base.

$\because$ Stability of carbanion $\propto$ Presence of electron withdrawing group $\propto$ –I group $\propto \frac{1}{+\text{I group}}$

$\therefore$ acidic strength $\propto$ Presence of electron withdrawing group $\propto$ –I group $\propto \frac{1}{+\text{I group}}$

The influence of the inductive effect on acidity can be summarised as follows :

Acidic strength of carboxylic acid

(a) $Cl–CH_2–COOH < Cl_2CH–COOH < CCl_3–COOH$

$-I \uparrow$ acid strength $\uparrow$

(b) $H–COOH > CH_3–COOH > CH_3–CH_2–COOH > CH_3–CH_2–CH_2–COOH$

$+I$ power of alkyl groups $\uparrow$ Acid strength $\downarrow$

Acidity of Alcohols : Acidity of alcohol depends on the stability of alkoxide ion (i.e., conjugate base of alcohol) which is obtained by the dissociation of alcohols.

$R - O - H \rightleftharpoons R - \overset{\ominus}{O} + \overset{\oplus}{H}$

Acid strength of alcohol $\propto$ stability of alkoxide ion

(a) $\underset{\text{I}}{\overset{\text{Cl}}{\overset{|}{CH_2 - OH}}} > \underset{\text{II}}{\overset{NO_2}{\overset{|}{CH_2 - CH_2 - OH}}}$

(b) $(CH_3)_3COH < (CH_3)_2CHOH < CH_3CH_2OH < CH_3OH$

(C) Basic Strength

Basicity of Amines :

Basicity is defined as the tendency to donate an electron pair for sharing. The difference in the base strength in various amines can be explained on the basis of +I - effect.

The groups producing +I effects (alkyl groups) tends to intensify electron density over N in amines thereby producing a base strengthening effect.

Thus, strength of base $\propto$ + I power of group present on $-NH_2 \propto K_b \propto \frac{1}{pK_b}$

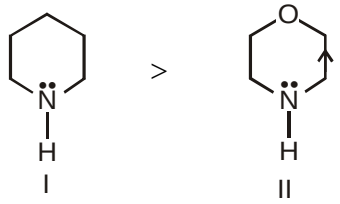
Whereas, a group producing -I effect [–Cl, $–NO_2$] tends to decrease electron density on N -atom in amines, there for producing a base weakning effect.

Thus, strength of base $\propto \frac{1}{-\text{I power of group present on} -NH_2} \propto K_b$

The order of basicity is as given below :

Alkyl groups (R—)	**Relative base strength**
(i) CH_3	$R_2NH > RNH_2 > R_3N > NH_3$
(ii) $(CH_3)_2CH$	$RNH_2 > NH_3 > R_2NH > R_3N$
(iii) $(CH_3)_3C$	$NH_3 > RNH_2 > R_2NH > R_3N$

Comparing with increasing + I effect, trend is rather surprising. This is due to the inability of 3° amines to give up their electrons due to presence of three bulky alkyl groups over N (steric effect).

Ex.  >

I II

QUESTION BASED ON I-EFFECT AND IT'S APPLICATION

Ex.1 Inductive effect refers to -

(A) σ electron displacement along a carbon chain

(B) complete transfer of one of the shared pair of electrons to one of the atoms joined by a double bond

(C) complete transfer of electron with the help of conjugation

(D) none of the above

Sol. **(A)** partial displacement of σ electron takes place.

Ex.2 Most acidic hydrogen is present in-

(A) Ethyne (B) Ethene (C) Benzene (D) Ethane

Sol. **(A)** Terminal alkyne are stronger acid because they contain sp - hybridized carbon which is more electronegative due to 50% s character.

$$H - C \equiv C - H > CH_2 = CH_2 > CH_3 - CH_3$$

Hybrid carbon atom	sp	sp^2	sp^3
% s-character	50%	33 %	25%

Ex.3 Which of the following groups has the highest + *I* effect ?

(A) $-\dot{C}H_3$ (B) $CH_3-\dot{C}H-$ (C) $(CH_3)_2\dot{C}H-$ (D) $(CH_3)_3\dot{C}-$

Sol. **(D)** ter. alkyl group have highest + I effect.

Ex.4 Maximum –I effect is exerted by the group-

(A) C_6H_5- (B) $-OCH_3$ (C) –Cl (D) $-NO_2$

Sol. **(D)** NO_2 has partial positive charge on nitrogen so shows maximum –I effect

Ex.5 The least acidic among the following acids is-

(A) Trichloroacetic acid (B) Dichloroacetic acid

(C) Monochloroacetic acid (D) Acetic acid.

Sol. **(D)** More the number of electron withdrawing atom attached stronger will be the acid. Trichloroacetic acid is strongest acid due to strong – I effect of three Cl atom

Ex.6 Basic nature of H_3O^+, H_2O and OH^- is in order -

(A) $H_3O^+ < H_2O < OH^-$ (B) $H_2O < OH^- < H_3O^+$

(C) $OH^- < H_2O < H_3O^+$ (D) $OH^- = H_3O^+ = H_2O$

Sol. **(A)** Anions are always more basic due to presence of real charge.

Ex.7 Among the following compounds, the weakest acid is-

(A) HC≡CH (B) C_6H_6 (C) C_2H_6 (D) CH_3OH

Sol. **(C)** Among hydrocarbon strength of acid depend upon hybrid state of carbon atom so alkyne possess sp hybridized carbon atom (50% s character) is stronger acid. Order of acid strength is given below

$$CH_3OH > H - C \equiv CH > C_6H_6 > CH_3 - CH_3$$

Ex.8 Among the following which one is most basic-

(A) NH_3 (B) CH_3NH_2 (C) $CH_3CH_2NH_2$ (D) $\underset{\underset{Cl}{|}}{CH_2}-NH_2$

Sol. **(C)** +I group increases the basicity of amine.

Ex.9 Which of the following compounds is most acidic ?

(A) CH_3COOH (B) CH_3CH_2OH (C) $CH_2ClCOOH$ (D) CCl_3COOH

Sol. **(D)** Electron withdrawing group (–Cl) increases the acid strength of acetic acid because of stabilization of carboxylate ion.

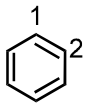
$$CCl_3COOH > \underset{\underset{Cl}{|}}{CH_2}-COOH > CH_3COOH > CH_3CH_2OH$$

3.2 Resonance

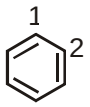
When a molecule or ion can not be represented by single lewis dot structure then more than one structure are needed to represent all properties of the molecule these structures are known as resonating structure and combind structure of all resonating structure is known as resonance hybride and this phenomenon is known as resonance.

- Resonating structure have the same arrangement of atomic nuclei but differ in distribution of electrons, (only π electron delocalised)
- Resonating structure are hypothetical and actual structure is a resonance hybrid.
- In the molecule if resonance is present then mesomeric effect may be present or may not be present. Resonance generally occurs when there is a conjugation of π-bonds (alternate double - single - double bond arrangement) known as conjugated system.

Consider structures of benzene :



I



II

I and II are resonating structures of C_6H_6.

Observations :

(a) According to resonating structure I, C, C bond length between C_1 and C_2 will be 1.34 Å.

(b) According to reasonating structure II, C, C bond bond length between C_1 and C_2 will be 1.54 Å.

(c) According to resonance, bond length between C_1 and C_2 will neither be 1.34 nor 1.54 Å but will be in between 1.34 and 1.54 Å, i.e., bond length between C_1 and C_2 is > 1.34 and < 1.54 Å.

(d) Experimental value is 1.39 Å, this result coincides with the result obtained by resonance, hence resonance theory or concept is correct.

Condition for Resonance :

(i) Planarity

(ii) Conjugation

Conjugation : Planer system in which orbitals are present parallel & continously. If π bond, positive charge, negative charge, odd electron or lone pair of electrons are present at alternate position then system is known as conjugative system & phenomenon is known as conjugation.

Type of Conjugation

(1) Negative charge, π bond conjugation : If in a conjugated system π bond and Θ charge are present at alternate position then conjugation is known as negative charge, π bond conjugation

$CH_2 = CH - \overset{\Theta}{C}H_2$

$CH_2 = CH - CH = CH - \overset{\Theta}{C}H_2$

(2) Lone pair, π bond conjugation : If in a conjugated system π bond and lone pair are present at alternate position so conjugation is known as ℓp, π bond conjugation.

$CH_2 = CH - \ddot{N}H_2$ $\qquad$ $CH_2 = CH - \ddot{X}:$

$CH_2 = CH - CH = CH - CH = CH - \ddot{N}H_2$

(3) π, π conjugation : If π bond alternate with π bond then conjugation is known as π, π conjugation

$CH_2 = CH - CH = CH_2$

$CH_3 - CH_2 - CH = CH - CH = CH - CH = CH_2$, 

All of the above compounds have π, π conjugation.

(4) π bond, Vacant orbital (Positive charge) conjugation : If π bond is present at alternate possition with vacant orbital so conjugation is known as positive charge, π conjugation.

$CH_2 = CH - \overset{\oplus}{C}H_2$

It has positive charge, π conjugation.

$CH_2 = CH - CH = CH - \overset{\oplus}{C}H_2$

This species has two type of conjugation π, π conjugation and positive charge, π conjugation.

(5) π bond, Odd electron (free radical) conjugation : If π bond and odd e^- are present at alternate position.

$CH_2 = CH - \dot{C}H_2$

$CH_2 = CH - CH = CH - \dot{C}H_2$

(6) Lone pair Vacant orbital (Positive charge) conjugation : If lone pair and vacant orbital are at alternate position then conjugation is known as lone pair vacant orbital conjugation.

Ex. 1 $\qquad CH_3 - \overset{\oplus}{C}H - \ddot{N}H_2 \longleftrightarrow CH_3 - CH = \overset{\oplus}{N}H_2$

2 $\qquad CH_3 - \overset{\oplus}{C}H - \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}H \longleftrightarrow CH_3 - CH = \underset{\cdot\cdot}{\overset{\oplus}{O}}H$

Rules to draw valid resonating structures

1. Position of atom cannot be change, only the π-electrons are delocalised.

Ex. $CH_3-\underset{(A)}{\overset{O}{\overset{||}{C}}}-\overset{\Theta}{O} \longleftrightarrow CH_3-\underset{(B)}{\overset{O^{\Theta}}{\overset{|}{C}}}=O$

A & B are Resonance forms.

$$CH_3-\underset{O}{\overset{||}{C}}-CH_3 \xleftrightarrow[\times]{} CH_2=\underset{OH}{\overset{|}{C}}-CH_3$$

Above forms are not resonating forms because position of H is changed.

2. Second period elements sould not violate the octet rule while drawing resonating structures

$$\underset{I}{CH_3-CH=CH-\overset{H}{\overset{|}{\underset{H}{\overset{|}{N}}}}\overset{\oplus}{-}H} \xleftrightarrow[\times]{} \underset{II}{CH_3-\overset{\oplus}{C}H-CH=\overset{H}{\overset{|}{\underset{H}{\overset{|}{N}}}}-H}$$

Above structures are not resonance form because in structure II, nitrogen has 10 valence electrons which violates octet rule.

3. Each Resonating structures must have the same number of unpaired and paired electrons.

$$\underset{I}{CH_2=CH-\dot{C}H_2} \longleftrightarrow \underset{II}{\dot{C}H_2-CH=CH_2}$$

I & II are resonating structure because both have 8 pair of electrons and 1 unpaired electron

4. Net charge should be conserved in all resonating structures.

$$\underset{\text{Net Charge}=0}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{\text{Net Charge}=0}{\overset{\oplus}{C}H_2-CH=CH-\overset{\Theta}{C}H_2}$$

Both structures have same net charge so both are resonance forms.

Rules for stability of resonating structures

1. Among various resonating structure non polar resonating structure is more stable than polar resonating structure or more number of covalent bonds is considered to be more contributing than others.

$$CH_2=CH-CH=CH_2 \longleftrightarrow \underset{\text{(more stable)}}{\overset{\oplus}{C}H_2-CH=CH-\overset{\Theta}{C}H_2}$$

2. If two resonance structures have same number of bonds then that structure in which octet of every atom is complete is more contributing than structure having incomplete octet.

$$CH_3-\overset{\oplus}{C}H-NH_2 \longleftrightarrow \underset{\text{(more stable)}}{CH_3-CH=\overset{\oplus}{N}H_2}$$

3. Neutral structure is more stable than charged structure and if both are charged Resonating structure then less charged resonating structure is more stable.

$$CH_3-\overset{O}{\overset{||}{C}}-OH \longleftrightarrow \underset{\text{(more stable)}}{CH_3-\overset{O^{-}}{\overset{|}{C}}=\overset{+}{O}H}$$

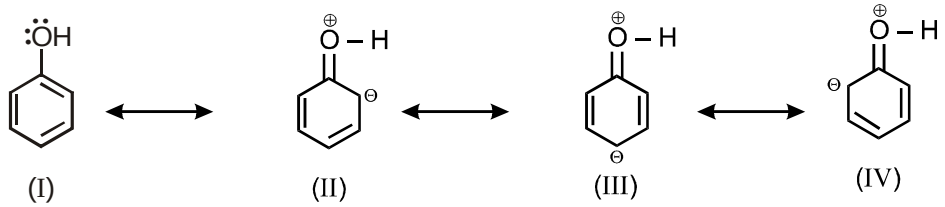
4. In case of charged resonating structures, the most stable one is that in which the positivie and negative charges reside on the most electropositive and most electronegative atoms of the structure respectively.

$$CH_2^{\ominus} - CH = O \longleftrightarrow CH_2 = CH - O^{\ominus}$$

(A) (B) (more stable)

stability of B > A

5. Resonating structure in which unlike charges are closer is more contributing than that structures in which unlike charges are far away.



(I) (II) (III) (IV)

Hence stability of II and IV will be the same and both will be more stable than III. The order of stability of resonating structures in decreasing order will be as follows :

I > II ≡ IV > III

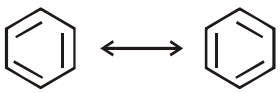
6. Resonating structure in which like charges are far away is more contributing as compared to structure in which like charges are closer.

Resonance Energy :

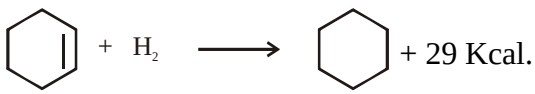
The energy difference between more stable resonating structure and resonance hybrid is known as resonace energy.

- It is an experimental value which is calculated by heat of hydrogenation (HOH)
- Higher the value of resonance energy, greater is the resonance stabilization.

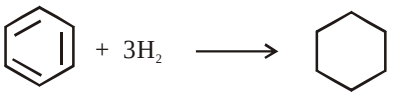
Resonance Energy of Benzene :



The resonance energy of benzene is calculated from the heat of hydrogenation as given below :



+ 29 Kcal.



+ 3 × 29 Kcal. = 87 Kcal. (Calculated theoretical vlaue)

but experimental value is 51 Kcal. so,

Resonance energy = Calculated value – Experimental value

= 87 – 51

= 36 Kcal.

QUESTION BASED ON RESONANCE

Ex.1 Polarisation of electrons in acrolein may be written as -

(A) $\overset{\delta+}{C}H_2 = CH - CH = \overset{\delta-}{O}$ (B) $\overset{\delta+}{C}H_2 = CH - \overset{\delta-}{C}H = 0$

(C) $\overset{\delta-}{C}H_2 = \overset{\delta+}{C}H - CH = 0$ (D) $\overset{\delta-}{C}H_2 = CH - CH = \overset{\delta+}{O}$

Sol. (A) O atom is more electronegative so negative charge is more stable on oxygen

Ex.2 In pyridine ;  Number of conjugated electrons are -

(A) 6 (B) 8 (C) zero (D) 5

Sol. (A) Lone pair of N-atom does not take part in resonance.

Ex.3 In which compound delocalisation is not possible -

(A) 2-butene (B) 1, 3-butadiene (C) 1, 3, 5-hexatriene (D) Benzene

Sol. (A) 2-butene, no conjugation present

Ex.4 Consider the following compound :

$\underset{1}{CH_2} = \underset{2}{CH} - \underset{3}{CH} = \underset{4}{CH_2}$

carbon-carbon bond length between C_2 and C_3 will be -

(A) 1.54 Å (B) 1.3 Å

(C) 1.21 Å (D) Less than 1.54 Å and greater than 1.34 Å

Sol. (D) $C_2 - C_3$ are at conjugated position.

Ex.5 + R power of the given groups -

(a) $-\overset{\ominus}{O}$ (b) $-NH_2$ (c) $-OH$ (d) $-NHCOCH_3$

increasing order is -

(A) a > b > c > d (B) d > c > b > a (C) a > c > b > d (D) a > d > c > b

Sol. (A)

3.3 Mesomeric effect

(a) This is a permanent effect where the displacement of conjugational π e– (s) are influenced by the group attached to carbon chain.

(b) There is a push or pull of π electrons of the conjugated system of molecule.

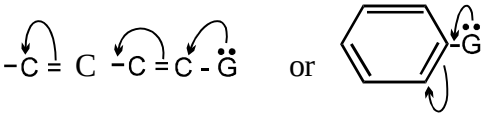
(c) M effect operates only in the conjugated system.

(d) If the conjugation is not available, M effect does not propagate further.

(e) M–effect has no correlation with the electronegativity of the connecting atom of the group

(f) M-effect is two type; +M and –M

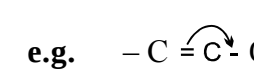
(g) **+M effect (+R) :** If the group pushes the electrons into the π e–system, the effect is said as +M effect and the group is called ERG (electron releasing group) or +M group.

e.g. 

+ M Effect is shown by : –Cl, –Br, $-NH_2$, –NHR, $-NR_2$, $-NHCOCH_3$, –OH , –OR

Condition : Electron pair must be present at first atom of group.

(h) **–M effect (–R) :** If the π e– system is pulled by the group then the effect is called –M effect and the group is called EWG group (electron withdrawing group) or –M group.

e.g.  or 

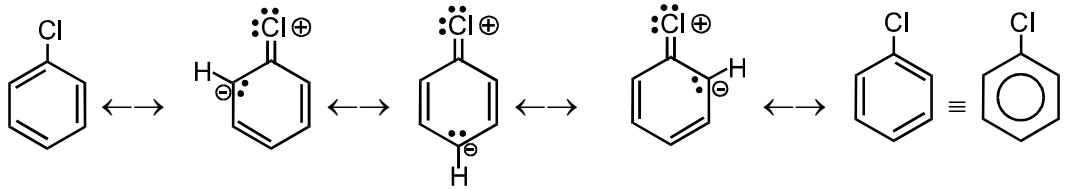
–M effect is shown by :

–CHO, > C = O, –COOH, $-NO_2$, –CN, $-SO_3H$, $-SO_2Cl$

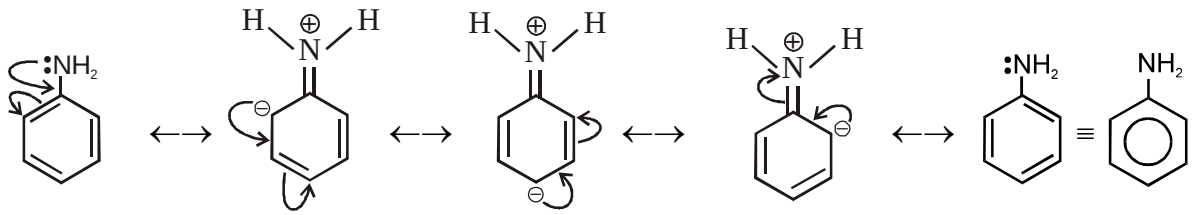
Condition : (i) Vacant orbital must be present

(ii) Multiple bond with more electron negative second atom.

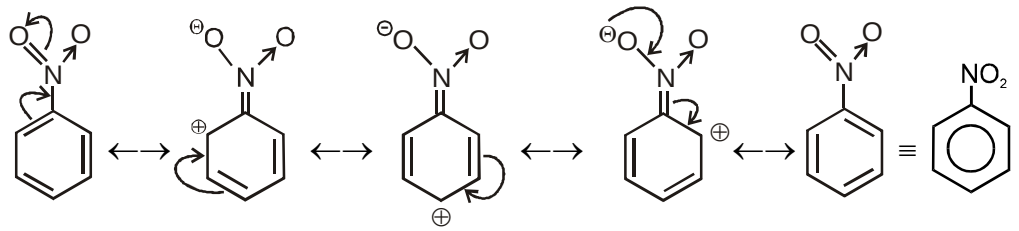
The various resonating structures of chlorobenzene, aniline and nitrobenzene are illustrated in following diagrams. Note that – Cl and – NH_2 show + M effect and – NO_2 show – M effect.



(a) (b) (c) (d) (e)



(a) (b) (c) (d) (e)



(a) (b) (c) (d) (e)

Note :

(i) Thus, mesomeric effect works at only ortho & para position, it is absent on meta position, while inductive effect works at all three position o, m, p however intensity of effect decreases as the distance increases.

(ii) Mesomeric effect always dominates on inductive effect except halogen (Cl, Br, I only).

Application of Mesomeric effect :

(A) Stability of reaction intermediates

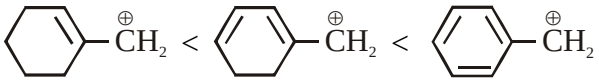
(i) Stability of carbocation

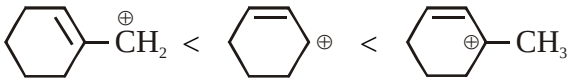
- More resonance in carbocation, more stable.
- Aromatic cations are more stable than non aromatic cations.

Example: Stability order :

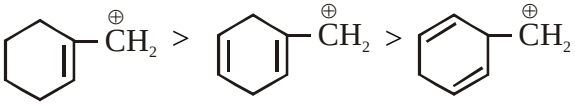
(i) $CH_3-\overset{\oplus}{C}(CH_3)-CH=CH_2 > CH_3-\overset{\oplus}{C}H-CH=CH_2 > \overset{\oplus}{C}H_2-CH=CH_2$

(ii) $CH_2=CH-\overset{\oplus}{C}H_2 > CH_3 \rightarrow CH_2-\overset{\oplus}{C}H_2 > CH_2=CH-CH_2 \leftarrow \overset{\oplus}{C}H_2$

(iii)  Maximum resonance

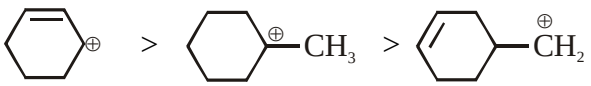
(iv) 

1° 2° 3°

(v) 

(vi) $(C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > C_6H_5\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 > (CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H >$

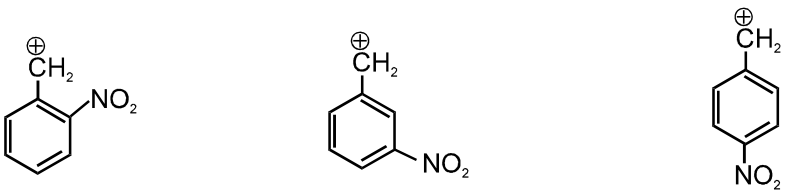
$CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H > CH \equiv \overset{\oplus}{C}$

(vii) 

(viii) $CH_2 = CH - \overset{\oplus}{C}H_2$ Number of resonating Structures = 2

$C_6H_5 - \overset{\oplus}{C}H_2$ Number of resonating Structures = 4

Hence the benzyl carbocation is more stable than the allyl carbocation.

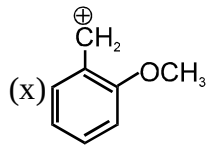
(ix) 

(I) Increase in positive charge by –I and – R effect

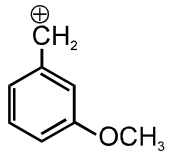
(II) Increase in positive charge only by –I effect

(III) Increase in Positive charge by –I and – R effect

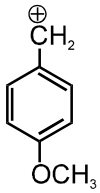
stability order II > III > I

(x) 

Stabilised by + R effect
destabilised by –I effect
–I power is maximum
(due to distance)



Stabilised by
–I effect only



Stabilised by + R effect
destabilised by –I effect
–I power is minimum
(due to distance)

stability order III > I > II

(ii) Stability of carbanion : More resonance in carbanion, more stable

Example: stability order for following

(i) $CH_2=CH-\overset{\ominus}{C}H_2$, $CH_2=\overset{\ominus}{C}H$, $CH_3-\overset{\ominus}{C}H_2$

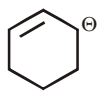
stability order I > II > III

(ii) $\overset{\ominus}{C}H_2-OH$ > $\overset{\ominus}{C}H_2-CH_2-OH$ > $\overset{\ominus}{C}H_2-CH_2-CH_2-OH$

maximum(–I) Minimum (–I) of OH

(iii) $\overset{\ominus}{C}H_2-NO_2$ $\overset{\ominus}{C}H_2-CH_2-NO_2$ $CH_3-\overset{\ominus}{C}H_2-NO_2$

stability order I > III > II

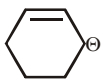
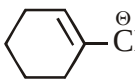
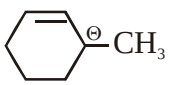
(iv)  ,  , 

resonance more resonance localized ⊖ charge

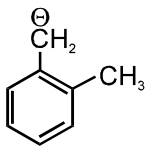
stability order II > I > III

(v) $(C_6H_5)_3\overset{\ominus}{C} > (C_6H_5)_2\overset{\ominus}{C}H > C_6H_5\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2 > CH_2=\overset{\ominus}{C}H$

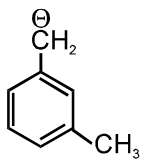
$\overset{\ominus}{C}H_3 > CH_3-\overset{\ominus}{C}H_2 > (CH_3)_2-\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

(vi)  >  > 

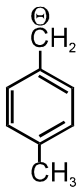
2° anion 1° anion 3° anion

(vii) 

+R effect decrease
stability
+I effect also decrease
stability
+I power is maximum

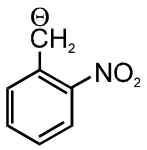
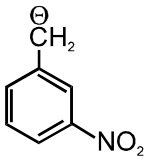
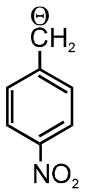


Destabilised only
only by +I effect only

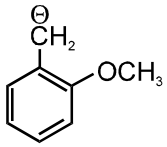
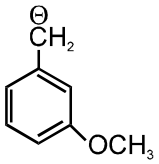
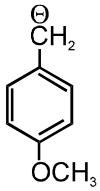


Destabilised only
by + R and + I effect
(+ I power is minimum)

Stability order II > III > I

(viii)   

stability order I > III > II

(ix)   

stability order II > I > III

(iii) Stability of free radicals.

- More resonance, more stable

Example: Stability order

(i) $CH_2=CH-\dot{C}H_2$ $CH_2=\dot{C}H$ $CH_2=CH-\dot{C}H-CH=CH_2$

less resonance no resonance more resonance

stability order III > I > II

(ii)  ,  , 

resonance more resonance localized

stability order II > I > III

(iii) $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > (C_6H_5)\dot{C}H_2 > CH_2=CH-\dot{C}H_2 > (CH_3)_3\dot{C}$

$> (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

(B) Acidic Strength

$$\text{Acidic strength} \propto \text{stability of conjugate base} \propto -\text{M effect} \propto \frac{1}{+\text{M}} \propto -\text{I} \propto \frac{1}{+\text{I}}$$

Acidity of Phenol v/s alcohol

$C_6H_5OH \longrightarrow C_6H_5\overset{\ominus}{O} + \overset{\oplus}{H}$

stabilized by resonance

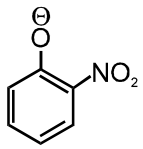
$R-OH \xrightarrow{-H^{\oplus}} R-O^{\ominus} + -H^{\oplus}$

no resonance

thus acidic strength of phenol > alcohol

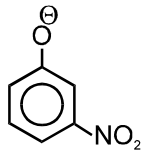
more is the stability of phenoxide ion more will be the acidity of phenol

Acidity of Substituted Phenols : Acidity of substitued phenols depend on the stability of the phenoxide ion because acidity is the function of conjugate base.



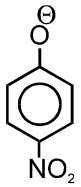
I

Stabilised by–R and –I effect and –I power is maximum



II

Stabilised by –I effect only



III

Stabilised by–R and –I effect and –I power is maximum

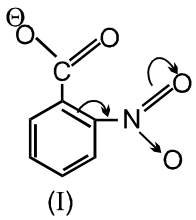
stability order I > III > II

Thus according to stability of anions o-derivative will be more acidic than p-derivative which will be more acidic than m-derivative. But result is as follows in case of nitrophenols, p-derivative is more acidic than o-derivative which is more acidic than m-derivative. In o-derivative , there is intramolecular hydrogen bonding which decrease acidity. Thus order of acidity is as follows :

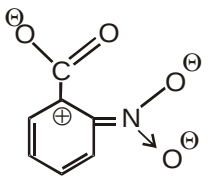
p-derivative > o-derivative > m- derivative > phenol.

Acidity in decreasing order

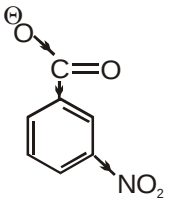
Acidity of substituted acids Ortho substituted banzoic acid is always a stronger acid than m- and p-derivative due to the ortho effect.



(I)

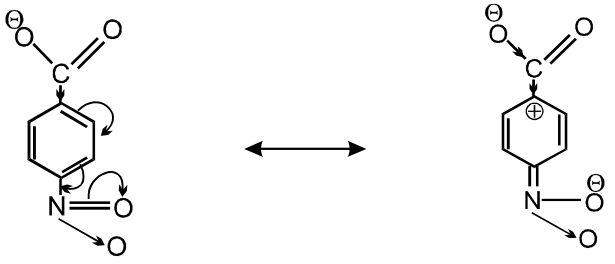


Thus, anion is stabilised by –R and –I effect and – I power is maximum.



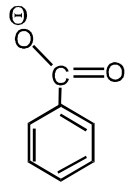
(II)

Anion is stabilised only by –I effect of NO_2 group



(III)

Anion is stabilised by -R and –I effect of NO_2 group



(IV)

Thus decreasing order of the stability of these anions is follows : I > III> II > IV

We know that ortho derivative is the most acidic therefore decreasing order of acidity of these acids is as follows :

o-derivative > p-derivative > m-derivative > benzoic acid

$\longrightarrow$

Acidity in decreasing order

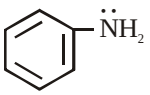
(C) Basic Strength

basic strength $\propto$ +M $\propto \frac{1}{-M} \propto$ + I $\propto \frac{1}{-I}$

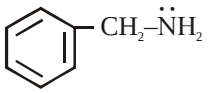
Basicity of Aromatic Amines : Basicity of nitrogen containing compounds $\propto$ Electron density on nitrogen.

In aromatic amines, lone pair of elecrons present on nitrogen is delocalised, hence electron density decrease due to resonance.

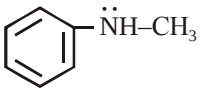
Ex. $C_6H_5NH_2$ is less basic than CH_3NH_2



ℓ.p. is participating in resonance
(I)



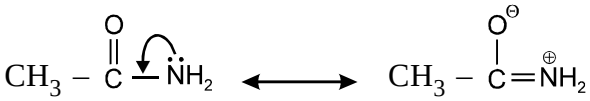
no reso. of ℓ.p. so maximum basic
(II)



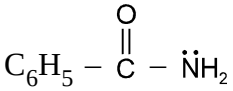
ℓ.p. is participating in resonance and +I of CH_3
(III)

basic order II > III > I

Effect of cross conjugation on basicity :



Due to delocalisation and – I effect of  group, amides are less basic than amines.



In this amide there is cross conjugation which increases basicity; thus $C_6H_5CONH_2$ is more basic than CH_3CONH_2. π bond of C = O group is in conjugation to benzene ring as well as lp of NH_2 group.

(D) Aromaticity

(a) Aromatic Character of Compounds : According to the **Hückel rule,** a compound will be aromatic if it fulfils the following four conditions :

(i) Compound should be cyclic

(ii) Compound should be planar or nearly planar.

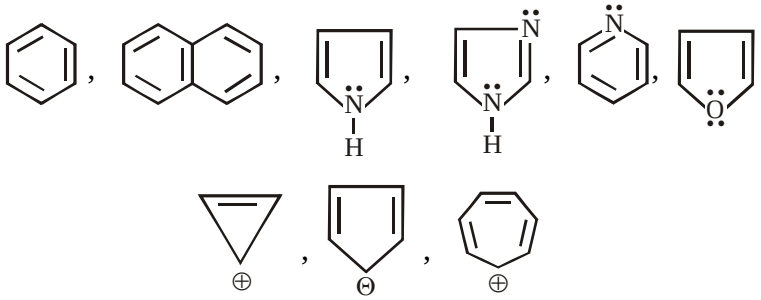
(iii) Compound should be conjugated through out ring and

(iv) Compound should have $(4n + 2)\pi$ conjugated or delocalised electrons where n is a whole number

n = 0, 1, 2, 3, 4, 5, 6, ...

n =		0,	1,	2,	3,	4,	5.....
$(4n + 2)\pi e^-$	=	2	6	10	14	18	22....

Exmples :



(b) Antiaromatic Compounds : According to Huckel rule, compound will be antiaromatic if it fulfits the following four conditions :

(i) Compound should be cyclic

(ii) Compound should be planar.

(iii) Compound should be conjugated through out ring and

(iv) Compound should have $(4n)\pi$ conjugated or delocalised electrons where n is a whole number

n = 1, 2, 3, 4, 5, 6

n =		1,	2,	3,	4,	5.....
$(4n)\pi e^-$	=	4	8	12	16	20.....

Example 

(c) Non aromatic compounds : these compounds are niether aromatic nor antiaromatic

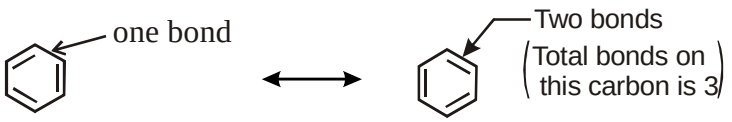
Example 

Although cyclooctatetraene has $(4n)\pi$ electrons but even then it is not an antiaromatic. Geometry of this compound is non planar. Thus it is non aromatic.

(E) Bond order : Bond order in conjugated compound or bond order in compounds which exhibit resonance

$$= \frac{\text{Total number of bonds on central atom}}{\text{Number of resonating structures}}$$

For examples :



Bond order of carbon in benzene = $\frac{2+1}{2}$ = 1.5

Example : Give the correct order of bond length of following mentioned compounds.

(i) $CH_3 - CH_2 - \overset{a}{\underset{\cdot\cdot}{N}}H_2$ (ii) $CH_2 = CH - \overset{b}{\underset{\cdot\cdot}{N}}H_2$

no resonance(only single bond charecters) resonance (partial double bond characters)

bond length order a > b

QUESTION BASED ON MESOMERIC EFFECT AND IT'S APPLICATION

Ex.1 Which of the following carboxylic acids is most acidic in character -

(A) o-methyl benzoic acid (B) m-methyl benzoic acid

(C) p-methyl benzoic acid (D) Benzoic acid

Sol. (A) due to ortho effect.

Ex.2 Which one of the following is most acidic-

(A) p-nitrophenol (B) phenol (C) m-nitrophenol (D) o-nitrophenol

Sol. (A) Electron withdrawing group ($-NO_2$) increases the acidity of phenol. Its effect is more dominant when it is present on o- & p- position rather than on m- position.

Ex.3 Consider the followig carbocations -

(a) $CH_3-\overset{\oplus}{C}H_2$ (b) $CH_2=\overset{\oplus}{C}H$ (c) $CH_2=CH-\overset{\oplus}{C}H_2$ (d) $C_6H_5-\overset{\oplus}{C}H_2$

Stability of these carbocations in decreasing order is -

(A) d > c > a > b (B) d > c > b > a (C) c > d > b > a (D) c > d > a > b

Sol. (A) d have more resonating structure than c

Ex.4 Increasing order of acid strength among p - methoxy phenol, p-methyl phenol and p-nitrophenol is-

(A) p- nitrophenol, p-methoxyphenol, p- methylphenol

(B) p- methylphenol, p- methoxyphenol, p-nitrophenol

(C) p- nitrophenol, p- methylphenol, p- methoxyphenol

(D) p- methoxyphenol, p- methylphenol, p- nitrophenol.

Sol. (D) Electron withdrawing group ($-NO_2$) increases acidity of phenol. Whereas electron releasing group ($-OCH_3$, $-CH_3$) decreases the acidity of phenol

Ex.5 The groups which when present in para position tend to decrease the acidity of phenol are-

(A) $-NO_2$ (B) $-CN$ (C) $-OCH_3$ (D) $-F$

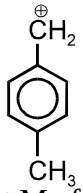
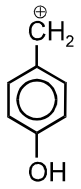
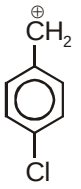
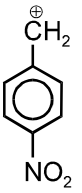
Sol. (C) Electron releasing group decreases the acidity of phenol whereas electron withdrawing group increase the acidity of phenol.

Ex.6 Which free radical is the most stable -

(A) $C_6H_5-\dot{C}H_2$ (B) $CH_2=CH-\dot{C}H_2$ (C) $CH_3-\dot{C}H-CH_3$ (D) $CH_3-\overset{\cdot}{\underset{|}{C}}(CH_3)-CH_3$

Sol. (A) more resonance due to phenyl group

Ex.7 Which carbocation is the most stable -

(A)  (B)  (C)  (D) 

Sol. (B) +M effect of –OH is highest, which decrease magnitude of charge thus stability increases.

3.4 Hyperconjugation :

(i) delocalization of conjugated (C–H) sigma electrons with π-bond or positive charge or free radical is called hyperconjugation or H-effect.

(ii) hyperconjugating structures may be written involving "no bond" between the alpha carbon and hydrogen atoms so known as **"no bond resonance."**

(iii) Nathan baker observed this effect so known as "Nathan baker effect"

(iv) It is also permanent effect

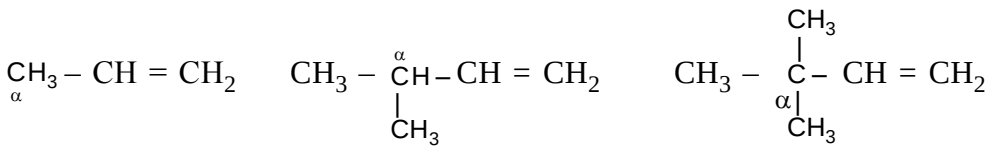
Condition for hyperconjugation:

(i) Compound should have at least one sp^2-hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.

(ii) α-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen. If both these conditions are fulfilled then hyperconjugation will take place in the molecule.

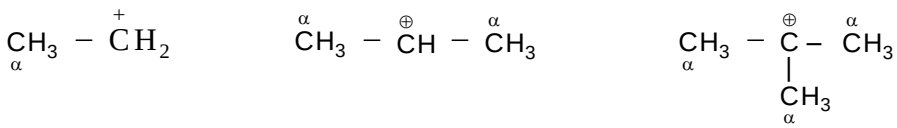
Hyperconjugation is of three types :

(i) σ (C – H), π hyperconjugation : This type of conjugation occurs in alkenes.



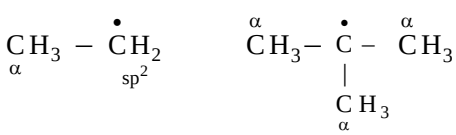
no. of α H = 3 no. of α H = 1 no. of α H = 0

(ii) σ (C – H), vacant orbital (positive charge) hyperconjugation : This type of conjugation occurs in alkyl carbocation.



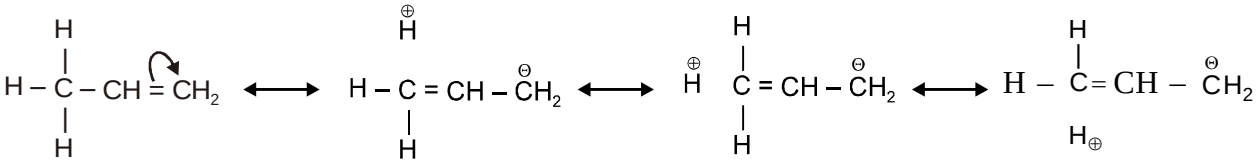
no. of α H = 3 no. of α H = 6 no. of α H = 9

(iii) σ (C – H), odd electron hyperconjugation : This type of conjugation occurs in alkyl free radicals -



Note: If there is one –C–H sigma bond alternate with negative charge then there will be no H-effect

(D) Resonating structures due to hyperconjugation may be written involving "no bond" between the alpha carbon and hydrogen atoms.

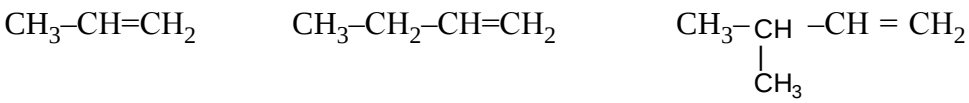


In the above resonating structures there is no covalent bond between carbon and hydrogen. From this point of view, hyperconjugation may be regarded as **" no bond resosnance "**.

Application of Hyperconjugation :

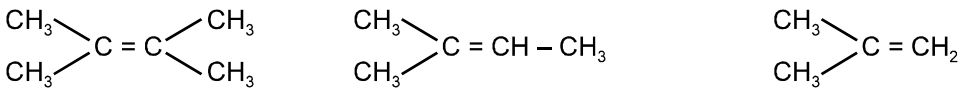
(A) **Stability of Alkenes :** Hyperconjugation explains the stability of certain alkenes over other alkenes:

Stability of alkenes ∝ Number of alpha hydrogens ∝ Number of hyperconjugating structures



(I) (II) (III)

stability order I > II > III



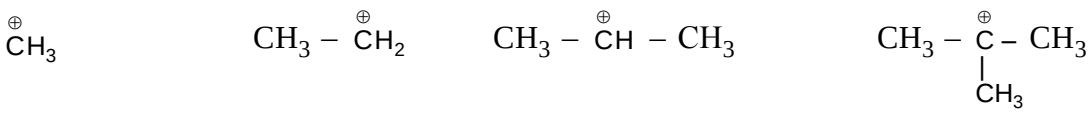
(I) (II) (III)

stability order I > II > III

(B) **Bond length in alkenes:** More is the number of hyperconjugating structures, the more will be single bond character in carbon-carbon double bond.

The bond length between carbon-carbon double bond ∝ number of hyperconjugating structures.

(C) **Stability of Alkyl Carbocations :** Stability of alkyl carbocations ∝ number of hyperconjugating structures ∝ number of α–hydrogens.



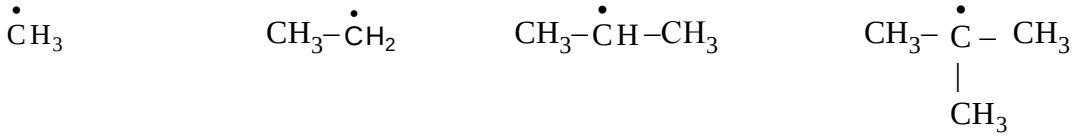
(I) (II) (III) (IV)

no. of α H = 0 no. of α H = 3 no. of α H = 6 no. of α H = 9

stability order IV > III > II > I

(D) Stability of Alkyl free radicals : Stability of alkyl free radicals can be explained by hyperconjugation. Stability depends on the number of hyperconjugating structures.

structure



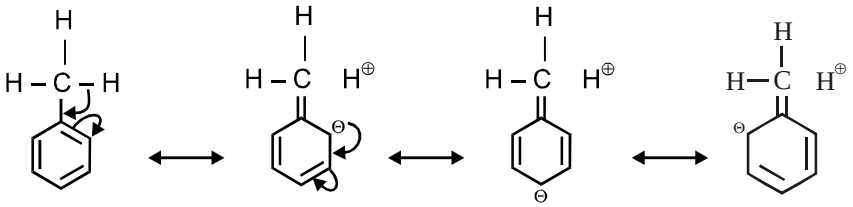
(I)	(II)	(III)	(IV)
no. of α H = 0	no. of α H = 3	no. of α H = 6	no. of α H = 9

No of hyperconjugating Str. 0 4 7 10

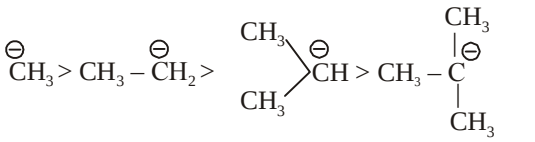
(i) Number of hyperconjugating structuresin increasing order

(ii) Stability is in increasing order

(E) Electron releasing (or donating) power of –R in alkyl benzene : CH_3 – (or alkyl group) is +H group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.



The electron donating power of alkyl group will depends on the number of resonating structures, this depends on the number of hydrogens present on α-carbon. The electron releasing power of some groups are as follows -



Electron donating power in decreasing order due to the hyperconjugation

(F) Heat of hydrogenation (HOH) :

$R–CH=CH_2 + H_2 \longrightarrow R–CH_2CH_3 + \Delta H$

(a) heat evolved when any unsaturated hydrocarbon are hydrogenated is called heat of hydrogenation (ΔH) If alkene is more reactive towards hydrogen then it will evolve more ΔH.

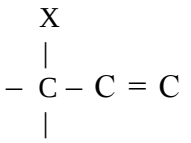
So, $\boxed{\Delta H \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\text{number of } \alpha\text{-H}}}$

(b) $\Delta H \propto$ number of π bonds

(c) It is exothermic process (energy release)

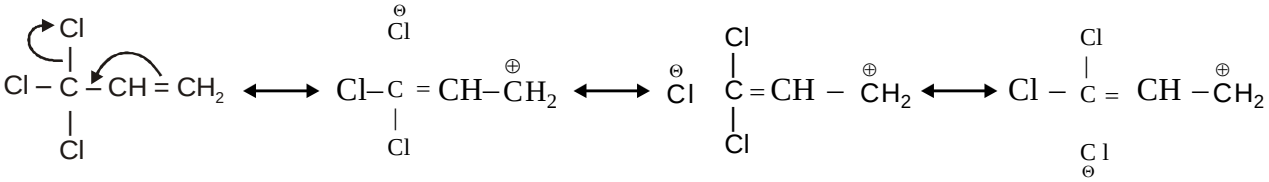
Note : Reverse Hyperconjugation (–H effect) :

The phenomenon of hyperconjugation is also observed in the system given below :

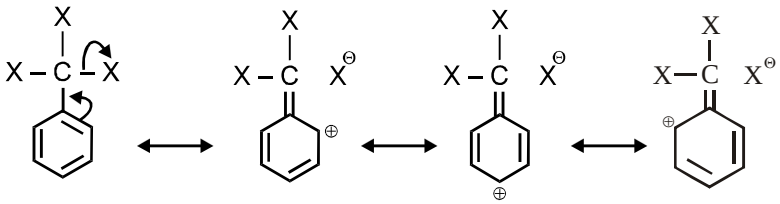


where X - halogen

In such system the effect operates in the reverse direction. Hence the hyperconjugation in such system is known as reverse hyperconjugation.



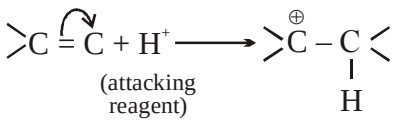
The meta directing influence and deactivating effect of $-CX_3$ group for electrophilic aromatic substitution reaction can be explained by this effect.



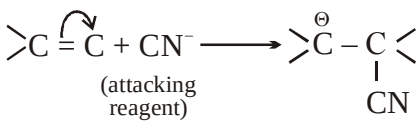
3.5 Electromeric Effect : (E-Effect)

- It is temporary effect.
- The organic compounds having a unsaturation (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.
- The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction.
- It is represented by E and the shifting of the electrons is shown by a curved arrow (↷).
- When inductive and electromeric effect operate in opposite directions, the electomeric effect predominates.
- There are two distinct types of electromeric effect.

(i) Positive Electromeric Effect (+E effect) : In this effect the π-electrons of the multiple bond are transferred to thet atom to which the reagent gets attached. For example :



(ii) Negative Electromeric Effect (–E effect) : In this effect the π-electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example.



QUESTION BASED ON HYPERCONJUGATION

Ex.1 Which of the following is most stable carbocation.

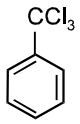
(A) $CH_3-\overset{+}{C}H_2$ (B) $CH_3-\overset{+}{C}H-CH_3$ (C) $CH_3-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-CH_3$ (D) $(CH_3-CH_2)_3\overset{+}{C}$

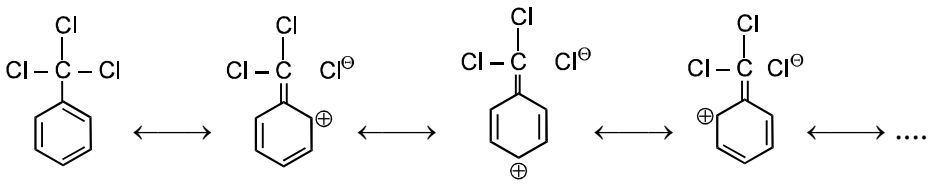
Sol. **(C)** Because $CH_3-\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-CH_3$ has '9' α H atoms which is maximum in all four examples.

Ex.2 Deactivating effect of $-CCl_3$ can be explained on the basis of

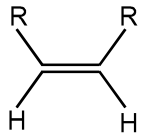
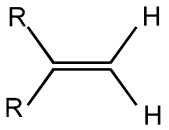
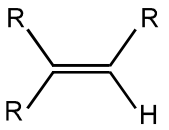
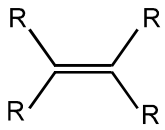
(A) –I effect (B) + R effect

(C) negative hyper conjugative effect (D) none

Sol. **(C)** There is a negative hyperconjugative in  as -



Ex.3 Which of the following alkenes will react fastest with H_2 under catalytic hydrogenation conditions-

(A)  (B)  (C)  (D) 

Sol. **(A)**

Ex.4 Which of following has maximum hydrogenation energy.

(A) $CH_3-CH_2-CH=CH_2$ (B) $CH_3-CH=CH-CH_3$ (cis)

(C) $CH_3-CH=CH-CH_3$ (trans) (D) All have the same

Sol. **(A)** Due to lower no. of α 'H' it is unstable than others.

Ex.5 Which statement is correct for electromeric effect -

(A) It is a temporary effect

(B) It is the porperty of π bond

(C) It takes place in presence of reagent, i.e., electrophile or nucleophile

(D) All are correct

Sol. **(D)**

4. ATTACKING REAGENTS

The species which attack on a substrate and form a product is called as attacking reagents. These are of two types

(A) Electrophile (B) Neucleophile

(A) Electrophiles or electrophilic reagents ($E^{\oplus}$):

(a) They are electron deficient species.

(b) They have a tendency to accept electron from another molecule

(c) In a reaction, an electrophile attacks the substrate at the point of maximum electron density.

Types of Electrophile :

(i) Positively charged electrophiles

$\overset{\oplus}{H}$, $\overset{\oplus}{NO}$, $\overset{\oplus}{R}(\overset{\oplus}{CH_3}, \overset{\oplus}{C_2H_5})$, $\overset{\oplus}{SO_3H}$

(ii) Neutral electrophiles

(a) All Lewis acids as : BF_3, $AlCl_3$, SO_3, $ZnCl_2$, $BeCl_2$, $FeCl_3$, $SnCl_4$

(b) Free radicals, carbenes acts as electrophiles.

(c) Transition metal cations are electrophiles, e.g. Fe^{3+}, Fe^{+}, Ag^{+}, Cd^{2+} etc.

(B) Neucleophlic reagents or nucleophiles :

(a) They are electron rich species so they have a tendency to donate electron pair.

(b) All nucleophiles are lewis bases.

(c) They attack the centre of minimum electron density in a molecule in a chemical reaction.

Types of Neucleophile :

(i) Negatively Charged nucleophiles :

F^-, Cl^-, Br^-, I^-, OH^-, CN^-, $RCOO^-$, RO^-, R^-, $R-C\equiv C^-$, NH_2^-, SH^- etc.

(ii) Neutral nucleophile containing lone pair :

$H_2\ddot{O}$, $R-\ddot{O}H$, $R-\ddot{O}-R$, $\ddot{N}H_3$, $R-\ddot{N}H_2$

(iii) π electron containing compounds

$CH_2=CH_2$, $CH\equiv CH$

(C) Ambiphiles :

Ambiphiles are those which act as both electrophile and nucleophile.

Example :

$R-CH=\ddot{O}$, RCOR, RCOOH etc.

S. No.	Electrophile	Nucleophile
1	Accept electron	Supplies the electron pair
2	Electron deficient (electron loving)	Electron rich
3	Usually positively charged species	Usually negatively charged species
4	Attacks the points of high electron density	Attacks the point of low electron denisty
5	e.g., $\overset{\oplus}{H}$, $\overset{\oplus}{CH_3}$, CO_2 $\overset{\oplus}{NO}$	e.g., F^-, Cl^-, Br^-, I^-, H_2O

QUESTION BASED ON ATTACKING REAGENTS

Ex.1 Select the nucleophile-

(A) BF_3 (B) Cl^+ (C) $AlCl_3$ (D) C_2H_4

Sol. **(D)**

Ex.2 An electrophile among the following is-

(A) NH_3 (B) CH_3NH_2 (C) H_2O (D) $AlCl_3$

Sol. **(D)**

Nucleophile : H–O–H, NH_3, CH_3–NH_2

Electrophile : $AlCl_3$ (6 electron)

Ex.3 A nucleophile is :

(A) electron-rich species (B) electron-deficient species

(C) a Lewis acid (D) Positively charged species

Sol. **(A)** A nucleophile is electron-rich species

Ex.4 Which of the following species is an electrophile ?

(A) NH_3 (B) OH^- (C) CH_4 (D) SO_3

Sol. **(D)** Nucleophile : OH^-, NH_3

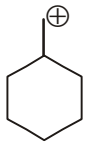
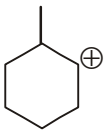
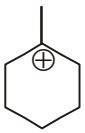
CH_4 is neither electrophile nor nucleophile.

EXERSICE # I

Q.1 The shape of CH_3^+ cation is likely to be:
(A) pyramidal (B) tetrahedral (C) linear (D) planar

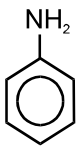
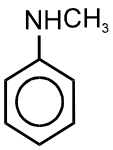
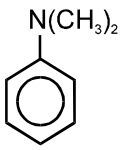
Q.2 Carbon free radicals are -
(A) Diamagnetic (B) Paramagnetic (C) Ferromagnetic (D) Non magnetic

Q.3 Which is the correct stability order of following intermediates:

(a)  (b)  (c) 

(A) a > b > c (B) a > c > b (C) c > b > a (D) b > a > c

Q.4 Arrange in Increasing of basic strength

I II III

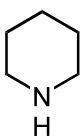
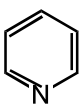
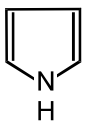
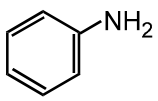
(A) II < III < I (B) I > II > III (C) III > II < I (D) I < II < III

Q.5 Which is the correct order of increasing basicity ?
(A) $CH_3CH_2CH_3 < CH_3CH_2SH < CH_3CH_2OH < CH_3CH_2NH_2$
(B) $CH_3CH_2CH_3 < CH_3CH_2OH < CH_3CH_2SH < CH_3CH_2NH_2$
(C) $CH_3CH_2NH_2 < CH_3CH_2SH < CH_3CH_2OH < CH_3CH_2CH_3$
(D) $CH_3CH_2CH_3 < CH_3CH_2OH < CH_3CH_2NH_2 < CH_3CH_2SH$

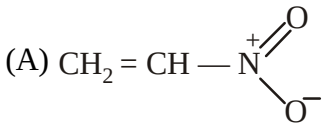
Q.6 Arrange in increasing order of basicity :
CH_3NH_2, $(CH_3)_2NH$, $C_6H_5NH_2$, $(CH_3)_3N$
(A) $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2 < C_6H_5NH_2$
(B) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > C_6H_5NH_2$
(C) $C_6H_5NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$
(D) $C_6H_5NH_2 > (CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$

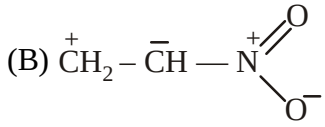
Q.7 Which of the following orders of acid strength is correct ?
(A) RCOOH > ROH > HOH > HC ≡ CH (B) RCOOH > HOH > ROH > HC ≡ CH
(C) RCOOH > HOH > HC ≡ CH > ROH (D) RCOOH > HC ≡ CH > HOH > ROH

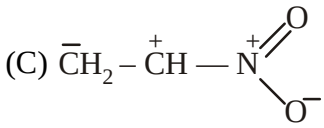
Q.8 Which of the following is the strongest base -

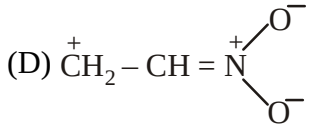
(A)  (B)  (C)  (D) 

Q.9 Select the least stable resonating structure among following carbocation.

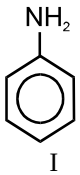
(A) 

(B) 

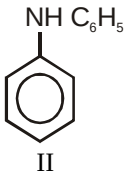
(C) 

(D) 

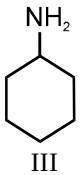
Q.10 Arrange the following in increasing of pH value



I



II



III

(A) II < I < III (B) III < I < II (C) III < II < I (D) II < III < I

Q.11 Polarisation of electrons in acrolein may be written as :

(A) $\overset{\delta+}{C}H_2 = CH - CH = \overset{\delta-}{O}$ (B) $\overset{\delta+}{C}H_2 = CH - \overset{\delta-}{C}H = O$

(C) $\overset{\delta-}{C}H_2 = \overset{\delta+}{C}H - CH = O$ (D) $\overset{\delta-}{C}H_2 = CH - CH = \overset{\delta+}{O}$

Q.12 Hyperconjugation occur due to overlaping of-

(A) π M.O. with 's' (B) 'p' orbital with σ

(C) σ M.O. with π M.O. (D) None

Q.13 Hyperconjugation is best described as:

(A) Delocalisation of π electrons into a nearby empty orbital.

(B) Delocalisation of σ electrons into a nearby empty orbital.

(C) The effect of alkyl groups donating a small amount of electron density inductively into a carbocation.

(D) The migration of a carbon or hydrogen from one carbocation to another.

Q.14 Which of the following properties cannot be explained on the basis of hyperconjugation.

(A) Dipole moment of $CH_3 - NO_2$ (B) o-p directing character of $-CH_3$ group.

(C) Greater stability of $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_2^{\oplus}$ (D) Meta directing character of CCl_3 group.

Q.15 Which of the following is an electrophilic reagent ?

(A) H_2O (B) OH^- (C) NO_2^+ (D) None

Q.16 Which among the following is not a Lewis acid

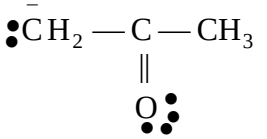
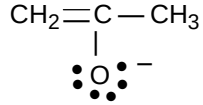
(A) BF_3 (B) $AlCl_3$ (C) NH_3 (D) Hg^{2+}

Q.17 Which of the following is an electrophile

(A) NH_3 (B) ROH (C) ^-OR (D) BCl_3

Q.18 Which of the following is not a nucleophile

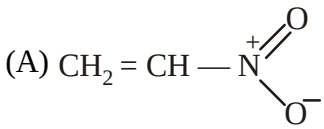
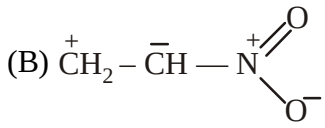
(A) NH_3 (B) BF_3 (C) ^-OH (D) HSO_3^-

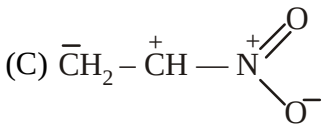
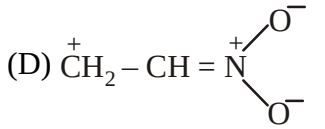
Q.19  and  are –

(A) resonating structures (B) tautomers

(C) geometrical isomers (D) optical isomers

Q.20 Select the least stable resonating structure among following carbocation.

(A)  (B) 

(C)  (D) 

Q.21 'M' effect is the resonance of -

(A) π electrons only (B) σ electrons only

(C) π and σ both (D) (+)ve and (-)ve charge.

Q.22 Which of the following is the strongest - I group -

(A) $-N^+(CH_3)_3$ (B) $-{}^+NH_3$ (C) $-{}^+S(CH_3)_2$ (D) –F

Q.23 Which of the following orders is correct regarding the – I effect of the substituents ?

(A) $-NR_2 > -OR > -F$ (B) $-NR_2 < -OR < -F$

(C) $-NR_2 > -OR < -F$ (D) $-NH_2 < -OR > -F$

Q.24 Zero inductive effect is exerted by :

(A) C_6H_5- (B) H (C) CH_3- (D) Cl

Q.25 Inductive effect refers to :

(A) Electron displacement along a carbon chain

(B) Complete transfer of one of the shared pair of electrons to one of the atoms joined by a double bond.

(C) Complete transfer of electrons either to unshared

(D) None of the above

Q.26 Heterolysis of propane will yield :

(A) CH_3 and C_2H_5 radicals (B) CH_3^- and $CH_3CH_2^+$ ions

(C) CH_3^+ and $CH_3CH_2^-$ ions (D) CH_3^+ and $CH_3CH_2^+$ ions

Q.27 Homolytic fission of C—C bond in ethane gives an intermediate in which carbon is

(A) sp hybridised (B) sp^2 hybridised (C) sp^3 hybridised (D) sp^2d hybridised

Q.28 The homolytic fission of a covalent bond produces

(A) free radicals (B) carbonium ions (C) carbanions (D) carbenes

Q.29 Which among the given acid has lowest pKa value -

(A) Chloroacetic acid (B) Bromoacetic acid

(C) Nitroacetic acid (D) Cyanoacetic acid

Q.30 Rank the following radicals in order of Decreasing stability

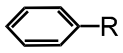


I II III IV

(A) III > II > I > IV (B) III > II < I < IV (C) II > III > II > IV (D) III < II < I < IV

EXERSICE # II

Q.1 In the following benzyl/alkyl system

$R - CH = CH_2$ or  (R is alkyl group)

increasing order of inductive effect is – **[AIEEE-2002]**

(A) $(CH_3)_3\ C - > (CH_3)_2\ CH \rightarrow CH_3CH_2$—

(B) $(CH_3CH_2 - > (CH_3)_2\ CH \rightarrow (CH_3)_3C$ —

(C) $(CH_3)_2\ CH - > CH_3CH_2 \rightarrow (CH_3)_3C$—

(D) $(CH_3)C - > CH_3CH_2 \rightarrow (CH_3)_2CH$—

Q.2 When $-CH_3$, $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{CH}}}-$ & $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}-$ groups are introduced on benzene ring then correct order

of their inductive effect is - **[AIEEE-2002]**

(A) $CH_3- > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{CH}}}- > CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}-$

(B) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}- > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{CH}}}- > CH_3-$

(C) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{CH}}}- > CH_3- > CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}-$

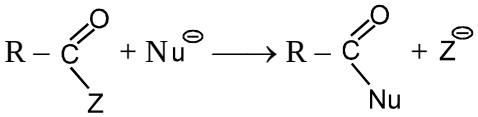
(D) $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}- > CH_3- > CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{|}{CH}}}-$

Q.3 The correct order of increasing basic no. of the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is – **[AIEEE-2003]**

(A) $NH_3 < CH_3NH_2 < (CH_3)_2NH$ (B) $CH_3NH_2 < (CH_3)_2NH < NH_3$

(C) $CH_3NH_2 < NH_3 < (CH_3)_2NH$ (D) $(CH_3)_2NH < NH_3 < CH_3NH_2$

Q.4 Rate of the reaction **[AIEEE-04,05]**



is fastest when Z is -

(A) Cl (B) NH_2 (C) OC_2H_5 (D) $OCOCH_3$

Q.5 Consider the acidity of the carboxylic acids : **[AIEEE-2004]**

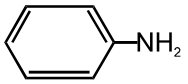
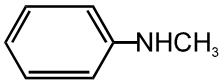
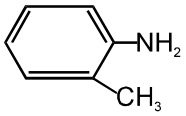
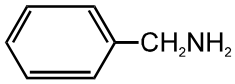
(a) PhCOOH (b) o – $NO_2C_6H_4COOH$

(c) p – $NO_2C_6H_4COOH$ (d) m – $NO_2C_6H_4COOH$

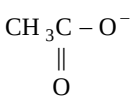
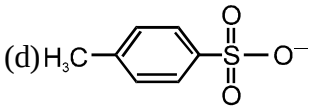
Which of the following order is correct ?

(A) a > b > c > d (B) b > d > c > a (C) b > d > a > c (D) b > c > d > a

Q.6 Which of the following is the strongest base - **[AIEEE-2004]**

(A)  (B)  (C)  (D) 

Q.7 The decreasing order of nucleophilicity among the nucleophiles **[AIEEE-2005]**

(a)  (b) CH_3O^- (c) CN^- (d) 

is

(A) d > c > b > a (B) a > b > c > d (C) c > b > a > d (D) b > c > a > d

Q.8 Amongst the following the most basic compound is– **[AIEEE-2005]**

(A) aniline (B) benzylamine (C) p–nitroaniline (D) acetanilide

Q.9 The increasing order of stability of the following free radicals is – **[AIEEE 2006]**

(A) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(B) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(C) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

(D) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

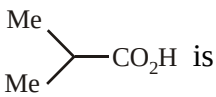
Q.10 $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is

[Nu^- = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-] **[AIEEE 2006]**

(A) D > C > B > A (B) A > B > C > D (C) B > D > C > A (D) D > C > A > B

Q.11 The correct order of increasing acid strength of the compounds **[AIEEE 2006]**

(a) CH_3CO_2H (b) $MeOCH_2CO_2H$ (c) CF_3CO_2H (d)  is

(A) d < a < c < b (B) d < a < b < c (C) a < d < c < b (D) b < d < a < c

Q.12 Which one of the following is the strongest base in aqueous solution ? **[AIEEE-2007]**

(A) Trimethylamine (B) Aniline (C) Dimethylamine (D) Methylamine

Q.13 Presence of a nitro group in a benzene ring- **[AIEEE 2007]**

(A) activates the ring towards electrophilic substitution

(B) renders the ring basic

(C) deactivates the ring towards nucleophilic substitution

(D) deactivates the ring towards electrophilic substitution

Q.14 Arrange the carbanions, $(CH_3)_3\overset{\ominus}{C}$, $\overset{\ominus}{C}Cl_3$, $(CH_3)_2\overset{\ominus}{C}H$, $C_6H_5\overset{\ominus}{C}H_2$, in order of their decreasing stability- **[AIEEE 2009]**

(A) $(CH_3)_2\overset{\ominus}{C}H > \overset{\ominus}{C}Cl_3 > C_6H_5\overset{\ominus}{C}H_2 > (CH_3)_3\overset{\ominus}{C}$

(B) $\overset{\ominus}{C}Cl_3 > C_6H_5\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

(C) $(CH_3)_3\overset{\ominus}{C} > (CH_3)_2\overset{\ominus}{C}H > C_6H_5\overset{\ominus}{C}H_2 > \overset{\ominus}{C}Cl_3$

(D) $C_6H_5\overset{\ominus}{C}H_2 > \overset{\ominus}{C}Cl_3 > (CH_3)_3\overset{\ominus}{C} > (CH_3)_2\overset{\ominus}{C}H$

Q.15 The correct order of increasing basicity of the given conjugate bases (R = CH_3) is : **[AIEEE 2010]**

(A) $RCO\overset{\ominus}{O} < \overset{\ominus}{N}H_2 < HC \equiv \overset{\ominus}{C} < \overset{\ominus}{R}$ (B) $RCO\overset{\ominus}{O} < HC \equiv \overset{\ominus}{C} < \overset{\ominus}{N}H_2 < \overset{\ominus}{R}$

(C) $RCO\overset{\ominus}{O} < HC \equiv \overset{\ominus}{C} < \overset{\ominus}{R} < \overset{\ominus}{N}H_2$ (D) $\overset{\ominus}{R} < HC \equiv \overset{\ominus}{C} < RCO\overset{\ominus}{O} < \overset{\ominus}{N}H_2$

Q.16 The strongest acid amongst the followng compounds is **[AIEEE 2011]**

(A) CH_3COOH (B) HCOOH

(C) $CH_3CH_2CH(Cl)CO_2H$ (D) $ClCH_2CH_2CH_2COOH$

Q.17 Electromeric effect :

(A) Comes into play at the demand of attacking reagent

(B) Involves displacement of electrons in a sigma bond

(C) Comes into play in the molecule when at least one atom has unshared pair of electrons

(D) Involves the distortion of the electron cloud

Q.18 Which of the following statements is correct about a carbonium ion ?

(A) It reacts with nucleophile (B) It can undergo rearrangement

(C) It can eliminate an H^+ to form an olefin (D) All are correct

Q.19 What is the decreasing order of strength of the bases ,OH^- (I), NH_2^- (II), H – C≡C^- (III), $CH_3CH_2^-$ (IV) ?

(A) IV > II > III > I (B) III > IV > II > I (C) I > II > III > IV (D) II > III > I > IV

Q.20 The meta-directing power of the groups $–NH_2$, $–OCH_3$, $–C_6H_5$ and $– NO_2$ follows the order

(A) $–NH_2 > –OCH_3 > –C_6H_5 > –NO_2$ (B) $–NO_2 > –C_6H_5 > –OCH_3 > –NH_2$

(C) $–OCH_3 > –NH_2 > –C_6H_5 > –NO_2$ (D) $–OCH_3 > –NO_2 > –NH_2 > –C_6H_5$

Q.21 Which one is the correct order of decreasing stability of carbanions ?

(A) P > S > T > $C_6H_5CH_2$ (B) $C_6H_5CH_2$ > P > S > T

(C) T > S > P > $C_6H_5CH_2$ (D) $C_6H_5CH_2$ > T > S > P

Q.22 The stability order in the following carbocations, $CH_3CH_2^+$ (I) $(CH_3)_2CH^+$ (II), $(CH_3)_3C^+$ (III) and $C_6H_5CH_2^+$ (IV) is :
(A) I > IV > III > II (B) I > II > III > IV (C) III > IV > I > II (D) IV > III > II > I

Q.23 Which is the increasing order of acidity in, HCOOH (I), CH_3COOH (II), CH_3CH_2COOH (III) and C_6H_5COOH (IV) ?
(A) I > II > III > IV (B) IV > III > II > I (C) IV > I > II > III (D) I > IV > II > III

Q.24 Which one of the following compounds is most acidic ?
(A) Phenol (B) Trichloro acetaldehyde
(C) Trichloro acetic acid (D) Benzoic acid

Q.25 Correct order of reactivity–
(A) $CH_2=CH_2 > CH_3—CH=CH_2 > (CH_3)_2C=CH_2$
(B) $CH_2=CH_2 > CH_3—CH=CH_2 > (CH_3)_2C=CH_2$
(C) $CH_2=CH_2 < (CH_3)_2C=CH_2 < CH_3—CH=CH_2$
(D) $CH_3—CH=CH_2 < CH_2=CH_2 < (CH_3)_2C=CH_2$

Q.26 In the following compounds phenol (I), p-cresol (II), m-nitrophenol (III) and p-nitrophenol (IV), the order of acidity is :
(A) III > IV > I > II (B) I > IV > III > II (C) II > I > III > IV (D) IV > III > I > II

Q.27 The order of stability of the following carbanion is :

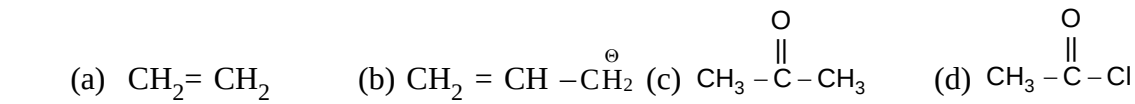


(I) (II) (III) (IV)

(A) I > II > III > IV (B) I > III > II > IV
(C) IV > III > II > I (D) III > IV > I > II

Q.28 Consider the following alkenes :
(a) $H_2C = C(CH_2CH_3)CH(CH_3)_2$ (b) $(CH_3)_2C = C(CH_3)CH_2CH_3$
(c) $CH_3CH = C(CH_3)CH(CH_3)_2$
The correct sequence of increasing order of stability of these alkenes is :
(A) a, b, c (B) c, b, a (C) b, a, c (D) a, c, b

Q.29 Which among the following compounds behave both as an electrophile as well as a nucleophile:



(a) $CH_2= CH_2$ (b) $CH_2 = CH - \overset{\Theta}{C}H_2$ (c) $CH_3 - \overset{O}{\overset{\|}{C}} - CH_3$ (d) $CH_3 - \overset{O}{\overset{\|}{C}} - Cl$

(A) Only a (B) a and b (C) c and d (D) b, c and d

Q.30 Which of the following is most basic ?
(A) N-methyl aniline (B) Aniline
(C) N, N-dimethyl aniline (D) p-nitroaniline

ANSWER KEY

EXERSICE # I

Q.1	D	Q.2	B	Q.3	C	Q.4	D	Q.5	A	Q.6	C	Q.7	B
Q.8	A	Q.9	C	Q.10	A	Q.11	A	Q.12	C	Q.13	B	Q.14	C
Q.15	C	Q.16	C	Q.17	D	Q.18	B	Q.19	A	Q.20	C	Q.21	A
Q.22	A	Q.23	B	Q.24	B	Q.25	A	Q.26	B	Q.27	B	Q.28	A
Q.29	C	Q.30	A										

EXERSICE # II

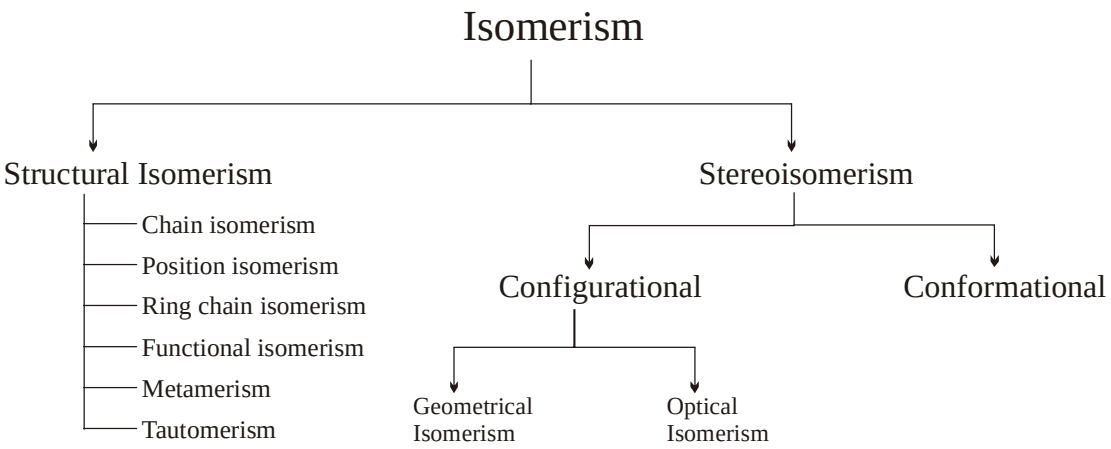
Q.1	A	Q.2	B	Q.3	A	Q.4	A	Q.5	D	Q.6	D	Q.7	D
Q.8	B	Q.9	D	Q.10	D	Q.11	B	Q.12	C	Q.13	D	Q.14	B
Q.15	B	Q.16	C	Q.17	A	Q.18	D	Q.19	A	Q.20	B	Q.21	B
Q.22	D	Q.23	D	Q.24	C	Q.25	B	Q.26	D	Q.27	D	Q.28	D
Q.29	C	Q.30	C										

INTRODUCTION

(i) The compound which have the same molecular formula but differ in physical and chemical properties are called as Isomer and the phenomenon is called Isomerism.

(ii) The term 'isomer' was given by Berzellius.

(iii) The isomer was derived from Greek word meaning 'equal or like part' (isos= equal; meros = parts)



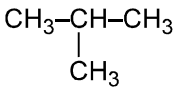
(I) **Structural Isomerism / Constitutional Isomerism** :

Structural isomers possess the same molecular formula but different connectivity of atoms. The term constitutional isomerism is a more modern term of structural isomerism. It is sub-classified into following types.

(i) Chain Isomerism : The different arrangement of carbon atoms gives rise to chain isomerism. Chain isomers possess different lengths of carbon chains (straight or branched). Such isomerism is shown by each and every family of organic compounds.

Butane : C_4H_{10}

$CH_3 - CH_2 - CH_2 - CH_3$ n- butane

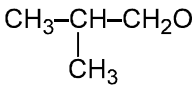


iso butane

n-butane has the chain of four carbon while isobutane has three. Hence they are chain isomers.

Butyl alcohol : C_4H_9OH

$CH_3 - CH_2 - CH_2 - CH_2OH$ n-Butyl alcohol



Isobutyl alcohol

These two butyl alcohols are chain isomers.

(ii) Position Isomerism -Position isomerism is shown by the compounds in which there is difference in the position of attachment of functional group, multiple bond or substituent along the same chain length of carbon atoms -

(i) The same molecular formula

(ii) The same length of carbon chain

(iii) The same functional group.

Example :

(a) $CH_3-CH_2-CH_2Cl$ and $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$

1- Chloropropane 2- Chloropropane

(b) $CH_3-CH_2-CH_2OH$ and $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

1 - propanol 2 - Propanol

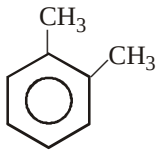
(c) $CH_3-CH_2-CH_2-NH_2$ and $CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3$

n-Propylamine Isopropylamine

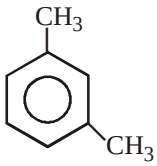
(d) $CH_3-CH_2-CH=CH_2$ and $CH_3-CH=CH-CH_3$

1-Butene 2-Butene

(e)



o-xylene



m-xylene



p-xylene

(iii) Ring chain isomerism –

Such isomerism arises because of the difference of carbon-chain or ring.

For example :

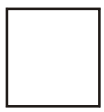
(i)



Cyclopropane $CH_3CH=CH_2$ Propene

Cyclopropane and propene are ring chain isomers.

(ii) $CH_3-CH_2-CH=CH_2$



Cyclobutane

Cyclobutane is the ring-chain isomer of 1-butene.

Note: Acyclic Alkanes do not exhibit ring-chain isomerism.

(iv) Functional group isomerism :

Compounds with the same molecular formula but differing in the type of functional group they possess are classed as functional isomers and isomerism between them is known as functional isomerism. For example:

(a) $CH_3 - CH_2 - OH$ and $CH_3 - O - CH_3$

Ethyl alcohol (Alcohol) — Dimethyl ether (Ether)

(b) $CH_3 - CH_2 - COOH$ and $CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3$

Propanoic acid (Acid) — Methyl acetate (Ester)

(c) $CH_3 - CH_2 - CH_2 - NH_2$ 1° amine

$CH_3 - CH_2 - NH - CH_3$ 2° amine

$CH_3 - \underset{\underset{CH_3}{|}}{N} - CH_3$ 3° amine

(d) Alkyne and Alkadienes

C_4H_6

$CH \equiv C - CH_2 - CH_3$ 1-Butyne

$CH_2 = CH - CH = CH_2$ 1,3-Butadiene

(v) Metamers : This type of Isomerism arises due to unequal distribution of alkyl substituents around a polyvalent functional group.

Some example of Polyvalent functional groups.

–O– Ether

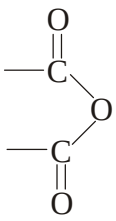
$-\overset{\overset{O}{\|}}{C}-$ Ketone

$-\overset{\underset{|}{}}{N}-$ tert.amine

–S– Thioether

$-\overset{\overset{S}{\|}}{C}-$ Thioketone

– COO – Ester



acid anhydride

Example :-

(i) $CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3 - CH_2$ and $CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3$

(2 – Pentanone) (3 – Pentanone)

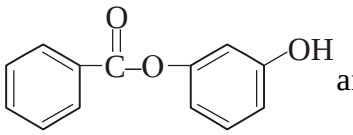
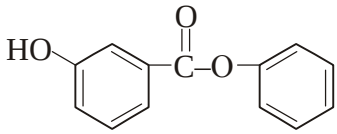
(ii) Diethyl ether and methyl propyl ether

$CH_3CH_2OCH_2CH_3$ (Diethyl ether); $CH_3OCH_2CH_2CH_3$(Methyl propyl ether)

(iii) Diethyl amine and methyl propylamine

$CH_3CH_2 - NH - CH_2CH_3$ (Diethyl amine);

$CH_3\,CH_2CH_2–NH–CH_3$(Methyl propyl amine)

(iv)  and  are metamers

(vi) Tautomerism -

(i) Tautomerism is a special type of functional group isomerism which arises due to the transfer of H-atom as proton from a polyvalent atom to other polyvalent atom.

(ii) Such isomers are directly and readily inter convertible under ordinary conditions, and the isomers are called tautomers.

(iii) Tautomers exist in dynamic equilibrium.

(iv) They have no separate existence under ordinary conditions like other isomers mentioned above.

(v) The other names of tautomerism are 'desmotroprism' or 'prototropy'.

(vi) Tautromerism is thus the property shown by certain compounds exhibiting different properties, as if they posses different structures and these constitutional isomers are called tautomers.

(vii) If the H atom oscillates between two polyvalent atoms linked together, the system is called as *Diad*.

$H - C \equiv N$	$\leftrightarrow$	$C \cong N - H$
Hydrocyanic acid		isocyanic acid

(viii) H atom oscillates in between first and third atoms in a chain, the system is called as triad.

$H - O - C \equiv N \quad \leftrightarrow \quad O = C = N - H$

(a) **Keto - Enol Tautomerism -**

(i) When the tautomers exist in the two forms keto & enol then, such type of tautomerism is called keto-Enol tautomerism'.

(ii) It was discovered by the scientist 'Knorr' in 1911 in acetoacetic ester.

(iii) The Keto means the compound has a Keto group > C = O, and the enol form has both double bond and OH (hydroxy) group Joined to the same carbon.

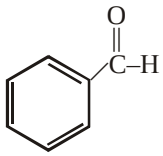


Keto forms Enol forms

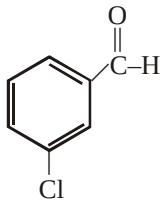
Conditions for tautomerism

(i) Presence of polyvalent atom

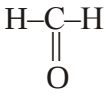
(ii) In order for conversion of a keto form to its enol form it must have an α-hydrogen (i.e., hydrogen attached to the carbon adjacent to the carbonyl group). Thus benzaldehyde, m-chlorobenzaldehyde (in general, aromatic aldehydes) formaldehyde, trimethylacetaldehyde do not exist as their enol forms.



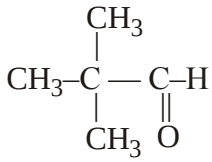
Benzaldehyde



m-Chlorobenzaldehyde



Methanal



Trimethyl-acetaldehyde

(iii) Keto enol tautomerism can occurs both in acidic and basic medium.

Example of Keto enol tautomerism :-

(i) 

Vinyl alcohol ⇔ Acetaldehyde

(ii) 

Aceto acetic ester (Keto form) ⇔ β - Hydroxy crotonic ester (Enol form)

(iii) 

Acetone ⇔ Isopropenyl alcohol

(iv) 

Malonic ester (keto) ⇔ (Enol)

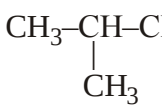
SOLVED EXAMPLE

Ex.1 Aldehydes show with each other -

(A) Chain isomers (B) Position isomers

(C) Functional isomers (D) Both A & B **(Ans. A)**

Sol. $CH_3-CH_2-CH_2-CHO \rightarrow$ 4 membered principal carbon chian



so both structure are chain isomers.

Ex.2 The molecules which exhibit metamerism are :

(A) $C_4H_{10}O$ (ether) (B) C_4H_8 (alkene)

(C) $C_5H_{10}O$ (ketone) (D) $C_4H_{11}N$ (amine) **(Ans. A,C,D)**

Sol. Compound having bivalent functional group like $-O-$, $-\overset{\overset{O}{\|}}{C}-$, $-S-$, $-NH$, $-\overset{\overset{O}{\|}}{C}-O-$ shows metamerism

(A) $C_4H_{10}O$ (ether)

$CH_3 - CH_2 - O - CH_2 - CH_3$ and $CH_3-O-CH_2 - CH_2 - CH_3$

(C) $C_5H_{10}O$ (ketone)

$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ and $H_3C-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$

(D) $C_4H_{11}N$(sec. amine)

$CH_3-CH_2-\underset{\underset{CH_2-CH_3}{|}}{NH}$ and $CH_3 - NH - CH_2 - CH_2 - CH_3$

(B) C_4H_8 (alkene) does not show metamerism.

Ex.3 Compound $C_4H_{10}O$ can show -

(A) Metamerism (B) Functional isomers

(C) Positional isomers (D) All above **(Ans. D)**

Sol. (A) Metamers :

$CH_3 - CH_2 - O - CH_2 - CH_3$

&

$CH_3 - O - CH_2 - CH_2 - CH_3$

(B) Functional isomers :

$CH_3 - CH_2 - CH_2 - CH_2 - OH$

&

$CH_3 - O - CH_2 - CH_2 - CH_3$

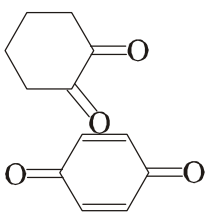
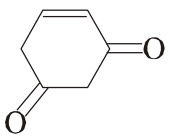
(C) Positional isomers :

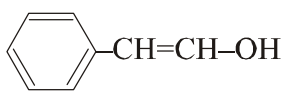
$H_3C - H_2C - CH_2 - CH_2 - OH$

&

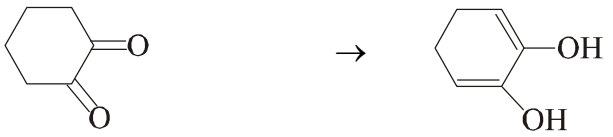
$CH_3 - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_3$

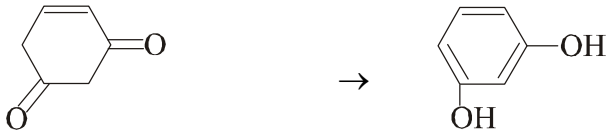
Ex.4 Which of the following compound can exhibit tautomerism.

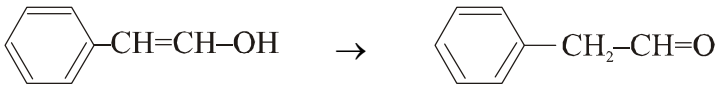
(A)  (B) 

(C) (D) 

(Ans. ABD)

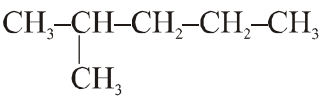
Sol. (A) 

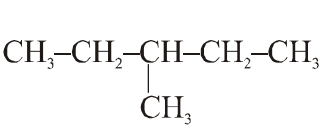
(B) 

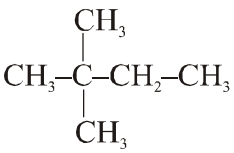
(D) 

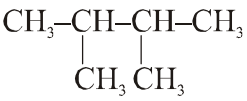
Ex.5 The number of structural isomers shown by C_6H_{14} :
(A) 4 (B) 5 (C) 6 (D) 8 **(Ans. B)**

Sol. Stuctural isomer of C_6H_{14} are shown below :

(A) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$ (B) 

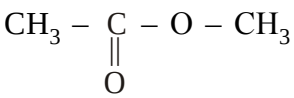
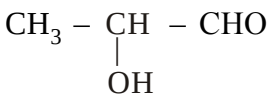
(C) 

(D) 

(E) 

Ex.6 Esters are functional isomers of -
(A) Hydroxy aldehyde (B) Ketone
(C) Diketone (D) Diol **(Ans. A)**

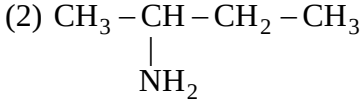
Sol. Ester are functional isomers of hydroxy aldehydes.

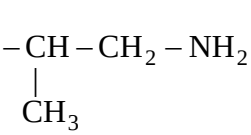
 & 

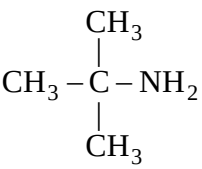
methyl ethenoate 2- hydroxy propanal

Ex.7 How many primary amines are possible for the formula $C_4H_{11}N$?
(A) 1 (B) 2 (C) 3 (D) 4 **(Ans. D)**

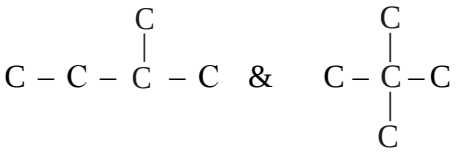
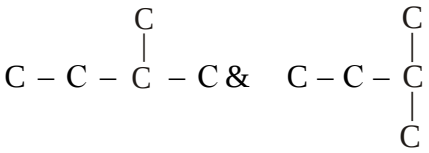
Sol. Primary amines of molecular formula $C_4H_{11}N$

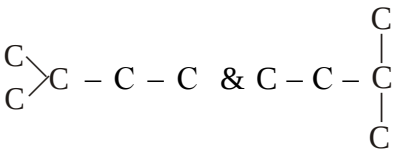
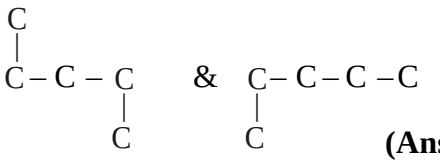
(1) $CH_3–CH_2–CH_2–CH_2–NH_2$ (2) 

(3) 

(4) 

Ex.8 Which of the following is an example of isomerism -

(A)  (B) 

(C)  (D) 

(Ans. A)

Sol. In the A option the compounds are 2-methyl butane and 2,2- dimethyl propane respectively. In B & C option both the compound are same i.e. 2-methyl butane.In D option both structure are same i.e. n-pentane.

(II) **Stereoisomerism / Space isomerism :**

Compound having same molecular formula, same connectivity and structure formula but differ due to spatial arrangement of group or atom is said to be stereo isomers and phenomenon is termed as stereoisomerism.

It is divided into two parts

(1) Configuration isomerism

(2) Conformational isomerism

1. Configuration isomerism : Stereoisomers which are not interconvertible at room temperature are known as configurational isomers

Configurational isomerism is further divided into two parts

(A) Geometrical isomerism

(B) Optical isomerism

A. Geometrical isomerism : It is type of configurational isomerism which arises due to restricted rotation of atoms or groups around a double bonded system or cyclic system.

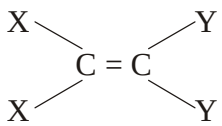
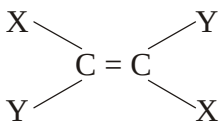
Conditions

(i) Planarity

(ii) Restricted rotation

(iii) Different functional group around system which is showing geometrical isomerism.

For example:

(a)  (b) 

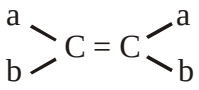
Not showing G.I. Showing G.I.

Geometrical isomers are named as

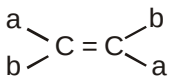
(a) cis- trans isomers (b) E and Z isomers

(c) Syn-anti isomers

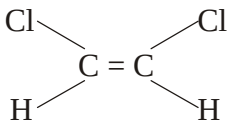
(a) *Cis- trans isomers.* When like atoms or groups attached at the same side of double bonded C-atom-called as cis. isomers. When like atoms or groups are on the opposite sides of doubly bonded carbon, are called. trans isomers.



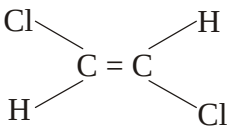
cis isomers



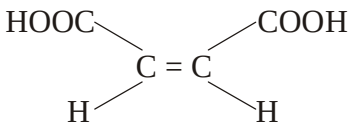
trans isomers



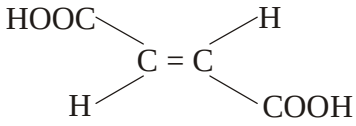
cis isomer



trans isomer



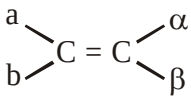
Maleic acid
(cis isomer)



Fumaric acid
(trans isomer)

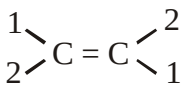
(b) E and Z isomers,

(i) The above system is used for derivatives of alkenes in which all the four substituents should be different



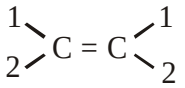
(ii) Following a set of rules (Cahn - Ingold-Prelog rules) the substituents on a double bond are assigned priorities.

(iii) The double bond is assigned the configuration E (From entgegen, the german word for opposite) if the two groups of higher priority are on the opposite sides of the double bond.



E form

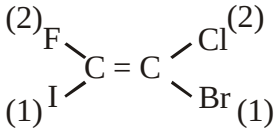
(iv) On the other hand, the double bond is assigned the configuration Z (From zusamenn, the German word for together) if the two groups of higher priority are on the same side of the double bond.



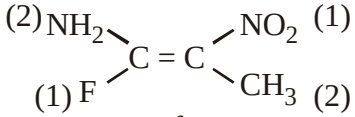
Z form

Proirity rule : chann, ingold & prelong proposed a sequence rule.

Rule-1 When atom or group of atom which are directly attach to the stereogenic centre have higher atomic number will have higher proirity. Example

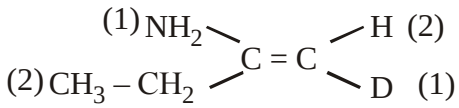


Z-form



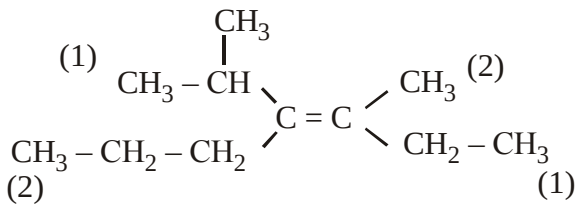
E-form

Rule-2 When the atomic number will be same, then higher atomic weight or group of atom have higher proirity

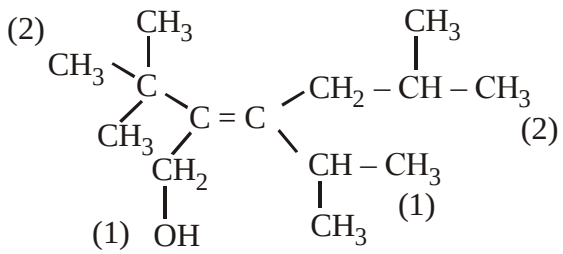


E-form

Rule-3 When both atomic number and atomic weight are same then proirity will be decided by the next joining atom.

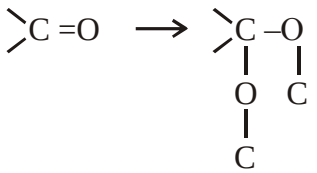


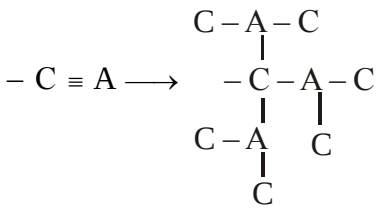
(E-form)



(Z-form)

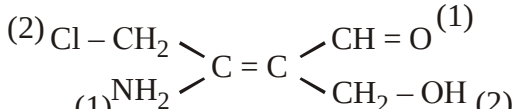
Rule-4 If multiple bonded group attach to the double bonded carbon, then they are considered in following manner.





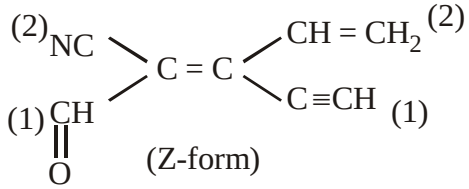
For example :

Ex.-1



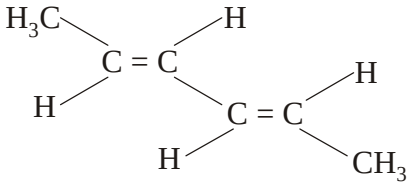
(E-form)

Ex.-2

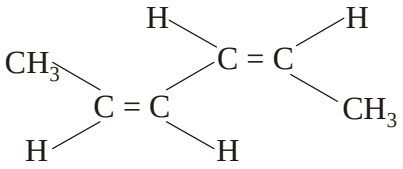


(Z-form)

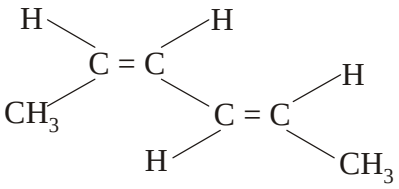
EX.-3 There are four geometrical isomers of 2,4-hexadiene.



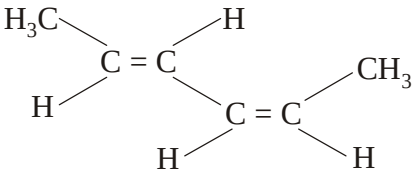
(2E, 4E) hexadiene



(2Z, 4Z) hexadiene

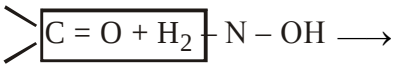


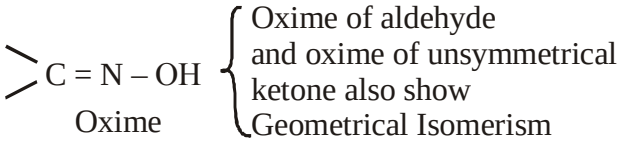
(2Z, 4E) hexadiene



(2E, 4Z) hexadiene

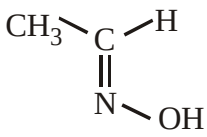
(c) Syn-anti isomers This type of isomerism exhibit by oximes and Azo compound. Oximes are the compounds formed by the reactions of aldehydes or ketones with hydroxyl amine. The products obtained have all the necessary conditions for Geometrical isomerism. i.e. restricted rotation they can be represented by the general formula



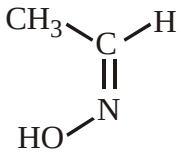


Oxime

Aldoximes

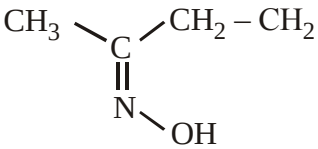


Syn form

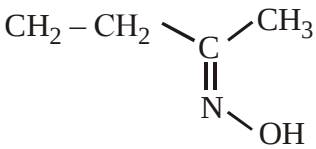


Anti form

When –OH group and H atom is same side, then it is syn form otherwise anti form



Syn form

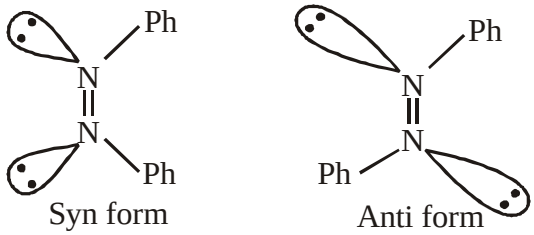


Anti form

In unsymmetrical Ketoxime, if-OH and the alphabetically alkyl present on the same side of double bond, then it is called as syn form and other isomer is anti form

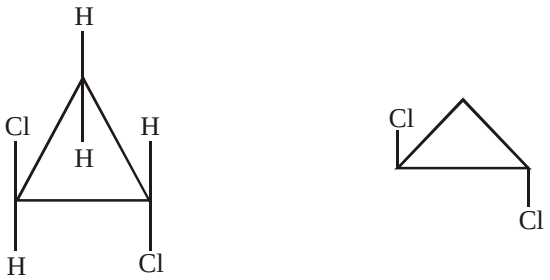
Geometrical Isomerism in AZO compound :

Eq. Ph – N = N – Ph



Geometrical Isomerism in cyclo alkane :

In cyclic compound the rotation about C – C single bond is not free because of the regidity caused by the presence of other carbon of the ring which keep them tightly held, thus a disubstituted cyclic compound (having the two substitution at the separate carbon) will also show Geometrical Isomerism.The substituents on the same side are cis-isomers while the substituents on opposite sides represent trans-isomers.



Trans form



Cis form



Cis form Trans form

No. of geometrical isomers in polyenes :

Case-1 Incase of unsymmetric alkene**.** If $R_1 \neq R_2$ (R_1 – CH = CH – CH = CH – R_2)

$$\boxed{\text{no. of G.I.} = 2^n}$$

n → number of double bond showing geometrical isomerism

Ex.- $CH_3 - CH = CH - CH = CH - CH_2 - CH_3$

$N = 2^n = 2^2 = 4.$

Case-2 Incase of symmetric alkene. If $R_1 = R_2$ ($R_1 - CH = CH - CH = CH - R_2$)

$$\boxed{\text{no. of G.I.} = 2^{n-1} + 2^{P-1}}$$

if n is even no. then , $P = \frac{n}{2}$

if n is odd no. then, $P = \frac{n+1}{2}$

Ex.- $CH_3 - CH = CH - CH = CH - CH = CH - CH_3$

here $\left| \begin{matrix} n = 3 \\ P = \frac{3+1}{2} \end{matrix} \right.$

$N = 2^2 + 2^1 = 6$

SOLVED EXAMPLE

Ex.1 Which of the following compounds exhibits geometrical isomers -

(A) C_2H_5Br (B) $(CH)_2(COOH)_2$

(C) CH_3CHO (D) $(CH_2)_2(COOH)_2$ **(Ans. B)**

Sol. $(CH)_2(COOH)_2$ in fact represents

HOOC – CH = CH – COOH and hence shows geometrical isomerism.

Ex.2 The number of geometrical isomers of

$CH_3CH = CH - CH = CH - CH = CHCl$ is -

(A) 2 (B) 4 (C) 6 (D) 8 **(Ans. D)**

Sol. Since both the carbon atoms of each of the three double bonds are differently substituted, therefore, $2^3 = 8$ geometrical isomers are possible.

Ex.3 Maleic and fumaric acids are:

(A) Geometrical isomer (B) Tautomers

(C) Optical isomers (D) Metamers **(Ans. A)**

Sol. Geometrical isomerism

$$\begin{matrix} H-C-COOH \\ \| \\ H-C-COOH \end{matrix} \qquad \begin{matrix} H-C-COOH \\ \| \\ HOOC-C-H \end{matrix}$$

(Maleic acid) (Fumaric acid)

Ex.4 Which of the following can exhibit cis-trans isomerism –

(A) $HC \equiv CH$ (B) $ClCH = CHCl$

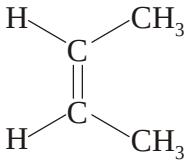
(C) $CH_3.CHCl.\ COOH$ (D) $ClCH_2 - CH_2Cl$ **(Ans. B)**

Sol. Remember that cis-tans geometrical isomerism is possible only in alkenes and further only in those alkenes in which the doubly bonded carbon atoms individually have different atoms/groups.

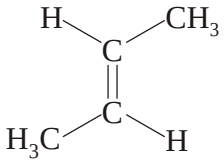
Ex.5 Geometrical isomerism is possible in case of:

(A) Pent-2-ene (B) Butane (C) 2-Butene (D) Ethene **(Ans. A & C)**

Sol. Geometrical isomerism is possible in case of 2-Butene and 2-Pentene

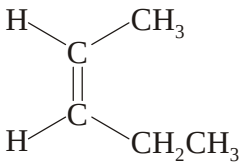


Cis

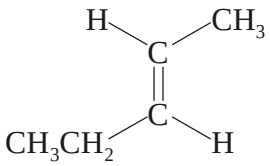


Trans

2-Butene



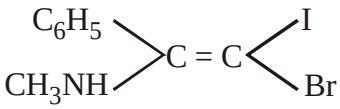
Cis



Trans

Pent-2-ene

Ex.6 Give the E-Z designation of the following compound -



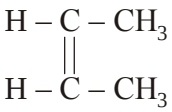
(A) E (B) Z (C) E-Z (D) E-E **(Ans. A)**

Sol. Priority order =

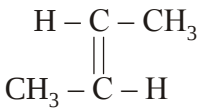
$-I > -Br$ (① ②), $-CH_3NH > -C_6H_5$ (① ②)

Ex.7 Which of the following compounds will exhibit trans (geometrical) isomerism?
(A) 2-butene (B) 2-butyne (C) 2-butanol (D) butanal **(Ans. A)**

Sol. Olefic compound shows geometrical isomerism due to restricted rotation around Carbon–Carbon single bond



Cis



Trans

2-Butene (β-Butylene)

B. Optical isomerism : Configurational isomers which are differ in their optical activity.

Optical Activity : The ability of optically active substances to cause rotation in the plane of oscillations of polarized light is called optical activity. The substances which do not have any interaction with plane polarized light are called optically inactive substances.

Following experiment was conducted to determine the optical activity of a substance

(a) Under ordinary conditions, the light waves oscillate in infinite number of planes passing through the line of propagation at right angle.

(b) Plane polarized light is a light whose vibrations take place in only one of these possible planes.

(c) Ordinary light can be turned into plane polarized light by passing it through Nicol prism (made up of calcite, a special crystalline form of CaCO3)

(d) When plane polarize light is passed through the liquid or dissolved state of such substances.

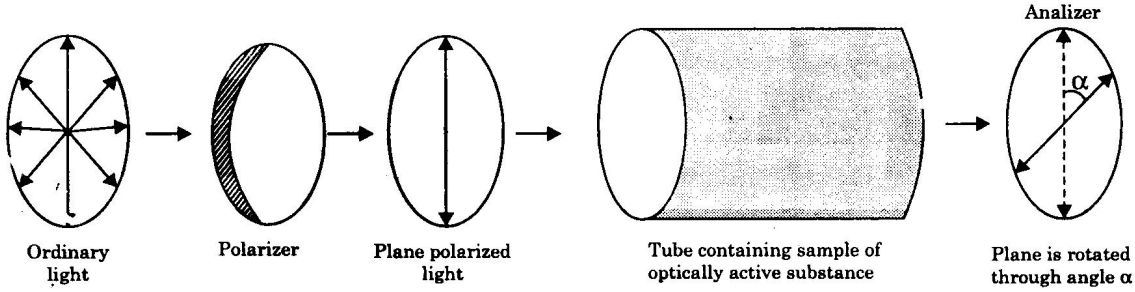
(e) The plane of oscillation gets rotated through some angle towards left or right of the original plane of oscillations. The substances which rotate the plane of polarized light are called optically active substances.

(f) The substances which rotate the plane of polarized light in the clockwise direction, i.e., towards right

are called dextrorotatory substances (Latin : dexter means right). This is indicated by putting a better d or (+) sign before the name of the substances.

(g) The substances which rotate the plane of polarized light in the anticlockwise direction, i.e., towards left are called leavorotatory substances (Latin : laevus means left). This is indicated by putting letter ' l ' or (–) sign before the name of the substance.

(h) The angle through which the plane of polarized light is rotated is represented by α and is called observed angle of rotation.



Polarimeter

(i) The amount of rotation caused by an optical active compound depends on various factors-

(a) Wavelength of light beam
(b) Temperature
(c) Density or concentration
(d) Length of the solution through which light beam has been passed.

SPECIFIC ROTATION : The specific rotation of optically active compound can be defined as the amount of optical rotation observed when plane polarised light is passed through a solution of 1 gm per ml concentration solution in a 1 dm long tube.

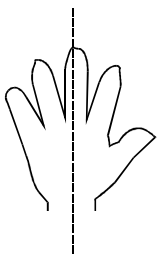
$$\text{Specific rotation} = [\alpha]^t_\lambda = \frac{\alpha}{l \times C}$$

Cause of optical activity:-

(a) In order to exhibit optical activity, an object or molecule must be chiral.

(b) Any molecule or object is said to be chiral if does not have any element of symmetry i.e. a plane of symmetry or a centre of symmetry.

Plane of symmetry:- A 'Plane' of symmetry' is a plane which divides an object in such a way that the part of it on one side of the plane is the mirror image of that on the other side for eg. a ball is symmetrical while a hand is asymmetric



A chiral molecule or object is non-superimposable on its mirror images.

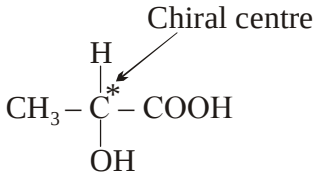
(c) Hence, chiral objects or molecules are also called dissymmetric objects or molecules the word chiral

in fact is derived from the Greek word cheir, meaning hard.

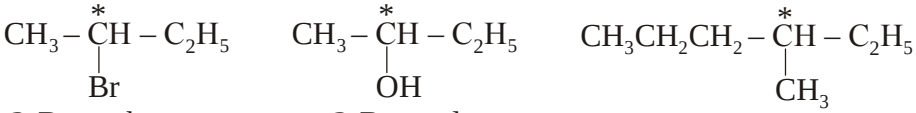
Chiral centre:-

(i) A carbon atom bonded to four different atoms / groups in the molecule is called Chiral centre.

(ii) The chiral centre in the molecule is represented by asterisk (*). For example, the second carbon in lactic acid is chiral centre because it is bonded to four different groups
(– H, – CH_3, – OH and – COOH).



(iii) Some more examples of molecules having one chiral centre are



(d) Compounds which are mirror images of each other and are not superimposable are termed *enantiomers* and the phenomenon is described as *enantiomerism.*

ENANTIOMERS :

Enantiomers are molecules which are mirror images of each other i.e. they should be non-superimposable.



CHARACTERISTICS OF ENANTIOMERS :

Some of the important characteristics of enantiomers are as given below :

(i) Enantiomers have identical physical properties such as melting point, boiling point, density, refractive index etc.

(ii) Enantiomers are optically active substances. They rotate the plane of polarized light in opposite directions but to the equal extent.

	(+)-2-Methyl-1-butanol	**(–)-2-Methyl-1-butanol**
Specific rotation :	+ 5.90º	– 5.90º
Relative density :	0.8193	0.8193
Boiling point :	128.9ºC	128.9ºC
Refractive index :	1.4107	1.4107

(iii) Enantiomers have identical chemical properties. This means that they form same products as a result of chemical combination. However, their reactivity, i.e., rates of reaction with other optically active substances are different.

(iv) Enantiomers have different biological properties. For example (+) -sugar plays significant role in animal metabolism. On the other (–)-sugar does not play any role in metabolism.

REPRESENTATION OF ENANTIOMERS :

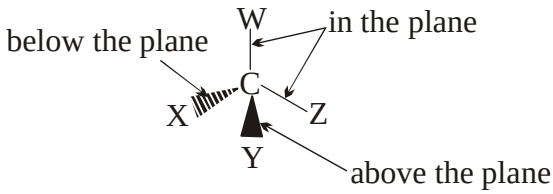
(a) Wedge and dash formulae (b) Fischer Projection Formulae

(a) Wedge and dash formulae :

(i) In this method, the four groups bonded to the chiral centre are represented by different means.

(ii) A normal line represents the bond lying in the plane of paper.

(iii) A broken line represents the bond going behind the plane of the paper and a solid wedge represents the bond projected out towards the viewer.



(b) Fischer Projection Formulae

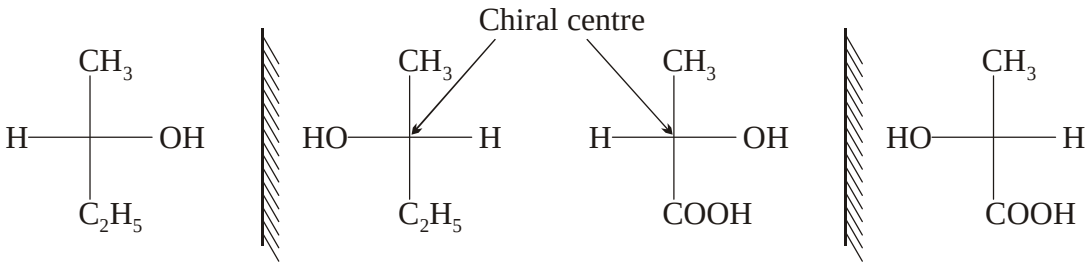
(i) Emily Fischer devised a most simple and convenient method to represent the three dimensional arrangement of groups bonded to chiral centre.

(ii) He used the point of intersection of two perpendicular lines to represent the chiral centre.

(iii) Horizontal lines represent the bonds projected out of the plane of the paper towards viewer.

(iv) Vertical lines on the other hand, represented the bonds projected back from the plane of the paper away from the viewer.

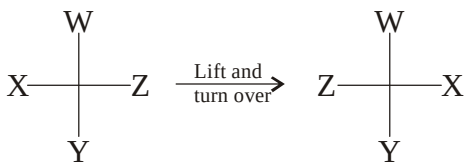
(v) The Fischer projection formulae of enantiomers of 2-butanol and lactic acid are as under



Enantiomers of 2-butanol Enantiomers of lactic acid

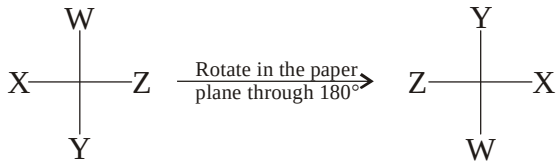
<u>Important Points About Fischer Projection Formula :</u>

(1) Fischer projection of a stereoisomer must not be lifted from the plane of the paper and turned over. Such an operation would result into an arrangement which is enantiomer of the original stereoisomer.



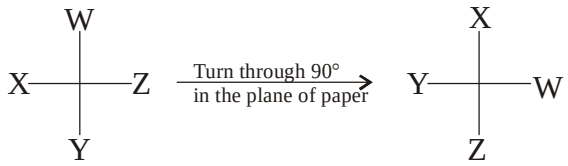
(A) Enantiomer of A

(2) Fischer's projection can be rotated in the plane of the paper about the chiral centre through 180º or its whole number multiple. Such an operation produces the same arrangement



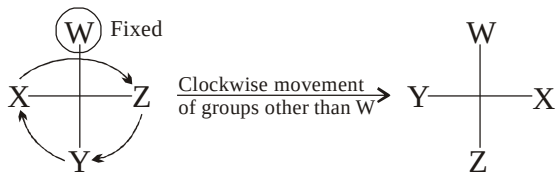
(A) (Same as A)

(3) Fischer projection should not be turned in the plane of the paper through angle of 90º about the chiral centre. Such an operation also produces enantiomer of the original compound.



(A) Enantiomer of A

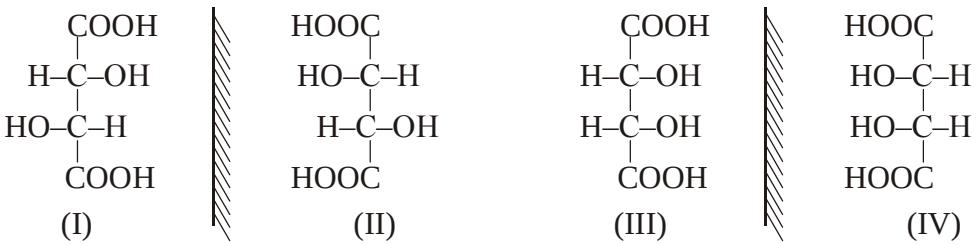
(4) Keeping one group as steady, the other groups in the Fischer projection can be rotated clockwise or anticlockwise simultaneously. Such operation would give same arrangement as the original.



(A) (Same as A)

DIASTEREOMERS :

The stereoisomers which are non-superimposable and do not bear mirror image relationship are called diastereomers. For Example, a compound having two asymmetric carbon atoms can have four stereoisomers as shown below in the case of tartaric acid :



One pair of enantiomers Second pair of enantiomers

(I) is mirror image of (II); similarly (III) and (IV are mirror images of each other. Thus, the four isomers are two pairs of enantiomers. Now compare (I) with (III); they are neither superimposable nor they are mirror images. They are called *diastereomers*. (I) and (IV) are also diastereomers, as are (II) and (III) and (II) and (IV).

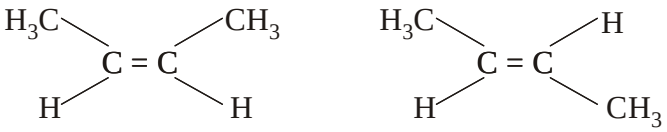
Characteristics of Diastereomers are :

(i) They show similar but not identical chemical properties. The rates of reactions are different.

(ii) They have different physical properties, such as melting points, boiling points, densities, solubilities, refractive indices, etc.

(iii) They can be easily separated through fractional crystallization, fractional distillation, chromatography, etc.

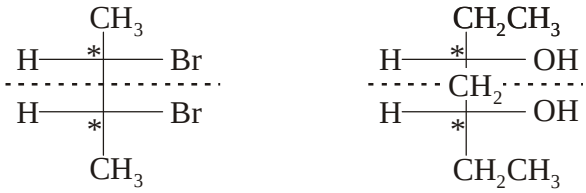
(iv) Diastereomers are also encountered in the case of geometrical isomers :



Cis Trans

MESO COMPOUND :

(a) The compounds containing two or more chiral centres but possessing achiral molecular structure because of having plane of symmetry, are called meso compounds.



(2S, 3R) (2S, 4R)

Meso Compound

Plane of symmetry is represented by dotted line ————————

(b) Meso compounds do not rotate the plane of polarized light in any direction, i.e., they are **optically inactive**.

(c) This is because of achiral nature of their molecules. Because of the present of plane of symmetry the optical rotation caused by half of the molecule is compensated by the rotation caused by the other half.

(d) This cancellation of rotation within the molecule is referred to as **internal compensation.**

(e) In short, the meso compounds are optically inactive due to internal compensation.

CONFIGURATION :

(i) Three dimensional arrangement of groups about the chiral centre is called configuration

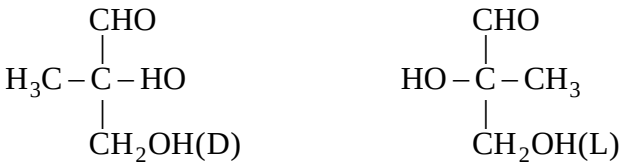
(ii) There are two methods for assigning configuration to a molecule :

(a) Relative method (b) Absolute method.

(1) **Relative method of configuration (D, L System) :**

(a) It uses D–Glyceraldehyde and L–Glyceraldehyde as the basis for the configuration determination.

(b) The stereochemical descriptor D refers to the arrangement in which – OH group attached to the chiral centre is on the right side of Fischer projection, whereas descriptor L refers to arrangement in which – OH group is on the left side of the Fischer projection of glyceraldehyde.



(d) This method was found suitable for the study of optically active sugars as the sugars are defined as *poly hydroxy aldehydes and ketones.*

(e) Glyceraldehyde also contains hydroxy and aldehyde groups but this method cannot be used for those molecules which do not process hydroxy aldehyde groups like CFCl BrI.

R–S system (Absolute configuration)

R → Rectus (Right)

S → Sinister (Left)

R-S nomenclature is assigned as follow :

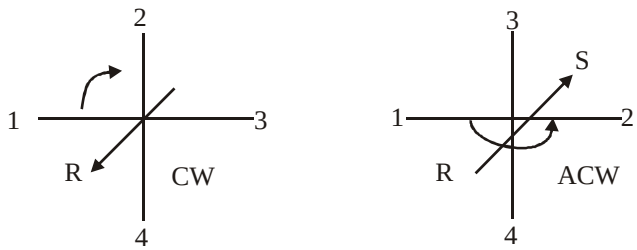
Step-I :- By the set of sequence rule, we give the priority order of atom or group connected through the chiral carbon.

Step-II :- If atom/group of minimum priority present on the verticle line, then

Movement of eyes in clockwise direction = R

Movement of eyes in anticlockwise = S

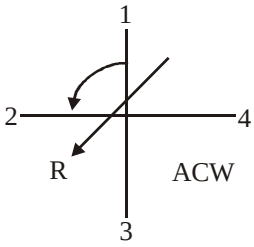
Movement of eyes taken from 1 → 2 → 3 through Low molecular weight group (if needed)

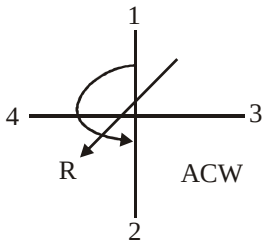


Step III :- If minimum proirity group present on the horizontal line, then

clockwise rotation $\Rightarrow$ S

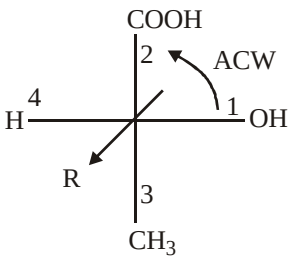
anticlockwise rotation $\Rightarrow$ R



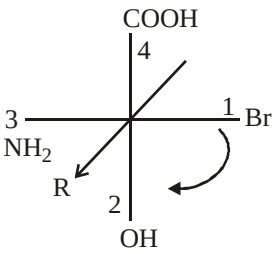


Example:-

(1)



(2)



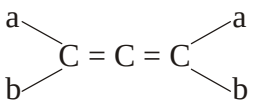
OPTICAL ISOMERISM IN COMPOUNDS CONTAINING NO CHIRAL CARBON ATOM :

Various types of compounds belonging to this group are allenes, alkylidene cycloalkanes, spiro compounds (spiranes) and properly substituted biphenyls.

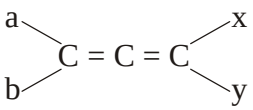
(i) **Allenes** These are the organic compounds of the following general formula.

$$> C = C = C <$$

Allenes containing even number of double bonds exhibit optical isomerism provided the two groups attached to each terminal carbon atom are

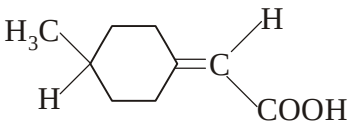


or



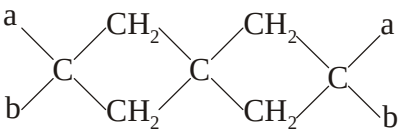
(ii) **Alkylidene, cycloalkanes and spiro compounds :**

When one or both of the double bonds in allenes are replaced by one and two rings, the resulting systems are respectively known as alkylidene cycloalkanes and spiranes.



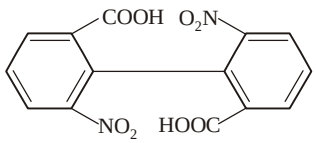
1-Methyl cyclo hexylidene-4-acetic acid
(Alkylidene cycloalkane)

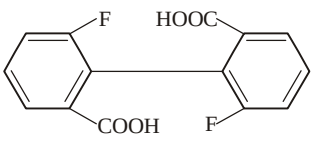
or



Spiranes

(iii) **Biphenyls :** Suitably substituted diphenyl compounds are also devoid of individual chiral carbon atom, but the molecules are chiral due to restricted rotation around the single bond between the two benzene nuclei and hence they must exist in two non-superimposable mirror images of each other.





Number of optical isomers :

Case - 1 When the molecule is unsymmetrical. (It cannot be divided into two halves)

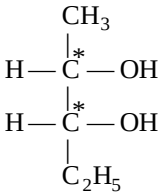
Number of d and *l* isomers = 2^n

Number of meso form = 0

Total number of optical isomers = 2^n

Where n is the number of chiral carbon atoms.

For eg. 2, 3 - Pentane diol



d and l isomers = $2^2 = 4$

Case - 2 When the molecule is unsymmetrical, number of chiral carbon = even number

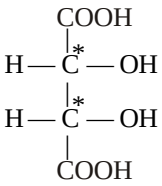
Number of d and l forms = $2^{(n-1)}$

Number of meso form = $2^{(n/2-1)}$

Total number = addition of the above

$= 2^{n-1} + 2^{\frac{n}{2}-1}$

For eg.: Tartaric acid



Number of d and l forms = $2^{(n2-1)} = 2$

Number of meso form = $2^{(2/2-1)} = 2^o = 1$

Total optical isomers = 3

Case- 3. When the molecule is symmetrical. Number of chiral carbon = add number of d and l form

$= 2^{(n-1)} - 2^{(n/2-½)}$

Number of meso form = $2^{(n/2-½)}$

Total number of isomers = 2^{n-1}

RACEMIC MIXTURE :

(a) An equimolecular mixture of a pair of enantiomers is called racemic mixture or racemic modification.

(b) A racemic mixture is optically inactive. This is because of the fact that in equimolecular mixture of enantiomeric pairs, the rotation caused by the molecules of one enantiomer is cancelled by the rotation caused by the molecules of other enantiomer.

(c) This type of compensation of optical rotation in a racemic mixture is referred to as **external compensation**. Thus, racemic mixture becomes optically inactive because of external compensation.

(d) Representation of Racemic mixture : The racemic mixture of a particular sample is indicated by using the prefix (d*l*) or (±). For example, racemic mixture of lactic acid is represented as (±) lactic acid.

RACEMIZATION :

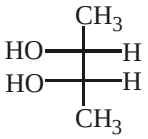
It is a process of conversion of an optically active compound into the racemic modification. Both (+) and (–) forms of the compound are capable of racemizations under the influence of heat, light or chemical reagents.

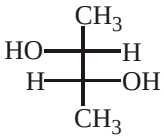
RESOLUTION :

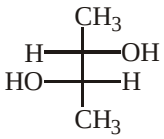
The process of separation of constituent enantiomeric forms from the racemic mixture is known as resolution.

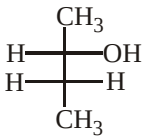
SOLVED EXAMPLE

Ex.1 A Fischer projection of (2R, 3S)-2,3-butanediol is : -

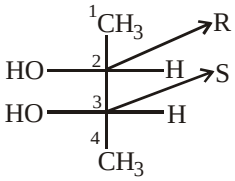
(A) 

(B) 

(C) 

(D) 

(Ans. A)

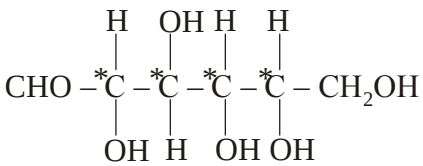
Sol. 

Ex.2 How many aldohexose stereo isomers exist ?

(A) 8 (B) 10 (C) 16 (D) 64

(E) 48 **(Ans. C)**

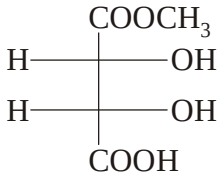
Sol. Aldohexose have 16 stereoisomer due to presence of 4 asymmetric carbon atom



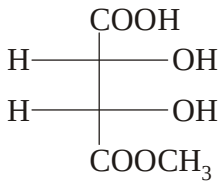
n = 4

No. of optical isomer = $2^n = 2^4 = 16$

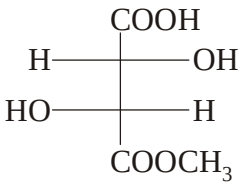
Ex.3 The correct statement about the compound A, B and C.



(A)



(B)

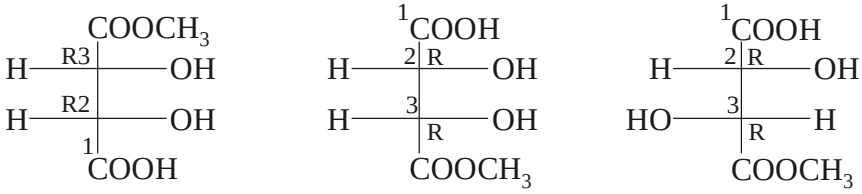


(C)

(A) 'A' and 'B' are identical (B) 'A' and 'B' are diastereomers

(C) 'A' and 'C' are enantiomers (D) 'A' and 'B' are enantiomers **(Ans. B)**

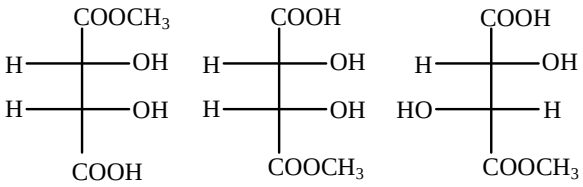
Sol.



(A) (B) (C)

A & B diastereomers

Ex.4 The correct statement about the compounds I, II and III

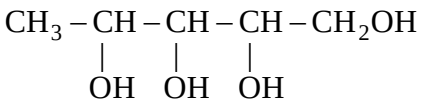


(I) (II) (III)

(A) I and II are identical (B) I and II are diastereomers

(C) I and III are enantiomers (D) I and II are enantiomers **(Ans. A)**

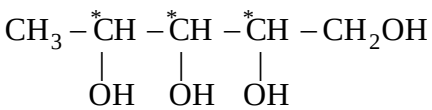
Ex.5 The number of optically active isomer possible for



is

(A) 2 (B) 4 (C) 6 (D) 8 (E) 10 **(Ans. D)**

Sol.



No. of asymmetric carbon atom = 3
Total optically active isomer.
Number are = $2^n = 2^3 = 8$

Ex.6 Which of the following compounds is chiral?

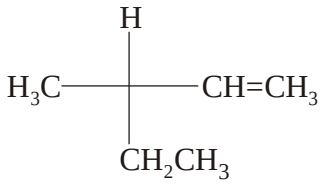
(A) $BrCH_2CH_2CH_2CH_2CH_3$ (B) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$

(C) $CH_3\underset{\displaystyle Br}{\underset{|}{C}} = C = CHCH_3$ (D) $BrCH = CHCH_2CH_2CH_3$

(E) None of these **(Ans. E)**

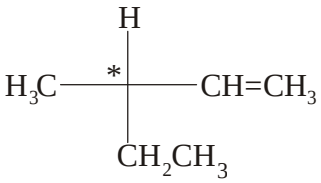
Sol. No compound is chiral because asymmetric carbon atom is absent in all the compound.

Ex.7 The following hydrocarbon can exhibit.



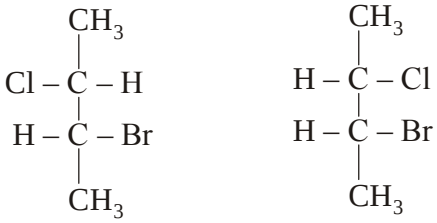
(A) Geometrical isomerism (B) Optical isomerism
(C) Both geometrical and optical isomerism (D) Tautomerism **(Ans. B)**

Sol.



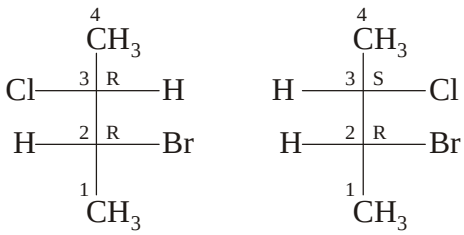
This compound shows optical isomerism due to presence of asymmetric carbon atom.

Ex.8



Structure I and II for 2-chloro-3-bromobutane represented in Fischer projection are
(A) Enantiomers (B) Diastereoisomers (C) Metamers (D) None of these
(Ans. B)

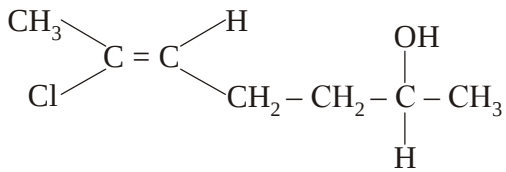
Sol.



(I) (II)

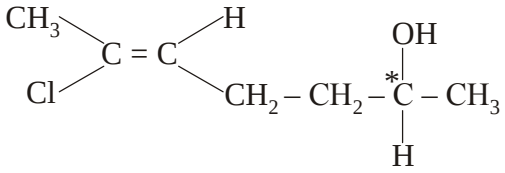
I & II are diastereoisomers.

Ex.9 The compound whose stereochemical formula is written below exhibits x geometrical isomers and optical isomers.

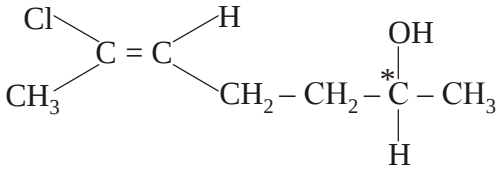


The values of x and y are
(A) 4 and 4 (B) 2 and 2 (C) 2 and 4 (D) 4 and 2
(E) None of these **(Ans. B)**

Sol. Geometrical isomers = 2



[Z]



[E]

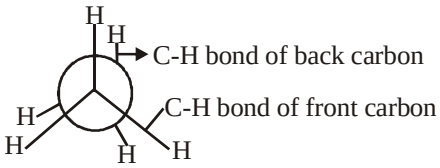
Optical isomers = 2
n =1
Number = $2^n = 2^1 = 2$

2. CONFORMATIONAL STEREOISOMERISMS

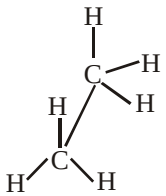
Different non-identical arrangement of atoms or group in a molecule that result by the rotation about a single bond and that can easily be reconverted at room temperature are known as conformational sterio isomers of conformers.

Projection of Tetrahedral Carbon Atom :

(1) Newman projection : In this method the molecule is observed along the central carbon-carbon bond. a circle is drawn and centre of the circle represents the front carbon. the bonds of the front carbon are drawn from the centre of the circle while the bonds at the hack carbon are drawn from the periphery.

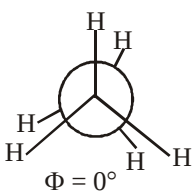


(2) Saw horse projection : In this method, central carbon-carbon bond of the molecule is represented by a straight line written in bond of the molecule is represented by a straight line written in slightly tilted manner and the molecule is observed from the right side.

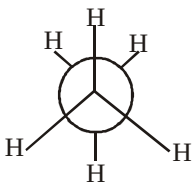


(3) Fischer projection (It is not used in conformation)

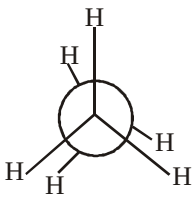
Conformation of ethane :



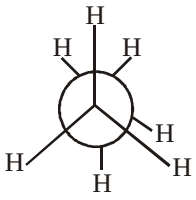
Φ = 0°
(I)



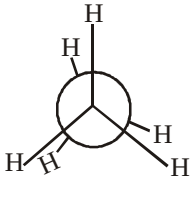
Φ = 60°
(II)



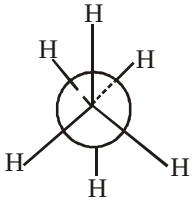
Φ = 120°
(III)



Φ = 180°
(IV)



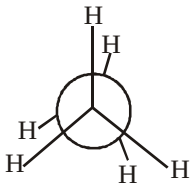
Φ = 240°
(V)



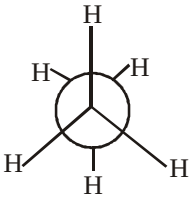
Φ = 300°
(VI)

Eclipsed = I = III = V

Staggered = II = IV = VI



Eclipsed conformation



Staggered conformation

Note: Here Φ denotes dihedral angle

***Dihedral angle** :– Angle between valencies of two adjescent atoms*

(i) Ethane molecule contains infinite number of conformers.

(ii) The extreme conformation of ethane molecules are staggered and eclipsed.

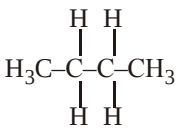
(iii) The energy of staggered conformation is lower than eclipsed conformation by 2.8 kcal/mole (11.7 kJ/mole).

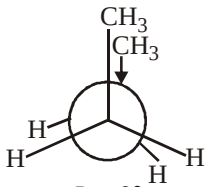
(iv) Staggered conformation is more stable than the eclipsed conformation.

(v) The mixture contains 99% staggered conformation and 1% eclipsed conformation.

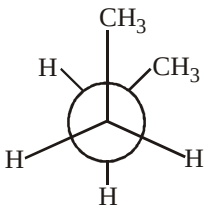
(vi) Eclipsed and staggered conformations are not isolated from the mixture.

Conformation of Butane :

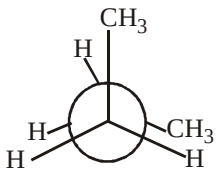




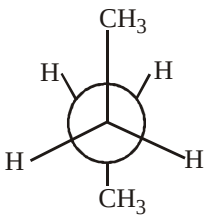
Φ = 0°
(I)



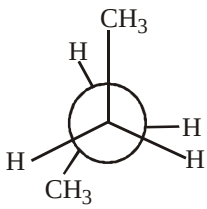
Φ = 60°
(II)



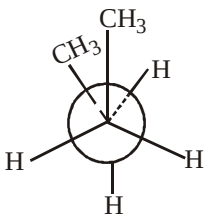
Φ = 120°
(III)



Φ = 180°
(IV)



Φ = 240°
(V)



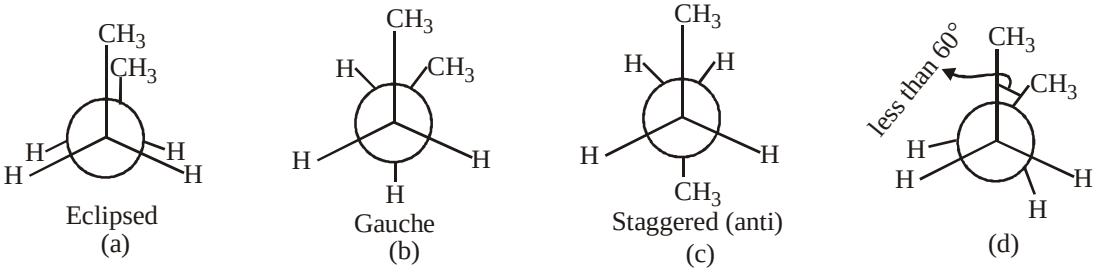
Φ = 360°
(VI)

(I) = Fully eclipsed (CH_3 group eclipsed by CH_3 group)

(II) = **(IV)** = Gauche (Staggered)

(IV) = anti or trans (Staggered)

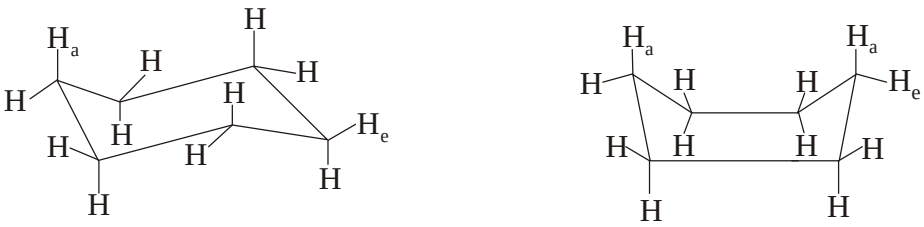
(III) = **(V)** = Partial eclipsed (CH_3 group eclipsed by H)



Eclipsed (a) Gauche (b) Staggered (anti) (c) (d)

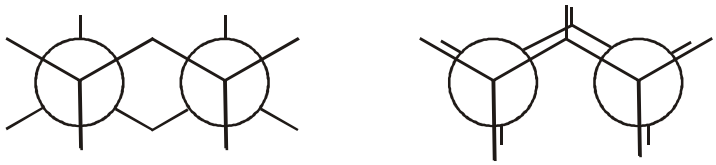
If the dihedral angle is less than 60. it is known as skew. Here stability of (c) > (b) > (d) > (a). Partial eclipsed stability > Fully eclipsed stability.

Conformers of Cyclohexane : The two important conformations of cyclohexane are the chair from and the boatform



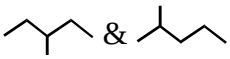
Chair conformer Boat conformer

Chair form is more stable than boat form.



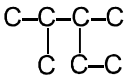
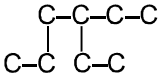
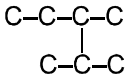
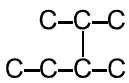
Chair conformation Boat conformation

EXERSICE # I

Q.1  are called as –

(A) Position isomers (B) Chain isomers (C) Function isomers (D) Ring chain isomers

Q.2 Out of following carbon chains which one is different from other three chains –

(A)  (B)  (C)  (D) 

Q.3  &  are –

(A) Tautomers (B) Functional (C) Position (D) All the above

Q.4 CH_3CONH_2 & $HCONHCH_3$ are called –

(A) Position (B) Chain (C) Tautomers (D) Functional

Q.5 Diethyl ether and methylpropyl ether are :

(A) metamers (B) chain isomers (C) position isomers (D) geometrical isomers

Q.6 Which of the following pairs exhibits chain isomerism ?

(A) α-butylene and β-butylene (B) α-butylene and isobutylene

(C) isobutylene and cyclobutene (D) cyclobutane and isobutylene

Q.7 Which pair of the following is not an example of position isomerism :

(A) Ethylene chloride and ethylidene chloride (B) n-Propyl alcohol and isopropyl alcohol

(C) n-Pentane and isopentane (D) n-butyl alcohol and sec butyl alcohol.

Q.8 Which pair of the followings is the example of both metamerism and position isomerism ?

(A) Diethylamine and methylisopropylamine (B) Propyl ethanoate and isopropyl ethanoate

(C) Ethoxyethane and 2-methoxypropane (D) Diethylketone and methyl n-propyl ketone.

Q.9 Geometrical isomerism is due to -

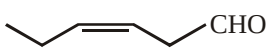
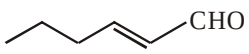
(A) The resticted rotation about a double bond

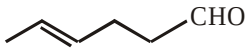
(B) The presence of keto group

(C) The presence of CH(OH) group

(D) The presence of an asymmetric carbon

Q.10 The correct structure of trans-2-hexenal is -

(A)  (B) 

(C)  (D) 

Q.11 cis-trans isomers can be differentiated by:

(A) Melting point (B) Dipole moment (C) Boiling point (D) All of these

Q.12 Compounds containing which of the following functional groups can exhibit geometrical isomerism ?
(A) > C = C < (B) > C = N – (C) –N = N – (D) All the three above

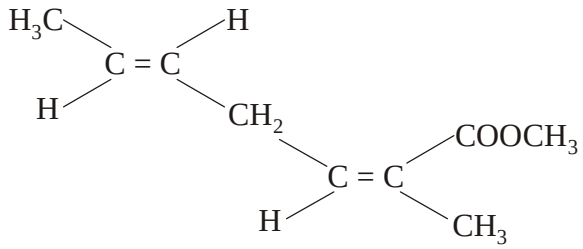
Q.13 Which among the following compounds will show geometrical isomerism :

(A) CH_3—CH=CH_2 (B) $CH_3 - \underset{\displaystyle CH_3}{\overset{|}{C}} = CH_2$

(C) $CH_3 - \underset{\displaystyle CH_3}{\overset{|}{C}} = CHD$ (D) CH_3—CH=CHD

Q.14 Which of the following compounds will show geometrical isomerism ?
(A) 2 - Butene (B) Propene (C) 1 -Phenylpropene (D) 2-Methyl -2 - butene

Q.15 The correct stereochemical name of

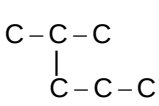
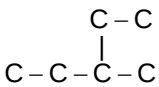
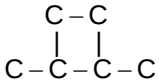
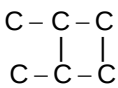


(A) methyl 2-methylhepta (2E, 5E) dienoate (B) methyl 2-methylhepta (2Z, 5Z) dienoate
(C) methyl 2-methylhepta (2E, 5Z) dienoate (D) methyl 2-methylhepta (2Z, 5E) dienoate

Q.16 The following are metamers of ethyl acetate except :
(A) methyl propanoate (B) methyl acetate
(C) isopropyl formate (D) propyl formate

Q.17 Which pair of the following exhibits different type of isomerism than the other three ?
(A) Methyl cyanide and methyl isocyanide (B) Methyl nitrite and nitromethane
(C) Ethyl methanoate and methyl ethanoate (D) 2-Butyne and 1, 3-butadiene

Q.18 The name of which carbon chain starts from 'iso' in the following chains –

(A)  (B)  (C)  (D) 

Q.19 How many aliphatic carbonyl compounds are possible having the molecular formula $C_5H_{10}O$ –
(A) 4 (B) 5 (C) 6 (D) 7

Q.20 The following classes of organic compounds exhibit metamerism except :
(A) secondary amines (B) esters (C) ethers (D) alkanols

Q.21 In keto-enol tautomerism of dicarbonyl compounds, the enol form is preferred in contrast to the keto-form, this is due to
(A) Presence of carbonyl group on each side of $-CH_2-$
(B) Resonance stabilization of enol form
(C) Presence of methylene group
(D) Rapid chemical exchange.

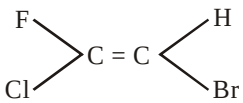
Q.22 The type of isomerism shown by nitromethane is-
(A) Metamerism (B) Optical isomerism (C) Tautomerism (D) Position isomerism

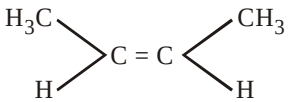
Q.23 The phenomenon involving the migration of a proton to give two structural isomers in equilibrium with each other is known is –
(A) Matamerism (B) Tautomerism
(C) Cis trans isomerism (D) Stereo isomerism

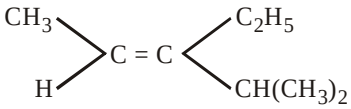
Q.24 Which of the following does not show tautomerism ?
(A) $C_6H_5COCH_3$ (B) CH_3CHO (C) CH_3COCH_3 (D) $C_6H_5COC(CH_3)_3$

Q.25 Which of the following can exhibit tautomerism ?
(A) $C_6H_5CH_2 - CO - CH_2CH_2CHO$
(B) $C_6H_5 - CO - CH_2 - CO - CH_2 - CH_2CH_3$
(C) $C_6H_5 - CO - CO - CH_2CH_2CH_3$
(D) All of the above.

Q.26 The 'E-isomer is -

(A) 

(B) 

(C) 

(D) None of the above

Q.27 How many non-cyclic structures may be written down for $C_3H_4Cl_2$, counting geometric isomers separately ?
(A) 5 (B) 7 (C) 4 (D) 6

Q.28 Which of the following will show geometrical isomerism ?
(A) 1-Butene (B) 1,2-Dibromoethene
(C) Propene (D) Isobutylene

Q.29 The number of isomeric aldehydes and ketones with formula $C_5H_{10}O$ are-
(A) 7 (B) 6 (C) 5 (D) 8

Q.30 The number of chain isomers for C_7H_{16} are-
(A) 6 (B) 7 (C) 8 (D) 9

EXERSICE # II

Q.1 Stereo - Isomerism includes - **[AIEEE-2002]**

(A) Geometrical isomerism only (B) Optical isomerism only

(C) Both geometrical & optical isomerism (D) Position & Functional isomerism

Q.2 Which of the following does not show geometrical isomerism - **[AIEEE-2002]**

(A) $CH_3 - CH = CH - CH_3$ (B) $CH_3 - CH_2 - HC = CH_2$

(C) $CH_3 - \underset{\displaystyle Cl}{\underset{|}{C}} = CH - CH_3$ (D) $ClHC = CH - CH_2 - CH_3$

Q.3 Racemic mixture is formed by mixing two – **[AIEEE-2002]**

(A) Isomeric compounds (B) Chiral compounds

(C) Meso compounds (D) Enanitiomers with chiral carbon

Q.4 Geometrical isomerism is not shown by – **[AIEEE-2002]**

(A) 1, 1– dichloro–1–pentene (B) 1, 2– dichloro–1–pentene

(C) 1, 3– dichloro–2–pentene (D) 1, 4– dichloro–2–pentene

Q.5 Racemic mixture is – **[AIEEE-2002]**

(A) A mixture of chiral carbons (B) A mixture of isomers

(C) A mixture of aldehydes and ketones (D) A mixture of alcohols and ethers

Q.6 Among the following four structures I to IV

(i) $C_2H_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_3H_7$ (ii) $C_2H_5 - \overset{\displaystyle O}{\overset{\|}{C}} - \underset{\displaystyle CH_3}{\underset{|}{CH}} - C_2H_5$

(iii) $H-\underset{\displaystyle H}{\overset{|}{\overset{\displaystyle H}{\underset{|}{C}}}}-H$ (iv) $C_2H_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_2H_5$

It is true that – **[AIEEE-2003]**

(A) Only (iii) is a chiral compound (B) Only (ii) and (iv) are chiral compounds

(C) All four are chiral compounds (D) Only (i) and (ii) are chiral compounds

Q.7 Which of the following compounds is not chiral ? **[AIEEE-2004]**

(A) 1 – chloropentane (B) 2 – chloropentane

(C) 1 – chloro –2–methyl pentane (D) 3 – chloro – 2 – methyl pentane

Q.8 Which of the following will have a mesoisomer also - **[AIEEE-2004]**

(A) 2 - Chlorobutane (B) 2, 3 - Dichlorobutane

(C) 2,3 - Dichloropentane (D) 2-Hydroxypropanoic acid

Q.9 Which types of isomerism is shown by 2,3–dichlorobutane ? **[AIEEE-2005]**

(A) Optical (B) Diastereo (C) Structural (D) Geometric

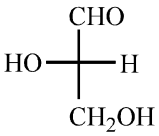
Q.10 Increasing order of stability among the three main conformations (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is **[AIEEE 2006]**

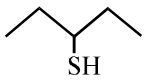
(A) Gauche, Eclipse, Anti (B) Eclipse, Anti, Gauche

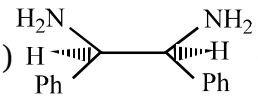
(C) Anti, Gauche, Eclipse (D) Eclipse, Gauche, Anti

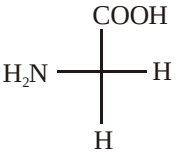
Q.11 Which of the following molecules is expected to rotate the plane of plane-polarised light?

[AIEEE-2007]

(A) 

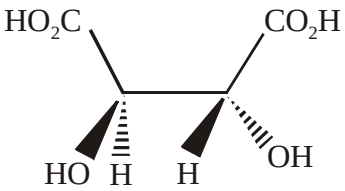
(B) 

(C) 

(D) 

Q.12 Which one of the following conformations of cyclohexane is chiral ? **[AIEEE-2007]**

(A) Twist boat (B) Rigid (C) Chair (D) Boat

Q.13 The absolute configuration of 

is **[AIEEE-2008]**

(A) R, R (B) R, S (C) S, R (D) S, S

Q.14 Out of the following, the alkene that exhibits optical isomerism is **[AIEEE-2010]**

(A) 3-methyl-1-pentene (B) 2-methyl-2-pentene
(C) 3-methyl-2-pentene (D) 4-methyl-1-pentene

Q.15 Identify the compound that exhibits tautomerism. [AIEEE-2011]

(A) 2-Butane (B) Lactic acid (C) 2-Pentanone (D) Phenol

Q.16 The compounds $C_2H_5OC_2H_5$ and $CH_3OCH_2CH_2CH_3$ are

(A) chain isomers (B) geometrical isomers
(C) metamers (D) conformational isomers

Q.17 The number of primary, secondary and tertiary amines possible with the molecular formula C_3H_9N respectively.

(A) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1

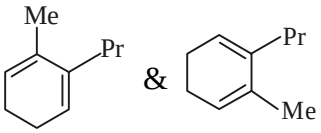
Q.18 Ethylethanoate and α – methyl propionic acid are –

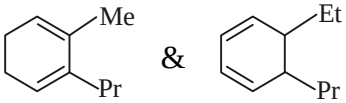
(A) Chain isomers (B) Functional isomers
(C) Geometrical isomers (D) Optical isomers

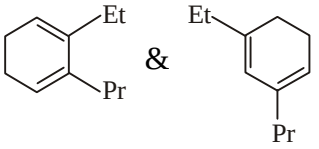
Q.19 Which of the following compounds will exhibit geometrical isomerism –

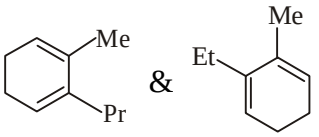
(A) 1–Phenyl–2–butene (B) 3–Phenyl–1–butene
(C) 2–Phenyl–1–butene (D)1,1–Diphenyl–1–propene

Q.20 Which of the following has **incorrect** relation

(A)  identical

(B)  positional isomers

(C)  positional isomers

(D)  homologues

Q.21 Which of the following compounds can exist as geometrical isomers –

(A) CH_2Cl_2 (B) CH_2Cl — CH_2Cl

(C) CHBr = CHCl (D) CH_2Cl — CH_2Br

Q.22 Which of the following paris of compounds are not isomers -

(A) Propyne and cyclopropene (B) Propyne and propadiene

(C) Propene and cyclopropene (D) 1-Propanol and methoxyethane

Q.23 The type of isomerism observed in urea molecule is

(A) Chain (B) Position (C) Geometrical (D) Functional

Q.24 Among the following compounds, the one which does not show geometrical isomerism is -

(A) $C_6H_5N = NC_6H_5$ (B) $C_6H_5CH = CHC_6H_5$

(C) $C_6H_5 - \underset{\displaystyle CH_3}{\underset{|}{C}} = N - OH$ (D) $C_6H_5 - \underset{\displaystyle C_6H_5}{\underset{|}{C}} = N - CH_3$

Q.25 How many minimum no. of C-atoms are required for position & geometrical isomerism in alkene?

(A) 4, 3 (B) 4, 4 (C) 3, 4 (D) 3, 3

Q.26 Structural isomers possible for $C_4H_8Br_2$ are -

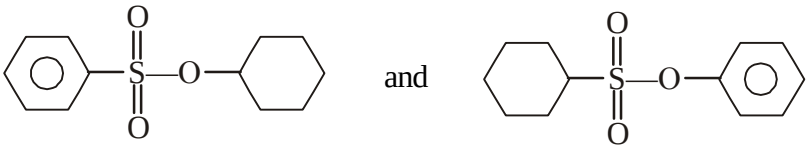
(A) 9 (B) 8 (C) 7 (D) 6

Q.27 Which of the following compounds has no geometrical isomer -

(A) 1-Phenylpropene (B) 1, 2-Diphenylethene

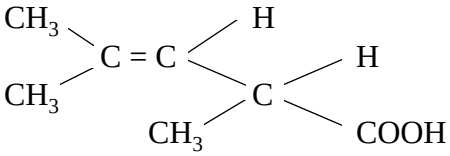
(C) 1, 2-Diphenylpropene (D) 1,1-Diphenylpropene

Q.28 Given compound shows which type of isomerism



(A) Chain isomerism
(B) Positional isomerism
(C) Metamerism
(D) Functional group isomerism

Q.29 The following compound can exhibit -



(A) Geometrical isomerism
(B) Geometrical and optical isomerisms
(C) Optical isomerism
(D) Tautomerism

Q.30 Which of the following does not show geometrical isomerism?
(A) 1, 2-dichloro-1-pentene
(B) 1, 3-dichloro-2-pentene
(C) 1, 1-dichloro-1-pentene
(D) 1, 4-dichloro-2-pentene

ANSWER KEY

EXERSICE # I

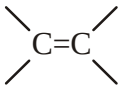
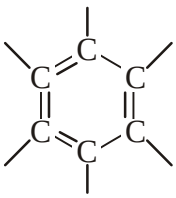
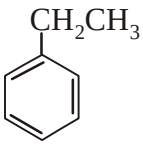
Q.1	A	Q.2	B	Q.3	B	Q.4	D	Q.5	A	Q.6	B	Q.7	C
Q.8	D	Q.9	A	Q.10	B	Q.11	D	Q.12	D	Q.13	D	Q.14	A
Q.15	D	Q.16	B	Q.17	C	Q.18	A	Q.19	D	Q.20	D	Q.21	B
Q.22	C	Q.23	B	Q.24	D	Q.25	D	Q.26	C	Q.27	B	Q.28	B
Q.29	A	Q.30	C										

EXERSICE # II

Q.1	C	Q.2	B	Q.3	D	Q.4	A	Q.5	A	Q.6	D	Q.7	A
Q.8	B	Q.9	A	Q.10	B	Q.11	A	Q.12	A	Q.13	A	Q.14	A
Q.15	C	Q.16	C	Q.17	C	Q.18	B	Q.19	A	Q.20	B	Q.21	C
Q.22	C	Q.23	D	Q.24	D	Q.25	B	Q.26	A	Q.27	D	Q.28	C
Q.29	C	Q.30	C										

ALKANE

Hydrocarbon :

Hydrocarbon	Functional group	Example
Alkanes	none (no double or triple bonds)	$CH_3–CH_2–CH_3$, propane
Alkenes	 double bond	$CH_2=CH–CH_3$, propene
Alkynes	–C≡C– triple bond	H–C≡C–CH_3, propyne
Aromatics	benzene ring 	 ethylbenzene

* **Introduction :**

Alkanes

(i) The alkanes or the paraffins are the saturated hydrocarbons. Many occur naturally, and the chief source of the alkanes is mineral oil or petroleum, which occurs in many parts of the world.

(ii) These are also called as 'Paraffins' (Parum + Affinis i.e. less reactive).

(iii) General formula is C_nH_{2n+2}.

(iv) Hybridisation state of carbon is sp^3.

(v) Geometry of carbon is tetrahedral.

(vi) Bond angle is 109º28'.

(vii) Number of bond angle in methane are six, while in ethane are twelve.

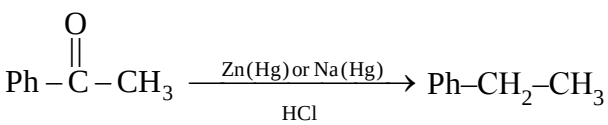
(viii) C – C bond length is 1.54 Å while C – H bond length is 1.11 Å.

Preparation of alkane

1. From aldehydes and ketones :

1.1 Clemmensen Reduction :

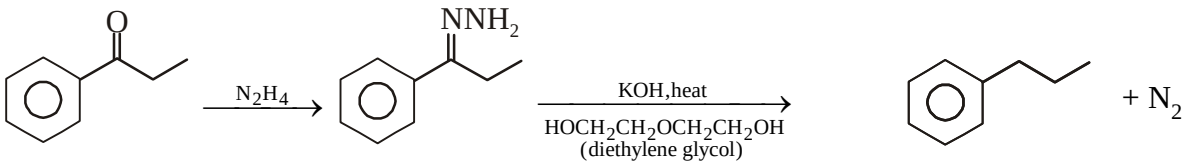
The Clemmensen reduction is most commonly used to convert acylbenzenes to alkylbenzenes, but it also works with other ketones and aldehydes that are not sensitive to acid. The carbonyl compound is heated with an excess of amalgamated zinc (zinc treated with mercury) and hydrochloric acid. The actual reduction occurs by a complex mechanism on the surface of the zinc.



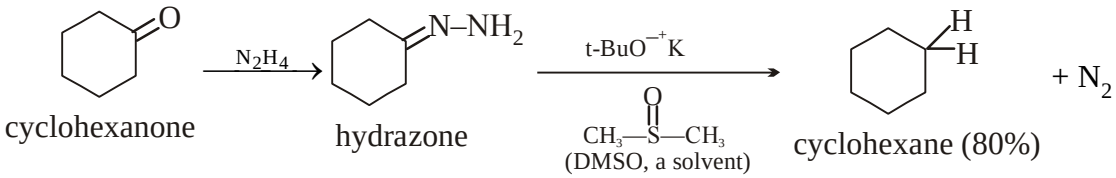
$$Ph-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[HCl]{Zn(Hg)\text{ or }Na(Hg)} Ph–CH_2–CH_3$$

1.2 Wolf-Kishner Reduction.

Compounds that cannot survive treatment with hot acid can be deoxygenated using the Wolf-Kishner reduction. The ketone or aldehyde is converted to its hydrazone, which is heated with a strong base such as KOH or potassium t-butoxide.



propiohenone hydrazone n-propylbenzene (82%)

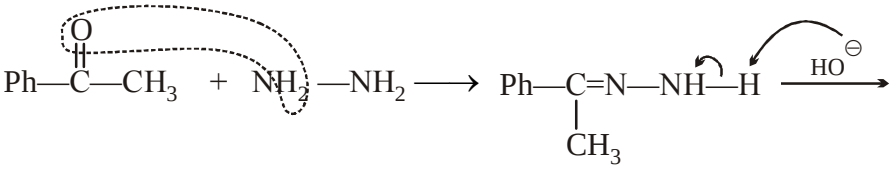


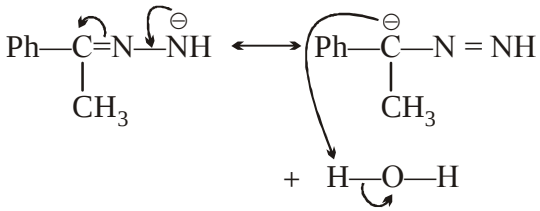
cyclohexanone hydrazone cyclohexane (80%)

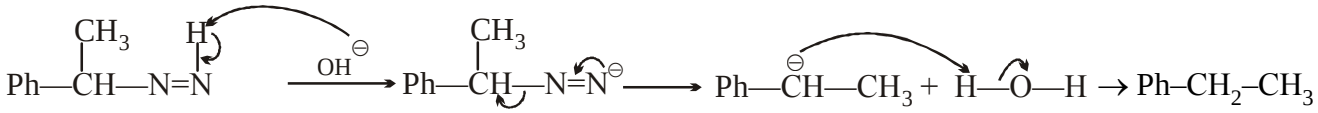
$$\text{(Aldehyde + Ketone)} \xrightarrow[HO^{\ominus},\Delta \text{ or } t-BuOK]{NH_2-NH_2} Ph-CH_2-CH_3$$

(basic medium)

Mechanism of wolf-kishner







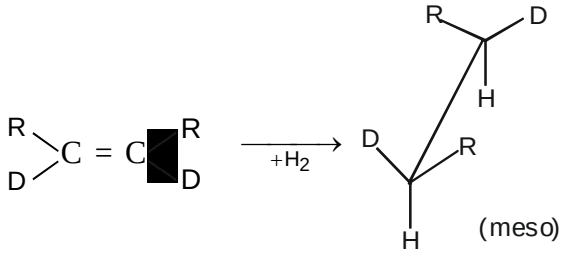
2. From alkene :

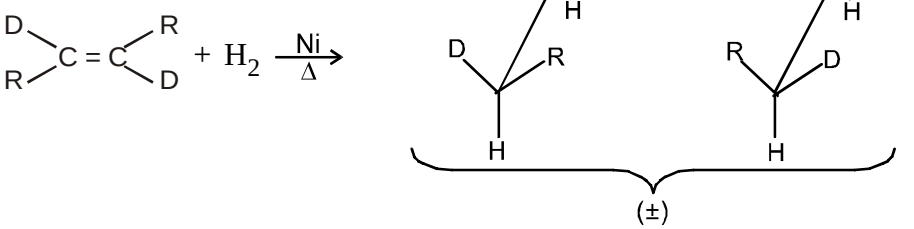
2.1 By catalytic hydrogenation : Addition of H_2 on alkene takes place in *cis manner* in the presence of Pt or Ni or Pd to give alkane.

eg.

(i) $CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$

(ii)





NOTE : This reaction is exothermic and heat of hydrogenation depend upon no. of 'α' hydrogen.

2.2 By hydroboration followed protolysis

(i) $CH_2=CH_2 + H-BH_2 \longrightarrow \overset{H}{\underset{|}{CH_2}}-\overset{BH_2}{\underset{|}{CH_2}} \xrightarrow{H^+} CH_3-CH_3$

(ii) $CH_3-CH=CH_2 \xrightarrow{H-BH_2} CH_3-\overset{H\cdots BH_2}{CH=CH_2} \longrightarrow CH_3-CH_2-\overset{BH_2}{\underset{|}{CH_2}}$

$$CH_3-CH_2-CH_2-BH_2 \xrightarrow{2CH_3-CH=CH_2} (CH_3-CH_2-CH_2-)_3B \xrightarrow{H_2O/H^+} 3CH_3-CH_2-CH_3$$

NOTE : Long- chain alkane may be possible by the coupling of alkyl boranes.

If $(AgNO_3 + NaOH)$ is used instead of H_2O/H^+

$$(R-)_3B \xrightarrow[NaOH]{AgNO_3} R-R$$

3. From alkyne - by reduction :

$$R-C\equiv C-H + H_2 \xrightarrow[2CH_3-OH]{Pt/Pd/Ni.} \underset{\text{alkene}}{R-\overset{H}{\underset{|}{C}}=\overset{}{\underset{H}{\underset{|}{C}}}-H} \xrightarrow[200°-300°C]{Pt/Pd/Ni. + H_2} \underset{\text{alkane}}{R-\overset{H}{\underset{H}{\underset{|}{\overset{|}{C}}}}-\overset{H}{\underset{H}{\underset{|}{\overset{|}{C}}}}-H}$$

in the above reaction if catalyst palladium or platinum is used, it is called simple reduction and if Ni is used, it is called ***Sabatier - Senderen's*** reaction (catalytic hydrogenation).

4. From Alkyl halides :

4.1 By reduction :

When alkyl halide is reduced with

Zn-Cu couple + ROH or Na + EtOH/ Na- Hg + H_2O or $LiAlH_4$, then we get respective alkane.

$$R-X + 2H \xrightarrow[R-OH]{Zn-Cu} RH + HX$$

$$CH_3Cl + 2H \longrightarrow CH_4 + HCl$$

$$CH_3I + 2H \longrightarrow CH_4 + HI$$

4.2 Wurtz's reaction :

When alkyl halide reacts with Sodium in presence of dry ether then we get higher alkane. Mechanism of the reaction is based on ionic and free radical both.

$$R-X + 2Na + X-R \xrightarrow{\text{dry ether}} R-R + 2NaX$$

$$CH_3Cl + 2Na + ClCH_3 \longrightarrow CH_3-CH_3 + 2NaCl$$

NOTE : * Current reaction is not suitable for tertiary alkyl halides

Mechanism : Two mechanism has been suggested for Wurtz's reaction.

(i) Via organometallic compound

$$C_2H_5Br + Na \xrightarrow[-NaBr]{} C_2H_5^-Na \xrightarrow[-NaBr]{CH_3-CH_2-Br} CH_3-CH_2-CH_2-CH_3$$

(ii) Via free radical

$$2C_2H_5-Br + 2Na \xrightarrow{-2NaBr} 2C_2H_5^{\bullet} \longrightarrow C_2H_5-C_2H_5$$

(iii) Corey-House Synthesis

$$R—X \xrightarrow[Ether]{Li} R—Li \xrightarrow{CuX} R_2CuLi$$

$$\underset{\text{Lithium dialkyl cuprate}}{R_2\,CuLi} + 2\,R'—X \longrightarrow 2\,R—R' + LiX + CuX$$
(should be 1°)

This method is better than Wurtz and can be used for preparing symmetrical as well as unsymmetrical alkanes (having an odd number of carbon atoms).

4.3 Frankland's reaction/Method :

If alkyl halide is treated with Zn dust in closed tube then higher symmetrical alkanes will be formed.

$$2RX + Zn \longrightarrow R - R + ZnX_2$$

This is known as Frankland's reaction, in this reaction first Frankland's reagent (R–Zn–R, dialkyl Zinc) is formed. Which then react with alkyl halide to give higher alkanes.

[Where $R = CH_3$]

For Example:-

$$CH_3 - Br + 2Zn + Br - CH_3 \longrightarrow CH_3 - Zn - CH_3 + ZnBr_2$$

$$CH_3 - Zn - CH_3 + CH_3 - Br \longrightarrow \underset{\text{ethane}}{CH_3 - CH_3} + CH_3ZnBr$$

4.4 Grignard reagents.

Alkyl halides in ether react with magnesium to form alkyl magnesium halides or Grignard reagents which, on treatment with water or dilute acid, are decomposed to alkanes.

(i) $RI + Mg \xrightarrow{ether} R — Mg — I \xrightarrow{H^+} RH$

(ii) $CH_3MgBr \xrightarrow{H-O-H} CH_4$

(iii) $CH_3MgBr \xrightarrow{R-O-H} CH_4$

(iv) $CH_3MgBr \xrightarrow{CH_3CO_2H} CH_4$

Preparation by Wurtz reaction, Kolbe electrolysis Ullmann, Fitting reaction, Wurtz-Fitting reaction already discussed in free radical reaction.

5. From Red P + HI :

It is a powerful reducing agent which will convert, aldehyde, ketone, alcohol, carboxylic acid to alkanes with same number of carbon.

(i) $R–CH_3–OH \xrightarrow{Red\ P + HI} R–CH_3$

(ii) $R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{Red\ P + HI} R–CH_3$

(iii) $R-\overset{\overset{O}{\|}}{C}-R \xrightarrow{Red\ P + HI} R–CH_2–R$

(iv) $R–COOH \xrightarrow{Red\ P + HI} R–CH_3$

SOLVED EXAMPLE

Ex.1 Grignard reagent give alkane with :

(A) C_2H_5OH (B) $C_2H_5NH_2$ (C) H_2O (D) None of these

Sol. **(A, B, C)**

Grignard reagent react with compounds containing active hydrogen like, NH_3, H_2O, ROH, RNH_2, R_2NH to form alkane

$$R–Mg–X + C_2H_5OH \rightarrow RH + Mg\begin{matrix}X\\OC_2H_5\end{matrix}$$

$$R–Mg–X + C_2H_5NH_2 \rightarrow R'–H + Mg\begin{matrix}X\\NHC_2H_5\end{matrix}$$

$$R''–Mg–X + HOH \rightarrow R''–H + Mg\begin{matrix}X\\OH\end{matrix}$$

Ex.2 The Kolbe synthesis of alkane using a sodium salt of butanoic acid gives -

(A) n-hexane (B) isobutane (C) n-butane (D) propane

Sol. **(A)**

Ex.3 Electrolysis of an aqueous solution of sodium butanoate gives main product –

(A) octane (B) heptane (C) hexane (D) butane

Sol. (C)

Koble electrolysis

$$2CH_3CH_2CH_2COONa \rightarrow 2CH_3CH_2CH_2COO^- + 2Na^+$$

$$\downarrow$$

$$2CH_3\dot{C}H_2CH_2COO^\bullet + e^-$$

$$\downarrow$$

$$2CH_3CH_2\dot{C}H_2^\bullet + 2CO_2$$

$$\downarrow$$

$$CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$$

Hexane.

Ex.4 Corey House reaction involves :

(A) An organometalic compound (B) A nucleophilic substitution

(C) A nucleophilic addition reaction (D) Development of a C–C bond.

Sol. (A, B, C)

Corey House reaction :

I– step : Formation of organometallic compound

$$R – X + 2Li \rightarrow R – Li + LiX$$

II–step : Organometallic compounds react with cuprous iodide (CuI) to form alkyl lithium cuprate.

$$2R – Li + CuI \rightarrow (R)_2\,CuLi + LiI$$

III step : This compound react with another alkyl halide by nucleophilic substitution reaction to form higher alkane containing both even and odd number of carbon atom which was otherwise not possible with Wurtz reaction.

$$(R)_2CuLi + R' – X \rightarrow R – R + LiX + CuR$$

overall this results in development of C – C bond.

$$CH_3–CH_2–Br \xrightarrow{Li} CH_3CH_2–Li \xrightarrow{CuI} (CH_3CH_2)_2CuLi$$

$$CH_3 – CH_2 – CH_2 – \underset{\displaystyle CH_3}{\underset{|}{C}}H – CH_3 \longleftarrow CH_3 – \underset{\displaystyle CH_3}{\underset{|}{C}}H – CH_2 – Br$$

isohexane

Ex.5 In Wurtz reaction if we take CH_3Cl & C_2H_5Cl then product will be -

(A) Propane + Ethane

(B) Propane

(C) Propane + Ethane + Butane + Ethene + CH_4

(D) Propane + Butane

Sol. **(C)**

(1) $CH_3\boxed{Cl + 2Na + Cl}CH_3 \longrightarrow \underset{\text{Ethane}}{CH_3–CH_3}$

(2) $CH_3\boxed{Cl + 2Na + Cl}CH_2–CH_3 \longrightarrow \underset{\text{Propane}}{CH_3–CH_2–CH_3}$

(3) $CH_3\,CH_2\boxed{Cl + 2Na + Cl}CH_2–CH_3 \longrightarrow \underset{\text{butane}}{CH_3–CH_2–CH_2–CH_3}$

Ex.6 Butane cannot be obtained by :

(A) Action of soda lime on sodium butanoate

(B) Clemmensen reduction (Zn amalgam in conc. HCl) of butanone

(C) Action of water on butyl magnesium iodide

(D) Sabatier Senderens hydrogenation of butene.

Sol. **(A)**

Butane formation :

(A) $RCOONa + NaOH \rightarrow R – H + Na_2CO_3$

$CH_3–CH_2CH_2COONa + NaOH \xrightarrow{CaO} CH_3CH_2CH_3 + Na_2CO_3$

(B) Clemmensen reduction : $> C = O + 4H \rightarrow > CH_2$

$$CH_3 – \underset{\underset{O}{||}}{C} – CH_2 – CH_2 + 4H \xrightarrow[\text{conc. HCl}]{} CH_3–CH_2–CH_2–CH_3$$

(C) $R–MgI + HOH \rightarrow R – H + Mg\begin{matrix} I \\ OH \end{matrix}$

$CH_3CH_2CH_2CH_2– MgI + HOH \rightarrow CH_3CH_2CH_2CH_3 + Mg\begin{matrix} I \\ OH \end{matrix}$

(D) Sabatier – Senderens hydrogenation of alkene

$R–CH=CH_2 + H_2 \xrightarrow[200°C]{NI} R – CH_2–CH_3$

$CH_3 – CH = CH – CH_3$

or $+ H_2 \xrightarrow[200°C]{NI} CH_3–CH_2–CH_2–CH_3$

$CH_3–CH_2–CH = CH_2$

Ex.7 Which of the following compounds cannot be prepared by Wurtz reaction :

(A) CH_3CH_3 (B) $CH_3\underset{\underset{CH_3}{|}}{C}H – CH_3$ (C) $(CH_3)_2CHCH_3$ (D) $CH_3CH_2CH_2CH_3$

Sol. **(B, C)**

Alkane containg even number of carbon atom can be obtained in good yield by Wurtz reaction.

$$R – Cl + R – Cl \xrightarrow[\text{ether}]{2Na} R – R$$

Alkane containing odd number of carbon atom can be obtained in good yield by Wurtz reaction.

$$R'–Cl + R – Cl \xrightarrow{2Na} R–R + R' – R' + R – R'$$

Ethane and butane are obtained in good yield because they contain even number of carbon atom.

$$2CH_3 – Cl + 2Na \xrightarrow{ether} CH_3–CH + 2NaCl$$

$$2CH_3CH_2–Cl + 2Na \xrightarrow{ether} CH_3–CH_2–CH_2CH_3 + 2NaCl$$

Isobutane contain odd number of carbon atom

$$CH_3–CH_2–Cl + \underset{\underset{CH_3}{|}}{CH_2}–Cl + 2Na \xrightarrow{ether} CH_3 – \underset{\underset{CH_3}{|}}{CH} – CH_3 + CH_3 – \underset{\underset{CH_3}{|}}{CH} – \underset{\underset{CH_3}{|}}{CH} – CH_3 + CH_3 – CH_3$$

Ex.8 Hydrolysis of an ester gives a carboxylic acid which on Kolbe's electrolysis yields ethane. The ester is :

(A) Methyl ethanoate (B) Methyl methanoate

(C) Ethyl methanoate (D) Methyl propanoate

Sol. **(A)**

Hydrolysis of ester forms carboxylic acid which on kolbe's electrolysis produces ethane.

$$CH_3 – \underset{\underset{O}{||}}{C} – OCH_3 \xrightarrow{H_3O^+} CH_3COOH + CH_3OH$$

Methyl ethanoate

$$CH_3COOH \xrightarrow{NaOH} 2CH_3COONa \rightarrow CH_3–CH_3$$

(B) $$H – \underset{\underset{O}{||}}{C} – O – CH_3 \xrightarrow{H_3O^+} H – \underset{\underset{O}{||}}{C} – OH + CH_3OH$$

(C) $$H – \underset{\underset{O}{||}}{C} – O – CH_2CH_3 \xrightarrow{H_3O^+} H – \underset{\underset{O}{||}}{C} – OH + CH_3CH_2OH$$

(D) $$CH_3 – CH_2 – \underset{\underset{O}{||}}{C} – OCH_3 \xrightarrow{H_3O} CH_3 – CH_2 – \underset{\underset{O}{||}}{C} – OH + CH_3OH$$

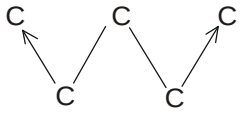
Physical Properties

1. The first four alkanes (from methane to butane) are colourless and odourless gases. The next thirteen (from pentane to heptadecane) are colourless and odourless liquids. And, the rest of higher alkanes (having 18 carbon atoms or more) are colourless solids at ordinary temperature.

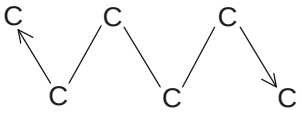
2. Alkanes being non-polar molecules, are soluble in non-polar solvents like benzene, ether, and chloroform. However, they are insoluble in polar solvents like water. Their solubility decreases with increase in their molecular weight.

3. Melting and boiling points are increases with molecular mass and decreases with No. branches. As far as melting point is concerned the alkane having even carbons has more M.P. than odd carbons, since the intermolecular forces in a crystal depend not only upon the size of the molecules but also upon how well they fit into a crystal lattice.

For e.g.



(both methyl group are directed on same side)



(both methyl group are adversely directed)

n- pentane n- hexane

M.P. even > odd no. of atoms

4. Boiling point decreases with the increment of branches.

(n-Pentane is liquid but neo-Pentane is gas due to increase in branching, surface area decrease therefore intermolecular forces & Vander Waals forces of attraction decreases).

5. Physical state:

Alkanes

$C_1 - C_4 \longrightarrow$ Gaseous state

$C_5 - C_{17} \longrightarrow$ Liquid state

(except neo pentane)

C_{18} & above $\longrightarrow$ Solid like wax

6. Alkanes are lighter than water, so it floats over water.

Chemical Properties :

1. Halogenation

Alkanes react with bromine or chlorine in the presence of sunlight or UV light or in dark at high temperatures (250°C– 400°C) forming a mixture of substituted products. For example,

$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow[h\nu]{Cl_2} CH_2Cl_2 \xrightarrow[h\nu]{Cl_2} CHCl_3 \xrightarrow[h\nu]{Cl_2} CCl_4$$

The yield of monohalogenated product can be increased by using substrate (alkane) in excess.

The reactivity of halogens follows the order: $F_2 > Cl_2 > Br_2 > I_2$.

Direct fluorination is explosive and can be achieved by the action of inorganic fluorides on bromo or iodo derivatives.

$$2C_2H_5Br + HgF_2 \rightarrow 2C_2H_5F + HgBr_2$$

Bromination is slower than chlorination and is carried out at higher temperatures.

Iodination is reversible and can be carried out sufficiently in the presence of strong oxidising agents like iodic acid (HIO_3) or nitric acid that destroys hydroiodic acid (HI) and shifts the equilibrium towards the right.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$5\,HI + HIO_3 \rightarrow 3I_2 + 3H_2O$$

Alkyl iodides can be prepared conveniently by **Contant-Finkelstein reaction** which involves treating chloro or bromoderivative with NaI in acetone or methanol solution.

$$R\,Cl + NaI \xrightarrow{acetone} RI + NaCl\downarrow$$

Alkyl chlorides or bromides cannot be prepared by this method of halide exchange because NaCl and NaBr are insoluble in acetone.

Mechanism of Halogenation :

The mechanism involves the following steps:

(i) Chain-initiation step

$$X_2 \xrightarrow[\text{or UV light}]{250\text{-}400^\circ C} 2X^\bullet$$

(ii) Chain-propagation step

$$X^\bullet + R{-}H \rightarrow H{-}X + R^\bullet$$

$$R^\bullet + X_2 \rightarrow R{-}X + X^\bullet$$

(iii) Chain-termination step

$$X^\bullet + X^\bullet \rightarrow X_2$$

$$R^\bullet + X^\bullet \rightarrow R{-}X$$

$$R^\bullet + R^\bullet \rightarrow R{-}R$$

Radical inhibitors stop chain propagation by reacting with free radical intermediates. Example:

$$R\bullet + \underset{\text{Peroxy radical}}{\bullet O{-}O\bullet} \rightarrow R{-}O{-}O\bullet$$

2. Nitration.

Under certain conditions, alkanes react with nitric acid, a hydrogen atom being replaced by a nitro-group, NO_2. This process is known as nitration. Nitration of the alkanes may be carried out in the vapour phase between 150° and 475 °C, whereupon a complex mixture of mononitroalkanes is obtained.

$$CH_3CH_2CH_3 \xrightarrow[400^\circ C]{HNO_3} CH_3CH_2CH_2NO_2 + \underset{\displaystyle CH_3CHCH_3}{\overset{\displaystyle NO_2}{|}} + C_2H_5NO_2 + CH_3NO_2$$

3. Sulphonation.

Sulphonation is the process of replacing a hydrogen atom by a sulphonic acid group, SO_3H. Sulphonation of a normal alkane from hexane onwards may be carried out by treating the alkane with oleum (fuming sulphuric acid). It has been shown that in concentrated sulphuric acid, hydrocarbons containing a tertiary hydrogen atom undergo hydrogen exchange (Ingold et. al. 1936). The mechanism is believed to occur via a carbonium ion:

$$R_3CH + 2H_2SO_4 \longrightarrow R_3C^+ + HSO_4^- + SO_2 + 2H_2O$$

$$R_3C^+ + R_3CH \longrightarrow R_3CH + R_3C^+ \text{, etc.}$$

This reaction is of particular interest since optically active hydrocarbons have been racemised in sulphuric acid; e.g., Burwell et. al. (1948) have shown that optically active 3-methylheptane is racemised in sulphuric acid.

$$CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{-}H \xrightarrow{H_2SO_4} CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{-}SO_3H$$

Imp. Rate of sulphonation $3^\circ > 2^\circ > 1^\circ$.

4 Chlorosulphonation/Reaction with SO_2 & Cl_2:

The reaction is also called as **Reed's reaction.** When propane reacts with SO_2 and Cl_2 in presence of ultraviolet light then propyl sulphonyl chlorides are formed.

$$CH_3\text{-}CH_2\text{-}CH_3 + SO_2 + Cl_2 \xrightarrow{\text{U.V. Light}} CH_3\text{–}CH_2\text{–}CH_2SO_2Cl + HCl$$

This process is used in the commercial formation of detergents.

$$CH_3 - (CH_2)_{10} - CH_2\text{–}CH_2\text{–}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{–}Cl + NaOH \xrightarrow[\text{hydrolysis}]{\text{Alkaline}} CH_3 - (CH_2)_{10} - CH_2\text{–}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{–}O^- \; Na^+$$

(detergent i.e. sodium salt of sulphonic acid)

5. Isomerisation : Lower alkanes are not isomerised but butane or higher number of alkanes if heated with aluminium chloride at high temperature then they convert into stable isomers by the rearrangement reaction. Isomerisation is also held by heating alkane with- (AlX_3 + HX; X = Cl, Br, I or $Al_2(SO_4)_3 + H_2SO_4$) at 200ºC.

$$CH_3\text{–}\underset{\underset{H}{|}}{CH}\text{–}CH_2\text{–}CH_3 \xrightarrow[400^\circ C]{AlCl_3} CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_3$$

n - butane iso butane

If we take n- heptane then it converts into most stable form Triptane (trivial name).

$$CH_3\text{-}(CH_2)_5\text{–}CH_3 \longrightarrow CH_3\text{–}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{–}\underset{\underset{CH_3}{|}}{CH}\text{–}CH_3$$

n- heptane 2, 2, 3- trimethyl butane

If we take n - octane, iso-octane is formed.

$$CH_3(CH_2)_6\,CH_3 \longrightarrow CH_3\text{–}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{–}CH_2\text{–}\underset{\underset{CH_3}{|}}{CH}\text{–}CH_3$$

n- octane iso-octane

Reaction is used in Petroleum industries, with the help of this reaction, we can convert unbranched alkane to branched alkane (i.e. lower octane number alkane to higher octane number alkane) or bad fuel to good fuel.

6. Combustion :

Combustion is a rapid oxidation that takes place at high temperatures, converting alkanes to carbon dioxide and water. Little control over the reaction is possible, except for moderating the temperature and controlling the fuel / air ratio to achieve efficient burning.

$$C_nH_{(2n+2)} + \text{excess } O_2 \xrightarrow{\text{heat}} nCO_2 + (n+1)\,H_2O$$

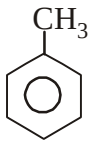
Example : $CH_3CH_2CH_3 + 5\,O_2 \xrightarrow{\text{heat}} 3\,CO_2 + 4\,H_2O$

Facilities that use these more environment- friendly heat sources are more expensive than those that rely on the combustion of alkanes, however.

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

7. Aromatization :

(i) n-Hexane $\xrightarrow[\Delta]{Cr_2O_3-Al_2O_3}$ 

(ii) n-Heptane $\xrightarrow[\Delta]{Cr_2O_3-Al_2O_3}$ 

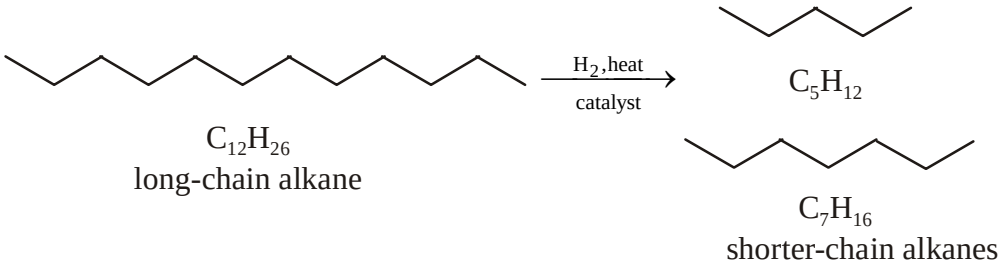
For converting aliphatic to aromatic.

(iii) n-Octane $\xrightarrow[\Delta]{Cr_2O_3-Al_2O_3}$ O + M + P (xylene)

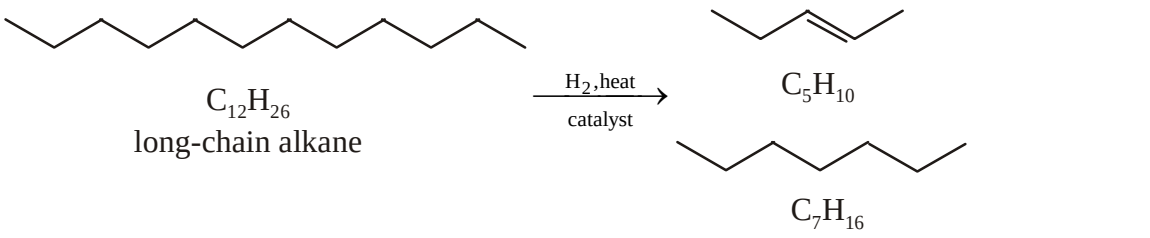
8. Cracking and Hydrocracking :

Cracking of large hydrocarbons at high temperatures produces smaller hydrocarbons. The cracking process usually operates under conditions that give the maximum yields of gasoline. In hydrocracking , hydrogen is added to give saturated hydrocarbons; cracking without hydrogen gives mixture of alkanes and alkenes.

Catalytic hydrocracking



Catalytic cracking



Knocking :

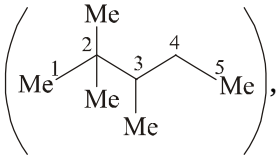
Knocking may be defined as the pre-ignition of fuel-air mixture in the cylinder aheadof the flame. It reduces the efficiency of the engine and also causes damage to the cylinder and piston of the engine.

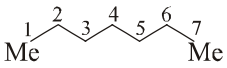
1. The extent of knocking depends on the quality of the fuel used. In other words, a fuel that produces minimum knocking is considered as a good-quality fuel
2. The anti-knocking property or the quality of a fuel is usually expressed in terms of the octane number.

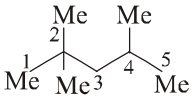
Octane Number :

Octane number is a scale that is used to determine the quality of a fuel.

It may be defined as the percentage of isooctane by volume in a mixture of isooctane and n-heptane that has the same anti-knocking properties as the fuel under examination.

1. Straight-chain aliphatic hydrocarbons have a higher tendency to knock than branched-chain hydrocarbons.
2. Two pure hydrocarbons have been selected as standards :
   (a) n-Heptane has poor anti-knocking property, therfore, arbitrarily it has been assigned an octane number of zero.
   (b) 2,24-Trimethylpentane (isooctane), a branched-chain hydrocarbon, has the highest anti-knocking property. Therfore, it has been given the octane number of 100. The octane number of nonane is –45 and that of 2,2,3-trimethylpentane , called as triptane, is 116.

 n-Heptane, octane number = 0

 2,2,4-Trimethylpentane or isooctane, octane number = 100

Alkanes	**Octane number**
CH_4	122
C_2H_6	101
C_3H_8	96
C_4H_{10}	89

3. Straight-chain alkanes have very low octane numbers. As the length of the chain increases, the octane number decreases.
4. Branched-chain alkanes have higher octane number. As the branching increases, the octane number increases.
5. Cycloalkanes have higher octane number. As the extent of branching increases, octane number further increases.
6. Unsaturated hydrocarbons, i.e., alkenes and alkynes, have higher octane numbers than the corresponding straight-chain alkanes.
7. Aromatic hydrocarbons have very high octane numbers.
8. It has been found that gasoline obtained by creacking has a higher octane number than gasoline obtained by direct distillation. This is because creacked gasoline contains higher precentage of alkenes, branched-chain aliphatic hydrocarbons, and aromatic hydrocarbons.

   The tendency of knocking decreases in the order : **straight-chain alkane > branched-chain alkane > alkenes > cycloalkanes > aromatic hydrocarbon.**

Anti-knocking agent or Gasoline additives :

Compounds that are added to gasoline and reduce knocking are called anti-knocking agents. The problem of knocking in engines can be checked by using fuels of high octane number and by addition certain compounds (anti knocking agents) that reduce knocking.

The best anti-knocking agent is tetraethyl lead (TEL) or $Pb(C_2H_5)_4$. This is added to the extent of 0.001% in gasoline. Such a gasoline is called ethyl gasoline or leaded gasoline. In the cylinder of an engine, TEL decomposes to produce ethyl radicals that combine with the radicals produced due to irregular combustion. As a reslt, reaction chains are broken and smooth burning of the fuel occurs. This prevents knocking.

$$Pb(C_2H_5)_4 \xrightarrow{\text{Heat}} Pb + 4C_2H_5 \text{ (Ethylradical)}$$

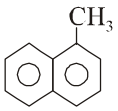
The lead deposited in the cylinder is removed by adding 1,2-dibromoethane (ethylene bromide) that decomposes into ehene (ethylene) and bromine. The bromine thus obtained combines with lead to form lead bromide which, being volatile, is carried of from the engine by exhaust gases.

$BrCH_2CH_2Br \rightarrow CH_2=CH_2 + Br_2$

$Pb + Br_2 \rightarrow PbBr_2$ (Volatile)

Cetane Number :

1. Cetane number is a scale that is used to determine the quality of a diesel fuel.
Cetane number is the percentage of cetane by volume in a mixture of cetane and α-methylnaphthalene that has the same ignition properties as the diesel under examination in a test engien.
C_6H_{34} (n-hexadecane), cetane number = 100 (ignites spontaneously)



α-Methylnapthalene, cetane number = 0 (ignites slowly)

or

1-Methylnapthalene

2. LPG and CNG : The term LPG (liquified petroleium gas) refers to the mixture of hydrocarbons containing three or four C atoms. This includes propane (C_3H_8), propene (C_3H_6), n-butane (C_4H_{10}), isobutane (methylpropane), and various butenes with a little amount of ethane (C_2H_6). The major sources of LPG are natural gas and refining and creacking of petroleium. Alkenes are mainly produced during creacking. LPG is mainly used in the manufacturing of chemicals, as a fuel for households, and in the petro-chemical industry.
CNG (compressed natural gas) is a highly compressed form of natural gas. Many vehicles are designed to operate on CNG. Natural gas has an octane rating of 130.

SOLVED EXAMPLE

Ex.1 The reaction conditions leading to the best yields of C_2H_5Cl are –

(A) C_2H_6 (Excess) + $Cl_2 \xrightarrow{\text{u.v.light}}$ (B) $C_2H_6 + Cl_2 \xrightarrow{\text{dark room temp.}}$

(C) $C_2H_6 + Cl_2$ (Excess) $\xrightarrow{\text{u.v.light}}$ (D) $C_2H_6 + Cl_2 \xrightarrow{\text{u.v.light}}$

Sol. **(A)**

Chlorination of ethane takes place by free radical substitution reaction can be prevented by using excess of C_2H_6.

$C_2H_6 + Cl - Cl \xrightarrow{\text{u.v.Light}} C_2H_5Cl + HCl$

(excess)

Ex.2 $C_2H_6 + SO_2 + Cl_2 \xrightarrow{\text{U.V.Light}}$ product. In this reaction product will be -

(A) C_2H_4 (B) CH_3CH_2Cl (C) $CH_3CH_2SO_2Cl$ (D) C_2H_2

Sol. **(C)**

Above reaction is Reed reaction and product is sulphonyl chloride.

Ex.3 Product of the Wolff-Kishner reduction is –

(A) Alkene (B) Alkyne (C) Alkane (D) Amine

Sol. **(C)**

In the Wolff-Kishner reduction carbonyl compound is converted into alkane by intermediate hydrazone.

Ex.4 Which of the following should be subjected to Wurtz reaction to obtain the best yield of n-hexane?

(A) Ethyl chloride and n-butyl chloride

(B) Methyl bromide and n-propyl bromide

(C) n-Propyl bromide

(D) Ethyl bromide and n-butyl bromide

Sol. **(C)**

Ex.5 2-Methylbutane on reacting with bromide in the presence of sunlight gives mainly -

(A) 1-Bromo-3-methylbutane (B) 2-Bromo-3-methylbutane

(C) 2-Bromo-2-methylbutane (D) 1-Bromo-2-methylbutane

Sol. **(C)** $CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_3 + Br_2 \xrightarrow{\text{Sunlight}} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}}-CH_2-CH_3 + HBr$.

Ease of substitution of H atom is $3^o > 2^o > 1^o$.

Ex.6 Which of the following alkyl bromides may be used for the synthesis of 2, 3-dimethylbutane by Wurtz reaction ?

(A) n-Propyl bromide (B) Isopropyl bromide

(C) Isobutyl bromide (D) s-Butyl bromide

Sol. **(B)**

REACTION CHART FOR ALKANES

GMP

(1) $R-C\equiv CH$ $\xrightarrow[200-300^\circ C]{H_2, Ni}$ or $R-CH=CH_2$ Sabatier senderens reaction

(2) $R-X$ $\xrightarrow[\text{Red P}-Hi, LiAlH_4]{Zn-Cu+HCl}$

(3) RX $\xrightarrow[\text{Wurtz reaction}]{Na, \text{dry ether}}$

(4) RX $\xrightarrow[\text{Frankland's reaction}]{Zn}$

(5) RX $\xrightarrow[(\text{Corey}-\text{House reaction})]{R_2CuLi}$

(6) $R-Mg-X$ $\xrightarrow[\text{or } NH_3 \text{ or } RNH_2]{+HOH \text{ or } ROH}$

(7) $R-OH$, $R-CHO$ $\xrightarrow{\text{Red P / HI}}$

$R-\underset{\underset{O}{\|}}{C}-R$, $RCOCl$, $RCOOH$

(8) $R-\underset{\underset{O}{\|}}{C}-R$ $\xrightarrow[\text{Clemension's reduction}]{Zn-Hg / \text{Conc.HCl}}$

(9) $R-\underset{\underset{O}{\|}}{C}-R$ $\xrightarrow[\text{Wolf / Kishner reduction}]{H_2N-NH_2}$

or

$(RCH_2CH_2)_3B$ $\xrightarrow{+H_2O}$

(10) $RCOONa$ $\xrightarrow{NaOH+CaO}$

(11) $RCOONa$ $\xrightarrow{\text{Kolbe's electrolytic synthesis}}$

$R-H$ or $R-R$ or C_nH_{2n+2} $\longrightarrow$

GR

(1) $\xrightarrow{X_2, h\nu \text{ or UV light or } 400^\circ C}$ RX

(2) $\xrightarrow{\text{Nitration}}$ $R-N\begin{matrix}O\\ \diagdown\\ \diagup\\ O\end{matrix}$

(3) $\xrightarrow{\text{Sulphonation } H_2S_2O_7}$ Alkyl Sulphonic acid

(4) $SO_2 + Cl_2 \xrightarrow[h\nu]{\text{Reed reaction}} RSO_2Cl$

(5) $\xrightarrow[\text{Isomerisation}]{AlCl_3 / HCl}$ branched alkanes

(6) $\xrightarrow[500-700^\circ C]{\text{Pyrolysis}}$ Alkenes + CH_4 or C_2H_6

(7) $\xrightarrow[+Al_2O_3\ 500^\circ C]{\text{Cr or Mo or V oxide}}$ Aromatic compound

(8) $\xrightarrow[\text{step up reaction}]{CH_2N_2}$ Higher alkane

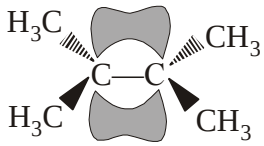
(9) $\xrightarrow[\Delta]{O_2}$ $CO_2 + H_2O$

Combustion

ALKENE

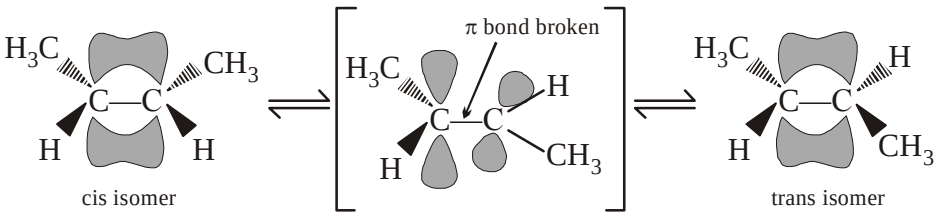
1. GENERAL INTRODUCTION

- Hydrocarbons that contain a carbon–carbon double bond are called alkenes.
- Early chemists noted that an oily substance was formed when ethene ($H_2C = CH_2$), the smallest alkene, reacted with chlorine. Based on this observation, early organic chemists called alkenes olefins (oil forming substance).
- Insects communicate by releasing pheromones, chemical substances that other insects of the same species detect with their antennae. There are sex, alarm, and trail pheromones, and many of these are alkenes.
- Many of the flavors and fragrances produced by certain plants also belong to the alkene family.
- Each double-bonded carbon of an alkene has three sp^2 orbital of another atom to form a σ bond.
- Thus, one of the carbon–carbon bonds in a double bond is a σ bond, formed by the overlap of an sp^2 orbital of one carbon with an sp^2 orbital of the other carbon.
- The second carbon-carbon bond in the double bond (the π bonds) is formed from side-to-side overlap of the remaining p-orbitals on the sp^2 carbons. Because three points determine a plane, each sp^2 hybridized carbon and two of the three atoms bonded to it are in a plane.
- In order to achieve maximum orbital-orbital overlap, the two p-orbitals must be parallel to each other. Therefore, all six atoms of the double bond system are in the same plane. A molecular orbital description of a carbon-carbon double bond.
- It is important to remember that the π bond represents the cloud of electrons that is above and below the plane defined by the two sp^2 carbons and the four atoms bonded to them.



p orbitals overlap
to form a π bond

- Because the two p orbitals that form the π bond must be parallel to one another to achieve maximum overlap, rotation about a double bond does not occur. If rotation about a doubel bond did occur, the two p-orbitals would ceases to overlap and the π bond would be destroyed.



cis isomer

trans isomer

2. Characteristics of Alkene :

(a) General formula : C_nH_{2n}.

(b) Functional group : in alkenes is >C=C<

(c) The double bond is made up of one sigma and one pi bond.

(d) The doubly bonded carbon atoms are sp^2 hybridized.

(e) Geometry of unsaturated 'C' carbon is trigonal planar.

(f) C = C bond length is 1.34 Å.

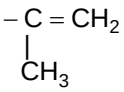
(g) C–H bond length is 1.10 Å.

(h) C = C bond energy is 143.1 k cal mol^{-1}.

(i) C – H bond energy is 98.69 k cal mol^{-1}.

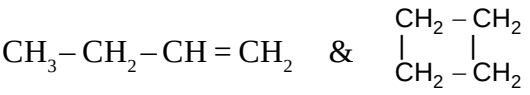
(j) Alkene shows chain, position, functional (ring chain), optical & geometrical isomerism.

NOTE : Cumulated polyene can exhibit geometrical as well as optical isomerism. for eg. Isomers of C_4H_8:

(i) Chain isomers → $CH_3-CH_2-CH=CH_2$ & 

(ii) Position isomers → $CH_2=CH-CH_2-CH_3$ & $CH_3-CH=CH-CH_3$

(iii) Functional isomers (ring chain isomerism)



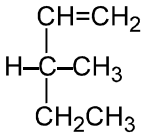
1-butene cyclobutane

(iv) Geometrical isomers →

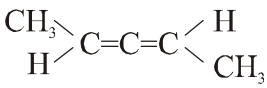


cis -2-butene Trans-2-butene

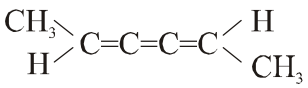
(v) Optical isomerism →



NOTE :



I



II

This molecule is simplest example of cumulated poly-ene which can exhibit optical isomerism. Because this is a chiral molecule. Similarly suitably substituted polyene containing odd no. of double bond can exhibit geometrical isomerism as because this is a planer molecule.

* Cumulated polyene having even no. of double bonds (eg. I) which has $=C<^{a}_{b}$ system at the both end can exhibit optical isomerism but cannot exhibit geometrical isomerism.

* Cumulated polyene having odd no. double bonds (eg. II) which have $=C<^{a}_{b}$ system at both end can exhibit geometrical isomerism but cannot exhibit optical isomerism.

3. METHODS OF PREPARATION OF ALKENES

3.1 ELIMINATION REACTIONS

Elimination reactions consist in removing the two groups (generally one being a proton and other is leaving group from one or two carbon atoms of a substrate to form an unsaturated linkage.
Elimination reactions are classified under two general categories.

TYPES OF ELIMINATION REACTIONS

1. α-elimination (1, 1)
2. β-elimination (1, 2)

1. α-elimination : When the two atoms or groups are eliminated from the same carbon, the process is called α–elimination.

2. β-elimination : When the two groups or atoms are removed from the two adjacent carbon atoms, the process is known as β-elimination.

SOME IMPORTANT TERMS

(1) **Substrate :** That molecule or ion which undergoes change is called substrate. Substrate may be alkyl halide, alcohol etc.

(2) **Base :** It is negative ion or neutral molecule which abstract the proton from the substrate.

(3) **Leaving Group :** It is an ion or molecule which leaves the substrate with a pair of electron. The tendency of leaving group is directly proportional to strength of its conjugated acid. Leaving group ability of different halide ions follows the sequence

$$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

β-ELIMINATION CAN OCCUR BY THREE DIFFERENT MECHANISM

(1) E-1 mechanism

(2) E-2 mechanism

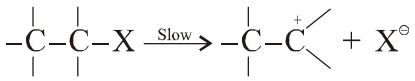
(3) E1 cB mechanism

CHARACTERISTICS OF E-1 MECHANISM :

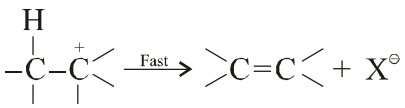
(a) It is called unimolecular elimination reaction.

(b) It takes place in two steps.

Ist Step : Departure of leaving group from a molecule to form carbocation.



IInd Step : Carbocation formed above loses a proton to the base and forms the alkene.



(c) Ist step of E-1 mechanism is the rate determining step (R.D.S.)

(d) Since in R.D.S. only substrate undergoes covalency change.
i.e. it follows first order kinetics with respect to substrate

$$\text{Rate} = K\,[\text{substrate}]$$

(e) Since in R.D.S. carbocation is formed as an intermediate so the reactivity order of different substrate follows the stability of order of carbocation formed.
Allylic > Tertiary > Secondary > Primary

(f) Loss of leaving group is the part of R.D.S. therefore the order of reactivity of alkyl halide in elimination reaction is

$$R–I > R–Br > R–Cl > R–F$$

Above order is parallel to order of leaving group ability

$$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

(g) E-1 mechanism does not show isotopic effect as the loss of hydrogen is not the part of R.D.S.

$$\frac{K_H}{K_D} = 1$$

(h) Since the ionization take place in step I. Therefore polar solvent favors the E-1 mechanism.

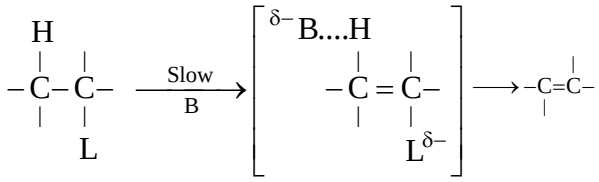
(i) E-1 mechanism involves carbocation as an intermediate so rearrangement of carbocation can take if possible. More stable carbocation forms the major product in the reaction.

E-2 MECHANISM

(a) It is known as bimolecular elimination mechanism.

(b) It take place in single step.

(c) It involves the formation of transition state



Transition State

(d) Formation of transition state is the rate determining step.

(e) Rate of reaction depends on the concentration of substrate as well as of base i.e. it follows the second-order kinetics.

Rate = [Substrate] [Base]

(f) E-2 mechanism shows the isotopic effect as the loss of hydrogen is a part of R.D.S.

$$\frac{K_H}{K_D} = \frac{7}{1}$$

(g) E-2 mechanism shows the halogen effect as loss of leaving group is a part of R.D.S.

$\therefore$ Reactivity of different alkyl halides follows the sequence

R – I > R – Br > R – Cl > R – F

Reactivity order of different substrate follows

3º > 2º > 1º

(h) The rate of reaction increases with increasing strength and concentration of the base.

(i) Non-polar solvent favors the E-2 mechanism.

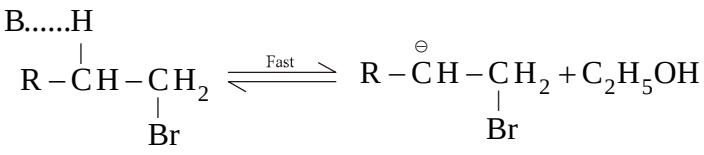
(j) Since E-2 mechanism involves the transition state rearrangement is not possible.

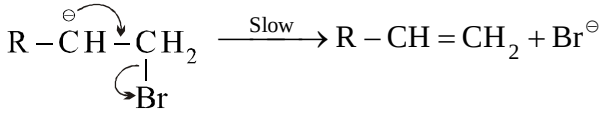
E1 cB MECHANISM

(a) In this mechanism, the reaction take place in two steps.

(i) The first step involves rapid removal of a proton from the α-carbon (carbon adjacent to the carbon bearing halogen atom) forming a carbanion.

(ii) The carbanion formed then loses the halides ion in the second rate determining step.





(b) The overall rate of the reaction is limited to slower second step & hence the rate of reaction depends only on the concentration of carbanion.

(c) Since carbanion is the conjugate base of the alkyl halide and rate of reaction depends on concentration of carbanion hence the mechanism is designated as E1cB mechanism.

MECHANISM OF α–ELIMINATION

α-elimination does not occur frequently and completes in two stages, the second of which is rate determining.

for eq.

$$CHCl_3 + OH^- \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} {}^{\ominus}CCl_3 + H_2O$$

$${}^{\ominus}CCl_3 \longrightarrow :CCl_2 + Cl^-$$

dichlorocarbene

Another example of α-elimination reaction is formation of diphenylacetylene from 2, 2-diphenyl vinyl bromide and sodamide.

$$(C_6H_5)_2C{=}C(H)(Br) \xrightarrow{\overset{\ominus}{N}H_2} C_6H_5{-}C{\equiv}C{-}C_6H_5$$

3.2 From Alkynes

$$R-C\equiv C-H + H_2 \xrightarrow[Pd-BaSO_4]{Lindlar's Catalyst} R-\underset{H}{\overset{H}{C}}=\underset{H}{\overset{}{C}}-H$$

poison of catalyst such as $BaSO_4$, $CaCO_3$ are used to stop the reaction after the formation of alkene, otherwise alkanes are formed.

Mechanism

(i) The reaction takes place at the surface of Pd, that is why it is ***cis addition*** and the product is cis form eg.

$$R-C\equiv C-R' \xrightarrow[-BaSO_4]{H_2/Pd} \underset{H}{\overset{R}{}}C=C\overset{R'}{\underset{H}{}}$$

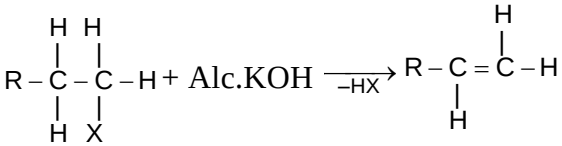
(ii) Alkyne can be reduced to trans alkene by using Na + NH_3, or Li AlH_4

$$R-C\equiv C-R \xrightarrow[NH_3 \text{ liq.}]{Na} \underset{H}{\overset{R}{}}C=C\overset{H}{\underset{R'}{}}$$

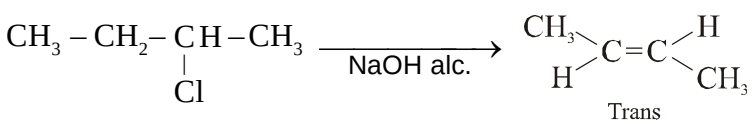
Terminal alkynes are not reduced by the Na – NH_3 untill presence of $(NH_4)_2SO_4$.

3.3 From mono halides

When mono halide react with alcoholic KOH or NaOH then respective alkenes are formed

(i)


Alkene

(ii)


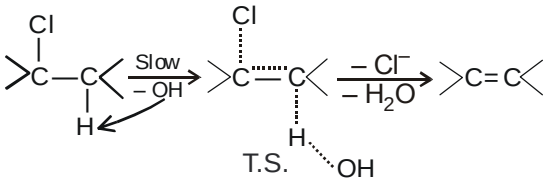
Trans

NOTE : $CH_3{-}CH_2CHX{-}CH_3 \longrightarrow \underset{\text{Minor}}{CH_3{-}CH_2{-}CH{=}CH_2} \longrightarrow \underset{\text{Major}}{CH_3{-}CH{=}CH{-}CH_3}$

CH_3—CH = CH —CH_3 (Trans) is the major product because it is more stable as having *six 'α' Hydrogen* in the comparison to $CH_3{-}CH_2{-}CH{=}CH_2$ having only two 'α' hydrogen.
This is in accordance with the **saytzeff rule.**

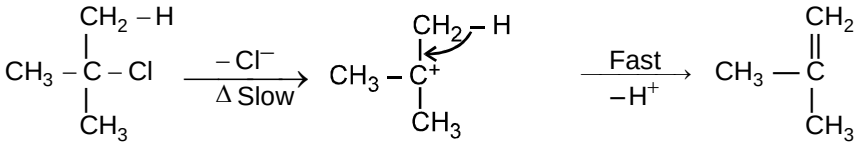
Mechanism : E2 and E1 are possible.

E2 Mechanism :



As molecularity of slowest step is two i.e. E2 mechanism.

E1 Mechanism :-

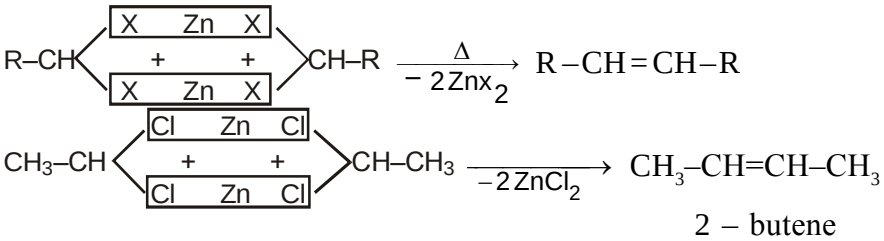


As molecularity of slowest step is **one**. That is why it is termed as E1.

Remember : Possibility of E1 increases with increasing stability of carbo cation . similarly possibility of E2 increases with decreasing stability of expected carbocation.

3.4 From Dihalides

3.4.1 From gem dihalides : When gem dihalide is heated with Na in ether then higher alkenes are formed.

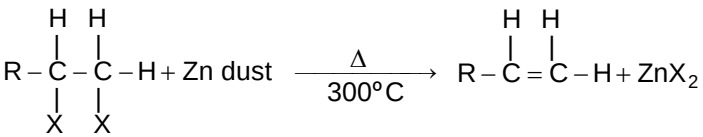


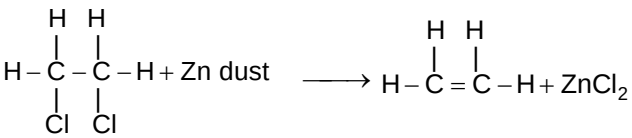
Conclusion – If we take two different types of gemdihalides then we obtain three different types of alkenes.

Note : The above reaction is used in the formation of symm. alkenes only, because if we take two different types of halides then mixture of alkenes is obtained so the yield of an individual alkene is reduced and it is improper to separate each alkene from the mixture because the difference of boiling points in alkenes is very less.

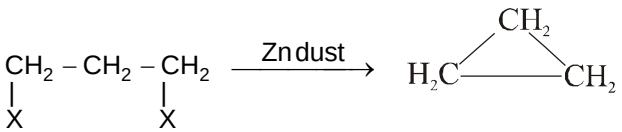
3.4.2 From vicinal dihalides :

When vicinal dihalides are heated with Zn dust, alkene of same no. of carbon is obtained.



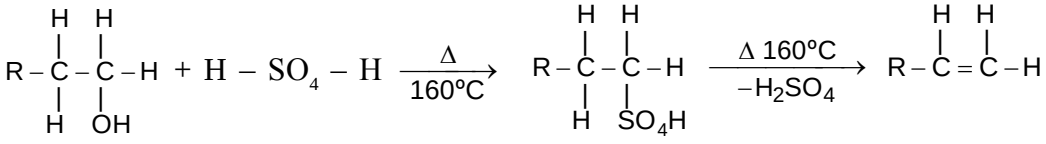


Note : Alkene is not formed from 1,3 dihalides. Cyclo alkanes are formed by dehalogenation of it. For eg.

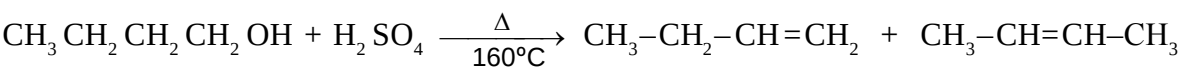


3.5 From Alcohols

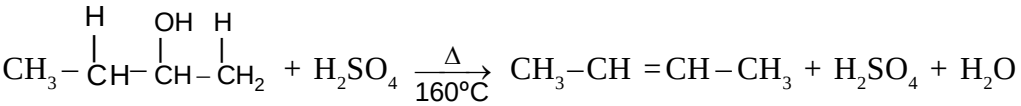
When alcohol is heated with conc. H_2SO_4 at about 160° C, alkenes are formed after dehydration.



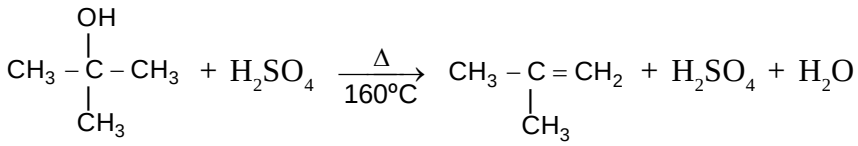
(Alkyl hydrogen sulphate) Alkene



1–butene (major product) 2–butene

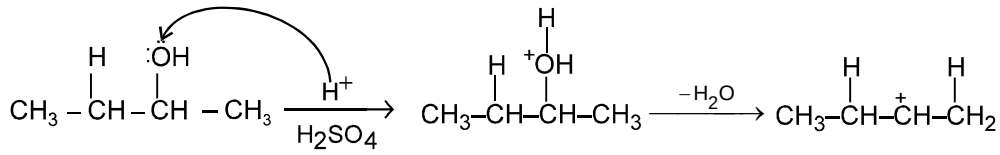


2–butene (chief product)

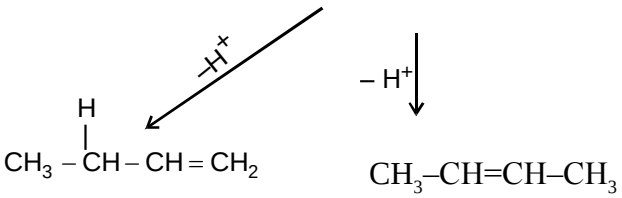


Iso butylene

Mechanism :-

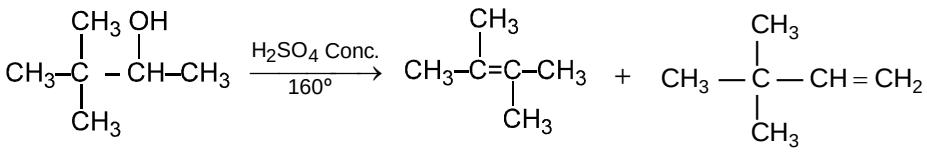


(+) or (–)



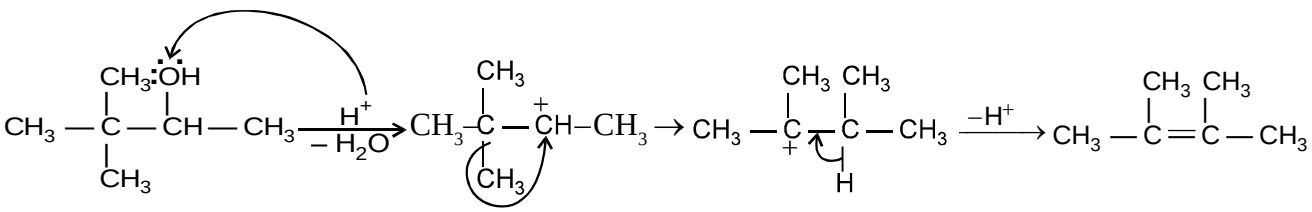
(Minor) (Trans major)

Note : Since the mechanism proceeds via- $\mathbf{C^+}$ ion therefore ***rearrangement*** is also possible eg.:



(Major) (Minor) Negligible

Mechanism :



Characteristics of dehydration of alcohol

(1) Since the carbocation is formed as an intermediate in the R.D.S. of dehydration of alcohol The relative reactivity of alcohols decreases in the order.

Tertiary > Secondary > Primary

(2) Since the R.D.S. is reversible it is necessary to remove the H_2O molecule produced in the reaction. Therefore in experimental condition conc. H_2SO_4 is added in a regular interval.

(3) For dehydration, different dehydrating agent like Al_2O_3, ThO_2 can also be employed.

(4) Rearrangement of carbocation can take place.

(5) –OH is not a good leaving group, in alcohols so turn it into a good leaving group, it is converted into $–H_2O$ by protonation

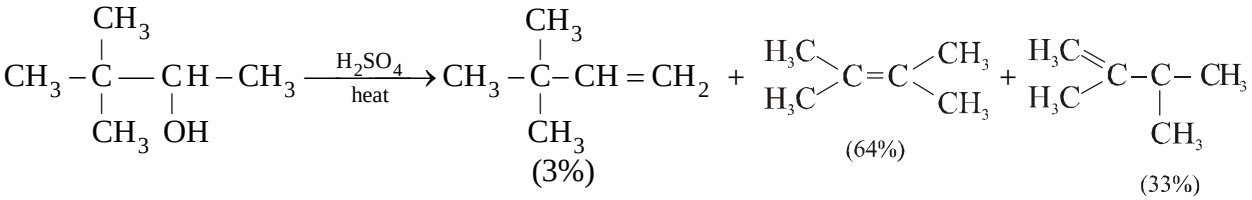
(6) H_2O is a good leaving group.

Rearrangement in Alcohol Dehydration

(1) Some alcohols undergo dehydration to form alkene having carbon skeleton different from those of the starting alcohol.

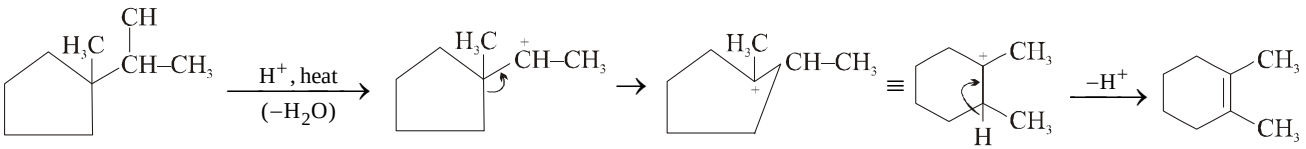
(2) This is due to rearrangement of carbocation formed in the reaction to more stable carbocation.

(3) An example of alcohol dehydration that is accompanied by rearrangement is.



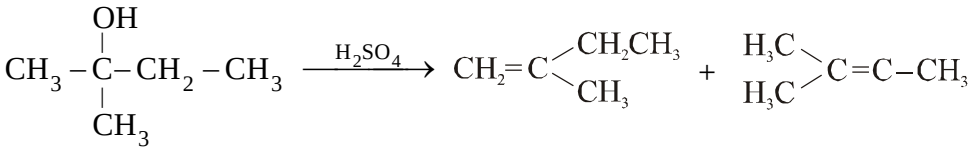
(4) Percent yield of alkenes formed from rearranged carbocation is greater than the percent yield of alkene obtained from unrearranged carbocation.

(5) Rearrangement of carbocations can also lead to a change in ring size, as the following example shows



Regioselectivity in alcohol dehydration :

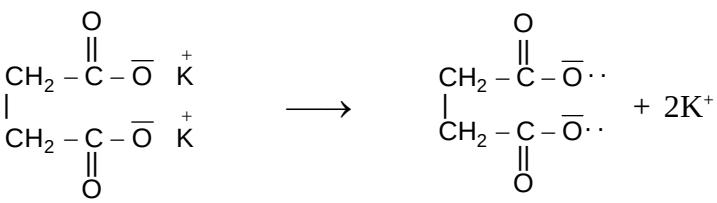
1. In alcohols such as 2-methyl-2-butanol, dehydration can occur in two different directions to give alkenes that are constitutional isomers.
2. More substituted alkene forms the major product and is called Saytzeff alkene or Zaitsev alkene.
3. Less substituted forms the minor product and is called Hofmann's alkene.



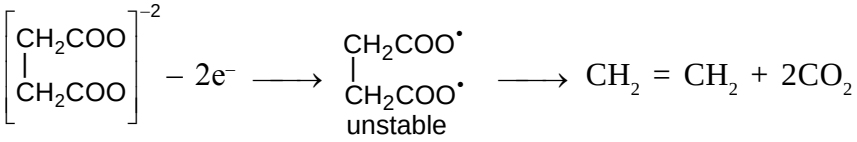
(Minor) (Major)

3.6 Kolbe's Synthesis

When aqueous solution of K or Na succinate is electrolysed, ethylene is released at anode.



At Anode



At Cathode

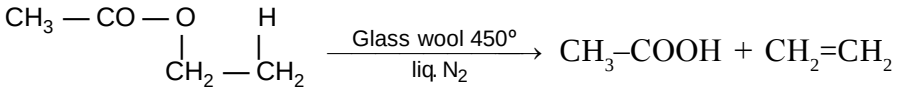
$$2K^+ + 2e^- \longrightarrow 2K$$

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

Note – If we use methyl succinic acid as reactant then propylene is formed.

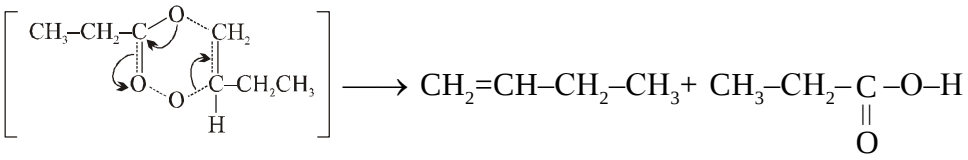
3.7 From Esters

When esters are heated in presence of liq. N_2 and glass wool, then alkyl part of ester converts into respective alkene while alkanoate part of ester is converted into respective acid.



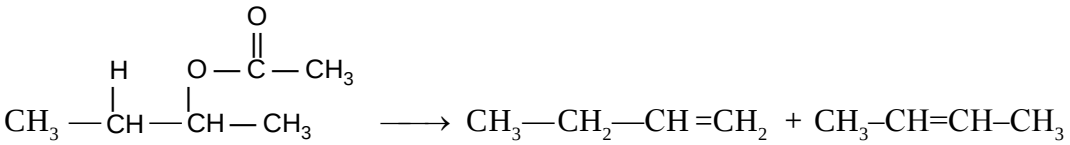
The reaction is called as '**Pyrolysis of Ester**'.

Mechanism : Pyrolysis of Ester is a type of E1 elimination which proceed via *cyclic T.S.* that is why the product becomes 'cis'



Cyclic Transition state

* It is interesting to note that, in this case major product is 1- alkene in the comparision to 2-alkene.

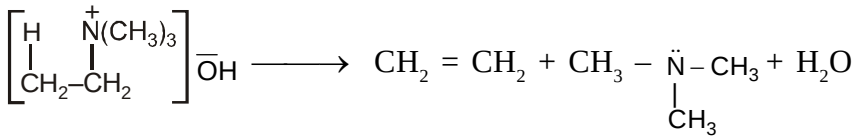


(Major) (minor)

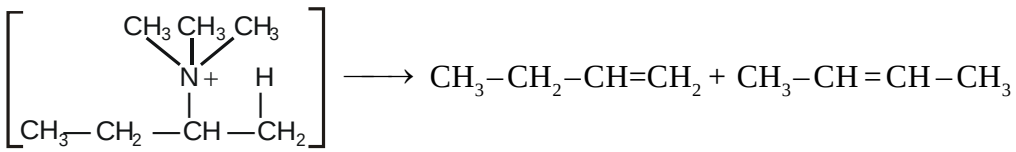
3.8 From quaternary ammonium hydroxide

When quaternary ammonium hydroxide is heated strongly it decomposes to give alkene. eg.

(i)



(ii)



(major) (minor)

This elimination is called **Hoffman's elimination.** It is markable that in this reaction more acidic H is preferably eliminated.

3.9 The wittig reaction

In this reaction methylene triphenyl phosphorane is reacted with carbonyl compound to give alkene.
eg. :

(i) $(Ph)_3P=CH_2 + \underset{\underset{O}{\|}}{CH-R} \longrightarrow (Ph)_3P=O + R-\underset{\underset{CH_2}{\|}}{CH}$

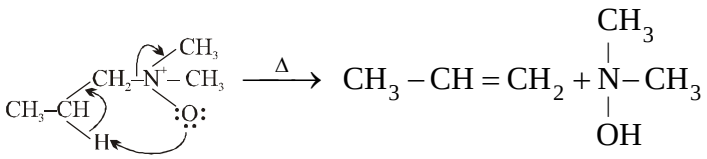
(ii) $(Ph)_3P=CH-R + \overset{\overset{O}{\|}}{CH}-R' \longrightarrow (Ph)_3P=O + R'-CH=CH-R$

3.10 The Cope Elimination :

Tertiary amine oxide undergoes the elimination of a dialkylhydroxyamine when they are heated. This reaction is called the Cope elimination.

$$\text{Reaction}: CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{O_\ominus}{|}}{N^+}}-CH_3 \xrightarrow{\Delta} CH_3-CH=CH_2 + \overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{N}}-CH_3$$

Mechanism :



SOLVED EXAMPLE

Ex. 1 The minimum number of C atoms required to be present in an optically active alkene are:
(A) 4 (B) 6 (C) 8 (D) 10 **(Ans.B)**

Sol. The minimum number of C atoms required to be present in an optically active alkene are 6.

e.g. $CH_3-\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH=CH_2$

Here the central carbon atoms is an asymmetric carbon atom.

Ex.2 Chloroethane reacts with alcoholic KOH to form –
(A) Propyl chloride (B) Ethyl chloride
(C) Ethene (D) None **(Ans.C)**

Sol. $H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-H + \text{Alc.KOH} \xrightarrow[-HX]{} H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}=C-H$

ethene

Ex.3 The synthesis of ethene from electrolysis of an aqueous solution of potassium succinate is known as:

(A) Faradays electrolysis (B) Kolbe - Schmidt reaction

(C) Hoffmann's rearrangement (D) Kolbe's electrolytic Synthesis

(Ans. D)

Sol. The synthesis of ethene from electrolysis of an aqueous solution of potassium succinate is known as Kolbe's Electrolysis synthesis. The reaction takes place as follows :

$$\begin{matrix}CH_2COOK\\|\\CH_2COOK\end{matrix} \longrightarrow \begin{matrix}CH_2COO^-\\|\\CH_2COO^-\end{matrix}$$

$$\begin{matrix}CH_2COO^-\\|\\CH_2COO^-\end{matrix} \xrightarrow{-2e,\ \text{At anode}} \underset{\text{Ethene}}{\begin{matrix}CH_2\\\|\\CH_2\end{matrix}} + 2CO_2$$

$$2K^+ + 2e \longrightarrow 2K \text{ (at cathode)}$$

$$2K + 2H_2O \longrightarrow 2\ KOH + H_2$$

Ex.4 $\begin{matrix}H\\|\\CH_2\end{matrix}-\begin{matrix}Cl\\|\\CH_2\end{matrix} \xrightarrow[\text{alk.}]{\text{NaOH}} CH_2=CH_2$. Most probable mechanism for this reaction is -

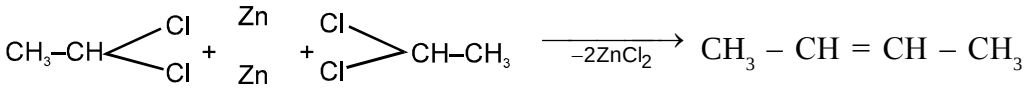
(A) E 1 (B) E 2 (C) $E1_{CB}$ (D) α elimination

Sol. **(B)** 1º halide generally gives E 2 mechanism.

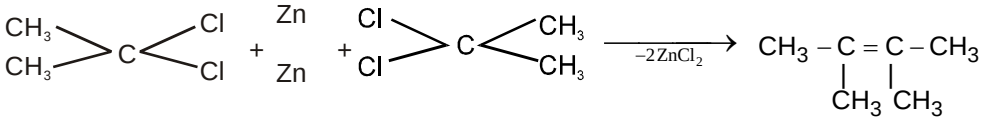
Ex.5 $RCH = CH_2$ can be obtained by :

(A) $R-\overset{\overset{O}{\|}}{C}-H$ and $(C_6H_5)_3 P = \underset{\downarrow}{CH_2}$ (B) By heating $RCH_2CH_2N(CH_3)_2$

$\qquad\qquad\qquad



2-butene



2,3-dimethyl-2-butene

Ex. 7 Identify 'Z' in the following reaction series,

$$CH_3CH_2CH_2Br \xrightarrow{NaOH(aq)} (X) \xrightarrow[heat]{Al_2O_3} (Y) \xrightarrow{Cl_2/H_2O} (Z)$$

(A) Mixture of $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$ and $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

(B) $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

(C) $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$ (D) $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$ **(Ans.B)**

Sol. $CH_3CH_2CH_2Br \xrightarrow{NaOH(aq.)} CH_3CH_2CH_2OH \xrightarrow[\Delta]{Al_3O_3} CH_3CH=CH_2 \xrightarrow{HOCl} CH_3\underset{OH}{\underset{|}{CH}}CH_2Cl$

Ex.8 $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-CH_3 \xrightarrow{Zn/dust} CH_3-CH=CH-CH_3.$

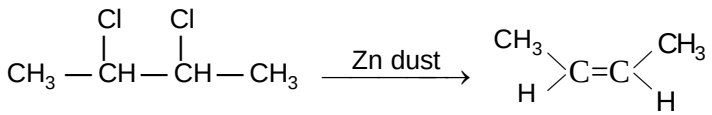
This 2-Butene is -

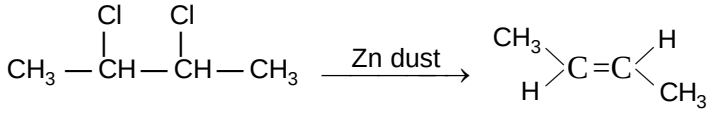
(A) Cis 2-Butene (B) Trans -2-Butene

(C) Depend upon reactant (D) Recemic mixture

Sol. **(C)**

$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-CH_3$ may be of two types. It may be asymmetrical or meso and they can give different compounds.





meso

4. PHYSICAL PROPERTIES

(i) From C_2–C_4 they are colourless, odourless gases, from C_5–C_{17} they are colourless liquids, C_{18} onwards alkenes are solids.

(ii) Alkenes are practically insoluble in water because they cannot form hydrogen bonds with H_2O molecule. They dissolve freely in organic solvents like benzene, chloroform, CCl_4 petroleum ether, etc. (Like dissolves like)

(iii) B.P and M.P. decreases with increasing branches in alkene.

(iv) The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans. Thus trans packs more tightly in the crystal lattice and hence has a higher melting point.

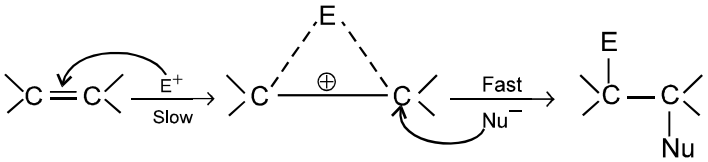
(v) The boiling points of cis isomers are higher than trans isomers because cis–alkenes has greater polarity (Dipole moment) than trans one.

(vi) These are lighter than water.

(vii) The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

5. CHEMICAL PROPERTIES

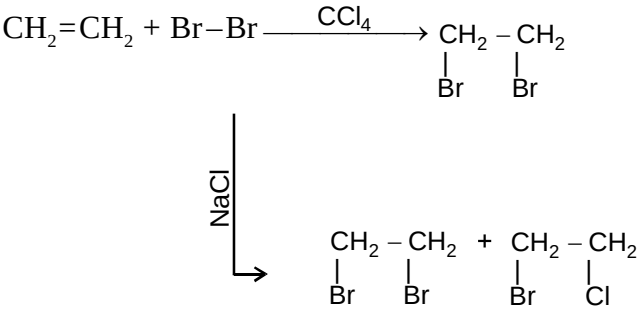
The main reactions of alkene are electrophilic addition reaction and the mechanism is based on ionic. It was proved by Francis.



Thus the electrophilic addition on alkene is trans addition.

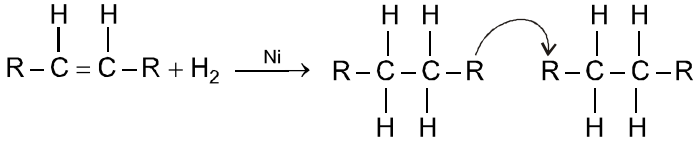
6. FRANCIS EXPERIMENT

According to Francis first attacks electrophile on the olefinic bond



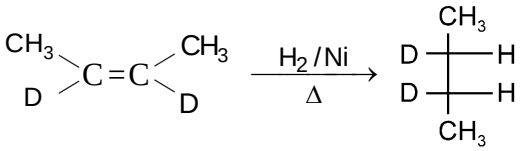
7. CHEMICAL REACTIONS

7.1 Reaction with Hydrogen –

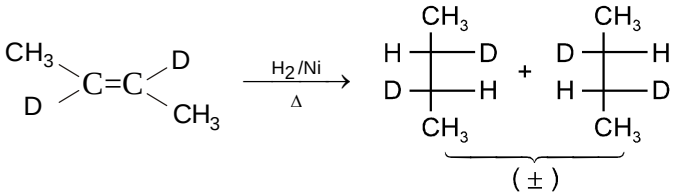


Mechanism : The reaction takes place at the surface of Ni, therefore the addition is cis addition.

eg :-



(meso)



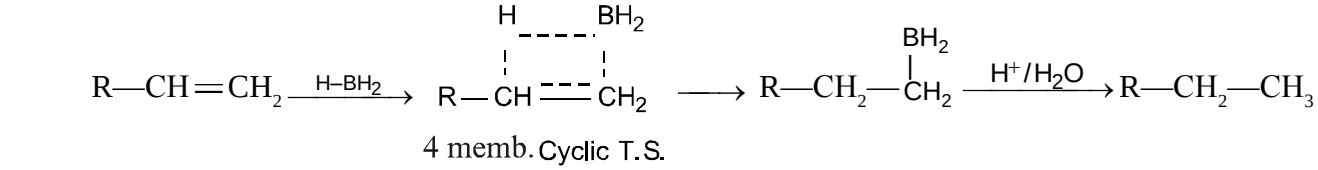
enontriomeric pair

Note : Hydrogenation (catalytic hydrogenation) of alkene is a cis addition and is an exothermic reaction. Thus the heat evolved decreases with increasing stability of alkene.

Remember, Stability of alkene depends upon hyperconjugation and type of geometrical isomerism

7.2 Reduction of alkene via hydroboration

(i) Alkene can be converted in to alkane by hydroboration followed by protolysis

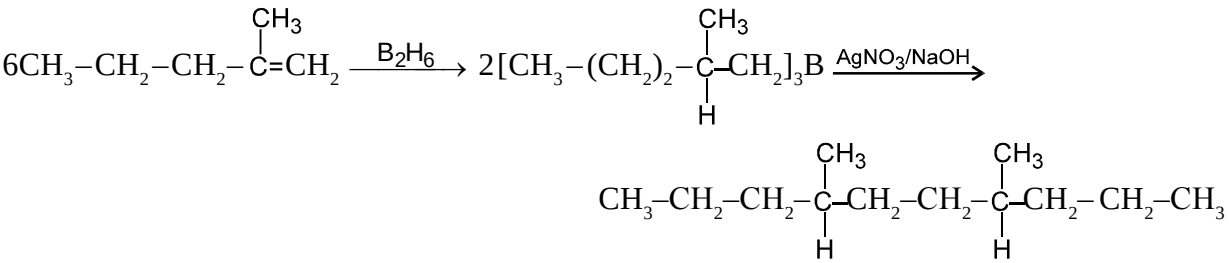


4 memb. Cyclic T.S.

This reaction is also represented as

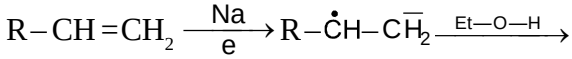
$$RCH=CH_2 \xrightarrow{H-BH_2} (R-CH_2-CH_2)_3B \xrightarrow{H^+/H_2O} 3R-CH_2-CH_3 + H_3BO_3$$

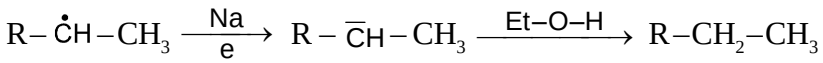
(ii) Alkene can be converted into alkane by hydroboration followed by treatment with $AgNO_3 + NaOH$. This method gives coupling.



7.3 Birch Reduction

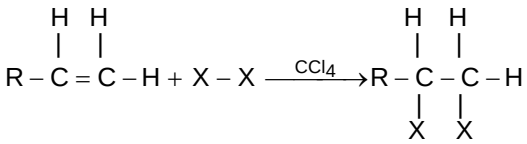
A terminal double bond may be reduced by sodium in liq. NH_3 in the presence of alcohol. This method is known as the **Birch Reduction** and is believed to proceed Via an anionic free radical





7.4 Halogenation –

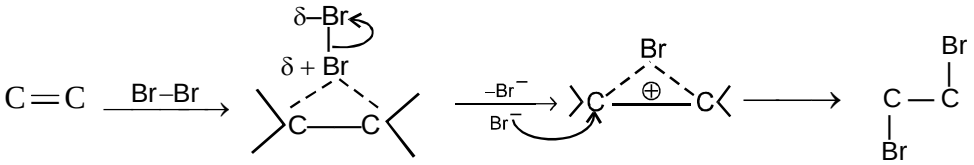
In presence of polar medium alkene form vicinal dihalide with halogen.



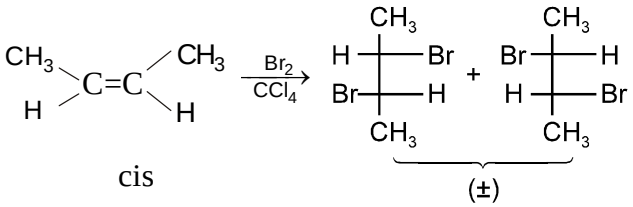
Vicinal dihalide

Order of reactivity of halogens is : $F_2 > Cl_2 > Br_2 > I_2$

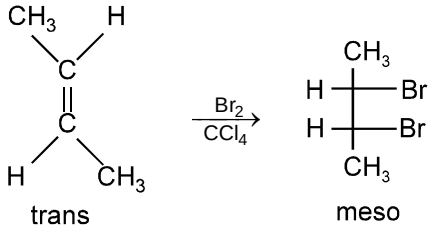
Mechanism : It is an electrophilic addition by molecular attack in which the addition takes place in trans manner.



that is why-



cis



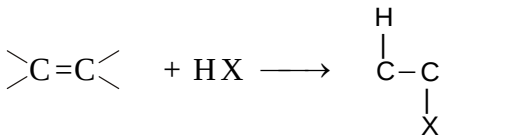
trans meso

Note : For suitable condition

(i) Cis addition on cis form results meso (ii) Cis addition on trans form results (±)

(iii) Trans addition on cis form results (±) (iv) Trans addition on trans form results meso.

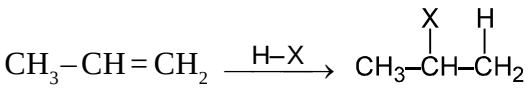
7.5 Reaction with HX (Hydrohalogenation) –



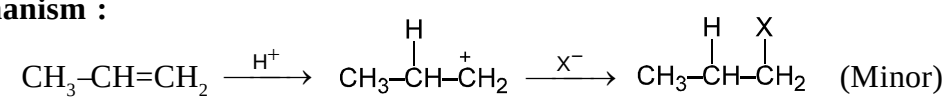
alkene alkyl halide

7.5.1 Markovnikoff's Rule

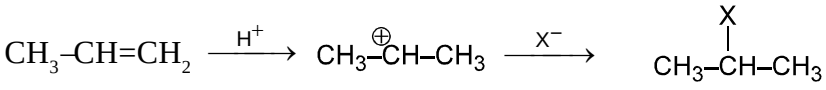
When an unsaturated unsymmetrical hydrocarbon reacts with HX then halogen goes on that unsaturated carbon which has minimum number of hydrogen atom. Mechanism of the reaction is based on $-\overset{|}{\underset{}{C^{+}}}-$.



Mechanism :



less stable



more stable major

(i) Formation of Carbocation is Rate determining step.

(ii) Rearrangement of carbocation to more stable carbocation can occur to form a more stable product.

(iii) Regiochemistry - Markownikoff's Addition of HX.

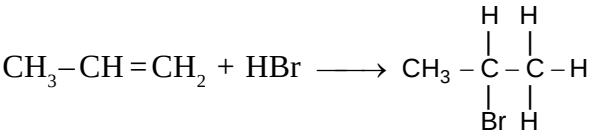
Addition of HX on unsymmetrical alkenes ($R–CH=CH_2$) takes place according to Markownikoff's rule which states that, "the negative part of abbendum is added on the carbon atom carrying lesser number of hydrogen atoms".

(iv) Reactivity order of different hydrogen halide towards addition

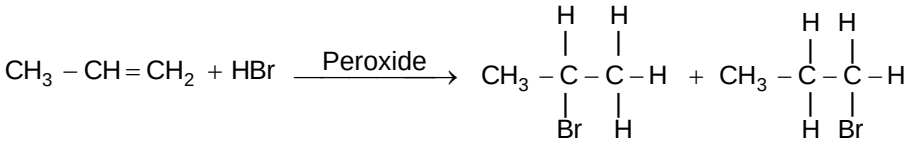
HI > HBr > HCl > HF

7.5.2 Anti Markownikoff's Principle / Kharasch Effect / Peroxide Effect –

To understand antimarkownikoff's principle let us consider the following reactions



(Markownikoff's rule)



(minor) (major)

(Anti markownikoff's rule)

It is based on free radical mechanism.

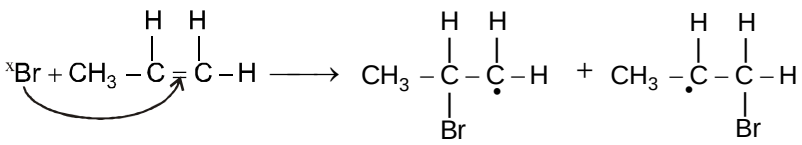
(a) Mechanism Concept –

(i) $R–O–O–R \longrightarrow RO^{\bullet} + {}^{\bullet}OR$

Peroxide

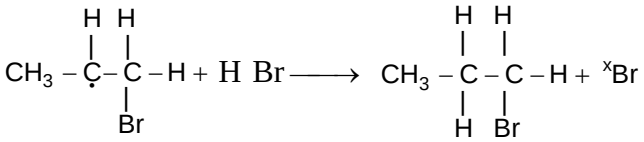
(ii) $RO^{\bullet} + H–Br \longrightarrow ROH + {}^{x}Br$

(iii)



minor 20% major 80%

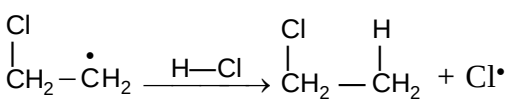
(iv)



(v) ${}^{x}Br + {}^{x}Br \longrightarrow Br_2$

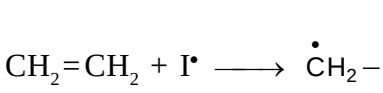
Note : It is interesting to note that anti markovnikov addition in the presence of peroxide is not applicable for HCl and HI

(i) In the case of H – Cl, the step



is endothermic (as $\Delta H^{\bullet} = + 12.6$ KJ mol^{-1})

(ii) In the case of H – I, the step

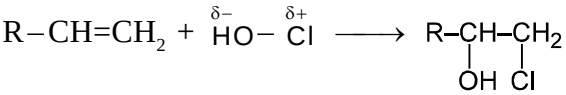


endothermic (as $\Delta H = +46$ KJ mol^{-1})

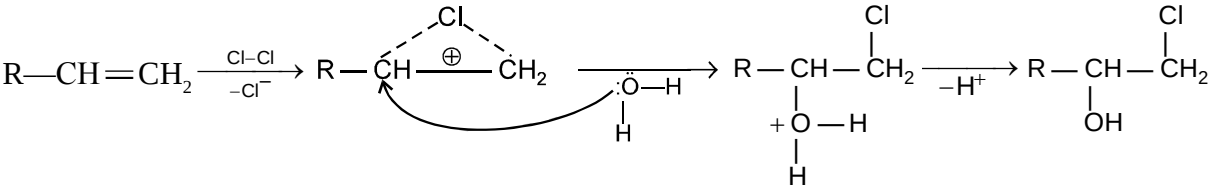
But in the case of HBr both of the steps are exothermic, which results spontaneous reaction.

* CCl_4, $CBrCl_3$ etc. can also be added to alkene in anti markovnikov manner.

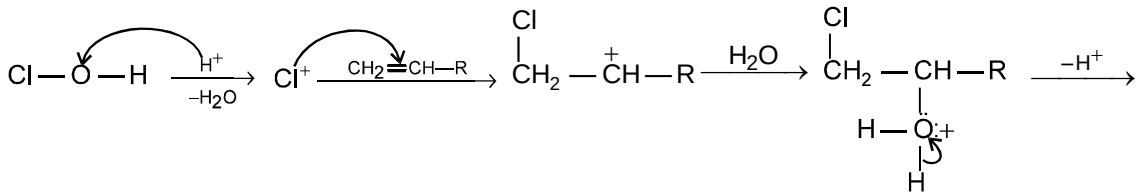
7.6 Reaction with Hypohalous Acid –

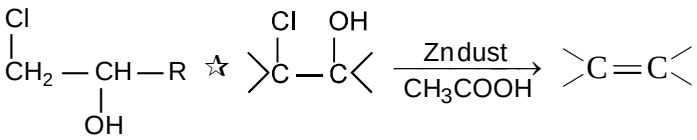


(i) When chlorine water or bromine water is used.



(ii) When aq. solution of HOCl is added in the presence of strong acid.

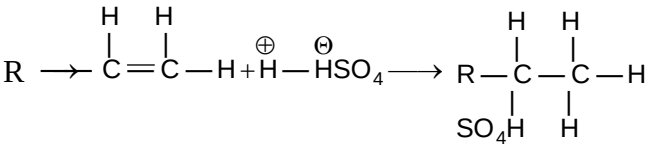




halohydrine

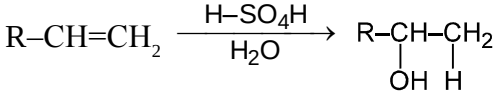
7.7 Reaction with H_2SO_4 –

(a) With conc. H_2SO_4

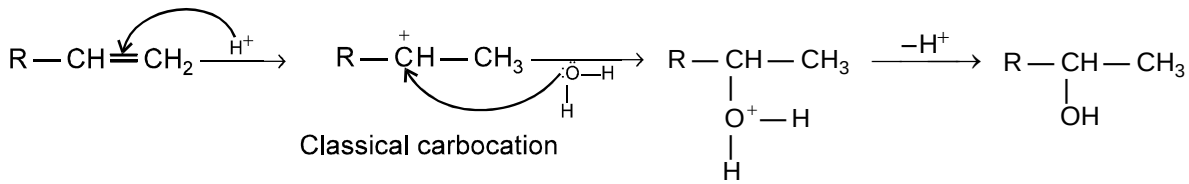


alkyl hydrogen sulphate

(b) With dil. H_2SO_4



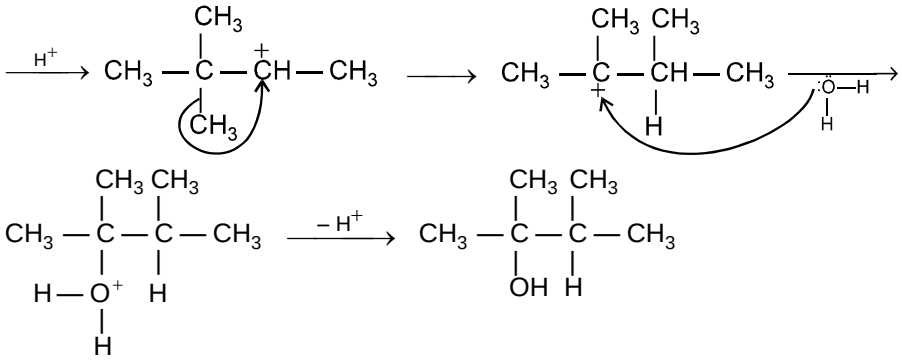
Mechanism:



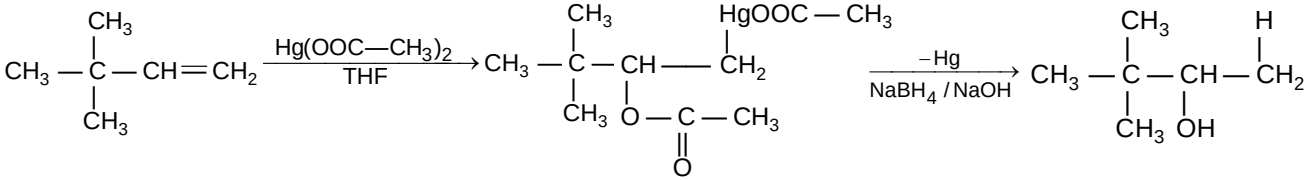
Classical carbocation

* The hydration of alkene is not stereoselective, as in the case of HCl addition. This fact can be explained on the basis of classical carbon cation formation.

* Since hydration proceeds via carbocation intermediate therefore rearrangement is always probable.

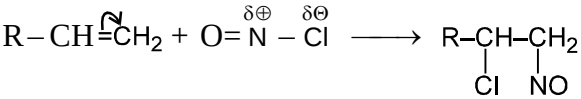


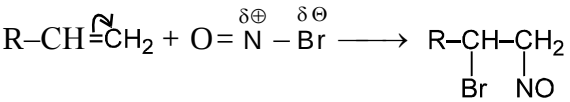
* Rearrangement, however, may be avoided by treatment of alkene by *oxymercuration-demercuration method*

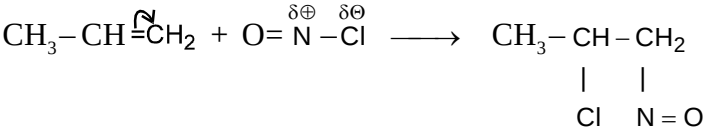


7.8 Addition of Nitrosyl halide –

Alkene with nitrosyl bromide or nitrosyl chloride (**Tillden reagent**) react according to Markovinikoff's rule to give alkene nitrosobromide and alkene nitrosochloride respectively.





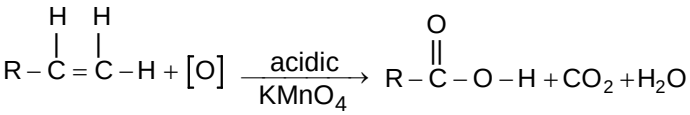


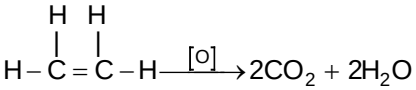
propelene nitrosochloride

7.9 Oxidation

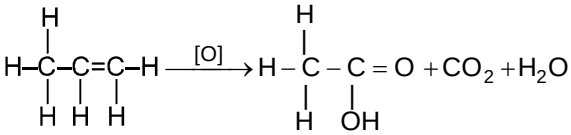
Oxidation is completed by the following ways.

7.9.1 With Acidic $KMnO_4$ / Hot $KMnO_4$

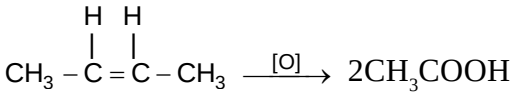




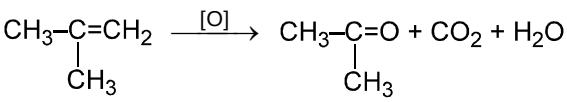
ethene



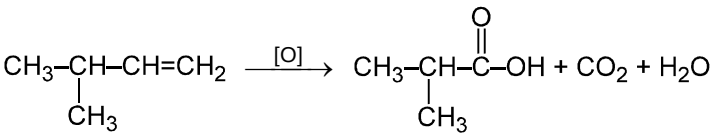
propenes acetic acid



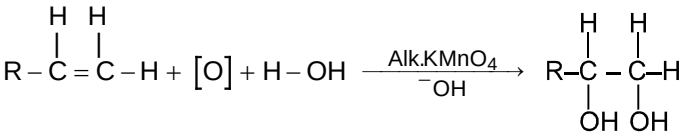
2-butene



isobutylene

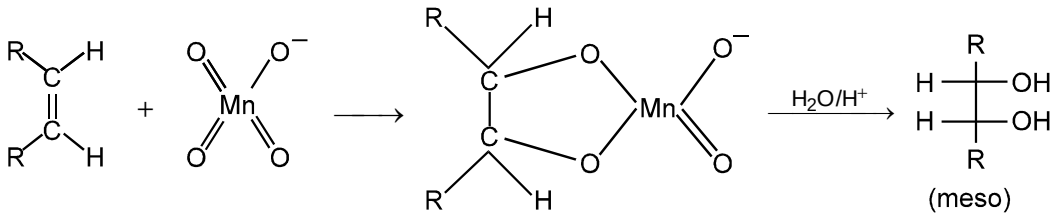


7.9.2 With alkaline $KMnO_4$ / Bayer's reagent



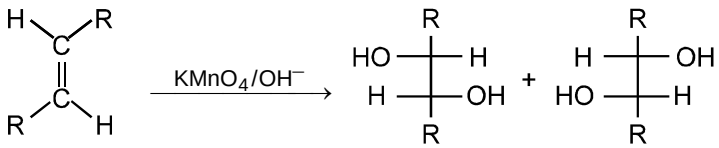
glycol

Mechanism: Hydroxylation by alkaline $KMnO_4$ (Bayer's reagent) is cis addition and the mechanism is cyclic.



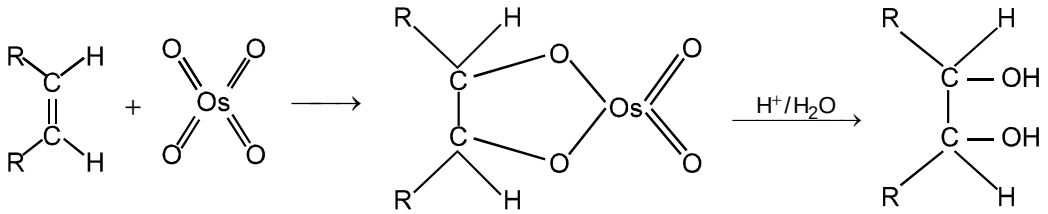
(meso)

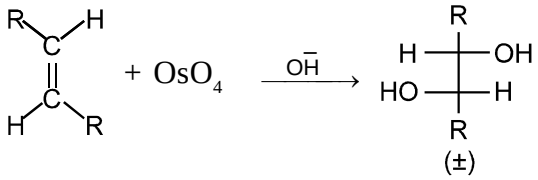
Similarly



(±)

7.9.3 Hydroxylation by OsO_4 :





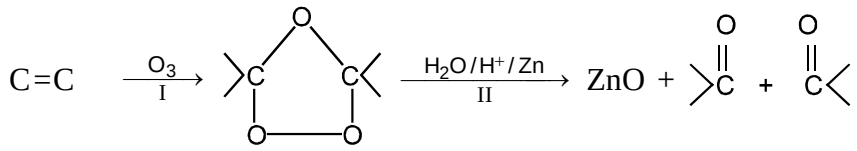
7.9.4 Ozonolysis :-

This is the two step reaction

(i) Ozonide formation

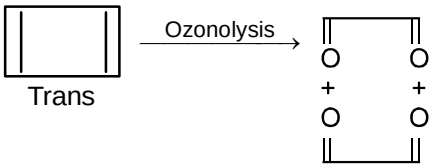
(ii) decomposition of ozonide (reductive hydrolysis)

eg:-

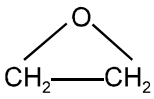


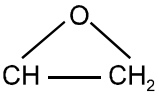
Remember : Ozonolysis gives oxidative cleavage of alkene to form two carbonyl group for each $\rangle C = C \langle$. Whether it is in acyclic or cyclic or in aromatic compound. eg :-

(a) $CH_2=CH-CH=CH_2 \xrightarrow{\text{Ozonolysis}} H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H$

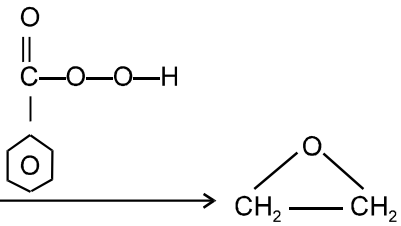
(b) 

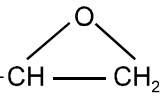
7.9.5 Epoxidation by O_2 /Ag

(i) $CH_2=CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag}$ 

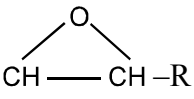
(ii) $CH_3-CH=CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag}$ 

7.9.6 Epoxidation by performic acid or perbenzoic acid

(i) $CH_2=CH_2 \xrightarrow{}$ 

(ii) $CH_3-CH=CH_2 \xrightarrow{H-\overset{O}{\overset{\|}{C}}-O-O-H}$ 

It is observed that $CF_3\overset{O}{\overset{\|}{C}}-O-OH$ is an excellent reagent for epoxidation

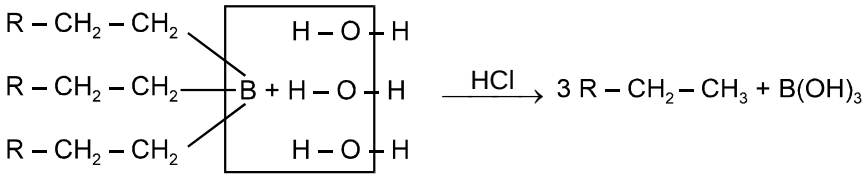
$R-CH=CH-R \xrightarrow{CF_3COOOH}$ 

7.10 Hydroboration

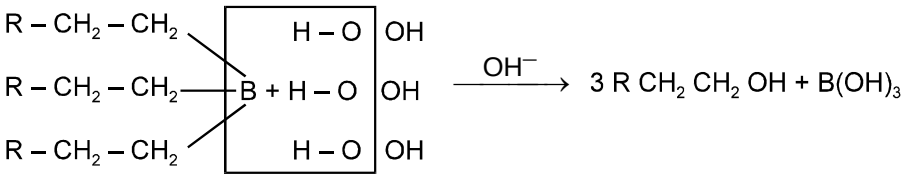
Alkene with borane hydride form an important compound called trialkyl borane.

$3R–CH=CH_2 + BH_3 \longrightarrow (R–CH_2–CH_2)_3B$

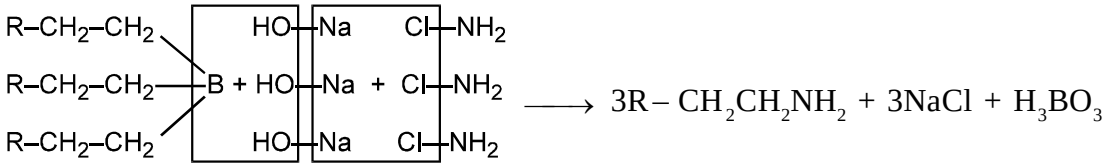
(a) Trialkyl borane is an important compound because it gives respective alkane on acidic hydrolysis.



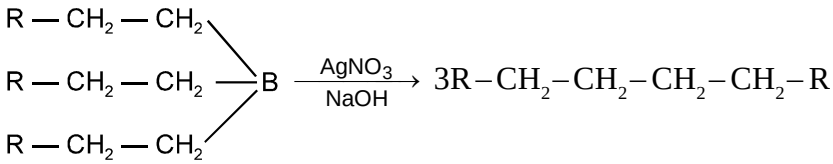
(b) It gives respective alcohol on alkaline hydrolysis



(c) It gives 1° amine on alkaline hydrolysis with chloramine



(d)



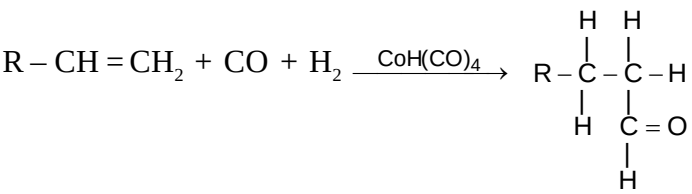
(e) In the overall hydroboration-oxidation reaction, three moles of alkene react with one mole of BH_3 to form three moles of alcohol.

(f) Because carbocation intermediates are not formed in the reaction carbocation rearrangement do not occur.

(g) Regiochemistry Anti-markownikoff's Addition of water.

(h) Alkyl boranes undergo coupling by means of silver nitrate in the presence of NaOH at 25°C. Higher alkanes are the products of this reaction.

7.11 Hydroformylation / Reaction with CO and H_2



Note : If $CO + H_2O$ is taken then respective acid is formed

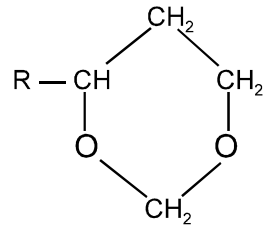
$$R-CH=CH_2 + CO + H_2O \xrightarrow{CoH(CO)_4} R-CH_2-\underset{\displaystyle COOH}{\underset{|}{CH_2}}$$

The above reaction is also called as '**Oxo reaction**' or '**Carbonylation**'.

7.12 Addition of formaldehyde :– In the presence of dil. mineral acids alkene react with formaldehyde to give 1, 3-diol or cyclic acetal. Mechanism, can be given as follows :

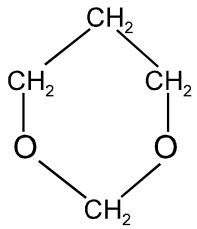
$$H_2C=O + \overset{\oplus}{H} \rightarrow [H_2C=\overset{\oplus}{O}H \longleftrightarrow H_2\overset{\oplus}{C}-OH] \xrightarrow{R-CH=CH_2} R-\overset{\oplus}{C}H-CH_2-CH_2-OH$$

$$\xrightarrow[-H^+]{HOH} R-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}} \xrightarrow{HCHO/\overset{\oplus}{H}}$$



1, 3-diol cyclic acetal

$$CH_2=CH_2 \xrightarrow{HCHO/H_3\overset{\oplus}{O}} \underset{\displaystyle OH}{\underset{|}{CH_2}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}} \xrightarrow{HCHO/\overset{\oplus}{H}}$$



1, 3 Propane diol 1, 3-dioxane

7.13 Polymerisation of Alkene

(a) Mechanism is based on ionic or free radicals both.

(b) In alkene polymer name of polymer is given on the basis of name of monomer, only 'Poly' prefix is used.

(c) If in polymerisation Zeigler-Natta catalyst (trialkyl aluminium + Titanium tetrachloride-$(C_2H_5)_3Al + TiCl_4$.) is used than polymerisation is named as Ziegler-Natta Polymerisation. e.g.

$$\begin{matrix} H & H \\ | & | \\ C=C \\ | & | \\ H & H \end{matrix} + \xrightarrow[1500°C/high\ pr.]{Trace\ O_2 + catalyst} \left(\begin{matrix} H & H & H & H \\ | & | & | & | \\ -C & -C & -C & -C- \\ | & | & | & | \\ H & H & H & H \end{matrix} \right)_n$$

Polymer or

$(-CH_2-)_n$ polythene

Note : (i) If propelene is reacted then polypropelene is formed its commercial name is '**Koylene**'.

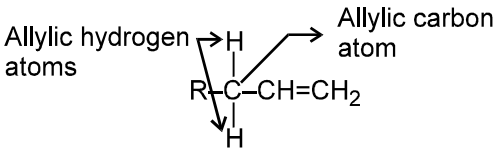
(ii) By the use of vinyl chloride polyvinyl chloride is formed.

(iii) By the use of Vinyl cyanide (Acrylonitrile), polyacrylonitrile or orlon is formed.

(iv) Zeigler-Natta catalyst is used in addition polymerisation.

7.14 Substitution reaction –

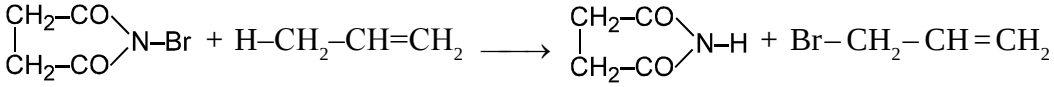
(a) Except ethene other higher alkene having allyl hydrogen when treated with chlorine or bromine 'α' H is substituted.



$$CH_3-CH=CH_2 + Cl_2 \xrightarrow{500-600°C} Cl-CH_2-CH=CH_2 + HCl$$

allyl chloride (3-chloropropene)

(b) Allylic bromination can be easily done by NBS (N–bromo succinamide)



NBS propene allyl bromide

7.15 Isomerisation :-

Alkenes isomerises when heated at high temperature or at lower temperature in the presence of various catalysts as $AlCl_3$

eg :-

(i) $CH_3-CH_2-CH_2-CH=CH_2 \xrightleftharpoons{AlCl_3} CH_3-CH_2-CH=CH-CH_3$

(ii) $CH_2(CH_3)-CH=CH_2 \xrightleftharpoons{AlCl_3} CH_2=C(CH_3)-CH_3$

the mechanism proceeds through carbocation

Solved Example

Ex.1 $R-CH=CH_2 \xrightarrow[C_2H_5OH]{Na/NH_3(l)} RCH_2CH_3$ is called

(A) Clemmensen's reduction (B) Fisher–Spier reduction
(C) Birch reduction (D) Arndt-Eistert reduction **(Ans.C)**

Sol. It is the name of reaction

Ex.2 What would be the product when 2-pentene reacts with HBr –
(A) 2-bromo pentane (B) 3-bromo pentane
(C) Both A and B (D) 1-bromo pentane **(Ans.C)**

Sol. $CH_3 \leftarrow CH_2 \leftarrow \overset{+\delta}{C}H=\overset{-\delta}{C}H-CH_3 \xrightarrow{HBr} CH_3-CH_2-CH(Br)-CH_2-CH_3$

3-bromo pentane

$CH_3-CH_2-\overset{-\delta}{C}H=\overset{+\delta}{C}H \leftarrow CH_3 \xrightarrow{HBr} CH_3-CH_2-CH_2-CH(Br)-CH_3$

2-bromo pentane

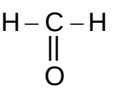
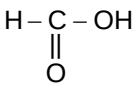
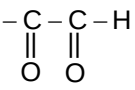
Ex.3 A hydrocarbon reacts with HI to give (X) which on reacting with aqueous KOH forms (Y). Oxidation of (Y) gives 3-methyl-2-butanone. The hydrocarbon is :

(A) $CH_3CH=C(CH_3)-CH_3$ (B) $CH_2=CH-CH(CH_3)-CH_3$

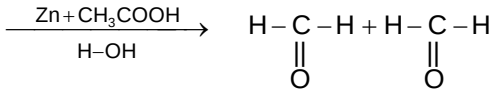
(C) $CH_3-CH_2-C(CH_3)=CH_2$ (D) $CH\equiv C-CH(CH_3)-CH_3$ **(Ans. B)**

Sol. $CH_2=CH-CH(CH_3)-CH_3 \xrightarrow{HI} CH_3-\overset{\oplus}{C}H-CH(CH_3)-CH_3 \xrightarrow{KOH(aq.)} CH_3-CH(OH)-CH(CH_3)-CH_3 \xrightarrow{[O]} CH_3-CO-CH(CH_3)-CH_3$

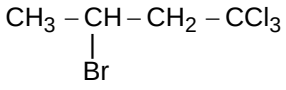
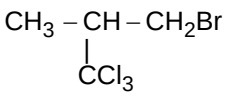
Ex.4 What would be the product when ethene is oxidised with ozone and forms ozonide which is hydrolysed in the presence of Zn and acetic acid?

(A)  (B) CH_3OH (C)  (D) 

(Ans. A)

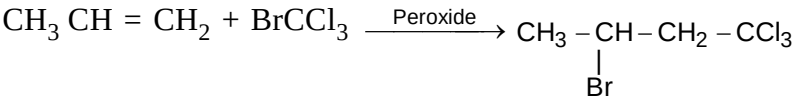
Sol. 

Ex.5 Reaction of $CH_3CH = CH_2$ with $Br.CCl_3$ in the presence of a peroxide yields the following product.

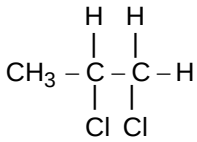
(A)  (B) 

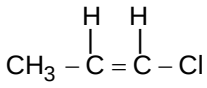
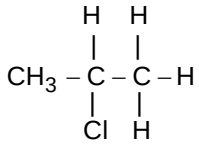
(C) $BrCH_2 - CH = CH_2$ and $CHCl_3$ (D) No reaction takes place **(Ans. A)**

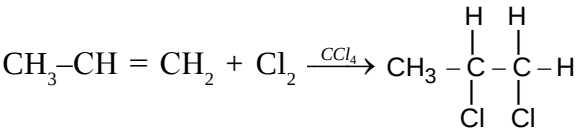
Sol. Compounds like CCl_4, $CHCl_3$, $Br.CCl_3$ etc also show kharash effect, hence they will show Anti Markownikoff's addition in the presence of peroxides. The reaction with $Br.CCl_3$ takes place as



Ex.6 What would be the product when propene reacts with chlorine in presence of CCl_4 –

(A)  (B) $Cl- CH_2 - CH = CH_2$

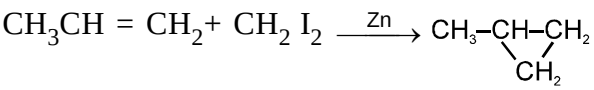
(C)  (D)  **(Ans. A)**

Sol. 

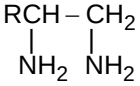
Ex.7 Propene on reaction with methylene iodide in presence of Zn–Cu couple gives :

(A) Cyclopropane (B) Cyclopropen

(C) Methyl Cyclopropane (D) Cyclobutene **(Ans.C)**

Sol. 

Ex.8 $RCH = CH_2 + BH_3 \rightarrow$ intermediate $\xrightarrow{OH^-/NH_2Cl}$ product,
product will be –

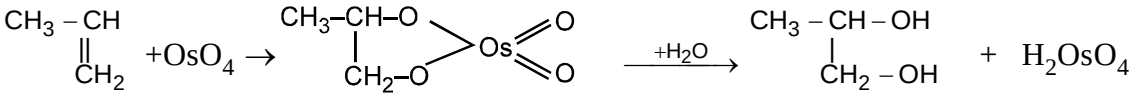
(A) $RCH_2–CH_2–NH_2$ (B) 

(C) $R–CH_2–NH_2$ (D) $RNH_2+CH_2=CH–NH_2$ **(Ans. A)**

Sol. Intermediate trialkyl, borane react with NH_2Cl in NaOH and gives same Carbon no alkyl amine.

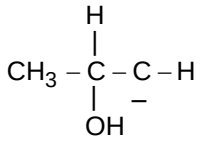
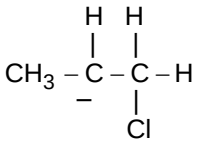
Ex.9 The addition of OsO_4 on an alkene followed by hydrolysis produces the following product
(A) H_4OsO_4 (B) H_3OsO_4 (C) Os_2O_3 (D) H_2OsO_4 **(Ans. D)**

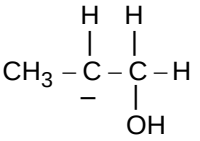
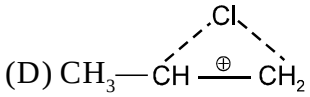
Sol. The addition of OsO_4 on an alkene followed by hydrolysis produces Osmic acid (H_2OsO_4). The reaction takes place as follows :

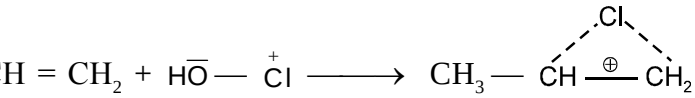


Cyclic Osmium Ester Propan 1,2 diol Osmic acid

Ex.10 Propene + HOCl → A → Final product. In the above reaction A will be

(A)  (B) 

(C)  (D)  **(Ans. D)**

Sol. 

Ex.11 In hydroboration it is evident that in the overall reaction a molecule of a water has been added to propene and the addition is :
(A) According to markownikoff's rule (B) Contrary to Markownikoff's rule
(C) Not concerned with markownikoff's rule (D) None of above **(Ans. B)**

Sol. In hydroboration it is evident that in the overall reaction a molecule of water has been added to propene and the addition is contrary to Markownikoff;s rule

$3CH_3\,CH = CH_2 + BH_3 \xrightarrow{0°C} (CH_3CH_2CH_2)_3B$

Tripropyl borane

$(CH_3CH_2CH_2)_3B + 3H_2O_2 + 3NaOH \rightarrow 3CH_3CH_2CH_2OH$

n–propyl alcohol

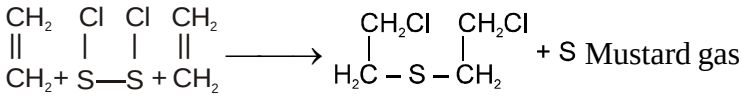
Ex.12 $R–CH=CH_2 + CO + H_2O \xrightarrow[200°–300°C]{Co/ThO_2} \underset{\displaystyle COOH}{\overset{\displaystyle R-CH_2}{|}}$,

Above reaction is known as –
(A) Oxo reaction (B) Carbonylation
(C) Both of the above (D) None of these **(Ans.C)**

Sol. Reaction is named as Oxo and Carbonylation. If $CO + H_2$ is taken than the reaction is named as a hydroformylation.

Ex.13 Ethylene adds on a molecule of sulphur monochloride to give a poisonous gas used in war, known as:
(A) Calor gas (B) Isocyanide gas
(C) Liquified petroleum gas (D) Mustard gas **(Ans. D)**

Sol. Ethylene adds on a molecule of sulphur monochloride to give a poisonous gas, known mustard gas and was used for the first time in first world war (1914-18)

 + S Mustard gas

(β, β'dichloro diethyl sulphide)

Ex.14 NBS react with 1-butene to give –

(A) 3-bromobutene-1 (B) 1,2-dibromobutane

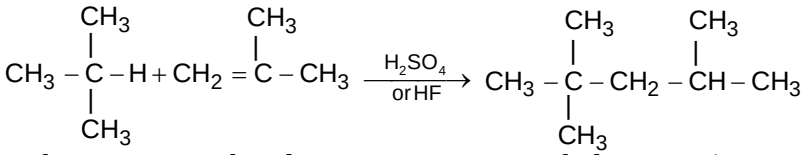
(C) 1-bromobutene (D) 1,2-dibromobutene-1 **(Ans. A)**

Sol. NBS is used for the bromo substitution of allylic hydrogen.

Ex.15 Isobutane reacts with the following to form isooctane :

(A) Isobutylene (B) n-Butene (C) n-Pentene (D) Isopentene **(Ans. A)**

Sol. Isobutane reacts with isobutylene in the presence of conc. H_2SO_4 to form isooctane



Isobutane Isobutylene 2,2,4 Trimethyl pentane(Isooctane)

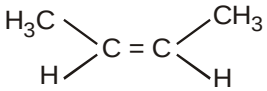
Ex.16 Reaction of alkene and peracid gives oxyrane. This reaction is named as –

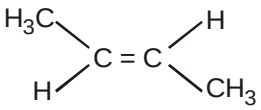
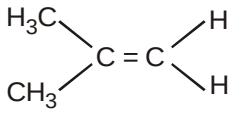
(A) Peroxidation (B) Oxidation

(C) Priles chaiev (D) None **(Ans. C)**

Sol. Reaction is known as Prileschaiev reaction.

Ex.17 The compound which reacts with HBr obeying Markownikov's rule is -

(A) $CH_2 = CH_2$ (B) 

(C)  (D)  **(Ans. D)**

Ex.18 Alkene and alkyne gives following types of polymerisation –

(A) Addition (B) Condensation

(C) Substitution (D) Replacement **(Ans.A)**

Sol. Due to unsaturation alkene and alkyne gives addition polymerisation.

Ex.19 Cyclic osmium ester of alkene after reacting with aqueous solution of sodium bisulphite gives –

(A) Diol (B) Cis-diol

(C) Trans-diol (D) Salt **(Ans. B)**

Sol. Cis-diol is the end product.

REACTION CHART FOR ALKENES

GMP **GR**

(1) $R–H \xrightarrow{\text{Pyrolysis}}$

(2) $R–C\equiv CH \xrightarrow[200–300°C]{Ni, H_2}$

(3) $R–CH_2–CH_2–X \xrightarrow[-HX]{\text{alc. KOH}}$

(4) $R–CH_2–CH\langle^{x}_{x} \xrightarrow[-X_2]{\text{Zn dust}}$ for higher alkene

(5) $R-\underset{X}{CH}-\underset{X}{CH_2} \xrightarrow{\text{Zn dust}}$

(6) $CH_2=CHCl \xrightarrow{CuR_2}$

(7) $R–CH_2–CH_2–OH \xrightarrow[-H_2O]{\text{conc. } H_2SO_4}$

(8) $R-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-R \xrightarrow{\text{Pyrolysis}}$

(9) $\begin{matrix}RCH-COOK\\ |\\ RCH-COOK\end{matrix} \xrightarrow{\text{Kolbe's electrolytic synthesis}}$

(10) $(C_2H_5)_4N^+OH \xrightarrow{\Delta}$

$R–CH=CH_2$ or C_nH_{2n}

(1) $\xrightarrow[200–300°C]{H_2, Ni} R–CH_2–CH_3$

(2) $\xrightarrow{X_2} R–CHX–CH_2X$

(3) $\xrightarrow{HX} R–CHX–CH_3$

(4) $\xrightarrow{HBr, \text{Peroxide}} R–CH_2–CH_2Br$

(5) $\xrightarrow{HOCl} R–CH(OH)–CH_2Cl$

(6) $\xrightarrow[+H_2O]{\text{dil. } H_2SO_4} R–CH_2(OH)–CH_3$

(7) $\xrightarrow[Ag\,300°C]{1/2\,O_2}$ R-CH-CH_2 (O)

(8) $\xrightarrow{+CH_2N_2}$ R-CH-CH_2 (CH_2)

(9) $\xrightarrow{BH_3} (RCH_2CH_2)_3B$

(10) $\xrightarrow[HCo(CO)_4]{CO+H_2} R-\underset{CHO}{CH}-CH_3 + R-CH_2-\underset{CHO}{CH_2}$

(11) $\xrightarrow[\Delta]{O_2} CO_2 + H_2O$

(12) $\xrightarrow{O_S O_4} R-\underset{OH}{CH}-\underset{OH}{CH_2}$

(13) $\xrightarrow[1\%\,\text{alkaline}\,KMnO_4]{\text{Bayer reagent}} R-\underset{OH}{CH}-\underset{OH}{CH_2}$

(14) $\xrightarrow{\text{strong oxidant}} R-\underset{\underset{O}{\|}}{C}-OH + CO_2 + H_2O$

(15) $\xrightarrow[\text{Priles–chalev's reaction}]{\text{Per acid}}$ R-CH-CH_2 (O)

(16) $\xrightarrow[\text{Ozonolysis}]{O_3+H_2O}$ $R-\underset{H}{\overset{O}{\|}}{C}-H + H-\underset{H}{\overset{O}{\|}}{C}-H$

(17) $\xrightarrow[200°C\,\text{high P}]{O_2}$ Polyalkene

(18) $\xrightarrow[500°C]{Cl_2}$ Substitution product

(19) $\xrightarrow[200–300°C]{Al_2(SO_4)_3}$ Isomerisation

(20) $\xrightarrow{\text{acetic anhydride}} R–CH_2=CH–COCH_3$ Methyl alkenyl ketone

(21) $\xrightarrow{\text{Alkane}}$ Higher alkane

ALKYNE

1. GENERAL INTRODUCTION :

(1) The chemistry of the carbon-carbon triple bond is similar to that of the double bond. In this chapter, we see that alkynes undergo most of the reactions of alkenes, especially the additions and the oxidations. We also consider reactions that are specific to alkynes : some that depend on the unique characteristics of the C ≡ C triple bond, and others that depend on the unusual acidity of the acetylenic C– bond.

(2) Alkynes are hydrocarbons that contain carbon–carbon triple bonds. Alkynes are also called acetylenes because they are derivatives of acetylene, the simplest alkyne.

(3) Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Cicutoxin is a toxic compound found in water hemlock, and capillin protects a plant against fungal diseases. The alkyne functional group is not common in drugs, but parsalmide is used as an analgesic, and ethynyl estradiol (a synthetic female hormone) is a common ingredient in birth control pills.

(4) Acetylene is by far the most important commercial alkyne. Acetylene is an important industrial feedstock, but its largest use is as the fuel for the oxyacetylene welding torch. Acetylene is a colourless, foul-smelling gas that burns in air with a yellow, sooty flame. When the flame is supplied with pure oxygen, however, the color turns to light blue, and flame temperature increases dramatically.

(5) Bond angle in alkyne is 180º.

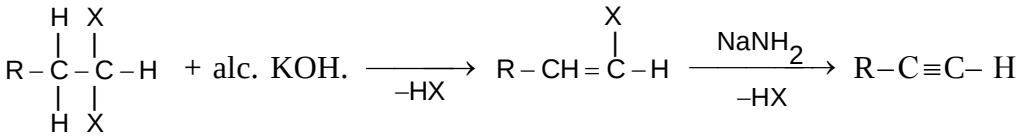
(6) Their general formula is C_nH_{2n-2}

(7) C–C triple bond length is 1.20 Å.

(8) C–H bond length is 1.08 Å.

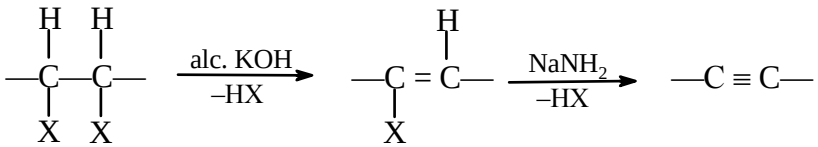
2. METHODS OF PREPARATION

2.1 From Gem Dihalides (Dehydrohalogenation) :



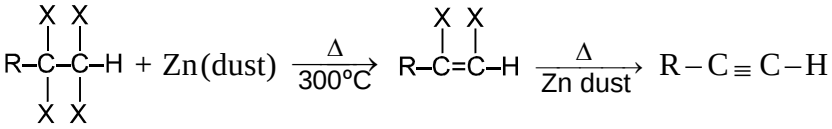
Note: Alc.KOH is not used for elimination in second step because in this case elimination takes place from doubly bonded carbon atom which is stable due to resonance so strong base $NaNH_2$ is used for elimination of HX.

2.2 From vicinal dihalides :



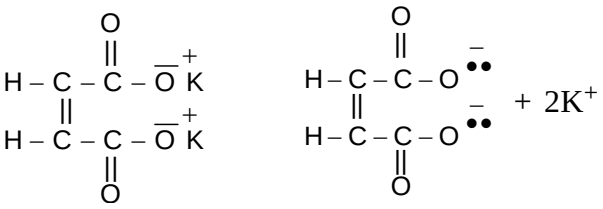
The elimination of one molecule of hydrogen halide yields vinyl halide which is very unreactive. Under mild conditions, the dehydrohalogenation stops at vinylic halide stage but more vigorous conditions—like the use of a stronger base like amide ion (NH_2^-)—are required for alkyne formation.

2.3 From Tetrahaloalkanes (Dehalogenation) :



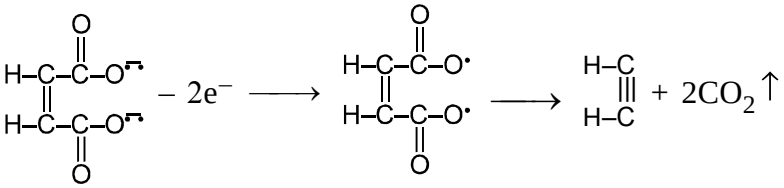
In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

2.4 From Kolbe's Synthesis :



Potassium Malaete

At Anode :



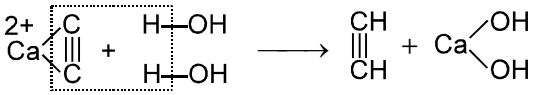
At Cathode :

$$2K^+ + 2e^- \longrightarrow 2K^\bullet$$

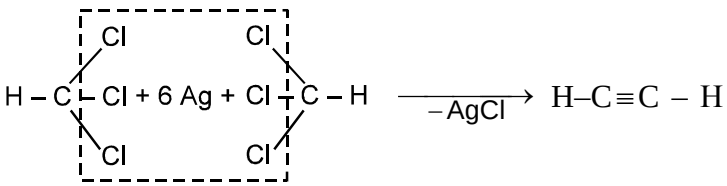
$$2K^\bullet + 2H_2O \longrightarrow 2KOH + H_2\uparrow$$

2.5 Laboratory method of preparation of Acetylene :

(a) In laboratory acetylene is prepared by hydrolysis of calcium carbide.



(b) It can also be prepared from $CHCl_3$ with Ag dust.



2.6 From Alkynes : (To form higher Alkynes)

2.6.1 With Na : When acetylene or 1- alkyne react with Na in presence of liq. NH_3 then an intermediate compound sodium acetylide or sodium alkynide is formed which gives higher alkyne with alkyl halide.

$$2H-C\equiv C-H + 2\ Na \xrightarrow[-H_2]{liq.NH_3} 2\,H-C\equiv \overline{C}\,^{+}Na \xrightarrow{X-R} H-C\equiv C-R$$

$$2R-C\equiv C-H + 2Na \xrightarrow[-H_2]{liq.NH_3} 2R-C\equiv \overline{C}\,^{+}Na \xrightarrow{X-R'} R-C\equiv C-R'$$

2.6.2 With GR : When acetyline or 1- alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.

$$H-C\equiv CH + R-Mg\text{-}X \xrightarrow[-RH]{} H\equiv C-MgX \xrightarrow[-MgX_2]{XR} H-C\equiv C-R$$

acetylene

$$R-C\equiv C-H + R-Mg-X \xrightarrow[-RH]{} R-C\equiv C-MgX \xrightarrow{R'-X} R-C\equiv C-R'$$

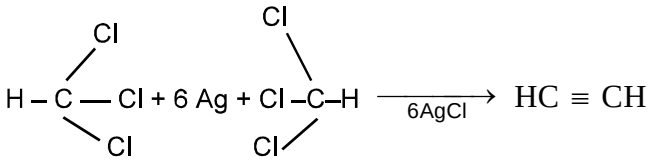
SOLVED EXAMPLE

Ex.1 What is the chief product of reaction between β-butylene chloride and alc. KOH/$NaNH_2$
(A) 1,2-butadiene (B) 1,3-butadiene (C) 2-butyne (D) 1-butyne **(Ans.C)**

Sol. 2-butyne is the chief product according to Saytzeff's rule -

Ex.2 Chloroform is heated with Ag powder in laboratory what will be the product -
(A) Acetylene (B) Ag_2O (C) CH_2Cl_2 (D) CH_4 **(Ans.A)**

Sol.



acetylene

Ex.3 Acetylene can be prepared from –
(A) Potassium fumarate (B) Calcium carbide
(C) Ethylene bromide (D) All **Ans. (D)**

Sol. These are methods of preparation of C_2H_2. Potassium fumerate on electrolysis, CaC_2 on hydrolysis and ethylene bromide on elimination gives acetylene.

Ex.4 Ethylene dibromide on treating with alcoholic KOH gives –
(A) C_2H_6 (B) CH_4 (C) C_2H_4 (D) C_2H_2 **Ans. (D)**

Sol. Alkynes can be prepared by dehydrohalogenation of alkyl dihalides

$$\underset{\text{Ethylene dibromide}}{CH_2Br\text{-}CH_2Br} \xrightarrow[-KBr\ -H_2O]{KOH\ alc.} \underset{\text{Vinylbromide}}{CHBr=CH_2} \xrightarrow[-KBr\ -H_2O]{KOH\ alc.} \underset{\text{Acetylene}}{CH\equiv CH}$$

Vinyl bromide being less reactive and thus to get better yield a stronger base $NaNH_2$ is used in second step.

Q.5 Which of the following on ozonolysis gives three different compound
(A) hex-1-en-4-yne (B) Penta-1,3-diene (C) oct-2, 5-diyne (D) Toluene

Sol. (A,B,C)

(A) $CH_2=CH-CH_2-C\equiv C-CH_3 \xrightarrow[Zn]{O_3/H_2O} H-\underset{\underset{O}{||}}{C}-H + CH_2(CHO)_2 + CH_3CHO$

hex-1-ene-4-yne

(B) $CH_2=CH-CH=CH-CH_3 \xrightarrow[Zn]{O_3/H_2O} H-\underset{\underset{O}{||}}{C}-H + \underset{\underset{CHO}{|}}{CHO} + CH_3CHO$

penta 1, 3-diene

(C) $CH_3–CH=CH–CH_2–CH=CH–CH_2–CH_3 \xrightarrow[Zn]{O_3/H_2O} CH_3CHO + CH_2(CHO)_2 + CH_3CH_2CHO$

(D) $\xrightarrow[Zn]{O_3/H_2O} CH_3-\underset{\underset{O}{||}}{C}-CHO + \underset{\underset{CHO}{||}}{C}HO + \underset{\underset{CHO}{|}}{C}HO$

Q.6 Treatment of an alkyne with H_2 in presence of palladised coke results in the formation of-

(A) Alkane (B) Alkane vigourously

(C) Trans-alkene (D) cis-alkene

Sol. (D)

Alkyne on treatment with H_2 in presence of palladised coke (Lindlar catalyst) Pd/C result in the formation of cis alkene

$$CH_3-C\equiv C-CH_3 + H_2 \xrightarrow[BaSO_4]{Pd/C} \underset{H}{\overset{CH_3}{}}C=C\underset{H}{\overset{CH_3}{}}$$

2-butyne cis-2-butene

3. PHYSICAL PROPERTIES :

(a) Alkynes are colourless, odourless and tasteless.

(b) Lower alkynes are partially soluble in H_2O. (It is due to its polarisibility).

(c) Higher alkynes are insoluble in water due to more % of covalent character.

(d) Completely soluble in organic solvents.

(e) Melting point and boiling point increases with molecular mass and decreases with number of branches.

(f) Upto C_4 alkynes are gaseous.C_5–C_{11} are liquid, C_{12} & above are solids.

(g) Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of Arsene (AsH_3) & Phosphine (PH_3).

(h) Acetylene & 1- alkyne are acidic in nature. It is due to greater electronegativity of sp hybridised 'C'.

(i) Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid. But the base should be very stronger as $^-NH_2$ or $^-CH_3$ etc.

4. CHEMICAL PROPERTIES

The chemical behaviour of alkynes is similar to that of alkenes. Alkynes form addition products with two or four univalent atoms or groups. They are generally less reactive than alkenes towards electrophilic addition reactions even though π electron density is higher in alkynes. This is because on moving from alkene to alkyne, the C—H bond has more of s character (33% in alkenes as compared to 50% in alkynes). Therefore, the π-electrons are more firmly held by carbon nuclei in alkynes and are thus less reactive to an electrophile.

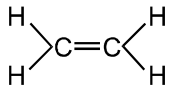
4.1 Hydrogenation

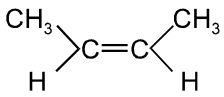
$$R-C\equiv C-H + H_2 \xrightarrow[High\ Temp.]{Ni,\ Pd,\ Pt} R-\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}H \longrightarrow R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

The above reaction is called as **Sabatier Senderson's reaction**.

4.1.1 Hydrogenation in the presence of lindelar's Catalyst :

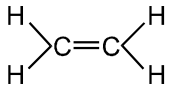
Addition up to alkene takes place in cis manner.

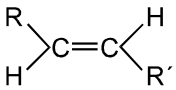
(i) $H-C\equiv C-H + H_2 \xrightarrow[\Delta]{Pd-BaSO_4}$ 

(ii) $CH_3-C\equiv C-CH_3 + H_2 \xrightarrow{Pd-BaSO_4}$ 

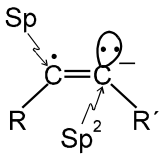
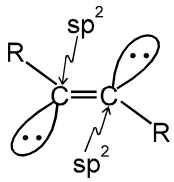
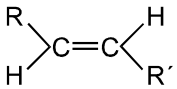
4.1.2 Hydrogenation by Na + NH_3 (liq.) :

Addition upto alkene takes place in trans manner

(i) $CH\equiv CH \xrightarrow[NH_3(liq.)]{Na}$ 

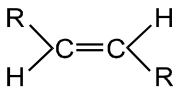
(ii) $R-C\equiv C-R' \xrightarrow{Na/NH_3 liq.}$ 

Mechanism :

$R-C\equiv C-R' \xrightarrow[e^-/-Na^+]{Na-NH_3}$  $\xrightarrow[e]{Na/NH_3}$  $\xrightarrow[-2NH_2^-]{2NH_2-H}$ 

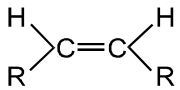
4.1.3 Hydrogenation by $LiAlH_4$:-

Addition upto alkene takes place in trans manner by $LiAlH_4$ also.

$R-C\equiv C-R \xrightarrow{LiAlH_4}$ 

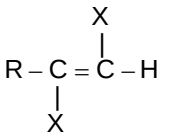
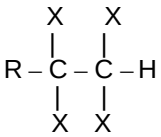
4.1.4 Reduction with the help of B_2H_6 :

Alkyne is first reacted with B_2H_6 and is follwed by acidic hydrolysis, cis alkene is obtained.

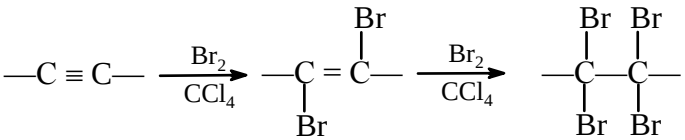
$R-C\equiv C-R \xrightarrow[2.H_2O/H^+]{1.\ B_2H_6}$ 

4.2 Halogenation :

In presence of Lewis acid as a catalyst alkyne form tetrahaloderivative with halogen.

$R-C\equiv C-H + X-X \xrightarrow[X = F,Cl,Br]{FeX_3}$  $\xrightarrow{X_2}$ 

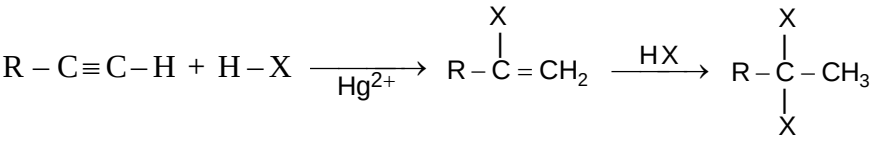
Example :



Alkynes add two molecules of Br_2 in CCl_4 and decoloration of bromine water is used to detect the presence of a double or triple bond.

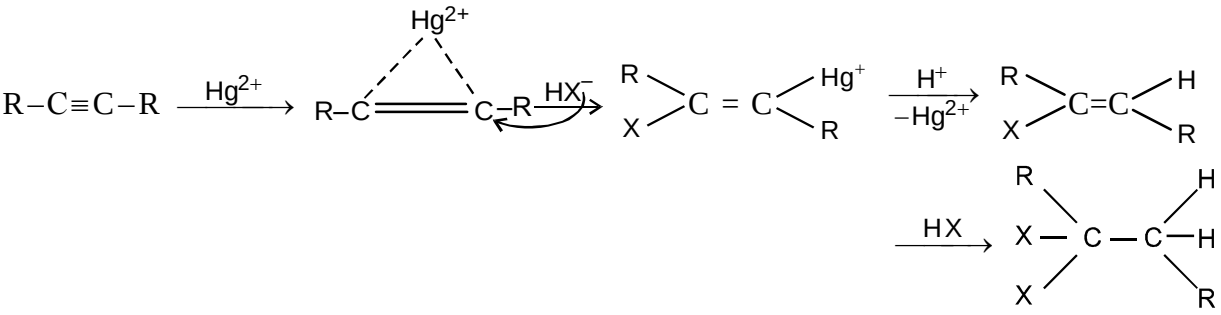
4.3 Reaction with HX (Hydrohalogenation) :

Alkyne form gem dihalide with HX because reaction follows markownikoff's Ist and IInd rule both.

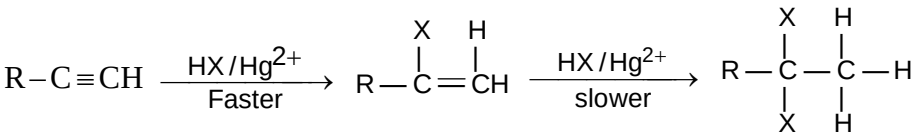


gem dihalide

Mechanism : The reaction takes place in the presence of Hg^{2+} ion.

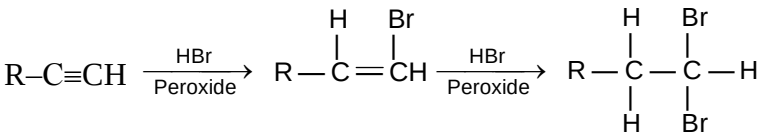


Note : (i) First step is faster than the second step among addition of two HX on alkyne.



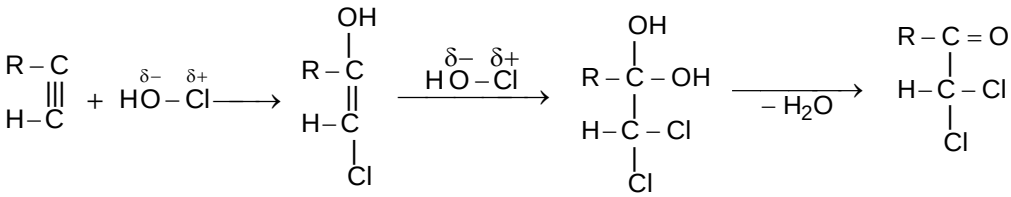
Slower rate of addition of 2nd molecule is caused by lower electron cloud density on C = C, due to – I effect of 'Cl'.

(ii) peroxide give same effect as in alkene



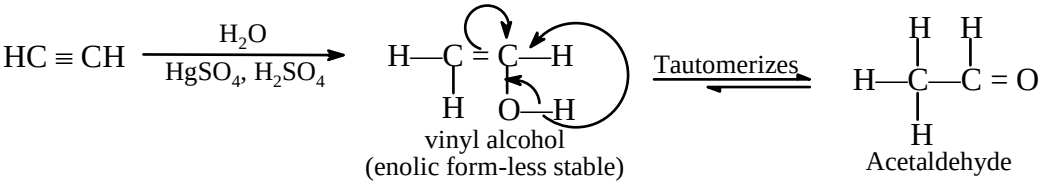
4.4 Reaction with Hypochlorous acid or Chlorine water :

Hypochlorous acid is broken into $O^{\ominus}H^{\oplus}$ Cl& ions & give addb. according to markonicoff's rule.



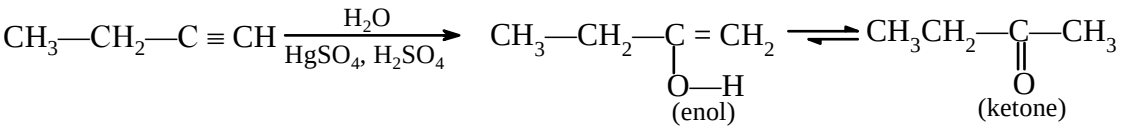
unstable

4.5 Hydration : Addition of water to alkynes is carried out in the presence of acid and mercuric sulphate.



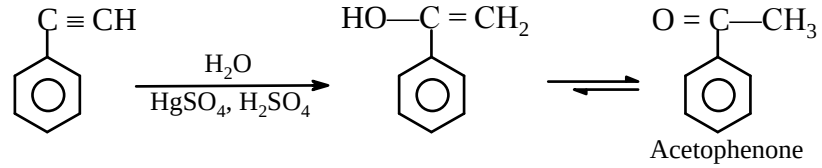
vinyl alcohol
(enolic form-less stable)

Acetaldehyde

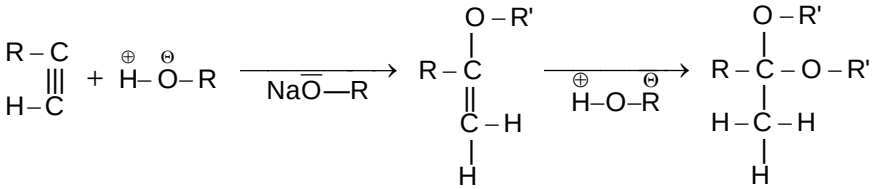


(enol)

(ketone)



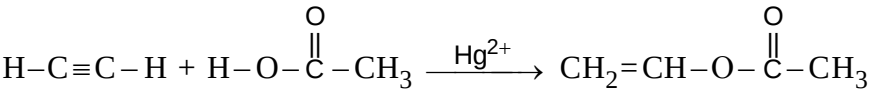
4.6 Addition of alcohol



olefinic ether acetal / ketal

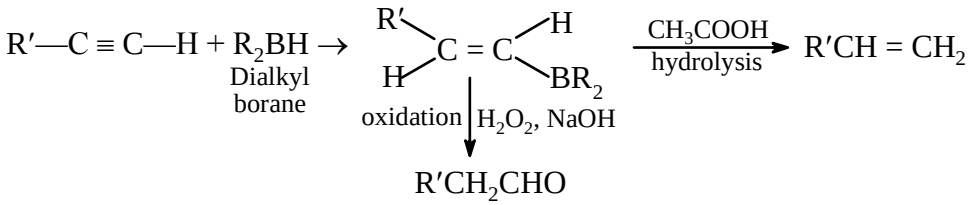
4.7 Addition of carboxylic acid :

In the presence of Hg^{2+} unioxylation of carboxylic acid takes place.

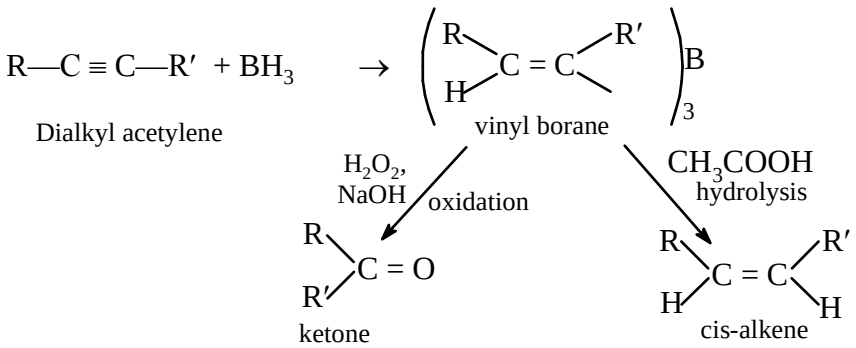


4.8 Adition of Boron Hydride (Hydroboration) :

(i) With mono-alkyl acetylene, R_2BH gives an intermediate which on hydrolysis gives alkene but on alkaline oxidation yields aldehyde.

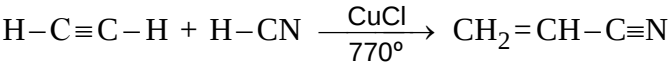


(ii) With dialkyl acetylenes, the product of hydrolysis is cis-alkene and that of oxidation is a ketone.



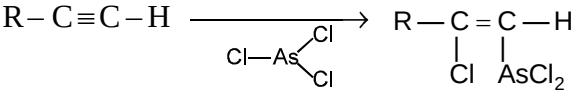
4.9 Addition of HCN :

Addition takes place in the presence of CuCl



4.10 Addition of $AsCl_3$:

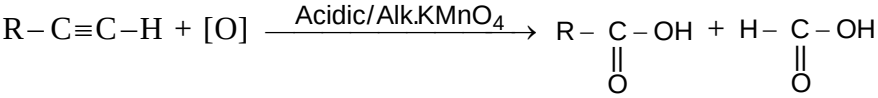
Lewisite is obtained

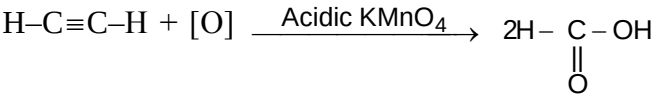


Lewisite

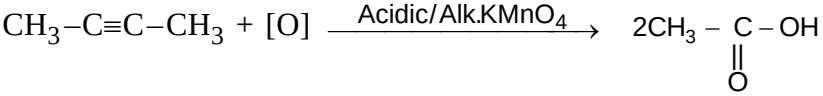
4.11 Oxidation :

4.11.1 With acidic or alkaline $KMnO_4$ alkyne break into two parts from triply bonded carbon and every part forms respective acid.

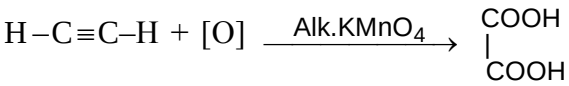






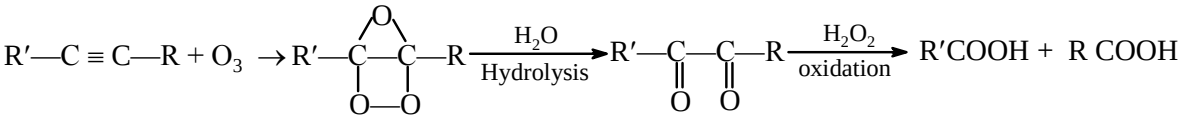


Exception : Acetylene forms oxalic acid with alkaline $KMnO_4$ exceptionally.



4.11 Ozonolysis

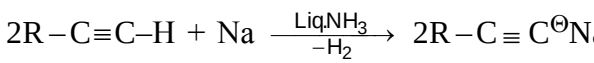
The ozonolysis of alkynes yields a mixture of carboxylic acids.



4.12 Acidic nature of 1- Alkyne or Acetylene

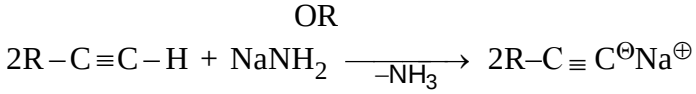
In 1- alkyne or acetylene, the H which is linked with sp hybridised carbon is called as acidic or active H. It can easily be substituted by metal or alkaline species. Hence 1- alkyne or acetylene are acidic in nature. eg.

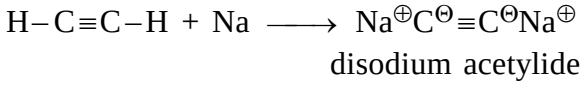
4.12.1 Reaction with Na :



sodium alkynide

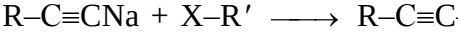
OR

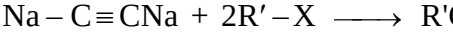




disodium acetylide

Note : Where this alkynide is treat with alkyl halide higher alkyne is obtained.





4.12.2 Reaction with Ammonical Silver Nitrate solution : (Tollen's Reagent)

$$2R-C\equiv C-H + AgNO_3 + NH_4OH \xrightarrow[-H_2O]{} 2R-C\equiv C^{\Theta}Ag^{\oplus}$$

silver alkynide (white ppt)

$$H-C\equiv C-H + AgNO_3 + NH_4OH \xrightarrow[-H_2O]{} Ag^{\oplus}C^{\Theta}\equiv C^{\Theta}Ag^{\oplus}$$

silver acetylide (white ppt)

4.12.3 Reaction with Ammoniacal Cuprous Chloride solution :

$$2R-C\equiv C-H + Cu_2Cl_2 + NH_4OH \xrightarrow[-2HCl]{} 2R-C\equiv C^{\Theta}Cu^{\oplus}$$

cuprous alkynide (red ppt.)

$$H-C\equiv C-H + Cu_2Cl_2 + NH_4OH \xrightarrow[-2\,HCl]{} Cu^{\oplus}C^{\Theta} \equiv C^{\Theta}Cu^{\oplus}$$

dicuprous acetylide (red ppt.)

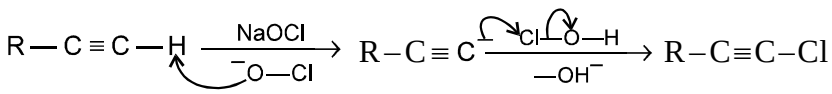
4.12.4 Reaction with NaOCl :

Acidic hydrogen is substituted by 'Cl'

(i) $H-C\equiv C-H \xrightarrow{NaOCl} Cl-C\equiv C-Cl$

(ii) $R-C\equiv C-H \xrightarrow{NaOCl} R-C\equiv C-Cl$

Mechanism :



Note : These (5.12.2) and (5.12.3) both reactions are used in the test of terminal alkynyl hydrogen. These ppt or metal acetylide or alkynide are insoluble in solution and in dry condication explode, therefore they are destroyed with HNO_3 before dryness (they form same compound again)

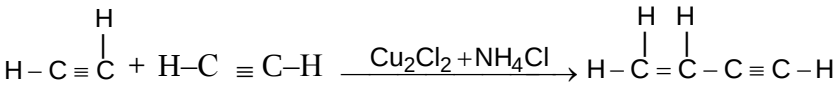
4.13 Polymerisation Reactions : Alkyne mainly shows addition polymerisation reactions.

4.13.1 Dimerisation and Cyclysation

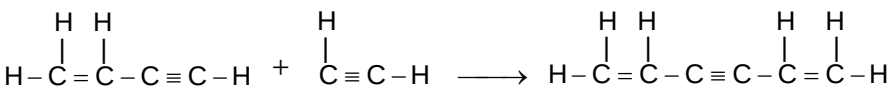
(a) Dimerisation :

Two mole acetylene reacts with Cu_2Cl_2 & NH_4Cl and forms vinyl acetylene.

Note : If acetylene would be in excess then product would be divinyl acetylene and the reaction is called *trimerisation.*



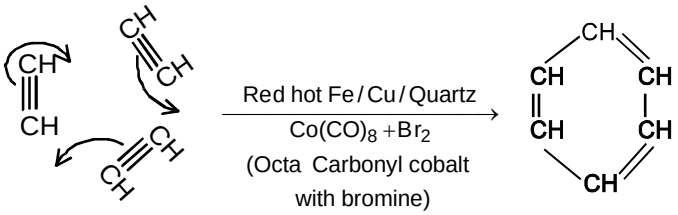
vinyl acetylene or butenyne



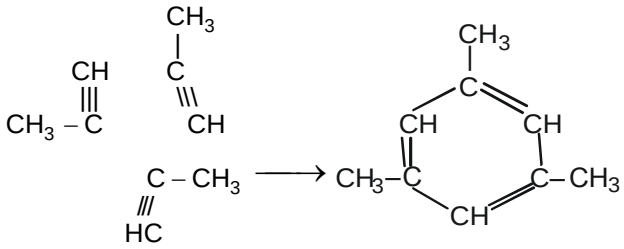
divinyl acetylene

(b) Trimerisation :

If three mole of acetylene is passed into red hot iron or Cu or quartz tube, then a cyclic trimer is formed which is called benzene.



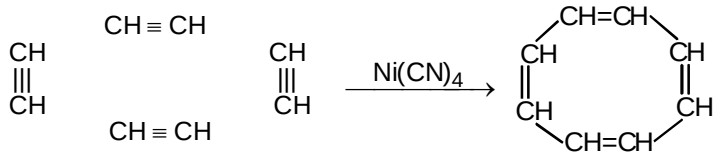
benzene



mesitylene (having 3-1º, 3-2º & 3-3º carbons)

Important : Mesitylene can also be obtained from acetone by condensation polymerisation.

(c) **Tetramerisation :** According to the name four moles of acetylene are heated with nickel tetra cyanide, then acetylene forms a cyclic tetramer cyclo octa tetraene.



(Nonaromatic) cyclooctatetraene

4.13.2 Coupling:-

(a) Alkyne form respective cuprous alkynide with ammonical cuprous chloride solution. When cuprous alkynide is reacted with pottasium ferri cyanide $[K_3Fe(CN)_6]$ they converted into conjugated diyne.

$$R-C\equiv CH + Cu(NH_3)_2Cl \longrightarrow \underset{\text{cuprous alkynide}}{R-C\equiv C.Cu}$$

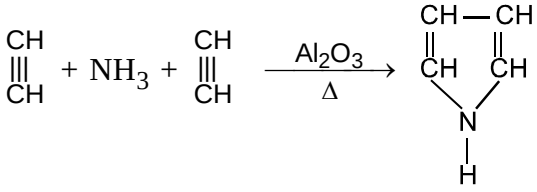
$$2R-C\equiv C.Cu \xrightarrow[\Delta]{O_2} \underset{\text{diyne}}{R-C\equiv C-C\equiv C-R}$$

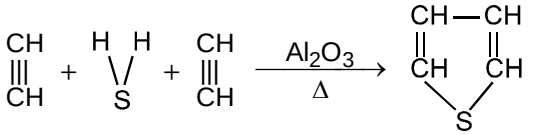
(b) Coupling is also done easily by 1-alkyne in the presence of Cu_2Cl_2 (cuprous compound) and amine (ie. pyridine + air) cuprous alkynide is formed (this coupling is known as oxidative coupling or glaser coupling)

$$2R-C\equiv CH + \frac{1}{2}O_2 \xrightarrow{Cu_2Cl_2/NH_3} R-C\equiv C-C\equiv C-R + H_2O$$

$$2CH_3-C\equiv CH + \tfrac{1}{2}O_2 \xrightarrow{Cu_2Cl_2/NH_3} \underset{\text{2,4–Hexadiyne.}}{CH_3-C\equiv C-C\equiv C-CH_3} + H_2O$$

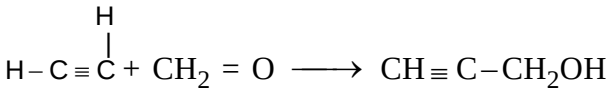
4.14 Formation of heterocyclic compounds :

(a)  (Pyrrole)

(b)  (Thiophene)

4.15 Reaction with Formaldehyde

1– Alkyne in the presence of copper react with methanal to form alkynol.

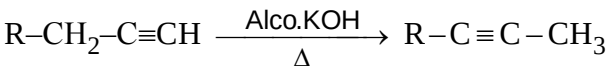


prop-2-yne-1-ol

Note : Acetylene react with two mole of HCHO (methanal) to give 2–butyne–1,4–diol. This reaction is used in the formation of 1,3 butadine. Which is used in the formation of buna rubber.

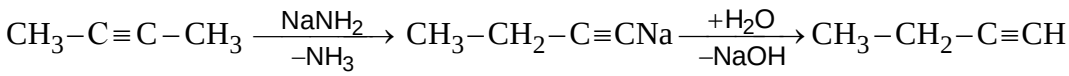
4.16 Isomerisation :–

(a) When 1-alkyne is treated with alcoholic KOH 2-alkyne is formed.



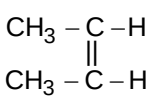
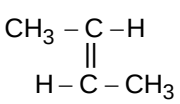
1–alkyne 2–alkyne

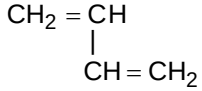
(b) When 2-alkyne is treated with sodamide then it is converted into 1-alkyne.



SOLVED EXAMPLE

Ex.1 What happens when 2- butyne reacts with H_2 in presence of Nickle Boride or lindlar's catalyst ($Pd/CaCO_3$–PbO) -

(A)  (B) 

(C) $CH_3 - CH_2 - CH_2 - CH_3$ (D)  **Ans.[A]**

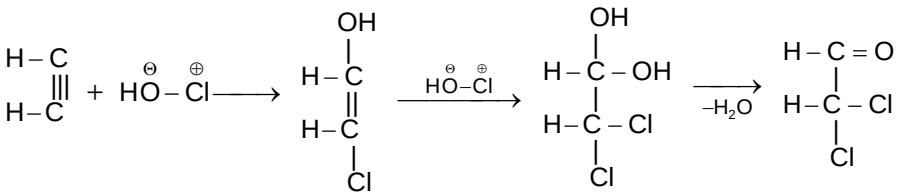
Sol. 2-butyne forms cis-2-butene with lindlar's catalyst.

Ex.2 What will be the product of chlorine water and acetylene -

(A) Dichloro propanol (B) Dichloroethanal

(C) Propanol (D) 2-Chloro ethanol **Ans.[B]**

Sol. Chlorine water ($HO^{\ominus} - Cl^{\oplus}$) when react with acetylene dichloro ethanal is formed



Ex.3 Product formed by the oxidation of acetylene in the presence of alkaline $KMnO_4$

(A) Glyoxal (B) Oxyrane (C) $CO_2 + H_2O$ (D) Oxalic acid **Ans.[D]**

Sol. This is the exceptional case of oxidation in which triple bonded carbon is not separated. The product is oxalic acid.

Ex.4 Acetylene on treating with HI gives –

(A) 1,1-Diiodoethane (B) Ethylene (C) Iodoethane (D) Ethane **Ans. (A)**

Sol. Acetylene on treating with HI gives 1,1-diiodoethane

$$\underset{\text{CH}}{\overset{\text{CH}}{|||}} + HI \xrightarrow{\text{dark}} \underset{\text{vinyl iodide}}{\overset{CH_2}{\overset{||}{CHI}}} \xrightarrow{\text{dark}} \underset{\text{ethylidene diiodide (1,1 – diiodoethane)}}{\overset{CH_3}{\overset{|}{CH-I_2}}}$$

The reactivity of halogen acids is

HI > HBr >HCl

Ex.5 Acetylene and ethylene react with alk $KMnO_4$ to give –

(A) Oxalic acid and formic acid (B) Acetic acid and ethylene glycol

(C) Ethyl alcohol and ethylene glycol (D) None **Ans. (A)**

Sol. Acetylene and ethylene react with alk. $KMnO_4$ to give oxalic acid and formic acid respectively.

$$\underset{\text{CH}}{\overset{\text{CH}}{|||}} + 4\,[O] \xrightarrow{\text{alk. } KMnO_4} \underset{\text{COOH}}{\overset{\text{COOH}}{|}}$$

acetylene oxalic acid

$$\underset{CH_2}{\overset{CH_2}{||}} + 4\,[O] \xrightarrow{\text{alk. } KMnO_4} 2HCOOH$$

ethylene formic acid

Ex.6 When 2-butyne reacts with sodamide in an inert solvent in the presence of dilute HCl, the product formed is:

(A) n-Butane (B) 2-Butene (C) 1-Butyne (D) 1-Propyne **Ans. (C)**

Sol. When 2-butyne is heated with $NaNH_2$ in an inert solvent, the sodium derivative of but-1-yne which is converted into but-1-yne by the action of dil HCl.

$$CH_3-C\equiv C-CH_3 + NaNH_2 \xrightarrow{\text{Paraffin}} NH_3 + CH_3CH_2C\equiv CNa \xrightarrow{\text{dil. HCl}} \underset{\text{1-butyne}}{CH_3CH_2C\equiv CH}$$

Ex.7 1-Pentyne reacts with :

(A) Sodium (B) Sodamide

(C) Ammonical silver nitrate (D) Ammonical cuprous chloride

Sol. (A, B, C, D)

Terminal alkyne having acidic hydrogen atom react with certain reagent like Na, NaNH2 ammonical silver nitrate, ammonical cuprous chloride

$CH_3–CH_2–CH_2–C\equiv CH + Na \rightarrow CH_3–CH_2–CH_2–C\equiv C^{\Theta}Na + 1/2H_2$

$CH_3–CH_2–CH_2–C\equiv CH + NaNH_2 \rightarrow CH_3–CH_2–CH_2–C\equiv C^{\Theta}Na + NH_3$

$CH_3–CH_2–CH_2–C\equiv CH + Ag(NH_3)_2^{+} \rightarrow CH_3–CH_2–CH_2–C\equiv CAg$

Ex.8 Which of the following can not react with ammonical silver nitrate-

(A) Acetylene (B) Hexyne-1 (C) Phenyl acetaldehyde (D) p-tolualdehyde

(E) hept-4-yne-2-ene

Sol. **(E)** Alkyne having acidic hydrogen atom react with ammonical silver nitrate i.e. Tollen's reagent.

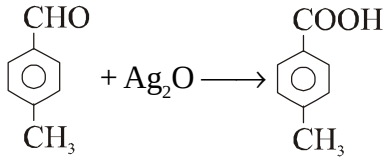
(A) $CH\equiv CH$

(B) $CH\equiv C–CH_2–CH_2–CH_2–CH_3$

Aldehyde reduces Tollen reagent to metallic silver.

(C) $C_6H_5CH_2CHO + Ag_2O \longrightarrow C_6H_5CH_2COOH + 2Ag$

Phenyl acetaldehyde

(D)  + 2AgCl

p-tolualdehyde

Note : Hept 4-yne-2-ene (CH_3–CH=CH–C≡C–CH_2–CH_3) does not contain acidic hydrogenso does not reacts with Tollen reagent.

Ex.9 The hydrocarbon that reacts with ammonical cuprous chloride is-
(A) Essentially aromatic (B) Ethane (C) Ethyne (D) Ethene

Sol. Ans. (C)
Terminal alkyne react with ammonical cuprous chloride CH ≡ CH

CH_3–CH_3, CH_2=CH_3 and  does not give test

Ex.10 The product of reaction $CH_3CH_2CH_2$ MgBr + HC ≡ CCH_3 →
is
(a) CH_3 CH_2 CH_3 (b) CH_3 CH_2 CH_2 C ≡ C CH_3
(c) CH_3 CH_2 CH_2 OH (d) CH_3 CH_2 CHO

Sol. Grignard reagent reacts with any compound having active hydrogen producing an alkane.
n—C_3H_7 MgBr + HC ≡ CCH_3 → n—C_3H_8 + CH_3C ≡ CMgBr
The answer is (a)

Ex.11 1-butyne can be distinguished from 2-butyne by using
(a) bromine water (Br_2 in CCl_4) (b) cold alk. $KMnO_4$ (Baeyer's Reagent)
(c) ammoniacal solution of silver (Tollen's Reagent) (d) diethyl ether

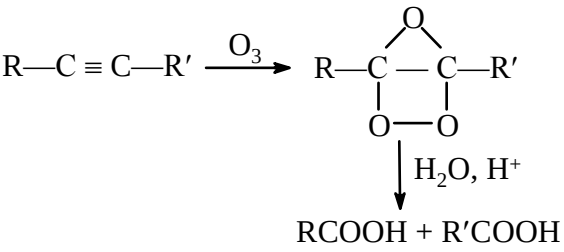
Sol. Terminal alkynes form a precipitate with Tollen's reagent.

$$RC \equiv CH + Ag^+ \rightarrow RC \equiv C^-\!:Ag^+ + \frac{1}{2} H_2$$

ppt. of Silver acetylide

1-butyne, a terminal alkyne gives this reaction but
2-butyne, a non-terminal alkyne does not give this reaction.
The answer is (c)

Ex.12 The ozonolysis of a triple bond produces
(a) a mixture of aldehydes and ketones (b) a mixture of ketones and carboxylic acids
(c) a mixture of carboxylic acids (d) none of the above

Sol. 

The answer is (c)

REACTION CHART FOR ALKYNES

GMP

(1) $CH_2Br–CH_2Br \xrightarrow{\text{alc.KOH or } NaNH_2}$

(2) $CH_3–CHBr_2 \xrightarrow{\text{alc.KOH, } NaNH_2}$

(3) $CHCl_3 \xrightarrow[\Delta]{\text{Ag powder}}$

(4) $CHBr_2–CHBr_2 \xrightarrow[\Delta]{\text{Zn dust}}$

(5) $\begin{matrix}CHBr\\ \|\\ CHBr\end{matrix} \xrightarrow{Zn}$

(6) $CH_2=CH–Cl \xrightarrow{\text{alc.KOH, } NaNH_2}$

(7) $\begin{matrix}HC-COONa\\ \|\\ HC-COONa\end{matrix} \xrightarrow{\text{Kolbe's electrolytic synthesis}}$

(8) $CaC_2 \xrightarrow{H_2O}$

(9) $2C + H_2 \xrightarrow[\text{Berthelot 's process}]{\text{electric arc, 1200°C}}$

(10) $CH_3–C\equiv CH \xrightarrow{\text{(i) Na (ii) R–X}}$

(10) $CH_3–C\equiv CH \xrightarrow{\text{(i) } CH_3MgI \text{ (ii) R–X}}$

$\rightarrow C_2H_2 \rightarrow$

GR

(1) $\xrightarrow[Ni]{H_2} C_2H_4,\ C_2H_6$

(2) $\xrightarrow{X_2} C_2H_2X_4$

(3) $\xrightarrow[\text{Peroxide}]{HBr} CH_3BrCH_2Br$

(4) $\xrightarrow[\text{No Peroxide}]{HBr} CH_3–CHBr_2$

(5) $\xrightarrow{HOCl} Cl_2CHCHO$

(6) $\xrightarrow{HCN,\ Ba(CN)_2} CH_2=CHCN$

(7) $\xrightarrow{CH_3COOH,\ Hg^{+2}} CH_3CH(OCOCH_3)_2$

(8) $\xrightarrow[\text{(Kucherov 's reaction)}]{Hg^{+2},\ 80°C,\ \text{dil.}\ H_2SO_4} CH_3CHO$

(9) $\xrightarrow{\text{Conc.}\ H_2SO_4} CH_3CH(HSO_4)_2$

(10) $\xrightarrow[\text{Ca det \& Bunsen reaction}]{AsCl_3} CHCl=CHAsCl_2$

(11) $\xrightarrow[HgSO_4]{C_2H_5OH\ /\ H_2O} CH_3CHO$

(12) $\xrightarrow[Ni(CO)_4]{CO+HOH} CH_2=CH–COOH$

(13) $\xrightarrow[Ni,160°C]{CO+EtOH} CH_2=CH–COOEt$

(14) $\xrightarrow{NaNH_2} Na–C\equiv C–Na$

(15) $\xrightarrow[\text{(Tollen's Reagent)}]{AgNO_3+NH_4OH} Ag–C\equiv C–Ag$

(16) $\xrightarrow{Cu_2Cl_2+NH_4OH} Cu–C\equiv C–Cu$

(17) $\xrightarrow{\text{Combustion } O_2} CO_2 + H_2O$

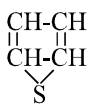
(18) $\xrightarrow{\text{Bayer Reagent}} \begin{matrix}CHO\\ |\\ CHO\end{matrix} \rightarrow HCOOH$

(19) $\xrightarrow[\text{Ozonolysis}]{O_3}$ $\xrightarrow{+H_2O} HCOOH$

(20) $\xrightarrow[\text{(Red hot iron tube)}]{\text{Trimerisation}}$ benzene

(21) $\xrightarrow[[Ni(CN)_2]]{\text{Trimerisation}} C_8H_8$ or 1,3,5,7-cyclo octa tetraene

(22) $\xrightarrow[[Cu(NH_3)_2]^+]{\text{Dimerisation}}$ butenyne

(23) $\xrightarrow[\Delta]{S}$ 

(24) $\xrightarrow[(BF_3–HgO)]{CH_3OH} \begin{matrix}CH(OCH_3)_2\\ |\\ CH_3\end{matrix}$ methylal

EXERCISE # I

ALKANE

Q.1 The simplest alkane which exhibits chain isomerism has how many carbon atoms :
(A) 4 (B) 5 (C) 6 (D) 3

Q.2 Which has least carbon bond length -
(A) Ethane (B) Ethyne (C) Ethene (D) Ethanol

Q.3 The compound with highest boiling point is
(A) n-hexane (B) n-pentane
(C) 2, 2-dimethyl propane (D) 2-methyl butane

Q.4 Which of the following will have least hindered rotation about carbon-carbon bond ?
(A) Ethane (B) Ethylene (C) Acetylene (D) Hexachloroethane

Q.5 Which reducing agent is used in Clemmensen reduction –
(A) Zn / HCl (B) $LiAlH_4$ (C) Zn-Hg / HCl (D) Na / C_2H_5OH

Q.6 CH_4 & C_2H_6 both are prepared. The compound is -
(A) CH_3COONa (B) CH_3Cl (C) CH_3MgBr (D) Both A and B

Q.7 Kolbe's reaction is convenient for the preparation of :
(A) Methane
(B) Alkanes containing even number of carbon atoms
(C) Alkanes containing even as well as odd number of carbon atoms
(D) Alkanes containing odd number of carbon atoms

Q.8 Which of the following reaction pairs constitutes the chain propagation step in chlorination of methyl chloride ?
(A) $^{\bullet}CH_3 + Cl_2 \rightarrow CH_3Cl + {}^{\bullet}Cl$ $CH_3Cl + {}^{\bullet}Cl \rightarrow {}^{\bullet}CH_2Cl + HCl$
(B) $CH_3Cl + {}^{\bullet}Cl \rightarrow CH_2Cl_2 + {}^{\bullet}H$ $^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + {}^{\bullet}Cl$
(C) $CH_3Cl + {}^{\bullet}Cl \rightarrow {}^{\bullet}CH_2Cl + HCl$ $^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + {}^{\bullet}Cl$
(D) $^{\bullet}CH_2Cl + {}^{\bullet}CH_2Cl \rightarrow CH_2Cl - CH_2Cl$ $^{\bullet}CH_2Cl + {}^{\bullet}Cl \rightarrow CH_2Cl_2$

Q.9 Name the reaction : $C_{10}H_{22} \xrightarrow{900\,K} C_4H_8 + C_6H_{14}$
(A) Alkylation (B) Cracking (C) Dehydrogenation (D) Fractionation

Q.10 Which of the following will not produce ethane-
(A) Reduction of CH_3COOH with HI/P_4
(B) Reduction of CH_3COCH_3 with HI/P_4
(C) Decarboxylation of sodium propionate with soda lime
(D) Hydrogenation of ethene in the presence of Ni.

ALKENE

Q.11 The carbon-carbon bond length in the following compounds -

$CH_2 = CH_2$ (I) $CH_2=CH–CH=CH_2$ (II) $CH_3—CH_3$ (III) $CH\equiv CH$ (IV)

(A) III < II < I < IV (B) IV < I < II < III (C) I < II < III < IV (D) I < IV < III < II

Q.12 Alkene can be formed from carbonium ion by

(A) Combination of proton (B) Elimination of hydride ion

(C) Elimination of proton (D) First combination of H then removal of H

Q.13 The compound 1,3-butadiene has-

(A) Only sp hybridized carbon atoms (B) Only sp^2 hybridized carbon atoms

(C) Both sp and sp^2 hybridized carbon atoms (D) sp, sp^2 and sp^3 hybridized carbon atoms.

Q.14 A carbocation undergoes following reactions except -

(A) Combination with a nucleophile

(B) Rearrangement to form a less stable carbocation

(C) Rearrangement to form a high stable carbocation

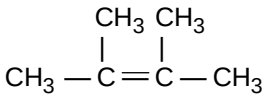
(D) Elimination of a proton to form C = C

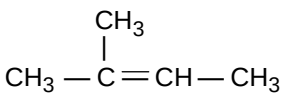
Q.15 Baeyer's reagent is used in the laboratory for-

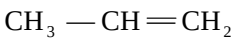
(A) Detection of double bonds (B) Detection of glucose

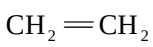
(C) Reduction (D) Oxidation

Q.16 The relative stability of the compounds


(I)


(II)


(III)


(IV)

is in the order -

(A) I > II > III > IV (B) IV > III > II > I

(C) I > III > II > IV (D) II > I > IV > III

Q.17 In dehydrohalogenations the base (alcoholic KOH) abstracts -

(A) The halide ion.

(B) The proton present on the carbon next to the carbon to which the halogen is attached.

(C) The proton present on the carbon to which the halogen is attached.

(D) The proton on the α-carbon.

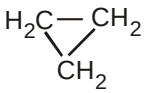
Q.18 In the sequence of reactions, $CH_3CH_2CH_2OH \xrightarrow{PCl_5} A \xrightarrow[KOH]{alc.} B$, the product B is -

(A) Propyne (B) Propylene (C) Propane (D) Propanol

Q.19 In the elimination of reactions, that is, in the formation of alkenes, the reactivity of halogens in alkyl halides is in the order -

(A) I > Br > Cl (B) Cl > Br > I (C) Br > Cl > I (D) None

Q.20 The ease of dehydrohalogenation of alkyl halide with alcoholic KOH is
(A) 3º > 2º > 1º (B) 3º < 2º < 1º (C) 3º > 2º < 1º (D) 3º < 2º > 1º

Q.21 $BrCH_2—CH_2—CH_2Br$ reacts with Na in the presence of ethanol at 100ºC to produce -
(A) $BrCH_2—CH=CH_2$ (B) $CH_2 = C = CH_2$
(C)  (D) all of these

Q.22 Alcohols undergo dehydration in the following sequence -
(A) 1º > 2º > 3º (B) 3º > 2º > 1º (C) 1º > 3º > 2º (D) 3º > 1º > 2º

Q.23 The catalyst used in kharash reaction, is -
(A) Only halogenated compound (B) Any peroxide
(C) $Al_2 (SO_4)_3$ (D) $TiCl_4$

ALKYNE

Q.24 Which can yield acetylene in single step
(A) Propyne (B) Ethene
(C) Ethylene dichloride (D) Sodium acetate

Q.25 Acetylene may be prepared using Kolbe's electrolytic method employing -
(A) Pot. acetate (B) Pot. succinate (C) Pot. fumarate (D) None of these

Q.26 Which of the following method is not applicable to the preparation of acetylene -
(A) Dehydro chlorination of a vicinal dihalide with two carbon atoms
(B) Debromination of tetrabromoethane
(C) Dehydration of glycol
(D) Heating of vinyl chloride with sodamide

Q.27 Which one of these will react with sodium metal -
(A) Ethyne (B) Ethene (C) Ethane (D) Ether

Q.28 Ethene can be separated from ethyne by passing the mixture through
(A) concentrated H_2SO_4 (B) ammonical Cu_2Cl_2
(C) pyrogallol (D) charcoal powder

Q.29 Lindlar's catalyst is :
(A) Na in liquid NH_3 (B) Pt in ethanol (C) Ni in ether (D) Pd with $BaSO_4$

Q.30 Addition of HCN to ethyne in presence of $Ba(CN)_2$ as catalyst gives-
(A) 1, 1-dicyanoethane (B) Ethyl cyanide
(C) Vinyl cyanide (D) Divinyl cyanide

EXERCISE # II

ALKANE

Q.1 On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be – **[AIEEE-2003]**

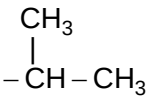
(A) Isopentane (B) Neopentane (C) Propane (D) Pentane

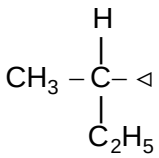
Q.2 Which one of the following has the minimum boiling point ? **[AIEEE-2004]**

(A) n – Butane (B) 1– Butyne (C) 1– Butene (D) isobutane

Q.3 Amongst the following compounds, the optically active alkane having lowest molecular mass is- **[AIEEE-2004]**

(A) $CH_3–CH_2–CH_2–CH_3$

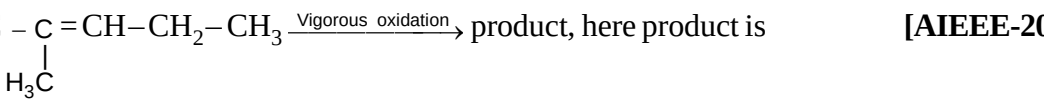
(B) 

(C) 

(D) $CH_3–CH_2 – C \equiv CH$

ALKENE

Q.4 The compound

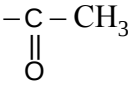


product, here product is **[AIEEE-2002]**

(A) CH_3COOH & 

(B) $CH_3 – CH_2 – COOH$ & 

(C) $CH_3 – CH_2 – COOH$ only

(D) HCOOH & 

Q.5 Butene-1 may be converted to butane by reaction with – **[AIEEE-2003]**

(A) zn – Hg (B) Pd / H_2 (C) Zn – HCl (D) Sn – HCl

Q.6 During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is - **[AIEEE-2003]**

(A) Elimination of water (B) Formation of an easter

(C) Protonation of alcohol molecule (D) Formation of carbocation

Q.7 Reaction of one molecule of HBr with one molecule of 1,3–butadiene at 40ºC given predominantly

(A)1–bromo–2–butene under thermodynamically controlled conditions **[AIEEE-2005]**

(B) 3–bromobutene under kinetically controlled conditions

(C) 1–bromo–2–butene under kinetically controlled conditions

(D) 3–bromobutene under thermodynamically controlled conditions

Q.8 Acid catalyzed hydration of alkenes except ethene leads to the formation of – **[AIEEE-2005]**

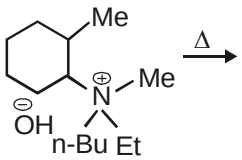
(A) secondary or tertiary alcohol (B) primary alcohol

(C) mixture of secondary and tertiary alcohols (D) mixture of primary and secondary alcohols

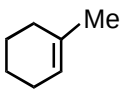
Q.9 Reaction of trans 2-phenyl-1 bromocyclopentane on reaction with alcoholic KOH produces

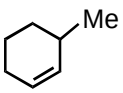
(A) 2-phenylcyclopentene (B) 1-phenylcyclopentene **[AIEEE 2006]**

(C) 3-phenylcyclopentene (D) 4-phenylcyclopentene

Q.10 

The alkene formed as a major product in the above elimination reaction is **[AIEEE 2006]**

(A) $CH_2 = CH_2$ (B) 

(C) 

(D) 

Q.11 Which of the following reactions will yield 2, 2-dibromopropane? **[AIEEE 2007]**

(A) $CH_3 - C \equiv CH + 2HBr \rightarrow$ (B) $CH_3CH = CHBr + HBr \rightarrow$

(C) $CH \equiv CH + 2HBr \rightarrow$ (D) $CH_3 - CH = CH_2 + HBr \rightarrow$

Q.12 In the following sequence of reactions, the alkene affords the compound 'B'

$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$, The compound B is **[AIEEE 2008]**

(A) CH_3COCH_3 (B) $CH_3CH_2COCH_3$

(C) CH_3CHO (D) CH_3CH_2CHO

Q.13 Out of the following, the alkene that exhibits optical isomerism is : **[AIEEE 2010]**

(A) 3-methyl-1-pentene (B) 2-methyl-2-pentene

(C) 3-methyl-2-pentene (D) 4-methyl-1-penten

ALKYNE

Q.14 Reaction

$H - C \equiv C - H + HOCl \longrightarrow$ product, here product will be - **[AIEEE-2002]**

(A) $CHCl_2 - CHO$ (B) $CHO - CHO$ (C) $CH - Cl = CHCl$ (D) $CHCl_2 - CHCl_2$

Q.15 Acetylene does not react with - **[AIEEE-2002]**

(A) $NaNH_2$ (B) NaOH (C) Na metal (D) Ammonical $AgNO_3$

Q.16 Which of the following reactions will yield 2, 2- dibromopropane? **[AIEEE 2007]**

(A) $CH_3 - C \equiv CH + 2HBr \longrightarrow$ (B) $CH_3CH = CHBr + HBr \longrightarrow$

(C) $CH \equiv CH + 2HBr \longrightarrow$ (D) $CH_3 - CH = CH_2 + HBr \longrightarrow$

Q.17 The treatment of CH_3MgX with $CH_3C \equiv C - H$ produces **[AIEEE 2008]**

(A) $CH_3C \equiv C - CH_3$ (B) $CH_3-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-CH_3$

(C) CH_4 (D) $CH_3–CH = CH_2$

Q.18 The hydrocarbon which can react with sodium in liquid ammonia is **[AIEEE 2008]**

(A) $CH_3CH_2 C\equiv CH$ (B) $CH_3CH = CHCH_3$

(C) $CH_3CH_2C \equiv CCH_2CH_3$ (D) $CH_3CH_2CH_2C \equiv CCH_2CH_2CH_3$

Q.19 The reactivity of the halogens towards methane decreases in the order -

(A) $F_2 > Cl_2 > Br_2 > I_2$ (B) $I_2 > Br_2 > Cl_2 > F_2$

(C) $F_2 > Cl_2 > I_2 > Br_2$ (D) $Cl_2 > F_2 > Br_2 > I_2$

Q.20 Both ionic and free radical mechanism involve in the reaction :

(A) Chlorination of alkane (B) Williamson's synthesis

(C) Electrolysis of potassium acetate (D) Friedel-Crafts reaction

Q.21 Propane can be best prepared by the reaction-

(A) $CH_3CH_2I + CH_3I + Na \xrightarrow{Et_2O}$ (B) $CH_3CH_2COONa + CH_3COONa \xrightarrow[\text{electrolysis}]{H_2O}$

(C) $CH_3CH_2Br + (CH_3)_2CuLi \xrightarrow{Et_2O}$ (D) $CH_3CH_2CH_2COONa \xrightarrow[CaO,\ heat]{NaOH}$

Q.22 Which of the following alkanes may be synthesized from a single alkyl halide by a process involving coupling reaction -

(A) 2-Methylbutane (B) 2-Methylpropane

(C) 2, 3-Dimethylbutane (D) Propane

Q.23 Addition of HI on double bond of propene yields isopropyl iodide and not n-propyl iodide as the major product, because addition proceeds through :

(A) A more stable carbonium ion (B) A more stable carbanion

(C) A more stable free radical (D) None

Q.24 $B \xleftarrow[\text{Catalyst}]{\text{Lindlar's}} R - C \equiv C - R \xrightarrow{Na/NH_3} A$. A and B are geometrical isomers (R–CH = CH – R) -

(A) A is trans, B is cis (B) A and B both are cis

(C) A and B both are trans (D) A is cis, B is trans

Q.25 In methyl alcohol solution, bromine reacts with ethylene to yield $BrCH_2CH_2OCH_3$ in addition to 1,2- dibromoethane because

(A) the ion formed initially may react with Br- or CH_3OH

(B) the methyl alcohol solvates the bromine

(C) the reaction follows Markownikoff's rule

(D) this is a free radical mechanism

Q.26 CH_2 = CHCl reacts with HCl to form -

(A) $CH_2Cl - CH_2Cl$ (B) $CH_3–CHCl_2$

(C) CH_2 = CHCl.HCl (D) None

Q.27 What is the slow, rate-determining step, in the acid-catalyzed dehydration of 2-methyl-2- propanol?

$(CH_3)_3COH \xrightarrow{H_2SO_4}$

(A) Protonation of the alcohol to form an oxonium ion

(B) Loss of water from the oxonium ion to form a carbocation.

(C) Loss of a β-hydrogen from the carbocation to form an alkene.

(D) The simultaneous loss of a β-hydrogen and water from the oxonium ion.

Q.28 Which of the following alkyne will form 2–butanone on hydration.

(i) $CH_3CH_2C{\equiv}CH$ (ii) $CH_3C{\equiv}C–CH_3$

(A) (i) (B) (ii) (C) Both (i) & (ii) (D) None of these

Q.29 Identify the products $HC \equiv CCH_2CH_2CH_3 \xrightarrow{\text{Warm alk. } KmnO_4}$

(A) $CO_2 + CH_3CH_2CH_2COOh$ (B) $CH_3CH_2CHO + OHC–CH_2–CH_3$

(C) $CO_2 + CH_3CH_2CH_2CHO$ (D) $CH_3CH_2CH_2CHO + 2CO_2$

Q.30 Which reagents would be best to perform the following reaction ?



(A) 1) BH_3, 2) NaOH, H_2O_2 (B) $HgSO_4$, H_2O, H_2SO_4

(C) 1) $NaNH_2$, 2) CH_3I, 3) $HgSO_4$, H_2SO_4 (D) 1) OsO_4, 2) HIO_4

ANSWER KEY

EXERCISE # I

Q.1	A	Q.2	B	Q.3	A	Q.4	A	Q.5	C	Q.6	D	Q.7	B
Q.8	C	Q.9	B	Q.10	B	Q.11	B	Q.12	C	Q.13	B	Q.14	B
Q.15	A	Q.16	A	Q.17	B	Q.18	B	Q.19	A	Q.20	A	Q.21	C
Q.22	B	Q.23	B	Q.24	C	Q.25	C	Q.26	C	Q.27	A	Q.28	B
Q.29	D	Q.30	C										

EXERCISE # II

Q.1	B	Q.2	D	Q.3	C	Q.4	B	Q.5	B	Q.6	C	Q.7	A
Q.8	C	Q.9	C	Q.10	A	Q.11	A	Q.12	C	Q.13	C	Q.14	A
Q.15	B	Q.16	A	Q.17	C	Q.18	D	Q.19	A	Q.20	C	Q.21	C
Q.22	C	Q.23	A	Q.24	A	Q.25	A	Q.26	B	Q.27	B	Q.28	C
Q.29	A	Q.30	C										

ALKYL HALIDE

CHARACTERISTICS :

(a) These are the organic compound in which halogen is directly linked with carbon atom.

(b) These are also called as Haloalkane.

(c) Their general formula is $C_nH_{2n+1}X$, (X = F, Br, Cl, I).

(d) In these compounds, hybridisation state of carbon is sp^3.

(e) In these compounds, geomerty of carbon is tetrahedral.

(f) Central carbon atom has a bond angle of 109º 28'.

(g) On the basis of no. of halogen atom, these are of following types –

(i) Monohalide – They possess single halogen atom.
eg. CH_3 - Cl, CH_3 - CH_2Br

(ii) Dihalide – These are of three types
eg. gem dihalide, vicinal dihalide and α, ω halide

(iii) Trihalide – They posses three halogen atoms.
eg. $CHCl_3$, CHI_3

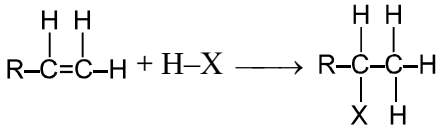
(iv) Tetrahalide – They possess four halogen atoms.
eg. CCl_4

(vi) Polyhalide – They possess more than four halogen atoms.

(h) Alkyl halide shows chain and position isomerism. If unsymmetrical or chiral carbon is present then it shows optical isomerism also.

METHODS OF PREPARATION OF ALKYL HALIDES

From Alkene (Hydrohalogenation) :–



Note : From alkyne we cannot obtain monoalkylhalide.

From Alcohol : –

(a) Using dry H - X : –

$$R–OH + H–X \xrightarrow[\Delta, 300^oC]{\text{Anhydrous } ZnCl_2} R–X + H_2O$$

(dry)

Note :

(i) The reactivity order of HX in the above reaction is – HI > HBr > HCl

(ii) The reactivity order of alcohols in the above reaction is – 3º > 2º > 1º > MeOH

The above reaction is called as '**Grove's Process**'.

(b) Using PCl_3 : –

$$3ROH + PCl_3 \longrightarrow 3R - Cl + H_3PO_3$$

(c) Using PCl_5 : – $ROH + PCl_5 \longrightarrow R - Cl + HCl + POCl_3$

Important Note : –

Bromine or Iodine derivatives can not be obtained from the above reaction becaues due to larger size of Bromine or Iodine, PBr_5 or PI_5 are unstable.

(d) Darzen's Process : – It is the best method for preparation of alkyl halide.

$$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + HCl\uparrow + SO_2\uparrow$$

From Silver Salt of Carboxylic Acid :

The reaction is called as '**Borodiene - Hunsdiecker**'reaction. It is also a good method for obtaining alkyl halide, but from this reaction we obtain only bromo derivatives because reaction is based upon free radical mechanism.

$$R-\underset{\underset{O}{\|}}{C}-O-Ag + Br-Br \xrightarrow{CCl_4} R-Br + CO_2\uparrow + AgBr\downarrow$$

Note : –

(i) In the above reaction the reactivity of alkyl group is : $1^o > 2^o > 3^o$

(ii) It is also an example of decarboxylation.

From Alkyl Halide :

Finkelstein Reaction :

$$R–Br \text{ or } R-Cl + KI \xrightarrow{\text{Acetone}} R-I + KCl$$

In this reaction only exchange takes place and the reaction is called as Halogen exchange reaction or '**Finkelstein Reaction**'.

Swarts reaction :

$$R–Br \text{ or } R-Cl \xrightarrow[\text{or } Hg_2F_2/\Delta]{AgF/\Delta} R-F$$

In this reaction is called as **'Swarts reaction'**

PHYSICAL PROPERTIES

(a) Alkyl halides are colourless with sweet smell or pleasant smell oily liquid, whereas

CH_3F, CH_3Cl, CH_3 - CH_2 - F, CH_3 - CH_2 - Cl are gaseous in nature.

(b) Alkyl halides having 18-carbon or more than it are solid in nature.

(c) Although carbon - halogen bond is polar in nature but alkyl halides are insoluble in H_2O because they cannot form bond with H_2O.

(d) These are completely soluble in organic solvents.

(e) M.P & B.P. $\propto$ molecular weight. For same alkyl group the order of B.P. is RI > RBr > RCl > RF

(f) Polarity order is RF > RCl > RBr > RI

(g) Reactivity order is RI > RBr > RCl > RF

(h) For same halide group reactivity order is 3^o halide > 2^o halide > 1^o halide

(i) Fluorides and Chlorides are lighter than water whereas bromides and iodides are heavier than H_2O due to more density of bromine than oxygen. CH_2I_2 is heavier liquid after Hg.

CHEMICAL PROPERTIES

Reduction :

Haloalkanes on reduction produces alkanes frequently, reduction is done as follows.

$$R-X + 2H \longrightarrow R-H + HX$$

(i) By Nascent hydrogen liberated from Na/C_2H_5OH or Sn / HCl or Zn / HCl or Zn-Cu couple/ C_2H_5OH etc.

$$R-X + 2H \longrightarrow R-H + HX$$

(ii) By hydride ion [$:H^{\Theta}$] liberated from $LiAlH_4$ or $NaBH_4$. It is completed by nucleophilic substitution reaction.

$$R-X + :H^{\Theta} \longrightarrow R-H + :X^{\Theta}$$

(iii) By catalytic hydrogenation of haloalkane -

$$R-X + H_2 \xrightarrow{\text{catalyst Pd}} R\text{-}H + HX$$

(iv) By reduction of RI with HI in presence of red P.

$$R-X + HI \xrightarrow{\text{redP /150°C}} R-H + I_2$$

Reaction with KOH : –

(a) With aqueous KOH : –

$$R-X + KOH(aq.) \longrightarrow R-OH + K-X$$

(b) With alcoholic KOH : – Dehydrohalogenation takes place and alkenes are formed.

$$R-CH_2-CH_2-X + KOH(alc.) \longrightarrow R-CH=CH_2$$

Reaction with KCN : –

$$R-X + KCN \longrightarrow R-C\equiv N + KX$$

Alkane nitrile

Alkane nitrile is an important compound which gives following products.

(i) $R-C\equiv N \xrightarrow[\text{Complete hydrolysis}]{H_3O^+} R-\overset{\overset{O}{\|}}{C}-O-H + NH_3$

(ii) $R-C\equiv N \xrightarrow[\text{Partial hydrolysis}]{H_2O} R-\overset{\overset{O}{\|}}{C}-NH_2$

(iii) $R-C\equiv N \xrightarrow{LiAlH_4 \text{ / Reduction}} R-CH_2-NH_2$

Reaction with AgCN :

$$R-X + AgCN \longrightarrow R-N\equiv C + AgX$$

$$R-N\equiv C \xrightarrow{\text{hydrolysis}} R-NH_2 + HCOOH$$

$$R-N\equiv C \xrightarrow{\text{Reduction}} R-\overset{\overset{H}{|}}{N}-CH_3$$

2°–amine

Reaction with KNO_2 :

$$R-X + \overset{+}{K}-\overset{-}{O}-N=O \longrightarrow R-O-N=O$$

alkyl nitrite

Reaction with $AgNO_2$:

$$R-X + Ag-O-N=O \longrightarrow R-N\begin{matrix}=O\\ \searrow O\end{matrix}$$

nitro alkane

Reaction with KSH :

$$R-X + K-SH \longrightarrow R\text{ - }SH$$

alkane thiol

Reaction with Na_2S :–

$$2R-X + Na_2S \longrightarrow R-S-R$$

dialkyl sulphide

Reaction with Na_2SO_3 :

$$R-X + Na_2SO_3 \longrightarrow RSO_3Na + NaX$$

alkyl sodium sulphonate

Reaction is know as **"Strecker reaction".**

Reaction with NaOR :

$$R-X + NaOR \longrightarrow R-O-R + NaX$$

The above reaction is called as "**Williamson ether synthesis**".

Reaction with Ag_2O :

(a) Using dry Ag_2O :

$$2R-X + Ag_2O \longrightarrow R-O-R + 2AgX$$

(b) Using moist Ag_2O :

$$2R-X + Ag_2O + H_2O \longrightarrow R-OH + 2AgX$$

Reaction with Silver Acetate :

$$R-X + Ag-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow R-O-\overset{\overset{O}{\|}}{C}-CH_3$$

ester

The reaction is called as '**Esterification**'.

Reaction with metals :

(a) With Na : – (Wurtz reaction)

$$R-X + 2Na + X-R \xrightarrow{\text{dry ether}} R-R + 2NaX$$

(b) With Mg : – (Grignard reaction)

$$R-X + Mg \xrightarrow{\text{dry ether}} R-Mg-X$$

(c) With Zn dust : – (**Frankland reaction**)

$$R-X + 2Zn + X-R \longrightarrow R-Zn-R + ZnX_2$$

dialkyl zinc

Dialkyl zinc is known as '**Frankland - Reagent**'.

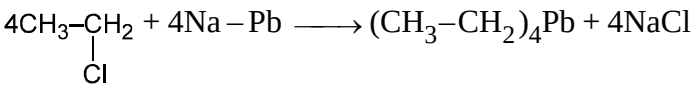
(d) With Li : –

$$R-Cl + 2Li \xrightarrow{\text{dry ether}} RLi + LiCl$$

alkyl lithium

Note : Alkyl lithium is more reactive than Grignard reagent.

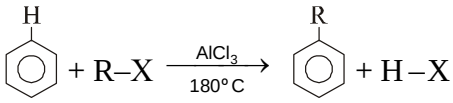
(e) With Na-lead alloy : –



TEL (tetra ethyl lead)

Note : Tetra ethyl lead is used as antiknocking agent.

Reaction with Benzene :



The reaction is called as '**Friedel-craft Reaction**'.

Important Note :– Alkyl halide shows electrophilic substitution reaction in the above reaction, which is exception in alkyl halide

TYPES OF DIHALIDES

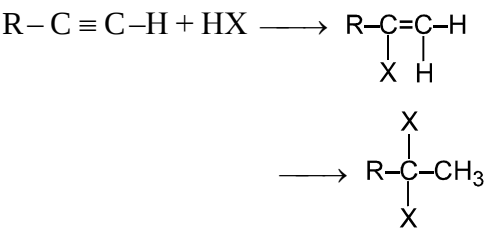
Dihalides are of two types : –

(a) **Gem dihalide :** These are the halides in which two identical halogen atoms are attached on same carbon.

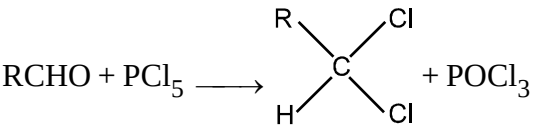
(b) **Vicinal dihalide :** In these halides two identical halogen atoms are attatched on adjacent carbon atoms.

Methods of Preparation of Gem dihalides :

(a) From Alkyne (By hydrohalogenation) : –



(b) From carbonyl compounds : –

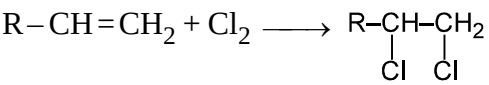


(terminal dihalide)

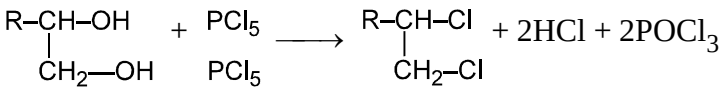
Note : If ketone is taken internal dihalide is formed.

Methods of preparation of Vicinal dihalides :–

(a) From Alkene (By halogenation) :–



(b) From Vicinal glycol : –



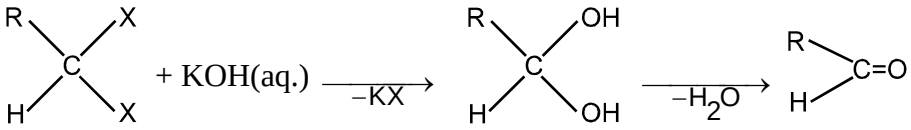
Physical properties of dihalides : –

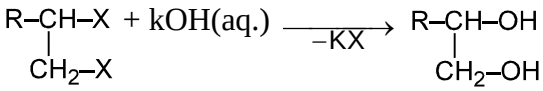
(a) Dihalides are colourless with pleasant smell liquid. Insoluble in water, soluble in organic solvent.

(b) Melting point and boiling points are directly proportional to molecular mass but boiling point of vicinal dihalides are more than gem dihalides. Also, reactivity of vicinal dihalide is more than gemdihalide, but these are less reactive than monohalide.

Chemical Properties of dihalides :

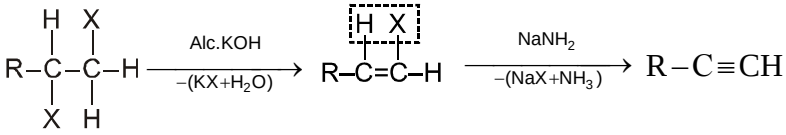
(a) Reaction with aqueous KOH : –

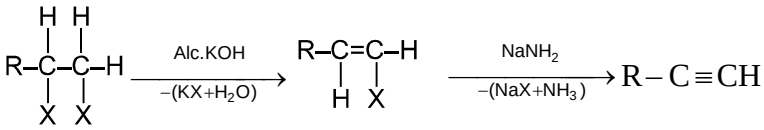




glycol

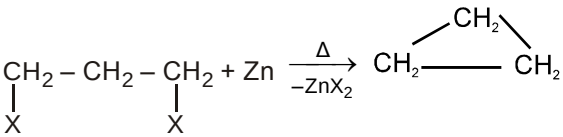
(b) Reaction with alcoholic KOH : –



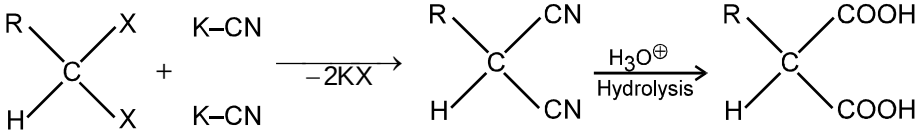


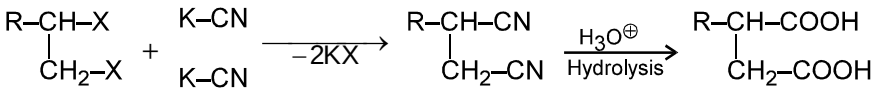
(c) **Reaction with zinc dust :** Gem dihalide reacts with Zn dust to form higher symmetrical alkene while vicinal dihalide reacts with Zn dust to form respective alkene.

Note – α, ω dihalide form cyclic alkane.

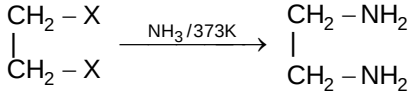


(d) Reaction with KCN :

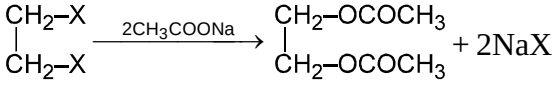




(e) Other substitution reaction : –



ethylene amine



TRIHALIDES :

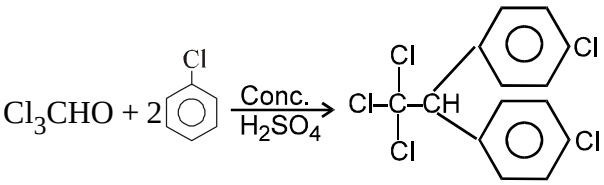
Trihalo derivatives of alkanes are known as trihalides. Reaction of method of preparation of trihalides is known as haloform reaction.

Haloform Reaction :

$$CH_3CHO \xrightarrow{Cl_2+aq.Ca(OH)_2} CHCl_3 + HCOONa$$

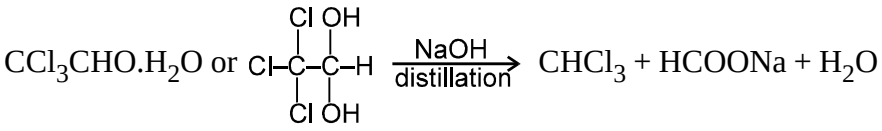
$$CH_3CH_2OH \xrightarrow{Br_2+aq.KOH} CHBr_3 + HCOONa$$

Note : (i) Chloral is an important compound and when it reacts with chlorobenzene in presence of conc. H_2SO_4, then it form an important compound DDT (Dichloro Diphenyl Trichloro ethane)



DDT [1,1,1-trichloro-2,2-bis (parachloro phenyl) ethane]

(ii) Preparation of pure Chloroform – Alkaline solution of chlorohydrate is used in the formation of chloroform. Which on distillation gives pure chloroform as follows :



chloro hydrate

Preparation of trihalide using 'Pyrene' :

$$CCl_4 + 2H \xrightarrow{Fe/H_2O \text{ reduction}} CHCl_3 + HCl$$

Physical Properties : –

(a) Chloroform is colourless with pleasant smell. Insoluble in water and soluble in organic solvent. Vapours of chloroform are poisonous in nature. It cause temporary unconsciousness, so used as an anasthetic agent.

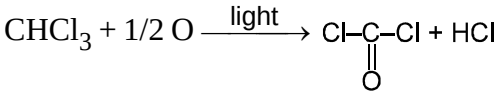
(b) Boiling point of $CHCl_3$ is 61° C.

(c) It is best solvent for fats, oil and wax.

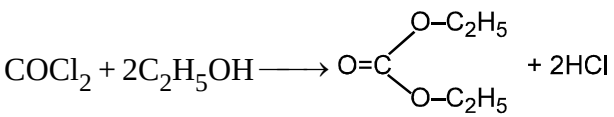
(d) Iodoform is yellow crystalline solid. It has melting point 119 °C.

Chemical Properties :

Oxidation : In presence of light it forms poisonous gas phosgene with atmospheric oxygen or with air.

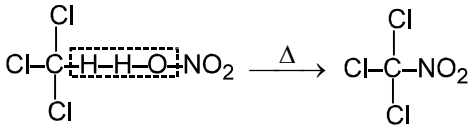


For protection it is kept into dark room in coloured bottle filling completely. For removal of phosgene we can use 0.5 to 1% ethanol solution which converts poisonous phosgene into non-poisonous salt diethyl carbonate.



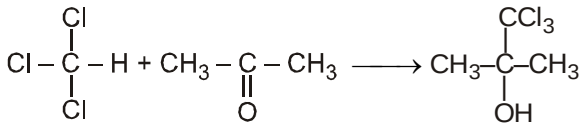
Note : We use silver nitrate solution to check the impurity of phosgene in solution which will form white ppt. of AgCl with HCl

Reaction with HNO_3 :



tear gas
(chloropicrin)

Reaction with Acetone :



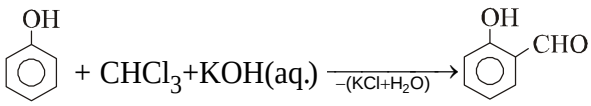
chloretone
chloretone is used as a hypnotic agent.

Reaction with Primary amine :

$R\ddot{N}H_2 + CHCl_3 + KOH\ (alc.) \longrightarrow R-N \cong C + KCl + H_2O$

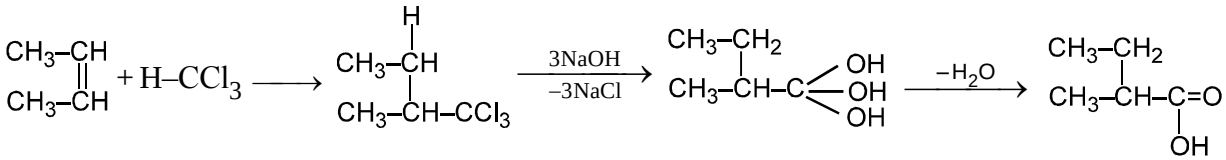
The reaction is called as 'Hoffman-carbylamine Reaction' or 'Isocyanide-test'. These isocyanides (product) has offensive smell. So, the reaction is used to test 1° amine. Reacting species of reaction is dichloro carbene.

Reaction with Phenol : The reaction is called as '**Reimer-tiemann Formylation**'.



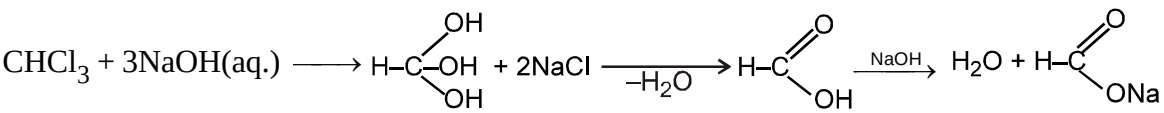
salicylaldehyde
or
(o-hydroxy benzaldehyde)

Reaction with 2- Butene :



2–methyl butanoic acid

Reaction with aq. NaOH :



Unstable

Reaction with silver powder
(Dehalogenation) :

$$CHX_3 + 6\,Ag \xrightarrow[\text{temp}]{\text{high}} CH \equiv CH + 6\,AgX$$

Reduction :

$$CHCl_3 \xrightarrow[Zn/HCl]{+2H} CH_2Cl_2 + HCl$$

$$CHCl_3 \xrightarrow[Zn/HCl]{+4H} CH_3Cl + 2HCl$$

$$CHCl_3 \xrightarrow[Zn/H_2O]{+6H} CH_4 + 3HCl$$

TETRAHALIDE 'PYRENE'

General method of preparation :

From CS_2 : –

$$CS_2 + 3Cl-Cl \xrightarrow[Fe\,dust+I_2]{\Delta\,500°C} CCl_4 + S_2Cl_2$$

sulphur monochloride

$$2S_2Cl_2 + CS_2 \longrightarrow CCl_4 + 6S\downarrow$$

The reaction is used for industrial production of CCl_4.

From CH_4 :

$$CH_4 + Cl_2 \longrightarrow CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

From $CHCl_3$:

$$CHCl_3 + Cl\text{-}Cl \xrightarrow{\text{ultra violet light}} CCl_4 + HCl$$

Physical Properties :

(a) It is colourless liquid with specific smell. It is insoluble in water and soluble in organic solvent.

(b) It is the only organic solvent which is non-combustible. So used as fire-extinguisher called as '**Pyrene**'.

Chemical Properties :

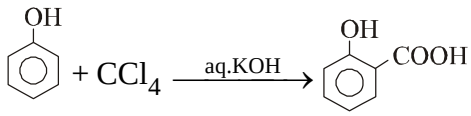
(a) It reacts with hot H_2O or with water vapour and forms poisonous gas '**Phosgene**'.

$$CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2HCl.$$

(b) It reacts with aqueous or alcoholic KOH and forms inorganic salt potassium carbonate.

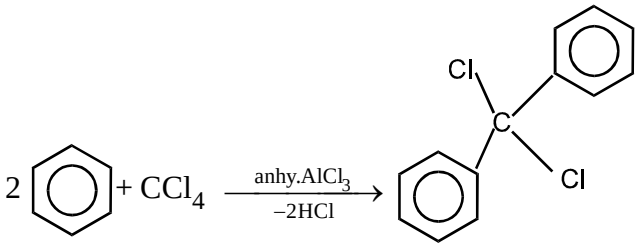
$$CCl_4 + 4KOH\ (aq.) \xrightarrow[-4KCl]{} \underset{\text{(unstable)}}{C(OH)_4} \xrightarrow[-2H_2O]{} CO_2 \xrightarrow{+2KOH} K_2CO_3 + H_2O$$

(c) It reacts with phenol and forms salicylic acid.



The reaction is called as '**Riemer-Tieman Carboxylation**'.

(d) Reaction with benzene.



dichloro diphenyl methane

FREONS

These are poly chlorofluoro derivative of alkane.

Preparation of freons :

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

$$C_2Cl_6 + 2HF \xrightarrow{SbCl_5} C_2F_2Cl_4 + 2HCl$$

hexachloro ethane freons–112

Nomenclature of Freons :

The common name of freons is Freon - cba or freon C - 1, H + 1, F, where
c = no. of carbon atom –1, b = no. hydrogen atom + 1, a = total no. of atoms of fluorine
eg. $CFCl_3$ C – 1 = 0, H + 1 = 1, F = 1 Freon - 11

Formula	**C-1**	**H + 1**	**F**	**Name**
$CFCl_3$	1 – 1 = 0	0 + 1 = 1	1	Freon-11
CF_2Cl_2	1 - 1 = 0	0 + 1 = 1	2	Freon-12
$C_2F_2Cl_4$	2 - 1 = 1	0 + 1 = 1	2	Freon-112
$C_2F_3Cl_3$	2 - 1 = 1	0 + 1 = 1	3	Freon-113
$C_2F_4Cl_2$	2 - 1 = 1	0 + 1 = 1	4	Freon-114
C_2F_5Cl	2 - 1 = 1	0 + 1 = 1	5	Freon-115

Properties & uses of freons : –

(a) Freons are colourless, odourless, unreactive & non-combustible liquids.

(b) Having very low boiling points (e.g CF_2Cl_2 = – 29.8ºC). They easily converted from gaseous state to liquid state, therefore they are used as a coolant in A.C. & Refrigerator.

(c) Used as a aerosole propellant in aroplane & rockets.

(d) Also used as a solvent.

Note : Main cause of Ozone layer decay (CFC – chlorofluoro carbon)

SOLVED EXAMPLES

Ex.1 The compound with no dipole moment is -
(A) Methyl chloride (B) Carbon tetrachloride
(C) Methylene chloride (D) Chloroform (**Ans.D)**

Sol. Carbon tetrachloride (CCl_4) has tetrahedral structure and its 4 polar C-Cl bond cancels each others dipole moment which results in net dipole moment zero.

Ex.2 True about alkyl halides is/are -
(A) Tertiary alkyl halides undergo S_N^2 substitutions
(B) Alkyl iodides on exposure to sunlight gradually darken
(C) Alkyl chlorides do not give beilstein test
(D) A nucleophilic substitution is most difficult in alkyl iodides **(Ans.B)**

Sol. When alkyl halides are exposed to sunlight they becomes darken.

Ex.3 The correct order of density is -
(A) $C_2H_5l > C_2H_5Br > C_2H_5Cl$ (B) $C_2H_5Cl > C_2H_5Br > C_2H_5l$
(C) $C_2H_5Cl > C_2H_5I > C_2H_5Br$ (D) None **(Ans.A)**

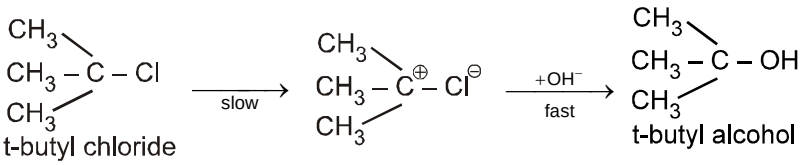
Sol. Density of a given alkyl group increases with increase in atomic weight of halogen atom. but for a given halogen density decreases with increase in size of alkyl group.

Ex.4 Action of alcoholic $AgNO_3$ on chlorobenzene is similar to the action on -
(A) Allyl chloride (B) Vinyl chloride
(C) Isopropyl chloride (D) Benzyl chloride **(Ans.B)**

Sol. Both vinyl chloride and chlorobenzene give no precipitate with alcoholic $AgNO_3$ because both have chlorine atoms which are not reactive.

Ex.5 Tertiary butyl halide on boiling with water gives tertiary butyl alcohol. The reaction follows -
(A) SE mechanism (B) S_N^I mechanism
(C) S_N^2 mechanism (D) E^1 mechanism (**Ans.B)**

Sol. Tertiary butyl halide on boiling with water gives tertiary butyl alcohol. The reaction following S_N^I mechanism.



The slow step is the formation of a carbonium ion, hence the reaction takes place via S_N^I mechanism.

Ex.6 Inversion of configuration of the product alcohol during the hydrolysis of an optically active halide is an experimental evidence for-
(A) S_N^2 mechanism (B) S_N^i mechanism
(C) S_N^1 mechanism (D) A carbanion **(Ans. A)**

Sol. Inversion of configuration of the product alcohol during the hydrolysis of an optically active halide is an experimental evidence for S_N^2 mechanism. The reaction takes place as follows :

$CH_3 – Cl + OH^- \rightarrow [HO \text{ ------- } CH_3 \text{ ----- } Cl] \rightarrow HO – CH_3 + Cl^-$

chloromethane transition state methanol

Here OH^- attacks from the back side on CH_3Cl molecule, hence the product formed has an inverted configuration.

Ex.7 Ethyl bromide and isopropyl chloride can be distinguished by -

(A) Alcoholic $AgNO_3$ (B) Comparing their colours

(C) Burning the compounds on spatula (D) Aqueous KOH solution **(Ans.A)**

Sol. With alcoholic $AgNO_3$, ethyl bromide gives a light yellow and isopropyl chloride gives white ppt.

Ex.8 The compound $C_2H_4Cl_2$ has two isomers and they can be distinguished by the reaction with -

(A) Aq. KOH (B) Alc. KOH

(C) Bromine water (D) $NaNH_2$ **(Ans.A)**

Sol. $CH_2Cl-CH_2Cl + 2KOH \xrightarrow{(aq.)} CH_2OH-CH_2OH + 2KCl$

1,2 dichloroethane ethane – 1,2 – diol

$CH_3-CHCl_2 + 2KOH \xrightarrow{(aq.)} [CH_3-CH(OH)_2] \xrightarrow{-H_2O} CH_3-CHO$

1,1 – di chloroethane

Ex.9 An unkown alkyl halide (A) reacts with alcoholic KOH to produce a hydrocarbon (C_4H_8). Ozonolysis of the hydrocarbon affords one mole of propionaldehyde and one mole of formaldehyde. Suggest which organic structure among the following is the correct structure of the above alkyl halide (A) -

(A) $CH_3(CH_2)_3Br$ (B) $CH_3CH(Br)CH(Br)CH_3$

(C) $CH_3CH_2CH(Br)CH_3$ (D) $Br(CH_2)_4Br$ **(Ans.A)**

Sol. $CH_3-CH_2-CH_2-CH_2-Br + KOH \xrightarrow{\Delta} CH_3-CH_2-CH=CH_2$

(Alcoholic) 1– butene

$CH_3-CH_2-CH=CH_2 + O_3 \longrightarrow CH_3-CH_2-CH(O-O)-CH_2 \xrightarrow{Zn/H_2O} H-CHO + CH_3-CH_2-CHO$

Ex.10 Which one of the following pairs of reaction types included in the reaction sequence below -

$CH_3CH=CHCH_3 + HI$ (in CH_3COOH) $\rightarrow CH_3CH_2CHICH_3$

$CH_3CH_2CHICH_3 + NaOH(aq) \rightarrow CH_3CH_2CH(OH)CH_3$

(A) Electrophilic addition and electrophilic substitution

(B) Electrophilic addition and nucleophilic substitution

(C) Nucleophilic addition and electrophilic substitution

(D) Nucleophilic addition and free radical substitution (**Ans.B)**

Sol. $CH_3-CH=CH-CH_3 + HI \xrightarrow{CH_3COOH} CH_3-CH_2-CHI-CH_3$

(electrophilic addition reaction)

$CH_3-CH_2-CHI-CH_3 + NaOH\ (aq.) \longrightarrow CH_3-CH_2-CH(OH)-CH_3$

(nucleophilic substitution reaction)

Ex.11 An alkyl isocyanide is prepared by -

(A) Heating an amide with P_2O_5 (B) Reacting an alcohol with NH_3

(C) The action of AgCN on alkyl halide (D) The action of KCN on alkyl halide **(Ans.C)**

Sol. An alkyl isocyanide is prepared by the action of AgCN on alkyl halide

$CH_3Cl + AgCN \longrightarrow CH_3N \equiv C + AgCl$

methanisonitrile

Isonitrile on reduction produces secondary amine.

Ex.12 $CH_3Br \xrightarrow{AgCN} A \xrightarrow{H_3O^+} B$, [B] is -

(A) CH_3NH_2 (B) $(CH_3)NH$ (C) $C_2H_5NH_2$ (D) CH_3COOH **(Ans. A)**

Sol. $CH_3 - Br + AgCN \longrightarrow CH_3 - N \equiv C$ (A) $\xrightarrow{H_3O^+} CH_3NH_2$ (B) + HCOOH

Ex.13 Action of sodium ethoxide on an alkyliodide is -

(A) A nucleophillic addition (B) An electrophillic addition

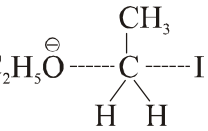
(C) A nucleophillic substitution (D) An electrophillic subsititution **(Ans.C)**

Sol. Action of sodium ethoxide on an alkyl iodide is a nucleophillic substitution.

$C_2H_5I + NaOC_2H_5 \rightarrow C_2H_5OC_2H_5 + NaI$

$C_2H_5I + EtO^- \rightarrow C_2H_5OC_2H_5 + I^-$

The reaction takes place by S_N2 mechanism

$C_2H_5O^- + C_2H_5I \rightarrow$  $\rightarrow C_2H_5OC_2H_5 + I^-$

(transition state)

Ex.14 Reaction of ethyl bromide and silver acetate gives -

(A) Ethyl ethanoate (B) Methyl ethanoate

(C) Ethanoic anhydride (D) 2-Butanone **(Ans.A)**

Sol. Reaction of ethyl bromide and silver acetate gives ethyl ethanoate It is an ester formation and has got a fruity smell.

$CH_3COOAg + BrC_2H_5 \rightarrow CH_3COOC_2H_5 + AgBr\downarrow$

silver acetate ethyl ethanoate

Ex.15 Ethyl bromide reacts with lead sodium alloy to form -

(A) Tetraethyl lead (B) Tetraethyl bromide

(C) (A) and (B) both (D) Lead bromide **(Ans.C)**

Sol. $C_2H_5 - Br + 4Pb/Na \xrightarrow[\Delta]{\text{High pressure}} (C_2H_5)_4Pb + 4\,NaBr + 3Pb$

tetraethyl lead

T.E.L. is used as antiknocking agent.

Ex.16 The name of the reaction of an alkyl halide with an arene in the presence of anhydrous $AlCl_3$ is –

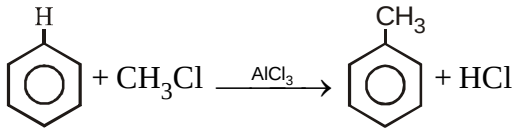
(A) Friedel Craft's reaction

(B) Grignard reaction

(C) Wurtz-fitting reaction

(D) Wurtz reaction **(Ans.A)**

Sol. The name of the reaction of an alkyl halide with an arene in the presence of anhydrous $AlCl_3$ is Friedel Craft's reaction



benzene toluene

It is an electrophillic substitution reaction.

Ex.17 Br - CH_2 - CH_2 - CH_2Br can be converted into HOOC - CH_2 - CH_2 - CH_2COOH by employing -

(A) NaCN, $H_2O + H_2SO_4$ (B) NaCl, $H_2O + H_2SO_4$

(C) $H_2O + H_2SO_4$, $KMnO_4$ (D) KCl, $H_2O + H_2SO_4$ **(Ans.A)**

Sol. $CH_2(Br) - CH_2 - CH_2(Br) + 2\,NaCN \longrightarrow CH_2(CN) - CH_2 - CH_2(CN)$

$\xrightarrow{\text{hydrolysis } (H_2O+H_2SO_4)} CH_2(COOH) - CH_2 - CH_2(COOH)$ (glutaric acid)

Ex.18 Which of the following statements is correct-

(A) Formaldehyde on heating with I_2 and alkali gives a yellow ppt.

(B) Ethanol is the only primary alcohol which gives haloform reaction.

(C) All secondary alcohols give haloform reaction.

(D) All ketones give haloform reaction. **(Ans.B)**

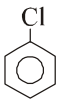
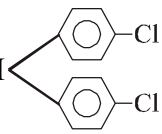
Sol. The correct statement is that ethanol is the only primary alcohol which gives haloform reaction.

$$CH_3CH_2OH \xrightarrow[+NaOH]{+I_2} I_3C.CHO \xrightarrow{+NaOH} CHI_3 \text{ (Iodoform)} + HCOONa$$

ethanol iodal

Ex.19 The main compound obtained when chlorobenzene is heated with chloral in presence of conc. H_2SO_4 -

(A) DDT (B) TNT (C) BHC (D) Chloretone **(Ans.A)**

Sol. $CCl_3CHO + 2$  $\xrightarrow[\text{conc.}H_2SO_4]{\Delta}$ $Cl_3C - CH$ 

(chloral) β, β ' - dichloro diphenyl trichloroethane (D.D.T)

Ex.20 Which of the following does not give white precipitate when boiled with alcoholic silver nitrate -

(A) Allyl chloride (B) t-butyl chloride (C) Chlorobenzene (D) Benzyl chloride

(Ans. C)

Sol. In chlorobenzene the electron lone pair of chlorine atom is in conjugation with benzene ring and hence chlorine atoms takes part in resonance and chlorobenzene does not show removal of chloride ion readily therefore it does not give white precipitate with alcoholic silver nitrate.

Ex.21 A sample of chloroform being used as an anaesthetic is tested by -

(A) Fehling solution (B) Ammoniacal CuCl solution

(C) $AgNO_3$ solution (D) $AgNO_3$ solution after boiling with alc. KOH

(Ans.C)

Sol. Chloroform is tested by silver nitrate solution if chloroform is oxidised to phosgene then HCl will also be present which reacts with $AgNO_3$ to form white precipitate (AgCl). If this reaction occur then chloroform is not used for anaesthesia.

Ex.22 The hydrogen atom in chloroform is -
(A) Acidic (B) Basic (C) Neutral (D) None **(Ans.A)**

Sol. Due to - I effect, Cl atoms tend to attract the electrons of C - H bond towards themselves.

Ex.23 Iodoform gives a precipitate with $AgNO_3$ on heating but chloroform does not because -
(A) Iodoform is ionic
(B) Chloroform is covalent
(C) C -I bond in iodoform is weak and C - Cl bond in chloroform is strong
(D) None **(Ans.C)**

Sol. On heating C - I bond breaks, but C - Cl bond does not break. Thus, $AgNO_3$ gives Agl with iodoform.

Ex.24 Pyrene is the commerical name of -
(A) Degreasing agent $CHCl_3$
(B) Fire extinguisher CCl_4
(C) Insecticide CHI_3
(D) Aerosol, propellant, $C_2Cl_4F_2$ **(Ans.B)**

Sol. Pyrene is the commerical name of a fire extinguisher CCl_4. It is the only organic cmpound which is non inflammable and which is used to extinguish fire.

Ex.25 In Hunsdiecker reaction -
(A) Number of carbon atoms decrease (B) Number of carbon atoms increase
(C) Number of carbon atoms remain same (D) None of the above **Ans.(A)**

Sol. Hunsdiecker reaction is a decarboxylation reaction.

Ex.26 Alkyl halides can be obtained by all methods except -
(A) $CH_3CH_2OH + HX/ZnCl_2$ (B) $CH_2 = CH - CH_3 + HBr$
(C) $C_2H_5OH + NaCl$ (D) $CH_3COOAg + Br_2 / CCl_4$
Ans.(C)

Sol. Alkyl halide can not be formed by the reaction between $C_2H_5OH + NaCl$.

$$C_2H_5OH + NaCl \longrightarrow C_2H_5ONa + HCl$$

Ex.27 Finkelstein reaction is -
(A) $2CH_3CH_2Cl + Ag_2O\ (dry) \longrightarrow CH_3CH_2OCH_2CH_3 + 2AgCl$
(B) $CH_3CH_2Br + NaI \xrightarrow{\text{acetone}} CH_3CH_2I + NaBr$
(C) $CH_3CH_2Br + Ag_2O\ (moist) \longrightarrow CH_3CH_2OH + AgBr$
(D) $CH_3CH_2Cl + NaOCH_3 \longrightarrow CH_3CH_2OCH_3 + NaCl$ **Ans.(B)**

Sol. The formation of alkyl iodide from alkyl bromide and alkyl chloride is known as Finkelstein reaction (Halogen exchange reaction).

Ex.28 Which of the following has the highest boiling point : –
(A) CH_3CH_2I (B) CH_3Cl (C) CH_3I (D) CH_3Br **Ans. (A)**

Sol. Boiling point $\propto$ molecular weight.

Ex.29 Ethyl chloride is soluble in : –

(A) C_2H_5OH (B) H_2O (C) Both A & B (D) None **Ans. (A)**

Sol. Alkyl halides are soluble in organic solvents.

Ex.30 What would be the product when tert. butyl chloride reacts with sodium ethoxide : -

(A) Tert. butyl alcohol (B) Tert. butyl ethyl ether

(C) Iso butyl ethyl ether (D) Isobutylene **Ans. (D)**

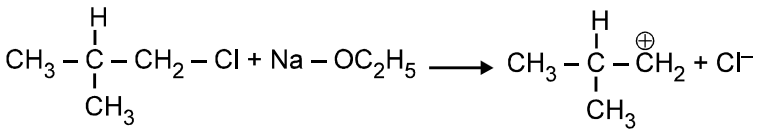
Sol. In the reaction halide is 3º and the nucleophile is bulky, reaction will be elimination E_1 and the product would be alkene.

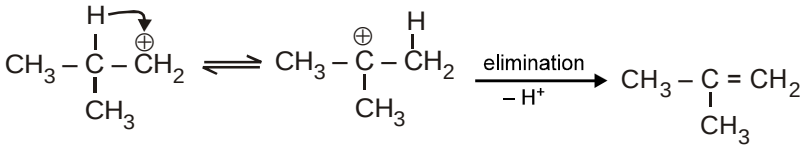
Ex.31 What would be the product when sodium ethoxide reacts with isobutyl chloride : -

(A) Tert. butyl alcohol (B) Tert. butyl ethyl ether

(C) Iso butyl ethyl ether (D) Isobutylene **Ans. (D)**

Sol.





Ex.32 Reduction of alkyl halide by $LiAlH_4$ is the type of reaction –

(A) Nueleophilic substitution reaction

(B) Electrophilic substitution reaction

(C) Electrophilic Addition reaction

(D) None of these **Ans. (A)**

Sol. $LiAlH_4$, provdies :$H^{\ominus}$ ion there fore this reaction is of Nucleophilic substitution reaction.

Ex.33 Alkyl halide with alcoholic KOH gives –

(A) Alkane (B) Acoholic salt (C) Alkene (D) Alcohol **Ans. (C)**

Sol. Alkyl halide with alcoholic KOH by elimination reaction gives alkene due to alkoxide reaction species.

Ex.34 Reduction of alkane nitrile gives –

(A) Primary amine (B) Secondary amine

(C) Acid (D) Nitro alkane **Ans. (A)**

Sol. By $LiAlH_4$ or any other reductant from alkane nitrile, primary amine is formed.

Ex.35 Tetra ethyl lead is used as an antiknocking agent, can be prepared by reacting ethyl chloride with –

(A) Sodium (B) Sodium lead alloy

(C) lead (D) Lead oxide **Ans. (B)**

Sol. TEL (tetra ethyl lead) is easily prepared by the reaction of ethyl chloride and Na-Pb alloy.

Ex.36 Ethylene glycol with PCl_5 gives –

(A) Ethylene chloride (B) Ethyl chloride

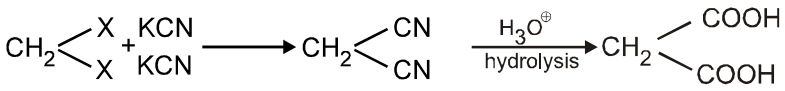
(C) 1, 1–Dichloro ethane (D) Oxyrane **(Ans. A)**

Sol. PCl_5 , replace-OH group by Cl to give chloroderivative., Here ethylene chloride is the product.

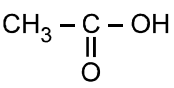
Ex.37 To form Malonic acid, we have to starts a reaction from –

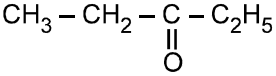
(A) Ethylidine chloride (B) Methyl chloride

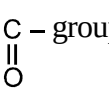
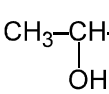
(C) Methylene chloride (D) Chloro ethane **(Ans.C)**

Sol. 

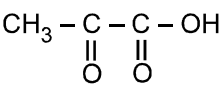
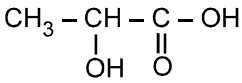
Ex.38 Which of the following shows haloform reaction : -

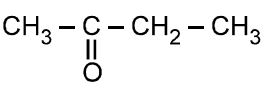
(A)  (B) 

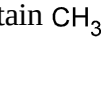
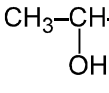
(C)  (D) None **(Ans. B)**

Sol. The compound containing  group or  group will show the haloform reaction.

Ex.39 Which of the following shows haloform reaction : -

(A)  (B) 

(C)  (D) All of above **Ans. (D)**

Sol. All of the above compounds contain  group or  group.

Ex.40 Carbyl amine reaction is used for the test of–

(A) Primary aliphatic amine (B) Primary aromatic amine

(C) Both of these (D) Secondary amine aliphatic **Ans. (C)**

Sol. In Hoffamann–Carbyl amine reaction, an offensive smell compound isocyanide is formed, therefore this reaction is used for the test of primary aliphatic and aromatic amine.

Ex.41 What will be the reduction product of following reaction –

$$CHCl_3 \xrightarrow[Zn/HCl(alc.)]{+2H} \xrightarrow[Zn/HCl(aq.)]{+4H} \xrightarrow[Zn/H_2O]{+6H}$$

(A) CH_2Cl_2, CH_3Cl, CH_4 (B) CH_4, CH_3Cl, CH_2Cl_2

(C) CH_3Cl, CH_2Cl_2, CH_4 (D) CH_3Cl, CH_4, CH_2Cl **Ans. (A)**

Sol. $CHCl_3 \xrightarrow[Zn/HCl(alc.)]{+2H} CH_2Cl_2 + HCl$

$$CHCl_3 \xrightarrow[Zn/HCl(aq.)]{+4H} CH_3Cl + 2HCl \xrightarrow[Zn/H_2O]{+6H} CH_4 + 3HCl$$

Ex.42 Which one is used as a fire-extinguisher–

(A) CCl_4 (B) Pyrene

(C) Tetra chloro methane (D) All the above **Ans. (D)**

Sol. Carbon tetra chloride (CCl_4) is also known as commercial name 'Pyrene' and used as a fire-extinguisher due to the incombustible vapour.

Ex.43 Water vapour react with CCl_4, to give a poisonous gas named as –

(A) Chloral (B) Chloroform

(C) Carbonyl chloride (D) tear gas **Ans. (C)**

Sol. $CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2HCl.$

Ex.44 $C_2F_3Cl_3$ is named as –

(A) Freon–112 (B) Freon–111 (C) Freon–113 (D) Freon–114 **Ans. (C)**

Sol. Named as follows –

C – 1, H + 1, F or C – 1 = 1, O + 1 = 1, 3

Ex.45 Addition of bromine on propene in the presence of brine yields a mixture of -

(A) $CH_3CHClCH_2Br$ and $CH_3CHBrCH_2Cl$

(B) $CH_3CHClCH_2Br$ and $CH_3CHBrCH_2Br$

(C) $CH_3CHClCH_2Cl$ and $CH_3CHBrCH_2Br$

(D) $CH_3CHClCH_2Cl$ and $CH_3CHBrCH_2Cl$ **(Ans. B)**

Sol. Addition of bromine on propene in the presence of brine solution yields a mixture of $CH_3CHClCH_2Br$ and $CH_3CHBrCH_2Br$.

$$CH_3-CH=CH_2 \xrightarrow[NaCl,\ \Delta]{Br_2} \underset{\text{1-bromo,2-chloro propane}}{CH_3-\underset{Cl}{CH}-\underset{Br}{CH_2}} + \underset{\text{1,2–dibromo propane}}{CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}}$$

Ex.46 The reaction of $SOCl_2$ on alkanols to form alkyl chlorides gives good yields because -

(A) Alkyl chlorides are immiscible with $SOCl_2$

(B) The other products of the reaction are gaseous and escape out

(C) Alcohol and $SOCl_2$ are soluble in water

(D) The reaction occurs via intermediate formation of an alkyl chloro sulphite **(Ans.B)**

Sol. The reaction of $SOCl_2$ on alkanols to form alkyl chlorides gives good yields because the other products of the reaction are gaseous and escape out.

$$\underset{\text{ethanol}}{C_2H_5OH} + Cl\text{-}SO\text{-}Cl \rightarrow \underset{\text{ethylchloride}}{C_2H_5Cl} + SO_2\uparrow + HCl\uparrow$$

It is one of the most important methods for preparing alkyl halides.

Ex.47 A carbon compound A forms B with sodium metal and again A forms C with PCl_5 but B and C form diethylether. Therefore A, B & C are -

(A) C_2H_5OH, C_2H_5ONa, C_2H_5Cl (B) C_2H_5Cl, C_2H_5ONa, C_2H_5OH

(C) C_2H_5OH, C_2H_6, C_2H_5Cl (D) C_2H_5OH, C_2H_5Cl, C_2H_5ONa **(Ans.A)**

Sol. $\underset{(A)}{2C_2H_5\text{-}OH} + 2Na \rightarrow \underset{(B)}{2C_2H_5ONa} + H_2$

$\underset{(A)}{C_2H_5\text{-}OH} + PCl_5 \rightarrow \underset{(C)}{C_2H_5\text{-}Cl} + POCl_3 + HCl$

$\underset{(B)}{C_2H_5\text{-}ONa} + \underset{(C)}{C_2H_5\text{-}Cl} \rightarrow \underset{\text{diethyl ether}}{C_2H_5\text{-}O\text{-}C_2H_5} + NaCl$

Ex.48 The best reagent for converting ethanol to chloroethane is -

(A) PCl_3 (B) PCl_5

(C) $SOCl_2$ (D) $HCl + ZnCl_2$ **(Ans.C)**

Sol. $ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$. It is evident that products other than RCl, are both gases (SO_2, HCl)

Ex.49 In Hunsdiecker reaction :

(A) A sodium salt of an acid reacts with bromine

(B) A calcuim salt of an acid reacts with HBr

(C) A silver salt of an acid reacts with bromine

(D) A silver salt of an acid reacts with HBr **(Ans.C)**

Sol. In Hunsdiecker reaction a silver salt of an acid reacts with bromine in the presence of CCl_4.

$$CH_3\,COOAg + Br_2 \xrightarrow{CCl_4} CH_3\,Br + CO_2\uparrow + AgBr$$

silver ethanoate bromomethane

It is an important method of preparing an alkyl halide from a silver salt of an alkanoic acid.

Ex.50 The yield of alkyl bromide obtained as a result of heating the dry silver salt of carboxyic acid with bromine what will be the order of formation w.r.t. alkyl bromide –

(A) $1^o > 3^o > 2^o$ bromides (B) $1^o > 2^o > 3^o$ bromides

(C) $3^o > 2^o > 1^o$ bromides (D) $3^o > 1^o > 2^o$ bromides **(Ans.B)**

Sol. $R - COOAg + Br_2 \xrightarrow{CCl_4} R - Br + CO_2 + AgBr\downarrow$

The yield of alkyl bromide has the following order

$$R{-}CH_2{-}Br > R{-}\underset{\displaystyle R}{\overset{}{CH}}{-}Br > R{-}\underset{\displaystyle R}{\overset{\displaystyle R}{C}}{-}Br$$

Since the mechanism of this reaction involves formation of free radicals.

EXERCISE – I

Q.1 In Finkelstein Reaction, which reactants are used -
(A) NaI + C_2H_5OH (B) NaCl + acetone
(C) NaBr + CH_3COCH_3 (D) NaI + CH_3COCH_3

Q.2 $C_2H_5Cl + AgF \longrightarrow C_2H_5F + AgCl$
The above reaction is called -
(A) Hunsdiecker (B) Swart (C) Strecker (D) Wurtz

Q.3 Which halide/ halides not prepared by Darzen reaction -
(A) R- Cl (B) RBr
(C) R I (D) (B) & (C) both

Q.4 In the Hunsdiecker reaction -
(A) Number of carbon atoms decrease (B) Number of carbon atoms increase
(C) Number of carbon atoms remain same (D) None of the above

Q.5 When propylene reacts with HBr in presence of peroxide, the product formed is -
(A) n-Propyl alcohol (B) Propylene peroxide
(C) n-Propyl bromide (D) 1,3 Dibromo propene

Q.6 The S_N2 reactivity order for halides :-
(A) R - F > R - Cl > R - Br > R - I (B) R - I > R - Br > R - Cl > R - F
(C) R - Br > R - l > R - Cl > R - F (D) R - Cl > R - Br > R - F > R - I

Q.7 Chlorobenzene is -
(A) More reactive than ethyl bromide
(B) More reactive than isopropyl chloride
(C) As reactive as methyl chloride
(D) Less reactive than benzyl chloride

Q.8 The correct order of polarity of alkyl halides is : -
(A) RI > RBr < RCl > RF (B) RF > RCl > RBr > RI
(C) RCl > RF > RBr > RI (D) None

Q.9 Ethylthioalcohol can be obtained when C_2H_5Br reacts with -
(A) KSH (B) NaOH (C) K_2S (D) Na_2S

Q.10 The reaction
$C_2H_5ONa + BrC_2H_5 \rightarrow C_2H_5–O–C_2H_5 + NaBr$ is called -
(A) Frankland reaction (B) Wurtz reaction
(C) Williamson's synthesis (D) Cannizzaro reaction

Q.11 Propylidene chloride when heated with zinc gives :
(A) Ethene (B) Propene (C) 1-Butene (D) 3-Hexene

Q.12 A gem dichloride is formed in the reaction except -
(A) CH_3CHO and PCl_5 (B) CH_3COCH_3 and PCl_5
(C) $CH_2 = CH_2$ and Cl_2 (D) $CH_2 = CHCl$ and HCl

Q.13 Iodoform test is not given by : -
(A) $CH_3COCH_2COOC_2H_5$ (B) CH_3COCH_3
(C) $CH_3CH_2COCH_3$ (D) $CH_3CH_2CHOHCH_3$

Q.14 $CHCl_3 + NaOH\,(aq.) \longrightarrow$
produces which intermediate –
(A) Benzyne (B) Carbene (C) Carbocation (D) Carbanion

Q.15 $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[Na_2CO_3]{I_2}$ (A) $\xrightarrow{Ag\ powder}$ (B) $\xrightarrow[Hg^{++}]{H_2SO_4}$ (C).

Product A, B & C are -
(A) Iodoform, Acetylene & Acetaldehyde
(B) Tri. iodomethane, Ethyne & Acetone
(C) Iodoform, Ethene & Ethylene glycol
(D) Ethene, iodoform & Ethylhydrogen sulphate

Q.16 Which of the following statement is wrong -
(A) All carbonyl compounds of the general structure $CH_3-\underset{\underset{O}{\|}}{C}-R$ give a positive iodoform test
(B) All secondary alcohols give iodoform reaction
(C) Alkanols of the structure $CH_3CH(OH)$ - R (where R = H, alkyl or aryl) give iodoform reaction.
(D) The only aldehyde giving iodoform reaction is acetaldehyde.

Q.17 The oxidation of $CHCl_3$ by air & light is prevented by adding -
(A) CH_3COOH (B) C_2H_5OH (C) CH_3CHO (D) CH_3COOCH_3

Q.18 Tear gas is -
(A) $C(NO_2)Cl_3$ (B) $COCl_2$ (C) CH_3Cl (D) CH_3COCl

Q.19 Chloroform when treated with aniline and alcoholic KOH forms -
(A) Phenyl cyanide (B) Phenyl isocyanide
(C) Phenyl cyanate (D) Phenyl isocyanate

Q.20 $CHCl_3$ is kept in brown bottles well stoppered and also with 1% alcohol so that it may not form-
(A) CH_2Cl_2 (B) $COCl_2$ (C) CCl_4 (D) None of these

Q.21 Which of the following compounds is used as a refrigerant -
(A) Acetone (B) CCl_4 (C) CF_4 (D) CCl_2F_2

Q.22 Catalyst used in the formation of dicholorodifluoromethane is generated from -
(A) $AlCl_3$ + HF (B) $SbCl_5$ + HF (C) $SbCl_4$ + HF (D) BF_3 + HF

Q.23 $CCl_4 + 4KOH \longrightarrow$ end product of the reaction is –
(A) K_2CO_3 (B) CO_2 (C) $C(OH)_4$ (D) HCOOK

Q.24 $CS_2 + Cl_2 \longrightarrow$ Product, Product is –
(A) $CHCl_3$ (B) CCl_4 (C) SCl_2 (D) C_2S_2

Q.25 Main cause of Ozone decay is –
(A) CFC (B) BFC (C) LMC (D) DKP

Q.26 In reaction : $C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X + H_2O$ the order of reactivity of HX is -
(A) HBr > HI > HCl (B) HI > HCl > HBr
(C) HCl > HBr > HI (D) HI > HBr > HCl

Q.27 Which of the following leads to the formation of an alkyl halide -
(A) $C_2H_5OH \xrightarrow{Red\ P + Br_2}$ (B) $C_2H_5OH \xrightarrow{SOCl_2}$
(C) $C_2H_5OH \xrightarrow{KBr + Conc, H_2SO_4}$ (D) All

Q.28 The reaction of silver carboxylates with bromine dissolved in carbon tetrachloride is called -
(A) Hofmann reaction (B) Borodine reaction
(C) Borodine - Hunsdiecker reaction (D) Hypobromide reaction

Q.29 The formation of an alkyl halide by reaction of hydrogen halide on an unsymmetrical alkene is an example of -
(A) A nucleophilic addition reaction (B) An electrophilic addition reaction
(C) A free radical reaction (D) An elimination reaction

Q.30 Which reaction is termed as Darzen's Reaction -
(A) ROH + HCl (B) ROH + PCl_5
(C) ROH + $SOCl_2$ (D) ROH + PCl_3

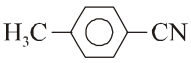
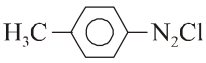
EXERCISE – IV

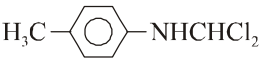
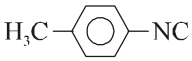
Q.1 The reaction $(CH_3)_3\,CBr + H_2O \longrightarrow (CH_3)_3\,COH + HBr$ is a - **[AIEEE-2002]**

(A) Substitution reaction (B) Debromination reaction

(C) Rearrangement reaction (D) Elimination reaction

Q.2 The reaction of chloroform with alcoholic KOH and p–toluidine form : **[AIEEE 2003]**

(A)  (B) 

(C)  (D) 

Q.3 The correct order of the thermal stability of hydrogen halides (H – X) is – **[AIEEE-2005]**

(A) HF > HCl > HBr > HI (B) HI > HBr > HCl > HF

(C) HI > HCl < HF > HBr (D)HCl < HBr > HBr < HI

Q.4 Tertiary alkyl halides are practically inert to substitution by S_{N^2} mechanism because of – **[AIEEE-2005]**

(A) instability (B) insolubility (C) steric hindrance (D) inductive effect

Q.5 Alkyl halides react with dialkyl copper reagents to give **[AIEEE-2005]**

(A) alkyl copper halides (B) alkenes

(C) alkenyl halides (D) alkanes

Q.6 Elimination of bromine from 2–bromobutane results in the formation of – **[AIEEE-2005]**

(A) predominantly 2–butene (B) equimolar mixture of 1 and 2–butene

(C) predominantly 2–butyne (D) predominantly 1–butene

Q.7 Among the following the one that gives positive iodoform upon reaction with I_2 and NaOH is – **[AIEEE 2006]**

(A) $C_6H_5CH_2CH_2OH$ (B) $CH_3 - \underset{\displaystyle CH_3}{\overset{}{C}}HCH_2OH$

(C) $PhCHOHCH_3$ (D) $CH_3CH_2CH(OH)CH_2CH_3$

Q.8 Which of the following is the correct order of decreasing SN^2 reactivity ? **[AIEEE 2007]**

(A) $RCH_2X > R_3CX > R_2CHX$ (B) $RCH_2X > R_2CHX > R_3CX$

(C) $R_3CX > R_2CHX > RCH_2X$ (D) $R_2CHX > R_3CX > RCH_2X$

(X = halogen)

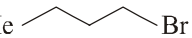
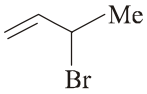
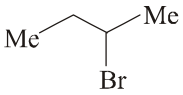
Q.9 The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction , is **[AIEEE 2008]**

(A) $(CH_3)_3CCl$ (B) $(CH_3)_2CHCl$ (C) CH_3Cl (D) $(C_2H_5)_2CHCl$

Q.10 Which of the following on heating with aqueous KOH produces acetaldehdye ? **[AIEEE 2009]**

(A) CH_3COCl (B) CH_3CH_2Cl (C) CH_2ClCH_2Cl (D) CH_3CHCl_2

Q.11 Consider the following bromides : **[AIEEE 2010]**

(a)  (b)  (c) 

The correct order of S_N1 reactivity is :

(A) a > b > c (B) b > c > a (C) b > a > c (D) c > b > a

Q.12 Which of the following reactions is not expected to give a satisfactory yield of alkyl iodide -

(A) $CH_3CH_2OH + KI + H_3PO_4 \longrightarrow$ (B) $CH_3CH_2OH + Pl_3 \xrightarrow{heat}$

(C) $CH_3CH_2Br + NaI \xrightarrow{acetone}$ (D) $CH_3CH_2COOAg + I_2 \xrightarrow[heat]{CCl_4}$

Q.13 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product is -

(A) trans-2-pentene (B) 2-ethoxypentane (C) 1-pentene (D) cis-2-pentene

Q.14 An aromatic primary amine (A) is heated with another compound (B) in the presence of alcoholic KOH to give a bad-smelling compound having the formula C_6H_5NC. The compound (B) can be prepared by heating another compound (C) with chlorine and slaked lime. The compound (C) is-

(A) $C_6H_5NH_2$ (B) C_2H_5OH (C) $CHCl_3$ (D) CH_3OCH_3

Q.15 Consider the following sequence of reactions.

$C_2H_5Cl \xrightarrow[DMSO,heat]{KCN} X \xrightarrow[prolonged\ heat]{H_3O^+} Y$. The products (X) and (Y) are, respectively -

(A) C_2H_5CN and $C_2H_5CH_2NH_2$ (B) C_2H_5CN and $C_2H_5CONH_2$

(C) C_2H_5NC and $C_2H_5NHCH_3$ (D) C_2H_5CN and C_2H_5COOH

Q.16 Which of the following, on being heated with alcoholic KOH, will respond positively to the carbylamine test -

(A) Chloroform and silver powder (B) Chloroform and aniline

(C) Methyl chloride and aniline (D) Methyl cyanide and aniline

Q.17 Arrange the following compounds according to their relative reactivity with alcoholic $AgNO_3$ - t-Butyl chloride (I), sec-butyl chloride (II) and CCl_4 (III)

(A) I > II > III (B) III > II > I

(C) II > I > III (D) II = III > I

Q.18 Of the following, which is an S_N1 reaction -

(A) $(CH_3)_3CBr + H_2O \longrightarrow$ (B) $CH_3CH_2CH_2Cl + I^- \longrightarrow$

(C) $(CH_3)_3CBr + CN^- \longrightarrow$ (D) $CH_3CHBrCH_3 + OH(alc.) \longrightarrow$

Q.19 In the reaction,

$C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X$

the order of reactivity of HX is -

(A) HBr > HI > HCl (B) HI > HBr > HCl

(C) HI > HCI > HBr (D) HCl > HBr > Hl

Q.20 $CH_3Br \xrightarrow{KCN} A \xrightarrow{+4H} CH_3CH_2NH_2$ IUPAC name of A is -

(A) Methyl cyanide (B) Mehyl isonitrile (C) Acetonitrile (D) Ethane nitrile

Q.21 An alkyl halide can not be converted into an alcohol by -

(A) Substitution (B) Addition

(C) Elimination (D) Dehydrohalogenation

Q.22 Function of bleaching powder in the formation of trichloro-methane from ethyl alcohol is -

(A) To provide nascent Cl for oxidation (B) To carry out chlorination of acetaldehyde

(C) To carry out hydrolysis of chloral (D) To carry out all the three processes

Q.23 Ethyl bromide can be converted into ethyl alcohol by -

(A) Heating with an alcoholic solution of KOH

(B) The action of moist silver oxide

(C) Heating with dil. HCl and Zn

(D) Refluxing with methanol

Q.24 Impure chloroform cannot be tested by -

(A) Concentrated sulphuric acid (B) Blue litmus

(C) Silver nitrate solution (D) Silver powder

Q.25 The reaction of ethyl bromide with a lead-sodium alloy gives -

(A) Tetraethyl bromide (B) Tetraethyl lead

(C) Sodium ethoxide (D) None of these

Q.26 A strong solution of alcoholic alkali will preferentially promote alkyl halide into an alkene by -

(A) Addition (B) Elimination

(C) Polymerisation (D) Substitution

Q.27 The Friedel-Crafts reaction of n-propyl bromide with benzene in the presence of anhydrous $AlCl_3$ gives-

(A) n-Propylbenzene (B) Isopropyl benzene

(C)1,4-Dipropyl benzene (D) 1,2-Dipropyl benzene

Q.28 Treatment of ammonia with excess ethyl chloride will give -

(A) Diethylamine (B) Ethane

(C) Methylamine (D) Tetraethyl ammonium chloride

Q.29 Most volatile alkyl chloride is -

(A) Ethyl chloride (B) Butyl chloride

(C) Amyl chloride (D) Propyl chloride

Q.30 The mixture of two organic chlorine compounds on treatment with sodium metal in ether solution gives isobutane as one of the products. The reactants are -

(A) Methyl chloride and propyl chloride (B) Methyl chloride and ethyl chloride

(C) Isopropyl chloride and ethyl chloride (D) Isopropyl chloride and methyl chloride

ANSWER KEYS

EXERCISE – I

Q.1	D	Q.2	B	Q.3	D	Q.4	A	Q.5	C	Q.6	B	Q.7	D
Q.8	B	Q.9	A	Q.10	C	Q.11	D	Q.12	C	Q.13	A	Q.14	B
Q.15	A	Q.16	B	Q.17	B	Q.18	A	Q.19	B	Q.20	B	Q.21	D
Q.22	B	Q.23	A	Q.24	B	Q.25	A	Q.26	D	Q.27	D	Q.28	C
Q.29	B	Q.30	C										

EXERCISE – II

Q.1	A	Q.2	D	Q.3	A	Q.4	C	Q.5	D	Q.6	C	Q.7	C
Q.8	B	Q.9	C	Q.10	D	Q.11	B	Q.12	D	Q.13	A	Q.14	B
Q.15	D	Q.16	B	Q.17	A	Q.18	A	Q.19	B	Q.20	D	Q.21	B
Q.22	D	Q.23	B	Q.24	D	Q.25	B	Q.26	B	Q.27	B	Q.28	D
Q.29	A	Q.30	D										