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HYDROCARBONS

Organic compounds composed of only carbon and hydrogen

Saturated Hydrocarbon (Al Kanes)

Represented by C_nH_{2n+2} (n = no of C-atoms)

Called paraffins (parum = little; affinis = affinity)

Bond angle is 109.5° or 109°28'

General methods of Preparation of Alkanes

1. Decarboxylation of carboxylic acids (Laboratory preparation)

An alkane is prepared by heating strongly the anhydrous sodium or potassium salt of a carboxylic acid with sodalime (NaOH + CaO).

$$R-COONa + NaOH \xrightarrow[CaO]{\Delta} R-H + Na_2CO_3$$

$$\underset{\text{Sodiumpropionate}}{CH_3CH_2COONa} + NaOH \xrightarrow[CaO]{\Delta} \underset{\text{Ethane}}{CH_3CH_3} + Na_2CO_3$$

Note :

(i) The alkane prepared contains one carbon atom less than that of the original acid.

(ii) CaO increases the porosity of the mixture and acts as a dehydrating agent and catalyst.

2. Sabatier-Senderen's Reaction

Alkane may be obtained by the catalytic hydrogenation of alkenes or alkynes is presence Ni catalyst at 200°C – 300°C.

$$\underset{\text{Alkene}}{R-CH=CH_2} + H_2 \xrightarrow[\Delta]{Ni} \underset{\text{Alkane}}{R-CH_2CH_3}$$

$$\underset{\text{Propyne}}{CH_3C\equiv CH} + 2H_2 \xrightarrow{Ni/\Delta} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

Note :

(i) Platinum or Palladium or Raney nickel may also be used as catalyst at ordinary temperature.

(ii) Methane cannot be prepared by this method.

3. By the Reduction of Alkyl Halides :

Alkyl halides are directly reduced by either of the following reducing agent to form alkanes.

(a) Zn/Cu + (C_2H_5OH)

(b) Zn + HCl

(c) Zn + Acetic acid (CH_3COOH)

(d) $LiAlH_4$

(e) Red phosphorous and hydrogen iodide

(f) H_2 + nickel or palladium or platinum

$$\underset{\text{Alkyl halide}}{RX} + 2H \xrightarrow[\text{Ethanol}]{Zn+Cu} RH + HX$$

4. Wurtz Reaction :

An ehterial solution of alkyl halide when treated with sodium metal forms alkane.

$$R - X + 2Na + X - R \xrightarrow[\Delta]{\text{dry Ether}} R - R + 2NaBr$$

$$\underset{\text{Methyl Bromide}}{H_3C - Br} + 2Na + BrCH_3 \xrightarrow[\Delta]{\text{dry ether}} \underset{\text{Ethane}}{CH_3CH_3} + 2NaBr$$

Note :

(i) Wrutz Reaction is useful only for the preparation of symmetrical alkanes containing even number of carbon atoms.

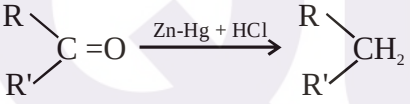
(ii) When a mixture of two different alkyl halides are used a mixture of three alkanes are obtained.

(iii) Methane cannot be prepared.

(iv) This reaction fails with tertiary alkyl halides.

5. Clemmensen's Reduction :

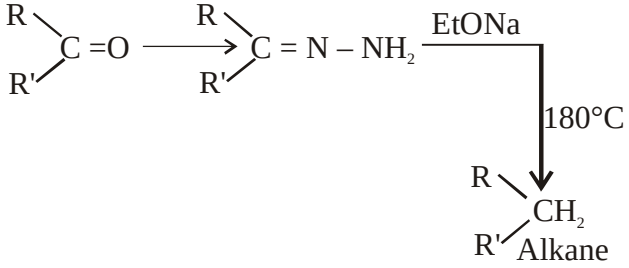
Carbonyl compounds like aldehydes and ketones are reduced by amalgamated zinc and conc. HCl to produce the corresponding alkanes having the same number of carbon atoms.



$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{Zn-Hg+HCl} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

6. Wolf-Kishner Reduction :

Carbonyl compounds can be reduced to hydrocarbons in presence of excess of hydrazine or semicarbazide and sodium alkoxide on heating.



7. Kolbe Reaction (Electrolytic Method) :

An alkane is prepared by the electrolysis of a concentrated aqueous solution of sodium or potassium salt of a saturated monocarboxylic acid using platinum electrodes.

$$2RCOOK + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Anode}}{R-R} + 2CO_2 + \underset{\text{Solution}}{2KOH} + \underset{\text{Cathode}}{H_2}$$

$$2CH_3COOK + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ehtane}}{CH_3CH_3} + 2CO_2 + 2KOH + H_2$$

8. Frank Land Method :

The alkyl halide is heated with zinc in inert solvent.

$$RX + Zn + XR \longrightarrow R - R + ZnX_2$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + Zn + BrC_2H_5 \longrightarrow \underset{\text{Butane}}{C_4H_{10}} + ZnBr_2$$

9. By the reduction of alcohols, aldehydes, Ketones and Carboxylic acids, by red phosophorus and HI

$$\underset{\text{Alcohol}}{R-OH} + 2HI \xrightarrow[150°C]{\text{Red P}} \underset{\text{Alkane}}{RH} + I_2 + H_2O$$

$$R - CHO + 4HI \xrightarrow[200°C]{\text{Red P}} RCH_3 + 2I_2 + H_2O$$

$$CH_3COCH_3 + 4HI \xrightarrow[250°C]{\text{Red P}} CH_3CH_2CH_3 + 2I_2 + H_2O$$

$$R - COOH + 6HI \xrightarrow[250°C]{\text{Red P}} R - CH_3 + 3I_2 + 2H_2O$$

10. By the Decomposition of Grignard Reagents :

A Grignard reagent can be decomposed by active hydrogencontaining compound to produce alkane.

$$RMgX + HOH \xrightarrow{\text{Ether}} \underset{\text{Alkane}}{R-H} + Mg(OH)X$$

$$RMgX + R' - OH \xrightarrow[\text{Zerewitnoff reaction}]{\text{Ether}} R - H + Mg(OR')X$$

11. Corey-House Alkane Synthesis :

Symmetrical as well as unsymmetricalalkanes can be prepared by the action of alkyl halides with an etherial solution oflithium dialkyl cuperate (LiR_2Cu)

$$RX + 2Li \xrightarrow{\text{Ether}} 2RLi + LiX$$

$$2RLi + CuI \longrightarrow \underset{\text{Lithium dialkyl Cuprate}}{LiR_2Cu} + LiI$$

$$LiR_2Cu + R'Br \longrightarrow \underset{\text{Alkane}}{R - R'} + R - Cu + LiBr$$

Note : R' should be mainly 1°.

Examples :

$$CH_3Br + 2Li \xrightarrow{\text{Ether}} CH_3Li + LiBr$$

$$2CH_3Li + CuI \longrightarrow Li(CH_3)_2 Cu + LiI$$

$$Li(CH_3)_2 Cu + C_2H_5Br \longrightarrow \underset{\text{Propane}}{C_2H_5 - CH_3} + CH_3Cu + LiBr$$

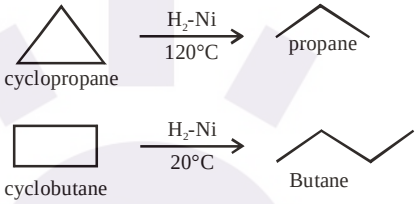
12. Hydroboration of Alkenes :

Diborane (B_2H_6) reacts with alkenes to form trialkyl-boranes which on treatment with acetic acid or propionic acid yields corresponding alkane.

$$R - CH = CH_2 \xrightarrow{B_2H_6} (R - CH_2 - CH_2)_3 B \xrightarrow{CH_3COOH} R - CH_2 - CH_3$$

13. By Cycloalkane :

Cycloalkanes can be reduced to alkanes by cleavage of C — C bond which minimises the strain.



14. Hydrolysis of Metal Carbides :

$$Al_4C_3 \xrightarrow{H_2O} Al(OH)_3 + CH_4$$

$$Be_2C \xrightarrow{H_2O} Be(OH)_2 + CH_4$$

N.B. :

This method is applied only for methane.

PROPERTIES

A. Physical Properties

First four members are gases, next 13 members are colourless liquids and rest are solids.

The alkanes are insoluble in water but soluble in organic solvents like ether, carbon tetrachloride, benzene etc.

The density and boiling points increase with the increase of molecular weights. The boiling points of isomeric branched chain alkanes, are generally lower than those of straight chain alkanes.

B. Chemical Properties

Alkanes are generally stable and chemically inert.

The C — H and C — C bonds in alkanes are almost non-polar, attacking reagents find no reaction sites to

which they could be attacked.

Under suitable conditions the alkanes undergo two types of reactions

(a) Free radical substitution Reaction

(b) Thermal; and Catalytic Reaction

(a) Substitution reaction

1. Halogenation :

In presence of diffused sunlight or in ultra violet light or at relatively high temperature (300°C – 500°C) the H-atoms (1°, 2°, 3° H) of alkanes are replaced by equal number of halogen atoms yielding a mixture of halogenated alkanes.

(i) Chlorination : (Free Radical Substitution)

$$\underset{\text{Excess}}{CH_4} + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV-light}} \underset{\substack{\text{Chloromethane}\\(\text{Methylchloride})}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV-light}} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV-light}} \underset{\substack{\text{Trichloromethane}\\(\text{Chloroform})}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV-light}} \underset{\substack{\text{Carbon tetrachloride}\\(\text{Pyrene})}}{CCl_4} + HCl$$

Note : Methyl Chloride is the major product if an excess of methane is used.

(ii) Bromination : Bromine reacts with alkanes in a similar manner but less vigorously.

(iii) Iodination : The reaction between iodine and alkane is reversible. Iodination can be done in the presence of an oxidising agent such as HIO_3 (or HNO_3) which removes the hydroiodic acid (HI).

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

(iv) Fluorination : Fluorine reacts with alkanes at ordinary temperature explosively. So fluorination can be done by diluting fluorine with an inert gas or indirectly.

$$2C_2H_5Br + HgF_2 \longrightarrow 2C_2H_5F + HgBr_2$$

2. Nitration : A mixture of an alkane and nitric acid vapours is heated at 400°C – 500°C, one hydrogen atom of the alkane is replaced by a nitro group. This reaction is also free radical substitution.

$$\underset{\text{Nitric Acid}}{R-H + HO-NO_2} \longrightarrow \underset{\text{Nitroalkane}}{R-NO_2} + H_2O$$

$$\underset{\text{(Vapourphase Nitration)}}{CH_4 + HNO_3} \xrightarrow{400°C-500°C} \underset{\text{Nitromethane}}{CH_3-NO_2} + H_2O$$

N.B. : This temperature (400°C – 500°C) is sufficient to break C–H as well as C–C bond homolytically and thus mixture of products are obtained.

$$CH_3CH_3 + HONO_2 \xrightarrow{400°C-500°C} \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2} + H_2O$$

3. Sulphonation : Sulphonation is carried out with fuming H_2SO_4.

$$R-H + \underset{\text{Fuming}}{HO-SO_3H} \xrightarrow{\Delta} \underset{\text{Alkane Sulphonic Acid}}{R-SO_3H} + H_2O$$

Note : R = C_6H_{13} or larger alkyl group

4. Oxidation :

(i) Complete Combustion :

In the presence of excess oxygen alkane burn to form carbon dioxide water.

$$\underset{\text{Methane}}{CH_4} + 2O_2 \longrightarrow CO_2 + 2H_2O + 212.8 \text{ Kcal/mole}$$

Note: $C_nH_{2n+2} + \frac{3n+1}{2}O_2 \xrightarrow{\text{Flame}} nCO_2 + (n+1)H_2O + \text{Heat}$

$$2CH_3CH_3 + 7O_2 \longrightarrow 4CO_2 + 6H_2O + 745.6 \text{ Kcal/mole}$$

(ii) Incomplete Combustion :

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow \underset{\text{Carbon black}}{C} + 2H_2O$$

(iii) Catalytic Oxidation :

I. $\underset{\text{Natural gas}}{CH_4} + O_2 \xrightarrow[200°, 100 \text{ atm.}]{Cu-tube} \underset{\text{Methyl alcohol}}{2CH_3OH}$

II. Alkane having 3° H on oxidation with $KMnO_4$ gives 3°-alcohol.

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H \xrightarrow{KMnO_4} \underset{\text{tert-butylalcohol}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH}$$

III. Higher alkane on oxidation with manganese acetate gives carboxylic acids.

$$R-CH_3 \xrightarrow{(CH_3COO)_2Mn} R-COOH$$

IV. $CH_4 + O_2 \xrightarrow[275°C]{Mo_2O_3} HCHO + H_2O$

5. Isomerisation : Normal alkanes are converted to their branched chain isomers in the presence of aluminium chloride and HCl at 25°C.

$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow[HCl]{AlCl_3} \underset{\text{Isobu tane}}{\underset{\text{(2–Methylpropane)}}{CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{|}}CH - CH_3}}$$

6. Prolysis (Cracking) : Decomposition of higher alkane into amixture of lower alkanes, alkenes and hydrogen on heating at high temperature in the absence of air.

$$3CH_3CH_3 \xrightarrow[\text{Absence of air}]{500°C} \underset{\text{Ethylene}}{2CH_2 = CH_2} + \underset{\text{Methane}}{2CH_4} + H_2$$

N.B. : In the presence of finely divided silica-alumina as catalyst, this reaction can be carried atless high temperature. This is called catalytic cracking.

7. Aromatisation :

$$CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow[600°C,10\,atm]{Cr_2O_3 + Al_2O_3} \text{C}_6\text{H}_6 + 4H_2$$

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_3 \xrightarrow[600°C,10\,atm]{Pt - Al_2O_3} \text{C}_6\text{H}_5\text{CH}_3 + 4H_2$$

8. $CH_4 + \underset{(\text{Steam})}{H_2O} \xrightarrow[1000°C]{\text{Ni on alumina}} \underset{\text{synthesis gas}}{CO + 3H_2}$

9. $2CH_4 \xrightarrow{1500°C} \underset{\text{Acetylene}}{HC \equiv CH} + 3H_2$

10. $CH_3CH_3 \xrightarrow[500°C-600°C]{Al_2O_3 + Cr_2O_3} \underset{\text{Ethylene}}{CH_2 = CH_2} + H_2 \uparrow$

11. Reaction with Alkenes

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}} + CH_2 = \underset{\displaystyle CH_3}{\overset{}{\underset{|}{\overset{|}{C}}}} - CH_3 \longrightarrow \underset{\text{Iso–oc tan e}}{CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}} - CH_3}$$

Uses :

C_1 to C_4 alkanes are used as domestic fuels.

In the manufacture of fuels.

Gasoline (petrol) is a mixture of alkanes alkenes and aromatic hydrocarbons. The quality of gasoline is determined by the amount of iso-octane (2, 2, 4-trimethyl pentane) present in it.

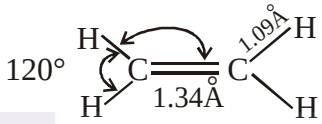
Methane is used in the manufacture of carbon black used in printer's ink, black paints etc.

ALKENE

H – C – C or H – C – H bond angle in ethylene is 120°.

C = C bond distance in ethylene is 1.34 Å

Alkenes are generally very active and due to the presence of pie-bond they exhibit addition reactions.



Generally represented by the general formula C_nH_{2n}.

Preparation

1. By the dehydration of alcohols :

$$CH_3CH_2OH \xrightarrow[160°C-180°C]{Conc.H_2SO_4} CH_2 = CH_2 + H_2O$$

$$\xrightarrow[\Delta]{\text{Syrupy Phosphoric acid}} CH_2 = CH_2 + H_2O$$

$$\xrightarrow[350°\text{-}400°C]{Al_2O_3} CH_2 = CH_2 + H_2O$$

Note :

(i) Here conc. H_2SO_4 acts as a dehyderating agent as well as catalyst.

(ii) The ease of dehydration of alcohols is

Tertiary alcohol > Secondary alcohol > Primary alcohol

$$\underset{\text{2-Butanol}}{CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3} \xrightarrow[180°C]{Conc.\ H_2SO_4} \underset{\substack{\text{But-2-ene}\\\text{(saytzeff's product major)}}}{CH_3CH = CHCH_3}$$

$$\xrightarrow[180°C]{Conc.\ H_2SO_4} \underset{\substack{\text{But-1-ene}\\\text{(Minor)}}}{CH_3CH_2CH = CH_2}$$

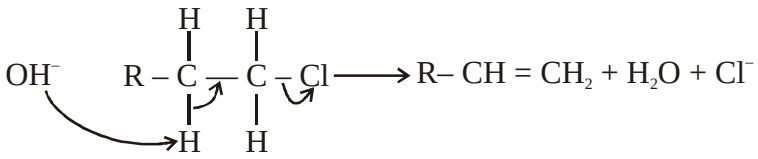
Note : Saytzeff's Rule :

During the dehydration of unsymmetrical alcohols the hydrogen atom is preferentially eliminated from that carbon atom which contains lesser number of hydrogen atoms (Dehydrohalogenation)

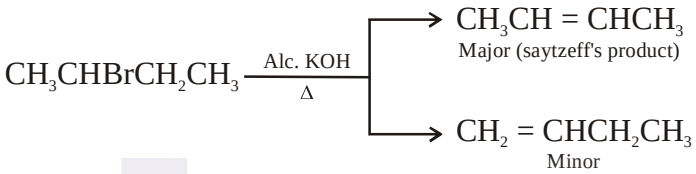
2. By the Removal of Hydrogen Halides from Alkyl Halides :

$$\underset{\text{Alkyl halide}}{R-CH_2CH_2X} \xrightarrow{\text{Alc.KOH}} R-CH=CH_2 + KX + H_2O$$

MECHANISM



For unsymmetrical alkyl halide.

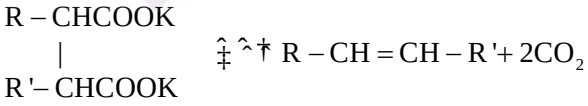


Note : If base taken in above reaction is highly hindered like $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O^-$ major product is

$CH_2 = CH - CH_2 - CH_3$ and it is Hoffmann's product.

Ease of reactivity is R – I > R – Br > R – Cl

3. By Kolbe's Electrolytic Method : When concentrated aqueous solution sodium or potasium salt of vicinal saturated dicarboxylic acid is electrolysed, the alkene and CO_2 liberate at anode where as alkali and H_2 at cathode.



4. By the Partial Hydrogenation of Alkynes :

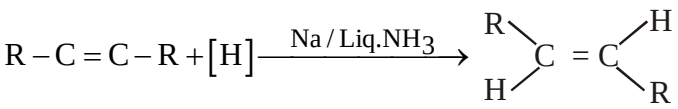
$$R-C\equiv C-R' + H_2 \xrightarrow[\text{Quinoline}]{\text{Pd}-CaCO_3} R-CH=CH-R'$$
$$\text{or, } Ni_2-B(P-2)$$

Note :

(i) Lindlar's Catalyst : Finely divided palladium or platinum deactivated by poisons like $BaSO_4$, $CaCO_3$ or quinoline. Partial reduction with Lindlar's catalyst gives cis alkene

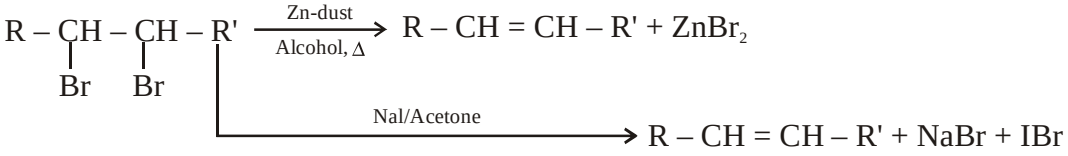
(ii) P-2 Catalyst = Nickel boride also gives cis-alkene.

(iii) Birch Reduction : Partial hydrogenation with Na and liquid NH_3 produces trans alkene.



(iv) B_2H_6 followed by treatment with CH_3COOH will give cis-alkene

4. By the dehalogenation of vicinal di-halides with Zn-dust in alcohol or NaI in acetone



7. By Dehydrogenation of Alkanes :

$$\underset{\text{n-Butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[500^\circ C]{Cr_2O_3\cdot Al_2O_3} \underset{\text{But-2-ene}}{CH_3-CH=CH-CH_3} + H_2$$

Properties

At room temperature, $C_2 - C_4 \rightarrow$ Gases

$C_5 - C_{13} \rightarrow$ Liquids

C_{13} Onwards $\rightarrow$ Solids

Gaseous alkenes are colourless and odourless. Only ethylene has a sweet smell.

All the alkenes are soluble in organic solvents like ether, benzene, etc.

The densities and boiling points increase with the increase of molecular weights. Their b.p. and m.p. are higher than corresponding alkanes. Cis-isomer has a higher boiling point than trans-isomer due to higher polarity whereas trans alkene has higher melting point than cis alkene.

Chemical :

Following types of reactions are given by alkenes

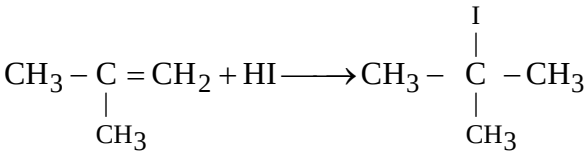
1. Addition Reaction (Electrophillic & radical addition)
2. Oxidation
3. Ozonolysis
4. Isomerisation
5. Substitution at α – carbon
6. Polymerisation

1. Addition Reaction

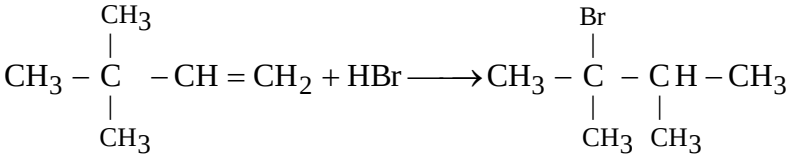
(a) Addition of HX(HCl, HBr and HI)

Electrophilic addition reaction.

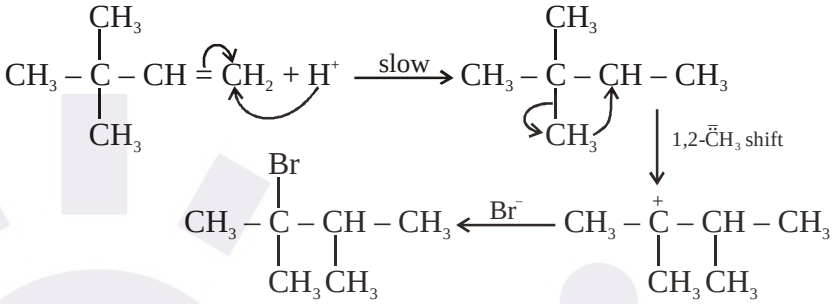
Product of formation takes place according to Markovnikov's rule.



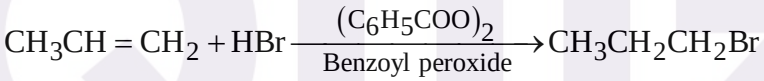
Note : Monosubstituted and disubstituted alkenes whose α – carbon is 4° give addition reaction through rearrangement.



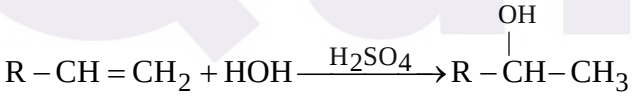
Mechanism :



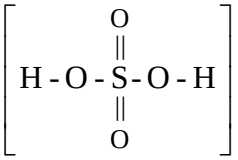
Product according to Anit Markownikoff's rule. (Free radical addition)

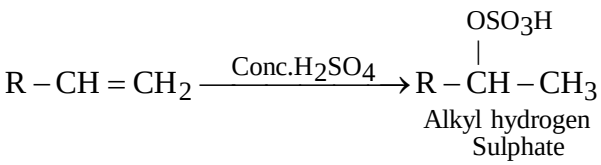


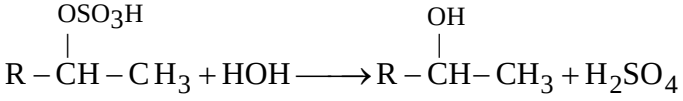
(b) Addition Reaction of Water : (Catalysed by acid) (Electrophillic addition)



Mechanism is exactly same as that of previous reaction.

(c) Addition Reaction of Conc. H_2SO_4  (Electrophillic addition)





(d) Addition of Hydrogen (Hydrogenation) :

$$R-CH=CH_2 \xrightarrow[\text{Heat, pressure}]{\text{Ni, Pt or Pd}} R-CH_2CH_3$$

(e) Addition of Halogens : (Electrophillic addition)

$$R-CH=CH_2 + \underset{\text{Brown}}{Br_2} \xrightarrow[(\text{Inert solvent})]{CCl_4} \underset{\substack{\text{Ethylene bromide}\\(\text{colourless})}}{CH_2Br-CH_2Br}$$

(Test for Unsaturation)

This reaction proceeds via cyclic intermediate that's why their no chance of rearrangement and it is anti addition.

(f) Addition of hypohalous acids :

$$CH_2=CH_2 + HOCl \longrightarrow \underset{\text{Ethylene Chlorohydrin}}{CH_2OHCH_2Cl}$$

Follow electrophillic addition via cyclic intermediati as in previous reaction.

(g) Hydroboronation oxidation :

$$6CH_3-CH=CH_2 + B_2H_6 \longrightarrow 2(CH_3CH_2CH_2)_3B$$

$$(CH_3CH_2CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} 3CH_3CH_2CH_2CH_2OH + H_3BO_3$$

Overall result of above reaction is anti Markonikoff addition of H_2O with Syn Stereochemistry.

(h) Oxy-Mercuration demercuration :

$$\underset{\text{3,3–Dimethylbut–1–ene}}{(CH_3)_3C-CH=CH_2} \xrightarrow[\text{THF}]{(CH_3COO)_2Hg/H_2O} (CH_3)_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2\cdot HgOOCCH_3$$

$$\downarrow NaBH_4, NaOH$$

$$\underset{\text{3,3–Dimethyl–2–bu tanol}}{(CH_3)_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3}$$

Overall result of above reaction is Markonikoff's addition of H_2O without rearrangement chance and with anti stereochemistry.

2. OXIDATION

(a) Addition of Oxygen :

$$R-CH=CH_2 + {}^{1}_{2}O_2 \xrightarrow[200°C\text{-}400°C]{Ag} R-\underset{\displaystyle O}{\underset{\diagdown\ \diagup}{CH-CH_2}} \xrightarrow{H_2O/H^+} R-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

oxirane

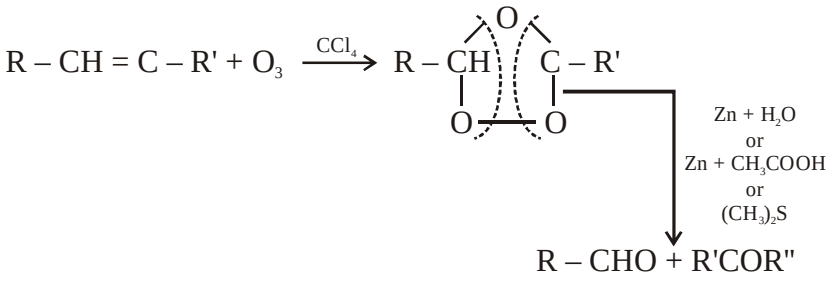
(b) Reductive ozonolysis :

$$>C=C<+O_3 \xrightarrow{CCl_4} >\underset{\displaystyle O}{\underset{|}{C}}\overset{\displaystyle O}{\overset{\diagup\ \diagdown}{\ }}\underset{\displaystyle O}{\underset{|}{C}}< \xrightarrow{Zn/H_2O} >C=O + O=C<$$

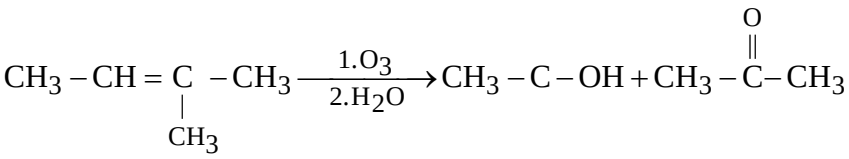
Ozonide

Carbonyl Compounds

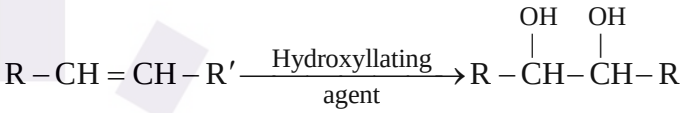
Note Zn-dust is added to prevent the oxidation of aldehyde into carboxylic group by H_2O_2



(c) Oxidative Ozonolysis :



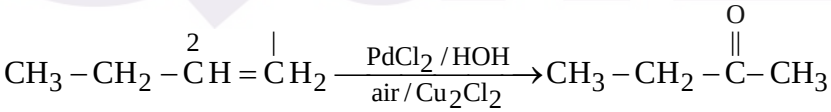
(d) Hydroxylation :



Hydroxylating agent

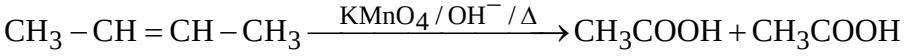
1. Cold dilute alkaline $KMnO_4$
2. OsO_4/H_2O_2
3. $R-\overset{O}{\overset{\|}{C}}-O-OH/H_3O^+$

(e) Wacker Process :



(f) Oxidation with hot basic $KMnO_4$.

In this reaction = CH_2 part gets oxidised to CO_2 and H_2O, = CHR part gets oxidised to RCOOH and = CR_2 part gets oxidised $\begin{matrix} R \\ R \end{matrix}\!\!>\!C=O$



(g) Combustion :

$$C_nH_{2n}+\frac{3n}{2}O_2 \longrightarrow nCO_2+nH_2O$$

$$C_2H_4+3O_2 \longrightarrow 2CO_2+2H_2O$$

3.SUBSTITUTION AT α-CARBON

(a) Allyllic oxidation :

$$CH_3-CH=CH_2 \xrightarrow{SeO_2} \underset{\text{Allyl alcohol}}{\overset{OH}{\overset{|}{C}}H_2-CH=CH_2}$$

$$CH_3-CH_2-\underset{CH_3}{\overset{|}{C}}H-CH=CH_2 \xrightarrow{SeO_2} CH_3-CH_2-\underset{CH_3}{\overset{OH}{\overset{|}{\overset{|}{C}}}}-CH=CH_2$$

(b) Allylic halogenation :

$$CH_3-CH=CH_2 \xrightarrow[\text{or } X_2/\Delta]{NBS/CCl_4} \underset{\text{Allyl bromide}}{\overset{Br}{\overset{|}{C}}H_2-CH=CH_2}$$

Uses

Ethylene is used in the preparation of polythene and also used in the manufacture of synthetic rubber, ethylene di chloride and mustard gas.

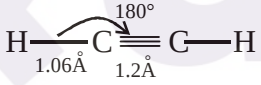
Ethene is used for artificial ripening of fruits.

Ethene is used as a general anaesthetic.

ALKYNES

General formula – C_nH_{2n-2}

The C – H bonds are formed by the overlapping of sp hybrid orbital of one carbon atom and s-orbital of hydrogen atom



$C \equiv C$ distance is $1.20\,\text{Å}$ and C – H bond length is $1.08\,\text{Å}$

H – C – C bond angle is 180°

General Methods of Preparation of Alkynes

1. By the reaction of calcikum carbide with water :

$$\underset{\text{Calcium carbide}}{\overset{C \quad C}{\diagdown\ \diagup}\ Ca} + 2HOH \xrightarrow{\text{Room Temp.}} \underset{\text{Acetylene}}{H-C\equiv -H} + Ca(OH)_2$$

2. Dehydrohalogenation of Vicinal Dihalides

$$R-\underset{Br}{\overset{H}{\overset{|}{\overset{|}{C}}}}-\underset{H}{\overset{Br}{\overset{|}{\overset{|}{C}}}}-H \xrightarrow[(ii)\ NaNH_2/\Delta]{(i)\ Alc.KOH/\Delta} R-C\equiv H + 2HBr$$

$$R-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{C}}-H \xrightarrow{NaNH_2/\Delta} R-C\equiv C-H+2HBr$$

3. Dehalogenation of Tetrahalides :

$$R-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-R+2Zn \xrightarrow[\Delta]{Alcohol} \underset{Alkyne}{R-C\equiv C-R}+2ZnX_2$$

Tetrahalide

4. Reaction of sodium acetylides with primary alkyl halides :

$$H-C\equiv C-Na+CH_3Br \longrightarrow CH_3-C\equiv CH+NaBr$$

5. Kolbe's Method :

$$\begin{matrix}CHCOONa\\ \|\\ CHCOONa\end{matrix} \xrightarrow{+2H_2O,\,Current} HC\equiv CH+2CO_2+2NaOH+H_2$$

Sodium Salt of maleic acid or fumaric acid

6. By heating Iodoform with Silver

$$CHI_3+6Ag+I_3CH \longrightarrow CH\equiv CH+6AgI$$

Properties

A. PHYSICAL

The first three members are gases. The next 8 members are liquids and the rests are solids. Alkynes are slightly soluble in water but dissolves in organic solvents like acetone, benzen, ethanol.

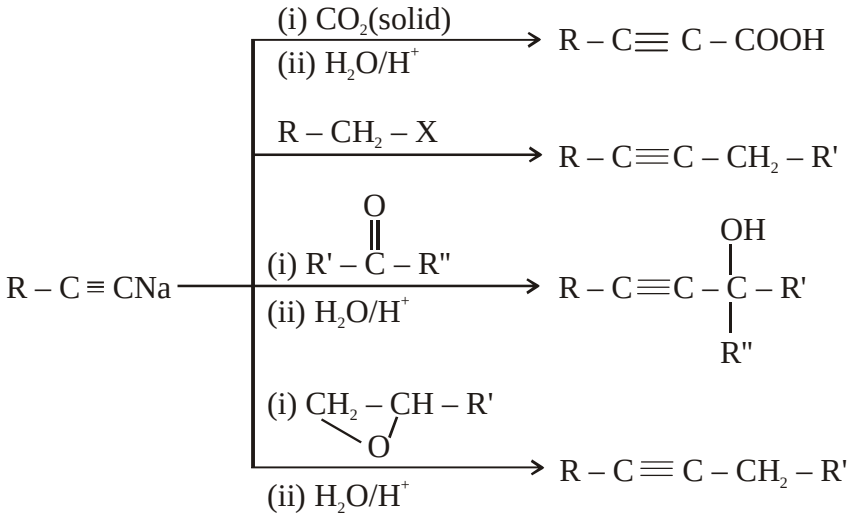
B. CHEMICAL

Alkynes give two types of chemical reaction

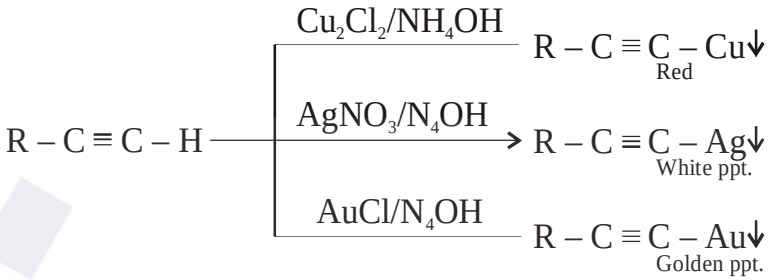
1. Reaction due to acidic hydrogen and
2. Reaction due to π – bonds.

1. Reaction due to Acidic Hydrogen

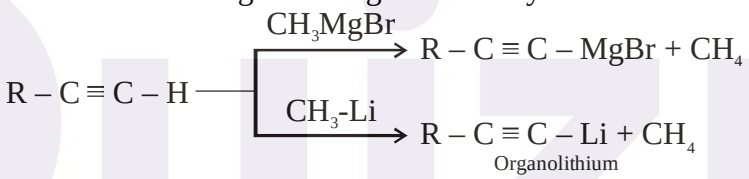
(a) $$R-C\equiv C-H \xrightarrow[NH_3(l)]{NaNH_2} R-C\equiv C^-Na^+ +\frac{1}{2}H_2$$



(b)



(c) Reaction with Grignard reagent and alkyl lithium :



2. Reaction due to π-bonds (Addition Reaction of Alkynes)

Alkynes generally gives electrophilic addition reaction and are less reactive than alkene for electrophilic addition reaction due to following reason

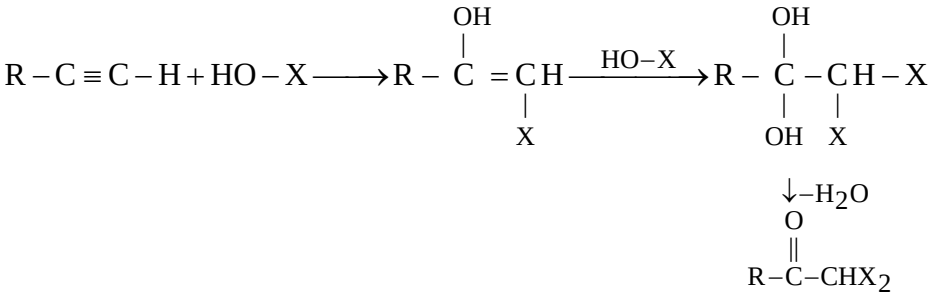
$$\underset{\text{Alkene}}{R-CH=CH_2} + H^+ \longrightarrow \underset{\substack{\text{(I)}\\ \text{Alkyl carbocation}}}{R-\overset{+}{C}H-CH_3}$$

$$R-C\equiv C-H + H^+ \longrightarrow \underset{\substack{\text{(II)}\\ \text{Vinyl carbocation}\\ \text{less stable than (I)}}}{R-\overset{+}{C}=CH_2}$$

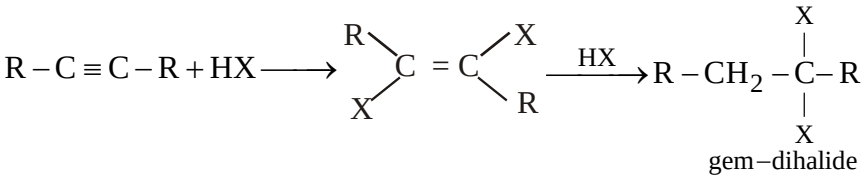
They also give nucleophilic addition reactions with HOH, HCN, ROH, RCOOH etc.

I. Electrophilic Addition Reaction

(a) Addition of HOX :

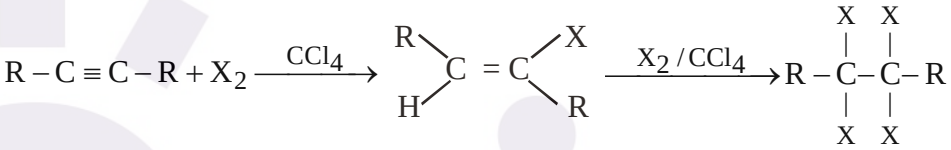


(b) Addition of HX :



Note : order of reactivity of HX is HI > HBr > HCl

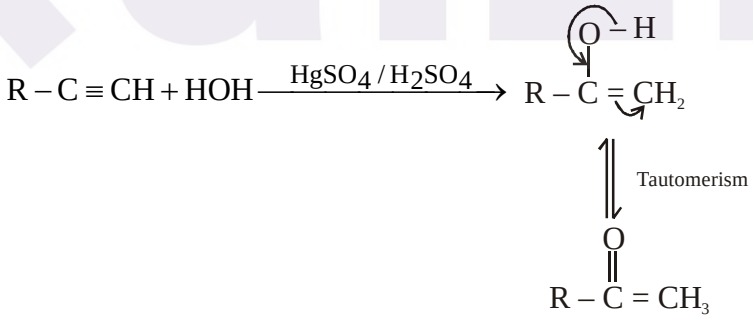
(c) Addition of X_2 (Cl_2, Br_2 and I_2) :



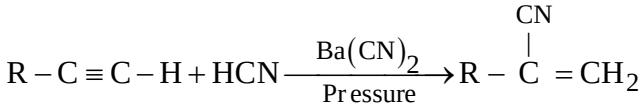
Note : The reactivity order of Halogen is $Cl_2 > Br_2 > I_2$

II. Nucleophilic Addition Reaction

(a) Addition of water



(b) Addition of HCN :



(c) Addition of $CH_3-\overset{\overset{O}{\|}}{C}-OH$:

3. Other Reactions :

I. Oxidation of Alkynes

(a) Baeyer's Test :

$$R-C\equiv C-R \xrightarrow[\text{Cold \& dil}]{KMnO_4/OH^-/HOH} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R$$

(b) Oxiation by SeO_2 :

$$R-C\equiv C-R \xrightarrow{SeO_2} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R$$

(c) $$R-C\equiv C-R \xrightarrow{KMnO_4/OH^-/\Delta} R-COOH + R'COOH$$

$$CH_3-C\equiv C-H \xrightarrow{KMnO_4/OH^-/\Delta} \underset{\downarrow[O]}{CH_3COOH} + \underset{CO_2+H_2O}{HCOOH}$$

II. Coupling Reaction (linear polymerisation)

$$H-C\equiv C-H + H-C\equiv C-H \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Vinylaccetylene}}{H_2C=CH-C\equiv CH}$$

III. Isomerisation

(a) $$CH_3-C\equiv C-CH_3 \xleftarrow{\text{alc.KOH}} CH_3-CH_2-C\equiv CH$$

$$\downarrow NaNH_2$$

$$CH_3-CH_2-C\equiv C^{-}\,Na^{+}$$

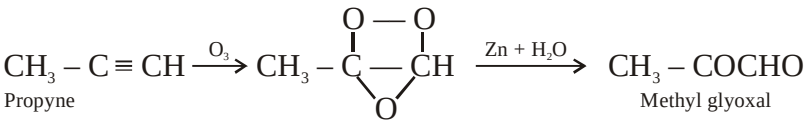
IV. Oxidative ozonolysis

$$R-C\equiv C-R' \xrightarrow{O_3} R-\underset{\underset{O}{|}}{\overset{O-O}{C}}-\underset{\underset{O}{|}}{\overset{O-O}{C}}-R' \xrightarrow{H_2O} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R' \xrightarrow{H_2O_2} R-COOH + R'COOH$$

e.g. $$CH_3C\equiv C-H \xrightarrow[(ii)H_2O]{(i)O_3} \underset{\text{Acetic Acid}}{CH_3COOH} + \underset{\downarrow[O]\\CO_2+H_2O}{\underset{\text{Formic Acid}}{[HCOOH]}}$$

V. Reductive ozonolysis

$$R-C=C-R' \xrightarrow{O_3} R-\underset{\underset{O}{|}}{\overset{O-O}{C}}-\underset{\underset{O}{|}}{\overset{O-O}{C}}-R' \xrightarrow{H_2O+Zn} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R'$$



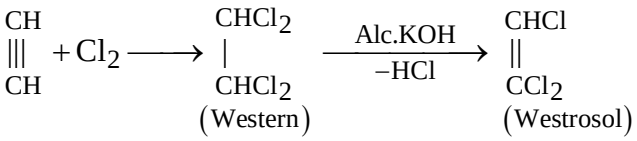
Uses :

(a) It is used for the production of oxy-acetylene flame, which is employed for cutting and welding of metals. it provides the temperature above 300°C.

(b) Acetylene on electrical decompositionproduces finely divided carbon and hydrogen.

Hydrogen is used in air ships. $C_2H_2 \rightarrow 2C + H_2$

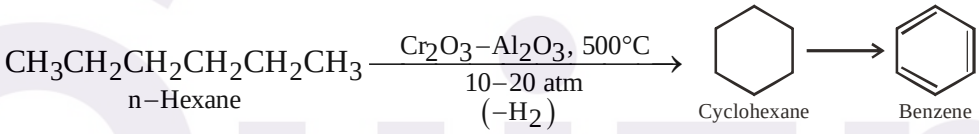
(c) It is used for the preparation of Westron and Westrosol (solvents).



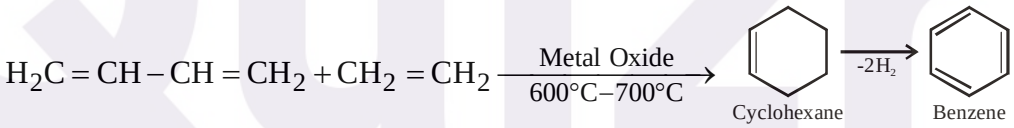
AROMATIC HYDROCARBON

Methods of Preparation :

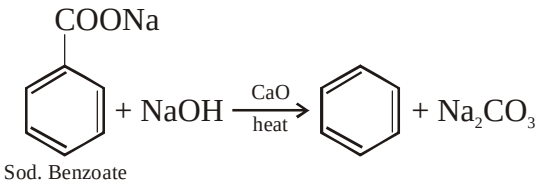
1. Hydrofroming or Catalytic reforming :



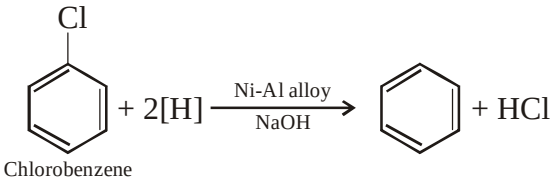
2. High Temperature Cracking :



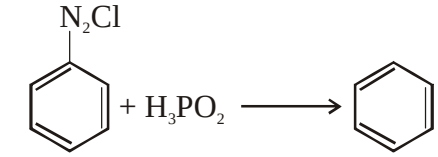
3. Laboratory Method :



4. From Chlorobenzene :

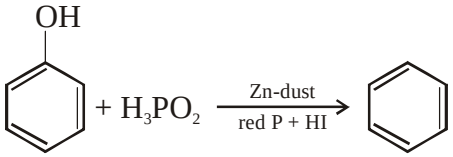


5. From Benzenediazonium Chloride :



Benzene diazomium chloride

6. From Phenol :

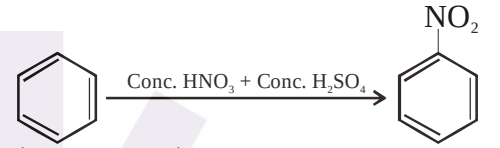


Phenol Benzen

CHEMICAL PROPERTIES

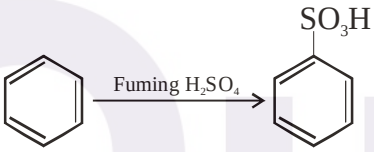
A. Electrophilic Aromatic Substitution -

1. Nitration



Nitrobenzene

2. Sulphonation

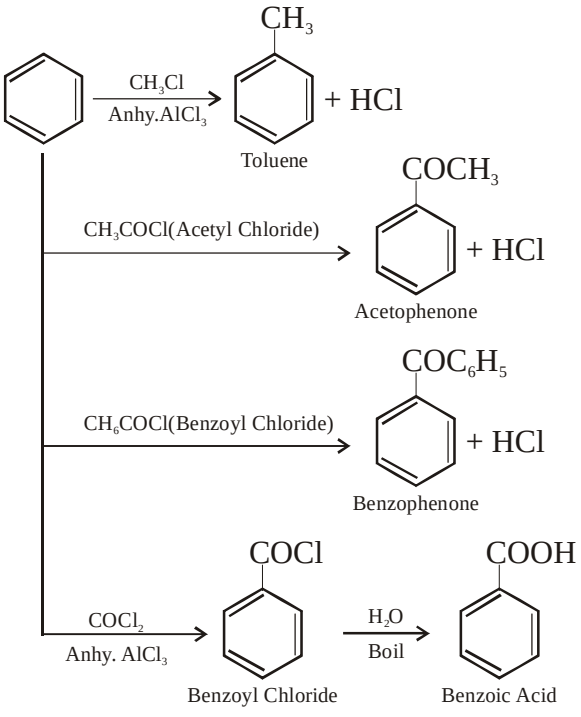


Benzene-sulphonic Acid

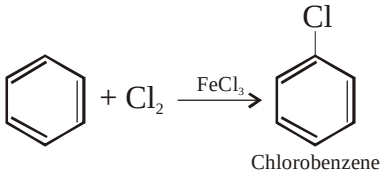
$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

Electrophile

3. Friedal Craft's Reaction



4. Halogneation :



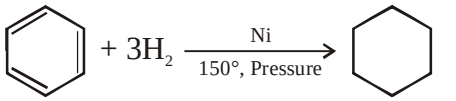
Chlorobenzene

$$FeCl_3 + Cl_2 \longrightarrow FeCl_4^- + Cl^+$$

Electrophile

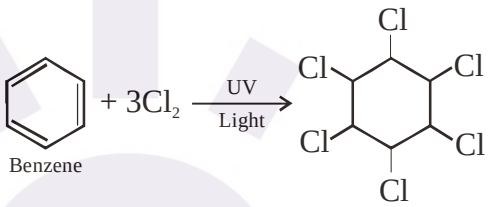
B. Addition Reaction

1. Addition of Hydrogen :



Benzene Chlorohexane

2. Addition of Halogens :

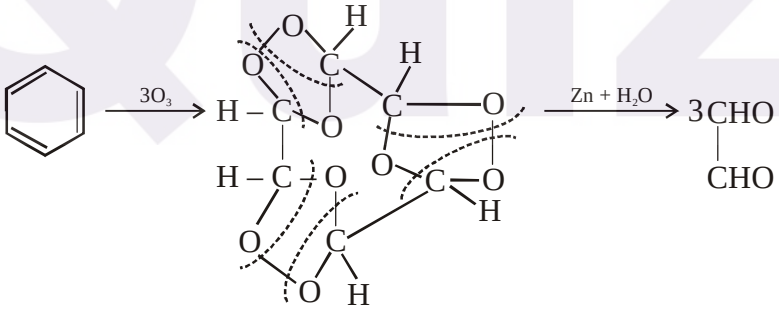


Benzene

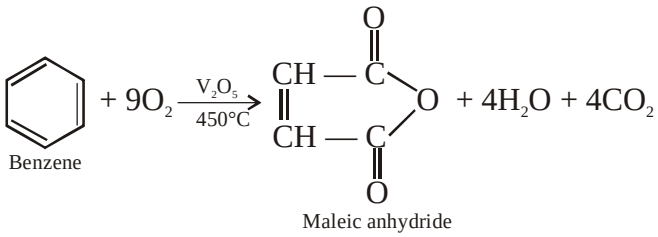
Benzene hexachloride (BHC)

3. Oxidation Reaction :

(a) Ozonolysis :

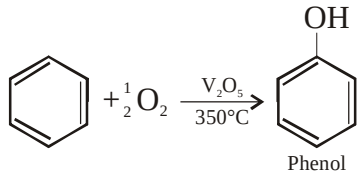


(b) Vapour Phase Oxiation :



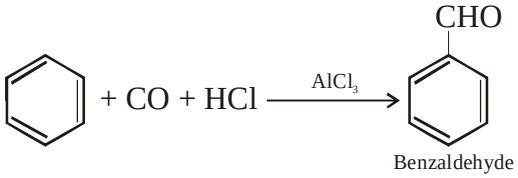
Benzene

Maleic anhydride

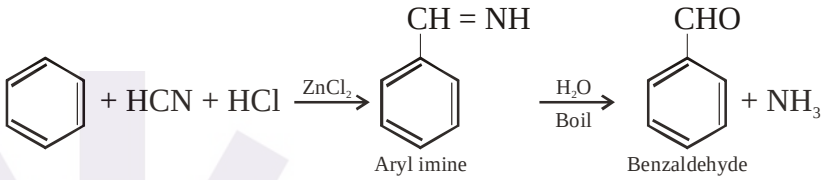
(c) 

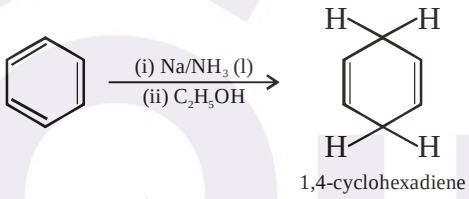
Other Reaction

1. Gattermann Koch Aldehyde Synthesis :



2. Gattermann Aldehyde Synthesis :



3. 

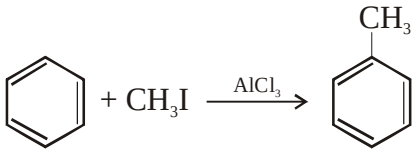
Uses of Benzene :

It is used as a solvent for oils and fats.
As synthethic liquid by mixing with petrol.
For the manufacture of toluene, nitrobenzene, acetophenone, etc.

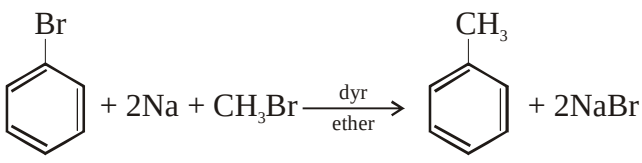
TOLUENE OR METHYL BENZENE

PREPARATION :

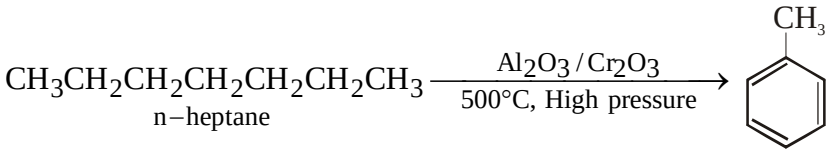
1. From Benzene



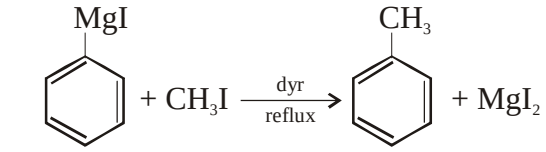
2. Wurtz Fittig Reaction



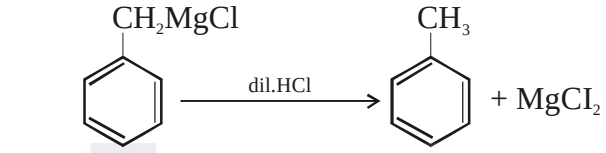
3. Aromatisation Reaction



4. From Grignard Reagent

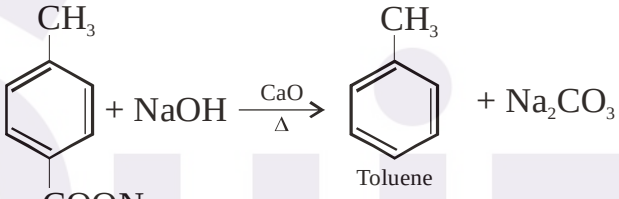


Phenyl magneisum iodide



Benzyl magneisum chloride

5. From Tolueic Acid



Toluene

Sodium Salt of para toluic acid

Properties

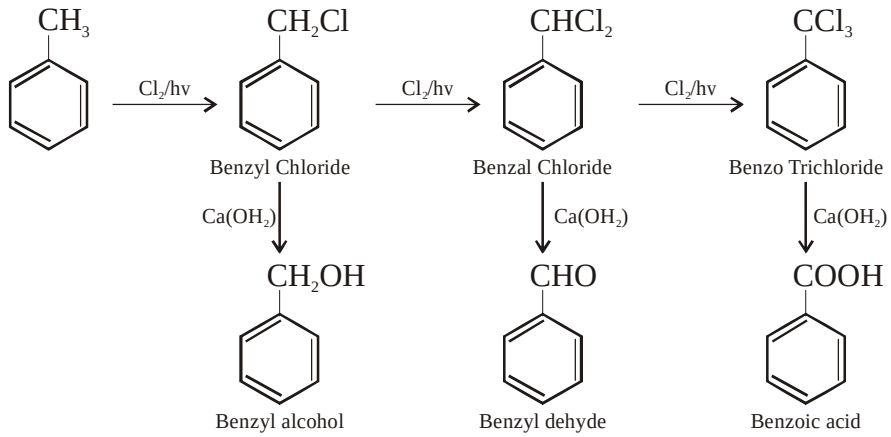
Toluene gives three types of Reaction

(a) Side Chain Reaction (b) Nuclear Chain Reaction

(c) Reduction Reaction

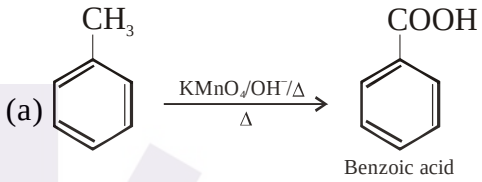
A. Side Chain Reaction

1. Chlorination

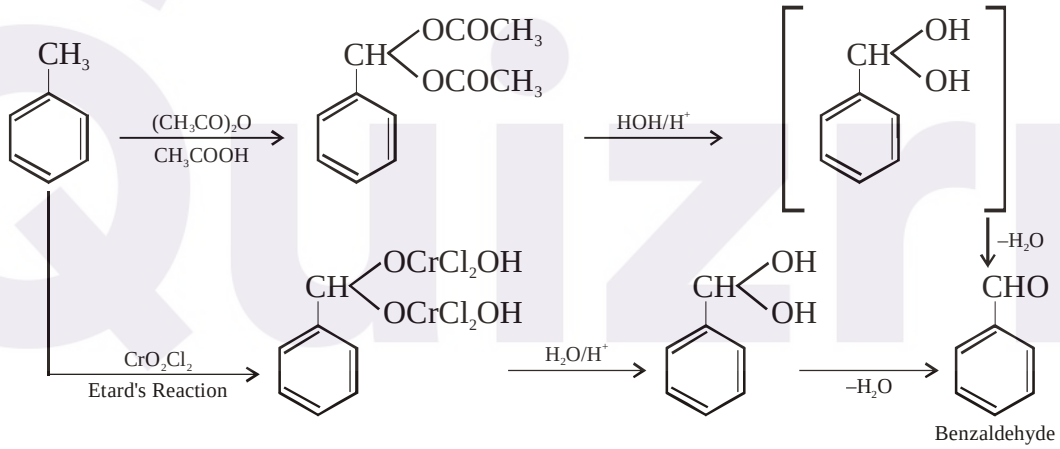


2. Side Chain Oxidation

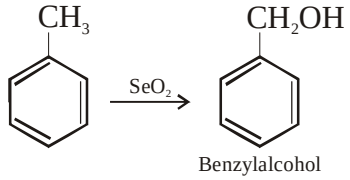
(a)



(b)

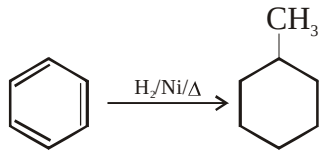


(c)

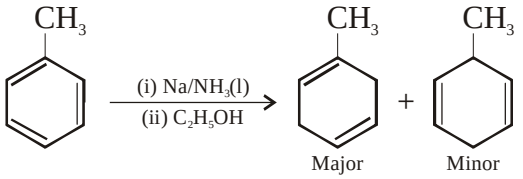


B. Reduction :

1. Total Reduction

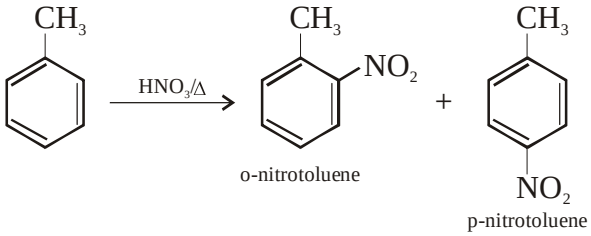


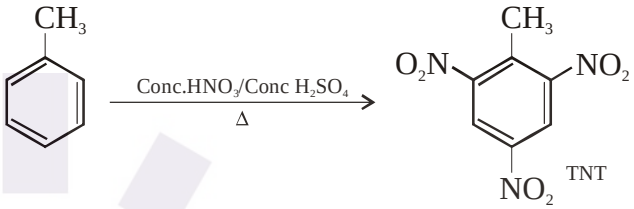
2. Birch Reduction :



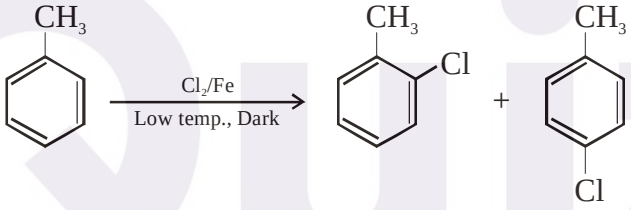
C. Nuclear Chain Reaction :

1. Nitration :

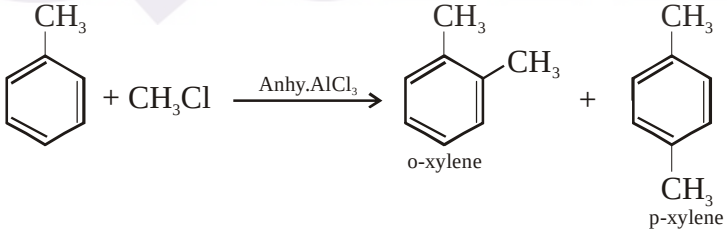




2. Reaction with Halogen :



3. Friedal Craft's Reaction :



4. Sulphonation :

