ORGANIC CHEMISTRY II

College of Pharmacy

2nd Stage/1st semester

A Lecturer :Mohammed S.Nawrooz

Pharmacognosist

Aromatic Hydrocarbons

Introduction:

- An aromatic hydrocarbon is an unsaturated cyclic hydrocarbon with a pattern of bonding that makes it chemically stable.

- Chemists have found it useful to divide all organic compounds into two broad classes: aliphatic compounds and aromatic compounds.

- The original meanings of the words "aliphatic" (fatty) and "aromatic" (fragrant).

- The word aromatic is used for historical reasons to refer to the class of compounds related structurally to benzene.

- Aromatic rings are a common part of many biological structures and are particularly important in nucleic acid chemistry and in the chemistry of several amino acids, also it is a part of chemical structures of active constituents in natural products.
- Benzene is the simplest aromatic hydrocarbon

- Disubstituted benzenes are named as ortho (1,2 disubstituted), meta (1,3 disubstituted), or para (1,4 disubstituted) derivatives.
- The C6H5 unit itself is referred to as a phenyl group, and the C6H5CH2 unit is a benzyl group.

- In the early days of organic chemistry, the word aromatic was used to describe Such fragrant substances as benzaldehyde (from cherries, peaches, and almonds), toluene (from Tolu balsam), and benzene (from coal distillate).

- Many naturally occurring compounds are aromatic in part, including steroids such as estrone and well-known pharmaceuticals such as the cholesterol-lowering drug atorvastatin(Lipitor.).

- Benzene itself causes a depressed white blood cell count (leukopenia) on prolonged exposure and should not be used as a laboratory solvent.

Properties of Aromatic Hydrocarbons

1. Some are liquids at room temperature while others are crystalline solids
2. Most are non-polar because of the symmetrical shape
3. Insoluble in water
4. Volatile
5. Carcinogenic
6. They burn with a strong sooty yellow flame because of the high carbon–hydrogen ratio

Importance of aromatic compounds

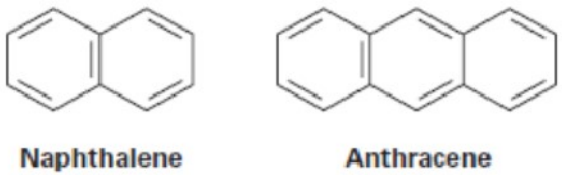
- Aromatic compounds play key roles in the biochemistry of all living things. The four aromatic amino acids histidine, phenylalanine, tryptophan, and tyrosine each serve as one of the 20 basic building-blocks of proteins. Further, all 5 nucleotides (adenine, thymine, cytosine, guanine, and uracil) that make up the sequence of the genetic code in DNA and RNA are aromatic purines or pyrimidines. Chlorophyll also has a similar aromatic system. Also, present in chemical structures of natural active constituents.

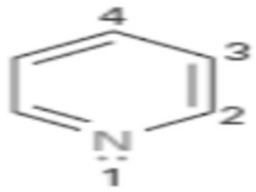
Types of aromatic compounds

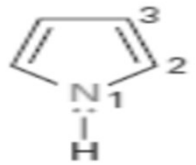
1.Neutral homocyclics : Benzene

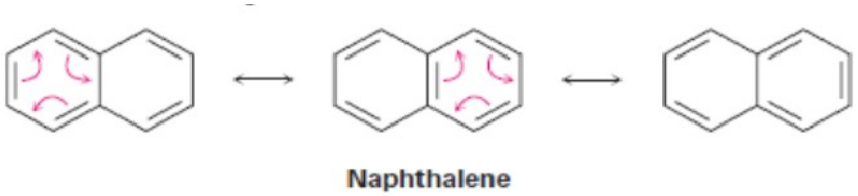
2.Heterocyclics A heterocycle is a cyclic compound that contains atoms of two or more elements in its ring, usually carbon along with nitrogen, oxygen, or sulfur. Pyridine and pyrimidine, for example, are six-membered heterocycles with nitrogen in their rings.

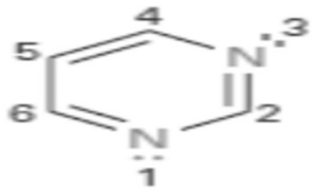
3. polycyclic aromatic compounds

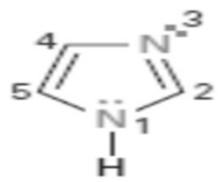












Sources of Aromatic Compounds

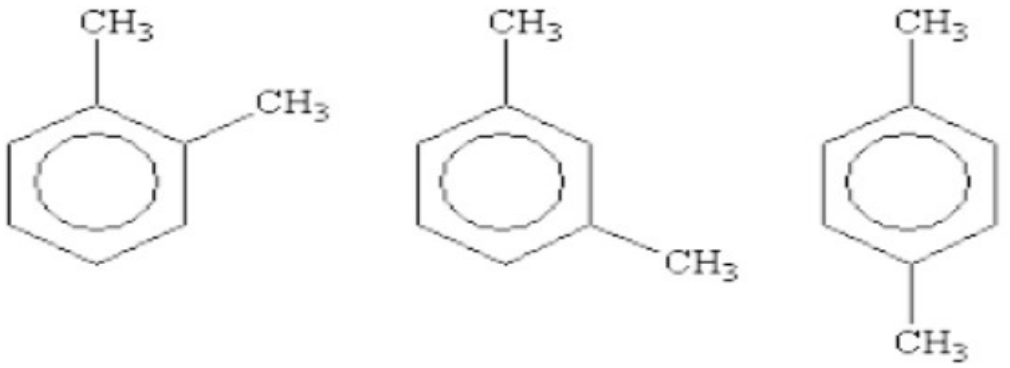
- Simple aromatic hydrocarbons come from two main sources: coal and petroleum. Coal is an enormously complex mixture made up primarily of large arrays of benzene-like rings joined together. Thermal breakdown of coal occurs when it is heated to 1000 °C in the absence of air, and a mixture of volatile products called coal tar boils off. Fractional distillation of coal tar yields benzene, toluene, xylene (dimethylbenzene), naphthalene, and other aromatic compounds

- Unlike coal, petroleum contains few aromatic compounds and consists largely of alkanes . During petroleum refining, however, aromatic molecules are formed when alkanes are passed over a catalyst at about 500 °C under high pressure.

- Aromatic substances, more than any other class of organic compounds, have acquired a large number of nonsystematic names. IUPAC rules discourage the use of most such names but do allow for some of the more widely used ones to be retained . Thus, methylbenzene is known commonly as toluene; hydroxybenzene, as phenol; aminobenzene, as aniline; and so on.

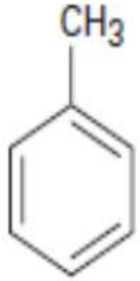
Nomenclature

- Sometimes you will see the greek prefixes ortho-, meta-, and para-used to represent the 1,2 position, 1,3 position, and 1,4 positions on the benzene ring respectively.

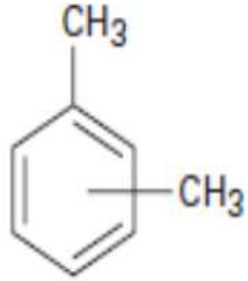




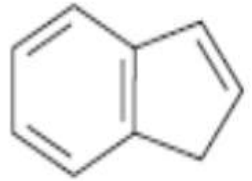
Benzene
(bp 80 °C)



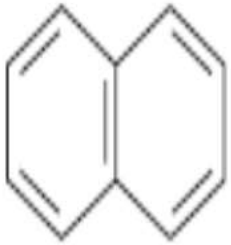
Toluene
(bp 111 °C)



Xylene
(bp: ortho, 144 °C;
meta, 139 °C; para, 138 °C)



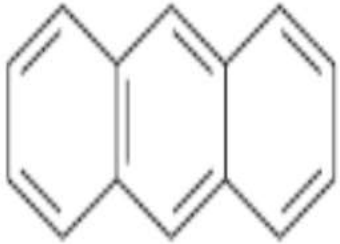
Indene
(bp 182 °C)



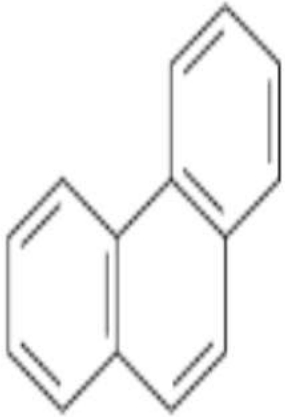
Naphthalene
(mp 80 °C)



Biphenyl
(mp 71 °C)

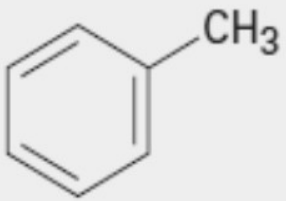
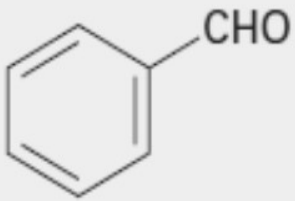
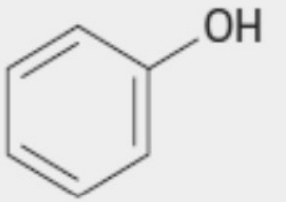
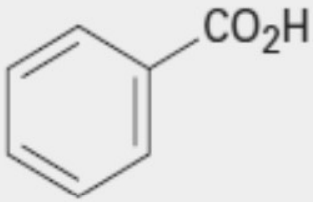
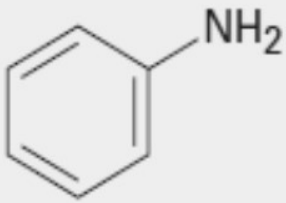
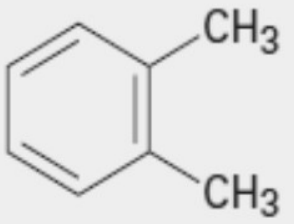
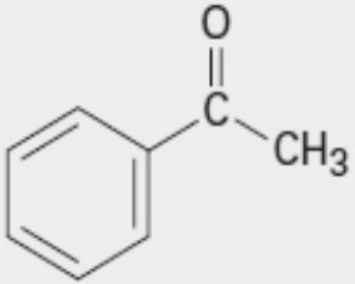
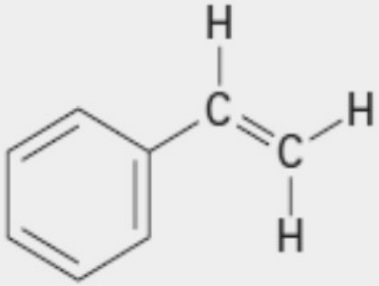


Anthracene
(mp 216 °C)



Phenanthrene
(mp 101 °C)

Table 15.1 Common Names of Some Aromatic Compounds

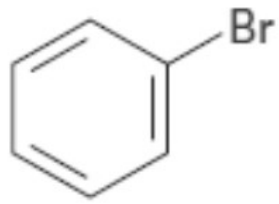
Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		ortho-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

1…Monosubstituted benzenes are named systematically in the same manner as other hydrocarbons, with -benzene as the parent name.

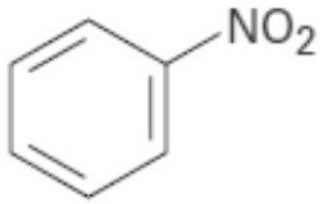
- Thus, C6H5Br is bromobenzene, C6H5NO2 is nitrobenzene, and C6H5CH2CH2CH3 is propylbenzene.

2…Alkyl-substituted benzenes are sometimes referred to as arenes and are named in different ways depending on the size of the alkyl group.

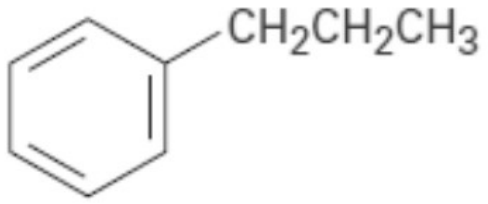
If the alkyl substituent is smaller than the ring (six or fewer carbons),the arene is named as an alkyl-substituted benzene .



Bromobenzene



Nitrobenzene



Propylbenzene

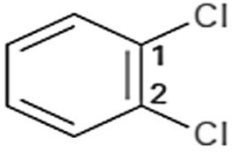
- If the alkyl substituent is larger than the ring

(seven or more carbons), the compound is named as a phenyl-substituted alkane.

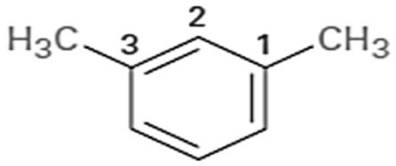
*Phenyl (C6H5)

3…Disubstituted benzenes are named using one of the prefixes ortho (o), meta (m), or para (p). An ortho-disubstituted benzene has its two substituents.

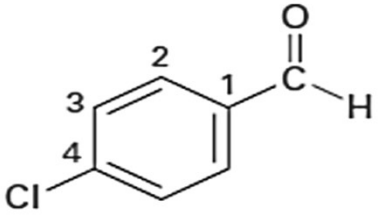
In a 1,2 relationship on the ring, a meta-disubstituted benzene has its two substituents in a 1,3 relationship, and a para-disubstituted benzene has its substituents in a 1,4 relationship.



ortho-Dichlorobenzene
1,2 disubstituted

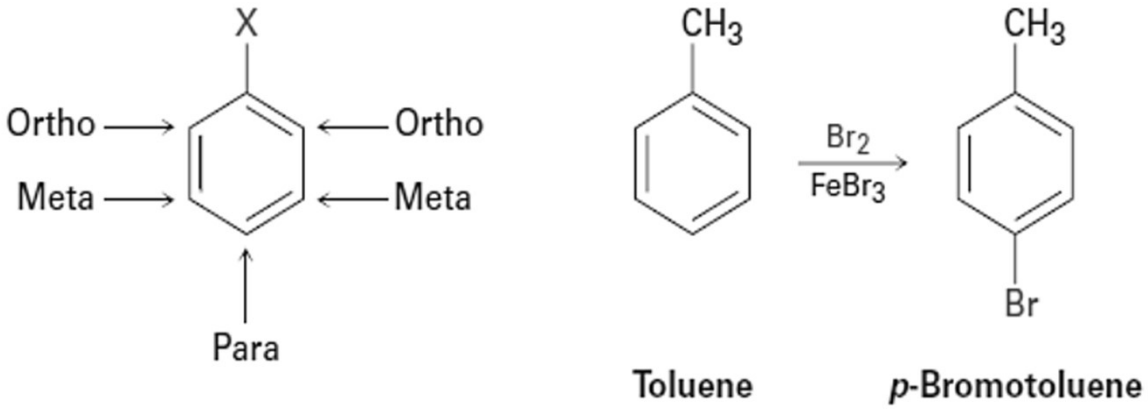


meta-Dimethylbenzene
(*meta*-xylene)
1,3 disubstituted

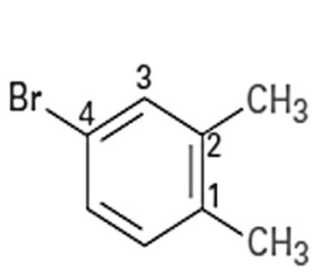


para-Chlorobenzaldehyde
1,4 disubstituted

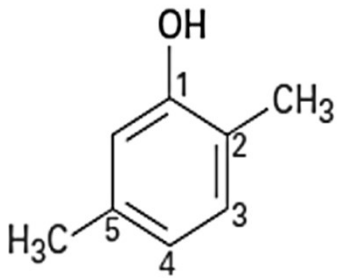
- The ortho, meta, para system of nomenclature is also useful when discussing reactions. For example, we might describe the reaction of bromine with toluene by saying, “Reaction occurs at the para position”—in other words, at the position para to the methyl group already present on the ring.



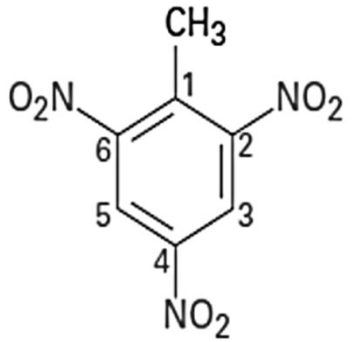
- As with cycloalkanes , benzenes with more than two substituents are named by choosing a point of attachment as carbon 1 and numbering the substituents on the ring so that the second substituent has as low a number as possible. If ambiguity still exists, number so that the third or fourth substituent has as low a number as possible, until a point of difference is found. The substituents are listed alphabetically when writing the name.



4-Bromo-1,2-dimethylbenzene



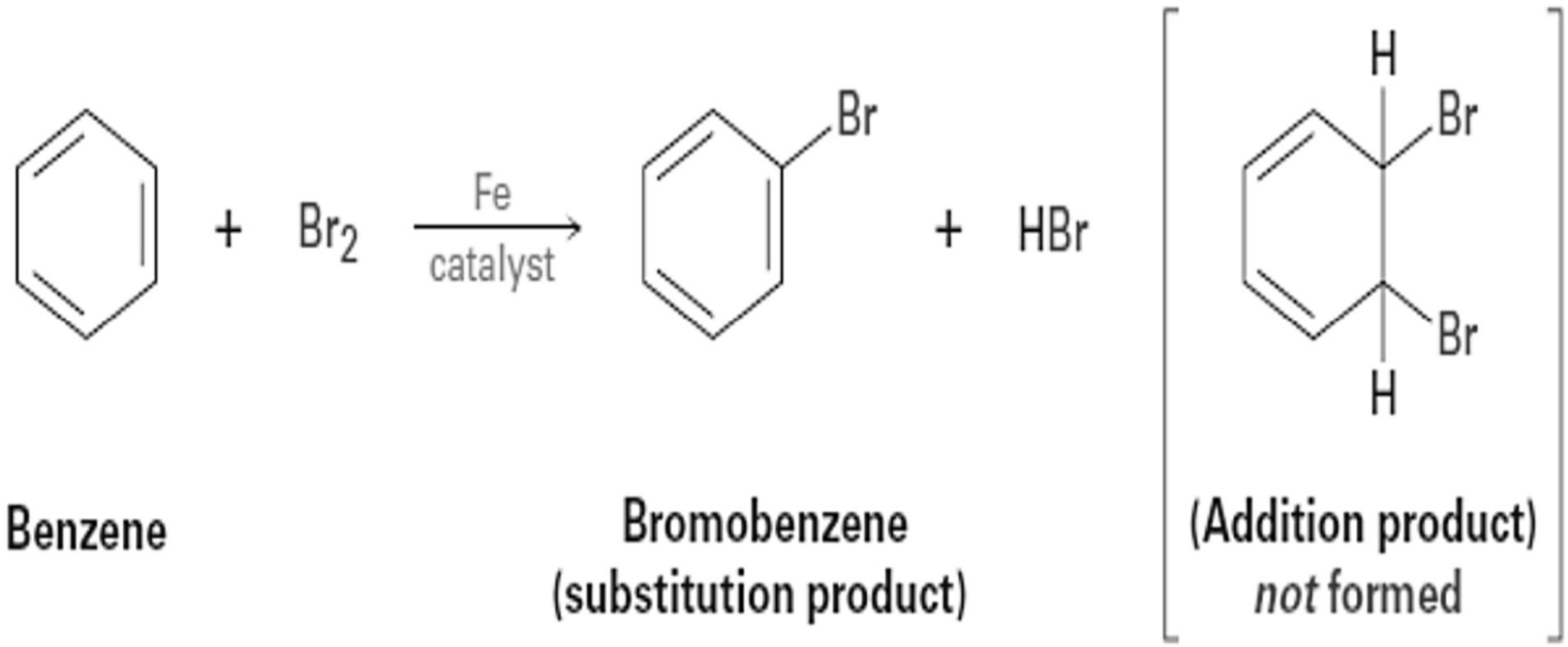
2,5-Dimethylphenol



2,4,6-Trinitrotoluene (TNT)

Structure and Stability of Benzene

- Benzene (C6H6) has six fewer hydrogens than the corresponding six-carbon cycloalkane (C6H12) and is clearly unsaturated, usually being represented as a six membered ring with alternating double and single bonds. Yet it has been known that benzene is much less reactive than typical alkenes and fails to undergo typical alkene addition reactions. Cyclohexene, for instance, reacts rapidly with Br2 and gives the addition product 1,2-dibromocyclohexane, but benzene reacts only slowly with Br2 and gives the substitution product C6H5Br.



Benzene

Bromobenzene
(substitution product)

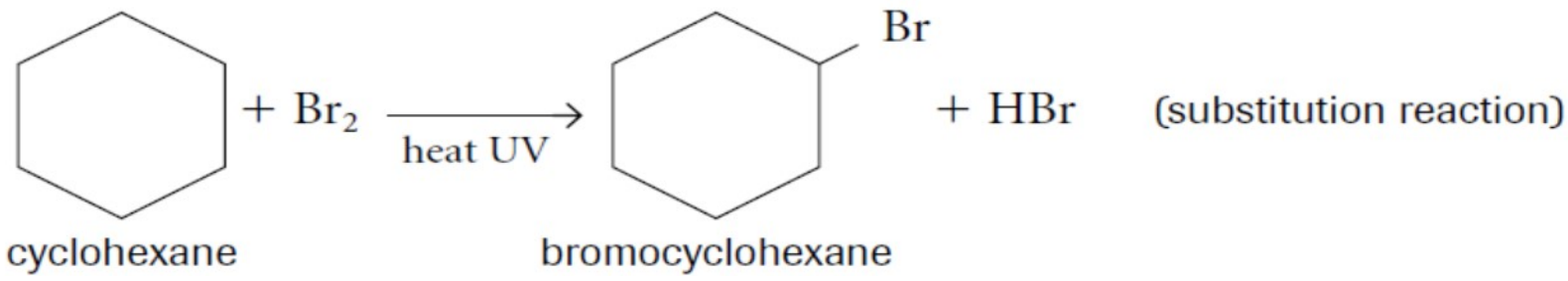
(Addition product)
not formed

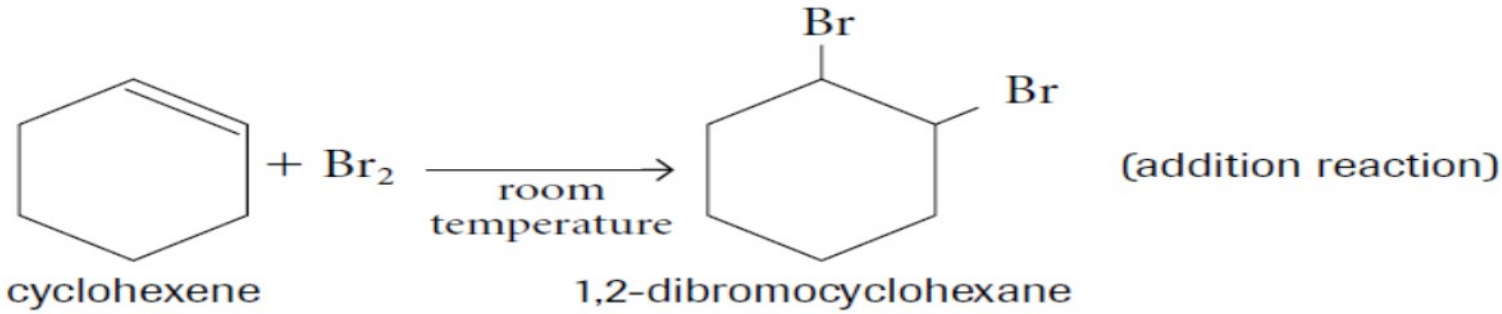
Reactions of Aromatic Compounds

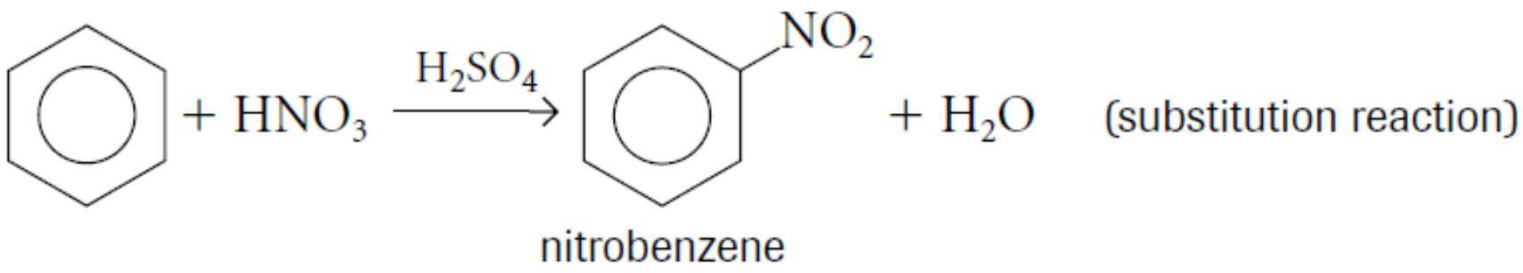
- **Halogenation:**

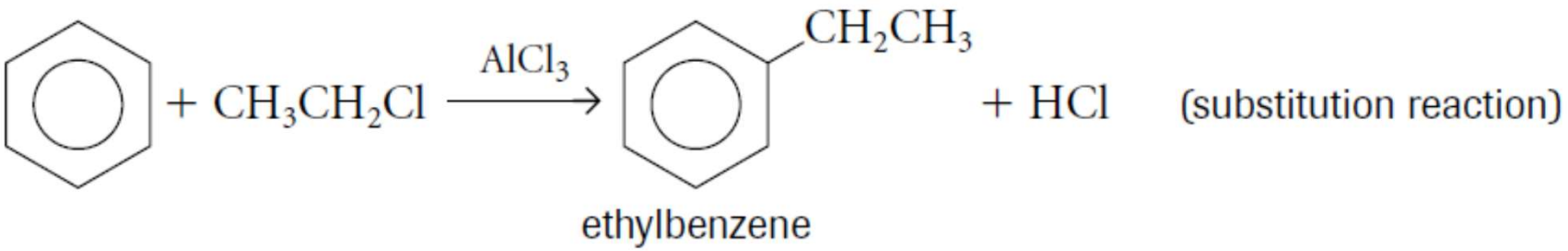
1. Alkanes react with halogens in a substitution reaction
2. Alkenes and alkynes react with halogens in an addition reaction
3. Aromatics also undergo substitution reactions with nitric acid

4. Aromatics undergo substitution reactions with alkyl halides


+ Br_2
heat UV
Br
+ HBr
(substitution reaction)
cyclohexane
bromocyclohexane


+ Br_2
room temperature
Br
Br
(addition reaction)
cyclohexene
1,2-dibromocyclohexane


+ HNO_3
H_2SO_4
NO_2
+ H_2O
(substitution reaction)
nitrobenzene


+ CH_3CH_2Cl
$AlCl_3$
CH_2CH_3
+ HCl
(substitution reaction)
ethylbenzene