الكلية : كلية الطب العام

القسم او الفرع : فرع الكيمياء والكيمياء الحياتية

المرحلة : الاولى

استاذ المادة : م.د.مثال رياض ضبع

اسم المادة باللغة العربية : الكيمياء العضوية

اسم المادة باللغة الانكليزية : **Organic Chemistry**

اسم المحاضرة الرابعة باللغة العربية : الهيدروكاربونات الاروماتية

اسم المحاضرة الرابعة باللغة الانكليزية: **Aromatic Hydrocarbons**

Organic chemistry

Aromatic Hydrocarbons

Dr. Mithal Riyadh AL-Kubais

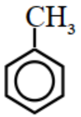
Aromatic Hydrocarbons

We have already studied in hydrocarbon introduction that aromatic hydrocarbons are a special type of hydrocarbons. Most of the aromatic hydrocarbons contain benzene ring. Benzene is a highly unsaturated hydrocarbon but in a majority of reactions, it does not lose its unsaturation.

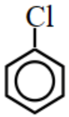
Substituted Benzene

When a hydrogen atom of benzene is replaced by any other atom, then benzene becomes a substituted benzene.

Substituted benzene examples

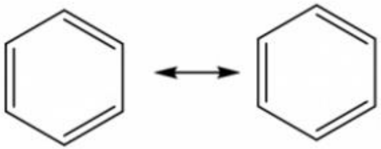


Methoxybenzene
(Toluene)



Chlorobenzene

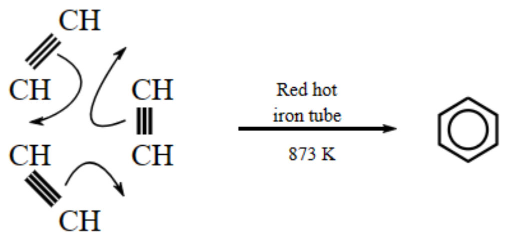
Based upon the number of substituents the benzene is known as monosubstituted (for one), disubstituted (for two), trisubstituted (for three) etc.



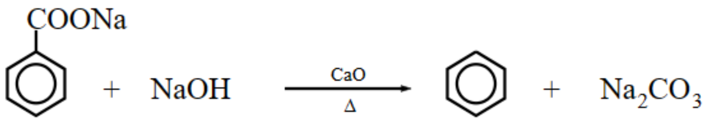
The benzene ring structure is stabilized by resonance. One of the few reactions that benzene rings will undergo are substitution reactions.

Preparation of Benzene

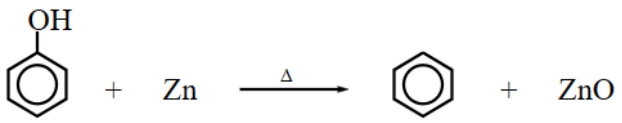
Cyclic Polymerisation of Ethyne : We have already discussed in reactions of alkynes that benzene is prepared by cyclic polymerisation of ethyne. The reaction is given below :



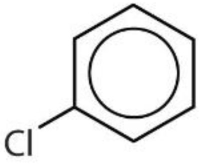
Decarboxylation of Aromatic Acids : Sodium salt of benzoic acid on heating with sodalime gives benzene.



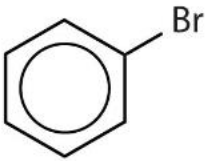
Reduction of Phenol : The vapours of phenols on passing over heated zinc dust are reduced to benzene.



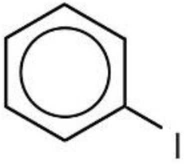
Aromatic Compounds name:



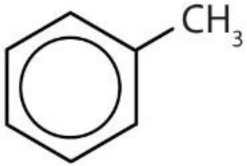
Chlorobenzene



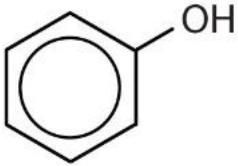
Bromobenzene



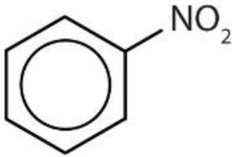
Iodobenzene



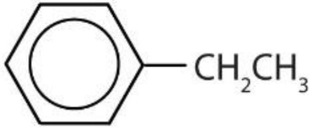
Toluene



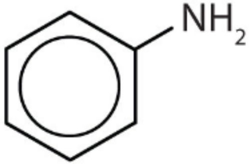
Phenol



Nitrobenzene

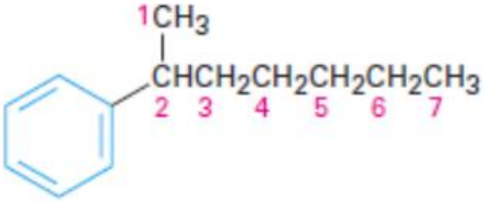


Ethylbenzene

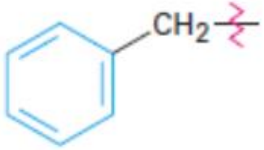


Aniline

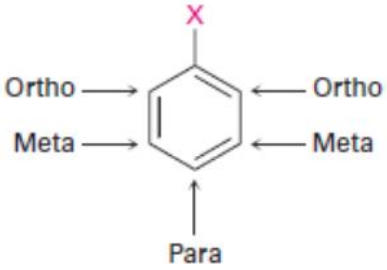
A phenyl group

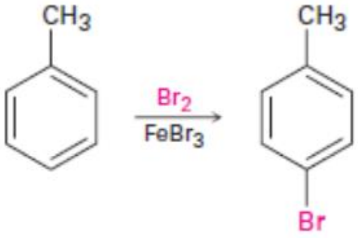


2-Phenylheptane



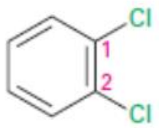
A benzyl group



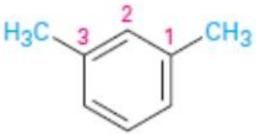


Toluene

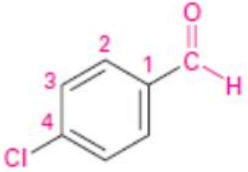
p-Bromotoluene



ortho-Dichlorobenzene
1,2 disubstituted

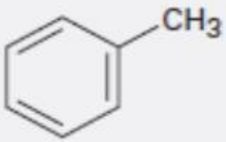
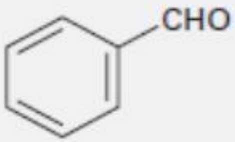
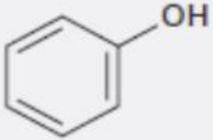
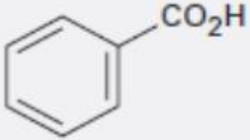
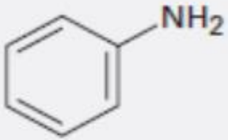
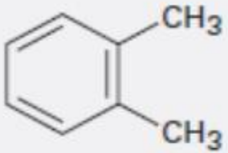
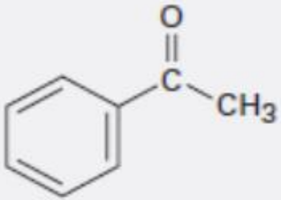
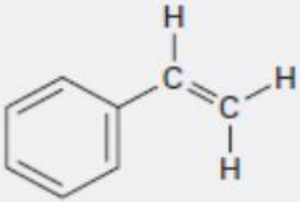


meta-Dimethylbenzene
(*meta*-xylene)
1,3 disubstituted



para-Chlorobenzaldehyde
1,4 disubstituted

Table-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)

Physical Properties of Aromatic Compounds:

Physical State and Odour of Arenes

Arenes up to eight carbon atoms are colourless liquids with characteristic odour. Higher members are solids.

Solubility of Arenes

Arenes are insoluble in water due to the presence of long hydrocarbon part (benzene ring) but fairly soluble in organic solvents.

Melting and Boiling Point of Arenes

The boiling points and melting points of arenes increase with increase in the mass due to the corresponding increase in the magnitude of van der Waal's forces of attraction. However, it may be noted that the melting point of benzene is higher than that of methylbenzene (toluene) because the molecules of benzene are closely packed in the crystal lattice which is not the case in toluene. Among isomeric arenes, p-isomers usually have higher melting point than the corresponding ortho and meta isomers which is again due to the fact that para-isomers being the most symmetrical fit closely in the crystal lattice.

Reactions of Arenes

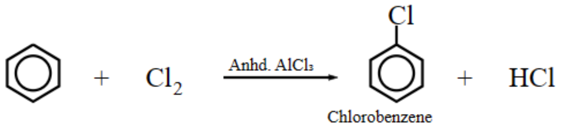
Arenes (aromatic hydrocarbons) usually undergo electrophilic substitution reactions. However, under special conditions they can also undergo addition and oxidation reactions.

Electrophilic Substitution Reactions

Some electrophilic substitution reactions of arenes are given below :

Halogenation

Arenes react with halogens in the presence of a Lewis acid such as anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$ to produce haloarenes.



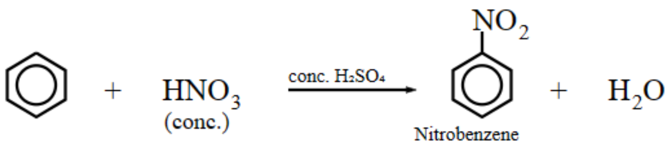
You may be wondering how Cl_2 acts as an electrophile. The reason lies in the following reaction :

Generation of Cl^+ electrophile :

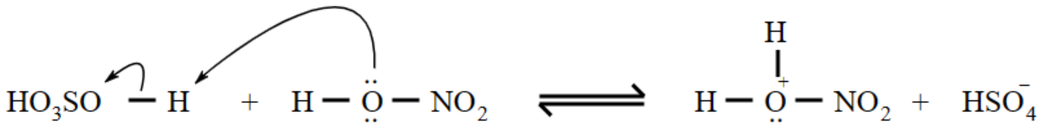
$$Cl-Cl + AlCl_3 \longrightarrow \overset{+}{Cl} + [AlCl_4]^-$$

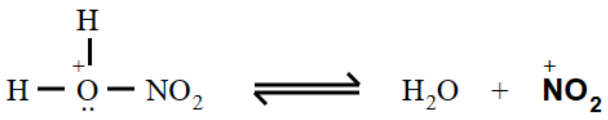
Nitration

Benzene on heating with a mixture of concentrated nitric acid and concentrated sulphuric acid yields **nitrobenzene**.



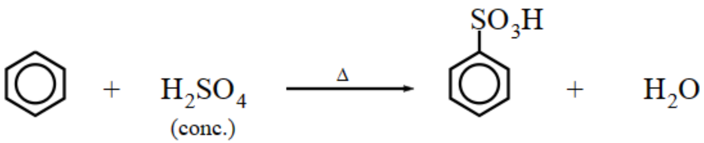
Generation of NO_2^+ electrophile : The following two steps may be followed to generate the NO_2^+ (nitronium ion) electrophile.





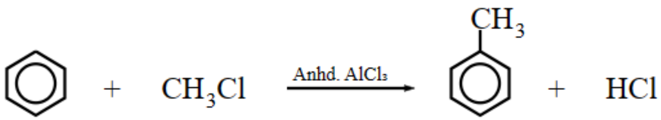
Sulphonation

When benzene is heated with fuming sulphuric acid, benzene sulphonic acid is formed.



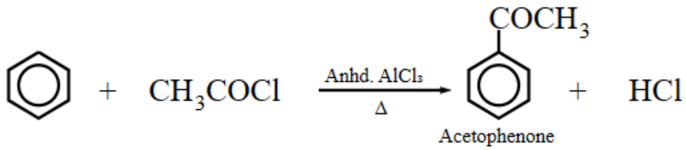
Friedel-Crafts Alkylation

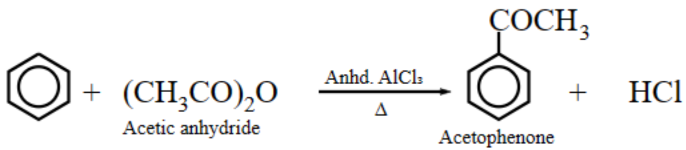
Benzene or its homologues on treatment with an alkyl halide in the presence of anhydrous aluminium chloride forms an alkylbenzene.



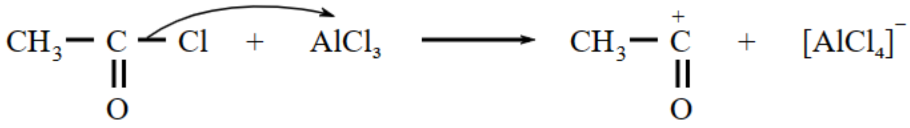
Friedel-Crafts Acylation

The reaction of benzene or its homologues with an acyl halide or acid anhydride in the presence of anhydrous aluminium chloride yields acyl benzene.





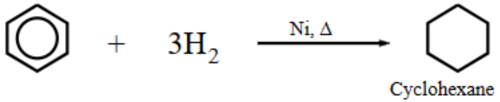
Generation of $CH_3-C^+=O$ electrophile :



Addition Reactions in Arenes

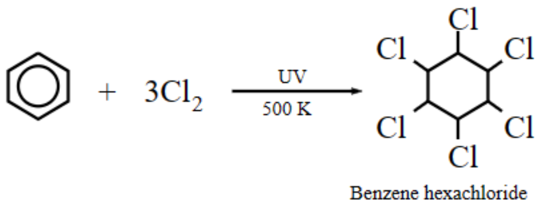
Formation of Cyclohexane

Hydrogenation of benzene at high temperature and/ or pressure in the presence of nickel yields cyclohexane.



Formation of benzene hexachloride (gammaxane)

In the presence of ultra-violet light, three chlorine molecules add to benzene to produce benzene hexachloride ($C_6H_6Cl_6$) or **gammaxane**.



Combustion of Arenes

Arenes easily burn on heating in air or oxygen producing CO_2 and H_2O with **sooty flames**.

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

Aromaticity and the Hückel (4*n* + 2) Rule

Let's list what we've said thus far about benzene and, by extension, about other benzene-like aromatic molecules.

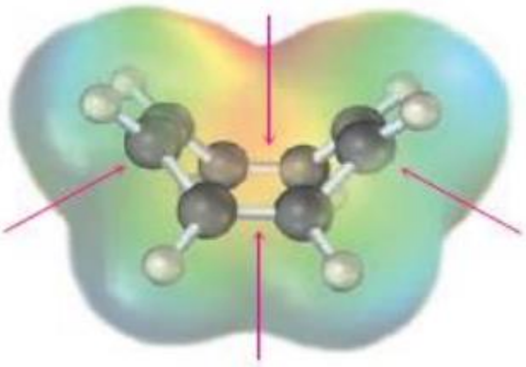
- Benzene is cyclic and conjugated.
- Benzene is unusually stable, having a heat of hydrogenation 150 kJ/mol less negative than we might expect for a conjugated cyclic triene.
- Benzene is planar and has the shape of a regular hexagon. All bond anglesare 120°, all carbon atoms are *sp*2-hybridized, and all carbon–carbon bond lengths are 139 pm.
- Benzene undergoes substitution reactions that retain the cyclic conjugation rather than electrophilic addition reactions that would destroy it.
- Benzene can be described as a resonance hybrid whose structure is intermediate between two line-bond structures.

- **Benzene** has six Π electrons ($4n + 2 = 6$ when $n = 1$) and is aromatic.

Benzene

Three double bonds;
six π electrons

- **Cyclooctatetraene** has eight Π electrons and is not aromatic. The Π electrons are localized into four double bonds rather than delocalized around the ring, and the molecule is tub-shaped rather than planar. It has no cyclic conjugation because neighboring *p* orbitals don't have the necessary parallel alignment for overlap, and it resembles an open-chain polyene in its reactivity.



Cyclooctatetraene

Four double bonds;
eight π electrons