

Aromatic Hydrocarbons Part 1

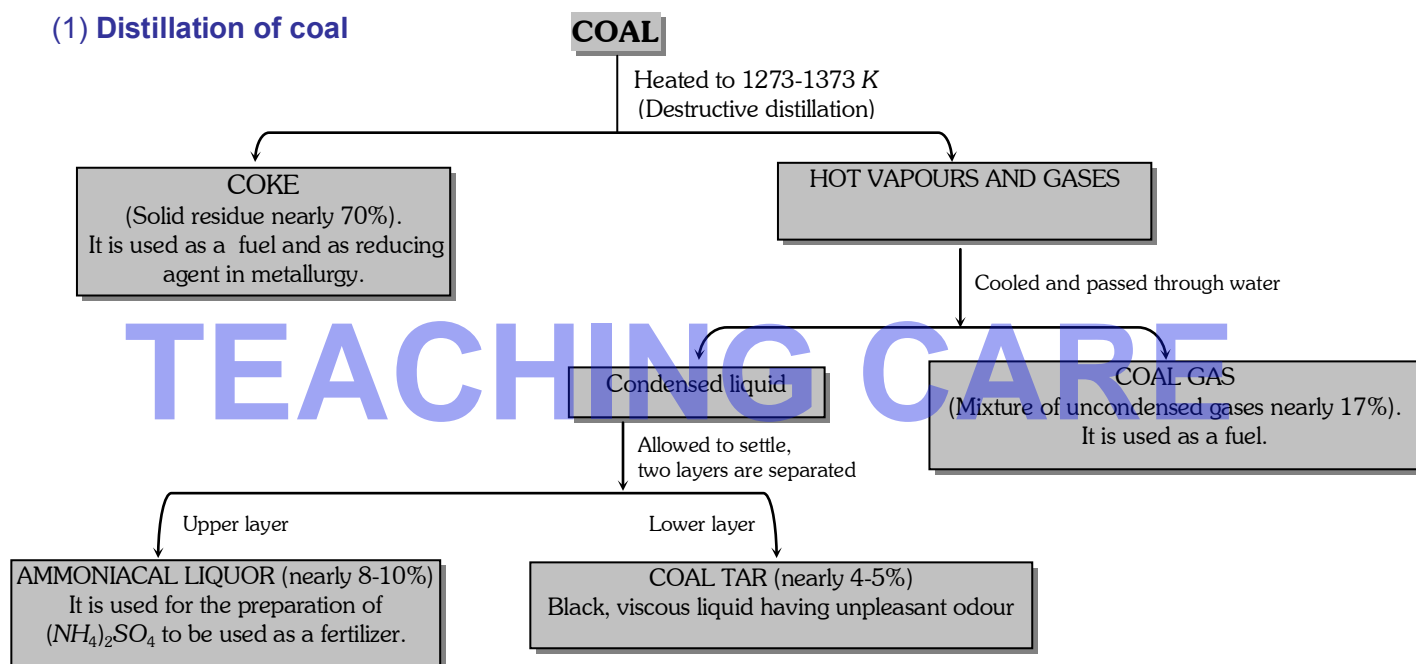
Word aromatic is now reserved for benzene and for the carbocyclic derivatives which resembles with benzene in chemical behaviour. These are also known as benzenoid compounds. All aromatic hydrocarbons (benzene, naphthalene, anthracene etc.) have been given a new name "Arenes".



Source of Arenes.

Source of arenes is coal. It contains benzene, xylene, naphthalene etc. Arenes are obtained by destructive distillation of coal.

(1) Distillation of coal



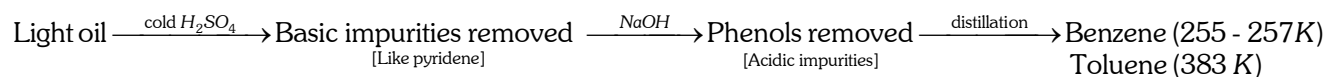
☐ Coal tar is a mixture of large numbers of arenes.

(2) Distillation of coal tar : Arenes are isolated by fractional distillation of coal tar,

Name of the fraction	Temperature range (K)	Main constituents
Light oil (or crude oil) fraction	Upto 443	Benzene, toluene, xylene
Middle oil fraction (Carbolic oil)	443-503	Phenol, naphthalene, pyridine
Heavy oil fraction (Creosote oil)	503-543	Naphthalene, naphthol and cresol
Green oil (Anthracene oil)	543-633	Anthracene, phenanthrene
Pitch (left as residue)	Non-volatile	Carbon

Note : * The residue left after fractional distillation of coal-tar is called pitch.

(3) Isolation of benzene



General characteristics of arenes.

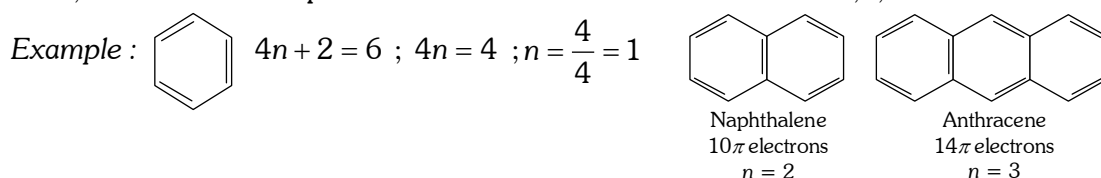
(1) All arenes have general formula $[C_nH_{2n-6y}]$. Where y is number of benzene rings and n is not less than 6.

(2) Arenes are cyclic and planar. They undergo substitution rather than addition reactions.

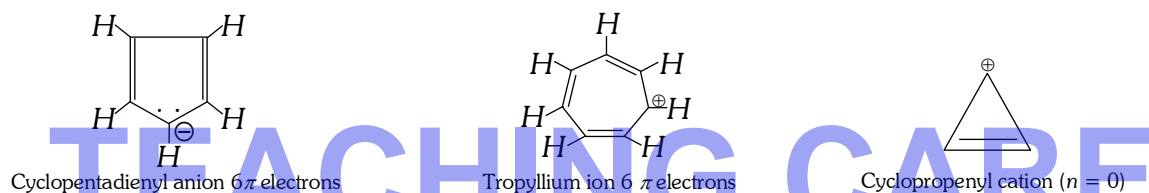
(3) **Aromaticity or aromatic character** : The characteristic behaviour of aromatic compounds is called aromaticity. Aromaticity is due to extensive delocalisation of π -electrons in planar ring system. Huckel (1931) explained aromaticity on the basis of following rule.

Huckel rule : For aromaticity the molecule must be planar, cyclic system having delocalised $(4n + 2)\pi$ electrons where n is an integer equal to 0, 1, 2, 3,-----.

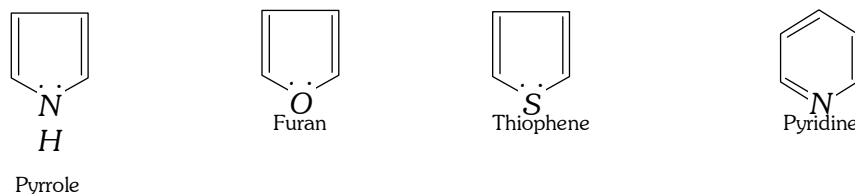
Thus, the aromatic compounds have delocalised electron cloud of 2,6,10 or 14 π electrons.



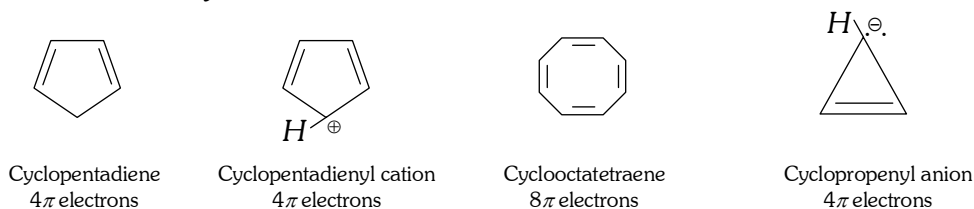
Similarly cyclopentadienyl anion or tropylium ion are also aromatic because of containing 6π electrons ($n=1$).



Heterocyclic compounds also have 6π electrons ($n = 1$).



Molecules do not satisfy huckel rule are not aromatic.



(4) **Antiaromaticity** : Planar cyclic conjugated species, less stable than the corresponding acyclic unsaturated species are called antiaromatic. Molecular orbital calculations have shown that such compounds have $4n\pi$ electrons. In fact such cyclic compounds which have $4n\pi$ electrons are called antiaromatic compounds and this characteristic is called antiaromaticity.

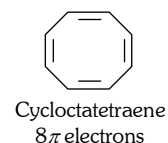
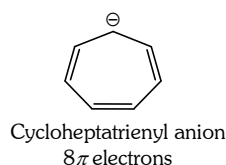
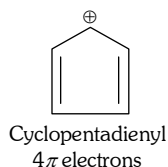
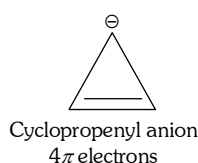
Example : 1,3-Cyclobutadiene, It is extremely unstable antiaromatic compound because it has $4n\pi$ electrons ($n = 1$).



Aromatic Hydrocarbons Part 1

Thus, cyclobutadiene shows two equivalent contributing structures and it has $n = 1$.

In terms of Huckel rule antiaromatic compounds have cyclic, planar structure with $4n\pi$ electrons. They are destabilised by resonance. Some other examples are,



Comparison of aromatic and aliphatic hydrocarbons

Characteristic	Benzene and its homologous	Aliphatic hydrocarbons
Composition	These are closed ring compounds. These are represented by general formula C_nH_{2n-6} .	These are open chain compounds. These are represented by general formulae; C_nH_{2n+2} (Alkanes), C_nH_{2n} (Alkenes) and C_nH_{2n-2} (Alkynes).
Carbon percentage	These contain high percentage of carbon. In benzene C_6H_6 , the carbon percentage is 92.3.	These have low percentage of carbon in comparison to aromatic hydrocarbons. In hexane, C_6H_{14} , the carbon percentage is 83.7.
Combustion	These burn with smoky flame.	These burn with non smoky flame.
Nature	These have high unsaturation. For example, benzene molecule consists three double bonds.	These are saturated as well as unsaturated.
Physical state	These are colourless liquids or solids. They have characteristic odour (Aromatic).	A few lower members are colourless gases while higher members are liquids or solids. Generally no characteristic odour exists.
Addition reactions	Inspite of the fact that these are unsaturated, generally resist addition reactions. These do not react with HCl, HBr, HI or $HClO$.	The unsaturated hydrocarbons show addition reactions.
Substitution reactions	Generally exhibit substitution (Electrophilic) reactions such as halogenation, nitration, sulphonation, Friedel-craft's reaction etc.	The saturated hydrocarbons show substitution reactions such as halogenation. The unsaturated hydrocarbons resist substitution reactions. Nitration and sulphonation occur with difficulty in higher alkanes. Friedel-craft's reaction is not shown by aliphatic hydrocarbons.
Stability	Highly stable.	The unsaturated hydrocarbons are less stable.
$(4n+2)$ rule	Follow $(4n+2)$ rule, i.e., contain $(4n+2)\pi$ electrons where $n = 0, 1, 2, 3, \dots$	$(4n+2)$ rule does not apply to aliphatic unsaturated hydrocarbons.
Oxidation	Except benzene, all oxidise easily.	Alkanes do not oxidise easily while unsaturated hydrocarbons oxidise easily.

Benzene (C₆H₆).

Benzene is the first member of arenes. It was first discovered by Faraday (1825) from whale oil. Mitscherlich (1833) obtained it by distilling benzoic acid with lime. Hofmann (1845) obtained it from coal tar, which is still a commercial source of benzene.

(1) **Structure of benzene** : Benzene has a special structure, which is although unsaturated even then it generally behave as a saturated compound.

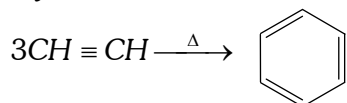
(i) **Kekule's structure** : According to Kekule, in benzene 6-carbon atoms placed at corner of hexagon and bonded with hydrogen and double bond present at alternate position.

(a) *Evidence in favour of Kekule's structure*

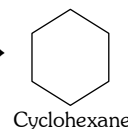
- Benzene combines with 3 molecules of hydrogen or three molecules of chlorine. It also combines with 3 molecules of ozone to form triozone. These reactions confirm the presence of three double bonds.

- Studies on magnetic rotation spectroscopy show the presence of three double bonds.

- The synthesis of benzene from three molecule of acetylene also favour's Kekule's structure.



- Benzene gives cyclohexane by reduction by hydrogen. $C_6H_6 + 3H_2 \xrightarrow{Ni} C_6H_{12}$



(b) *Objections against Kekule's formula*

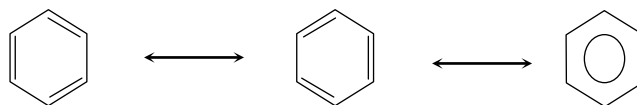
- Unusual stability of benzene.

- According to Kekule, two ortho disubstituted products are possible. But in practice only one ortho disubstituted product is known.

- Heat of hydrogenation of benzene is 49.8 kcal/mole, whereas theoretical value of heat of hydrogenation of benzene is 85.8 kcal/mole. It means resonance energy is 36 kcal/mole.

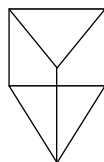
- C – C bond length in benzene are equal, although it contains 3 double bonds and 3 single bonds.

Kekule explained this objection by proposing that double bonds in benzene ring were continuously oscillating between two adjacent positions.

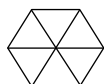


(ii) **Some other structures of benzene**

(a) *Ladenberg's prism formula* : This formula shows benzene three dimensional structure where X-ray studies of benzene molecule indicate a planar.



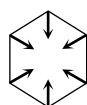
(b) *Claus diagonal formula* :



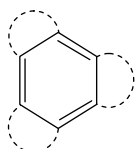
(c) *Dewar's parallel formula* :



(d) *Armstrong and Baeyer's centric formula* :

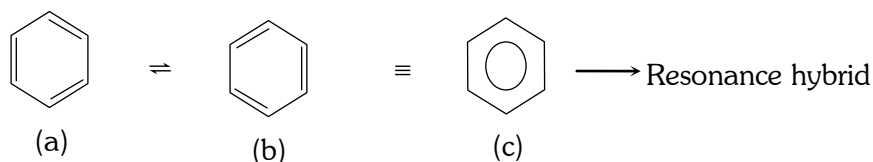


(e) *Thiele's formula* :



(iii) **Valence bond theory** [Resonance theory] : According to this theory, benzene can not be represented by only one structural formula but as a hybrid of structure.

Aromatic Hydrocarbons Part 1

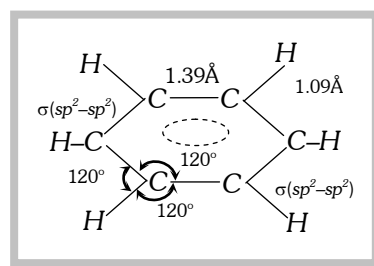


The resonance hybrid structure of benzene explain all the properties of benzene. The resonance structure of benzene is supported by the following facts,

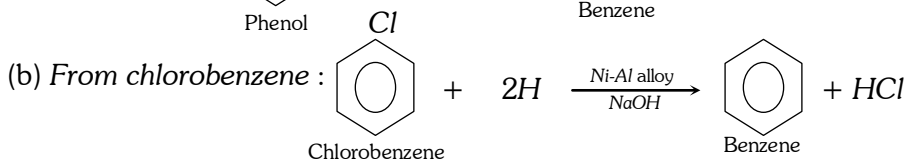
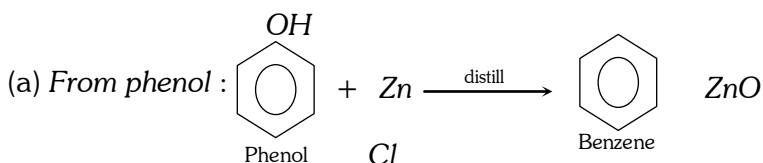
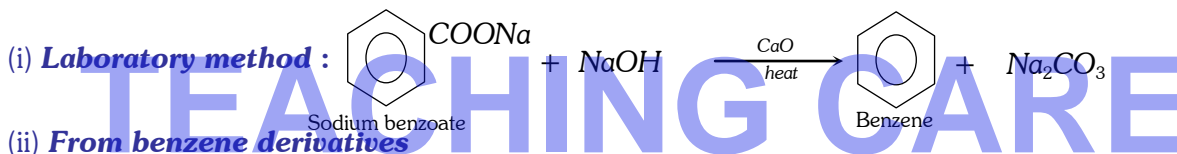
(a) The C – C bond length in benzene is 139 pm which is intermediate between bond lengths for C – C bond (154 pm) and C = C (134 pm).

(b) Due to resonance the π electron charge in benzene get distributed over greater area. As a result of delocalisation the energy of resonance hybrid decrease as compared to contributing structure by about 50 kJ/mole. The decrease in energy is called resonance energy.

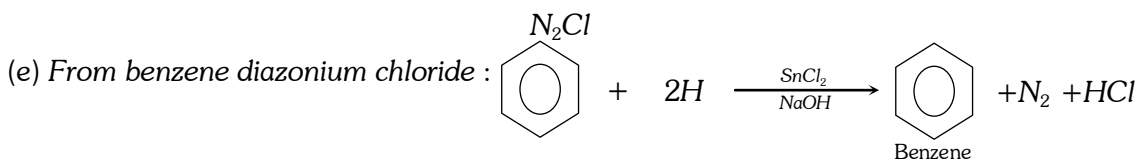
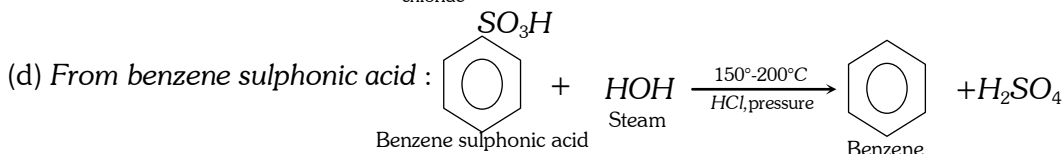
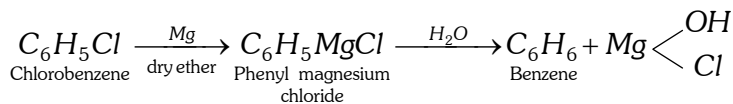
(iv) **M.O.T.** [Modern concept] : According to the orbital concept each carbon atom in benzene is sp^2 hybridised and one orbital remains unhybridised. Out of three hybrid orbitals two overlap with neighbouring carbon atoms and third hybrid orbital overlap with hydrogen atom for σ bonds. Thus benzene has a planar structure with bond angle of 120° each.



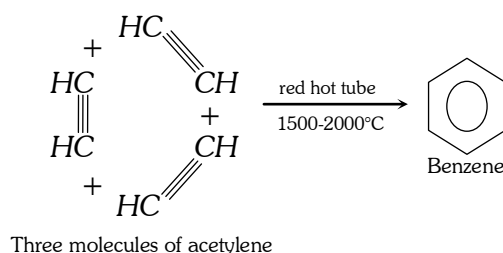
(2) Methods of preparation of benzene



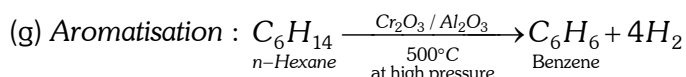
(c) **By preparing grignard reagent of chlorobenzene and then hydrolysed**



(f) From acetylene :



Note : * Cyclic polymerisation takes place in this reaction.



(3) Properties of benzene

(i) Physical properties

(a) Benzene is a colourless, mobile and volatile liquid. Its boiling point is 80°C and freezing point is 5.5°C . It has characteristic odour.

(b) It is highly inflammable and burns with sooty flame.

(c) It is lighter than water. Its specific gravity at 20°C is 0.8788.

(d) It is immiscible with water but miscible with organic solvents such as alcohol and ether.

(e) Benzene itself is a good solvent. Fats, resins, rubber, etc. dissolve in it.

(f) It is a non-polar compound and its dipole moment is zero.

(g) It is an extremely poisonous substance. Inhalation of vapours or absorption through skin has a toxic effect.

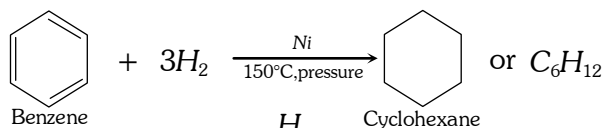
(ii) **Chemical properties :** Due to the presence of π electron clouds above and below the plane benzene ring, the ring serves as a source of electrons and is easily attacked by electrophiles (Electron loving reagents). Hence electrophilic substitution reaction are the characteristic reactions of aromatic compounds.

Substitution reactions in benzene rather than addition are due to the fact that in the former reactions resonance stabilised benzene ring system is retained while the addition reactions lead to the destruction of benzene ring. Principal reactions of benzene can be studied under three heads,

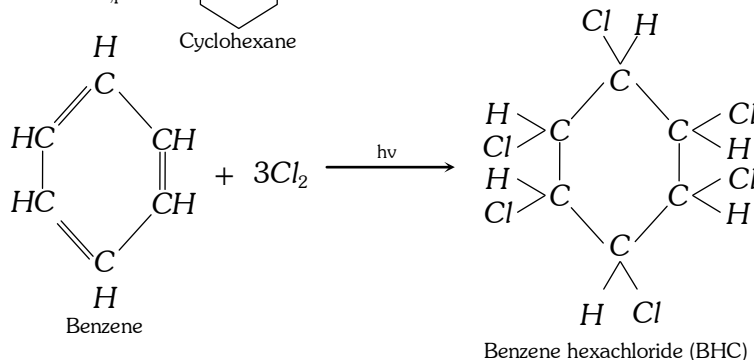
(a) Addition reactions (b) Substitution reactions (c) Oxidation reactions

(a) **Addition reactions :** In which benzene behaves like unsaturated hydrocarbon.

• Addition of hydrogen : Benzene reacts with hydrogen in the presence of nickel (or platinum) catalyst at 150°C under pressure to form cyclohexane.

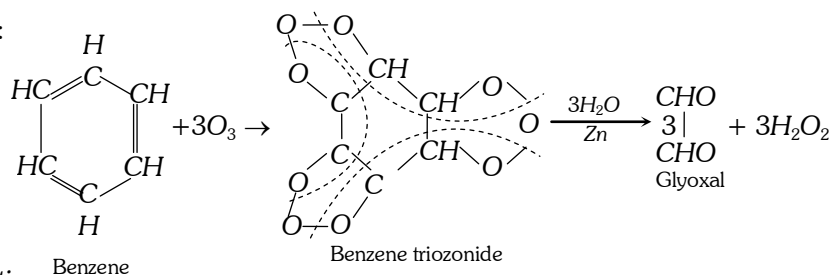


• Addition of halogen :



Aromatic Hydrocarbons Part 1

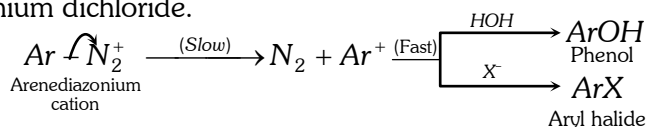
- Addition of ozone :



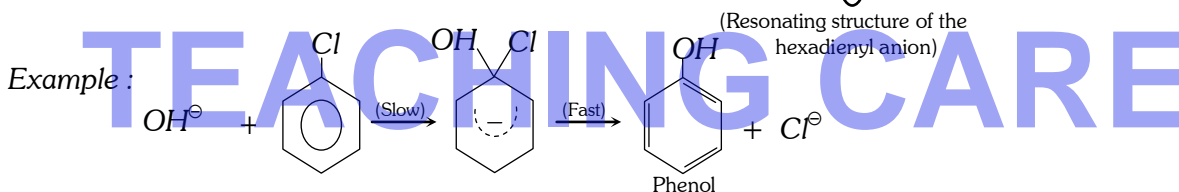
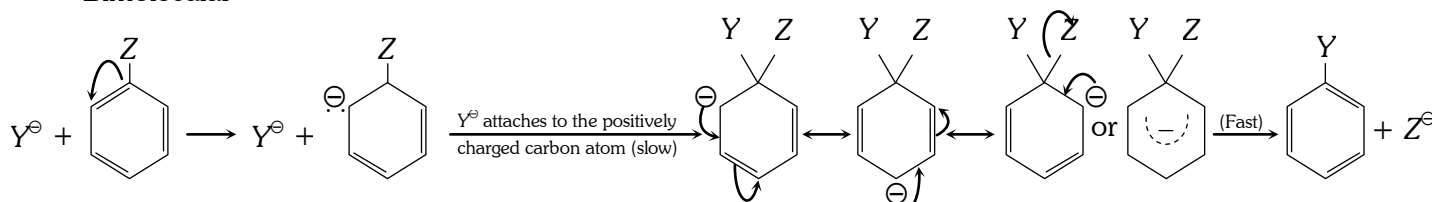
(b) Substitution reactions

- Nucleophilic mechanism

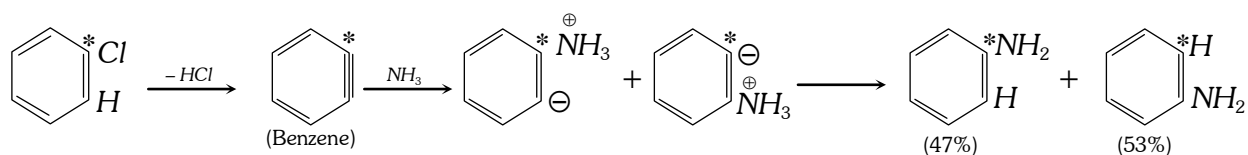
• Unimolecular : Mostly uncommon in aromatic substitution, there is only one example which obtain in benzene diazonium dichloride.



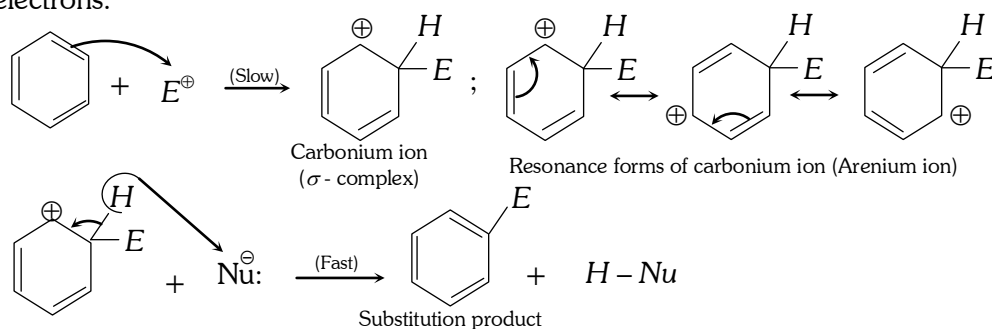
- Bimolecular



- Elimination-addition mechanism (Benzyne mechanism)



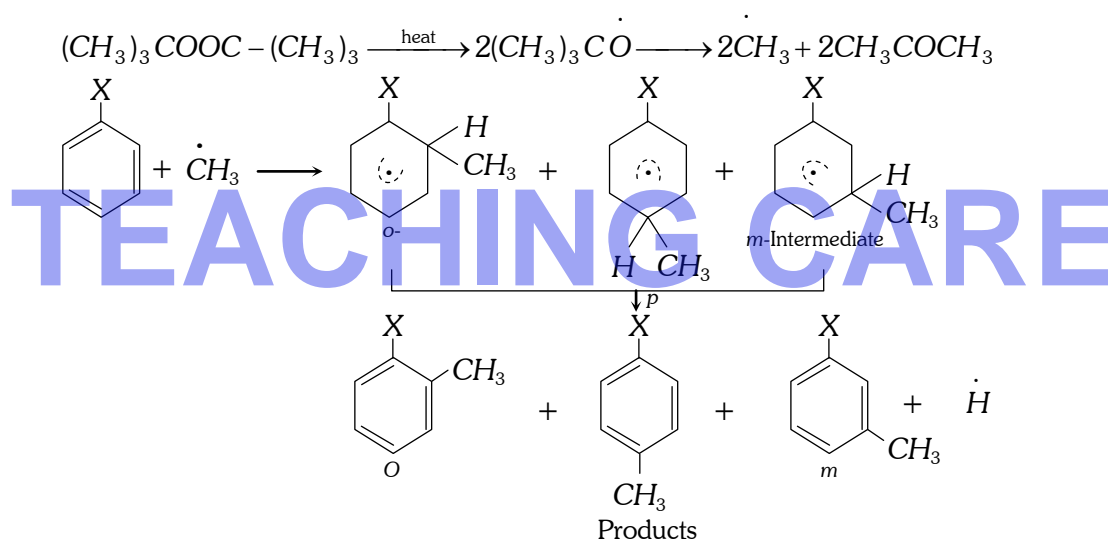
- Electrophilic substitution reaction : Benzene undergoes this reaction because it is an electron rich system due to delocalized π electrons.



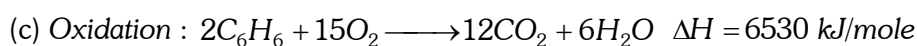
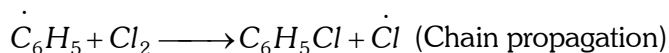
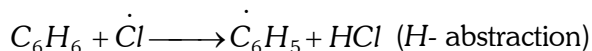
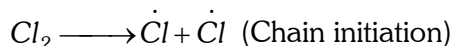
Aromatic Hydrocarbons Part 1

Electrophile (E^{\oplus})	Name	Source	Name of substitution reaction
Cl^+	Chloronium	$Cl_2 + AlCl_3$ or $FeCl_3$	Chlorination
Br^+	Bromonium	$Br_2 + AlBr_3$ or $FeBr_3$	Bromination
NO_2^+	Nitronium	$HNO_3 + H_2SO_4$	Nitration
SO_3	Sulphur trioxide	Conc. H_2SO_4 , Fuming sulphuric acid	Sulphonation
R^+	Alkyl carbonium	$RX + AlX_3$ ($X = Cl$ or Br), $ROH + H^+$	Friedel-Craft's (Alkylation)
$R-\overset{+}{C}=O$	Acyl carbonium	$RCOCl + AlCl_3$	Friedel-Craft's (Acylation)

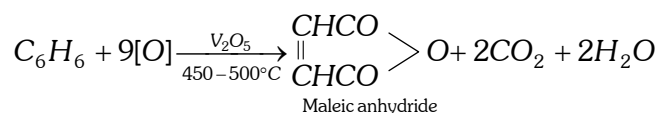
- Free radical aromatic substitution : The aromatic substitution reactions which follow free radical mechanisms are very few and have limited synthetic value. But some typical example of these reactions are:



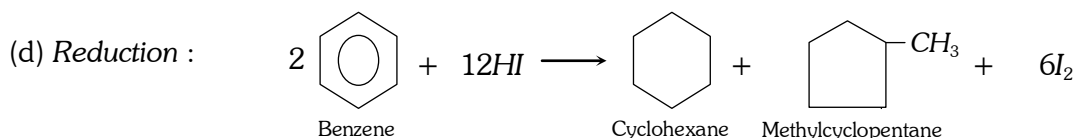
The mechanism of chlorination of benzene at high temperature is similar to that of the free radical aliphatic substitution



When vapours of benzene and air are passed over vanadium pentoxide at 450 – 500°C, maleic anhydride is obtained.



Note : * Strong oxidising agents converts benzene slowly into CO_2 and water on heating.



(iii) **Uses** : (a) In dry cleaning (b) As a motor fuel when mixed with petrol. (c) As a solvent. (d) In the manufacture of gammexane (As insecticide). (e) In the preparation of nitrobenzene, chlorobenzene, benzene sulphonic acid, aniline, styrene, etc. Many of these are employed for making dyes, drugs, plastics, insecticides, etc.

Directive effect in substituted benzene derivatives.

(1) **Directive effect in mono substituted benzene derivatives** : The substituent already present on the benzene ring directs the incoming substituent to occupy ortho (2 or 6), meta (3 or 5) or para (4) position. This direction depends on the nature of the first substituent and is called **directive or the orientation effect**.

The substituent already present can increase or decrease the rate of further substitution, i.e., it either activates or deactivates the benzene ring towards further substitution. These effects are called **activity effects**.

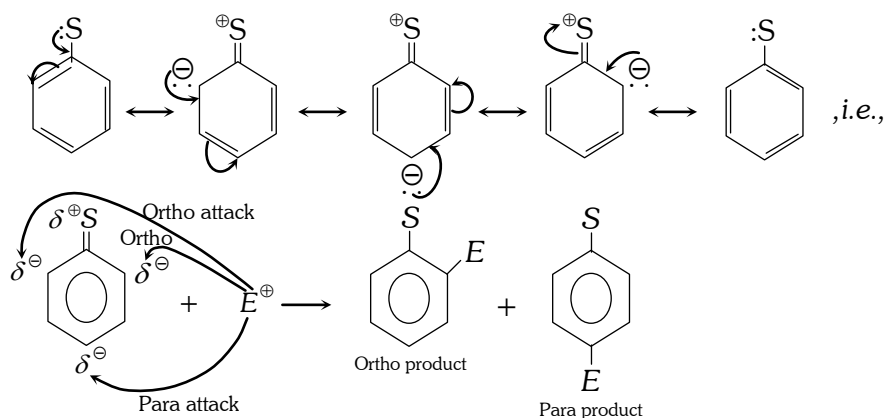
There are two types of substituents which produce directive effect are,

(i) Those which direct the incoming group to ortho- and para-positions simultaneously (Neglecting meta all together).

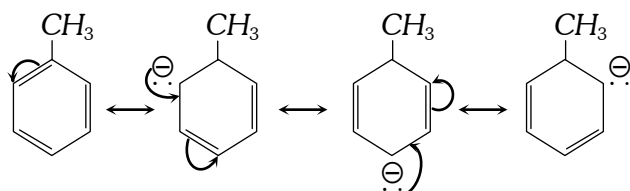
(ii) Those which direct the incoming group to meta-position only (Neglecting ortho- and para-positions all together).

Ortho-para directors	Meta directors
<p>Strongly activating $-\text{NH}_2, -\text{NHR}, -\text{NR}_2, -\text{OH}, -\text{O}^-$</p> <p>Moderately activating $-\text{NHCOCH}_3, -\text{NHCOR}, -\text{OCH}_3, -\text{OR}$</p> <p>Weakly activating $-\text{CH}_3, -\text{C}_2\text{H}_5, -\text{R}, -\text{C}_6\text{H}_5$</p> <p>Weakly deactivating $-\text{F}, -\text{Cl}, -\text{Br}, -\text{I},$</p>	<p>Moderately deactivating $-\text{C}\equiv\text{N}, -\text{SO}_3\text{H}, -\text{COOH}, -\text{COOR}, -\text{CHO}, -\text{COR}$</p> <p>Strongly deactivating $-\text{NO}_2, -\text{NR}_3^+, -\text{CF}_3, -\text{CCl}_3$</p>

Theory of ortho - para directing group



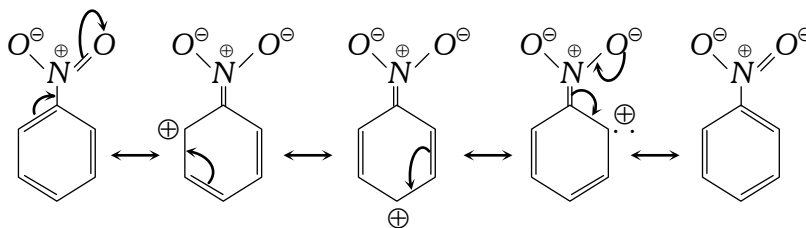
The above mechanism is followed when S is $-\text{OH}, -\text{NH}_2, -\text{Cl}, -\text{Br}, -\text{I}, -\text{OR}, -\text{NR}_2, -\text{NHCOR}$ etc.



In methyl or alkyl group, the $+I$ effect of the methyl group or alkyl group initiates the resonance effect.

Thus, methyl or alkyl group directs all electrophiles to ortho and para positions.

Theory of meta directing group : The substituent, S withdraws electrons from ortho and para positions. Thus, m -position becomes a point of relatively high electron density and further substitution by electrophile occurs at meta position. For example, $-NO_2$ group is a meta directing (Electron withdrawing). Its mechanism can be explained as :



All meta-directing groups have either a partial positive charge or a full positive charge on the atom directly attached to the ring.

TEACHING CARE