

Chemistry

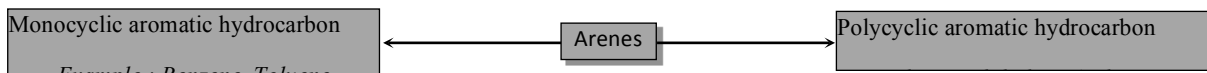
Aromatic Hydrocarbons

Table of Content

- I. Sources of Arenes.
2. General characteristic of arenes.
3. Benzene (C_6H_6).
4. Directive effect in substituted benzene derivatives.
5. Toluene, methyl benzene or phenyl methane.
6. Xylenes (Dimethyl benzene).
7. Ethyl benzene ($C_6H_5C_2H_5$).
8. Styrene ($C_6H_5CH=CH_2$).
9. Bi-phenyl ($C_6H_5 - C_6H_5$).
10. Diphenyl methane.
- II. Polynuclear hydrocarbons.
12. Heterocyclic compounds.

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**".

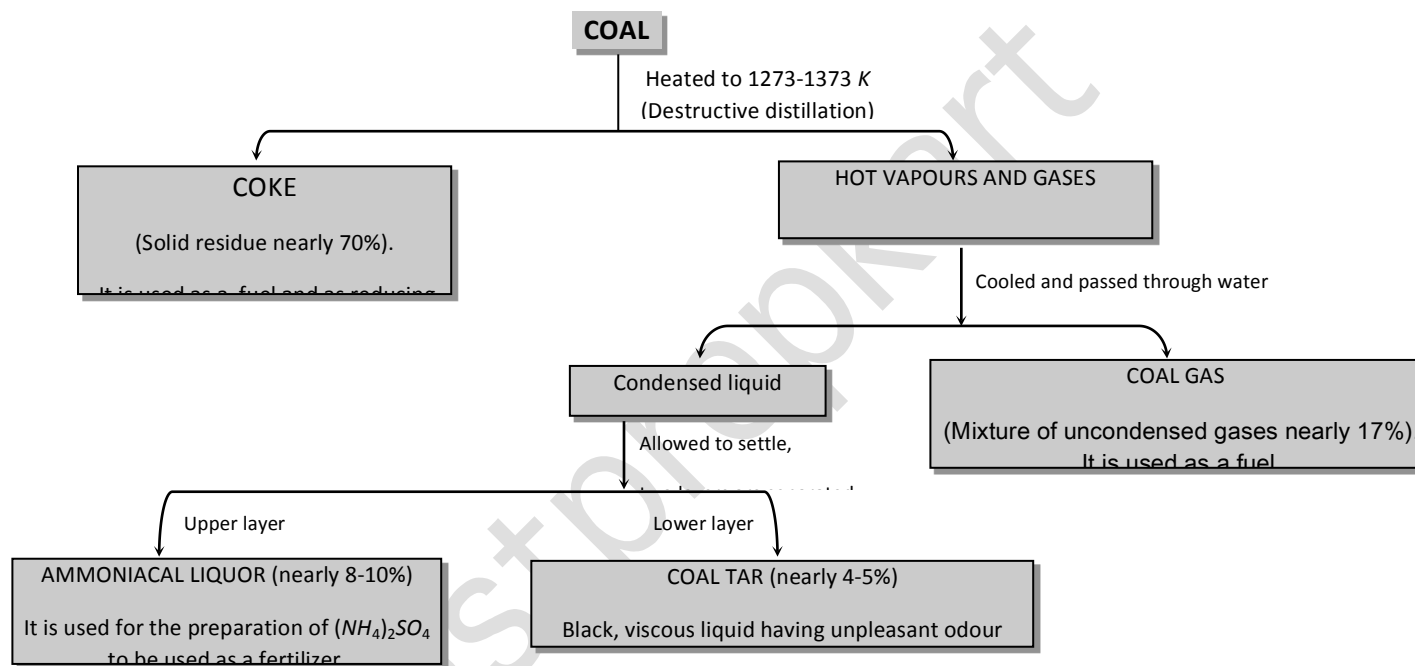




I. Source of Arenes.

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

(1) Distillation of coal



Note: Coal tar is a mixture of large numbers of arenes.

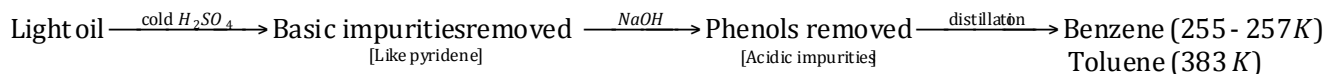
(2) Distillation of coal tar: Arenes are isolated by fractional distillation of coal tar,

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



2. General characteristics of arenes.

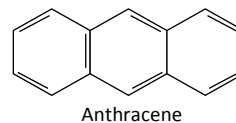
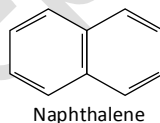
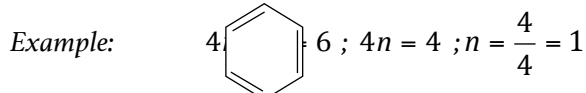
(1) All arenes have general formula $[C_n H_{2n - 6y}]$. Where y is number of benzene rings and n is not less than 6.

(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,-----.

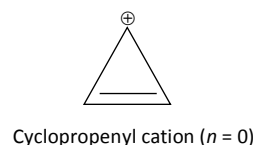
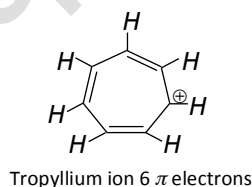
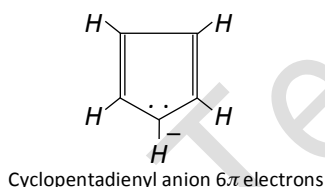
Thus, the aromatic compounds have delocalised electron cloud of 2,6,10 or 14 π electrons.



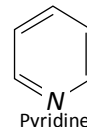
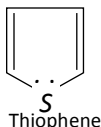
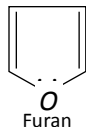
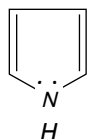
10 π electrons

14 π electrons

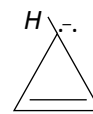
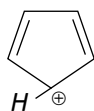
Similarly cyclopentadienyl anion or tropylium ion are also aromatic because of containing 6 π electrons ($n=1$).



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

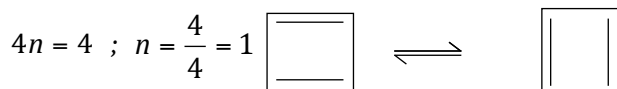


Molecules do not satisfy huckel rule are not aromatic.



(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 ($n = 1$).



Thus, cyclobutanediene 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	In spite 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.

3. Benzene (C_6H_6).

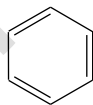
Benzene is the first member of arenes. It was first discovered by Faraday (1825) from whale oil. Mitscherlich (1833) obtained it by distilling benzoic acid with lime. Hofmann (1845) obtained it from coal tar, which is still a commercial source of benzene.

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

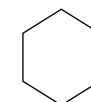
(i) **Kekule's structure:** According to Kekule, in benzene 6-carbon atoms placed at corner of hexagon and bonded with hydrogen and double bond present at alternate position.

(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. $C_6H_6 + 3H_2O \xrightarrow{Ni}$



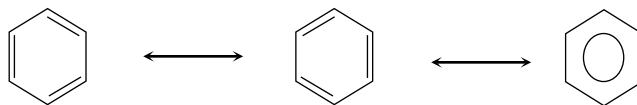
Cyclohexane

(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.

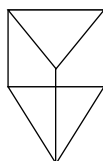


Kekule explained this objection by proposing that double bonds in benzene ring were continuously oscillating between two adjacent positions.

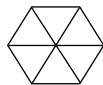


(ii) **Some other structures of benzene**

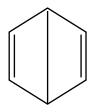
(a) **Ladenberg's prism formula:** This formula shows benzene three dimensional structure where X-ray studies of benzene molecule indicate a planar.



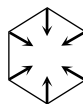
(b) **Claus diagonal formula:**



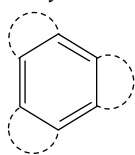
(c) **Dewar's parallel formula:**



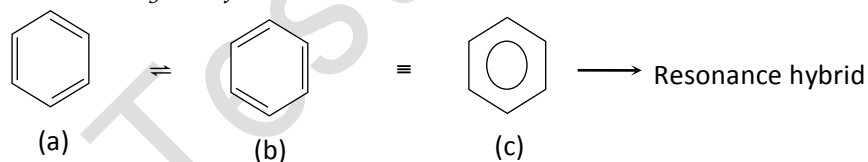
(d) **Armstrong and Baeyer's centric formula:**



(e) **Thiele's formula:**



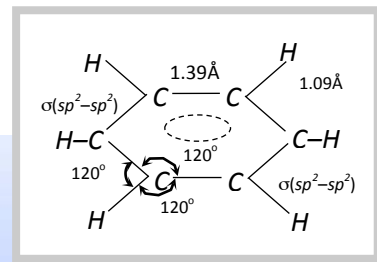
(iii) **Valence bond theory [Resonance theory]:** According to this theory, benzene cannot be represented by only one structural formula but as a hybrid of structure.



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).

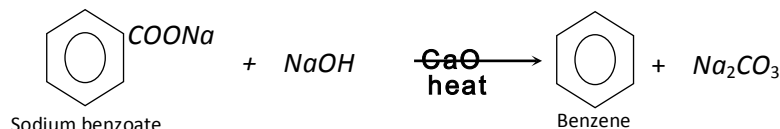
(b) Due to resonance the π electron charge in benzene get distributed over greater area. As a result of delocalisation the energy of resonance hybrid decrease as compared to contributing structure by about 50 kJ/mole. The decrease in energy is called resonance energy.



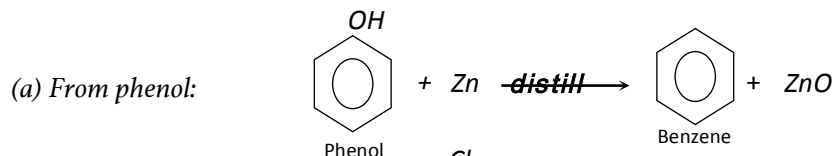
(iv) **M.O.T. [Modern concept]:** According to the orbital concept each carbon atom in benzene is sp^2 hybridised and one orbital remains unhybridised. Out of three hybrid orbitals two overlap with neighbouring carbon atoms and third hybrid orbital overlap with hydrogen atom for σ bonds. Thus benzene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

(2) Methods of preparation of benzene

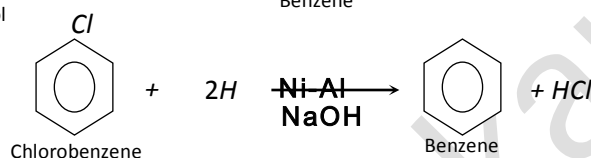
(i) Laboratory method:



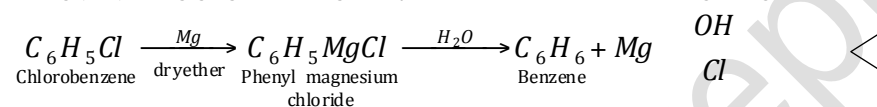
(ii) From benzene derivatives



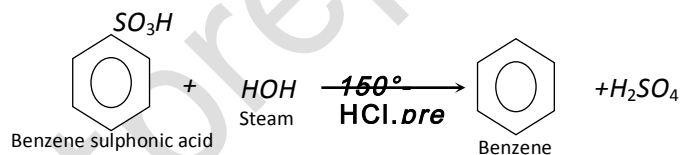
(b) From chlorobenzene:



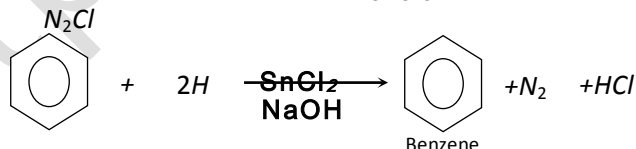
(c) By preparing grignard reagent of chlorobenzene and then hydrolyzed



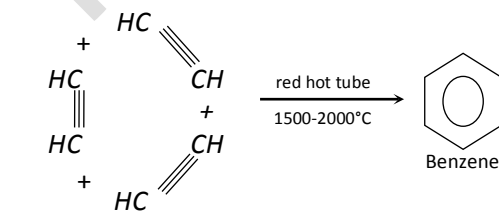
(d) From benzene sulphonic acid :



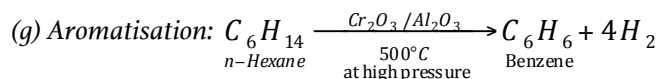
(e) From benzene diazonium chloride :



(f) From acetylene:



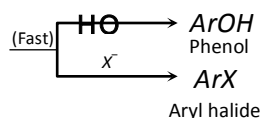
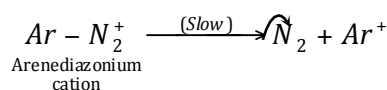
Note: Cyclic polymerization takes place in this reaction.



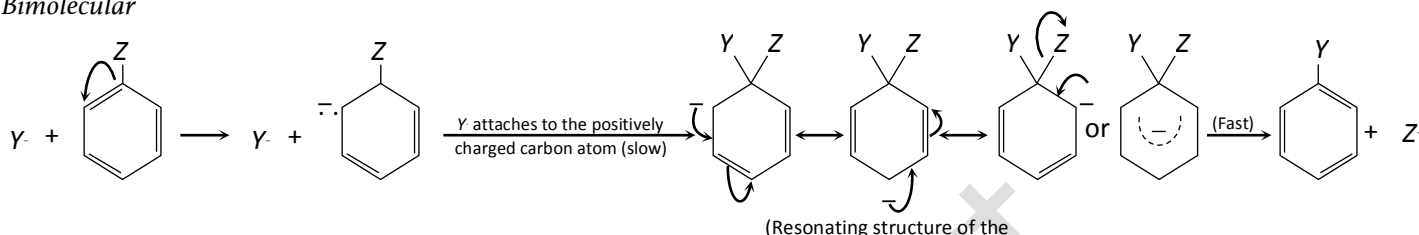
(b) Substitution reactions

• Nucleophilic mechanism

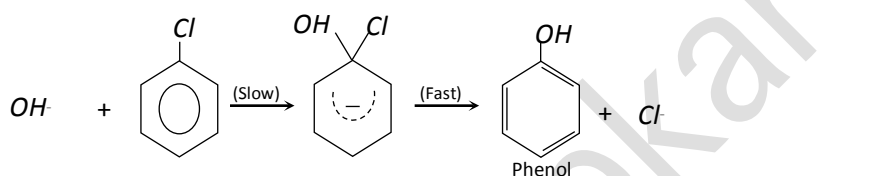
• Unimolecular: Mostly uncommon in aromatic substitution, there is only one example which obtain in benzene diazonium dichloride.



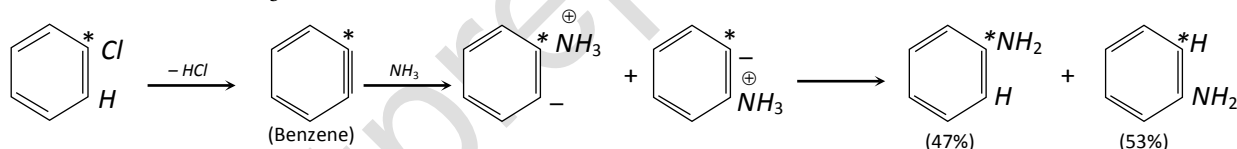
• Bimolecular



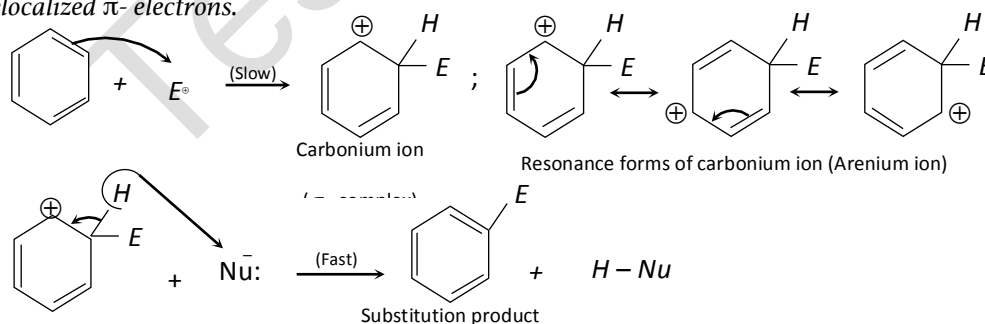
Example:



• Elimination-addition mechanism (Benzyne mechanism)



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

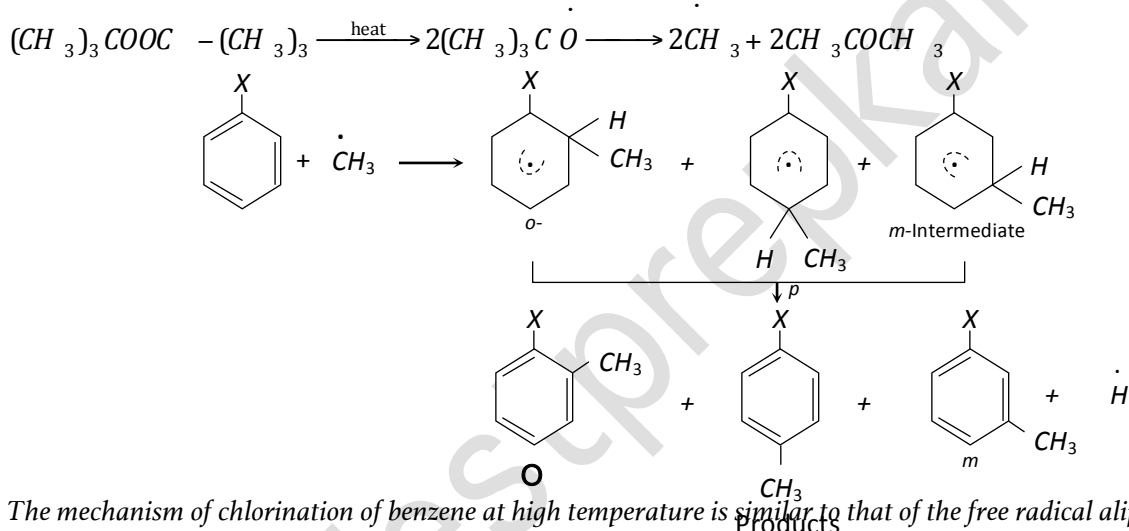


Electrophile (E^+)	Name	Source	Name of substitution reaction
Cl^+	Chloronium	$\text{Cl}_2 + \text{AlCl}_3$ or FeCl_3	Chlorination
Br^+	Bromonium	$\text{Br}_2 + \text{AlBr}_3$ or FeBr_3	Bromination
NO_2^+	Nitronium	$\text{HNO}_3 + \text{H}_2\text{SO}_4$	Nitration

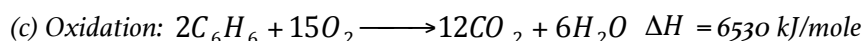
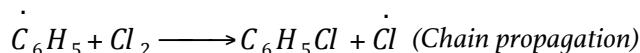
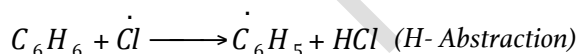
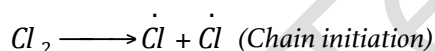


SO_3	Sulphur trioxide	Conc. H_2SO_4 , Fuming sulphuric acid	Sulphonation
R^+	Alkyl carbonium	$RX + AlX_3$ ($X = Cl$ or Br), $ROH + H^+$	Friedel-Craft's (Alkylation)
$R-\overset{+}{C}=O$	Acyl carbonium	$RCOCl + AlCl_3$	Friedel-Craft's (Acylation)

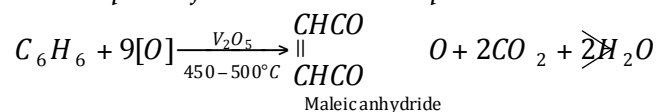
• **Free radical aromatic substitution:** The aromatic substitution reactions which follow free radical mechanisms are very few and have limited synthetic value. But some typical example of these reactions are:



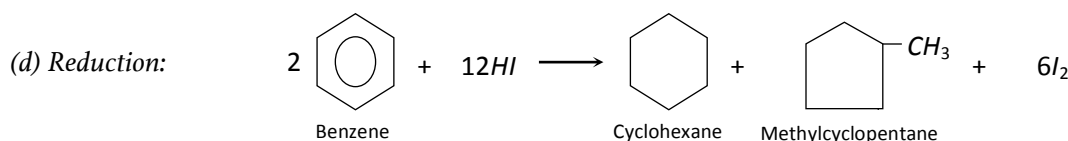
The mechanism of chlorination of benzene at high temperature is similar to that of the free radical aliphatic substitution



When vapours of benzene and air are passed over vanadium pentoxide at $450 - 500^\circ C$, 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.

4. Directive effect in substituted benzene derivatives.

(i) **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**.

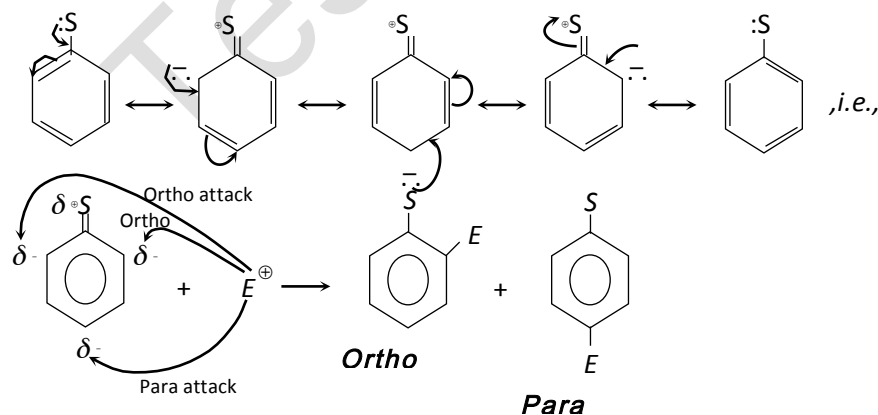
The substituent already present can increase or decrease the rate of further substitution, i.e., it either activates or deactivates the benzene ring towards further substitution. These effects are called **activity effects**.

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

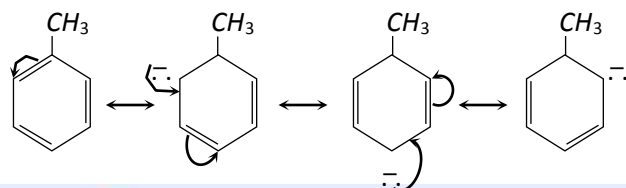
- Those which direct the incoming group to ortho- and para-positions simultaneously (Neglecting meta all together).
- Those which direct the incoming group to meta-position only (Neglecting ortho- and para-positions all together).

Ortho-para directors	Meta directors
Strongly activating $-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{HR}, -\ddot{\text{N}}\text{R}_2, -\ddot{\text{O}}\text{H}, -\ddot{\text{O}}^-$	Moderately deactivating $-\text{C}\equiv\text{N}, -\text{SO}_3\text{H}, -\text{COOH}, -\text{COOR}, -\text{CHO}, -\text{COR}$
Moderately activating $-\ddot{\text{N}}\text{HCOCH}_3, -\ddot{\text{N}}\text{HCOR}, -\ddot{\text{O}}\text{CH}_3, -\ddot{\text{O}}\text{R}$	Strongly deactivating $-\text{NO}_2, -\text{NR}_3^+, -\text{CF}_3, -\text{CCl}_3$
Weakly activating $-\text{CH}_3, -\text{C}_2\text{H}_5, -\text{R}, -\text{C}_6\text{H}_5$	
Weakly deactivating $-\text{F}, -\text{Cl}, -\text{Br}, -\text{I}$	

Theory of ortho – para directing group



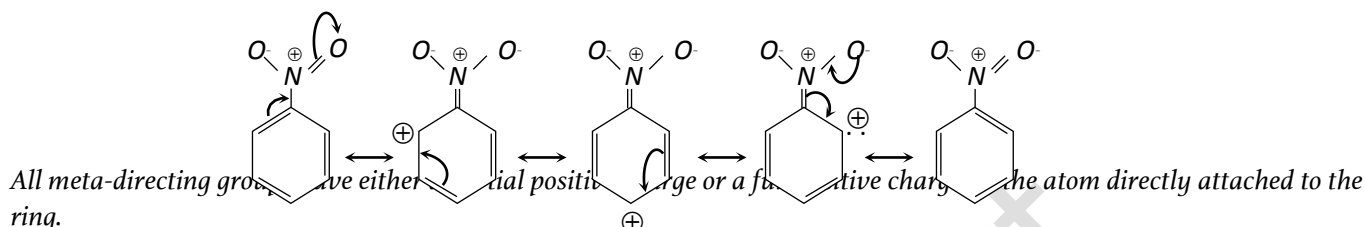
The above mechanism is followed when S is $-\text{OH}, -\text{NH}_2, -\text{Cl}, -\text{Br}, -\text{I}, -\text{OR}, -\text{NR}_2, -\text{NHCOR}$ etc.



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

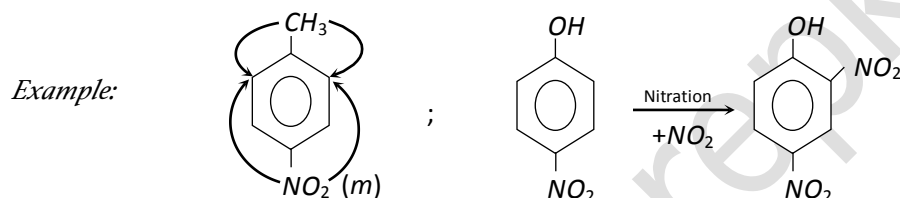
Thus, methyl or alkyl group directs all electrophiles to ortho and para positions.

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, $-\text{NO}_2$ group is a meta directing (Electron withdrawing). Its mechanism can be explained as :



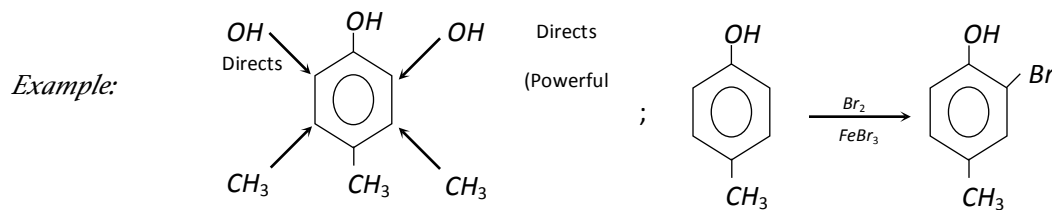
(2) Directive effect in disubstituted benzene

(i) If the directive effects of two substituents reinforce, then a single product is formed.

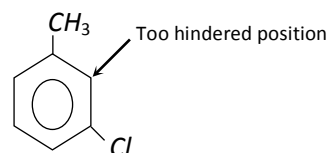


Thus, both $(\text{CH}_3, \text{NO}_2)$ direct further substitution to the same position (Orth).

(ii) If the directing effect of two groups oppose each other strongly activating groups win over deactivating or weakly activating group. The sequence of directing power is



(iii) There is normally little substitution when the two groups are meta to each other. Aromatic rings with three adjacent substituents are generally prepared by same other routes.

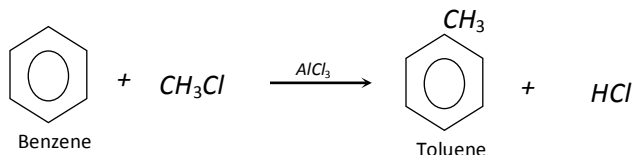


5. Toluene, methyl benzene or phenyl methane.

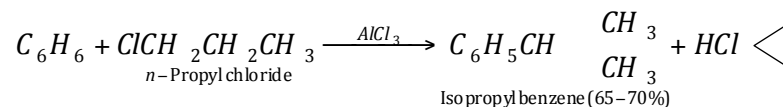
Toluene is the simplest homologue of benzene. It was first obtained by dry distillation of tolu balsam and hence named toluene. It is commercially known as tolual.

(i) Methods of preparation

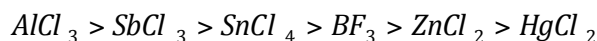
(i) From benzene [Friedel-Craft's reaction] :



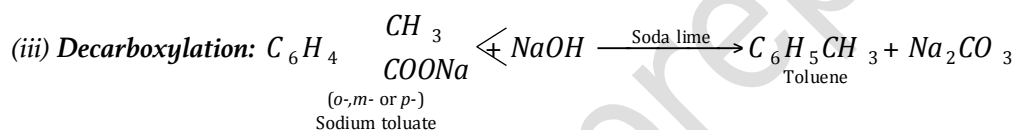
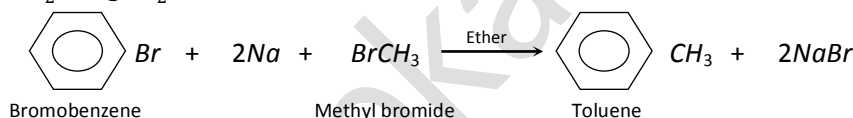
Note: Alkyl halide employed may undergo an isomeric change



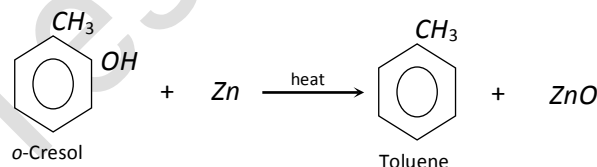
Catalysts can be used in place of anhydrous AlCl₃ are,



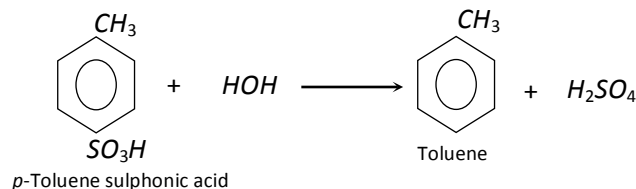
(ii) Wurtz fitting reaction:



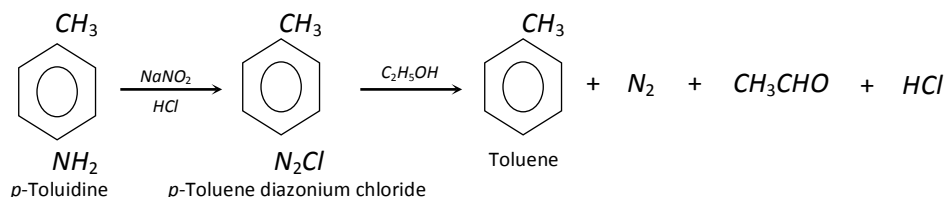
(iv) From cresol:



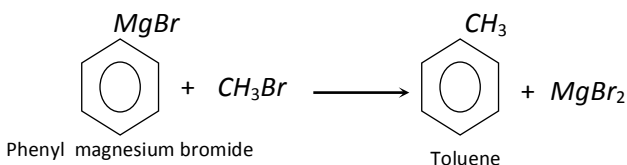
(v) From toluene sulphonic acid:



(vi) From toluidine:



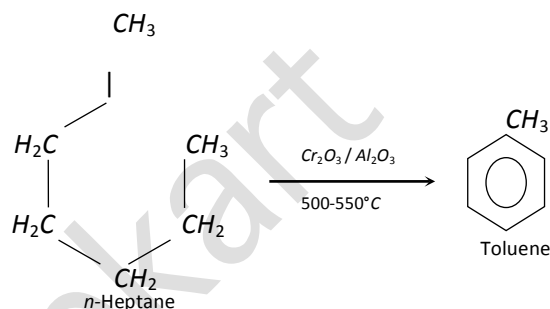
(vii) **From grignard reagent:**



(viii) **Commercial preparation**

From coal tar: The main source of commercial production of toluene is the light oil fraction of coal-tar. The light oil fraction is washed with conc. H_2SO_4 to remove the bases, then with NaOH to remove acidic substances and finally with water. It is subjected to fractional distillation. The vapours collected between $80 - 110^\circ\text{C}$ is 90% benzol which contains 70 – 80% benzene and 14 – 24% toluene. 90% benzol is again distilled and the portion distilling between $108 - 110^\circ\text{C}$ is collected. It is toluene.

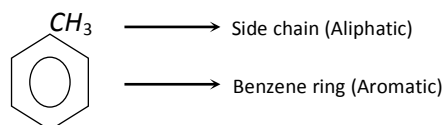
(ix) **From n-heptane and methyl cyclohexane**



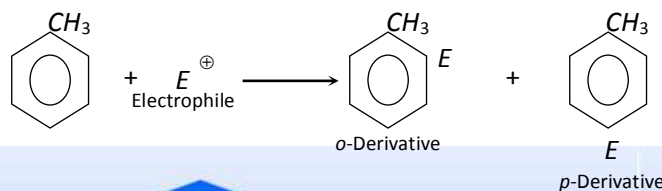
(2) **Physical properties**

- (i) It is a colourless mobile liquid having characteristic aromatic odour.
- (ii) It is lighter than water (sp. gr. 0.867 at 20°C).
- (iii) It is insoluble in water but miscible with alcohol and ether in all proportions.
- (iv) Its vapours are inflammable. It boils at 110°C and freezes at -96°C .
- (v) It is a good solvent for many organic compounds.
- (vi) It is a weak polar compound having dipole moment 0.4D.

(3) **Chemical properties:** Toluene shows the behavior of both

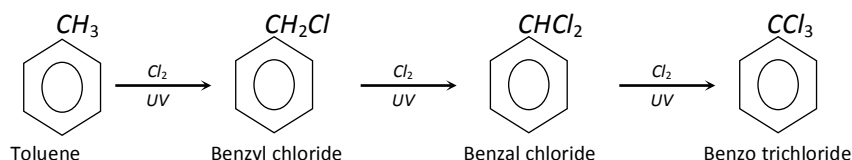


(i) **Electrophilic substitution reactions:** Aromatic character (More reactive than benzene) due to electron releasing nature of methyl group.

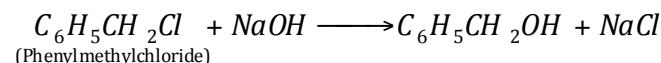


(ii) Reactions of side chain

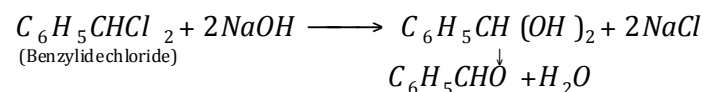
(a) *Side chain halogenation :*



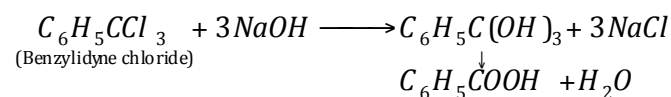
Note: Benzyl chloride on hydrolysis with aqueous caustic soda forms benzyl alcohol.



Benzal chloride on hydrolysis forms benzaldehyde.

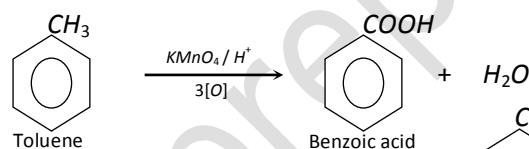


Benzo trichloride on hydrolysis forms benzoic acid.

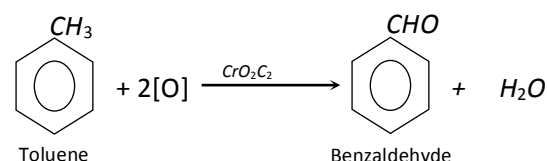


(b) Oxidation:

- *With hot acidic KMnO_4 :*

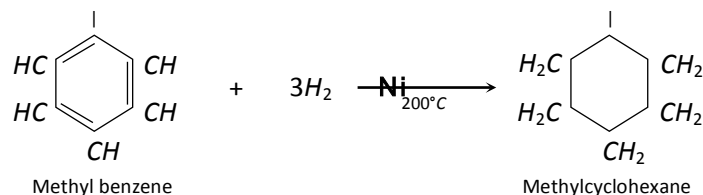
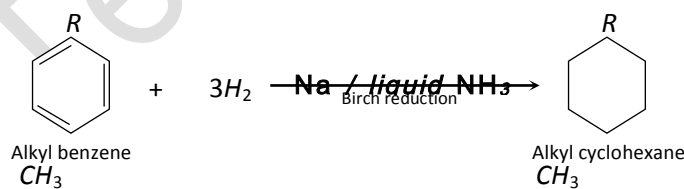


- *With acidic manganese or chromyl chloride (Etards reaction) :*



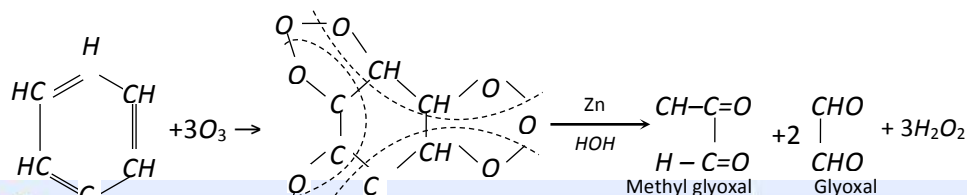
Note: All alkyl benzenes on oxidation with hot acidic KMnO_4 or $\text{Na}_2\text{Cr}_2\text{O}_7$ form benzoic acid. The length of the side chain does not matter.

(c) *Hydrogenation:*



(d) Combustion: $C_6H_5\overset{\text{Methyl benzene}}{CH_3} + 9O_2 \longrightarrow 7CO_2 + 4H_2O$

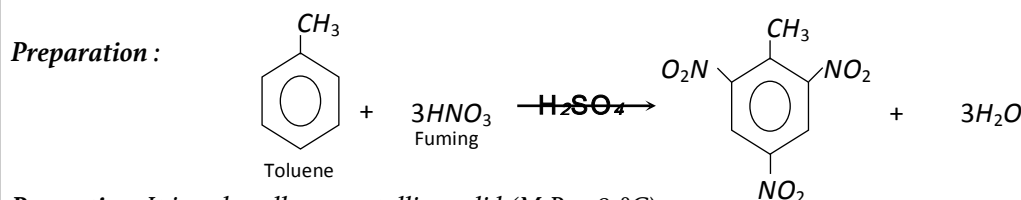
(e) *Ozonolysis:*



(4) Uses

- (i) In the manufacture of benzyl chloride, benzal chloride, benzyl alcohol, benzaldehyde, benzoic acid, saccharin, etc.
- (ii) In the manufacture of trinitrotoluene (TNT), a highly explosive substance.
- (iii) As an industrial solvent and in dry-cleaning.
- (iv) As a petrol substitute.
- (v) In the manufacture of certain dyes and drugs.

T.N.T. (Tri-nitro toluene)

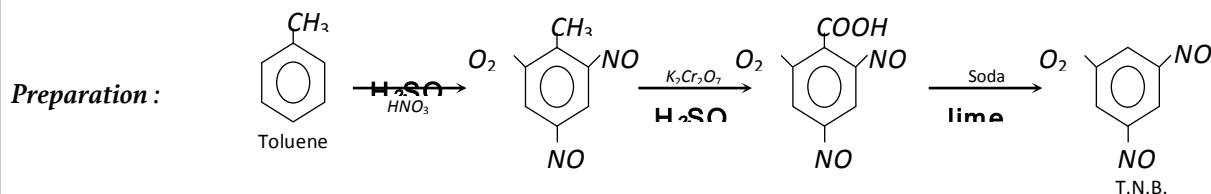


Properties : It is pale yellow crystalline solid (M.P. = 81°C).

Uses : • It is used as an explosive in shells, bombs and torpedoes under the name trotyl.

- When mixed with 80% ammonium nitrate it forms the explosive **amatol**.
- TNT is also used as a mixture of aluminium nitrate, alumina and charcoal under the name **ammonal**.

T.N.B. (Tri-nitro benzene)

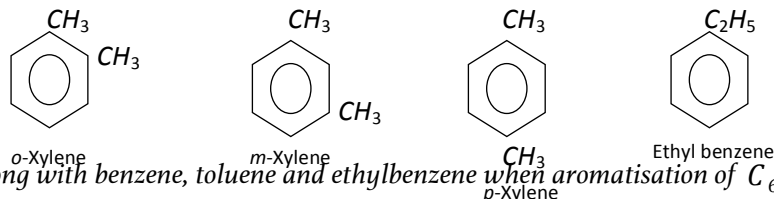


Properties and uses: It is colorless solid (M.P. = 122°C). It is more explosive than T.N.T. and used for making explosive.



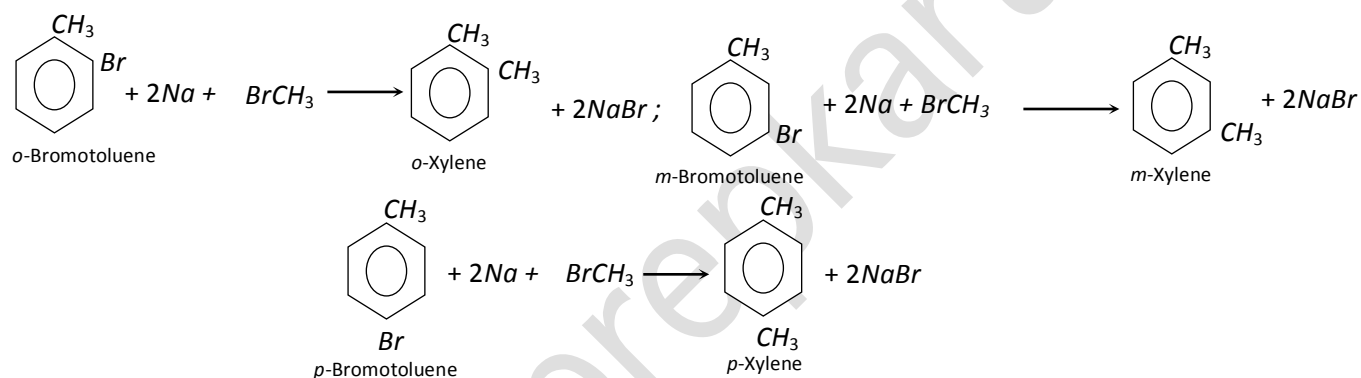
6. Xylenes (Dimethyl benzene) $C_6H_4(CH_3)_2$.

The molecular formula, C_8H_{10} represents four isomers.

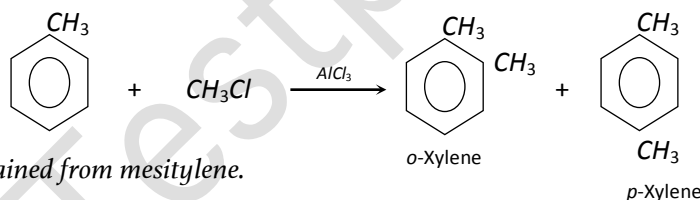


These are produced along with benzene, toluene and ethylbenzene when aromatisation of $C_6 - C_8$ fraction of petroleum naphtha is done. The xylenes are isolated from the resulting mixture (BTX) by fractional distillation.

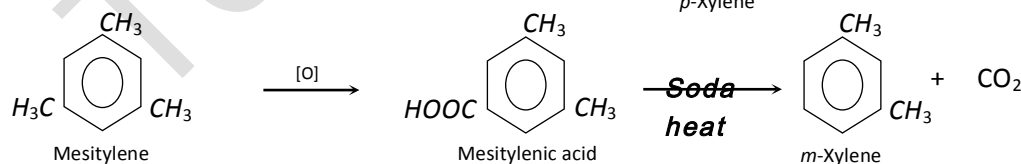
These can be prepared by Wurtz – Fittig reaction. A mixture of bromotoluene and methylbromide is treated with sodium in dry ethereal solution to form the desired xylene.



• These can also be obtained by Friedel – craft's synthesis,



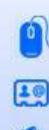
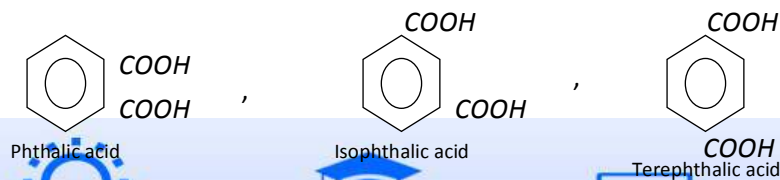
• m-Xylene can be obtained from mesitylene.



Xylenes are colourless liquids having characteristic odour. The boiling points of three isomers are,

o-Xylene = $144^\circ C$; m-Xylene = $139^\circ C$; p-Xylene = $138^\circ C$.

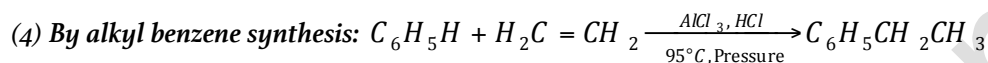
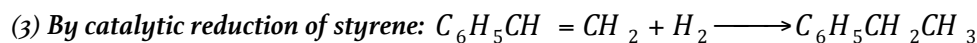
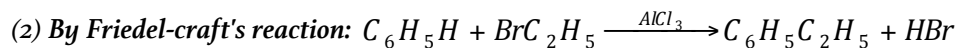
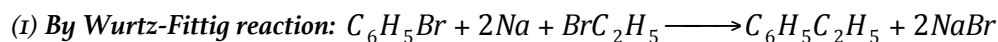
Xylenes undergo electrophilic substitution reactions in the same manner as toluene. Upon oxidation with $KMnO_4$ or $K_2Cr_2O_7$, Xylenes form corresponding dicarboxylic acids.



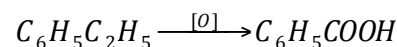
Xylenes are used in the manufacture of lacquers and as solvent for rubber. o-Xylene is used for the manufacture of phthalic anhydride.

7. Ethyl benzene ($C_6H_5C_2H_5$).

It can be prepared by the following reactions,



It undergoes electrophilic substitution reactions in the same way as toluene. When oxidised with dil. HNO_3 or alkaline $KMnO_4$ or chromic acid it forms benzoic acid.

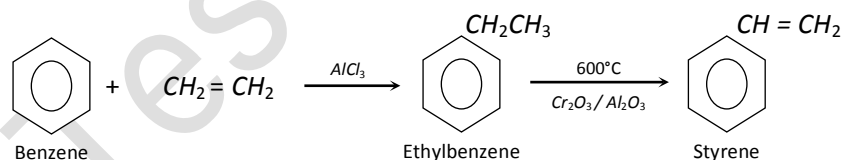


8. Styrene ($C_6H_5CH=CH_2$).

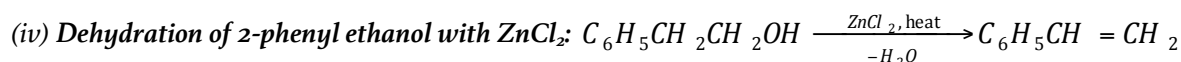
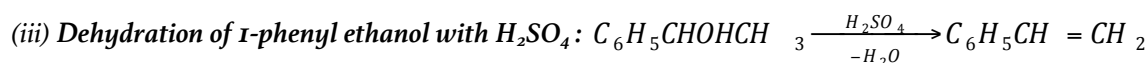
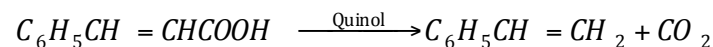
It is present in storax balsam and in coal-tar traces.

(i) Preparation

(i) **Dehydrogenation of side chain of ethylbenzene:** Dehydrogenation of side chain is affected by heating ethylbenzene to high temperature in presence of a catalyst.

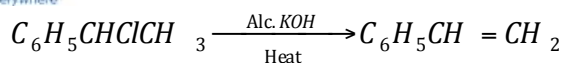


(ii) **Decarboxylation of cinnamic acid:** This is the laboratory preparation. It involves heating of cinnamic acid with a small amount of quinol.



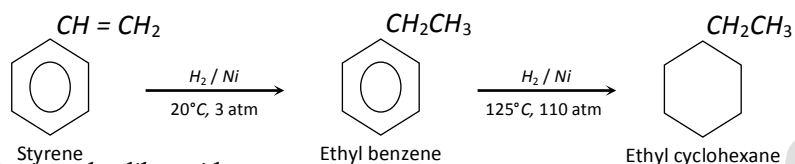
(v) **Dehydrohalogenation of 1-phenyl-1-chloro ethane:** On heating with alcoholic potassium hydroxide, a molecule of hydrogen chloride is eliminated by the chloroderivative.



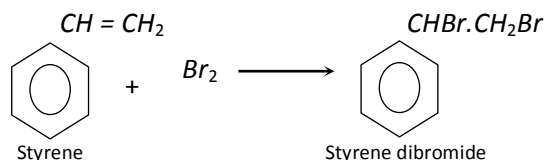


(2) **Properties:** It is a colorless liquid, boiling point 145°C. On keeping, it gradually changes into a solid polymer called metastyrene. The polymerization is rapid in sunlight or when treated with sodium. It shows properties of benzene ring (Electrophilic substitution) and unsaturated side chain (Electrophilic addition). However, the side chain double bond is more susceptible to electrophilic attack as compared to benzene ring.

At lower temperature and pressure, it reacts with hydrogen to produce ethylbenzene and at higher temperature and pressure, it is converted into ethyl cyclohexane.

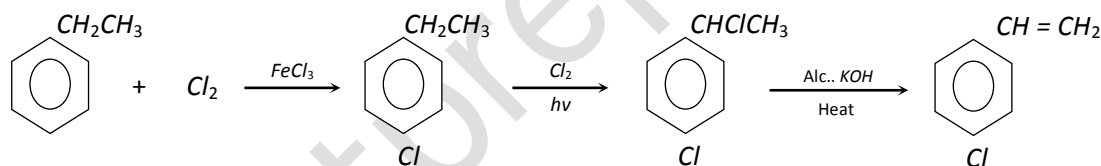


With bromine, it gives the dibromide.

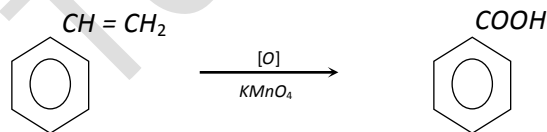


Halogen acids add to the side chain. $C_6H_5CH=CH_2 + HX \longrightarrow C_6H_5CHXCH_3$

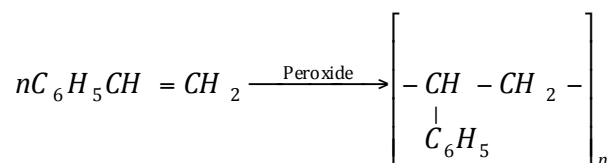
Preparation of ring substituted styrenes is not done by direct halogenation but through indirect route.



When oxidised under drastic conditions, the side chain is completely oxidised to a carboxyl group.



In presence of peroxides, styrene undergoes free radical polymerisation resulting in the formation of polystyrene – an industrially important plastic.



Co-polymers of styrene with butadiene and other substances are also important since many of them are industrially useful products such as SBR (A rubber substitute).

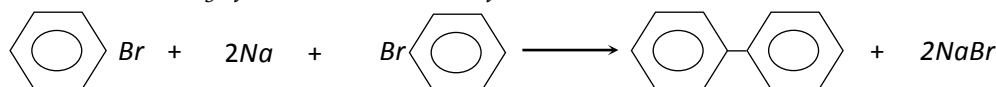


9. Bi-phenyl ($C_6H_5 - C_6H_5$).

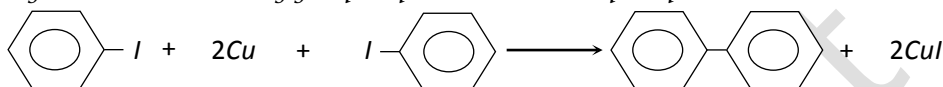
It occurs in coal-tar. It is the simplest example of an aromatic hydrocarbon in which two benzene rings are directly linked to each other.

(1) Methods of formation

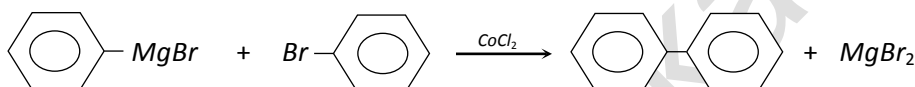
(i) **Fittig reaction:** It consists heating of an ethereal solution of bromobenzene with metallic sodium.



(ii) **Ullmann biaryl synthesis:** Iodobenzene, on heating with copper in a sealed tube, forms biphenyl. The reaction is facilitated if a strong electron withdrawing groups is present in ortho or para position.



(iii) **Grignard reaction:** Phenyl magnesium bromide reacts with bromo benzene in presence of CoCl_2 .



(2) **Properties:** It is a colorless solid, melting point 71°C . It undergoes usual electrophilic substitution reactions. Since aryl groups are electron withdrawing, they should have deactivating and m-orientating effect. But, it has been experimentally shown that presence of one benzene ring activates the other for

electrophilic substitution and directs the incoming group to o- and p- positions. It has been shown that monosubstitution in the bi-phenyl results in the formation of para isomer as the major product.

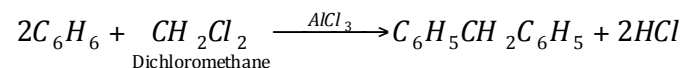
Another special feature of the biphenyl is the behaviour towards second substitution in a monosubstituted biphenyl. The second substituent invariably enters the unsubstituted ring in the ortho and para position no matter what is the nature of substituent already present.



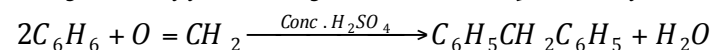
10. Diphenyl methane.

(1) Methods of preparation

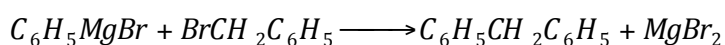
(i) **Friedel-craft's reaction :** $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{C}_6\text{H}_6 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_5 + \text{HCl}$ or
Benzylchloride Benzene Diphenyl methane



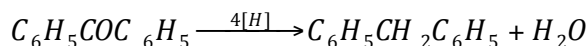
(ii) **By action of formaldehyde on benzene in presence of conc. sulphuric acid**



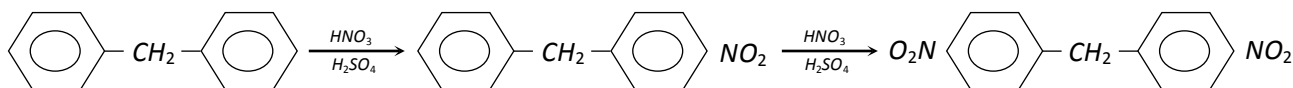
(iii) **By Grignard reaction :** Phenyl magnesium bromide reacts with benzyl bromide to form diphenyl methane.



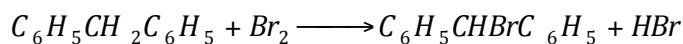
(iv) **By reduction of benzophenone** : Reduction can be done with LiAlH_4 or P and HI .



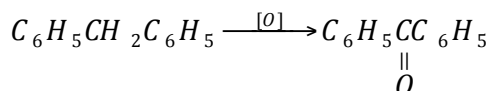
(2) **Properties** : It is a colourless solid, melting point 26°C . Like biphenyl, it also easily undergoes electrophilic substitution reactions.



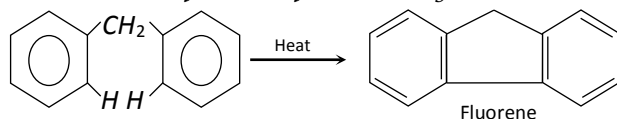
The methylene hydrogens of diphenylmethane are situated on carbon atom linked by two electron attracting benzene rings. Thus, these are somewhat acidic in nature.



When oxidised with $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$ mixture, it forms benzophenone.

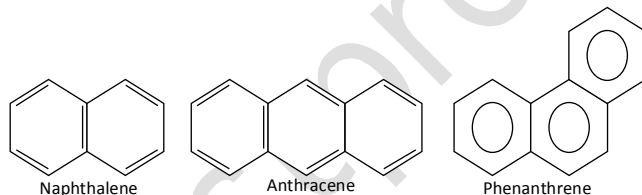


It forms fluorene when its vapours are passed through a red hot tube.



II. Polynuclear hydrocarbons.

Compounds having two or more benzene rings fused together in ortho positions are termed as fused polynuclear hydrocarbons. These hydrocarbons also called fused ring hydrocarbons.

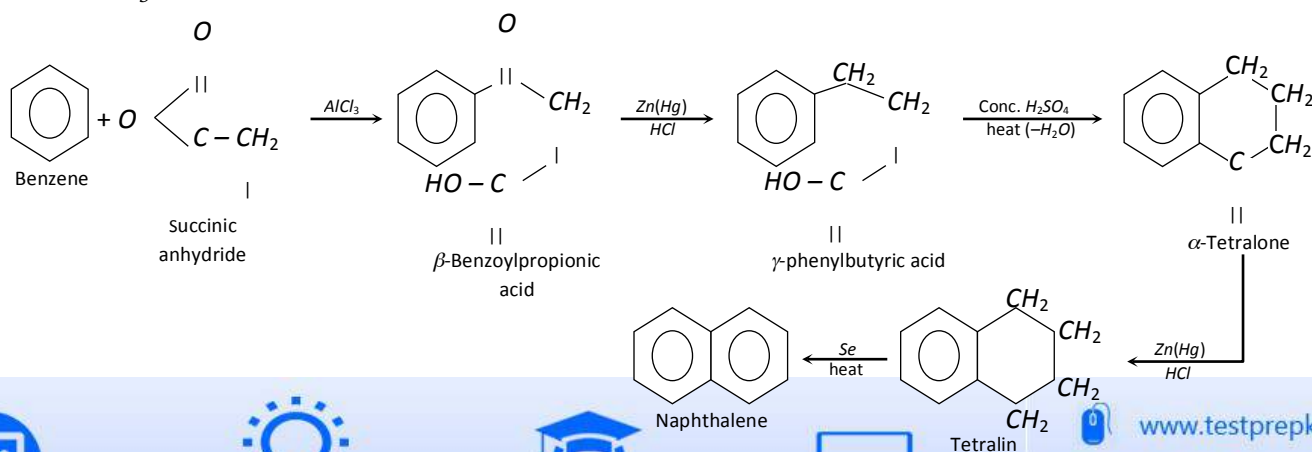


(I) Naphthalene

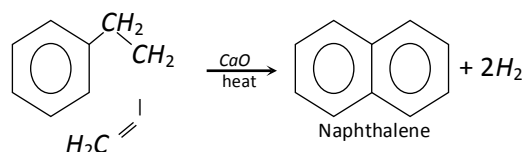
Naphthalene is the largest single constituent of coal-tar (6-10%). It is obtained in the middle oil fraction of coal-tar distillation. It is recovered as crude product when the middle oil fraction is cooled. The crude crystalline product is separated by centrifugation and purified by washing successively with dilute H_2SO_4 (to remove basic impurities), sodium hydroxide solution (to remove acidic impurities) and water. Finally, the solid is sublimed to get pure naphthalene.

(i) Methods of preparation

(a) Haworth synthesis



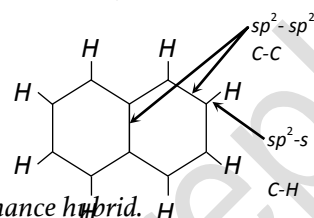
(b) By 4-phenyl-1-butene :



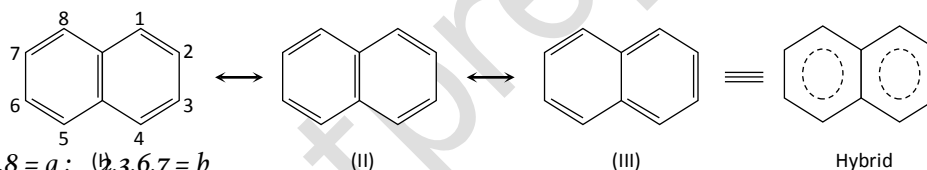
(ii) **Structure**

(a) In naphthalene all carbon atoms are sp^2 - hybridized. sp^2 - hybrid orbital overlap with s- orbital of hydrogen atoms forming C – C and C – H sigma bond.

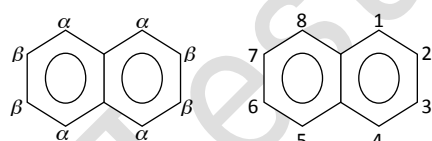
(b) All carbon and hydrogen atoms lie in one plane in naphthalene.



(c) According to resonance theory. It is a resonance hybrid.



(d) Position: 1,4,5,8 = a ; (2,3,6,7 = b

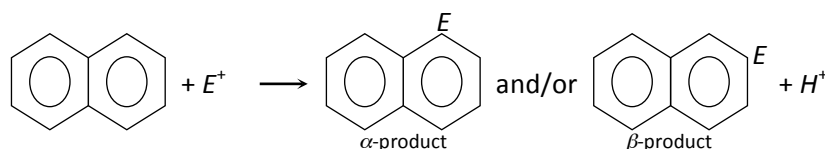


(e) Resonance energy of naphthalene is 61 kcal/mol. Which is less than of benzene. So that naphthalene is less aromatic i.e. more reactive than benzene.

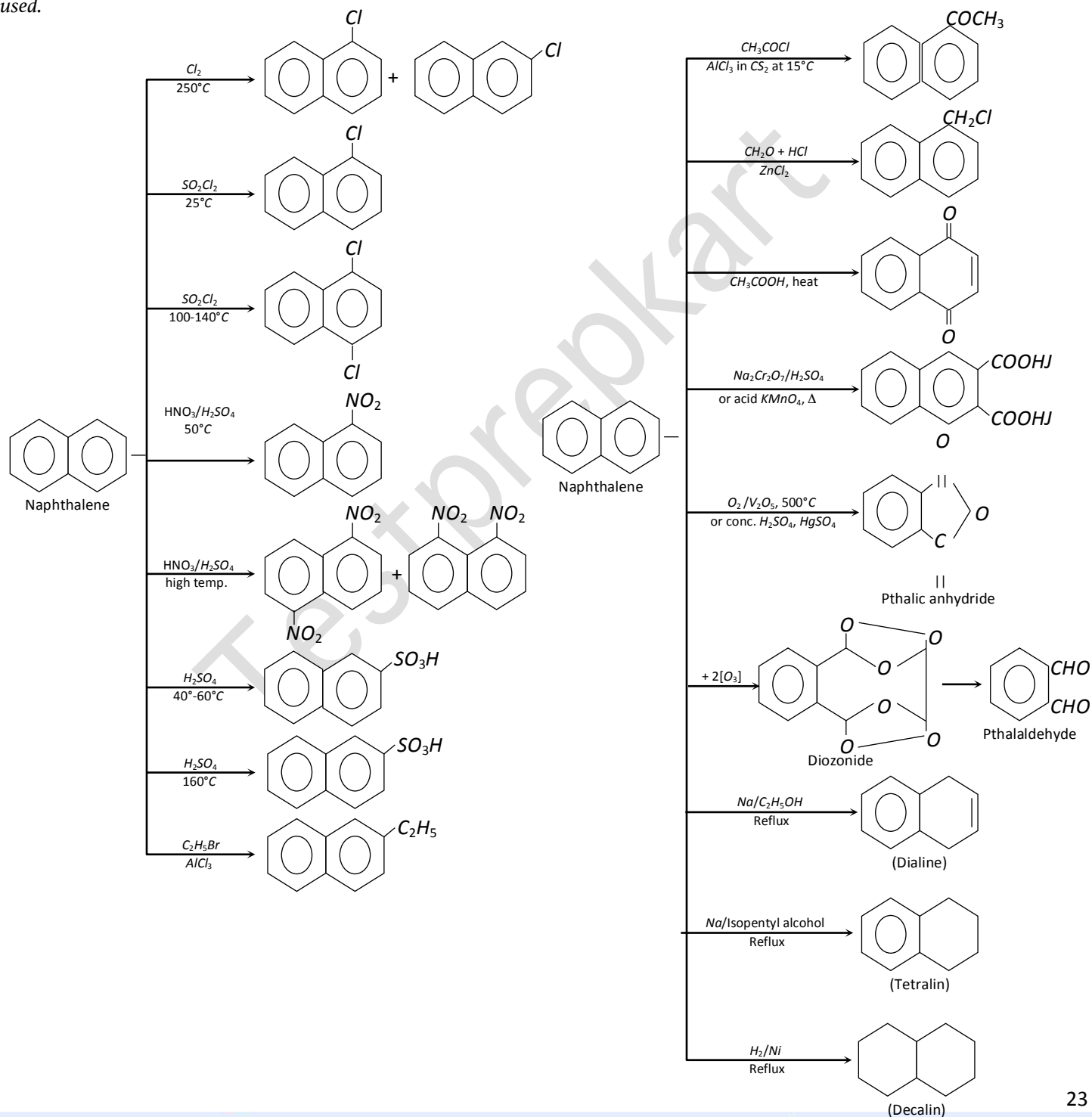
(f) In naphthalene $C_1 - C_2$ bond length is shorter (1.36Å) i.e. C = C and $C_2 - C_3$ is 1.40Å i.e. single bond.

(iii) **Physical properties:** It is a colorless crystalline compound. It melts at 80.2°C. It is very volatile and sublimates slowly even at room temperature. It has strong characteristic odour. It is insoluble in water but very soluble in ether, benzene and hot alcohol. It burns with smoky flame.

(iv) **Chemical properties:** It undergoes usual aromatic electrophilic substitution reactions. The product of monosubstitution is either a or b -depending on conditions, but the a -product always predominates.



Substitution at *b*-position occurs only when the reaction is carried at high temperatures or when bulkier solvents are used.



(v) Uses

- (a) As moth repellent. It is, however, now being replaced by more powerful insecticides such as *p*-dichlorobenzene and DDT.
- (b) For commercial production of phthalic anhydride, *a*-naphthol, *b*-naphthol, etc.
- (c) For manufacture of dyes, explosives and synthetic resins.
- (d) For increasing the illuminating power of coal gas.

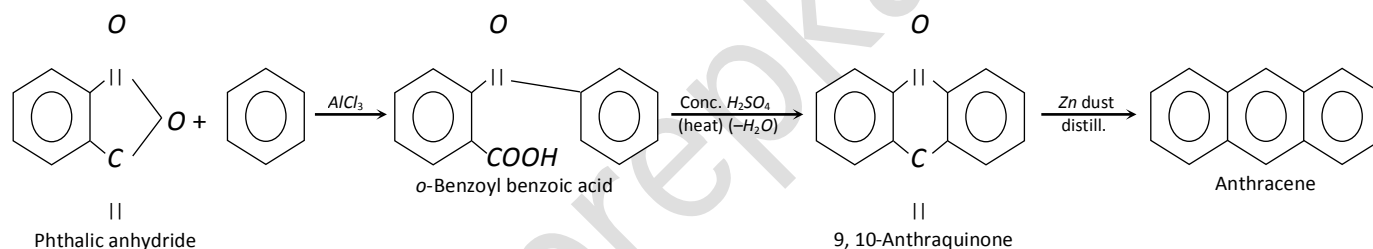
(2) Anthracene

The hydrocarbon derives its name from the word anthrax (Greek = coal) as coal is the chief source from which it is manufactured. It is present in coal-tar (Less than 0.5%) and is obtained from the anthracene oil or green oil fraction (because of its dark green fluorescence) formed during coal-tar distillation. This fraction is collected between 270 - 360°C.

The anthracene oil fraction is cooled when crude anthracene crystallizes out. The crude product consists phenanthrene and carbazole as impurities. The crude product is successively washed with solvent naphtha as to remove phenanthrene and pyridine to remove carbazol. Finally, the solid is sublimed to get pure anthracene.

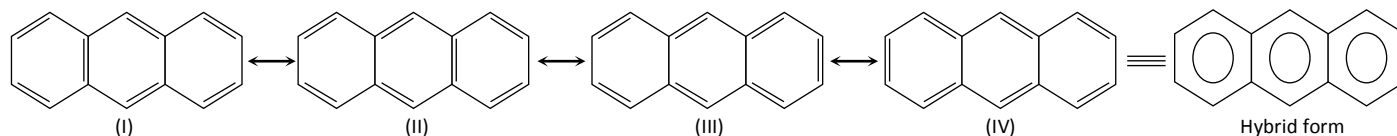
(i) Methods of preparation

Haworth synthesis



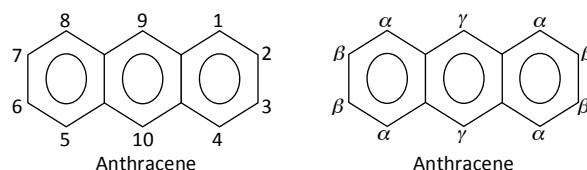
(ii) Structure

- (a) Anthracene is tricyclic aromatic hydrocarbon.
- (b) All carbon atoms in anthracene are sp^2 hybridized.
- (c) resonance hybrid are as follows



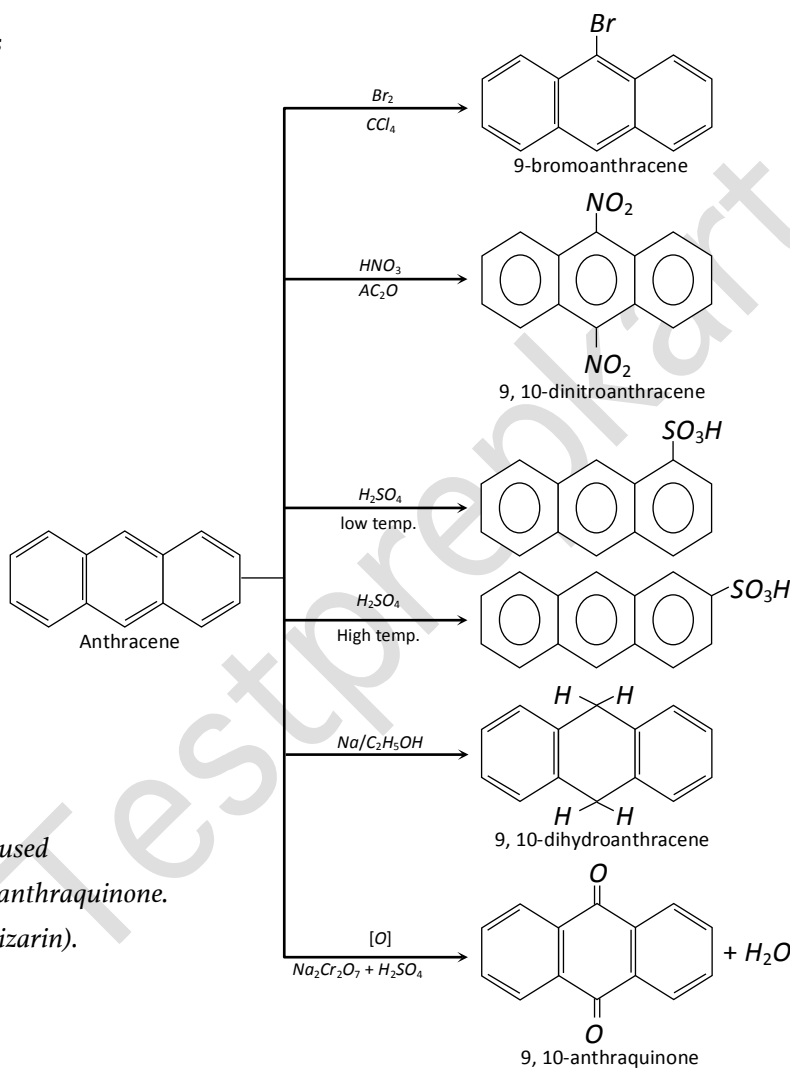
(d) It gives both addition and electrophilic substitution reaction.

(e) In anthracene the numbering of carbon atom is



(iii) **Physical properties:** Anthracene is a colorless solid. It melts at 217°C . It is insoluble in water but soluble in alcohol and ether in small amounts. It is comparatively more soluble in hot benzene. With picric acid, it forms a red color picrate.

(4) Chemical properties



(v) **Uses:** Anthracene is used

(a) For manufacture of anthraquinone.

(b) For making dyes (Alizarin).

(c) In smoke screens.

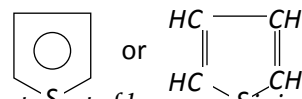
12. Heterocyclic compounds.

These are cyclic compounds in which the ring includes in addition to carbon atoms at least one atom of another element (Hetero = other, different). The common hetero atoms present in the carbon rings are O, N and S.

(1) Thiophene



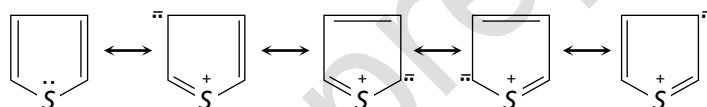
It is found in the benzene fraction of coal-tar and petroleum. The benzene fraction is shaken with cold concentrated sulphuric acid. Thiophene present in the fraction combines with sulphuric acid more readily than benzene to form thiophene sulphonic acid which is separated with water being soluble. Thiophene sulphonic acid is treated with super-heated steam to recover thiophene.



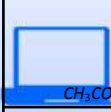
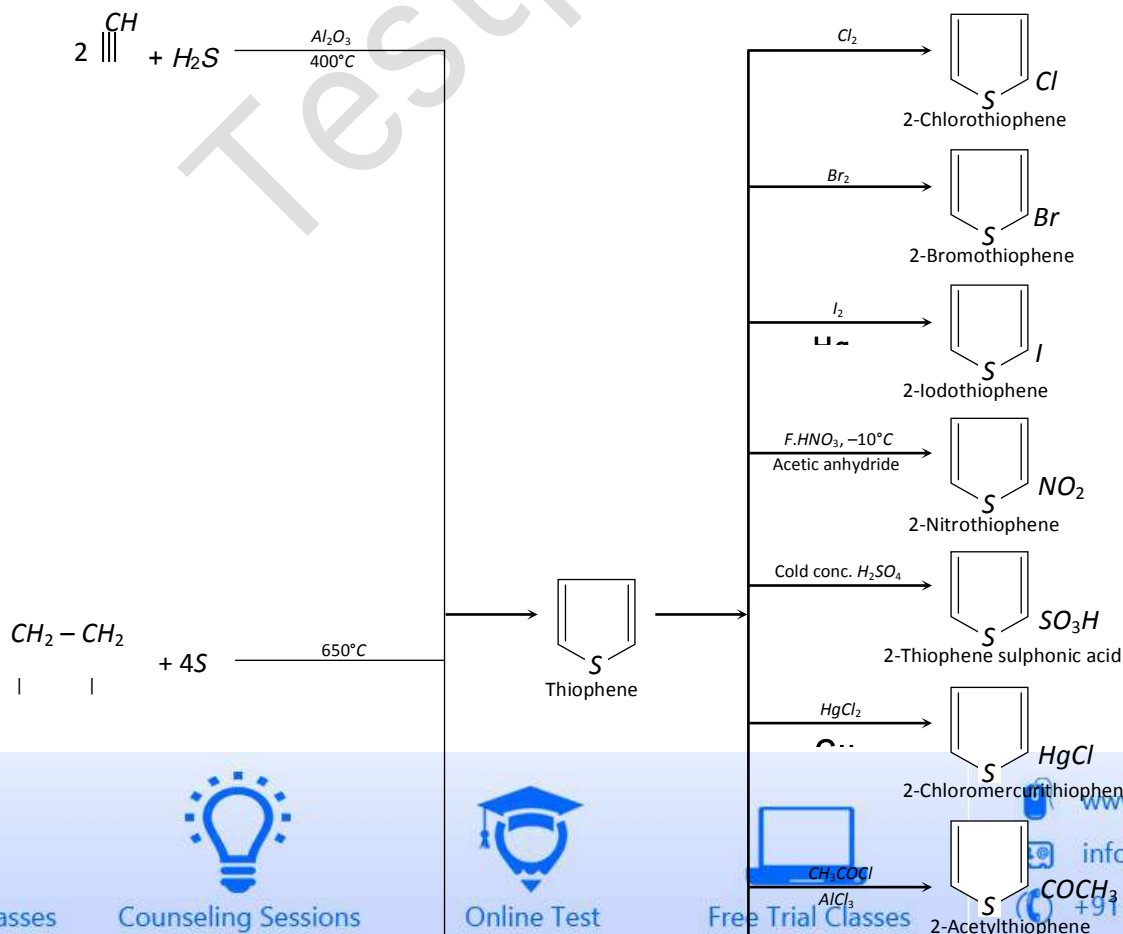
Properties: It is a colourless liquid. Its boiling point is 84°C . Its odour is similar to that of benzene. It is insoluble in water but soluble in organic solvents. It is flammable and toxic in nature.

Its resonance energy is 31 k cal mol^{-1} . Hence, it is more stable and resembles benzene more closely than furan

(23 k cal mol^{-1}) and pyrrole (25 k cal mol^{-1}). It does not show basic properties and does not undergo Diels-Alder reaction.



Thiophene as a resonance hybrid (Resonance energy is 31 k cal/mol)



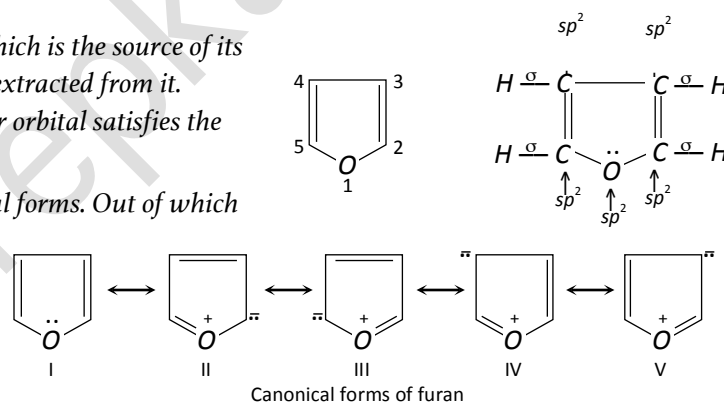
(2) Furan

Furan derives its name from *furfur* meaning bran in Greek which is the source of its aldehyde, *furfural*. It is present in pine-wood tar and may be extracted from it.

Furan shows aromatic behavior because resulting p -molecular orbital satisfies the Huckel rule $((4n + 2)\pi$ where, $n = 1$.

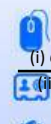
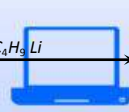
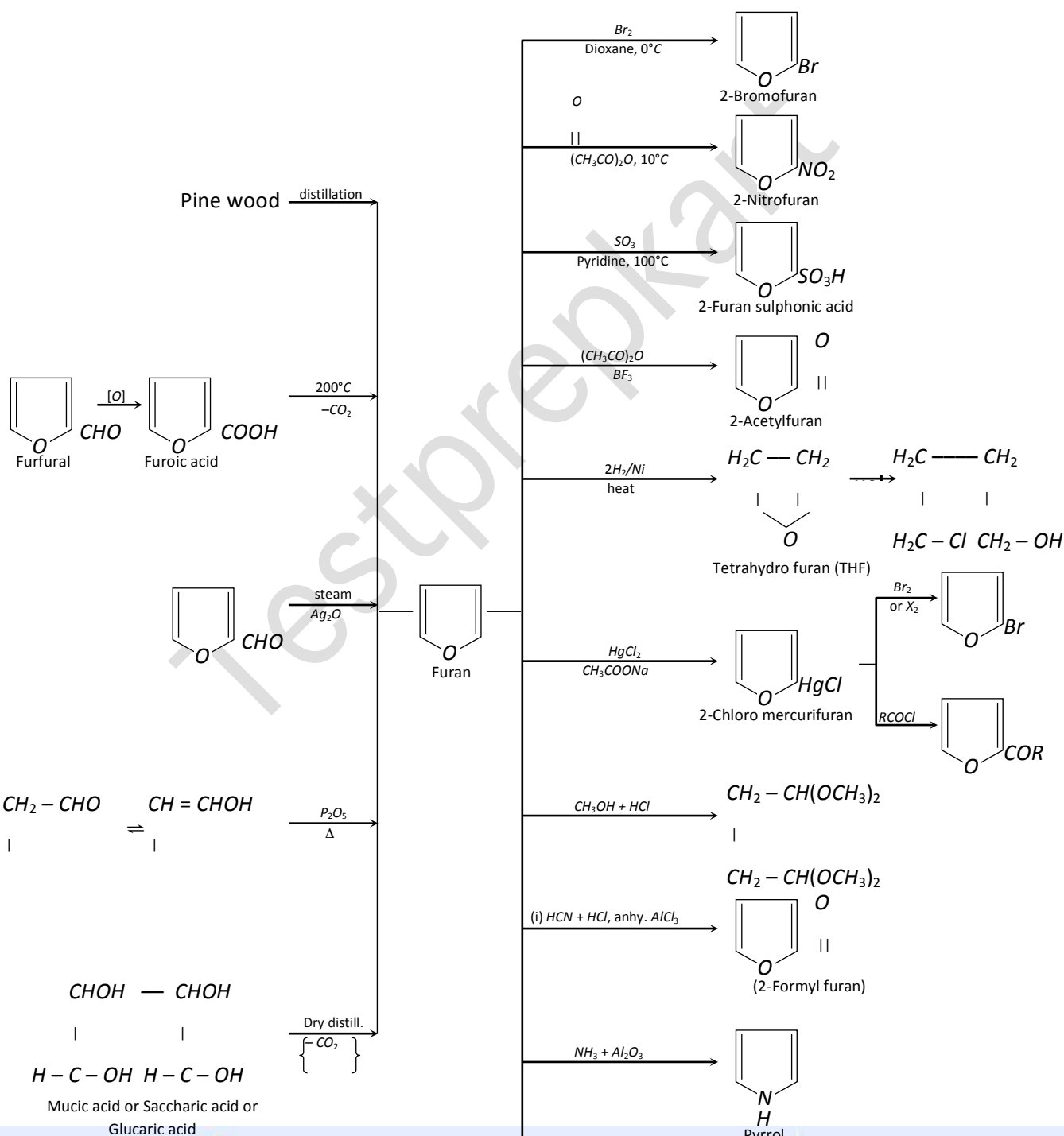
Furan is also considered as a resonance hybrid of the canonical forms. Out of which the first three are the main contributing structures.

Furan has resonance energy about $23 \text{ k cal mol}^{-1}$ which is less than benzene. However it is less aromatic and more reactive than benzene.



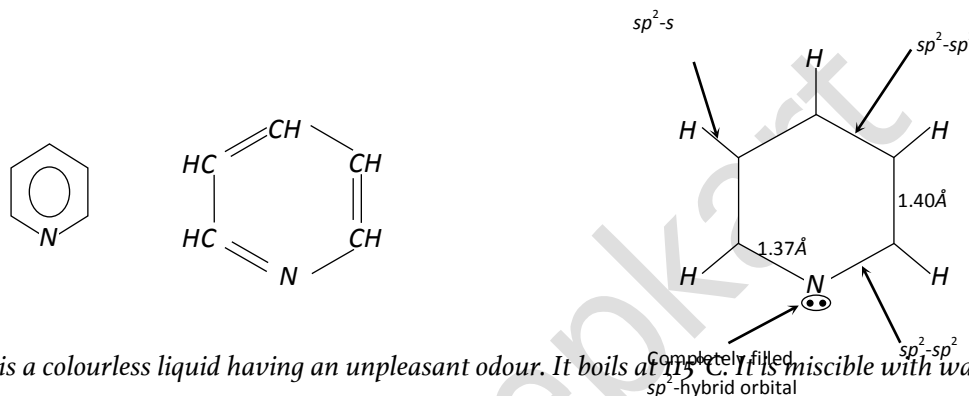
Properties: Furan is a colorless liquid. Its boiling point is 32°C . It is insoluble in water but soluble in organic solvents. It is a reactive compound. It is a weak base. In Furan electrophilic substitution reactions take place preferably at 2 and 5 position where electron density is high. If these positions are occupied, substitution occurs at 3 and 4 positions. It undergo **Diels-Alder reaction**.





(3) Pyridine

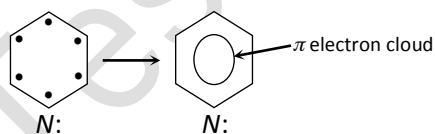
Pyridine is a six membered aromatic heterocycle with one nitrogen atom in the ring. It may be supposed to have been derived by replacement of = CH – group of benzene by = N –. Hence, it is isoster of benzene. Its systematic name is **azabenzene**. (Prefix aza stands for nitrogen). The hybrid structure of pyridine is represented as:



(i) **Properties:** It is a colourless liquid having an unpleasant odour. It boils at 115°C . It is miscible with water and is hygroscopic. It is a good solvent for many organic compounds and inorganic salts.

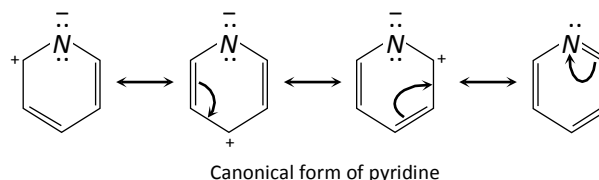
(ii) **Aromatic character:** Each carbon atom and nitrogen atom in the ring have sp^2 hybridized and one unhybrid p -orbital containing one electron. These orbitals overlap to form π molecular orbital consisting six electrons. The π molecular orbital satisfies Huckel's rule ($4n + 2$) and thus aromatic properties are observed in pyridine.

The resonance energy is 43 k cal/mol and bond length of C – C bond is 1.40 Å and C – N 1.39 Å.

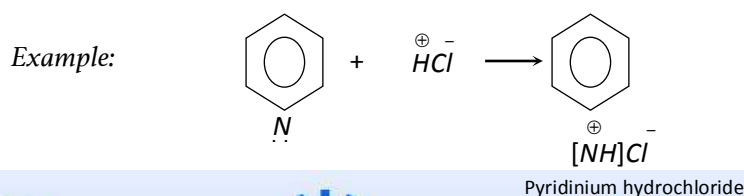


$$4n + 2 = 6; n = 1$$

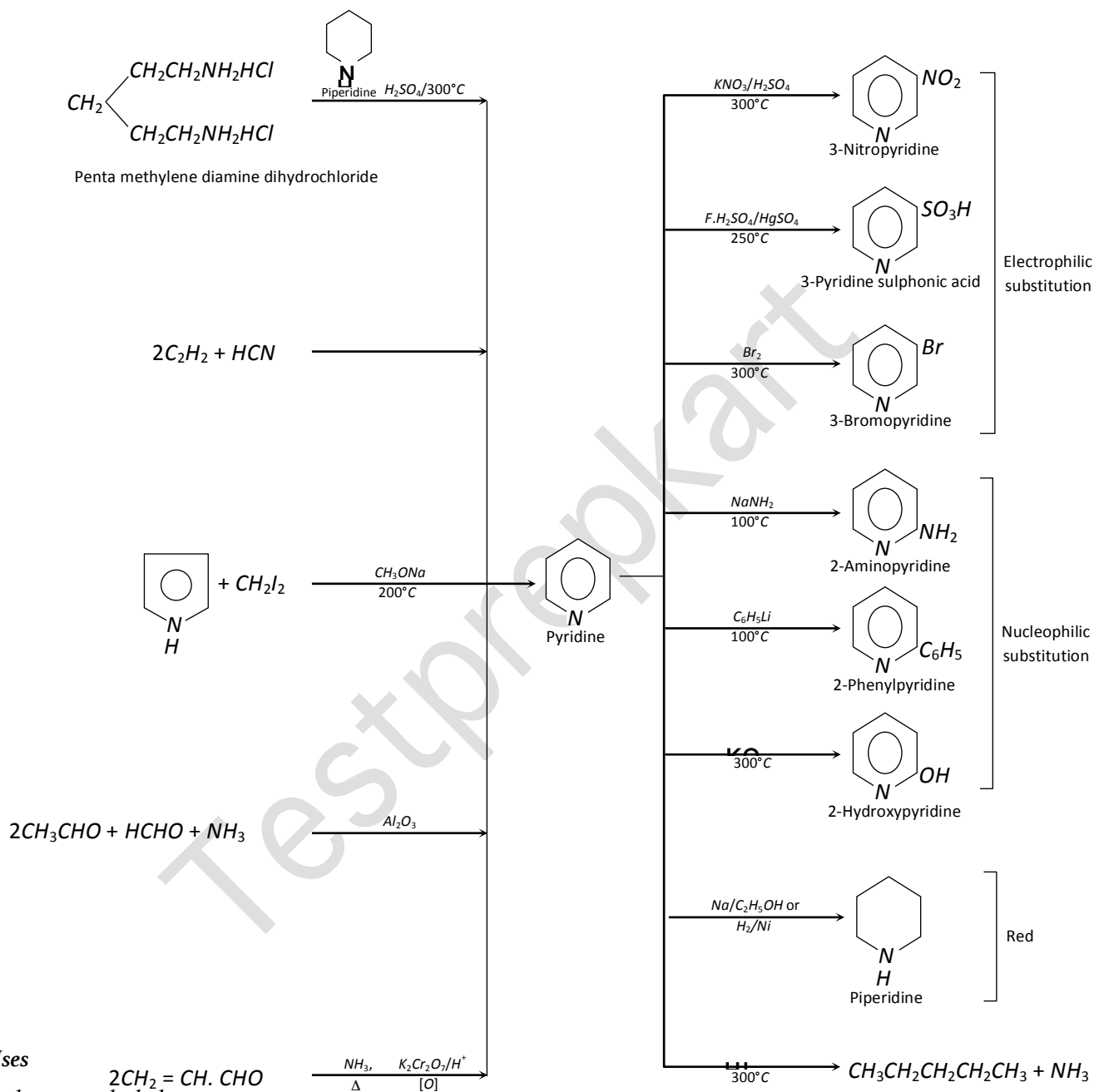
(iii) **Resonance structure:**



(iv) **Basic nature:** Pyridine is basic in nature due to presence of lone pair nitrogen atom. It is more and more basic than pyrrole and less basic than aliphatic amine.



(v) Chemical properties:



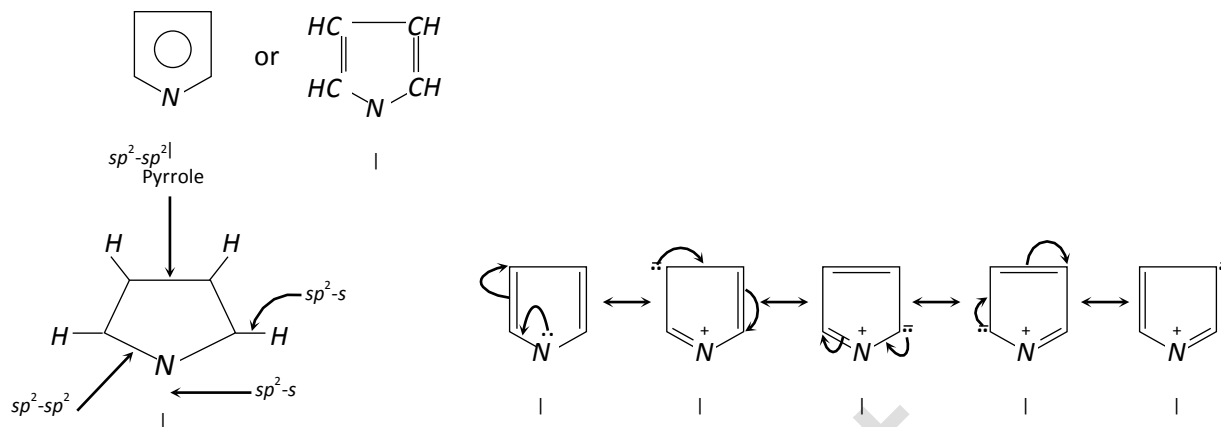
(vi) Uses

- To denature alcohol.
- As a basic solvent in organic reactions.
- For preparing sulpha-pyridine and vitamin B₆.
- As a catalyst in many reactions, e.g., in the formation of Grignard reagent, in Perkin and Knoevenagel reactions.

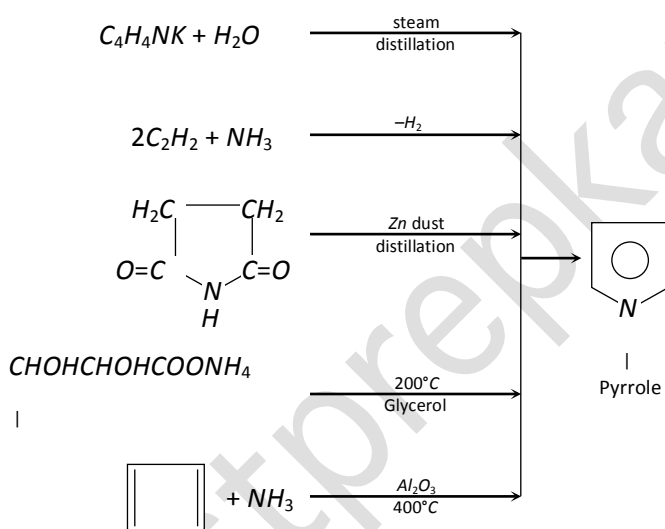
(4) Pyrrole



It occurs in coal-tar and bone oil and is found in many natural products including chlorophyll, haemoglobin and alkaloids.



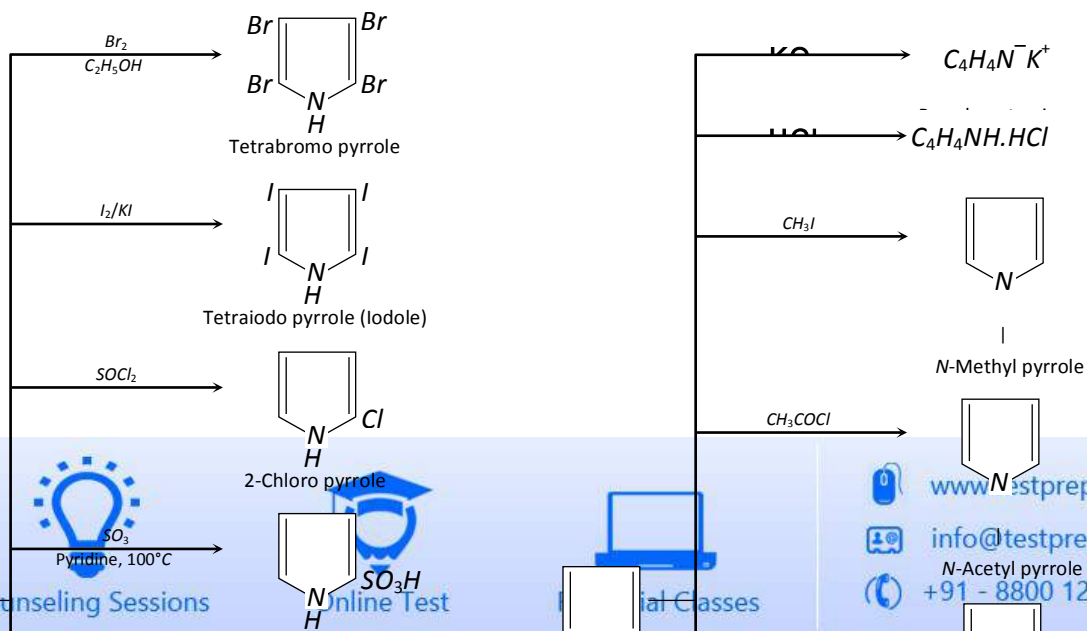
(i) Preparation:

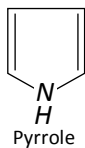


Note: Furan needed for the process is obtained from agricultural waste materials which are rich in pentosans. The pentosans on acid hydrolysis yields furfural which is decarbonylated.

(ii) Properties: Pyrrole is a colorless liquid. Its boiling point is $131^\circ C$. It is slightly soluble in water but highly soluble in alcohol and ether. Its odour is similar to chloroform. It rapidly becomes brown when exposed to air. Vapours of pyrrole turn a pine splint moistened with HCl red. Pyrrole derives its name from this property.

Chemical properties:





(iii) *Uses:* It is used as a commercial solvent, as an intermediate in the production of nylon and for making pharmaceuticals.

