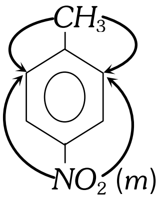
Aromatic Hydrocarbons Part 2

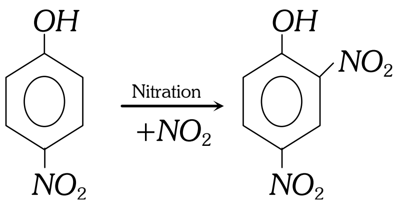
(2) Directive effect in disubstituted benzene

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

Example :



;

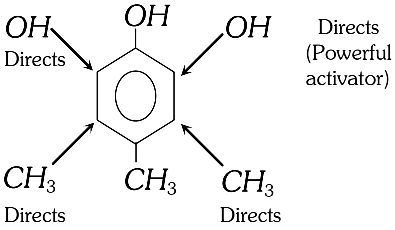


Thus, both (CH_3, NO_2) direct further substitution to the same position (Orth).

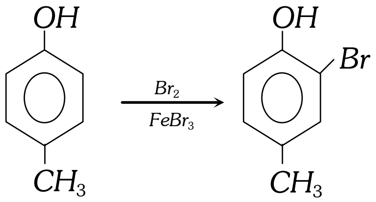
(ii) If the directing effect of two groups oppose each other strongly activating groups win over deactivating or weakly activating group. The sequence of directing power is

$$-NH_2 > -OH > -OCH_3 - > NHCOCH_3 > -C_6H_5 > CH_3 > \text{meta directors}$$

Example :



;



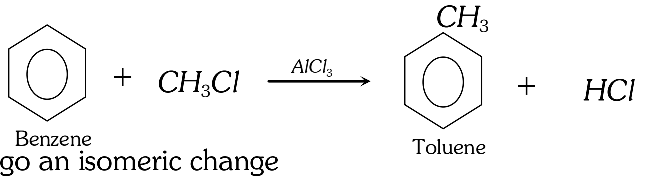
(iii) There is normally little substitution when the two groups are meta to each other. Aromatic rings with three adjacent substituents are generally prepared by same other routes.

Toluene, methyl benzene or phenyl methane.

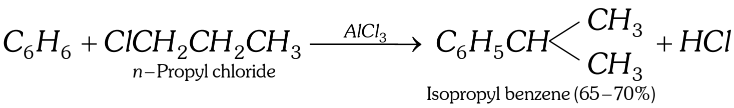
Toluene is the simplest homolouge of benzene. It was first obtained by dry distillation of tolubalsam and hence named toluene. It is commercially known as tolual.

(1) Methods of preparation

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



Note : ✹ Alkyl halide employed may undergo an isomeric change

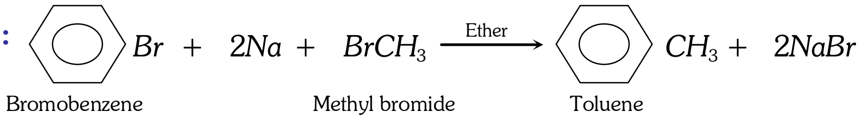


$$\underset{n-\text{Propyl chloride}}{C_6H_6 + ClCH_2CH_2CH_3} \xrightarrow{AlCl_3} \underset{\text{Isopropyl benzene (65–70\%)}}{C_6H_5CH\begin{matrix} CH_3 \\ CH_3 \end{matrix}} + HCl$$

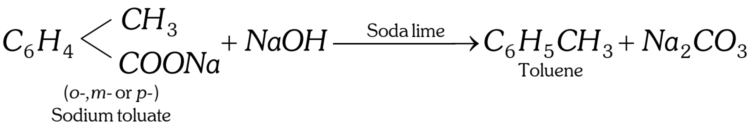
✹ Catalysts can be used in place of anhydrous $AlCl_3$ are,

$$AlCl_3 > SbCl_3 > SnCl_4 > BF_3 > ZnCl_2 > HgCl_2$$

(ii) ***Wurtz fitting reaction :***

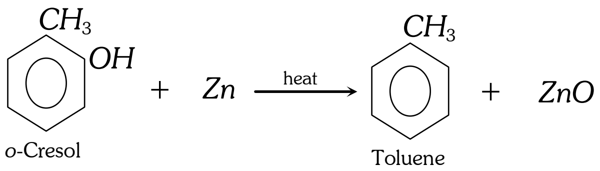


(iii) ***Decarboxylation :***

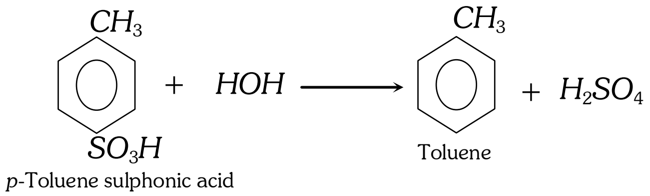


$$\underset{\substack{(o\text{-}, m\text{- or } p\text{-})\\ \text{Sodium toluate}}}{C_6H_4\begin{matrix} CH_3 \\ COONa \end{matrix}} + NaOH \xrightarrow{\text{Soda lime}} \underset{\text{Toluene}}{C_6H_5CH_3} + Na_2CO_3$$

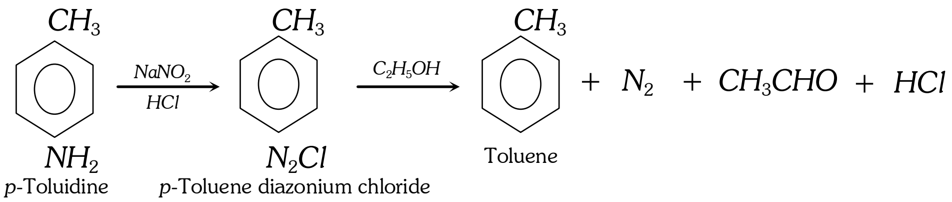
(iv) **From cresol :**



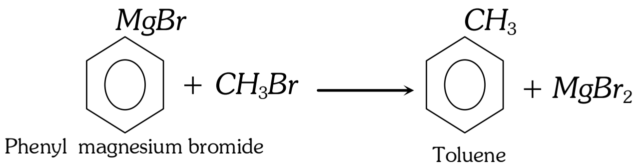
(v) **From toluene sulphonic acid :**



(vi) **From toluidine :**



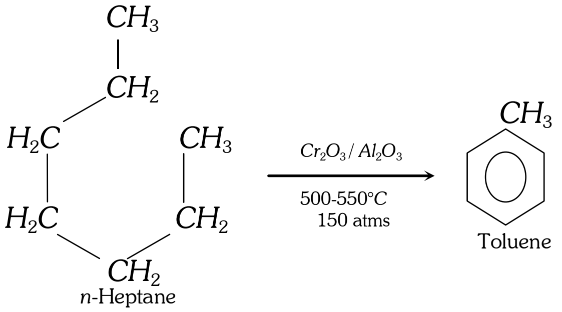
(vii) **From grignard reagent :**



(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 $80-110°C$ is 90% benzol which contains $70-80\%$ benzene and $14-24\%$ toluene. 90% benzol is again distilled and the portion distilling between $108-110°C$ 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).

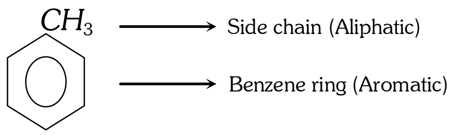
(iii) It is insoluble in water but miscible with alcohol and ether in all proportions.

(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.

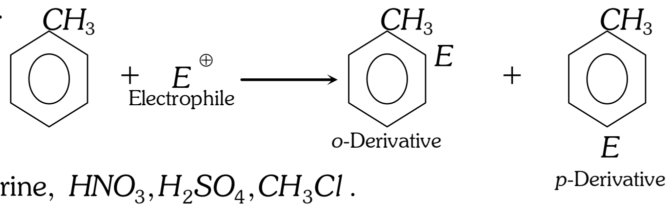
(vi) It is a weak polar compound having dipole moment 0.4*D*.

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



Aromatic Hydrocarbons Part 2

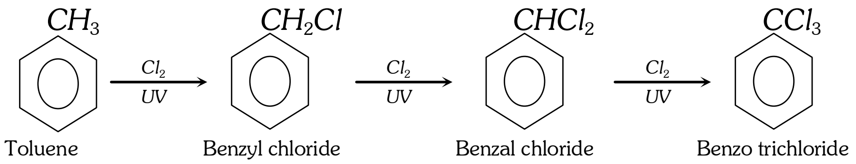
(i) ***Electrophilic substitution reactions*** **:** Aromatic character (More reactive than benzene) due to electron releasing nature of methyl group.



Note : ✹ E^+ may be chlorine, HNO_3, H_2SO_4, CH_3Cl.

(ii) ***Reactions of side chain***

(a) *Side chain halogenation* :



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

$$\underset{\text{(Phenyl methyl chloride)}}{C_6H_5CH_2Cl} + NaOH \longrightarrow C_6H_5CH_2OH + NaCl$$

✹ Benzal chloride on hydrolysis forms benzaldehyde.

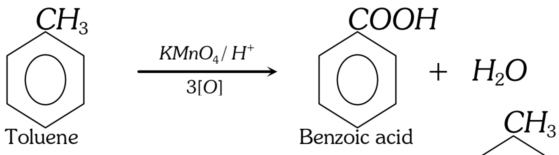
$$\underset{\text{(Benzylide chloride)}}{C_6H_5CHCl_2} + 2NaOH \longrightarrow \begin{array}{c} C_6H_5CH(OH)_2 + 2NaCl \\ \downarrow \\ C_6H_5CHO + H_2O \end{array}$$

✹ Benzo trichloride on hydrolysis forms benzoic acid.

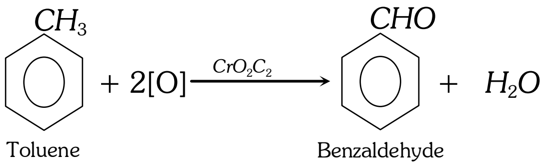
$$\underset{\text{(Benzylidyne chloride)}}{C_6H_5CCl_3} + 3NaOH \longrightarrow \begin{array}{c} C_6H_5C(OH)_3 + 3NaCl \\ \downarrow \\ C_6H_5COOH + H_2O \end{array}$$

(b) *Oxidation* :

- With hot acidic KMnO$_4$:

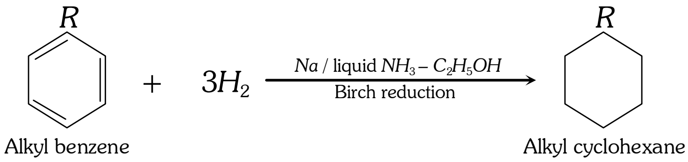


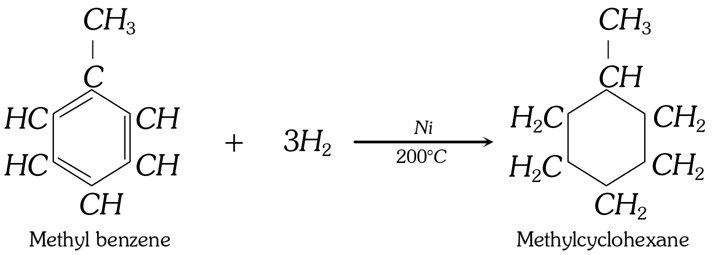
- With acidic manganese or chromyl chloride (Etards reaction) :



Note : ✹ All alkyl benzenes on oxidation with hot acidic $KMnO_4$ or $Na_2Cr_2O_7$ form benzoic acid. The length of the side chain does not matter.

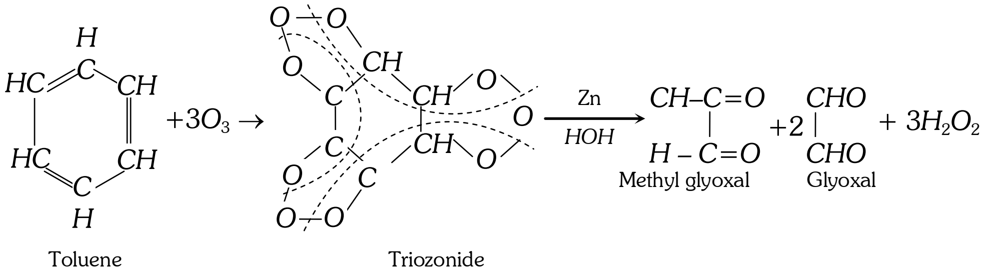
(c) *Hydrogenation* :





(d) *Combustion* : $C_6H_5CH_3 + 9O_2 \longrightarrow 7CO_2 + 4H_2O$

(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.

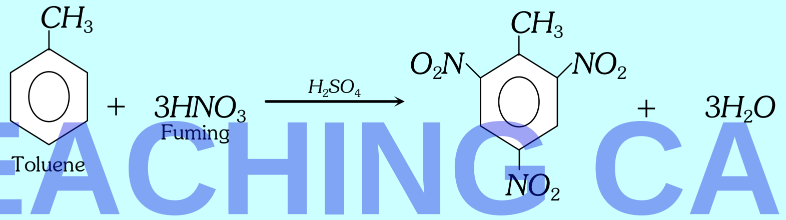
(iii) As an industrial solvent and in drycleaning.

(iv) As a petrol substitute.

(v) In the manufacture of certain dyes and drugs.

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

Preparation :

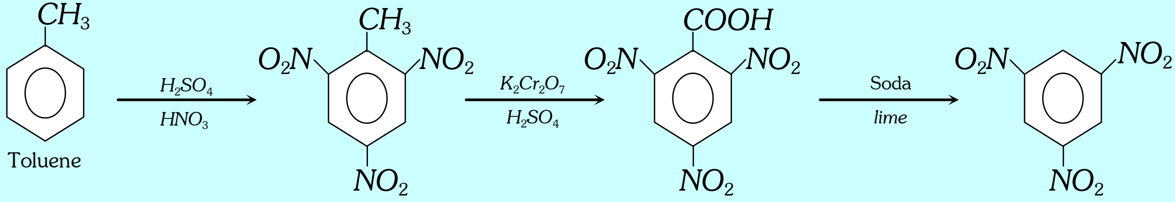


Properties : It is pale yellow crystalline solid (M.P. = 81°C).

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)

Preparation :

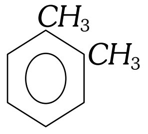


T.N.B.

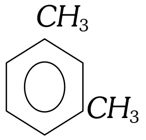
Properties and uses: It is colourless solid (M.P. = 122°C). It is more explosive than T.N.T. and used for making explosive.

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

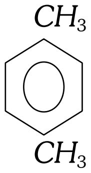
The molecular formula, C_8H_{10} represents four isomers.



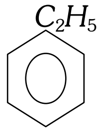
o-Xylene



m-Xylene



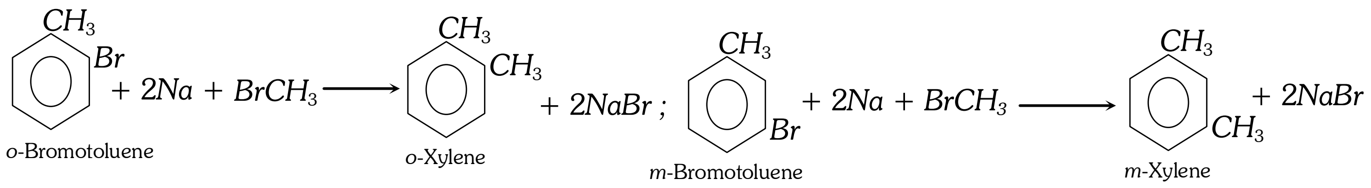
p-Xylene

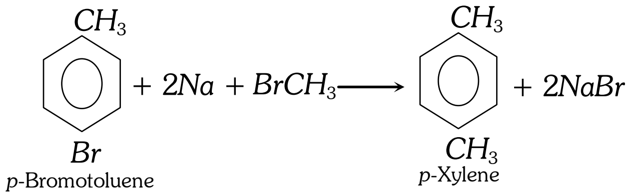


Ethyl benzene

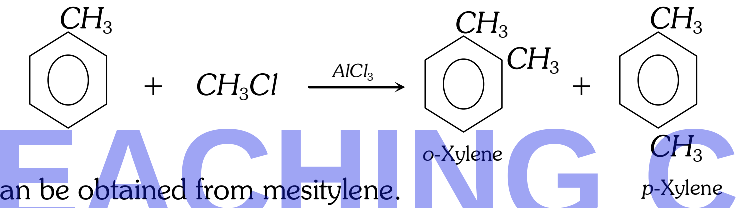
These are produced along with benzene, toluene and ethylbenzene when aromatisation of $C_6 - C_8$ fraction of petroleum naphtha is done. The xylenes are isolated from the resulting mixtrue (BTX) by fractional distillation.

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.

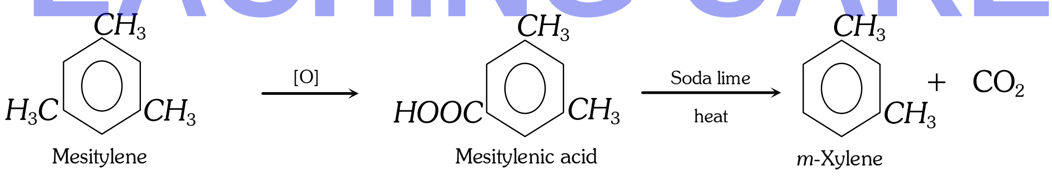




- These can also be obtained by Friedel – craft's synthesis,



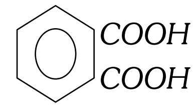
- *m*-Xylene can be obtained from mesitylene.



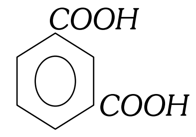
Xylenes are colourless liquids having characteristic odour. The boiling points of three isomers are,

o-Xylene = 144°C; *m*-Xylene = 139°C; *p*-Xylene = 138°C.

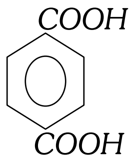
Xylenes undergo electrophilic substitution reactions in the same manner as toluene. Upon oxidation with $KMnO_4$ or $K_2Cr_2O_7$, Xylenes form corresponding dicarboxylic acids.



Phthalic acid ,



Isophthalic acid ,



Terephthalic acid

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

Ethyl benzene ($C_6H_5C_2H_5$).

It can be prepared by the following reactions,

(1) **By Wurtz-Fittig reaction :** $C_6H_5Br + 2Na + BrC_2H_5 \longrightarrow C_6H_5C_2H_5 + 2NaBr$

(2) **By Friedel-craft's reaction :** $C_6H_5H + BrC_2H_5 \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HBr$

(3) **By catalytic reduction of styrene :** $C_6H_5CH=CH_2+H_2\longrightarrow C_6H_5CH_2CH_3$

(4) **By alkyl benzene synthesis :** $C_6H_5H+H_2C=CH_2\xrightarrow[95°C,\text{Pressure}]{AlCl_3,HCl}C_6H_5CH_2CH_3$

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.

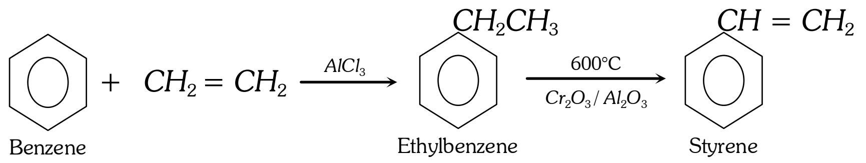
$$C_6H_5C_2H_5\xrightarrow{[O]}C_6H_5COOH$$

Styrene ($C_6H_5CH=CH_2$).

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

(1) 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.

$$C_6H_5CH=CHCOOH\xrightarrow{\text{Quinol}}C_6H_5CH=CH_2+CO_2$$

(iii) ***Dehydration of 1-phenyl ethanol with H_2SO_4* :** $C_6H_5CHOHCH_3\xrightarrow[-H_2O]{H_2SO_4}C_6H_5CH=CH_2$

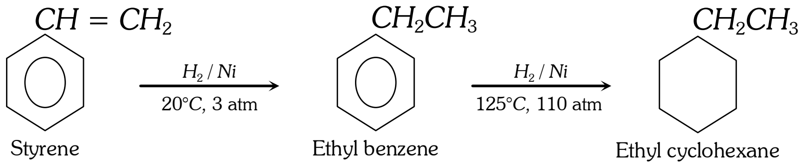
(iv) ***Dehydration of 2-phenyl ethanol with $ZnCl_2$* :** $C_6H_5CH_2CH_2OH\xrightarrow[-H_2O]{ZnCl_2,\text{heat}}C_6H_5CH=CH_2$

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

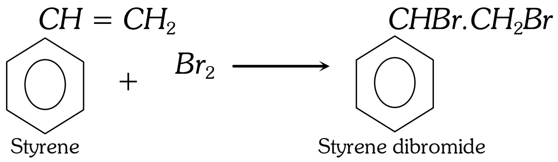
$$C_6H_5CHClCH_3\xrightarrow[\text{Heat}]{\text{Alc.}KOH}C_6H_5CH=CH_2$$

(2) **Properties :** It is a colourless liquid, boiling point 145°C. On keeping, it gradually changes into a solid polymer called **metastyrene**. The polymerisation 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.

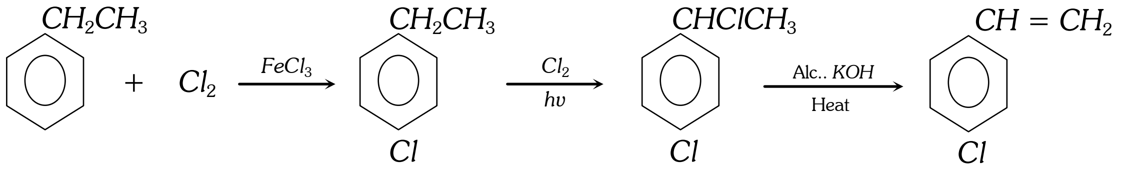


With bromine, it gives the dibromide.

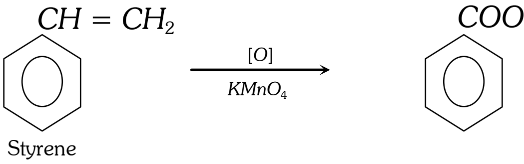


Halogen acids add to the side chain. $C_6H_5CH=CH_2+HX \longrightarrow C_6H_5CHXCH_3$

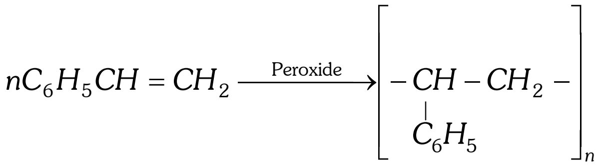
Preparation of ring substituted styrenes is not done by direct halogenation but through indirect route.



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.



$$nC_6H_5CH=CH_2 \xrightarrow{\text{Peroxide}} \left[-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2- \right]_n$$

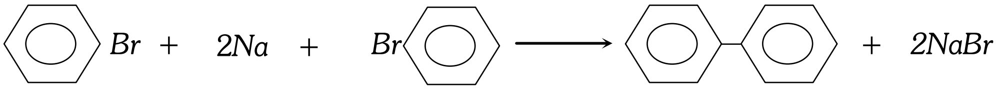
Co-polymers of styrene with butadiene and other substances are also important since many of them are industrially useful products such as *SBR* (A rubber substitute).

Bi-phenyl ($C_6H_5-C_6H_5$).

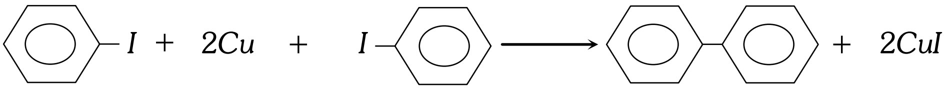
It occurs in coal-tar. It is the simplest example of an aromatic hydrocarbon in which two benzene rings are directly linked to each other.

(1) Methods of formation

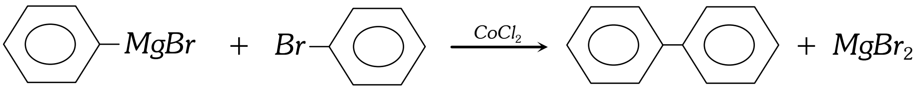
(i) ***Fittig reaction*** **:** It consists heating of an ethereal solution of bromobenzene with metallic sodium.



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

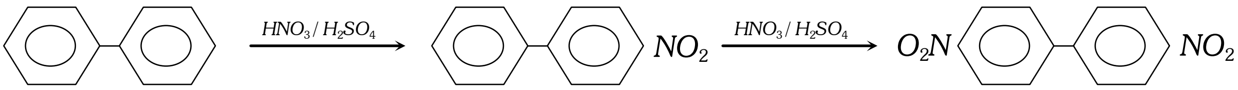


(iii) ***Grignard reaction*** **:** Phenyl magnesium bromide reacts with bromo benzene in presence of $CoCl_2$.



(2) **Properties :** It is a colourless 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.



Diphenyl methane.

(1) Methods of preparation

(i) **Friedel-craft's reaction :** $\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{AlCl_3} \underset{\text{Diphenyl methane}}{C_6H_5CH_2C_6H_5} + HCl$ or

$$2C_6H_6 + \underset{\text{Dichloromethane}}{CH_2Cl_2} \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + 2HCl$$

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

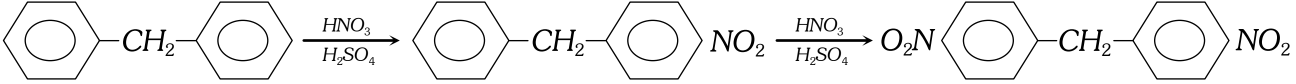
$$2C_6H_6 + O = CH_2 \xrightarrow{Conc.\,H_2SO_4} C_6H_5CH_2C_6H_5 + H_2O$$

(iii) **By Grignard reaction :** Phenyl magnesium bromide reacts with benzyl bromide to from diphenyl methane. $C_6H_5MgBr + BrCH_2C_6H_5 \longrightarrow C_6H_5CH_2C_6H_5 + MgBr_2$

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

$$C_6H_5COC_6H_5 \xrightarrow{4[H]} C_6H_5CH_2C_6H_5 + H_2O$$

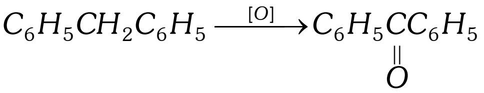
(2) **Properties :** It is a colourless solid, melting point 26°C.Like biphenyl, it also easily undergoes electrophilic substitution reactions.



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

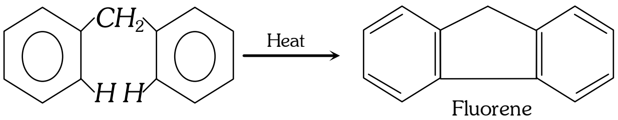
$$C_6H_5CH_2C_6H_5 + Br_2 \longrightarrow C_6H_5CHBrC_6H_5 + HBr$$

When oxidised with $K_2Cr_2O_7 / H_2SO_4$ mixture, it forms benzophenone.



$$C_6H_5CH_2C_6H_5 \xrightarrow{[O]} C_6H_5\underset{\underset{O}{\|}}{C}C_6H_5$$

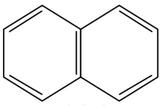
It forms fluorene when its vapours are passed through a red hot tube.



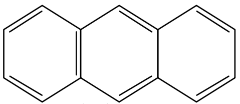
Fluorene

Polynuclear hydrocarbons.

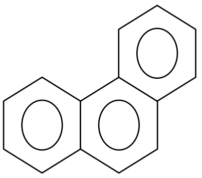
Compounds having two or more benzene rings fused together in ortho positions are termed as fused polynuclear hydrocarbons. These hydrocarbons also called fused ring hydrocarbons.



Naphthalene



Anthracene



Phenanthren

(1) **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.