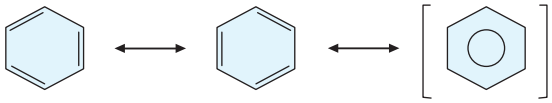
AROMATIC HYDROCARBONS Section - 6

Benzene : [C_6H_6]

Structure :

Its molecular formula is C_6H_6. This implies unsaturation in benzene. It shows addition reactions : addition of 3 molecules of Hydrogen, 3 moles of Cl_2 and 3 moles of Ozone (like alkenes).

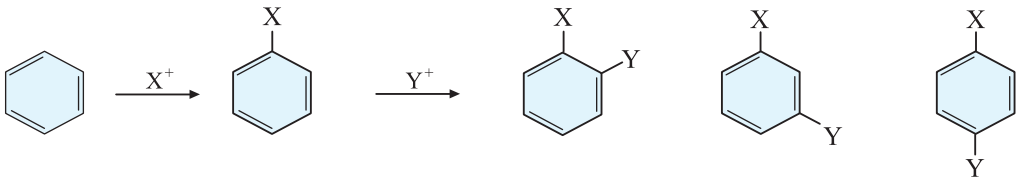
This leads to idea of three double bonds. However, benzene fails to give unsaturation test (i.e., Baeyer's test or decolouration of bromine water). Benzene also gives substitution reactions like halogenation, nitration etc. (like alkanes). On addition of H_2, benzene forms cyclohexane (a cyclic hydrocarbon) C_6H_{12}. Kekule (1865) proposed following structure the basis of the structure of cyclohexane. But this structure fails to explain ozonolysis of Xylene [$C_6H_4-(CH_3)_2$], a derivative of benzene. So benzene is found to be a resonance hybrid of two Kekule structures :



Kekule structures Resonance hybrid

This is supported by ozonolysis of o-Xylene, which gives a mixture of Glyoxal, Methyl glyoxal, Dimethyl glyoxal which can not be explained by either of Kekule structures.

Now benzene is considered as resonance hybrid of two Kekule structures. Resonance imparts stability to the benzene due to delocalisation of π electrons over entire benzene ring. Since π electrons are not concentrated in any specific region, addition reaction (electrophillic) are not common is benzene. However, in benzene electrophillic substitution reactions are common as they are stabilized by resonance stabilisation of intermediate Carbonium ion. When a group is introduced in benzene nucleus (ring), only one product (monosubstitued) is obtained. On the other hand, when a group of electrophillic nature is introduced in a mono-substituted benzene, three different isomers are possible.



Ortho (o) Meta (m) Para (p)

In the above sequence, nature of X (group over mono-substituted benzene) is responsible for the formation of either 'm' or 'o' & 'p' derivatives.

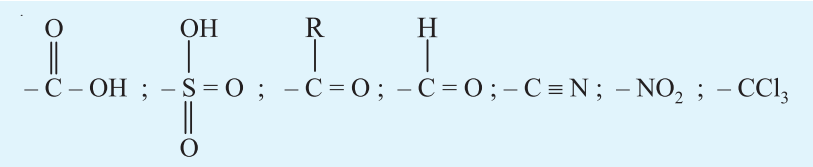
Directive (orienting) influence of groups :

(a) ***o* and *p* directing groups :** These groups direct the incoming group predominantly to the 'o' & 'p' position. Some important groups are :

$-NH_2$; $-NHR$; $-\ddot{O}H$; $-\ddot{O}R$; $-\ddot{X}$; $-R$

All of these groups exerts +M effect over benzene and tends to increase electron-density over benzene and make benzene strongly nucleophillic towards electrophiles. These groups are called activating group. –I effect (electronegative or electron withdrawing nature) of these groups is weaker as compared to +M effect. Halogens exerts +M effect over benzene but their –I effect is very powerful. Though they are *o* and *p* directing (+M effect) but are de-activating in nature and hence it is difficult to carry out electrophillic substitution in halo benzenes. Alkyl group (R) are *o* and *p* directing due to hyperconjugation (to be discussed later).

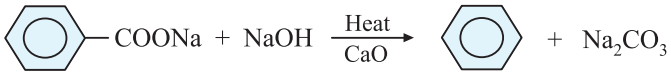
(b) m-directing groups : These groups direct the incoming groups predomintly to m-positions. Some of the important groups are :



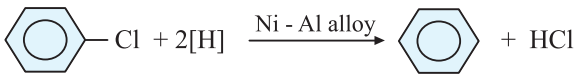
All m-directing groups, (except $-CCl_3$) either possess a positive charge or the key atom of substituents has an electronegative atom linked by a multiple bond. The benzene nucleus containing these groups undergo strong –M, –I, effect such that the displacement of electron takes place away from the benzene ring. These groups tends to deactivate the benzene ring and hence makes it less nucleophillic towards electrophiles. These are called as de-activating groups. Benzene having these groups will have greater difficulty in electrophillic substitution reactions.

Preparation of Benzene :

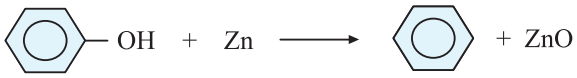
1. Decarboxylation of Sodium Benzoate :



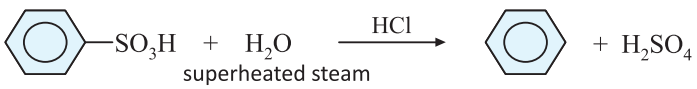
2. From Chlorobenzene :



3. From Phenol :



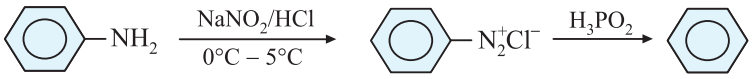
4. From Sulphonic Acid :



5. Synthesis :

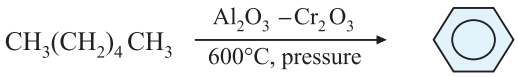
$$3C_2H_2 \xrightarrow{\text{Red hot Fe tube}} C_6H_6$$

6. From Benzene Diazonium Chloride :



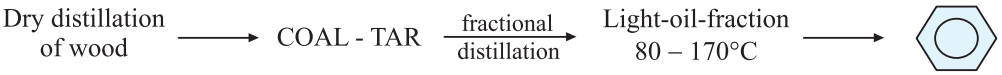
7. Manufacture :

(a) n-hexane :



This is known as Hydroforming or catalytic Reforming or aromatisation

(b) Coal Tar :



Physical properties of Arenes :

1. Benzene and its homologues containing upto eight carbon atoms are colourless liquids with characteristic smell.
2. Due to large hydrophobic hydrocarbon part, arenes are not soluble in water but are soluble in organic solvents.
3. The melting points and boiling points of arenes increase with increase in the molecular size due to a corresponding increase in the magnitude of van der Waal's forces of attraction. Amongst isomeric arenes, i.e., *o*-, *m*- and *p*-Xylenes, the *p*-isomer is most symmetrical, has the highest melting point.

Reaction of Benzene :

When benzene is treated with bromine in carbon tetrachloride in the dark or with aqueous potassium in the dark or with aqueous potassium permanganate or with dilute acids, none of the expected reactions (addition reactions)occurs. Benzene does add hydrogen in the presence of finely divided nickel, but only at high temperature and under high pressures.

Benzene does react with bromine except in the presence of catalyst such as ferric bromide. The interesting aspect of this reaction is that benzene show substitution not addition (like alkenes).

Substitution :

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$

Addition : Benzene does not show addition reaction of Br_2 or H_2 at all under normal conditions.

When benzene reacts with bromine, only one monobromobenzene is formed. That is, only one compound with the formula C_6H_6Br is found among the products. Similarly, when benzene is chlorinated, only one monochlorobenzene results.

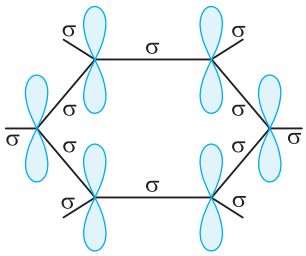
Two possible explanations can be given for these observations. The first is that only one of the six hydrogen atoms in benzene is reactive toward these reagents. The second is that all six hydrogen atoms in benzene are equivalent, and replacing any one of them with a substituent results in the same product. From the concept of Resonance we know all six carbon atom form equivalent C – C and C – H bonds. Hence this is the correct explanation.

Structure of Benzene

The fact that the bond angles of the carbon atoms in the benzene ring are all 120° strongly suggests that the carbon atoms are sp^2 hybridized. If we accept this suggestion and construct a planar six-membered ring from sp^2 carbon atoms, a representation like and shown in figure emerges. In this model, each carbon is sp^2 hybridized and has a p-orbital available for overlap with p-orbitals of its neighbouring carbons. If we consider favaourble overlap of these p-orbitals all around the ring, the result is the model shown in figure.

(a) Six sp^2-hybridized carbon atoms are joined in a ring (each carbon also bears a hydrogen atom). Each carbon has a p-orbital with lobes above and below the plane of the ring. Fig.(1)

Fig. (1)



(b) Overlap of the p-orbitals forming pi(π) bonds around the ring results in the delocalisation of pi(π) electrons on the ring. [Refer to Fig.(2), (3), (4)]

Fig. (2)

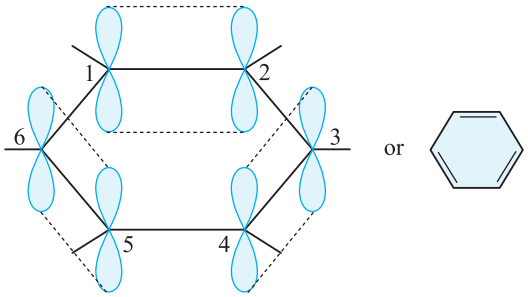


Fig. (3)

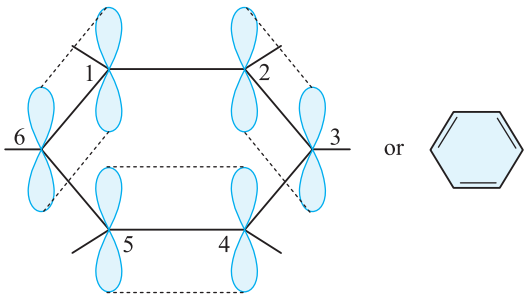
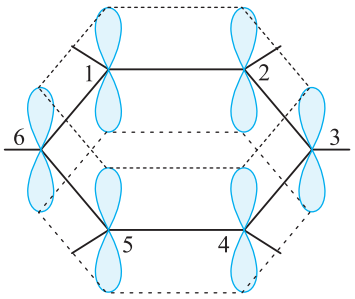


Fig. (4)



or

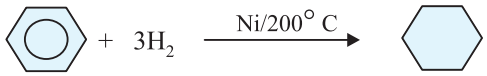
(electron cloud)

≡

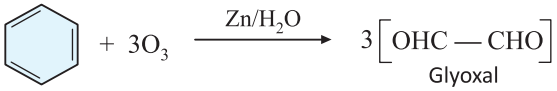
(Resonance hybrid)

The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in figure (4). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable than the hypothetical cyclohexatriene. X-Ray diffraction data reveals that benzene is a planar molecule. It also indicates that all the six C – C bond lengths are of the same order (139 pm) which is intermediate between C – C single bond (154 pm) and C – C double bond (133 pm). This absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene.

1. Addition of Hydrogen (H_2) :



2. Ozonolysis :



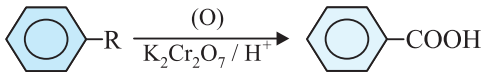
3. Oxidation :

Benzene is unreactive towards even strong oxidising agents such as : $KMnO_4/K_2Cr_2O_7$. However in drastic conditions, it can be oxidised slowly to CO_2 and H_2O. It can be burned (i.e., combustion) to give luminous and smoky flame.

(a) Controlled oxidation with air :

Benzene on oxidation with air at 773 K in presence of V_2O_5 as catalyst gives Maleic anhydride.

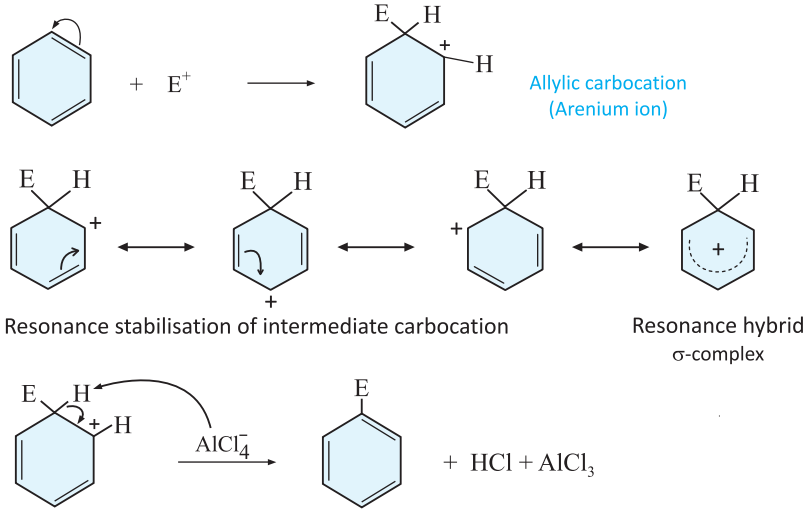
(b) Oxidation of alkyl benzene :



Note : If R is a 3° alkyl group, then it resists oxidation the benzene ring is destroyed.

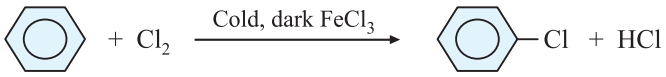
3. Substitution Reactions :

Most important reactions of benzene are electrophillic substitution reactions. These are also denoted as S_E reactions.



Electrophiles : Cl^+ (Chloronium ion), $\overset{+}{N}O_2$ (Nitronium ion), SO_3 (Sulphur trioxide), $\overset{+}{R}$ (Carbocation), $R-C\equiv\overset{+}{O}$ (Acylium ion)

(a) Halogenation :



$$FeCl_3 + Cl_2 \longrightarrow FeCl_4^- + Cl^+$$

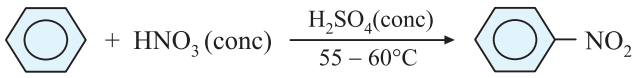
Note : **(i)** In iodination, oxidising agents like HNO_3 or HIO_3 are used to oxidise HI, a reducing agent.

(ii) In presence of sunlight and absence of halogen carriers (i.e., $AlCl_3$, $FeBr_3$, etc), benzene adds three molecules of chlorine to form Benzene hexachloride (BHC) or Gammexane.

$$C_6H_6 + 3Cl_2 \xrightarrow{h\nu} C_6H_6Cl_6$$

It may be noted that this is an addition reaction, not a substitution reaction.

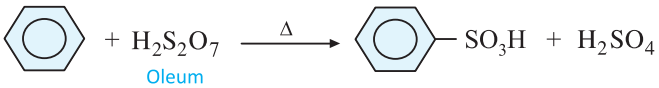
(b) Nitration :



$$\underset{\text{Base}}{HNO_3} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow HSO_4^- + \overset{+}{H}O(H) - NO_2 \longrightarrow NO_2^+ + H_2O$$

(Nitrating mixture)

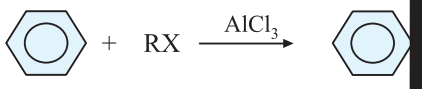
(c) Sulphonation :

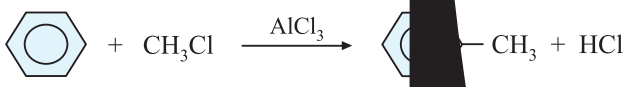


$$H_2S_2O_7 \longrightarrow \underset{\text{electrophile}}{SO_3} + H_2SO_4$$

(d) Introduction of alkyl and acyl groups in pres ce of Catalysts : $AlCl_3$, $FeCl_3$, $SbCl_3$ (acting as Lewis acids) or protonating agents like HF, H_2SO_4, H_3PO_4 etc. T ese are known as Friedal Craft reactions.

(i) Alkylation :





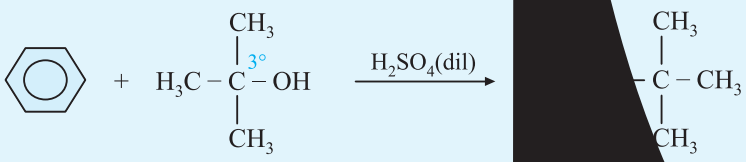
$RCl + AlCl_3 \longrightarrow AlCl_4^- + R^+$ l carbocation)

Electrophile

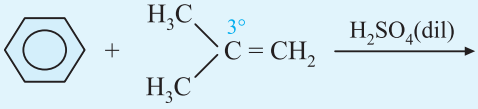
Note : The above reaction can be achieved with :

(a) An alcohol in HF or dil H_2SO_4 **(b)** HF or dil. H_2SO_4 (at low temperature)

(a)

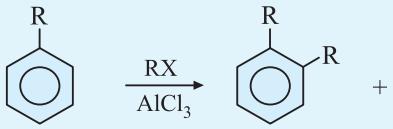


(b)



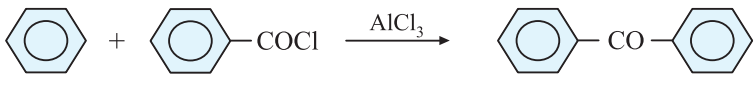
Observe that 3° carbon is attached to the ring.

While doing alkylation, we expect formation of polyalkylated - and *p*-directing and activating



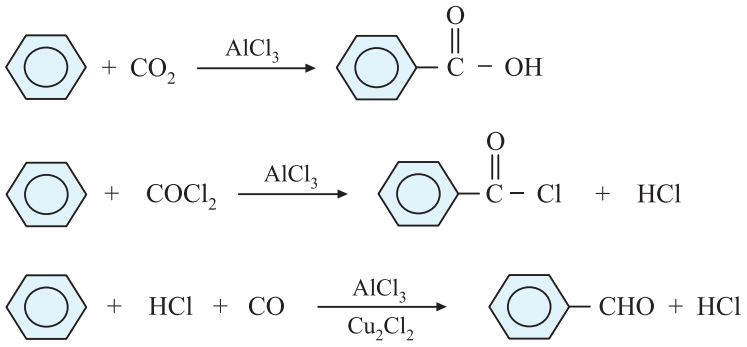
(ii) Acylation :

$RCOCl + AlCl_3 \longrightarrow R-C^{+}=O$ $AlCl_4^-$



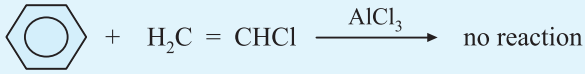
The above two reactions are called as Acetylation and Benzoylation respectively.

Some Friedal Craft acylation are shown below :

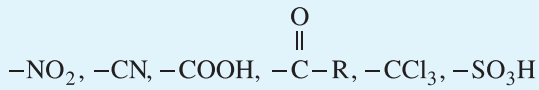


The above reaction is also known as Gatterman - Koch reaction.

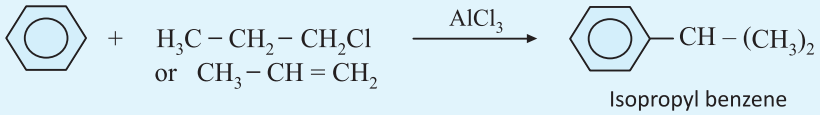
Note : **(i)** Aryl and vinylic halides cannot be used in Friedal craft reactions as they do not form carbocations easily.



(ii) In substituted benzenes, Friedal Craft reactions gives poor yield when electron withdrawing (de-activating) groups are present on the ring. These include :

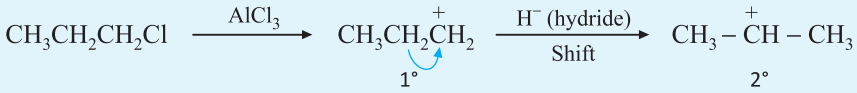


(iii) In Friedal craft alkylation most stable carbocation (from alkyl halide or alkene) determines the final substitution product.



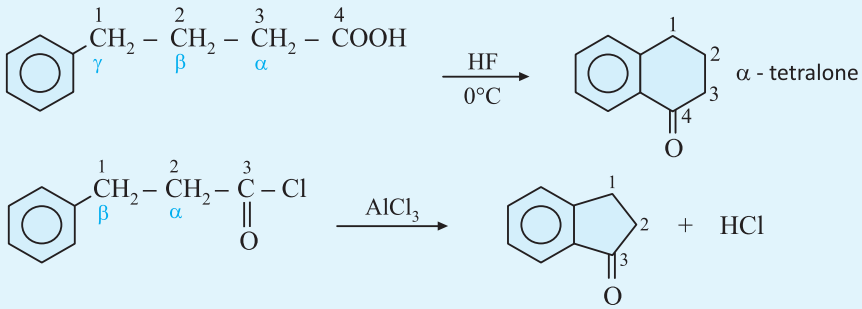
Isopropyl benzene

It does not give n–propyl benzene since $CH_3 - \overset{+}{\underset{2^\circ}{C}}HCH_3$, being a 2° carbocation is more stable than $CH_3CH_2CH_2$(1°).

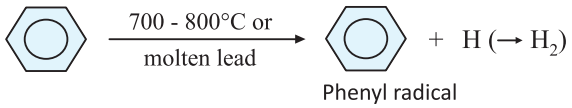


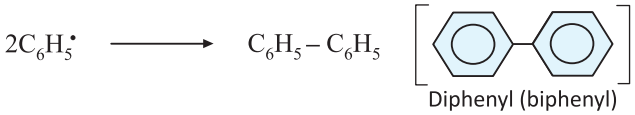
* The detailed mechanism of SE reaction will be discussed later in the chapter "Organic Concepts".

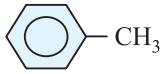
(iv) Intramolecular Friedal Craft reactions of β- & -γ phenyl alkanoic acid or alkanoyl chlorides give cyclic products.



4. Dehydrogenation :

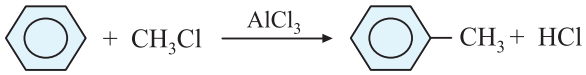




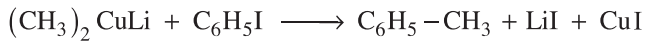
Toluene : 

Preparation of Toluene :

1. Friedal craft alkylation :

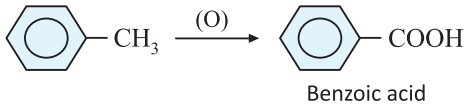


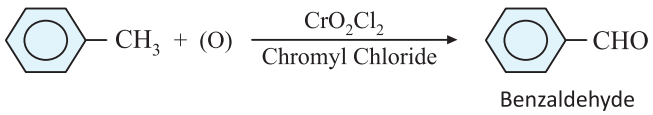
2. From dialkyl cuprates :



Reactions :

1. Oxidation :

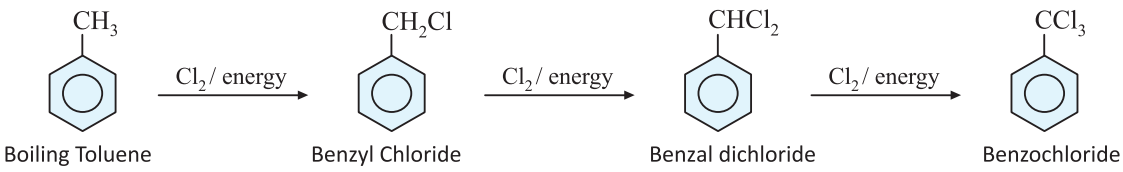
(a) 

(b) 

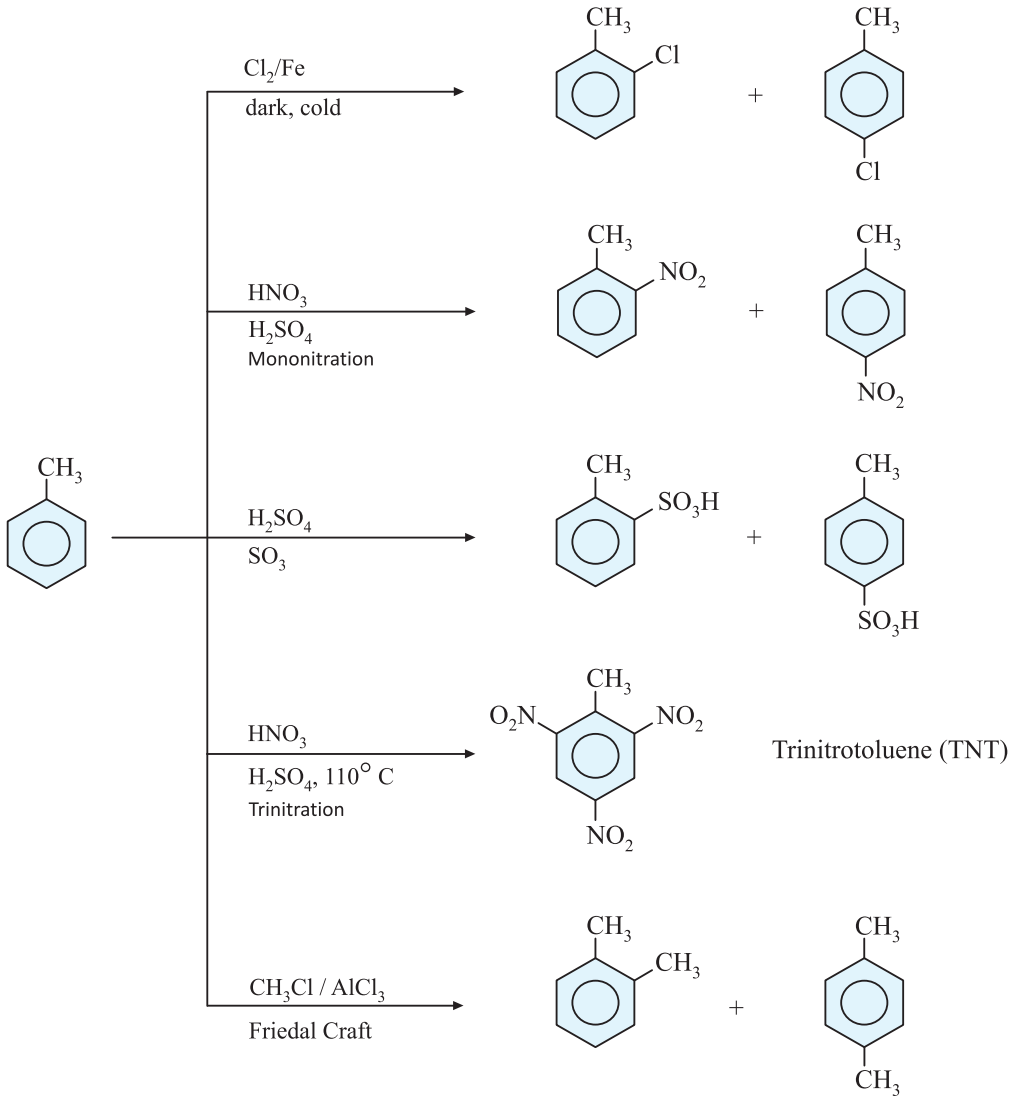
This is also known as Etard reaction.

2. Substitution :

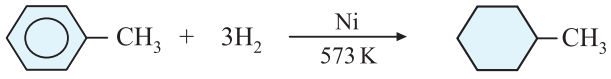
(a) Side chain substitution :



(b) CH_3 group being *o* and *p* directing directs incoming electrophile to *o* and *p* position :



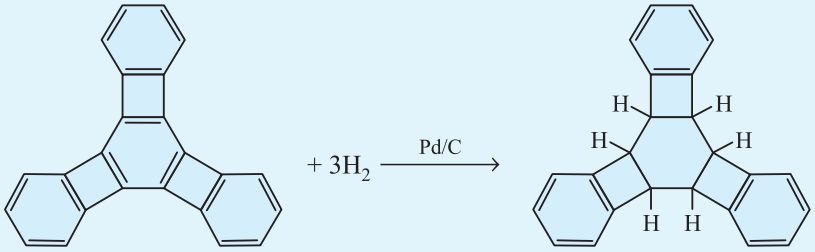
3. Addition Reactions :



Methyl Cyclohexane

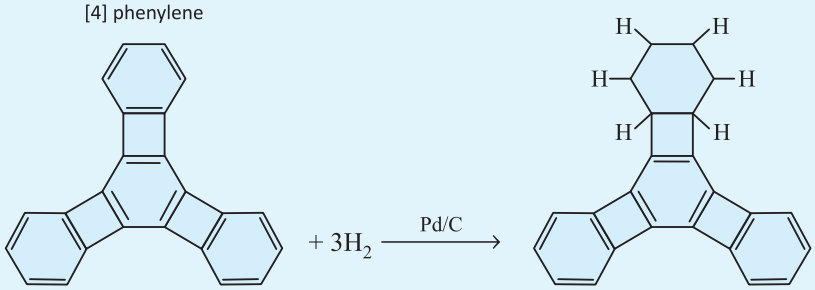
Illustration - 11 *One of the benzene ring of* [4] *phenylene undergoes catalytic hydrogenation readily under conditions usually used for ordinary alkenes, but the other benzene rings do not. Identify which of these two reactions correctly represent product of hydrogenation of* [4] *phenylene* ?

I.



[4] phenylene

II.

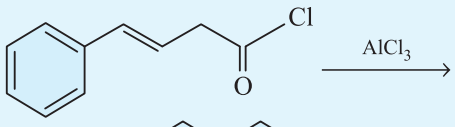


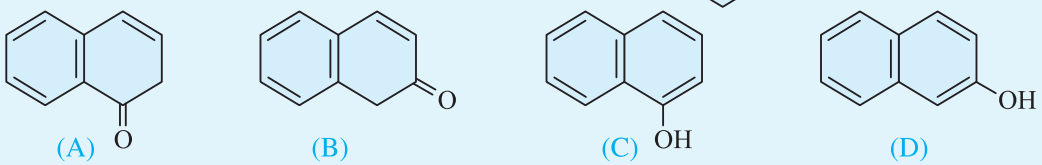
(A) *Only I* **(B)** *Only II* **(C)** *Both I and II* **(D)** *None*

SOLUTION :

Reaction I correctly represent product of hydrogenation of [4]-phenylene because of loss in anti-aromatic characters of all four membered rings.

Illustration - 12 *Which is the major product of the following intramolecular F.C. acylation reaction* ?

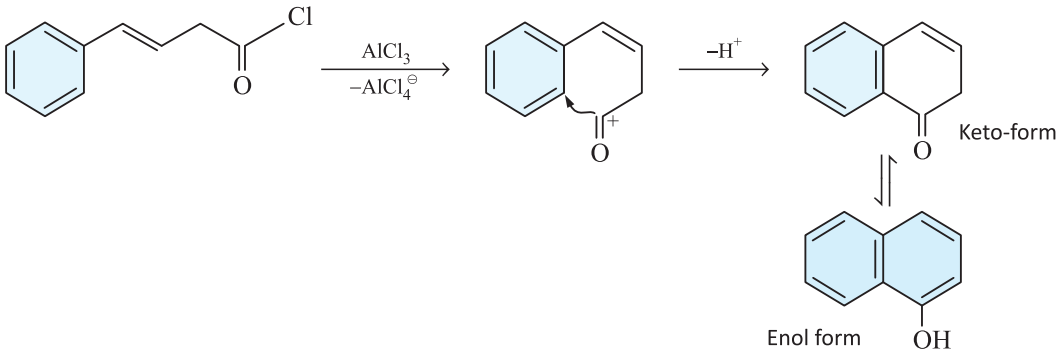




(A) (B) (C) (D)

SOLUTION : (C)

Enolic form is more stable than keto form due to more aromatic characters in enolic form.



IN-CHAPTER EXERCISE-F

1. *Identify the products A, B, C. . . . .*

(i) + $CH_2 - CH = CH_2 \xrightarrow[0°C]{HF} A$
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