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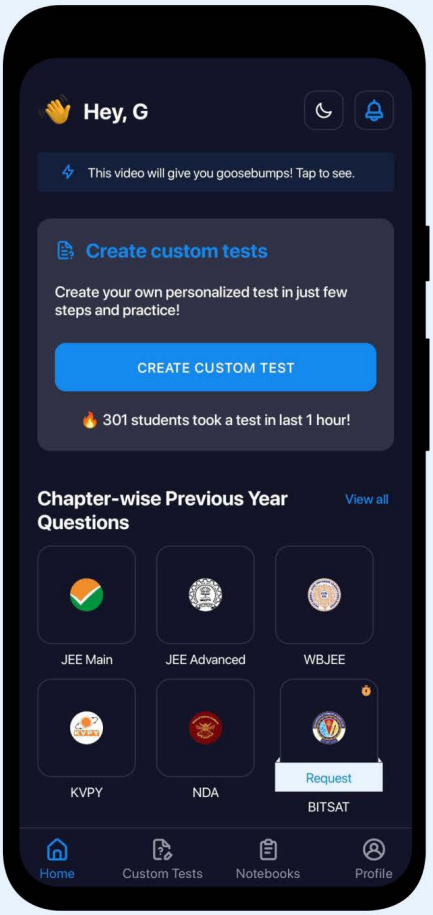

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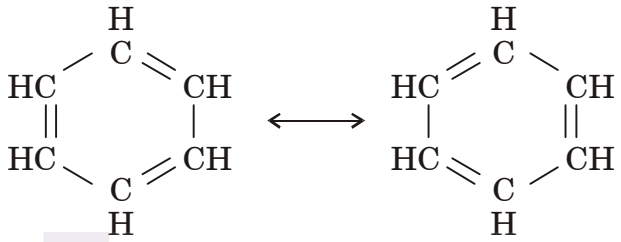
ElectropHilic Aromatic Sustitution

ElectropHilic Aromatic Sustitution

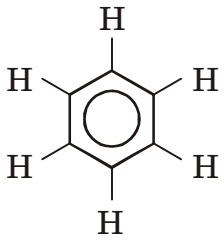
1. AROMATICITY



In **organic chemistry**, the structures of some rings of atoms are unexpectedly stable. Aromaticity is a chemical property in which a conjugated ring of **unsaturated bonds, lone pairs,** or **empty orbitals** exhibit a stabilization stronger than would be expected by the stabilization of conjugation alone. It can also be considered a manifestation of cyclic **delocalization** and of **resonance.**

This is usually considered to be because **electrons** are free to cycle around circular arrangements of **atoms,** which are alternately single and double-**bonded** to one another. These bonds may be seen as a hybrid of a single bond and a double bond, each bond in the ring identical to every other. The **benzene** consists of two **resonance** forms, which corresponds to the double and single bonds' switching positions. Benzene is a more stable molecule than would be expected without accounting for charge delocalization.

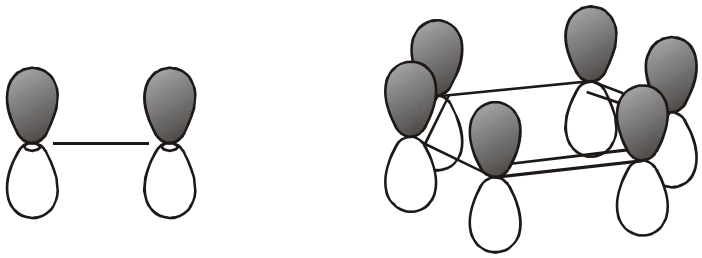
1.1 Theory



A C=C bond is shorter than a C–C bond, but benzene is perfectly hexagonal–all six carbon-carbon bonds have the same **length,** intermediate between that of a **single** and that of a **double bond.**

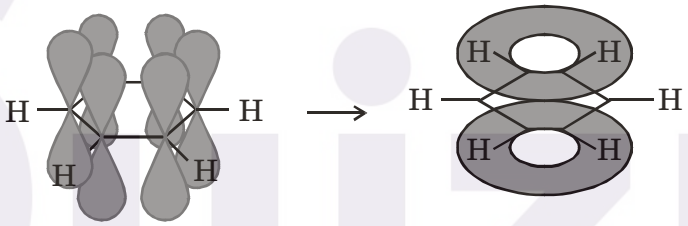
A better representation is that of the circular π bond in which the electron density is evenly distributed through a **π-bond** above and below the ring. This model more correctly represents the location of electron density within the aromatic ring.

The single bonds are formed with electrons in line between the carbon nuclei–these are called **σ-bonds.** Double bonds consists of a σ-bond and a π-bond. The π-bonds are formed from overlap of **atomic p-orbitals** above and below the plane of the ring. The following diagram shows the positions of these p-orbitals :



Side view **Projection**

Since they are out of the plane of the atoms, these orbitals can interact with each other freely, and become delocalised. This means that instead of being tied to one atom of carbon, each electron is shared by all six in the ring. Thus, there are not enough electrons to form double bonds on all the carbon atoms, but the "extra" electrons strengthen all of the bonds on the ring equally. The resulting **molecular orbital** has π symmetry.



6-p-orbitals delocalised orbital clouds

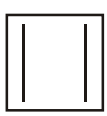
1.2 Characteristics of aromatic (Aryl) compounds

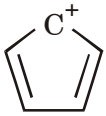
An aromatic compound contains a set of **covalently-bound** atoms with specific characteristics :

1. A **delocalized** conjugated **π** system, most commonly an arrangement of alternating single and double **bonds.**
2. **Coplanar** structure, with all the contributing atom in the same plane.
3. Cyclic in nature
4. A number of π delocalized electrons that is **even, but not a multiple of 4.** That is, 4n + 2 of π electrons, where n = 0, 1, 2, 3 and so on. This is known as **Huckel's Rule.**

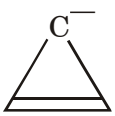
- Aromatic molecules typically display enhanced chemical stability, compared to similar non-aromatic molecules. A molecule that can be aromatic will tend to alter its electronic or conformational structure to be in this situation. This extra stability changes the chemistry of the molecule.
- Many of the earliest-known examples of aromatic compounds, such as benzene and toluene, have distinctive pleasant smells. This property led to the term "aromatic" for this class of compounds, and hence the term "aromaticity" for the eventually-discovered electronic property.

1.3 Antiaromaticity

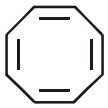

A



B



C


Cyclooctatetraene

Antiaromatic molecules are **cyclic** systems containing alternating single and **double bonds,** where the **pi electron** energy of antiaromatic compounds is higher than that of its open-chain counterpart. Therefor antiaromatic compounds are unstable and highly reactive; often antiaromatic compounds distort themselves out of planarity to resolve this instability. Antiaromatic compounds usually fail **Huckel's rule** of **aromaticity.**

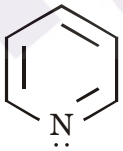
Examples of antiaromatic systems are **cyclobutadiene** (A), the cyclopentadienyl cation (B) and the cyclopropenyl anion (C). **Cyclooctatetraene** is a 4n system but neither aromatic or antiaromatic because the molecule escapes a planar geometry.

By adding or removing an electron pair via a **redox** reaction, a π system can become aromatic and therefore more stable than the original non- or anti-aromatic compound, for instance the **cyclooctatetraenide dianion.** The **IUPAC** criteria for **antiaromaticity** are as follows :

1. The molecule must have 4n π electrons where n is any integer.
2. The molecule must be cyclic.
3. The molecule must have a conjugated pi electron system.
4. The molecule must be planar.

Example 1

Is this compound aromatic or antiaromatic ?



Solution :

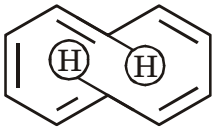
The given compound, pyridine is aromatic as total no. of conjugated electrons

= 6 = 4n + 2 where n = 1.

Here lone pair of Nitrogen is not involved in delocalisation.

EXCEPTIONS

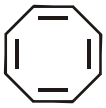
(1)



Here no. of π e^- = 10

Molecule will be aromatic if planar. But due to the repulsion between hydrogens, molecule lose its planarity.

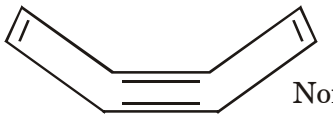
(2)



Here no. of π e^- = 8

This molecules should be antiaromatic.

But its not planar. Its real structure is non planar.



Nonplanar

Therefore this molecule is nonaromatic.

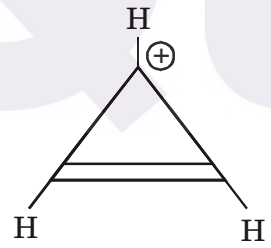
1.4 Stability of Compounds

Order of stability is :

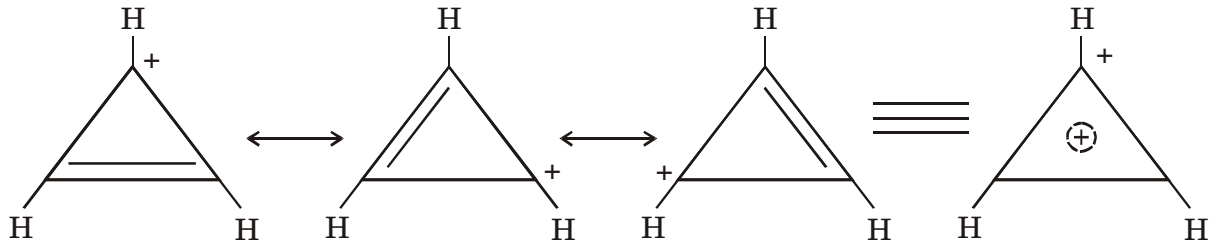
aromatic > nonaromatic > antiaromatic

Stability order is explained on basis of constructive and destructive resonance in aromatic and antiaromatic compound respectively; which comes under molecular orbital theory.

1.5 Cyclopropenium salts



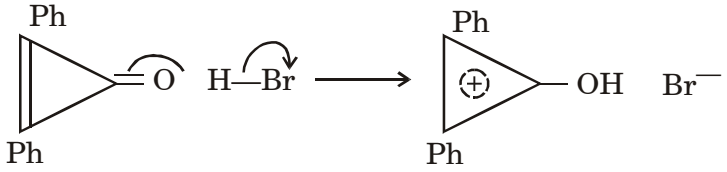
This is the cyclopropenyl cation and may be represented as a resonance hybrid.

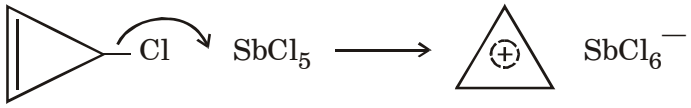


Hence the cyclopropenyl cation should be stable. Many cyclopropenium salts have actually been prepared.

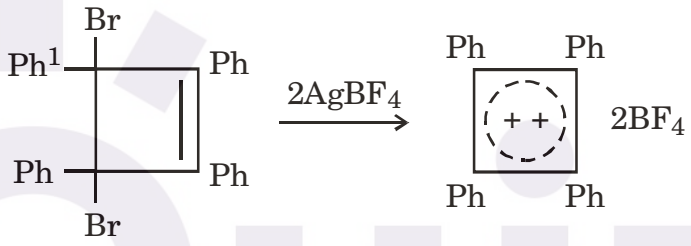
e.g. (i) hydroxydiphenyl propenyl bromide

(ii) cyclopropenyl hexachloroantimonate.

(i) 

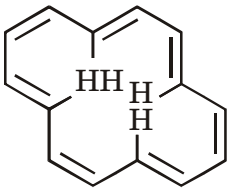
(ii) 

1.6 Cyclobutenium salts

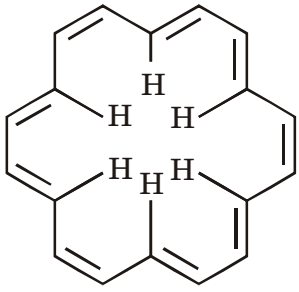


1.7 Annulenes

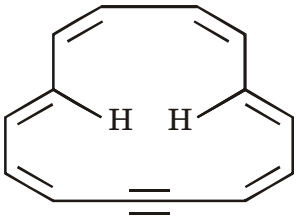
Conjugated monocyclic polyenes, C_nH_n, in which n ≥ 10 are usually called onnulenes. The annulenes prepared have n = 12, 14, 16, 18, 20, 24 and 30, of these only [14], [18] and [30] annulenes are (4n + 2) π electron molecules and rest ore 4nπ molecules.



[14] annulene

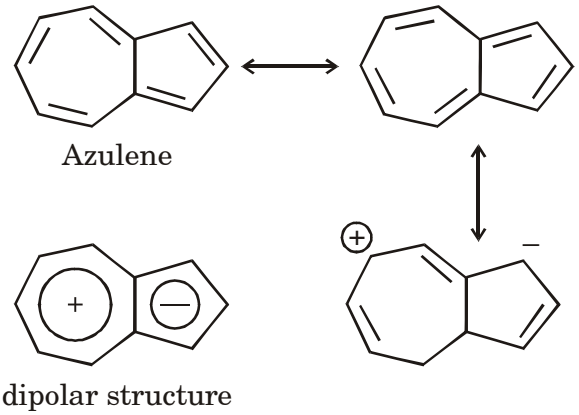


[18] annulene



dehydro
[14] annulene

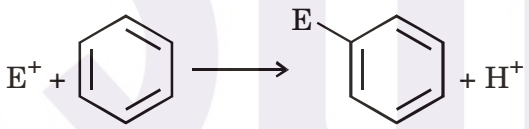
1.8 Azulene



There are two KeKule resonating structures containing 10 π electrons (n = 2; and 10 peripheral π-electrons). The five membered ring has five and the seven membered ring has seven π–electrons (two π–electrons are common to both rings). If one π–electron is transferred from seven to the five ring each ring will now have a closed shell of six π–electrons. In this condition, the molecule will have a dipolar structure.

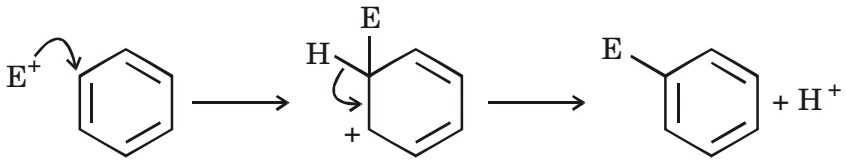
2. ELECTROPHILIC AROMATIC SUBSTITUTION

Overall an electrophilic aromatic susbtituton can be represented as follows :



There are three fundamental compounds to an electrophilic substitution reaction :

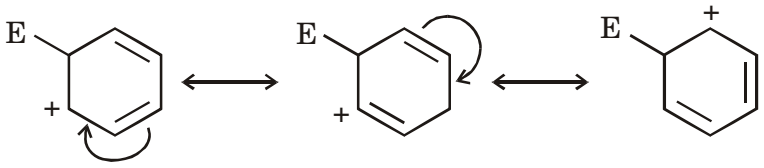
1. Formation of the new σ bond from a C=C in the arene nucleophile
2. removal of the proton by breaking the C-H σ bond
3. reform the C=C and restore aromaticity



The mechanism is represented by the following series of events :

- Formation of the reactive electrophile, **E^+**
- Slow reaction of the arene C=C with the **E^+** to give a resonance stabilised **carbocation** (see below)

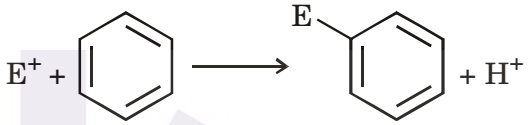
ı Loss of H^+ from the carbocation to restore the **C=C** and the aromatic system



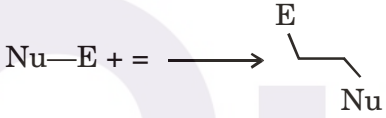
The reaction of the electrophile E^+ with the arene is the slow step since it results in the loss of aromaticity even though the resulting cation is still resonance stablised.

Why Substitution not Addition ?

Overall an electrophilic aromatic substitution can be represented as follows :

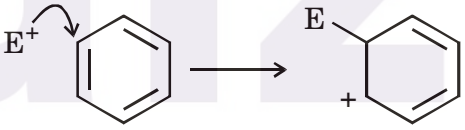


But we have **previously** seen the **C=C** generally react via an electrophilic addition pathway :

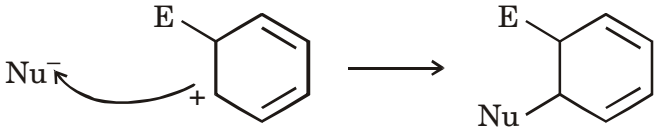


So why don't arenes react in a similar fashion to alkenes and give overall addition ?

The first step is common to both, E^+ adds a **C=C** to give a carbocation intermediate.

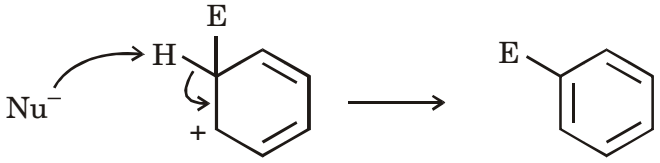


For an **addition** pathway, the nucleophile then adds to the electrophilic carbocation giving a cyclohexadien e derivative.



addition

For a **substitution** pathway "nucleophile" functions as a base and removes a proton from the sp^3 C to recreate the **C=C** and restore the aromaticity.



+ NuH
substitution

The resonance energy of benzene is about 152 kJ / mol (36 kcal / mol) and a conjugated diene is 16 kJ / mol (4 kcal / mol).This extra stability of the aromatic system is responsible for favouring the substitution reaction.

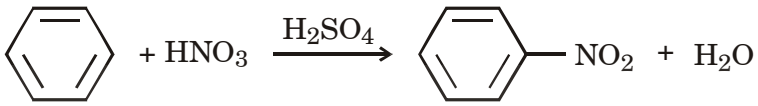
ı An electrophilic substitution reaction on benzene does not always result in monosubstitution. While electrophilic substituents usually withdraw electrons from the aromatic ring and thus deactivate it against further reaction, a sufficiently strong electrophile can perform a second or even a third substitution. This is especially the case with the use of **catalysts.**

3. SOME BASIC REACTIONS

3.1 Nitration

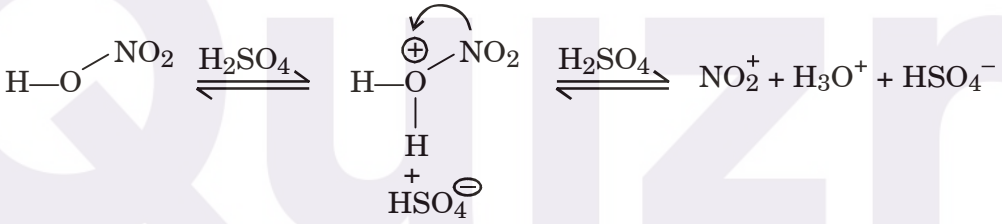
Aromatic nitration

In a **aromatic nitration, aromatic organic compounds** are nitrated via an **electrophilic aromatic substitution** mechanism involving the attack of the electron-rich **benzene** ring by the **nitronium ion.**



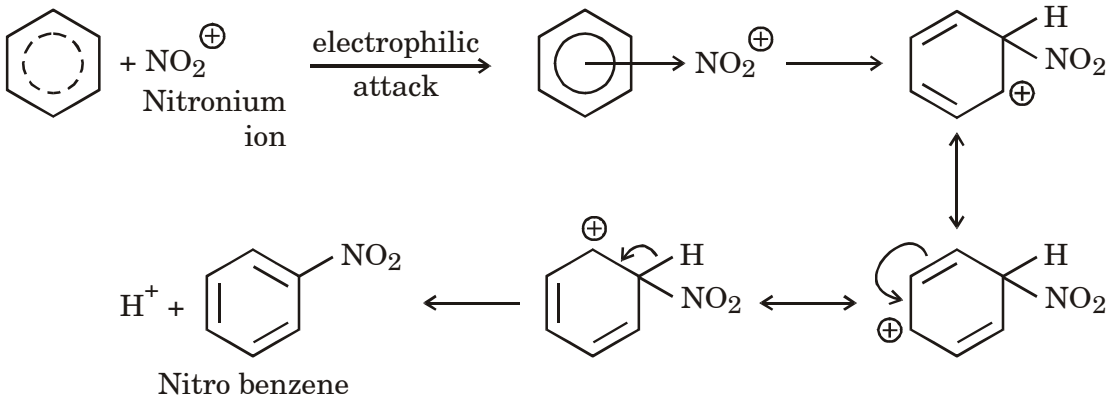
Benzene is nitrated by refluxing with concentrated sulfuric acid and concentrated nitric acid at 50 C. The sulfuric acid is regenerated and hence acts as a **catalyst.** It also absorbs water.

The formation of a nitronium ion (the electrophile) from nitric acid and sulfuric acid and subsequent reaction of the ion with benzene is shown below :



i.e. $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^{\oplus} + 2HSO_4^{\ominus}$

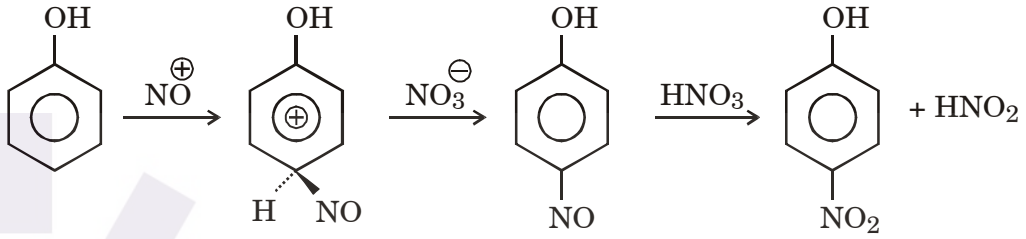
Now the NO_2^+ ion attacks the benzene nucleus and forms an intermediate cation, a benzenonium ion; which loses a proton to yield the nitro derivative.



The nitronium ion is well known existing in salts such as $NO_2^+ \ ClO_4^-$ and $NO_2^+ \ BF_4^-$ which smoothly nitrate benzene at room temperature. It supports the mechanism in which the electrophile species attacking the aromatic compound is nitronium ion NO_2^+.

Highly reactive aromatic compounds such as phenol, are found to undergo ready nitration even in dilute nitric acid and at a far more rapid pace than can be explained on the basis of the concentration of $NO_2^{\oplus}$ that is present in the mixture. This has been shown due to the presence of nitrous acid in the system which nitrosates the reactive nucleus via the nitrosonium ion $\overset{\oplus}{N}O$.

$$HNO_2 + 2HNO_3 \rightleftharpoons H_3O^{\oplus} + 2NO_3^{\odot} + \overset{\oplus}{N}O$$



3.2.1 Some Important Points

NO_2^+ can be generated by :

(i) Mixture of HNO_3 & any other acid stronger than HNO_3 to generated NO_2^+.

HNO_3 / conc. H_2SO_4

It is behaves base — It is behaves as an acid

$$H_2SO_4 + OH - NO_2 \longrightarrow NO_2^+ + HSO_4^- + H_2O$$

(ii) Conc. $HNO_3 + HO\text{-}NO_2 \rightarrow NO_2^+ + H_2O + HNO_3^-$

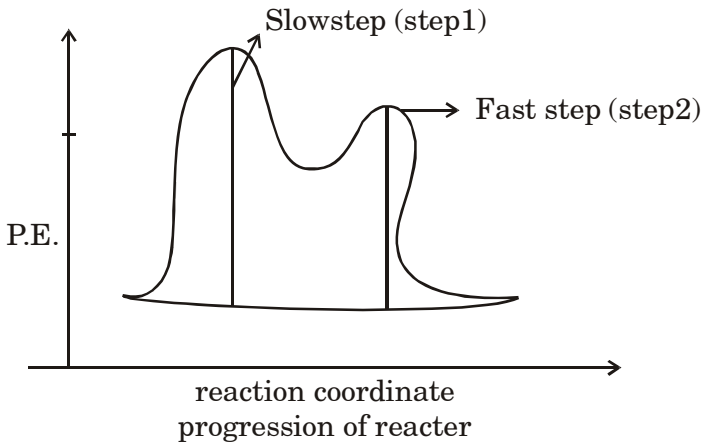
(iii) $N_2O_5 \rightarrow NO_2^+ + NO_3^-$

(iv) $NO_2^+ \ BF_4^- \rightarrow NO_2^+ + BF_4^-$

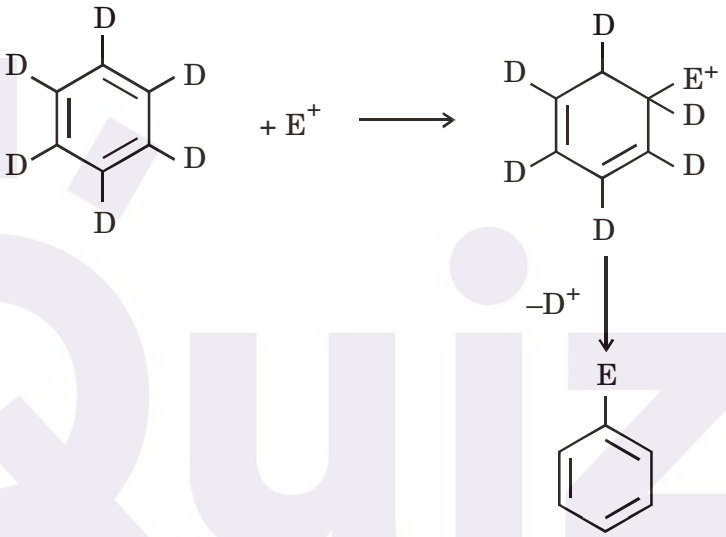
Ist step is slow step mechanism because compound loses its aromaticity.

In IInd step compound gains aromaticity, it is highly fast.

Potential energy curve with the progression of reaction is given by :



If H in Benzene is replaced by D, then



Here $E^+ = NO_2^+$

Comparison of rates

Let for the first reaction the value of rate constant is k_H and that for IInd is k_D then which can be true.

(i) $k_H > k_D$

(ii) $k_H < k_D$

(iii) $k_H = k_D$

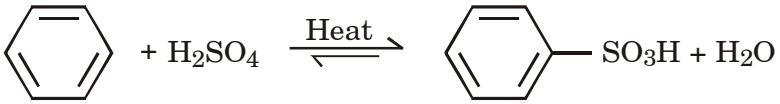
(iv) can't say **Ans. :** $K_H > K_D$

Explanation

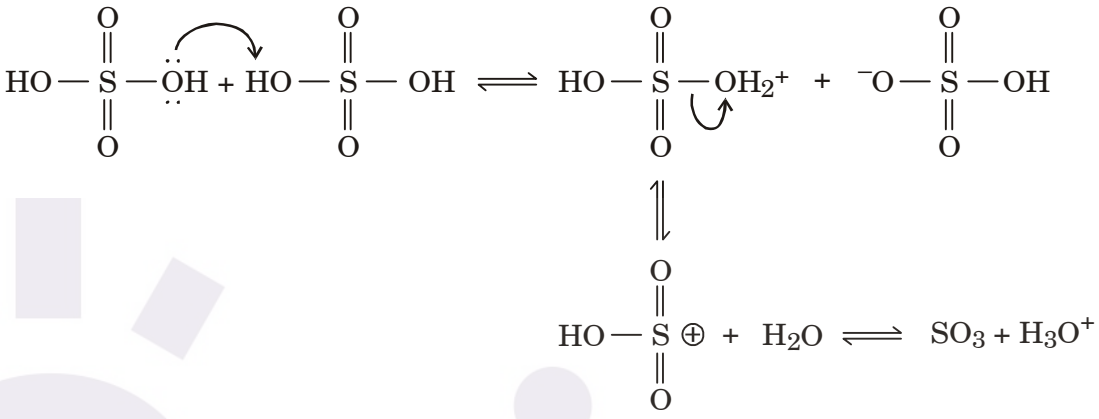
C – D bond is stronger than C-H.

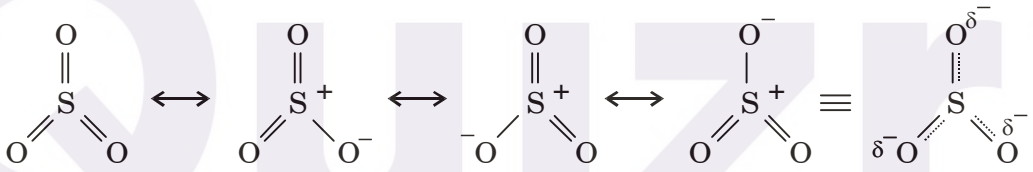
3.2 Aromatic Sulfonation

Aromatic sulfonation is an **organic reaction** in which a hydrogen atom on an **arene** is replaced by a **sulfonic acid functional group** in an **electrophilic aromatic substitution.**



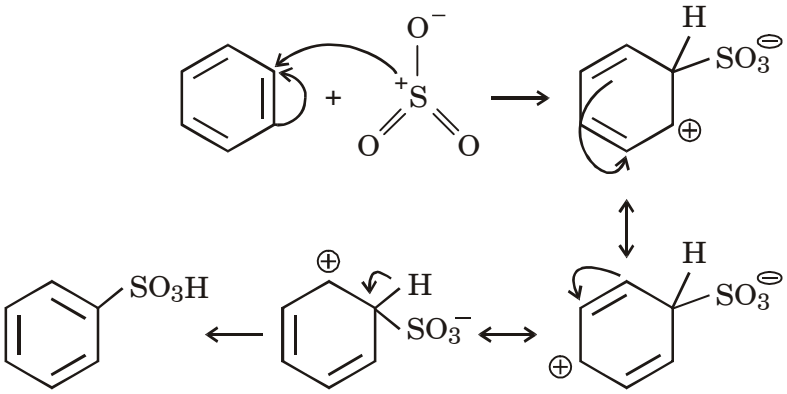
Sulfur trioxide is the **electrophile** in this reaction generated from concentrated **sulfuric acid** (or fuming sulfuric acid) when heated.





In contrast to **aromatic nitration** and other electrophilic aromatic substitution this reaction is **reversible.** Sulfonation takes place in concentrated acidic conditions and desulfonation is the mode of action in a dilute hot aqueous acid.

Mechanism of sulphonation



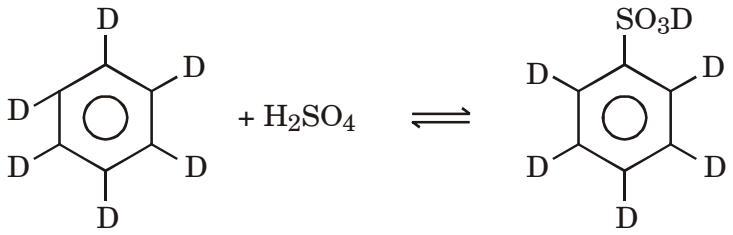
S is bonded to three more electronegative oxygen atoms. Hence, S is electron deficient, acting as electrophile.

More Important Points

Increase of sulphonation **the electrophile is SO_3.**

- SO_3 has vacant orbital, therefore it is electrophile.
- Both the steps are in equilibrium in the mechanism.

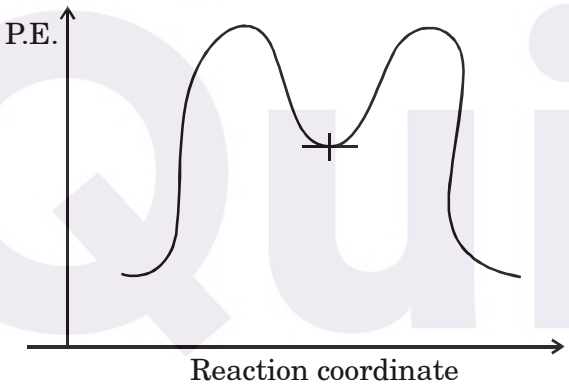
Comparison with Deutrobenzene :



$$K_H > K_D$$

This reaction is reversible.

Energy Profile

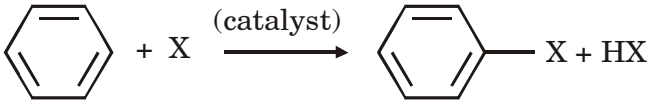


Reaction is reversible. Carbocation can proceed in both forward and backward direction. IInd step is not the fast step. Both the step will contribute to stability of product.

C – D bond is stronger than C-H bond.

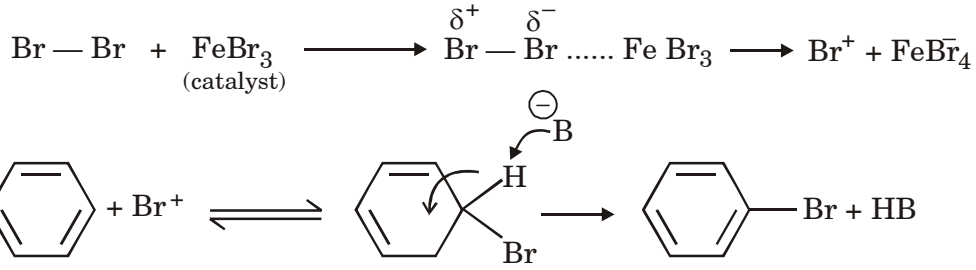
3.3 Electrophilic halogenation

In **organic chemistry,** an **electrophilic aromatic halogenation** is also a type of **electrophilic aromatic substitution.** This **organic reaction** is typical of **aromatic** compounds and a very useful method for adding substituents to an aromatic system.



A few types of aromatic compounds, such as **phenol,** will react without a **catalyst,** but for typical benzene derivatives with less reactive substrates, a **Lewis acid catalyst** is required. Typical Lewis acid catalysts include $AlCl_3$, $FeBr_3$, and $ZnCl_2$. These work by forming a highly **electrophilic complex** which attacks the benzene ring.

Reaction mechanism

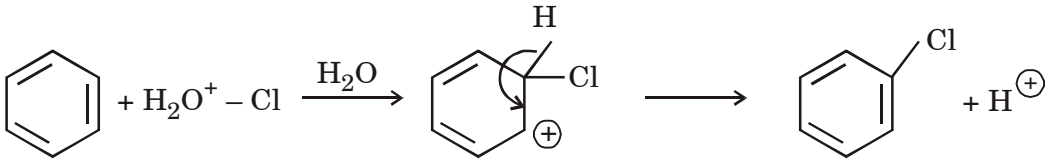


- The **reaction mechanism** for chlorination of benzene is the same as bromination of benzene. **Ferric bromide** and **ferric chloride** become inactivated if they react with water, including moisture in the air. Therefore, they are generated in situ by adding iron filings to bromine or chlorine.
- Halogenation of aromatic compounds differs from the halogenation of **alkenes,** which do not require a **Lewis Acid** catalyst. The formation of the **arenium ion** results in the temporary loss of **aromaticity,** which has a higher **activation energy** compared to carbocation formation in alkenes. In other words, alkenes are more reactive and do not need to have the Br-Br or Cl-Cl bond weakened.

Important point

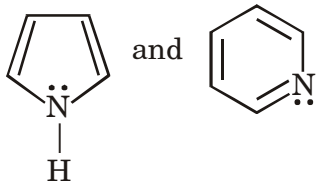
A similar dual mechanism can also operate when halogenation is carried out with hypochlorous and hypobromous acid. The reaction is acid catalysed.

$H–O–Cl+H^+ \rightarrow H_2O^+–Cl$



Example 4

Among pyrrole and pyridine, Which is more basic and why?



(pyrrole) (pyridine)

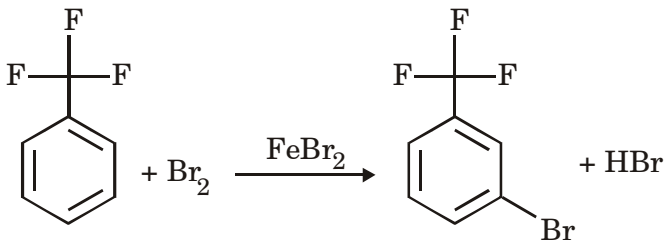
Solution :

Pyridine is more basic than pyrrole because in case of pyridine nitrogen lone pair does not participate in aromaticity.

Example 5

Write the product of mono bromination of $C_6H_5CF_3$.

Solution :

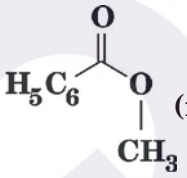


$-CF_3$ shows (– I) effect. Hence it is behave as M-directing group.

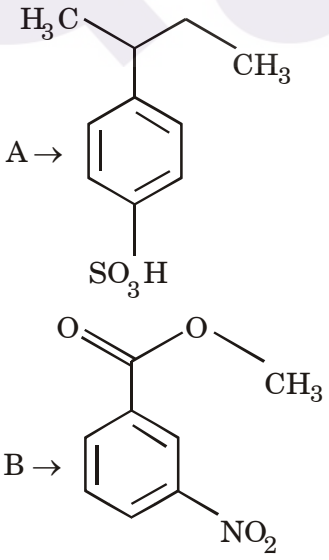
Example 6

Find out products in following conversion.

(i) $C_6H_5CH\ (CH_3)CH_2CH_2$ (monosulfonation) → (A)

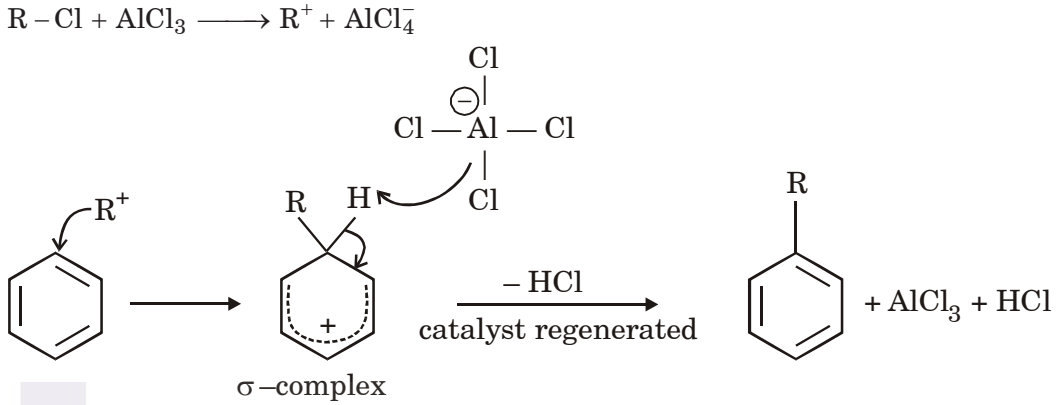
(ii)  **(mononitration) ⟶ (B)**

Solution :



3.4 Friedel-Crafts alkylation

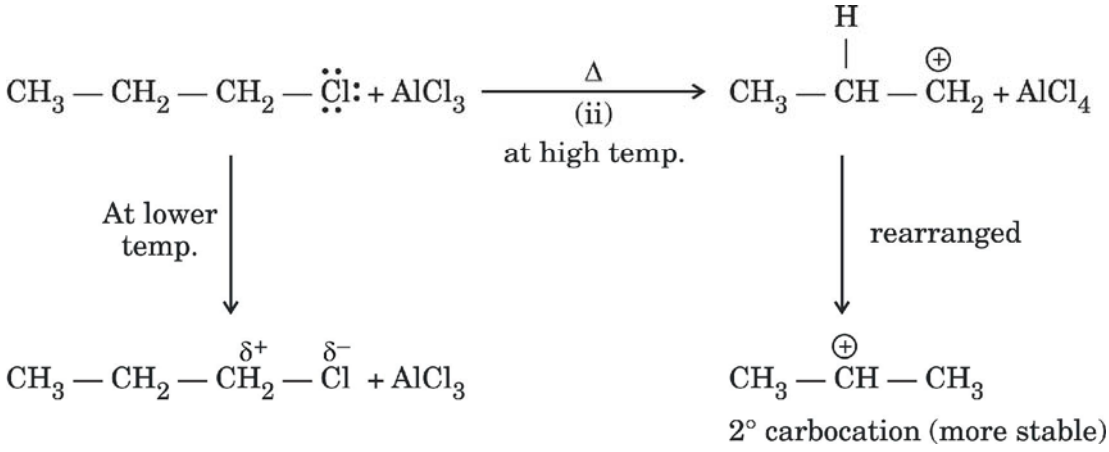
Friedel-Crafts alkylation involves the alkylation of an **aromatic ring and an alkyl halide** using a strong **Lewis acid** catalyst. With anhydrous **Aluminium chloride** as a **catalyst,** the alkyl group attaches at the former site of the chloride ion. The general mechanism is shown below.

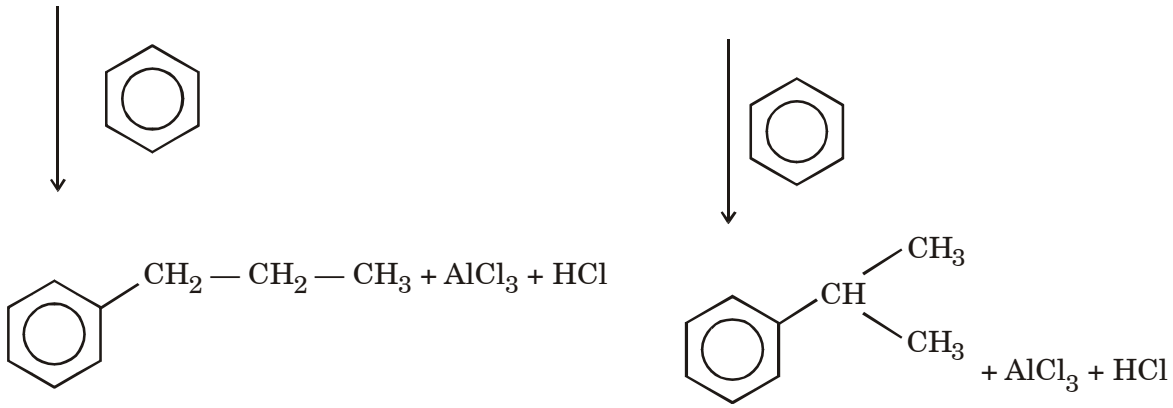


Important points

1. This reaction has one big disadvantage, namely that the product is more **nucleophilic** than the reactant due to the election donating alkyl-chain. Therefore, another hydrogen is substituted with an alkyl-chain, which leads to overalkylation of the molecule.
2. Also, if the chlorine is not on a **tertiary carbon, carbocation rearrangement reaction** will occur. This is due to the relative stability of the tertiary **carbocation** over the secondary and primary carbocations.

   Alkylations are not limited to alkyl halides : Friedel-Crafts reactions are possible with any **carbocationic** intermediate such as those derived from **alkenes.**
3. Not only nature of alkyl group, but also temperature determines the nature of electrophile. e.g. n-alkyl group can be introduced to a fair extent without rearrangement at low temperature, because ionisation of oduct is retarted. But at higher temperature, carbonium ion is formed which rearranges and the product is rearranged alkyl benzene. Thus n-propylchloride gives isopropyl benzene.





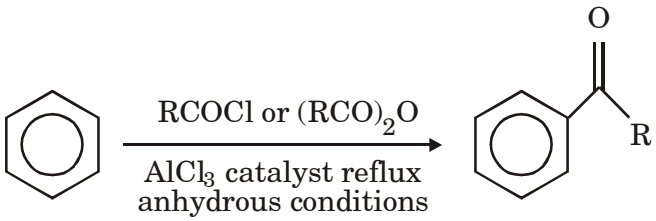
4. The order of effectiveness of Lewis acid catalysts has been shown to be

$AlCl_3 > FeCl_3 > BF_3 > TiCl_3 > ZnCl_2 > SnCl_4$

The action of $Me_3CCH_2/AlCl_3$ on benzene is found to yield almost completely the rearranged product $PhCMe_2\ CH_2Me$, while $Me_3CCH_2Cl/FeCl_3$ on benzene is found to yield almost completely the unrearranged product.

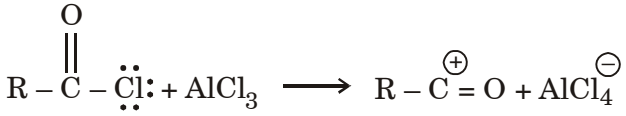
3.4.2 Friedel-Crafts acylation

- Friedel-Crafts acylation is the **acylation** of aromatic rings with an **acyl chloride** using a strong **Lewis acid** catalyst.
- Friedel-Crafts acylation is also possible with **acid anhydrides.**
- Reaction conditions are similar to the Friedel-Crafts alkylation mentioned above. This reaction has several advantages over the alkylation reaction. Due to the electron-withdrawing effect of the **carbonyl** group, the **ketone** product is always less reactive than the original molecule, so multiple acylations do not occur. Also, there are no **carbocation** rearrangements, as the carbonium ion is stabilized by a resonance structure in which the positive charge is on the oxygen.

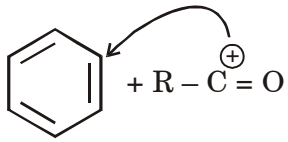


Reaction mechanism

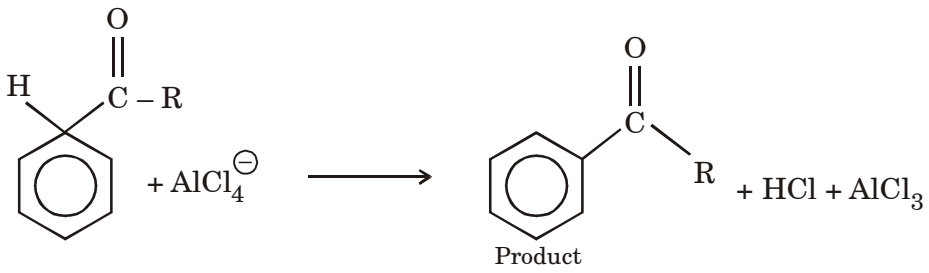
In a simple mechanism view, the first step consists of dissociation of a chlorine atom to form an **acyl** cation



This is followed by electrophilic acylcation toward the arene.



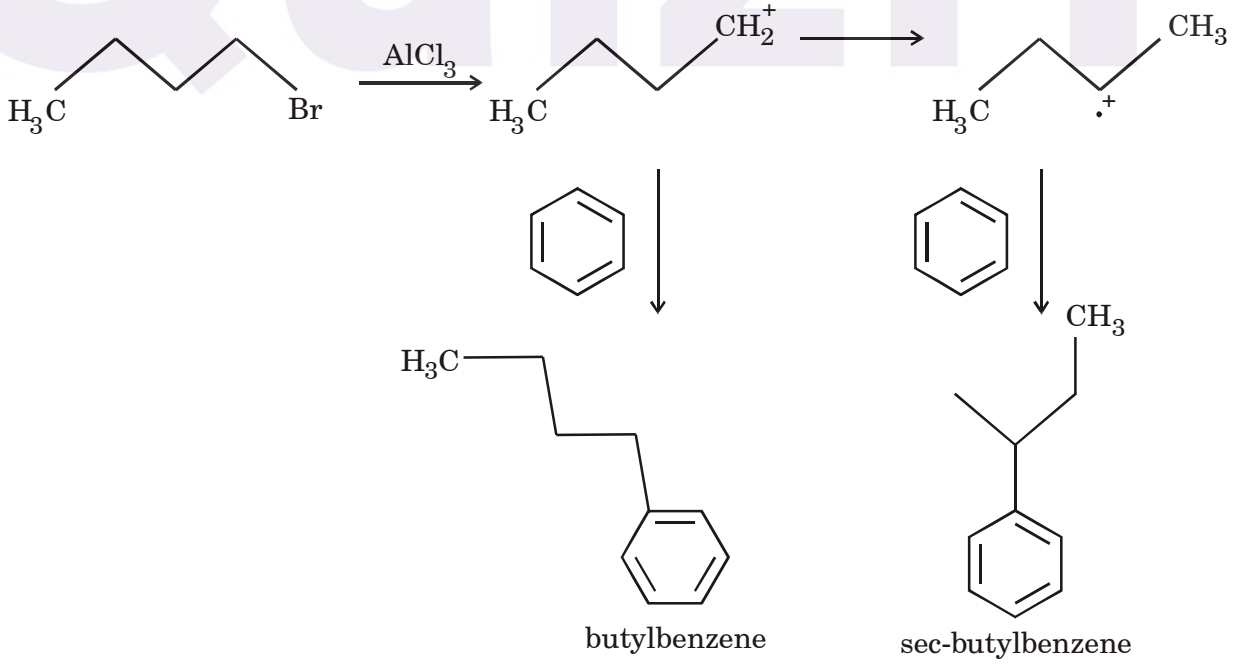
Finally, a chlorine atom reacts to form HCl, and the $AlCl_3$ catalyst is regnerated.



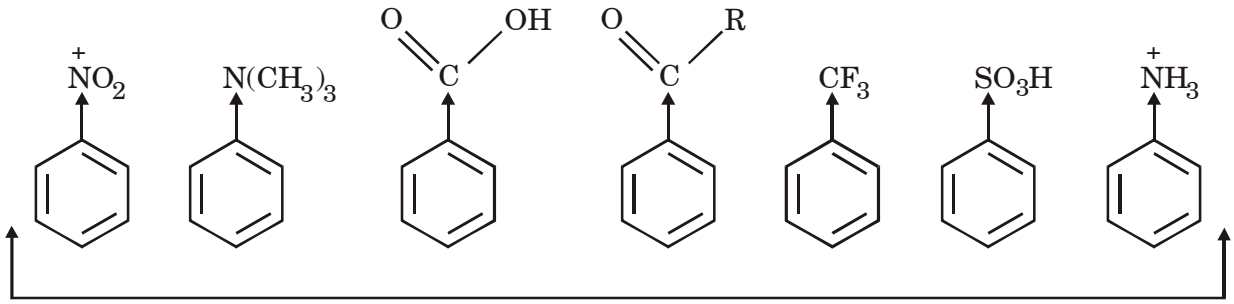
Limitations of Friedel-Crafts reactions

Several restrictions limit the usefulness of Friedel-Crafts reactions :

(1) When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation, it usually does so and the major product obtained from the reaction is usually the one from the more stable carbocation. When benzene is alkylated with butyl bromide, for example, some of the developing butyl cations rearrange by a hydride shift – some developing 1 carbocations (see following reactions) become more stable 2 carbocations. Then benzene reacts with both kinds of carbocations to form both butylbenzene and sec-butyl benzene.

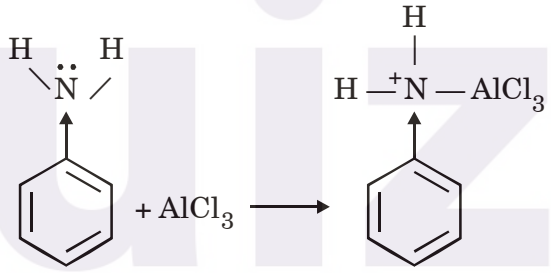


(2) Friedel-Crafts reactions do not occur when powerful electron-withdrawing groups are present on the aromatic ring or when the ring bears an $-NH_2$, – NHR, or $-NR_2$ group. This applies to alkylations and acylations.



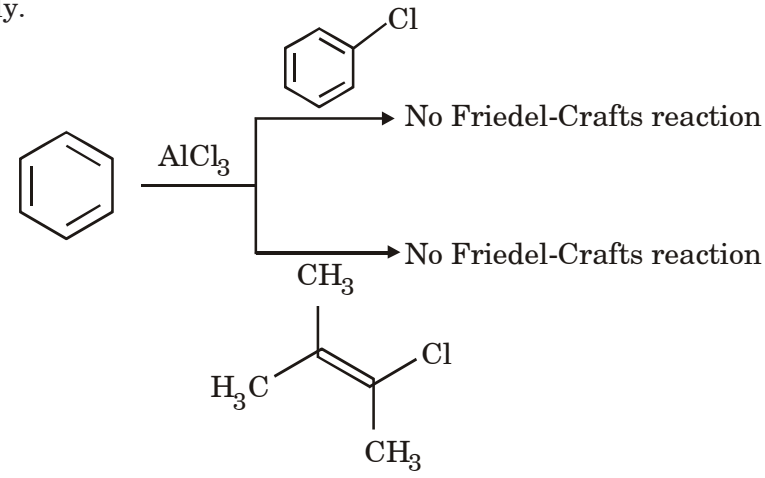
These do not undergo Friedel-Crefts reactions

We shall learn that the groups present on an aromatic ring can have large effect on the reactivity of the ring towards electrophilic aromatic substitution. Electron-withdrawing groups make the ring less reactive by making it electron deficient. Any substituent more electron withdrawing (or deactivating) than a halogen, that is, any meta-directing group, makes an aromatic ring too electron deficient to undergo a Friedel-Crafts reaction. The amino groups, $-NH_2$, – NHR, and $-NR_2$ are changed into powerful electron-withdrawing groups by the Lewis acids used to catalyze Friedel-Crafts reactions. For example :

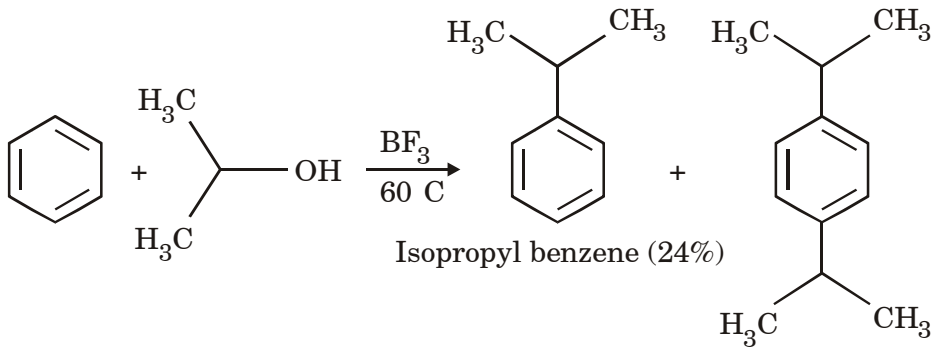


Does not undergo a
Friedel-Crafts reaction

(3) Aryl and vinyl halides cannot be used as the halide component because they do not form carbocations readily.



(4) Polyalkylations often occur. Alkyl groups are electron -releasing groups, and once one is introduced into the benzene ring it activates the ring toward further substitution.



Polyalkylations are not a problem in Friedel-Crafts acylations, however the acyl group (RCO–) by itself is an electron-withdrawing group, and when it forms a complex with $AlCl_3$ in the last step of the reaction, it is made even more electron withdrawing. This strongly inhibits further substitution and makes monoacylation easy.

Example 7

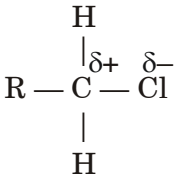
What happens when benzene is treated with methyl chloride in presence of anhydrous $AlCl_3$ and the product is treated with excess of chlorine in presence of UV light ?

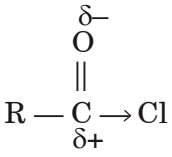
Solution :

$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \xrightarrow[AlCl_3]{\text{anhy}} C_6H_5CH_3 \xrightarrow[\text{UV light}]{Cl_2} C_6H_5CH_2Cl \xrightarrow{Cl_2} C_6H_5CHCl_2 \xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3}$$

Comparison between alkylation and acylation

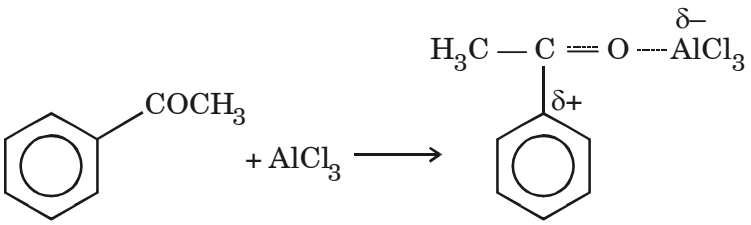
(i) A comparison of the electrophilic nature of both alkyl and acyl group indicates that acyl group is a better electrophile on account of two electron withdrawing atoms attached to C.





Effective +ve charge density on carbonyl compound is greater.

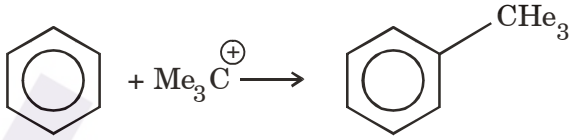
(ii) Acylation requires more catalyst than alkylation because much of the catalyst is removed by the formation of a complex with the product (ketone) and is removed from further participation in the reaction.



(iii) Unlike polyalkylation, polyacylation does not take place as the product ketone is much less reactive than the original hydrocarbon.

(iv) Rearrangement of R does not take place in acylation, but decarbonylation can take place, especially where R would form a stable carbonium ion, so that the end result is then alkylation rather that the expected anylation.

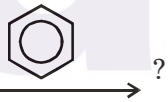
e.g. $Me_3C - C^{\oplus} = O \xrightarrow{\Delta} CO + Me_3C^{\oplus}$

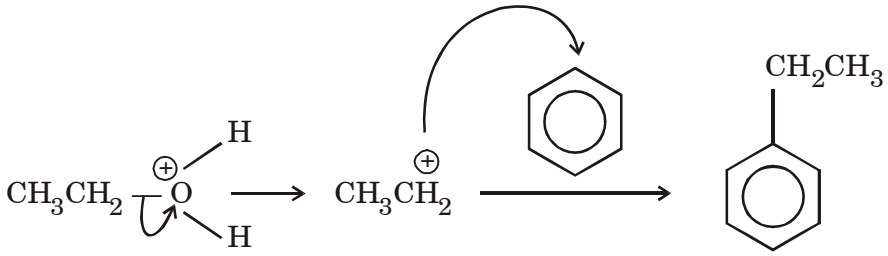


3.5 Some Important Reactions

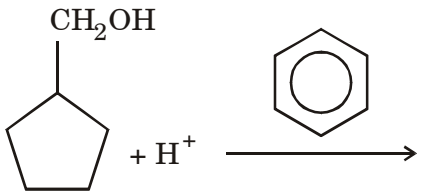
(1) Reaction of alcohols + Acid + 

Solution :

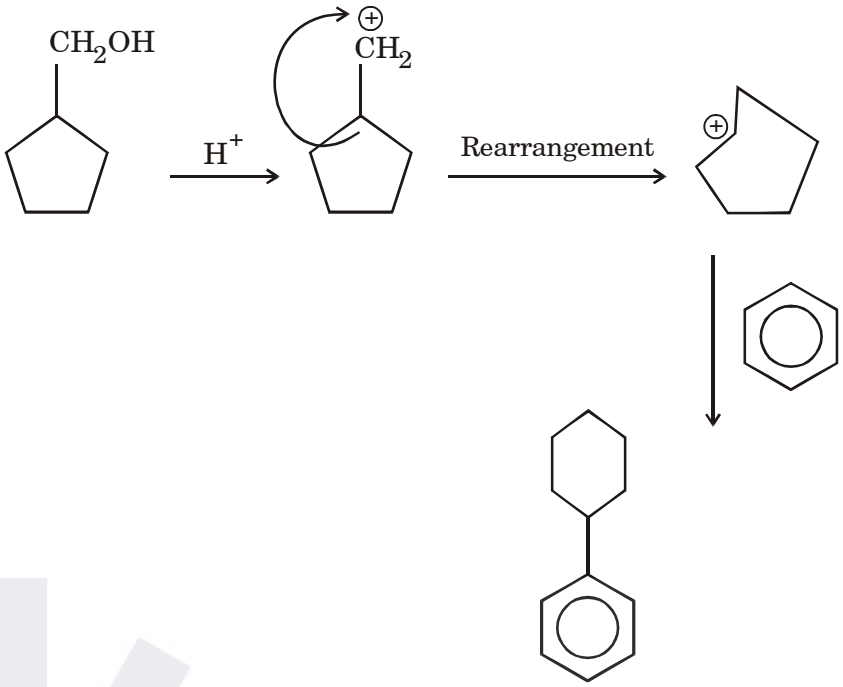
(i) $CH_3\ CH_2OH + H^+$  ?



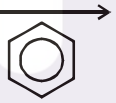
(ii)



Solution :



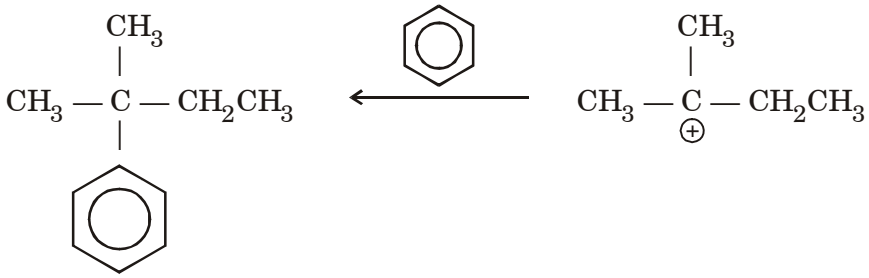
(2) Reaction of Alkene + Acid + 

(i) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow{H^+}$ 

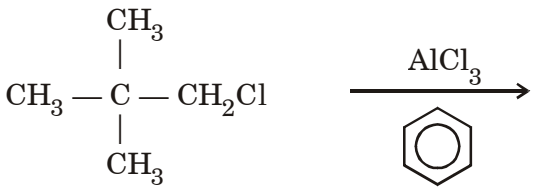
Solution :

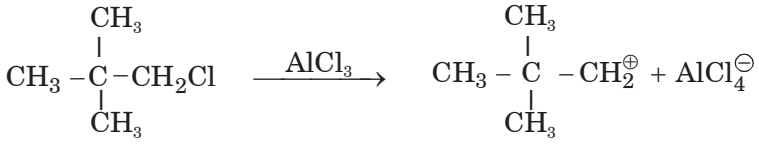
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow{H^+} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\oplus}{CH}-CH_3$$

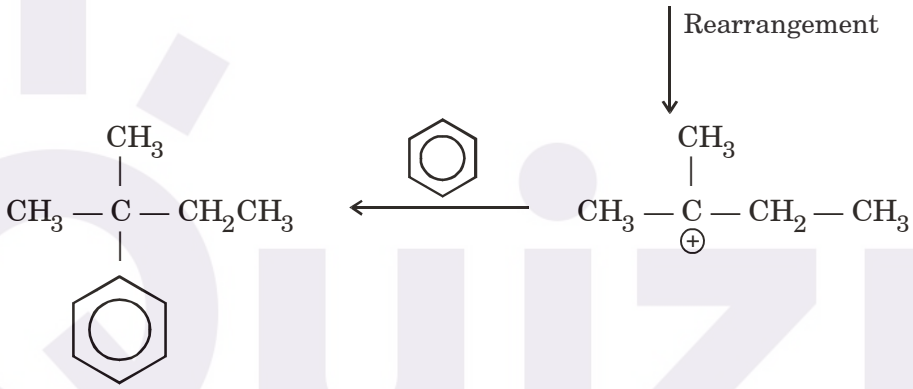
1, 2 hydride shift



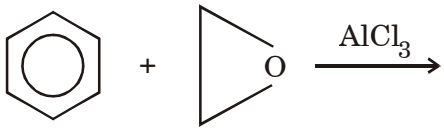
(3) Reaction of Alkyl Halide + Lewis Acid + 

(i) 

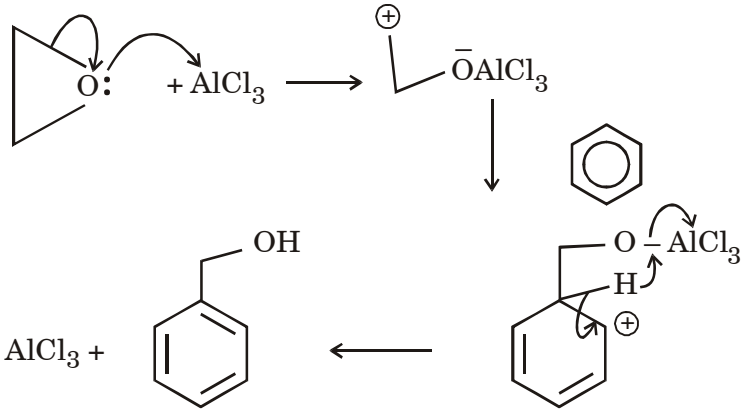




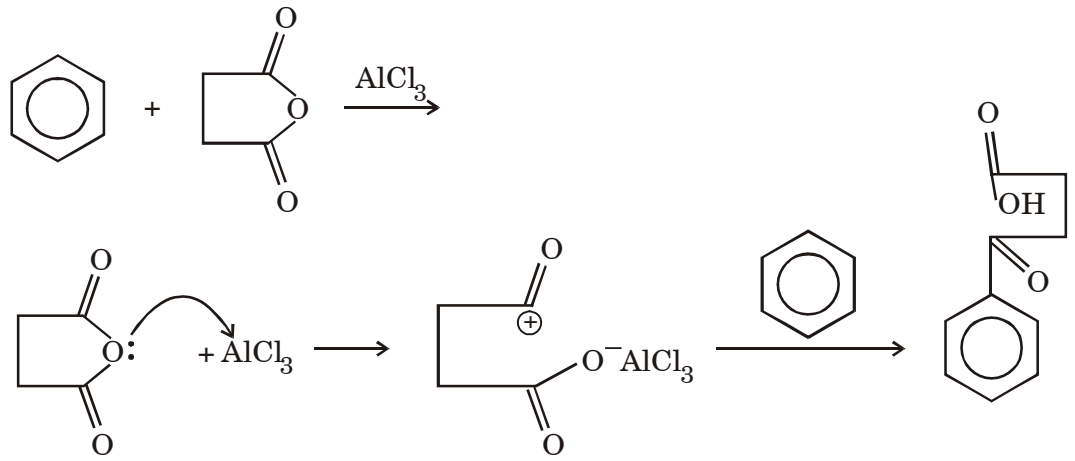
Example 8



Solution :



(3)



(4)

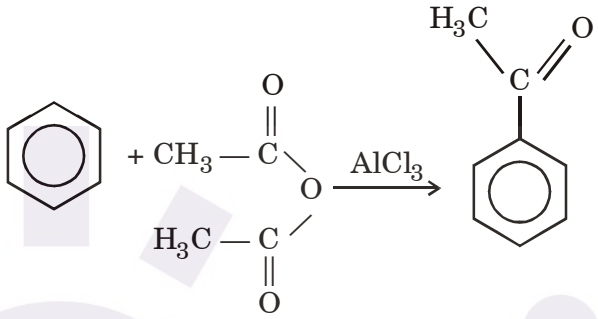
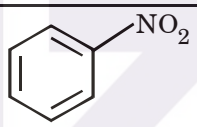
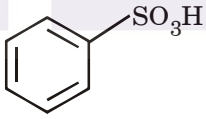
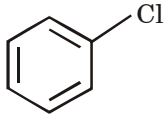
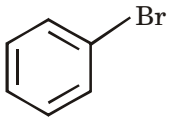
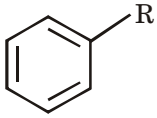
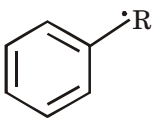
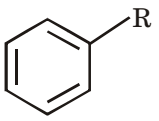
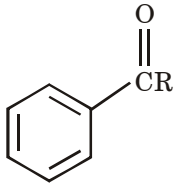
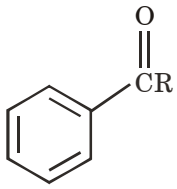


Table for reactions

Reaction	Reagents	Electrophile	Product	Comments
Nitration	HNO_3 / H_2SO_4	NO_2^+		E^+ formed by loss of water from nitric acid
Sulfonation	H_2SO_4 or SO_3/H_2SO_4	SO_3		Reversible
Halogenation	Cl_2/Fe or $FeCl_3$	Cl^+		E^+ formed by Lewis acid removing Cl^-
	Br_2/Fe or $FeBr_3$	Br^+		E^+ formed by Lewis acid removing Br^-
Alkylation	R-Cl/$AlCl_3$	R^+		E^+ formed by Lewis acid removing Cl^-

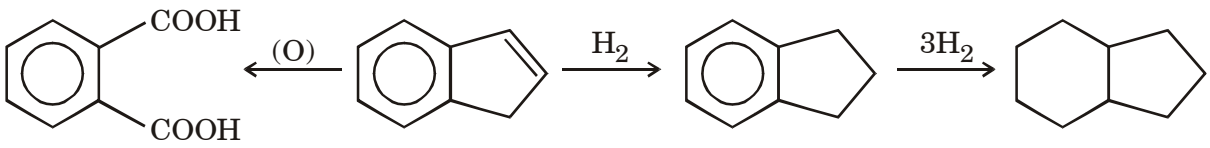
	$R\text{-}OH/H^+$	R^+		E^+ formed by loss of water from alcohol
	$C{=}C/H^+$	R^+		E^+ formed by protonation of alkene
Acylation	$RCOCl/AlCl_3$	RCO^+		E^+ formed by Lewis acid removing Cl^-
	$RCO_2COR/AlCl_3$	RCO^+		E^+ formed by Lewis acid removing RCO_2^-

Example 9

Deduce the structure of compound A, C_9H_8 from the following experimental data : A decolorizes Br_2 in CCl_4 and adds one eq. of H_2 under mild conditions, forming B, C_9H_{10}. At high temperature and pressure A adds four eq. of H_2.Vigorous oxidation of A yields phthalic acid, 1, 2–$C_6H_4(COOH)_2$.

Solution :

A has 6 of unsaturation, four of which often signal the presence of benzene ring, as confirmed by isolation of phthalic acid on vigorous oxidation. Reaction with Br_2 and one eq. of H_2 indicate there is a C=C. Addition of three more eq. of H_2 further indicates the presence of a benzene ring. So far 5 of unsaturation have been accounted for –the sixth degree resists reduction and must be a ring with C=C. Oxidation to the ortho-dicarboxylic acid indicates the ring is fused to the benzene ring. The structure is indene.



Phthalic acid Indene, (A) Indane, (B) Bicyclo (4.3.0) nonane

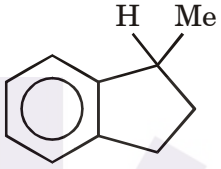
Example 10

(a) Give the structures for all possible chiral compounds, $C_{10}H_{12}$, that do not decolorize Br_2 and that can be oxidized to phthalic acid.

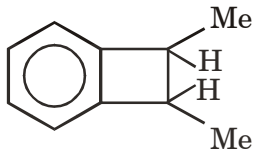
(b) Identify E, also chiral, with the same formula, but which is oxidized to PhCOOH.

Solution :

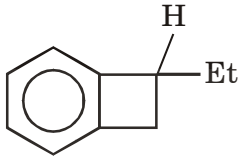
(a) The formula reveals a fifth degree of unsaturation in addition to the four of the benzene ring. This fifth degree of unsaturation must be a ring, not C=C, because the Br_2 test is negative. Production of phthalic acid means the ring is fused to the benzene ring. This fused ring has the chiral carbon and must be a mono–R–substituted five–membered or di–R–substituted four–membered ring. Only in this way can we account for the additional four C's of the formula.



1-Methylindane

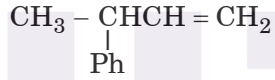


trans-1,2-Dimethylbenzcyclobutane



1-Ethylbenzcyclobutane

(b) The extra unsaturation is in the single side chain. E is 3–phenyl–1-butene,



3.6 Substituted aromatic rings

1. Electrophiles may attack aromatic rings with **functional groups.** Performing an electrophilic substitution on an already substituted benzene compound raises the problem of addition. In case of a monosubstituted benzene, there are 4 different reactive positions. For a monosubstituted benzene, the ring carbon atom bearing the **substituent** is position 1 or **ipso,** the next ring atom is position 2 or **ortho,** position 3 is **meta** and position 4 is **para.** Positions 5 and 6 are respectively equal to 3 and 2.
2. Substituents can generally be divided into two classes regarding electrophilic substitution : activating and deactivating towards the aromatic ring. **Activating substituents** or **activating groups** stablize the cationic intermediate formed during the substitution by donating electrons into the ring system, by either **inductive effect** or **resonance effects.** Examples of activated aromatic rings are **toluene, aniline** and **phenol.**
3. The extra electron density delivered into the ring by the substituent is not equally divided over the entire ring, but is concentrated on atoms 2, 4 and 6 (the ortho and para positions). These positions are thus the most reactive towards an electron-poor electrophile. The highest electron density is located on both ortho positions, though this increased reactivity might be

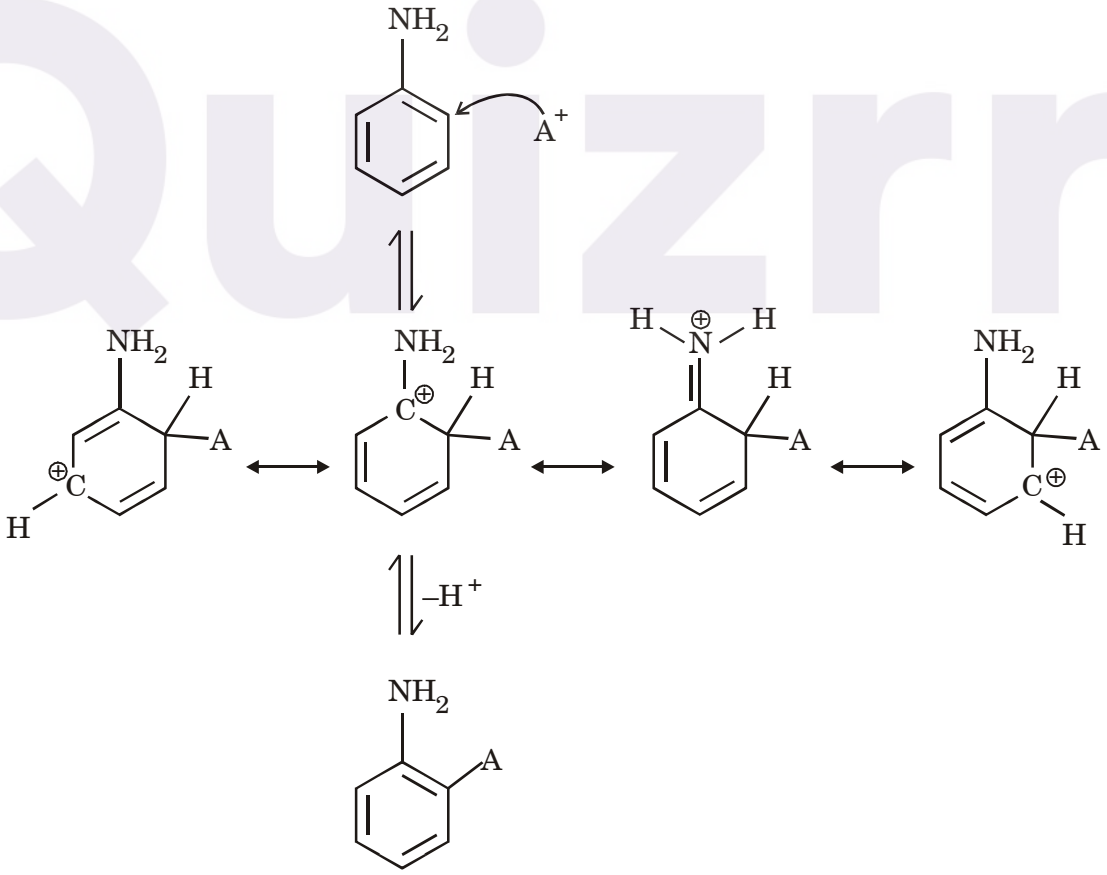
offset by **steric hindrance** between substituent and electrophile. The final result of the electrophile aromatic substitution might thus be hard to predict, and it is usually only established by doing the reaction and determining the ratio of ortho versus para substitution.

4. On the other hand, **deactivating substituents** destablize the intermediate cation and thus decrease the **reaction rate.** They do so by withdrawing electron density from the aromatic ring, though the positions most affected are again the ortho and para ones. This means that the most reactive positions (or, least unreactive) are the meta ones (atoms 3 and 5). Examples of deactivated aromatic rings are **nitrobenzene, benzaldehyde** and **trifluoromethylbenzene.**

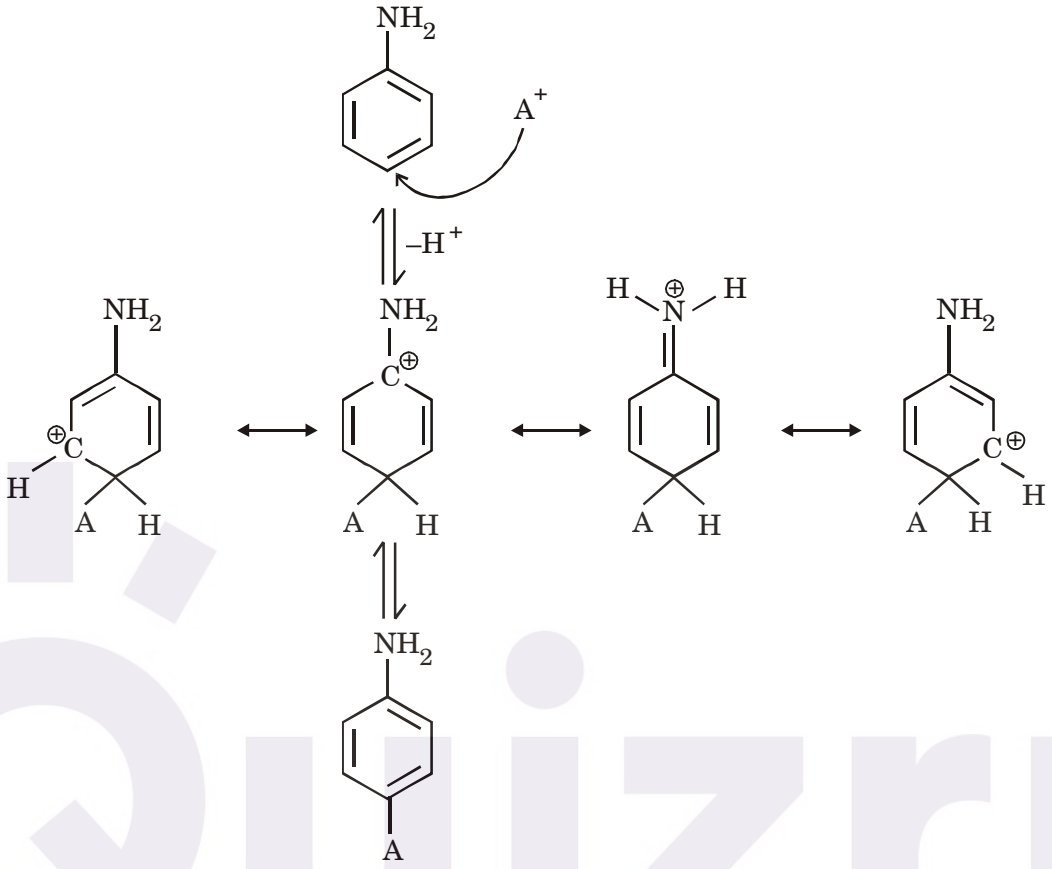
5. Functional groups thus usually tend to favour one or two of these positions above the others; that is, they direct the electrophile to specific positions. A functional group that tends to direct attacking electrophiles to the meta positions, for example is said to be **meta-directing.**

3.6.1 Ortho/para directors

Groups with **unshared pairs** of electrons, such as the **amino** group of **aniline,** are strongly activating and ortho/ para-directing. Such **activating groups** donate those unshared electrons to the pi system.

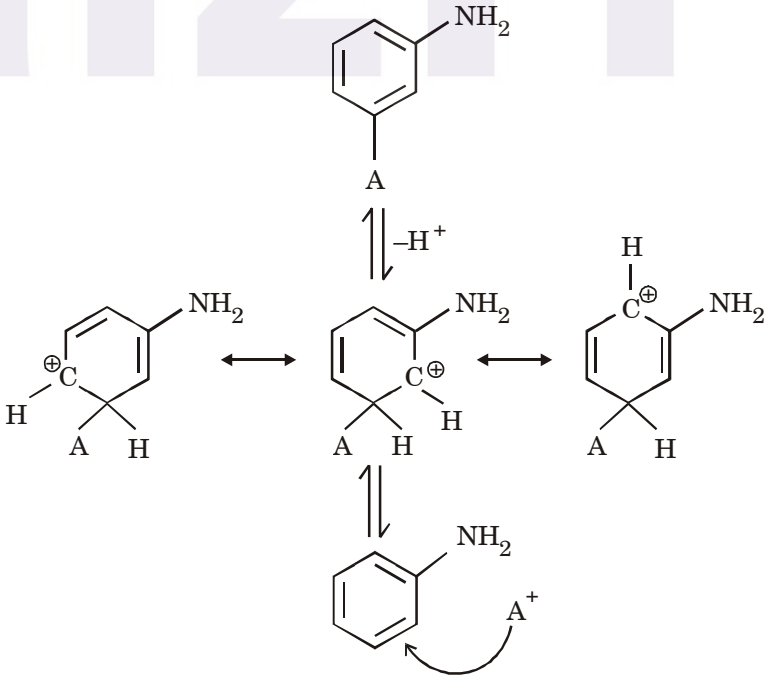


When the electrophile attacks the ortho and para positions of aniline, the **nitrogen** atom can donate electron density to the pi system (forming an **iminium ion**), giving four **resonance structures** (as opposed to three in the basic reaction). This substantially enhances the stability of the cationic intermediate.



Compare this with the case when the electrophile attacks the meta position. In that case, the nitrogen atom cannot donate electron density to the pi system, giving only three resonance contributors. For this reason, the meta-substituted product is produced in much smaller proportion to the ortho and para products.

Other substituents, such as the **alkyl** and **aryl substituents,** may also donate electron density to the pi system; however, since they lack an available unshared pair of electrons, their ability to do this is rather limited. Thus they only weakly activate the ring and do not strongly disfavor the meta position.

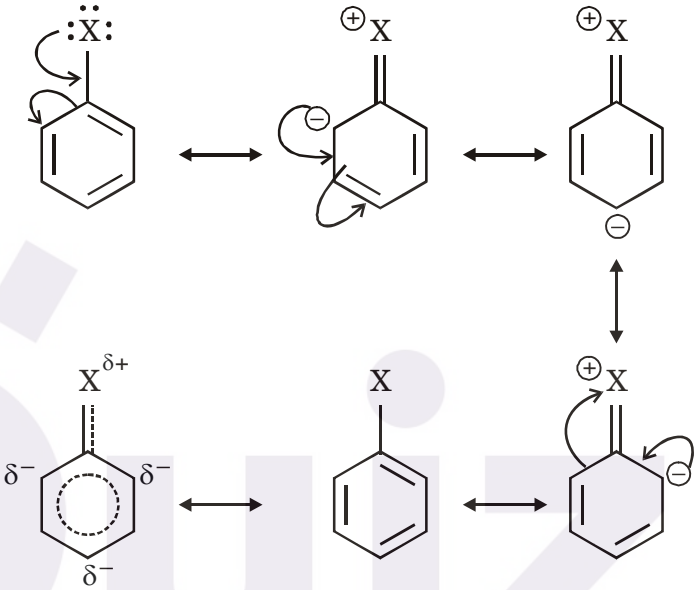


3.6.2 Special Effect of Halogens

- **Halogens** are ortho/ para directors, since they possess an unshared pair of electrons just as nitrogen does. However, the stability this provides is offset by the fact that halogens are substantially more **electronegative** than carbon, and thus draw electron density away from the pi system. This destablizes the cationic intermediate, and EAS occurs less readily. Halogens are therefore **deactivating groups.**

Hence we can say that halogens are de-activating yet ortho, para directing.

A halogen substituted benzene (C_6H_5-X) by virtue of the presence of unshared electron pair on the halogen, exhibits resonance. Thus it can be represented by the resonance hybrid of following :

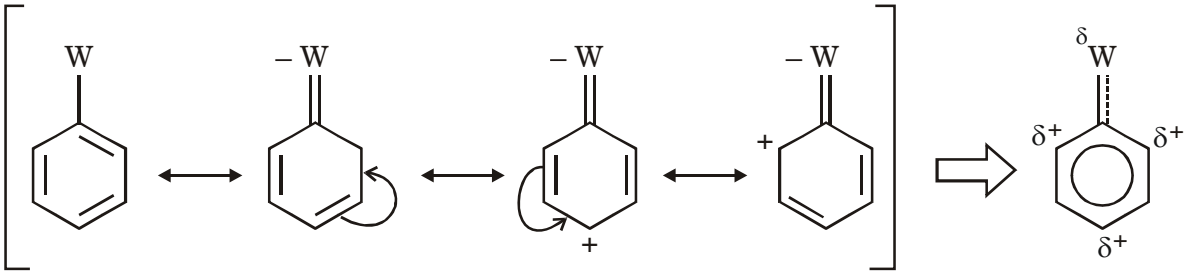


Halogens withdraw electrons through its inductive effect (– I) and releases electrons through its resonance or mesomeric effect (+ M). Thus for halogen, the two effects are more evenly balanced and we observe the operation of both.

3.6.3 Meta directors

Non-halogen groups with atoms that are more electronegative than carbon, such as the **nitro** group (NO_2) draw substantial electron density from the pi system. These groups are strongly **deactivating groups.** Additionally, since the substituted carbon is already electron-poor, the resonance contributor with a positive charge on this carbon (produced by ortho/ para attack) is less stable than the others. Therefore, these electron-withdrawing groups are meta directors. $–CF_3$, $–CCl_3$, $–CBr_3$, $–Cl_3$ are meta directors.

Electron withdrawing groups (EWG) with π bonds to **electronegative atoms** (e.g. –C=O, $–NO_2$) adjacent to the π system **deactivate** the aromatic ring by decreasing the electron density on the ring through a **resonance withdrawing effect.** The resonance only decreases the electron density at the ortho- and para- positions. Hence these sites are **less** nucleophilic, and so the system tends to react with electrophiles at the **meta** sites.

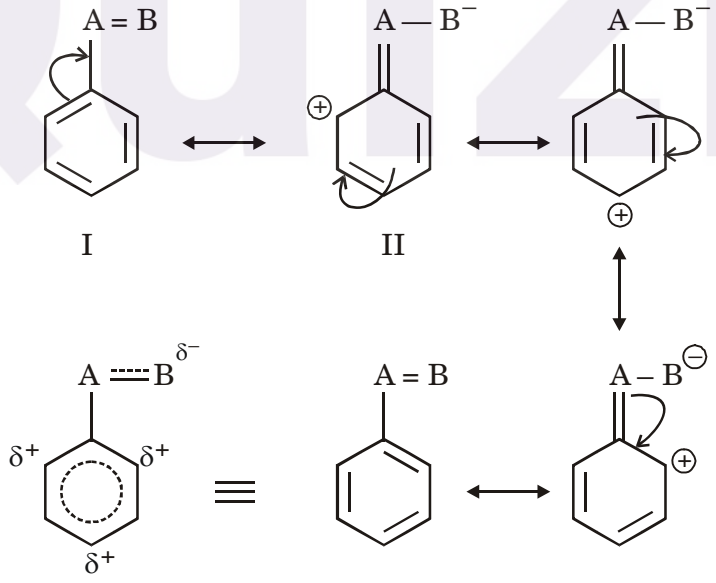


ı The deactivation of the aromatic system also means that generally harsher conditions are required to drive the reaction to completion. An example of this is the **nitration** of toluene during the production of **trinitrotoluene** (TNT). While the first nitration, on the activated toluene ring, can be done at room temperature and with dilute acid, the second one, on the deactivated nitrotoluene ring, already needs prolonged heating and more concentrated acid, and the third one, on very strongly deactivated dinitrotoluene, has to be done in boiling concentrated **sulfuric acid.**

Examples :

When the substituent has at least one strongly electronegative atom and a multiple bond in conjugation with benzene ring :

Let –A = B represent the group in which B is more electronegative than A. The highly electronegative atom pulls the electron pair of the multiple bond which is form withdraws electron from benzene ring (–M effect) giving rise to the following five cononical forms :



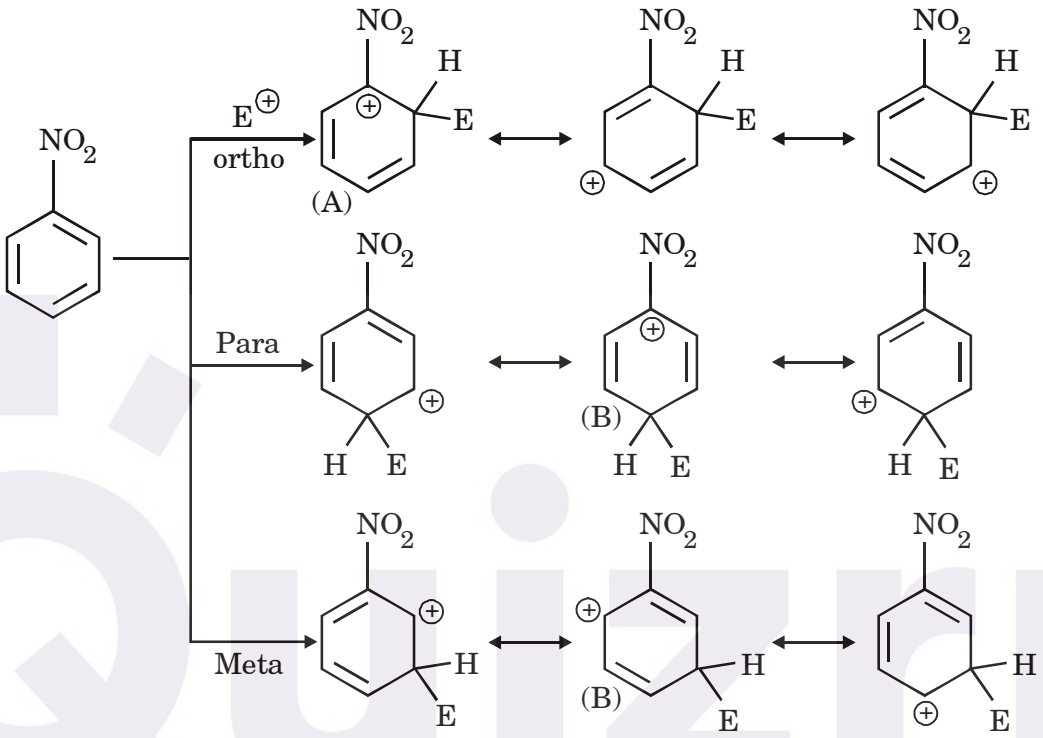
Evidently electrons are withdrawn by the substituent group from the ring and more so from –O –P positions where electron density declines. Also, the meta positions have relatively more electron density and therefore electrophilic substitution takes place at the meta positions.

The nitro and sulphuric acid groups are examples of the type of electron withdrawing substituents which one characterized by the presence of a strong electronegative atom attached to another more electronegative atom by a multiple bond.

Example 11

Draw the resonance structure for electrophilic substitution reactions of nitro benzene and explain why it is meta-directing group ?

Solution :

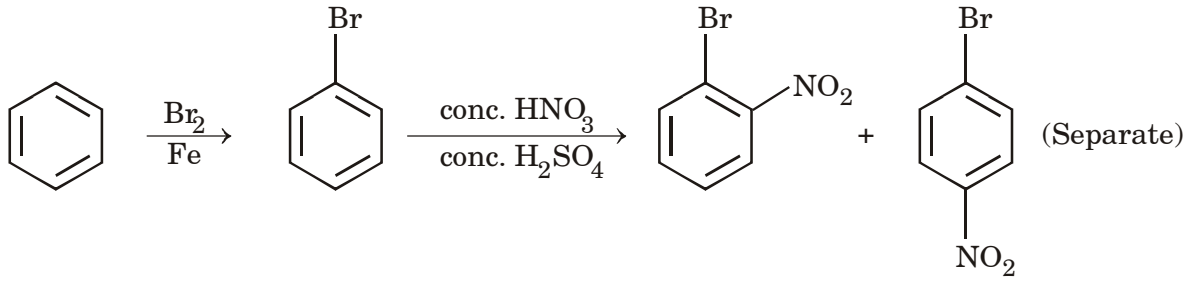


In ortho-para attack of electrophile on nitrobenzene, we are getting two structures (A) and (B) in which positive charge is appearing on the carbon atom directly attached to the nitro group. As nitro group is electron withdrawing by nature, it decreases the stability of such product and hence meta attack is more feasible when electron withdrawing substituents are attached.

Example 12

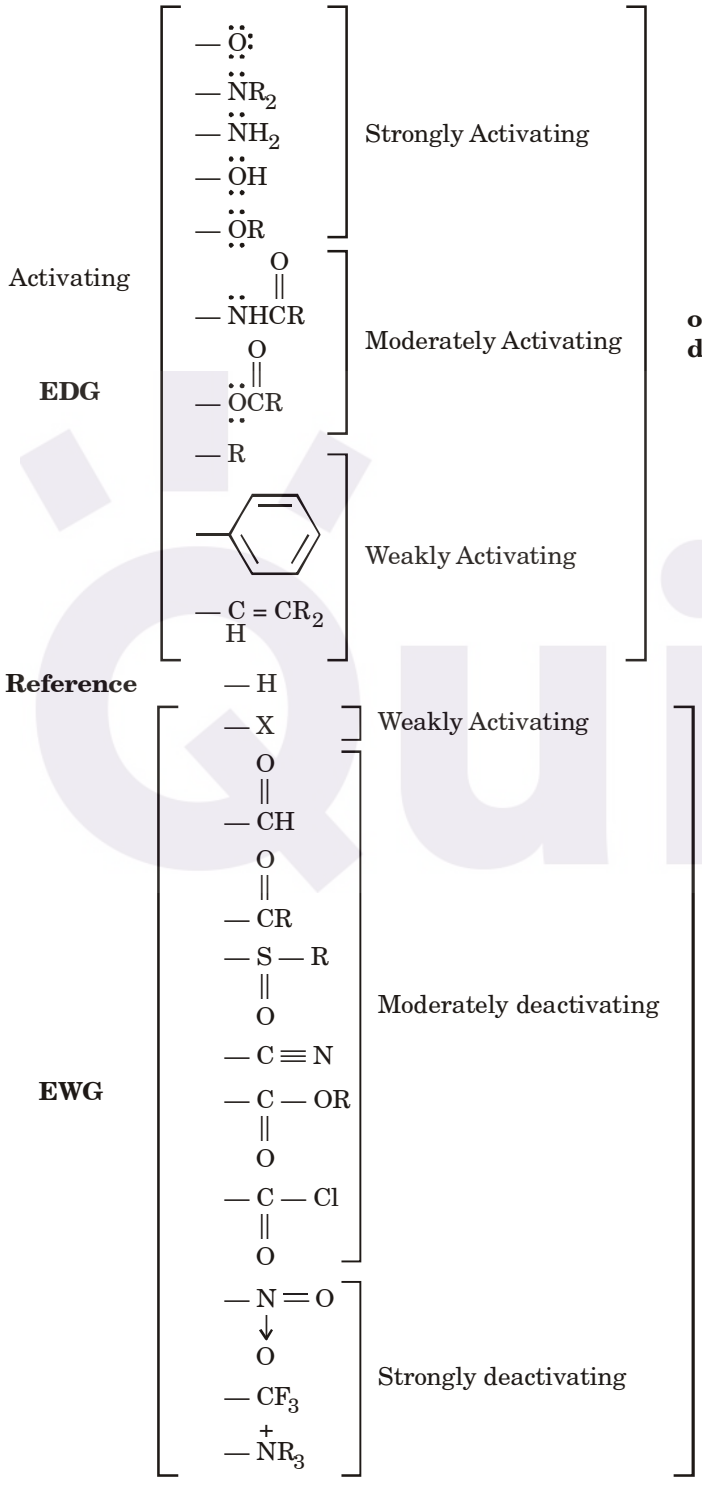
Convert benzene → p-bromonitrobenzene

Solution :



Here is a table that shows the effect of substituents on a benzene ring have on both the rate and orientation of electrophilic aromatic substitution reactions.

These effects are a combination of **Resonance** and **Inductive** effects. The effects are also important in other reactions and properties (e.g. acidity of the substituted benzoic acids).



Here are some **general pointers** for recognising the substituent effects :

- The **H** atom is the standard and is regarded as having no effect.
- **Activating** groups increase the rate
- **Deactivating** groups decrease the rate
- **EDG = electron donating group**
- **EDG** can be recognised by lone pairs on the atom adjacent to the π system, eg : OMe
- except **-R**, -Ar or -vinyl (hyperconjugation, π electrons)
- **EWG = electron withdrawing**

(i) The directing power of electron donating group is generally in the following order.

$O- > NH_2 > NR_2 > OH > OM_e$, $NHA_C > M_e > X$

(ii) The directive power of electron withdrawing group is generally in the following order :

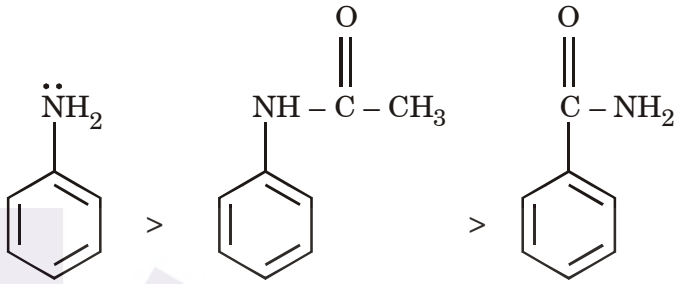
$Me_3N^+ > NO_2 > CN > SO_3H > CHO > COM_e > CO_2H$

Example 13

Arrange the following substances in order to activating a benzene ring.

Benzamide, Aniline, Acetanilide

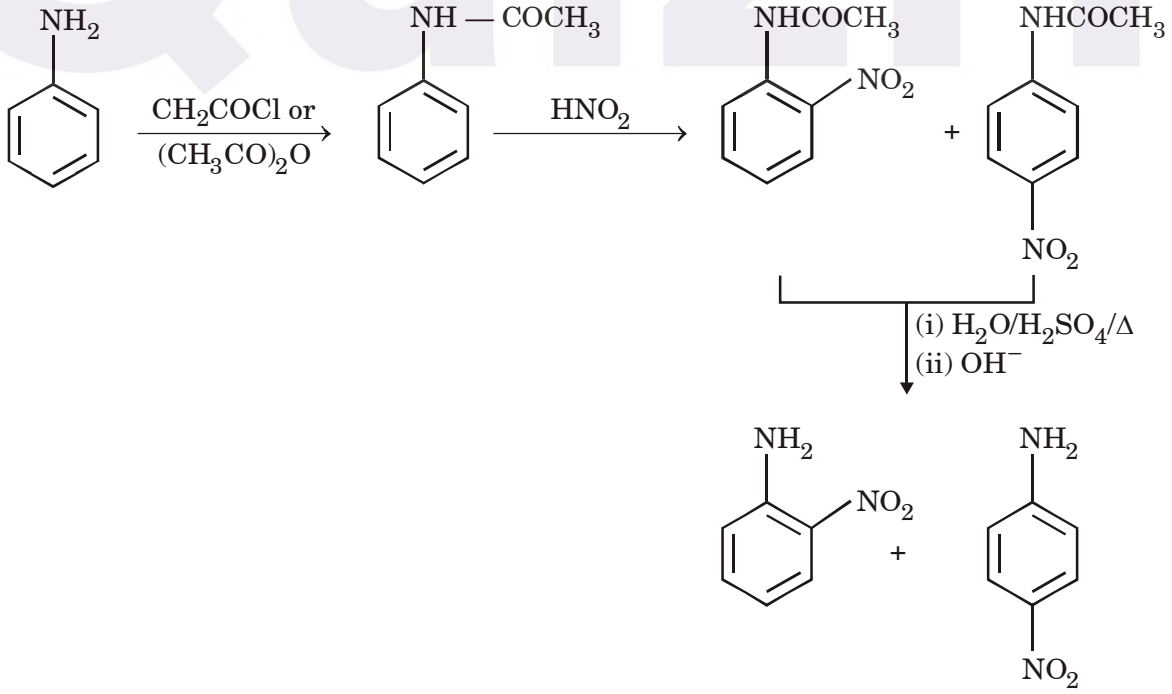
Solution :



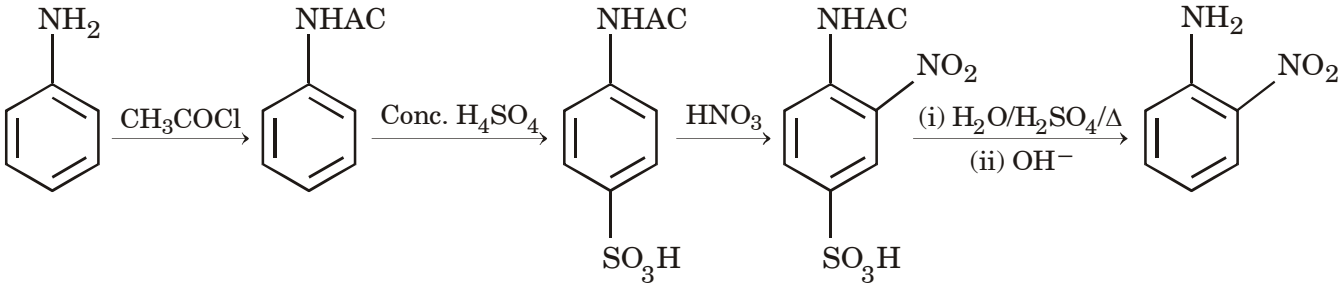
In aniline, benzene ring is directly attached to $-NH_2$ which releases electrons by resonance effect, where as the activation of $-NH_2$ group can be decreased by converting it to anilide and in amide, ring is attached to electron withdrawing group which deactivates the ring.

3.6.4 Use of protecting group

Groups like $-NH_2$ and –OH activate the benzene ring to a great extent and cause undesirable reactions e.g. nitration of aniline with nitric acid is not possible directly as nitric acid oxidizes and destroys the highly activated ring. But its nitration can be carried out by use of protecting group as follows :



In the above reaction, a mixture of ortho and para substituted products is formed. If we desire to form only ortho product then the para position is blocked with help of blocking reagents e.g. conc. H_2SO_4 and tert butyl halides.



P - position blocked

Please note that the blocking reagents are bulky, hence they do not form ortho substituted product.

Thus they can be used to block p positions.

3.6.5 Orientation in disubstituted Benzene

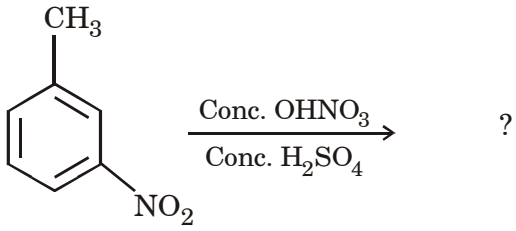
Both the group present on ring collectively decide the position of incoming third group.

Case I : If both are electron donating group then position of incoming group is decided by the group with more electron donating power.

Case II : If one group is e^- donating and other is e^- withdrawing, then position of incoming group is governed by e^- donating group.

Case III : When both are e^- withdrawing groups, then position of incoming group is decided by group which is more deactivating power. But it is difficult to introduce the incoming group.

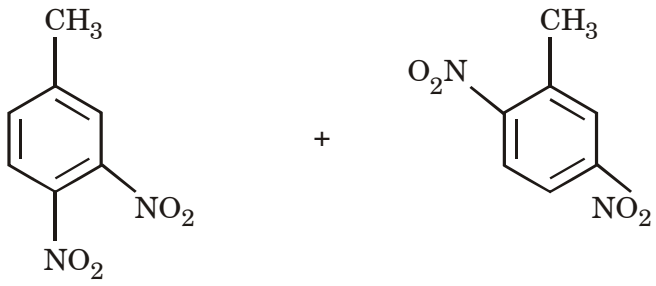
Example 16



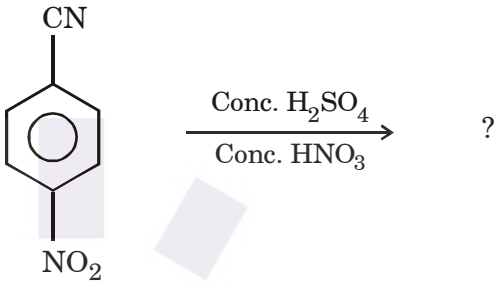
Solution :

$-CH_3$ is e^- donating and NO_2 is e^- withdrawing. Therefore incoming group position will be decided by $- CH_3$.

Hence products are



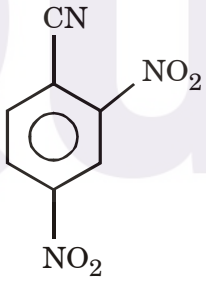
Example 17



Solution :

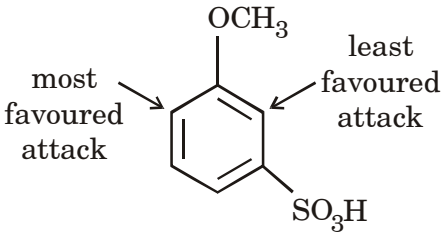
Both are e^- withdrawing group; CN being less withdrawing. Therefore $-NO_2$ will decide the position of incoming group.

Hence product is



Case IV : All other things being equal, a third group is least likely to enter between two groups in the meta position. This is the result of steric hindrance and increases in importance with the size of the groups on the ring and with the size of attacking electrophile.

Example :

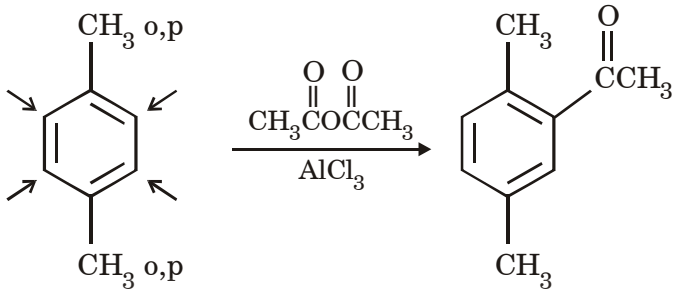


3.6.5.1 Selective Addition

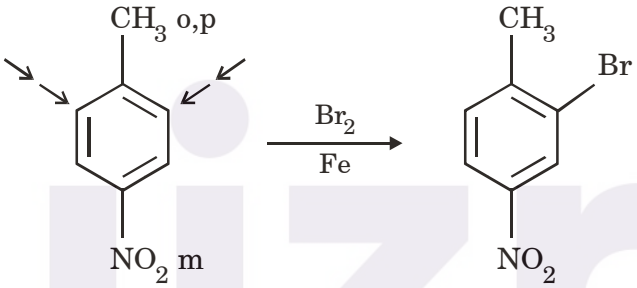
The selective addition for further substitution of disubstituted benzenes can usually be predicted by looking at the cumulative effects of the substituents.

As a suggested method, look at each of the substituents, label their directing effects, then indicate the sites where they would promote reactivity with small arrows. Some issues that can arises are shown by the following worked examples :

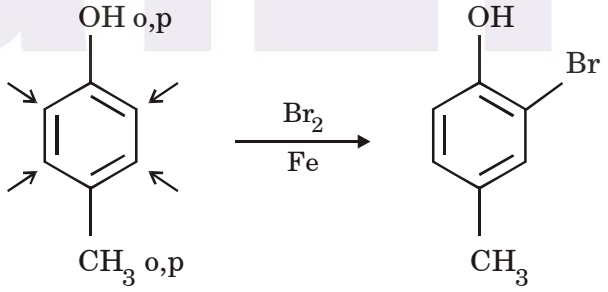
all positions equal



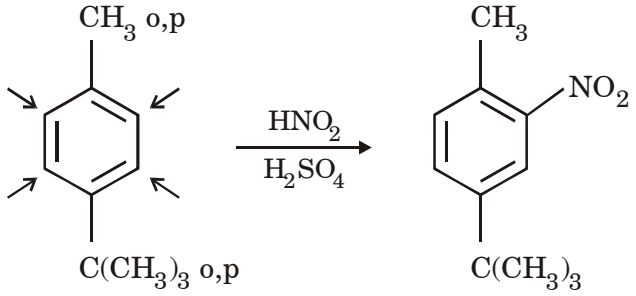
substituents reinforce each other



stronger activator controls



activating effects similar, but steric effects favour ortho to the smaller methyl group



Example 18

The alkylation of phenol and aniline with alkyl halide in presence of $AlCl_3$ gives poor yields. Explain.

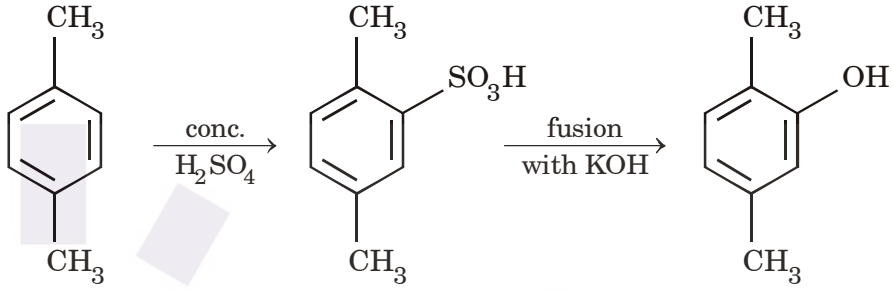
Solution :

In presence of Lewis acid (e.g. $AlCl_3$), the group ($-NH_2$ or $-OH$) becomes electron withdrawing.

Example 19

What happens when p-xylene is treated with concentrated sulphuric acid and the resultant product is fused with KOH ?

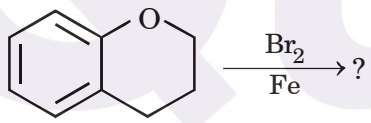
Solution :



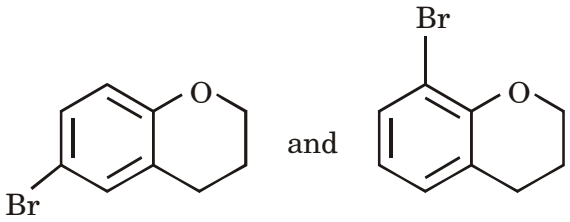
p-Xylene 2-5. Dimethyphenol

Example 20

Explain the product formation in following reaction.



Solution :

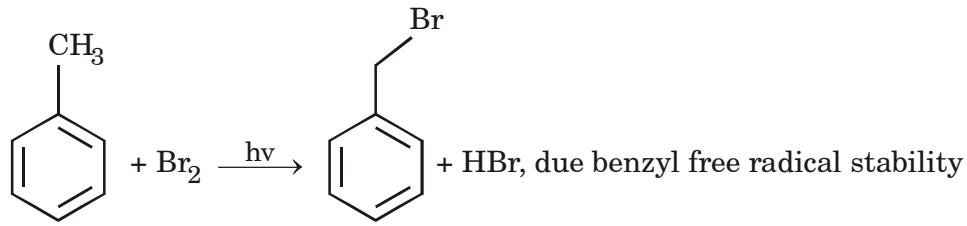


The oxygen-containing ring can be viewed as an OR group and an R group attached to the benzene ring. Although both groups are activating. The OR group is more strongly activating. So the positions ortho and para so it will be faster than the bromination of benzene which requires a catalyst.

Example 21

What happens when toluene reacts with Br_2 in presence of light ?

Solution :



3.6.6 Making Polysubstituted Benzenes

Since the position of electrophilic attack on a substituted benzene ring is controlled by the substituent already present rather than the approaching electrophile, the order of events in the synthesis of polysubstituted benzenes need careful planning to ensure success.

The two factors that need to be monitored are :

- regiochemistry (selective addition)
- reactivity (for example Friedel-Crafts reactions are limited to halobenzenes and activated benzenes)

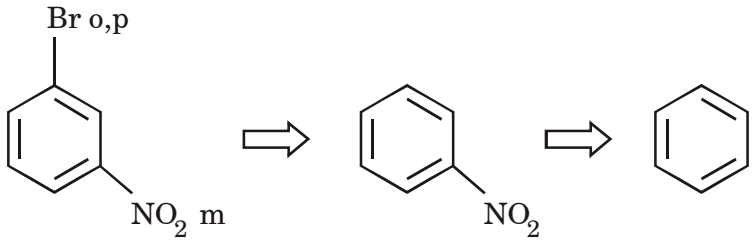
Tip : Students often get this concept of what component is in control confused. Try thinking about it in terms of an aircraft (the $\mathbf{E^+}$) coming into land at an airport (the **Ar-X**)... it is the control tower at the airport on the ground. **(-X)** that does the "directing" of which runway and which ramp the aircraft should go to.

- Draw the target product and label the substituents with their directing effects
- Look at these directing effects to see which align to allow the introduction of the appropriate group
- If there is a choice, introduce the more activating group first.... it will make the subsequent reactions easier
- Remember that some functional groups can undergo reactions that changes their directing effects
- Check the order of reactions for compatibility

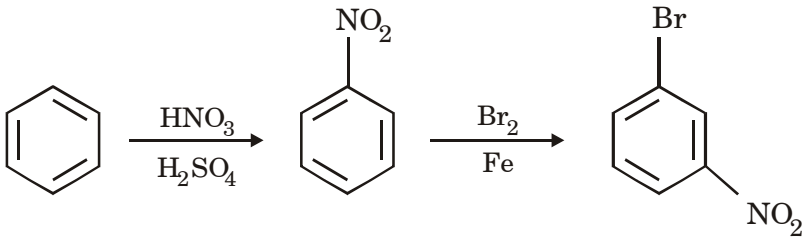
Here are a couple of examples :

1. Here the nitro group could direct to bromine to the correct position

   Therefore in planning the synthesis we should use the nitro group to introduce the bromine

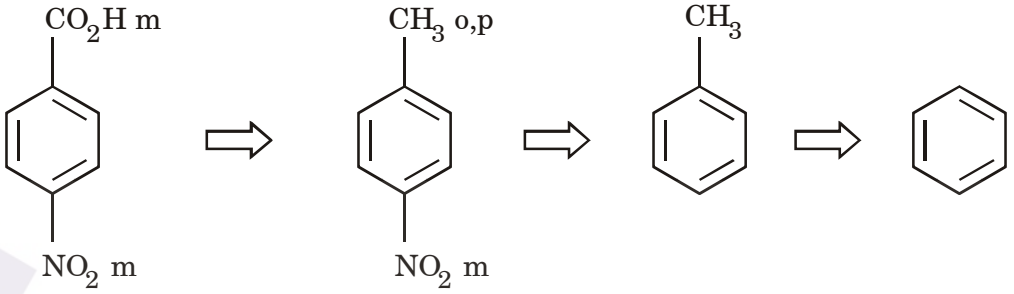


Actual Synthesis :

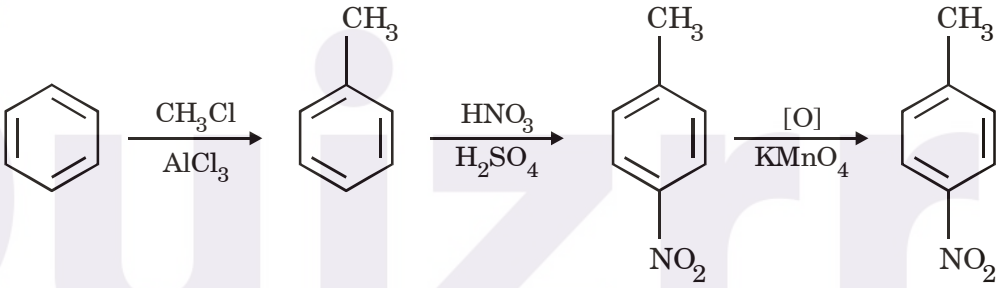


2. Here neither group directs to the correct location of the other.

But since the carboxylate could be introduced by the oxidation of a methyl group, which directs o, p- we can use the methyl to direct the nitro group to the correct position.



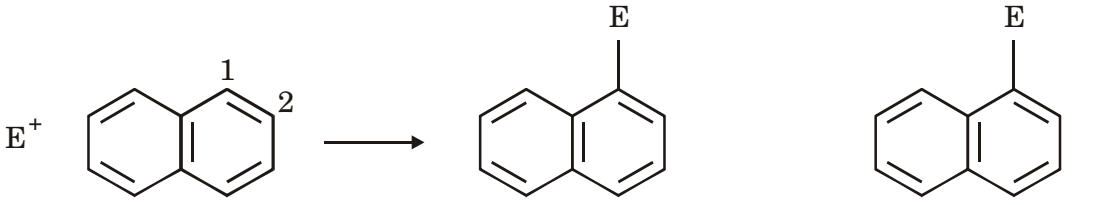
Actual Synthesis :



Note that the oxidation has to be after the nitration to get the correct orientation and that the Friedel-Crafts alkylation has to before the nitration since nitrobenzene is too deactivated to undergo alkylation.

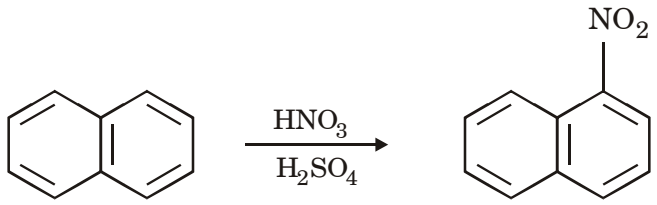
3.6.7 Electrophilic Aromatic Substitution of Polycyclic Aromatics

- Polycyclic aromatics such as naphthalene, anthracene etc. react with similar reagents to those used for benzene
- Typically they are more reactive than benzene
- Reactions are usually less selective than those of benzene and mixtures of products are often obtained



1 - or α – substitution 2 - or β – substitution

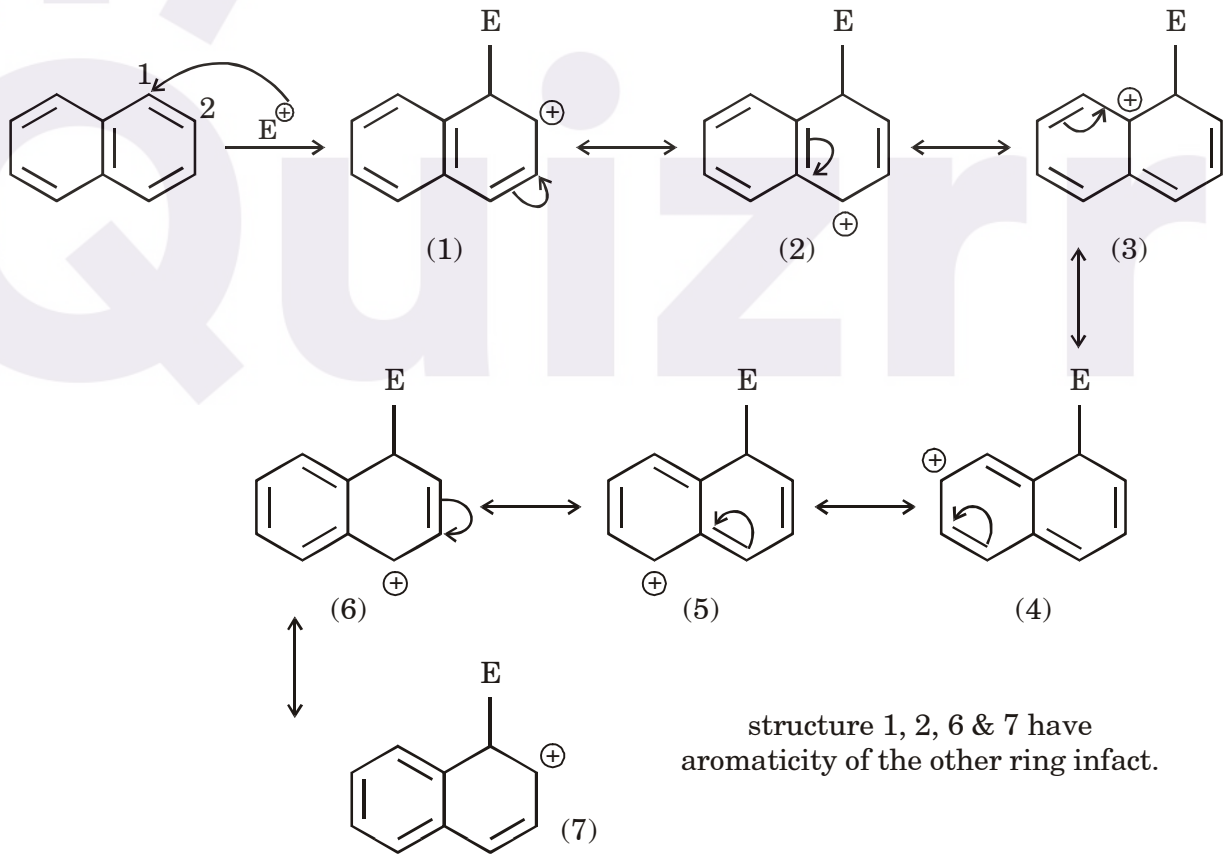
For example, the nitration of naphthalene proceeds to give mainly 1-nitronaphthalene.



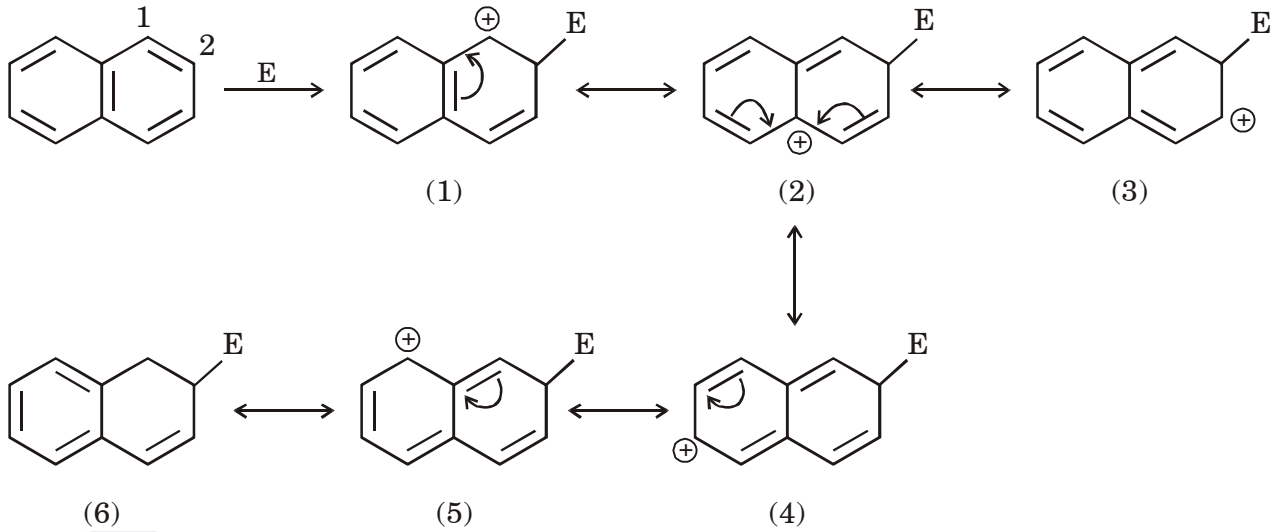
napthalene

This selectivity can be rationalised by drawing the resonance structures for intermediates produced by attack of the electrophile at the 1- and 2- positions. Attack at the 1-position gives an intermediate that is represented by 7 resonance contributors of which 4 leaves the aromaticity of the other ring intact. In contrast attack at the 2-positions gives an intermediate with 6 resonance contributors in which only 2 have the aromaticity of the other ring intact.

Attack at position-1

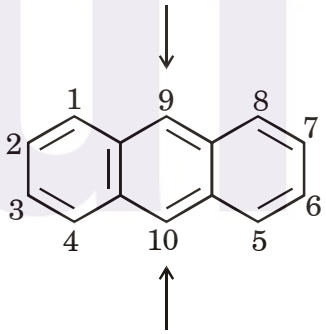


Attack at position-2



There are 6 resonating structure out of them only 2 have aromaticity of the other ring intact.

In anthracene, the electrophile attacks preferentially at the 9 or 10 positions since the arenium ion formed by the electrophilic attack at any of these positions can have two intact benzene ring in its canonical forms, while attack of electrophile at any other position (1 or 2) would give arenium ion having a naphthalene ring in its canonical forms. The resonance energy of 2 benzene rings is more than the resonance energy of a naphthalene ring.



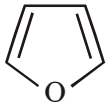
(here position 1, 4, 5 and 8 are identical, positions 2, 3, 6 and 7 are identical and positions 9 and 10 are same).

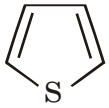
3.6.8 Electrophilic Aromatic Substitution of Heteroaromatics

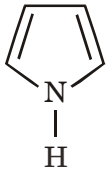
1. Aromatic compounds which contain **heteroatoms** (e.g. O, N, S) are called heteroaromatics.
2. The presence of the heteroatom influences the reactivity compared to benzene.
3. The 5-membered ring heterocycles **(furan, pyrrole, thiophene**) are **π-electron rich aromatics** (6 π electrons over 5 atoms).
4. This makes them more reactive than benzene (since the aromatics the nucleophilic component in these electrophilic substitution reactions)
5. For example **furan** is similar to an activated benzene like methoxybenzene
6. **Pyridine** is less reactive than benzene (more like nitrobenzene) due to the electronegativity of N, it is described as a **π-electron deficient aromatic**

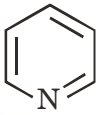
7. The basic nature of the N atom of pyridine often interferes and interacts with the electrophile **E+** which further deactivates the system.

Compound Name Line Drawing 3D Model

Furan 

Thiophene 

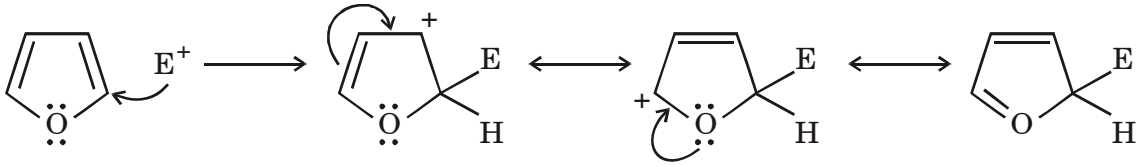
Pyrrole 

Pyridine 

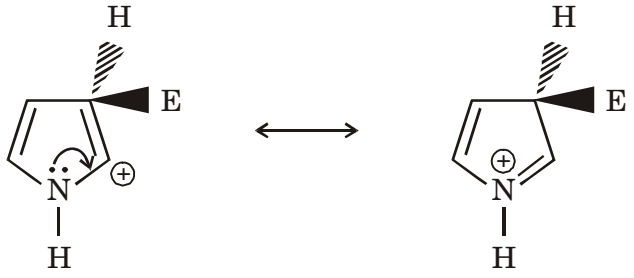
3.6.8.1 Five Membered Heterocyclic Ring

The 5 membered heterocycles react in a similar way. As an example here is the general pattern for the electrophilic aromatic substitution reactivity of furan, complete with the 3 important resonance structures that justify the reactivity of the 2-position.

Mechanism :



3–substitution:



(Stable contributor–octet of every atom is complete)

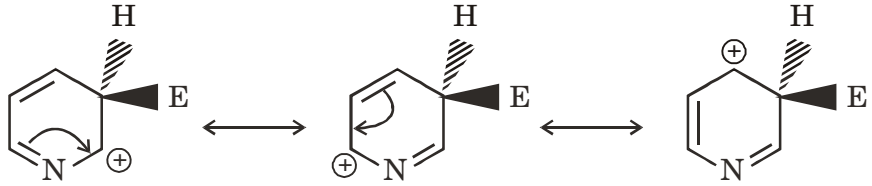
Furan and thiophen are also activated towards electrophiles and react predominantly at the 2-position. Theory is similar to that for pyrrole, namely, that the heteroatom is able to delocalize the positive charge on the transition state. Since oxygen accommodates a positive charge less readily than nitrogen, furan is less reactive than pyrrole. Just as phenol is less reactive than aniline. The +M effect of sulphur is smaller than that of oxygen because the overlap of the differently sized p–orbitals of carbon and sulphur is less than furan. Thus, the reactivity order of 5–membered heterocyclics towards electrophilic substitution would be

pyrrole > furan > thiophene

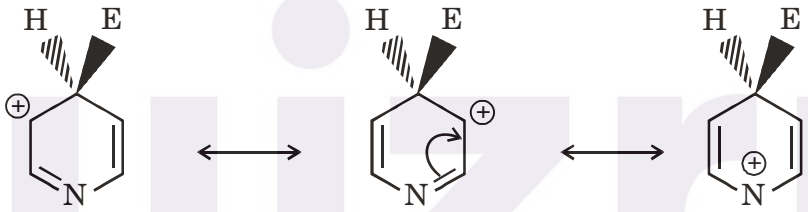
3.6.8.2 Six-Membered Heterocyclic Rings

The principles governing the reactivity of these compounds are illustrated by reference to pyridine. The transition states for substitution at the 3– and 4–positions can be represented as the hybrids.

3–substitution:



4–substitution:



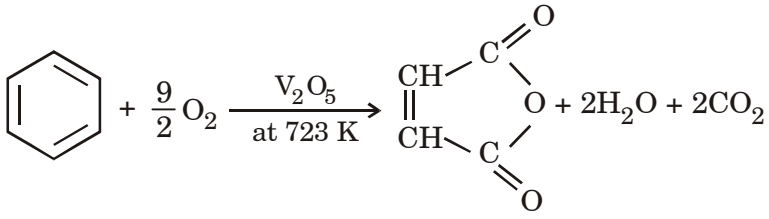
In each case, the positive charge is less well accommodated than in reactions on benzene because nitrogen is more electronegative than carbon. Hence, both the 3– and 4–positions are deactivated, the latter more strongly because of the high energy of the contributing structure which contains divalent positive nitrogen. The 2–position resembles the 4–position, as reference to the appropriate resonance structures will show.

3.6.9. Reactions of Benzene and Its Homologues

(i) Benzene on vigorous oxidation (combustion) gives CO_2 and H_2O.

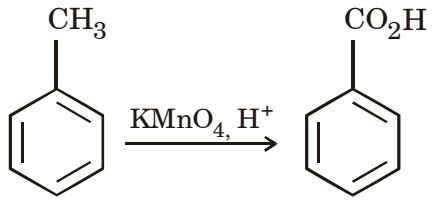
$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

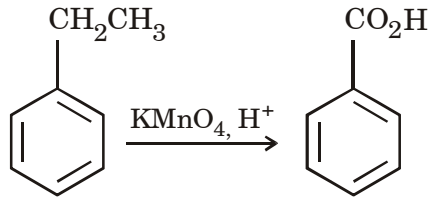
Benzene on oxidation by air at 723 K in presence of V_2O_5 gives maleic anhydride.

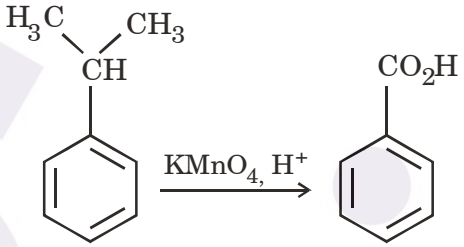


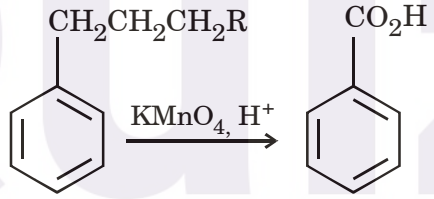
(ii) Side chain oxidation of alkyl benzenes

An alkyl benzenes (irrespective of the chain length) on oxidation by acidified or alkaline $KMnO_4$ (followed by acidification) are degraded to benzoic acid provided they have a benzylic hydrogen.

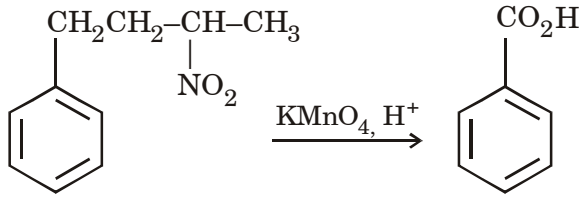


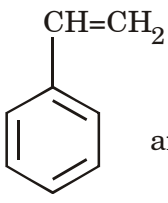




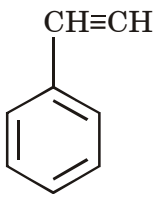


Even if the side chain contains some functional groups, whether they are electron pushing or electron withdrawing, are also degraded to benzoic acid on oxidation.



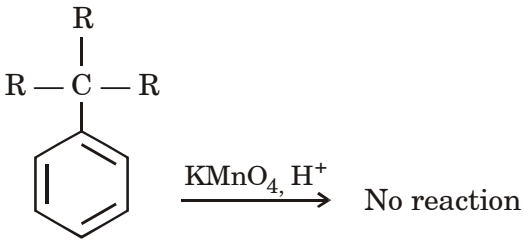


and

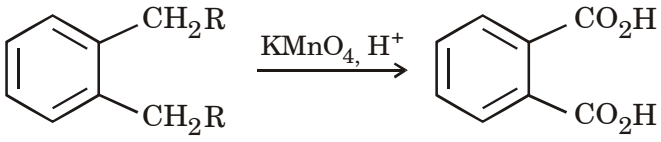


are also oxidised by $KMnO_4$, H^+ or $KMnO_4$, OH^- to give benzoic acid due to oxidative cleavage of  and –C≡C–

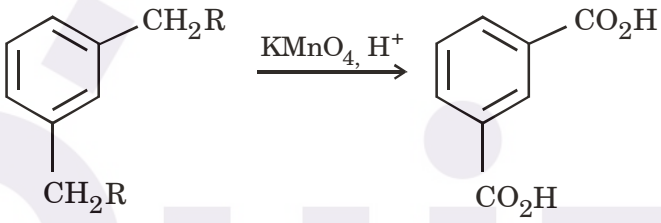
Compounds that do not contain a benzylic hydrogen will not get oxidised to benzoic acid.



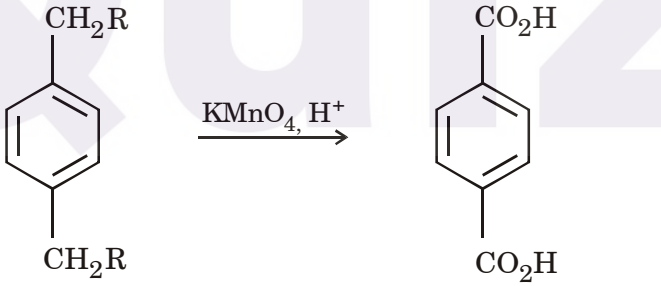
Compounds which contain, two alkyl carbons bearing benzylic hydrogen are oxidised to give two $-CO_2H$ groups on the benzene ring.



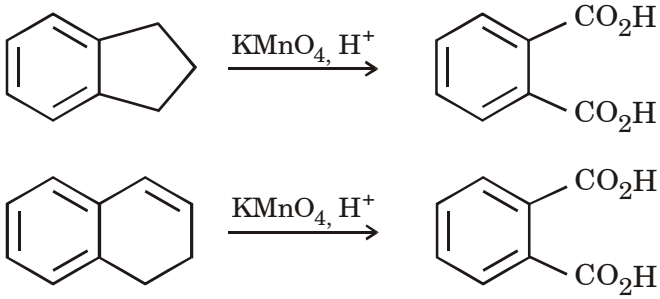
Phthalic acid



Isophthalic acid

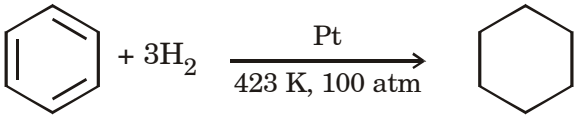


Terephthalic acid

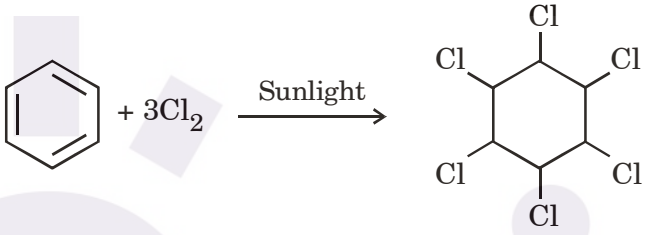


(iii) Addition reactions :

Benzene is so stable that it gives addition reactions much less readily. It can be reduced by catalytic hydrogenation, when three molecules of hydrogen add to it in presence of Pt as a catalyst.

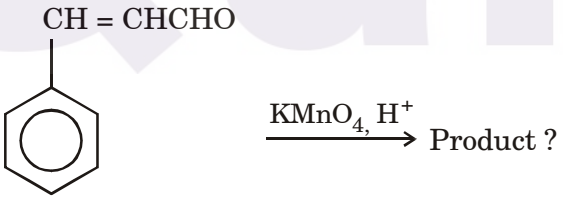


Addition of 3 molecules of chlorine also takes place to one molecule of benzene in presence of sunlight. The product formed is 1, 2, 3, 4, 5, 6–hexachlorocyclohexane (also called as benzene hexachloride). This compound is used as an important insecticide and is sold commercially in the name of BHC or gammaxene.

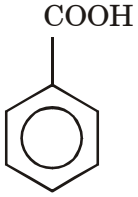


Example 22

Find the product

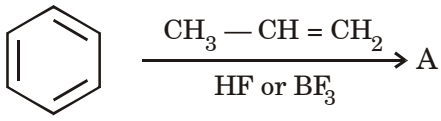


Solution :



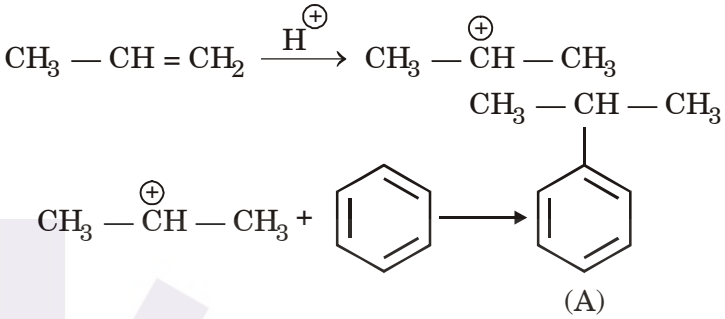
MISCELLANEOUS EXAMPLES

Example 1



Identify A and also the electrophile involved in the reaction.

Solution :

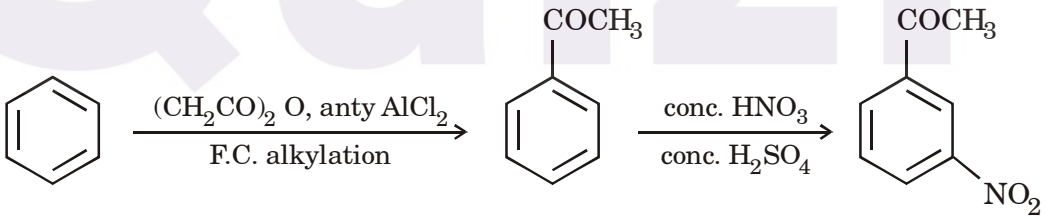


is iso propyl benzene or cumene and electrophile involved is $CH_3 - CH^{\oplus} - CH_3$ (isopropyl carbocation). Rearrangements are also possible in Friedel Crafts reactions when benzene is treated with n-butyl chloride and Lewis acid the product obtained is isobutyl benzene.

Example 2

Synthesize m–nitroacetophenone from benzene.

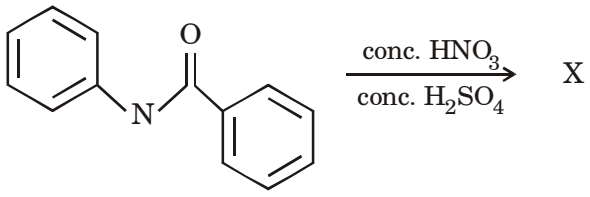
Solution :



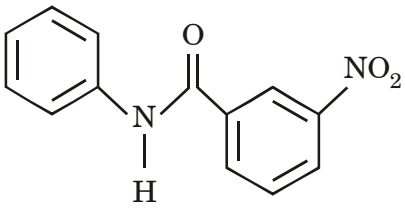
Acetophenone

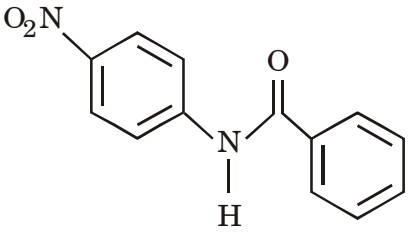
Example 3

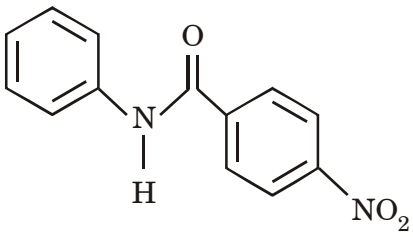
In the following reaction,

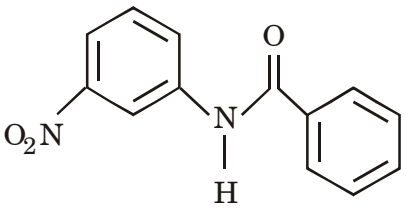


the structure of the major product 'X' is

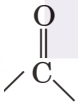
(a) 

(b) 

(c) 

(d) 

Solution :

The ring to which –NH group is attached is activated due to the lone-pair on N; while the ring to which  is attached is deactivated. Hence, the electrophile would go to the para-position of the activated ring.

∴ (b)

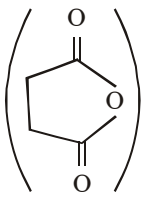
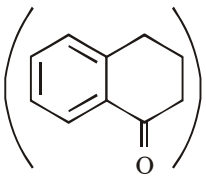
Example 4

Irradiation of an equimolar mixture of cyclohexane and $PhCH_3$ gives mostly cyclohexyl chloride with Cl_2 and $PhCH_2Br$ with Br_2. Explain.

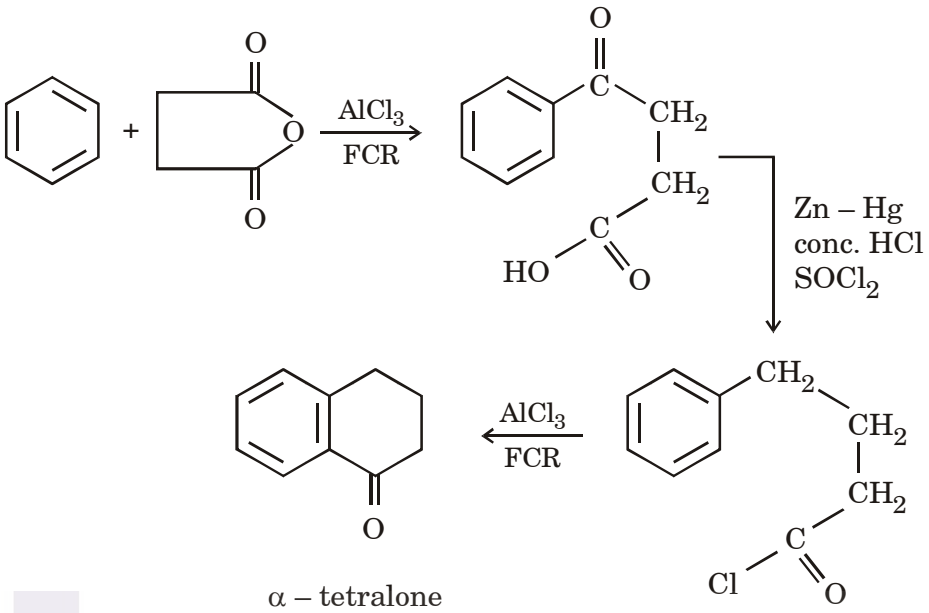
Solution :

In these competitive reactions the reactivities of cyclohexane and toluene are compared $Cl^{\bullet}$, being more reactive and less reactive than $Br^{\bullet}$, reacts with the kind of H present in greatest number, which in this case is one of the twelve equivalent H's of cyclohexane. The less reactive and more selective $Br^{\bullet}$ reacts with the most reactive H, in this case one of the three alkyl H's of $PhCH_3$.

Example 5

Starting with benzene and succinic  **anhydride synthesise α-tetralone.** 

Solution :



α – tetralone

Example 6

Compound (A), B and (C) are three isomeric derivatives of benzene. Identify which is O–, m– or p– from the products of nitration ?

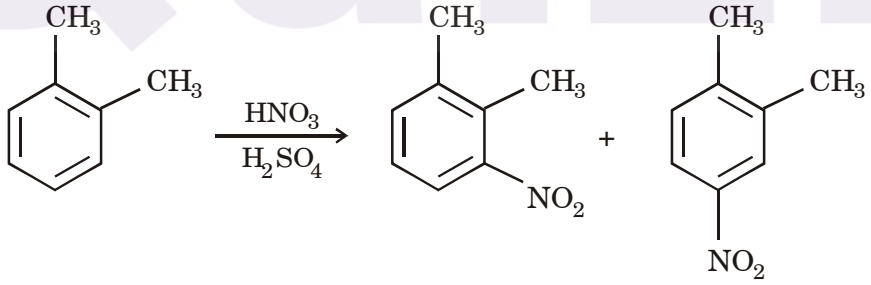
A $\xrightarrow[H_2SO_4]{\text{conc. } HNO_3}$ **two mononitro product**

B $\xrightarrow[H_2SO_4]{\text{conc. } HNO_3}$ **three mononitro product**

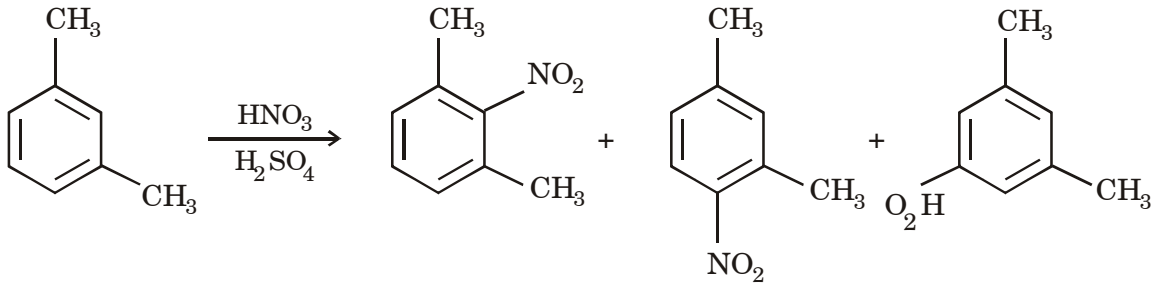
C $\xrightarrow[H_2SO_4]{\text{conc. } HNO_3}$ **one mononitro product**

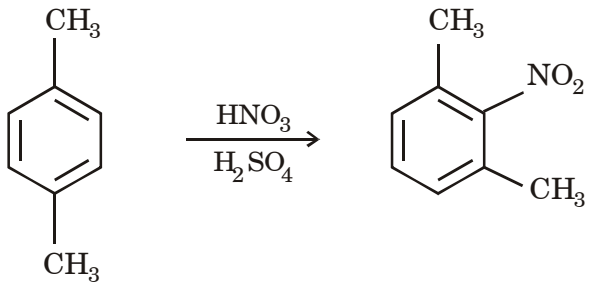
Solution :

(A)



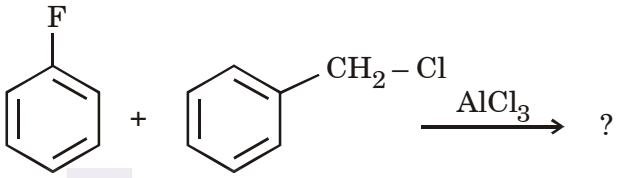
(B)



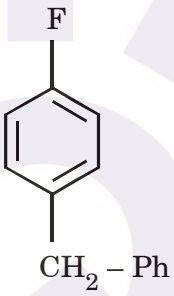
(C) 

Example 7

Write the structure of the major product (only mono-substitution is involved in each case).

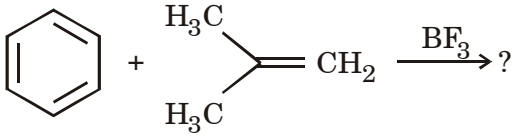


Solution :

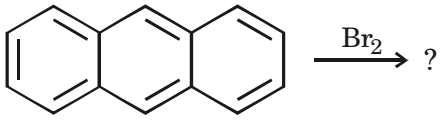


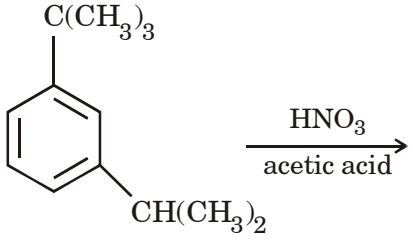
Example 8

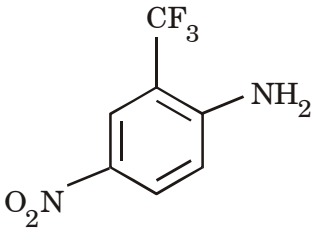
Complete the following :

(a) 

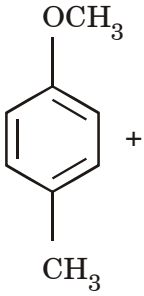
(b) 

(c) 

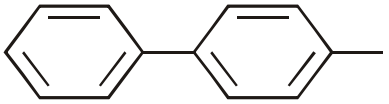
(d) 

(e) 

$\xrightarrow{Br_2}$?

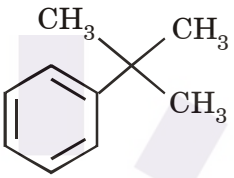
(f) 

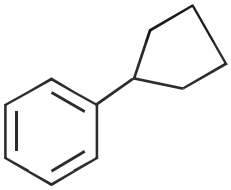
$+ (CH_3)_2C = CH_2 \xrightarrow{H_2SO_4}$?

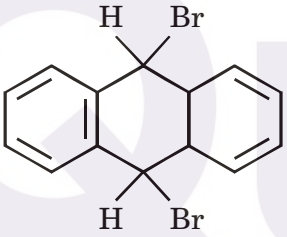
(g) 

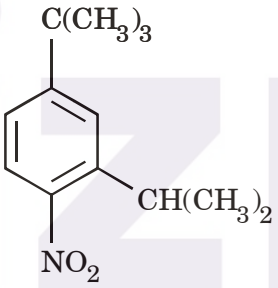
$\xrightarrow[CHCl_3]{Br_2}$?

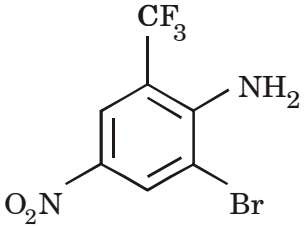
Solution :

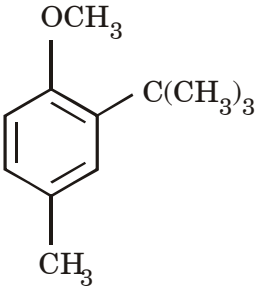
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

(g)