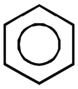
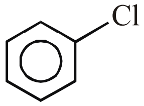
# AROMATIC COMPOUNDS

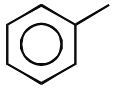
## INTRODUCTION

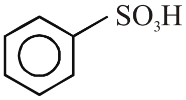
Aromatic hydrocarbons are known generally as arenes. An aryl group is one derived from an arene by removal of a hydrogen atom and its symbol is Ar—. Thus, arenes are designated ArH just as alkanes are designated RH.

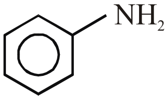
## SOME IMPORTANT AROMATIC COMPOUNDS

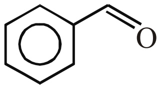
1.

Benzene

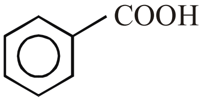
2.

Chlorobenzene

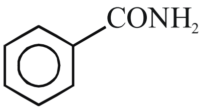
3.

Toluene

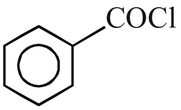
4.

Benzene sulphonic acid

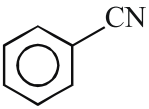
5.

Aniline

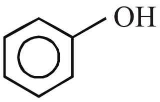
6.

Benzaldehyde

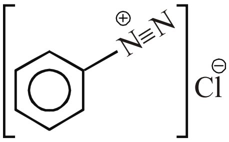
7.

Benzoic acid

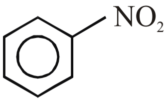
8.

Benzamide

9.

Benzoyl chloride

10.

Benzonitrile

11.

Phenol

12.

Benzene diazonium salt

13.

Niterobenzene

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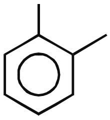
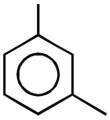
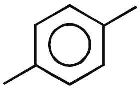
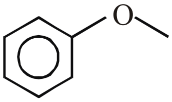
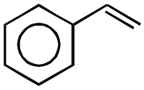

o-Xylene

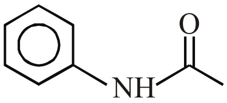
15.

m-Xylene

16.

p-Xylene

17.

Anisole

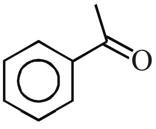
18.

Styrene

**19.**



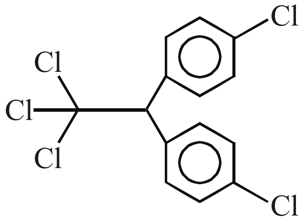
Acetanialide

**20.**



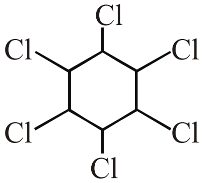
Acetophenone

**21.**



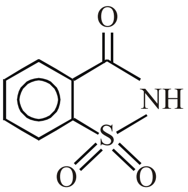
DDT
(Dihlorodiphynl trichloroethane)

**22.**



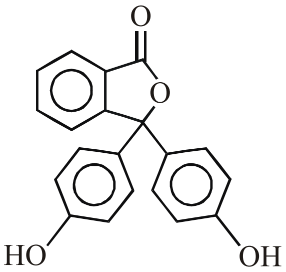
BHC
(Benzene Hexachloride)

**23.**



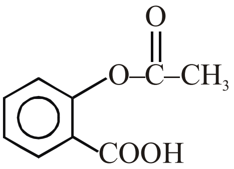
Saccharin

**24.**



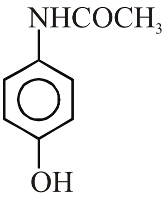
Phenolphtlalein

**25.**



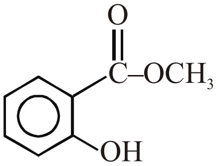
Aspirine

**26.**



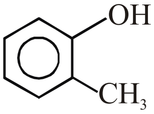
Paracetamol

**27.**



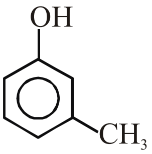
Oil of wintergreen

**28.**



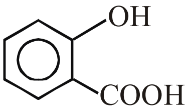
o-Cresol

**29.**



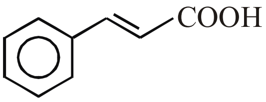
m-Cresol

**30.**



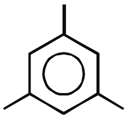
Salicylic acid

**31.**



Cinnamic acid

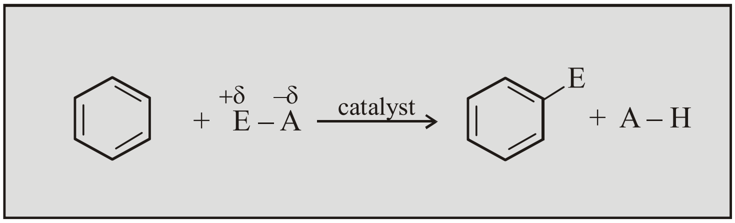
**32.**



Mesitylene

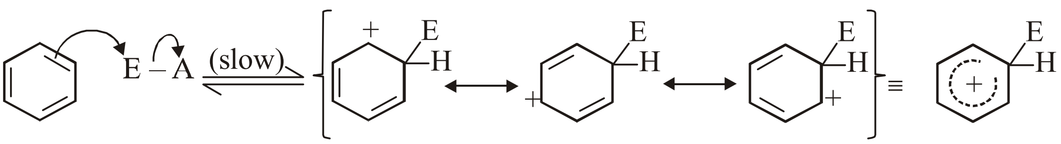
## ❑ REACTION OF AROMATIC COMPOUNDS

### (A) Electrophilic substitution reaction :



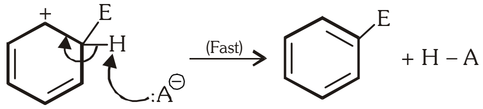
**General Mechanism for electrophilic Aromatic substitution** :

Step I



Arenium ion (σ-complex)

Step II



**The effects of various substituents on the reactivity of a benzene ring toward electrophilic substituion:**

**Strong activating groups :** —$NH_2$, —NHR, —$NR_2$, —OH, —OR.

**Moderately activating groups :** $—NH\overset{O}{\overset{\|}{C}}R$, $—O\overset{O}{\overset{\|}{C}}R$,

**Weakly activating groups :**—R, —Ar, —$CH{=}CR_2$

**Weakly deactivating groups :**—F, —Cl, —Br, —I

Ortho/para directing

**Moderately deactivating groups :** —CHO, —COR, —COOR, —COOH, —COCl

**Strong deactivating groups :** —C≡N, —$SO_3H$, $—\overset{+}{N}H_3$, $—\overset{+}{N}H_2R$, $—\overset{+}{N}HR_2$, $—\overset{+}{N}R_3$, —$NO_2$

Meta directing

## ❑ NITRATION

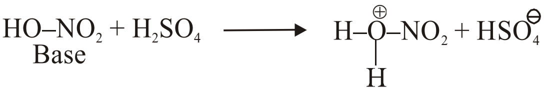
Nitration reaction is generally carried out with a mixture of concentrated nitric acid and sulphuric acid. The reagents which is used for nitration are called nitrating agents.

**Mechanism** :

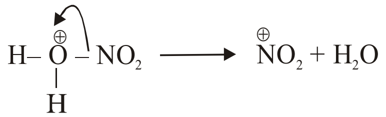
**Generation of electrophile from nitrating agent.**

**Step 1 :**

(a) In a mixture of nitric acid and sulphuric acid an acid base reaction takes place in which nitric acid acts as the base.



$$\underset{\text{Base}}{HO{-}NO_2} + H_2SO_4 \longrightarrow H{-}\underset{\underset{H}{|}}{\overset{\oplus}{O}}{-}NO_2 + HSO_4^{\ominus}$$



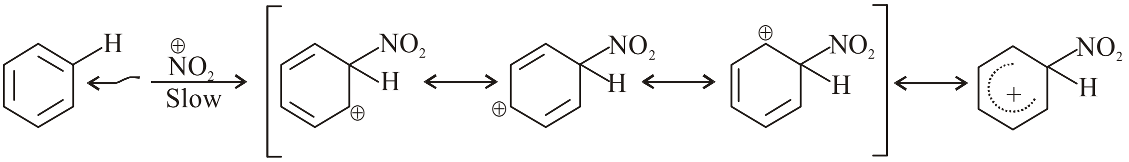
$$H-\overset{\oplus}{O}(H)-NO_2 \longrightarrow \overset{\oplus}{N}O_2 + H_2O$$

$$H_2O + H_2SO_4 \longrightarrow H_3O^{\oplus} + HSO_4^{\ominus}$$

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{\oplus}{N}O_2 + H_3O^{\oplus} + 2\ HSO_4^{\ominus}$$

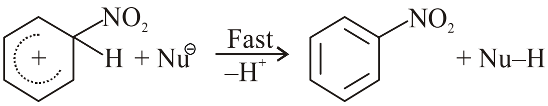
**Step :**

**Attack of electrophile on aromatic System :**



**Step :**

**Transfer of Proton to a base/nucleophile**



**KEY POINTS :**

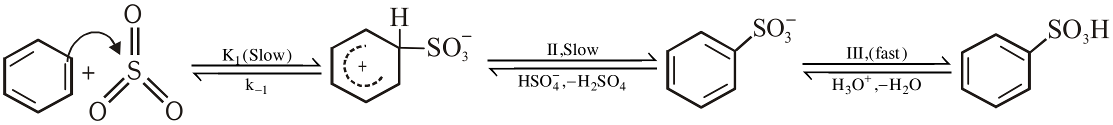
- In nitration, electrophile is $NO_2^+$
- Conc. ($H_2SO_4$ + $HNO_3$) is known as nitrating mixture.
- In nitrating mixture ($HNO_3$) work as bronsted base and $H_2SO_4$ as bronsted acid.
- Kinetic isotopic effect is not occurs here on rate of reaction. Hence benzene, $C_6D_6$, $C_6T_6$ reacts with same rate.

## ☐ SULPHONATION

Sulphonation is another synthetically important reaction. It is often accomplished with concentrated sulphuric acid or fuming sulphuric acid containing excess of $SO_3$ or chlorosulphonic acid, $ClSO_2OH$.

$H_2SO_4$ ($SO_3$ + $H_2O$) or $H_2S_2O_7$)

$$2H_2SO_4 \rightleftharpoons HSO_4^- + H_3O^+ + SO_3$$



**KEY POINTS:**

- In sulphonation, $SO_3$ is electrophile.
- $ClSO_3H$ in $CCl_4$ can also be used for sulphonation in some cases.
- Kinetic isotopic effect occurs here on rate of reaction. Hence benzene reacts more fast than $C_6D_6$ than $C_6T_6$.

## ☐ HALOGENATION

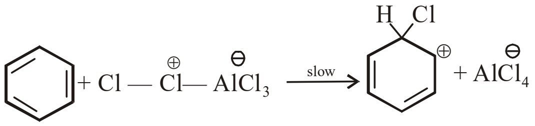
Halogenation is catalysed by a Lewis acid like $AlCl_3$, or $FeCl_3$, Reactivity of halogens has the following order,

$$I_2 < Br_2 < Cl_2$$

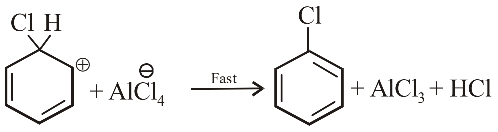
Let us take chlorination as a representative reaction to understand the mechanism of halogenation. Chlorine, in the presence of $AlCl_3$ or $FeCl_3$ forms a complex, $Cl_2$—$AlCl_3$. This complex can itself be the reactive electrophile or it may dissociate to give $Cl^+$.

Step 1 : $\mathrm{Cl{-}\ddot{C}l{:}} + \underset{\text{(anhydrous)}}{\mathrm{AlCl_3}} \rightleftharpoons \mathrm{Cl{-}\overset{\oplus}{Cl}{-}\overset{\ominus}{Al}Cl_3}$

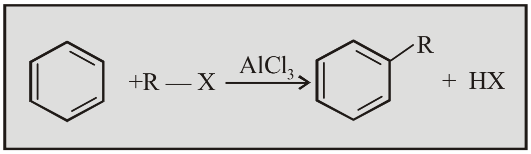
Step 2 :



Step 3 :

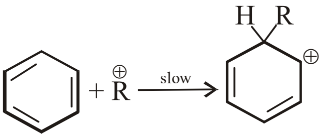


## ❑ FRIDEL-CRAFT'S ALKYLATION

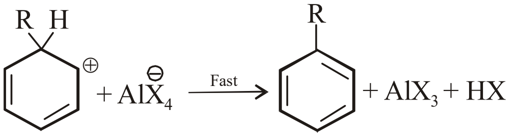


Step 1 : $\mathrm{R{-}X} + \underset{\text{(anhydrous)}}{\mathrm{AlX_3}} \rightleftharpoons \mathrm{\overset{\oplus}{R} + \overset{\ominus}{AlX_4}}$

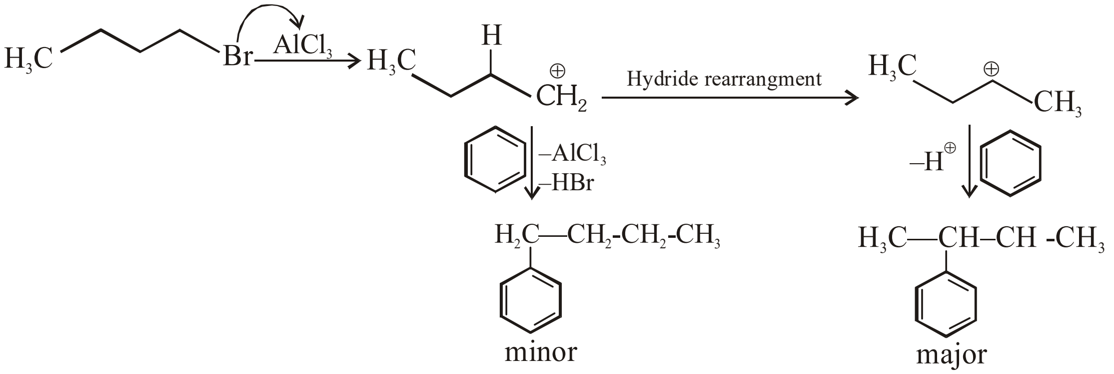
Step 2 :



Step 3 :



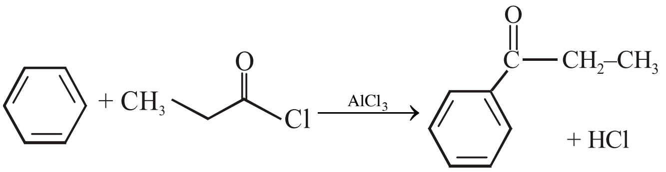
**Note :** Carbocations intermediat is formed so rearrangment is possible.



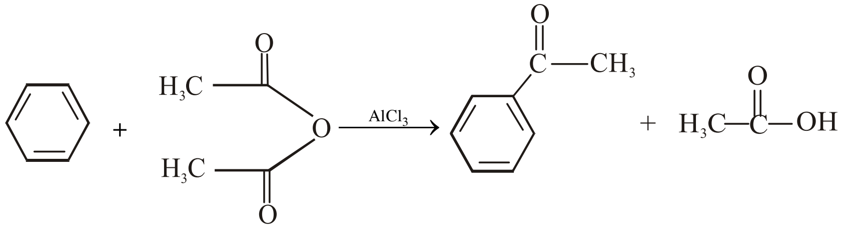
## ❑ FRIEDEL-CRAFTS ACYLATION

The reaction where an acyl group is introduced into an aromatic compound compound is called an acylation reaction.

The Friedel-Crafts acylation reaction is an effective means of introducing an acyl group into an aromatic ring. The reaction is often carried out by treating the aromatic compound with an acyl halide.



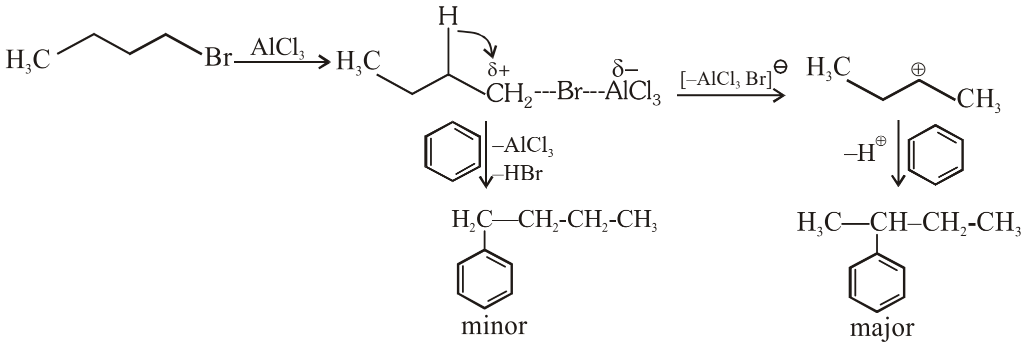
Friedel-Crafts acylations can also be carried out using carboxylic acid anhydrides. eg.



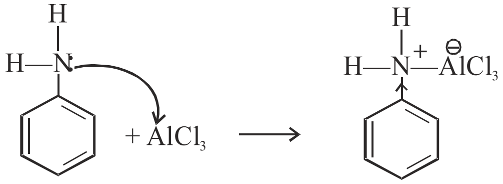
**Limitations of Friedel - Crafts Reactions :**

(a) 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. The benzene reacts with both kinds of carbocations to form both butylbenzene and sec-butylbenzene.

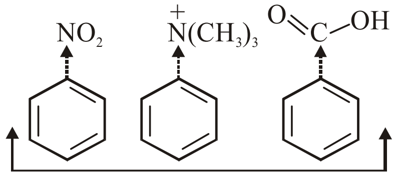


(b) Aromatic ring containing $-NH_2$, $-NHR$, $-NR_2$, groups do not undergo Friedal-Craft's alkylation due to formation of anilinum complex which is meta directing and has more electron withdrawing power than halogen in benzene ring.



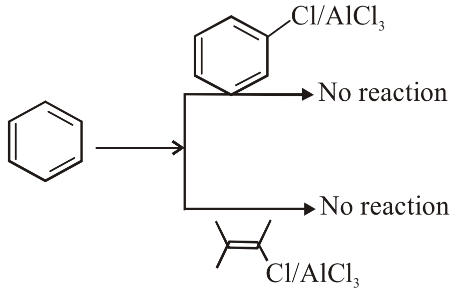
Meta directing group
and does not undergo
Friedal Craft's reaction

(c) Friedel-Crafts reactions (alkylationi and acylation) do not occur when powerful electron-withdrawing groups are (like $-NO_2$, $-\overset{\oplus}{N}R_3$ etc) present on the aromatic ring.

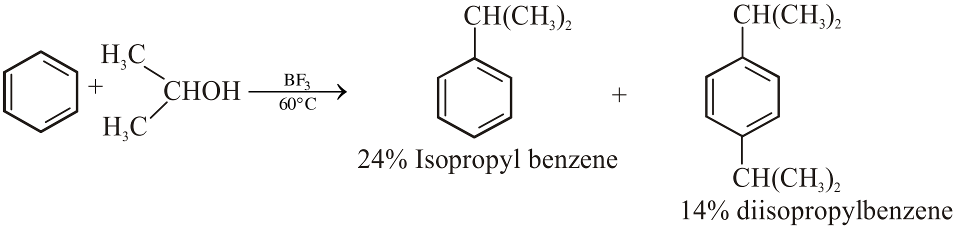


These do not undergo Friedel -Crafts reactions

(d) Aryl and vinylic halides can not be used as the halide component because they do not form carbocations readily.



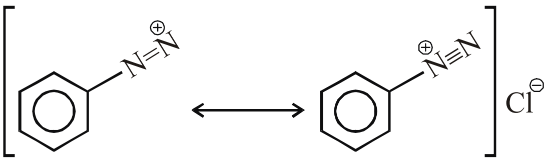
(e) Polyalkylations often occur because alkyl groups are electron releasing groups, and once one is introduced into the benzene ring it activates the ring towards further substitution.



Polyacylations are not a problem in Friedel-Crafts acylations. 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.

## COUPLING REACTION

Coupling reaction is used for formation of coloured compound dye & indicator. In this reaction benzene diazonium salt is electrophile.

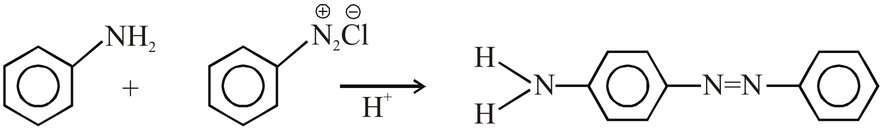


Resonating structures of Benzene diazonium chloride.

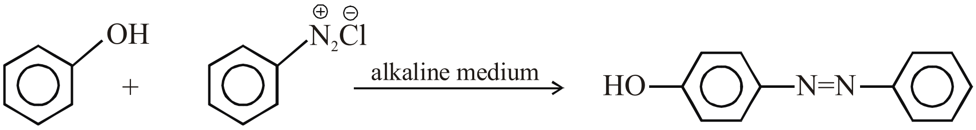
**C–N coupling :**

The reaction in which coupling occurs between carbon & nitrogen is called C–N coupling.

The reaction in which coupling occurs between nitrogen & nitrogen is called N–N coupling.



(Yellow colour dye)



(Red colour dye)