

## AROMATIC HYDROCARBONS

### MAIN SOURCE

Bituminous coal when subjected to destructive distillation in the absence of air [1000°–1200°C] the chief constituent obtained is coal tar.

**Fractional distillation of coal tar :** Different fractions are :

	Fraction	Temperature	Main constituents
(a)	Light oil	80 – 170°C	Benzene, toluene, xylene etc.
(b)	Middle oil (carbolic oil)	170° – 230°C	Naphthalene, Phenol etc.
(c)	Heavy oil	230° 270°C	Cresols, naphthalene
(d)	Green oil	270° – 360°C	Anthracene
(e)	Pitch	Residue	Carbon

### BENZENE

[i] Discoverer : Michael Faraday

[ii] C-hybridisation :  $sp^2$

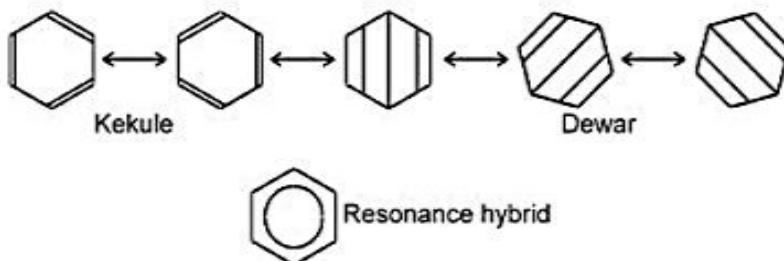
[iii] Geometry – Hexagonal

[iv] Bond angle : 120°

[v] C-C Bond length : 1.39 Å

[vi] C-H Bond length : 1.09 Å

[vii] Resonance in benzene :

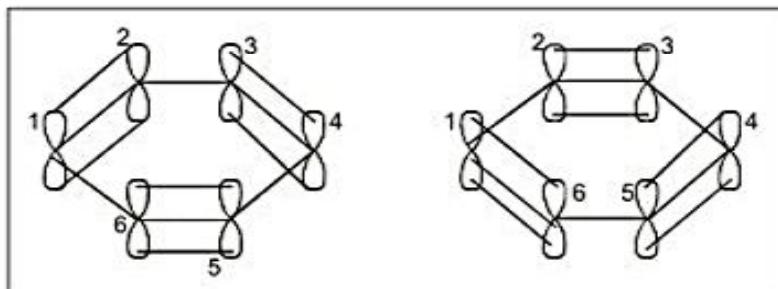


[ix] Number of angles of 120° : 18

[x] Localized and delocalized  $\pi$ -orbital

Localized  $\pi$ -orbital

Localized  $\pi$ -orbital

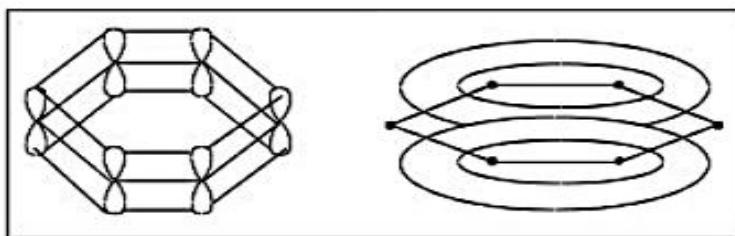


Partial overlapping  
of p-orbital C<sub>1</sub>—C<sub>2</sub>,  
C<sub>3</sub>—C<sub>4</sub> and C<sub>5</sub>—C<sub>6</sub>

Partial overlapping  
of p-orbital C<sub>2</sub>—C<sub>3</sub>,  
C<sub>4</sub>—C<sub>5</sub> and C<sub>1</sub>—C<sub>6</sub>

Obviously, each orbital formed in the partial overlapping is attracted by two carbon nucleus hence less stable.

### Delocalized p-orbital :



### Methods of Preparation of Benzene :

#### Isolation From 'Light Oil Fraction – Industrial method :

In 'light oil', at least 60–65% benzene is present. Alkaline impurities (aniline, pyridine, quinolene, etc.) are removed by washing 'light oil' with cold and conc. H<sub>2</sub>SO<sub>4</sub>. The acidic impurities are removed by washing with dilute NaOH solution. After that, NaOH is removed by washing with water. Three fractions are obtained at different temperature ranges by fractional distillation of the neutral sample of oil.

- [i] 90% Benzol (90's benzol). 80–110°
- [ii] 50% Benzol (50's benzol). 110–140°
- [iii] Solvent naphtha – 140°–170°

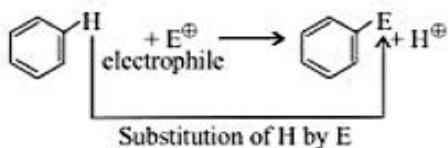
The 90% benzol contains about 70% benzene 24% toluene and remaining xylenes. Fractional distillation gives benzene at 80°, toluene at 110° and a mixture of all the three xylenes at 137–145°. Crystals are formed on cooling benzene from which pure benzene can be obtained by melting the crystals.

## ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

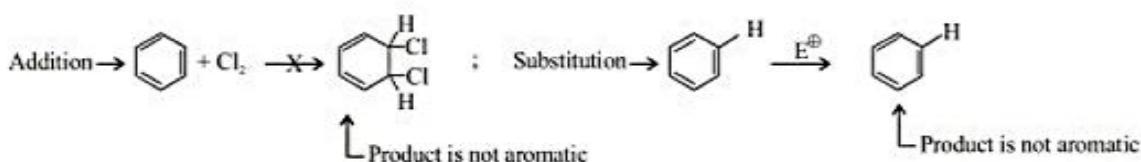
Based on its structure and properties, what kind of reaction should benzene undergo ? Are any of its bond particularly weak does it have electron rich or electron deficient atom.

- \* Benzene has six p-electron delocalized in six p-orbitals that overlap above and below the plane of ring. These loosely held π-electron make the benzene ring electron rich, and so it reacts with electrophile.
- \* Because benzene six π-electron satisfy Huckel's rule, benzene is especially stable. Reactions that keep the aromatic ring intact are therefore, favoured.
- \* Electron cloud above and below the plane of benzene shields the ring carbon from the attack of a nucleophile.

As a result, the characteristic reaction of benzene is electrophilic aromatic substitution - a hydrogen atom is replaced by an electrophile.



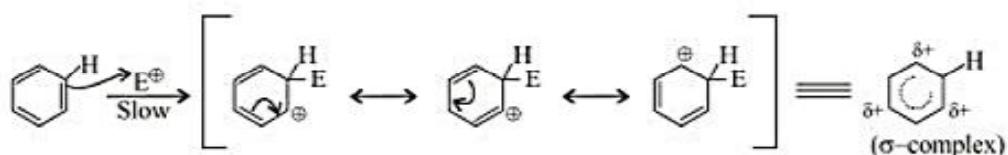
Benzene does not undergo addition reaction like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic. Substitution of a hydrogen on the other hand, keeps the aromatic ring intact.



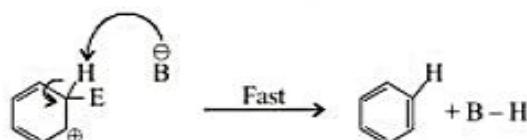
## THE GENERAL MECHANISM OF EAS

EAS reactions occur via a two steps mechanism.

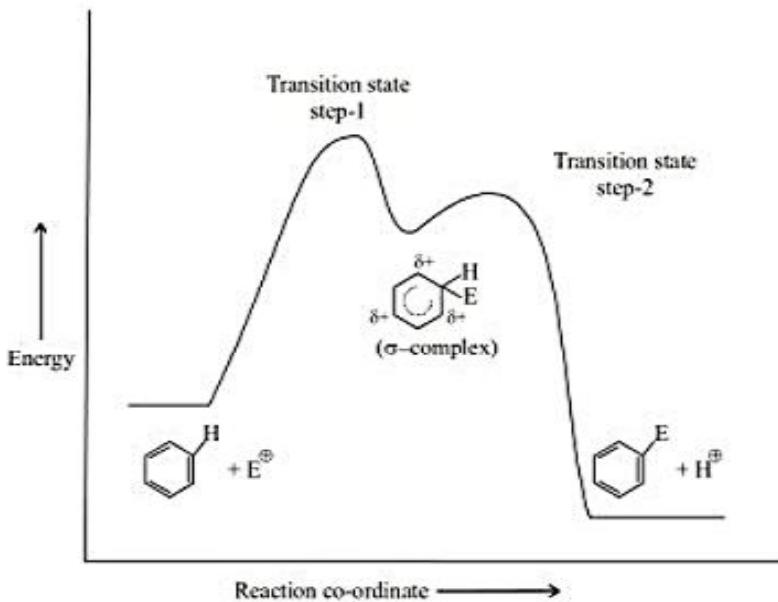
### **Step 1: Addition of the electrophile**



### **Step 2. Loss of a proton to reform the aromatic ring**



Any of the three resonance structures of the carbocation intermediate can be used to draw the product. The energy changes in EAS are shown in figure. The mechanisms consist of two steps, so energy diagram has two energy barriers. Because the first step is rate-determine, its transition state is higher in energy.



Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004533.jpg

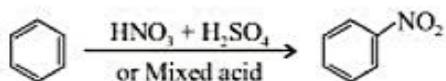
**Most examples of EAS proceed by this sequence of events :**

1. Generation of an electrophile
2. Attack of the aromatic ring on the electrophile
3. The resulting carbocation is stabilized by the resonance
4. A proton is eliminated from the carbocation
5. A substituted aromatic compound is formed

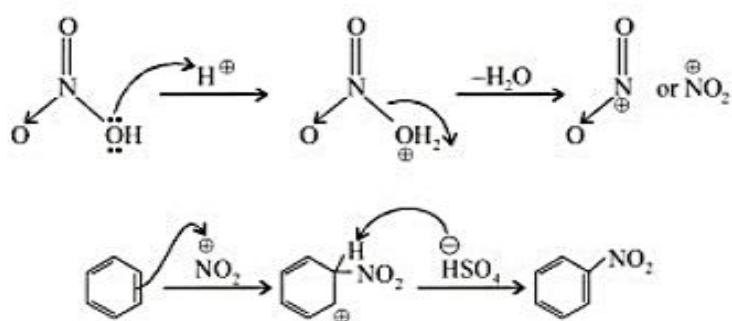
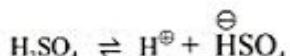
## NITRATION OF BENZENE

The introduction of a nitro ( $-NO_2$ ) group on benzene known as nitration of benzene. The most common reagent for the nitration of aromatic compound is mixture of concentration  $HNO_3$  and concentration  $H_2SO_4$  (mixed acid).

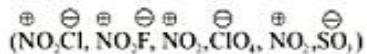
The electrophile required for the nitration is nitronium ion ( $\text{NO}_2^+$ ).



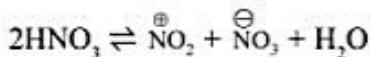
**Mechanism :**



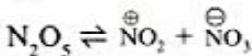
Besides mixed acid, other reagents have also been used for nitration such as nitronium salts



In the case of fuming  $HNO_3$  alone  $\text{NO}_2^+$  is formed as follow



In nonpolar solvent  $N_2O_5$  get dissociated and produces  $\text{NO}_2^+$



**Problem :** Compare rate of nitration among  $C_6H_6$ ,  $C_6D_6$  and  $C_6T_6$ .

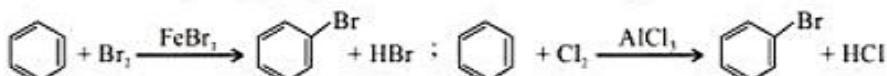
**Solution :**  $C_6H_6 = C_6D_6 = C_6T_6$

Therefore nitration of benzene does not show primary kinetic isotopic effect.

Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004535.jpg

## HALOGEN OF BENZENE

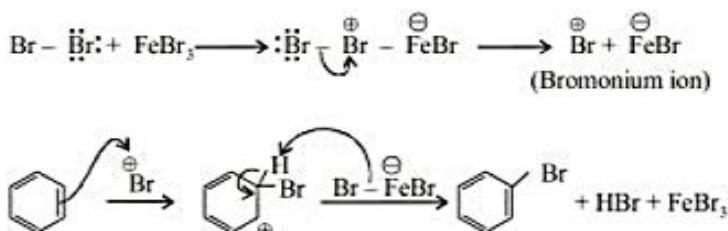
The introduction of halo (-X) group on benzene known as halogenation of benzene



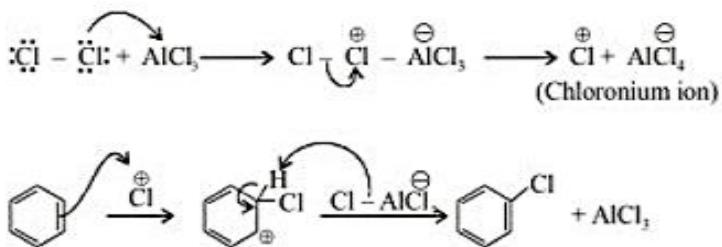
The bromination or chlorination of benzene requires a Lewis acid catalyst such as  $\text{FeBr}_3$ ,  $\text{AlBr}_3$ ,  $\text{FeCl}_3$  or  $\text{AlCl}_3$ .

Sometime Fe or Al is used but real catalyst is not Fe or Al itself but  $\text{FeX}_3$  or  $\text{AlX}_3$  is formed from the reaction between halogen and Fe or Al.

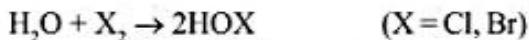
### Mechanisms for Bromination



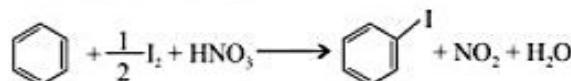
### Mechanisms for Chlorination



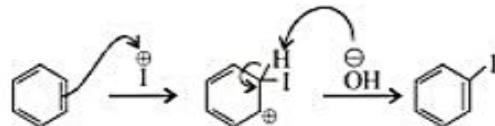
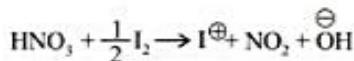
Bromination and chlorination also occur by  $\text{HOBr}$  and  $\text{HOCl}$ , obtained by reaction between  $\text{H}_2\text{O}$  and  $\text{X}_2$ .



Iodination of benzene requires an acidic oxidizing agent such as nitric acid. Nitric acid is consumed in the reaction, so it is a reagent rather a catalyst.



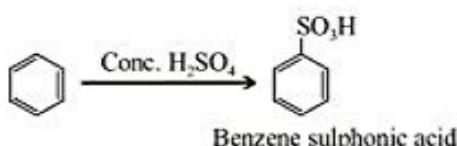
### Mechanisms for Iodination



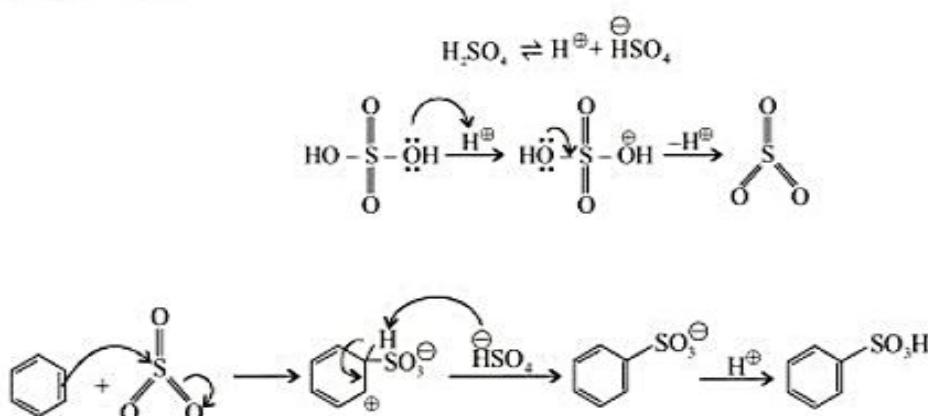
The electrophile required for halogenation reaction is halonium ion ( $\text{X}^\oplus$ )

### Sulphonation of Benzene

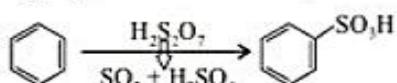
Sulphonation is usually done with concentration  $\text{H}_2\text{SO}_4$ . Electrophile required for sulphonation reaction is  $\text{SO}_3^+$ .



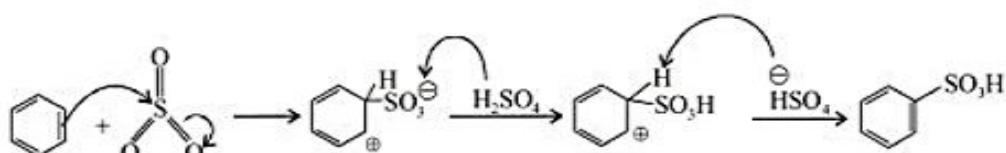
### Mechanisms :



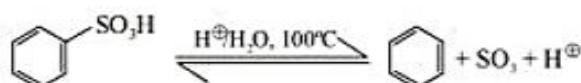
Fuming sulphuric acid or oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ) is also used to sulphonate aromatic ring.



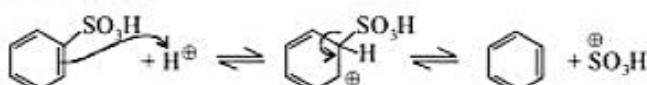
### Mechanisms :



Sulphonation of benzene is a reversible reaction. If benzenesulfonic acid is heated in dilute acid, the reaction proceed in reverse direction.



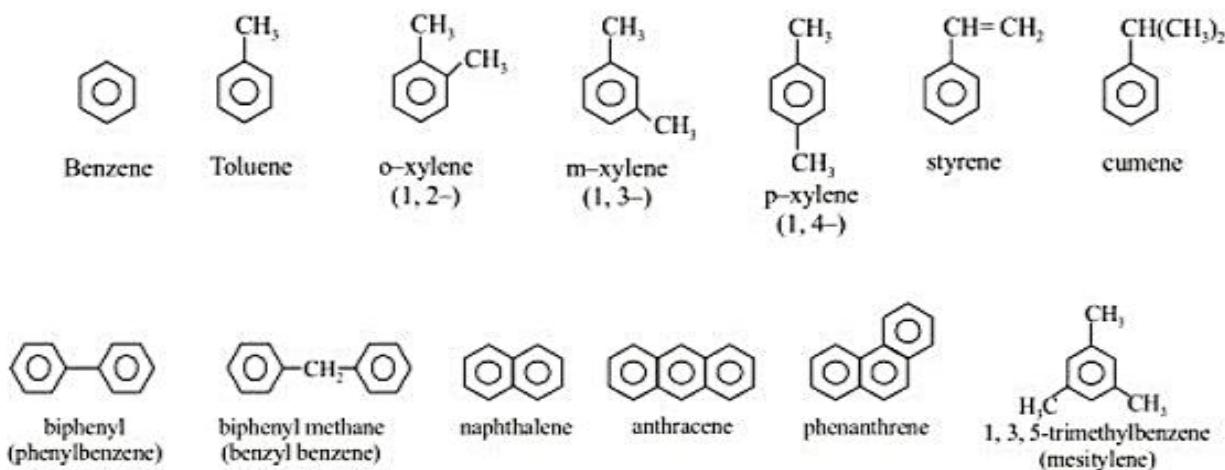
### Mechanisms of desulphonation



## RELATIVE REACTIVITY OF SUBSTITUTED BENZENE

Ortho para directors Strongly activating	Meta directors Moderately deactivating
$-\text{O}^\ominus\text{--}\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{R}_2, -\ddot{\text{O}}\text{H}, -\ddot{\text{O}}\text{R}$	$-\overset{\text{O}}{\parallel}\text{C--H}, -\overset{\text{O}}{\parallel}\text{C--}, -\overset{\text{O}}{\parallel}\text{C--Cl}, -\overset{\text{O}}{\parallel}\text{C--NH}_2, -\overset{\text{O}}{\parallel}\text{C--OH}, -\overset{\text{O}}{\parallel}\text{C--OR}$
Moderately activating	Strongly deactivating
$-\ddot{\text{N}}\text{H}-\overset{\text{O}}{\parallel}\text{C--CH}_3, -\ddot{\text{O}}-\overset{\text{O}}{\parallel}\text{C--CH}_3$	$-\overset{\oplus}{\text{NH}}_2, -\overset{\oplus}{\text{N}}\text{R}_2, -\text{NO}_2, -\text{C}=\text{N}, -\text{CF}_3, -\text{CCl}_3$
Weakly activating	
$-\text{CH}_3, -\text{CH}_2\text{CH}_3, -\text{R}$	
	
Weakly deactivating	
$-\ddot{\text{F}}, -\ddot{\text{Cl}}, -\ddot{\text{Br}}, -\ddot{\text{I}}$	

## AROMATIC HYDROCARBONS



### Source

(a) **Fractional distillation of Coal tar**

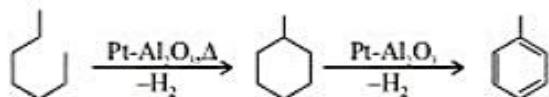
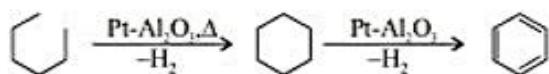
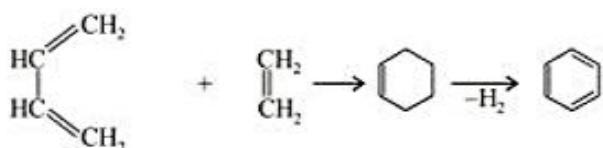
The dark-brown sticky liquid called coal-tar is a mixture of several aromatic hydrocarbons, phenols, bases etc. The first step in the separation of coal-tar into its components is distillation in a fractionating column as given in table.

(b) **High temperature cracking**

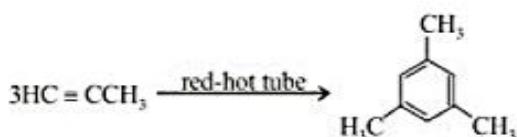
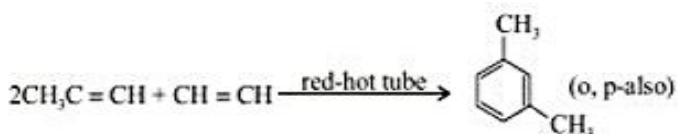
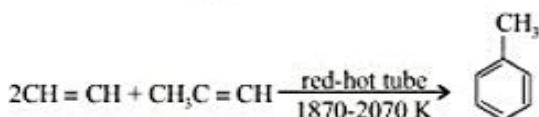
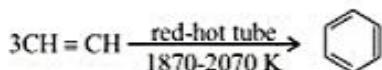
Petroleum (kerosene and low boiling fractions)  $\xrightarrow{\text{cracking}}$  mixture of alkenes and alkanes.

$\xrightarrow{\text{cyclisation/aromatisation}}$  aromatic hydrocarbon

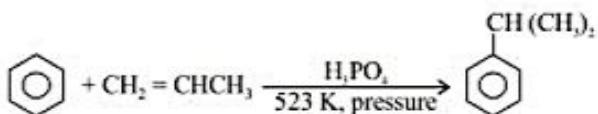
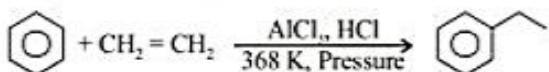
Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004541.jpg



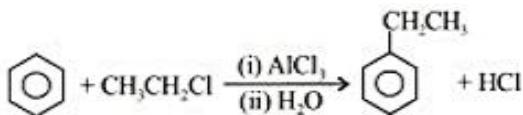
**(c) Polymerisation**



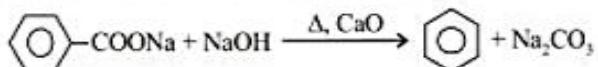
**(d) Alkyl benzene synthesis**

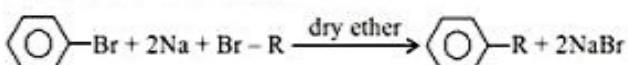
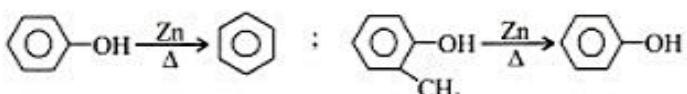
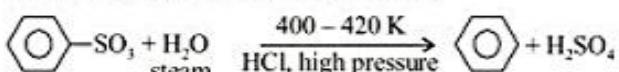


**(e) Friedel-Crafts reaction**



**(f) Decarboxylation of Aromatic acids**



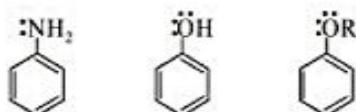
(g) **Wurtz-Fitting reaction**(h) **Deoxygenation of Phenols**(i) **Reduction of Diazonium salts**(j) **Desulphonation of sulphonic acids**

Mechanisms of the above reactions have been given in further section.

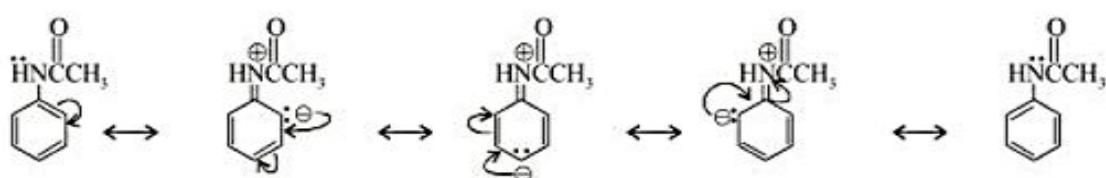
1. All meta-directing groups are deactivating groups;
2. All ortho, para-directing groups except for the halogen are activating groups.
3. The halogens are deactivating groups

The activating substituents make the benzene ring more reactive towards electrophilic substitution, the deactivating substituents make the benzene ring less reactive towards electrophilic substitution.

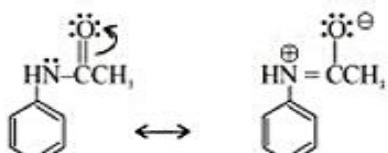
All the strong activating substituents donate electrons into the ring by resonance and withdraw electrons inductively. The fact that they are strong activators indicate that electron donation into the ring by resonance (which increases electron-density hence, nucleophilicity) is much greater than electron withdrawal from the ring by the inductive effect (which decreases electron-density hence nucleophilicity). Strongly activating substituents are :



The moderately activating substituents also donate electrons into the ring by resonance and withdraw electrons from the ring inductively. However they donate electrons into the ring by resonance less effectively than do not strongly activating substituents. These substituents are less effective at resonance donation since, they can donate electrons by resonance in two competing directions- into the ring and away from the ring and thus net resonance effect is diminished and still electron donation by resonance is more than the electron withdrawal by induction and thus, these substituents are activators though moderately.

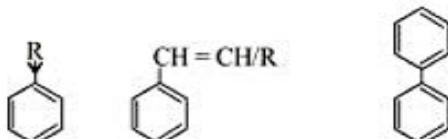


(substituents donates electrons by resonance into the benzene ring)



(substituents donates electrons away from the benzene ring)

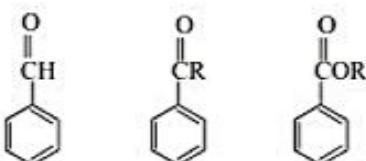
Alkyl, aryl and  $\text{CH} = \text{CHR}$  groups are weakly activating substituents. Two of the three groups (aryl and  $\text{CH} = \text{CHR}$ ) can donate electrons into the ring by resonance and can also withdraw from the ring by resonance. The fact that they are weak activators indicates that they are slightly more electron-donating than they are electron-withdrawing. An alkyl substituent is a weak electron donor because of hyperconjugation.



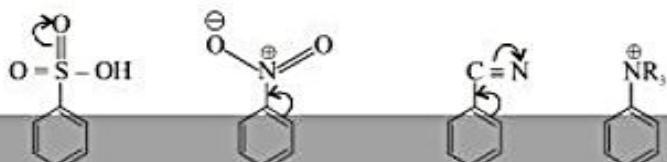
The halogen are weakly deactivating substituents. They donate electrons into the ring by resonance and withdraw electrons inductively. Since, they have been found deactivators, we can conclude that they withdraw electrons inductively more strongly than they donate electrons by resonance.



The moderately deactivating substituents all have carbonyl groups directly attached to the benzene ring. They withdraw electron both inductively and by resonance.

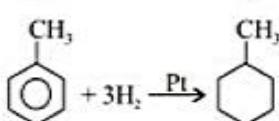
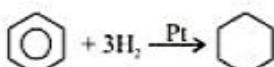


The strongly deactivating substituents are powerful electron withdrawers. With the exception of  $-\overset{\oplus}{\text{NH}_3}$ ,  $-\overset{\oplus}{\text{NH}_2}\text{R}$ ,  $-\overset{\oplus}{\text{NHR}_2}$ , and  $-\overset{\oplus}{\text{NR}_3}$ , and they withdraw electrons both inductively and by resonance. The ammonium ions have no resonance effect, but the positive charge on the nitrogen atom causes them to strongly withdraw electron inductively.

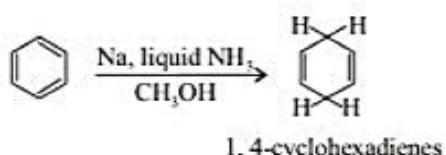


Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004549.jpg

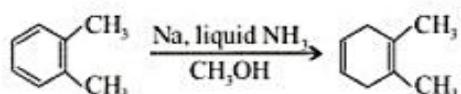
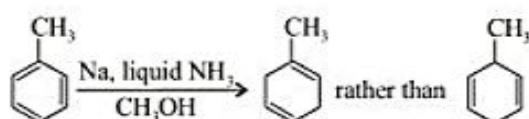
**(a) Catalytic hydrogenation**



Treatment of arenes with group I metal (like sodium, lithium) and methanol (or ethanol) in liquid reduces arenes to non-conjugated dienes.

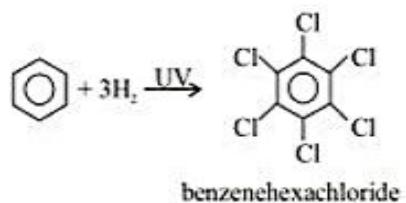


Alkyl substituted arenes give 1, 4-cyclohexadienes in which the alkyl group is a substituent on the double bond.



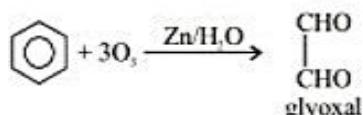
Metal ammonia -alcohol reduction of aromatic ring is known as Birch reduction and is one type of a more general class of reactions called dissolving metal reduction.

**(b) Addition of Halogen**



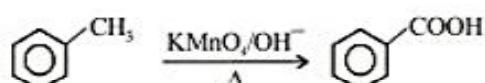
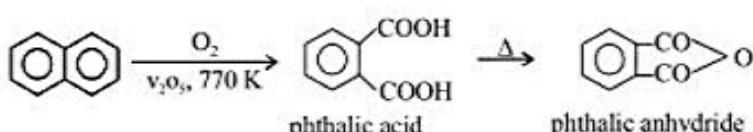
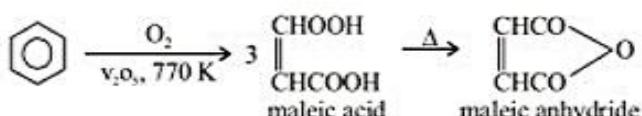
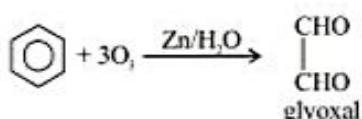
Benzenehexachloride (BHC,  $\text{C}_6\text{H}_6\text{Cl}_6$ ) is also called Lindane or Gammaxene ( $\gamma$ -isomer) and is used insecticide.

**(c) Ozonolysis**

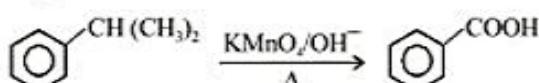


Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004551.jpg

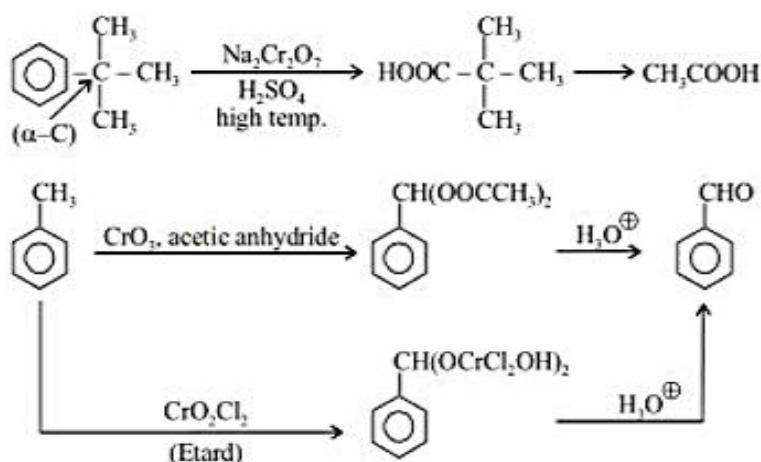
## (d) Oxidation



When oxidised using  $\text{KMnO}_4/\text{OH}^-$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ,  $\text{KMnO}_4/\text{H}^+$  the entire side chain, with at least one H at  $\alpha$ -C, regardless of length is oxidised to  $-\text{COOH}$ .



The conversion of alkyl benzenes to benzoic acid with strong oxidations suggest that benzene ring is more stable than the side chains; this is correct so long as the side-chain contains at least one benzylic C–H bond. The first step in the mechanism is the removal of hydrogen from the benzylic carbon. If the side-chain has no C–H bond at the  $\alpha$ -carbon (w.r.t. benzene nucleus), then benzene ring is cleaved.

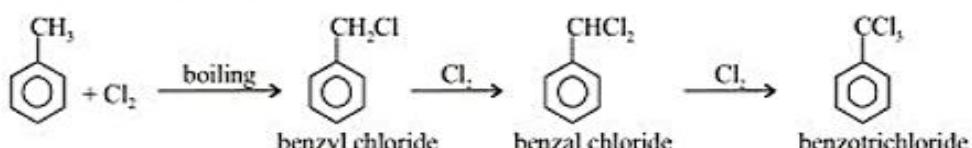


## (e) Combustion

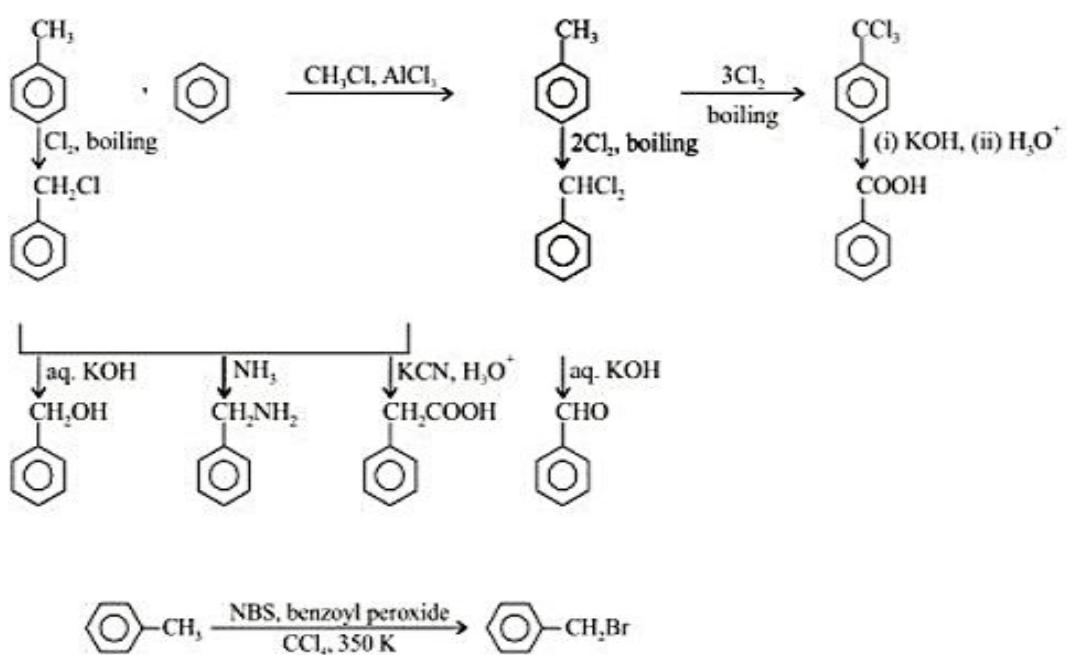


Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004553.jpg

### (f) Side-chain halogenation

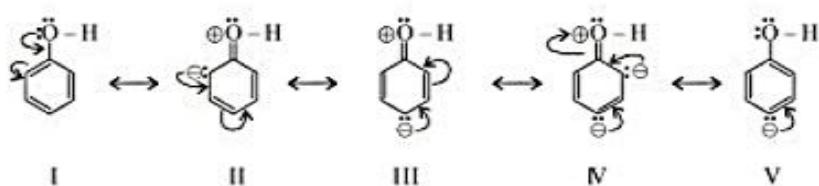


This provides a source of preparing other derivatives from benzene and toluene.

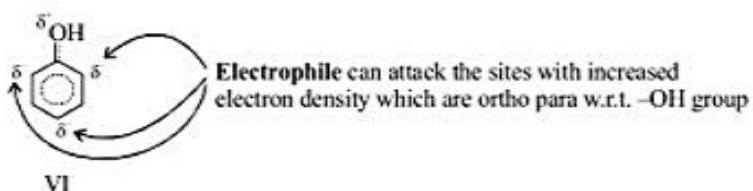


## DIRECTING INFLUENCE AS DECTED BY ELECTRON DENSITY

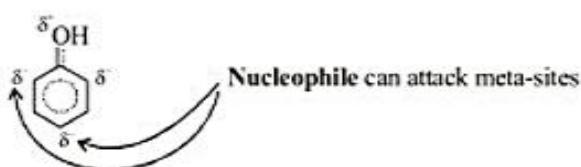
- OH group is ortho and para-directing since it increases electron-density at ortho and para-positions for electrophilic attacks; electron-density at meta-position is decreased hence, electrophilic attack at this position is least.



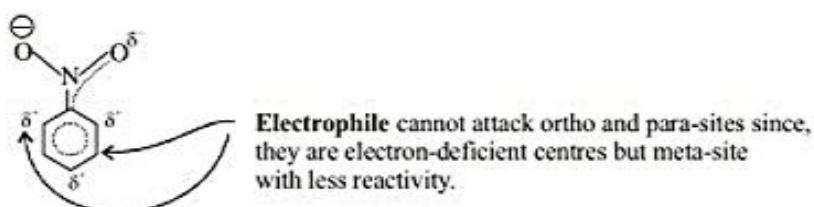
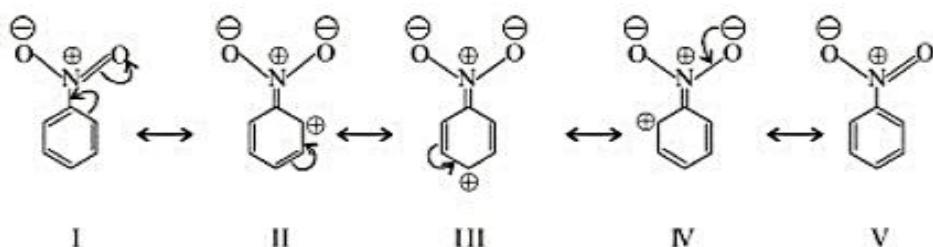
I to V are different resonance structures and VI resonance hybrid structure.



Naturally nucleophile cannot attack ortho and para-sites but can attack at meta-site (but less reactive)



- NO<sub>2</sub> group is electron-withdrawing group. It deactivates ortho and para-position for electrophilic attack and thus electrophile can occupy meta-position. I to V are resonance and VI is resonance hybrid.

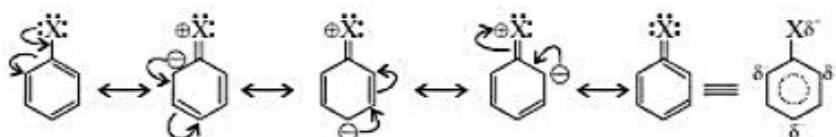


In this case nucleophilic attack at electron-rich ortho and para-sites is favoured.

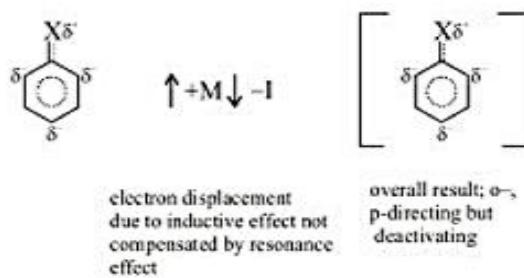


## ANAMALOUS BEHAVIOUR OF HALOGEN SUBSTITUENT

- X(F, Cl, Br, I) is o-, p-directing but is **deactivating** group.

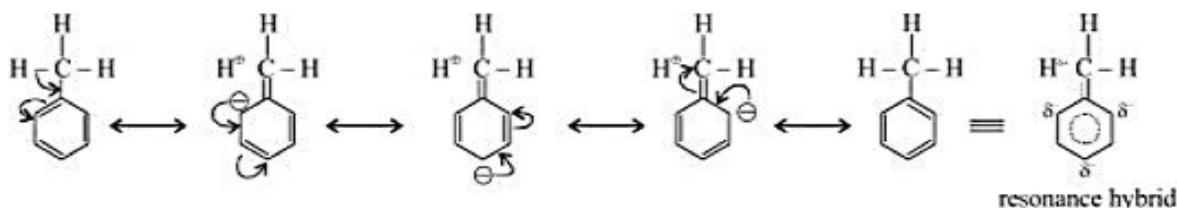


This deactivating nature is attributed to high electronegativity of the halogen atom due to which they withdraw electrons; resonance effect explains its electron-donating behaviour.



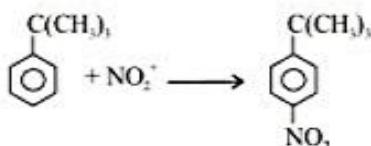
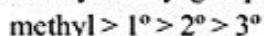
## Alkyl groups and Orientation

Alkyl groups ( $-\text{CH}_3$ ,  $-\text{CH}_2\text{CH}_3$ , etc.) have complete octet and are without one-pair of electrons; but they are ring activators and o-, p-directors. They not only show electron-pumping effect, but also when attached to conjugated system show hyperconjugated effect (no-bond resonance). This type of resonance requires the interaction of  $\sigma$ -electrons instead of usual lone-pair of electrons. In toluene, hyperconjugation is shown below :



Thus, hyperconjugation helps in increasing-density at o-and p-sites in case of alkyl groups.

There must be at least one H-atom on the carbon of the alkyl group joined to the ring carbon to take part in hyperconjugation and relative ability of alkyl groups for this effect is

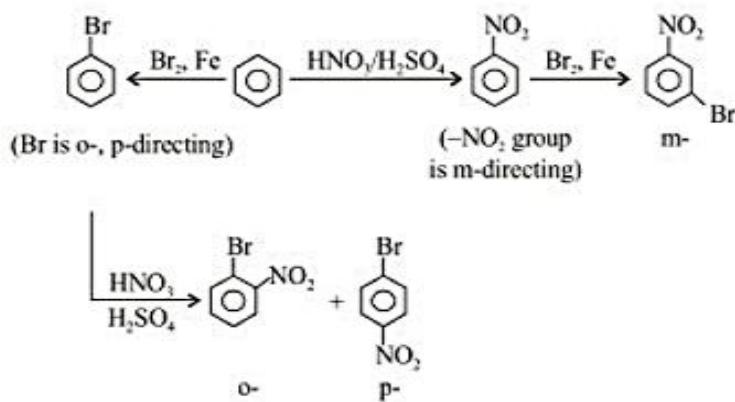


In this case, only p-isomer is obtained. It is due to steric influence of the substituents  $-\text{C}(\text{CH}_3)_3$ , and due to its inability to show hyperconjugation.

## Orientation and Synthesis

By using the nature of directing group (substituent), it is possible to prepare variety of products.

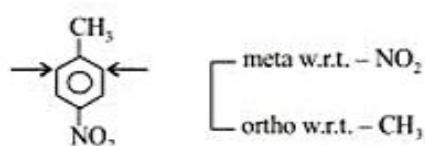
To prepare meta-bromo nitrobenzene from benzene, we have to first carry out nitration and then bromination; and to prepare o-and p-derivatives, sequence will be bromination and then nitration.



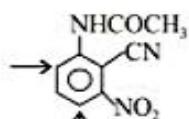
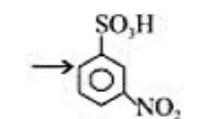
## Orientation in Disubstituted benzene

When two substitution are present, orientation of the third coming  $S_F$  is complicated.

$-\text{CH}_3$  group is o-, p-directing and  $-\text{NO}_2$  group is m-directing, thus in p-nitrotoluene, new electrophile can be in a position shown by arrow :



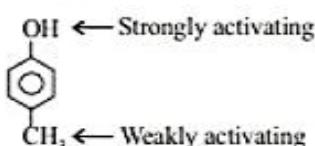
Similarly we can decide the position of the new electrophile in other disubstituted compounds.



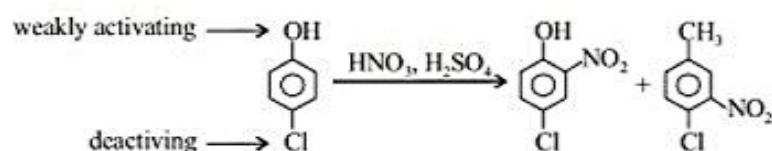
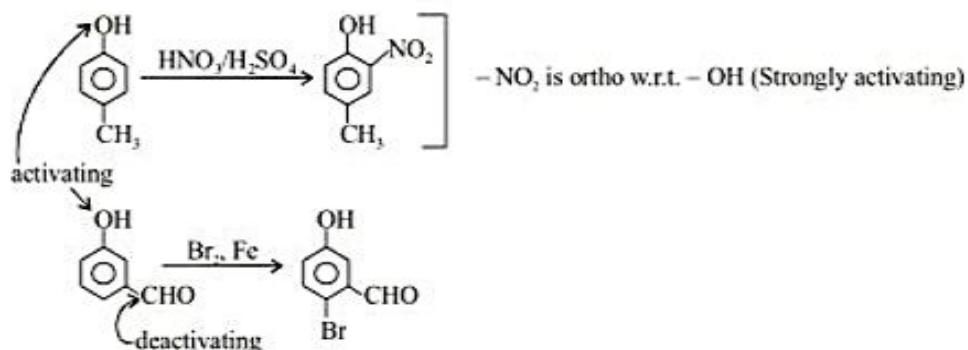
both meta-directing

- NHCOCH<sub>3</sub> ortho, para and  
- CN meta-directing

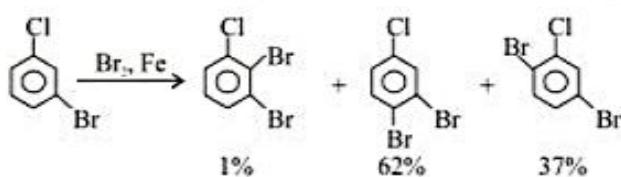
### Problems may arise in the following cases :



Both are ortho, para-directing and none of the vacant positions are ortho-and para, w.r.t. each. In such cases we follows : (a) Strongly activating groups generally win over deactivating or weakly activating groups.



(b) If the substitution are meta to each other, S<sub>E</sub> in between vacant sites takes place rarely.

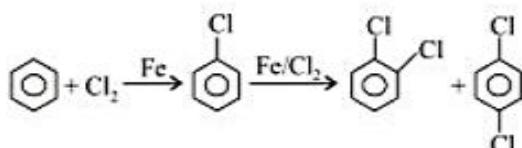


## HALOGEN COMPOUND

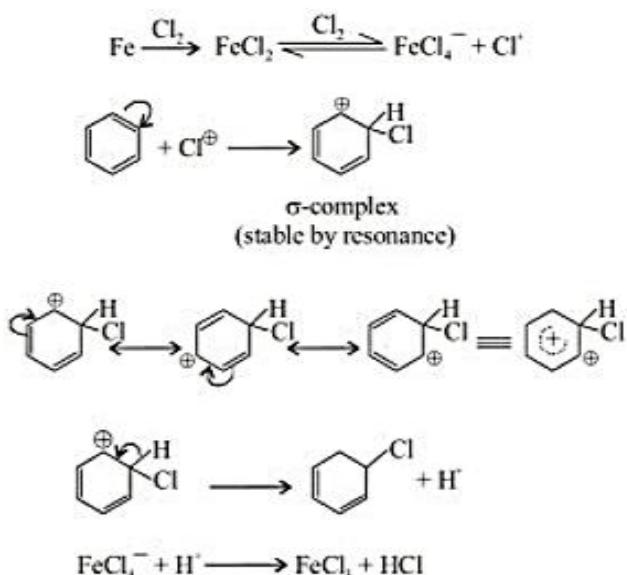
### Aryl Halides

#### Source/Preparation

- Direct halogenation:

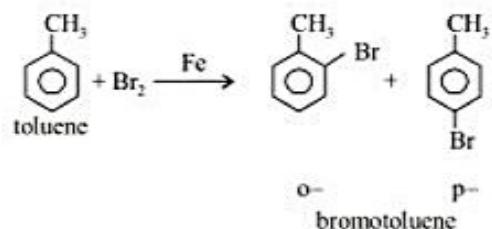


Low temperature and the presence of a halogen carrier favour nuclear substitution. The chlorides or bromides of Al, Fe, Sb may be used:

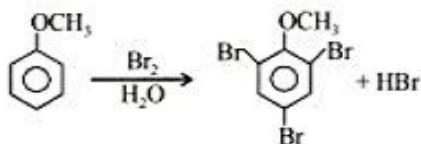


Iron is most commonly used being converted to Lewis acid  $\text{FeCl}_3$  as shown above.

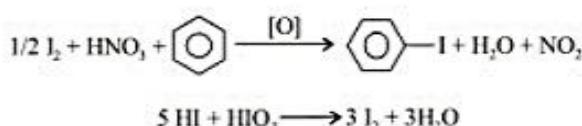
It is again  $S_E$  reaction and without halogen-carrier (Lewis acid),  $\text{Cl}^+$  (halonium) is not formed and hence, reaction is not possible:



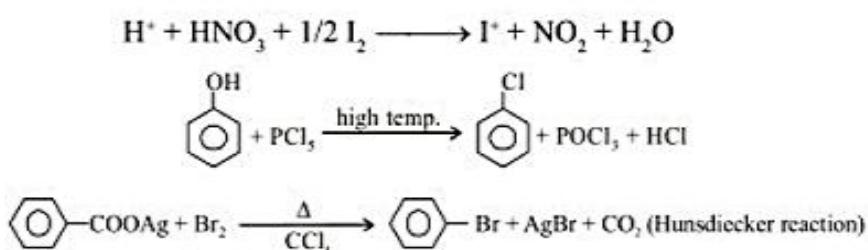
A methoxy group is so strongly activating that anisole quickly brominates in water without a catalyst:



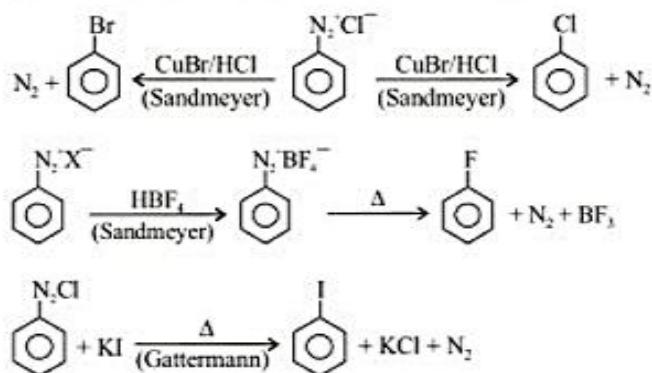
Direction iodination is not possible since, iodine is least reactive and HI formed makes reaction reversible. In presence of oxidising agents like  $\text{HNO}_3$  or  $\text{HIO}_3$ , iodination of benzene is possible and HI formed is converted to  $\text{I}_2$ :



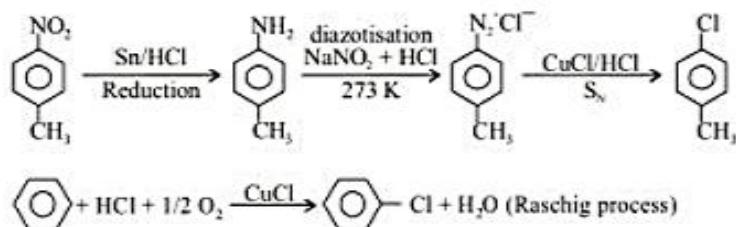
Iodination probably involves an electrophilic aromatic substitution with iodonium ( $I^+$ ) acting as the electrophile.  $I^+$  is formed from iodine by oxidation with  $HNO_3$ .



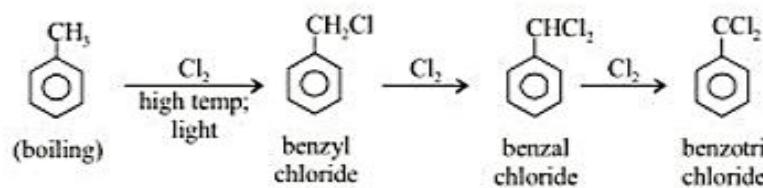
**Diazonium salts are converted to halogen compounds :**



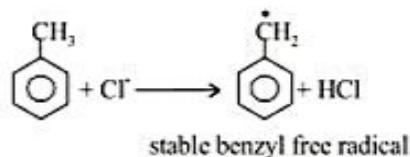
Diazonium salts are obtained by diazotisation of amino compounds and this provides a better route to convert amino compounds into halogen compounds :



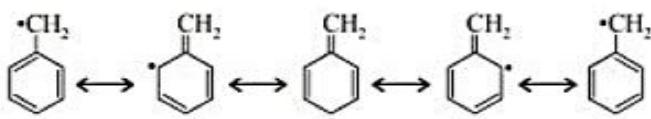
### **Side-Chain Derivatives**



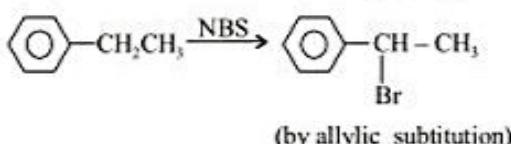
Side-chain halogenation involves free radical mechanisms due to lower bond energy of the benzyl C-H bond:



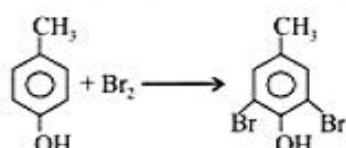
Benzyl radical is stabilised by resonance due to delocalisation of odd electrons into ring:



NBS can also be used for bromination of side-chain alkyl group:



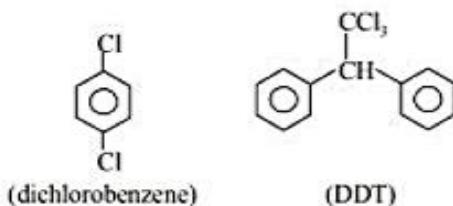
In presence of an activating group –OH or –NH<sub>2</sub>, side chain halogenation is difficult:



## Properties

## Physical

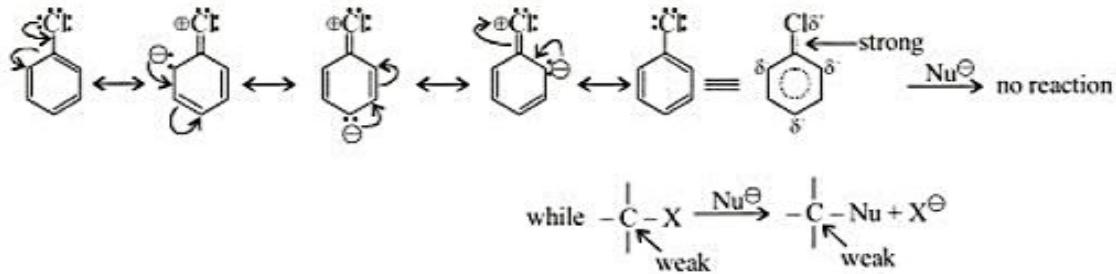
- Less polar, insoluble in water but soluble in organic solvents like ethanol and ether.
  - They show physiological activity and are used as insecticides. Examples are :



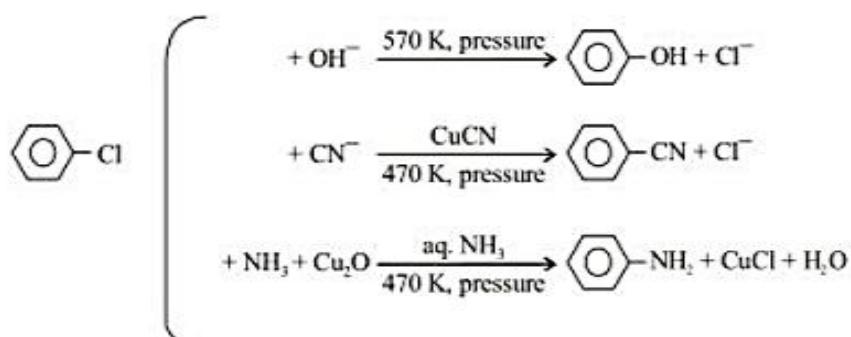
## Chemical

(a) Low reactivity of Aryl halide for  $S_N$  reaction

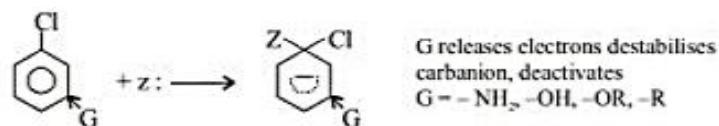
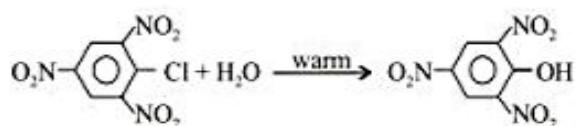
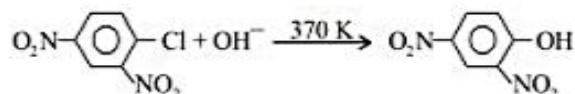
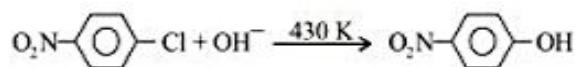
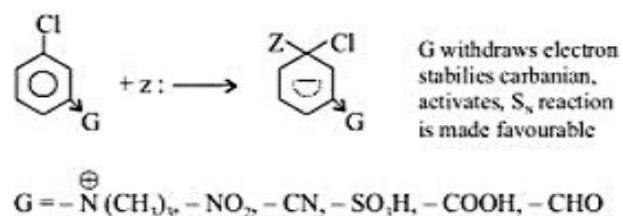
C-X bond in aryl halide is stable due to delocalisation of electrons by resonance. Also (C-X) bond possesses a double bond character like vinyl chloride and is stronger than C-X bond in alkyl halide.



Hence,  $S_N$  reaction is not possible in benzene nucleus under ordinary conditions. However, under high temperature and pressure,  $S_N$  reaction is made possible.

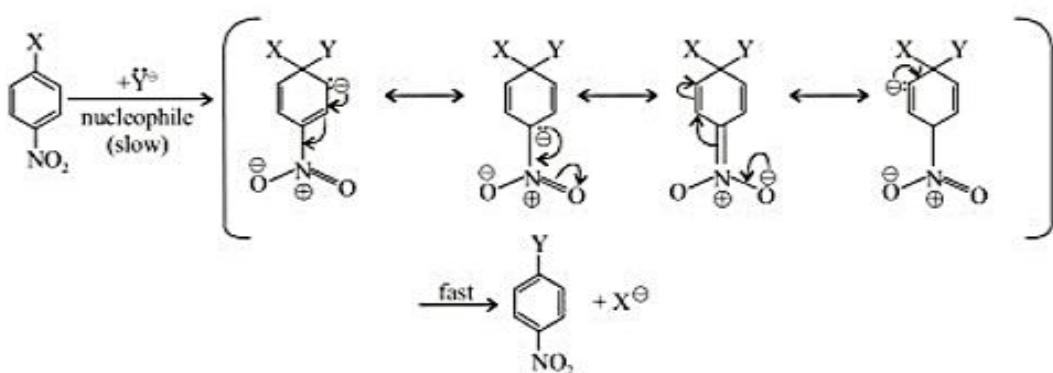


If the benzene ring has (1) one or more substituents that strongly withdraw electrons from the ring by resonance, and (2) a good leaving group (such as halogens), nucleophilic aromatic substitution reactions can occur without using extreme conditions. These electron-withdrawing groups must be positioned ortho or para to the leaving group. The greater the number of electron-withdrawing substituents, the easier it will be to carryout the nucleophilic aromatic substitution reactions.



Nucleophilic aromatic substitution takes place by a two-step reaction known as an  $S_N$  Ar reaction by following mechanisms :

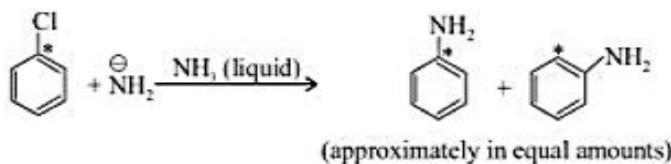
**Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004616.jpg**



### (b) Elimination-Addition Through Benzyne Intermediate

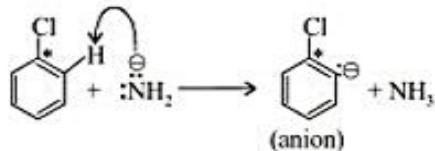
An aryl halide can undergo a nucleophilic substitution reaction in the presence of a very strong base such as NH<sub>2</sub><sup>-</sup>.

When chlorobenzene – that has the carbon to which chlorine is attached isotopically labelled with <sup>14</sup>C – is treated with amide ion in liquid ammonia, aniline is obtained as a product. Half of the product has the amino group attached to the isotopically labelled carbon (\*) as expected, but the other half has the amino group attached to the carbon adjacent to the labelled carbon.

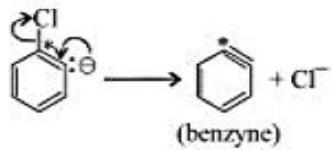


The mechanisms that accounts for the experimental observations involves formation of a benzene intermediate which has two equivalent carbon atoms to which amino group can be attached. Benzyne has an extra π-bond between two adjacent carbon atoms of benzene and can be formed as :

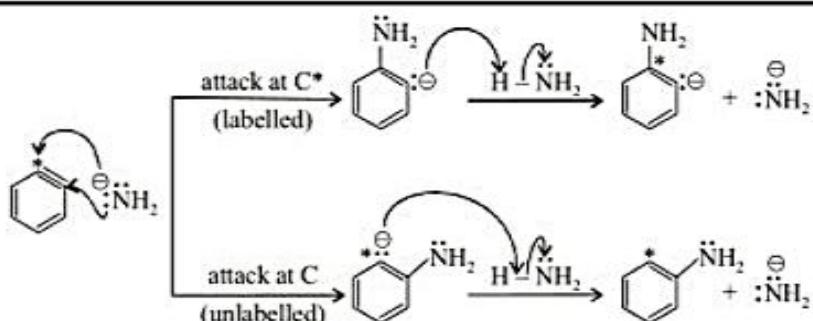
**Step-I :** Strong base NH<sub>2</sub><sup>-</sup> removes a proton from the position ortho to halogen :



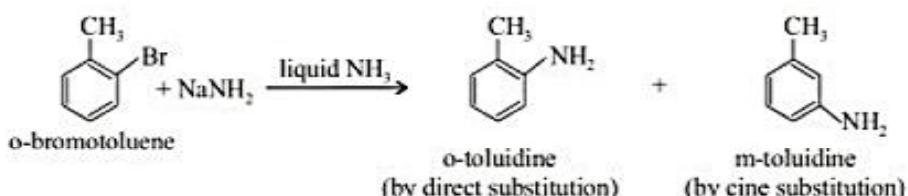
**Step-II :** Anion formed in step I eliminates the halide ion, thereby forming benzyne :



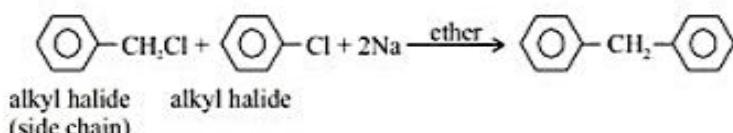
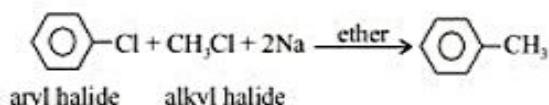
The incoming nucleophile can attack either of the carbons of the “triple bond” of benzyne. Protonation of the resulting anion form the substitution product. The overall reaction is an elimination-addition reaction; benzyne is formed in an elimination reaction and immediately undergoes an addition reaction.



Substitution at the carbon (\*) that was attached to the leaving group is called direct substitution. Substitution at the adjacent carbon is called cine substitution.

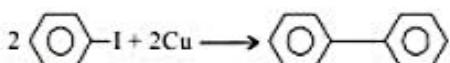


### (c) Wurtz-Fitting Reaction



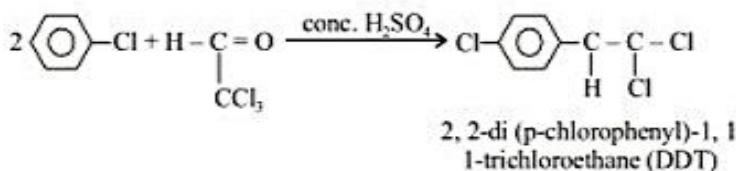
If only aryl halide is involved, diphenyl is formed (**Fitting reaction**)

### (d) Ullman synthesis



### (e) Reaction with Chloral

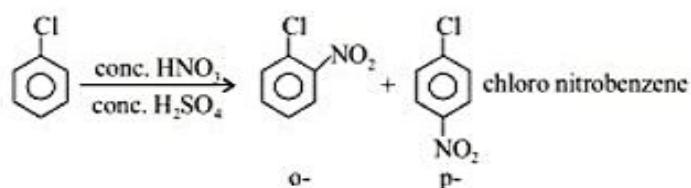
DDT is formed when chloral reacts with chlorobenzene in presence of concentrated  $\text{H}_2\text{SO}_4$ .



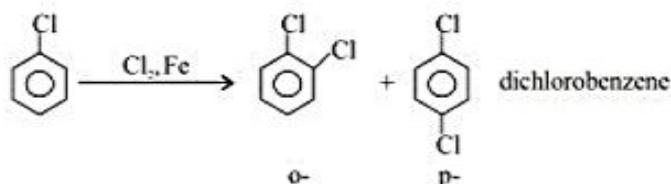
DDT is causing ecological problems, its use as insecticides is being banned.

Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004621.jpg

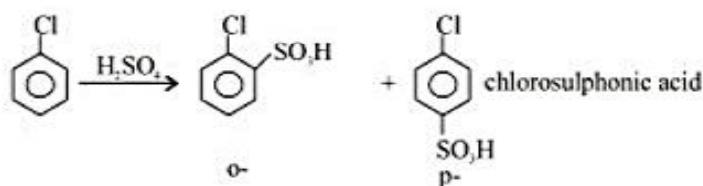
### Nitration



### Chlorination

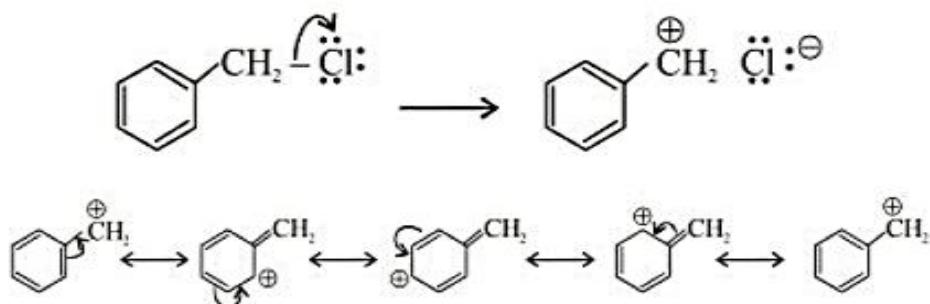


### Sulphonation

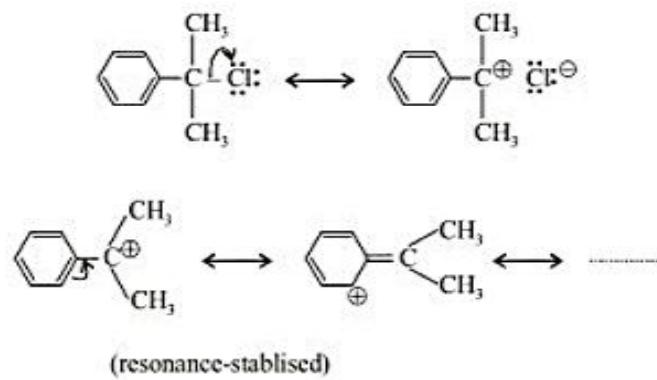


- Chlorine is not a good donor of electrons by resonance due to its high electronegativity. Thus, the inductive effect of the Cl atom overcomes the resonance effect, and thus, it deactivates the benzene ring.

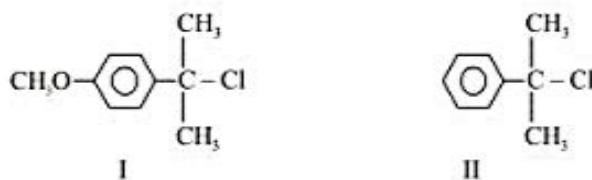
- (g) **Substitution on benzyl carbon ( $S_N$ )**: The greater reactivities of benzylic halides result from the stabilities of the carbocation intermediates that are formed when they react.



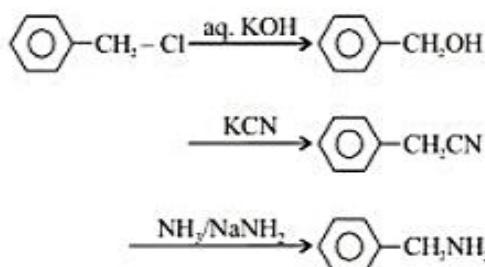
Tertiary cumyl chloride ionises to a carbocation with four important resonance structure :



Because of the possibility of resonance, ortho and para substituent group on the benzene ring that activate electrophilic aromatic substitution further accelerate S<sub>N</sub> 1 reaction at the benzylic position. Thus p-methoxy tert-cumyl chloride (I) undergoes hydrolysis about 3400 times faster than tert-cumyl chloride II.

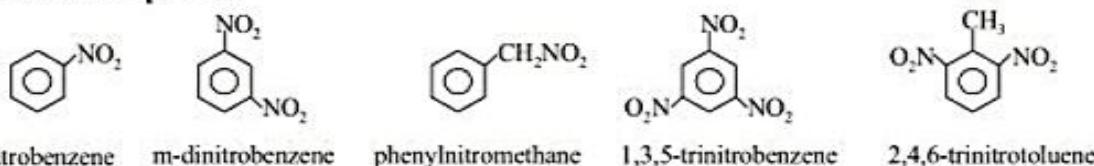


Benzylic halides undergo S<sub>N</sub> reactions like aliphatic halides.



This provides a path of converting toluene into so many other compounds from benzyl chloride.

### Aromatic Nitro Compounds



### Source

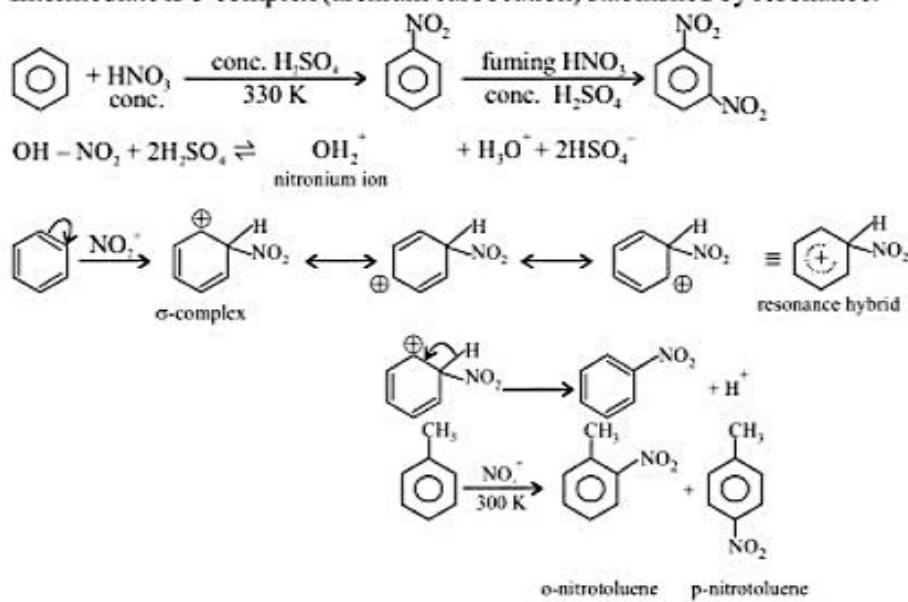
- Direct nitration

Nitrating agent is

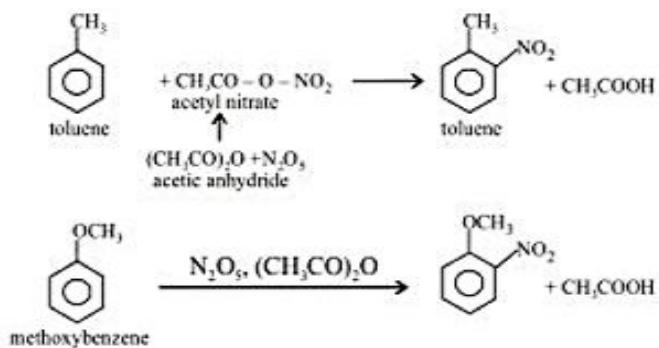
(a) conc. HNO<sub>3</sub> + conc. H<sub>2</sub>SO<sub>4</sub> or (b) acetyl nitrate (N<sub>2</sub>O<sub>5</sub> in acetic anhydride)

-NO<sub>2</sub> is deactivating group, hence, further nitration takes place with fuming HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> mixture.

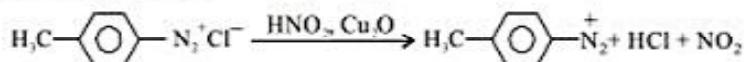
Intermediate is o-complex (arenium carbocation) stabilized by resonance.



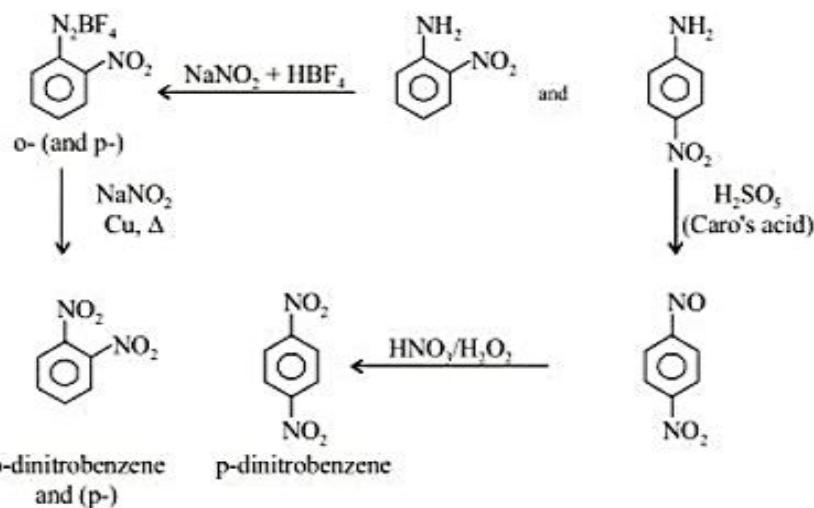
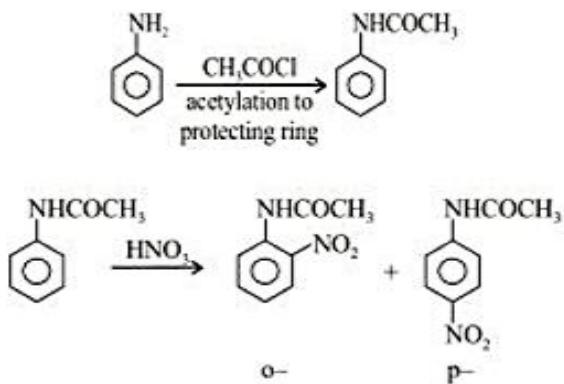
- CH<sub>3</sub> and -OCH<sub>3</sub> groups are activating groups hence, nitration of toluene and methoxy benzene (anisole) is easier than that of benzene.



- From Diazonium salts :



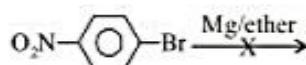
- Oxidation of Amino compounds : (using trifluoroperbenzoic acid)



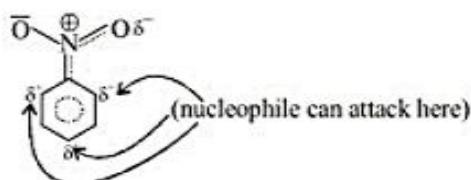
Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004628.jpg

### Properties

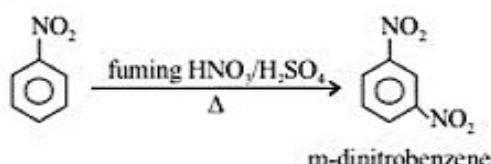
- Nitro-compounds are yellow crystalline solids (nitrobenzene is yellow liquid)
  - Steam-volatile, denser than water in which they are insoluble.
  - Nitro group is attacked by Grignard reagent; nitro-substituted aryl halides cannot be used for the preparation of these reagents.



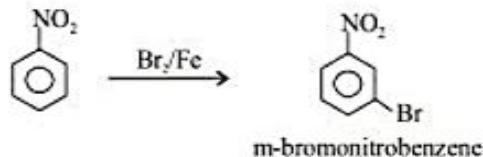
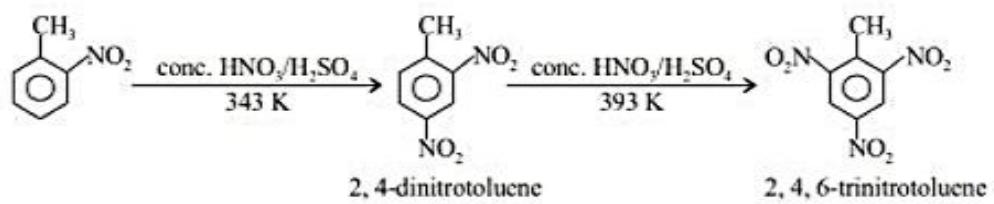
There is also partial positive charge on the ortho and para-positions. Thus,  $\text{--NO}_2$  activates the benzene nucleus for nucleophilic substitution at the ortho and para-positions.



### **Electrophilic substitution ( $S_E$ )**



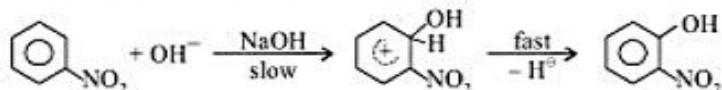
Further nitration to form trinitrobenzene takes place under drastic conditions. Presence of electron-releasing group activates benzene nucleus for  $S_N$ . Toluene can be nitrated only once but nitro group introduced retards a second nitration on the same ring.

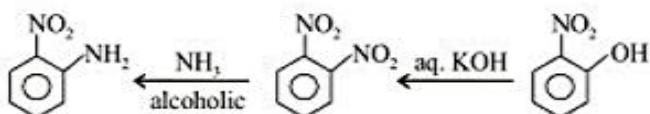
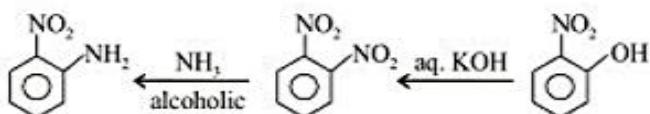
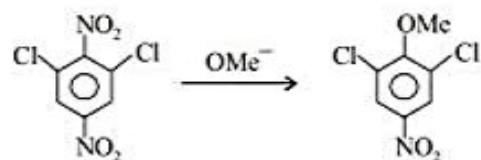
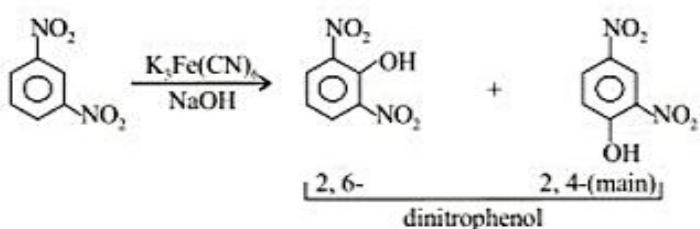


- NO<sub>2</sub> group also deactivates benzene nucleus for alkylation by Friedel-Crafts reaction.

## NUCLEOPHILIC SUBSTITUTION REACTIONS

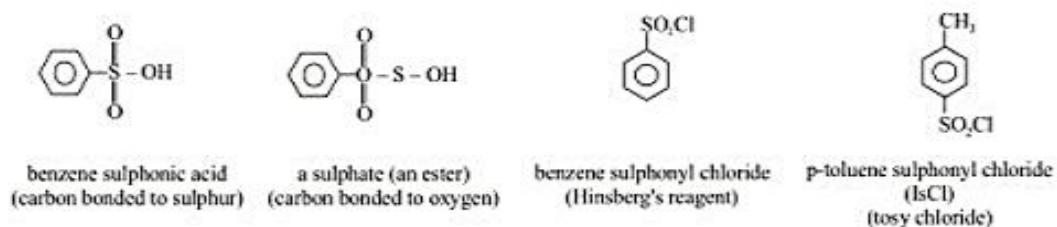
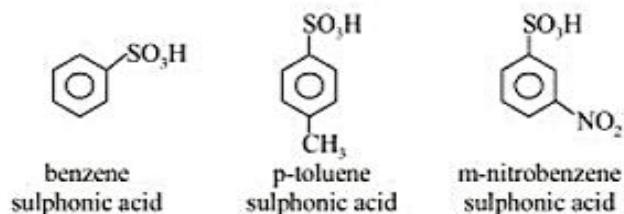
- Substitution of hydrogen by a nucleophile does not occur in benzene itself, but the presence of one nitro group is sufficient to activate the *o*-and *p*-positions.





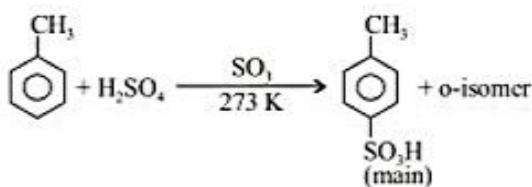
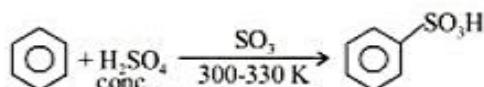
## AROMATIC SULPHONIC ACIDS

They are derivatives of aromatic hydrocarbons in which one or more hydrogen of the benzene ring have been replaced by the function  $-\text{SO}_3\text{H}$ , called the sulphonic group.

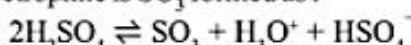


### Source

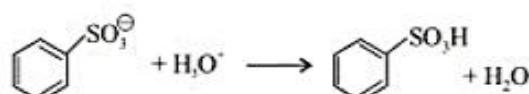
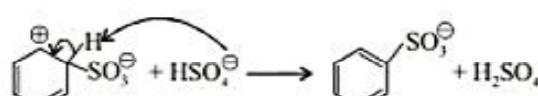
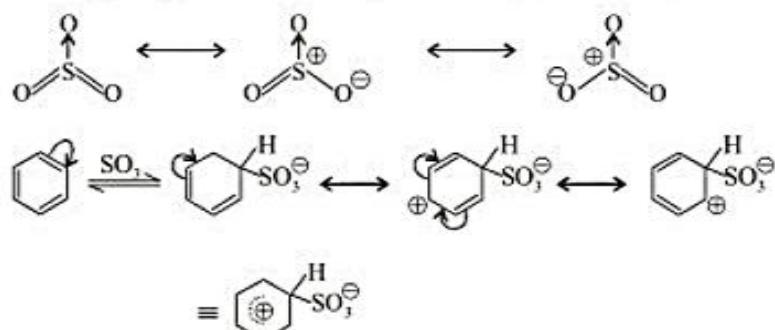
- **Direct sulphonation :**



In the sulphonation, electrophile is  $\text{SO}_3^+$  formed as :



Although it appears neutral, sulphur carries positive charge due to resonance :

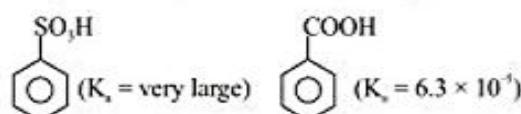


### Properties

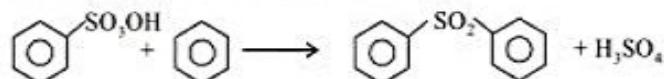
- Colourless crystalline deliquescent solid.
- Very soluble in water and solution is strongly acidic.



They are stronger acid than carboxylic acid.

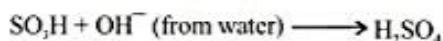
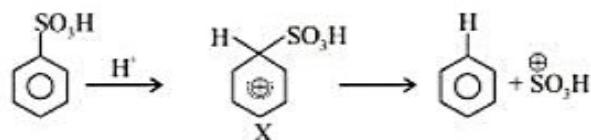


- **Formation of diphenyl sulphone :**



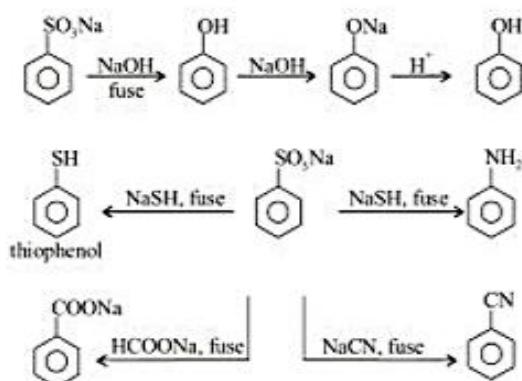
- **Desulphonation :**

The knocking out of sulphonic acid group from benzene nucleus is called **desulphonation**.



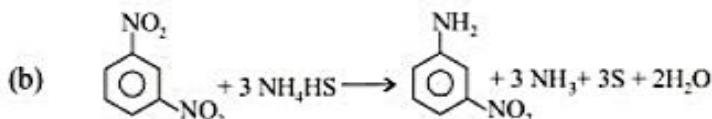
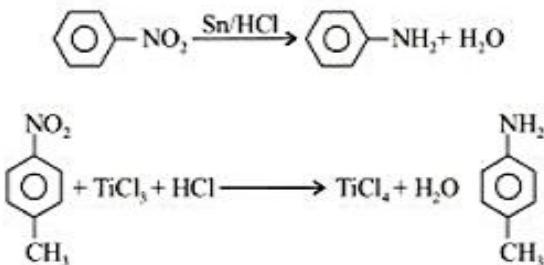
The desulphonation is very useful for preparation of certain isomers which are otherwise not obtained in pure state.

**Reactions of sodium salt of benzene sulphonic acid :**  
(conversion into other derivatives)

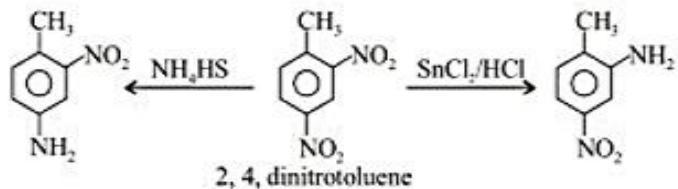


**Source**

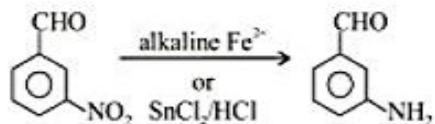
- (a) Nitrobenzene can be reduced under different media to produce aniline and related compounds.



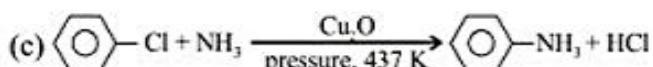
$\text{NH}_4\text{HS}$  is suitable reagent where only one  $-\text{NO}_2$  (in stages) is to be reduced.



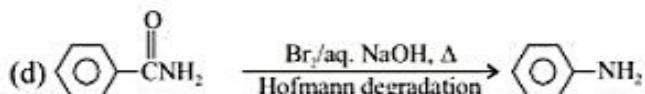
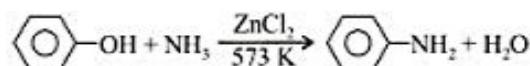
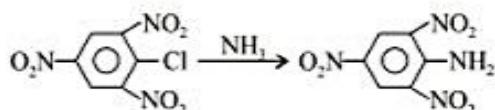
Action of  $\text{NH}_4\text{HS}$  and  $\text{SnCl}_2/\text{HCl}$  is specific.  $\text{NH}_4\text{HS}$  reduces  $-\text{NO}_2$  para to  $-\text{CH}_3$  while  $\text{SnCl}_2/\text{HCl}$  reduces  $-\text{NO}_2$  ortho to  $-\text{CH}_3$ .



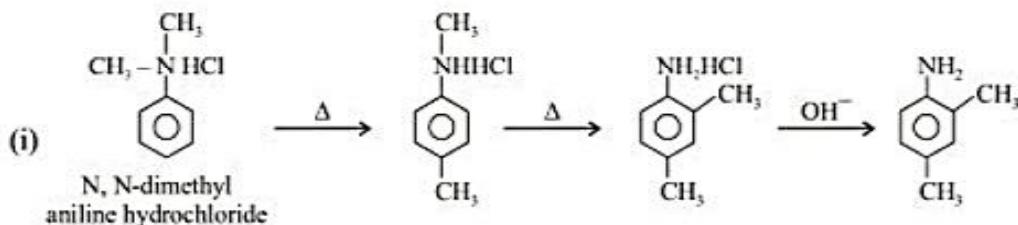
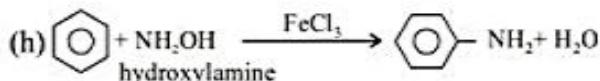
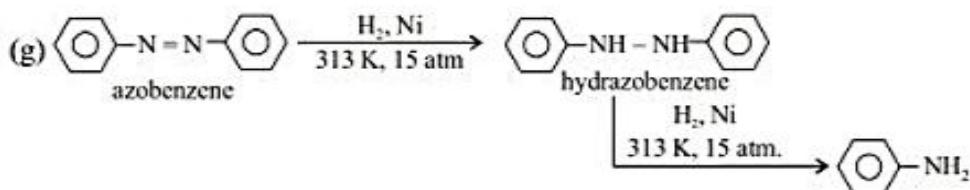
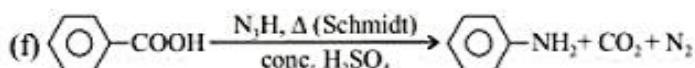
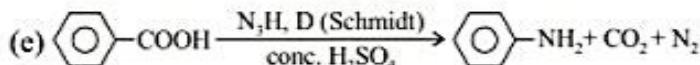
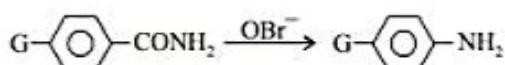
Alkaline  $\text{Fe}^{2+}$  does not reduce  $-\text{CHO}$  into  $-\text{CH}_2\text{OH}$ .  $\text{SnCl}_2/\text{HCl}$  can also be used here.



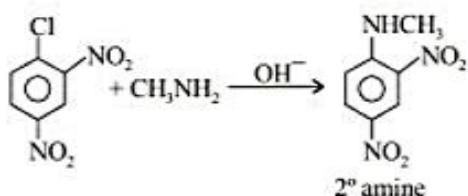
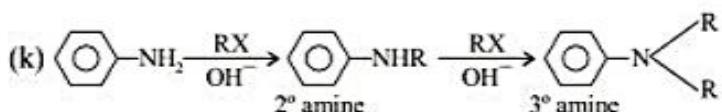
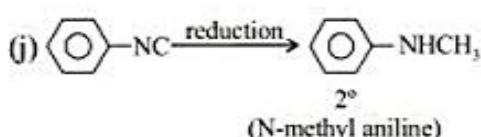
C-Cl bond is stable, hence ammonolysis of aryl halide takes place under high temperature and pressure. However electron withdrawing group in benzene nucleus makes C-Cl bond highly reactive.



When the migrating group is aryl, the rate of the Hofmann degradation reaction is increased by the presence of electron releasing substituents in the aromatic ring.



This is called Hofmann-Martius rearrangement and alkyl group preferentially migrates to p-position and if it is occupied, then to o-position.

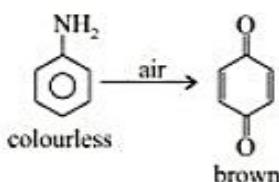


Some other methods are very similar to that used for aliphatic amines.

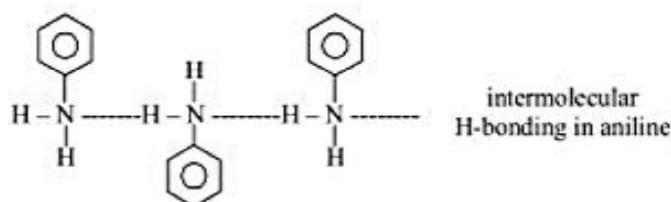
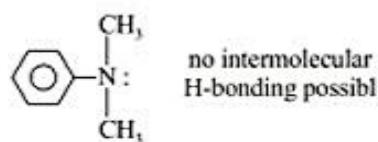
## Properties

### Physical

- Colourless liquid/solids, but due to air oxidation, they turn brown.



- Slightly soluble in water (polar solvent) but highly soluble in benzene and other organic solvents.
- High b.p. due to intermolecular H-bonding. N, N-dimethyl aniline has lower b.p. due to lack of H-bonding but molecular weight is also important affecting b.p.

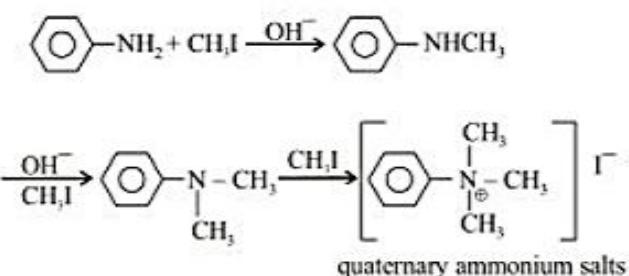


- Para-substituted aniline, being the most symmetric, have the highest melting points. Thus p-toluidine is solid at room temperature while o-toluidines are liquids.

Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004645.jpg

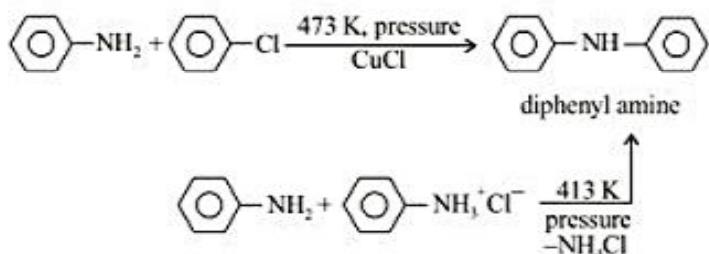
### Relations of the $-NH_2$ group

#### (a) Methylation (Alkylation)

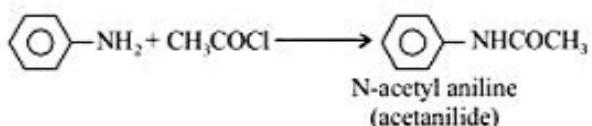


#### (b) Arylation

Arylation of aniline with  $C_6H_5Cl$  is difficult.

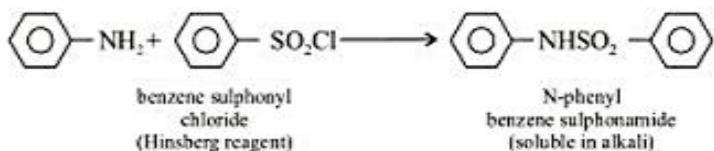


#### (c) Acylation



Acetyl group deactivates  $-NH_2$  group, whenever aniline is subjected to nitration, acetylation is necessary to protect the ring from being oxidised.

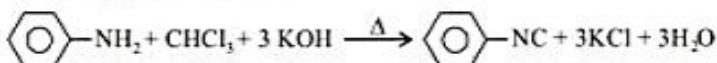
#### (d) Sulphonylation



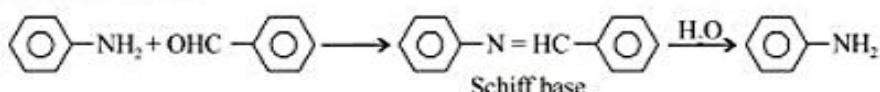
$2^\circ$  amine also reacts but the product is insoluble in alkali. This provides a method (called Hinsberg method) of separation of mixture of  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines.

#### (e) Carbyl Amine Reaction

Only  $1^\circ$  amines give this reaction when unpleasant smell of isocyanides is obtained on heating a mixture of alcoholic KOH,  $\text{CHCl}_3$ , and  $1^\circ$  amine.

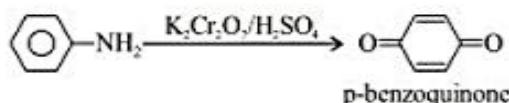


## (f) Formation of Schiff base

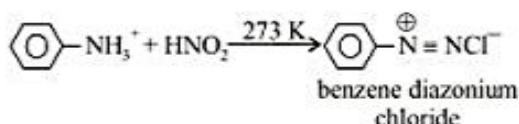
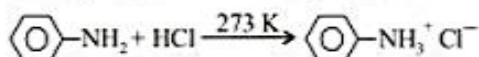
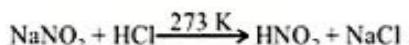


These Schiff bases are easily hydrolysed to the free amines and so their formation offers a mean of 'protecting' an amino group (during nitration).

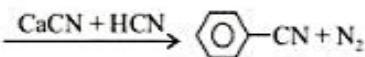
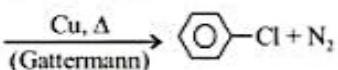
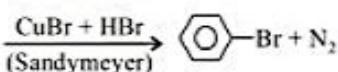
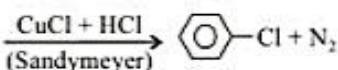
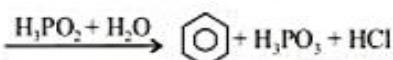
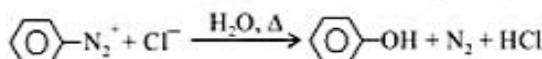
## (g) Oxidation

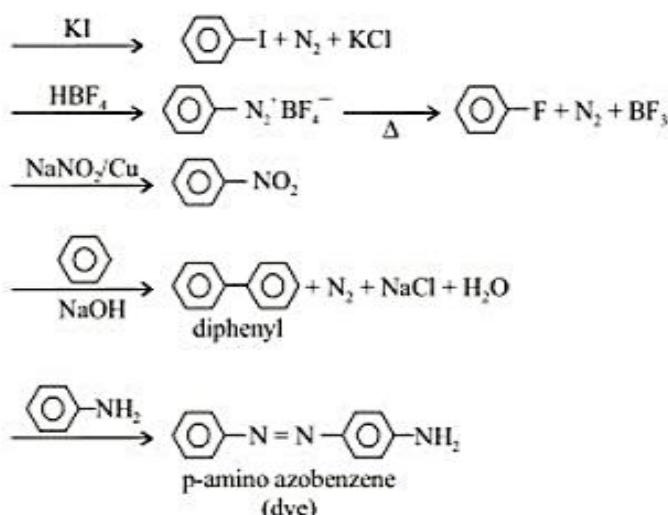
(h) Reaction with  $\text{HNO}_2$ 

1° amines form diazonium salts at low temperature (273–278 K). A reaction in which  $-\text{NH}_2$  group is converted into diazo group ( $-\overset{\oplus}{\text{N}}=\text{N}^-$ ) is called diazotisation. Diazonium salts are stable in cold aqueous solution.



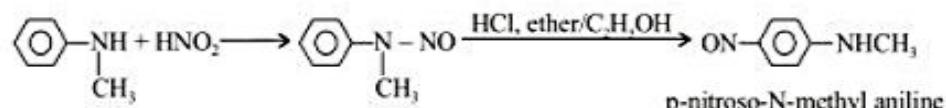
Aniline can be converted into so many other compounds through the formation of diazonium salts.



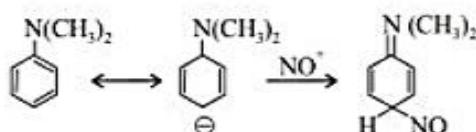
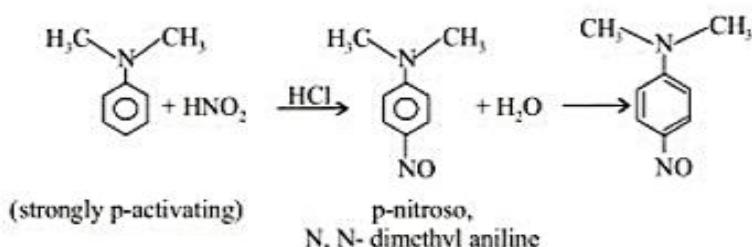


More reactions are given in sec. 16.8 (diazonium salts)

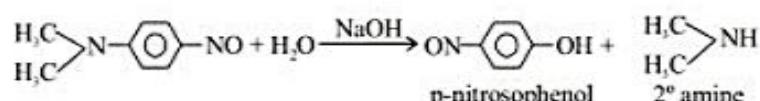
2° amines form nitrosamine (yellow oily liquid) which is stable at room temperature. However on reaction with HCl in ether and alcohol – NO group migrates to para-position (Fischer-Hepp)



**3° amines form p-nitroso derivatives :**

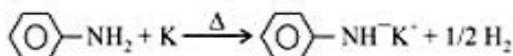


**Hydrolysis of p-nitroso derivative gives 2° amines :**

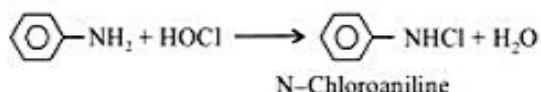


Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004653.jpg

This provides a path of the preparation of 2° amines :

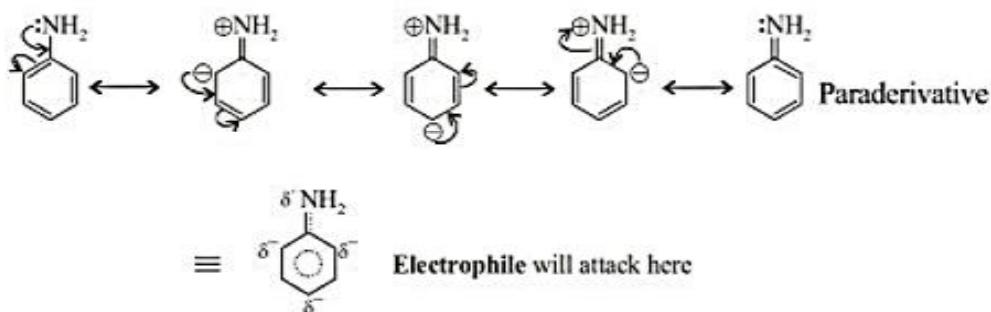


This represent acidic nature of aniline. Hypochlorous acid also reacts with aniline in which active H is replaced. :

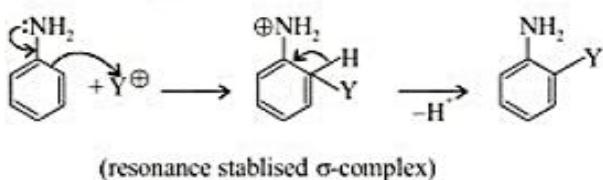


### Electrophilic substitution in benzene nucleus

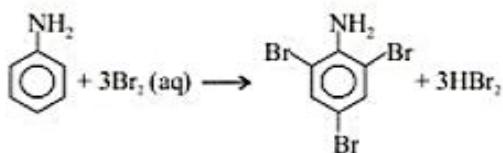
-NH<sub>2</sub> group is o, -p directing and activating group.



Hence, -NH<sub>2</sub> group activates benzene nucleus for ortho and para-electrophilic attack.



#### (a) Bromination



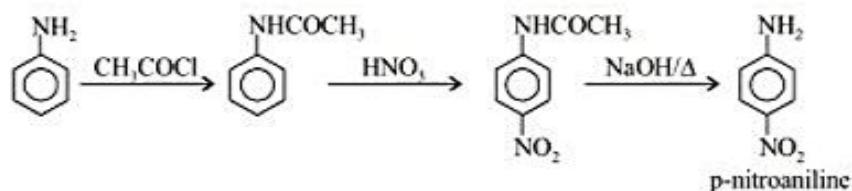
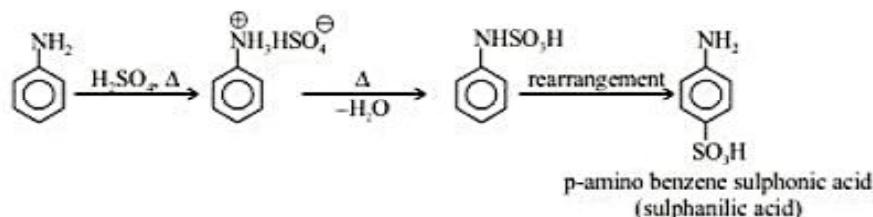
-NH<sub>2</sub> group is greatly activating group hence reaction takes place rapidly. However if ring is deactivated by acetylation, o-and p-isomers are obtained.



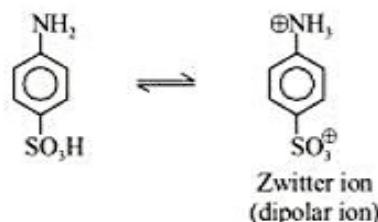
Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004655.jpg

**(b) Nitration**

Direct nitration of aniline with nitric acid gives a complex mixture of mono-, di- and tri-nitro compounds and oxidation products. If  $-\text{NH}_2$  group is protected by acetylation and then nitrated, p-isomer is the main product.

**(c) Sulphonation**

Like antranilic acid, sulphanilic acid also exists as Zwitter ion due to internal neutralisation.

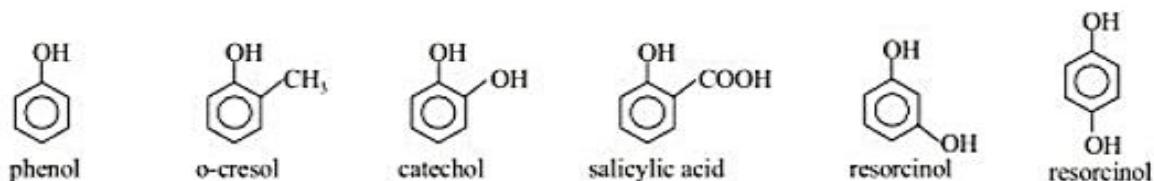
**Distinction between Aliphatic and Aromatic Amines**

S.No.	Test	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{CH}_3\text{NH}_2$
1.	Diazotisation (reaction with $\text{HNO}_2$ )	Diazonium salt is formed $\text{C}_6\text{H}_5\text{N}^+$ which forms azo dye with phenolic compounds.	$-\text{NH}$ is replaced by $-\text{OH}$
2.	$\text{S}_E$	can be halogenated, sulphonated, nitrated.	no
3.	Basic nature	less basic than $\text{CH}_3\text{NH}_2$ , $\text{NH}_3$	more basic than $\text{NH}_3$

Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004656.jpg

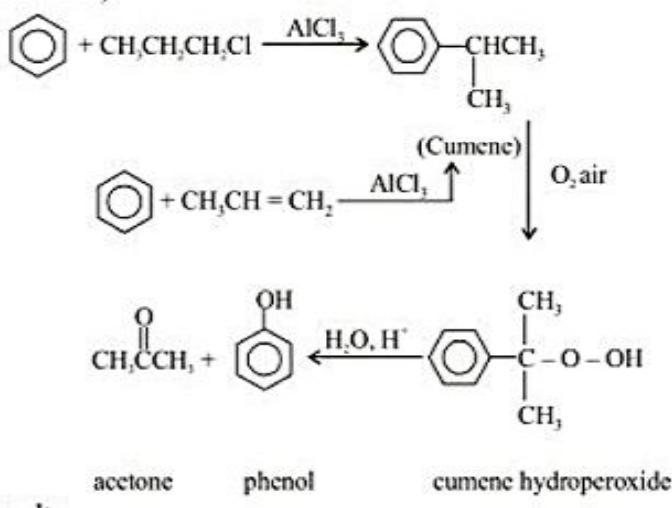
## Phenolic compounds

Phenols are the compounds of the general formula  $\text{ArOH}$ , where, Ar is phenyl or substituted phenyl. Phenols differs from alcohols in having the  $-\text{OH}$  group attached directly to an aromatic ring.

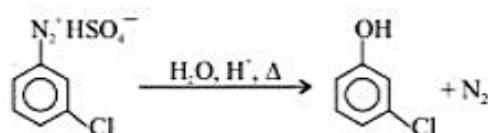


### Source

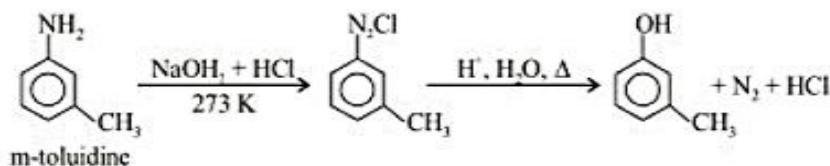
- From Cumene (Isopropyl benzene)



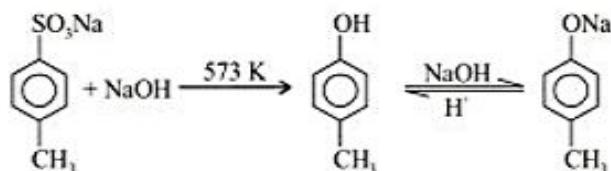
- Hydrolysis of Diazonium salts



Diazonium salts are obtained from aniline and its derivatives by a process called **diazotisation**.



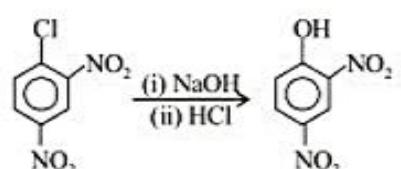
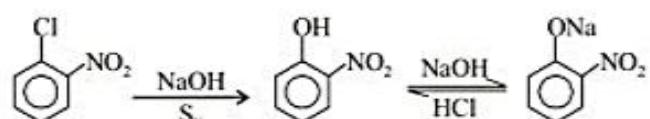
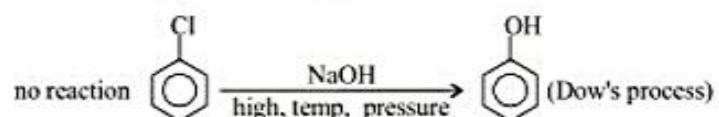
- Alkali Fusion of Benzene Sulphonic Acid salts



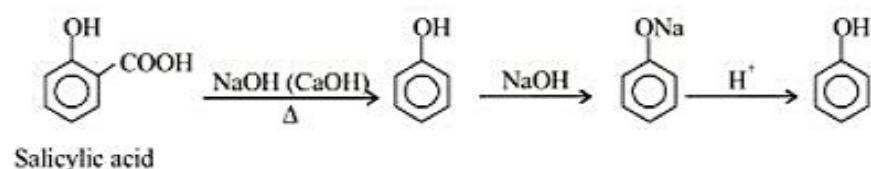
Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004658.jpg

• **Hydrolysis of Aryl Halides**

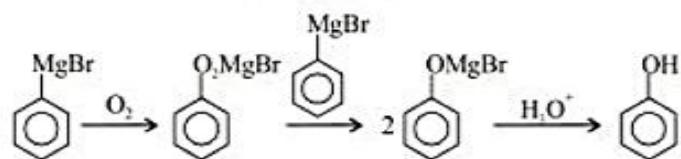
Halogen atom attached to benzene nucleus does not give  $S_N2$  reaction since C–X bond is stable due to resonance. However, in presence of electron withdrawing group in o- and p-positions,  $S_N1$  reaction is favoured and phenolic compounds are formed.



• **Distillation of Phenolic Acids**



• **Oxidation of Grignard Reagent**



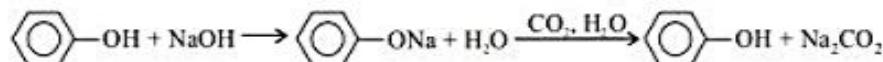
## MIDDLE OIL OF COAL-TAR DISTILLATION

Middle oil of coal-tar distillation has naphthalene and phenolic compounds. Phenolic compounds are isolated in following step :

**Step-I :** Middle oil is washed with  $H_2SO_4$ . It dissolves basic impurities like pyridine (base).

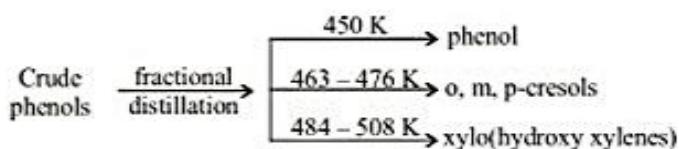
**Step-II :** Excessive cooling separates naphthalene (a low melting solid)

**Step-III :** Filtrate of step II is treated with aqueous  $NaOH$  when phenols dissolves as phenoxides. Carbon dioxide is then blown through the solution to liberate phenols.



**Step-IV :** Drude phenol (of step III) is subjected to fractional distillation.

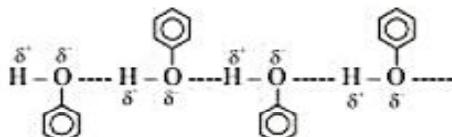
Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004700.jpg



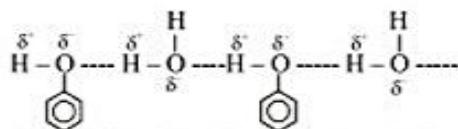
## Properties

### Physical

- Simplest phenols are liquids or low-melting solids.
- They are capable of forming intermolecular H-bonding among themselves and with water. Thus,
  - they have high b.p.
  - they are soluble in water.



(intermolecular H-bonding among phenol molecules)



(crossed intermolecular H-bonding between water and phenol molecules)

– due to intermolecular H-bonding and high dipole moment, m.p. and b.p. of phenol are much higher than that of hydrocarbon of comparable molecular weights.

Solute	mol. wt.	b.p.	m.p.
phenol	94 g mol <sup>-1</sup>	455 K	314 K
toulene	92 g mol <sup>-1</sup>	384 K	178 K

## Comparison of properties of nitrophenols

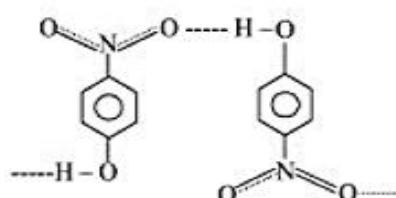
Isomer	b.p. at 760 mm	Solubility g/100 g	
o-nitrophenol	373 K	0.2	volatile in steam
p-nitrophenol	decomposes	1.69	non-volatile in steam
m-nitrophenol	467 K	1.35	non-volatile in steam

From the above table, it is clear that o-nitrophenol has much lower b.p. and much lower solubility in water than its isomer and is only steam-volatile.

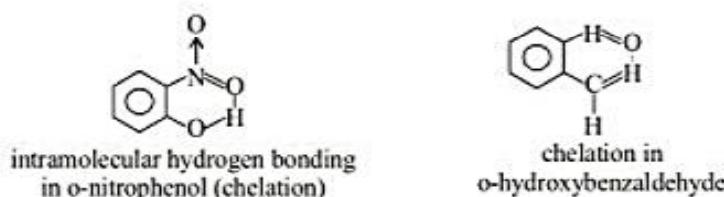
– m and p-isomer have high b.p. because of intermolecular H-bonding and high solubility in water is again due to crossed intermolecular H-bonding with H<sub>2</sub>O.

*o*-isomer has intramolecular H-bonding due to which association with different molecules decreases hence, b.p. is low giving volatile character to it and also H-bonding with  $\text{H}_2\text{O}$  molecules is not possible which makes it water soluble to a very small extent.

– Steam distillation depends upon a substance having an appreciable vapour pressure at the b.p. of water, by lowering the v.p., intermolecular hydrogen bonding inhibits steam distillation of the *m*-and *p*-isomer.



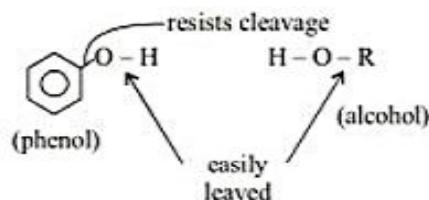
intermolecular hydrogen bonding in *p*-nitrophenol molecules



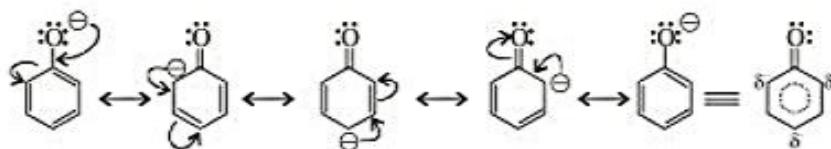
## ACIDITY OF PHENOLS AND EFFECT OF SUBSTITUENTS ON IT



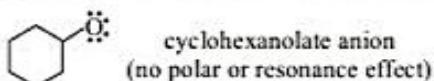
Phenols are converted into their salts by aqueous NaOH, but not by aqueous bicarbonates. The salts are converted to free phenols by aqueous mineral acids (HCl, etc.) carboxylic acid or carbonic acids. Phenol is more acidic than alcohols but less than carboxylic acid. Enhanced acidity of phenol is due to (a) polar effect (b) resonance effect.



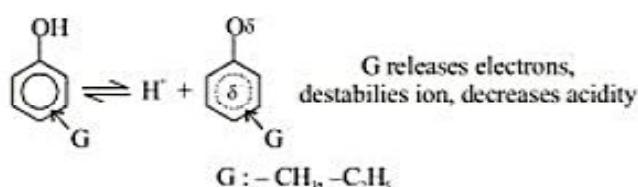
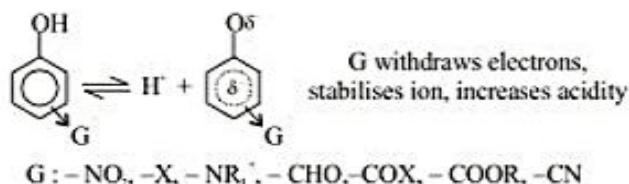
$\text{C}_6\text{H}_5$  - (phenyl) group is electron-withdrawing and phenoxide ion is more resonance stabilised than phenol, hence following equilibrium is displaced towards the right where stable phenoxide ion is formed.



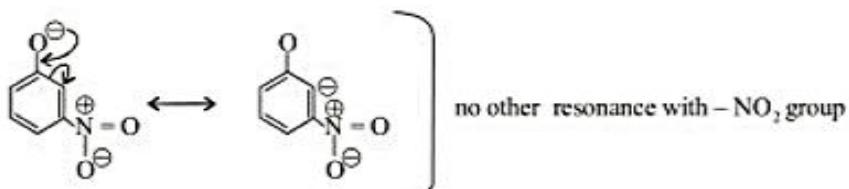
Alkoxides are stabilised neither by resonance nor by the polar effect of benzene rings or double bonds.



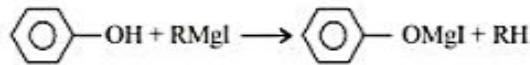
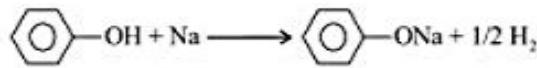
- Electron-attracting substituents like  $-X$ , or  $-NO_2$  increase the acidity of phenols and electron-releasing substituents like  $-CH_3$ , decrease acidity.



$K_a$  (acidity constant) and  $pK_a$  of different substituted phenols are given in table. The marked lower acidity in case of meta-isomer is explained by the fact that m-nitrophenoxide ion is stabilized by inductive effect only and no resonance effect operates with  $-NO_2$  group.

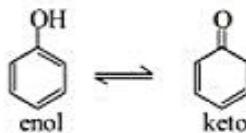


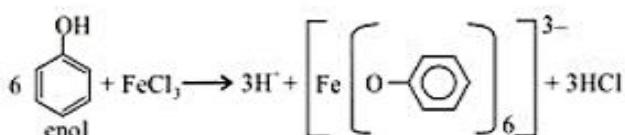
- Reactions in which phenol is a source of active H are :



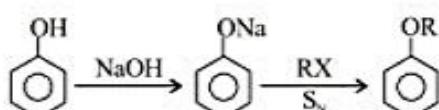
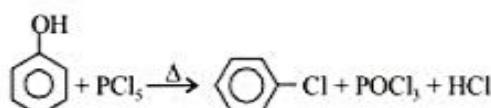
### FORMATION OF COMPLEXES WITH $\text{FeCl}_3$

Phenols form coloured iron complexes when related with neutral  $\text{FeCl}_3$  solution. The formation of iron complexes is attributed to the existence of keto-enol tautomerism in phenols. Phenol predominantly exists in enolic form, hence colour formation is used to identify phenols.

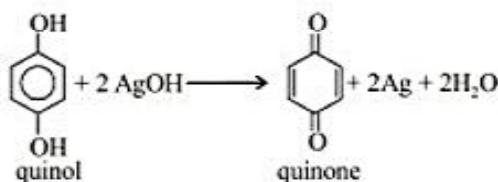
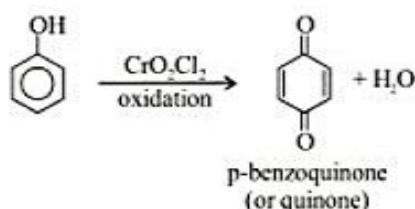
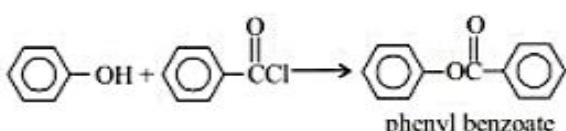
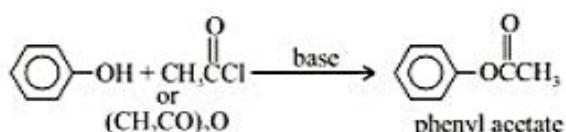
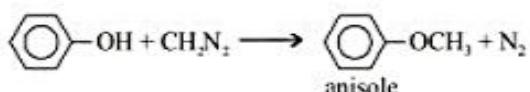




### Other Reaction of -OH Groups



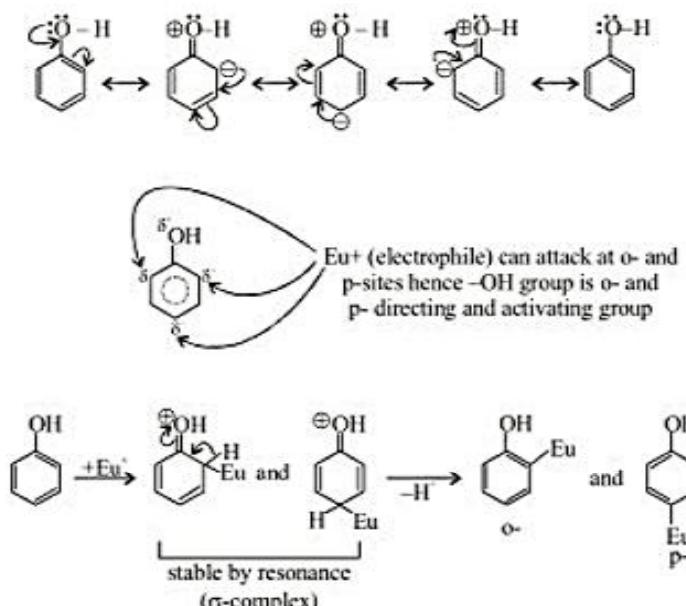
This is called Williamson's synthesis. The phenoxide ion is a nucleophile and will replace halogen of the alkyl halide.



Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004712.jpg

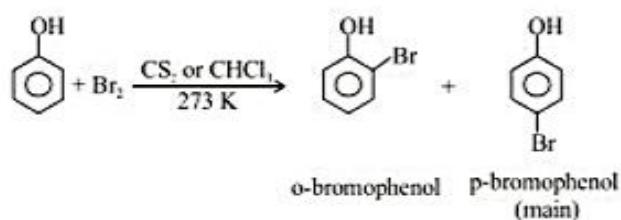
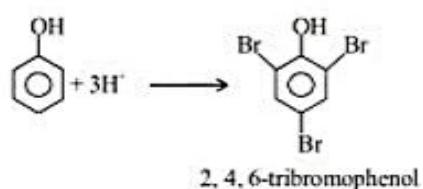
## ELECTROPHILIC SUBSTITUTION IN BENZENE NUCLEUS

-OH group is o- and p-directing and activating group for SE reactions.

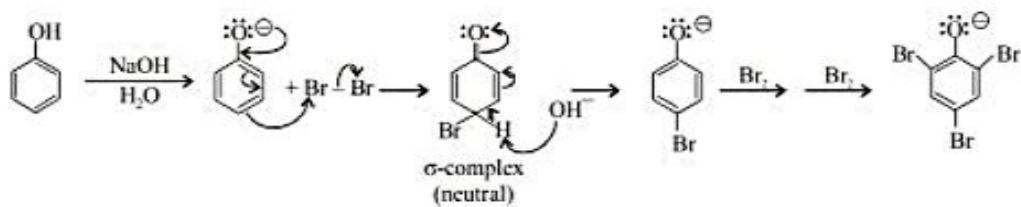


## HALOGENATION

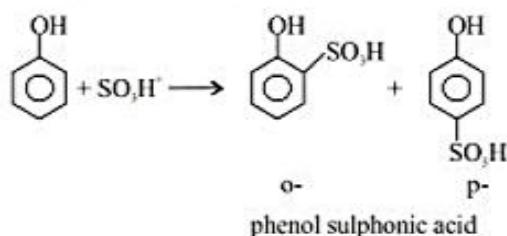
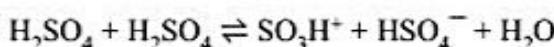
With excess of  $\text{Br}_2$  solution :



In presence of  $\text{NaOH}$ , phenoxide ion is formed which is more reactive than phenol towards electrophilic aromatic substitution.



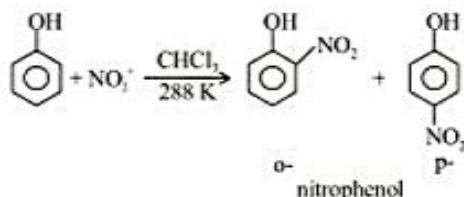
• Sulphonation



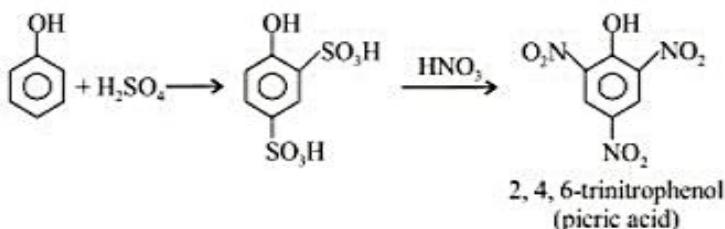
At room temperature, ortho-isomer while at 373 K the para-isomer is the main product.

• Nitration

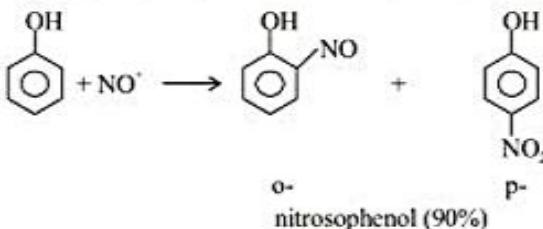
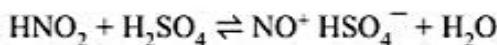
-OH group is activating group, hence, nitration is possible with dil.  $\text{HNO}_3$ .



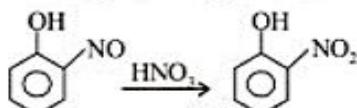
$\text{HNO}_3$  is oxidising agent and may lead to cleavage of benzene ring hence, further nitration is done carefully. However ring can be deactivated by sulphonation and then nitration will give picric acid in better yield.



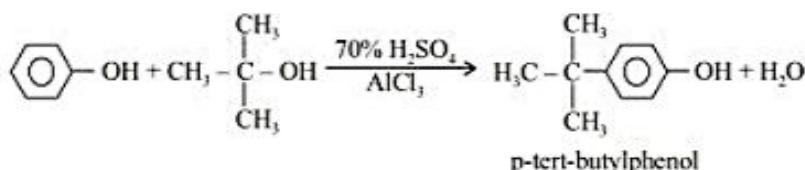
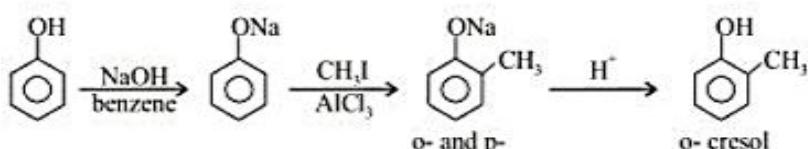
• Nitrosation



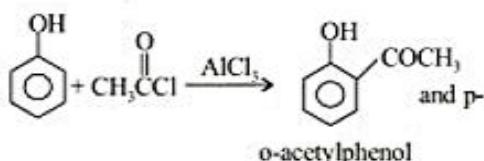
Nitrosophenol can be oxidised to  $-\text{NO}_2$  by  $\text{HNO}_3$ ; this provides a path of preparing nitrophenol.



• Alkylation (Friedel-Crafts Reaction)



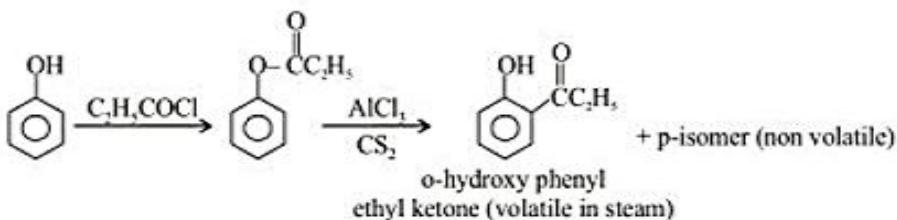
• Acylation (Friedel-Crafts Reaction)



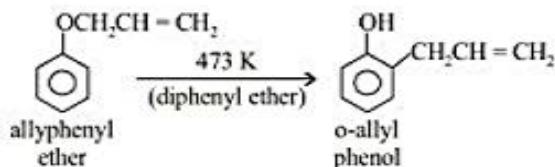
Intermediate of this reaction is  $\text{CH}_3\text{C}^{\oplus}\text{O}$  (acylium ion).

• Fries rearrangement

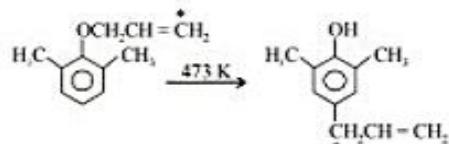
When esters or phenols are heated with AlCl<sub>3</sub>, the acyl group migrates from the phenolic oxygen to an ortho or para-position of the ring thus, yielding a ketone. This reaction is called the Fries rearrangement and appears to involve generation of an acylium ion, RCO<sup>+</sup>, which then attack the ring as in ordinary Friedel-Crafts acylation.



• Claisen rearrangement



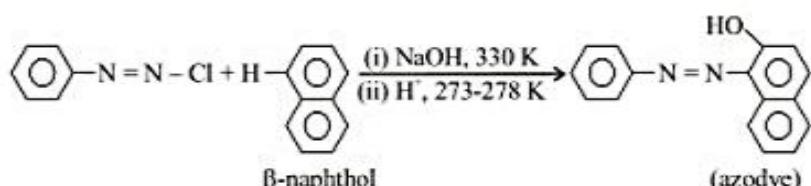
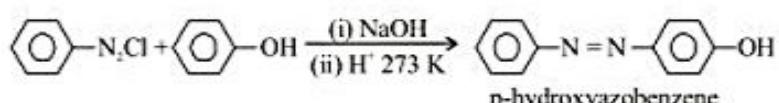
This is the arrangement of allyl ethers to allyl phenols. Allyl group migrates to ortho-position. If ortho-position is already occupied, para-isomer is obtained.



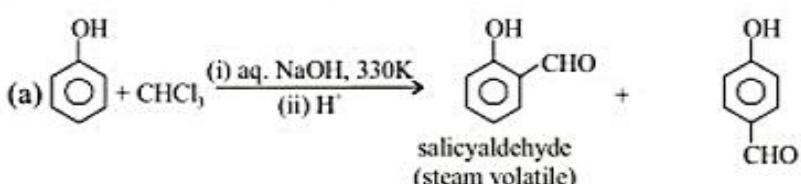
In this Claisen rearrangement, carbon which gets attached to benzene nucleus is vinylic and not allylic.

#### • Coupling reactions (Azo dye formation)

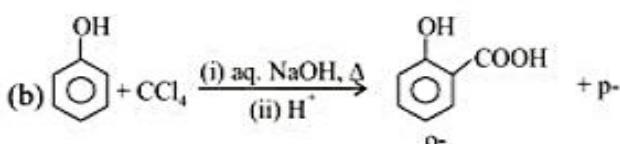
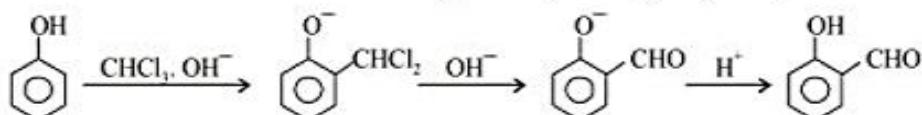
Phenol reacts with aryl diazonium salts in presence of alkali at low temperature to form form azo dyes.



- Reimer-Tiemann Reaction

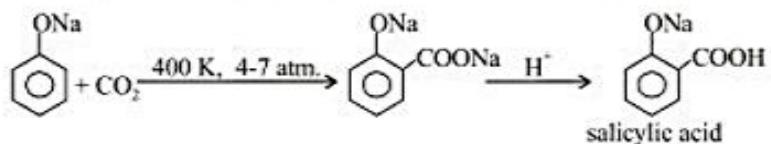


A substituted benzal chloride is initially formed, but is hydrolysed by the alkaline medium.

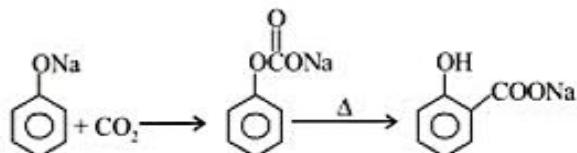


#### • Kolbe reaction (Carbonation)

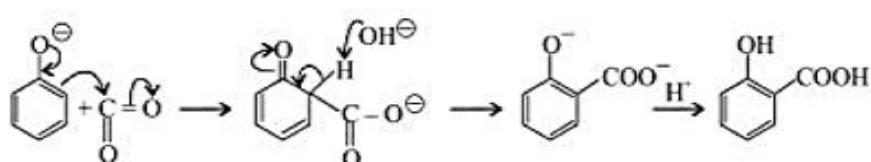
Treatment of the salt of a phenol with  $\text{CO}_2$  under pressure brings about substitution of the carboxyl group,  $-\text{COOH}$ , for hydrogen of the ring. This is called Kolbe reaction.



This provides a path of conversion of phenol into hydroxy carboxylic acids. It seems likely that  $\text{CO}_2$  attaches itself initially to phenoxide oxygen rather than to the ring.

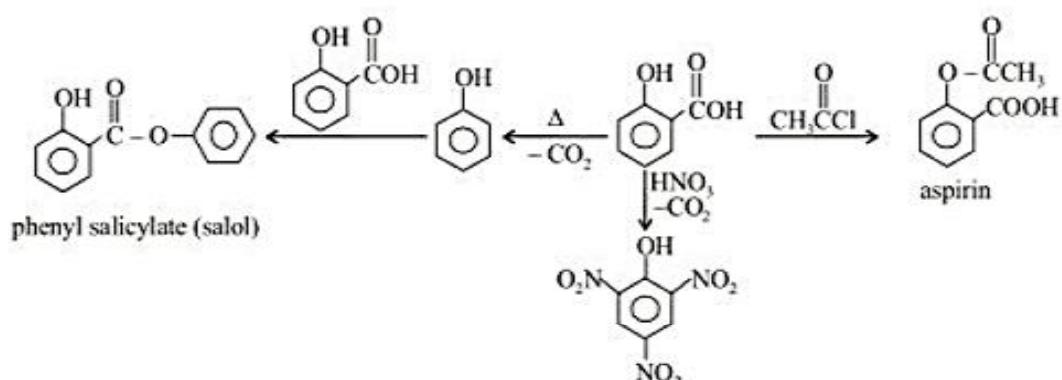


At high temperature (525 – 575 K), p-isomers is obtained.

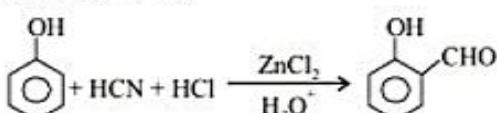


H-atom attached to the ortho-position combines with phenoxide oxygen.

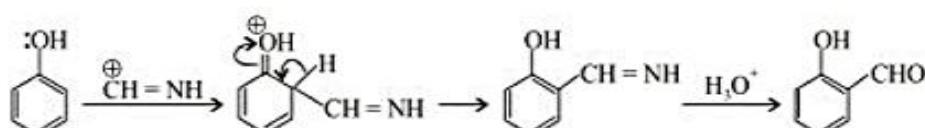
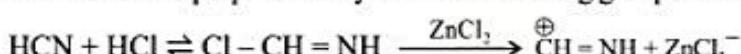
Salicylic acid is used to prepare aspirin, salol and picric acid :



#### • Gattermann Reaction (Formylation)

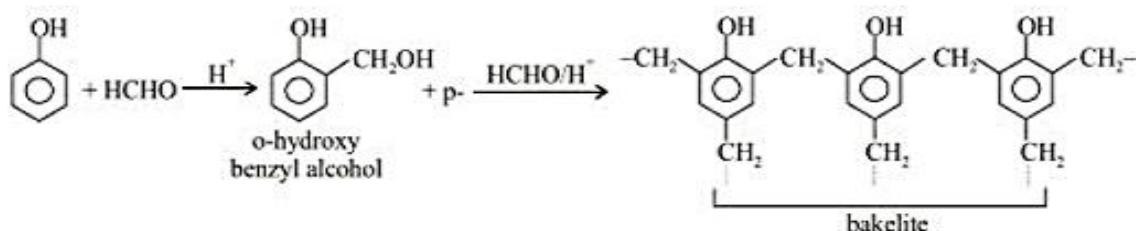


This reaction is used to prepare aldehyde when activating groups like  $-\text{OH}$ ,  $-\text{NH}_2$  are present.



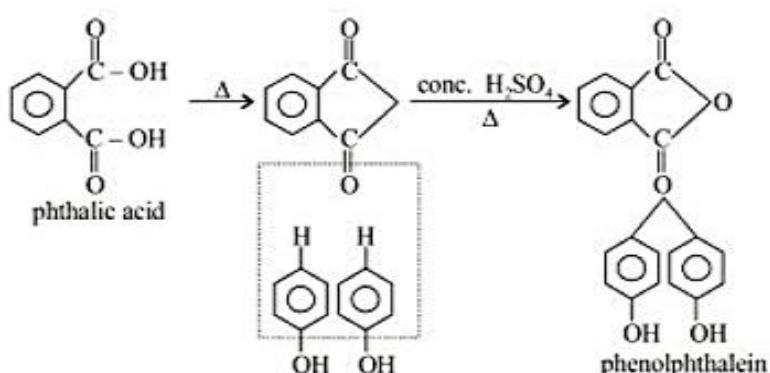
#### • Condensation Reaction

(a) Condensation of phenol with  $\text{HCHO}$  in presence of acid forms bakelite.



(b) Condensation of phenol with phthalic acid in presence of concentration  $\text{H}_2\text{SO}_4$  forms phenolphthalein (an indicator) which gives pink colour with  $\text{NaOH}$  (phthalein test of dibasic acid)

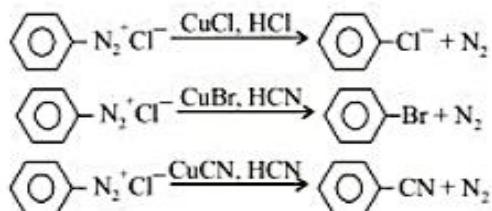
Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004727.jpg



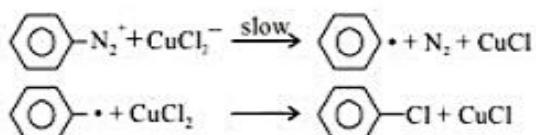
S.No.	Test		$\text{CH}_3\text{CH}_2\text{OH}$
1. 2.	Neutral $\text{FeCl}_3$ Azo dye test	violet colour with benzene diazonium chloride is formed  $\text{C}_6\text{H}_5\text{N}_2^+ \text{Cl}^- + \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{NaOH, 273 K}} \text{C}_6\text{H}_5\text{N}_2^+ \text{C}_6\text{H}_4\text{OH}$	no reaction no dye formation
3. 4. 5.	Phthalein test Litmus test Iodoform test	is given turns blue not given	no given no change is given

- **Sandmeyer Reaction**

Nucleophiles such as  $\text{CN}^-$ ,  $\text{Cl}^-$  etc., replace the diazonium group if appropriate cuprous salt is added to the solution containing diazonium salt.

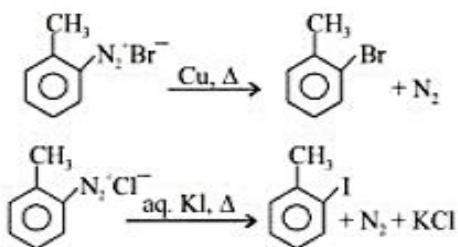


**Sandmeyer reaction involves :**  $\text{CuCl} + \text{Cl}^- \rightarrow \text{CuCl}_2^-$

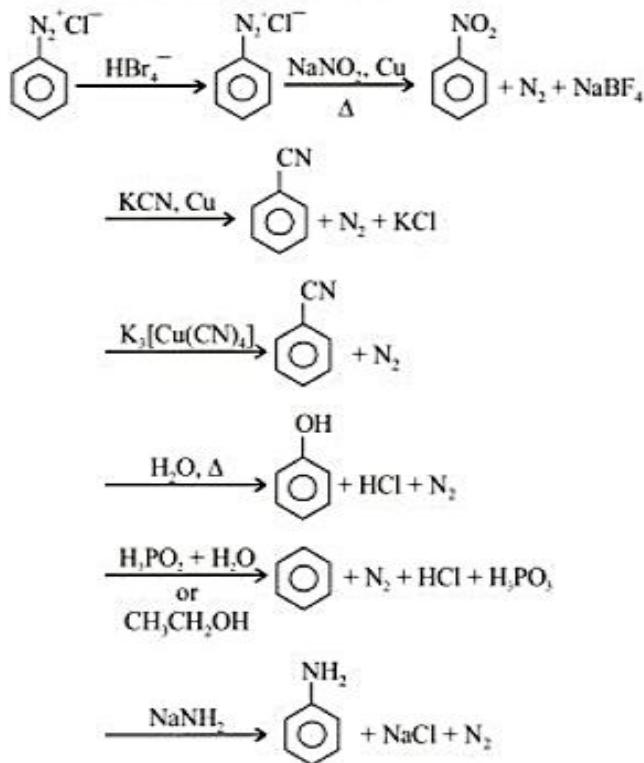


Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004729.jpg

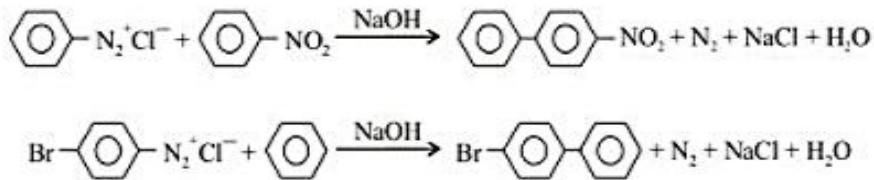
### Gattermann Reaction



### Other Replacement Reactions



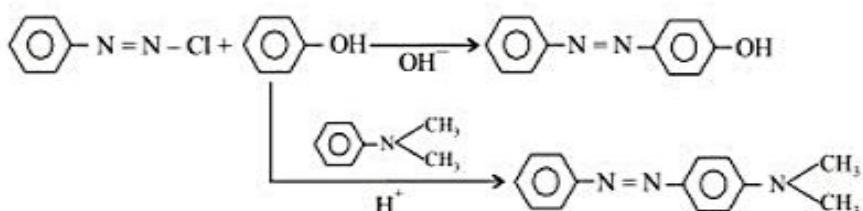
### Gomberg Reaction



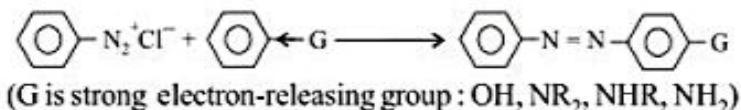
### Coupling reaction

Diazonium salts undergo coupling reactions with phenols, naphthols and aromatic amines to form highly coloured azo-compounds.

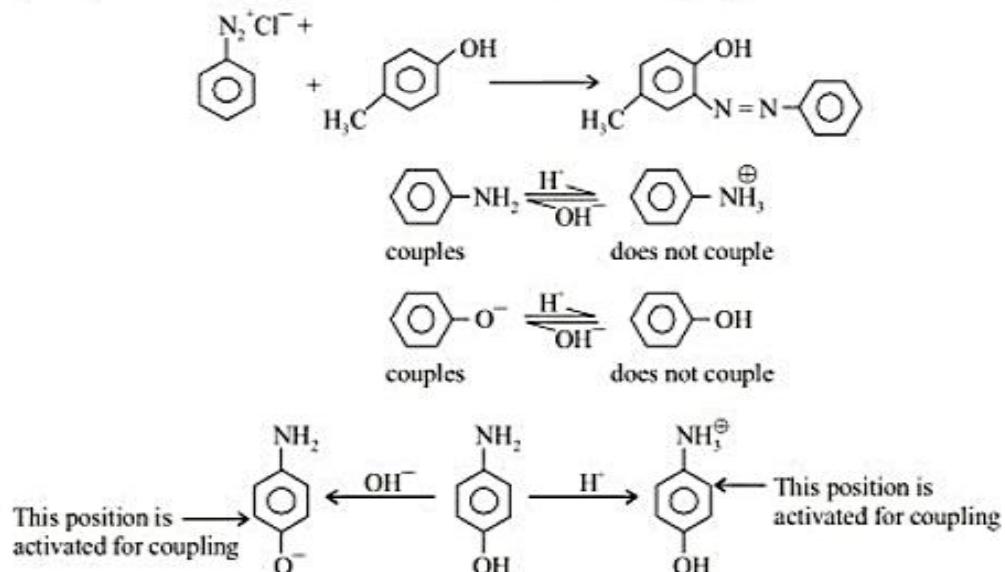
Arene diazonium ions acts as weak electrophiles in (aromatic) electrophilic substitution. The products have the structure Ar – N = N – Ar, containing the –N = N – azo linkage. Thus products are called azo compounds and reactions is called diazo coupling. Because diazonium salts are weak electrophiles, they react only with strongly activated ring (such as phenol, aniline).



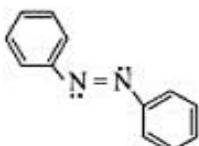
In general :



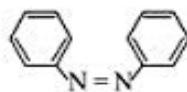
Coupling with benzene substrates occurs preferentially at the less sterically hindered p-position to the hydroxy or amino group, but if this is blocked, then o-coupling occurs.



Azo compounds, like alkenes, can exist in cis and trans forms and because of steric strain, the trans-isomer is more stable than cis-isomer.

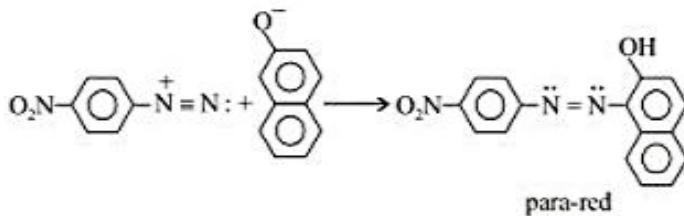


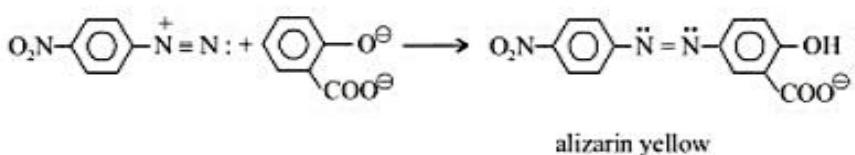
trans-azobenzene



cis-azobenzene

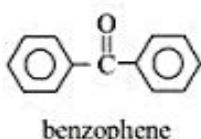
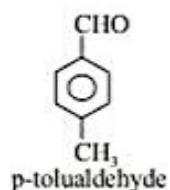
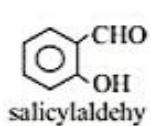
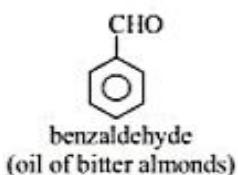
Azo compounds bring two substituted aromatic rings into conjugation with an azo group, which is a strong chromophore (a functional group absorption of light/colour). Thus most azo compounds are strongly coloured and they make azo dyes.





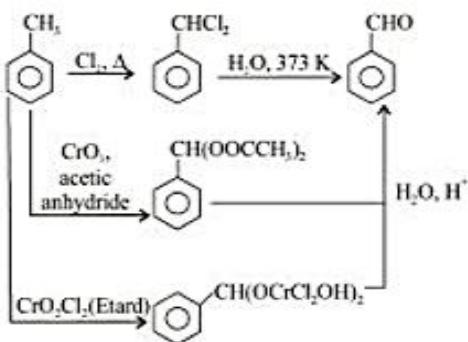
Diazo coupling often takes place in basic solutions since due to deprotonation of the phenolic –OH group or benzene sulphonic acid and carboxylic groups, activate the aromatic ring for S<sub>E</sub> reaction. Common azo dyes have sulphonate/carboxylate groups to enhance solubility of the azo dye in water and to help bind the dye to the polar surface of common fibres such as cotton and wool.

## CARBONYL COMPOUNDS

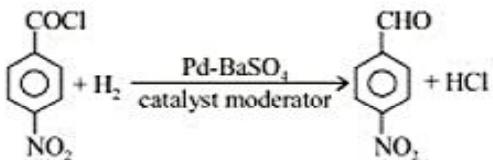


### Source

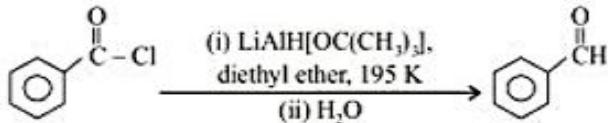
- From Toluene



- Rosenmund Reaction

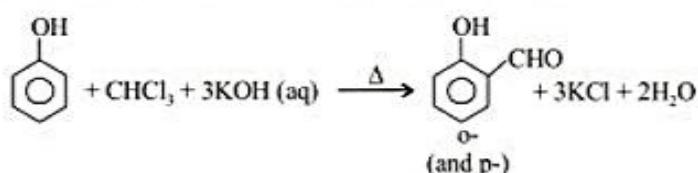


- Acylic chlorides can be reduced to aldehyde by treating them with lithium tri-ter-butoxy aluminium hydride, LiAlH[OC(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, at 195 K.

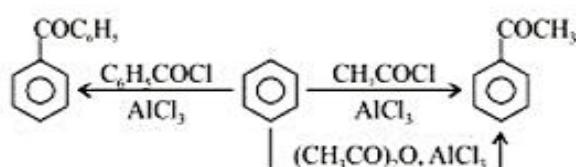


The reduction is brought by the transfer of a hydride ion from the aluminum atom to the carbonyl carbon of the acyl chloride. Subsequent hydrolysis frees the aldehyde.

- Reimer-Tiemann reaction is used to prepare phenolic aldehydes

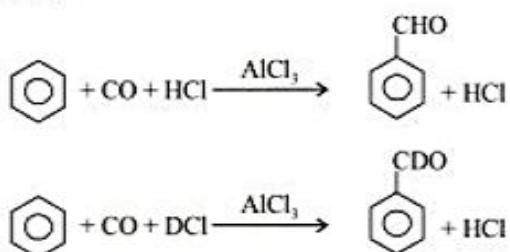


- Friedel-Crafts Acylation



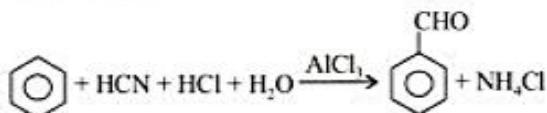
This reaction cannot be used on strongly deactivated aromatic systems.

### Gattermann-Koch Reaction

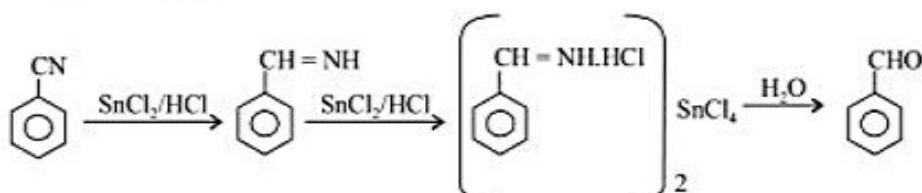


Thus, HCl (reactant) and HCl (product) are different. H of HCl (reactant) and CO appear in the form of -CHO in the benzene nucleus. It is confirmed by the fact that using isotopic DCI instead of HCl, would form -CDO and not -CHO. This reaction also succeeds only with benzene and activated benzene derivative.

- Gattermann-Aldehyde Synthesis

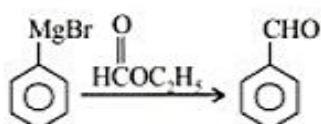


- Stephan Reaction

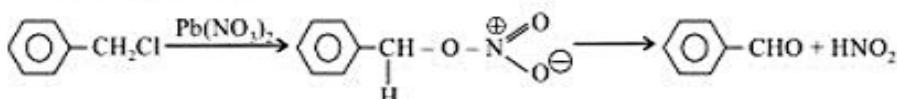


Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004740.jpg

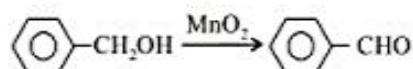
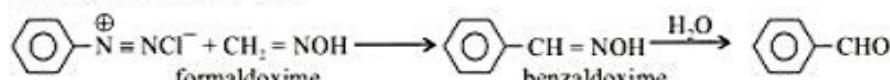
- **Grignard Reagent**



- **Oxidation of Benzyl Chloride**



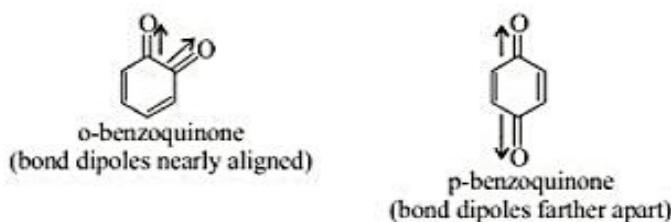
- **Using Diazonium Salts**



### Properties

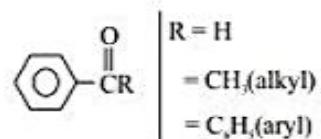
#### Physical

- $\text{C}_6\text{H}_5\text{CHO}$  is a colourless liquid with smell of bitter almond, sparingly soluble in water but readily in ethanol and ether.
- $\text{C}_6\text{H}_5\text{COCH}_3$  is crystalline solid and is steam volatile; soluble readily in ethanol and ether but sparingly soluble in water. It produces natural type of sleep when administered orally.
- Ortho-quinones, particularly ortho-benzoquinone are less stable than their para-quinone isomers. It is due to the fact that in ortho-isomer, the C=O bond dipoles are nearly aligned and these have a repulsive destabilising interaction. In para-isomers, these dipoles are farther apart.



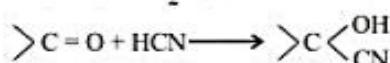
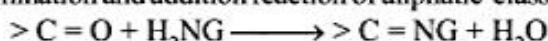
#### Chemical

Aromatic carbonyl compounds with following structure

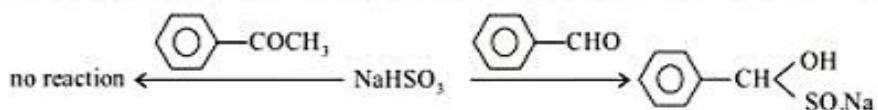


- Conjugation of the carbonyl carbon with the aryl ring reduces the electrophilic reactivity of the carbonyl carbon atom due to delocalisation of  $\pi$ -electrons. Hence, aromatic aldehydes and ketones are less reactive than aliphatic classes.
- Benzaldehyde, like aliphatic aldehydes, reduces Tollen's reagent (silver-mirror test). However, it does not reduce Fehling's solution. (a distinction from aliphatic class).

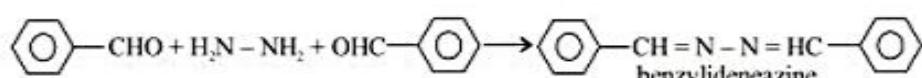
- They show elimination and addition reaction of aliphatic classes.



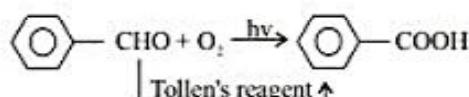
However, acetophenone does not form bisulphite complex, probably due to steric hindrance.



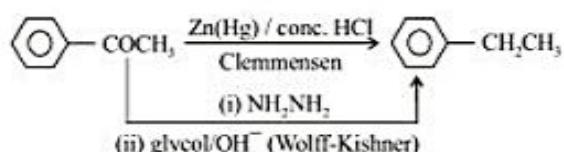
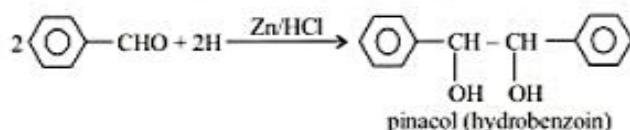
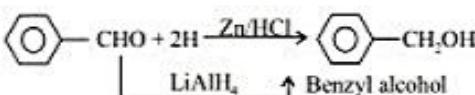
Benzaldehyde can react with hydrazine to form benzylideneazaine.



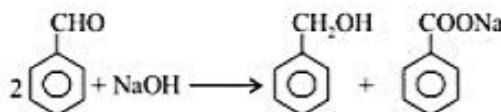
- Oxidation**



- Reduction**



- Cannizzaro Reaction**

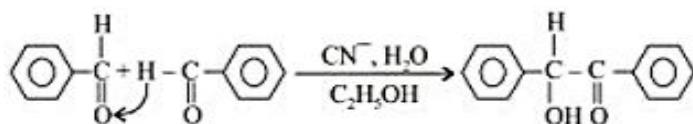


- It is given by those aldehydes which do not have H at  $\alpha$ -carbon, and also by HCHO.
- It is a disproportionation reaction.
- Benzoin condensation

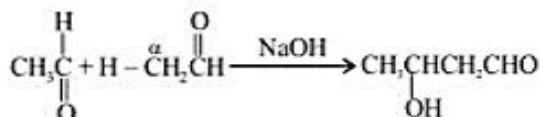
When benzaldehyde is heated with aqueous ethanolic NaCN or KCN, it dimerises to form an  $\alpha$ -hydroxy ketone ketone called benzoin, and reaction is called benzoin condensation.

It involves self condensation of an aromatic aldehyde in the presence of  $\text{CN}^-$  as catalyst.

Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004744.jpg

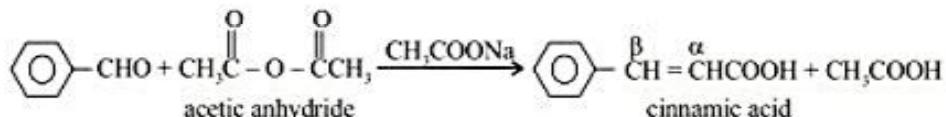


It resembles Aldol condensation of aliphatic aldehyde in which  $\alpha$ -H condenses, but  $-\text{CHO}$  group is free.



## PERKIN REACTION

It is the condensation reaction in which aromatic aldehyde is heated with an anhydride of an aliphatic acid in the presence of sodium salt of the same acid form  $\alpha$ ,  $\beta$ -unsaturated acid.

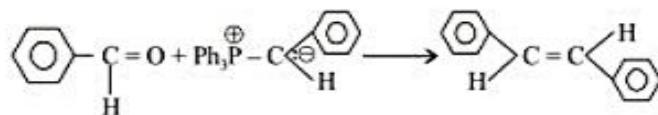
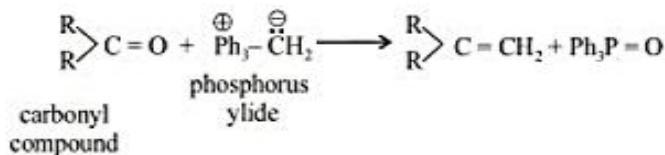


However, with cyclic anhydride (succinic anhydride),  $\beta$ ,  $\gamma$ -unsaturated acid is formed.

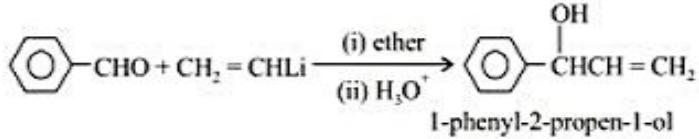
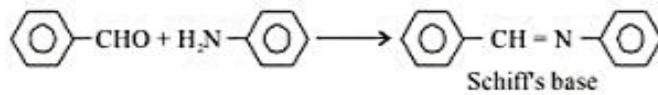


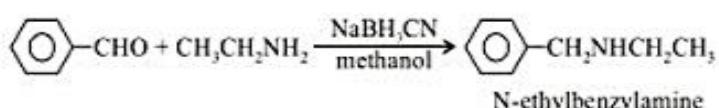
## **Witting Reaction**

It converts the carbonyl group of a ketone or aldehyde into a new double bond on reaction with phosphorus ylides.

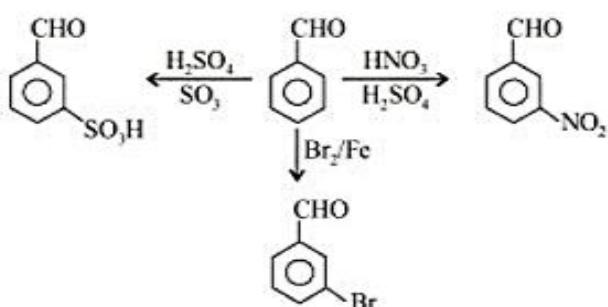
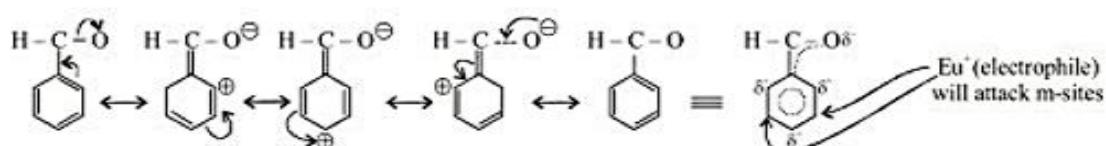


Mixture of cis and trans-isomers often result when geometric isomerism is possible.





- Reactions of Benzene Nucleus**



Saved /storage/emulated/0/Pictures/TouchShot/  
20170809\_004749.jpg