FOCUS NEET/JEE 2019

Class XII

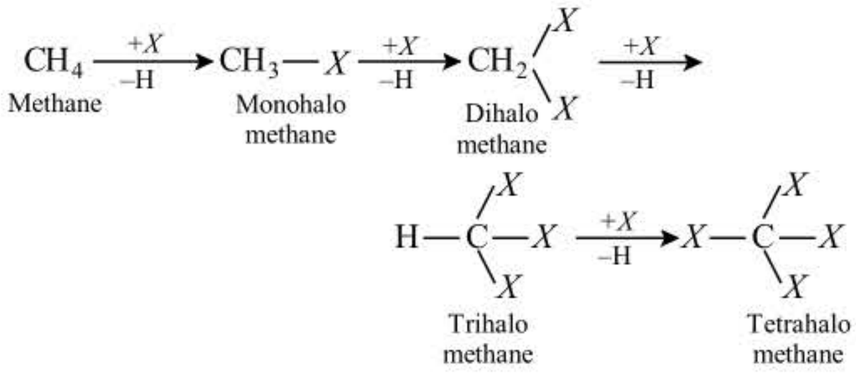
Focus more to get high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

UNIT - 5 : Haloalkanes & Haloarenes | Alcohols, Phenols & Ethers

HALOALKANES AND HALOARENES

Haloalkanes (Alkyl Halides)

- Compounds in which one or more hydrogen of alkane is (are) replaced by halogen are known as haloalkanes.



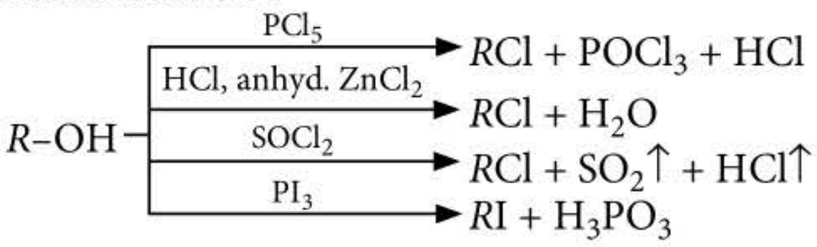
Nomenclature

- According to common or trivial system, monohaloderivatives are named as alkyl halides. *e.g.*, $CH_3—Cl$ (methyl chloride)
- According to IUPAC system, the monohaloderivatives of alkanes are named as haloalkanes.

e.g., $CH_3—\underset{\underset{Br}{|}}{CH}—CH_3$ (2-bromopropane)

Preparation

- **From alcohols :**



- **Halogentaion of alkanes :** $R-H + X_2 \xrightarrow{h\upsilon} RX + HX$
- **Finkelstein reaction :** $R-Cl + NaI \xrightarrow{\text{Acetone, }\Delta} RI + NaCl$
- **Hunsdiecker reaction :**

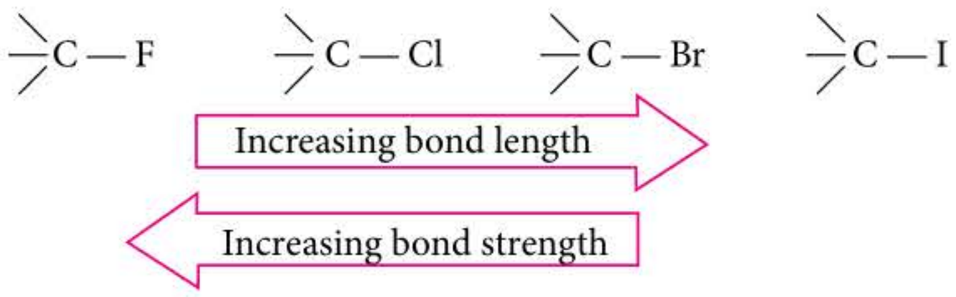
$$RCOOAg + Br_2 \xrightarrow{CCl_4} RBr + CO_2 + AgBr$$

Nature of C — *X* Bond

- In haloalkanes, the halogen atom is bonded to an alkyl group. The carbon atom is sp^3-hybridised.
  - The C — *X* bond is highly polarised covalent bond due to large difference in the electronegativities of carbon and halogen atoms. Halogen tends to pull the electrons away from carbon due to high electronegativity.

$$—C^{\delta+} \rightarrow\rightarrow X^{\delta-}$$

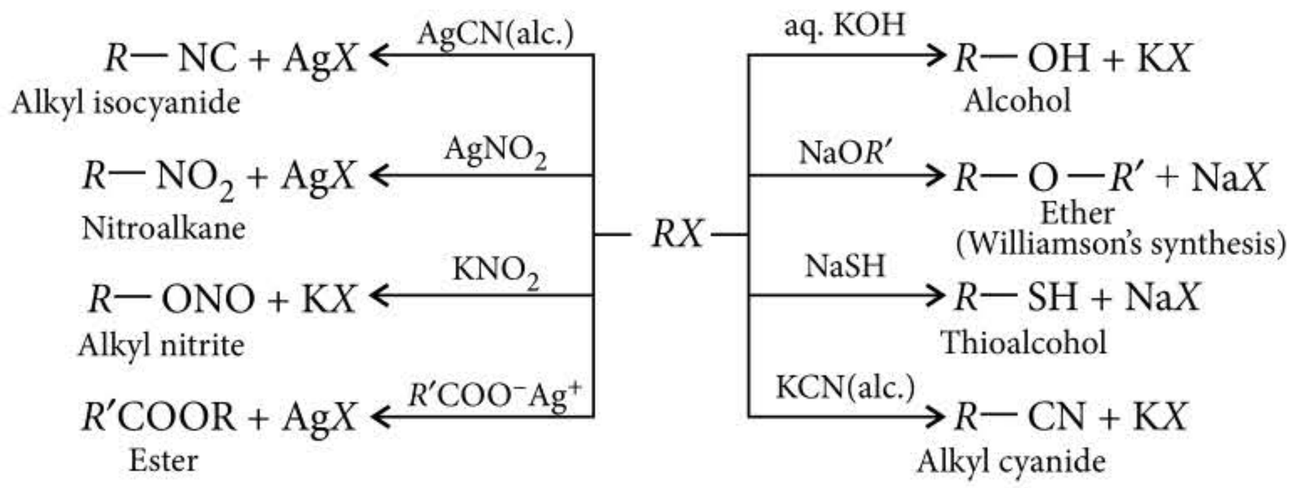
    This positive charge on carbon makes it susceptible for nucleophilic attack.
  - In haloalkanes bond strength of C — *X* bond decreases with an increase in bond length as one moves from fluorine to iodine.



Chemical Properties

- **Nucleophilic substitution reactions :** Alkyl halides easily undergo nucleophilic substitution reactions. Weakly basic halide ion is a good leaving group and gets replaced by other nucleophile easily.

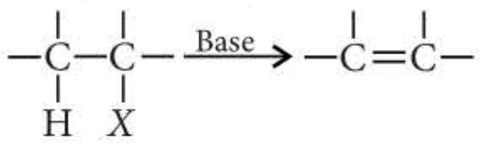
$$R - X + Nu^- \longrightarrow R - Nu + X^-$$



➤ The nucleophilic substitution can proceed via S_N1 mechanism or S_N2 mechanism :

Unimolecular (S_N1)	Bimolecular (S_N2)
It is first order reaction.	It is second order reaction.
Generally carried out in polar protic solvents like water, alcohol and acetic acid.	Carried out in polar aprotic solvents like acetone, DMSO, acetonitrile, or DMF.
Takes place in two steps through carbocation as the intermediate.	Takes place in one step through transition state.
Rate of reaction : $3° > 2° > 1° > {}^+CH_3$ (fastest) (slowest) Greater the stability of carbocation, faster will be the reaction.	Rate of reaction : $CH_3 > 1° > 2° > 3°$ halides (fastest) (slowest) Lesser the steric hindrance in transition state, faster will be the reaction.
Tends to proceed with weak nucleophiles *e.g.*, CH_3OH, H_2O, CH_3CH_2OH, etc.	Tends to proceed with strong nucleophiles, *e.g.*, CH_3O^-, CN^-, OH^-, etc.
Configuration is retained but in front attack inversion takes place (racemisation and inversion).	Inversion of configuration takes place (Walden inversion).

- **Dehydrohalogenation :**



- **Wurtz reaction :**

$$R\text{—}X + 2Na + X\text{—}R \xrightarrow{\text{Ether}} R\text{—}R + 2NaX$$

- **Reaction with Mg metal :**

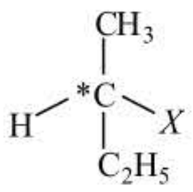
$$CH_3I + Mg \xrightarrow{\text{Ether}} CH_3MgI$$

$$CH_3MgI + H_2O \longrightarrow CH_4 + Mg(OH)I$$

Optical Rotation

- Substances which rotate the path of plane polarised light to either left or right are known as optically active and the rotation is known as optical rotation.
- If the substance rotates the plane polarised light in clockwise direction (*i.e.*, to the right) it is called dextrorotatory or *d*-form and if the substance rotates the plane polarized light in anticlockwise direction (*i.e.*, to the left), it is called laevorotatory or *l*-form.
- The compounds which differ only in the behaviour towards polarised light are called optical isomers and the phenomenon is called optical isomerism.
- Alkyl halides show optical isomerism. Basic requirement for the presence of optical isomerism is
  - ➤ Compounds must have a chiral or asymmetric carbon atom *i.e.*, a carbon atom should be linked to four different groups.
  - ➤ Mirror images must be non-superimposable (non superimposable mirror images are said to be enantiomers).

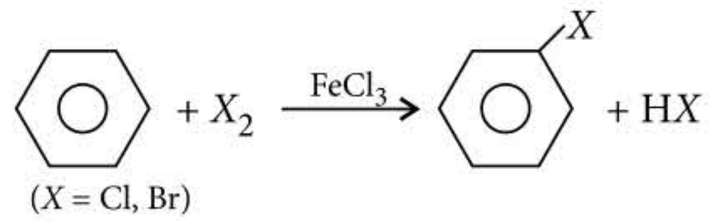
- **Diastereomers :** They are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation.
- **Meso compounds :** These compounds have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to internal compensation.
- Lowest molecular mass, optically active haloalkane must contain four carbon atom.



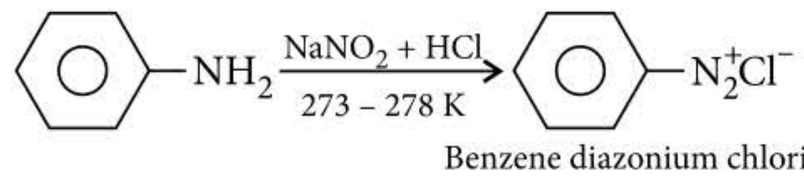
HALOARENES

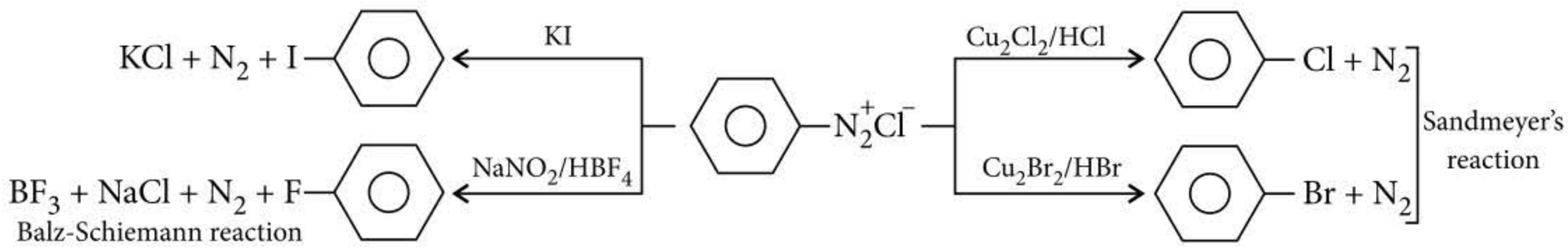
Preparation

- **Direct halogenation of benzene (electrophilic substitution reactions) :**



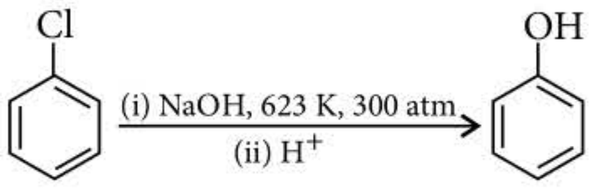
➤ **From benzene diazonium chloride :**





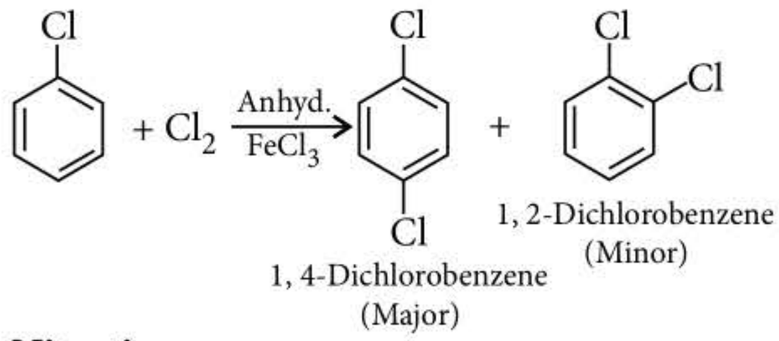
Chemical Properties

- The aryl halides are relatively less reactive towards nucleophilic substitution reactions as compared to alkyl halides. This low reactivity can be attributed due to the following factors :
  - ➤ The C—*X* bond in halobenzene has a partial double bond character due to involvement of halogen electrons in resonance with benzene ring.
  - ➤ The C—*X* bond in aryl halides is less polar as compared to that in alkyl halides as sp^2 hyridised carbon is more electronegative than sp^3 hybridised carbon.
- **Nucleophilic substitution reactions :**

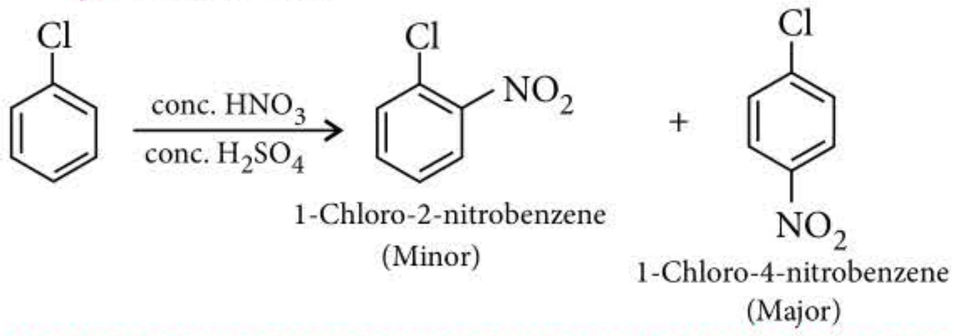


The presence of an electron withdrawing group ($-NO_2$) at *ortho*- and *para*-positions increases the reactivity of haloarenes.

- **Electrophilic substitution reactions :**
  - ➤ **Halogenation :**



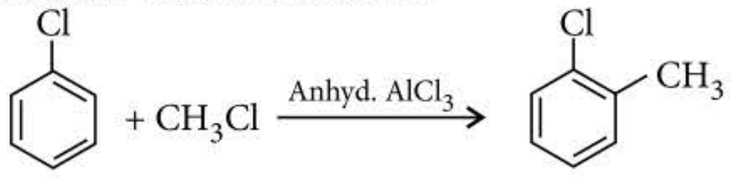
  - ➤ **Nitration :**



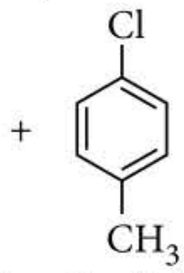
MONTHLY TUNE UP CLASS XI ANSWER KEY

1.	(b)	**2.**	(a)	**3.**	(a)	**4.**	(a)	**5.**	(a)
6.	(a)	**7.**	(b)	**8.**	(a)	**9.**	(b)	**10.**	(a)
11.	(d)	**12.**	(b)	**13.**	(a)	**14.**	(b)	**15.**	(c)
16.	(a)	**17.**	(b)	**18.**	(d)	**19.**	(b)		
20.	(b,c,d)	**21.**	(b,c)	**22.**	(a,d)	**23.**	(a,b,c)		
24.	(4×10^{-9})			**25.**	(33)	**26.**	(9)	**27.**	(b)
28.	(b)	**29.**	(b)	**30.**	(d)				

- **Friedal–Crafts reaction :**

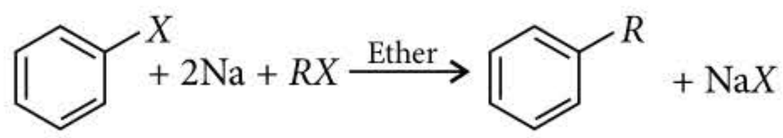


1-Chloro-2-methylbenzene
(Minor)

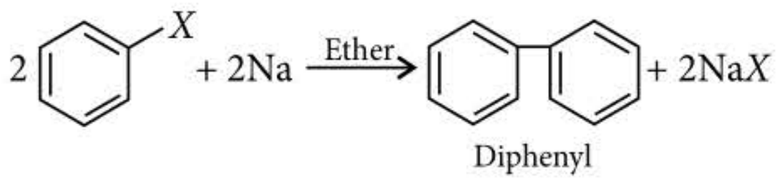


1-Chloro-4-methylbenzene
(Major)

- **Wurtz—Fittig Reaction :**



- **Fittig reaction :**

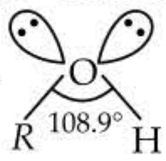


Diphenyl

ALCOHOLS, PHENOLS AND ETHERS

ALCOHOLS

- **General formula :** Alcohols are the hydroxy derivatives of alkanes having general formula $C_nH_{2n+1}OH$.
- **Nomenclature :** In common system, alcohols are named as alkyl alcohol. According to IUPAC system, alcohols are called 'alkanols', by replacing '*-e*' of alkane by '*-ol*'.
- **Structure :** In alcohols, $R-OH$, the O atom of hydroxyl group is attached to C-atom by a sigma (σ) bond formed by the overlap of sp^3-hybridised orbital of C-atom with sp^3-hybridised orbital of O atom.



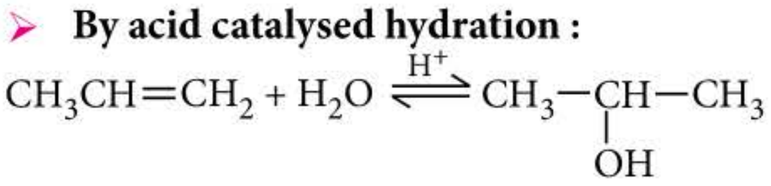
- Monohydric alcohols are of three types :

Monohydric alcohols

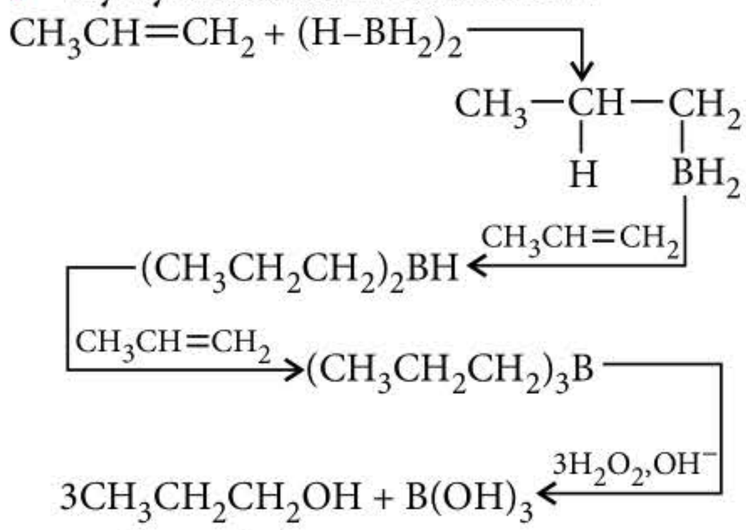
Primary Alcohols	**Secondary Alcohols**	**Tertiary Alcohols**
–OH group attached to primary C-atom.	–OH group attached to secondary C-atom.	–OH group attached to tertiary carbon atom.
$R-CH_2OH$	R_2CH-OH	R_3C-OH

Preparation

- **From alkenes :**
  - **By acid catalysed hydration :**

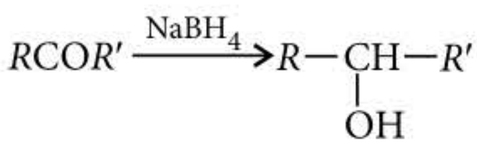


  - **By hydroboration-oxidation :**

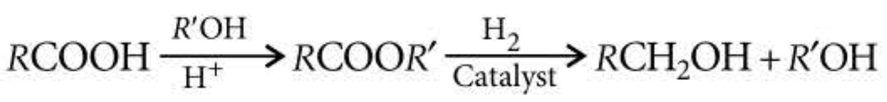


Propan-1-ol

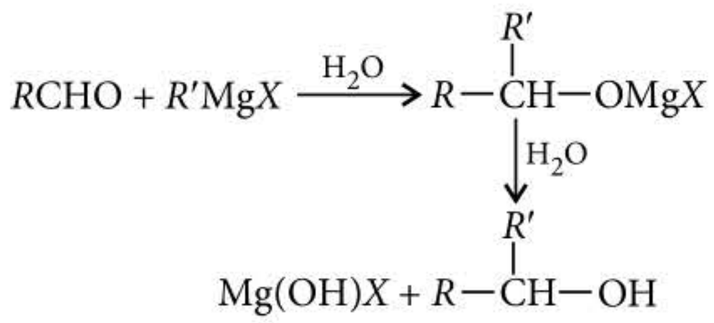
- **From carbonyl compounds :**
  - **By reduction of aldehydes and ketones :**



  - **By reduction of carboxylic acids and esters :**

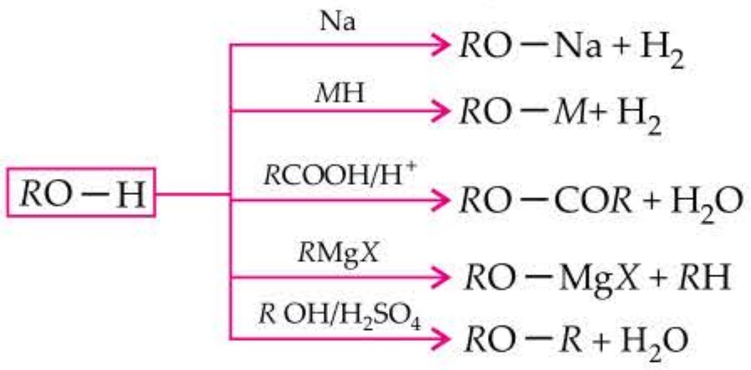


  - **From Grignard reagents :**

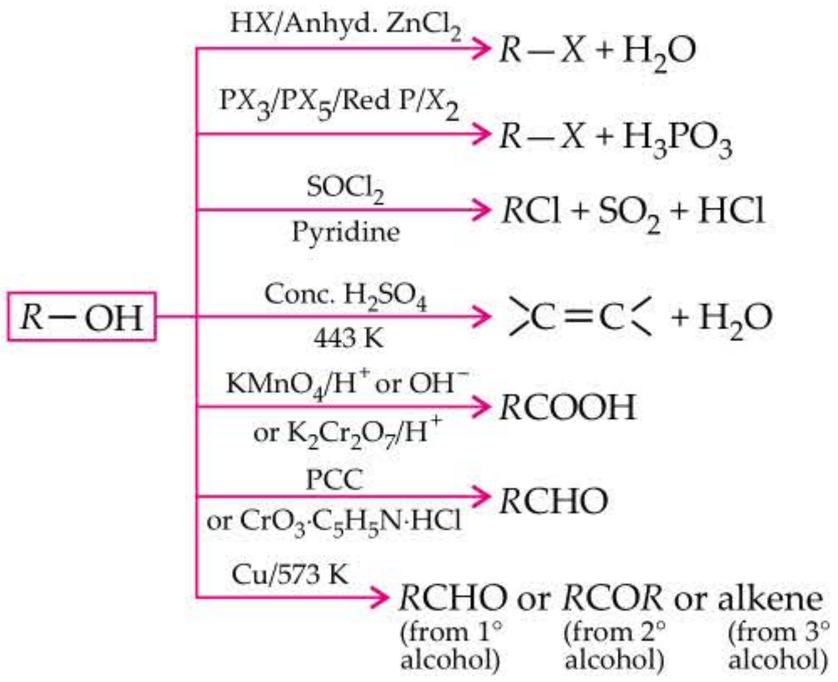


Chemical Properties

- **Reactions involving cleavage of O – H bond**



- **Reactions involving cleavage of C – O bond**



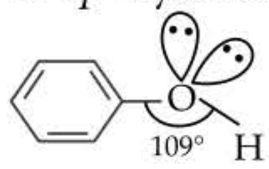
Identification Tests

- **Lucas test** : Lucas reagent is a solution of conc. HCl with anhyd. $ZnCl_2$.
  With Lucas reagent : Primary alcohols (No cloudiness), Secondary alcohols (Cloudiness in 5 minutes), Tertiary alcohols (Cloudiness immediately).
  By this reaction it is clear that 1° alcohol is most acidic and 3° alcohol is most basic amongst alcohols.
- **Victor Meyer's test :**

Primary alcohol	Secondary alcohol	Tertiary alcohol
RCH_2OH ↓ $P + I_2$ RCH_2-I ↓ $AgNO_2$ RCH_2-NO_2 ↓ HNO_2 $R-C(=N-OH)-NO_2$ Nitrolic acid ↓ NaOH $R-C(=N-O^-Na^+)-NO_2$ Red colour	R_2CHOH ↓ $P + I_2$ R_2CH-I ↓ $AgNO_2$ R_2CH-NO_2 ↓ HNO_2 $R_2C(NO_2)(NO)$ Pseudonitrol ↓ NaOH Blue colour	R_3C-OH ↓ $P + I_2$ R_3C-I ↓ $AgNO_2$ R_3C-NO_2 ↓ HNO_2 No reaction ↓ NaOH Colourless

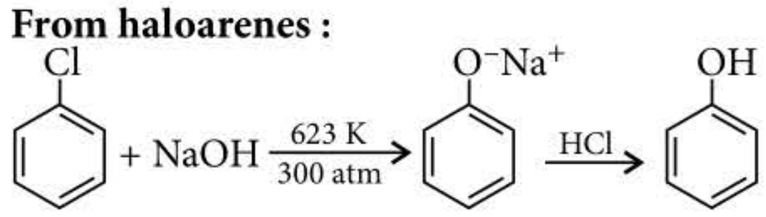
PHENOLS

- **General formula :** Phenols are the compounds in which hydroxy (–OH) group is directly linked to aromatic ring having formula C_6H_5OH.
- **Nomenclature :** The simplest hydroxy derivative of benzene is phenol which is also called carbolic acid. It is its common name and, which is also an accepted IUPAC name.
- **Structure :** In phenols, the –OH group is attached to sp^2-hybridised C-atom of an aromatic ring.

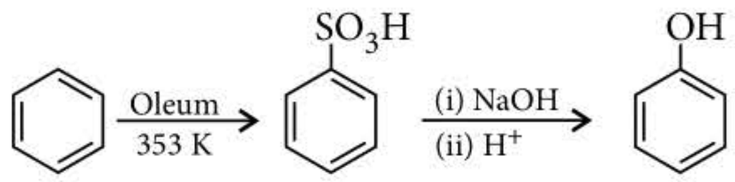


Preparation

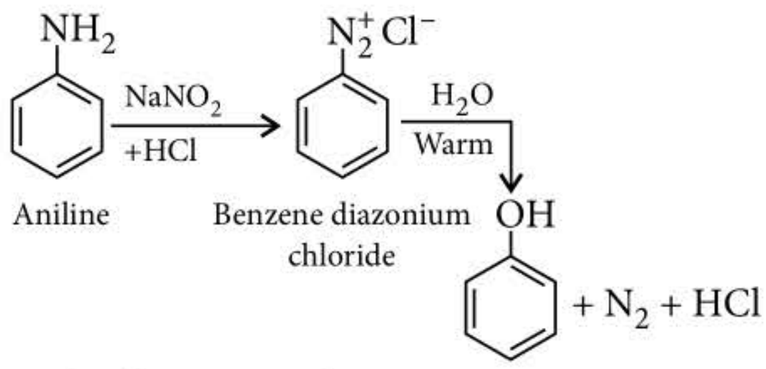
- **From haloarenes :**



- **From benzenesulphonic acid :**



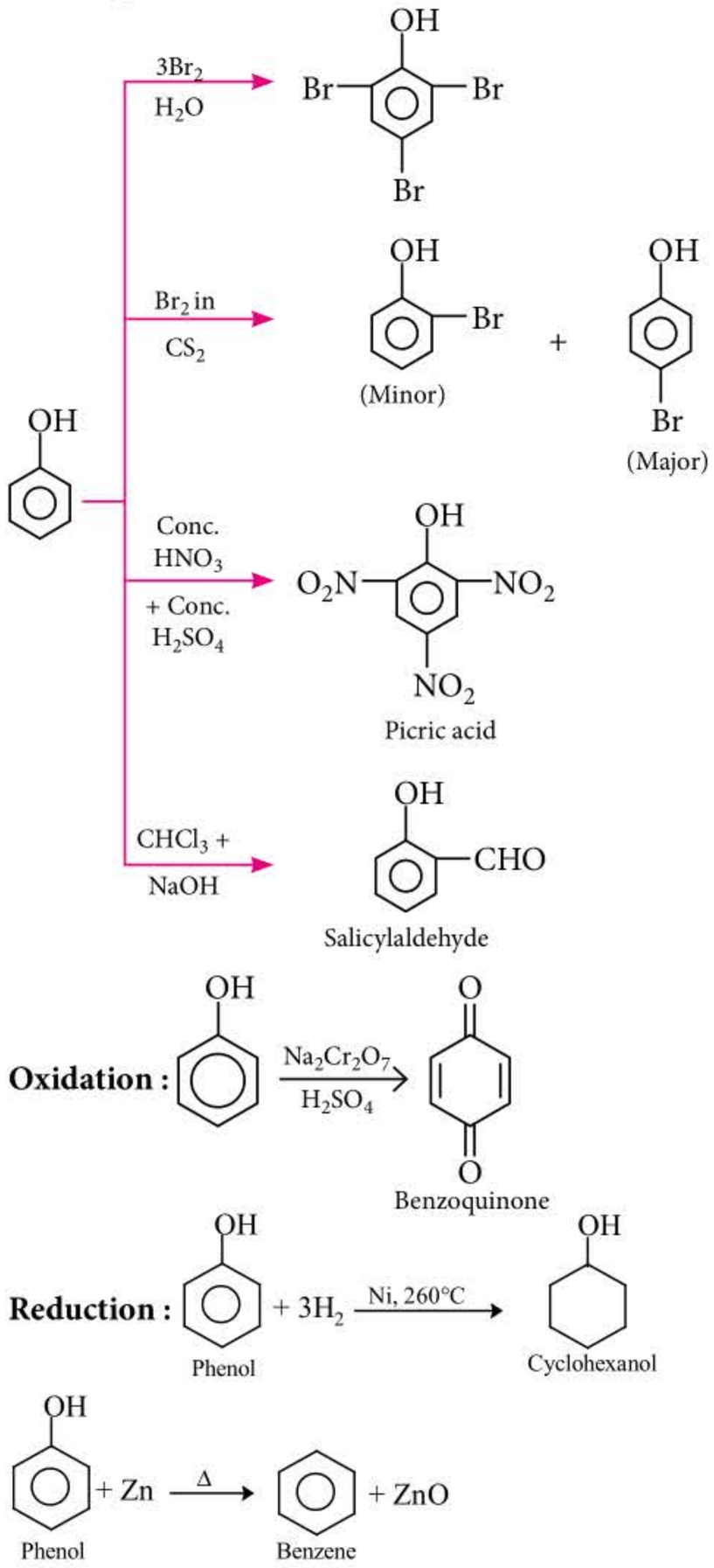
- **From diazonium salts :**



Chemical Properties

- **Acidity of phenols :** Phenols are weakly acidic in nature due to polar O – H bond directly attached to sp^2-hybridised C-atom.
  - They turn blue litmus red and react with alkali metals and alkalies to form their salts.
  - Phenol is weaker acid than carboxylic acid. It does not react with sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$).
  - Phenols are more acidic than alcohols which can be explained on the basis of resonance.
  - Electron withdrawing groups increase the acidic strength of phenols.
  - Electron releasing groups decrease the acidic strength of phenols.

- **Electrophilic Substitution Reactions**



- **Oxidation :**
- **Reduction :**

ETHERS

- **General formula :** Ethers are the compounds having general formula $C_nH_{2n+2}O$; where, n is always greater than 1.
- **Nomenclature :** Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word '*ether*' at the end. According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an $-OR$ or $-OAr$ group, where R and Ar represent alkyl and aryl groups, respectively.
- **Structure :** In ethers, the four electron pairs, *i.e.*, the two bond pairs and two lone pairs of electrons on O-atom are arranged approximately in a tetrahedral arrangement.

Preparation

By dehydration of alcohols

$$R\text{OH} + \text{HO}R \xrightarrow[413\ \text{K}]{\text{Conc. } H_2SO_4}$$

$$R\text{OH} + \text{HO}R \xrightarrow{Al_2O_3,\ 633\ \text{K}}$$

$$R\text{OH} + CH_2N_2 \xrightarrow{HBF_4}$$

From alkyl halides

$$2R{-}X + Ag_2O \xrightarrow{\Delta}$$

$$R{-}X + R\text{ONa} \xrightarrow{\Delta}$$

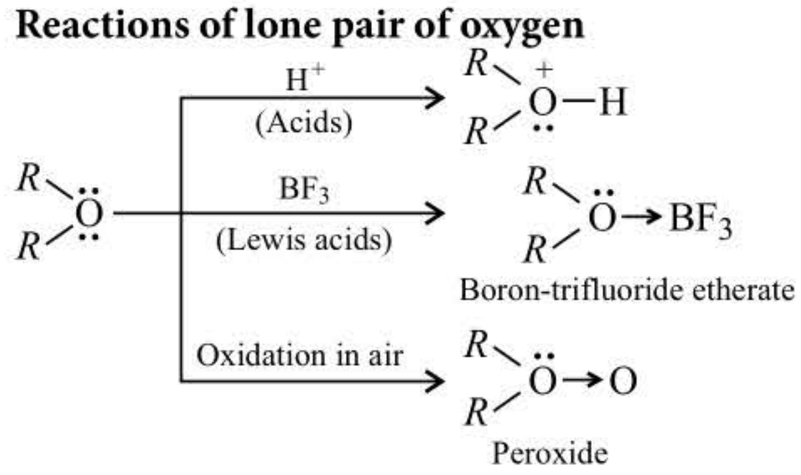
Preparation of cyclic ethers (or epoxides)

$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[200\text{–}400^\circ C]{Ag} \underset{CH_2}{\overset{CH_2}{|}}\!\!>\!O$$

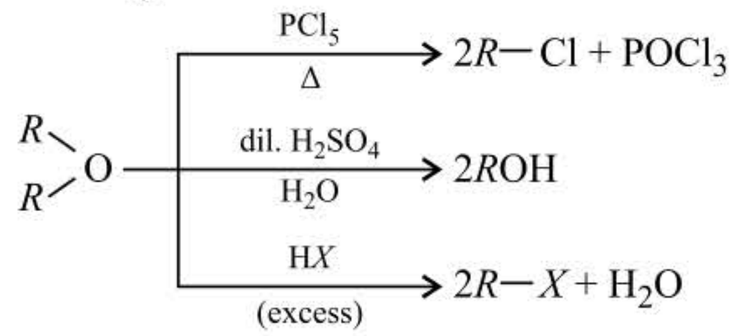
ETHERS

Chemical Properties

Reactions of lone pair of oxygen



Cleavage of R—O—R bond



Quotable Quote

The greatest enemy of knowledge is not the ignorance, it is the illusion of knowledge.

Stephen Hawking