Haloalkanes And Haloarenes

⇒ Haloalkanes :-

The halogen derivatives of alkanes are called haloalkanes. These are also called alkyl halide.

$$R-H \xrightarrow[-H]{+X} R-X$$

$$CH_4 \xrightarrow[-H]{+Cl} CH_3-Cl$$

general formula → $C_nH_{2n+1}-X$ (R-X)

↳ Halogen (F, Cl, Br, I)

↳ Alkyl Group

⇒ Haloalkenes or Alkenyl halides :- The halogen derivatives of alkenes, also called alkenyl halides

eg $CH_2=CH-Br$, $CH_2=CH-CH_2-I$

⇒ Haloalkynes or alkynyl halides :-

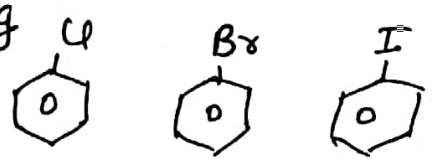
These are the halogen derivatives of alkynes.

$CH_3-C\equiv C-Br$

⇒ Aromatic Halogen Compounds

These are the halogen derivatives of aromatic hydrocarbons.

In haloarenes, the halogen atom is directly bonded to benzene ring



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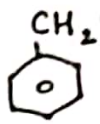
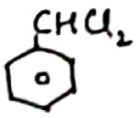
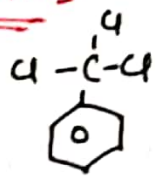
⇒ Side Chain Halogen derivatives



Benzyl chloride



Benzal dichloride



Benzotrichloride

⇒ Classification of Haloalkanes and Haloarenes

(A) Types of halogen atom

fluorobenzene

Chlorobenzene

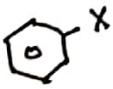
bromobenzene

iodobenzene

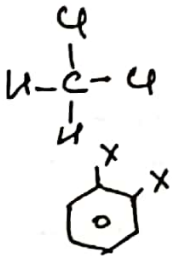
(B) Number of halogen atoms

Monohalo

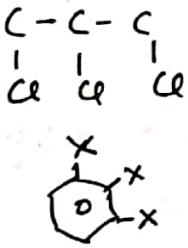
CH_3CH_2Br



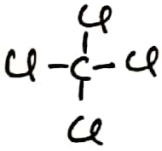
Dihalo



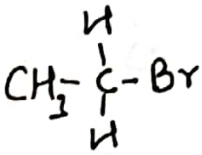
Trihalo



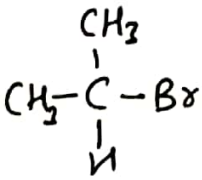
Tetrahalo



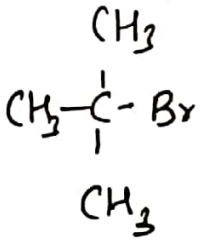
(C) Nature of Carbon Atoms



(1°)



(2°)



(3°)

(d) Hybridisation Of Carbon

(sp^3)

CH_3-CH_2-I,

(sp^2)

$CH_2=CH_2$ (Cl),

(sp)

$CH_3-C\equiv C-Cl$

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* Some Special Type

(a) Vinylic Halides :-

$CH_2 = CH$
$\quad\quad\;\; |$
$\quad\quad\;\; X$

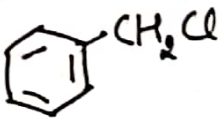
Halogen bonded to double bonded C atom

(b) Allylic Halides

$CH_2 = CH - CH_2 - X$

Halogen bonded to next to double bonded C-atom.

(c) Benzylic or Aralkyl halides



Halogen bonded to side chain C-atom of benzene ring.

(d) gem-dihalides

$CH_3 - CH\begin{matrix} Cl \\ Cl \end{matrix}$

(e) vicinal-dihalides

$CH_2 - CH_2$
$\quad\;\; |\quad\quad\; |$
$\quad\;\; Cl\quad\;\; Cl$

(e) Propargyl halides

$HC \equiv C - CH_2 - Br$

$HC \equiv C - CH - CH_3$
$\quad\quad\quad\;\; |$
$\quad\quad\quad\; Cl$

halogen atom is bonded to a sp^3 hybridised carbon atom next to a carbon-carbon triple bond.

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⇒ Nomenclature of Haloalkanes & Haloarenes

CH_3-Cl	methyl chloride	chloro methane
CH_3-CH_2-Br	Ethyl bromide	bromo ethane
$CH_3-CH_2-CH_2-I$	n-propyl iodide	iodopropane
$CH_3-CH(CH_3)-CH_2-Cl$	Isobutyl chloride	2-methyl-1-chloro propane

Remember

n- is used for alkyl group having continuous chain of C-atom

(n-) $CH_3-CH_2-CH_2-CH_2-$ or $CH_3-CH_2-CH_2-CH_2-CH_2-$

iso - one methyl group is attached to the next to end C-atom

(iso-) $CH_3-CH(CH_3)-$ or $CH_3-CH(CH_3)-CH_2-$

neo - when two methyl groups attached to the next to end C-atom

(neo-) $CH_3-C(CH_3)_2-CH_2-$ or $CH_3-C(CH_3)_2-CH_2-CH_2-$

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(•) $CH_3CH_2CH_2F$ — n-Propyl fluoride — 1-Fluoro propane

(•) $CH_3-\overset{I}{CH}-CH_3$ — isopropyl iodide — 2-iodopropane

(•) $CH_3-\underset{CH_3}{CH}-CH_2-Cl$ — isobutyl chloride — 1-chloro-2-methyl propane

(•) $CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_3$ — tert-Butyl chloride — 2-chloro-2-methyl propane

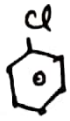
(•) $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$ — tert-Pentyl chloride — 2-chloro-2-methyl butane

IUPAC Nomenclature

$C-\overset{C}{C}-C-Cl$ → 1-chloro-2-methyl propane

$C-C-\overset{C}{\underset{C}{C}}-C-Br$ → 1-Bromo-2,2-dimethylbutane

$C-\underset{Br}{C}-C-C-C$ → 2-Bromopentane


→ chlorobenzene

1,2-Dichlorobenzene (o-Dichlorobenzene)

1-chloro-4-methyl benzene

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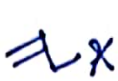
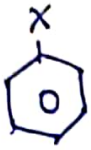
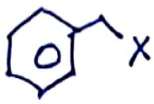
Special Names

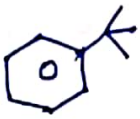
Vinyl


Allyl

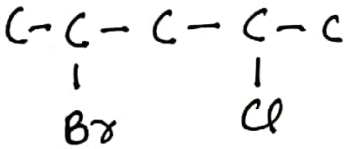

Phenyl


Benzyl

Benzal


Benzo

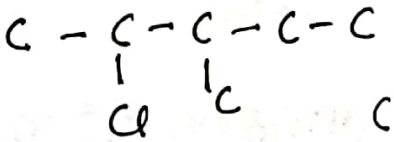
⇒ Previous Year Questions

- 
(A.I - 2013)

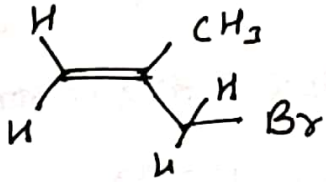
  2-bromo-4-chloropentane

- $CH_2 = CH - CH_2 - Br$ (A.I - 2011)

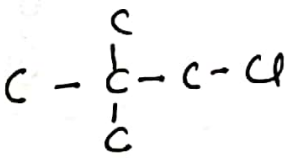
  3-bromoprop-1-ene

- 
(2011 C)

  (2-chloro-3-methylpentane)

- 
(A.I - 2010)

  (3-bromo-2-methylprop-1-ene

- 
(A.I - 2010 C)

  1-chloro-2,2-dimethylpropane

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Isomerism in Haloalkanes and Haloarenes

- Haloalkanes show two types of isomerism

(a) **Chain isomerism**:- isomers differ in the chain of carbon atoms.

C_4H_9Br has three chain isomers

$CH_3-CH_2-CH_2-CH_2-Br$

$CH_3-CH(CH_3)-CH_2-Br$

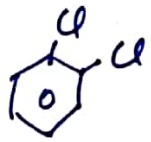
$CH_3-C(CH_3)_2-Br$

(b) **Position isomerism** isomers differ in the position of halogen atom.

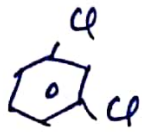
$CH_3-CH_2-CH_2-Cl$

$CH_3-CH(Cl)-CH_3$

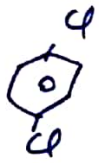
Haloarenes show position isomerism



1,2- Dichlorobenzene



1,3-dichlorobenzene



1,4-dichloro benzene

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Nature of C-X Bond

$\overset{\delta+}{C}-X^{\delta-}$ Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised

Size of halogen atom increases as we move down the group in the periodic table, fluorine atom is the smallest and iodine the largest

As a result, the carbon-halogen bond length increases and bond enthalpy decreases from C-F to C-I

Halomethane	C-X bond length (in pm)	C-X bond enthalpy (KJ/mol)	Dipole moment /Debye
CH_3-F	139	452	1.847
CH_3-Cl	178	351	1.860
CH_3-Br	193	293	1.830
CH_3-I	214	234	1.636

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Preparation Of Haloalkane

From Alcohol

1.) $R\text{-}OH + HCl \xrightarrow{ZnCl_2} R\text{-}Cl + H_2O$

(Groover's Process)

ग्रोवर शराबी है एकली का जादु

$C_2H_5\text{-}OH + HCl \xrightarrow{ZnCl_2} C_2H_5\text{-}Cl + H_2O$

→ $*R\text{-}OH + SOCl_2 \longrightarrow R\text{-}Cl + HCl_{(g)} + SO_{2(g)}$

S
O O
Cl H
Cl

$C_2H_5\text{-}OH + SOCl_2 \longrightarrow C_2H_5\text{-}Cl + HCl + SO_2$

→ $R\text{-}OH + PCl_5 \longrightarrow R\text{-}Cl + HCl + POCl_3$

P Cl Cl Cl Cl Cl
OH

$C_2H_5\text{-}OH + PCl_5 \longrightarrow C_2H_5\text{-}Cl + HCl + POCl_3$

→ $3(R\text{-}OH) + PCl_3 \longrightarrow 3(R\text{-}Cl) + P(OH)_3$ or H_3PO_3

$3(C_2H_5\text{-}OH) + PCl_3 \longrightarrow 3(C_2H_5\text{-}Cl) + H_3PO_3$

Physical Properties Of Haloalkanes

Solubility

Haloalkanes are insoluble in water because they can't form H-bond with water. These are soluble in organic solvents like alcohol, benzene, ether. etc

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Physical State

Lower Haloalkanes are colourless ~~liquid~~ ~~or~~ gases while higher members are liquid or solid But bromide and iodides are coloured when exposed in light. They have sweet smell

M.Pt and B.Pt

M.Pt $\propto$ Mol. Mass

(i) $CH_3Cl < CH_3-CH_2-Cl < CH_3-CH_2-CH_2-Cl$

(ii) $CH_3-CH_2-F < CH_3-CH_2-Cl < CH_3-CH_2-Br < CH_3-CH_2-I$

(iii) $CH_3-CH_2-CH_2-CH_2-Cl > CH_3-CH(CH_3)-CH_2-Cl > CH_3-C(CH_3)_2-Cl$

Note: M.Pt and B.Pt decreases with increase in no. of branches in isomeric Haloalkanes

(iv) $H-CH_2-Cl < H-CH(Cl)-Cl < H-CCl_2-Cl < Cl-CCl_3$

~~Solubili~~

Density

These are heavier than water

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⇒ By Halogen Exchange

(a) Finkelstein Reaction

$$R\text{-}X + NaI \xrightarrow{\text{Acetone}} R\text{-}I + NaX$$

$$CH_3\text{-}CH_2\text{-}Br + NaI \xrightarrow[\Delta]{\text{Acetone}} CH_3\text{-}CH_2\text{-}I + NaBr$$

$$CH_3\text{-}CH_2\text{-}Cl + NaI \xrightarrow{\text{Acetone}} CH_3\text{-}CH_2\text{-}I + NaCl$$

Only iodo alkanes are prepared by this method.

(b) Swarts Rxn

The only method for the preparation of fluoroalkanes

These are prepared by treating alkyl chlorides or bromides with heavy metal fluorides like Hg_2F_2, AgF, CoF_3, SbF_3 etc

$$CH_3\text{-}Br + AgF \longrightarrow CH_3F + AgF$$

⇒ Hunsdiecker Reaction

$$CH_3\text{-}COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + CO_2 + AgBr$$

⇒ Addition of HX to Unsymmetrical Alkenes :

$$CH_3\text{-}CH = CH_2 + HCl \xrightarrow{\text{M.Rule}} CH_3\text{-}\underset{\underset{Cl}{|}}{CH}\text{-}CH_3 \ (\text{sor.}) + CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl \ (\text{lor.})$$

- The addition of HBr takes place acc. to Markownikov's rule in absence of peroxide but in presence of peroxide, the addition of HBr is acc. to anti-Markownikov's Rule. This is called peroxide effect or Kharasch effect

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$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{M.Rule}} CH_3-\underset{Br}{CH}-\underset{H}{CH_2}$$

$$\xrightarrow[\text{A.M Rule}]{\text{Peroxide}} CH_3-\underset{H}{CH}-\underset{Br}{CH_2}$$

- **Markovnikov's Rule**

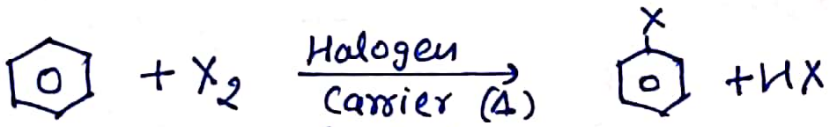
This rule states that negative part of the ~~addition~~ addendum attached to that C-atom which has lesser number of Hydrogen.

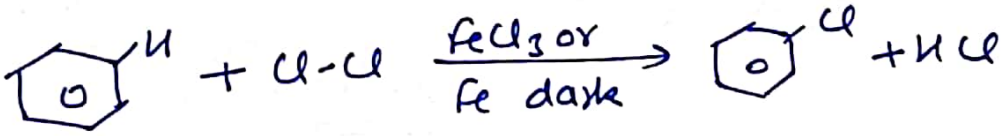
- **Anti. Markownikov's Rule** or **Peroxide effect** or **Kharasch effect**

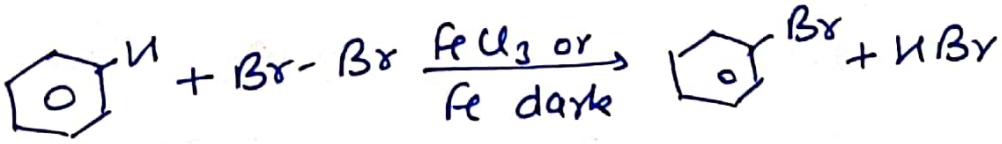
Acc. to this rule, the negative part of the adding reagent goes to that doubly bonded carbon which has more hydrogen.

Methods of Preparation of Haloarenes

⇒ By electrophilic substitution







- The reaction with fluorine is violent and can not be controlled

⇒ Iodoarenes are also difficult to prepare. The HI formed during reaction behave as reducing agent and cause the reaction in backward direction. So reaction is carried out in presence of oxidising agent

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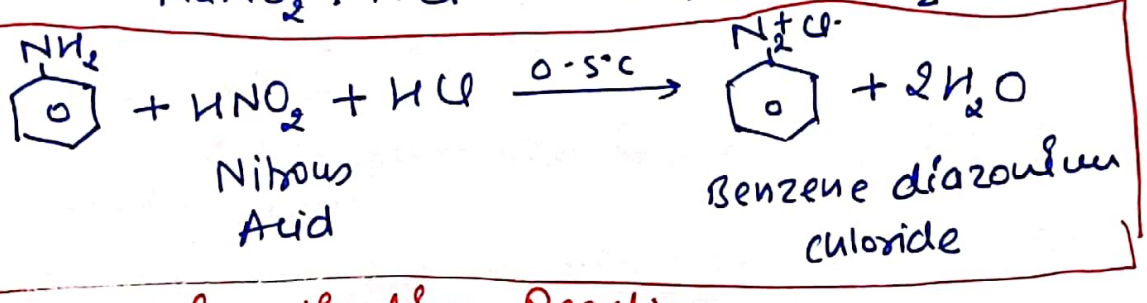
$$5HI + HIO_3 \longrightarrow 3H_2O + 3I_2$$

Iodic acid

From Diazonium Salts

(a) Sandmeyer's Reaction

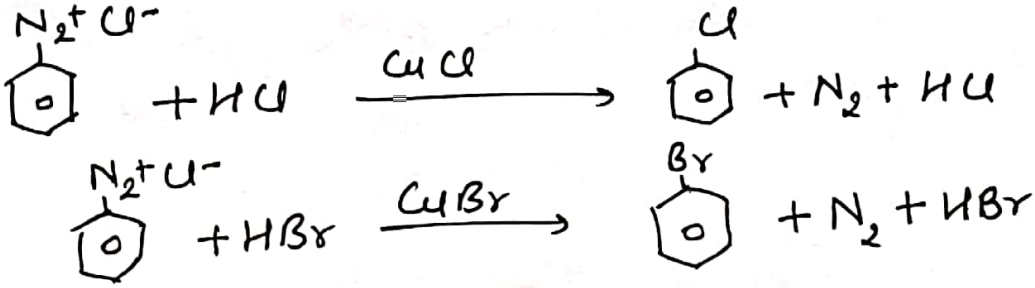
$$NaNO_2 + HCl \xrightarrow{0\text{-}5^\circ C} NaCl + HNO_2$$



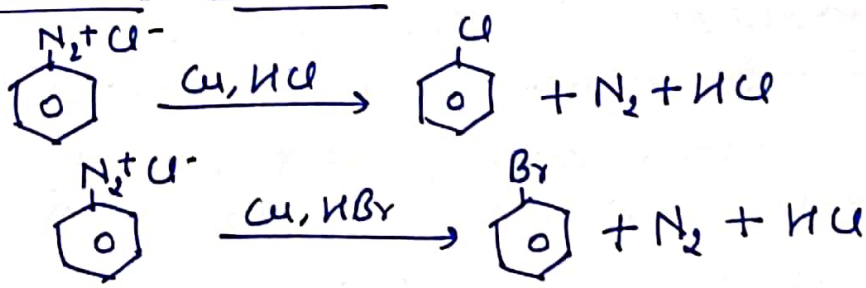
Nitrous Acid

Benzene diazonium chloride

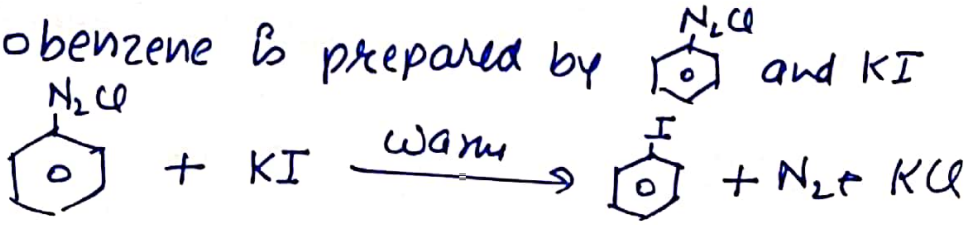
Diazotization Reaction



(b) Gattermann's Reaction



(c) Iodobenzene is prepared by



and KI

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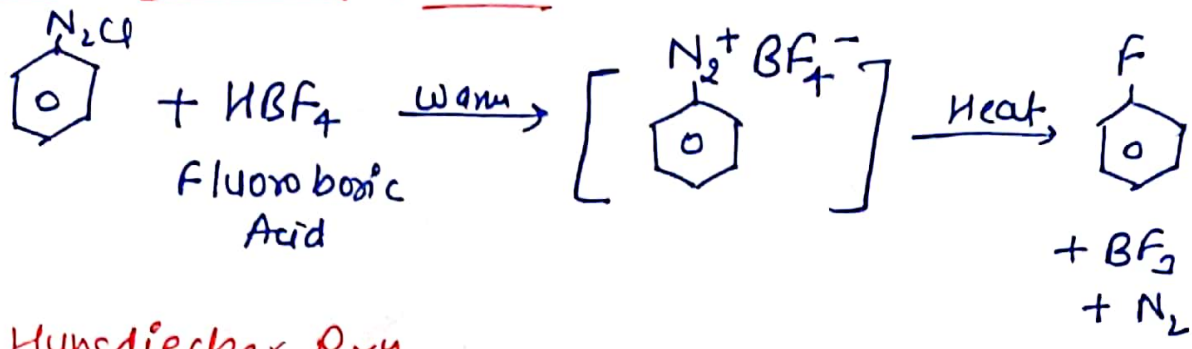
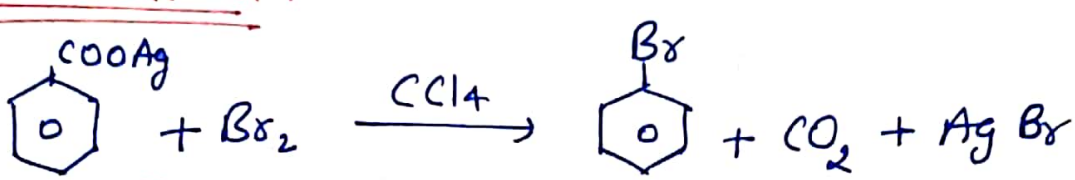
(d.) Balz - Schiemann Reaction



(e) Hunsdiecker Rxn



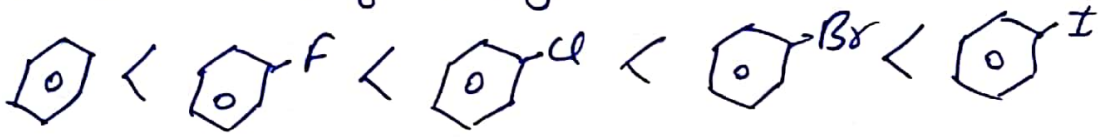
Physical Properties of Haloarenes

1.) These are either colourless liquids or colourless crystalline solids.

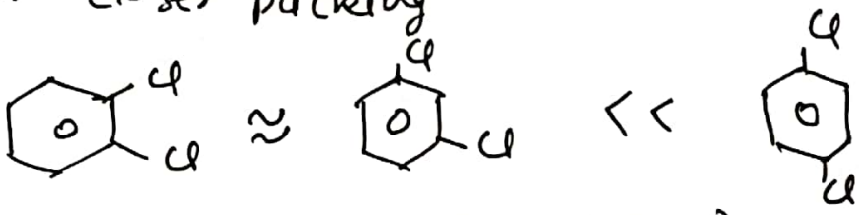
2.) These are insoluble in water but soluble in organic solvents.

3.) They have higher density than water

4.) The m.pt and b.pt go on increasing with increase in size of halogens



5.) In dihalo arenes, the orthodichlorobenzene and meta dichlorobenzene have almost same m.pt and b.pt but the m.pt of para dichlorobenzene is quite higher than 'o' and 'm' isomers because it is symmetrical and so has more closer packing



Increasing order of melting pt.

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Nucleophilic Substitution Reaction

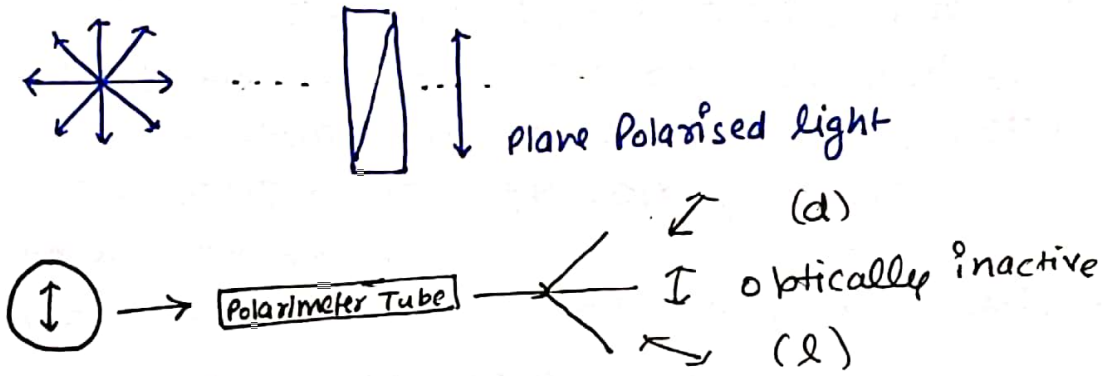
C-X bond in haloalkanes is polar and halide ion can be replaced by a stronger nucleophile

$$Nu + \overset{\delta+}{C} - \overset{\delta-}{X} \longrightarrow C-Nu +$$

- SN^1 (Substitution Nucleophilic Unimolecular)
- SN^2 (Substitution Nucleophilic Bimolecular)

⇒ **Plane Polarized Light**

when a normal light from a light source (also called diffused light) is passed through nicol prism, then the light is changed into PPL (plane polarised light)



Optically active substance

when this plane polarized light is passed through a solution of an organic compound, then the light may rotate either clockwise or anti clockwise

Such substance are called optically active substance

dectro rotatory ↗

If plane polarized light is rotated clockwise. It is called dextro rotatory or d or (+)

laevorotatory ↖

If plane polarised light is rotated anti-clockwise. It is called laevo-rotatory or l or (−)

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⇒ **Stereocentre**

If all the substituent attached to a carbon are different, then such a carbon is called asymmetric carbon or stereocentre or chiral carbon

- The asymmetry of the molecule is responsible for the optical activity in such organic compounds. The asymmetry is also called disymmetry

⇒ **Chirality**

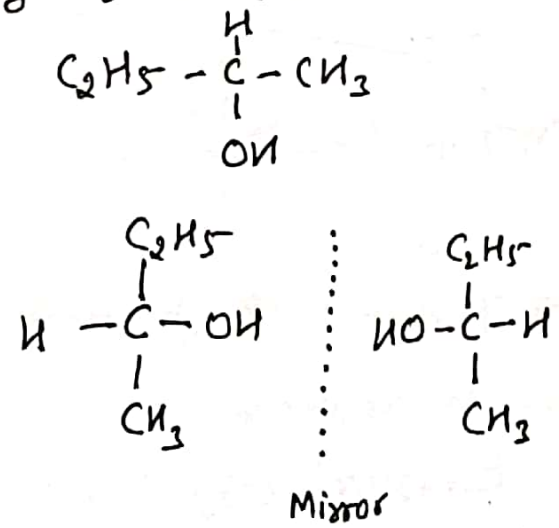
The carbon which is bonded to four different atoms or group of atoms is called chiral carbon. Such carbon do not have a plane of symmetry. This property of compound is called chirality or dissymmetry

⇒ **Enantiomers**

The non superimposable mirror images of an organic compound are optically active. And one of them will be dextro rotatory and other will be laevo rotatory. So, such pair of d and l isomers are called enantiomers.

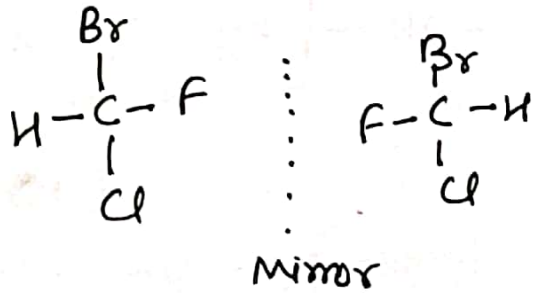
- Essential condition for enantiomerism is disymmetry.

e.g Butan-2-ol has chiral carbon



a pair of enantiomers

e.g Bromo chloro fluoromethane



a pair of enantiomers.

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Racemic Mixture

equimolar mixture of d and l substance so that net rotation is zero is called racemic mixture. The process of making a racemic mixture is called racemization. These are represented as prefixes dl or ±

Resolution

The separation of dextro rotatory (d) and laevo rotatory (l) isomers from racemic mixture by suitable method is called resolution

S_N2 Mechanism

Bimolecular Nucleophilic Substitution Rxn

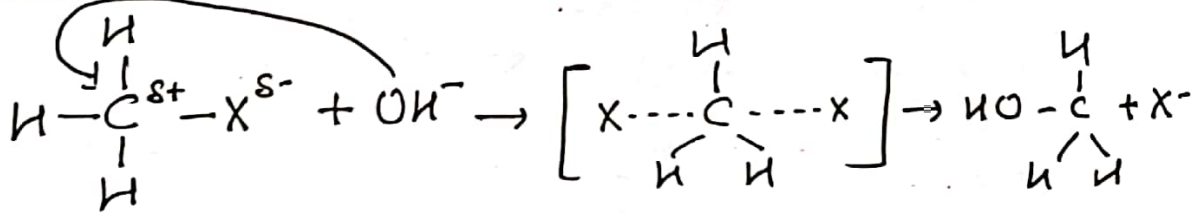
Order = 2 , molecularity = 2

because the rate of reaction depends upon the conc. of both reactants i.e alkyl halide and Nucleophile

ex. Substitution by hydroxy group.

$$R-X + \underbrace{OH^-}_{\text{Nucleophile}} \longrightarrow R-OH + \underset{\text{leaving Group.}}{X^-}$$

Mechanism



Rate of Rxn = $K[CH_3X][OH^-]$

- In this mechanism, the configuration of alkyl halide gets inverted. This is called inversion of configuration or Walden inversion.

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S_N1 Mechanism

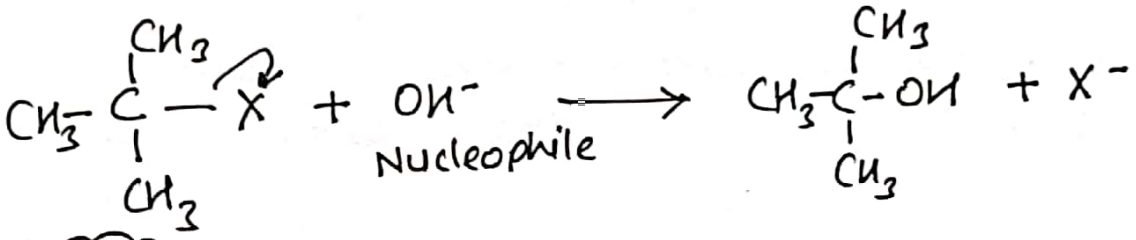
Unimolecular Nucleophilic Substitution Rxn.

The rate of reaction depends only on the conc. of 1 reactant i.e alkyl halide

e.g order of reaction = 1

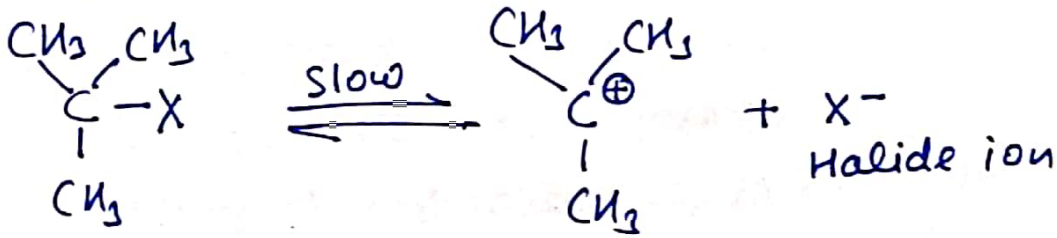
molecularity of reaction = 1

This reaction takes place in two steps.

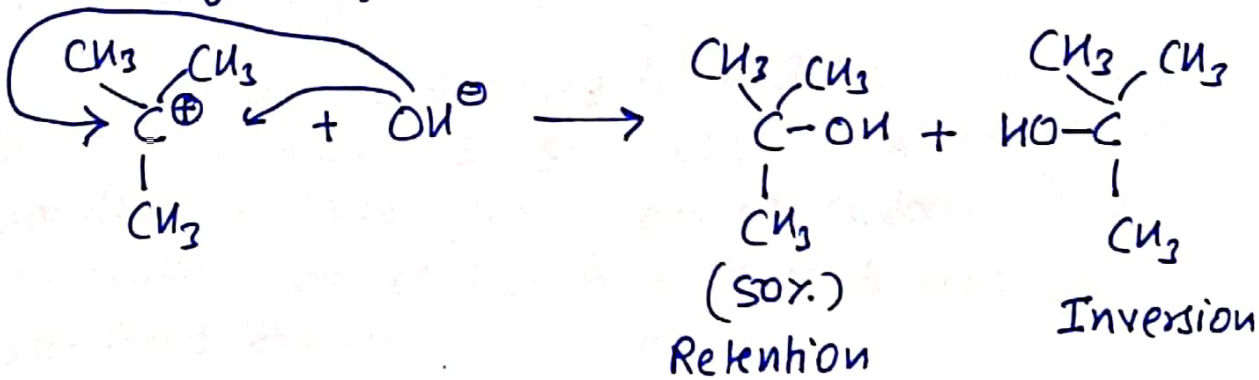


Mechanism

Step-I Formation of intermediate carbocation



Step-II Attack of nucleophile on C⁺ may occur either from front side or from backside



Rate of Rxn = $K[(CH_3)_3X]$

Order = 1

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Order of reactivity of Alkyl Halide

S_N2

$CH_3X > 1^\circ > 2^\circ > 3^\circ$

$$CH_3X > CH_3CH_2X > CH_3-\overset{CH_3}{\overset{|}{CH}}-X > CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-X$$

$\longrightarrow$ Reactivity decreases for S_N2

As steric hindrance increases and rate of S_N2 reaction decreases. It becomes more difficult for a nucleophile to approach C-X carbon due to steric hindrance

In S_N1

The order of reactivity is

$3^\circ > 2^\circ > 1^\circ > CH_3X$

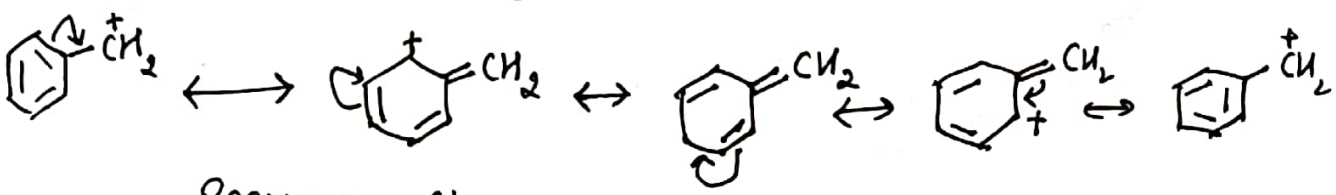
In this, an intermediate C^+ is formed

More is the stability of carbocation is, faster is the substitution reaction. As tertiary carbocation is more stable, So nucleophilic substitution is faster in 3° alkyl halide.

⇒ The allylic and benzylic halides show high reactivity towards S_N1 reaction. Although the substitution takes place from 1° carbon. The carbocation. The carbocation thus formed gets stabilized through resonance

$$CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$$

Resonance str. of allylic carbocation



Resonance str. of Benzylic carbocation

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⟹ For a given alkyl group the reactivity of the halides, R-X follows the same order in both mechanism.

i.e

R-I > R-Br > R-Cl > R-F

Spectrochemical Aspects

S_N2 reaction proceeds with spectrochemical inversion

S_N1 reaction proceeds with racemization.

Unimolecular (S_N1)	Bimolecular (S_N2)
1.) It is first order Rxn	1.) It is second order Rxn
2.) Generally carried out in polar protic solvents like water, alcohol & acetic acid	2.) Carried out in polar aprotic solvents like acetone, acetone or DMF ~~or~~ DMSO.
3.) Takes place in two steps through carbocation as the intermediate	3.) Takes place in one step through transition state.
4.) Rate of Reaction $3° > 2° > 1° > CH_3X$ Greater the stability of carbocation, faster will be the reaction.	4.) Rate of Reaction $CH_3X > 1° > 2° > 3°$ Less the steric hindrance in transition state, faster will be the reaction.
5.) Tends to proceed with weak nucleophiles e.g CH_3OH, H_2O, CH_3CH_2OH etc.	5.) Tends to proceed with strong nucleophiles e.g CH_3O^-, CN^-, OH^-
6.) Both retention and inversion of configuration takes place	6.) Inversion of configuration takes place (Walden Inversion)

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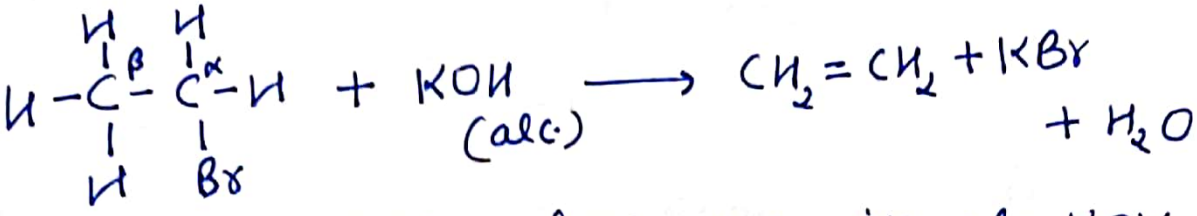
Eliminate

Elimination Reaction

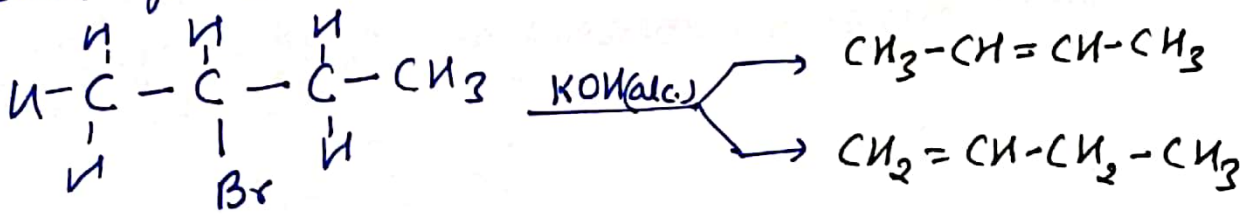


when an alkyl halide is treated with alc. KOH, then hydrogen of β-carbon is eliminated alongwith halogen. A saturated compound is changed into unsaturated compound and alkenes are formed

Saytzeff Rule

If there is the possibility of β-hydrogen from two carbons, then that alkene is preferred which is more alkylated

It means the major product of alkenes formed is that which has greater number of alkyl group attached to doubly bonded C-atoms.



The stability order of alkenes is

$CH_2=CH_2 < CH_3-CH=CH_2 < CH_3-CH=CH-CH_3 < CH_3-C(CH_3)=CH-CH_3 < CH_3-C(CH_3)-C(CH_3)-CH_3$

More the alkylated alkene is more is the stability

Reaction with Metals:

(a) Wurtz Reaction — Alkanes with even number of carbons are formed.

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$$R-X + 2Na + X-R \xrightarrow[\text{ether}]{\text{Dry}} R-R + 2NaX$$

$$C_2H_5-Br + 2Na + Br-C_2H_5 \xrightarrow[\text{ether}]{\text{Dry}} C_4H_{10} + 2NaBr$$

Action with magnesium Metal

Formation of Grignard Reagent

$$R-X + Mg \xrightarrow[\text{ether}]{\text{Dry}} R.MgX \quad (X = Cl, Br, I)$$

(Grignard Reagent)

$$CH_3CH_2Br + Mg \xrightarrow[\text{ether}]{\text{Dry}} CH_3CH_2MgBr$$

ethyl magnesium bromide

Nature of Grignard Reagent

Although carbon-magnesium bond is covalent but it is highly polar because carbon is more electronegative than magnesium whereas magnesium - halogen bond is mainly ionic

$$\overset{\delta-}{R}-\overset{\delta+}{Mg}-\overset{\delta-}{X}$$

Reduction

$$CH_3CH_2Br \xrightarrow{\text{Reducing Agent}} CH_3CH_3 + HBr$$

(i) Zn-Cu, 95% C_2H_5OH
(ii) Zn/HCl
(iii) Sn/HCl
(iv) $LiAlH_4$
(v) $NaBH_4$
(vi) HI in RedP
(vii) H_2 in Ni/Pt/Pd

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Rearrangement

On heating alkyl halides with anhydrous aluminium chloride, isomeric haloalkane is formed.

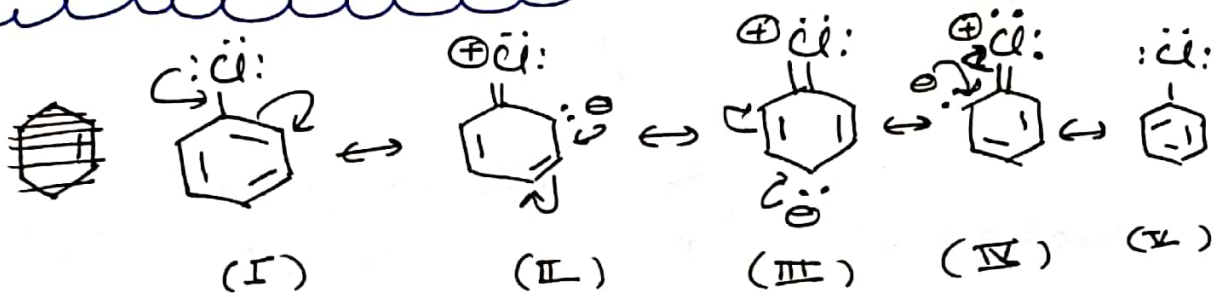
$$CH_3CH_2CH_2Cl \xrightarrow{AlCl_3,\ 573K} CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$$

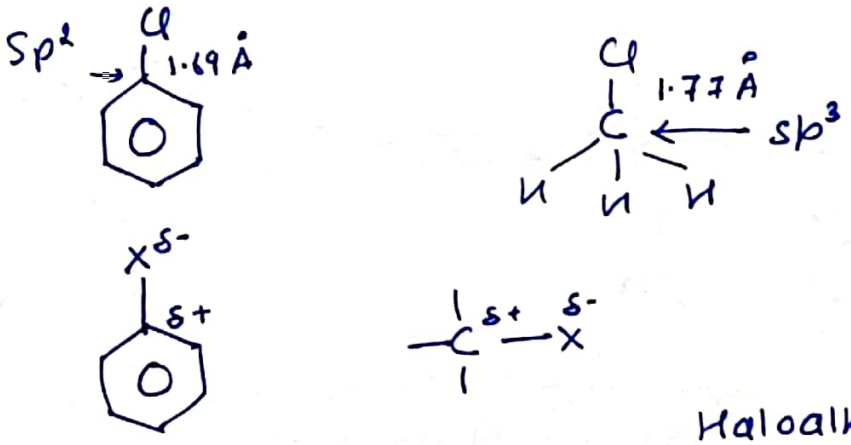
Chemical Properties of Haloarenes

Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reaction due to resonance, C-Cl bond acquires partial double bond character and C-Cl carbon is sp^2 hybridized.

Haloarenes are less reactive than haloalkanes

Resonance in Haloarenes





Haloarene

(C-X bond is less polar and hence X can't be easily displaced by Nucleophile)

Haloalkane

(C-X bond is more polar than in aryl halides and hence X can be easily displaced by nucleophile)

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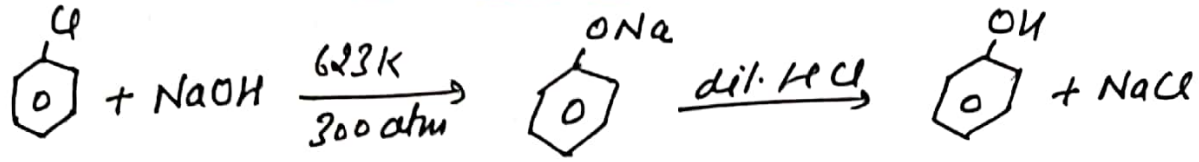
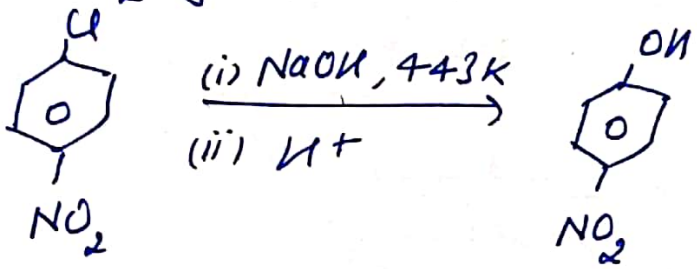
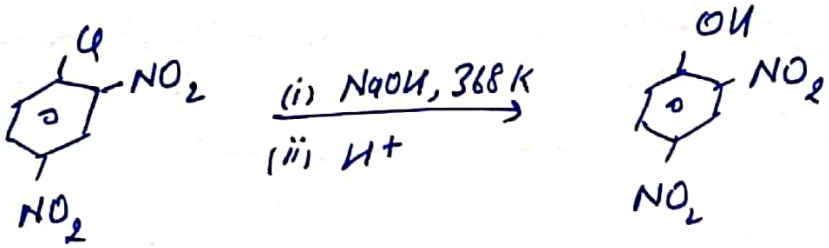
(I) Nucleophilic Substitution Reaction

(a) Replacement by Hydroxy group or DOWS PROCESS

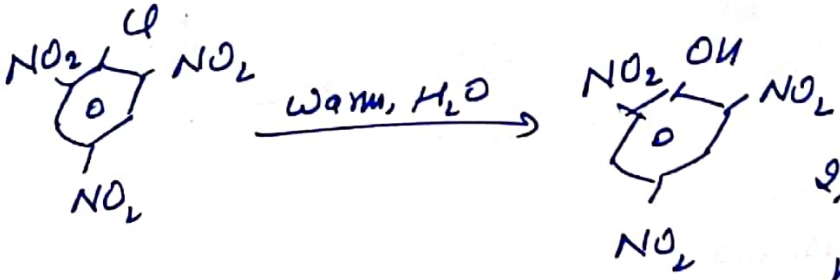


Note → The presence of e⊖ withdrawing group like ($-NO_2$) at ortho and para-positions increases the reactivity of haloarenes. Larger the number of $-NO_2$ groups is faster is the reaction



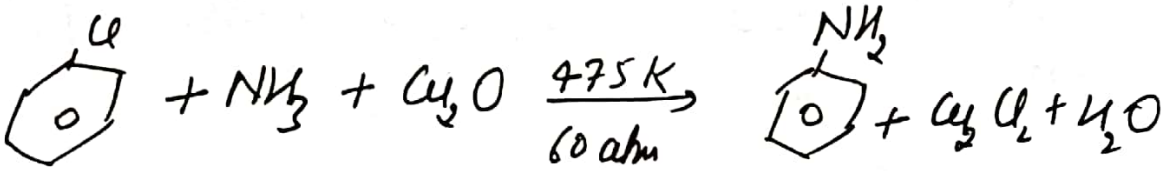


2,4-Dinitrophenol



2,4,6-Trinitrophenol or picric acid

(b) Substitution by Amino Group



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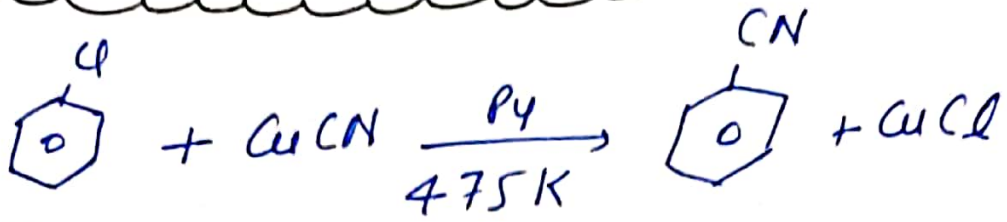
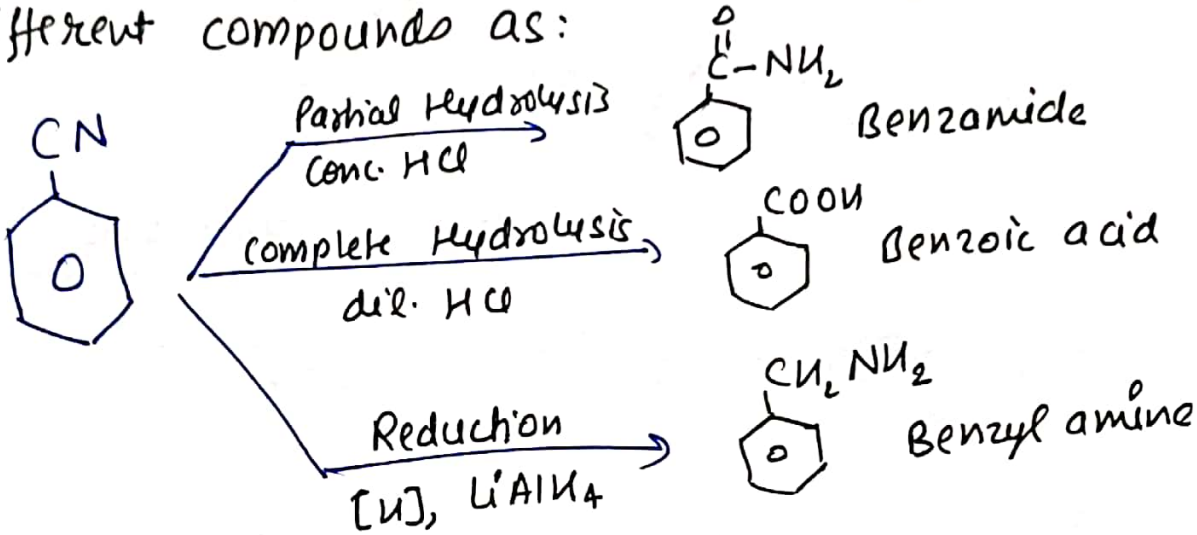
Substitution By Cyano Group



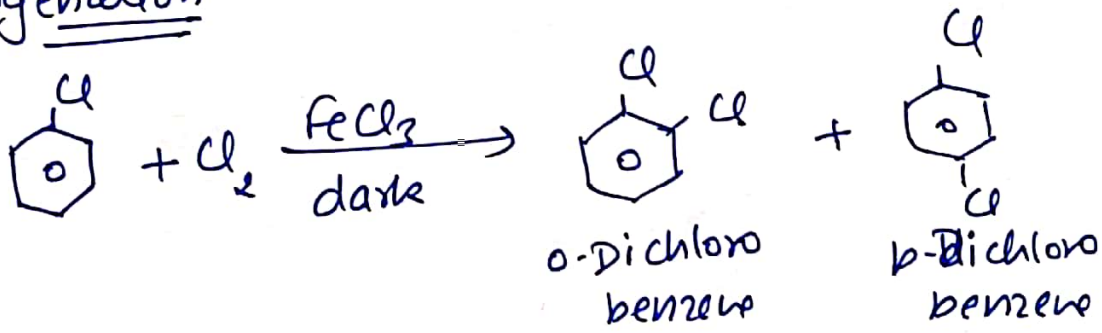
Imp Note

Benzonitrile further can be changed into different compounds as:

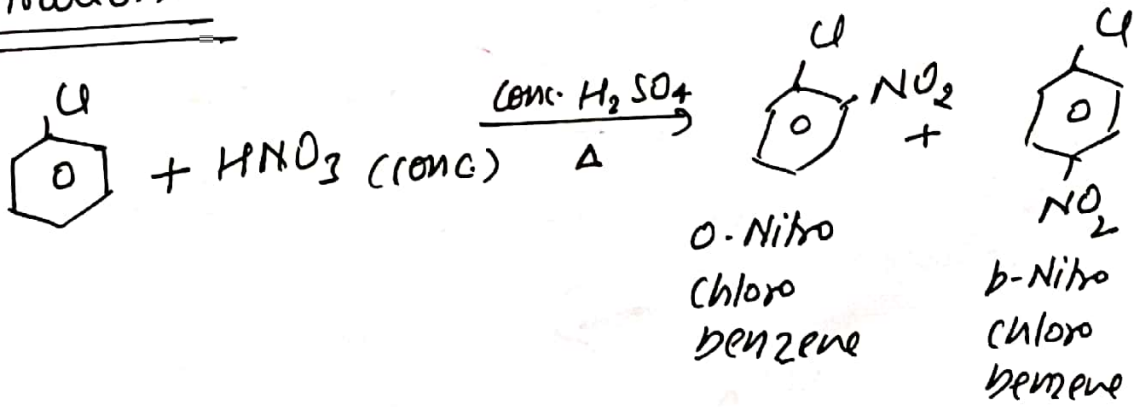


Electrophilic Substitution Reaction

- **Halogenation**



- **Nitration**



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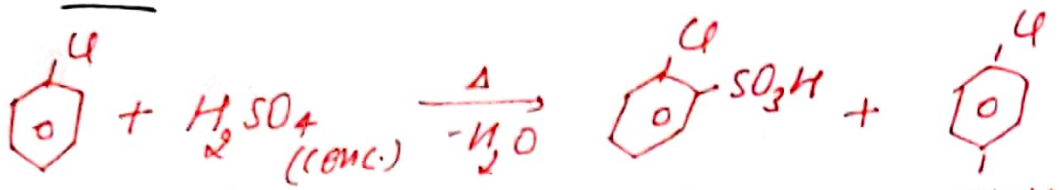
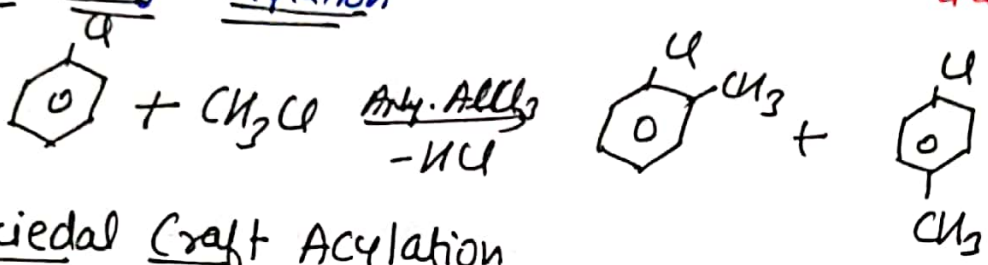
Sulphonation



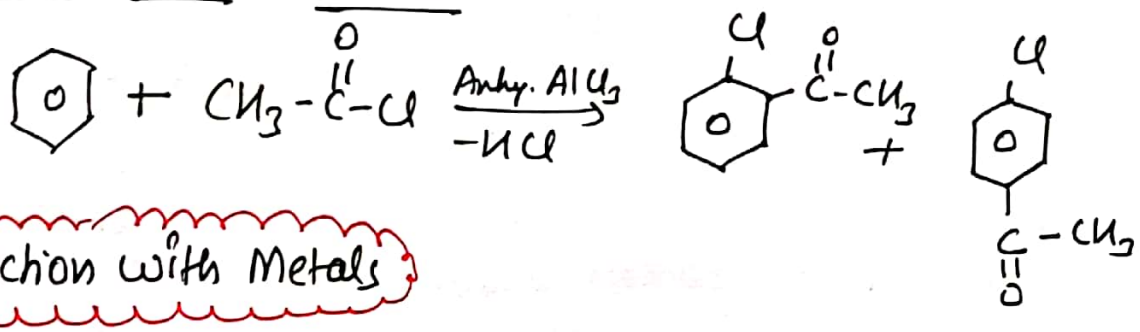
o-chloro benzene sulphonic Acid

p-chloro benzene sulphonic acid.

⇒ **Friedal Craft Alkylation**

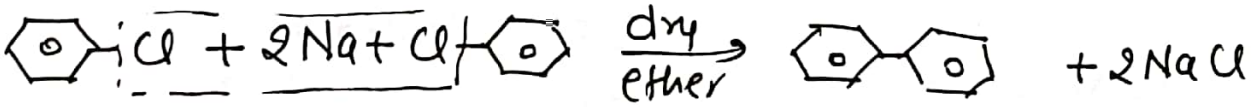


⇒ **Friedal Craft Acylation**

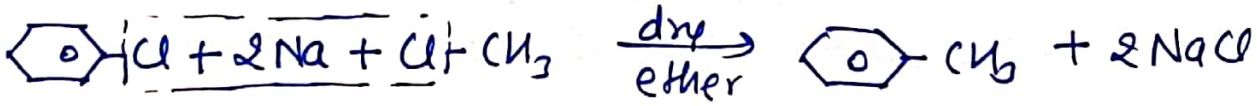


(III) Reaction with Metals

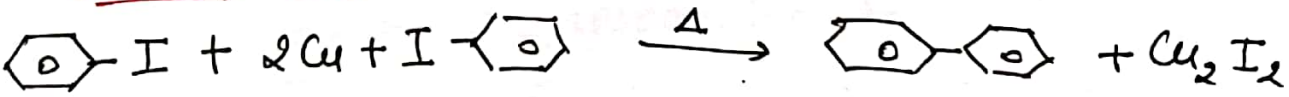
(a) **Fitting Reaction**



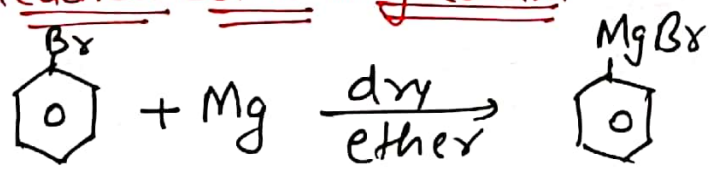
(b) **Wurtz - Fitting Rxn**



(c) **Ullmann's Rxn**



(d) **Reaction with Magnesium**



phenyl magnesium bromide

Phenyl magnesium chloride

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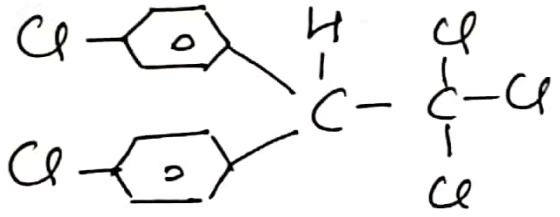
Polyhalogen Compounds

⇒ **DDT** (p,p' - Dichloro diphenyl ethane)

It is the first chlorinated organic insecticide. It is very effective against the mosquitos that spread malaria. It is very toxic for fishes. It is not metabolised ~~by~~ in animals, instead it is stored in fatty tissues

Str. of DDT



⇒ **Freons**

The chlorofluoro carbon compounds of methane and ethane are collectively known as freons. They are very stable, unreactive, non-toxic, non-corrosive and easily liquefiable gass.

Freon 12 (CCl_2F_2) is the most widely used freons

Uses – These are used for aerosol propellants in refrigeration and in air conditioning.

Harms: The freons are responsible to initiate free radical chain reaction in stratosphere where they deplete the ozone layer and causes holes in ozone layer.

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