Flow Chart

Haloalkanes and Haloarenes

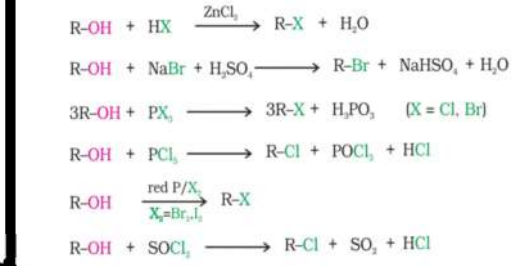
Methods of preparation
- From Alcohols
- From Hydrocarbons
- Halogen Exchange

Physical Properties
- B.P.
- M.P.
- Solubility

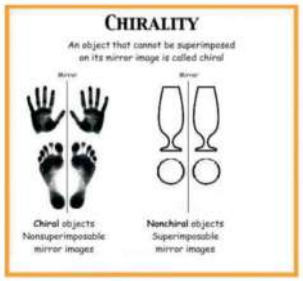
Classification

Nomenclature

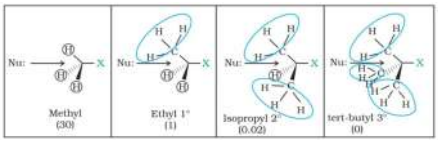
Nature of C–X bond

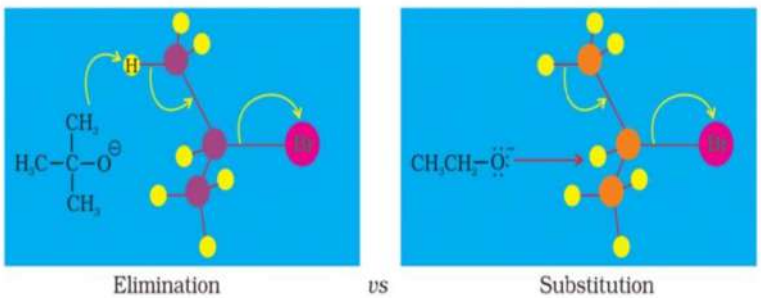


Reaction of Haloarenes
- Nucleophilic Substitution
- Electrophilic Substitution
- Reaction with metals



Reactions of Haloalkane
- Nucleophilic Substitution
  - S_N1 and S_N2
- Elimination Reaction
- Reaction with metals



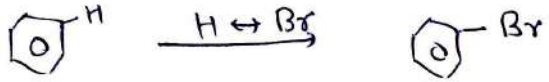


Haloalkanes and Haloarenes

→ Aliphatic hydrocarbon $\xrightarrow{H \leftrightarrow X}$ Alkyl halide [haloalkane]

Aromatic hydrocarbon $\xrightarrow{\text{Replacement of hydrogen by halogen atom}}$ Arylhalide [haloarene]

Example –: $CH_4 \xrightarrow{H \leftrightarrow Cl} CH_3Cl$ Methyl Chloride



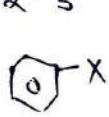
Classification on basis of number of halogen atoms

→ If one halogen atom is present in structure of alkanes / arenes : Monohalo alkane / Monohalo arenes

→ If two halogen atoms are present : Dihaloalkane / Dihaloarene

→ Similarly, If three halogen atoms are present : Trihaloalkane / Trihaloarene

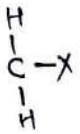
Example –: C_2H_5X : Monohaloalkane (X → Halogen)

 : Monohaloarene  : Dihaloarene

Monohalo compounds

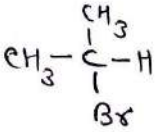
- Compounds containing sp^3 C–X bond
- Compounds containing sp^2 C–X bond

① **Alkyl halides** : (R–X)

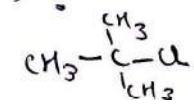
→ Primary Alkyl halide : 

Example –: CH_3-CH_2-Br

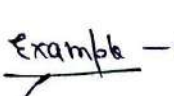
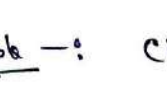
→ Secondary (2°) :

Example –: 

→ Tertiary (3°) :

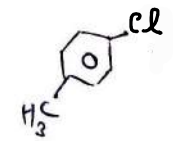
Example –: 

① **Vinylic Halide** :– X is bonded to carbon – carbon double bond.

Example –:  , 

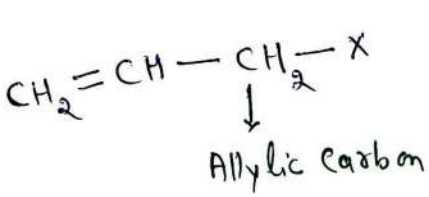
 , $CH_3-CH=CBr-CH_3$

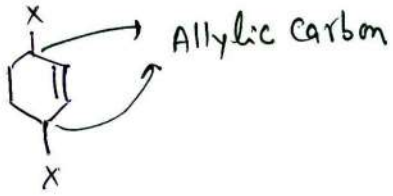
② **Aryl halide** –: X (halogen atom) is bonded to the carbon of aromatic ring (benzene)

Example –:  ,  etc.

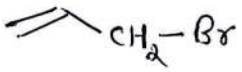
(2) **Allylic Halides** : X is bonded to sp^3 hybridised carbon atom next to carbon - carbon double bond.

Example -:



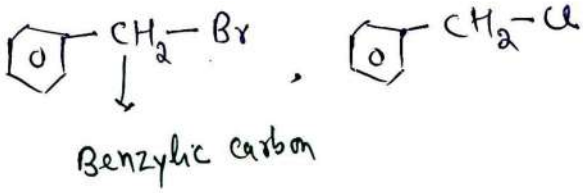


Allyl bromide -:



(3) **Benzylic halide** -: Compounds in which the halogen atom is bonded to an sp^3 hybridised carbon atom next to benzene ring.

Example :



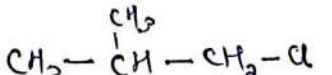
Nomenclature

→ As we know about selection of main chain and numbering of hydrocarbon, same rule is here also (considering halogen atoms (F, Cl, Br, I) as substituents.

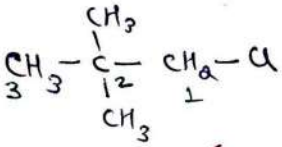
→ Rule : No. of carbon > Max. no. of substituent > Lowest set of locants > Alphabetic order

→ Example -:

IUPAC → 1 - Bromopropane



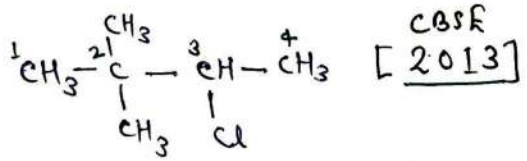
1 - Chloro - 2 - methyl propane



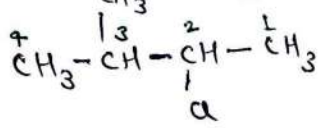
1 - Chloro - 2,2 - dimethyl propane

[Delhi 2013]

CBSE [2013]

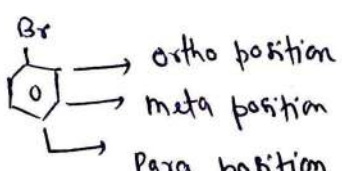


3 - chloro - 2,2 - methylbutane

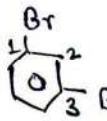


2 - Chloro - 3 - methyl butane

→

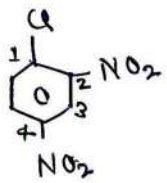


Bromobenzene



Common name : m - Dibromo benzene

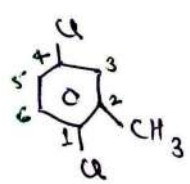
IUPAC : 1,3 - Dibromo benzene



Delhi 2017

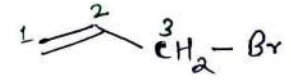
2,4 - Dinitro chloro benzene

→

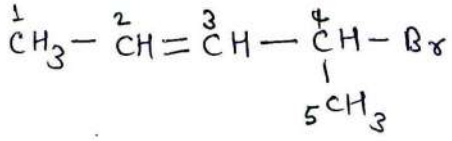


⇒ 1,4 - Dichloro - 2 - methyl benzene

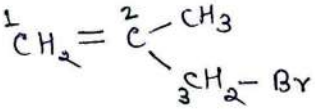
[CBSE 2013]

→  [CBSE 2011] (1M)

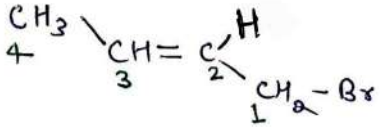
3-Bromopropene

 [CBSE 2010] (1M)

4-Bromopent-2-ene

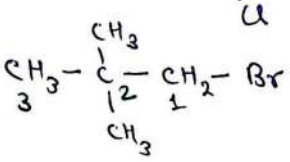
 [2010] (1M)

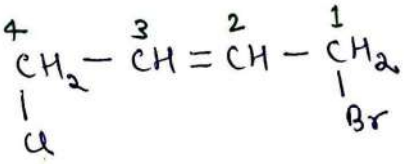
3-Bromo-2-methylpropene

 : 1-Bromobut-2-ene

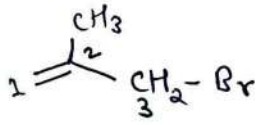
→ Draw the structure of following compounds?

a.] sec-Butyl chloride (2-Chlorobutane : IUPAC)

b.] Neo-Pentyl bromide  (1-Bromo-2,2-dimethylpropane : IUPAC)

c.] 1-Bromo-4-chloro.but-2-ene : 

[Delhi 2017] (1M)

d.] 3-Bromo-2-methylprop-1-ene : 

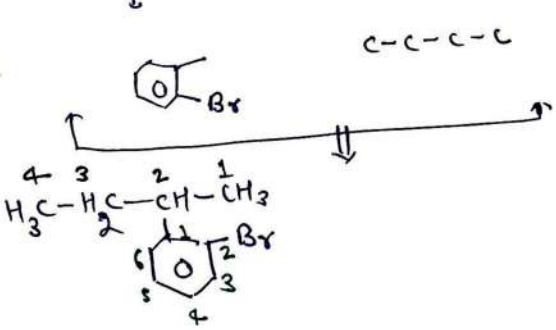
[Delhi 2017] (1M)

NOTE : **Benzene as substituent : Phenyl**

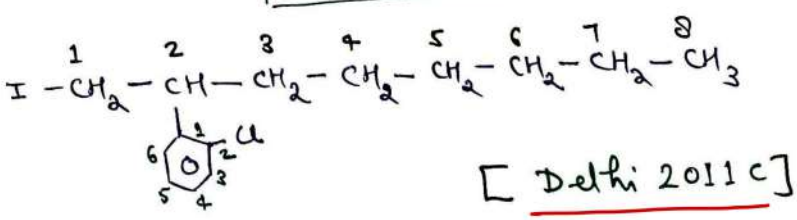
Example -: Chloromethyl benzene [X]

Chlorophenylmethane [✓] is correct name of  .

→ 2-(2-bromophenyl) butane [Delhi 2011c] (1M)

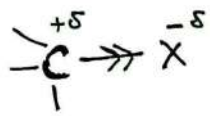


2-(2-chlorophenyl)-1-iodooctane



[Delhi 2011c]

Nature of C–X bond

→ Due to electronegative nature of halogens, C–X bond is polar. 

→ Size of halogen : I > Br > Cl > F

→ Carbon-halogen bond length : C–I > C–Br > C–Cl > C–F

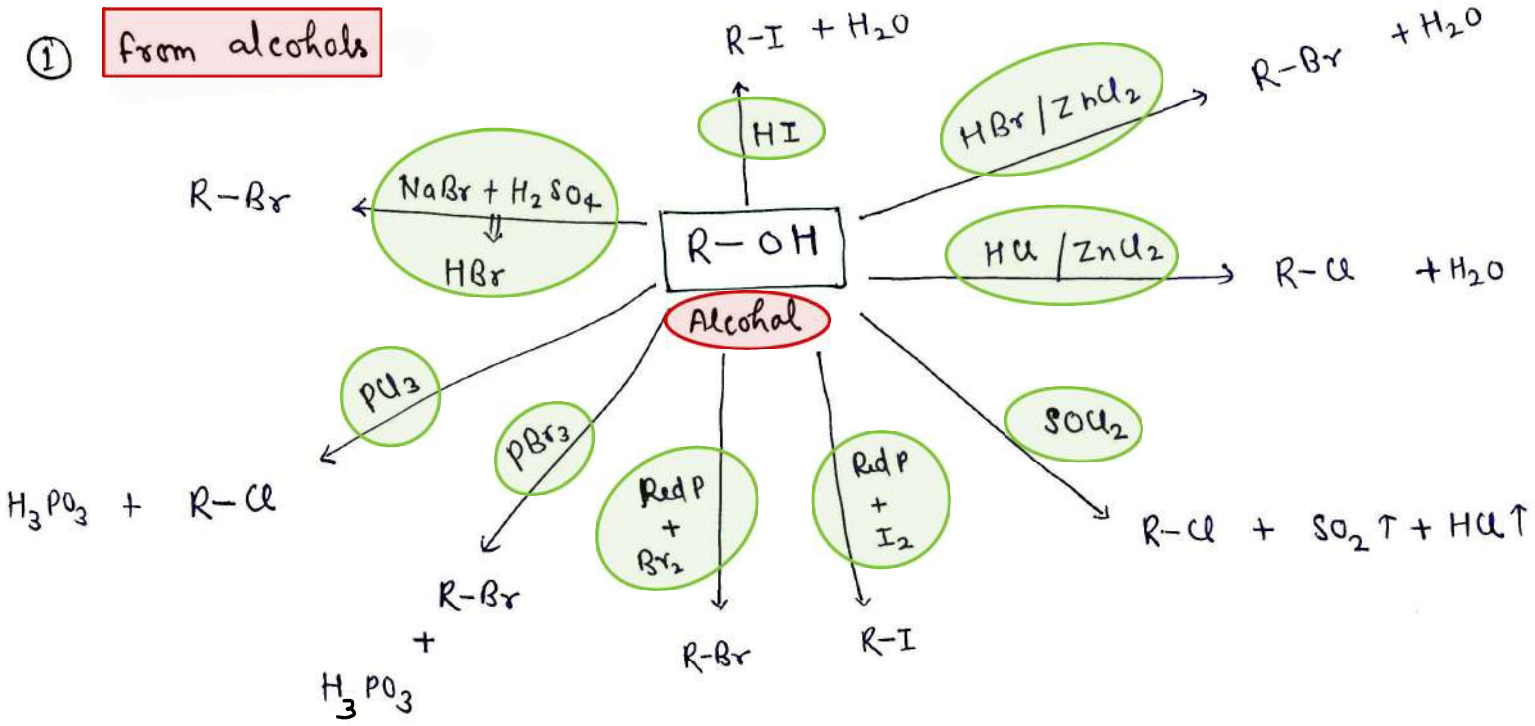
→ **Bond Length of C–X ∝ 1/C–X bond enthalpies**

→ **Bond Enthalpy** : C–F > C–Cl > C–Br > C–I

→ **Order of dipole moment** : $CH_3-Cl > CH_3-F > CH_3-Br > CH_3-I$

Methods of preparation

① From alcohols



→  [All India 2014] 1M

→ Above method is not applicable for the preparation of aryl halides because the carbon – oxygen bond in phenol has partial double bond character.

Breaking of this bond is tough.

2.] From Hydrocarbon

a → Free Radical Halogenation : $CH_4 \xrightarrow[h\nu]{Cl_2\ (1\ equivalent)} CH_3-Cl + HCl$

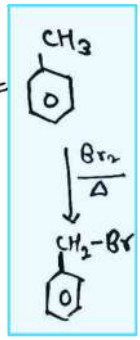
$CH_3-CH_3 \xrightarrow[h\nu]{Cl_2\ (1\ equivalent)} CH_3-CH_2-Cl$

$CH_3-CH_2-CH_3 \xrightarrow[UV\ light]{Cl_2}$ only monochloro structural isomers.

→ $CH_3-CH_2-CH_2-Cl$

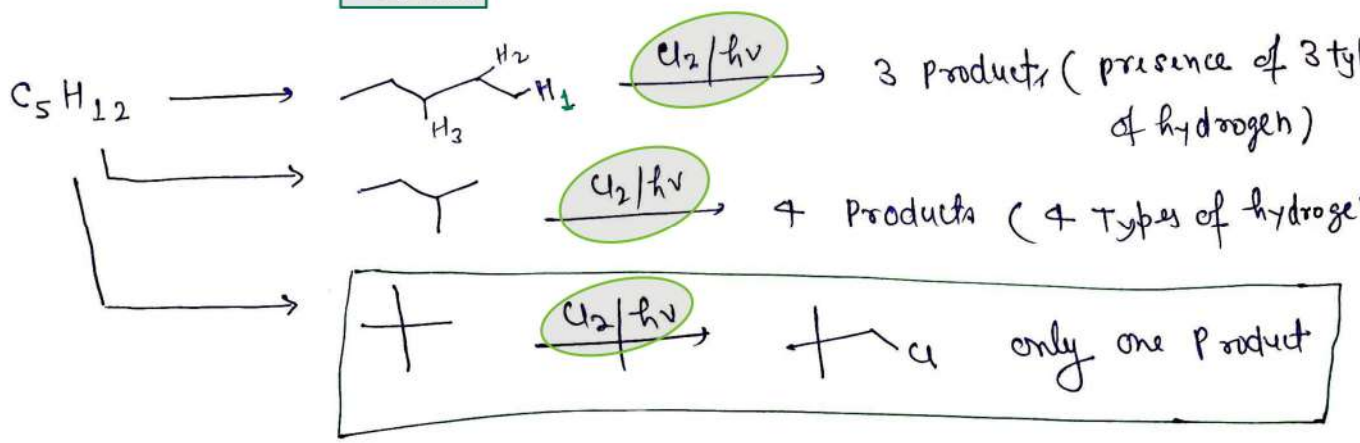
→ $CH_3-\underset{Cl}{CH}-CH_3$

Mono, di, tri, Poly halo alkanes ← $Cl_2/h\nu$

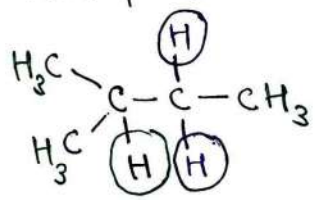


A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon. [Delhi 2013C] (2M)

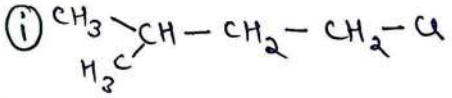
Isomers

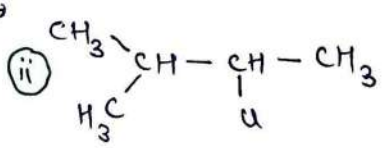


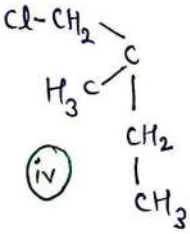
→ Find possible monochloro structural isomers of $(CH_3)_2CH-CH_2-CH_3$.

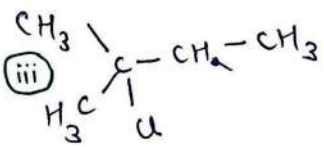


⇒ There are 4 different hydrogens are present. So, by replacing these hydrogen by Chlorine atom we get product

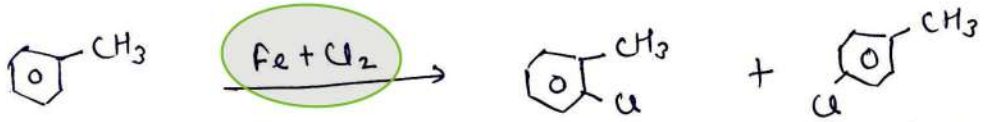


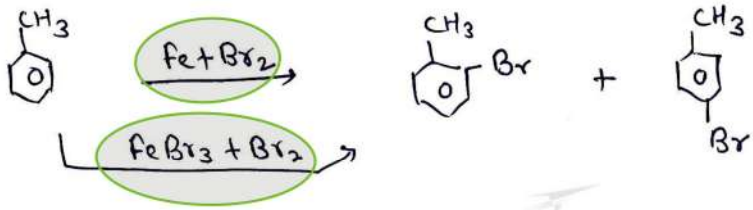




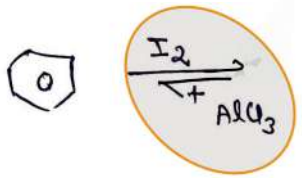


b.] By Electrophilic Substitution :-

→ 

→ 

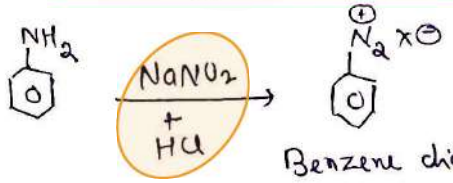
→ Reactions with I_2 are reversible in nature.



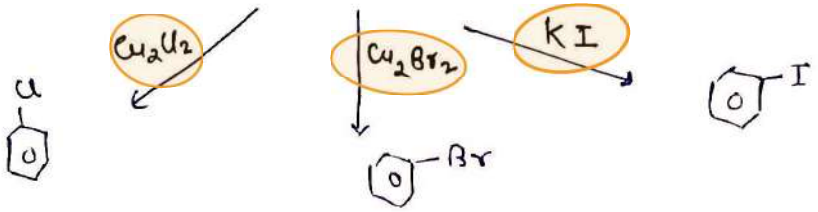
This reaction requires present of oxidising agent to oxidise HI formed during iodonation.

→ Due to high reactivity of flourine (there is probability of explosion) fluoro compounds are not prepared by this method.

c.] **Sandmeyer's Reaction** —: Primary aromatic amine $\xrightarrow[+\ NaNO_2]{HCl}$ Diazonium salt

→ 

Benzene diazonium halide



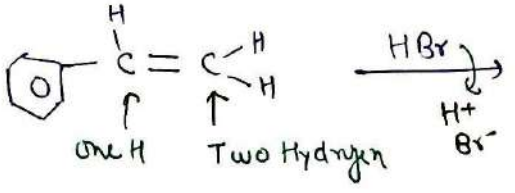
d.] **From alkenes** —:

(i) Addition of hydrogen halide (HCl, HBr, HI, HF)

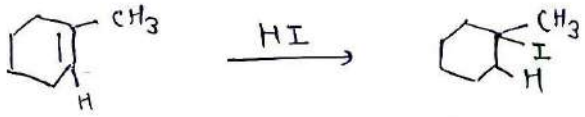
→ $CH_2=CH_2 \xrightarrow{HCl} CH_2(H)-CH_2(Cl)$

→ $CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-CH(Br)-CH_2(H) + CH_3-CH(H)-CH_2(Br)$

Add to that carbon which has more no. of hydrogen. ← Major product: Markovnikov's; Minor product: Anti-Markovnikov's

→ 

(Major)

→ 

But in presence of peroxide only addition of HBr ⇒ Anti markovnikov's fashion

(ii) Addition of halogens (Cl_2, Br_2) —:

$CH_2=CH_2 \xrightarrow[CCl_4]{Br_2} CH_2(Br)-CH_2(Br)$

Halogen Exchange

Finkelstein Reaction

$CH_3-CH_2-Cl \xrightarrow[Acetone]{NaI} CH_3-CH_2-I + NaCl\downarrow$

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

In Acetone : NaI is soluble but not NaCl / NaBr.

Swarts Reaction

$CH_3-Br \xrightarrow{\text{Metallic fluoride}} CH_3-F$

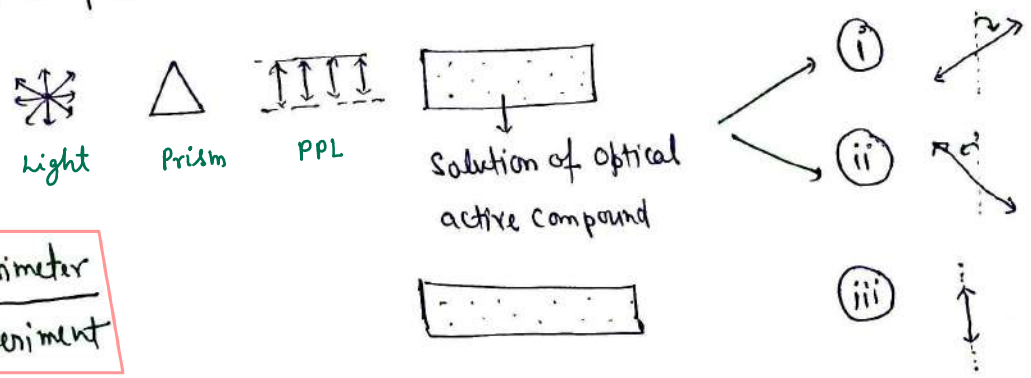
$AgF / Hg_2F_2 / SbF_3$

$+\ AgBr\downarrow$

In water AgF is soluble but not AgCl, AgBr.

Optical active compound —:

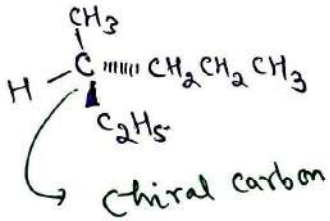
"The compound which can rotate the plane polarised light"

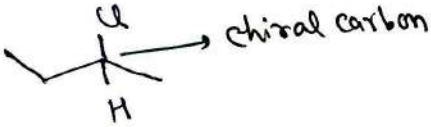


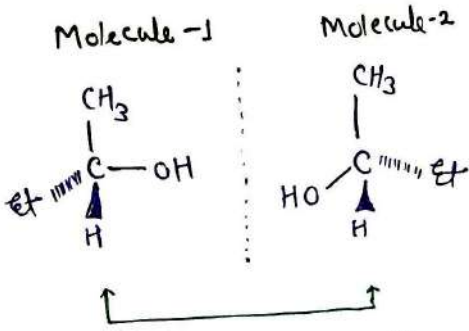
Polarimeter / Experiment

→ dextro-rotatory compound and laevo-rotatory compounds are optical isomers. This phenomenon is known as **optical isomerism**.

→ **Asymmetric Carbon** [chiral carbon] —: sp^3 hybridised carbon attached with 4 different substituents is known as chiral carbon.

→ 





Non-Superimposable mirror images.

⇓

Chiral molecule

⇓

Optical active Compound.

→ **Chiral** —: The objects which are non-superimposable on their mirror image are said to be chiral.

"molecule having a chiral carbon is always optical active."

→ **Enantiomers** :— Stereoisomers with non-superimposable mirror image character.

→ **Diastereomer** —: Stereoisomers which are not mirror image of each other.

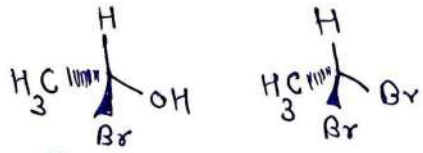
→ In above example molecule-1 & molecule-2 are enantiomer of eachother as they are non-superimposable mirror images.

→ **Racemic mix** —: A mixture containing two enantiomers in equal proportions is known as racemic mixture.

→ It is represented by dl or (±).

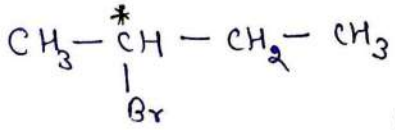
→ The process of forming racemic mixture is known as **racemisation**.

Question :— Identify chiral and achiral molecule —:

a.] 

Chiral

Achiral

b.] 

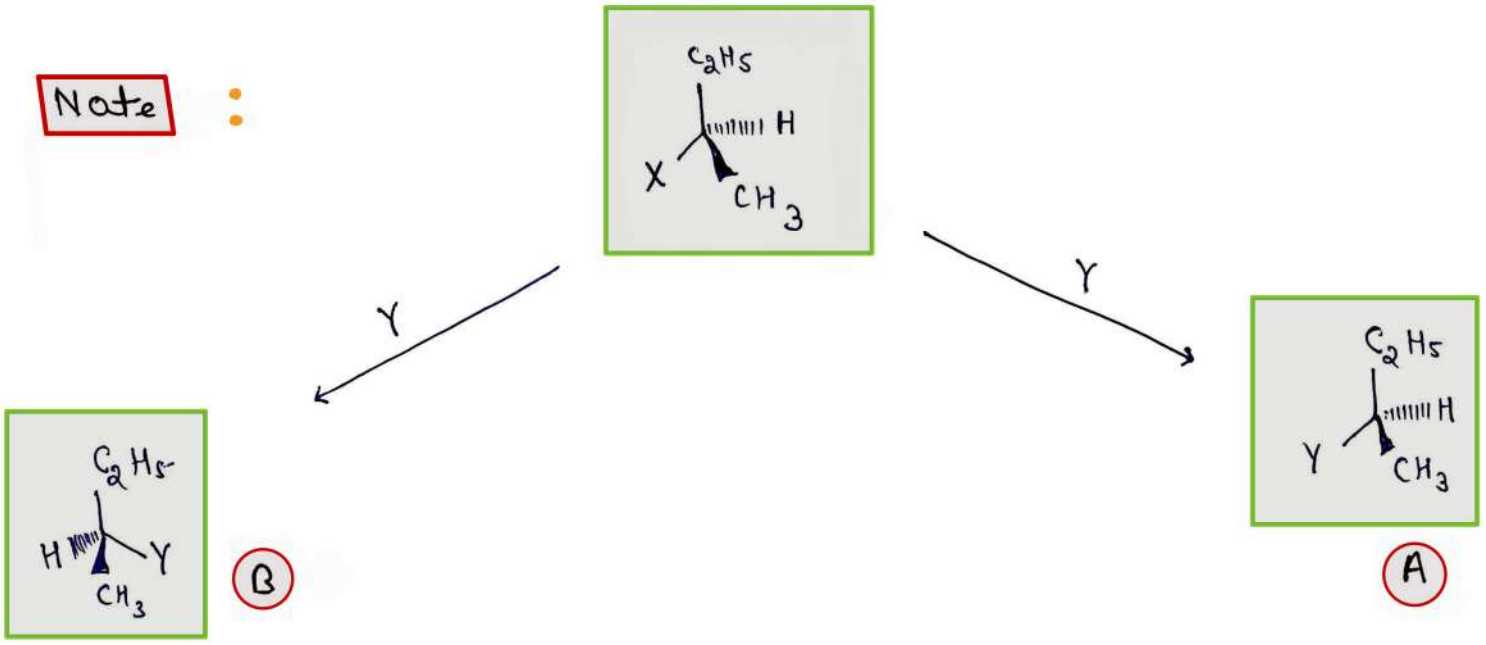
one chiral carbon ⇓ Optical Active

Chiral

$CH_3-CH_2-CH_2-CH_2-Br$

↳ Achiral

Note :



→ **Retention** :— If A is the only product in reaction. Then this process is called retention.

→ **Inversion** :— If B is the only product in reaction, then this process is called inversion.

→ **Racemisation** —: If A and B both are 50%. then this process is called racemisation. And mixture of A+B : Racemic mixture.

→ Mixture of A and B with 50-50%. Concentration is optically inactive As one isomer will rotate light in the direction opposite to another.

Physical Properties

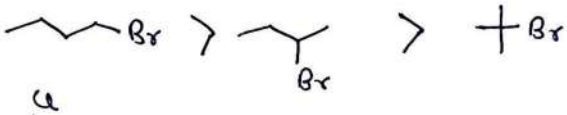
B.P. & M.P.

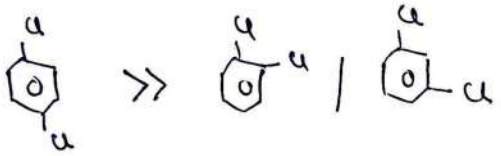
→ Molecules of organic halogen compounds are generally polar, due to greater polarity as well as higher molecular mass as compared to parent hydrocarbon, the dipole - dipole and vander Waals force of attraction are stronger in halogen derivatives.

So. B.P. : Halogen Derivative compound > Parent hydrocarbon.

→ For a given halogen atom —: B.P. : 

→ For a given alkyl group —: B.P. : R-I > R-Br > R-Cl > R-F

→ B.P. $\alpha \frac{1}{\text{Branching}}$ —: B.P. : 

→ Melting point :  : Due to symmetry of para isomer that fits in crystal lattice better as ortho/meta

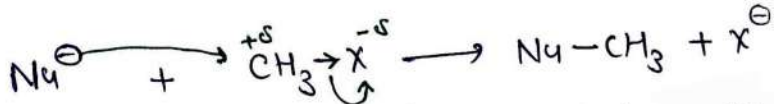
[CBSE 2019] 1M

Solubility :— The solubility of haloalkanes in water is low. Because force of attraction between haloalkanes is greater than haloalkanes - water interaction.

Chemical Reactions of Haloalkanes

- Nucleophilic substitution Reaction
- Elimination Reaction
- Reaction with metals

Nucleophilic substitution Reaction —:



Nucleophile — Alkyl halide — Product — Leaving group

In this reaction, substitution reaction is initiated by a nucleophile so, it is called NSR.

Nucleophile → Nucleus loving species (+ve charge loving)

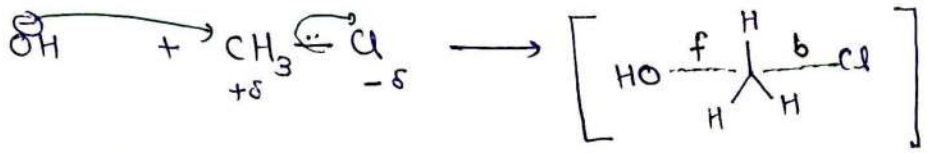
→ Two different mechanisms can explain above reaction → S_N2 / S_N1

i Bimolecular Nucleophilic Substitution —: S_N2

(Bimolecular → 2, Nucleophilic → N, Substitution → S)

Consider a reaction : $HO^{\ominus} + H_3C-Cl \longrightarrow HO-CH_3 + Cl^{\ominus}$

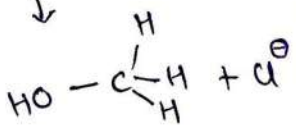
Mechanism –:



→ It follows second order kinetics.

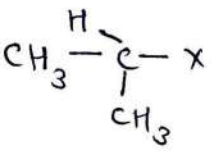
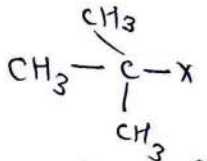
Rate = $K[OH^{\ominus}][CH_3-Cl]$

Rate $\propto$ [Nu$^{\ominus}$] [Substrate]



→ It is a single step (Concerted) reaction.

→ Order of reactivity : Primary halide > secondary halide ≫ Tertiary halide

: $CH_3-X > CH_3-CH_2-X >$  ≫ 

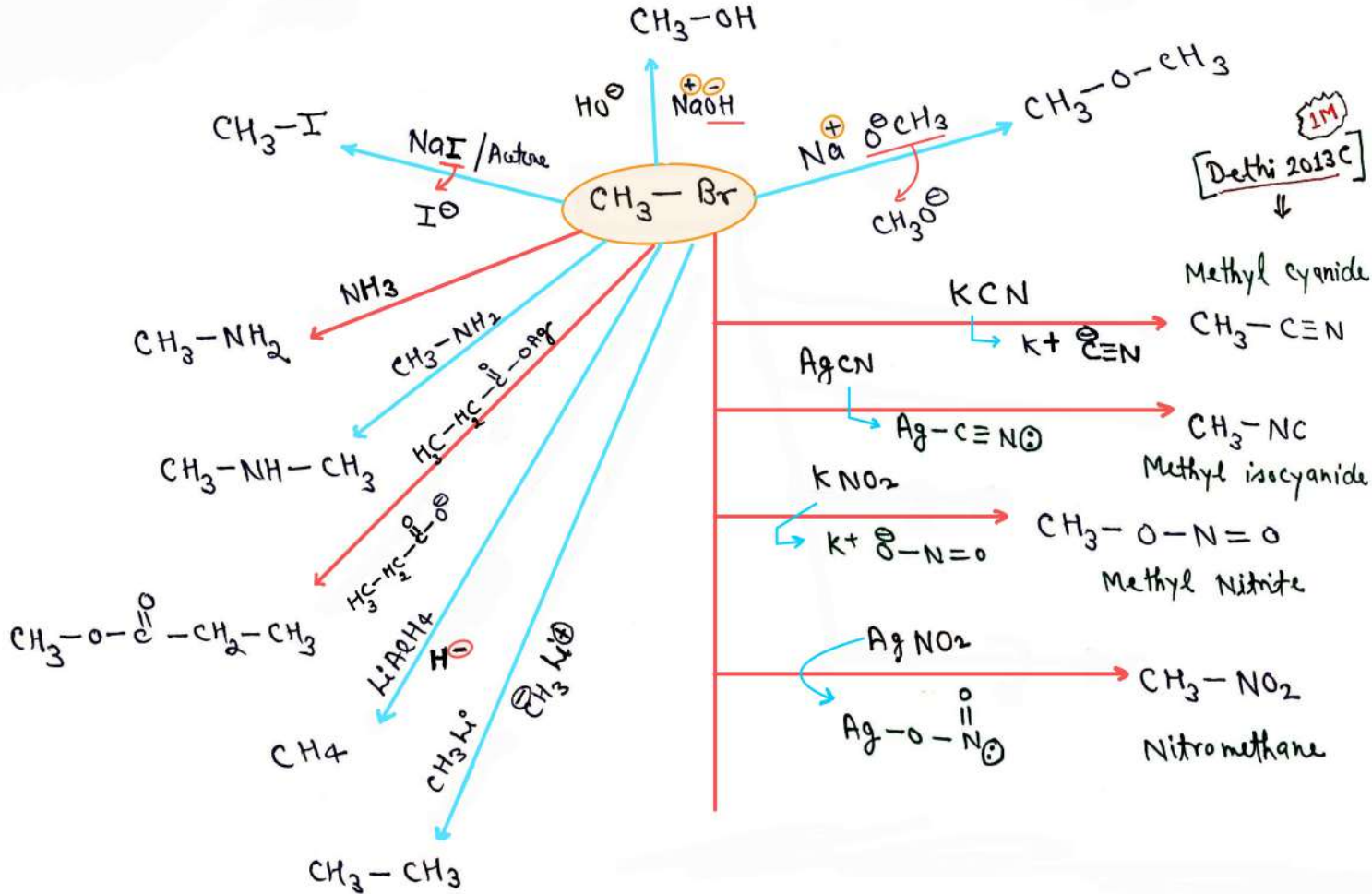
Most reactive : Less hindrance

Least reactive because bulky groups hinder the approaching of nucleophile towards carbon.

→ Order of reactivity with different halogen atoms : R–I > R–Br > R–Cl > R–F

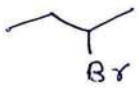
Weak Bond strength So, easy to break.

Strong Bond, So tough to break.



Substrate having less crowding is more effective than more crowding substrate for S_N2 reaction.

Example –:

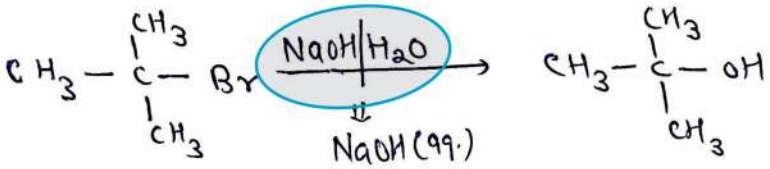
Rate of reaction :  (2°) <  (1°) → [CBSE 2014] (1M)

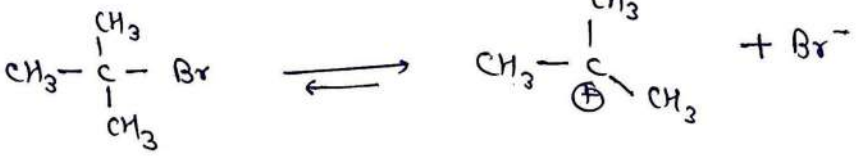
: $CH_3-I > CH_3-Br$

: $H_3C-C(CH_3)_2-Cl < CH_3-Cl$

→ [Delhi 2014 / CBSE 2014 / CBSE 2010] (1M)

Unimolecular Substitution nucleophilic reaction : S_N1

→ 

Mechanism –: Step (i) 

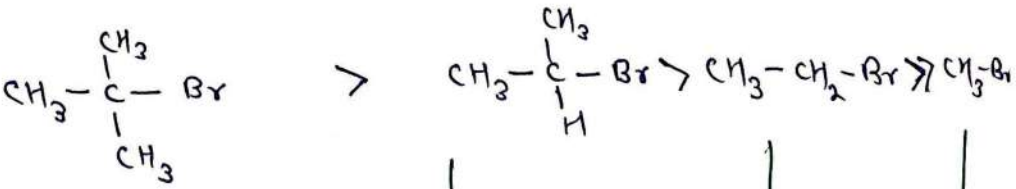
Step (ii) 

→ Above reaction follows first order kinetics.

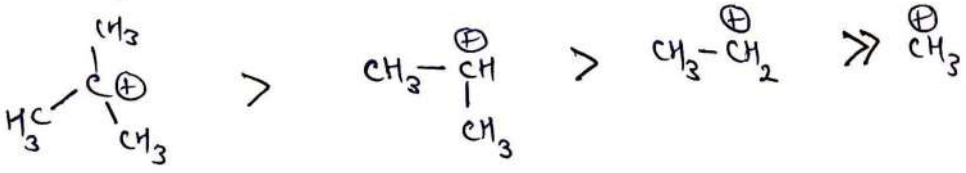
Rate ∝ [Alkyl halide]

→ It is a two step reaction and carbocation reaction intermidiate is formed.

→ Step (i) is slow and reversible & Rate of reaction depends on slowest step.

Order of reactivity : 

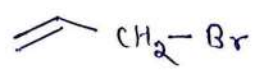
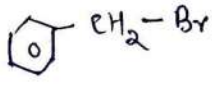
During reaction → ↓

Stability of Carbocation : 

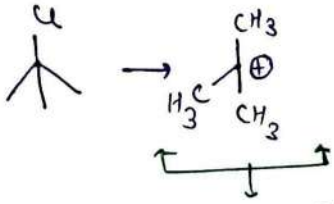
→ If carbocation intermidiate is stable then that substrate gives fast S_N1 reaction

→ **Order of reactivity** : R–I > R–Br > R–Cl > R–F

→ Find the order of reactivity for SN1 reaction ?

→ ① CH_3-CH_2-Br < ②  < ③  : Reactivity

: Stability of carbocation

→ ①  ② 

[Delhi 2013] 1M

3° carbocation : more Stable carbocation

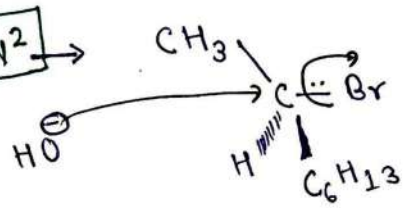
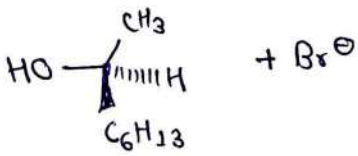
order of reactivity : ① > ②

Stereochemistry of SN^1 Vs SN^2 –:

S_N2 reaction gives inverted product.

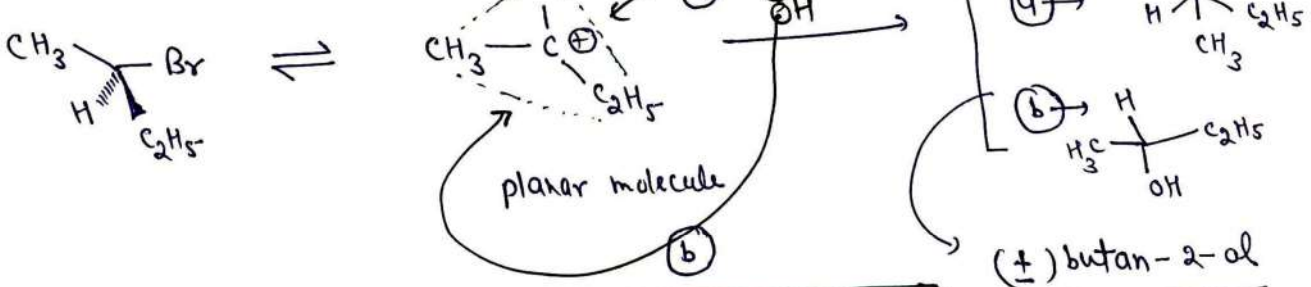
But S_N1 reaction gives racemic mixture (It go through racemisation)

Example –:

S_N2 →  

$\ominus OH$ attacks on the opposite side of carbon – bromine bond. So inversion of configuration happens.

S_N1 –:



Order of reactivity for S_N1 : Tert. Halide > sec. Halide > 1° Halide > CH_3-X

for S_N2 : CH_3-X > 1° Halide > sec. Halide >> tri Halide

→ SN1 : $(CH_3)_3CBr$ > $CH_3-CH(Br)-CH_2-CH_3$ > $CH_3-CH_2-CH_2-CH_2-Br$

SN2 : $(CH_3)_3CBr$ < $CH_3-CH(Br)-CH_2-CH_3$ < $CH_3-CH_2-CH_2-CH_2-Br$

Elimination Reaction :-

Dehydrohalogenation Reaction

Haloalkane with β-hydrogen atom $\xrightarrow[\text{(alcoholic)}]{KOH}$ Alkene

$CH_3-\overset{H}{\underset{H}{C}}-CH_2 \xrightarrow{\ominus OH} CH_3-CH=CH_2 + H_2O + Br^-$

$CH_3-CH_2-\underset{H_2}{CH}-\underset{H_1}{CH}-CH_2(Br) \xrightarrow[H_2 \& Br]{\text{Elimination of}} CH_3-CH_2-CH=CH-CH_3$ (Major) ← Stable Alkene

$\xrightarrow{\text{Elimination of } H_2 \& Br} CH_3-CH_2-CH_2-CH=CH_2$ (Minor)

Reaction with metals :-

$R-Br \xrightarrow[\text{Dry ether}]{Mg} R-Mg-X$ [Grignard Reagent]

$R-MgX \xrightarrow[H^+ \bar{O}H]{H_2O} R-H$

$R-X + Na + X-R \longrightarrow R-R + NaX$

Reactions of haloarenes

Nucleophilic Substitution :- Aryl halides are extremely less reactive toward NSR due to following reasons :- [Delhi 2013] (2M)

(i) **Resonance effect :-** [Delhi 2013] (1M)

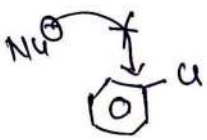
$\longleftrightarrow$

C-Cl bond acquires a partial double bond character due to resonance as a result bond breaking in haloarene is difficult than haloalkane. Therefore haloarenes are less reactive than haloalkane towards NSR.

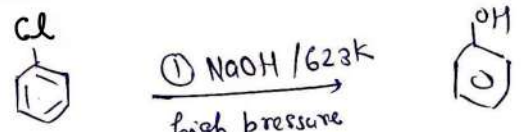
CH_3-Cl ↳ Always single bond character

(ii) **Instability of phenyl cation :-** Haloarenes can not follow S_N1 path because during first step we get phenyl cation which is not stable.

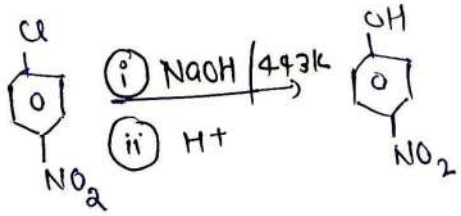
(iii) Because of possible repulsion, it is less likely for electron rich nucleophile to approach electron rich arenes.



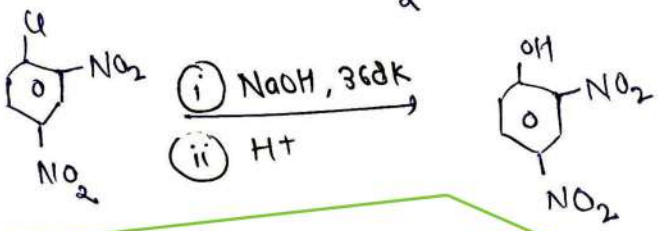
→ **Replacement by hydroxyl group :–**

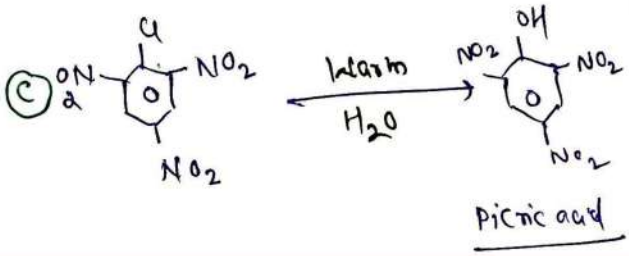


The presence of an electron withdrawing group ($-NO_2$ / $-CN$) at ortho and para positions increases the reactivity of halo-arenes.

(a) 

[Delhi 2019] 1M

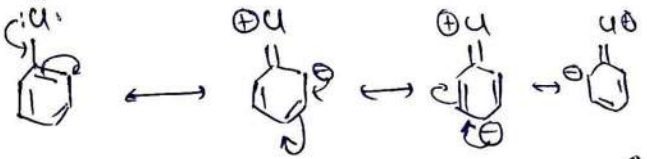
(b) 

(c) 

Picric acid

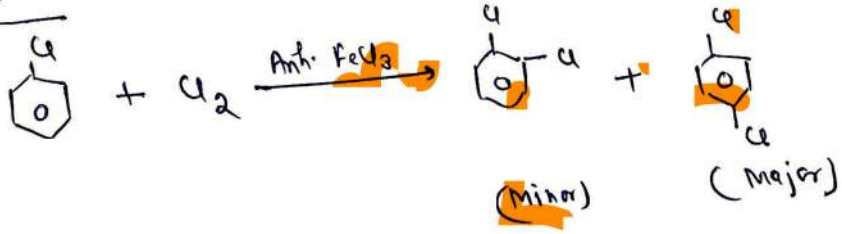
Electrophilic Substitution Reaction :-

→ Halogens are ortho – para directing in nature for ESR. [Delhi 2012] 3M



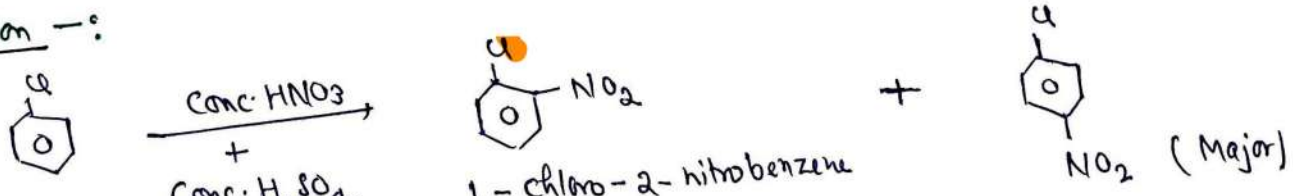
Due to resonance, the electron density increases more at ortho and para position.

(i) Halogenation :–

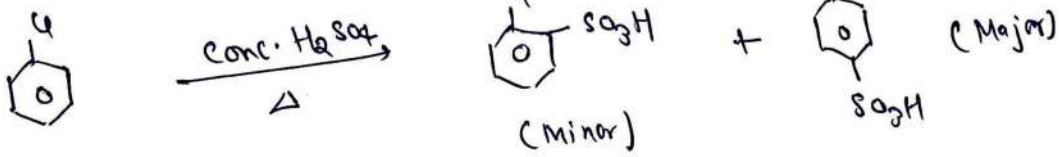


→ [CBSE 2015] 1M

(ii) Nitration :–



(iii) Sulphonation :–



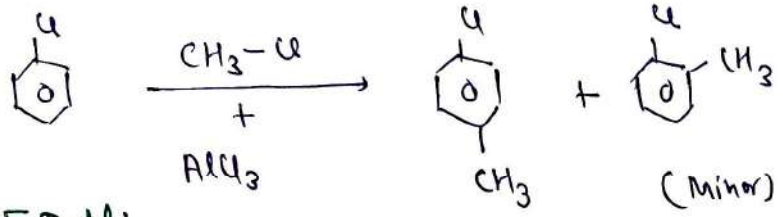
(iv)

Friedel - Craft's Reaction

[Delhi 2010] 1M

Alkylation

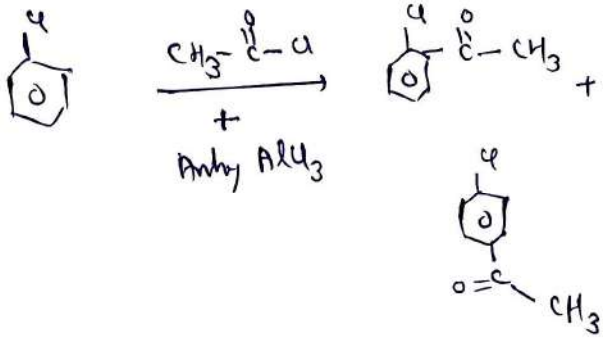
Addition of alkyl group on benzene



[Delhi 2014C] 1M

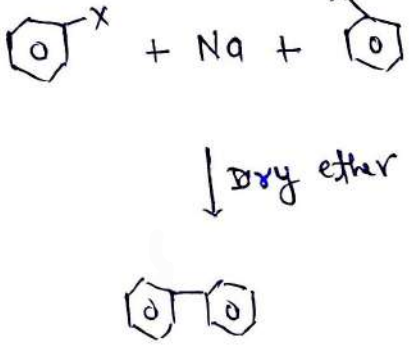
Acylation

Addition of acyl group on benzene

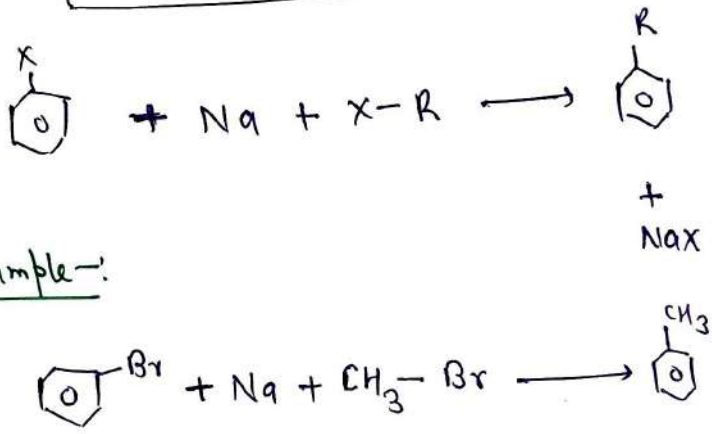


Reaction with metal :-

Fittig Reaction



Wurtz - Fittig Reaction

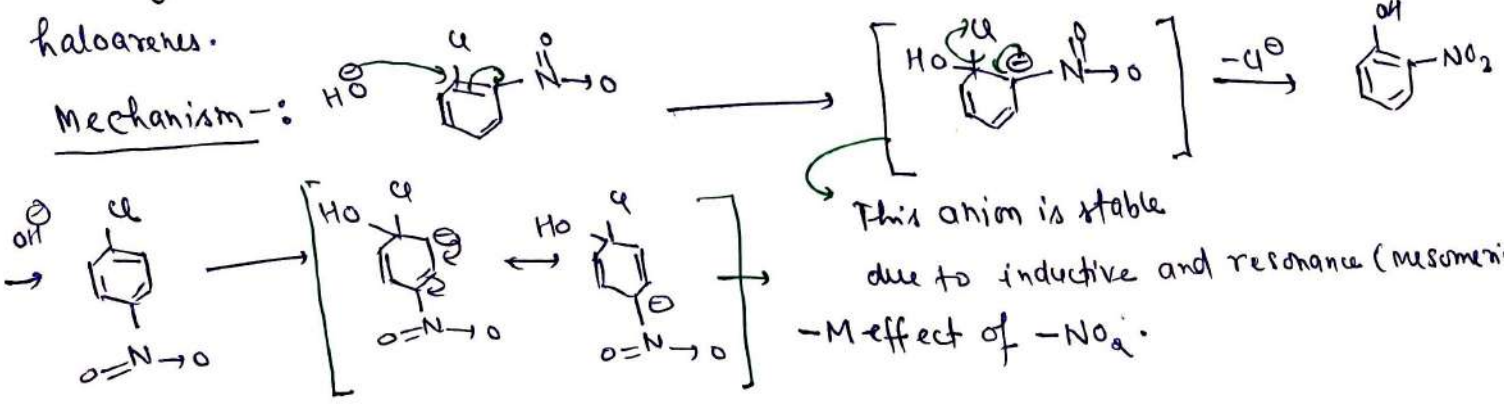


Example :-

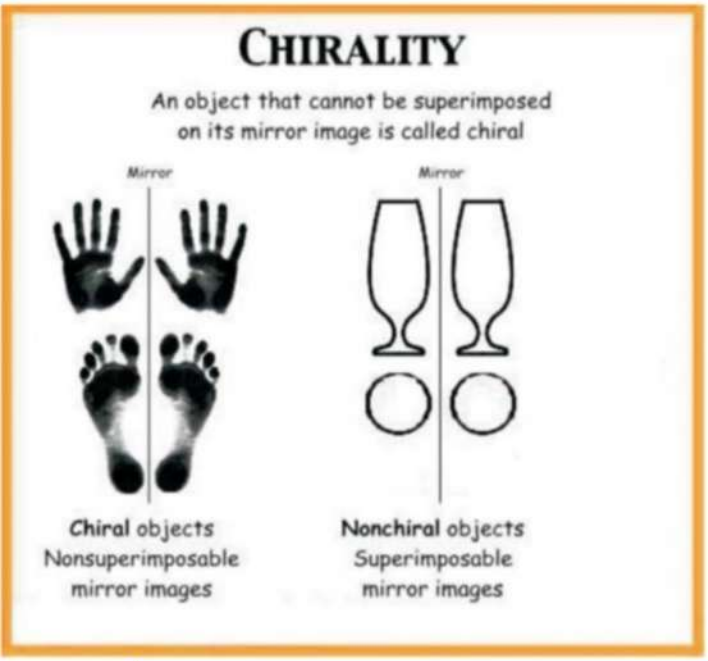
Question :- The presence of nitro group at ortho-para positions increases the reactivity of haloarenes towards NSR, Why? [CBSE 2019] 1M

Answer :- Because $-NO_2$ group at ortho and para positions withdraw electron density from the benzene ring and thus facilitates the nucleophilic attack on haloarenes.

Mechanism :-

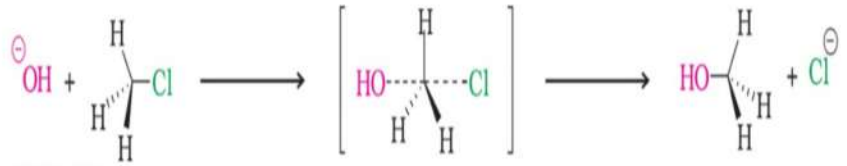


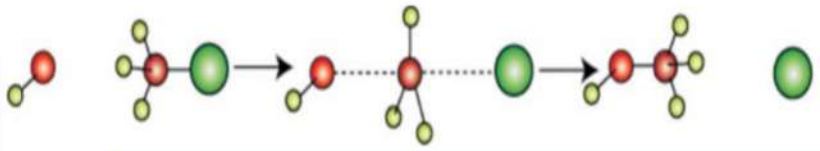
This anion is stable due to inductive and resonance (mesomeric) -M effect of $-NO_2$.



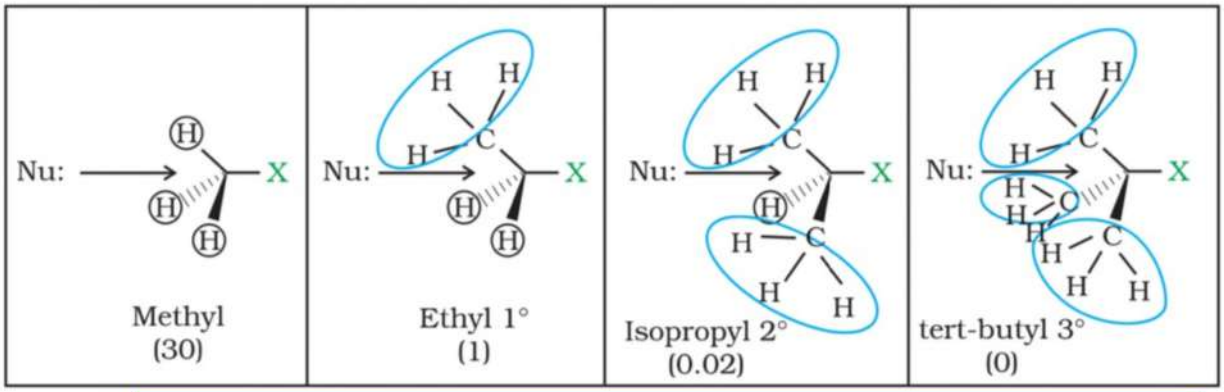
Some common examples of chiral and achiral objects

SN^2 Reaction





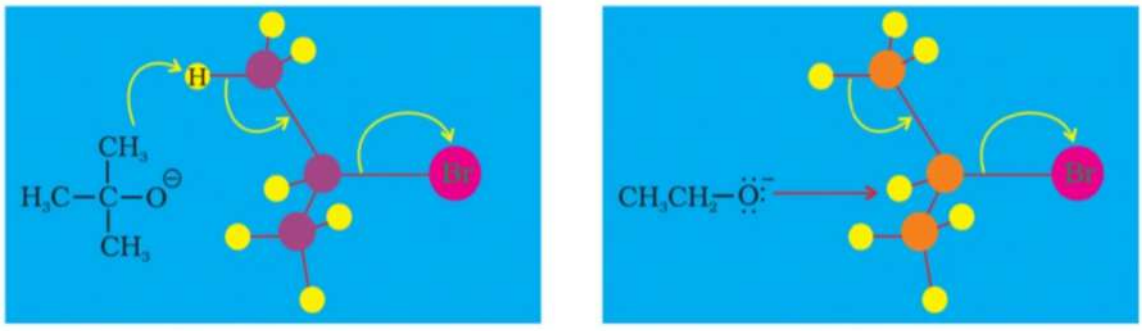
Red dot represents the incoming hydroxide ion and green dot represents the outgoing halide ion



Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis

Elimination versus substitution

A chemical reaction is the result of competition; it is a race that is won by the fastest runner. A collection of molecules tend to do, by and large, what is easiest for them. An alkyl halide with α-hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution (S_N1 and S_N2) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. Thus, a bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and *vice versa*. Similarly, a primary alkyl halide will prefer a S_N2 reaction, a secondary halide- S_N2 or elimination depending upon the strength of base/nucleophile and a tertiary halide- S_N1 or elimination depending upon the stability of carbocation or the more substituted alkene.



Elimination *vs* Substitution

Polyhalogen Compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture.

Dichloro- methane (Methylene chloride) CH_2Cl_2

Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system.

In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

Trichloro- methane (Chloroform) $CHCl_3$

Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, such as ether.

Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.

$$2CHCl_3 + O_2 \longrightarrow 2COCl_2 + 2HCl$$

Triiodo- methane (Iodoform) CHI_3

It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Tetrachloro-methane (Carbon tetrachloride) CCl_4

It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

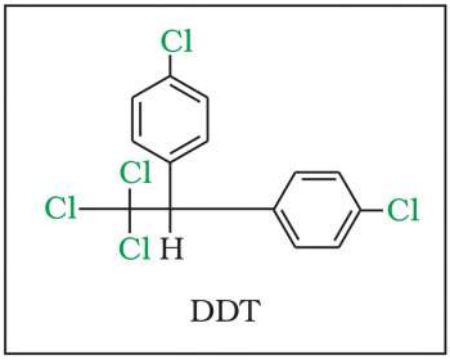
When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.

Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.

p,p'-Dichlo- rodiphenyl-trichloro- ethane (DDT)



DDT

DDT, the first chlorinated organic insecticides, was originally prepared by Paul Muller .

Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus.