HALOALKANES & HALOARENES

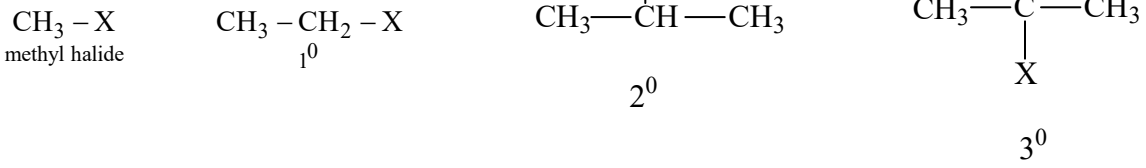
Organic Halogen Compound

They are formed by replacement of H atoms on hydrocarbons by an equal number of halogen atoms.

Classification

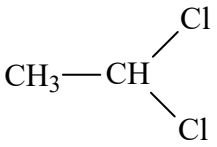
1. Alkyl halides

The mono-halogen derivatives of alkanes are alkyl halides. The general formula for an alkyl halide is $C_nH_{2n+1}X$



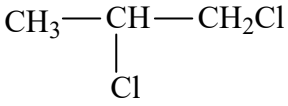
2. Gem dihalides/Alkylidene halides

Two halogen atoms are present on a single C.



3. Vicinal Dihalides/Alkylene halides

Two halogen atoms are present on two adjacent C atoms.

eg : 

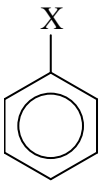
4. Vinyl halides

Halogen is bonded to a double-bonded carbon.

eg : $CH_3 – CH = CH – X$

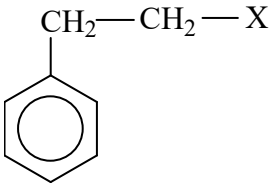
5. Aryl Halides

Halogen is bonded to aromatic ring.

eg : 

6. Aralkyl Halides

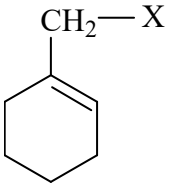
Halogen is bonded to side-chain

eg : 

7. Allylic Halides

An sp^3 hybridised C bonded to sp^2 hybrid C of C = C double bond is called allylic carbon.

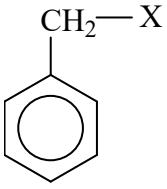
Replacement of H atoms on allylic C by halogen atoms produce allylic halides.

eg : $CH_2 = CH – CH_2 – X$ and 

8. Benzylic Halides

An sp^3 hybridised C bonded to sp^2 hybridised C of aromatic ring is called benzylic C.

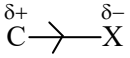
Replacement of H atoms of benzylic C by halogen atoms produce benzylic halides.

eg : 

Nature of C - X bond

Halogen is more electronegative as compared to C.

$\therefore$ C - X bond pair is slightly shifted towards X, $\therefore$ C - X bond is polar in nature.



Electronegativity of halogens decreases down the group. As a result, C - X bond, polarity and dipole moment $(\mu = qd)$ decreases from C - F bond to C - I bond.

NOTE

The μ of $CH_3 - Cl$ is slightly greater than that of $CH_3 - F$ due to greater C – Cl bond length as compared to C – F bond length (magnitude of change is more in F)

Dipole moment order :

$CH_3 - Cl > CH_3 - F > CH_3 - Br > CH_3 - I$

Physical properties of organic halogen compounds

1. Melting & boiling points

Organic halogen compounds have greater boiling point as compares to hydrocarbons of comparable molecular mass due to their polar nature.

Alkyl halides

a) For same alkyl group, boiling point increases from F to I

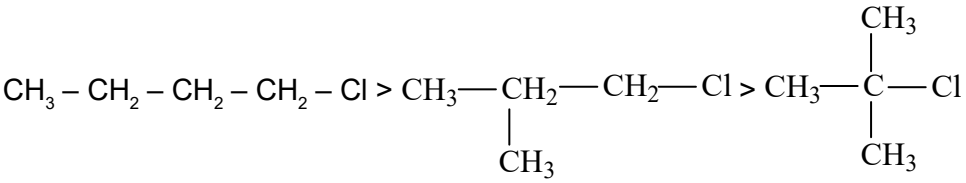
R - I < R - Cl < R - Br < R - I

Reason : Surface area increases

b) For same halogen atom, boiling point increases with increase in size of alkyl group.

$CH_3 - Cl < CH_3 - CH_2 - Cl < CH_3 - CH_2 - CH_2 - Cl$

c) For isomeric halides, boiling point decreases with increase in branching



Reason : Surface area decreases

d) Boiling point increases with increase in number of halogen atoms

$CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$

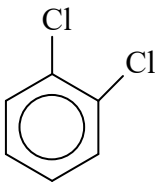
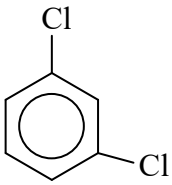
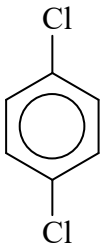
Reason : Surface area increases

Aryl Halides

For same aryl group boiling point increases from F to I and for same halogen atom, boiling point increases with increase in size of aryl group.

NOTE

Boiling point of isomeric dichloro benzenes are almost identical but melting point of p-dichlorobenzene is much more greater as compound to o - and m - isomers. ∴ p-isomers is symmetrical and therefore can fit closely in the crystal lattice. Due to the same reason, p-isomer is least soluble in a given solvent.

B.P	453 K	446 K	448 K
M.P	256 K	249 K	323 K

2. Density

Densities of alkyl fluorides and chlorides are less than that water whereas bromides, iodides & poly-halides have greater densities as compared to water.

a) For same alkyl group, density increases from F to I

R – F < R – Cl < R – Br < R – I

Reason : Molecular mass increases

b) Density decreases with increase in size of alkyl group

CH_3Cl – Cl > CH_3 – CH_2 – Cl > CH_3 – CH_2 – CH_2 – Cl

c) Density increases with increase in number of halogen atoms

$CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$

Reason : molecular mass increases

3. Solubility

Organic halogen compounds are generally polar in nature. ∴ They are soluble in polar solvents but not in water, because energy released as a result of solvation is less than energy required to break H-bonds in water. They are soluble in common organic solvents such as ether, CCl_4, benzene, etc.

4. Stability

The C - X bond strength decreases from F to I.

∴ Stability of various alkyl halides follows the order :

R – F > R – Cl > R – Br > R – I

5. Dipole moments

Dipole moments of chloromethane :

$$\underset{\mu=1.92\,D}{CH_3Cl} > \underset{\mu=1.6\,D}{CH_2Cl_2} > \underset{\mu=1.04\,D}{CHCl_3} > \underset{\mu=0}{CCl_4}$$

Dipole moments of dichlorobenzene

According to parallogram law of dipole moment

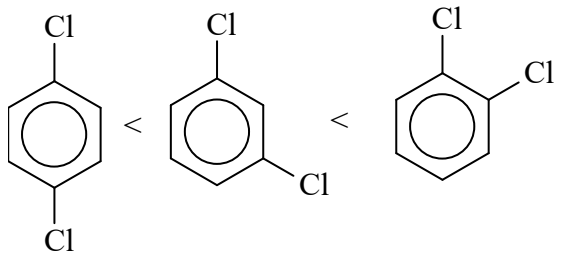
$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

μ - dipole moment of C - X bond

θ - angle between bonds

When $\theta = 180^0$, $\cos\theta = -1 \Rightarrow \mu = 0$

As value of θ decreases, value of $\cos\theta$ increases and hence μ also decreases.



$\mu = 0$

Preparation of aliphatic halogen compounds

1. Preparation from alcohols

a. Reaction with HX

$$R - OH + HX \rightarrow R - X + H_2O$$

Mechanism :

$$HX \rightarrow H^+ + X^-$$

$$R - \ddot{O}H + H^+ \rightarrow R - \overset{\oplus}{\ddot{O}}H_2$$

Tertiary and secondary carbocations are quite stable.

$\therefore$ Tertiary and secondary alcohols react through S_N1 mechanism.

$$R - \overset{\oplus}{\ddot{O}}H_2 \rightarrow R^+ + H_2O$$

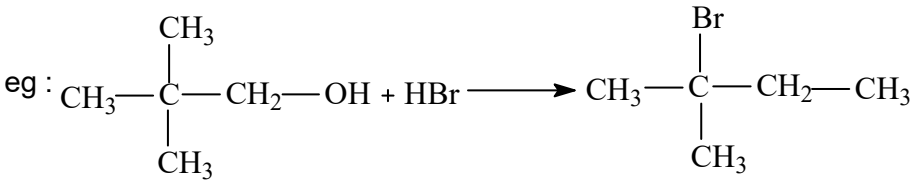
$$R^+ + X^- \rightarrow RX$$

Primary carbocations are highly unstable. $\therefore$ 1^0 alcohols react through S_N2 mechanism.

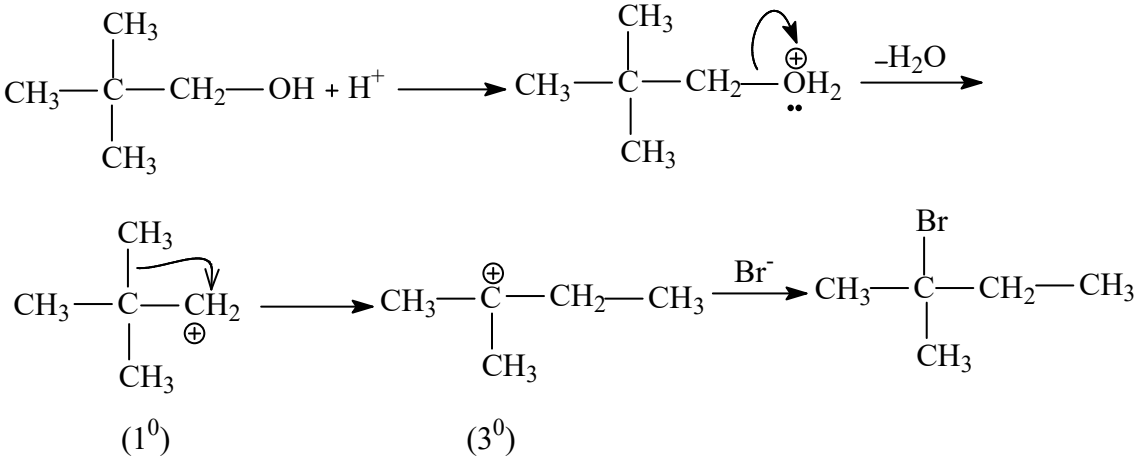
$$X^- + R - \overset{\oplus}{\ddot{O}}H_2 \rightarrow R - X + H_2O$$

NOTE

If β carbon of primary alcohol is 3^0 or 4^0, 1^0 alcohols react by S_N1 mechanism (rearrangements are possible)



Mechanism :



Grove's process

1^0 and 2^0 alcohols react with HCl in the presence of anhy. $ZnCl_2$ to produce corresponding chlorides and reaction is called Grove's process.

$$CH_3 - CH_2 - OH + HCl \xrightarrow[\Delta]{ZnCl_2} CH_3 - CH_2 - Cl$$

$$CH_3 - \underset{}{\overset{CH_3}{\underset{|}{CH}}} - OH + HCl \xrightarrow{ZnCl_2} CH_3 - \overset{CH_3}{\underset{|}{CH}} - Cl$$

Function of $ZnCl_2$

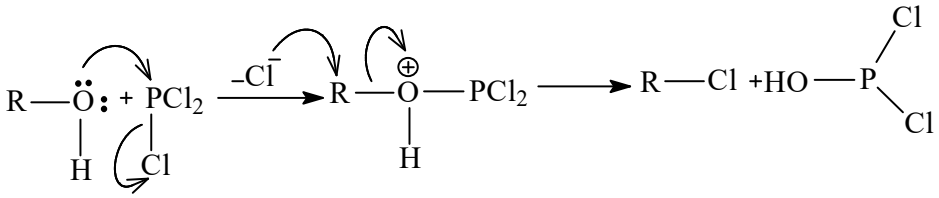
The Lewis acid $ZnCl_2$ coordinates with the oxygen of alcohol and thus weakens C - O bond.

Reaction with phosphorous halides

$$R - OH + PCl_5 \rightarrow R - Cl + POCl_3 + HCl$$

$$3R - OH + PCl_3 \rightarrow 3R - Cl + H_3PO_3$$

Mechanism :



PBr_5 and PI_5 are highly unstable. PBr_3 and PI_3 are less stable.

$\therefore$ In order to prepare bromides and halides by this reaction, we prepare PBr_3 or PI_3 along with the reaction (prepared in situ)

$$R-OH+X_2 \xrightarrow{\text{Red P}} R-X \ (X_2 \to Br_2 / I_2)$$

$$P_4+6X_2 \to 4PX_3$$

Reaction with thionyl chloride

$$R-OH+SOCl_2 \xrightarrow{\text{Pyridine}} R-Cl+SO_2\uparrow+HCl\uparrow$$ (Darzen's reaction)

Free-radical halogenation of hydrocarbon

$$CH_4+Cl_2 \xrightarrow{h\nu} CH_3Cl+CH_2Cl_2+CHCl_3+CCl_4$$

Mechanism :

(i) $Cl-Cl \xrightarrow{h\nu} 2Cl^{\cdot}$ ⟶ Initiation

(ii) $CH_4+\dot{Cl} \to \dot{C}H_3+HCl$

(iii) $\dot{C}H_3+Cl_2 \to CH_3Cl+\dot{Cl}$

} Propagation

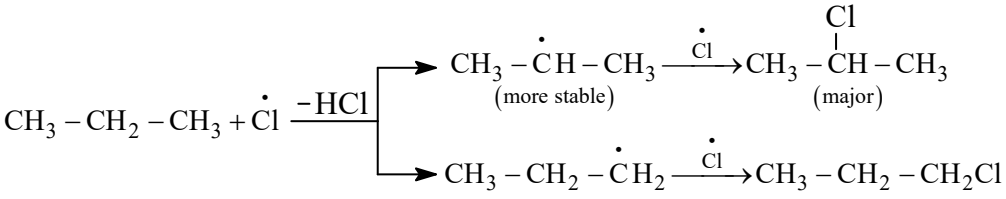
(iv) $\dot{C}H_3+\dot{Cl} \to CH_3Cl$

(v) $\dot{C}H_3+\dot{C}H_3 \to CH_3-CH_3$

} Termination

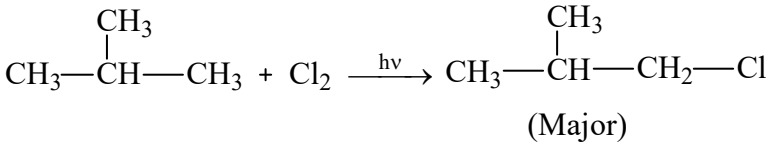
$$CH_3-CH_2-CH_3+Cl_2 \xrightarrow{h\nu} \underset{(\text{MAJOR})}{CH_3-\overset{Cl}{\overset{|}{C}}H-CH_3}+CH_3-CH_2-CH_2-Cl$$

Mechanism :



Reactivity of various H atoms towards free radical sub. depends on intermediate free radical generated. The stability of free radicals follows the order $3^0 > 2^0 > 1^0$.

$\therefore$ Reactivity of various H atoms towards free radical substitution follows order $3^0 > 2^0 > 1^0$.



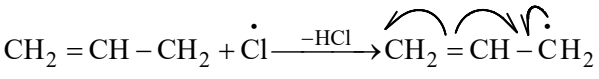
(Major)

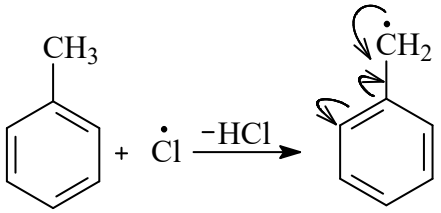
Different types of H - atom	1^0	2^0	3^0
Reactivity of corresponding H-atoms (x)	1	3.8	5
Total no. of corresponding H-atom(y)	9	0	1
Total possibility of corresponding products (xy)	9	0	5
% yield of corresponding products	$\frac{9}{9+5}\times 100$	0	$\frac{5}{9+5}\times 100$

NOTE

- Reactivity ratio of 1^0, 2^0 & 3^0 H towards free radical bromination is 1 : 84 : 1600
- Allylic and benzylic free radicals are resonance stabilized.

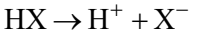
  $\therefore$ Reactivity of allylic and benzylic H towards free radical substitution reaction is greater than that of a tertiary H.

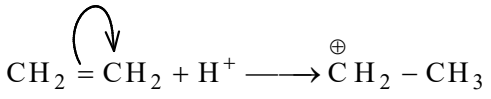




3. Electrophilic addition reaction of HX to alkenes

Mechanism

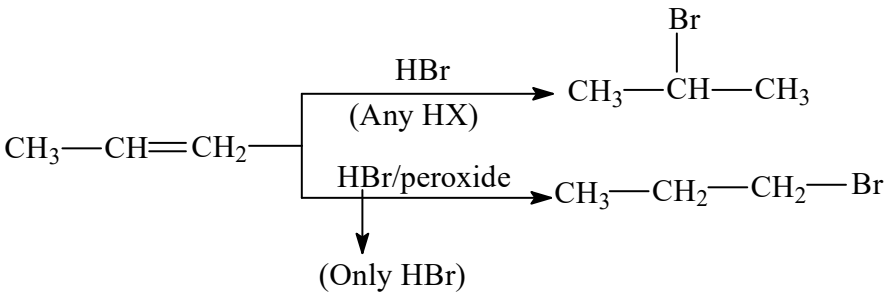




$$\overset{\oplus}{C}H_2 - CH_3 + X^- \longrightarrow CH_3 - CH_2 - X$$

NOTE

In the case of a unsymmetrical alkene, there is a possibility for both Markownikove's & Anti-markownikove's addition.



4. Addition of halogen molecules to alkenes

$$CH_3 - CH = CH_2 \xrightarrow{Br_2/CCl_4} CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_2 - Bt$$

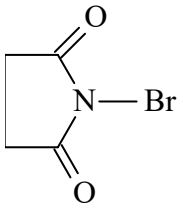
Allylic and benzylic halogens

Allylic and benzylic free radicals are resonance stabilized.

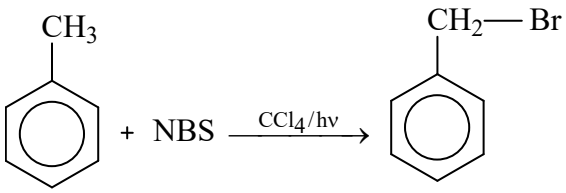
$\therefore$ Free radical substitution reactions are easy at allylic & benzylic positions.

$$CH_2 = CH - CH_3 \xrightarrow[(\text{or } Cl_2/793\,K)]{Cl_2/h\nu} CH_2 = CH - CH_2 - Cl$$

A specific reagent for allylic & benzylic bromination is NBS (N-Bromo succinimide)



$$CH_2 = CH - CH_3 + NBS \xrightarrow{CCl_4/h\nu} CH_2 = CH - CH_2 - Br$$

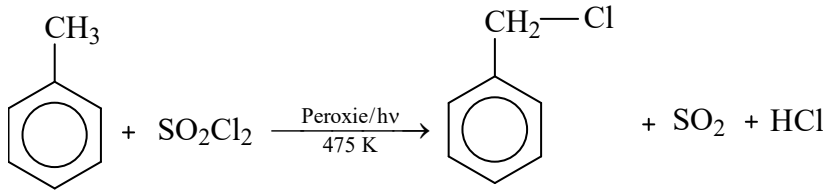


NOTE

The function of NBS is the production of Br free radical.

A specific reagent for allylic & benzylic chlorination is SO_2Cl_2.

$$CH_2=CH-CH_3+SO_2Cl_2 \xrightarrow[475\ K]{Peroxide/h\nu} CH_2=CH-CH_2-Cl+SO_2+HCl$$



NOTE

SO_2Cl_2 will also produce chlorine free radical

5. Halogen exchange reaction

a) Finkelstein reaction

$$R-X+NaI \xrightarrow{Acetone/\Delta} R-I+NaX \quad [X \to Cl, Br]$$

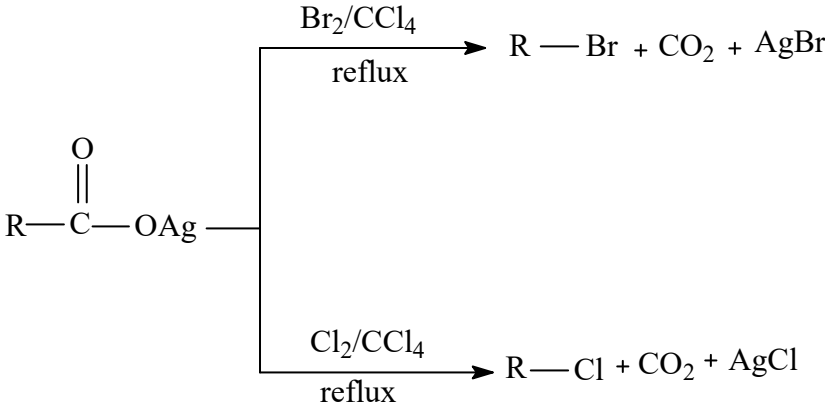
b) Swartz reaction

$$R-Cl+AgF \xrightarrow{\Delta} R-F+AgCl$$

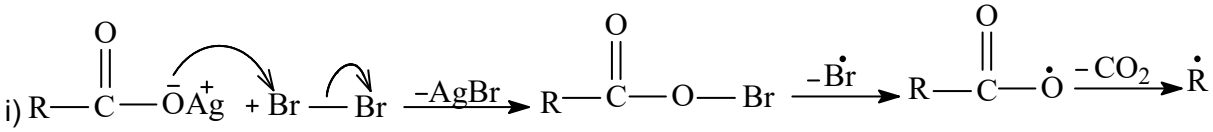
$$\downarrow$$

$$[SnF_2, AsF_3, Hg_2F_2, SbF_3, ...]$$

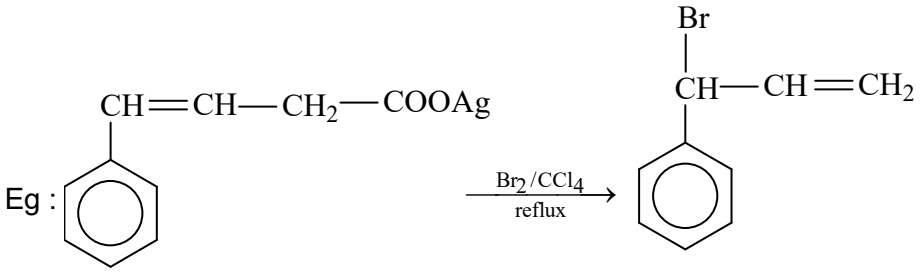
6. Preparation from silver salts of carboxylic acids (Hundsdiecker reaction)



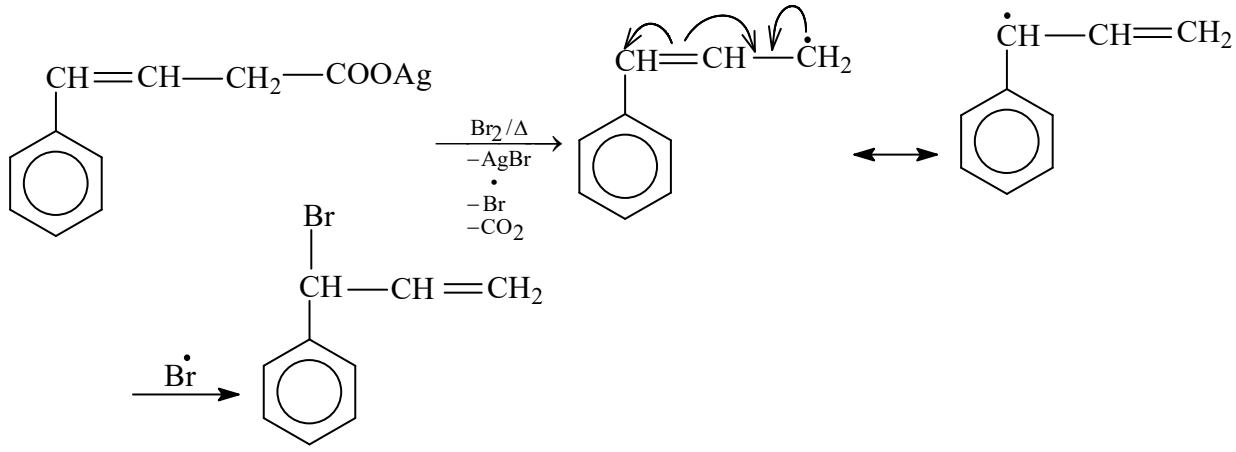
Mechanism



ii) $\dot{R} + \dot{Br} \longrightarrow R - Br$



Mechanism



NOTE

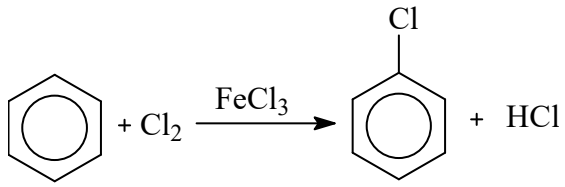
Silver salts of acids react with I_2 to produce an ester & reaction is called Birnbaum simonini reaction.

$$2R - \overset{O}{\overset{\|}{C}} - OAg + I_2 \longrightarrow R - \overset{O}{\overset{\|}{C}} - OR + CO_2 + 2AgI$$

Preparation of aryl halides

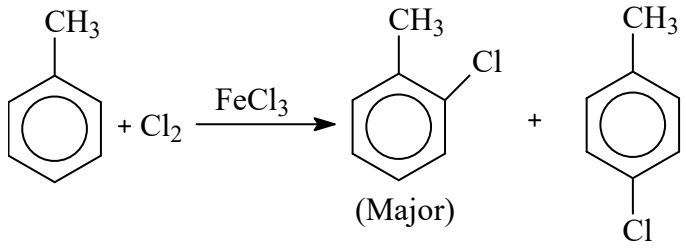
1. Electrophilic substitution

a. Chlorination

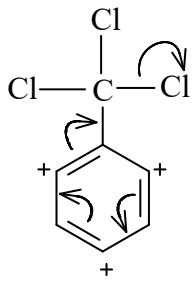


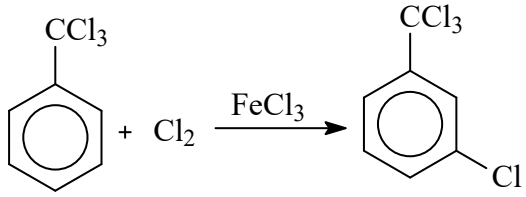
NOTE

→ CH_3 group is a ring activating group and o-, p- directing for electrophiles through their hyper conjugative effect

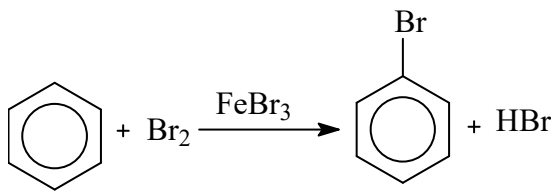


→ $-CCl_3$ group is a ring deactivating and m-directing group through reverse hyperconjugative effect.



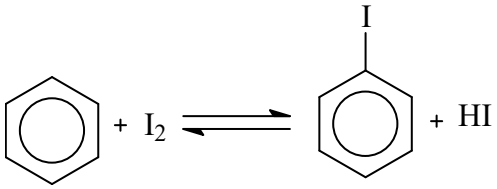


b. Bromination



c. Iodination

Direct iodination of benzene is not a convenient method for the preparation of iodobenzene because biproduct HI is a strong reducing agent and reduces back iodobenzene to benzene.



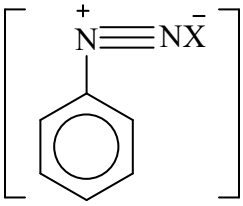
In order to avoid this problem, iodination is carried out in presence of HNO_3, HIO_3 or HgO

$$2HNO_3 + 2HI \longrightarrow I_2 + 2NO_2 + 2H_2O$$

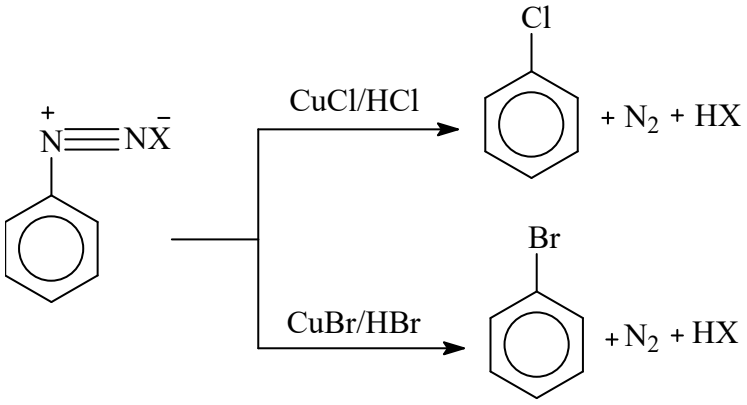
$$HIO_3 + 5HI \longrightarrow I_2 + 3H_2O$$

$$HgO + 2HI \longrightarrow HgI_2 + H_2O$$

2. Preparation from benzene diazonium salts



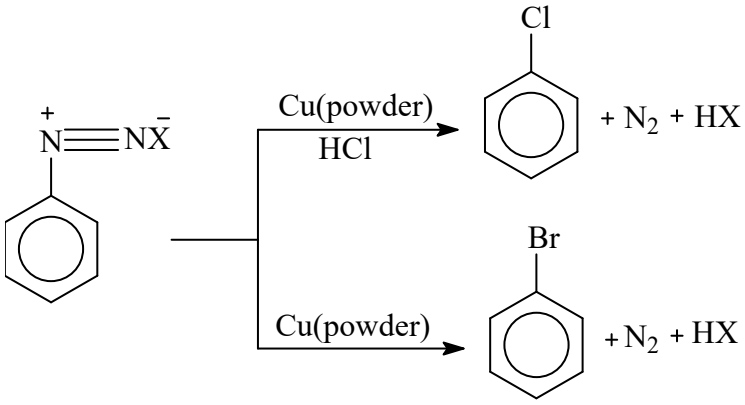
a. Sandmayer's reaction



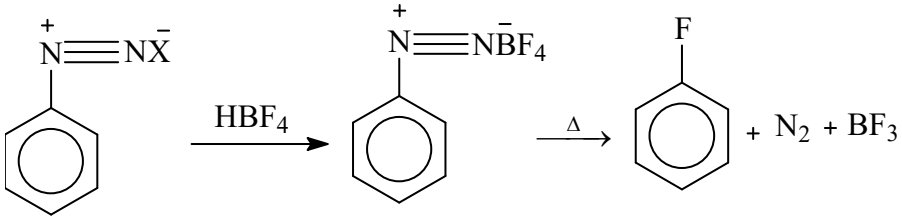
NOTE

The halogen in the ring is coming from CuX_2 which is generated by reaction of CuX and HX.

b. Gatterman's reaction

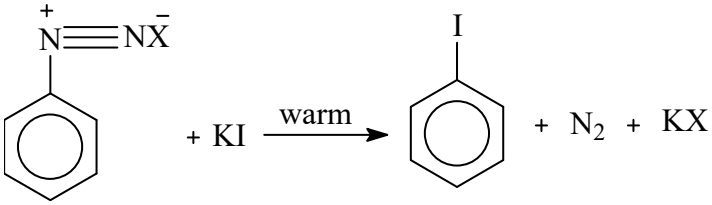


c. Balz-schiemann reaction



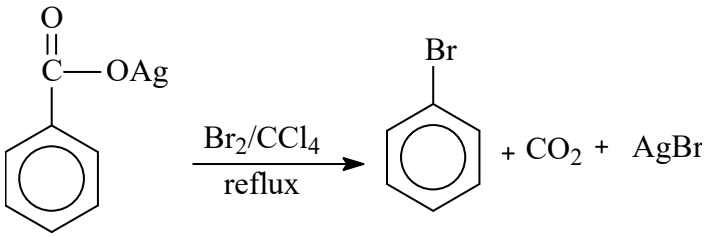
Benzene Diazonium
Tetrafluoro Borate

d.



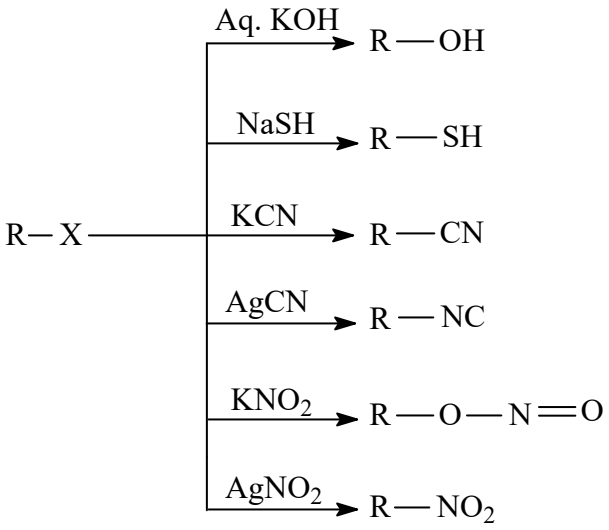
3. Preparation from silver salt of benzoic acid

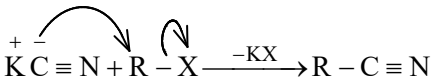
a. Hundsdiecker reaction

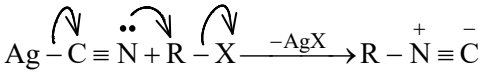


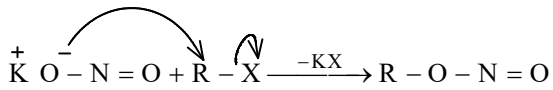
Chemical properties of alkyl halides

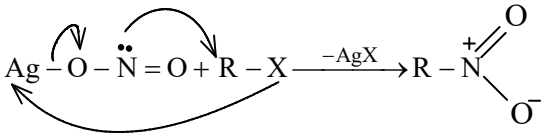
1. Nucleophilic substitution











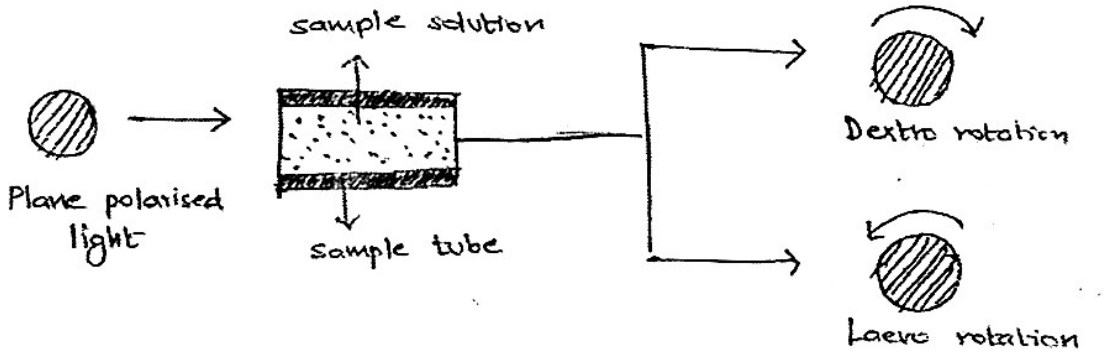
Some stereochemical aspects

1. Optical activity

The ability of a compound to rotate the plane of vibration of plane polarised light.

Towards right ⟶ dextro rotation [d/(+)]

Towards left ⟶ laevo rotation [ℓ /(–)]

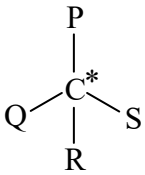


2. Chirality

The objects which give non-superimpossible mirror images are called chiral objects and the phenomenon is called chirality. Chirality of the molecule is the neccessary condition for optical activity.

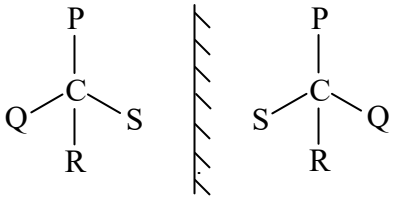
Asymmetric carbon (chiral carbon)

In 1874, vant Hoff and Le-Bell pointed out independently that the 4 valencies of C are directed towards the corners of a regular tetrahedron. If the valencies are satisfied by 4 different groups or atoms, molecule becomes chiral and it is therefore optically active. Such type of a carbon is called asymmetric carbon.



Enantiomers

They are optical isomers of the same compound and rotates the plane of vibration of plane polarised light equally but through opposite directions. They are non-superimpossible mirror images of each other.



Racemic mixture

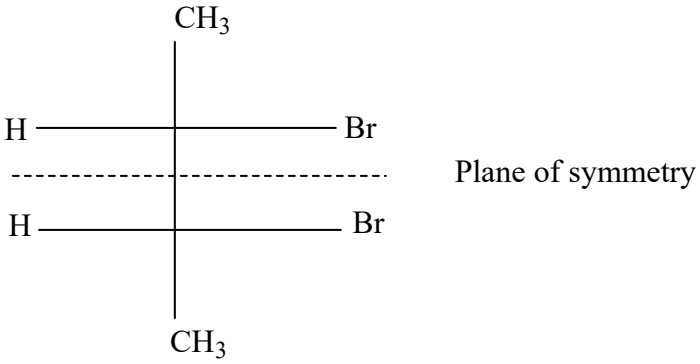
An equimolar mixture of enantiomers are called racemic mixture. The optical activity of racemic mixtures are zero due to external compensations.

Racemisation

The process of conversion of an optically active compound into the racemic modification is called racemisation

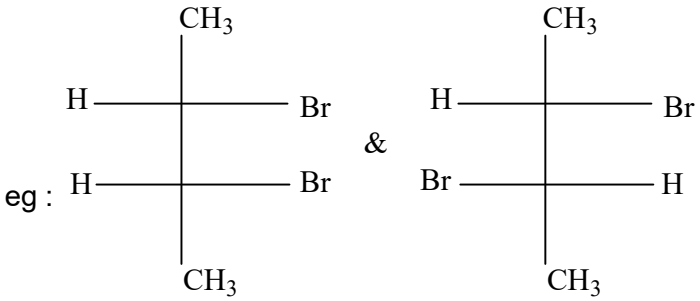
Meso compounds

They are optically inactive compounds but they contain asymmetric carbon atoms. They are optically inactive due to presence of a plane of symmetry in the compound (internal compensation)



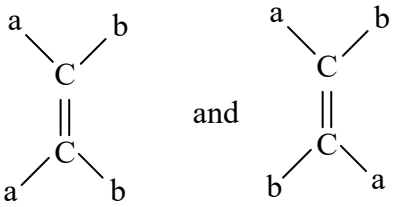
Diastereomers

They are the stereoisomers of same compound but they are not mirror images

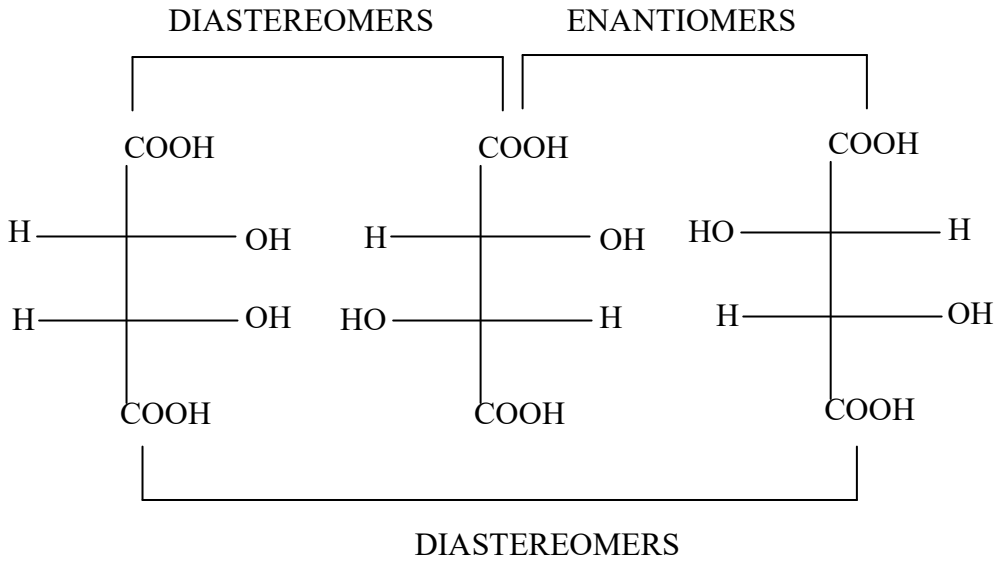


NOTE

Geometrical isomers are considered as diastereomers

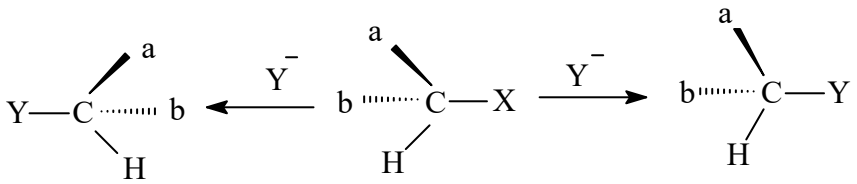


Relation between different stereoisomers of Tartaric acid



Configuration

The spacial arrangement of different groups of atoms around a central carbon is called configuration. In a chemical reaction, if the configuration of different bonds around central C is preserved, it is called retention of configuration and if configuration is not preserved, it is called inversion of configuration.

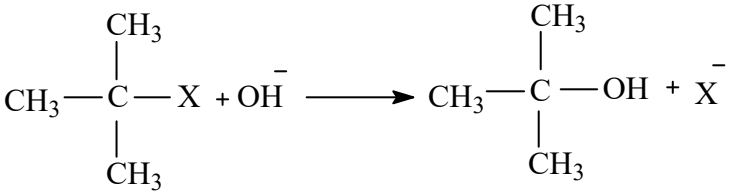


Inversion Retention

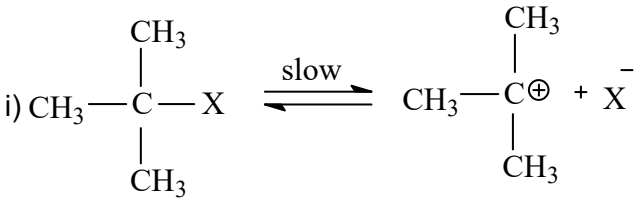
I. Mechanism of nucleophilic substitution reaction

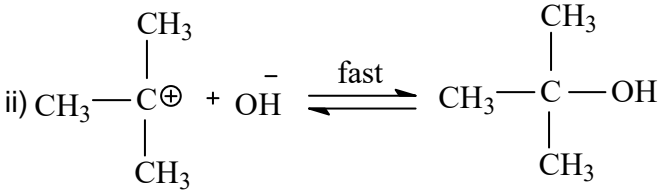
S_N1 mechanism (Substitution nucleophilic unimolecular mechanism)

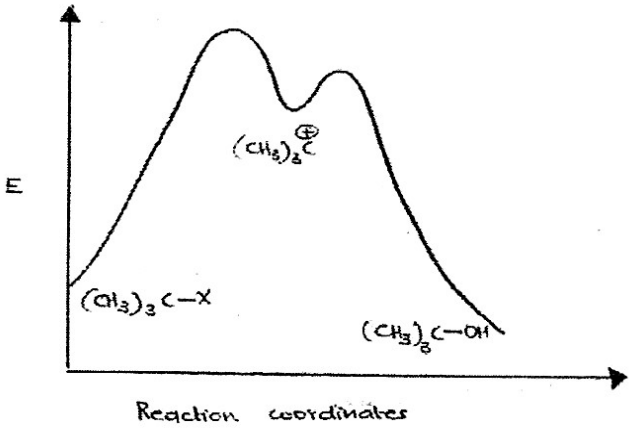
Consider the reaction



The S_N1 mechanism for this reaction can be explained as :







The first step is the slowest step and it is therefore the rate determining step. This step involves only a single reactant molecule.

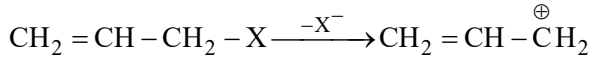
$\therefore$ The mechanism is called as unimolecular.

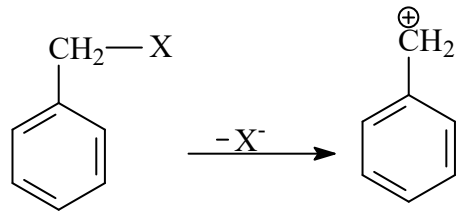
The rate of S_N1 reaction depends on stability of intermediate carbocation, formed in the first step. The stability of carbocation follows the order $3^0 > 2^0 > 1^0 > \overset{\oplus}{C}H_3$. $\therefore$ Reactivity of various alkyl halides towards S_N1 reaction follows the order $3^0 > 2^0 > 1^0 > CH_3 - X$.

NOTE

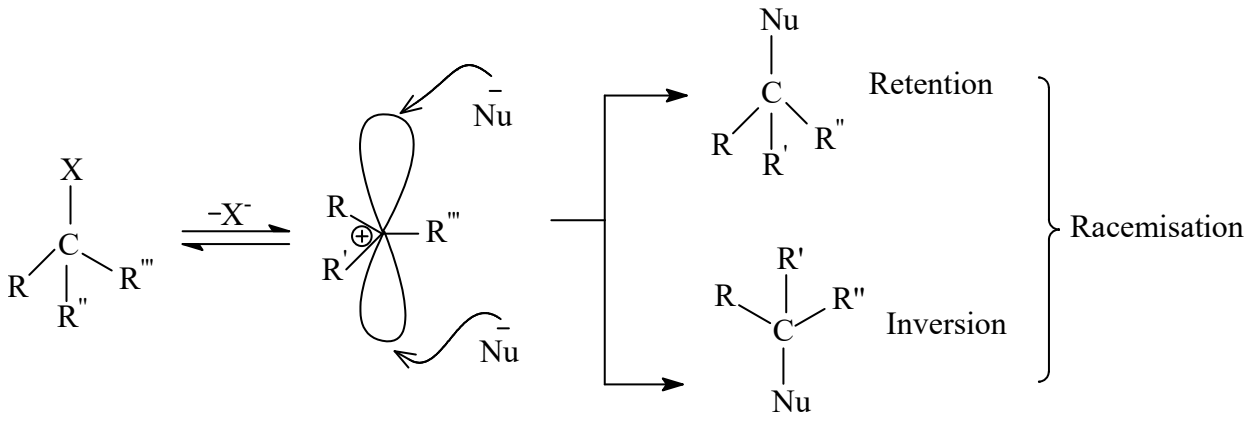
Allylic and benzylic carbocation are resonance stabilized.

$\therefore$ The reactivity & allylic and benzylic halides are highly reactive towards S_N1 even though they are 1^0 halides.





Stereochemistry of S_N1 reaction

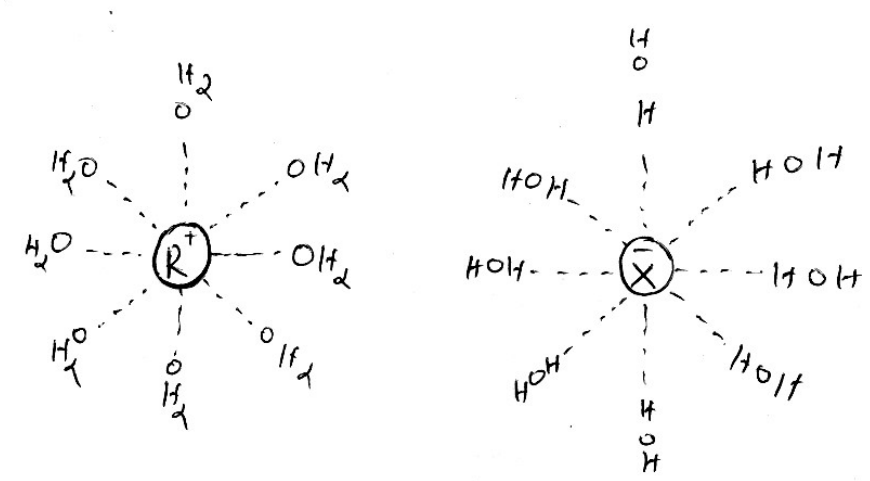


∴ S_N1 reaction at an optically active centre gives a partial racemisation with slight excess of inversion product.

Reason : The attack of nucleophile through the side of leaving group is partially hindered by X^- ions from this position.

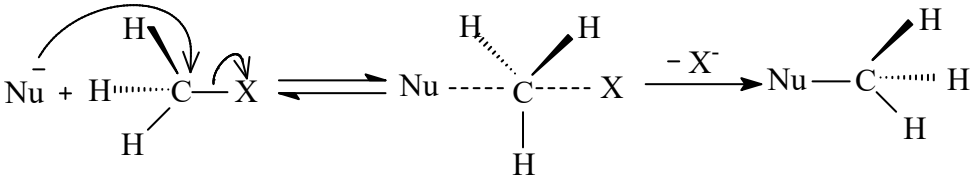
Effect of solvents on S_N1 reaction

The rate determining step of S_N1 mechanism involves two ions R^+ and X^-. Polar solvents easily solvate these two ions. ∴ Rate of S_N1 reaction are greater in polar solvents. Polar protic solvents such as water, alcohol etc are even more effective solvents for S_N1 because X^- ions form H-bonds with the hydrogen of OH group and R^+ ions coordinate with O of OH group using its non-bonding electrons.

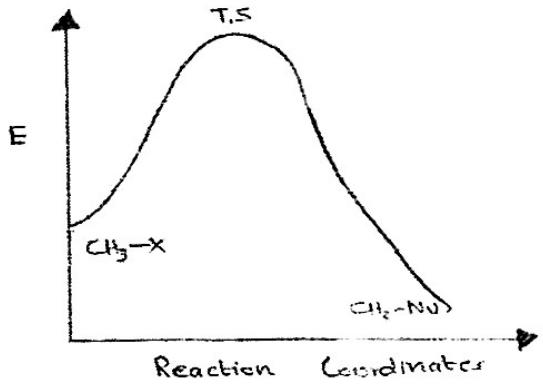


S_N2 mechanism (Substitution nucleophilic biomolecular reaction)

S_N2 reaction involves only a single step in which nucleophilic attacks from the backside of leaving group and as a result, we get corresponding inversion product and is called Walden inversion.



Transition state



The single step (rate determining step) involves two reactant species. ∴ Mechanism is called bimolecular.

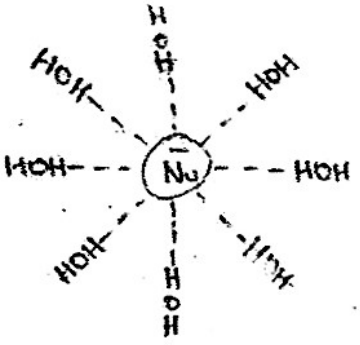
Bulky groups sterically retard the backside attack of nucleophile. As a result, S_N2 reaction in various alkyl halide follows the order $CH_3 - X > 1^0 > 2^0 > 3^0$

Allylic and benzylic halides are also highly reactive towards S_N2 reaction because the π-electrons help in the cleavage of C - X bond.

S_N2 reaction at an optically active isomer gives only a single stereoisomer and its optical activity is unpredictable (may be dextro or laevo)

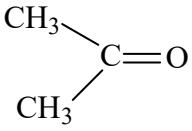
Effect of solvent on S_N2 reaction

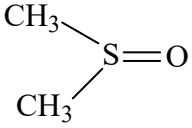
The rate of S_N2 reaction involves nucleophile also. In polar protic solvents, the nucleophile forms H - bonds with the solvent molecules.

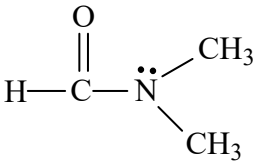


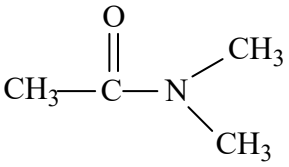
$\therefore$ The nucleophile is in a cage of H-bond and hence it has less nucleophilicity. $\therefore$ S_N2 reactions are slow in polar protic solvents.

The commonly used solvents for S_N2 reactions are polar aprotic solvents such as

(i) Acetone 

(ii) D.M.S.O 

(iii) D.M.F 

(iv) D.M.A 

	S_N1	S_N2
i)	Nucleophilic strength is unimportant	Strong nucleophiles are required
ii)	$3^0 > 2^0 > 1^0 > CH_3 - X$	$CH_3 - X > 1^0 > 2^0 > 3^0$
iii)	Polar protic solvents	Polar aprotic solvents
iv)	r = K[R - X]	r = K[R - X] [Nu^-]
v)	Rearrangements are common	Rearrangement is not possible

NOTE

The rate determining step of both S_N1 and S_N2 reactions involves cleavage of a C – X bond. C – X bond strength decreases from F to I.

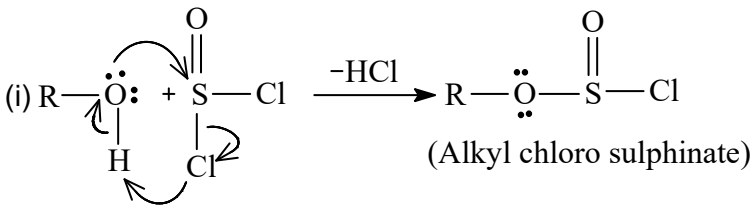
$\therefore$ Nucleophilic substitution reactivity order for various halides follows the order : R – I > R – Br > R – Cl > R – F

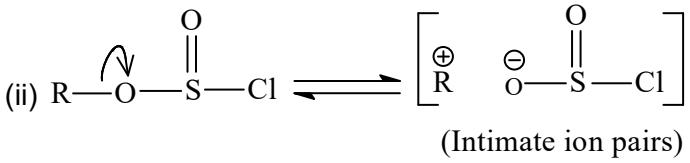
S_Ni reaction (Internal nucleophilic substitution)

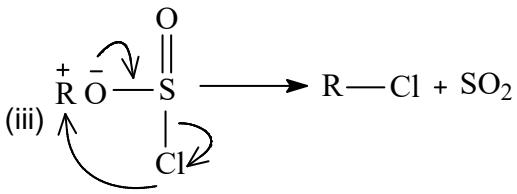
S_Ni mechanism proceeds through 100 % retention of configuration.

$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$$

Mechanism

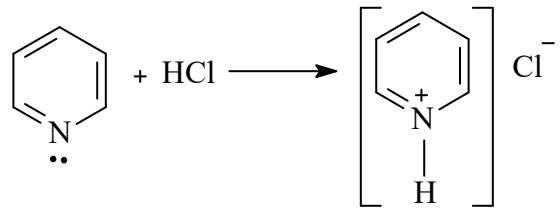




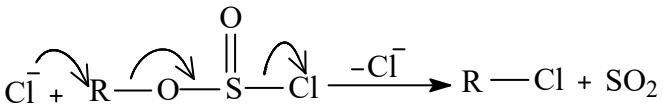


Geometry of intimate ion pair forces the Cl^- ion to attack R^+ ion from the same side in which the R – O bond is originally located. $\therefore$ we get the corresponding retention product.

If the reaction is taking place in pyridine medium, protonation of pyridine occurs.

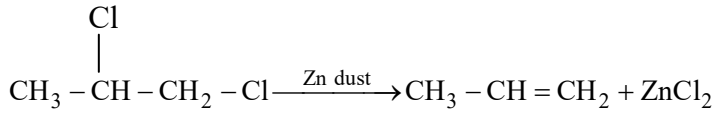


$\therefore$ The medium contains good conc. of Cl^- ions. These Cl^- ions give S_N2 reaction on alkyl chlorosulphinate and produce corresponding inversion product.

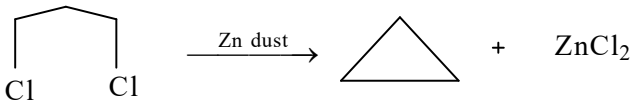


Elimination Reactions

Dehalogenation reaction



$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-Br \xrightarrow[(\text{or KI})]{\text{NaI}} CH_3-CH=CH_2+IBr+NaBr$$



Dehydrohalogenation reactions

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle H}{\underset{|}{CH_2}} \xrightarrow[-HCl]{\text{alc. KOH}} CH_3-CH=CH_2$$

The reaction involves $R-\overset{\ominus}{O}$ as nucleophile $R-\overset{\ominus}{O}$ is a bulkier nucleophile and strong base. $\therefore$ It prefers to attack $\beta-H$ and produces corresponding elimination product.

Saytzseff's rule

In a dehydrohalogenation reaction, the more substituted alkene will be the major products.

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[-HCl]{\text{alc.KOH}} CH_2=CH-CH_2-CH_3+\underset{(\text{Major})}{CH_3-CH=CH-CH_3}$$

Reason

More substituted alkenes have more number of $\alpha-H$ atoms and it is therefore stabilised by hyperconjugation.

Exceptions for Saytzseff's elimination

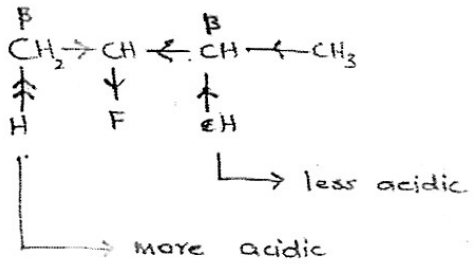
1. Dehydrofluorination reaction (Hoffmann's elimination)

$$CH_3-\underset{\displaystyle F}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[-HF]{\text{alc. KOH}} CH_2=CH-CH_2-CH_3$$

Reason

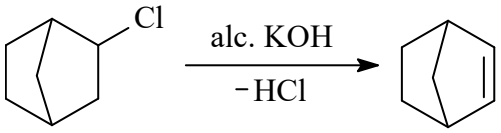
The C – F bond strength is greater than C – H bond strength

$\therefore$ The more acidic $\beta-H$ (less sterically crowded $\beta-H$) will be eliminated in first step.



2. Bredt's rule

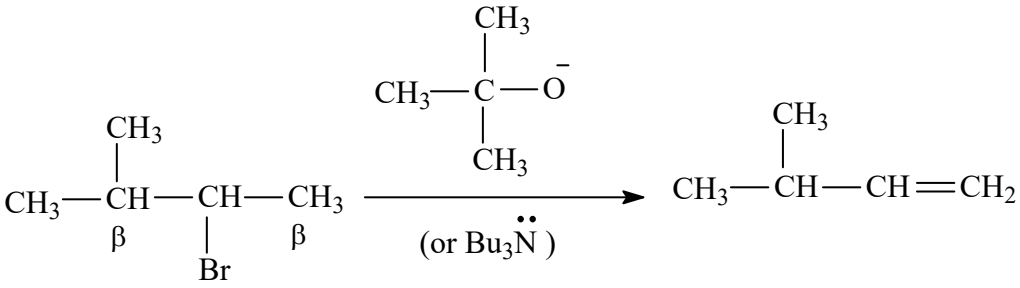
Bridgehead carbon has pyramidal geometry. In order to maintain pyramidal geometry, its hybridisation should be sp^3. Double bonds on bridgehead carbon makes the hybridisation sp^2 (planar). Therefore double bonds are not formed through bridgehead carbon.



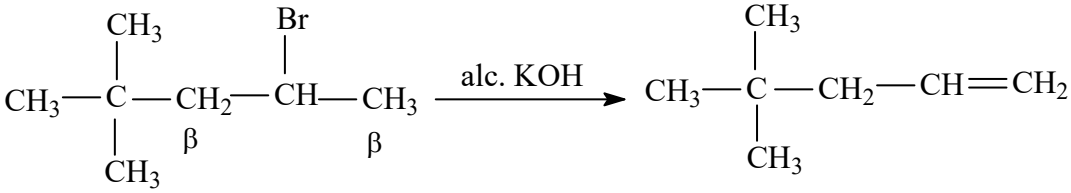
NOTE

Nucleophilic substitutions (both S_N1 and S_N2) are also difficult on bridgehead carbon.

3. Bulkier bases prefer to attack less sterically crowded $\beta - H$ and produce corresponding Hoff-man elimination.

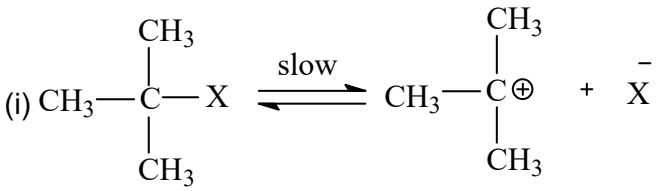


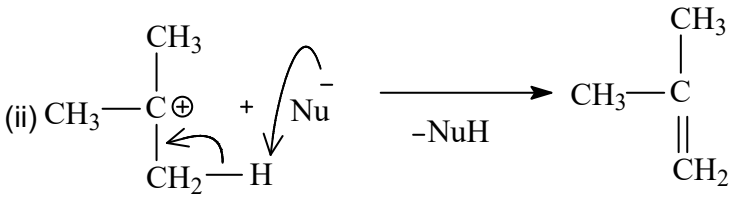
4. Bulkness around a particular $\beta - H$ directs the incoming base to another $\beta - H$ which is less sterically crowded and produce corresponding Hoffmann's elimination product.

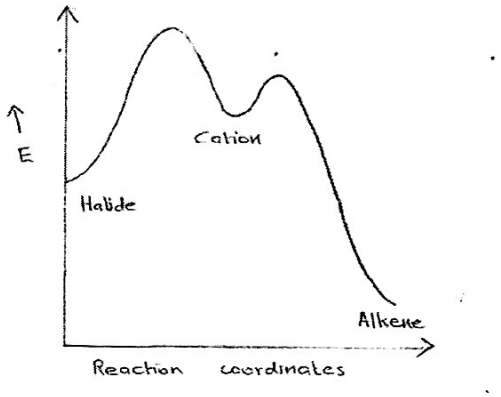


Mechanism of β - elimination reactions

1. E_1 reaction (Elimination unimolecular mechanism)

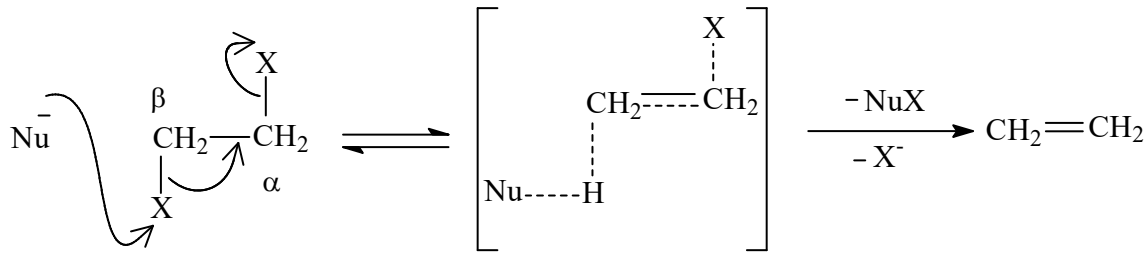


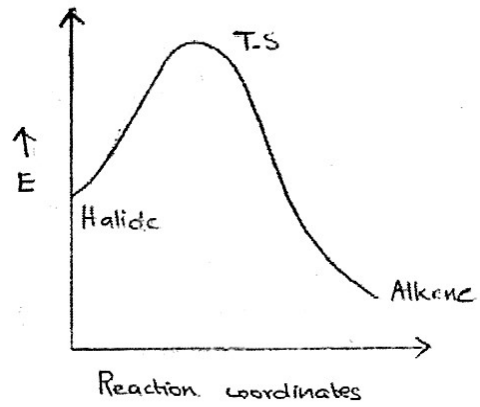




Since the rds of E_1 reaction involves the formation of a carbocation intermediate, E_1 reactivity order of various alkyl halides follows the sequence $3^0 > 2^0 > 1^0$

2. E2 mechanism (Elimination biomolecular mechanism)





Bulkness around α C, sterically retards the attack of nucleophile on that carbon and directs the incoming nucleophile to $\beta-H$. $\therefore$ E2 reactivity order of various alkyl halides follows the sequence. $3^0 > 2^0 > 1^0$.

	E1 mechanism	E2 mechanism
1	weak base	strong base
2	$3^0 > 2^0 > 1^0$	$3^0 > 2^0 > 1^0$
3	Polar protic solvent	Non-polar or weakly polar solvents
4	Better leaving group required	Better leaving group required
5	Saytzeff's rule	Saytzeff's rule

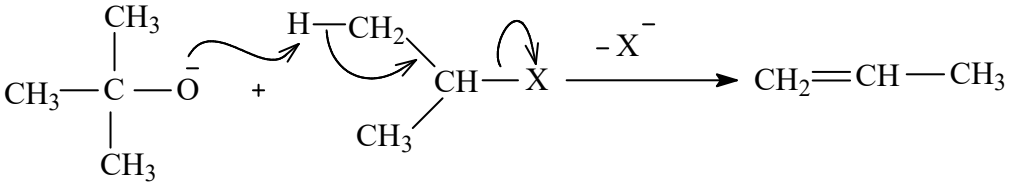
S_N2 v/s E2

	SN2 mechanism	E2 mechanism
1	$1^0 > 2^0 > 3^0$	$3^0 > 2^0 > 1^0$
2	Weak bases having strong nucleophilicity Eg : I^-, Br^-, ...	Strong bases having weak nucleophilicity Eg : $R-O^-$, NH_2^-, ...

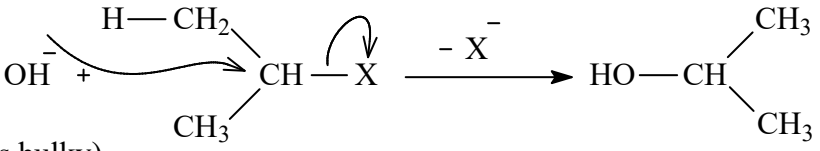
Elimination v/s substitution

1. Bulkness of nucleophile

More bulky nucleophile gives elimination & less bulky Nu^- gives substitution.



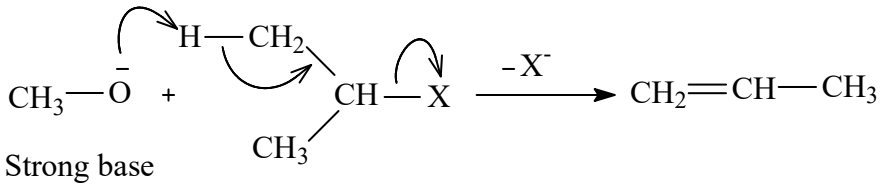
(more bulky)



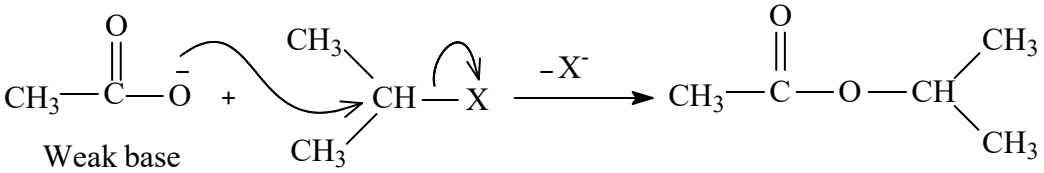
(less bulky)

2. Basicity of nucleophile

Strong bases give elimination reaction where as weak base gives substitution



Strong base



Weak base

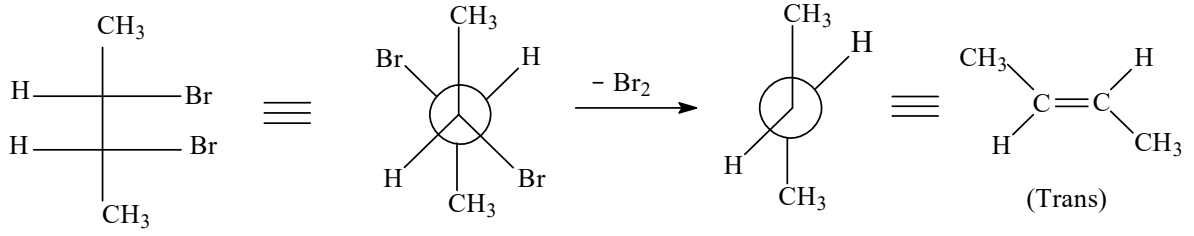
3. Temperature

Elimination reaction involves cleavage of large number of bonds. It requires high activation energy. ∴ High temperature favours elimination reaction.

Stereochemistry of E2 elimination

The stereo electronic requirement (SER) for E2 elimination reaction is that the groups to be eliminated are conformationally anti to each other. The reason for this is that the bonding orbitals of groups to be eliminated are in same plane so as to overlap to form π-bond (anti-periplanar conformation)

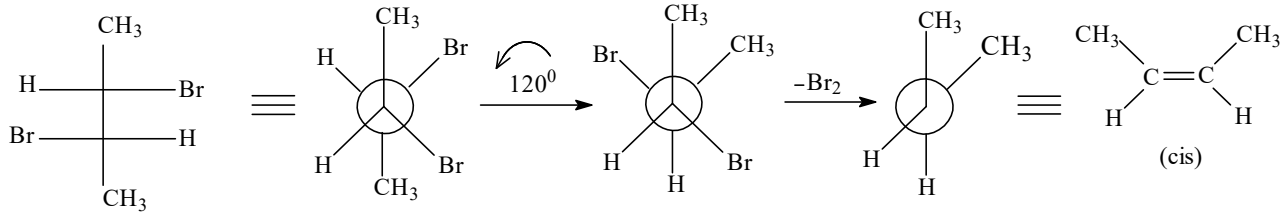
eg : (i) Debromination of meso-2,3-dibromo butane

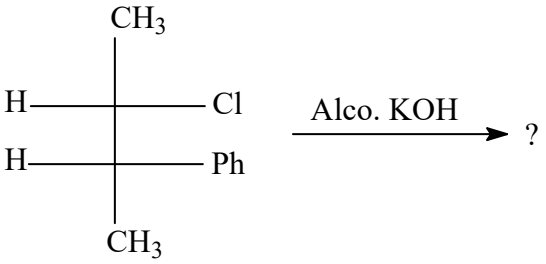


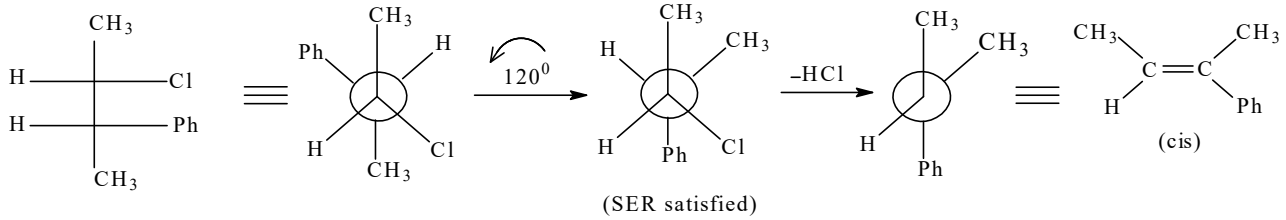
(S.E.R. statisfied)

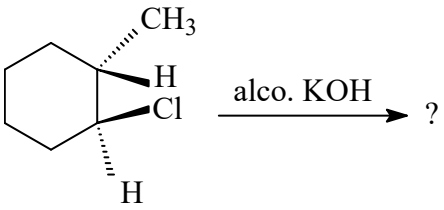
(Trans)

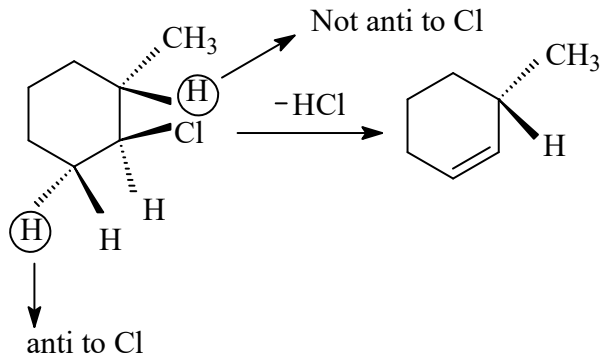
(ii) Debromination of optically active 2,3-dibromobutane











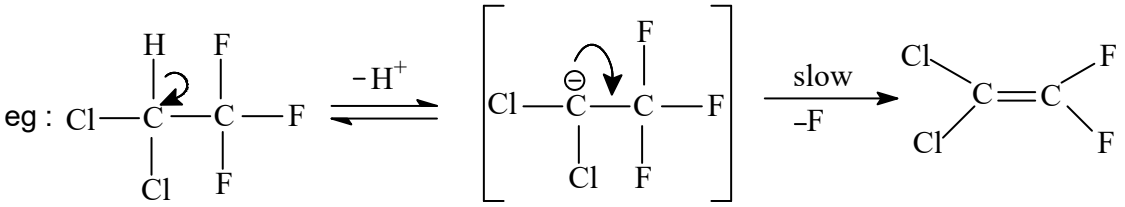
E_{cb}^{1} mechanism (Elimination unimolecular conjugate base mechanism)

In E_{cb}^{1} mechanism, $\beta - H$ eliminates first and then the leaving group.i.e, reaction proceeds through a carbanion intermediate (conjugate base)

Conditions for E_{cb}^{1} mechanism

(i) Presence of poor leaving group

(ii) Presence of strongly acidic H



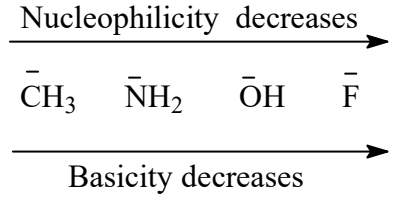
conjugate base

Nucleophilicity and basicity

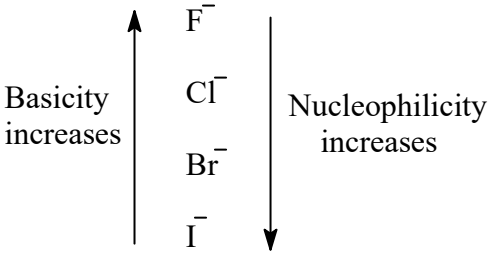
They are chemical species having at least one lone pair with or without – ve charge.

The ability of a reagent to attack electron deficient carbon is called nucleophilicity & that to attack electron deficient H is called basicity.

For reagents having the attacking atom on same period of periodic table, nucleophilicity is parallel to basicity.



If the attacking atom is in the same group of periodic table, nucleophilicity is antiparallel to basicity.



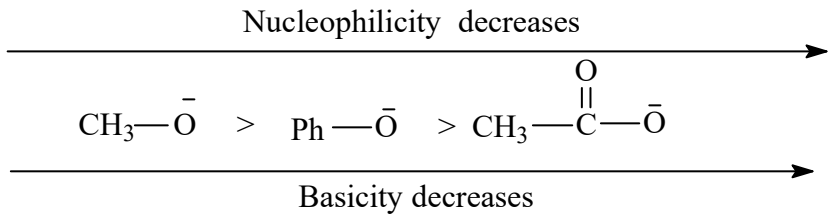
- In polar protic solvents, smaller F^- ions hydrated, strongly and hence are less nucleophilic. $\therefore$ The nucleophilicity of halide ions in polar protic solvents follow the order :

$$F^- < Cl^- < Br^- < I^-$$

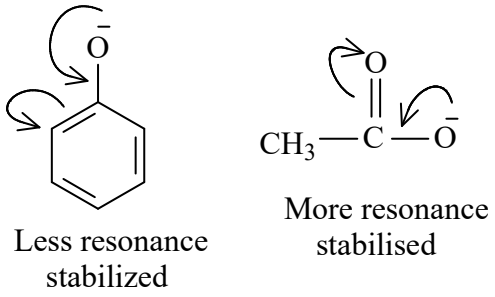
- In polar aprotic solvents, the hard acid $\overset{\oplus}{C}$ prefer hard base such as F^-. ∴ In polar aprotic solvents, the nucleophilicity follows the order :

$$F^- > Cl^- > Br^- > I^-$$

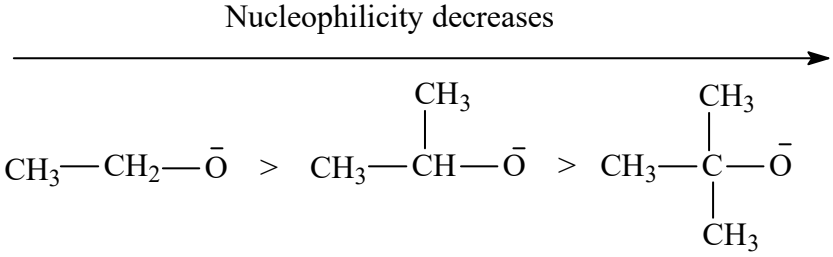
- If the attacking atom is same, nucleophilicity of reagent is parallel to basicity.



NOTE



- Nucleophilicity of a reagent decreases with increase in bulkness but basicity is not much affected by bulkness of reagent.



III. Reaction with metals

a. Reaction with Na (Wurtz reaction)

$$R-X+2Na+X-R \xrightarrow[-2\,NaX]{Ether} R-R \quad (X \rightarrow Cl, Br)$$

Ionic mechanism

(i) $R-X+2Na \longrightarrow \overset{-}{R}\overset{+}{Na}+NaX$

(ii) $\overset{-}{R}\overset{+}{Na}+R-X \longrightarrow R-R+NaX$

R^- is a strong base. ∴ we can expect elimination product also in this reaction.

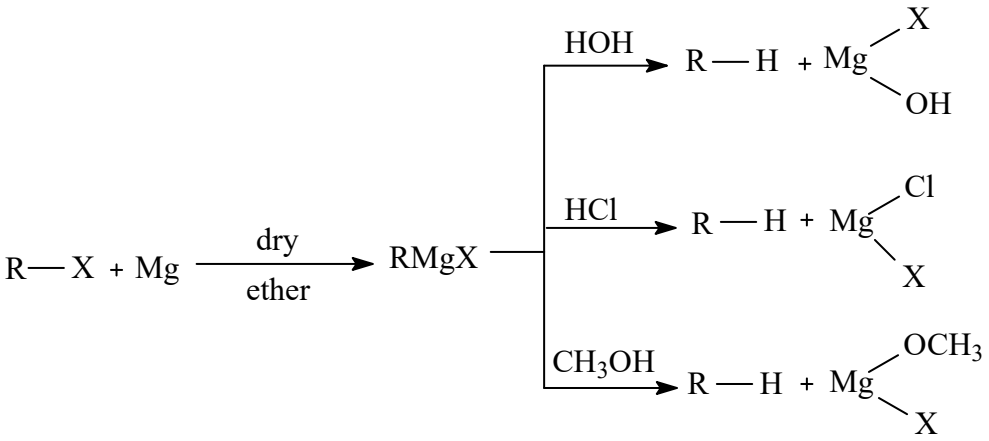
Radical mechanism

(i) $R-X+Na\longrightarrow \dot{R}+NaX$

(ii) $\dot{R}+\dot{R}\longrightarrow R-R$

b. Reaction with Mg

Alkyl halides react with Mg in the presence of dry ether producing corresponding Grignard reagent. Grignard reagent reacts with compounds containing active H to produce corresponding hydrocarbons.



Mechanism

(i) $2R-X+2MgX\longrightarrow R-R+2\dot{M}g-X$

(ii) $R-X+\dot{M}gX\longrightarrow \dot{R}+MgX_2$

(ii) $\dot{R}+\dot{M}gX\longrightarrow RMgX$

c. Reaction with Zn (Frankland's reaction)

$R-I+Zn+I-R\longrightarrow R-R+ZnI_2$

NOTE

The reaction involves highly inflammable dialkyl zinc (R_2Zn) intermediate.

Chemical properties of aryl halides

I. Nucleophilic substitution reactions

Nucleophilic substitution in aryl halides are difficult as compared to alkyl halides due to :

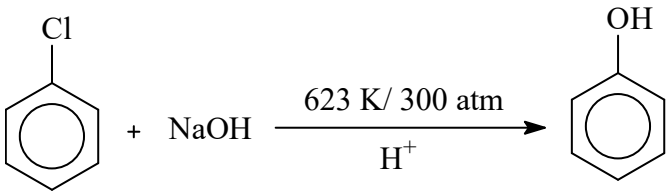
1) Resonance

2) The carbon in C – X bond is sp^2 hybridised (electronegative). ∴ The C of holds C – X bond pair more strongly.

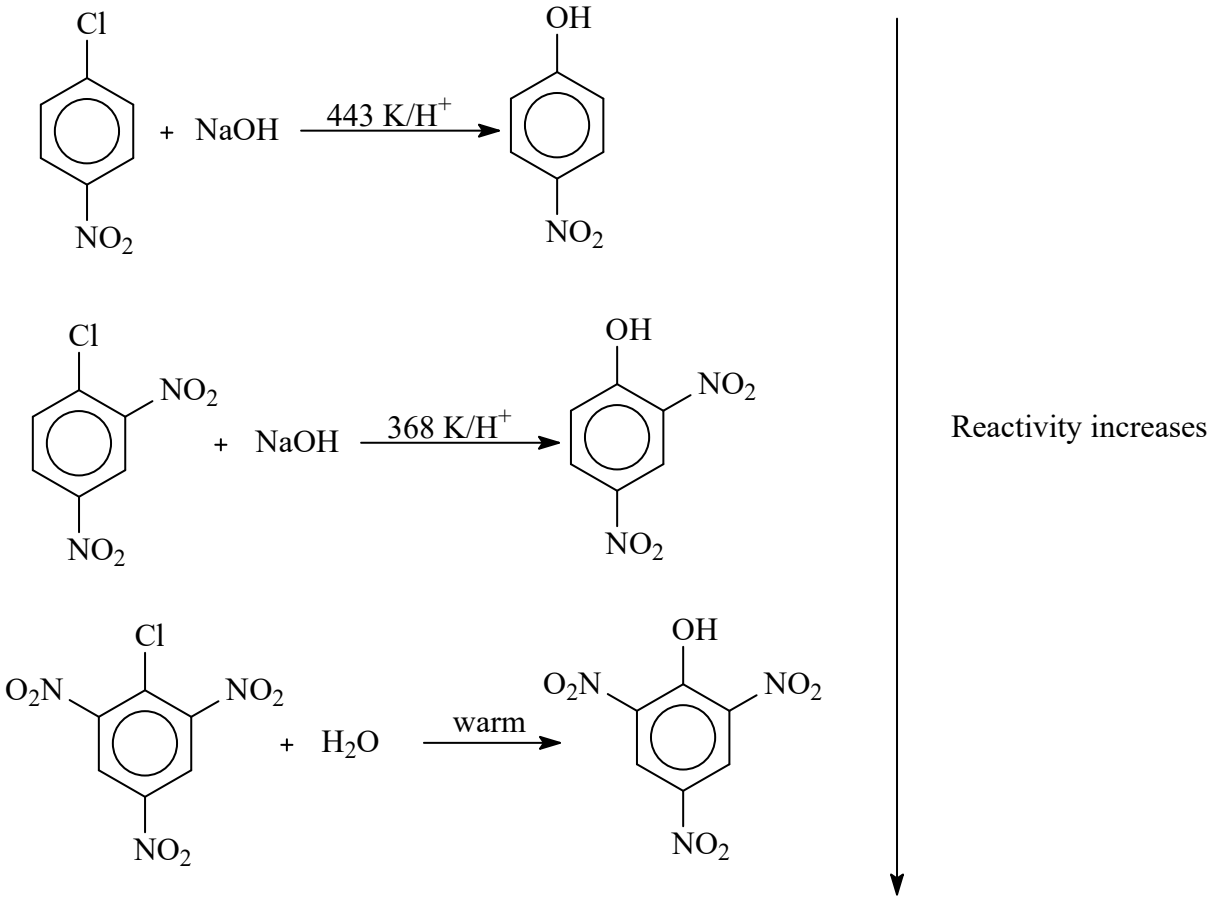
3) The phenyl carbocation  is highly unstable. ∴ S_N1 reactions are difficult in aryl halides.

4) Electron rich nucleophile experiences repulsion with electron rich aromatic ring.

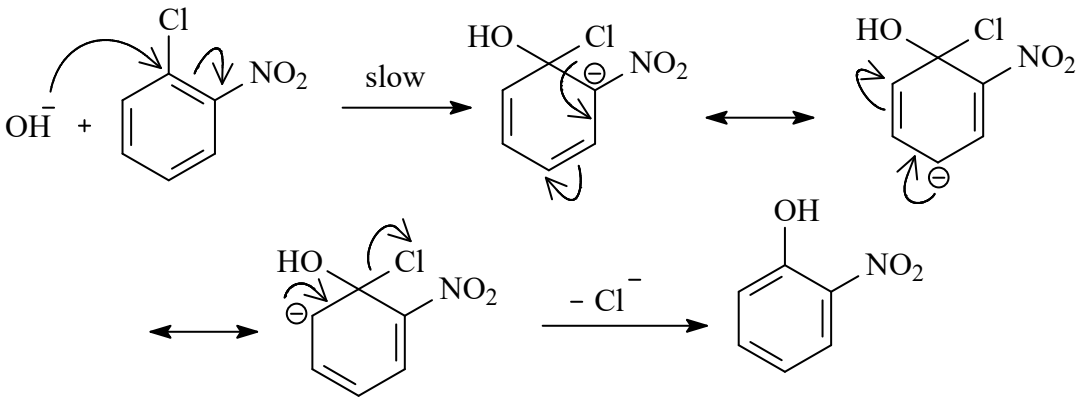
a. Substitution with OH^-



Presence of electron withdrawing groups such as – NO_2, – CN, – SO_3H etc. on ortho, para positions increases the rate of reaction.



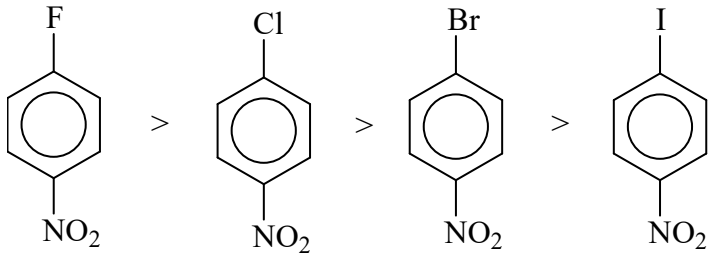
Mechanism (Addition-elimination mechanism)



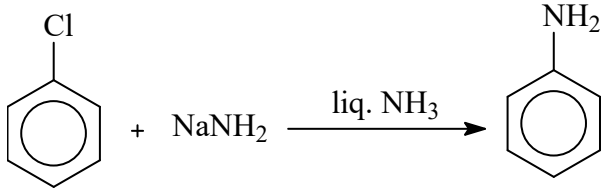
NOTE

Strongly electron withdrawing F decreases electron density on α -carbon through its – I effect. $\therefore$ Aryl fluorides gives aromatic nucleophilic substitution faster than all other aryl halides.

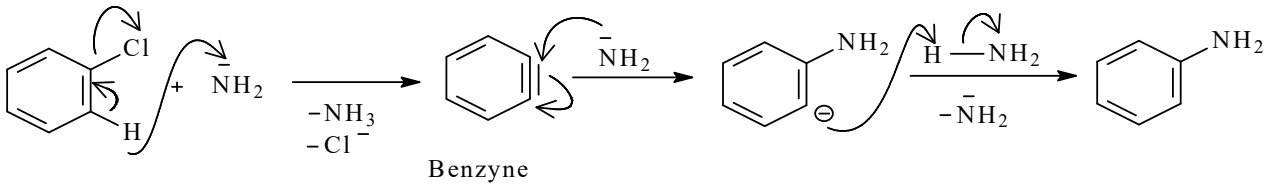
Overall reactivity order :



b. Substitution by NH_2^-

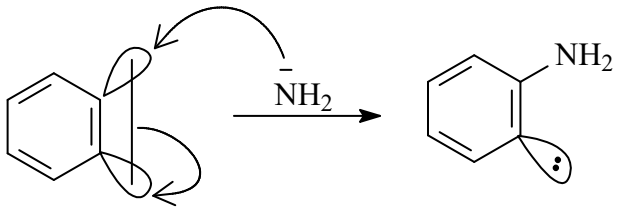


Mechanism (Elimination - addition mechanism)



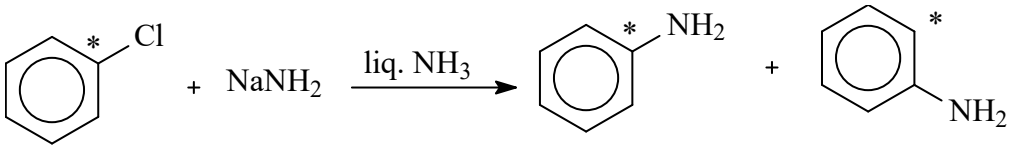
Benzyne

In benzyne intermediate, the two triply-bonded carbons are sp^2 hybridised, i.e, the third bond is formed by the overlapping of two sp^2 hybridised orbitals from each carbon. The anion generated from benzyne has its unshared electron pair on one of the sp^2 hybridised orbital.



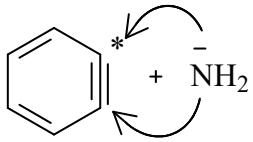
$\therefore$ Only inductive effect (both – I and + I) can affect the electrons of benzyne intermediate and the corresponding anion.

Applications



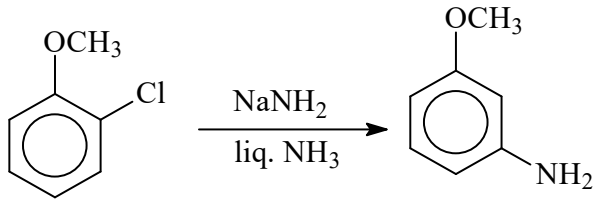
(41 %) (53 %)

Reason



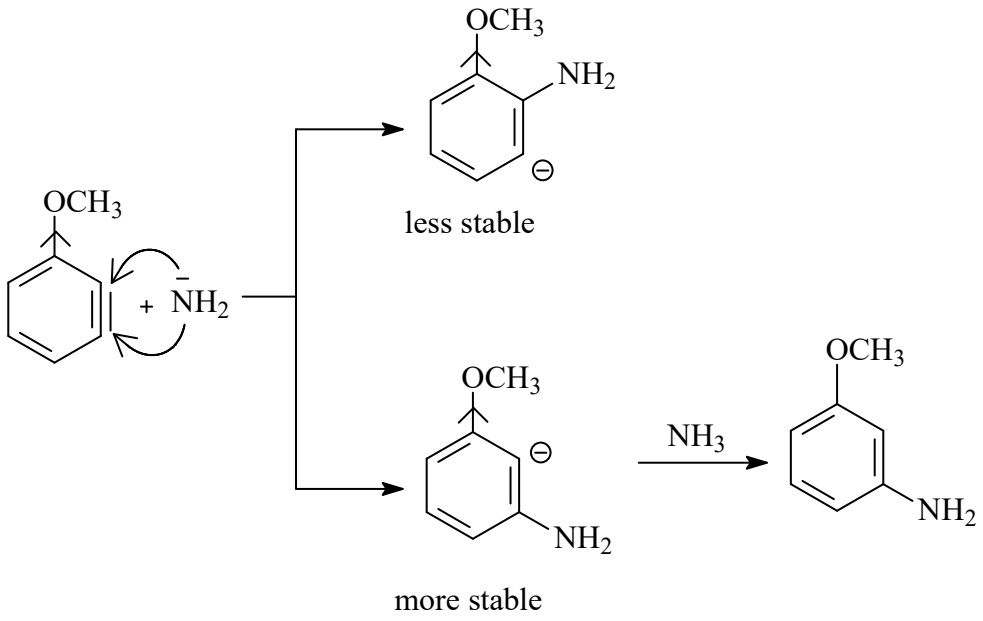
The attack of NH_2^- at the labelled carbon is partially hindered by the leaving X^- ions from this position.

2.

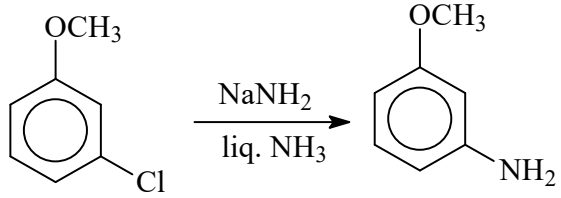


o - chloro anisole m - anisidine

Reason



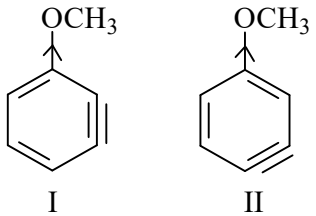
3.



m - anisidine

Reason

There is the possibility for following benzyne intermediates

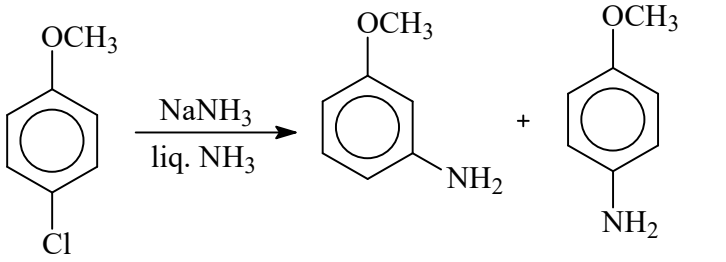


I II

Intermediate I is more stable due to – I effect of – OCH_3 group.

$\therefore$ From I, m - anisidine is generated as final product.

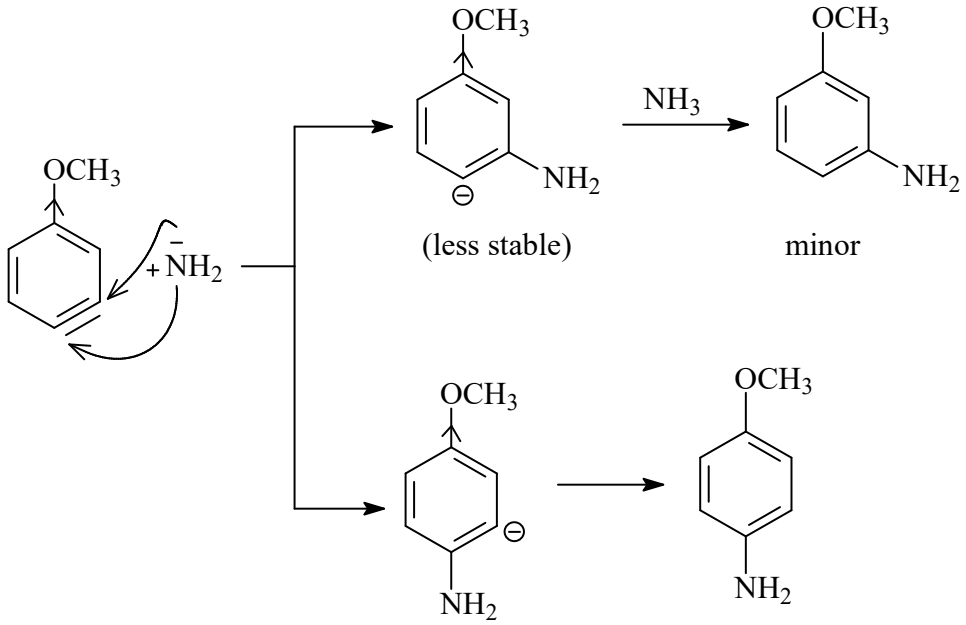
4.



(p - chloro anisol) (m - anisidine) (p - anisidine)

Major

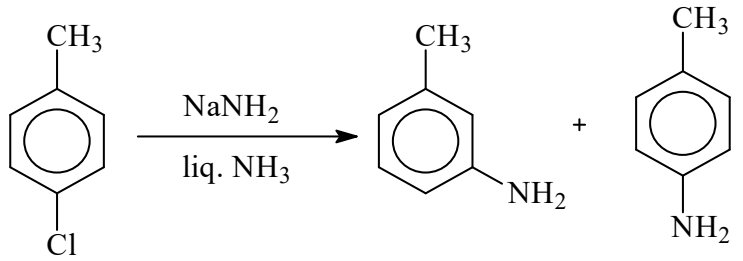
Reason



(less stable) minor

(more stable) major

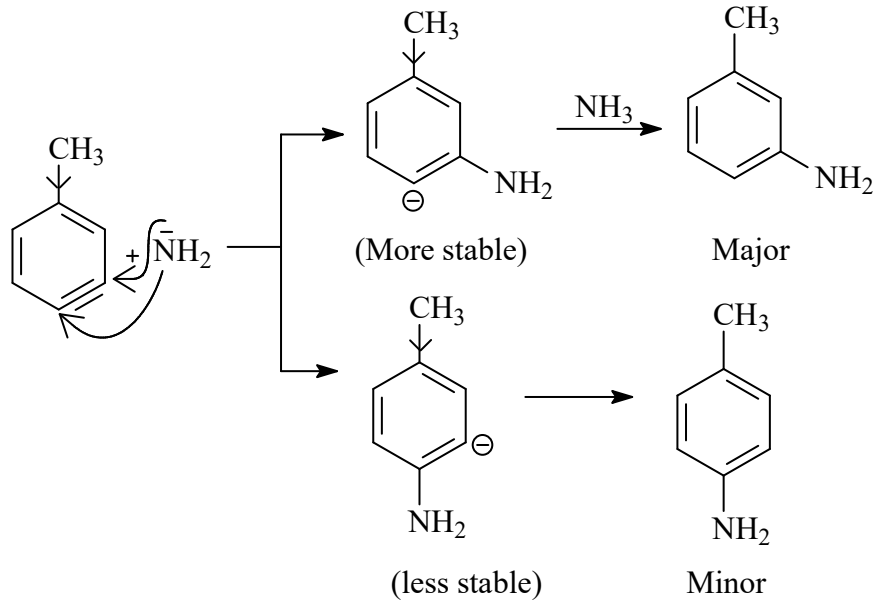
5.



p- chloro toluene m - toludine p - toludine

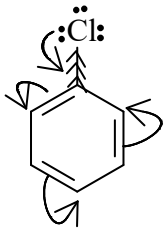
(Major)

Reason

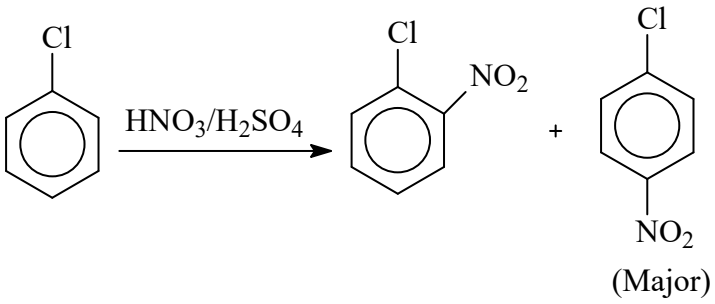


Electrophilic substitution reactions

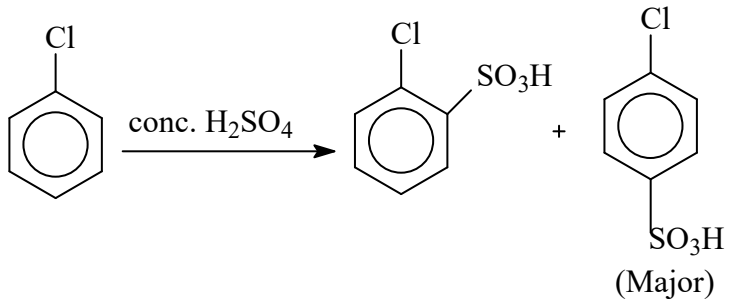
Halogens are ring deactivating groups for electrophilic substitution reactions through their strong – I effect, but they are o, p -directing groups for electrophiles through their weak + R effect. ∴ Halogens are o,p-directing deactivators, i.e, reactivity of the ring is controlled by its strong – I effect and orientation of electrophile is controlled by its weak + R effect .



a. Nitration

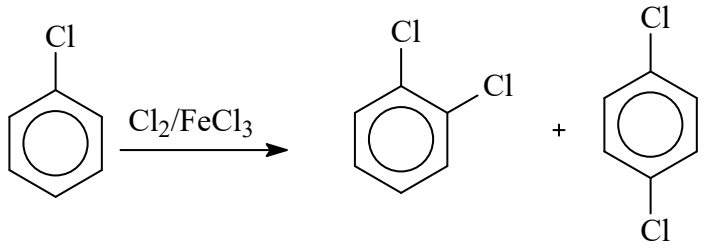


b. Sulphonation



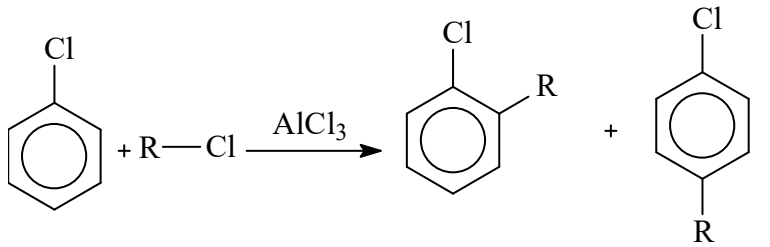
(Major)

c. Halogenation



(Major)

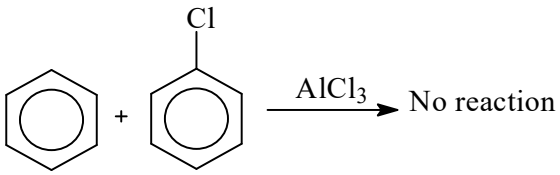
d. Friedel craft's reaction

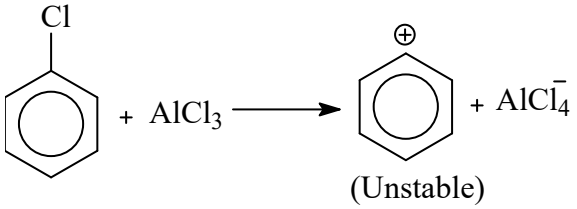


(Major)

NOTE

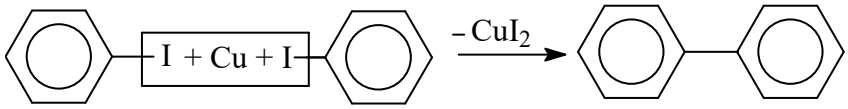
Benzene with chlorobenzene does not give friedel craft's reaction because the phenyl cation is highly unstable.



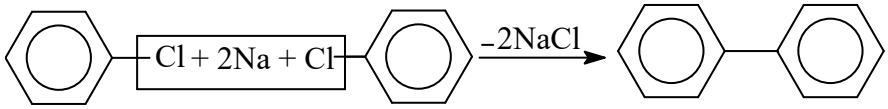


III. Reaction with metals

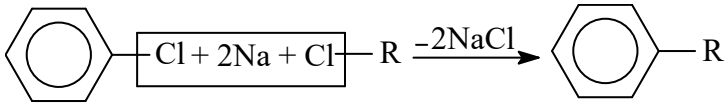
a. Ullmann reaction



b. Fittig reaction



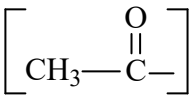
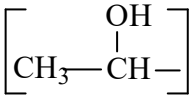
c. Wurtz-fittig reaction



Polyhalogen compounds

I. Chloroform ($CHCl_3$)

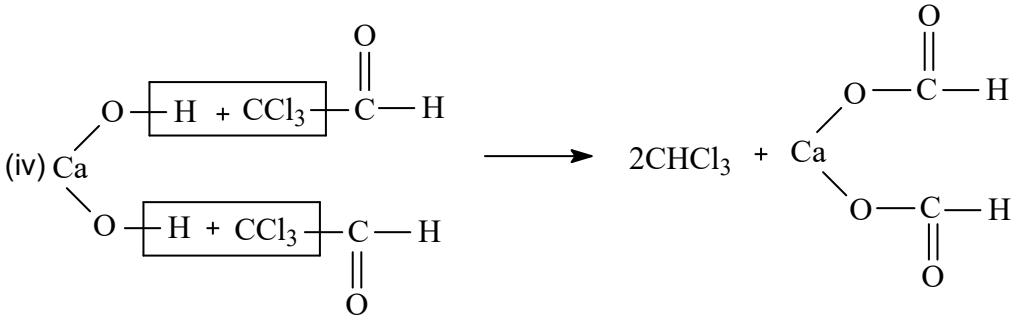
Preparation

Compounds containing methyl ketone  or methyl carbinol  bonded to C or H reacts with bleaching powder to produce chloroform.

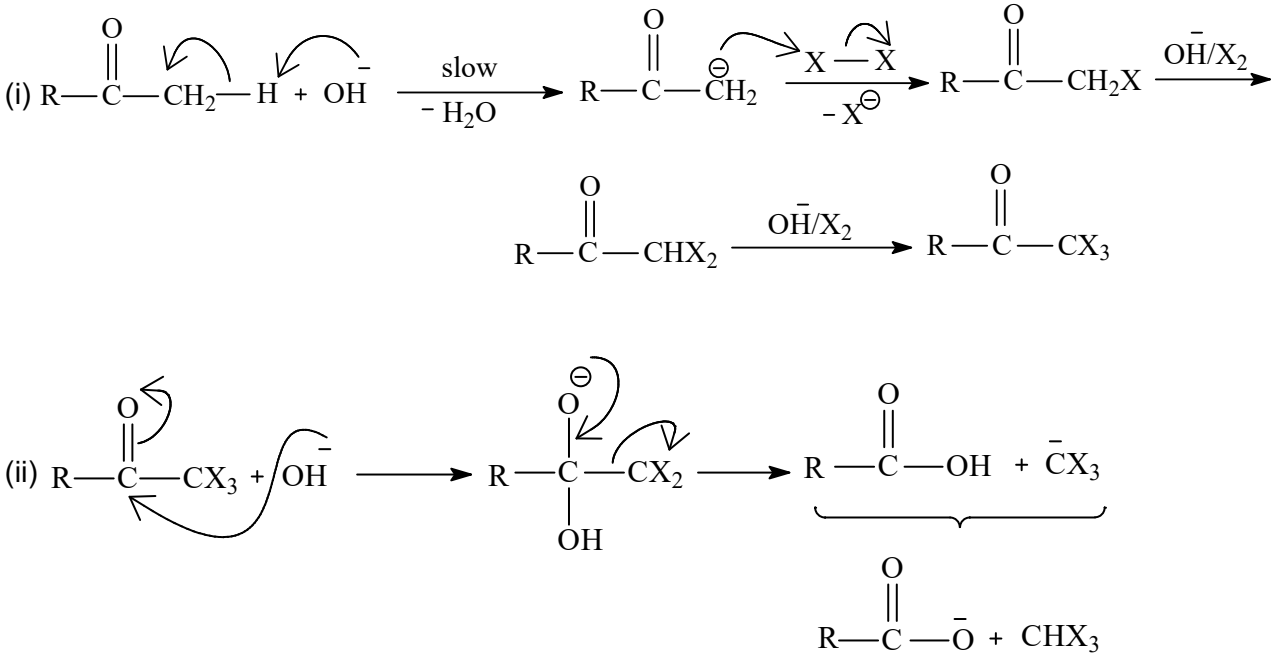
(i) $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

(ii) $CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - H + Cl_2 \longrightarrow CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - H + 2HCl$

(iii) $CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - H + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3 - \overset{\displaystyle O}{\overset{\|}{C}} - H} + 3HCl$



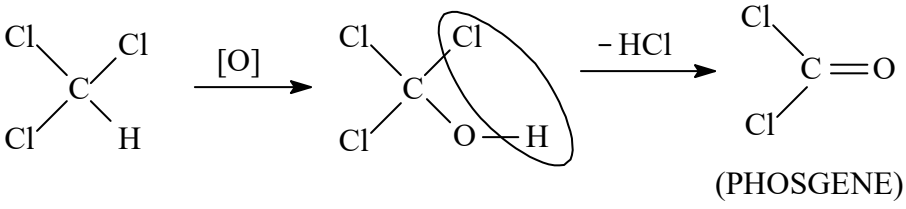
Mechanism of haloform reaction



Since halogen molecules is not involved in rate determining step, all halogens give chloroform reaction at same rate.

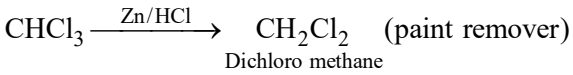
Chemical properties

1. Oxidation

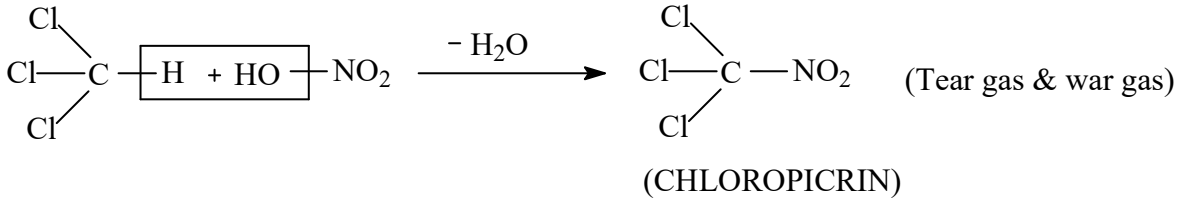


(PHOSGENE)

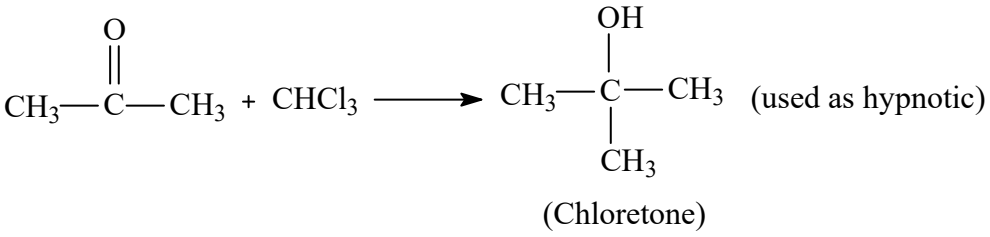
2. Reduction



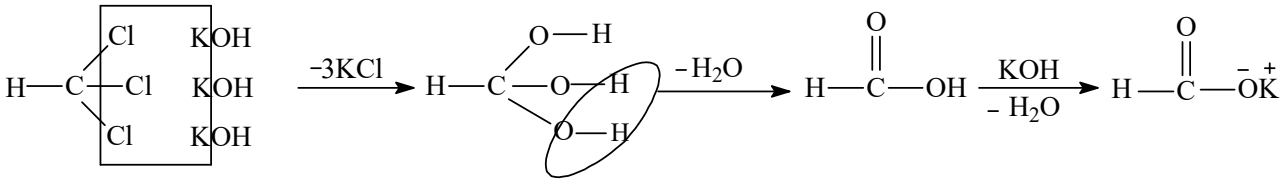
3. Nitration



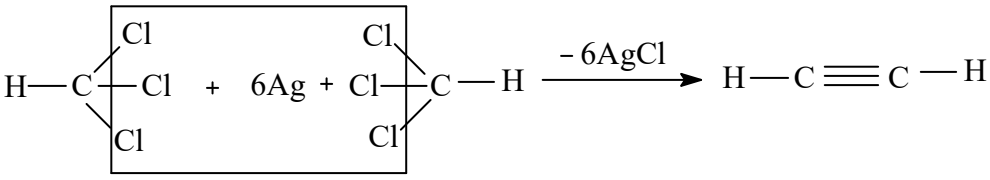
4. Reaction with acetone



5. Hydrolysis



6. Reaction with Ag powder

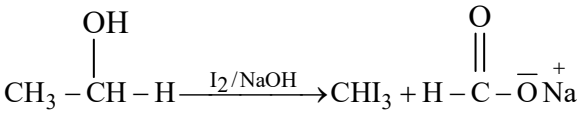


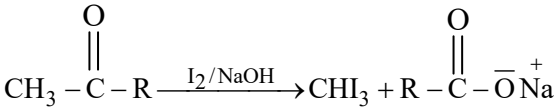
II. Iodoform (CHI_3)

→ **Antiseptic**

Preparation (Iodoform test)

Compound containing methyl ketones or methyl carbinols bonded to C or H reacts with I_2 and NaOH to produce yellow crystals of iodoform





III. CCl_4 (pyrene)

Preparation

$$CS_2 + 2S_2Cl_2 \rightarrow CCl_4 + 6S$$

CCl_4 is a well-known fire extinguisher. After using CCl_4 as a fire extinguisher in a room, the room should be well-ventilated. Because CCl_4 at high temperature reacts with steam to produce poisonous gas phosgene.

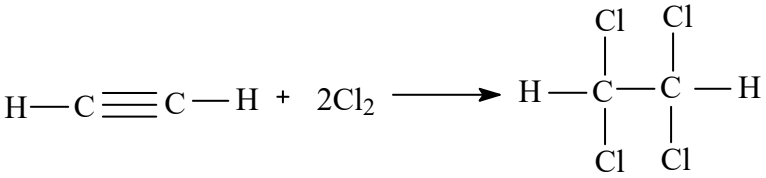
$$CCl_4 + H_2O_{(v)} \xrightarrow{\Delta} COCl_2 + 2HCl$$

IV. Freons

Chlorofluorocarbons of CH_4 and C_2H_6 are collectively called freons.

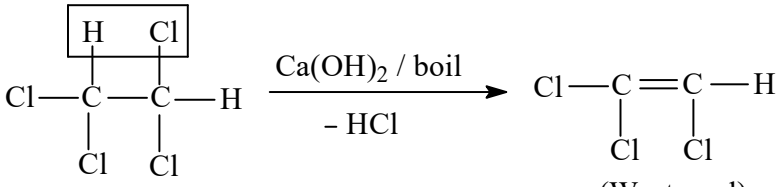
CF_2Cl_2 is used as a refrigerant and it is also causes ozone layer depletion

V. Westron ($C_2H_2Cl_4$)



(westron)

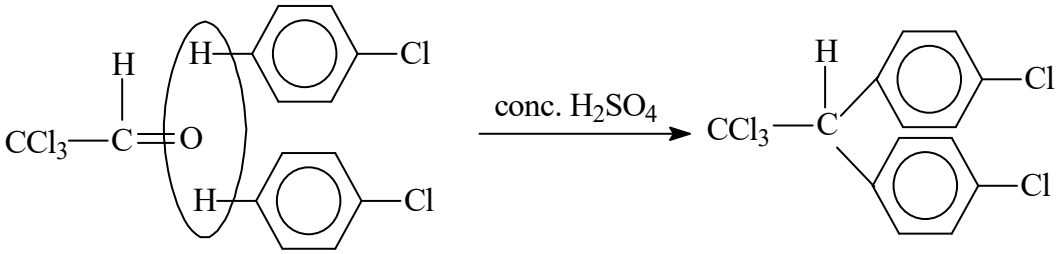
VI. Westrosol



(Westrosol)

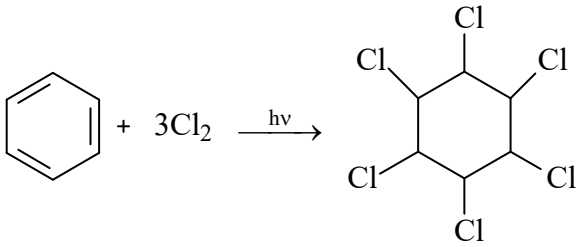
Both westron and westrosol are used as solvents for points varinishes, etc.

VIII. D.D.T (Dichloro Diphenyl Trichloro ethane)



DDT

VIII. BHC (Benzene Hexa Chloride)



$(C_6H_6Cl_6)$

It is a famous insecticide known under the name gammexane, 666 or lindane