

CHAPTER - 7

HALOALKANES & HALOARENES, STEREOCHEMISTRY

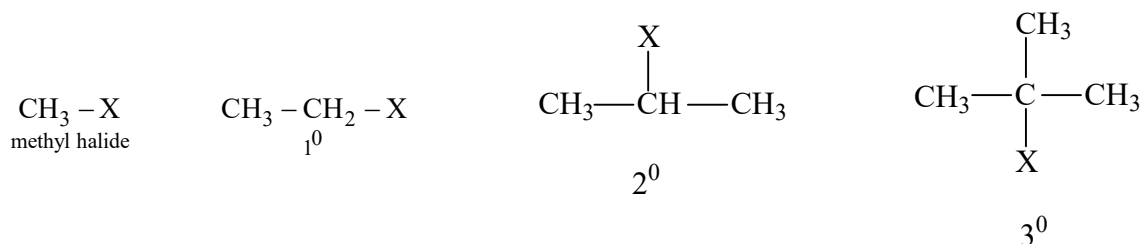
Organic Halogen Compound

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

Classification

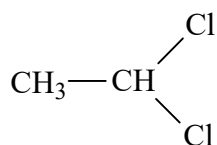
1. Alkyl halides

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



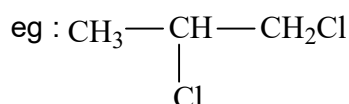
2. Gem dihalides/Alkylidene halides

Two halogen atoms are present on a single C.



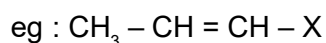
3. Vicinal Dihalides/Alkylene halides

Two halogen atoms are present on two adjacent C atoms.



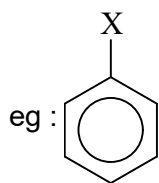
4. Vinyl halides

Halogen is bonded to a double-bonded carbon.

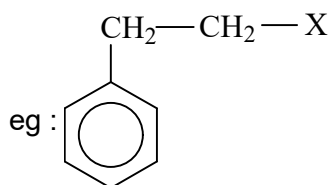


5. Aryl Halides

Halogen is bonded to aromatic ring.

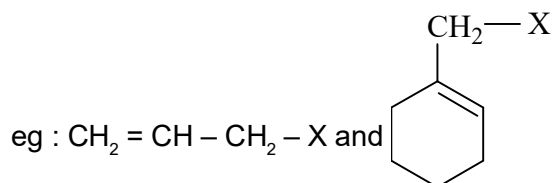
**6. Aralkyl Halides**

Halogen is bonded to side-chain

**7. Allylic Halides**

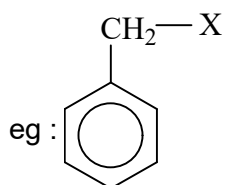
An sp^3 hybridised C bonded to sp^2 hybrid C of $C = C$ double bond is called allylic carbon.

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

**8. Benzylic Halides**

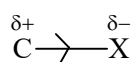
An sp^3 hybridised C bonded to sp^2 hybridised C of aromatic ring is called benzylic C.

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

**Nature of C - X bond**

Halogen is more electronegative as compared to C.

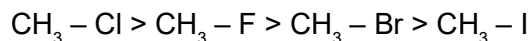
\therefore C - X bond pair is slightly shifted towards X, \therefore C - X bond is polar in nature.



NOTE

The μ of $\text{CH}_3 - \text{Cl}$ is slightly greater than that of $\text{CH}_3 - \text{F}$ due to greater C – Cl bond length as compared to C – F bond length (magnitude of change is more in F)

Dipole moment order :



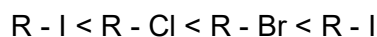
Physical properties of organic halogen compounds

1. Melting & boiling points

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

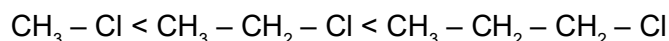
Alkyl halides

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

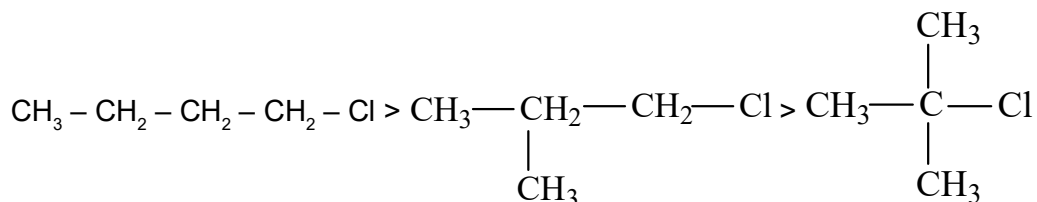


Reason : Surface area increases

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

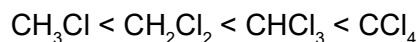


c) For isomeric halides, boiling point decreases with increase in branching



Reason : Surface area decreases

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



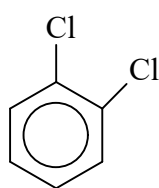
Reason : Surface area increases

Aryl Halides

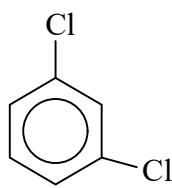
For same aryl group boiling point increases from F to I and for same halogen atom.

NOTE

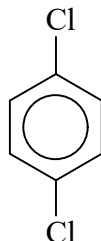
Boiling point of isomeric dichloro benzenes are almost identical but melting point of p-dichlorobenzene is much more greater as compound to o - and m - isomers. \therefore p-isomers is symmetrical and therefore can fit closely in the crystal lattice. Due to the same reason, p-isomer is least soluble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



B.P 453 K
M.P 256 K



446 K
249 K

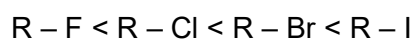


448 K
323 K

2. Density

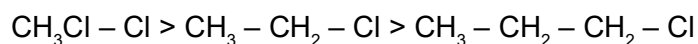
Densities of alkyl fluorides and chlorides are less than that water whereas bromides, iodides & polyhalides have greater densities as compared to water.

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

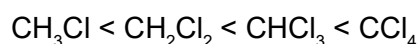


Reason : Molecular mass increases

b) Density decreases with increase in size of alkyl group



c) Density increases with increase in number of halogen atoms



Reason : molecular mass increases

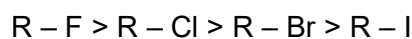
3. Solubility

Organic halogen compounds are generally polar in nature. \therefore 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.

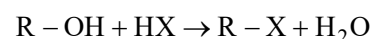
\therefore Stability of various alkyl halides follows the order :



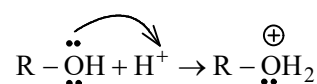
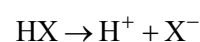
Preparation of aliphatic halogen compounds

1. Preparation from alcohols

a. Reaction with HX

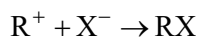
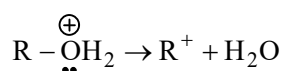


Mechanism :

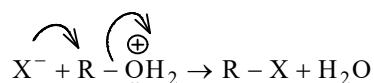


Tertiary and secondary carbocations are quite stable.

\therefore Tertiary and secondary alcohols react through S_N1 mechanism.

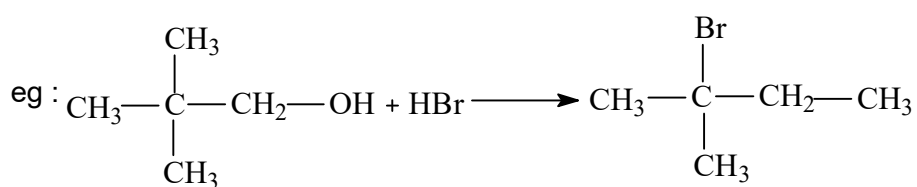


Primary carbocations are highly unstable. \therefore 1° alcohols react through S_N2 mechanism.

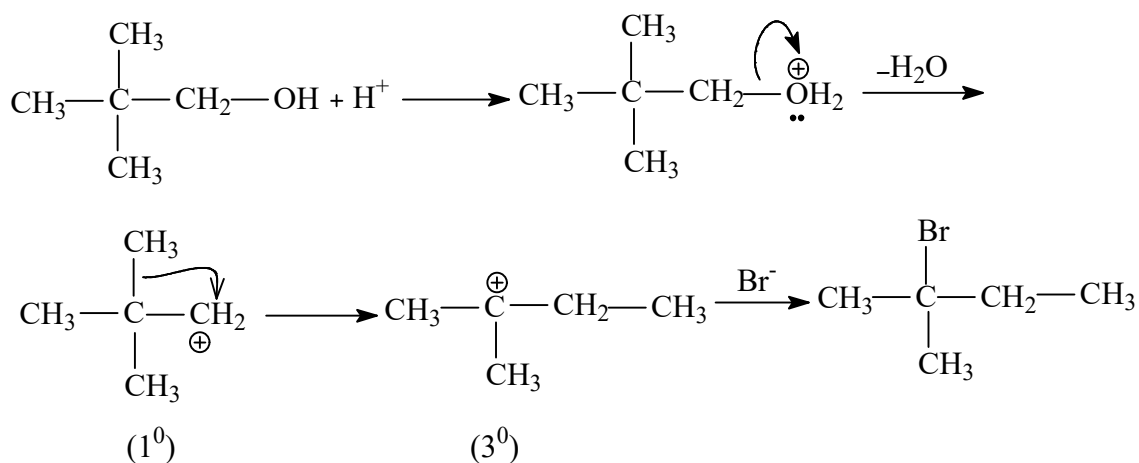


NOTE

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

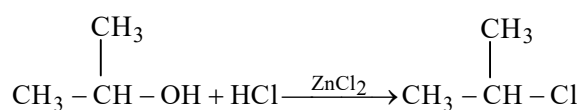
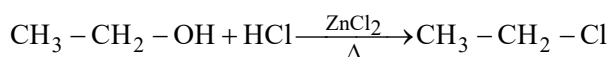


Mechanism :



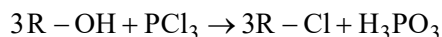
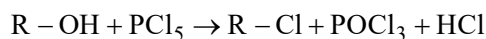
Grove's process

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



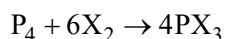
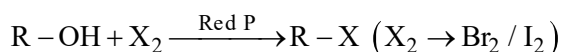
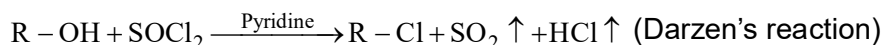
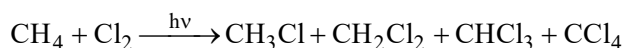
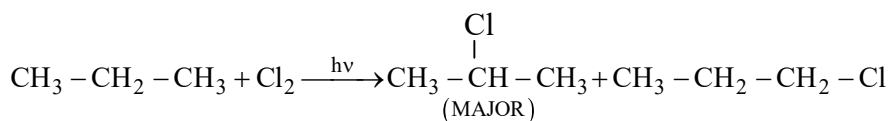
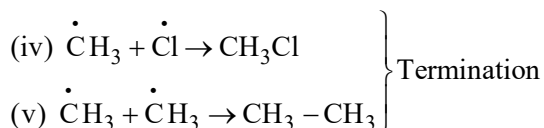
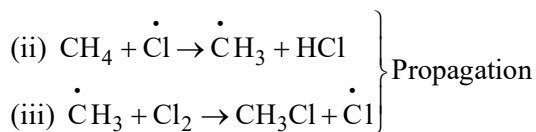
Function of ZnCl_2

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

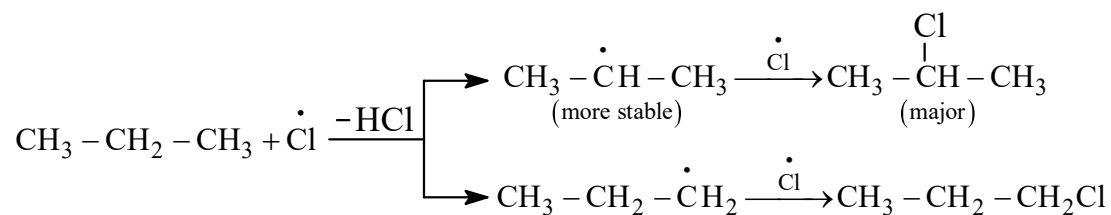
Reaction with phosphorous halides

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)

**Reaction with thionyl chloride****Free-radical halogenation of hydrocarbon****Mechanism :**

Mechanism :



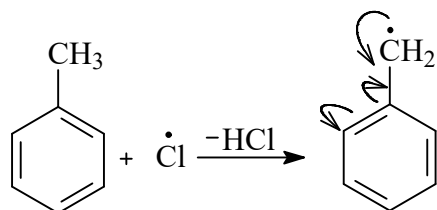
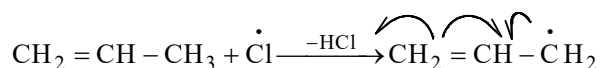
Reactivity of various H atoms towards free radical sub. depends on intermediate free radical generated. The stability of free radicals follows the order $3^\circ > 2^\circ > 1^\circ$.

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

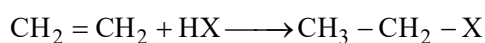
NOTE

- ♦ Allylic and benzylic free radicals are resonance stabilized.

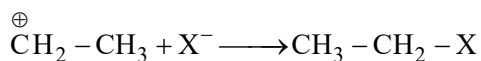
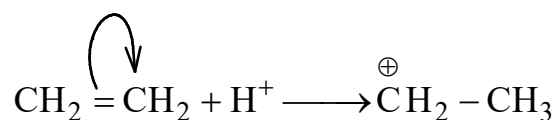
\therefore Reactivity of allylic and benzylic H towards free radical substitution reaction is greater than that of a tertiary H.



3. Electrophilic addition reaction of HX to alkenes

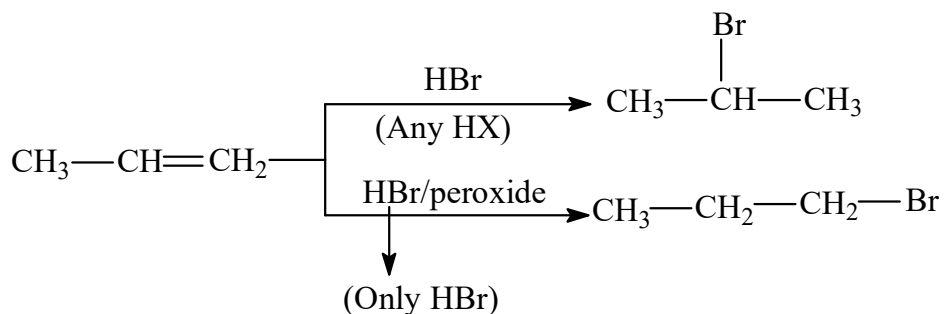
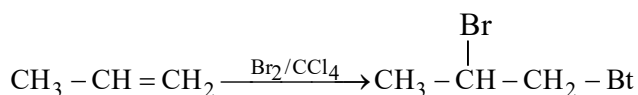


Mechanism



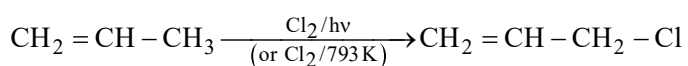
NOTE

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

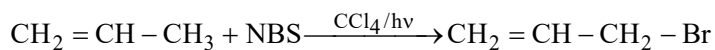
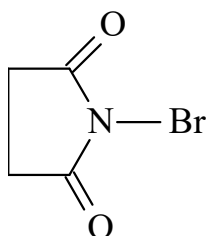
**4. Addition of halogen molecules to alkenes****Allylic and benzylic halogens**

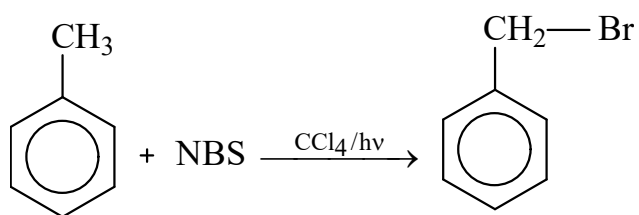
Allylic and benzylic free radicals are resonance stabilized.

∴ Free radical substitution reactions are easy at allylic & benzylic positions.



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

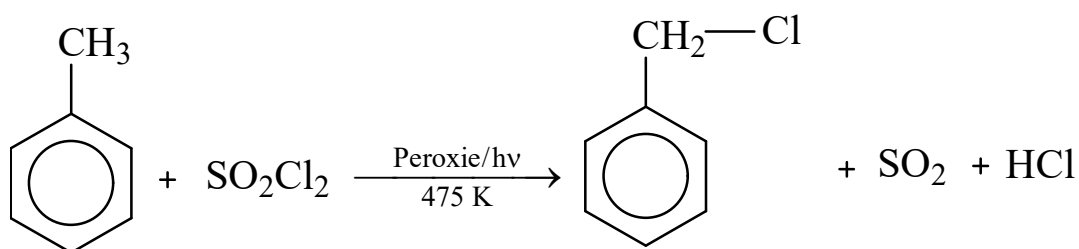
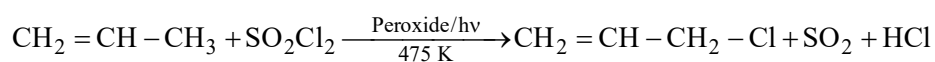




NOTE

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

A specific reagent for allylic & benzylic chlorination is SO_2Cl_2 .

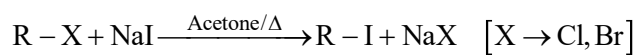


NOTE

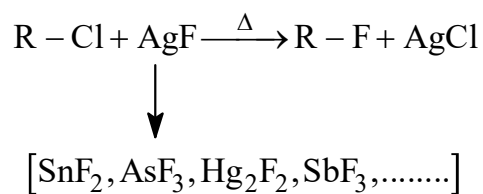
SO_2Cl_2 will also produce chlorine free radical

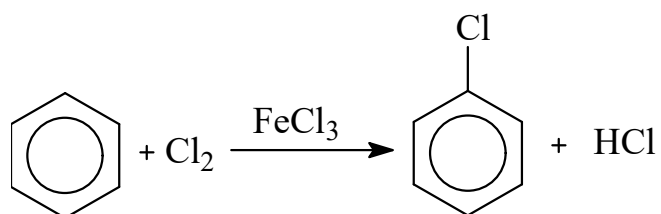
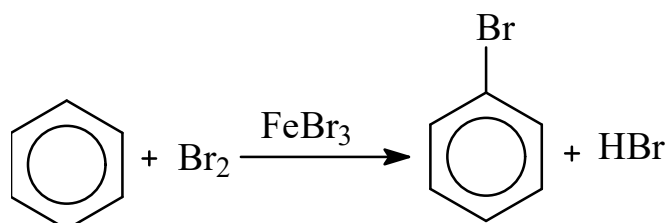
5. Halogen exchange reaction

a) Finkelstein reaction

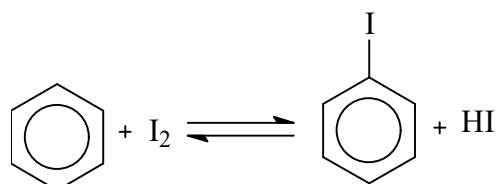


b) Swartz reaction

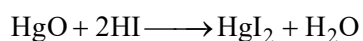
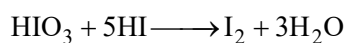
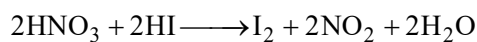
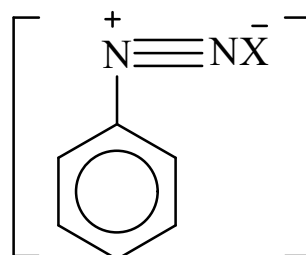


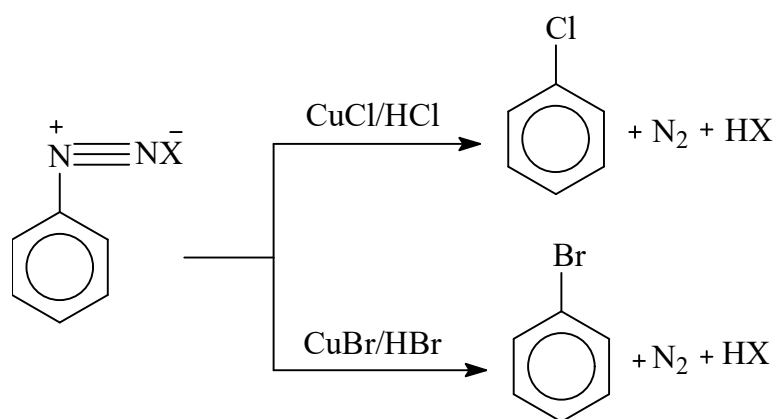
Preparation of aryl halides**1. Electrophilic substitution****a. Chlorination****b. Bromination****c. Iodination**

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

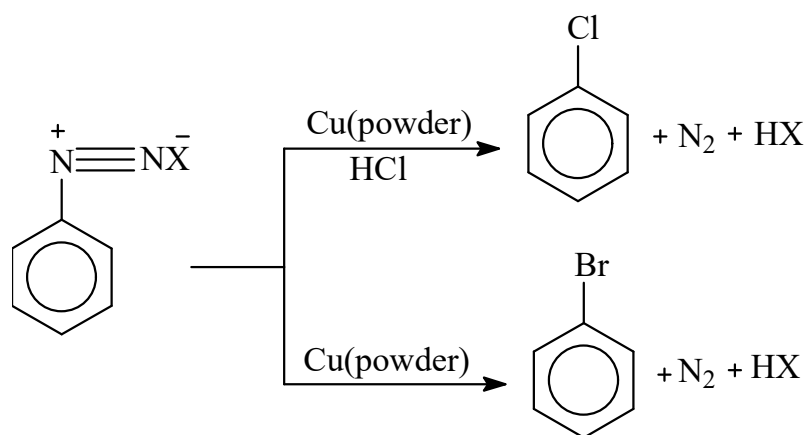


In order to avoid this problem, iodination is carried out in presence of HNO_3 , HIO_3 or HgO

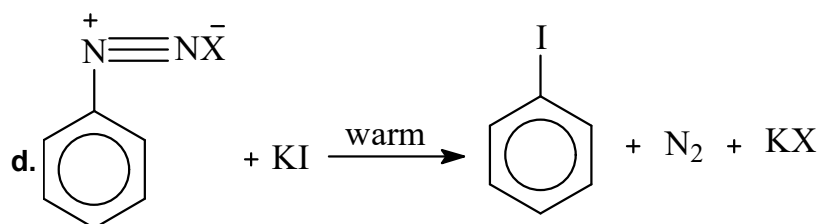
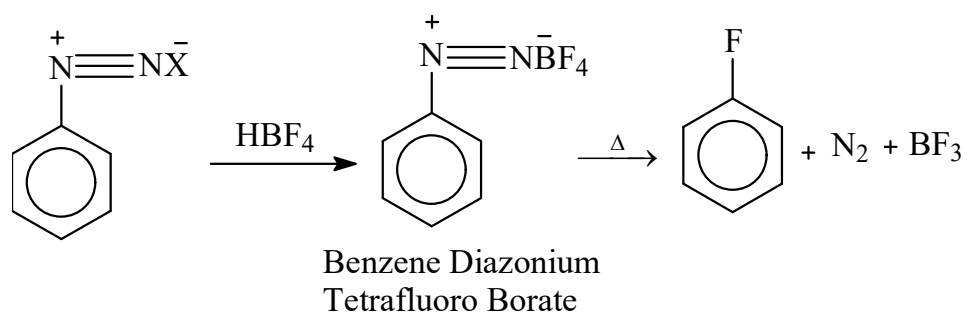
**2. Preparation from benzene diazonium salts****a. Sandmeyer's reaction**

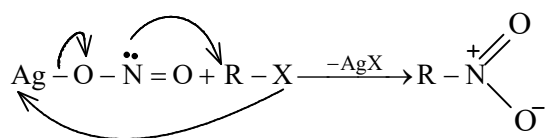
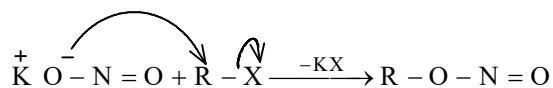
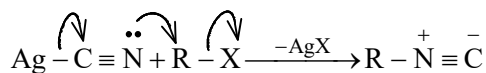
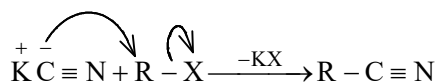
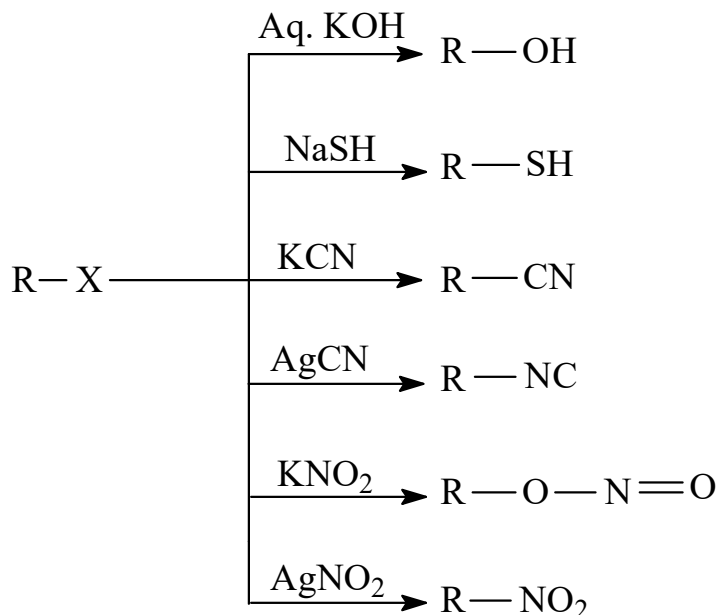


b. Gatterman's reaction



c. Balz-schiemann reaction

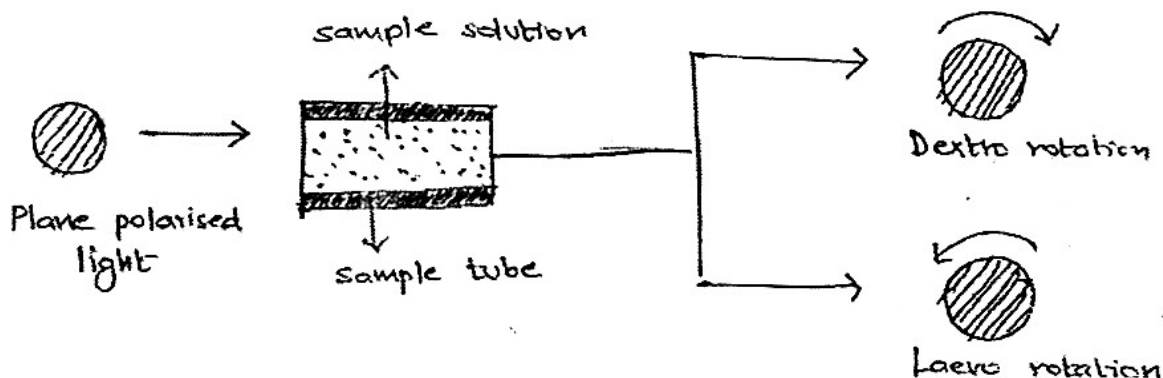


Chemical properties of alkyl halides**1. Nucleophilic substitution****Some stereochemical aspects****1. Optical activity**

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

Towards right \longrightarrow dextro rotation [$d/(+)$]

Towards left \longrightarrow laevo rotation [$\ell/(-)$]

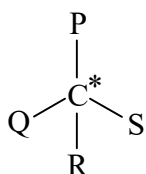


2. Chirality

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

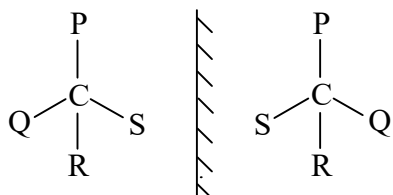
Asymmetric carbon (chiral carbon)

In 1874, van 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 rotate the plane of vibration of plane polarised light equally but through opposite directions. They are non-superimposable mirror images of each other.



Racemic mixture

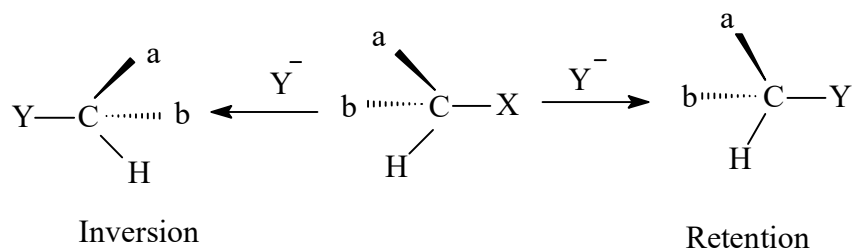
An equimolar mixture of enantiomers are called racemic mixture. The optical activity of racemic mixtures are zero due to external compensations.

Racemisation

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

Configuration

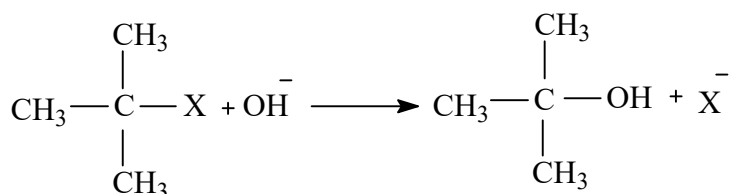
The spatial arrangement of different groups of atoms around a central carbon is called configuration. In a chemical reaction, if the configuration of different bonds around central C is preserved, it is called retention of configuration and if configuration is not preserved, it is called inversion of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



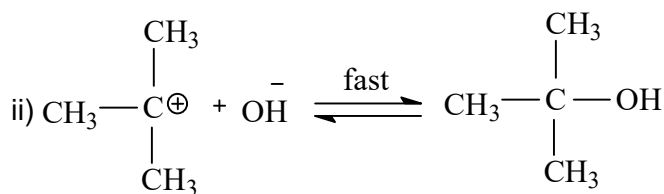
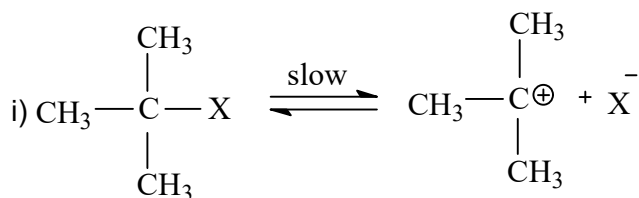
I. Mechanism of nucleophilic substitution reaction

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

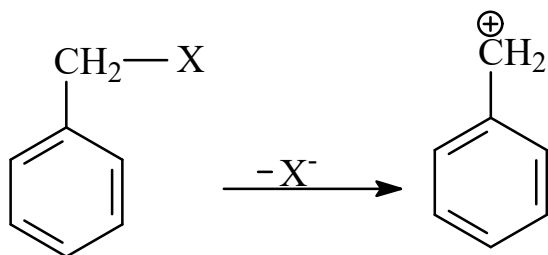
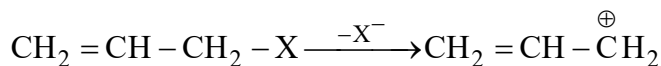
stability of carbocation follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$. \therefore Reactivity of various alkyl halides

towards S_N1 reaction follows the order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3 - \text{X}$.

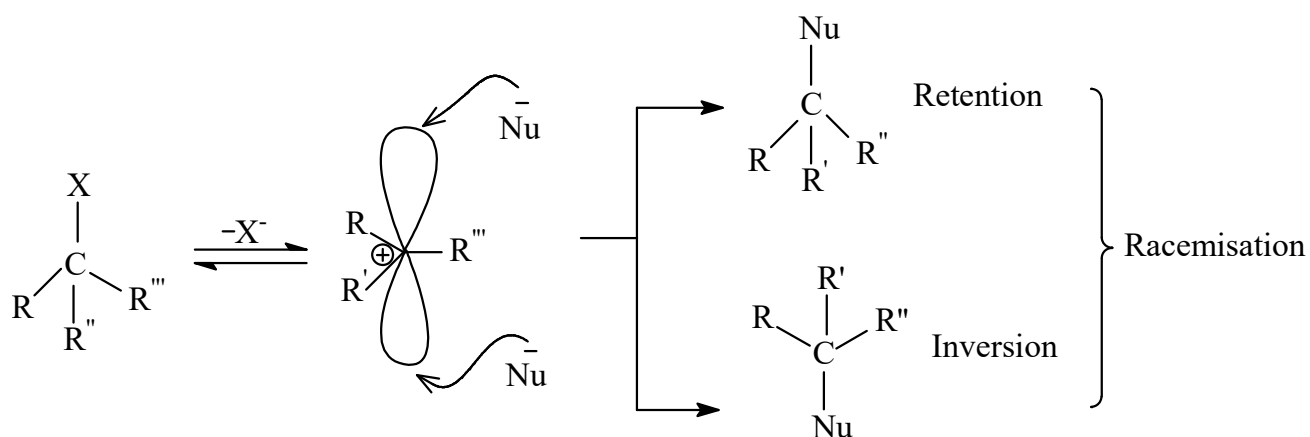
NOTE

Allylic and benzylic carbocation are resonance stabilized.

\therefore The reactivity of allylic and benzylic halides is highly reactive towards S_N1 even though they are 1° halides.



Stereochemistry of S_N1 reaction

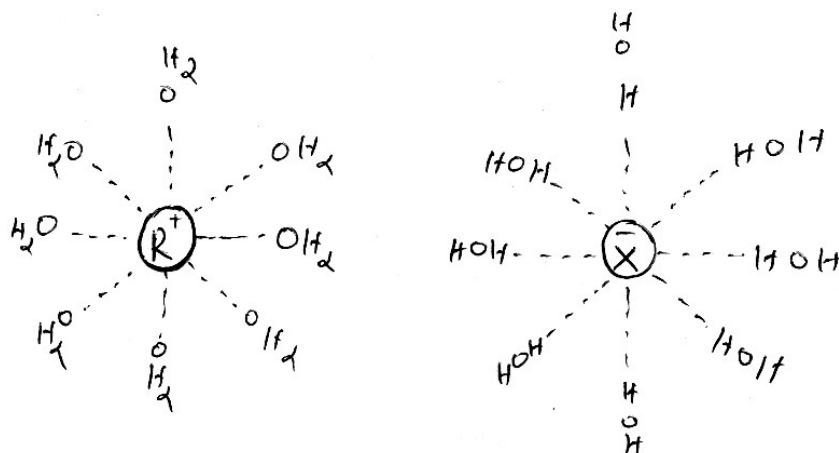


\therefore S_N1 reaction at an optically active centre gives a partial racemisation with slight excess of inversion product.

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

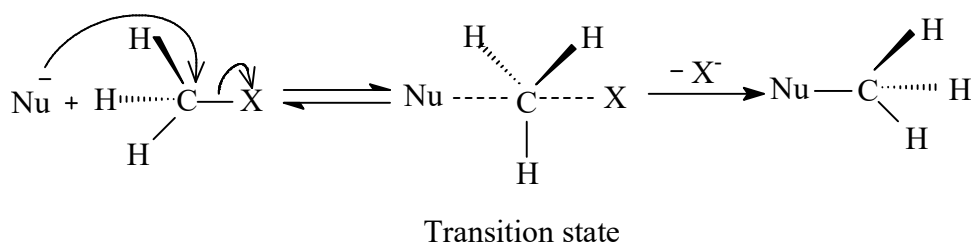
Effect of solvents on S_N1 reaction

The rate determining step of S_N1 mechanism involves two ions R^+ and X^- . Polar solvents easily solvate these two ions. \therefore 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 bimolecular 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.



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

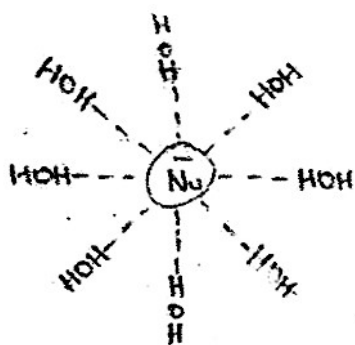
Bulky groups sterically retard the backside attack of nucleophile. As a result, S_N2 reaction in various alkyl halide follows the order $CH_3 - X > 1^\circ > 2^\circ > 3^\circ$

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)

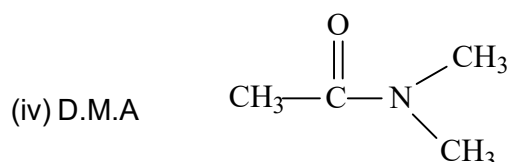
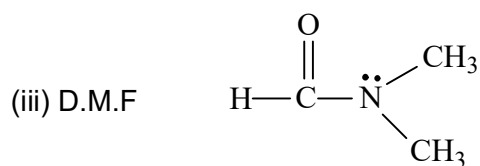
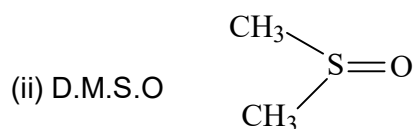
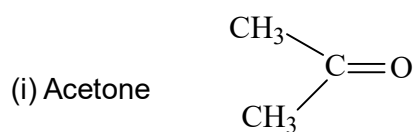
Effect of solvent on S_N2 reaction

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



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

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



	S_N1	S_N2
i)	Nucleophilic strength is unimportant	Strong nucleophiles are required
ii)	$3^\circ > 2^\circ > 1^\circ > \text{CH}_3 - \text{X}$	$\text{CH}_3 - \text{X} > 1^\circ > 2^\circ > 3^\circ$
iii)	Polar protic solvents	Polar aprotic solvents
iv)	$r = k[\text{R} - \text{X}]$	$r = k[\text{R} - \text{X}][\text{Nu}^-]$
v)	Rearrangements are common	Rearrangement is not possible

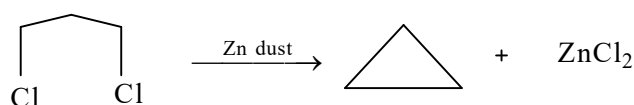
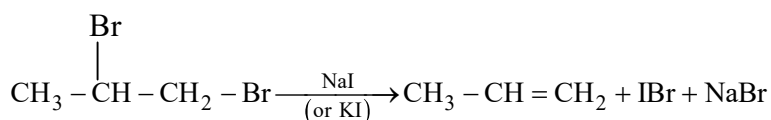
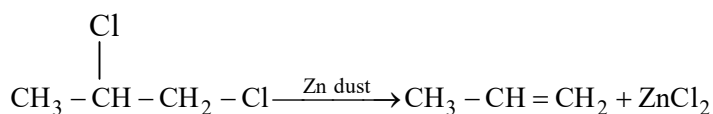
NOTE

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.

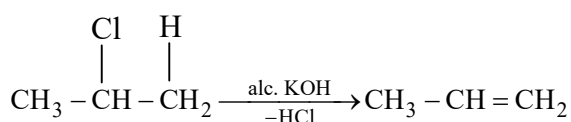
∴ Nucleophilic substitution reactivity order for various halides follows the order : $\text{R} - \text{I} > \text{R} - \text{Br} > \text{R} - \text{Cl} > \text{R} - \text{F}$

Elimination Reactions

Dehalogenation reaction



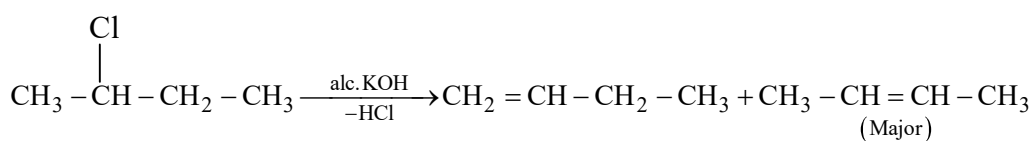
Dehydrohalogenation reactions



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

Saytzeff's rule

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

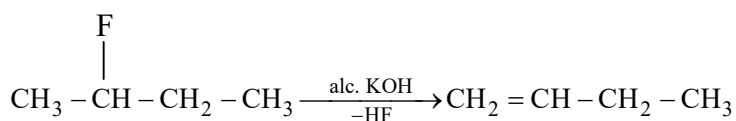


Reason

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

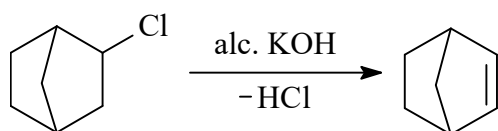
Exceptions for Saytzeff's elimination

1. Dehydrofluorination reaction (Hoffmann's elimination)

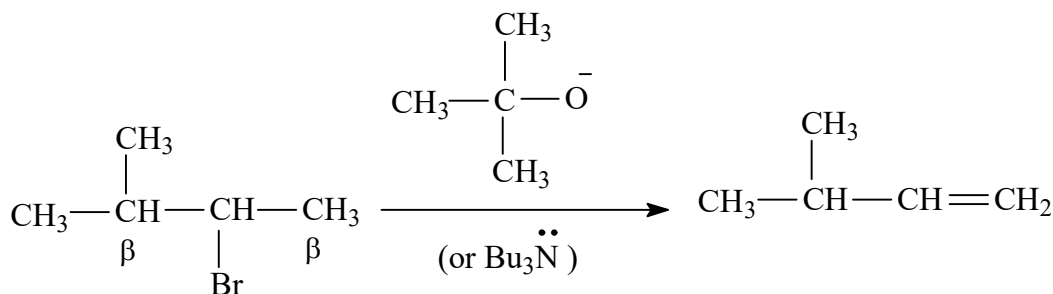


2. Bredt's rule

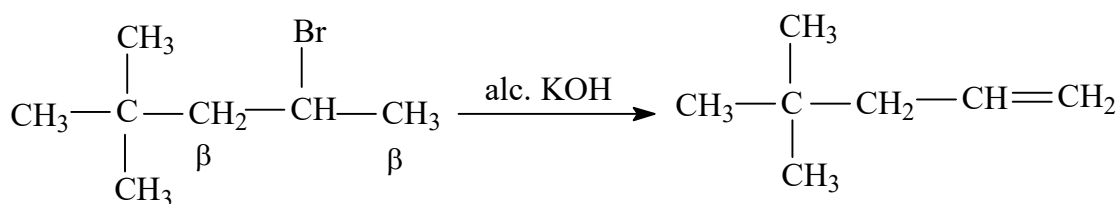
Bridgehead carbon has pyramidal geometry. In order to maintain pyramidal geometry, its hybridisation should be sp^3 . Double bonds on bridgehead carbon makes the hybridisation sp^2 (planar). Therefore double bonds are not formed through bridgehead carbon.



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



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

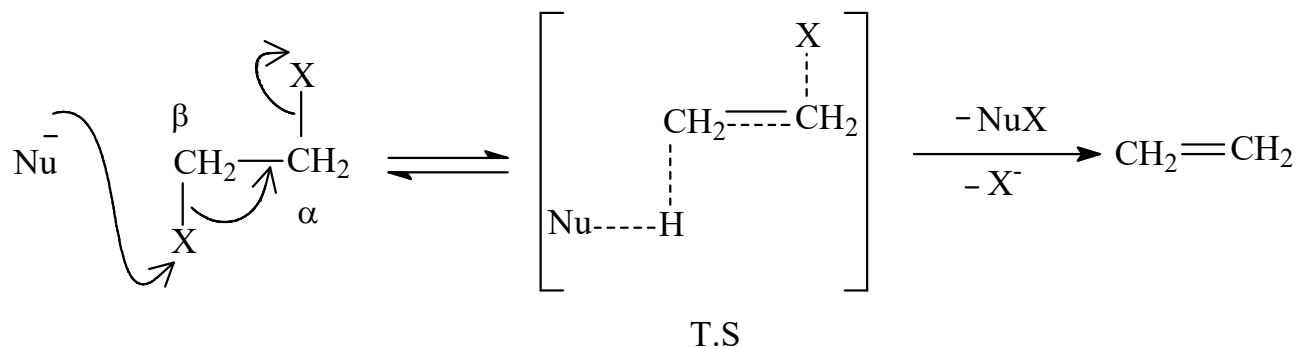


Mechanism of β -elimination reactions

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

2. E2 mechanism (Elimination biomolecular mechanism)



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

	E1 mechanism	E2 mechanism
1	weak base	strong base
2	$3^\circ > 2^\circ > 1^\circ$	$3^\circ > 2^\circ > 1^\circ$
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

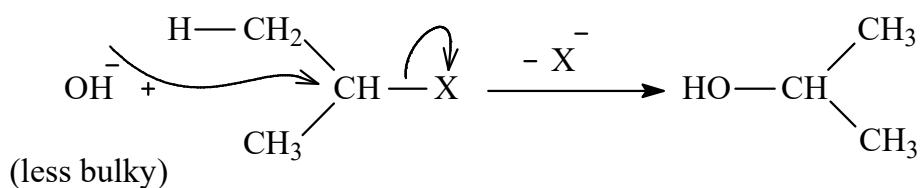
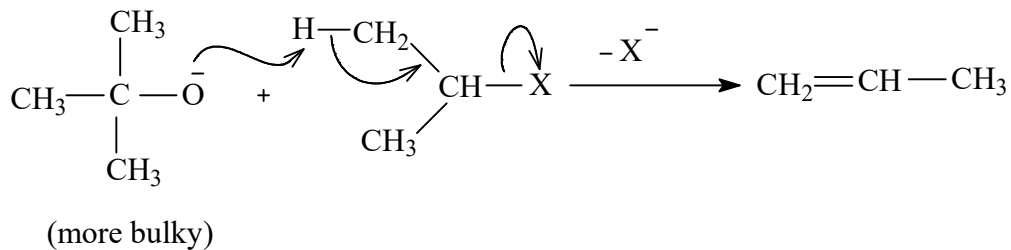
S_N2 v/s E2

	S_N2 mechanism	E2 mechanism
1	$1^\circ > 2^\circ > 3^\circ$	$3^\circ > 2^\circ > 1^\circ$
2	Weak bases having strong nucleophilicity Eg : I^- , Br^- ,	Strong bases having weak nucleophilicity Eg : $R-O^-$, NH_2^- ,

Elimination v/s substitution

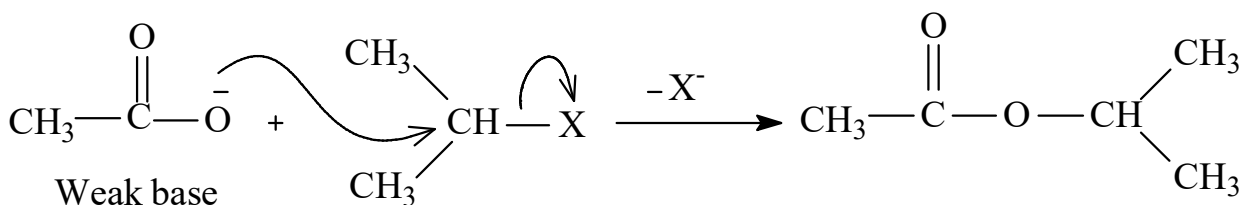
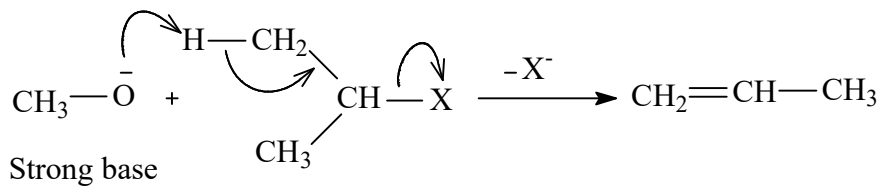
1. Bulkiness of nucleophile

More bulky nucleophile gives elimination & less bulky Nu⁻ gives substitution.



2. Basicity of nucleophile

Strong bases give elimination reaction where as weak base gives substitution

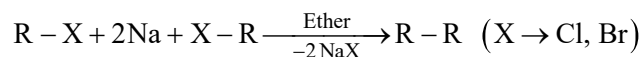


3. Temperature

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

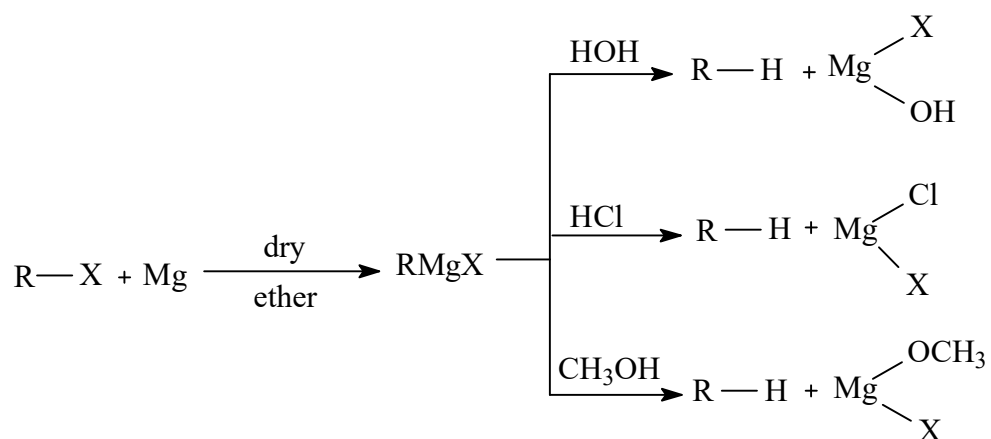
III. Reaction with metals

a. Reaction with Na (Wurtz reaction)



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.

**NOTE**

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

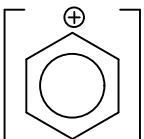
Chemical properties of aryl halides**I. Nucleophilic substitution reactions**

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

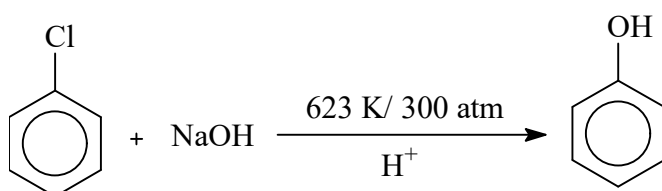
1) Resonance



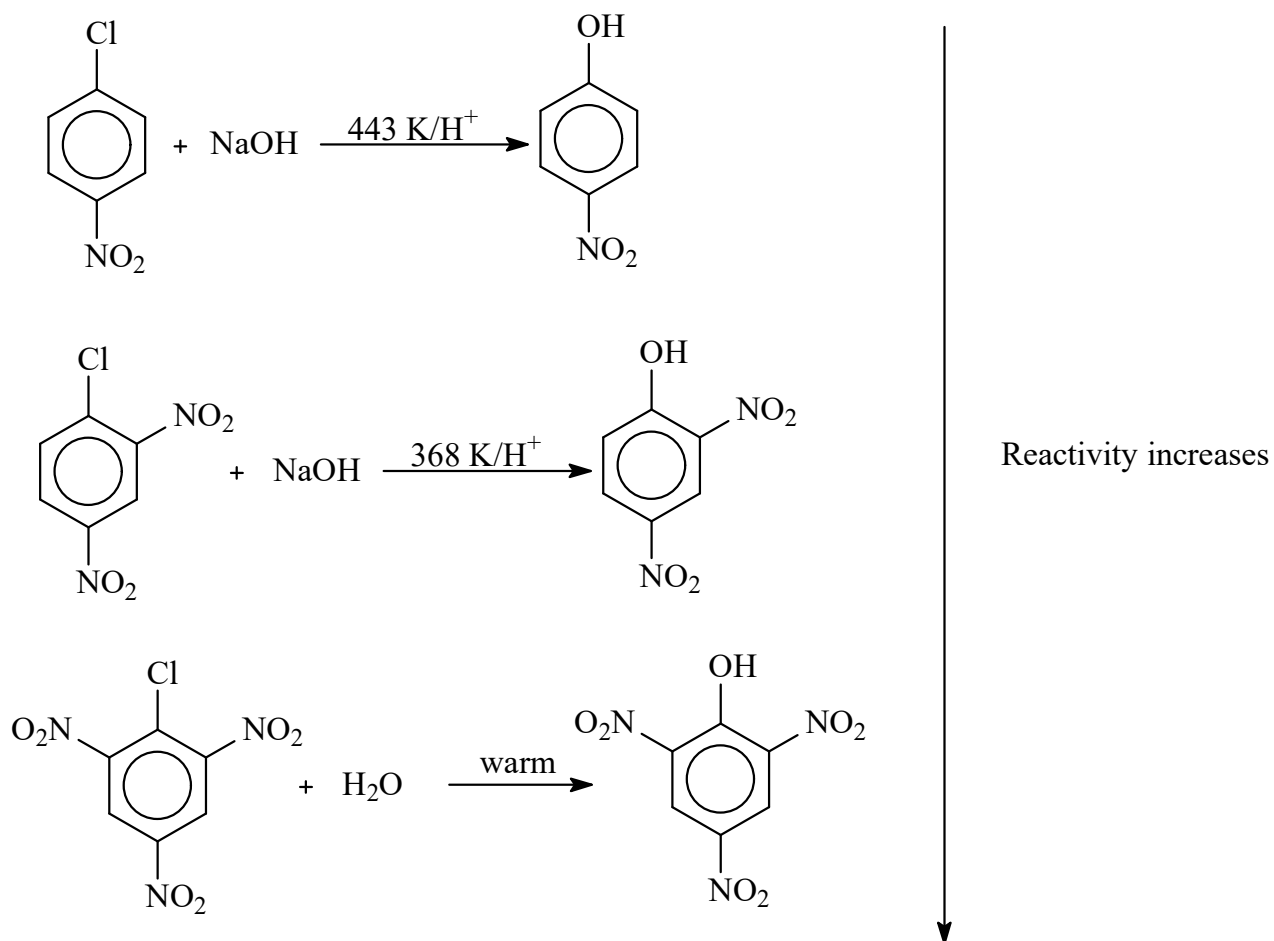
2) The carbon in $\text{C}-\text{X}$ bond is sp^2 hybridised (electronegative). \therefore The C of holds $\text{C}-\text{X}$ bond pair more strongly.

3) The phenyl carbocation  is highly unstable. \therefore $\text{S}_{\text{N}}1$ reactions are difficult in aryl halides.

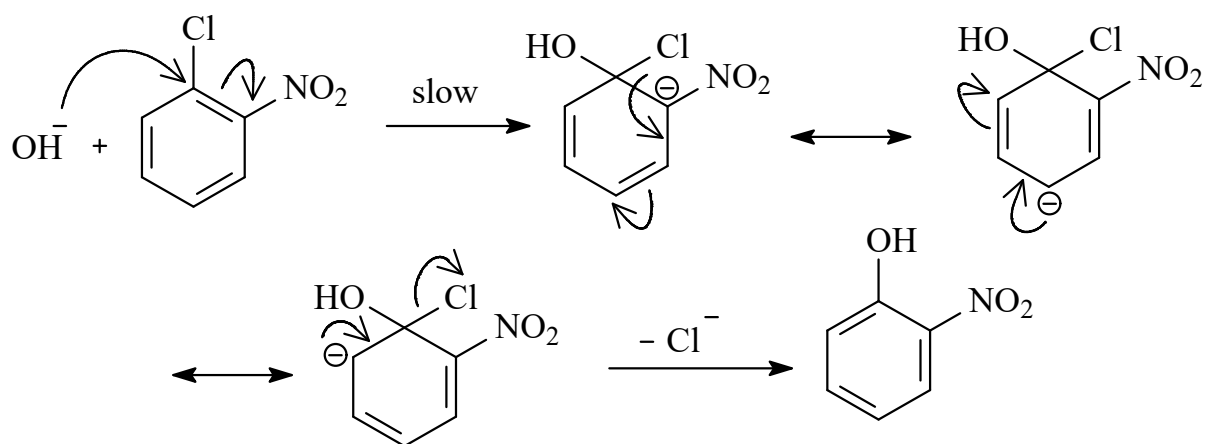
4) Electron rich nucleophile experiences repulsion with electron rich aromatic ring.

a. Substitution with OH^- 

Presence of electron withdrawing groups such as $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$ etc. on ortho, para positions increases the rate of reaction.

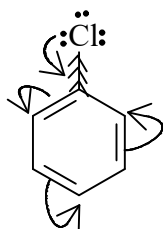


Mechanism (Addition-elimination mechanism)

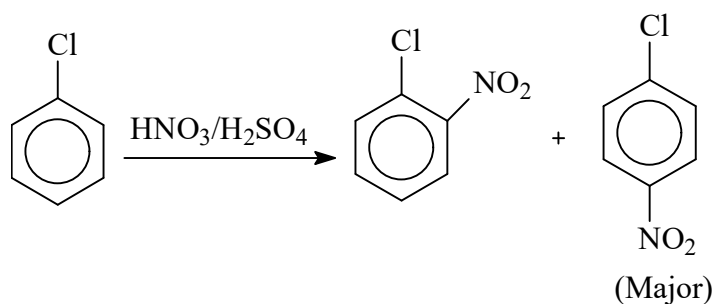


Electrophilic substitution reactions

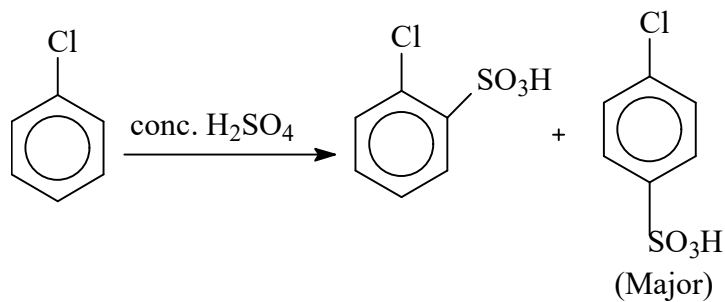
Halogens are ring deactivating groups for electrophilic substitution reactions through their strong $-I$ effect, but they are o, p -directing groups for electrophiles through their weak $+R$ effect. \therefore Halogens are o,p-directing deactivators, i.e, reactivity of the ring is controlled by its strong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



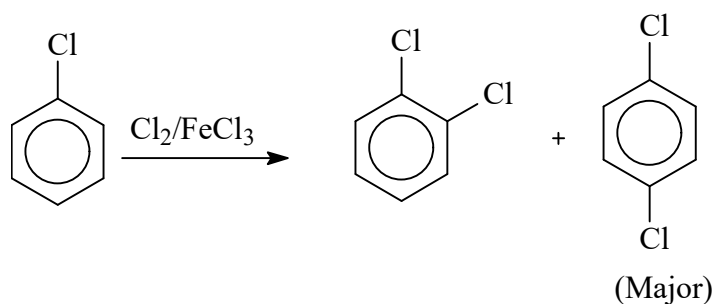
a. Nitration



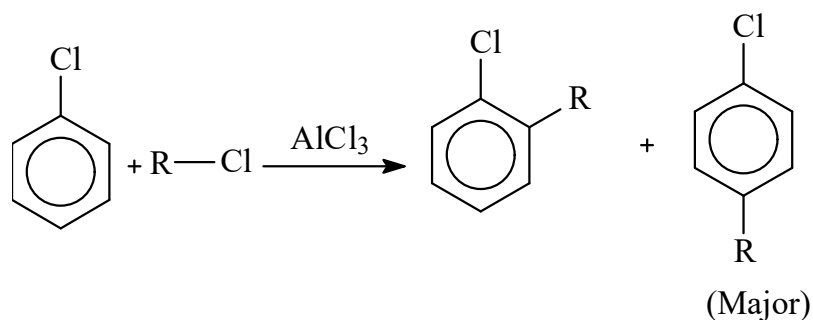
b. Sulphonation



c. Halogenation

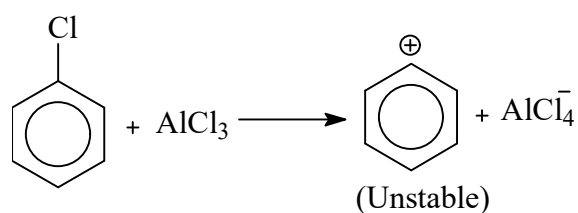
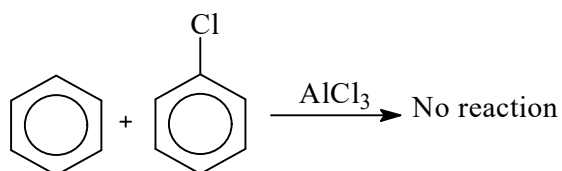


d. Friedel craft's reaction



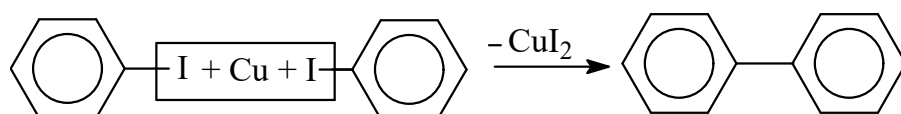
NOTE

Benzene with chlorobenzene does not give Friedel-Craft's reaction because the phenyl cation is highly unstable.

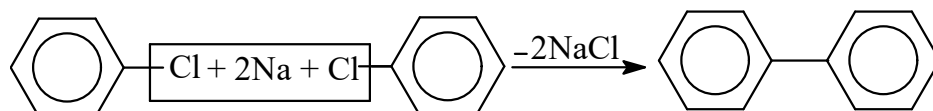


III. Reaction with metals

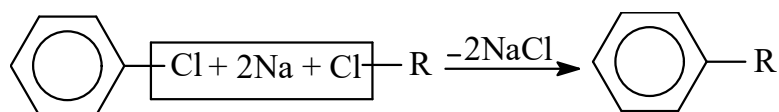
a. Ullmann reaction

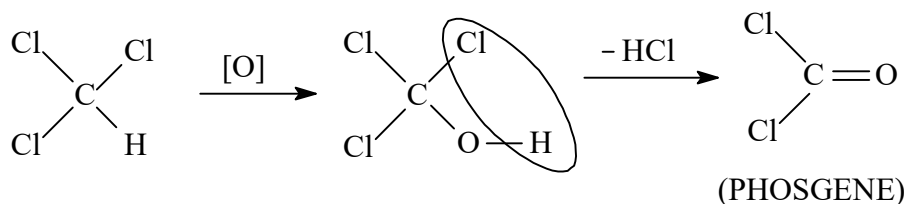


b. Fittig reaction

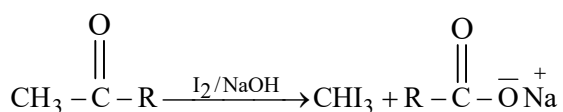
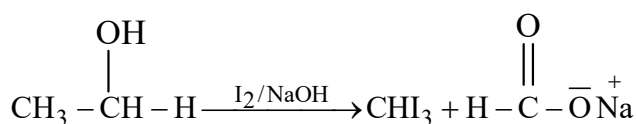
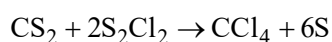


c. Wurtz-Fittig reaction

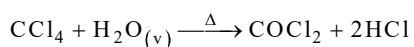


Polyhalogen compounds**1. Chloroform(CHCl₃)****II. Iodoform (CHI₃)**→ **Antiseptic****Preparation (Iodoform test)**

Compound containing methyl ketones or methyl carbinols bonded to C or H reacts with I₂ and NaOH to produce yellow crystals of iodoform

**III. CCl₄ (pyrene)****Preparation**

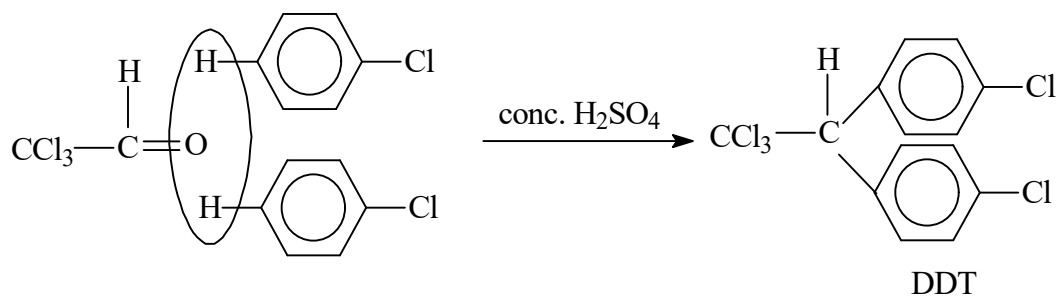
CCl₄ is a well-known fire extinguisher. After using CCl₄ as a fire extinguisher in a room, the room should be well-ventilated. Because CCl₄ at high temperature reacts with steam to produce poisonous gas phosgene.

**IV. Freons**

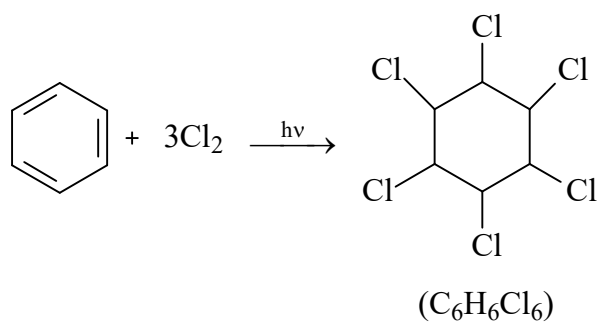
Chlorofluorocarbons of CH₄ and C₂H₆ are collectively called freons.

CF₂Cl₂ is used as a refrigerant and it also causes ozone layer depletion

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



VI. BHC (Benzene Hexa Chloride)



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