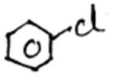
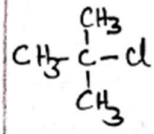
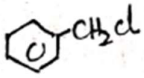
HALOGEN COMPOUNDS

NOMENCLATURE

Compound	Common name	IUPAC name
CH_3-CH_2-Br	Ethyl Bromide	Bromo ethane
$CH_3-CH=CHCl$	Propenyl chloride	1-chloropropene
	phenyl chloride	Chloro Benzene
	t-Butyl Chloride	2-chloro 2-methyl propane
	Benzyl chloride	phenyl methyl chloride
CH_3Cl	methyl chloride	Chloromethane

CH_4
Methane

CH_3Cl
Methyl chloride
(Chloromethane)

CH_2Cl_2
Methylene chloride
(Dichloromethane)

$CHCl_3$
Chloroform
(Trichloromethane)

CCl_4
Carbon tetra chloride
(Tetra chloro methane)

CLASSIFICATION OF HALOGEN COMPOUNDS

1. **Alkyl halides:** Alkyl halides are classified in to three types based on the nature of the carbon atom to which halogen atom is attached. They are

A) Primary alkyl halides or 1° alkyl halides: In 1° alkyl halides, halogen atom is attached to 1° carbon atom (R-$\underline{CH_2}$-X).

Example: Ethyl bromide CH_3-$\underline{CH_2}$-Br

n-Propyl bromide CH_3-CH_2-$\underline{CH_2}$-Br

B) Secondary alkyl halides or 2° alkyl halides: In 2° alkyl halides, halogen atom is attached to 2° carbon atom (R_2-$\underline{CH}$-X).

Example: Iso propyl bromide $(CH_3)_2$-$\underline{CH}$-Br

C) Tertiary alkyl halides or 3° alkyl halides: In 3° alkyl halides, halogen atom is attached to 3° carbon atom (R_3-$\underline{C}$-X).

Example: t- butyl bromide $(CH_3)_3$-$\underline{C}$-Br

2. **Aryl halides:** A class of Halogen compounds where a halogen atom (like chlorine, bromine, etc.) is directly bonded to an aromatic ring, such as benzene. They are also known as haloarenes and are represented by the general formula Ar-X

Example : Chloro benzene C_6H_5-Cl

Bromo benzene C_6H_5-Br

3. **Aryl Alkyl halides:** An aryl alkyl halide is a molecule that combines features of both aryl halides and alkyl halides. It contains a halogen atom attached to an alkyl group, which is itself connected to an aromatic (aryl) ring. The halogen is not directly bonded to the aromatic ring. Example: Benzyl Chloride C_6H_5-CH_2-Cl

4. **Allyl halides:** An allyl halide is an organic compound containing a halogen atom (like chlorine, bromine, etc.) bonded to a carbon atom that is directly adjacent to a carbon-carbon double bond (C=C). This specific carbon is sp^3 hybridized.

Example: Allyl chloride CH_2=CH-CH_2-Cl

Allyl bromide CH_2=CH-CH_2-Br

5. **Vinyl halides:** A vinyl halide is a compound having halogen atom directly bonded to a carbon atom within a carbon-carbon double bond (C=C)

Example: Vinyl Chloride CH_2=CH-Cl

Vinyl Bromide CH_2=CH-Br

NUCLEOPHILIC ALIPHATIC SUBSTITUTION REACTIONS

Nucleophilic substitution reactions are classified into 2 types

i Unimolecular Nucleophilic substitution reactions (S_N1)

ii Bimolecular Nucleophilic substitution reactions (S_N2)

1. UNIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTION (SN^1)

1.1 MECHANISM FOR UNIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTION (SN^1)

i) UNIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTION (S_N1)

In unimolecular substitution substitution reactions, the rate of reaction depends only on the Concentration of Alkyl halide (RX) and is independent on the Concentration of base ion Nucleophile

$$\text{Rate} \propto [RX]$$

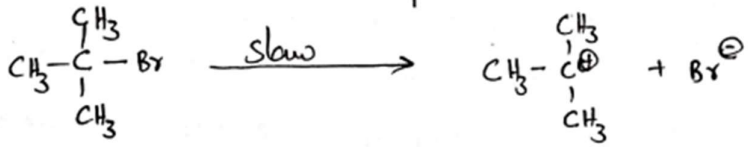
This reaction takes place in two steps.

Example for S_N1 reaction

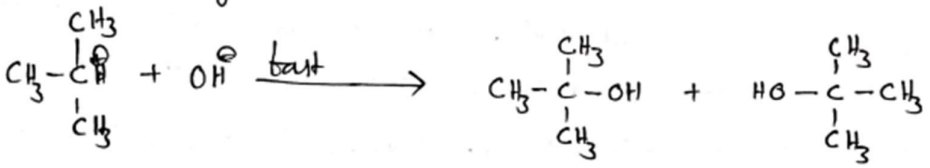
Hydrolysis of t-butyl bromide to give t-butyl alcohol is taken as a typical example for S_N1 reaction.

$$(CH_3)_3CBr + OH^{\ominus} \longrightarrow (CH_3)_3C-OH + Br^{\ominus}$$

In the first step t-butyl Bromide ionises to give t-butyl Carbocation and bromide ion. This is the slowest step and rate determining step.



In the second step attack of Nucleophile ($OH^{\ominus}$) on the Cat t-butyl Carbocation takes place resulting in the formation of t-butyl alcohol



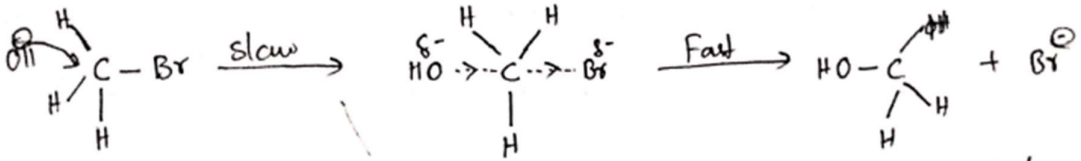
2. BIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTION (SN^2)

2.1 MECHANISM FOR BIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTION (SN^2)

In bimolecular nucleophilic substitution reaction, the rate of reaction depends on the concentration of Alkyl halide (RX) and Nucleophile ($Nu^{\ominus}$)

$$\text{Rate} \propto [RX][Nu^{\ominus}]$$

The reaction takes place in one step.
Let us consider the hydrolysis of Methyl bromide by aq. NaOH. The Nucleophile (OH^-) starts to share its electrons with the substrate carbon from the side opposite to the bromine atom. Simultaneously the bromine atom starts parting away with its shared pair of electrons from the carbon. This state is represented in the form of transition state in which carbon is sp^2 hybridised. the three hydrogen atoms lie in a plane with a bond angle 120°.



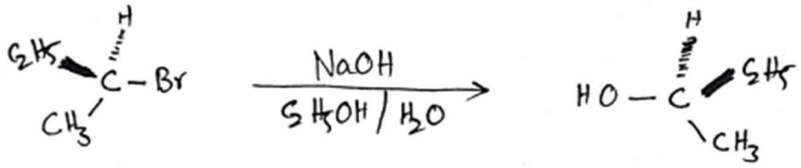
Methyl bromide — Transition state — Methyl alcohol

Finally the C–Br bond is fully cleaved and C–OH bond is fully formed occupying the opposite position to –Br. Thus the alcohol formed is with inverted configuration is called Walden inversion.

2.2 BIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTION IN OPTICALLY ACTIVE ALKYL HALIDE (SN^2)

Mechanism of Bimolecular Nucleophilic substitution in optically active alkyl halide was explained by taking 2-bromobutane as an example.

Stereochemistry of SN^2 reactions can be best demonstrated by taking Alkyl halide having chiral Carbon eg: 2-Bromobutane. When (+)-2-Bromobutane is allowed to react with Aq NaOH under SN^2 condition (−)-2-Butanol is obtained.



(+)-2-Bromobutane (−)-2-Butanol.

The change in specific rotation (sign) from (+) to (−) indicates that the configuration changes during the reaction. The inversion of configuration is referred as Walden inversion.

It is proved by the fact that a sample of 83% pure optically pure (+)-2-Bromo butane give 83% optically pure (−)-2-Butanol on SN^2 reaction.