

HALOGEN COMPOUNDS

II B.Sc.

SEMESTER – III

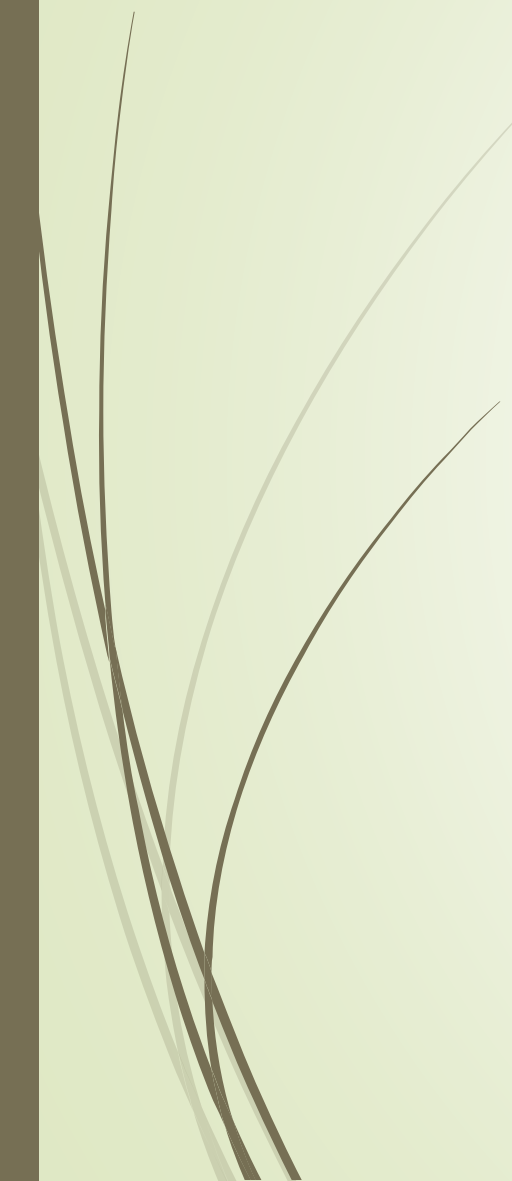
Dr. Narayana Rao Vykunthapu

Lecturer in Chemistry

P.R. Govt. College (A), Kakinada



Outline

- Introduction
 - Nomenclature
 - Classification of alkyl halides
 - Nucleophilic aliphatic substitution reactions
 - Summary
- 



Introduction

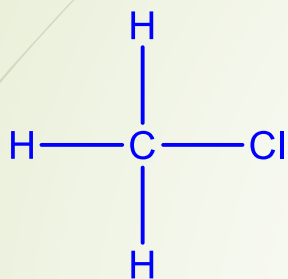
- Fluorine, Chlorine, Bromine and Iodine are called as Halogens.
- These derivatives are obtained by replacing of one or more hydrogen atoms in Hydrocarbons.
- General symbol for alkyl halides is $R-X$, where X is halogen
- Reactivity of Halogen compounds is high, so these compounds used as starting material in the preparation of many organic compounds.



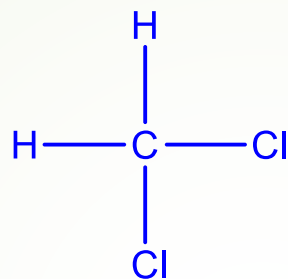
Alkyl Halides in day to day life

- Due to stable, non-toxic, non-inflammable and non-corrosive nature these are used as Solvents, Coolants in fridges and Propellants
- Fire Extinguishers
- Anaesthetic and Medicine
- Pesticides, Fungicides
- Feedstock's for PVC, PTFE and Teflon

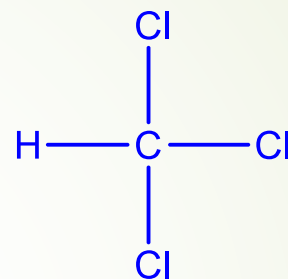
Examples:



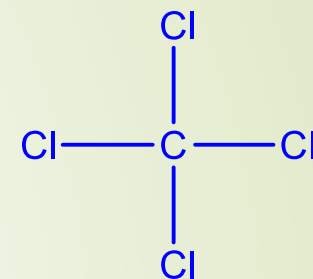
Methyl chloride
(Monohalogen derivative)



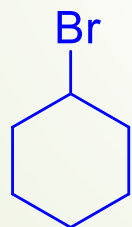
Dichloro Methane
(Dihalogen derivative)



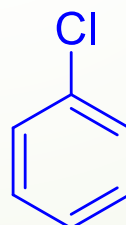
Trichloro Methane
(Trihalogen derivative)



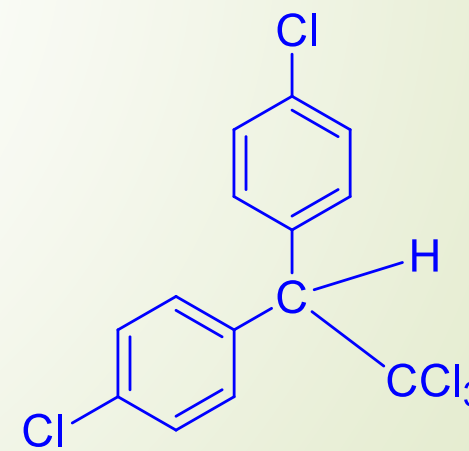
Tetrachloro Methane
(Tetrahalogen derivative)



Bromocyclohexane



Chlorobenzene

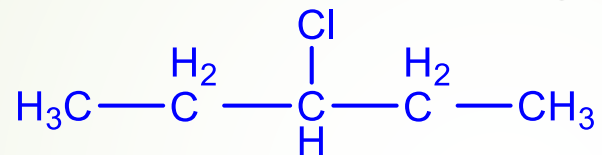


DDT

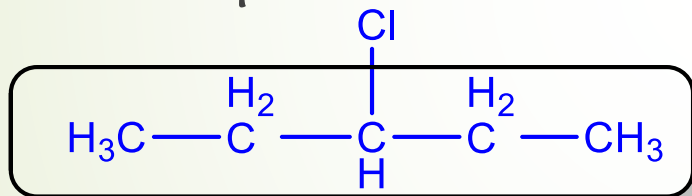
Nomenclature

➤ IUPAC system:

Ex:1 Give the IUPAC name of the following alkyl halide



Step-1: Find the parent carbon chain containing the halogen



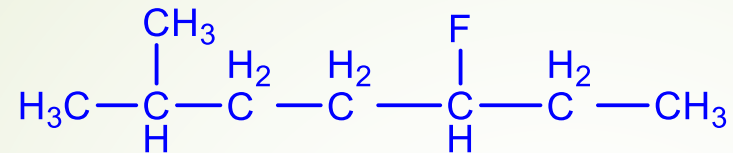
Five carbons in the longest chain

5 C's -----Pentane

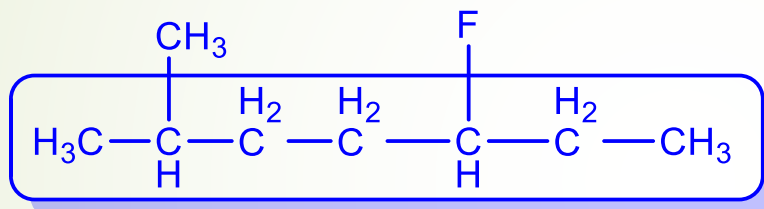
Step-2 Apply all other rules of IUPAC: Name and position of Substituents

Chloro at 3rd position, hence name is **3 – Chloro pentane**

Ex: 2. Give the IUPAC name of the following alkyl halide

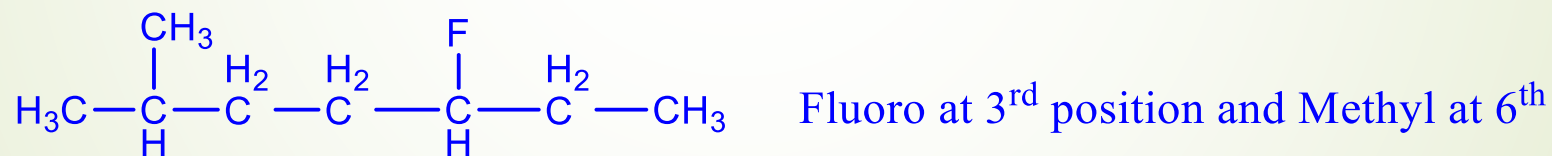


Step-1: Find the parent carbon chain containing the halogen



Seven Carbons in the longest chain
7 C's -----Heptane

Step-2 Apply all other rules of IUPAC: Name and position of Substituents



Hence the name of the compound is **3- Fluoro, 6- methyl heptane**

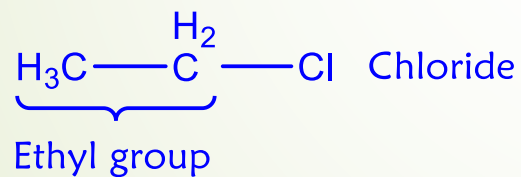
➤ Common Names

- Common names are often used for simple alkyl halides

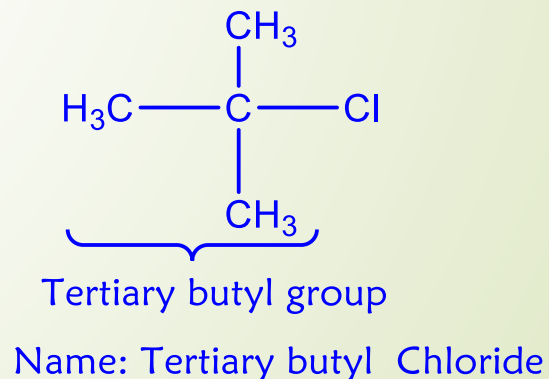
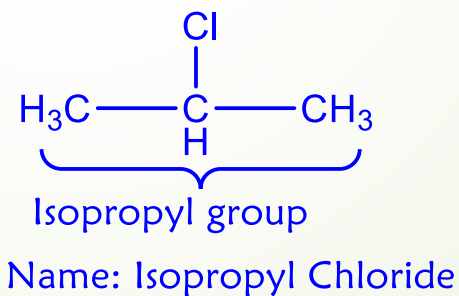
Rules to assign:

- Name all the carbon atoms of the given molecule as a single alkyl group.
- Name the halogen bonded to the alkyl group
- Combine the names of alkyl group and halide

EX:



Name: Ethyl Chloride



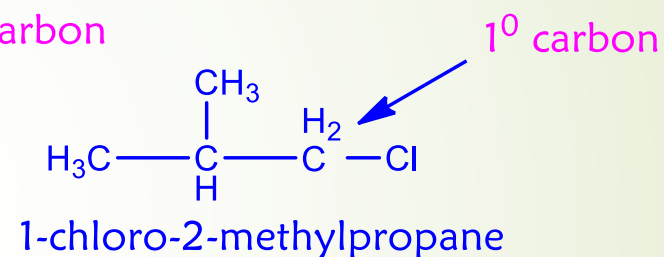
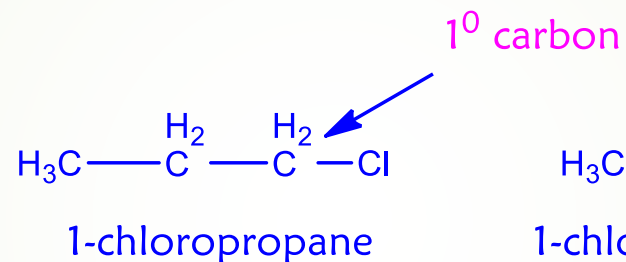
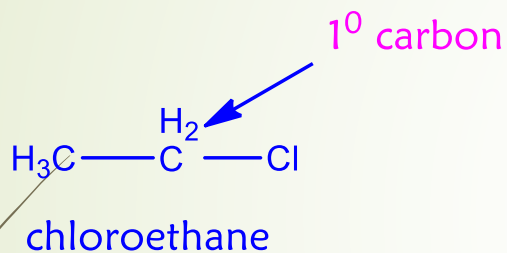
Classification of alkyl halides

- Generally Halides of Alkanes, Alkenes and Alkynes are called as **Alkyl halides, Alkenyl halides and Alkynyl halides**.
- Based on number of hydrogen atoms replaced by halogen, these compounds are classified as mono, di, tri and tetra halogen compounds.
- **Mono alkyl halides** further classified as Primary (1°), Secondary (2°) and Tertiary (3°) based on the alkyl group linked to the halogen atom.

□ Classification of Mono halogen derivatives:

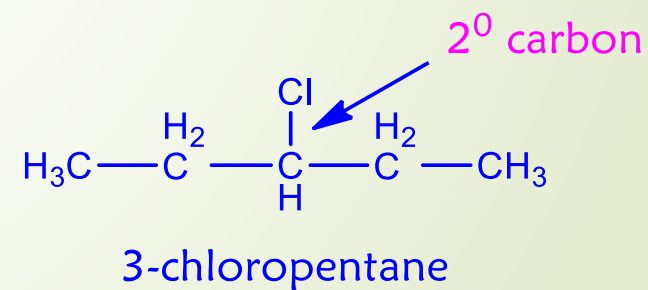
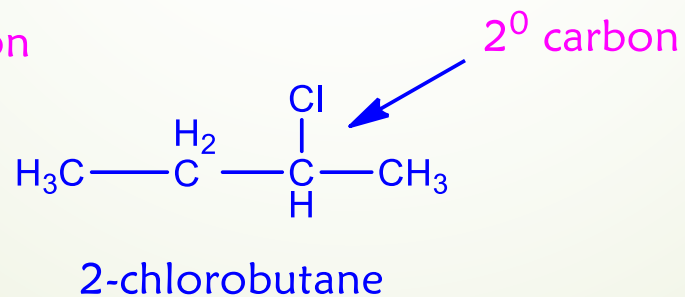
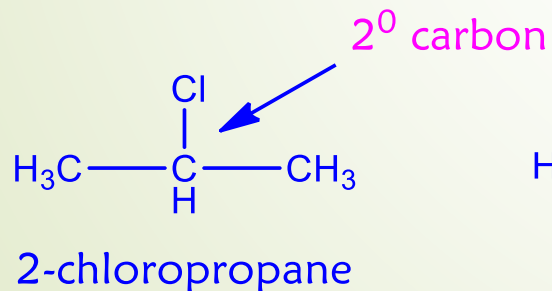
- **Primary alkyl halides:** Halogen atom is linked to primary carbon atom.

Examples:



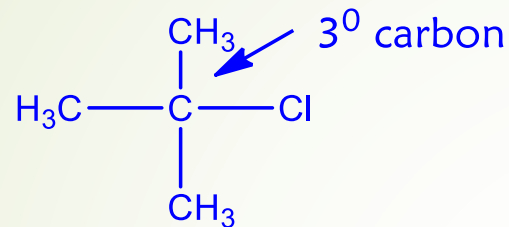
- **Secondary alkyl halides:** Halogen atom is linked to secondary carbon atom.

Examples:

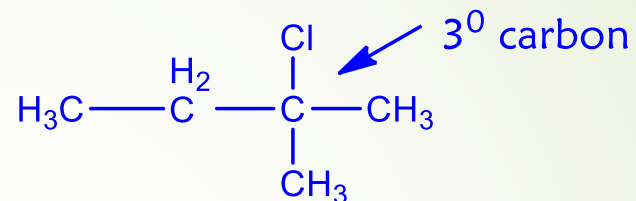


- **Tertiary alkyl halides:** In this type halogen atom is linked to tertiary carbon atom.

Ex:



2-chloro-2-methylpropane



2-chloro-2-methylbutane

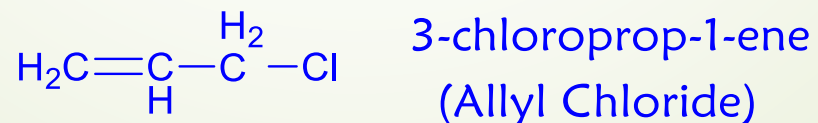
- ❑ **Halo alkenes or alkenyl halides:** In this type halogen atom is directly linked to alkenyl carbon atom or C-C double bond

Ex:



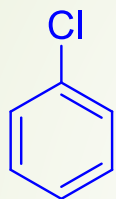
- ❑ **Allylic Halides:** in this type halogen atom is bonded to carbon atom adjacent to the C-C double bond

Ex:

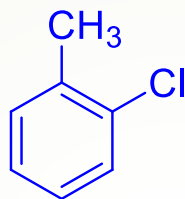


- ❑ **Aromatic Halogen compounds:** These are obtained by replacement of hydrogen atoms of an aromatic hydrocarbon with an equal number of halogen atoms, i.e. halogen atom is directly attached to aromatic ring.

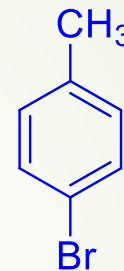
Ex:



chlorobenzene



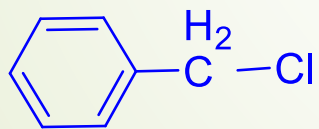
o-chlorotoluene



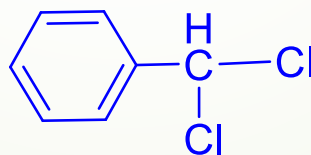
p-bromotoluene

- ❑ **Aralkyl halides (side chain halogen derivatives):** In these compounds halogen atom is directly linked to one of the carbon atoms of the side chain carrying the aryl group.

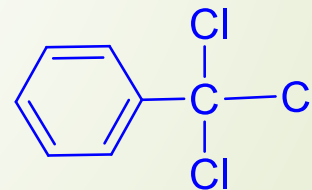
Ex:



Benzyl Chloride



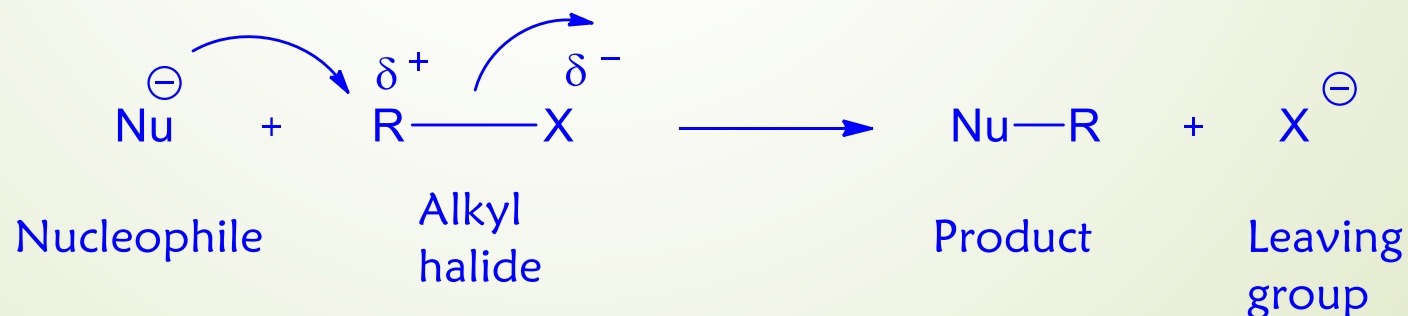
Benzal Chloride



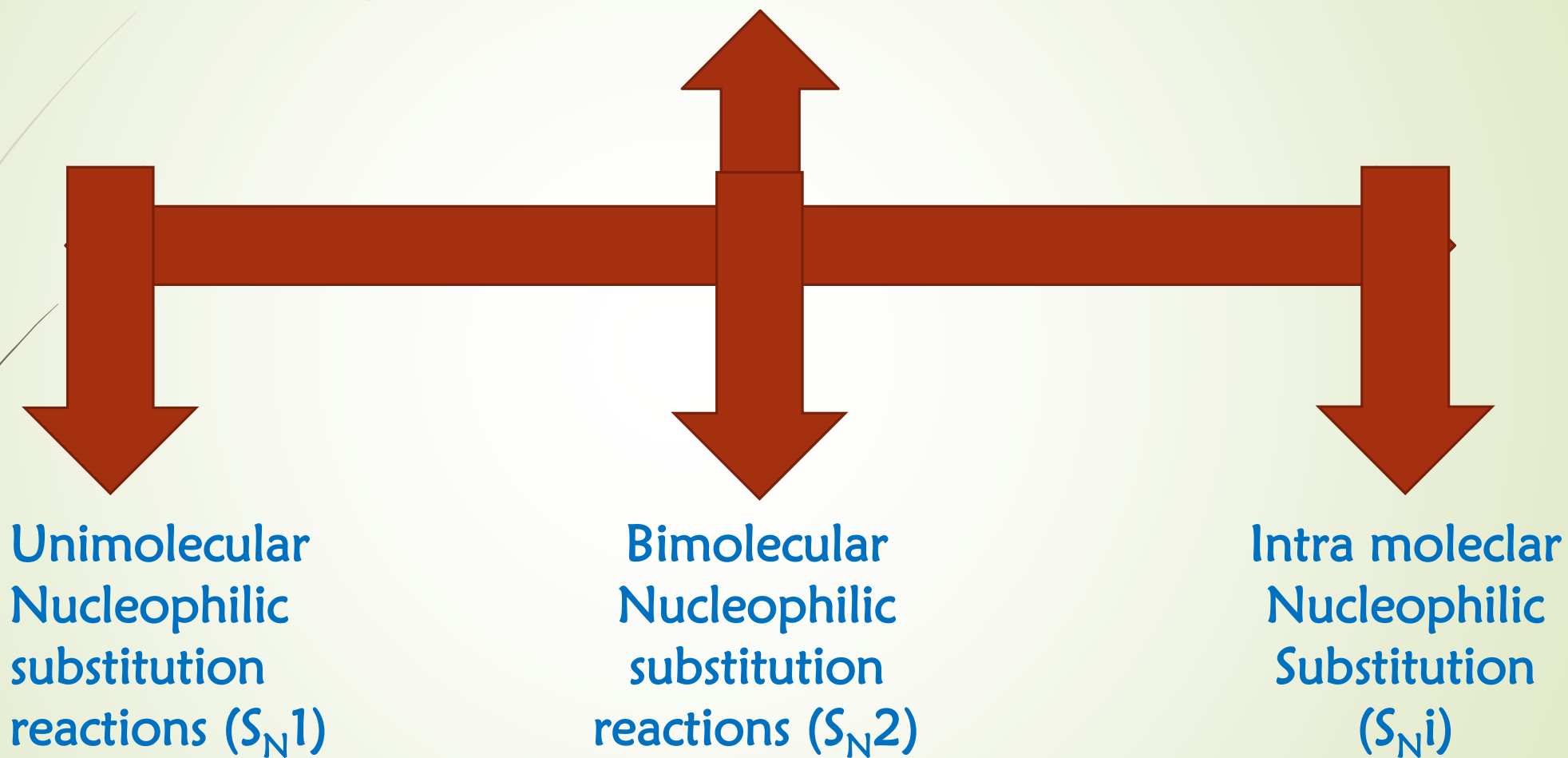
Benzo trichloride

Nucleophilic Substitution reactions

- The substitution reactions in which one nucleophile is replaced by another incoming strong nucleophile is called as Nucleophilic Substitution reactions.
- Generally alkyl halides participated in Nucleophilic Substitution reactions. Since halogen atoms electro negativity is higher than carbon, so bond pair electrons of C-X bond are attracted towards halogen atom as a result halogen atom gets partial negative charge and carbon will get same magnitude of positive charge.
- General representation of reaction is



Nucleophilic substitution reactions



Unimolecular Nucleophilic substitution reactions (S_N1):

- In these reactions rate determining step of the reaction involves only alkyl halide not nucleophile, i.e. rate of the reaction depends on only concentration of alkyl halide, so these are called as Unimolecular reactions.

Rate of reaction \propto [Alkyl Halide][Nucleophile]

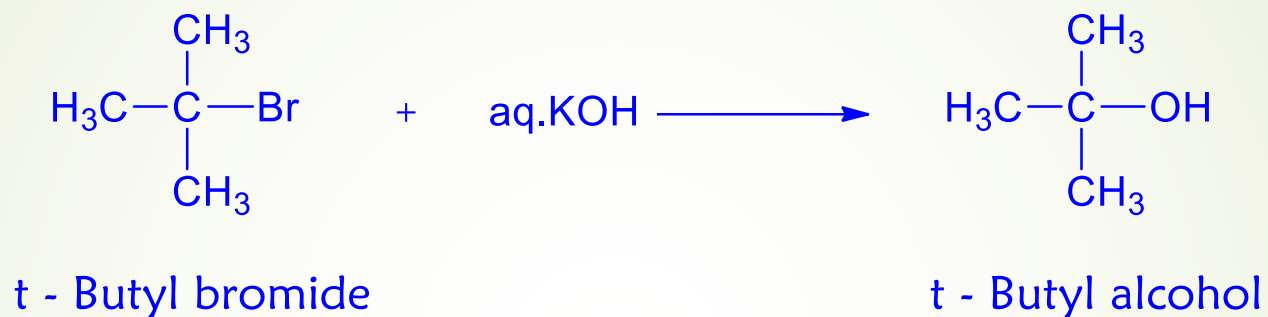
- It is a two – step process, in the first step ionization of $R - X$ takes place, resulting in the formation of carbocation intermediate. It is the slow step hence is the rate determining step.
- In the second step Nucleophile vigorously combining with Carbocation intermediate and forms product.

- 
- Generally tertiary alkyl halide participates in SN1 reaction and relative reactivity of alkyl halides in SN1 reactions is:

Benzyl halide > Allyl > Tertiary halide > Secondary > Primary > Methyl.

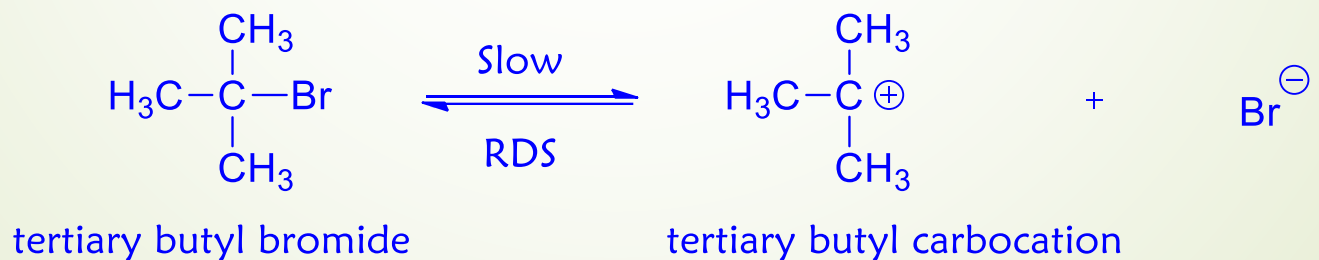
- Polar protic solvents (ROH, H₂O etc.) favors SN1 reaction mechanism.
- In SN1 reaction racemic mixture is formed if substrate is asymmetric molecule.

Ex: Base hydrolysis of tertiary butyl bromide with aqueous alkali such as NaOH or KOH to form tertiary alcohol as a product.



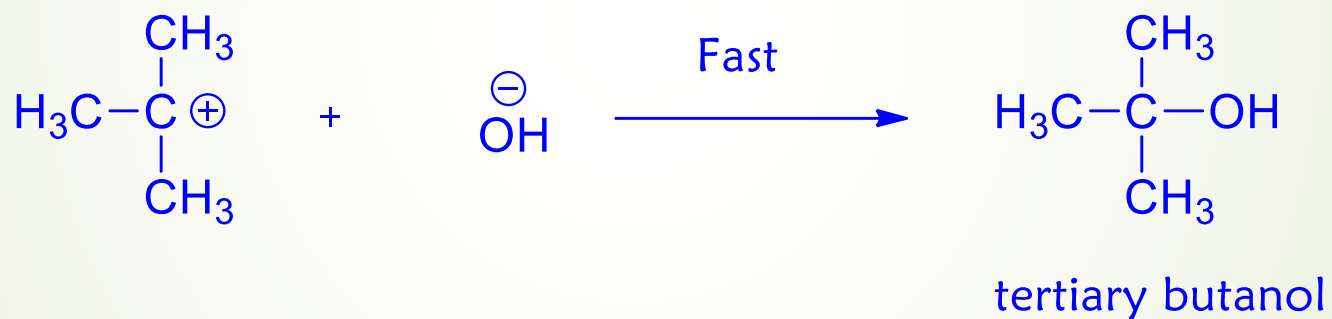
Mechanism:

Step-1: Heterolysis of the C – Br bond Forms a Carbocation Intermediate



Step-2: Nucleophile attack on Carbocation Intermediate

Nucleophile attack on carbocation forms the new C-O bond in the product. This is a Lewis acid – base reaction the nucleophile is the Lewis base and carbocation is the Lewis acid

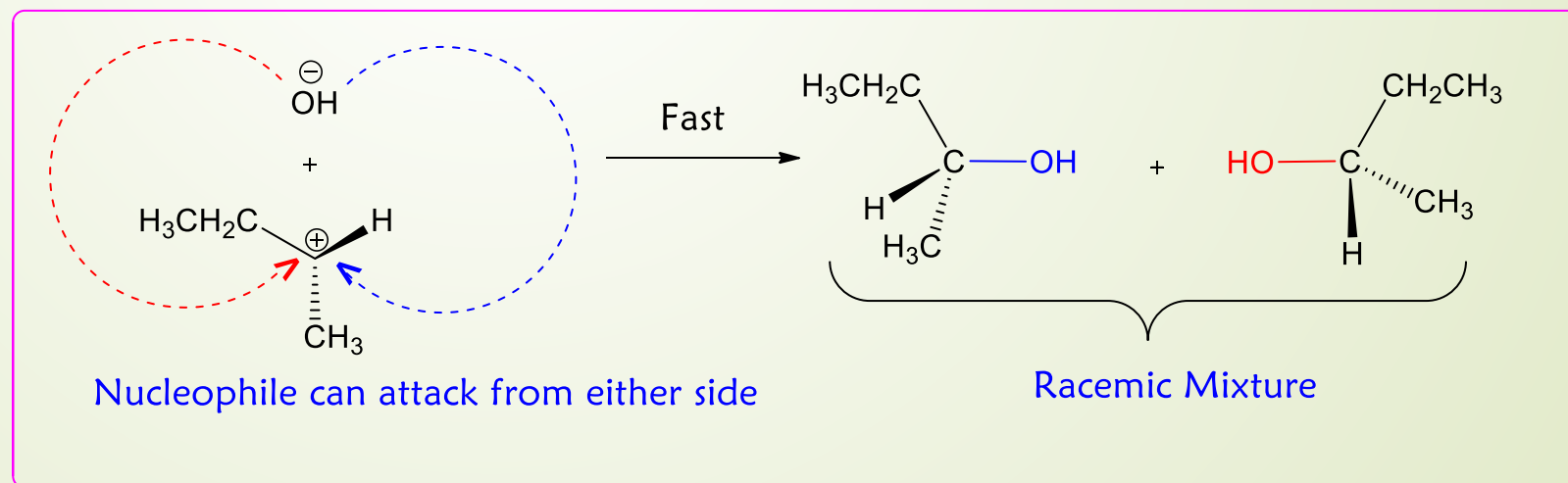
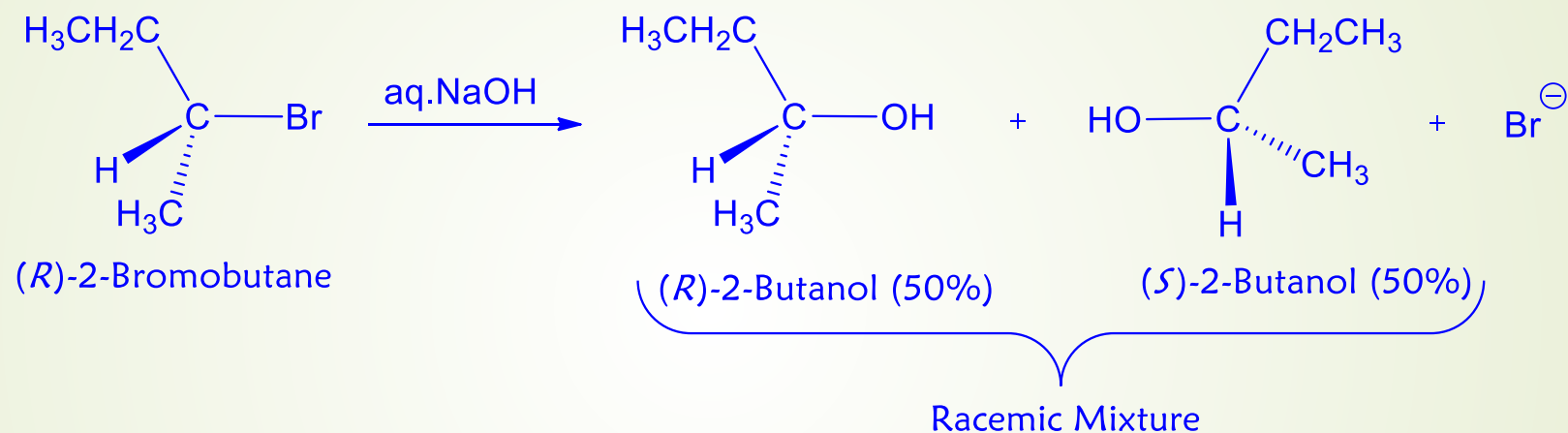




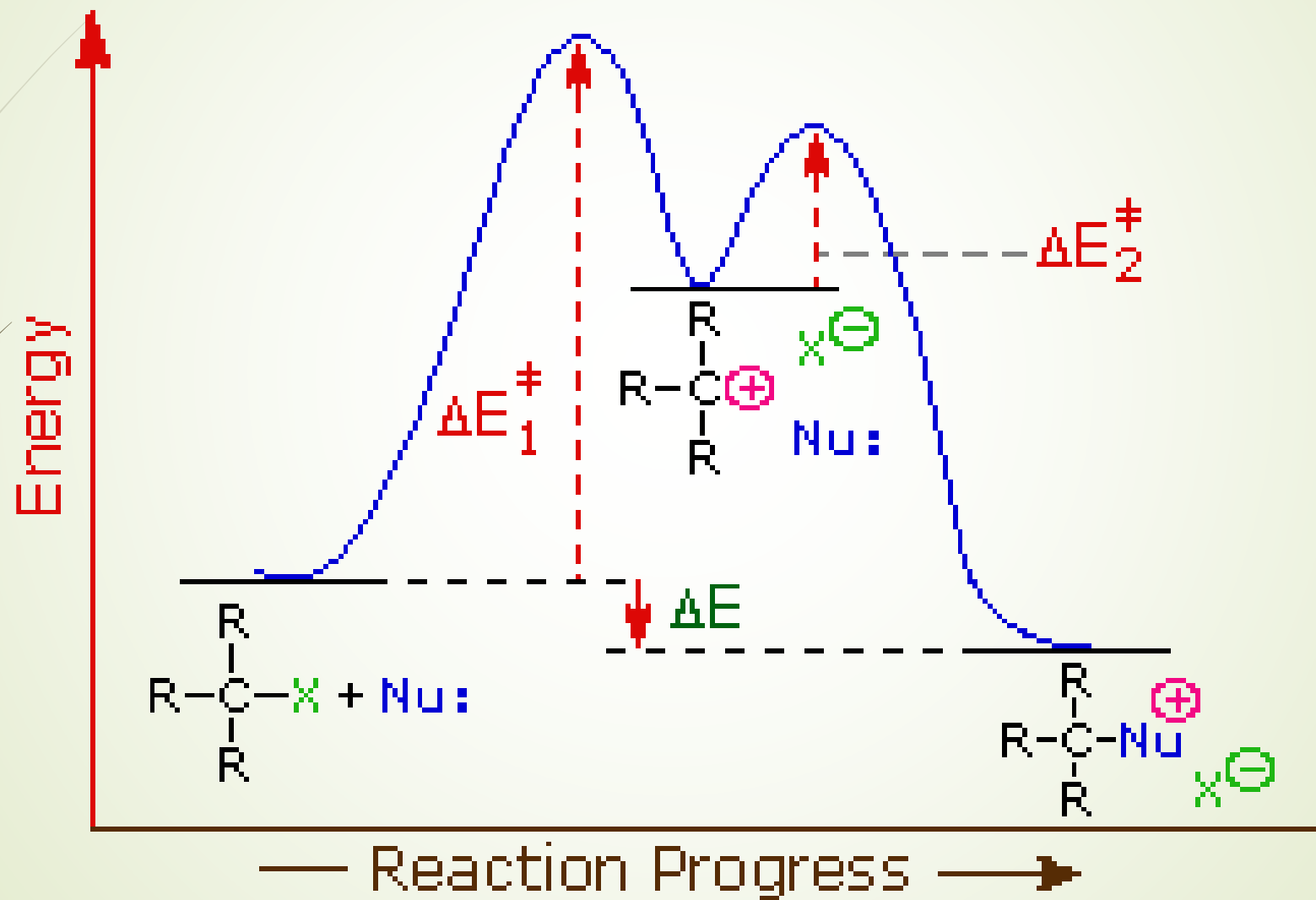
Stereochemistry in SN1 reactions:

- if the reaction takes place at a stereo center in asymmetric molecule, racemic mixture of enantiomers is formed.
- Since the Carbocation intermediate is formed in the SN1 reaction is a sp^2 hybridized carbon with **Trigonal Planar** molecular geometry. This allows two different possibilities for the Nucleophile attack on either side of the planar molecule to afford two products which are a pair of enantiomers.
- Because there is no preference for nucleophilic attack from either direction, an equal amount of the two enantiomers is formed a racemic mixture. We say that **racemization** has occurred

Ex: Base hydrolysis of **2-Bromo butane** with aqueous alkali such as NaOH or KOH to form racemic **2-butyl alcohol** as a product.

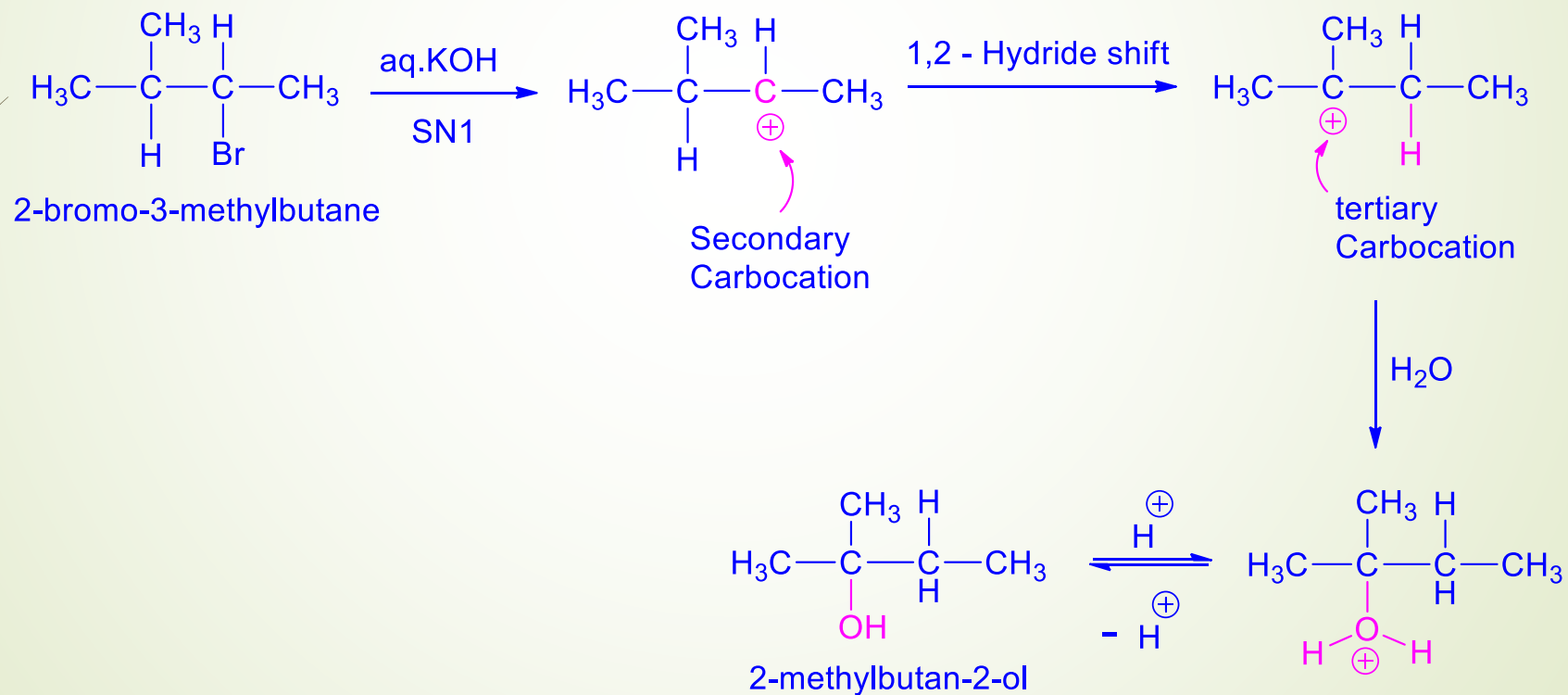


Energy profile diagram for SN1:



The SN1 Reaction: Carbocation Rearrangements:

- In SN1 reaction Carbocation rearrangement takes place, i.e. involve 1,2-hydride shift or 1,2-alkyl shifts




Bimolecular Nucleophilic substitution reactions (SN²):

- In these reactions rate determining step of the reaction involves both alkyl halide and nucleophile, i.e. rate of the reaction depends on both the concentrations of alkyl halide and Nucleophile, so these are called as Bimolecular reactions.

Rate of reaction \propto [Alkyl Halide][Nucleophile]

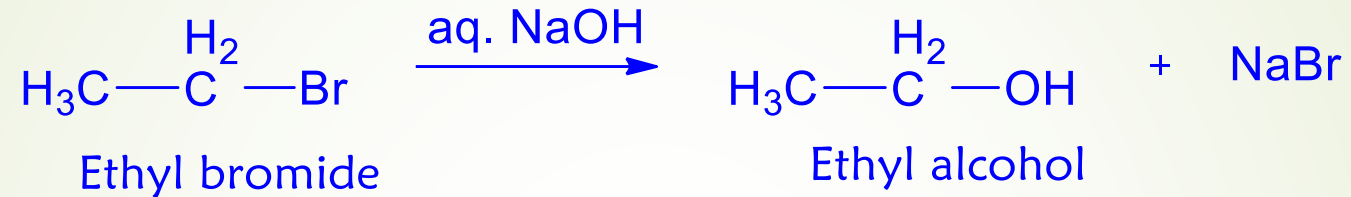
- This is a single step reaction process, in these reactions Nucleophile attacks on alkyl halide from the side opposite to the leaving group (X).
- In this the bond between Nucleophile and carbon formation and C-X bond breakage happens simultaneously, this state is called as transition state. this is highly energized and unstable state, so it can easily break and form products.

- 
- The SN2 reaction is a concerted reaction because bond formation and breaking occur simultaneously in a single transition state.
 - Generally primary alkyl halides participates in SN2 reactions and relative reactivity of alkyl halides is

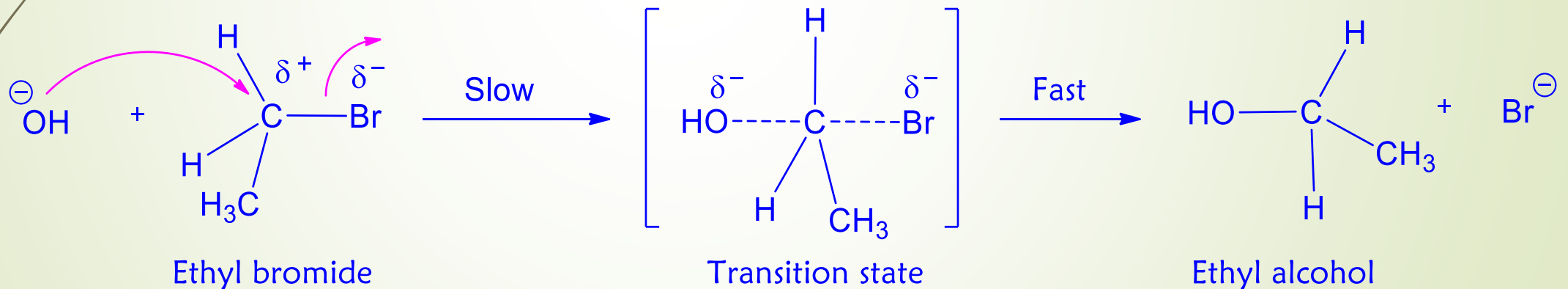
Methyl halide > Primary > Secondary > Tertiary

- Polar aprotic solvents (Like: DMSO, DMF etc.) favors SN2 reaction mechanism
- In this reaction Walden inversion takes place if substrate is asymmetric molecule.

Ex: Base hydrolysis of Ethyl bromide with aqueous alkali such as NaOH or KOH to form Ethyl alcohol as a product.



Mechanism:

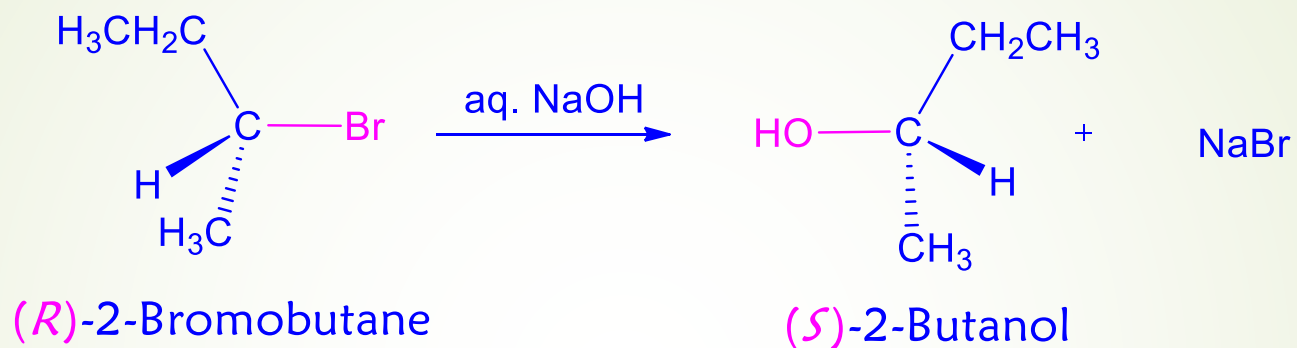




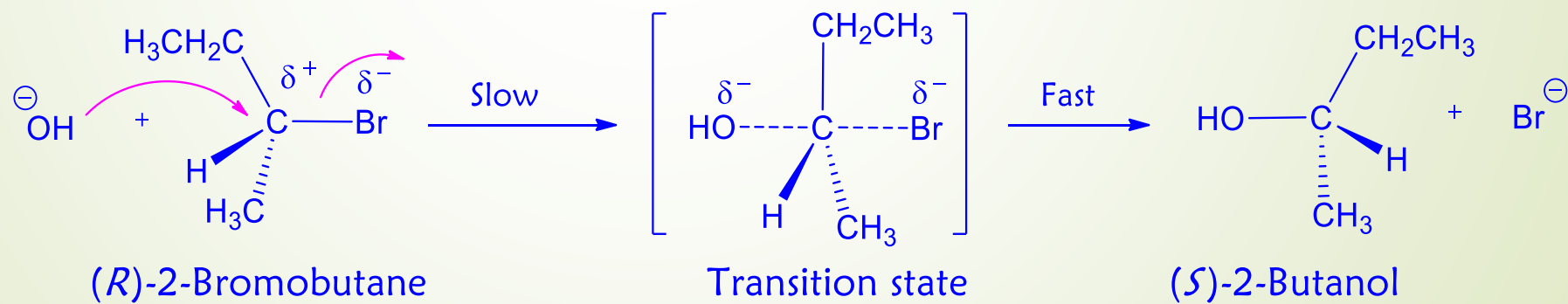
Stereochemistry in SN2 reactions:

- All SN2 reactions proceed with backside attack of the nucleophile, resulting in inversion of configuration takes place.
- if the reaction takes place at a stereo center in asymmetric molecule, spatial orientation of groups around the central carbon atom is inverted like reverted umbrella in a very strong wind, i.e. 100% inversion of product formation taking place in SN2 Reactions. It is called as **Walden inversion**

- Ex: Base hydrolysis of (*R*)-2-Bromo butane with aqueous alkali such as NaOH or KOH to form inverted (*S*)-2-butyl alcohol as a product.

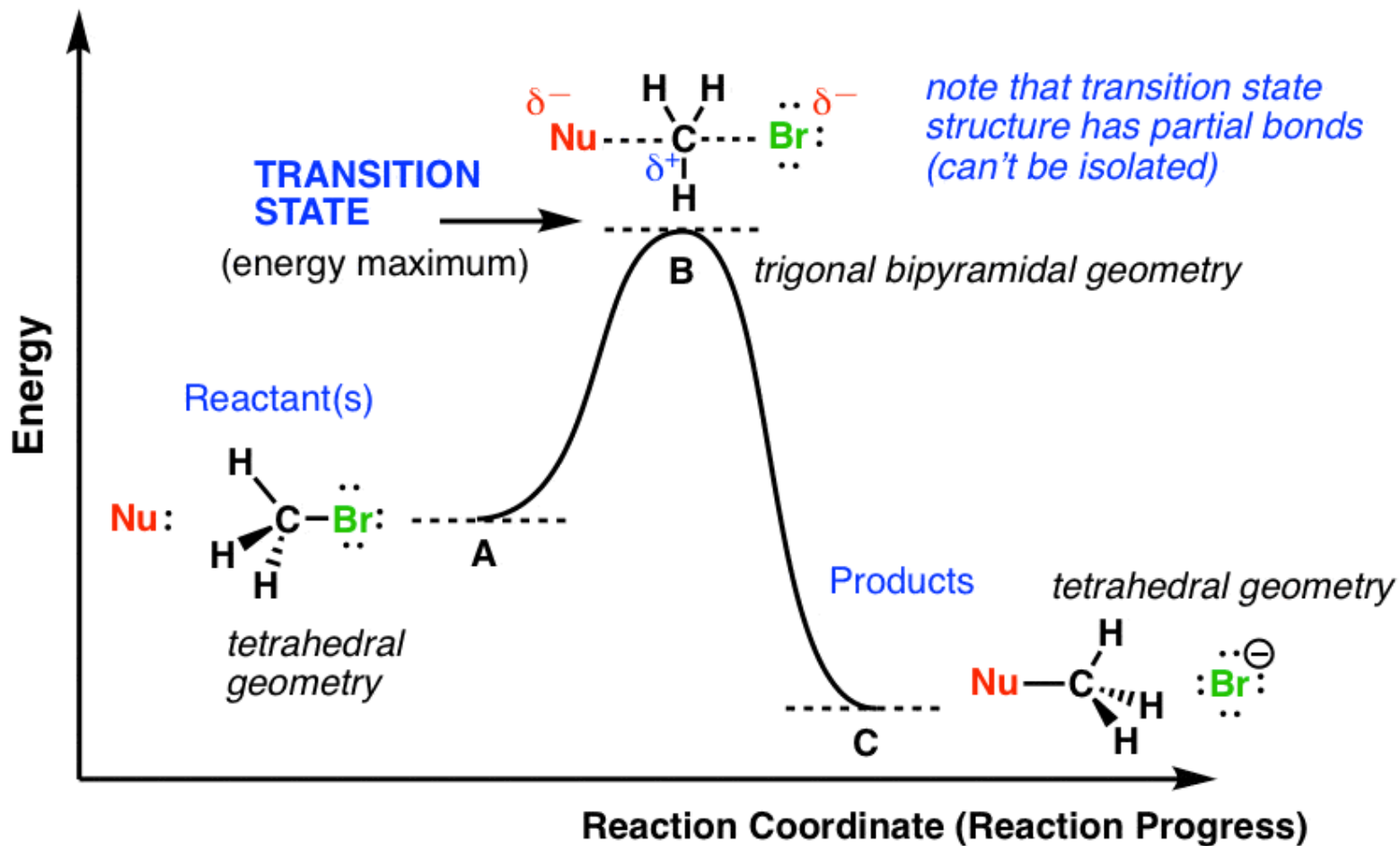


Mechanism:



Energy profile diagram for S_N2:

Reaction Energy Diagram For A Simple Substitution Reaction (S_N2)



Factors affecting the rate of Nucleophilic Substitution reactions of Alkyl Halides:

□ Nature of alkyl group:

- In SN1 reactions, a carbocation intermediate is formed, hence as the stability of carbocation increases rate of reaction increases. Therefore order of reactivity of alkyl halides in SN1 reaction is **Benzyl > Allyl > Tertiary > Secondary > Primary > Methyl halide**
- In SN2 reaction back side attack of the Nucleophile on carbon atom occurs, so as the crowding increases on carbon atom in alkyl halides backside attack of the Nucleophile becomes more difficult. Therefore the reactivity of alkyl halides in SN2 reaction is **Methyl > Primary > Secondary > Tertiary halide.**

□ Nature of Leaving group (Halogen):

- A better leaving group increases the rate of both SN1 and SN2 reactions. Usually leaving group carries negative charge hence groups which best stabilize a negative charge are the best leaving groups, i.e., the weakest bases are stable as anions and are the best leaving groups.

Increasing basicity
→

pKb values	23	22	21	11	-1.7	-2	-21
Ions	I ⁻	Br ⁻	Cl ⁻	F ⁻	OH ⁻	OR ⁻	NH ₂ ⁻
Leaving ability	30,000	10,000	200	1	0	0	0

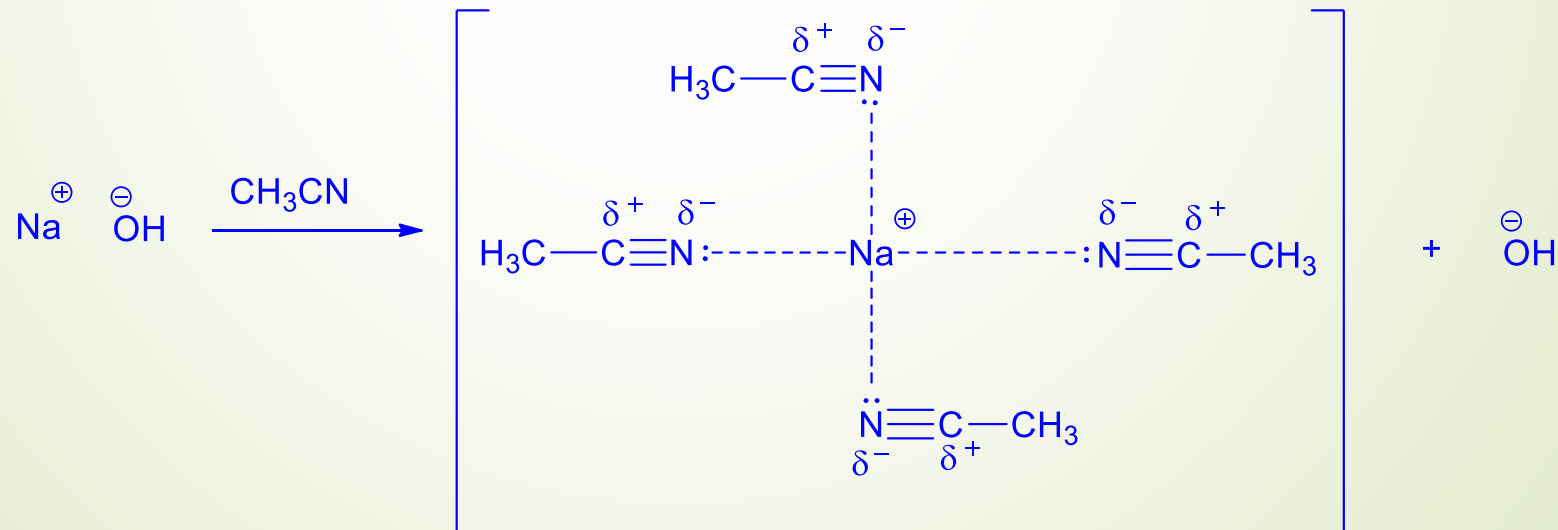
←
Increasing leaving ability

therefore the reactivity of alkyl halides in both SN1 and SN2 reactions is



□ Nature of Solvent:

- Polar protic solvents like H_2O and ROH favors $\text{S}_\text{N}1$ reactions, this is due to polar solvents stabilizes the ionic intermediates (carbocation and anion) by solvation.
- Polar aprotic solvents like acetonitrile (CH_3CN), Acetone (CH_3COCH_3), Dimethyl sulfoxide (DMSO) and Dimethyl Formamide (DMF) favor $\text{S}_\text{N}2$ reaction since these are well solvates the metal cations but not the nucleophiles hence they are more nucleophilic.





☐ Nature and Concentration of Nucleophile:

- In SN1, Rate of reaction does not depend on concentration of Nucleophile, so weak (like H_2O and ROH) and low concentrated Nucleophiles accelerate the rate of SN1 reaction.
- In SN2, Rate of reaction is depending on concentration of Nucleophile, so strong and high concentrated Nucleophiles accelerate the rate of SN2 reaction.

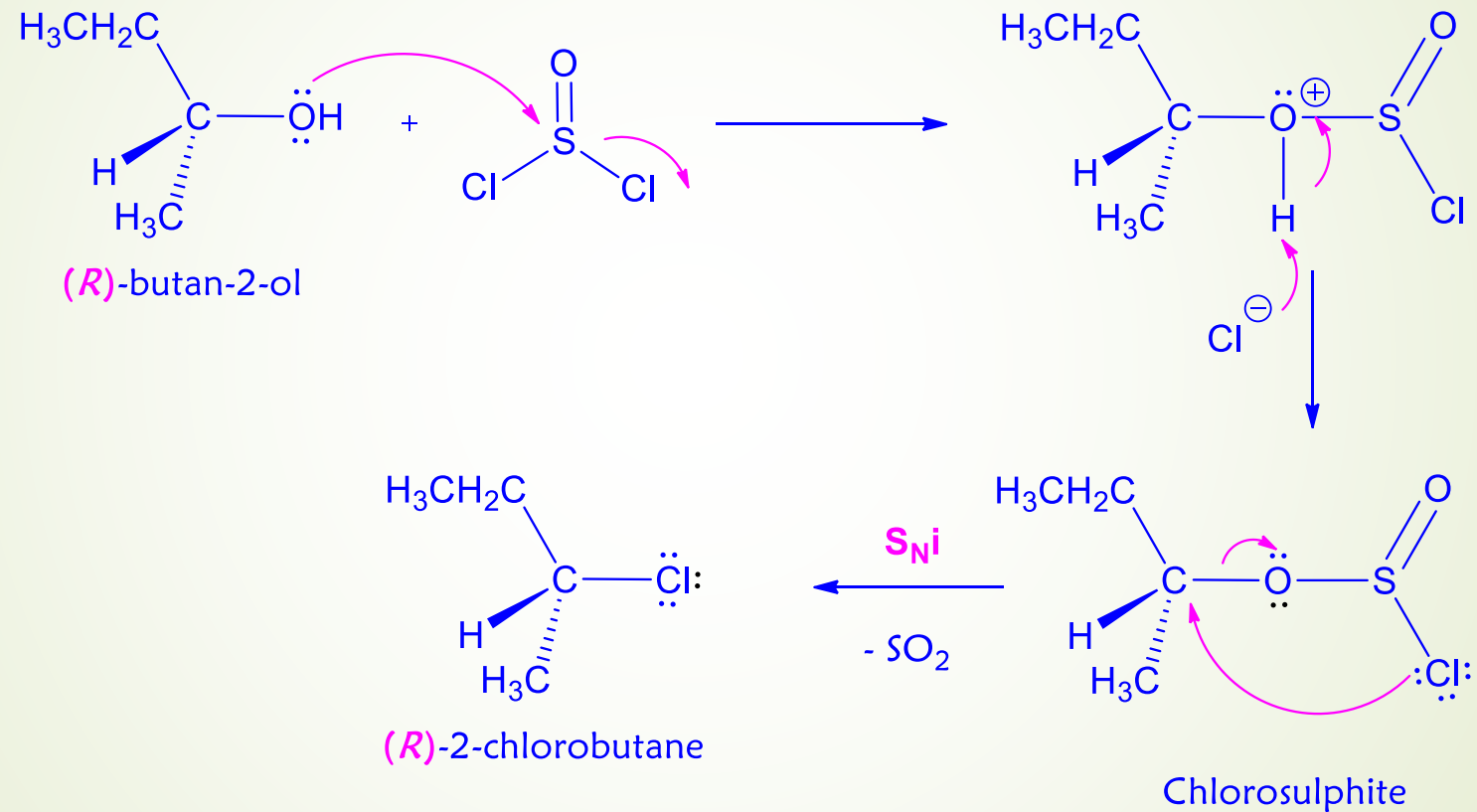
Differences between SN1 and SN2 Reactions:

<u>SN1 Reaction</u>	<u>SN2 Reaction</u>
Unimolecular Reactions	Bimolecular Reactions
It is two step reaction process	It is a single step reaction process
Carbocation intermediate is formed	No Carbocation intermediate is formed
Racemic mixture is formed	Walden inversion takes place
Reactivity of alkyl halides is Tertiary Halide > Secondary > Primary > Methyl halide	Reactivity of alkyl halides is Methyl halide > Primary > Secondary > Tertiary halide
Weak and low concentrated Nucleophiles favors	Strong and high concentrated Nucleophiles favors
Polar protic solvents Favors this reaction	Polar aprotic solvents Favors this reaction

Intra molecular Nucleophilic Substitution (S_{Ni})

- In these reactions alcohols with $SOCl_2$ to give corresponding halide
- Retention of configuration takes place
- First alcohol reacts with $SOCl_2$ to form an alkyl chloro sulphite
- Next step is loss of a SO_2 molecule and its replacement by the chloride, which was attached to the sulfite group and it is concerted.

EX: Conversion of (R)-butan-2-ol to (R)-2-chlorobutane



Summary

- Applications of Alkyl halides in day to day life.
- Classification of Alkyl halides into aliphatic (primary, secondary, tertiary) aromatic and aralkyl.
- Nomenclature of Alkyl halides; IUPAC and Common names.
- Nucleophilic aliphatic substitution reactions.
Unimolecular (S_N1) and Bimolecular (S_N2) reactions and their mechanisms.
- Stereochemistry and Energy profile diagrams of Unimolecular (S_N1) and Bimolecular (S_N2) reactions.
- Factors influencing on Unimolecular (S_N1) and Bimolecular (S_N2) reactions and their mechanisms.
- Differences between S_N1 and S_N2 reactions.



Thank you