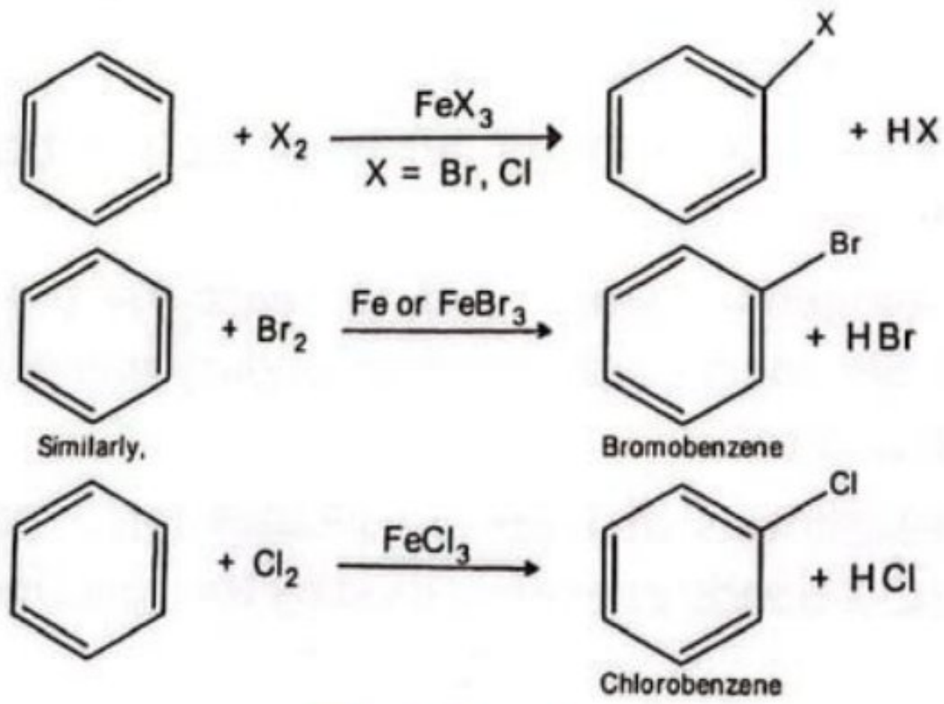
HALOGENOALKANES

Preparation Halogenoarenes

Halogenation of benzene occurs with halogens (X_2) in the presence of Fe or Lewis acid catalyst FeX3.



Reactivity of Halogenoalkanes

The **strength of the C–X bond** (where *X* is a halogen) is an important factor that determines the **reactivity of alkyl halides** and **aryl halides**.

In an **alkyl halide**, the molecule is **polarized** because halogens are more **electronegative** than carbon. As a result, the **carbon atom becomes partially positive (δ^+)**, and the **halogen becomes partially negative (δ^-)**.

This makes the halogen atom nucleophilic in nature and allows it to be **replaced by another nucleophile**.
For example, **chloroethane** undergoes a **nucleophilic substitution reaction** as follows:

$$CH_3 - CH_2 - Cl + Nu^- \rightarrow CH_3 - CH_2 - Nu + Cl^-$$

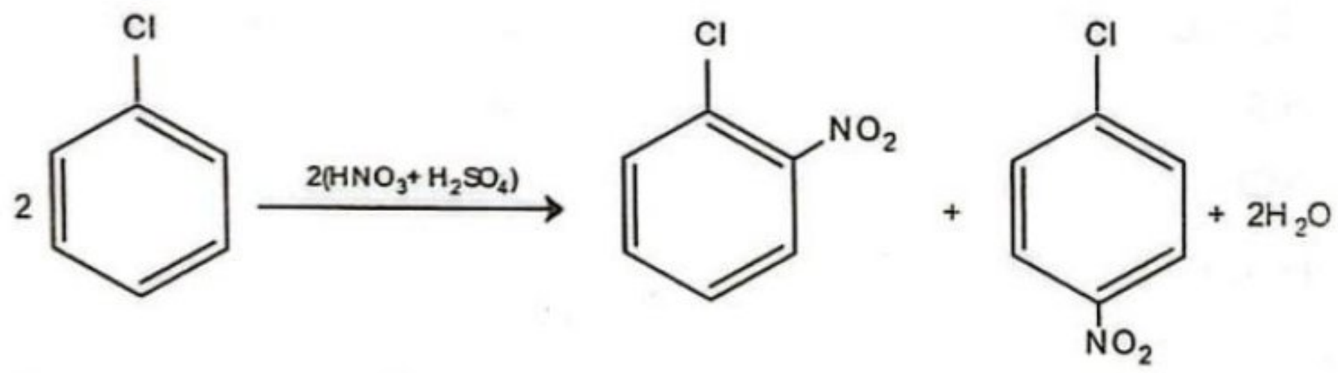
In this reaction, the **nucleophile (Nu^-)** attacks the **carbon atom** attached to chlorine, replacing the chlorine atom.

Reactivity of Aryl Halides (e.g., Chlorobenzene)

In **chlorobenzene**, the **lone pair of electrons** on the chlorine atom is **delocalized into the benzene ring**. This gives the **C–Cl bond partial double bond character**, making it **stronger and harder to break**. Therefore, **chlorine cannot be easily replaced by a nucleophile**.

Moreover, due to **resonance**, chlorine increases the **electron density** of the benzene ring, especially at the **ortho** and **para** positions. Hence, chlorobenzene undergoes **electrophilic substitution reactions** rather than nucleophilic substitution.

Example:
During **nitration of chlorobenzene**, a mixture of **ortho-nitrochlorobenzene** and **para-nitrochlorobenzene** is formed.



Reactions of Halogenoalkanes (Alkyl Halides)

In an **alkyl halide** molecule, the **carbon–halogen (C–X) bond** is **polarized** because the **halogen atom** is more **electronegative** than the **carbon atom**.

As a result, the **bonding electrons** are drawn closer to the halogen atom, making the **halogen partially negative (δ^-)** and the **carbon partially positive (δ^+)**.

$$C^{\delta+} - X^{\delta-}$$

The **polar character** of the **C–X bond** is responsible for the **chemical reactivity** of alkyl halides.

Types of Reactions of Alkyl Halides

Alkyl halides mainly undergo **two types of reactions**:

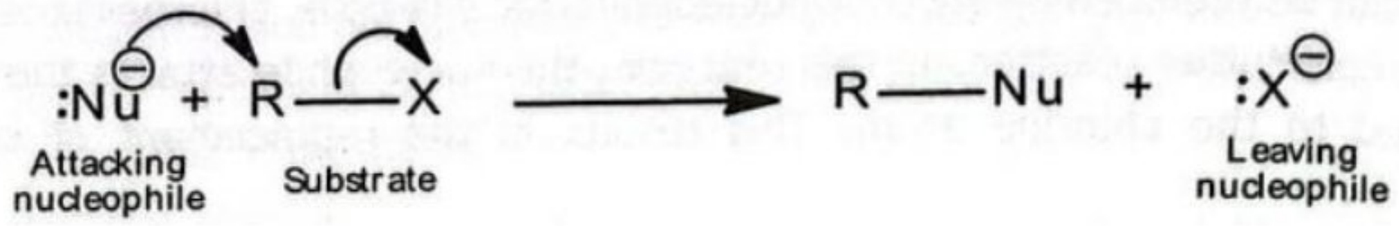
1. **Nucleophilic Substitution Reactions (SN Reactions)**
   In these reactions, a **nucleophile** (electron-rich species) attacks the **positively charged carbon atom**, replacing the halogen atom.
2. **Elimination Reactions**
   In these reactions, the **halogen atom** and a **hydrogen atom** from an adjacent carbon are removed (eliminated), forming an **alkene**.

Nucleophilic Substitution (SN) Reactions of Alkyl Halides

A **nucleophilic substitution reaction** is a chemical reaction in which the **halogen atom** of an **alkyl halide** is **substituted (replaced)** by a **nucleophile**.

A **nucleophile (Nu^-)** is a species that is **electron-rich** and attacks the **electron-deficient carbon atom** (the one bonded to the halogen).

The **general equation** for a nucleophilic substitution reaction is:



where:

- **R–X** = alkyl halide
- **Nu^-** = nucleophile
- **X^-** = halide ion (leaving group)

Such reactions are called **nucleophilic substitution reactions** or **SN reactions**.

Substrate, Nucleophile, and Leaving Group

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1. Substrate Molecule

The **substrate** is the **alkyl halide molecule** on which the **nucleophile attacks**.
It contains the **carbon–halogen (C–X) bond**, where carbon is partially positive and halogen is partially negative.

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2. Nucleophile

A **nucleophile** is a species that has a **lone pair of electrons** and can **donate** this pair to an **electron-deficient carbon atom** (electrophilic carbon) of the alkyl halide.
Nucleophiles can be **negatively charged** or **neutral molecules**.

Examples of Nucleophiles:

Nucleophile	Name
OH^-	Hydroxide ion
NH_2^-	Amide ion
$C_2H_5O^-$	Ethoxide ion
Cl^-	Chloride ion
Br^-	Bromide ion

HS^-	Hydrogen sulfide ion
SCN^-	Thiocyanate ion
NH_3	Ammonia
H_2O	Water

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3. Leaving Group (LG)

The **halogen atom** of an alkyl halide is called the **leaving group**.
It departs from the molecule along with an **unshared pair of electrons** when replaced by a nucleophile.

A **good leaving group** is one that can easily carry away its electron pair and form a stable ion.

Good Leaving Groups:
Cl^-, Br^-, I^-, HSO_4^-

Poor Leaving Groups:
OH^-, OR^-, NH_2^-

Note: The **iodide ion (I^-)** is both a **good nucleophile** and a **good leaving group**.

Steps in a Nucleophilic Substitution Reaction

There are two main events in a nucleophilic substitution reaction:

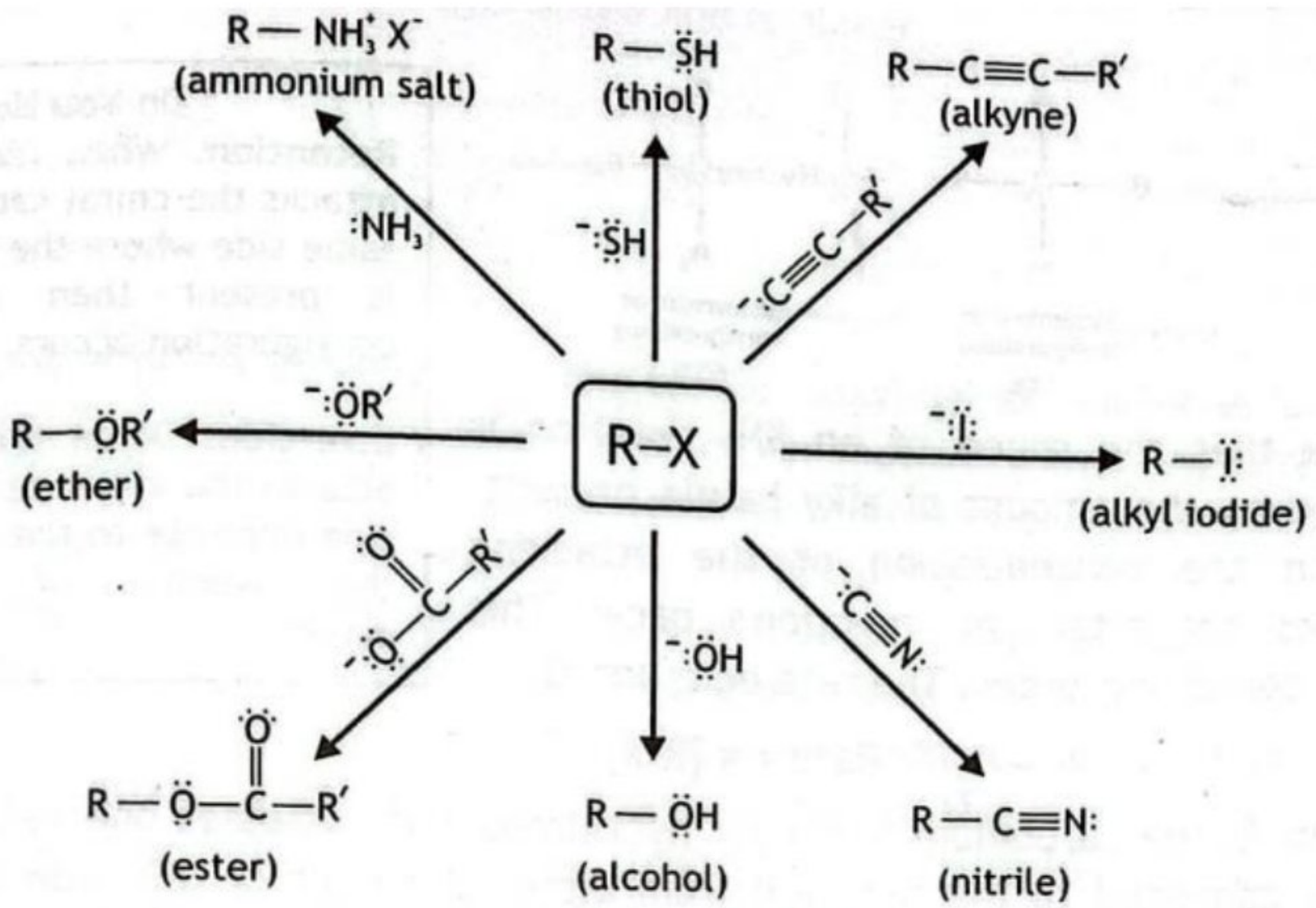
1. **Breaking** of the bond between **carbon and halogen**.
2. **Formation** of a new bond between **carbon and the incoming nucleophile**.

Mechanisms of Nucleophilic Substitution Reactions

The course of substitution depends on the nature of the substrate, nucleophile, and leaving group.

- In **primary and secondary alkyl halides**, the **attack by the nucleophile** and **departure of the leaving group** occur **in a single step**.
  → This follows the **SN2 mechanism**.
- In **tertiary alkyl halides**, the **leaving group departs first**, forming a **carbocation**, and then the **nucleophile attacks** in the second step.
  → This follows the **SN1 mechanism**.

Examples of Nucleophilic Substitution Reactions



Carbocations and their Stability

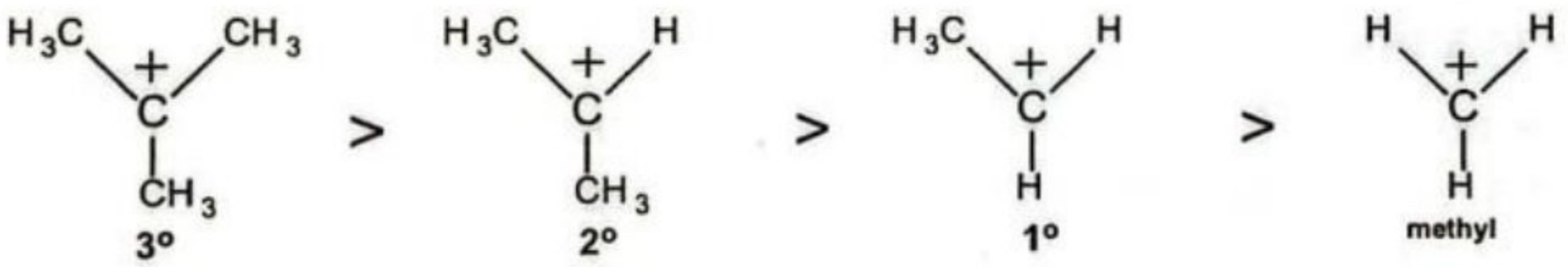
Carbocation:
A carbon atom that is attached to three atoms or groups and carries a **positive charge** is known as a **carbocation**.
It is formed when a covalent bond breaks in such a way that the carbon atom loses an electron pair.

Stability of Carbocations

The general order of stability of simple alkyl carbocations is:

$$3^\circ > 2^\circ > 1^\circ > \text{methyl}$$

(most stable) → (least stable)



Reason for Stability Order

This order is due to the **electron-donating effect** of alkyl groups, which stabilizes the positively charged carbon atom in two ways:

1. **Inductive Effect:**
   Alkyl groups push electrons towards the positively charged carbon atom through sigma bonds, reducing the positive charge density.
2. **Hyperconjugation (No-bond Resonance):**
   The hydrogen atoms attached to the adjacent carbon atoms can overlap with the empty p-orbital of the carbocation.
   This delocalizes the positive charge and increases stability.
   The greater the number of alkyl groups, the greater the hyperconjugation.

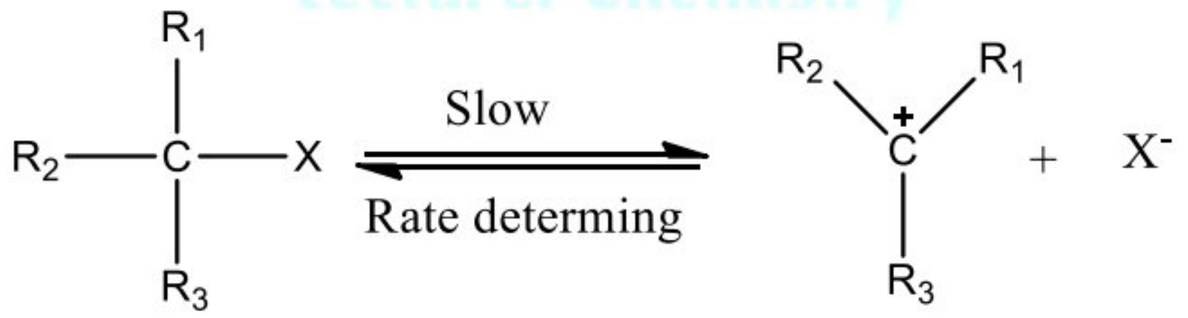
SN1 Mechanism

Definition:
An **SN1 reaction** (Substitution Nucleophilic Unimolecular) is a **two-step** nucleophilic substitution mechanism.
The name "SN1" comes from:

- **S** = Substitution
- **N** = Nucleophilic
- **1** = Unimolecular (rate depends on one molecule only)

Step 1: Formation of Carbocation (Slow Step)

The **substrate (R–X)** ionizes **reversibly** to form a **carbocation (R^+)** and a **halide ion (X^-)**.
This is the **rate-determining step** (slow step).



Carbonium Ion

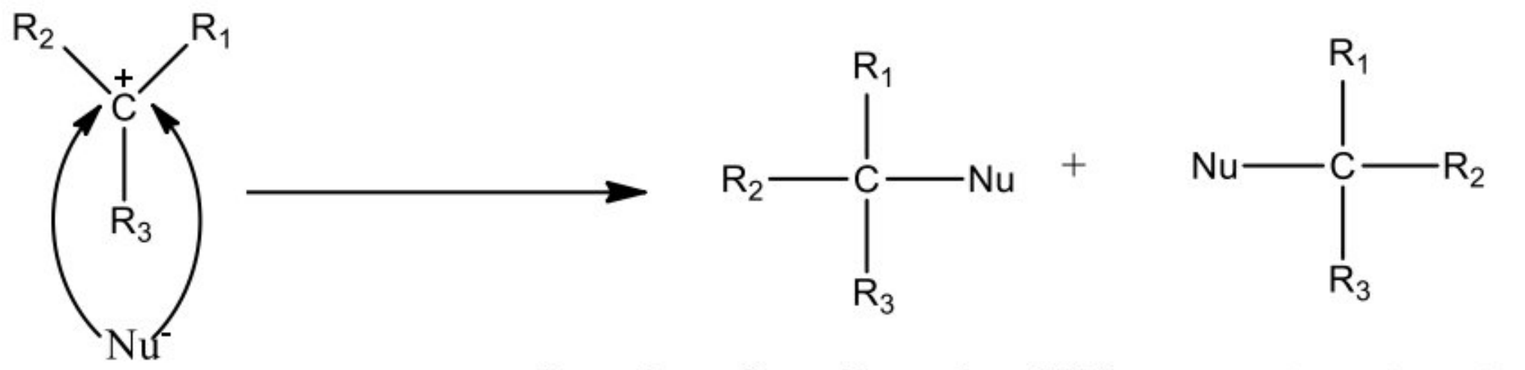
The rate of reaction depends **only** on the concentration of the alkyl halide:

$$\text{Rate} = k[\text{R–X}]$$

That is why this reaction is called **first order** or **unimolecular**.

Step 2: Attack of Nucleophile (Fast Step)

The **nucleophile (Nu^-)** attacks the **planar carbocation**, forming the **substituted product (R–Nu)**:



Retenion of configuration 50% Inversion of configuration 50%

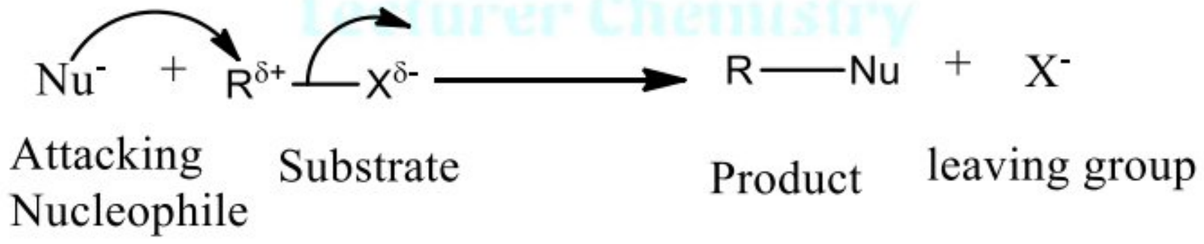
Hybridization and Structure

The **carbocation (R^+)** is **sp^2 hybridized** and has a **planar structure** with an empty **p-orbital**.
The nucleophile can attack **from either side** of the plane.

SN_2 Mechanism

Definition:
SN_2 stands for **Substitution Nucleophilic Bimolecular** reaction.
It is a **one-step mechanism** in which the **nucleophile attacks** the carbon atom **at the same time** as the **leaving group departs**.
Hence, bond-making and bond-breaking occur **simultaneously**.

Mechanism:



- The nucleophile attacks the carbon atom **from the side opposite** to the leaving group (called **backside attack**).
- The **C–Nu bond** forms while the **C–X bond** breaks **in one step**.
- This **single transition state** determines the rate of the reaction.

Rate of Reaction

The rate depends on the **concentration of both** the **alkyl halide (R–X)** and the **nucleophile (Nu^-)**:

$$Rate = k[R - X][Nu^-]$$

Thus, the reaction is:

- **First order** in alkyl halide
- **First order** in nucleophile
- **Second order overall**

Transition State

During the reaction, the carbon atom:

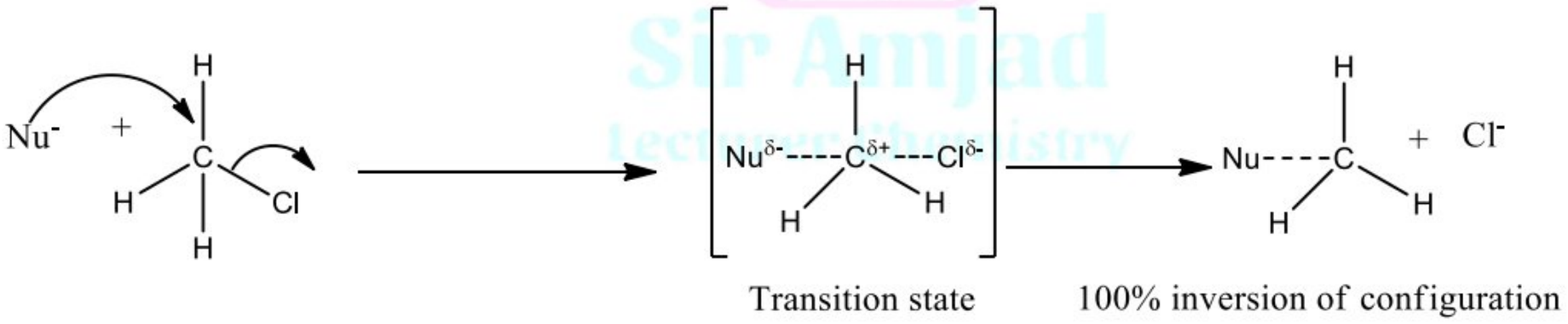
- Is **sp^2 hybridized**
- Has a **planar, trigonal transition state**
- Is partially bonded to both the **nucleophile** and the **leaving group**

$$Nu \text{ - - - } C \text{ - - - } X$$

Stereochemical Outcome (Inversion of Configuration)

- The nucleophile attacks **from the back side**, opposite to the leaving group.
- This causes **inversion of configuration**, also known as **Walden inversion**.
- The product has a configuration **opposite** to that of the reactant (100% inversion).

Example:



Effect of Structure of Alkyl Halides

The rate of SN_2 reaction decreases with increasing size of the alkyl group due to **steric hindrance**.

$$\text{Methyl halide} > 1^\circ > 2^\circ > 3^\circ$$

- **Methyl halide** reacts very fast (least steric hindrance).
- **Tertiary halide** does not undergo SN_2 reaction (too bulky).
- **Secondary halide** can undergo both SN_1 and SN_2 depending on conditions.

Example:

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

Methyl bromide reacts with hydroxide ion to form methanol via the SN_2 mechanism.

Effect of Solvent on SN Reactions

Effect of Solvent on SN_2 Reactions

Polar protic solvents can interact with the nucleophile through hydrogen bonding. This reduces the nucleophile's strength and slows down the reaction. Therefore, **polar protic solvents decrease the rate of SN2 reactions** because the nucleophile is part of the rate-determining step.

Effect of Solvent on SN_1 Reactions

In SN1 reactions, a **carbocation intermediate** is formed. Polar protic solvents help stabilize this carbocation through solvation, making its formation easier. Hence, **polar protic solvents increase the rate of SN1 reactions** by stabilizing the intermediate species.

Predicting SN_1 and SN_2 Mechanisms

To predict whether a nucleophilic substitution reaction will occur via the **SN_1** or **SN_2** mechanism, the following factors must be considered:

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1. The Nature of the Electrophile (Alkyl Halide)

When the leaving group is attached to a **primary carbon atom**, an **SN_2 mechanism** is favoured. This is because the electrophile is unhindered, and the nucleophile can easily attack it.

However, when the leaving group is attached to a **tertiary carbon atom**, the **tertiary carbocation** formed is relatively stable, and the attack of the nucleophile is **sterically hindered**. Therefore, the **SN_1 mechanism** is favoured in such cases.

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2. The Nature of the Nucleophile

Powerful nucleophiles, especially those having **negative charges**, favour the **SN_2 mechanism**. For example, **OH^-**, **CN^-**, and **I^-** favour SN_2 reactions.

On the other hand, weaker nucleophiles such as **water (H_2O)** or **alcohols (ROH)** favour the **SN_1 mechanism**.

3. The Nature of the Solvent

Polar aprotic solvents (such as **acetone**) enhance the reactivity of the nucleophile and thus favour the **SN_2 mechanism**.

In contrast, **polar protic solvents** stabilize the **carbocation intermediate** and therefore favour the **SN_1 mechanism**.

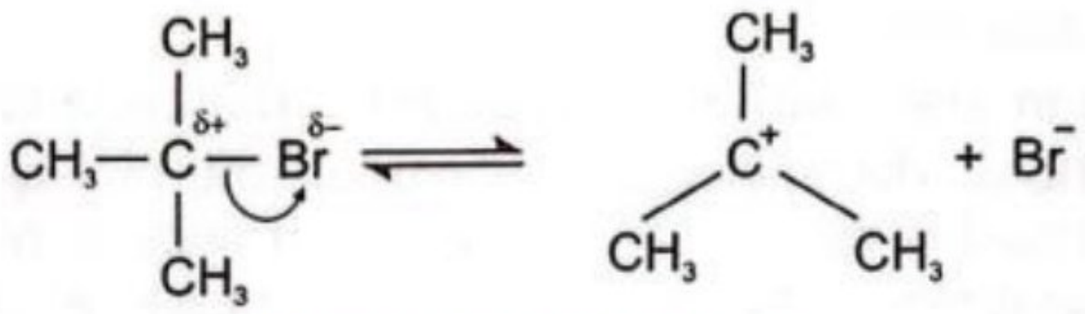
Elimination Reactions

E1 Reaction (Unimolecular Elimination)

Alkyl halides also undergo E, and E_2 reactions, in which a substrate loses a proton to form a double bond. E1 Reaction (Unimolecular Elimination) E, is a two-step reaction.

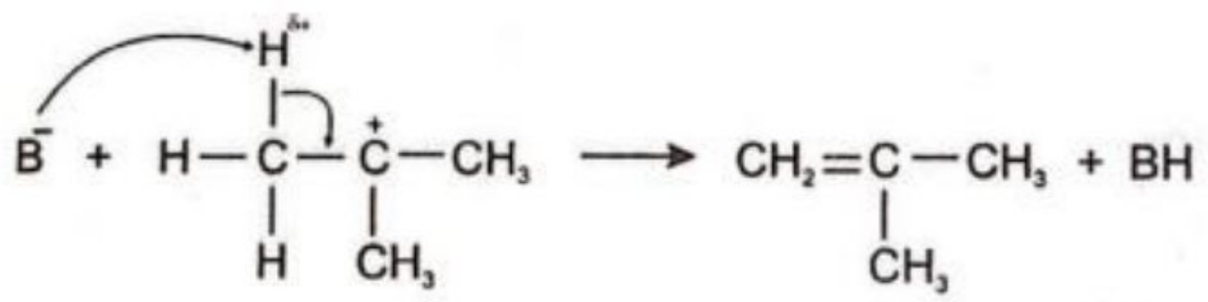
Step 1:

Formation of a carbocation intermediate by the departure of the leaving group (rate. determining step).



Step 2:

A base abstracts a proton from a ß-carbon, resulting in the formation of a double bond.



Rate law

The rate of reaction depends only on the concentration of the substrate.

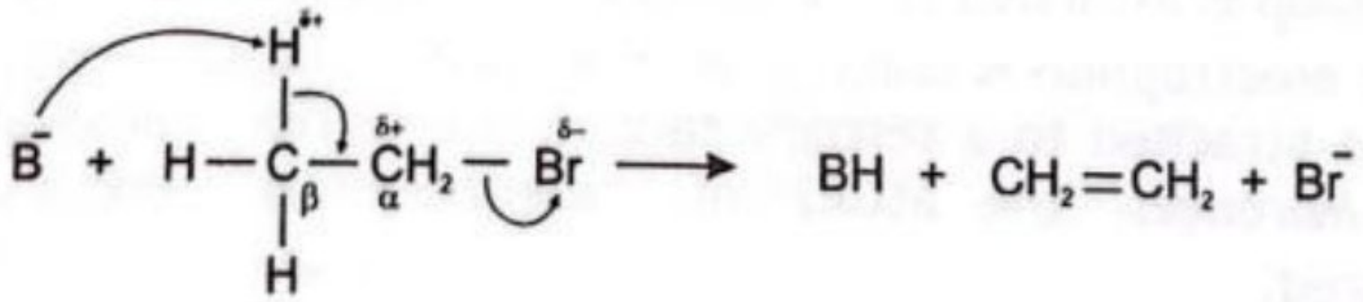
Rate = k[substrate]

Favoured by:

It is favoured by weak bases and polar protic solvents (e.g., water, ethanol) that stabilize the carbocation.

E2 Reaction (Bimolecular Elimination)

E_2 is a one-step reaction. The base abstracts a proton from the ß-carbon simultaneously as the leaving group departs, forming the double bond.



Rate law

The rate of reaction depends on the concentrations of both the substrate and the base.

Rate = k[substrate][base]

Favoured by:

This reaction is favoured by strong bases and polar aprotic solvents (e.g., DMSO, acetone).

Conditions for SN and E Reactions

The type of mechanism (SN_1, SN_2, E_1, or E_2) for alkyl halides depends on several factors — including the type of alkyl halide, the strength of the nucleophile or base, and the solvent.

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1. Primary Alkyl Halides

- Tend to undergo **SN_2 reactions** regardless of the strength of the nucleophile.
- **Elimination (E_2)** is less common because primary carbocations are unstable.

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2. Secondary Alkyl Halides

- With **strong nucleophiles or bases** → reaction may proceed by **SN_2 or E_2**.
- With **weak nucleophiles or bases** → reaction may proceed by **SN_1 or E_1**.

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3. Tertiary Alkyl Halides

- With **strong bases** → reaction favours **E_2** (elimination).
- With **weak nucleophiles or bases** → reaction favours **SN_1 or E_1** (substitution/elimination).

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4. Effect of Solvent

- **Polar aprotic solvents** (e.g., DMSO, acetone) favour **SN_2 and E_2** reactions.
- **Polar protic solvents** (e.g., water, alcohols) favour **SN_1 and E_1** reactions.

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5. Nucleophile or Base Strength

- **Good nucleophile but weak base** → favours **SN_2**.
- **Weak nucleophile but strong base** → favours **E_2**.

Test to Assess the Reactivity of Haloalkanes

1. Reactivity and the Carbon–Halogen (C–X) Bond

The reactivity of haloalkanes depends mainly on the strength of the **carbon–halogen bond (C–X)**, where **X = F, Cl, Br, or I**.

- **C–F bond** is the **strongest** because fluorine is small and highly electronegative.
- **C–I bond** is the **weakest**, as iodine has a larger atomic size and lower bond energy.
- Therefore, as we move **down the halogen group**, bond strength decreases and **reactivity increases**.

Order of bond strength:
C–F > C–Cl > C–Br > C–I

Order of reactivity:
RI > RBr > RCl > RF

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2. Reaction with Aqueous Silver Nitrate ($AgNO_3$)

A common test to compare the reactivity of haloalkanes is their **reaction with aqueous silver nitrate**.

Reaction:

Where **R** = alkyl group and **X** = Cl, Br, or I.

- The **silver ion (Ag^+)** replaces the **halide ion (X^-)** to form a **precipitate of silver halide (AgX)**.

- **Alkyl fluorides (R–F)** do **not react readily** because the **C–F bond is very strong**, so fluoride ion is not displaced.

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3. Observation: Colour of Precipitates

Halogen (X)	Silver Halide Formed	Colour of Precipitate	Solubility in NH_4OH (Aqueous Ammonia)
Cl	AgCl	White	Soluble
Br	AgBr	Cream	Partially soluble
I	AgI	Yellow	Insoluble

Alkyl Halides and Retrosynthesis

Alkyl halides (haloalkanes) are **important starting materials** in organic synthesis.
They can be converted into a variety of organic compounds by substitution or elimination reactions.

General Reaction

When a **haloalkane (R–X)** reacts with a **nucleophile (Nu^-)**, the nucleophile attacks the **carbon atom** bonded to the halogen.
The **halogen leaves** as a halide ion (X^-), forming a new compound.

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

Concept of Retrosynthesis

Retrosynthesis is a method used to identify the **starting materials** needed to synthesize a desired organic product.
It involves working **backwards** from the product to determine possible precursors.

For a product of the form **R–Nu**, the likely starting material is a **haloalkane (R–X)** that can react with the nucleophile **Nu^-**.

$$R - Nu \Rightarrow R - X + Nu^-$$

Example: Preparation of Ethyl Alcohol

Target molecule:

$$CH_3CH_2OH$$

Step 1: Work backwards
Break the molecule at the oxygen–carbon bond:

$$CH_3CH_2OH \Rightarrow CH_3CH_2^+ + OH^-$$

Step 2: Identify possible starting material
The positive fragment **$CH_3CH_2^+$** suggests an **ethyl group** bonded to a halogen in the starting compound.
Hence, the starting haloalkane is **bromoethane (CH_3CH_2Br)**.

Forward Reaction

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

Product: Ethyl alcohol (ethanol)
By-product: Bromide ion (Br^-)

For More Information:

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