# B: Organic Chemistry

## Paper II - Physical and organic Chemistry

B.Sc. Part I (Honours)

By
Sonu Ram Shankar
Assistant Professor
Department of Chemistry

Marwari College, Darbhanga

A constituent Unit of
Lalit Narayan Mithila University, Kameshwar Nagar, Darbhanga

# Reaction Mechanism: Substitution

## Substitution

When a group is replaced with another group.

Substitution Reaction are two types: Nucleophilic and electrophilic

## Nucleophilic:

When nucleophilic reagents bring out the reaction.

There are two types of substitution reaction based on molecularity: **$S_N2$ and $S_N1$**

**$S_N2$, (Substitution nucleophilic bimolecular)**: One step concerted reaction
**$S_N1$, (Substitution nucleophilic unimolecular):** Two step reaction
First step: Slow formation of carbonium ion, unimolecular, rate determining
Second step: Fast combination of carbanion ion and nucleophile

# Reaction Mechanism: Substitution

*Table 1: Comparison of $S_N2$ and $S_N1$ reaction*

| **Factor** | | **$S_N2$** | **$S_N1$** |
|---|---|---|---|
| **Order** | Reactants in comparable concentration | 2nd | 1st |
| | One reactant in excess concentration | 1st | 1st |
| **Stereochemistry** | | Inversion | Inversion, retention, or racemization |
| **Rearrangement** | | No | Possible |
| **Rate constant dependency** | With substrate | On nucleophile | |
| | With nucleophile | On leaving group | |

# Reaction Mechanism: Substitution

Mechanism:

**$S_N2$** $Y^- + R\text{-}X \rightarrow Y^{\delta-}\text{----}R\text{------}X^{\delta-} \rightarrow Y\text{-}X$

Transition state: $Y^{\delta-}\text{----}R\text{------}X^{\delta-}$ ; Carbonium: Pentavalent $C^+$

**$S_N1$** $R\text{-}X \rightarrow X^{\delta-}\text{----}R^{\delta+} \rightarrow X^- + R^+$

$R^+ + Y^- \rightarrow Y^{\delta-}\text{----}R^{\delta+} \rightarrow Y\text{-}X$

Intermediate; $R^+$; Carbenium: Traivalent $C^+$

Intermediate can be isolated: $ph_3C^+$ $ClO_4^-$/ $BF_4^-$, $CH_3C^+$ $SbF_6^-$

# Reaction Mechanism: Substitution

*Variation:*

**$S_N2(C^+)$ Mechanism**: If step 2 in $S_N1$ is slower than step 1

*Example*:

Step 1: $Ar_2CHOH + H^+ \rightarrow Ar_2CHOH_2^+ \rightarrow Ar_2C^+ + H_2O$

Step 2: $Ar_2CH^+ + ArH \rightarrow Ar_2CHAr$

Effect of substitution:

| | |
|---|---|
| p-methyl benzylchloride → p-methyl benzyl cation | Fast; due to hyper conjugation |
| p-Nitro benzylchloride → p-nitro benzyl cation | Slow; due to -I effect |