



B: Organic Chemistry

Paper II - Physical and organic Chemistry

B.Sc. Part I (Honours)

By

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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

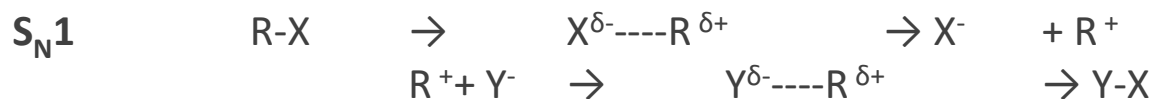
Factor		S_N2	S_N1
Order	Reactants in comparable concentration	2 nd	1 st
	One reactant in excess concentration	1 st	1 st
Stereochemistry		Inversion	Inversion, retention, or racemization
Rearrangement		No	Possible
Rate constant dependency	With substrate	On nucleophile	
	With nucleophile	On leaving group	

Reaction Mechanism: Substitution

Mechanism:



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



Intermediate; R⁺; Carbenium: Trivalent C⁺

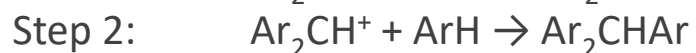
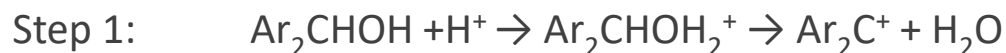
Intermediate can be isolated: $ph_3C^+ ClO_4^- / BF_4^-$, $CH_3C^+ SbF_6^-$

Reaction Mechanism: Substitution

Variation:

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

Example:



Effect of substitution:

p-methyl benzylchloride \rightarrow p-methyl benzyl cation

Fast; due to hyper conjugation

p-Nitro benzylchloride \rightarrow p-nitro benzyl cation

Slow; due to -I effect