B.Sc. I

Paper II Organic Chemistry

TYPES OF ORGANIC REACTIONS
NUCLEOPHILIC SUBSTITUTION: SN1, SN2

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BROAD CLASSIFICATION

1. SUBSTITUTION REACTION
    1. NUCLEOPHILIC SUBSTITTION – **SN^1 , SN^2**
    2. ELECTROPHILIC SUBSTITUTION
    3. FREE RADICAL SUBSTITUTION
2. ADDITION REACTIONS
    1. NUCLEOPHILIC ADDITION
    2. ELECTROPHILIC ADDITION
    3. FREE RADICAL ADDITION

3. ELIMINATION REACTIONS - **E1, E2**

4. REARRANGEMENT REACTIONS

5. POLYMERIZATION REACTION –
    1. CATIONIC,
    2. ANIONIC,
    3. FREE RADICAL

6. REACTIONS WHICH OCCUR DUE TO REORGANIZATION OF PI [π] ELECTRONS

SUBSTITUTION REACTIONS

1. NUCLEOPHILIC SUBSTITTION – Substitution brought about by a Nucleophile **[Nu]**$^{-}$

SN^{1} REACTION – Tertiary alkyl halide and KOH [OH]$^{-}$
SN^{2} REACTION – Primary alkyl halide and KOH [formation of transition state]

2. ELECTROPHILIC SUBSTITUTION - Substitution brought about by an Electrophile **[E]**$^{+}$
Characteristic reaction of aromatic compounds – Nitration of Benzene

3. FREE RADICAL SUBSTITUTION - Substitution brought about by Free Radicals **[X]**$^{\bullet}$
Characteristic reaction is Halogenation of Alkanes in sunlight

SUBSTITUTION REACTION

Nucleophilic substitution reactions are a class of reactions in which an electron rich Nucleophile attacks a positively charged electrophile to replace a leaving group.

Nucleophilic substitution reaction is a class of organic reactions where one Nucleophile replaces another.

In a nucleophilic substitution reaction, a stronger Nucleophile replaces a weaker Nucleophile from its compound.

Generally strong bases are stronger nucleophile.

$$R{-}LG + Nu\Theta \rightarrow R{-}Nu + LG\Theta$$

Where,

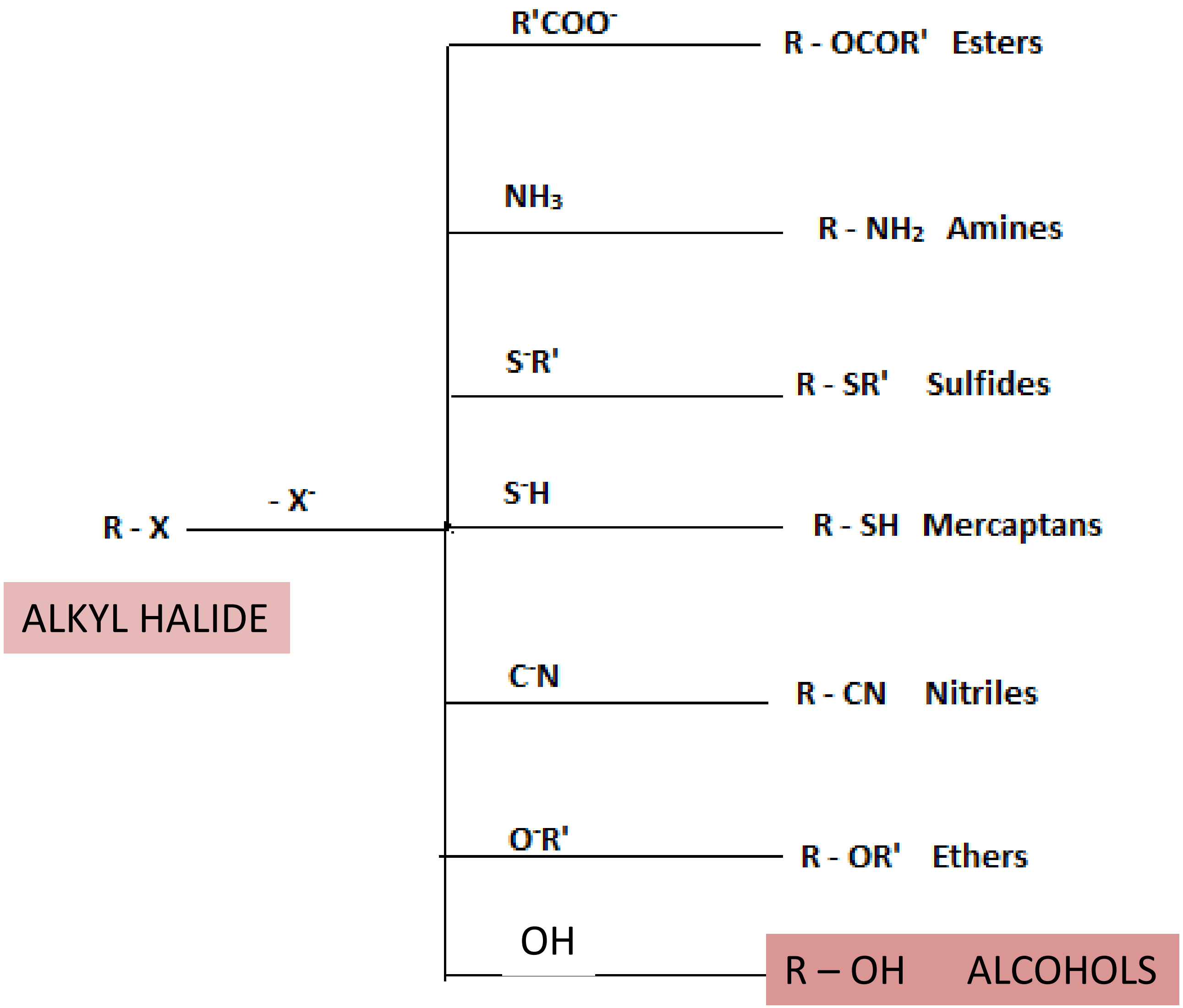
R = Alkyl group

LG = Leaving group (weak Nucleophile)

NuΘ→ Stronger Nucleophile

SUBSTITUTION REACTION

The leaving group leaves as a neutral molecule or anion



$R - X$ $\xrightarrow{-X^-}$

ALKYL HALIDE

$R'COO^-$ → $R - OCOR'$ Esters

NH_3 → $R - NH_2$ Amines

S^-R' → $R - SR'$ Sulfides

S^-H → $R - SH$ Mercaptans

C^-N → $R - CN$ Nitriles

O^-R' → $R - OR'$ Ethers

OH → R – OH ALCOHOLS

UNIMOLECULAR NUCLEOPHILIC SUBSTITUTION – SN1

It is called **unimolecular nucleophilic substitution reaction.**

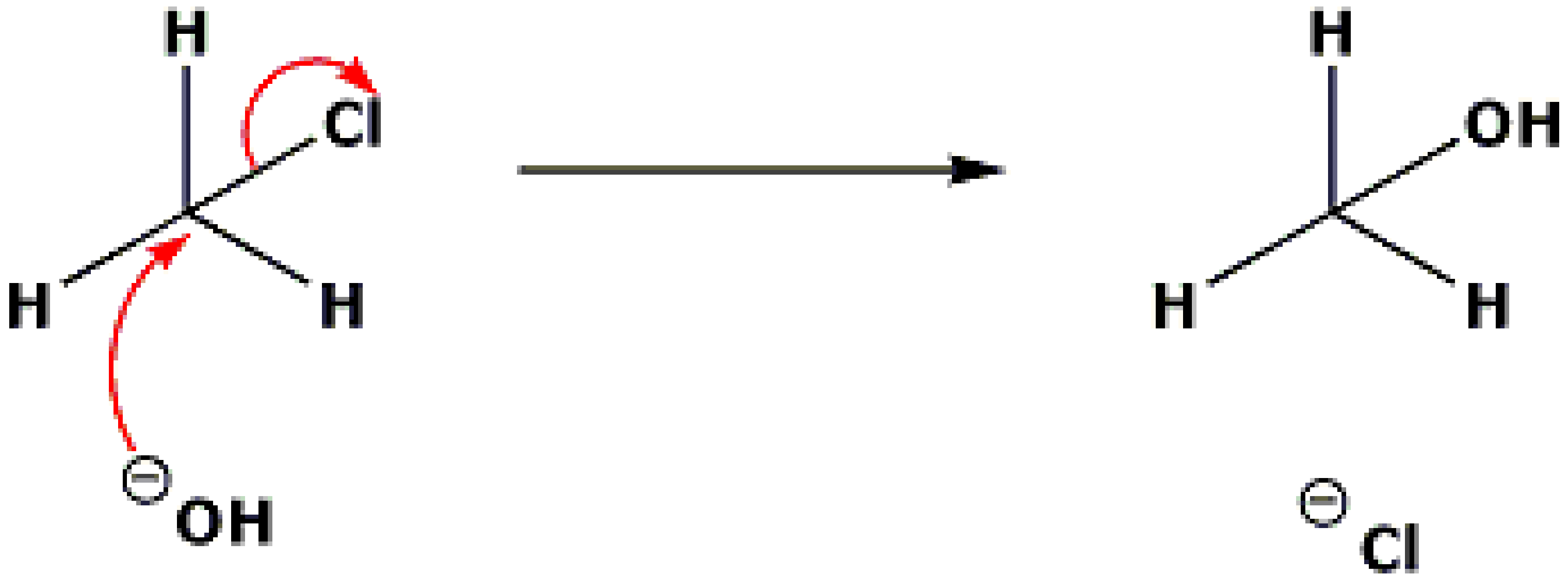
S_N1 mechanism depends only on the concentration of the substrate and is independent of the concentration of the incoming Nucleophile.

S_N1 reaction mechanism follows a step-by-step process.

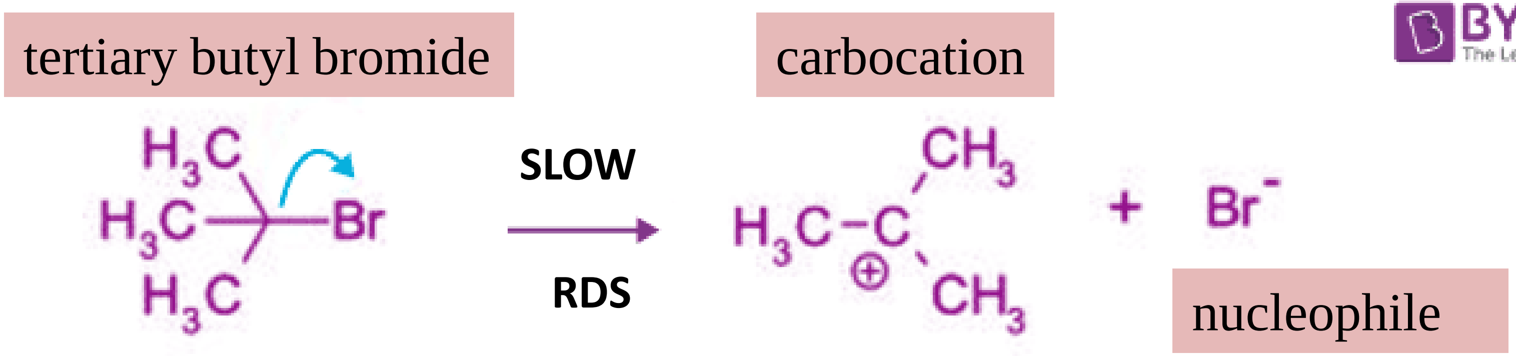
First, the Carbocation is formed from the removal of the leaving group.

Then the Carbocation is attacked by the Nucleophile.

Finally, the deprotonation of the protonated Nucleophile takes place to give the required product.



HYDROLYSIS OF TERTIARY BUTYL BROMIDE



<u>STEP 1</u> [Carbocation is formed from the removal of the leaving group]

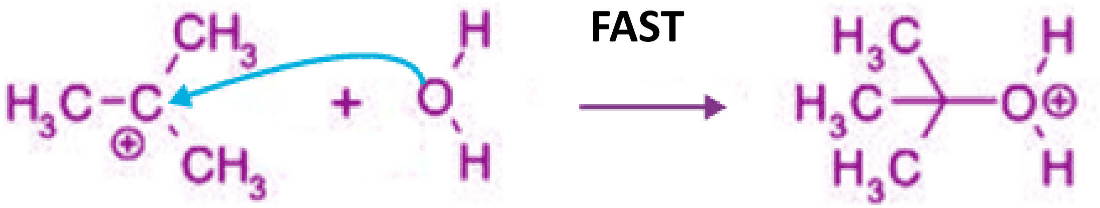
The carbon-bromine bond is a polar covalent bond. The cleavage of this bond allows the removal of the leaving group (bromide ion).

When the bromide ion leaves the tertiary butyl bromide, a Carbocation intermediate is formed.

This is the slowest step , so this is the **Rate Determining Step (RDS)** of the S_N1 mechanism.

The breaking of the carbon-bromine bond is endothermic

HYDROLYSIS OF TERTIARY BUTYL BROMIDE



carbocation

Oxonium ion

STEP 2 [Carbocation is attacked by the Nucleophile.]

In the second step of the SN1 reaction mechanism, the carbocation is attacked by the nucleophile.

Since water is used as a solvent, an oxonium ion intermediate is formed.

Since the solvent is of a neutral nature, a third step where deprotonation occurs is necessary.

HYDROLYSIS OF TERTIARY BUTYL BROMIDE

STEP 3 [deprotonation of the protonated Nucleophile]

The positive charge on the carbocation was shifted to the oxygen in the previous step.

The water solvent now acts as a base and deprotonates the oxonium ion to yield the required alcohol along with a hydronium ion as the product.

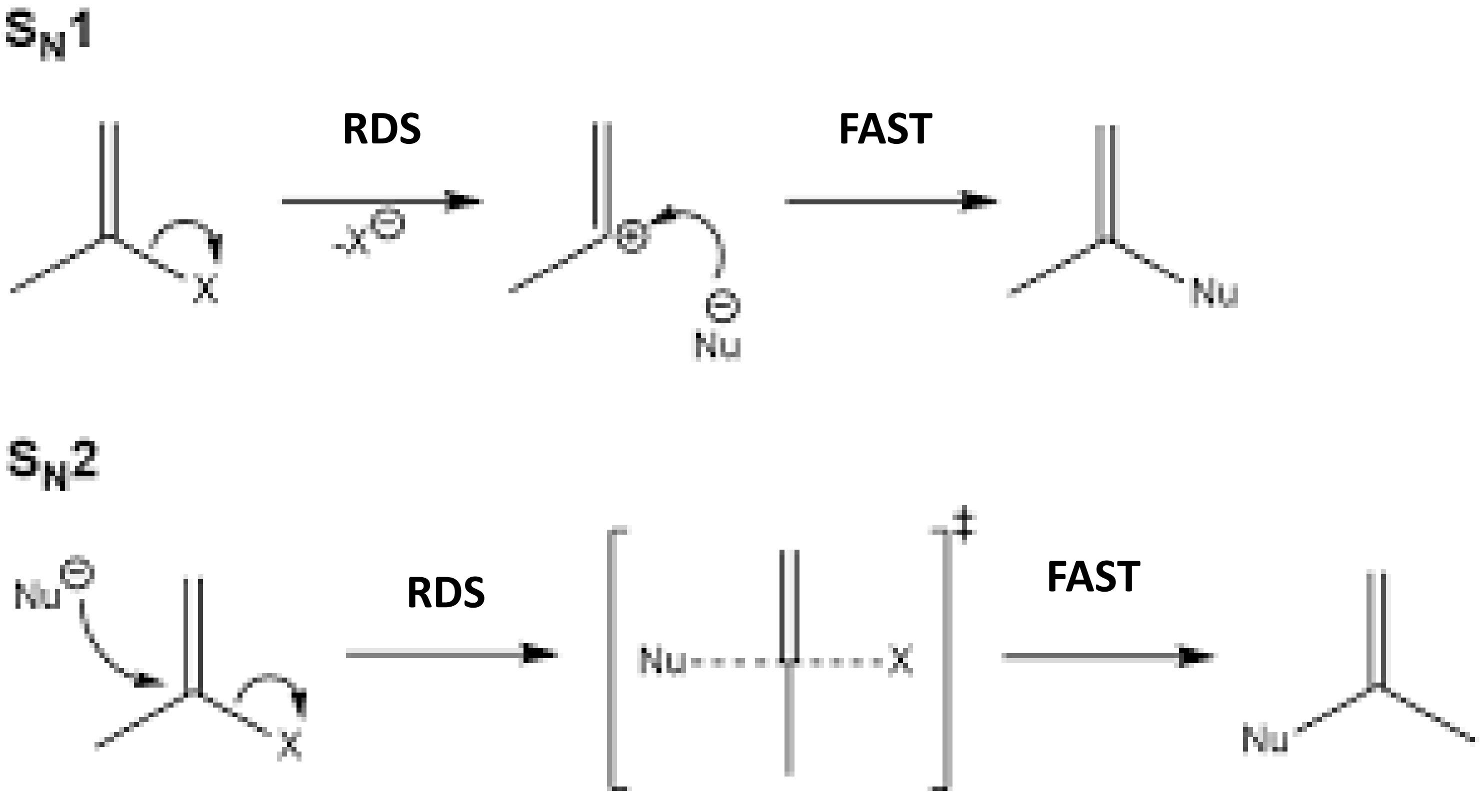
Step 2 and Step 3 of this reaction are fast.

BIMOLECULAR NUCLEOPHILIC SUBSTITUTION – SN2

It is called substitution nucleophilic bimolecular mechanism. It is a single step process consisting of one intermediate.

The order of reactivity of 1°, 2°, 3° halides is as follows.

1° > 2° > 3° (steric hindrance).



HYDROLYSIS OF METHYL CHLORIDE

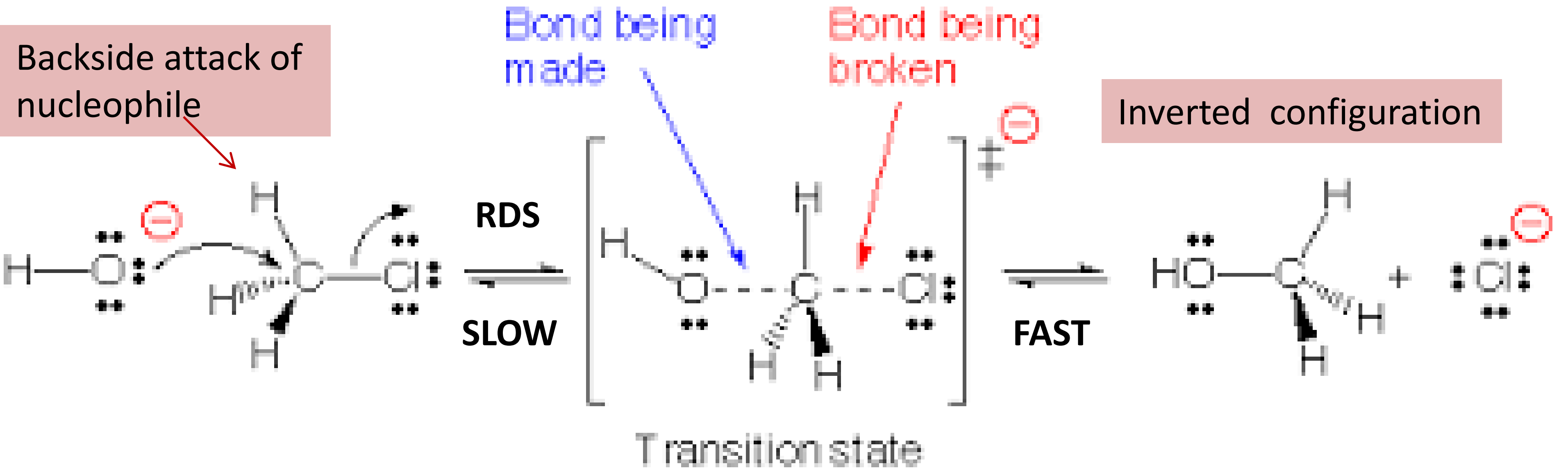
It proceeds through the backside (of the LG) attack of the incoming nucleophile to avoid repulsions.

This leads to formation of an intermediate which is indicated using two dotted lines between carbon – OH (Nu) and carbon-Cl (LG). The two dotted lines in the intermediate indicate that the C – Cl bond is broken and the C – OH bond is formed simultaneously.

Finally, C – Cl bond is completely broken and the C– OH bond is completed formed.

Since it is a backside attack of the nucleophile, the product will always have an inverted configuration with respect to the substrate (CH3 Cl).

Therefore, the SN_2 mechanism always results in “Inversion of configuration”.



Backside attack of nucleophile

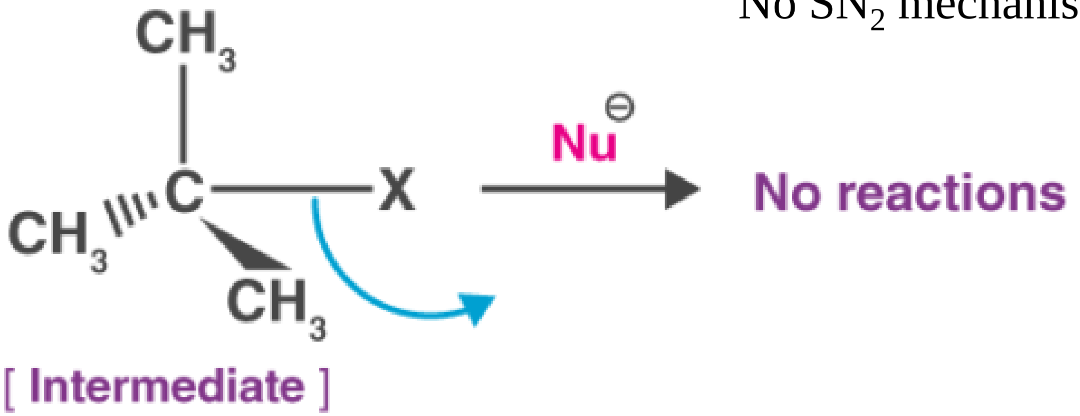
Inverted configuration

HYDROLYSIS OF METHYL CHLORIDE

In case of t-butyl of chloride, SN_2 mechanism becomes difficult as the nucleophile will find it difficult to attack from the backside due to the presence of bulky methyl groups.

Highly crowded substrates will be less reactive towards the SN2 mechanism.

No SN_2 mechanism.



CHARACTERISTICS OF SN_2

1. Sensitive to the steric effect.

2. A reaction occurs with inversion of molecule.

3. Methyl halides and primary halides undergo SN2, secondary halides may react but tertiary halides do not undergo SN2.

5. The reaction between the negatively charged nucleophile with the substrate will give a neutral product.

6. The reaction between the neutral nucleophile with the substrate will give rise to the positively charged product.

7. A weak base (stable anions) are good leaving groups.