

**SRIMAAN COACHING CENTRE-TRICHY-UG-TRB-CHEMISTRY**

**GRADUATE TEACHERS / BLOCK RESOURCE TEACHER EDUCATORS (BRTE)**

**UNIT-VIII- STUDY MATERIAL-TO CONTACT:8072230063.**

**2023-24**

**SRIMAAN**

# SRIMAAN

## UG-TRB

## CHEMISTRY

**GRADUATE TEACHERS / BLOCK RESOURCE TEACHER EDUCATORS (BRTE)**

**UNIT-VIII- ORGANIC CHEMISTRY STUDY MATERIAL (NEW SYLLABUS 2023)**

### UG-TRB MATERIALS

**TAMIL / ENGLISH / MATHS / CHEMISTRY / PHYSICS /  
BOTANY / ZOOLOGY / HISTORY / GEOGRAPHY AVAILABLE.**

**PG-TRB STUDY MATERIALS:-TAMIL / ENGLISH / MATHEMATICS / PHYSICS  
CHEMISTRY / COMMERCE (T/M & E/M) / BOTANY (T/M & E/M) / ZOOLOGY  
HISTORY (T/E) / ECONOMICS (T/E) / GEOGRAPHY / BIO-CHEMISTRY**

**PGTRB-COMPUTER INSTRUCTOR GRADE-I -TO CONTACT -8072230063.**

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## **TRB POLYTECHNIC LECTURER MATERIALS:**

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**UG-TRB: ALL SUBJECT STUDY MATERIALS AVAILABLE.**

**SCERT/DIET/GTTI STUDY MATERIAL AVAILABLE.**

**DEO & BEO (T/M & E/M) STUDY MATERIALS AVAILABLE.**

**TNPSC (CESSE)-(T/M & E/M) STUDY MATERIAL AVAILABLE.**

**PG-TRB COMPUTER INSTRUCTOR GRADE-1 -FULL STUDY  
MATERIAL WITH QUESTION BANK AVAILABLE**

**TNPSC-ASSISTANT DIRECTOR OF CO-OPERATIVE AUDIT  
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**TNEB-(ASSESSOR/AE/JA) MATERIALS WITH QUESTION BANK AVAILABLE**

**TNTET / PG-TRB / TRB-POLYTECHNIC / DEO & BEO  
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**PG-TRB STUDY MATERIALS:-TAMIL/ENGLISH/ MATHEMATICS/ PHYSICS  
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**UG-TRB:CHEMISTRY**

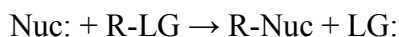
**Graduate Teachers / Block Resource Teacher Educators (BRTE)**

**UNIT-VIII- ALIPHATIC NUCLEOPHILIC SUBSTITUTION**

## **INTRODUCTION (ORGANIC CHEMISTRY:-TYPES OF REACTIONS)**

In organic chemistry, nucleophilic substitution is a fundamental class of reactions in which an electron rich nucleophile selectively bonds with or attacks the positive or partially positive charge of an atom or a group of atoms to replace a leaving group; the positive or partially positive atom is referred to as an electrophile. The whole molecular entity of which the electrophile and the leaving group are part is usually called the substrate.

The most common aliphatic nucleophilic reaction may be given as the following:



The electron pair (:) from the nucleophile (Nuc) attacks the substrate (R-LG) forming a new bond, while the leaving group (LG) departs with an electron pair. The principal product in this case is R-Nuc. The nucleophile may be electrically neutral or negatively charged, whereas the substrate is typically neutral or positively charged.

## **NUCLEOPHILIC REACTION**

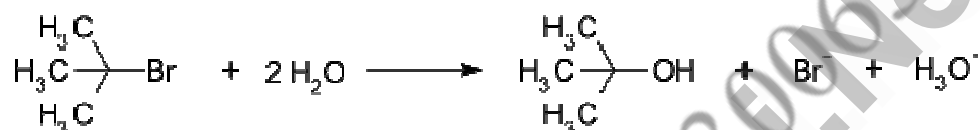
**The SN<sub>2</sub>, SN<sub>1</sub> Reaction: SN<sub>1</sub> reaction:**

The SN<sub>1</sub> reaction is a substitution reaction in organic chemistry. "SN" stands for nucleophilic substitution and the "1" represents the fact that the rate-determining step is unimolecular. Thus, the rate equation is often shown as having first-order dependence on electrophile and zero-order dependence on nucleophile. This relationship holds for situations where the amount of nucleophile is much greater than that of the carbocation intermediate.

This type of mechanism involves two steps. The first step is the reversible ionization of Alkyl halide in the presence of aqueous acetone or an aqueous ethyl alcohol. This step provides a carbocation as an intermediate. In the second step this carbocation is attacked by the nucleophile to form the product.

### Mechanism:

An example of a reaction taking place with an SN1 reaction mechanism is the hydrolysis of tertbutyl bromide with water forming tert-butanol.:



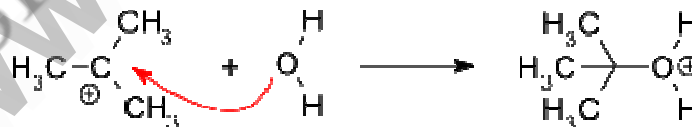
This SN1 reaction takes place in three steps:

**Step 1: Formation of carbocation:** Formation of a tert-butyl carbocation by separation of a leaving group (a bromide anion) from the carbon atom; this step is slow and

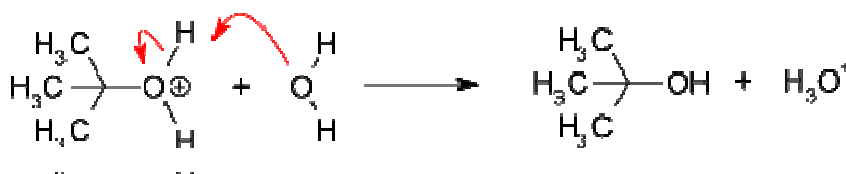


**Step 2: Nucleophilic attack:** the carbocation reacts with the nucleophile. If the nucleophile is a neutral molecule (i.e. a solvent) a third step is required to complete the reaction.

When the solvent is water, the intermediate is an oxonium ion. This reaction step is fast.



**Step 3: Deprotonation:** Removal of a proton on the protonated nucleophile by water acting as a base forming the alcohol and a hydronium ion. This reaction step is fast.



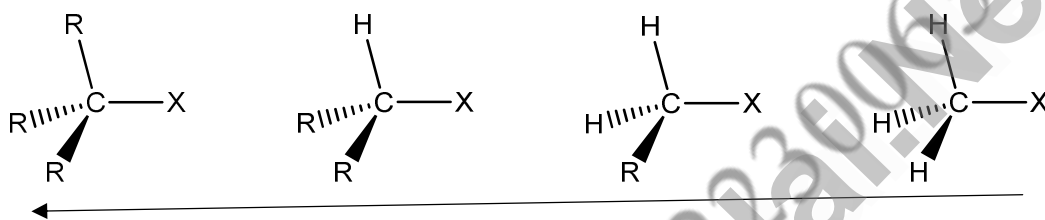
**Factor Affecting the  $S_N^1$  reaction:**

Some of the factor which can affect the  $S_N^1$  reaction are given below:

**(a) Nature of substrate:**

For  $S_N^1$  reaction reactant should be of the such type that can generate stable carbocation intermediate.

According to the concept reactivity order of the alkyl halide for  $S_N^1$  reaction can be given as:



-Increase stability of corresponding carbocation.

-Increase reactivity of alkyl halide toward the  $S_N^1$  reaction.

**(b) Nature of Nucleophile:**

Nature of Nu does not affect the  $S_N^1$  reaction because Nu does not involve in the slow step of  $S_N^1$  reaction.

**(b) Nature of leaving group:**

For the  $S_N^1$  reaction always leaving group less basic in nature.

**Stereochemistry of  $S_N^1$  reaction:**

Reaction is the two step reaction during which there can occur the inversion as well as retention of configuration i.e. there can occur racemization during the  $S_N^1$  reaction

**Effect of the solvent on the rate of  $S_N^1$  reaction:**

During the slow step or rate determining step of the  $S_N^1$  reaction there occurs the formation of polar nature of transition state before generating the carbocation. The polar solvent with high dielectric constant value stabilize the transition state by which energy of activation for the slow step or rate determining step is decrease in the dielectric constant value of polar solvent.

Relative rate of  $\text{SN}^1$  in t-butyl chloride according to the dielectric constant of same polar solvent can be given as:

Solvent	Dielectric constant	Relative rate
Acetic acid	6	1
Methanol	33	4
Formic acid	58	5,000
Water	78	1,50,000

Potential energy diagram for  $\text{SN}^1$  reaction:

$\text{SN}^1$  reaction is the two step reaction for with P.E diagram can be represented as:

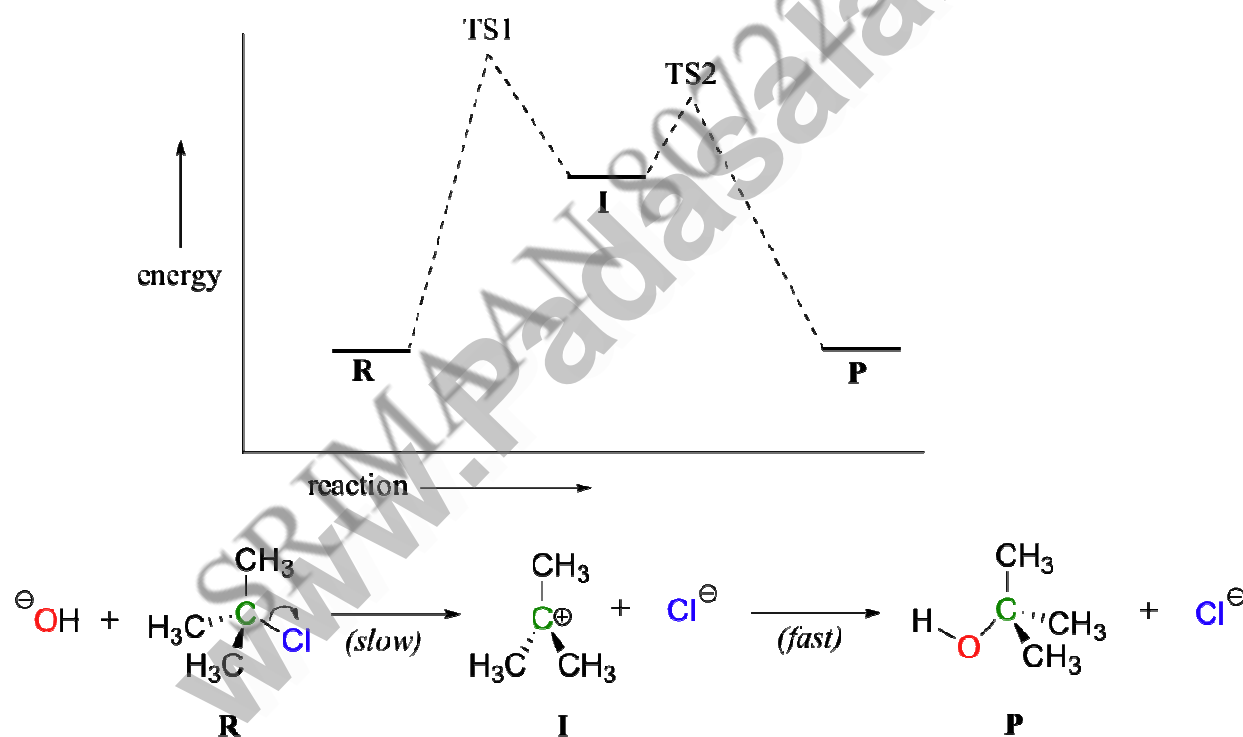


Figure.2

## SN2 Reaction:

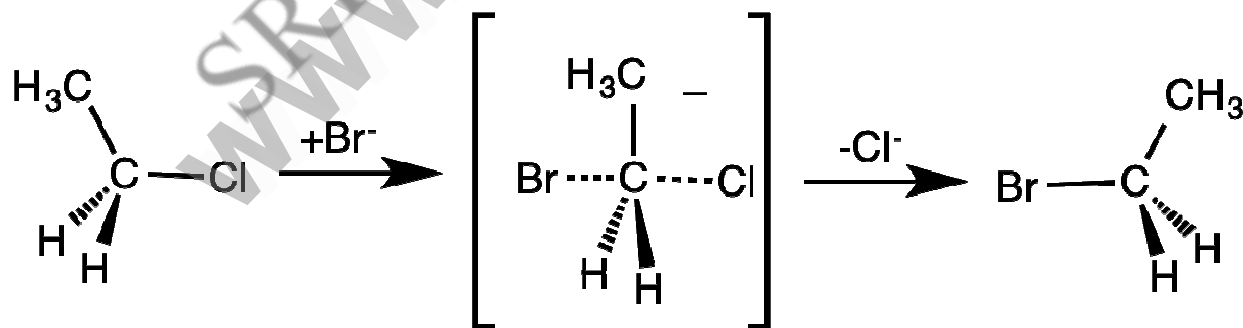
The SN2 reaction is a type of reaction mechanism that is common in organic chemistry. In this mechanism, one bond is broken and one bond is formed synchronously, i.e., in one step. SN2 is a kind of nucleophilic substitution reaction mechanism. Since two reacting species are involved in the slow (rate-determining) step, this leads to the term substitution nucleophilic (bi-molecular) or SN2, the other major kind is SN1. Many other more specialized mechanisms describe substitution reactions.

### Mechanism of SN2 reaction:

The reaction most often occurs at an aliphatic  $sp^3$  carbon center with an electronegative, stable leaving group attached to it (often denoted X), which is frequently a halide atom. The breaking of the C–X bond and the formation of the new bond (often denoted C–Y or C–Nu) occur simultaneously through a transition state in which a carbon under nucleophilic attack is pentacoordinate, and approximately  $sp^2$  hybridised.

The nucleophile attacks the carbon at  $180^\circ$  to the leaving group, since this provides the best overlap between the nucleophile's lone pair and the C–X  $\sigma^*$  antibonding orbital. The leaving group is then pushed off the opposite side and the product is formed with inversion of the tetrahedral geometry at the central atom.

In an example of the SN<sub>2</sub> reaction, the attack of Br<sup>–</sup> (nucleophile) on an ethyl chloride (electrophile) results in ethyl bromide, with chloride ejected as the leaving group.:



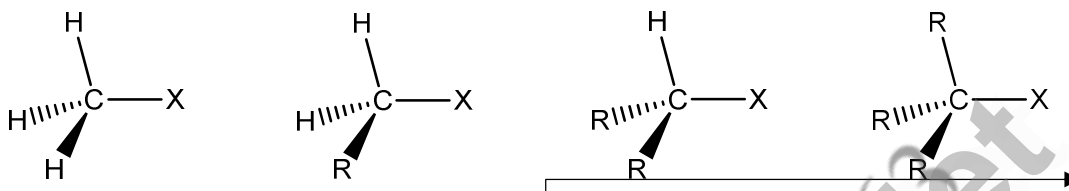
### Factor affecting SN<sup>2</sup> Reaction:

Some of the factors which can affect the SN<sup>2</sup> reaction are given below:



**(a) Nature of Substrate:**

For the  $S_N2$  reaction substrate should contain less bulky atoms or group otherwise backside attack of nucleophile will not be possible. On the basis of the above given concept the order of reactivity for  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  alkyl halide toward the  $S_N2$  reaction will become as:



-Increase number of bulky substituent.

-Decrease possibility of back attack of Nu.

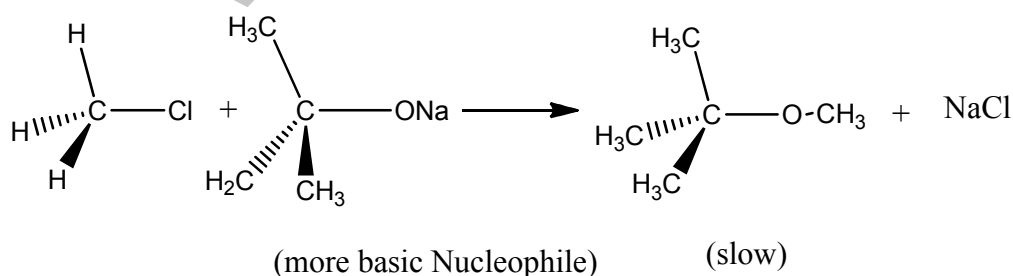
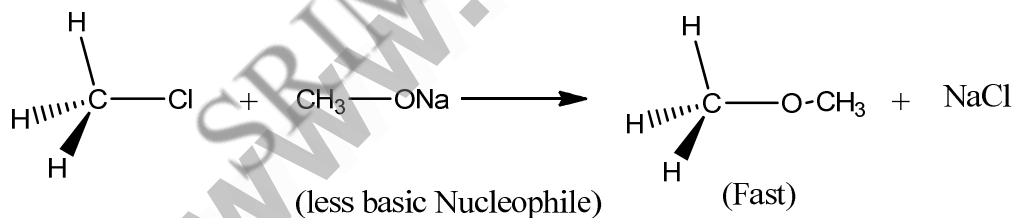
-Decrease reactivity of alkyl halide toward the  $S_N2$  reaction.

**(b) Nature of nucleophile:**

(i) For the  $S_N2$  reaction nucleophile should be less bulky otherwise back side attack of Nu will not be possible due to steric reason.

(ii) For the  $S_N2$  reaction Nu should be more basic in nature. Sometime bulkiness factor of Nu can be dominated over the basicity factor.

**Example:**  $\text{CH}_3\text{Cl}$  exhibit 1000 times faster reaction with  $\text{CH}_3\text{O}^-$  in compare to the reaction with more basic  $(\text{CH}_3)_3\text{CO}^-$ .

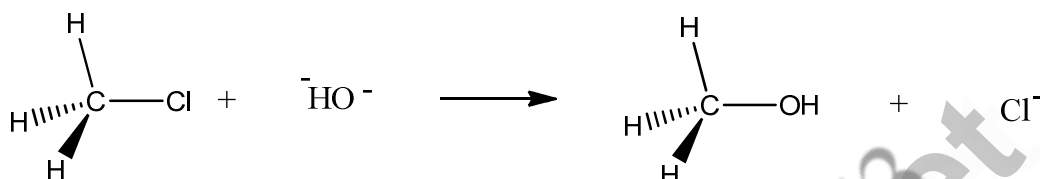




(c) **Nature of leaving group:** For the  $S_N^2$  reaction leaving group should be less basic in nature.

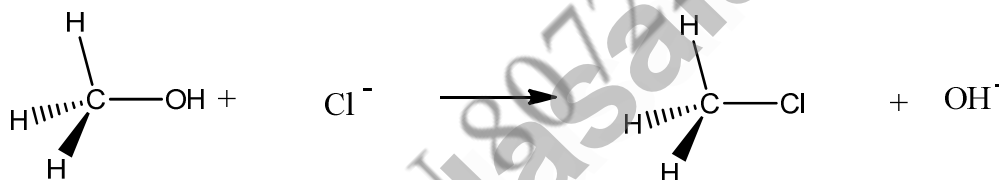
(d) Always basicity of Nu should be more in compare to the basicity of leaving group otherwise reaction will not be possible.

**EXAMPLE:**



This reaction is possible due to more basic strength of  $OH^-$  ion (nucleophile) than the  $Cl^-$  ion (leaving group)

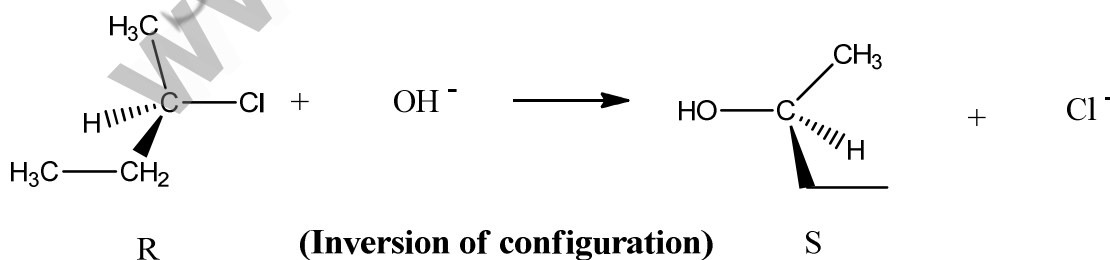
**Example:**



This reaction is not possible due to less basic strength of  $Cl^-$  ion (Nucleophile) than the  $OH^-$  ion (leaving group)

**Stereochemistry of  $S_N^2$  reaction:**

During the  $S_N^2$  reaction attack from the back side in the substrate due to which always there will occur the inversion in configuration.



**Walden Inversion:**

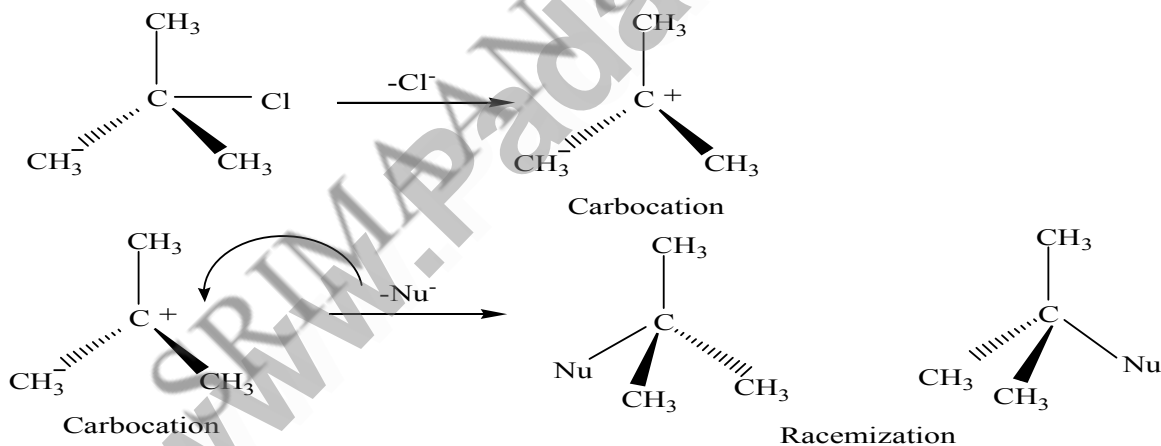
If the inversion in configuration occur at chiral center by the  $SN^2$  reaction than such type of inversion in configuration is called as Walden inversion.

### Mixed $SN1$ and $SN2$ Nucleophilic Substitution:

Mixed  $SN1$  and  $SN2$  reaction consists of a nucleophile and a substrate. When a nucleophile reacts with a substrate, substitution takes place. This substitution is known as nucleophilic substitution reaction. A substitution reaction occurs and the leaving group from the substrate departs. The nucleophile is an electron pair donor. The substrate acts an electrophile (electron pair acceptor). The electrophile has  $sp_3$  hybridization. There must be a leaving group in the electrophile.

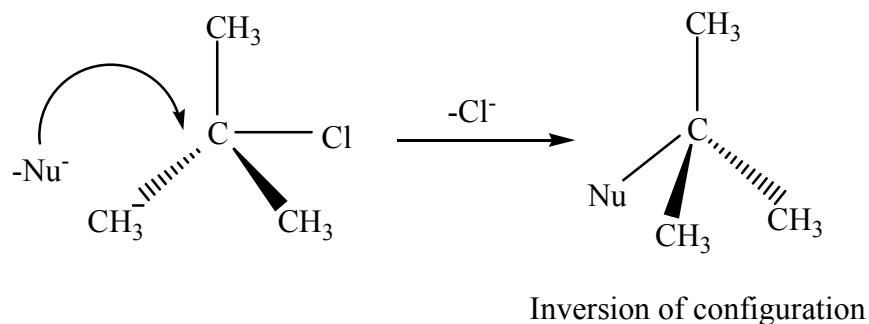
### Substitution Nucleophilic Unimolecular ( $SN1$ ) Reaction:

In  $SN1$  reaction, there is one molecule reacting in the reaction intermediate state or the transition state. A carbocation which is planar in nature is first formed. Then a nucleophile attacks on the carbocation to form the intermediate or the transition state. Here the nucleophile is free to attack from either side of the substrate. Therefore, there occurs racemization.



### Substitution Nucleophilic Bimolecular ( $SN2$ ) Reaction:

In  $SN2$  reaction, there are two molecules react in the reaction intermediate state or the transition state. The leaving group departs simultaneously as soon as the nucleophile attacks the molecule or the substrate from the backside. Hence in the product side, there occurs inversion of the configuration.



In the above, both nucleophilic substitution reactions (mixed SN1 and SN2), there is a competition between the leaving group and the nucleophile.

**SNi Mechanism:** SNi or Substitution Nucleophilic internal stands for a specific but not often encountered nucleophilic aliphatic substitution reaction mechanism. This reaction type is linked to many forms of neighbouring group participation, for instance the reaction of the sulfur or nitrogen lone pair in sulfur mustard or nitrogen mustard to form the cationic intermediate.

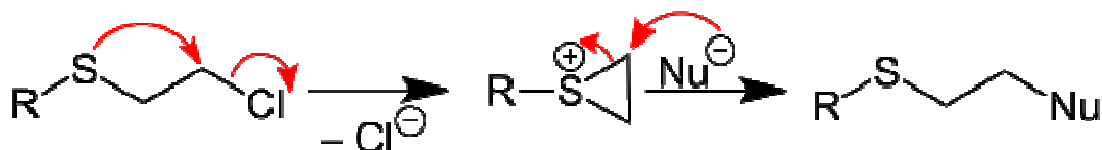
This reaction mechanism is supported by the observation that addition of pyridine to the reaction leads to inversion. The reasoning behind this finding is that pyridine reacts with the intermediate sulfite replacing chlorine. The dislodged chlorine has to resort to nucleophilic attack from the rear as in a regular nucleophilic substitution.

## THE NEIGHBOURING GROUP MECHANISM

During the SN2 reaction if hydrocarbons of heteroatom like N, S etc. being present at  $\beta$  position or  $\pi$  bond being present at the  $\gamma$ - position with respect to the leaving group than there occur the enhancement (increase) in the rate of the SN2 reaction. The mechanism operating in such neighboring group participation.

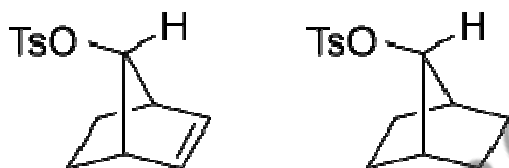
During the neighbouring group mechanism there occurs the formation of highly reactive three membered cyclic intermediate by the intramolecular reaction but the final substitution product formation occur with the retention of configuration because there occur the two consecutive SN2 reactions.

Due to the formation of highly reactive three membered cyclic intermediate these reaction being thousand times faster than the normal SN2 reaction.

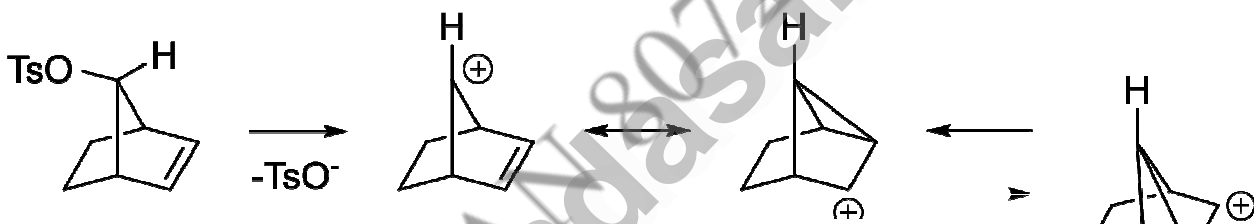


### NGP by an alkene:

The  $\pi$  orbitals of an alkene can stabilize a transition state by helping to delocalize the positive charge of the carbocation. For instance the unsaturated tosylate will react more quickly ( $10^{11}$  times faster for aqueous solvolysis) with a nucleophile than the saturated tosylate.

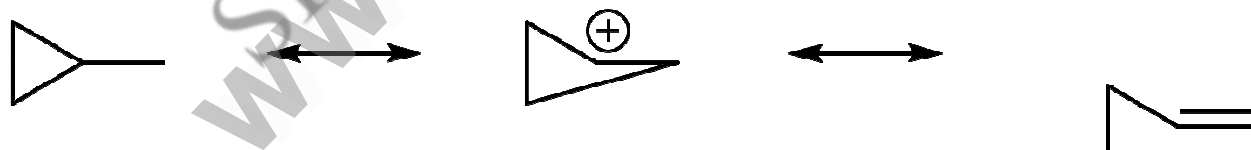


The carbocationic intermediate will be stabilized by resonance where the positive charge is spread over several atoms; in the diagram below this is shown.



### NGP by a cyclopropane, cyclobutane or a homoallyl group:

If Cyclopropylmethyl chloride is reacted with ethanol and water then a mixture of 48% cyclopropylmethyl alcohol, 47% cyclobutanol and 5% homoallyl alcohol (but-3-enol) is obtained. This is because the carbocationic intermediate is delocalised onto many different carbons through a reversible ring opening.



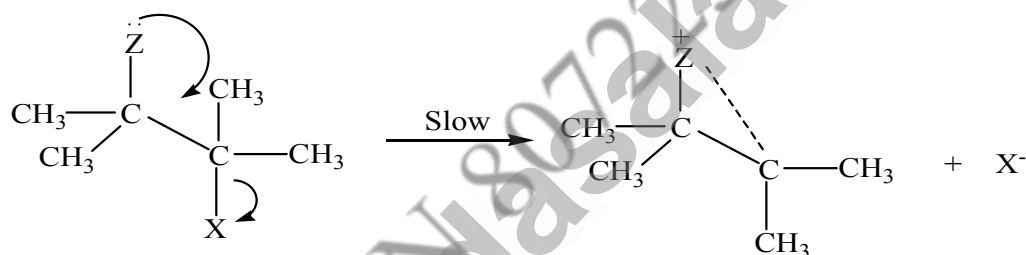
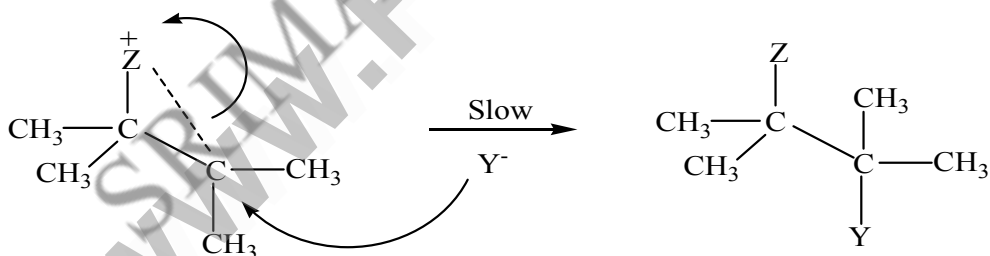
## ANCHIMERIC ASSISTANCE

When a catalytic functional group or atom is part of the reacting molecule, the catalysis is called intra-molecular catalysis. Anchimeric assistance (anchimeric in Greek means "adjacent parts") is a case of intra-molecular catalysis where a suitably placed intra-molecular nucleophile assists in a substitution reaction by enhancing rate of reaction.

**Mechanism of anchimeric assistance:**

The bimolecular mechanisms for nucleophilic substitution are termed SN2 reactions. SN2 reactions follow second order rate kinetics. The geometric alignment of transition state for SN2 mechanism is such that the nucleophile attacks from the rear of the leaving group, leading to inversion of configuration.

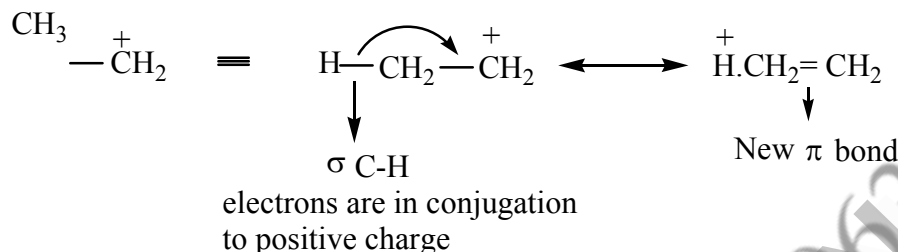
However, there are some examples of retention of configuration in SN2 reactions, where an atom or group (Z) close to the carbon undergoing substitution assist in the reaction with its available pair of electrons. Such a group is called a neighbouring group (NG) and the assistance provided is termed neighbouring group participation (NGP). If such participation leads to an enhanced reaction rate, the group is said to provide anchimeric assistance.

**Step-I****Step-2**

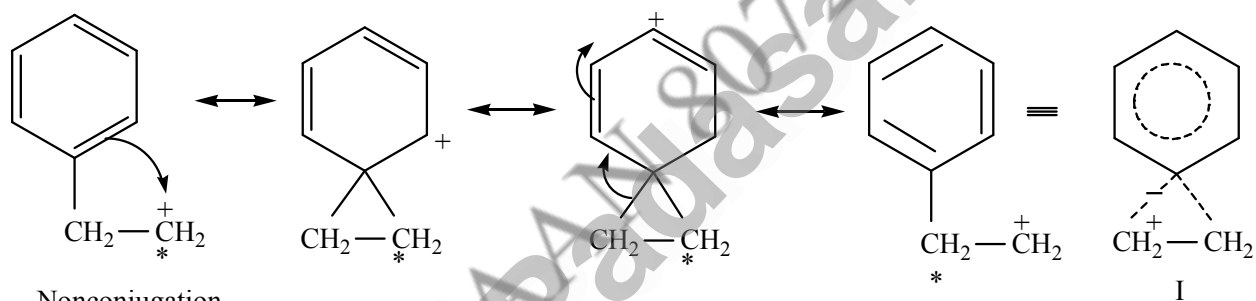
The mechanism for anchimeric assistance is a two step mechanism where two consecutive SN2 reaction leads to retention of configuration. In the first step, the neighbouring group (Z) acts as a nucleophile, attacking the substitution centre and expelling out the leaving group. In the next step, the external nucleophile (Y) attack from backside displacing the neighbouring group and retaining the overall configuration. Since the first step is slow and is rate determining, the reaction follows first order kinetics and there is no effect of concentration of Y<sup>-</sup> on rate of reaction.

## CLASSICAL AND NON-CLASSICAL CARBOCATIONS

Carbocations discussed so far are called classical carbocations. Classical carbocations are those which get stabilised by the movement of either the lone pair of electrons or C-H sigma electrons or pi electrons, in conjugation to the positive charged carbon atom to form a new pi bond.



On the other hand, if in a carbocation the positive charge does not get conjugated with the pi bond, and then the resonance structure cannot be written in a normal way. However, in some cases the resonance structures can be written by the participation of the neighbouring groups. The resultant is the formation of bridged cation which are called non-classical carbocation.



Nonconjugation

In structure (I) two carbons, carbon-1 and carbon-2 are bonded together by sigma bond. The third carbon is bonded with other two carbons by two electrons three centered bond. The third atom however, can also be a hydrogen atom. This leads to the formation of bridged structure. These bridged structures which involve delocalisation of sigma electrons and formation of three centered, two electron bonds are called non-classical ions. In classical carbocation positive charge is either located on one carbon or is delocalised due to conjugation of pi electrons or lone pair of electrons in allylic position.

## NORBORNYL CATION

Various naturally occurring terpenes are derivatives of Norbornane. Molecular rearrangements are common among these bicyclic terpenes. Winstein and Roberts (1950) actively pursued the mechanism of the rearrangements and the associated stereochemical problems using the basic norbornyl system.

### Acetolysis of 2-norbornyl brosylates:

Each of the isomeric brosylates (1 and 2) is prepared and subjected to acetolysis. (solvolysis using acetic acid as solvent and nucleophile)

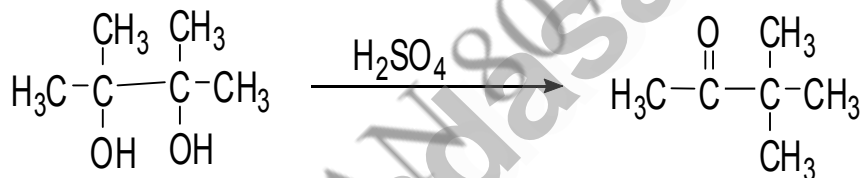
In the above reactions following observations takes place:

- (i) Rate of solvolysis of 1 to 2 is about 400
- (ii) Both 1 and 2 give 3, the exo-acetate
- (iii) Optically active exo-brosylate (1) gives 3 which is racemic ( $\pm$ )
- (iv) The recovered brosylate (1) is also racemic
- (v) The rate of racemisation (measured from specific Rotation) is greater than solvolysis in the case of the exo-isomer
- (vi) The rate of racemization is equal to the rate of solvolysis in the case of endoisomer.

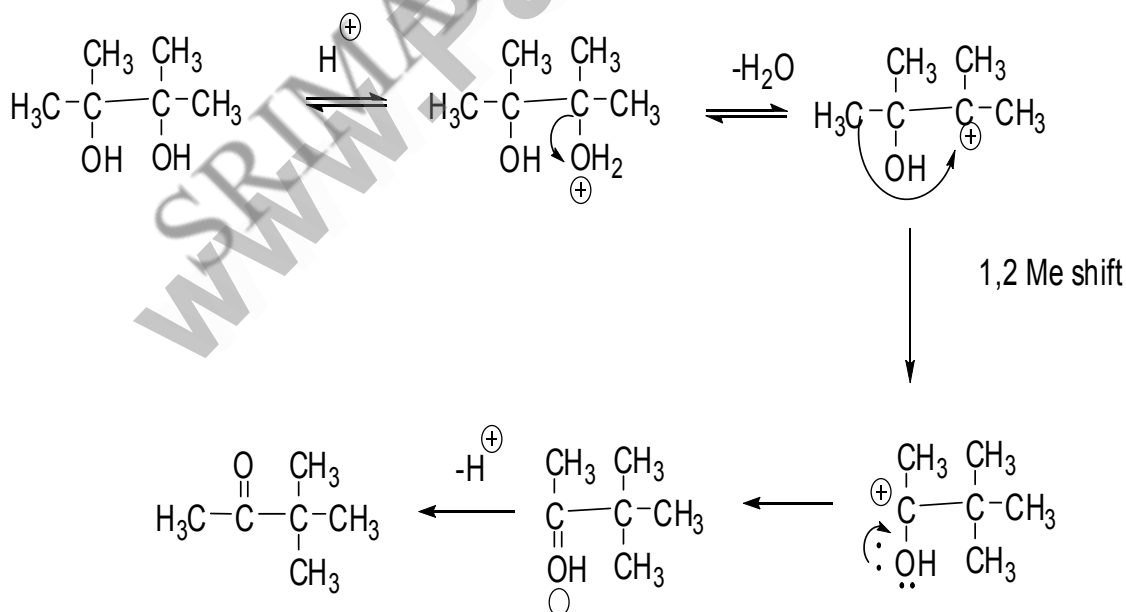
## COMMON CARBOCATION REARRANGEMENTS

### Pinacol-Pinacolone rearrangement:

Acid catalysed rearrangement of vicinal diol (Pinacol) into ketone or aldehyde (Pinacolone) is known as Pinacol-Pinacolone Rearrangement.



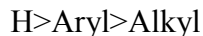
#### Mechanism:



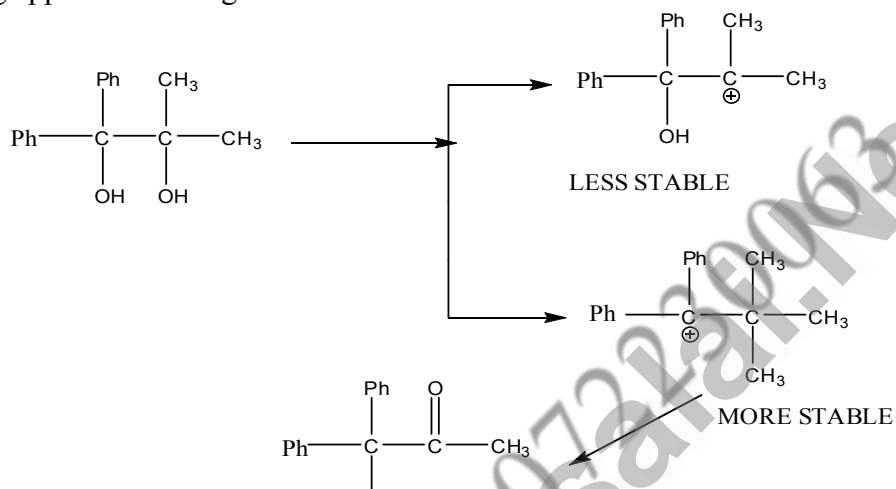


This reaction can be catalysed by the protic acids like H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HClO<sub>4</sub> etc.

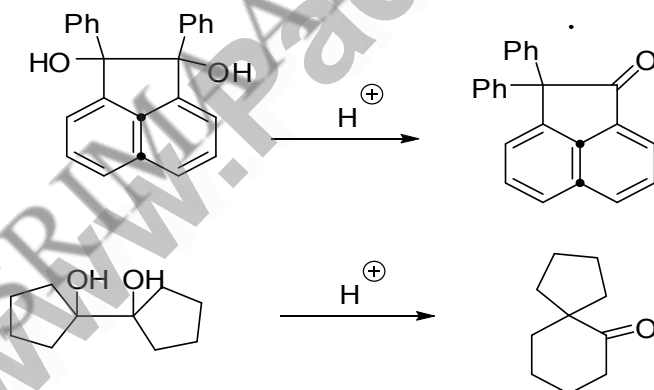
During the Pinacol-Pinacolone Rearrangement the migrating aptitude of various atoms or groups having following order:



Some of the examples related to these reactions can be given as: This order of the migrating aptitude being applicable during reactions.

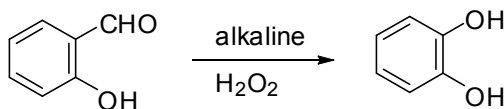


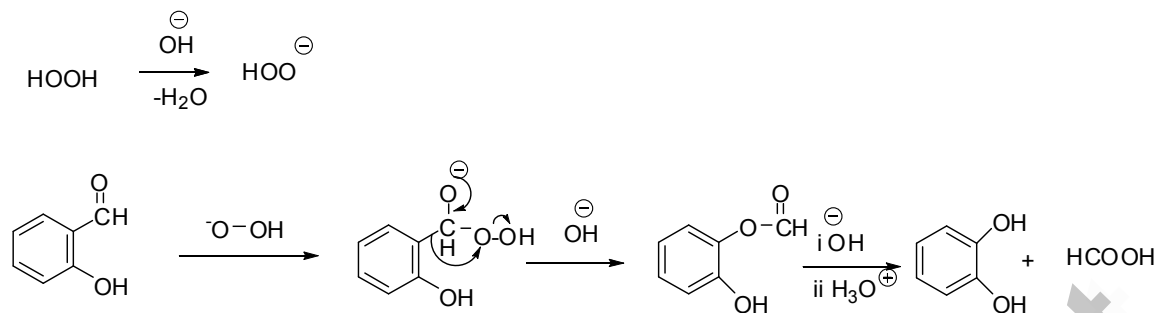
In the case of aryl substituent if there will be EDG in the aryl-substituent then migrating aptitude will further be higher while there will be EWG in the aryl substituent then migrating aptitude will be lower than an unsubstituted aryl group.



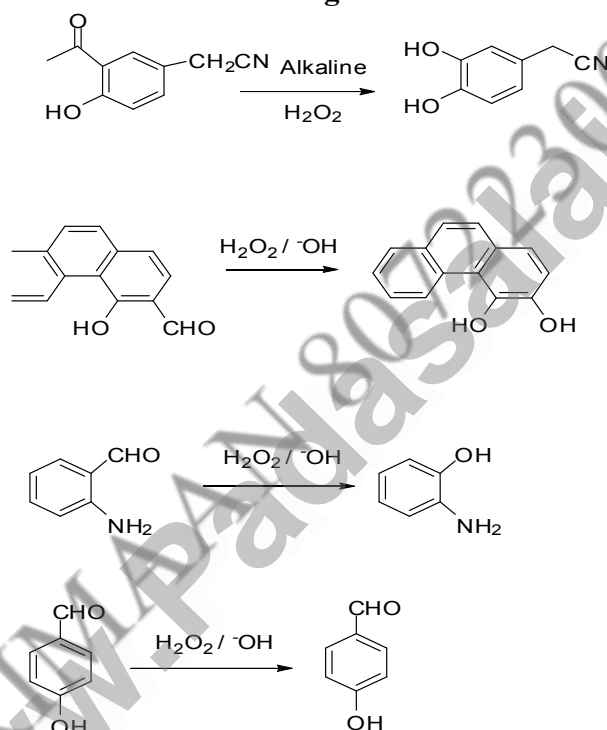
### Dakin Reaction:

Replacement of an aldehyde or keto group by the hydroxyl group when it is present ortho or para with respect to the hydroxyl or amino group, on treating with alkaline H<sub>2</sub>O<sub>2</sub> is called as Dakin Reactions.



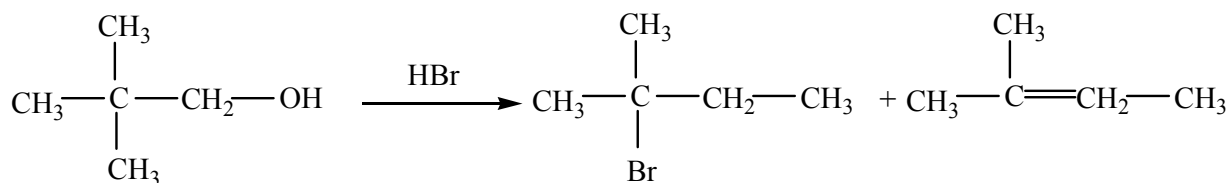
**Mechanism:**

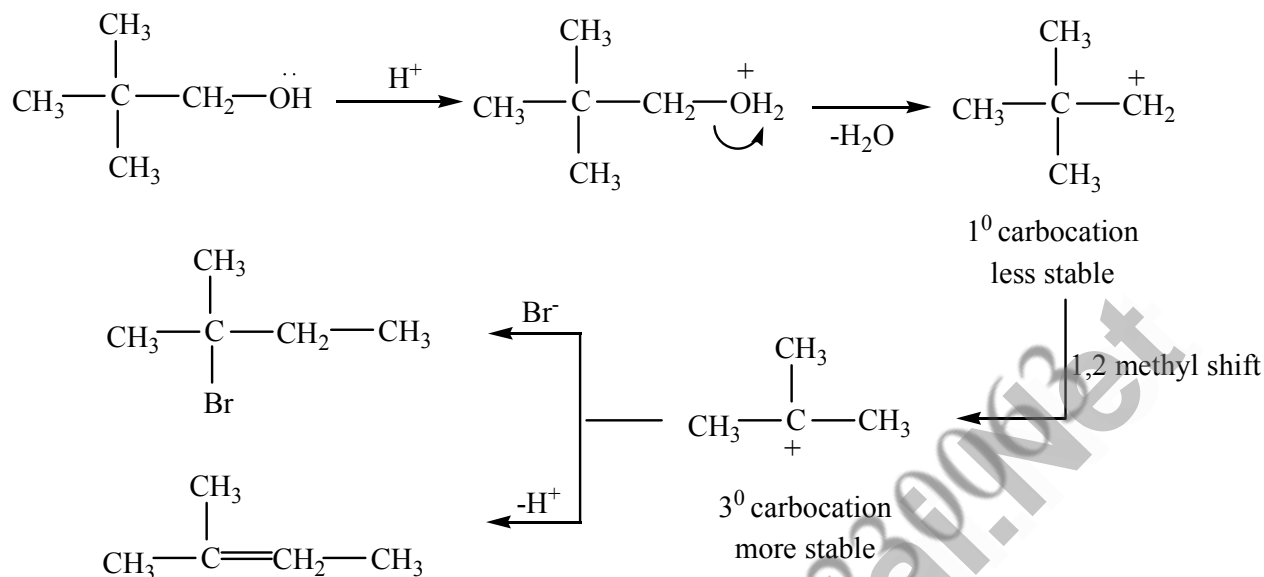
Some other examples of these reactions can be given as:

**Wagner-Meerwein rearrangement:**

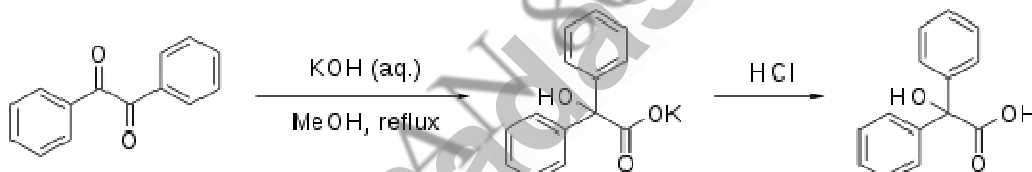
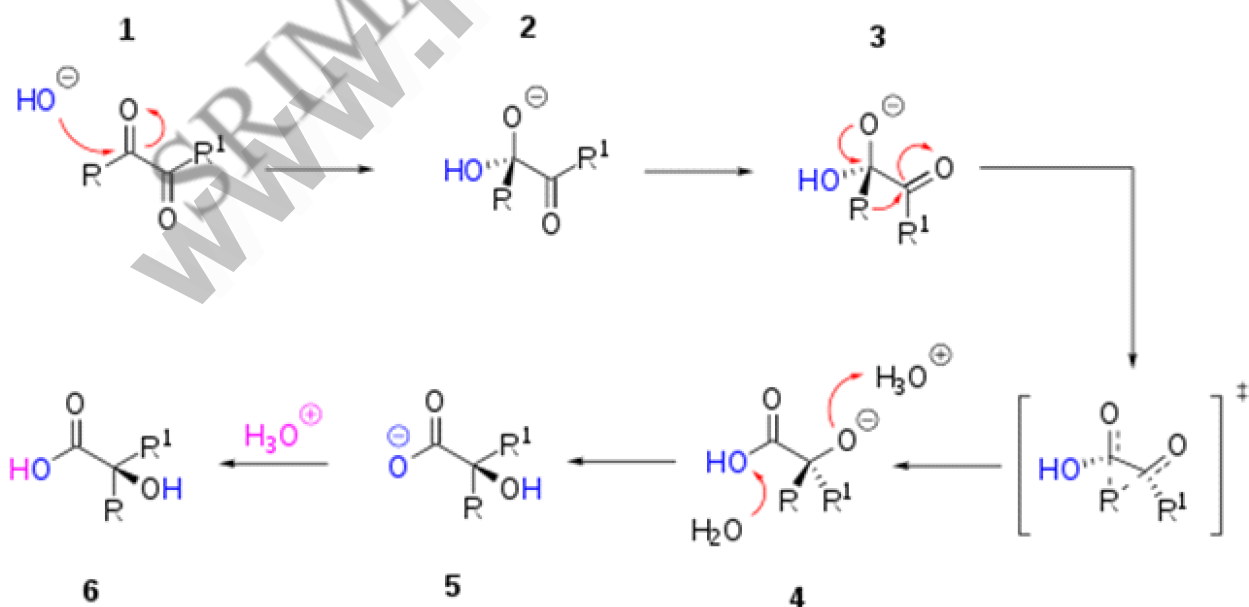
All those chemical reactions (Generally substitution or elimination reactions) which give the product through the carbocation intermediate with the rearranged carbon skeleton are called as Wagner-Meerwein Rearrangement reactions.

During these reaction carbocation intermediate having the tendency to increase their stability.



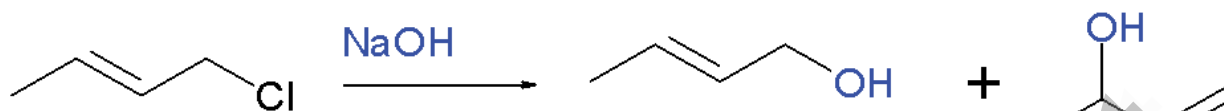
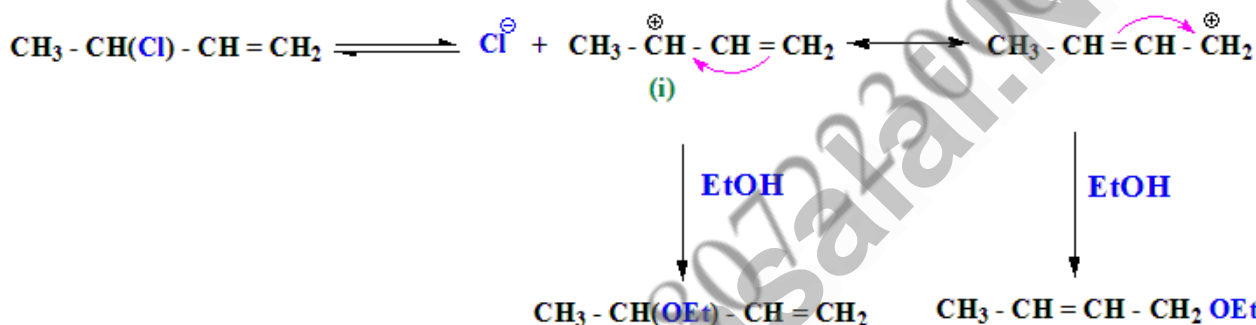
**Mechanism:****Benzilic acid rearrangement:**

Rearrangement of  $\alpha$ -diketone into  $\alpha$ -hydroxyl acid in the presence of any strong base is known as benzilic Acid rearrangement.

**Mechanism:**

**Allylic rearrangement:**

An allylic rearrangement or allylic shift is an organic reaction in which the double bond in an allyl chemical compound shifts to the next carbon atom. It is encountered in nucleophilic substitution.

**Mechanism:****TO BE CONTINUED.....****STUDY MATERIALS AVAILABLE**

**IF YOU NEED : UG-TRB: CHEMISTRY FULL STUDY MATERIAL AVAILABLE.**

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TO CONTACT:8072230063.**

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# **UG-TRB MATERIALS**

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- **UG TRB: ENGLISH STUDY MATERIAL +Q. BANK (T/M)**
- **UG-TRB: MATHEMATICS MATERIAL WITH Q. BANK (E/M)**
- **UG TRB: PHYSICS MATERIAL WITH QUESTION BANK (E/M)**
- **UG TRB: CHEMISTRY MATERIAL + QUESTION BANK (E/M)**
- **UG TRB: HISTORY MATERIAL + Q.BANK (T/M & E/M)**
- **UG TRB: ZOOLOGY MATERIAL + QUESTION BANK (E/M)**
- **UG TRB: BOTANY MATERIAL +QUESTION BANK (T/M& E/M)**
- **UG TRB: GEOGRAPHY STUDY MATERIAL (E/M)**

**SCERT/DIET/GTTI (LECTURER) STUDY MATERIAL AVAILABLE.**

**TRB-POLYTECHNIC LECTURER-(NEW SYLLABUS)  
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- **ECE STUDY MATERIAL with Question Bank.**
- **EEE STUDY MATERIAL With Question Bank.**
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- **CIVIL STUDY MATERIAL With Question Bank.**
- **EIE STUDY MATERIAL with Question Bank.**
- **ICE STUDY MATERIAL with Question Bank.**

## **PG-TRB MATERIALS**

- **PG TRB: TAMIL STUDY MATERIAL +QUESTION BANK (T/M)**
- **PG TRB: ENGLISH MATERIAL WITH QUESTION BANK.**
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- **PG TRB: PHYSICS MATERIAL WITH QUESTION BANK (E/M)**
- **PG TRB: CHEMISTRY MATERIAL + QUESTION BANK (E/M)**
- **PG TRB: COMMERCE MATERIAL WITH Q.BANK (T/M)&(E/M)**
- **PG TRB:ECONOMICS MATERIAL+Q. BANK (T/M & E/M)**

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- **PG TRB: HISTORY MATERIAL + Q. BANK (T/M & E/M)**
- **PG TRB: ZOOLOGY MATERIAL + QUESTION BANK (E/M)**
- **PG TRB: BOTANY MATERIAL +QUESTION BANK (T/M& E/M)**
- **PG TRB: GEOGRAPHY STUDY MATERIAL (E/M)**

**TNPSC-(CESE /JSO) STUDY MATERIAL AVAILABLE.**

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TNPSC-GROUP-I C**

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(TAMIL & ENGLISH MEDIUM) STUDY MATERIAL AVAILABLE.**

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