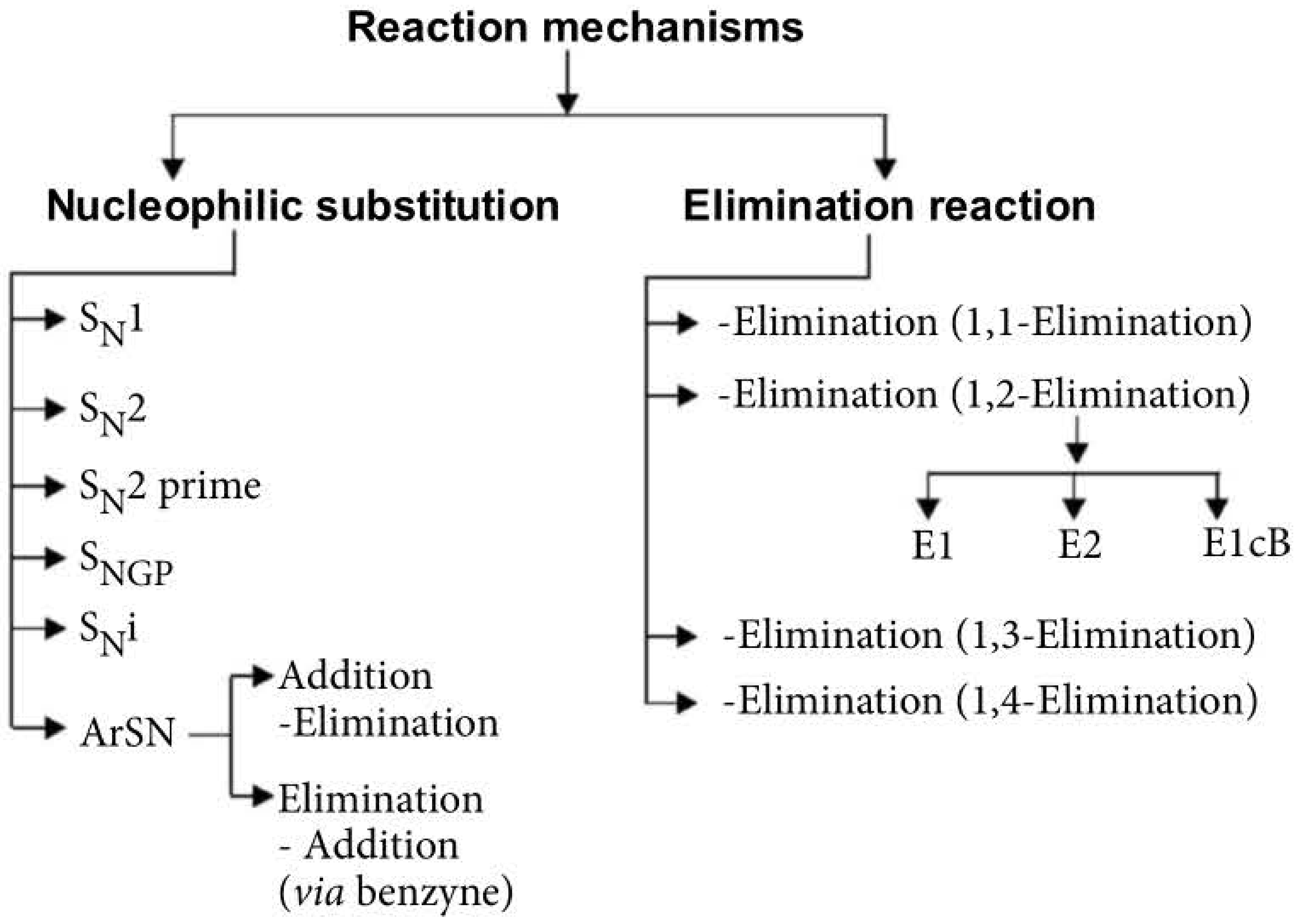
Rank Enhancer

This column is specially designed to make your concepts crystal clear.



NUCLEOPHILIC SUBSTITUTION

S$_N$1

- It takes place in two steps.

  Step-1 : $R - X \xrightarrow{\text{slow}} R^+ + X^-$ (Rate determining step)

  Step-2 : $R^+ + \text{Nu}^- \xrightarrow{\text{fast}} R - \text{Nu}$

  As rate determining step contains one molecule (R — X), it is unimolecular reaction and called S$_N$1.
- It involves formation of reaction intermediate "carbocation". Hence, methyl shift, hydride shift and phenyl shift are possible.
- Stability order of carbocation, favourable for this mechanism is :

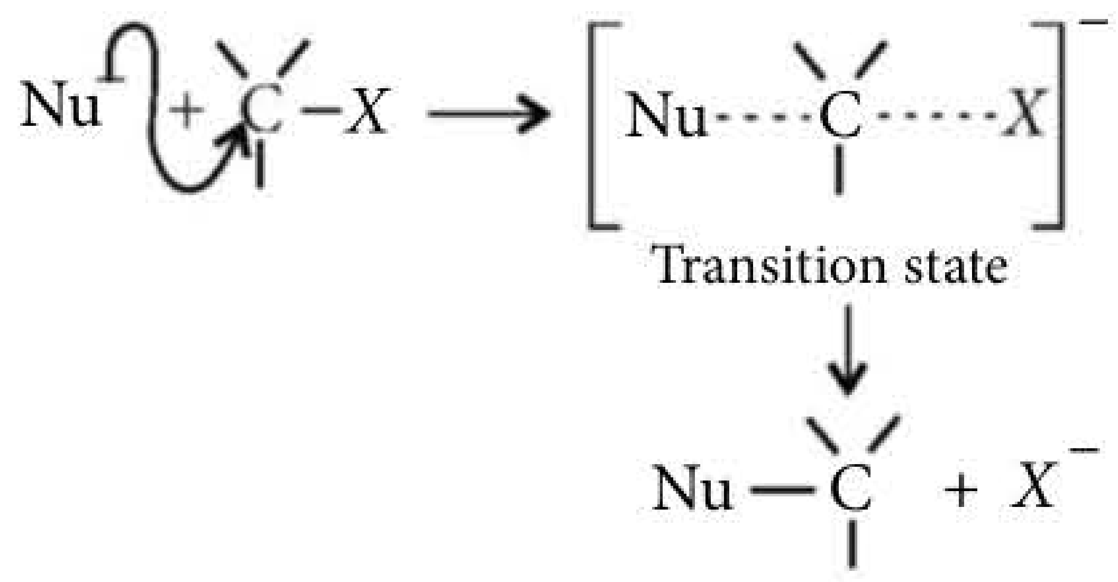
  Benzyl > Allyl > 3° > 2° > 1° > Vinyl
- Presence of heavy metal ions (Pb^{2+}, Ag^+) catalyses S$_N$1 reaction by facilitating ionisation of $R - X$.
- Solvents with higher dielectric constant such as H_2O, RCOOH (polar protic) and DMSO (polar aprotic) favour S$_N$1 reaction due to solvation of cation.
- Stable leaving group with higher leaving tendency favours S$_N$1 reaction.

  e.g., $CF_3 - SO_3^-$ (Triflate ion) is a good leaving group because of its resonance stabilisation.
  - Among halogens, leaving tendency follows the sequence :

    $R - I > R - Br > R - Cl > R - F$

S$_N$2

- It takes place in one step.



- As rate determining step involves two species, it is bimolecular reaction and called S$_N$2.

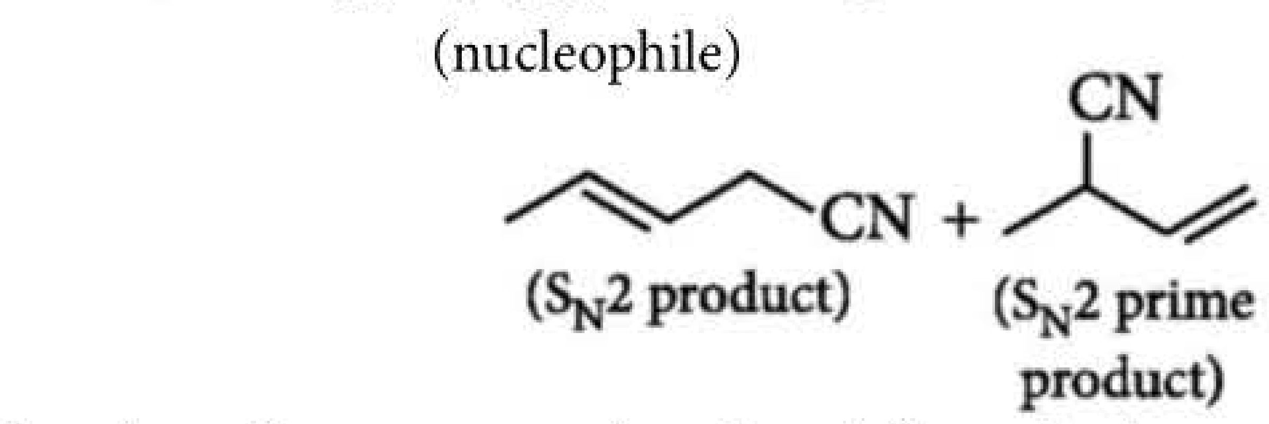
By K. Vijay Bhasker, Senior faculty at Sri Chaitanya Educational Institution, Visakhapatnam

- It does not involve formation of reaction intermediate but forms "transition state". Hence, no rearrangement is possible.
- Rate of reaction depends on steric factors. Lesser the number of steric groups on target C, more will be the reactivity.
  ∴ Order of reactivity of alkyl halides in S_N2 reaction is $CH_3X > 1° > 2° > 3° >$ Allyl > Benzyl.
- This reaction is favourable when stronger base replaces weaker base.
- Nucleophilic attack will be from opposite side of the leaving group. Hence, inversion takes place. It is called as **Walden inversion**.

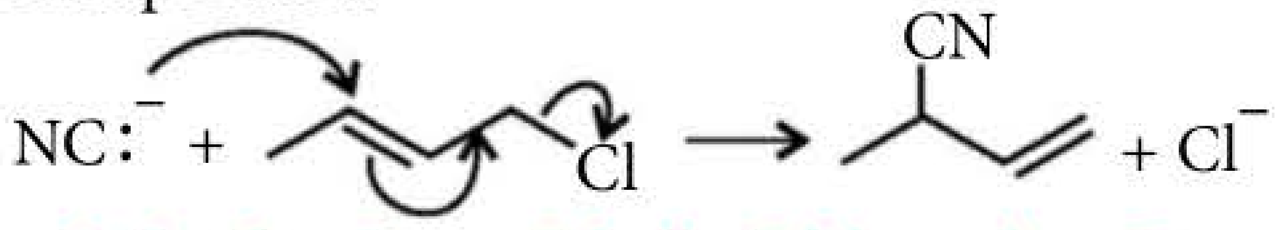
S_N2 prime

- When allylic rearrangement takes place in S_N2 reaction, it is called S_N2 prime reaction.

  e.g.,

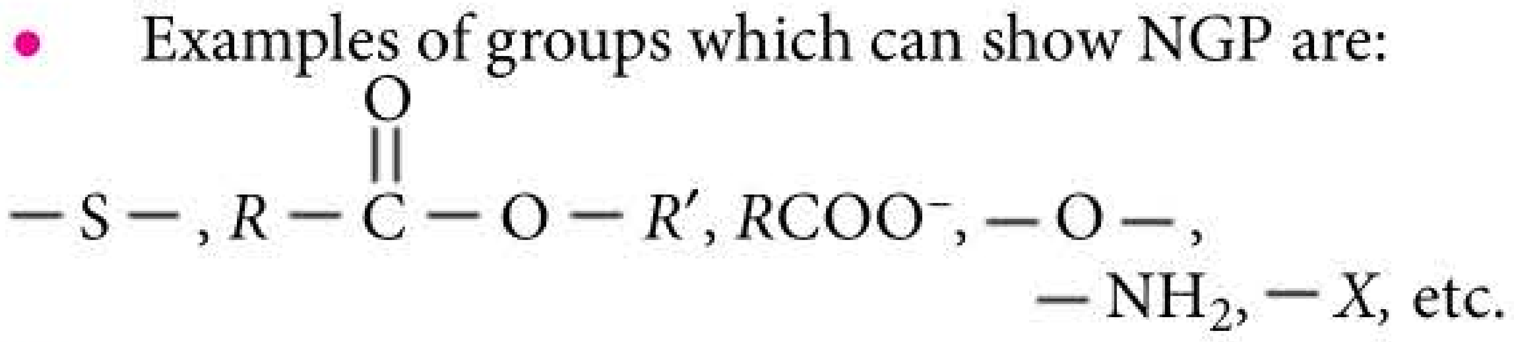


  Mechanism : In presence of nucleophile, π electrons move towards leaving group and result in S_N2 prime product.



S_{NGP} – Substitution with Neighbouring Group Participation

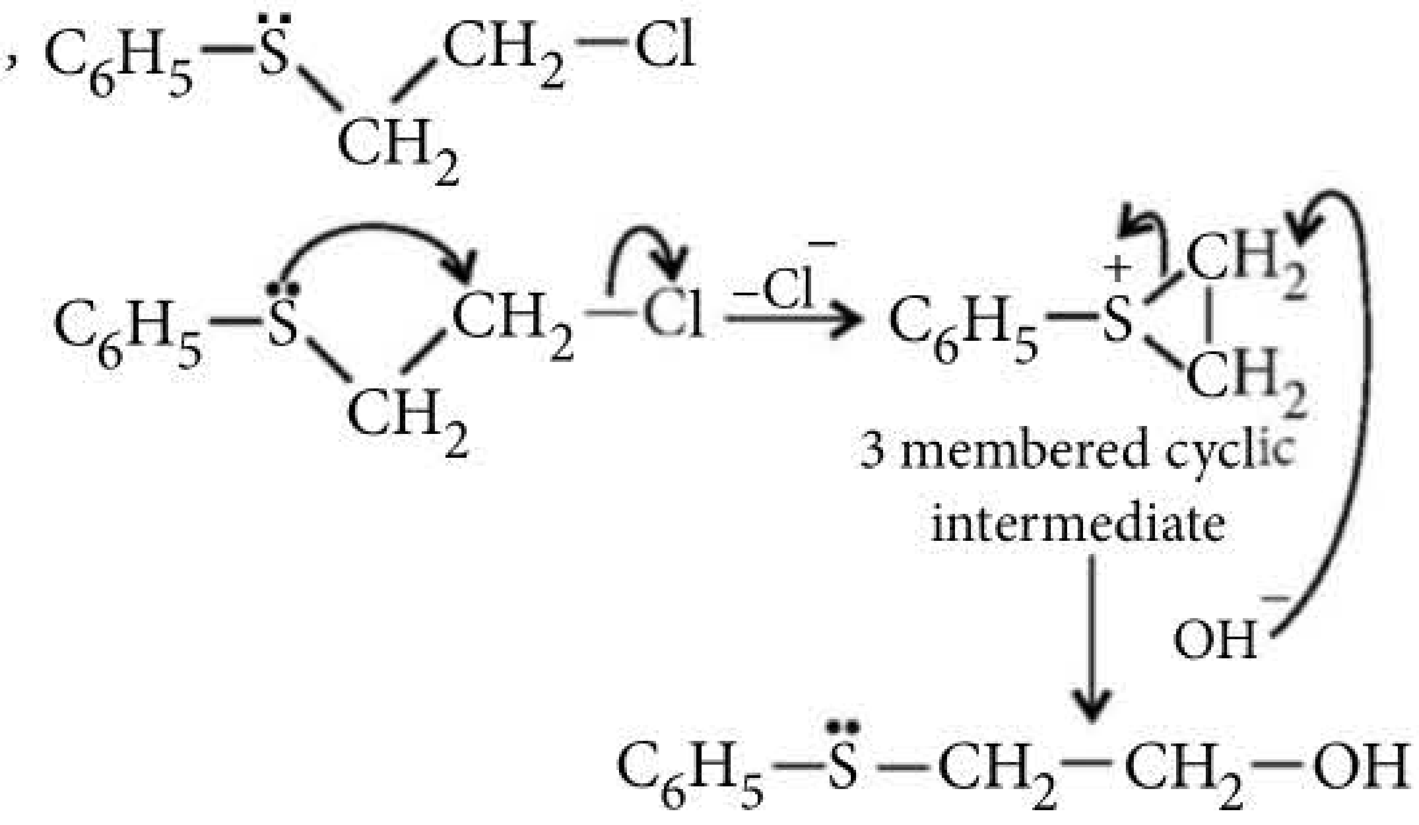
- This reaction takes place when an atom or group having lone pair of electrons is present at β-position or far away with respect to the leaving group.
- This atom or group displaces leaving group and produces 3,4,5 or 6 membered cyclic intermediate.
- Examples of groups which can show NGP are:



$$-S-,\ R-\overset{\overset{\displaystyle O}{||}}{C}-O-R',\ RCOO^-,\ -O-,\ -NH_2,\ -X,\ \text{etc.}$$

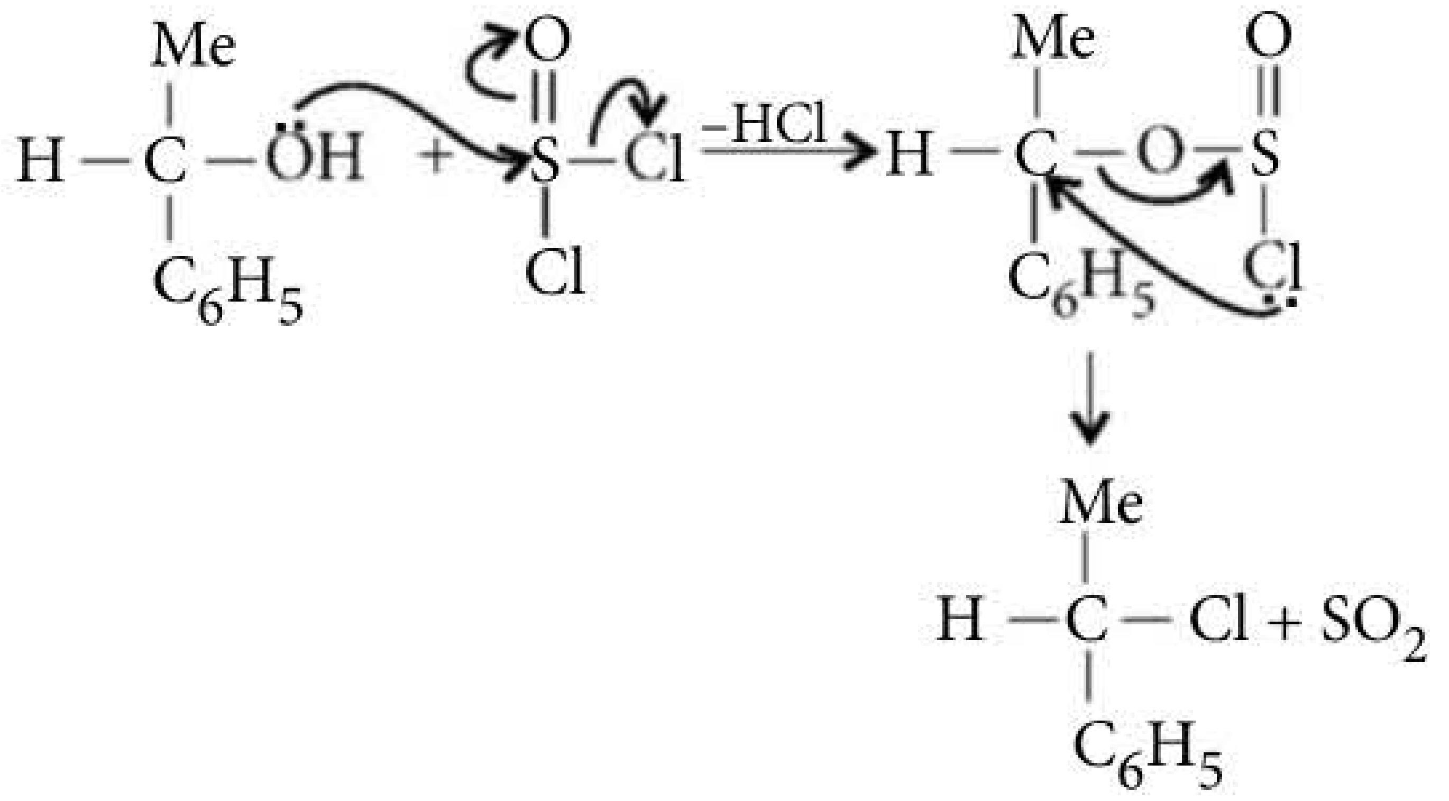
- In NGP, rate of reaction increases.

e.g.,



S_Ni (Nucleophilic Substitution Internal)

- Darzen's process of preparation of haloalkane from alcohol in absence of pyridine is called S_Ni.
- This reaction proceeds with retention of configuration.



(ArSN–) Aromatic Substitution of Nucleophilic Reaction

- Nucleophilic substitution in aryl halides when electron withdrawing groups (such as $-NO_2$) are present at ortho or para position w.r.t halide group is called ArSN reaction.

ELIMINATION REACTION

α-Elimination or 1,1-Elimination

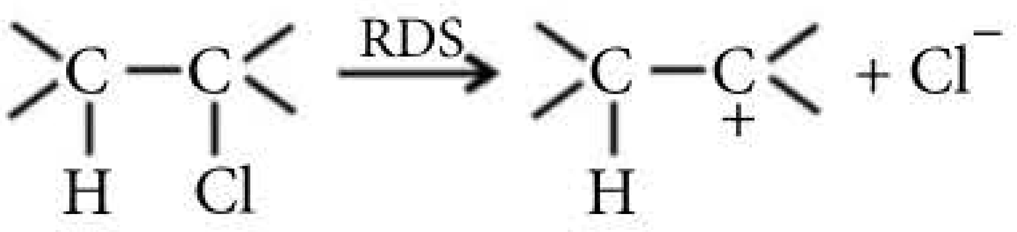
- When two groups or atoms are being eliminated from same C-atom, results in the formation of carbene is called α-elimination or 1,1-elimination.

β-Elimination or 1,2-Elimination

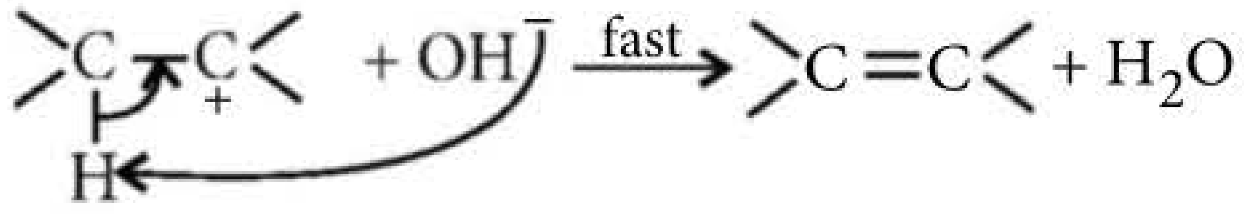
- When two groups or atoms are being eliminated from adjacent C-atoms, results in the formation of π-bond, such reactions are called β-elimination or 1,2-elimination.
- They are further classified into following three types:

E1 (Elimination unimolecular reaction)

- It takes place in two steps.
- Rate of reaction depends only on concentration of substrate such as alkyl halide but not on concentration of base.
- Ist step is the rate determining step. It involves heterolytic dissociation of alkyl halide.



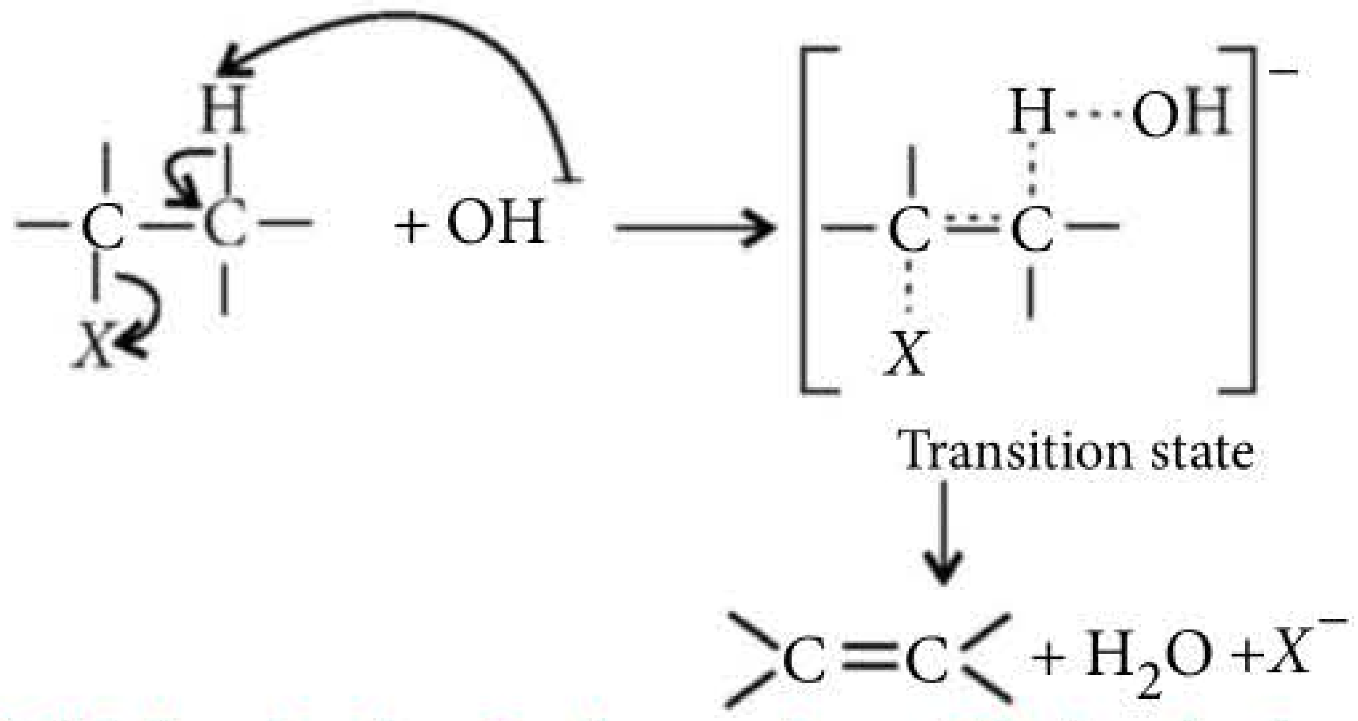
- 2nd step is the removal of H^+ from carbon atom adjacent to carbocation formed in the above step by base.



- Order of reactivity towards E1 elimination :
  - With respect to substrate, 3° benzylic ≃ 3° allylic > 2° benzylic ≃ 2° allylic > 1° benzylic ≃ 1° allylic > 3° > 2° > 1° > vinylic
  - With respect to leaving group - weaker base have better leaving tendency.
    $\therefore\ R-I > R-Br > R-Cl > R-F$

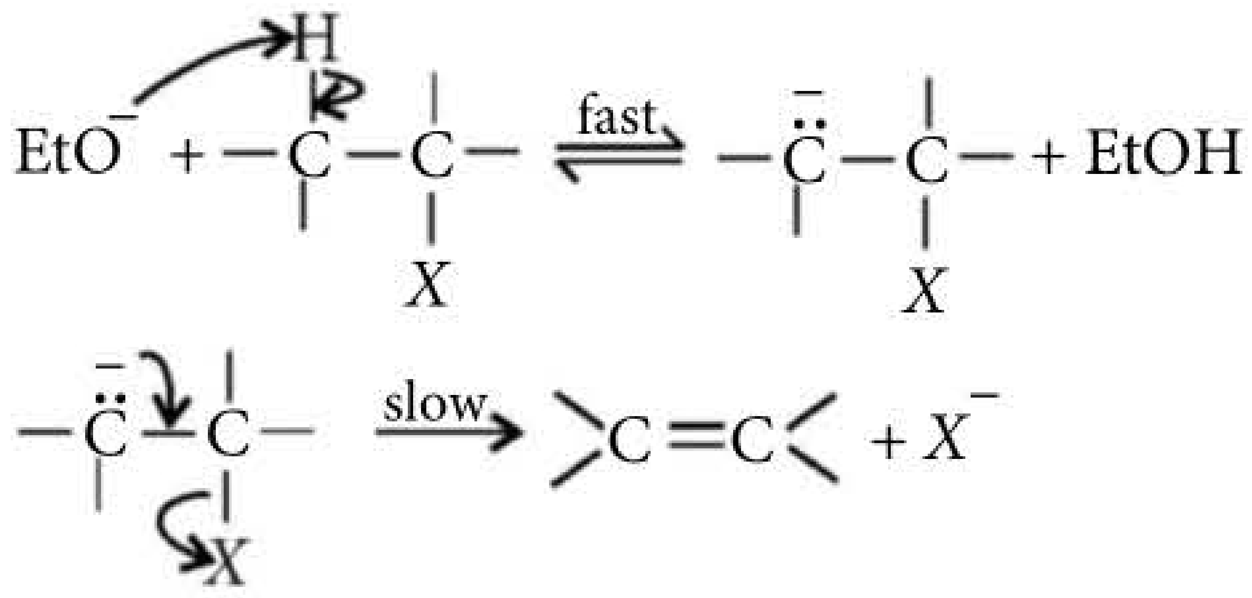
E2 (Elimination Biomolecular Reaction)

- It takes place in single step.
- Rate of reaction depends both on concentration of substrate ($R-X$) and reagent [OH^-].
- It involves the formation of transition state rather than carbocation reaction intermediate.
- *Trans*-elimination takes place more readily than *cis*.
- Order of reactivity towards E2 reaction increases with decrease in steric hindrance at carbon atom.
  $\therefore$ 1° > 2° > 3°
- Among halogens leaving tendency follows the sequence :
  $\therefore\ R-I > R-Br > R-Cl > R-F$



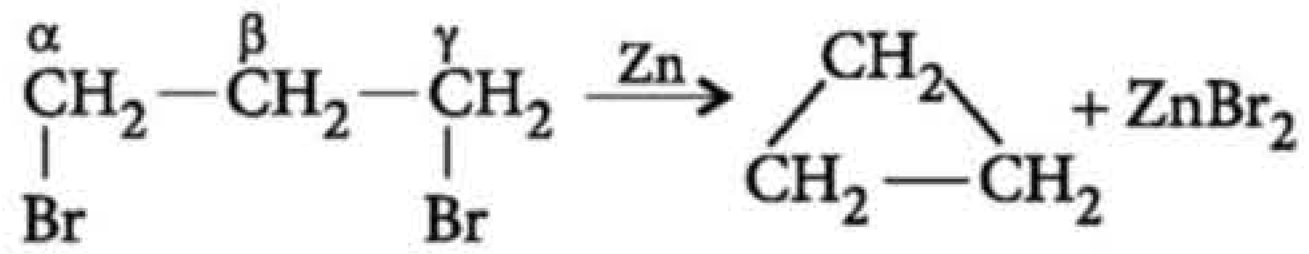
E1CB (Unimolecular Conjugate base Elimination)

- It also takes place in two steps like E1 reaction.
- Step-1 is fast and step-2 is slow. Hence step-2 is RDS.
- It involves fast reversible removal of proton from the β-carbon with the formation of a carbanion which then loses the leaving group in the second slow rate-*d*-determining step.



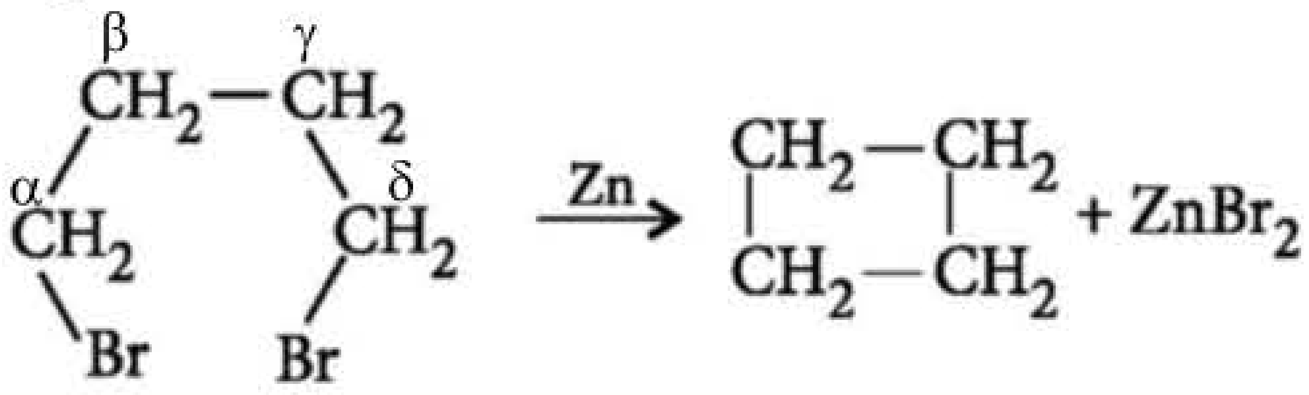
γ-Elimination or 1, 3-Elimination

- In this elimination, atoms or groups are being removed from the carbon atoms which lie three bonds away from each other *i.e.*, from α and r positions.
- It results in the formation of three membered cyclic ring.



δ-Elimination or 1, 4-Elimination

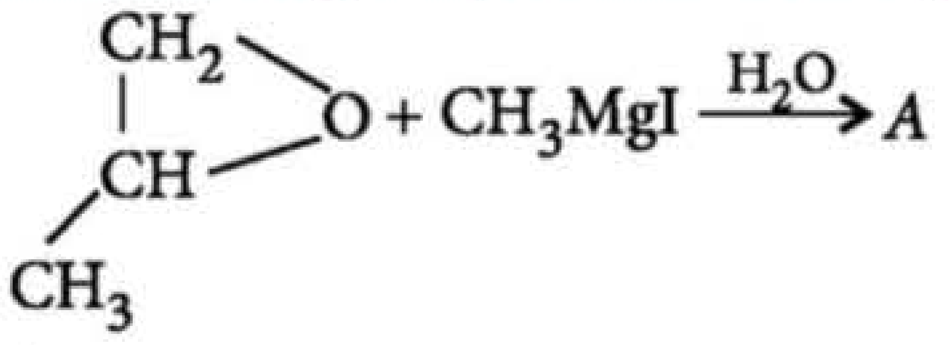
- In this elimination, atoms or groups are being removed from carbon atoms which lie four bonds away. *i.e.*, from α and δ-positions.
- It results in the formation of cyclic four membered ring.



QUESTIONS FOR PRACTICE

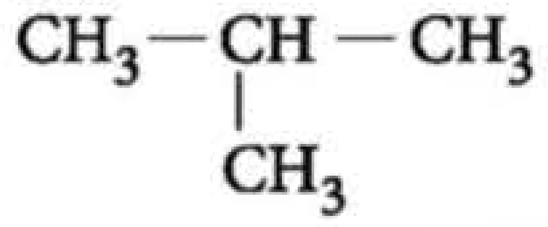
Single Option Correct Type

1.

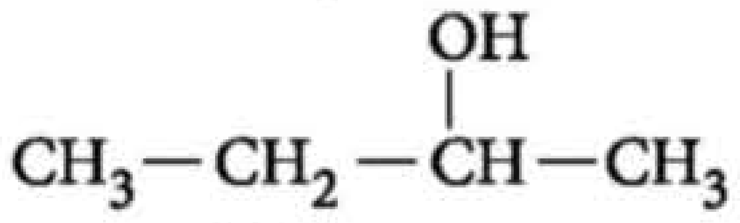


A is

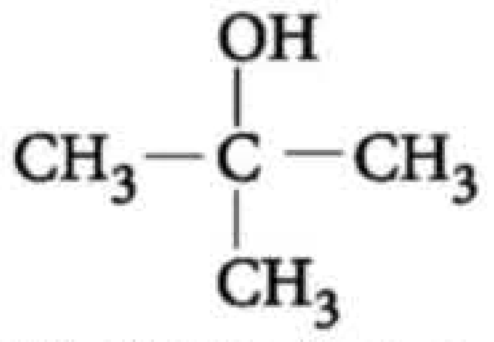
(a)


$CH_3-CH(CH_3)-CH_3$

(b)


$CH_3-CH_2-CH(OH)-CH_3$

(c)


$CH_3-C(OH)(CH_3)-CH_3$

(d) none of these.

2. E2 elimination is

(a) stereoselective (b) stereospecific
(c) both (a) and (b) (d) none of these.

UNSCRAMBLED WORDS

DECEMBER 2019

1-c- CREOSOTE
2-f- ASPHALTITES
3-a- EXCIPLEX
4-b- FUGACITY
5-h- MULLITE
6-g- OXANTHROL
7-d- PATINA
8-e- PERICLASE

CONCEPT BOOSTER

Hello boys and girls!! Wish you all a very happy new year. I believe this year will bring prosperity to you all. My suggestion to you is try to be imperturbable while preparing for the exam as well as while giving the exam. Your anxiety and panic will bring incongruity between your knowledge and performance. I have always suggested you that try to complete the basics first and then go to the unconventional parts. After this do rigorous practice. I believe this will bring success and success. Good luck. This article with an unconventional but important topic will make you feel confident.

*Arunava Sarkar

ORGANOSILICON COMPOUNDS

These are very useful reagents in a number of organic synthesis. Most commonly used such reagents are chlorotrialkyl silanes like Me_3SiCl (chlorotrimethyl silane) or Et_3SiCl (chlorotriethyl silane) etc. These reagents are used mostly as protecting groups, stabilisation of carbocations, carbanions etc. On the other hand, we have silicon hydrides like triethyl silane (Et_3SiH) which are used as reducing agents and specially to reduce alkenes and carbonyl compounds.

Short Method of Preparation of organosilicon compounds

A short outline of the preparation of organosilicon compound can be given as below :

$$\underset{\text{(Starting material)}}{SiCl_4} \xrightarrow{CH_3MgX\text{ (3 times)}} \underset{\text{Chlorotrimethyl silane}}{(CH_3)_3SiCl}$$

Taking $(CH_3)_3SiCl$ as a starting material we can prepare other organosilicon compounds too.

$$RMgCl + (CH_3)_3SiCl \longrightarrow RSi(CH_3)_3 + MgCl_2$$

R can be suitable group including any allylic group like $RCH_2 - CH = CH -$, etc.

Now, let us be specific about the reagents and their functions.

Chlorotrialkyl silane

Function 1 : As a protecting group for alcohols, amines, thioalcohols and terminal alkynes.

Let us take ethyl alcohol (C_2H_5OH). Here, the reactive part is the hydrogen atom of the —O—H group. So, if we wish to protect the —OH group we can take the following action :

$$CH_3CH_2\underset{\cdot\cdot}{\ddot{O}}H + \underset{\text{Chlorotri-methyl silane}}{(CH_3)_3SiCl} \xrightarrow{Et_3N:} \underset{\text{Silyl ether}}{CH_3CH_2O}\underset{\substack{\uparrow \\ \text{Protected}}}{Si(CH_3)_3}$$

In this type of reaction the order of reactivity of alcohols is 1° > 2° > 3° (alkyl alcohols) and alkyl alcohols > phenols or phenolic derivatives.

Silyl ether thus obtained can be cleaved with aqueous acid or base or sometimes even under some normal aqueous conditions.

$$CH_3CH_2OSi(CH_3)_3 \xrightarrow{CH_3COOH/H_2O} CH_3CH_2OH + (CH_3)_3SiOH$$

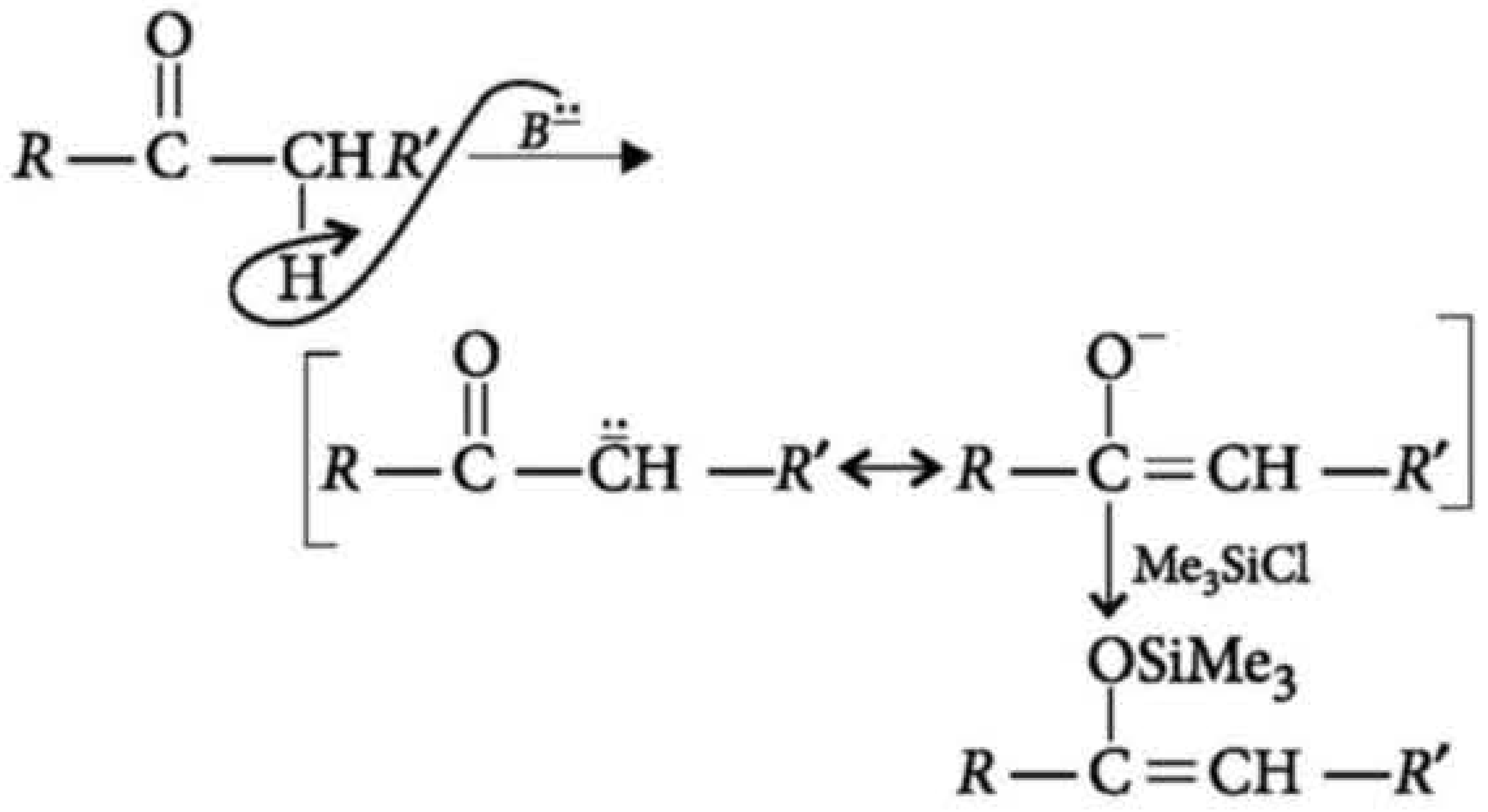
Take another example :

$$CH_3CH_2OSi(CH_3)_2C_4H_9\text{-}t \xrightarrow{CH_3COOH/H_2O} CH_3CH_2OH + t\text{-}C_4H_9\,(CH_3)_2SiOH$$

There is another way by which the deprotection of silyl ether can be done and that is fluoride ion. Such fluoride ion can be obtained from HF, KF or ammonium fluoride salt. Actually, Si — F bond is stronger bond than Si—O bond. This is the driving force for the readily cleavage of Si — O bond by F^- in order to produce Si — F bond.

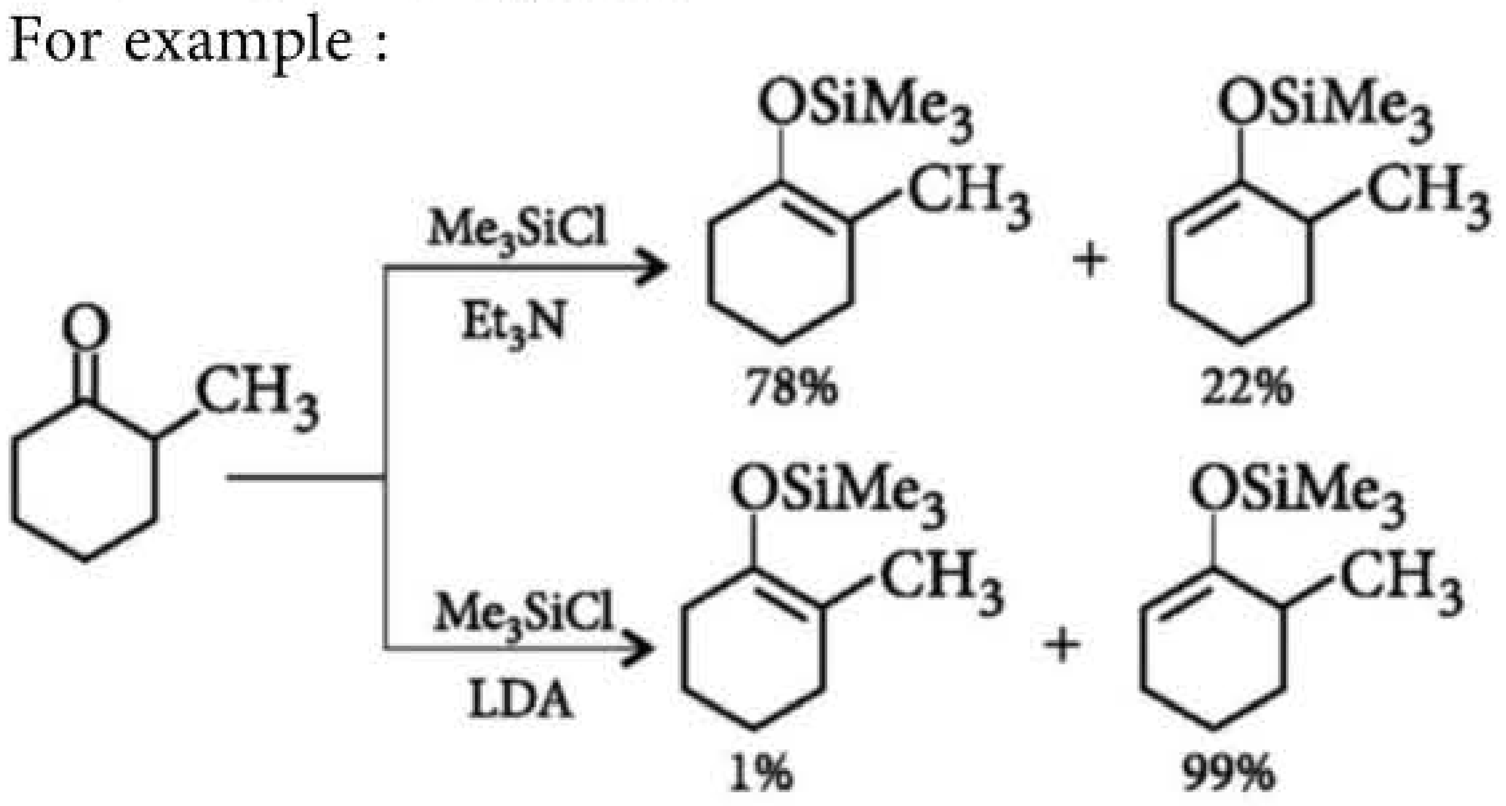
Function 2 : Reaction with enolates :

Let us see at first how a chlorotrimethyl silane reacts with an enolate :

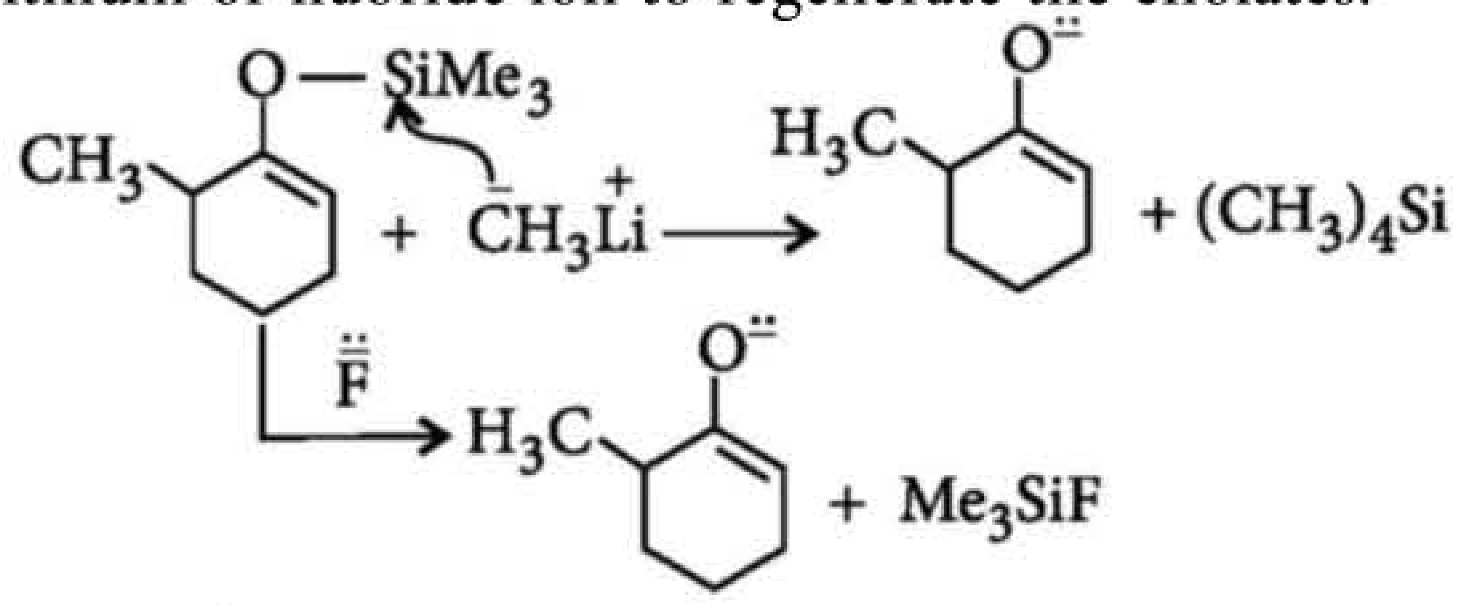


Now, amount of product in such cases depends on the kind of base being used.

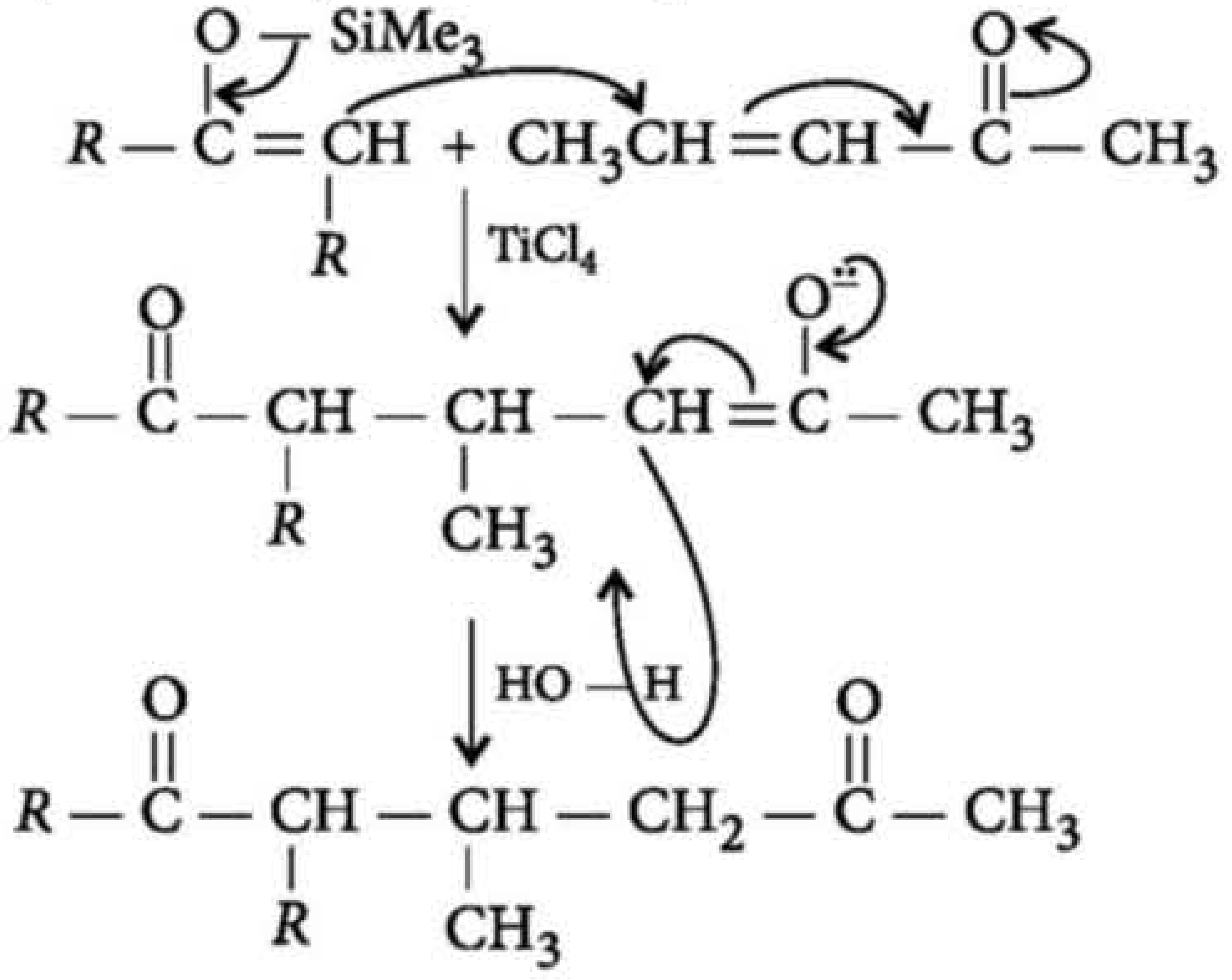
For example :



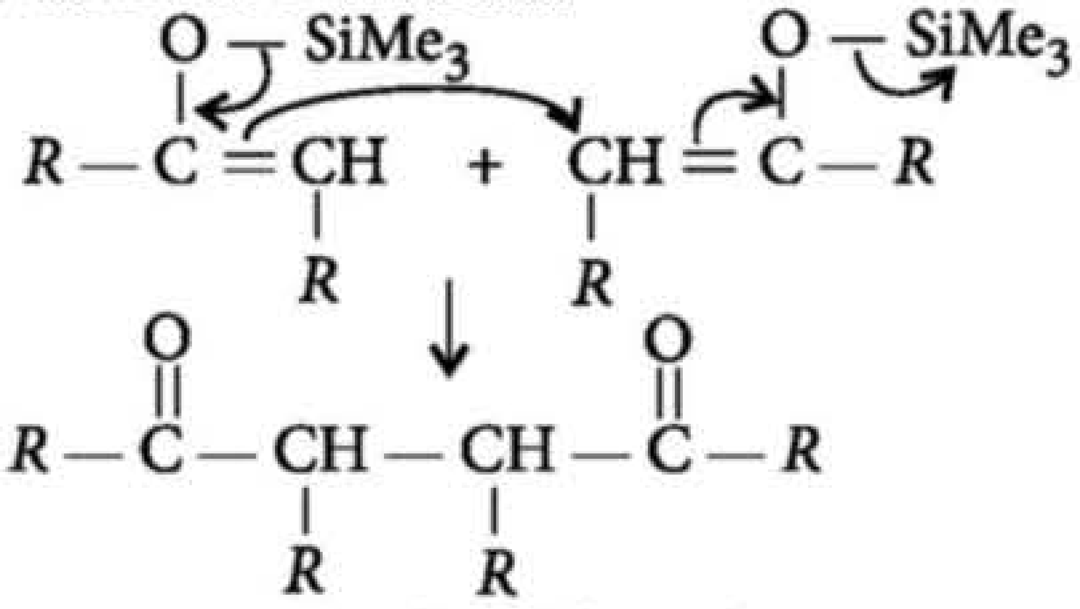
LDA is a bulky base, so gives kinetically controlled enolate but Et_3N gives thermodynamically controlled enolate. Here, the silyl enol ethers undergo reaction with methyl lithium or fluoride ion to regenerate the enolates.



With α, β-unsaturated compounds, silyl ethers of enols add to yield Michael addition product in presence of $TiCl_4$ as a catalyst. For example,



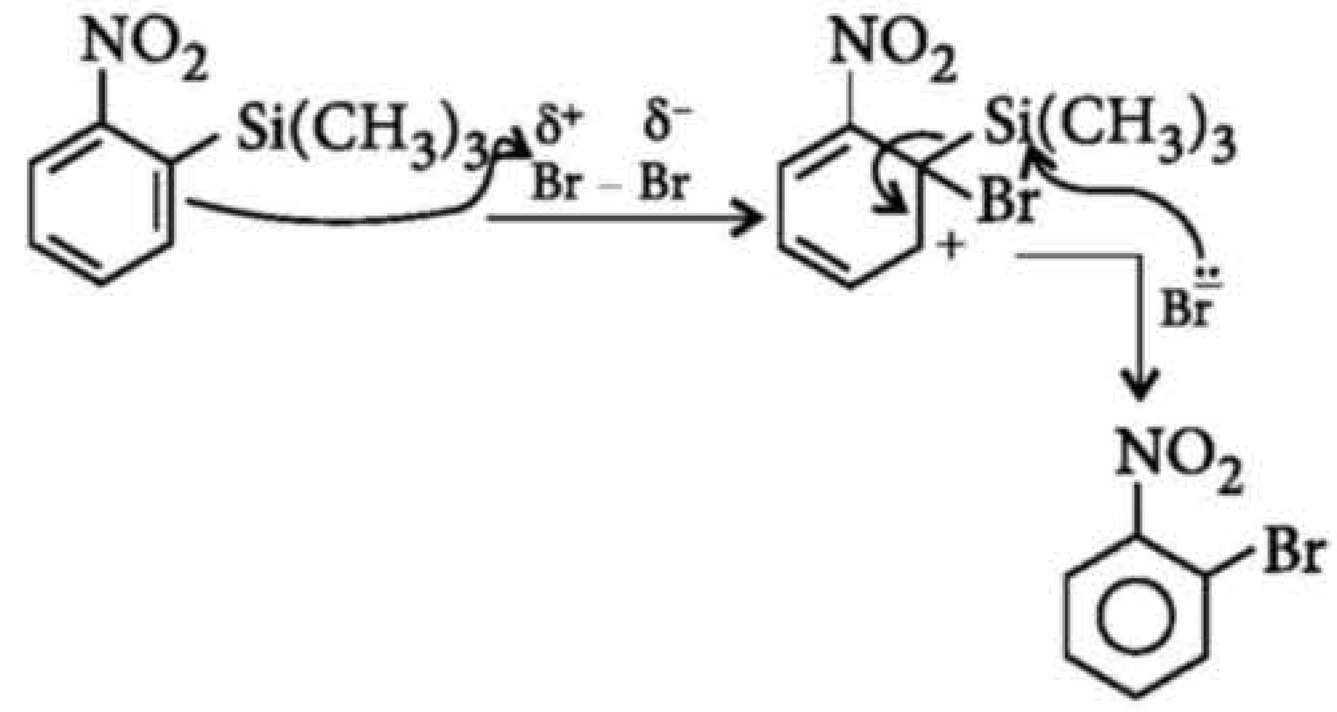
Silyl ethers also can undergo dimerisation in presence of Ag_2O in DMSO medium.



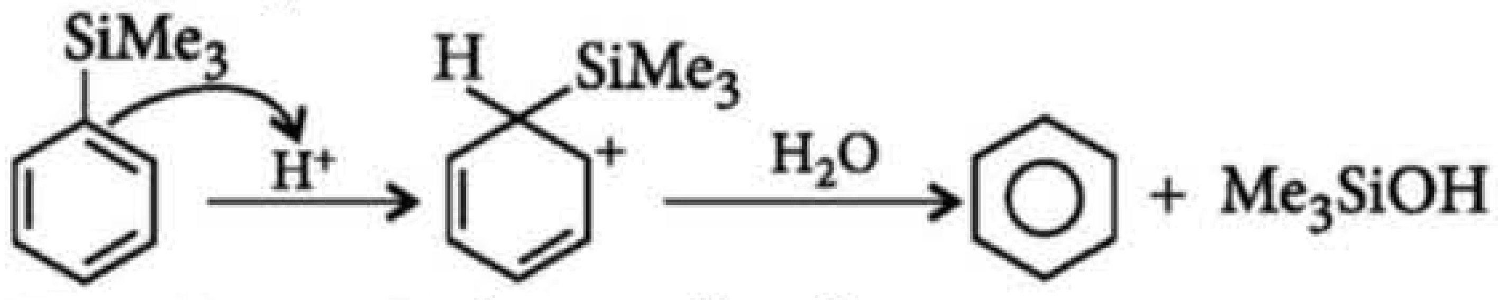
(1, 4-Diketone)

Function 3 : Ipso substitution :

Silicon has a vacant *d* orbital and it can undergo hyperconjugation with carbon atom so, it can stabilise a nearby carbocation. When an electrophile attacks the carbon atom bearing the trimethylsilyl group, then the trimethylsilyl group is replaced by the incoming electrophile. As you know this is an ipso-substitution.

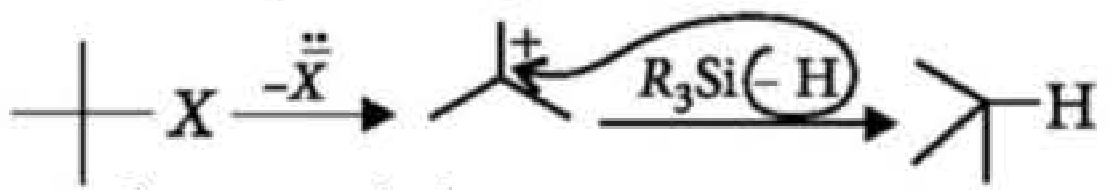


Ipso substitution can also take place during the course of hydrolysis.

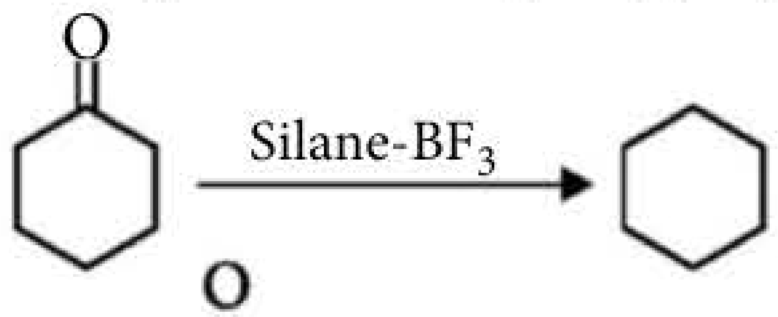


Function 4 : Reduction by silanes :

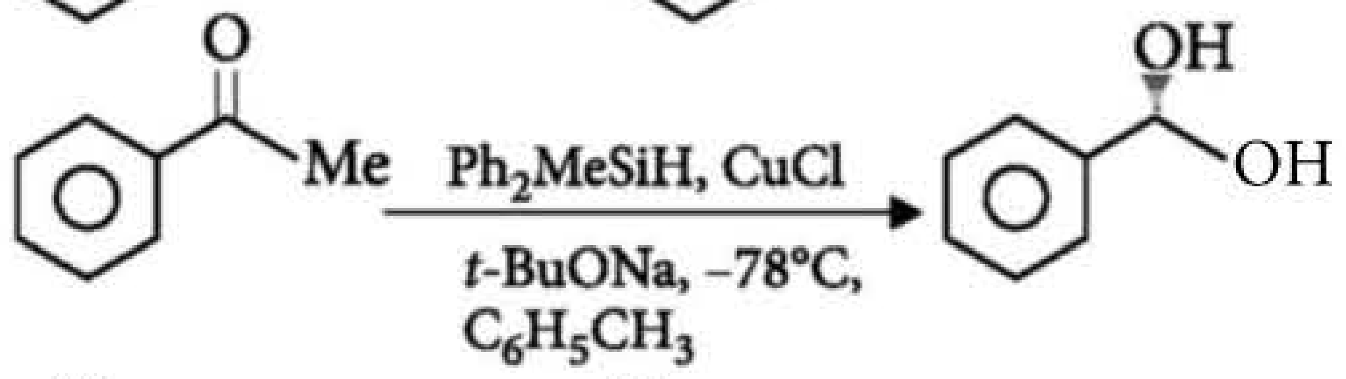
For selective reductions silanes are very useful. Some specific examples are given below :

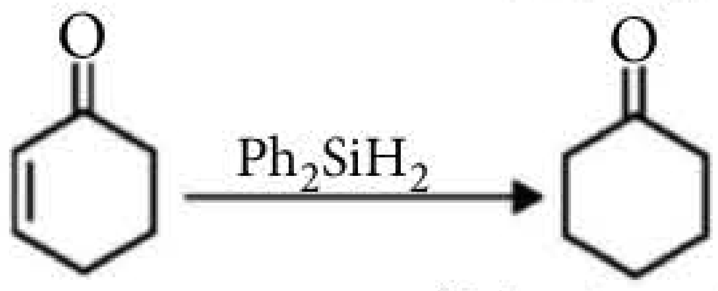
(A) 

Remember, Si (Electronegativity = 1.9) is less electronegative than hydrogen (2.20).

(B) 

but,

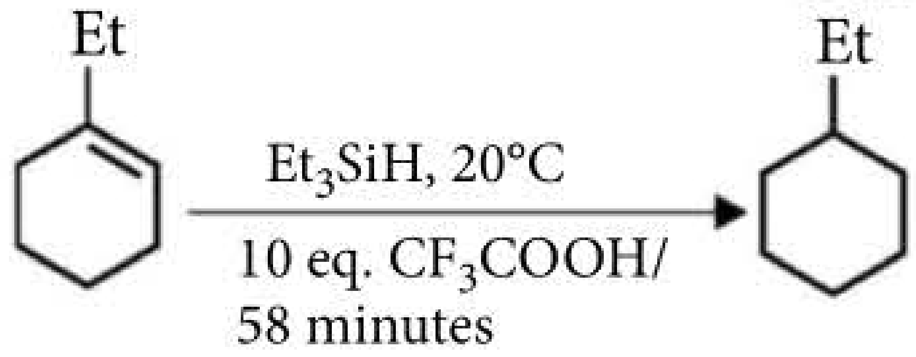
(C) 

(D) 

(Selective reduction)

(E) $Ph-CH{=}CH-CHO \xrightarrow[KF]{(EtO)_2SiHMe} Ph-CH{=}CHCH_2OH$

(Selective reduction)

(F) 

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