UNIT-6 : ELIMINATION REACTIONS

INTRODUCTION

Removal of two atoms or two groups or one atom and one group from a molecule is known as **elimination reaction**. In elimination reactions the leaving group is removed as a nucleophile and is called a nucleofuge.

The following are examples of leaving groups :

$$X \text{ (halogens), OH, OR, } \overset{\oplus}{N_2}, N_3, H_2\overset{\oplus}{O}, R_3\overset{\oplus}{N}, R_2\overset{\oplus}{S}$$

Elimination reactions are generally endothermic and take place on heating.

Types of Elimination Reactions

Elimination reactions can be classified into two categories :

(1) α-elimination reactions or 1, 1-elimination reactions

(2) β-elimination reactions or 1, 2-elimination reactions

(1) α-Elimination Reactions : A reaction in which both the groups or atoms are removed from the same carbon of the molecule is called α-elimination reaction. This reaction is mainly given by *gem* dihalides and *gem* trihalides having at least one α-hydrogen.

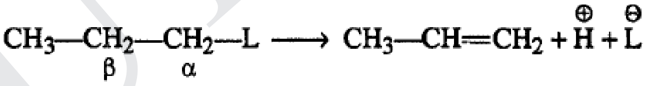
$$CHX_3 \xrightarrow{\text{Alc. KOH}/\Delta} \ddot{C}X_2 + \overset{\ominus}{X} + \overset{\oplus}{H}$$

$$CH_2X_2 \xrightarrow{\text{Alc. KOH}/\Delta} \ddot{C}HX + \overset{\ominus}{X} + \overset{\oplus}{H}$$

$$CH_3CHI_2 + Zn \xrightarrow{\Delta} CH_3\ddot{C}H + ZnI_2$$

Product of the reaction are halocarbenes or dihalocarbenes. Carbenes are key intermediates in a wide variety of chemical and photochemical reactions.

(2) β-Elimination Reactions : Consider the following reaction :



$$CH_3\text{—}\underset{\beta}{CH_2}\text{—}\underset{\alpha}{CH_2}\text{—}L \longrightarrow CH_3\text{—}CH{=}CH_2 + \overset{\oplus}{H} + \overset{\ominus}{L}$$

(a) Removal of functional group (i.e., leaving group) from α-carbon and other group (generally hydrogen atom) from the β-carbon is called β-elimination reaction.

(b) In this reaction there is loss of two σ bonds and gain of one π bond.

(c) Product of the reaction is generally less stable than the reactant.

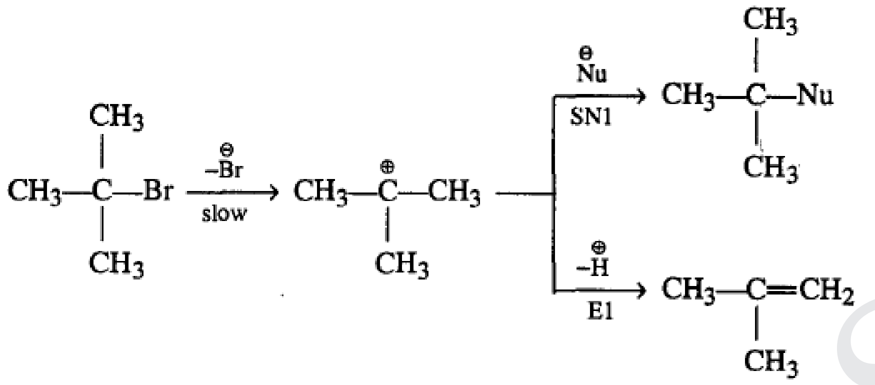
(d) Reaction is generally endothermic reaction which takes place on heating.

Types of β-Elimination Reactions

In analogy with substitution reactions, β-elimination reactions are divided into E_1 (elimination unimolecular), E_2 (elimination bimolecular) and E_{1cb} (elimination unimolecular conjugate base) reactions.

E1 Reactions

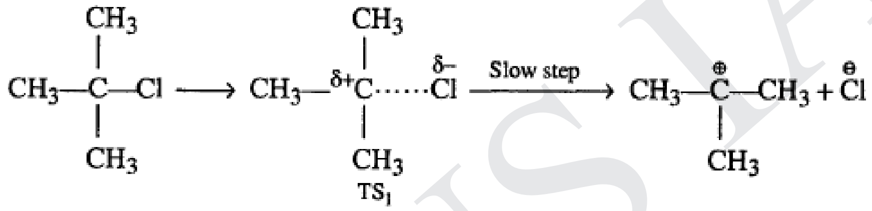
In case of SN1 reaction (for details of SN1 and SN2 reactions see Section 7.6) formation of product takes place *via* the formation of intermediate carbocation. This carbocation is a high energy, unstable intermediate that quickly undergoes further reaction. One way a carbocation can reach a stable product is by combining with nucleophile. This is known as SN1 reaction. However, there is alternative; the carbocation can lose a proton to a base leading to overall elimination reaction resulting in the formation of an alkene. In this case, the reaction is known as E1 elimination.



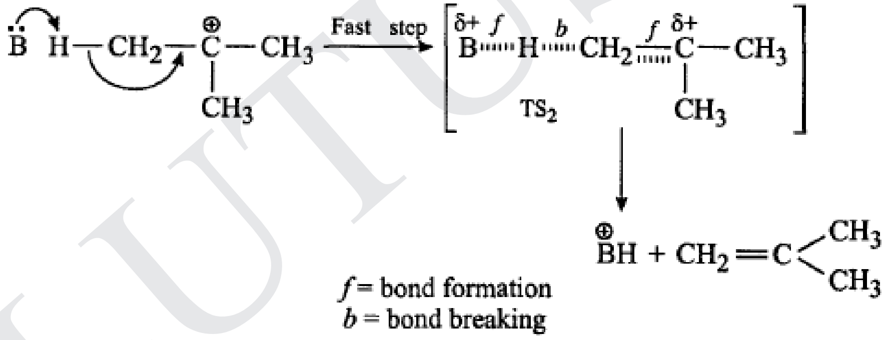
E1 mechanism

The mechanism of E1 reaction involves the following two steps :

Step I.: Formation of carbocation intermediate :



Step II.: Removal of proton by a base :



Energy profile diagram of E1 reaction is given in Fig. 5.1.

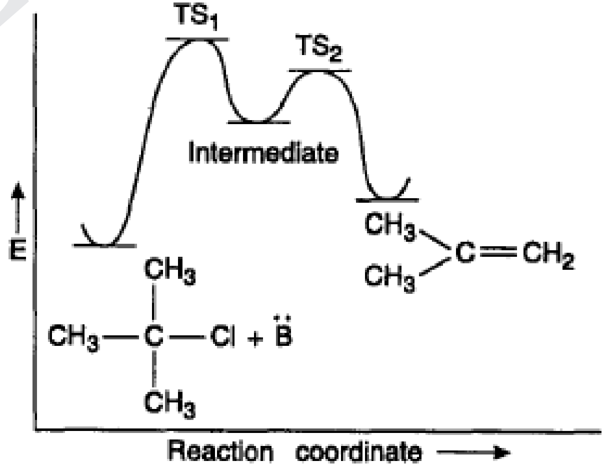


Fig. 5.1.

Characteristics of E1 Reactions

(i) The rate of the El reactions depends only on the concentration of substrate. The rate is independent of the concentration of the base.

$$\text{Rate} \propto [\text{Substrate}]$$

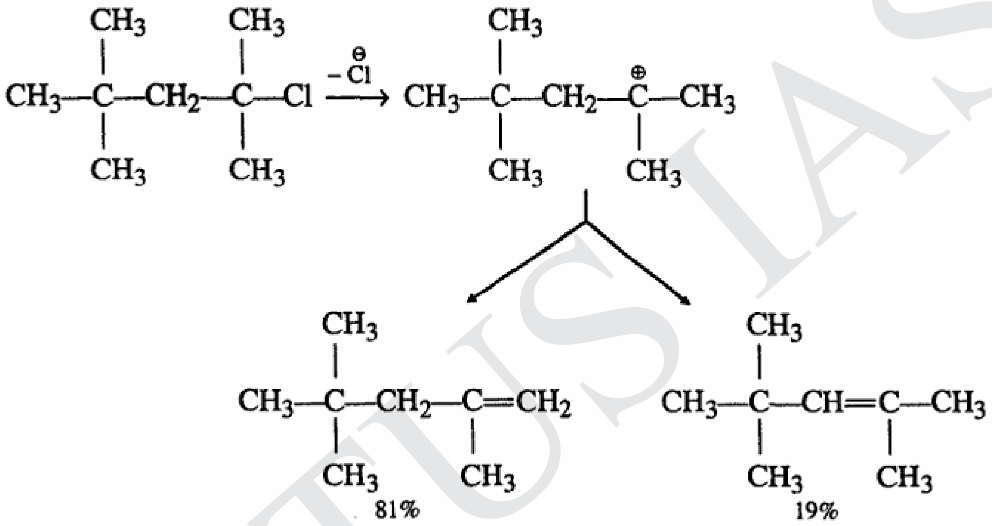
(ii) The rate of the reaction depends on the nature of the leaving group. In general, iodides react faster than bromides which react faster than chlorides.

$$R—I > R—Br > R—Cl > R—F$$

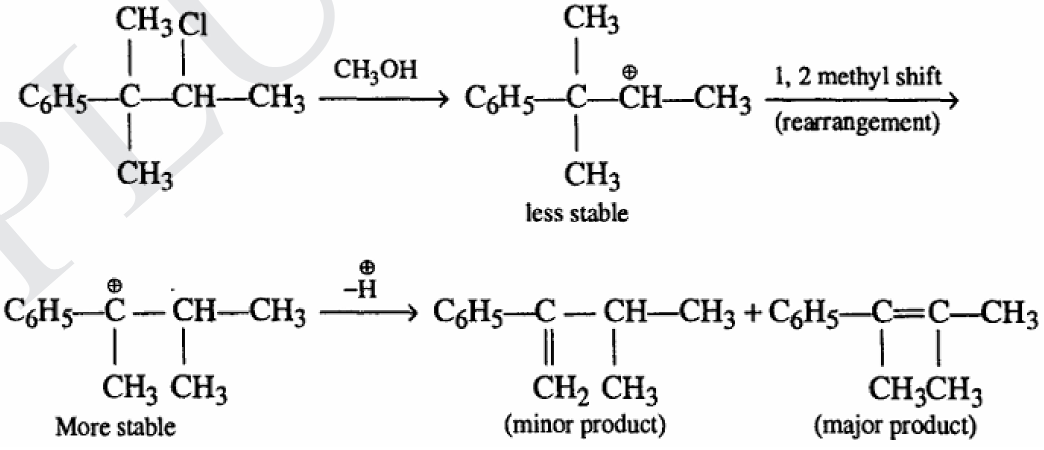
(iii) The reaction does not show primary kinetic isotope effect that is C—D bond and C—H bond are broken with the same ease.

(iv) Product formation takes place by Saytzeff rule but there are some exceptions, i.e., in some cases product formation takes place by Hofmann rule. For example :

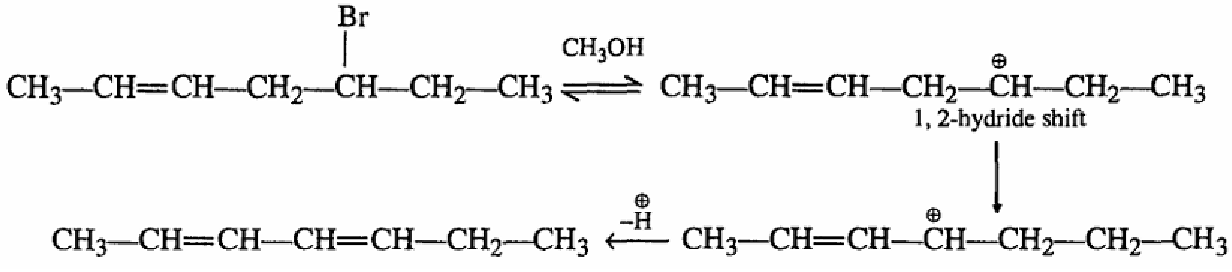
The E1 reaction of 2-chloro-2, 4, 4-trimethylpentane is interesting because it produces an excess of less substituted alkene. This is due to steric effect which leads to Hofmann elimination in an E1 reaction.



(v) **Rearrangement :** Because the E1 reaction involves the formation of a carbocation intermediate, rearrangement of the carbon skeleton can occur before the proton is lost. For example, the secondary carbocation that is formed from 3-chloro-2-methyl-2-phenylbutane undergoes a 1, 2 methyl shift to form a more stable tertiary benzyl carbocation.



In the following example, the secondary alkyl carbocation undergoes a 1, 2-hydrlde shift to form a more stable secondary allylic carbocation.



Factors Influencing E1 Reaction Rate

(1) Substrate structure and the reactivity: Carbocation being an intermediate in the E1 reaction, the rate and the reactivity of the reaction depends on the stability of the carbocation. Since +I effect, hyperconjugative effect and conjugative effect stabilise carbocation, any structure which forms stable carbocation will be reactive. Taking all these the order of the reactivity of the compounds is expected to be :

3° benzyl ≈ 3° allylic > 2° benzyl ≈ 2° allylic ≈ 3° alkyl > 1 ° benzyl ≈ 1 ° allylic
≈ 2° alkyl > 1° alkyl > vinyl

Thus alkyl or aryl substituents on α and β-positions with respect to the leaving group increases reactivity and the rate of the E1 reactions.

(2) Basicity and concentration of the base: Since E1 reactions do not usually require any added base (the solvent molecules surve the purpose), the strength and the concentration of the base have nothing to do with the rate of the E1 reactions. Usually the SN1 product dominates over E1 product because of the weak base character of the solvent.

(3) Nature of the leaving group: Reactivity of the substrate depends largely on the nature of the leaving group. Thus reactivity order is as follows :

$$\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{F}$$

(4) Nature of the solvents: Since E1 reactions involve an ionic intermediate, the carbocation, the rate of the E1 reaction increases with increasing polarity of the solvent. Polar solvents of poor nucleophilicity favour E1 reactions. If the temperature of the reaction is increased, E1 reactions are favoured. Thus increase in temperature increases E1/SN1 ratio.

E2 Reactions

The given reaction is an example of E2 reaction.

$$CH_3—CH_2—CH_2—Br \xrightarrow[\Delta]{\text{Base}} CH_3—CH{=}CH_2 + \overset{\oplus}{H} + \overset{\ominus}{X}$$

Energy profile diagram of-this reaction is given in Fig. 5.2.

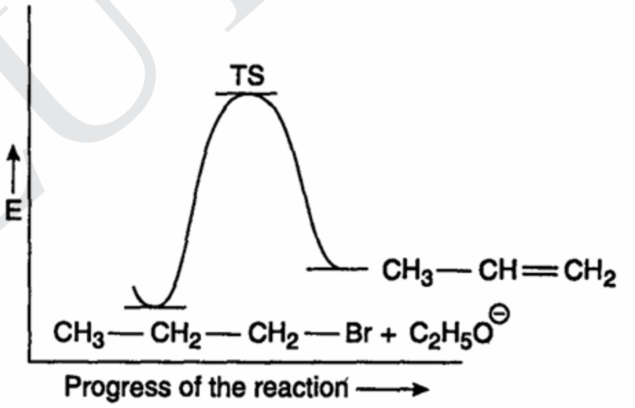


Fig. 5.2.

Characteristics of E2 reactions

(i) Rate ∝ [R—X] [Base]

(ii) Rate depends on the nature of leaving group, .i.e., Rate ∝ leaving power of the group, e.g., bromides react faster than chlorides.

(iii) Reaction has high primary kinetic isotope effect:

$CH_3—CH_2—Br$ K_H (velocity constant of the reaction)
$CD_3—CD_2—Br$ K_D (velocity constant of the reaction)

$$\frac{K_H}{K_D} = 7$$

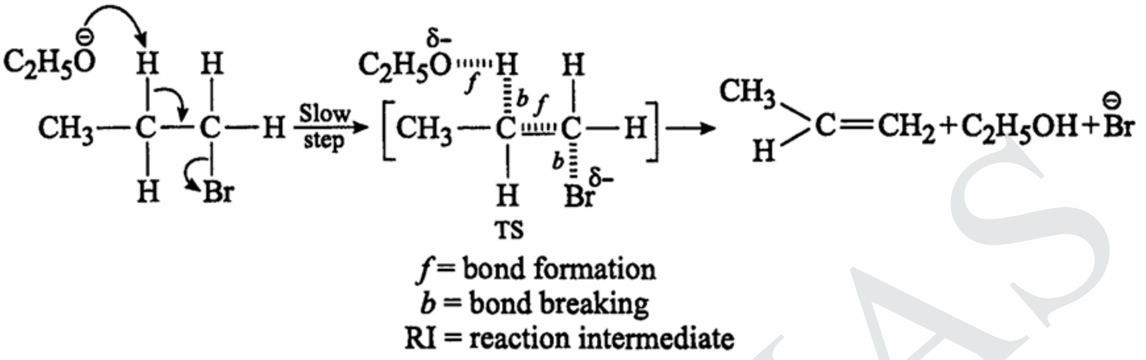
Results (ii) and (iii) show that C—X bond breaking and C—H bond breaking take place in the rate determining step.

(iv) Since the reaction is a bimolecular reaction, the product formation will take place by formation of transition state.

Reaction:

$$CH_3-CH_2-CH_2-Br+C_2H_5\overset{\ominus}{O}\longrightarrow CH_3-CH=CH_2+C_2H_5OH+Br^{\ominus}$$

Mechanism:



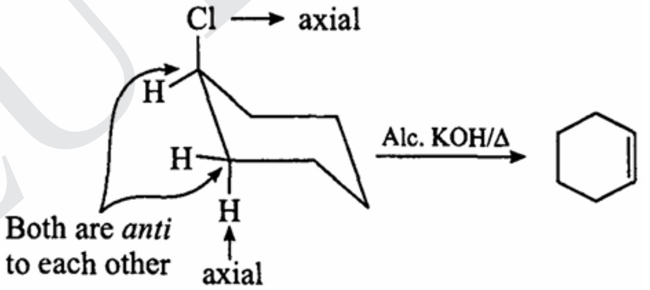
f = bond formation
b = bond breaking
RI = reaction intermediate

(v) In E2 reaction product formation takes place by formation of TS which is neutral species and has less energy content (whereas in E1, RI is carbocation and in E1*cb*, RI is carbanion, both species are charged species having high energy content). Thus E2 elimination is lowest energy path [<<<<E_a] in comparison to E1 and E_{1cb} reactions. Due to this E2 reaction is the most common reaction.

(vi) In E2 reaction, both the leaving groups should be *anti*-periplanar, i.e., both leaving groups should be in the same plane but should have anti conformation (i.e., angle is 180°) i.e., E2 mechanism is stereospecific.

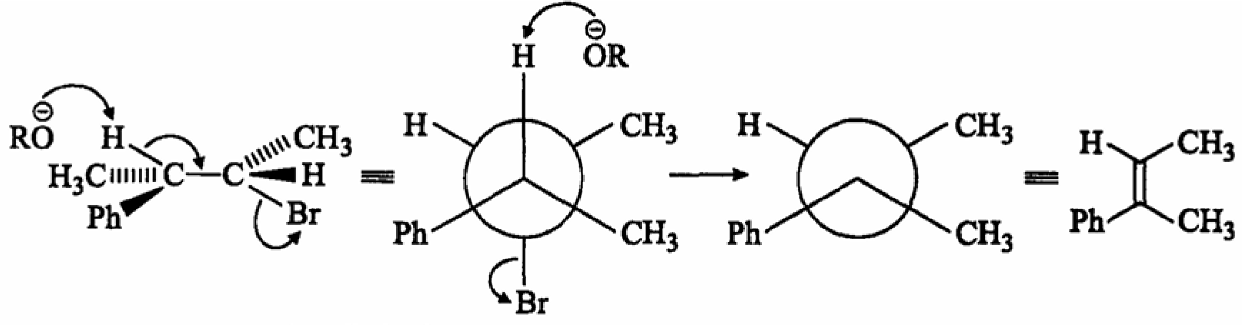
(vii) In acyclic compounds, E2 elimination is given by the most stable conformation in which both leaving groups are *anti*-periplanar.

(viii) The elimination in six membered cyclic compounds (i.e., cyclohexane derivatives) proceeds best when leaving groups are diaxial (*trans* or *anti*). In this case *anti*-peri planarity is available. 1, 2-Diaxial groups are always periplanar and *anti* to each other.



Stereochemistry of E2 reactions

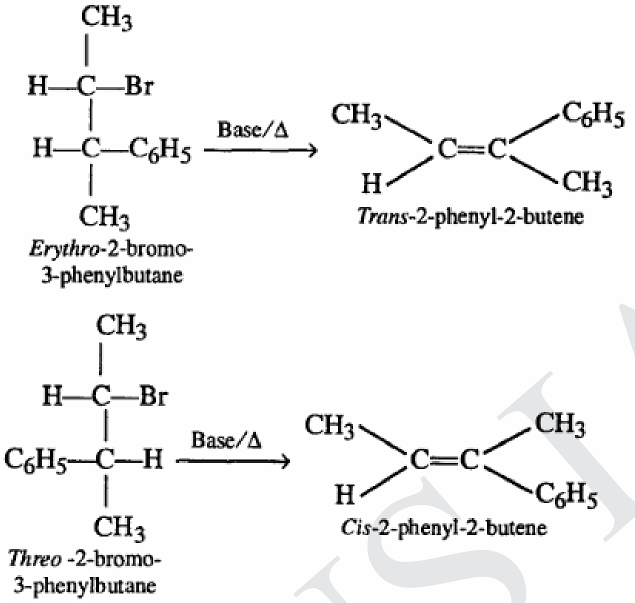
It has been observed that in the transition state of E2 elimination, the attacking base and the leaving group are generally *anti* or as far apart as possible. For this reason, the E2 elimination is often referred as *anti*-elimination. In majority of cases, *anti*-elimination is favoured over *syn* elimination because TS for the former has staggered conformation with lower energy than that for the eclipsed or gauche conformation in the *syn* elimination.



Anti elimination

The interesting feature about *anti*-elimination is that *anti*-positioning of the eliminating groups (H and Br) determines the stereochemistry of the product alkene.

For example, *erythro* form of halide gives *E* or *trans* alkene whereas *threo* form gives *Z* or *cis* alkene.



Erythro-2-bromo-3-phenylbutane

Trans-2-phenyl-2-butene

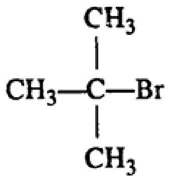
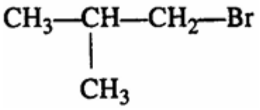
Threo -2-bromo-3-phenylbutane

Cis-2-phenyl-2-butene

In open chain compounds the molecules can easily adopt the *anti*-periplanar conformation owing to free-rotation about C—C single bond. Hence, *anti* (*trans*) E2 reaction is a general rule in the case of open chain compounds. Some cyclic compounds also show the *trans* E2 reaction. However, some cyclic compounds which have *cis* coplanar groups, are incapable of adopting *anti*-periplanar conformation do not follow *trans* E2 elimination and undergo *syn* E2 elimination.

Factors Influencing E2 Reaction Rate

(1) Structure of Substrate: It has been found that the increasing branching at α and β-carbon increases the rate of the E2 reaction. This is because as the number of alkyl or aryl groups increases on the carbon atoms of the developing double bond, the stability of the TS increases.

Substrate	% yield	Rate
$CH_3—CH_2—Br$	0.9	1.0×10^5
$CH_3—CH_2—CH_2—Br$	8.9	5.3×10^5
 $(CH_3)_3C—Br$	97	4.7×10^5
 $CH_3—CH(CH_3)—CH_2—Br$	59.5	8.5×10^5

The above table shows that the order of the rate and reactivity is 3° > 2° > 1°.

Since the TS of SN2 reaction involves high steric strain, the α and β-branches slow down the SN2 reaction rate while speed up to E2 reaction rate. Thus with increasing branching at α and β-carbons, the E2/SN2 ratio increases.

It has also been found that electron withdrawing groups (–*I* or –*R* group) on the β-carbon increases the rate of the E2 reaction. This is because –*I* group or –*R* group increases acidity of the β-hydrogen and stabilises the carbocation character of the T.S.

(2) Nature of the Leaving Group: In general, the better the leaving group, the higher is the rate of the E2 reaction.

Substrate	$PhCH_2—CH_2—Cl$	$PhCH_2CH_2Br$	$PhCH_2CH_2I$
Rate	0.007×10^3	4.2×10^3	27×10^3

It has also been found that with the increasing leaving power of the halogen atom E2/SN2 ratio increases but to a minimum extent.

(3) Strength and Concentration of the Base : With the increasing basicity and the concentration of the added base, the rates of the E2 reactions have been found to increase. In the presence of strong base the E2/SN2 ratio increases.

(4) The Nature of the Solvent: The yield of the E2 product decreases with the decrease in the polarity of the solvent.

(5) The Effect of Temperature: As the temperature of the E2 reaction increases, the rate of the reaction also increases. Thus the E2/SN2 ratio also increases.

Competition Between E2 and E1 Reactions

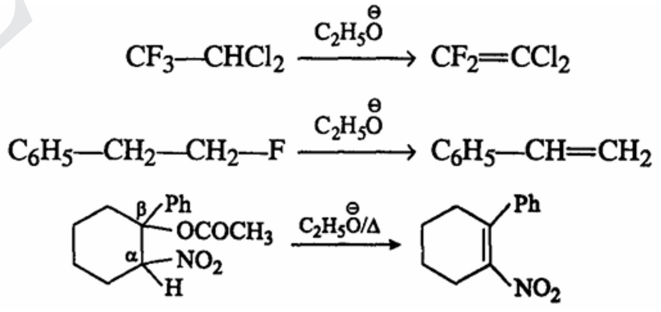
Primary alkyl halides undergo only E2 elimination reactions. They cannot undergo E1 reactions because of the difficulty encountered in forming primary carbocations. Secondary and tertiary alkyl halides undergo both E1 and E2 reactions. For those alkyl halides that can undergo both E2 and E1 reactions, the E2 reaction is favoured by a high concentration of a strong base and an aprotic solvent (e.g., DMSO, DMS, acetone). An E1 reaction is favoured by a weak base and a protic solvent (e.g., HOH, ROH).

Substrate	Elimination Reaction
Primary alkyl halide	E2 only
Secondary alkyl halide	E1 and E2
Tertiary alkyl halide	E1 and E2

E1*cb* Reactions :

There is third mechanism of β-elimination reactions. This begins with the rapid loss of a proton to a base. Loss of this proton leads to a formation of a carbanion. The carbanion is then converted to, an alkene. Conversion of carbanion to alkene is slow step and hence the rate determining step. Since this reaction proceeds through the conjugate base of the starting material, this elimination is abbreviated as E1*cb* (elimination unimolecular conjugate base).

The following are some examples of E1*cb* reactions :

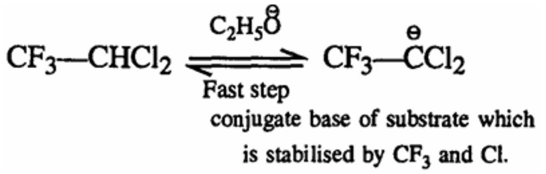


$$CF_3—CHCl_2 \xrightarrow{C_2H_5\overset{\ominus}{O}} CF_2=CCl_2$$

$$C_6H_5—CH_2—CH_2—F \xrightarrow{C_2H_5\overset{\ominus}{O}} C_6H_5—CH=CH_2$$

Mechanism of E1*cb* reaction :

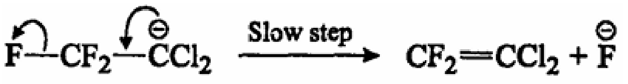
First step:



$$CF_3—CHCl_2 \underset{\text{Fast step}}{\overset{C_2H_5\overset{\ominus}{O}}{\rightleftharpoons}} CF_3—\overset{\ominus}{C}Cl_2$$

conjugate base of substrate which is stabilised by CF_3 and Cl.

Second step :



$$F—CF_2—\overset{\ominus}{C}Cl_2 \xrightarrow{\text{Slow step}} CF_2=CCl_2 + \overset{\ominus}{F}$$

The E1*cb* reaction is first order in base and first order in substrate just like the E2 reaction. However, it is unimolecular, because only one species is involved in the rate—determining step. That species is the carbanion.

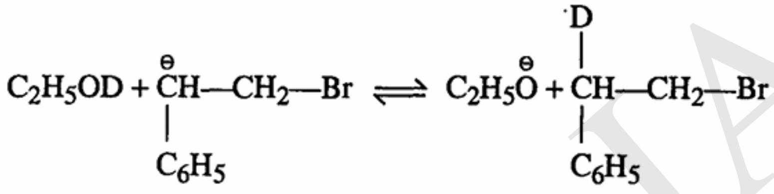
The following are important points regarding E1*cb* reaction :

(1) E1*cb* mechanism is limited to substrates with substituents which can stabilise the carbanion as reaction intermediate. Thus β-carbon should contain strong –*I* group, e.g., carbonyl group, nitro group, cyano group, sulphonyl group or other carbanion stabilising group.

(2) This reaction is given by those compounds which have poor leaving group, otherwise carbanion will not be formed.

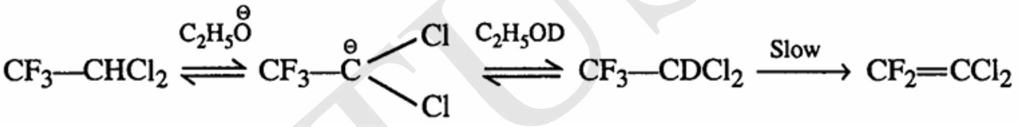
(3) β-hydrogen should be highly acidic so that it can easily be removed as proton to give carbanion.

The E1*cb* reaction completes with the E2 reaction. The use of deuterium labelling can help to distinguish the E1*cb* from the E2 pathway. The first step of the E1*cb* mechanism is reversible, when the reaction is carried out in C_2H_5OD instead of C_2H_5OH, the intermediate carbanion should pick up deuterium, and one would recover deuterated substrate after partial transformation.



$$C_2H_5OD + \underset{C_6H_5}{\overset{\ominus}{C}H}-CH_2-Br \rightleftharpoons C_2H_5\overset{\ominus}{O} + \underset{C_6H_5}{\overset{D}{C}H}-CH_2-Br$$

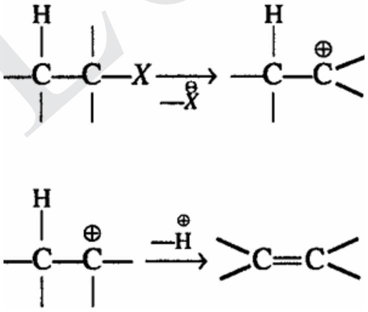
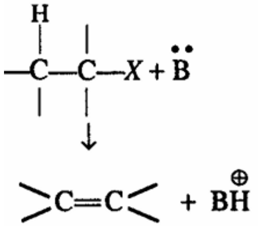
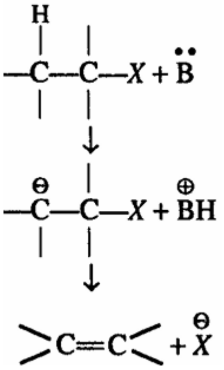
On the other hand, there should be no deuterium uptake if E2 mechanism is operating. E1*cb* mechanism operates only in some special cases where the intermediate carbanion is stabilised either by inductive or mesomeric effect. For instance, 1, 1, 1 trifluoro-2, 2-dichloroethane undergoes β-elimination *via* E1*cb* pathway.



$$CF_3-CHCl_2 \overset{C_2H_5\overset{\ominus}{O}}{\rightleftharpoons} CF_3-\overset{\ominus}{C}Cl_2 \overset{C_2H_5OD}{\rightleftharpoons} CF_3-CDCl_2 \xrightarrow{Slow} CF_2=CCl_2$$

Comparison between E1, E2 and E1*cb* pathways

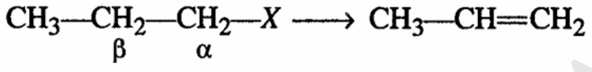
Comparison between these reaction pathways are given in the table below :

	E1	E2	E1*cb*
1. Steps	Two step process 	One step process 	Two step process 
2. RI or TS	Carbocation as *RI*	*TS*	Carbanion as *RI*
3. Kinetics	First order, unimolecular; Rate = $K_1[RX]$; rate of ionisation	Second order, bimolecular Rate = $K_2[R—X][B]$	Second order, Rate = $K_2[R—X][B]$
4. Driving force	Ionisation of *R—X*	Attack by base on β-hydrogen	Attack by base on β-hydrogen
5. Stereochemistry	Nonstereospecific and non-stereoselective	Stereoselective and stereo specific	Nonstereospecific and non-stereoselective
6. Regioselectivity	Saytzeff	Saytzeff as well as Hofmann	Hofmann

7. Rearrangement	Common	No rearrangement except for, allylic (SN2')	No rearrangement
8. Completing reaction	SN1	SN2	No
9. Reactivity order	3° > 2° > 1°	3° > 2° > 1°	3° > 2° > 1°

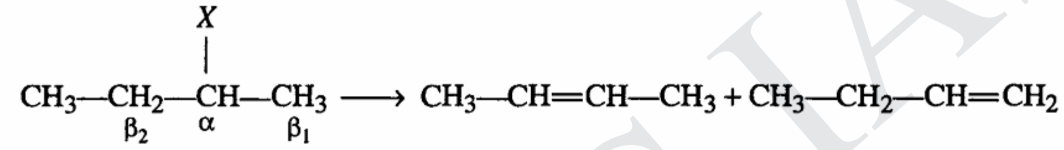
Number of Products in β-Elimination Reactions

Number of products depends on the number of different types of β-carbons having hydrogen(s). Number of products in a β-elimination reaction = Number of different types of β-carbons having hydrogen(s).



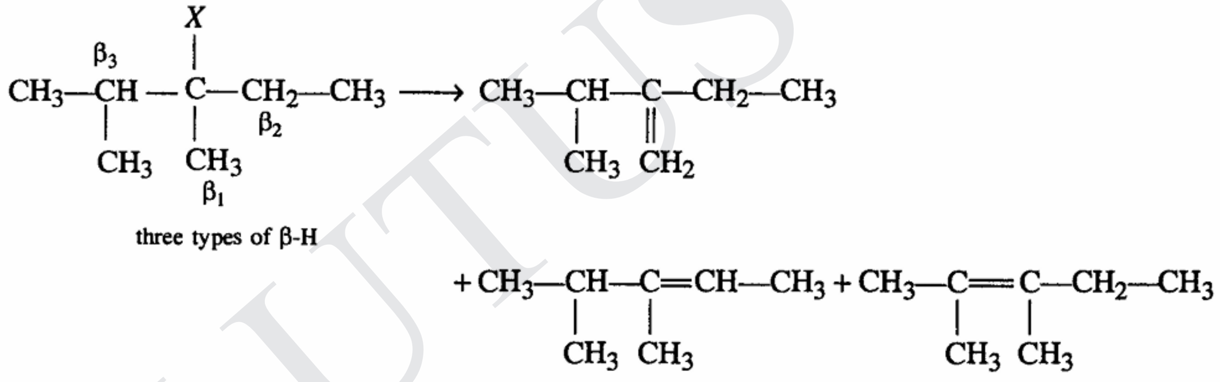
$$CH_3-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-X \longrightarrow CH_3-CH=CH_2$$

only one type of β—H only one product



$$CH_3-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{X}{CH}}-\underset{\beta_1}{CH_3} \longrightarrow CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$$

two types of β-H two products



$$CH_3-\underset{CH_3}{\overset{\beta_3}{CH}}-\underset{\underset{\beta_1}{CH_3}}{\overset{X}{C}}-\underset{\beta_2}{CH_2}-CH_3 \longrightarrow CH_3-\underset{CH_3}{CH}-\underset{CH_2}{\overset{}{C}}-CH_2-CH_3$$

three types of β-H

$$+ CH_3-\underset{CH_3}{CH}-\underset{CH_3}{C}=CH-CH_3 + CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_2-CH_3$$

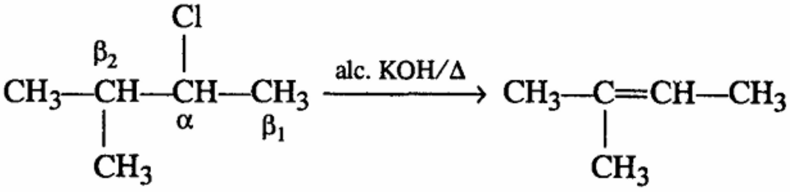
three products

ORIENTATION IN ELIMINATION REACTIONS

If a substrate has different types of β-hydrogens then it will give more than one product. Major product of the reaction can be known by two empirical rules.

Saytzeff Rule

According to this rule, major product is the most substituted alkene, i.e., the most stable alkene. Thus, the major product is obtained by elimination of $\overset{\oplus}{H}$ from that β-carbon which has the least number of hydrogen. Product of the reaction in this case is known as Saytzeff product.

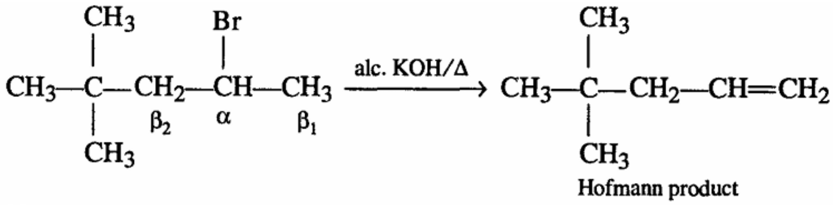


$$CH_3-\underset{CH_3}{\overset{\beta_2}{CH}}-\underset{\alpha}{\overset{Cl}{CH}}-\underset{\beta_1}{CH_3} \xrightarrow{\text{alc. KOH}/\Delta} CH_3-\underset{CH_3}{C}=CH-CH_3$$

Saytzeff product

Hofmann Rule

According to this rule major product is always least substituted alkene, i.e., the least stable alkene. Thus, the major product is formed from β-carbon which has maximum number of hydrogens. Product of the reaction in this case is known as Hofmann product.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{Br}{CH}}-\underset{\beta_1}{CH_3}\xrightarrow{\text{alc. KOH}/\Delta}CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH=CH_2$$

Hofmann product

Note:

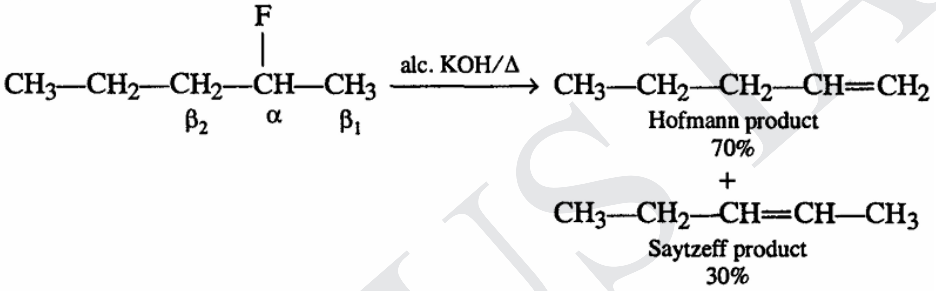
(i) In E1 reactions, product formation always takes place by Saytzeff rule.

(ii) In E1*cb* reactions, product formation always takes place by Hofmann rule.

(iii) In E2 reaction, product formation takes place by Saytzeff as well as Hofmann rule.

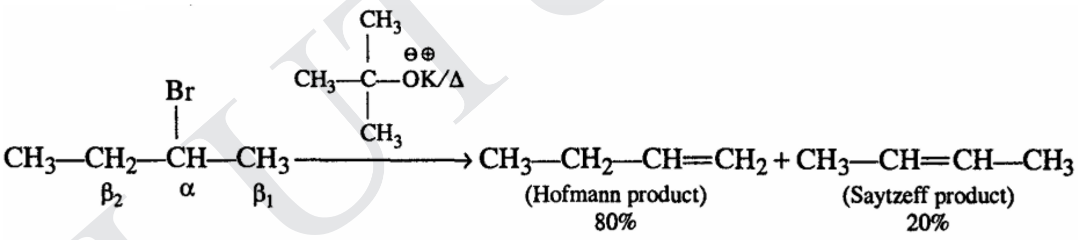
In almost all E2 reactions product formation takes place by Saytzeff rule. **Only in four cases product formation takes place by Hofmann Rule.**

(1) Dehydrohalogenation of alkyl halides when leaving group is very poor, e.g., alkyl fluoride (primary or secondary)



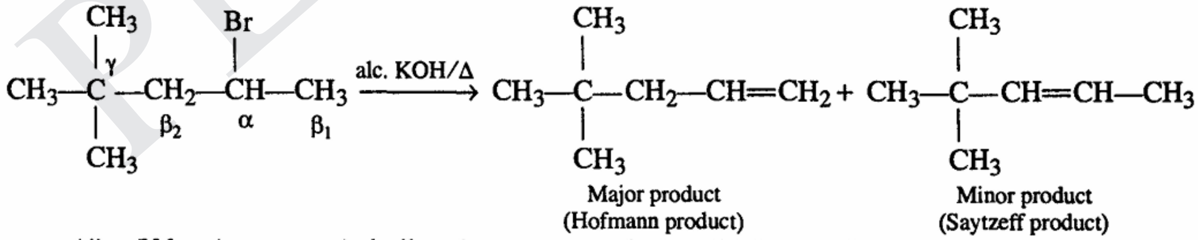
$$CH_3-CH_2-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{F}{CH}}-\underset{\beta_1}{CH_3}\xrightarrow{\text{alc. KOH}/\Delta}\underset{\substack{\text{Hofmann product}\\70\%}}{CH_3-CH_2-CH_2-CH=CH_2}+\underset{\substack{\text{Saytzeff product}\\30\%}}{CH_3-CH_2-CH=CH-CH_3}$$

(2) Primary and *sec*-alkyl halides gives Hofmann elimination when the size of the base is bulky, i.e., sodium or potassium *ter*-butoxide.



$$CH_3-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{Br}{CH}}-\underset{\beta_1}{CH_3}\xrightarrow{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\ominus\oplus}{OK}/\Delta}\underset{\substack{\text{(Hofmann product)}\\80\%}}{CH_3-CH_2-CH=CH_2}+\underset{\substack{\text{(Saytzeff product)}\\20\%}}{CH_3-CH=CH-CH_3}$$

(3) Primary and *sec*-alkyl halides having quarternary γ-carbon gives Hofmann elimination

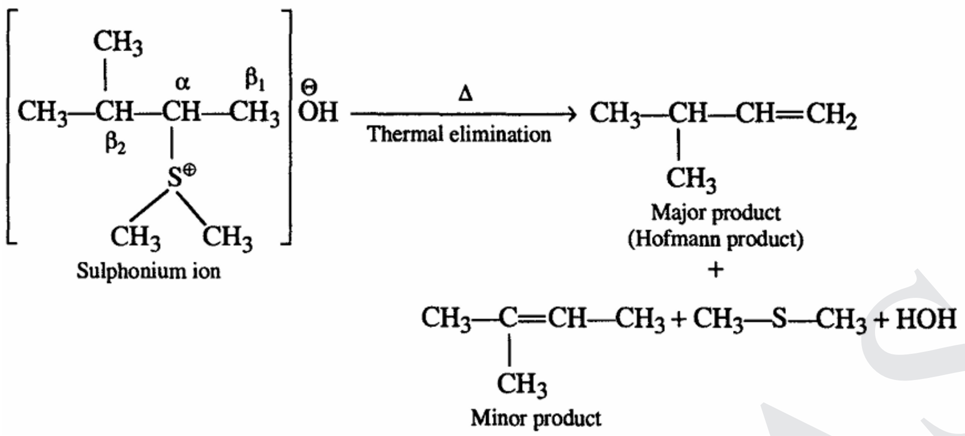


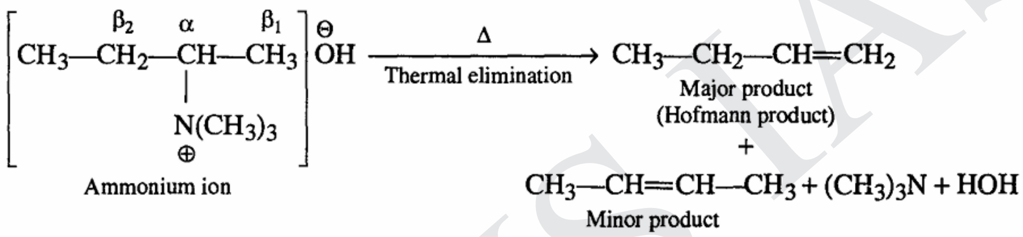
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{\gamma}{C}}}-\underset{\beta_2}{CH_2}-\underset{\alpha}{\overset{Br}{CH}}-\underset{\beta_1}{CH_3}\xrightarrow{\text{alc. KOH}/\Delta}CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH=CH_2+CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH-CH_3$$

Major product (Hofmann product)

Minor product (Saytzeff product)

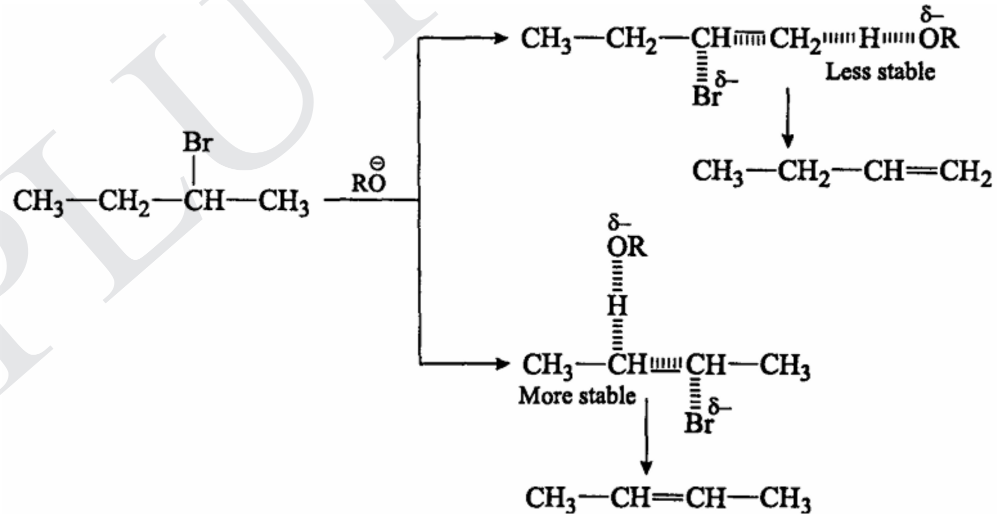
(4) If leaving group is bulky, then compound gives Hofmann elimination reaction. The most common type of large, bulky leaving groups which lead to Hofmann products have positively charged nitrogen $(\overset{\oplus}{N}R_3)$ or positively charged sulphur $(\overset{\oplus}{S}R_2)$





Theoretical Explanation for Saytzeff Rule

Explanation for the more stable alkene (Saytzeff product) being formed in preference to the less stable alkene, is available from the transition states leading to these two alkenes. In either transition state, the removal of a proton and the formation of the double bond is taking place simultaneously. The transition state has some double-bond character which is represented by the dotted line.



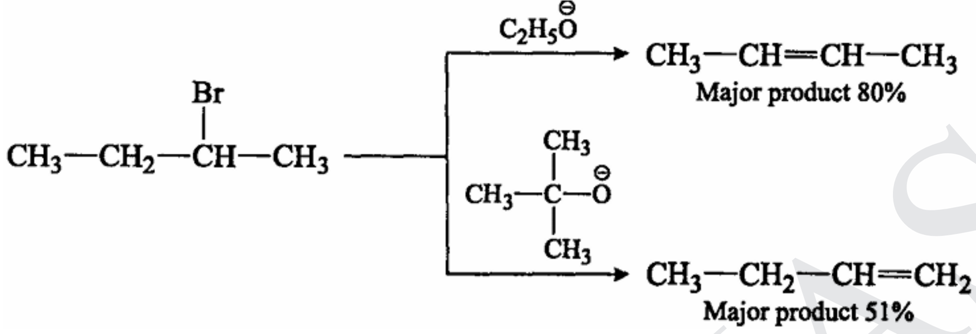
Because both transition states leading to the alkene have some double bond character, the transition state leading to the more stable alkene is itself more stabilised and is of lower energy. The reaction with the lower energy transition state proceeds at a faster rate; therefore the more stable alkene is the predominant product (Fig. 5.3).

In the case of E1 reactions the Saytzeff product (most stable alkene) is always the major product because it is formed through a lower energy TS from the carbocation intermediate. As we have noted above, the TS leading to the more stable alkene is itself more stabilised and is of lower energy.

Theoretical Explanation of Hofmann Rule

A common phenomenon leading to the less substituted alkene (Hofmann product) is steric hindrance in the transition state leading to the least substituted alkene. Steric hindrance can raise the energy of this transition state so much so that the reaction follows a different course and yields the less substituted alkene. The steric hindrance is caused by anyone of the following four factors.

(1) Size of attacking base: In the elimination reaction of 2-bromopentane with ethoxide the most substituted alkene predominates but with the bulky *t*-butoxide ion, the 1-butane predominates.



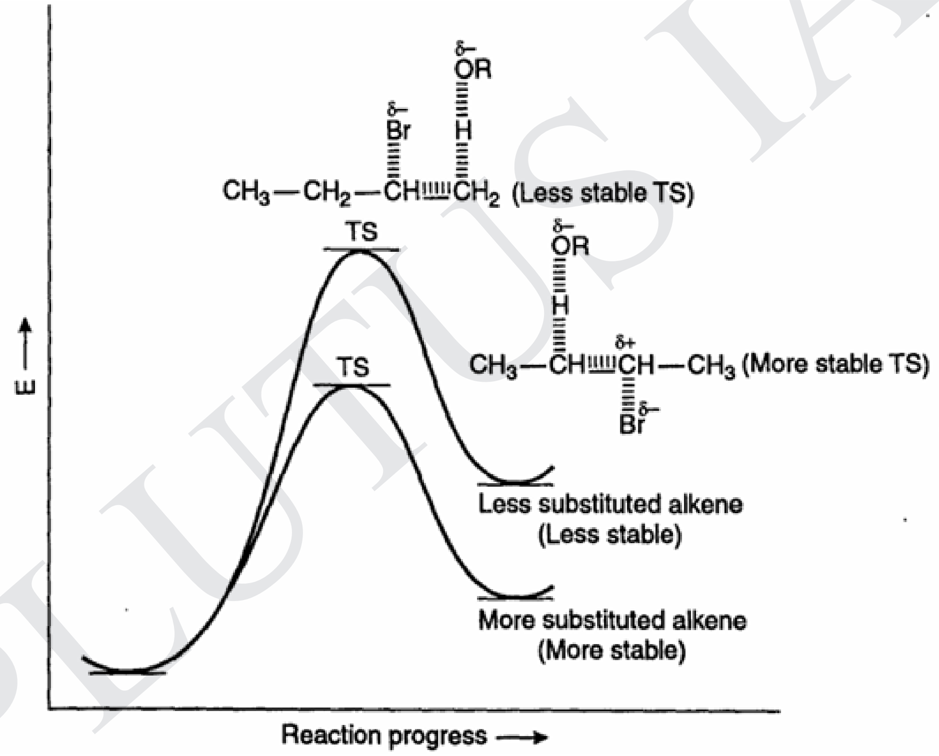
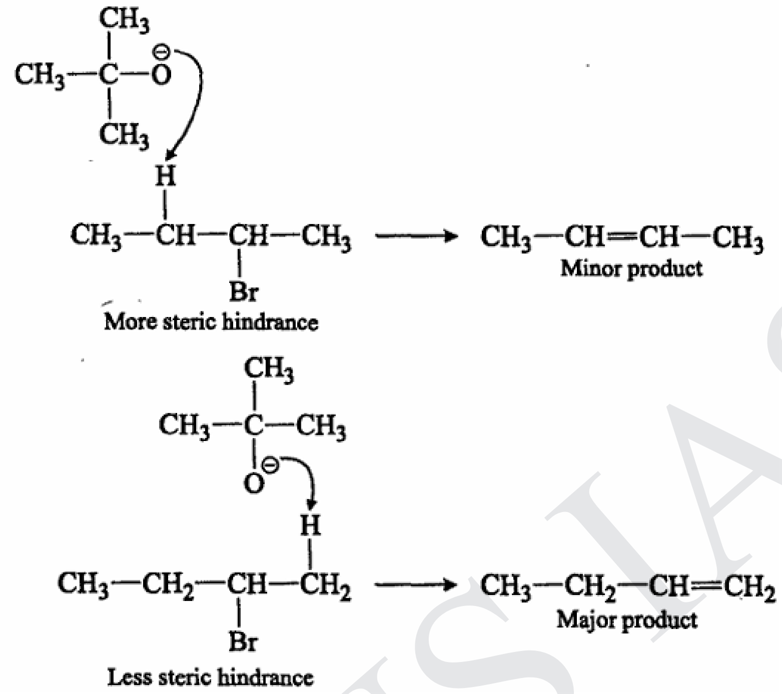
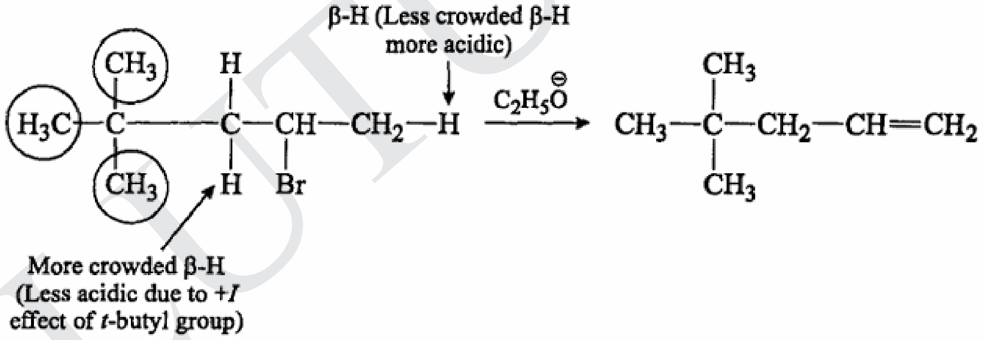


Fig. 5.3.: Energy diagram for a typical E2 reaction, showing why the more substituted alkene predominates.

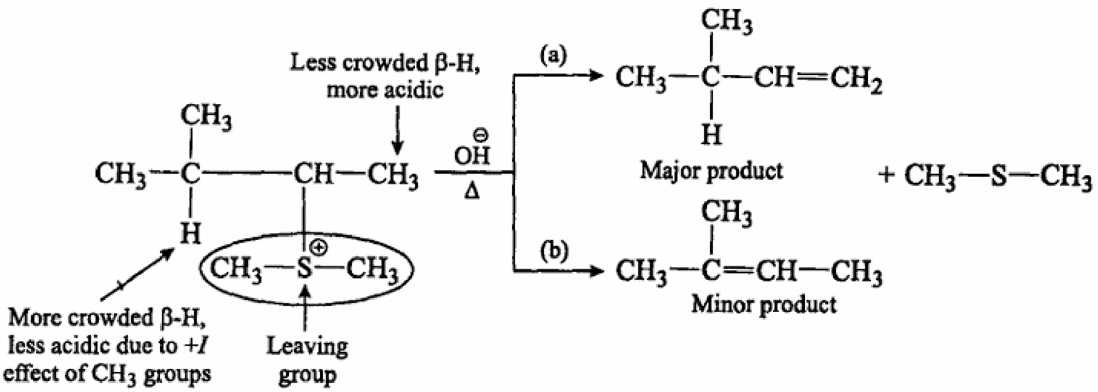


(2) Bulkiness of groups surrounding the leaving group: The hindered β-hydrogen (i.e., ϒ-carbon is quaternary) yields the less substituted alkene in E2 reaction even with a small base like the ethoxide ion.

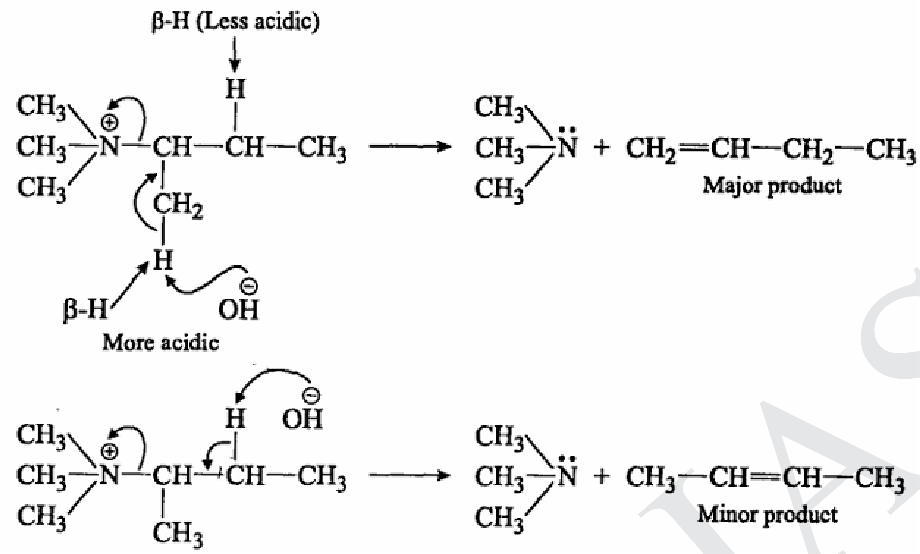


Above two factors decide whether the orientation of elimination will follow Saytzeff rule or Hofmann rule.

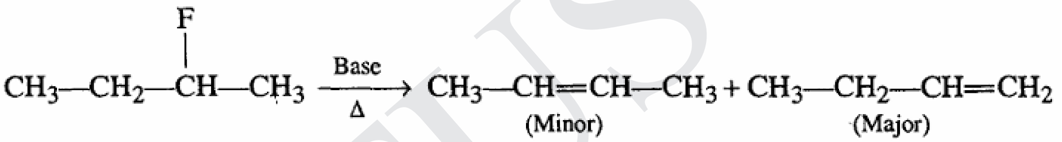
(3) Large and bulky leaving groups: The most common type of large bulky leaving groups which lead to Hofmann products have positively charged nitrogen $(-\overset{\oplus}{N}R_3)$ or positively charged sulphur $(-\overset{\oplus}{S}R_2)$.



Similarly *sec*-butyl trimethyl ammonium cation has two different types of β-hydrogen. The loss of one type leads to 1-butene while the loss of the other type leads to 2-butene.



(4) Poor leaving groups: The presence of poor leaving groups, e.g., F, $\overset{\oplus}{N}R_3$ and $\overset{\oplus}{S}R_2$ leads to the formation of Hofmann product.



$$CH_3-CH_2-\overset{\overset{\displaystyle F}{|}}{C}H-CH_3 \xrightarrow[\Delta]{Base} \underset{(Minor)}{CH_3-CH=CH-CH_3} + \underset{(Major)}{CH_3-CH_2-CH=CH_2}$$

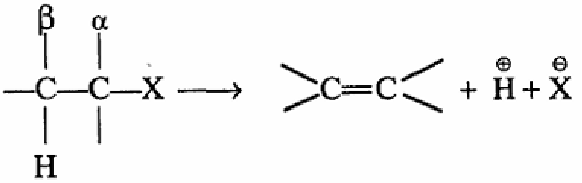
In general, in the case of alkyl halides the size of attacking base and the bulkiness of groups surrounding the leaving group govern the orientation, i.e., the formation of Saytzeff or Hofmann product. On the either hand, in the case of substrates with F, $\overset{\oplus}{N}R_3$ and $\overset{\oplus}{S}R_2$ leaving groups, the acidity of the eliminating hydrogen governs the orientation. The most acidic hydrogen is preferably removed to give the major product.

TYPES OF E1 AND E2 REACTIONS

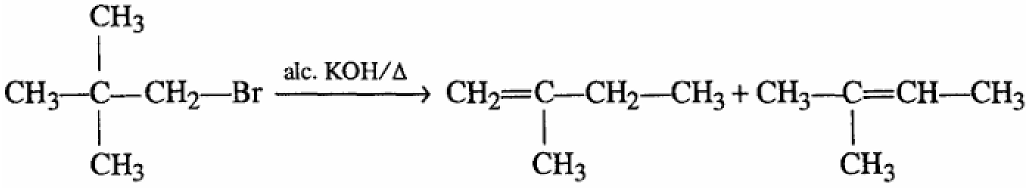
There are various classes of organic compounds that undergo E1 and E2 reactions. The following are most important of these reactions:

Dehydrohalogenation

(1) This reaction is given by aliphatic halides having at least two carbon atoms.

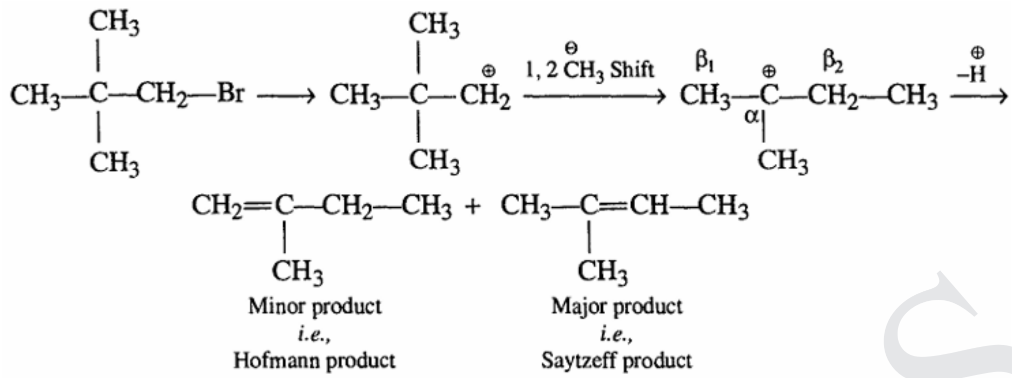


(2) Tertiary alkyl halides always give E1 reaction, secondary and primary alkyl halides whose β-carbon is either 3° or 4° also give E1 reaction.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-Br \xrightarrow{alc.\ KOH/\Delta} CH_2=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_2-CH_3 + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH_3$$

The above reaction takes place as follows:



(3) *p*-Alkyl halides whose β-carbon is 1° or 2° give E2 reaction.

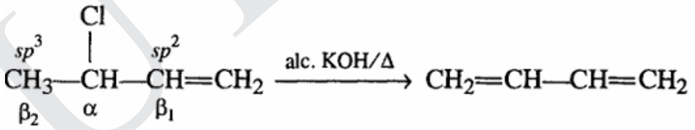
(4) E2 reaction is carried out with a high concentration of a strong base (thus, a high concentration of a strong nucleophile), i.e., alc. KOH/Δ, NaH/Δ, $NaNH_2$/Δ and sodium or potassium alkoxide.

(5) E1 reaction is carried out in the presence of a weak base and above the room temperature. Weak base is generally NaOH/Δ, KOH/Δ and $C_2H_5\overset{\ominus}{O}$/ Δ.

(6) Following factors favour E1 and E2 reactions

		Favours E1	Favours E2
(a)	Alkyl group	3° > 2° > 1°	3° > 2° > 1°
(b)	Base strength	Weak base	Strong base
(c)	Leaving group	Good leaving group	Good leaving group
(d)	Catalyst	$Ag^{\oplus}$, $AlCl_3$	Phase transfer catalyst

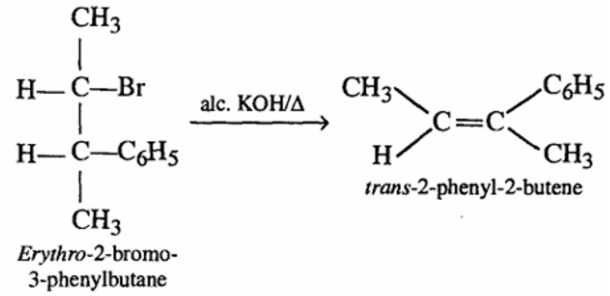
(7) If halide has sp^3 as well as sp^2 hybrid β-carbons then elimination takes place only with sp^3 hybrid β-carbon because in this case diene is conjugated.

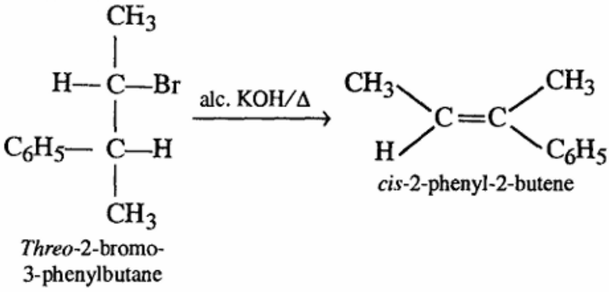


Stereochemistry of E2 Elimination Reactions of Dehydrohalogenation: Optically active alkyl halides, in which α and β carbons are chiral, give stereoselective as well as stereospecific dehydrohalogenation reaction. Geometry of alkene depends on the configuration of the substrate as follows:

(i) *Erythro* form gives *E* or *trans* alkene and (ii) *Threo* form gives *Z* or *cis* alkene.

Examples are :





Dehydration of Alcohols

(1) Secondary and tertiary alcohols always give E1 reaction. Primary alcohols whose β-carbon is 3° or 4° also give E1 reaction.

(2) Primary alcohols whose β-carbon is 1° or 2° give E2 reaction.

(3) Dehydrating reagents for alcohols are :

$$\text{conc. } H_2SO_4/\Delta,\ KHSO_4/\Delta,\ H_3PO_4/\Delta,\ \text{anhy. } Al_2O_3/\Delta$$
$$\text{anhy. } PCl_5/\Delta,\ \text{anhy. } ZnCl_2/\Delta,\ BF_3/\Delta \text{ and } P_2O_5/\Delta.$$

(4) Reactivity of alcohols for elimination reaction is as follows:

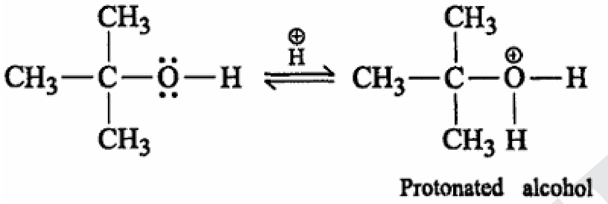
$$\xrightarrow[\text{Reactivity in decreasing order}]{\text{ter. alcohol> sec. alcohol> prim. alcohol}}$$

(5) Rearrangement occurs in E1 as well as in E2 reactions.

Mechanism of Dehydration of Alcohols

Mechanism of E1 reaction :

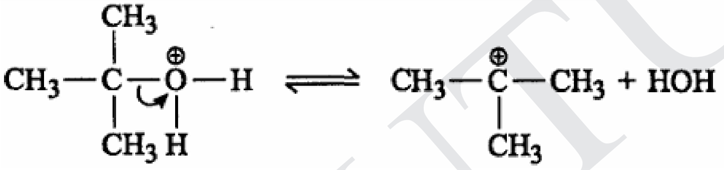
Step-I:



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\ddot{O}-H \overset{\overset{\oplus}{H}}{\rightleftharpoons} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{\underset{H}{O}}-H$$

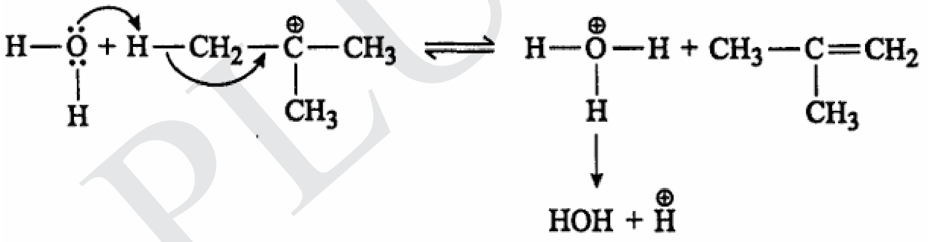
Protonated alcohol

Step-II :



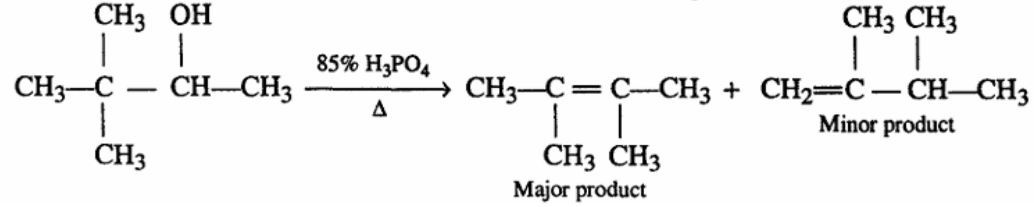
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{\underset{H}{O}}-H \rightleftharpoons CH_3-\overset{\oplus}{\underset{CH_3}{C}}-CH_3 + HOH$$

Step-III:



$$H-\underset{H}{\ddot{O}} + H-CH_2-\overset{\oplus}{\underset{CH_3}{C}}-CH_3 \rightleftharpoons H-\overset{\oplus}{\underset{H}{O}}-H + CH_3-\underset{CH_3}{C}=CH_2$$
$$\downarrow$$
$$HOH + \overset{\oplus}{H}$$

Rearrangement in E1 reactions : Consider the following E1 reaction.

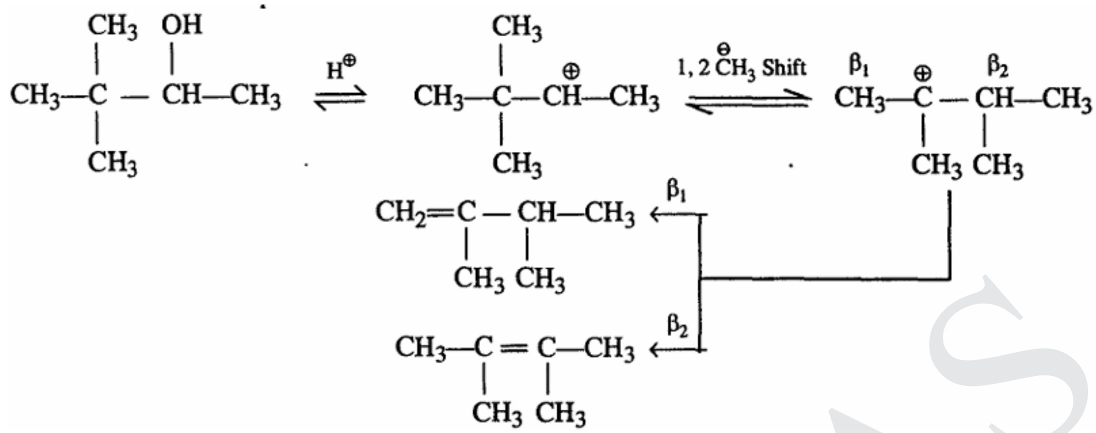


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{OH}{CH}-CH_3 \xrightarrow[\Delta]{85\%\ H_3PO_4} CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_3 + CH_2=\overset{CH_3}{C}-\overset{CH_3}{CH}-CH_3$$

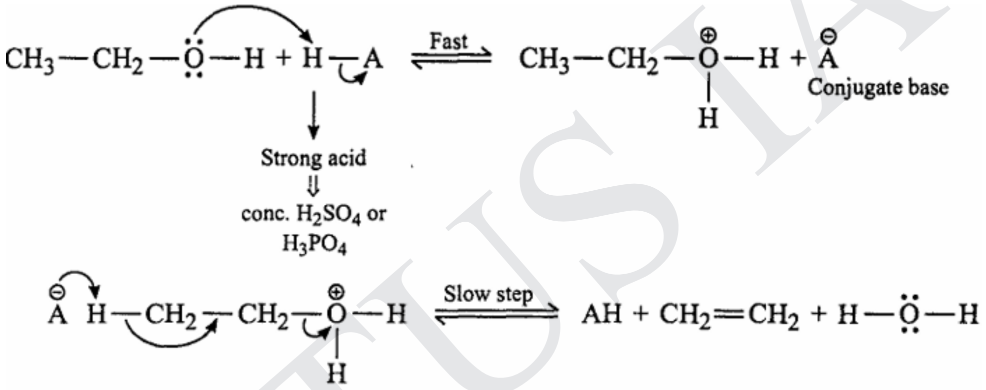
Major product

Minor product

This reaction takes place as follows :



Mechanism of E2 reaction



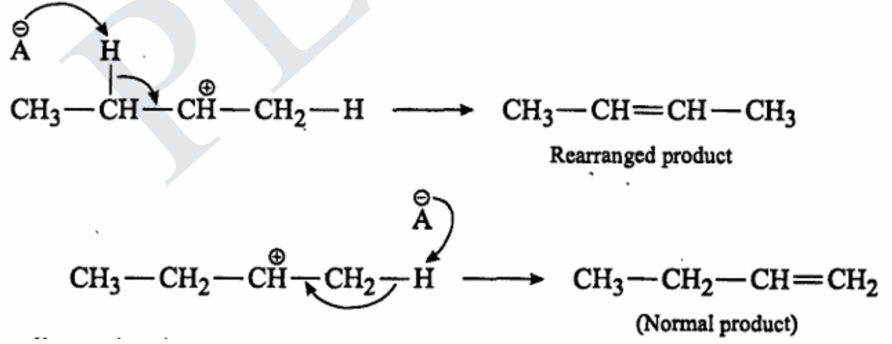
Rearrangement in E2 reactions: The given reaction is E2 reaction :

$$CH_3-CH_2-CH_2-CH_2-OH\xrightarrow[\Delta,\ E_2]{HA}CH_3-CH_2-CH=CH_2+HOH+CH_3-CH=CH-CH_3$$

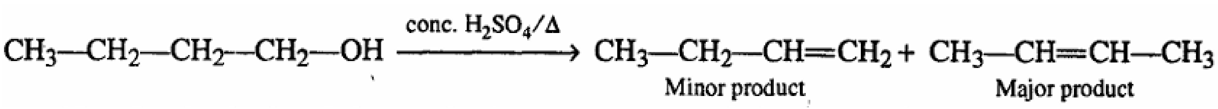
In E2 reactions rearrangement take place after the formation of alkene because alkene reacts with $\overset{\oplus}{H}$ of acid to give carbocation. This carbocation gives rearranged product.

Step I : $CH_3-CH_2-CH=CH_2+\overset{\oplus}{H}\longrightarrow CH_3-CH_2-\overset{\oplus}{C}H-CH_3$

Step II :



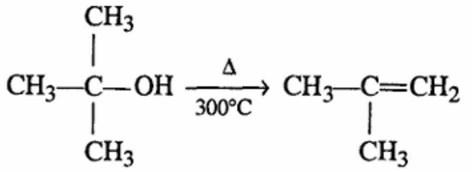
Thus the overall reaction is



$$CH_3-CH_2-CH_2-CH_2-OH\xrightarrow{conc.\ H_2SO_4/\Delta}\underset{\text{Minor product}}{CH_3-CH_2-CH=CH_2}+\underset{\text{Major product}}{CH_3-CH=CH-CH_3}$$

(6) On the basis of the mechanism, one can conclude that product formation takes place according to Saytzeff rule in E1 as well as in E2 reaction.

(7) Tertiary alcohols are so reactive that they undergo dehydration on strong heating even in the absence of dehydrating agent. In this process Cu works as catalyst.



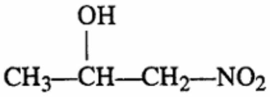
$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH \xrightarrow[300^\circ C]{\Delta} CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$$

(8) (a) –*I* group present in an alcohol increases its reactivity for dehydration, and

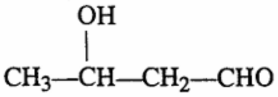
Reactivity ∝ –*I* power of the group present in the alcohol.

(b) Alcohols having –*I* group undergo dehydration in the presence of acids as well as bases.

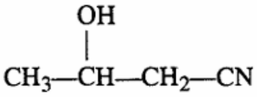
Problem. Which alcohol will be most reactive for dehydration reaction?

(a)


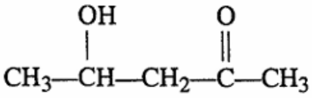
$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-NO_2$

(b)


$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO$

(c)


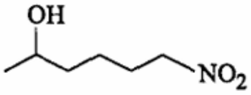
$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CN$

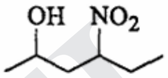
(d)


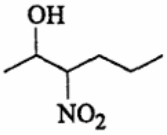
$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

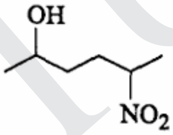
Solution: (a)

Problem. Arrange reactivity of given four alcohols in decreasing order for dehydration reaction.

(A)


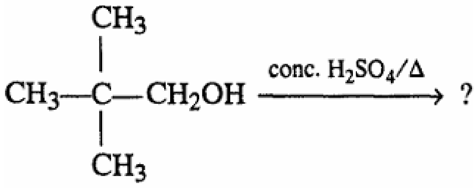
(B)


(C)


(D)


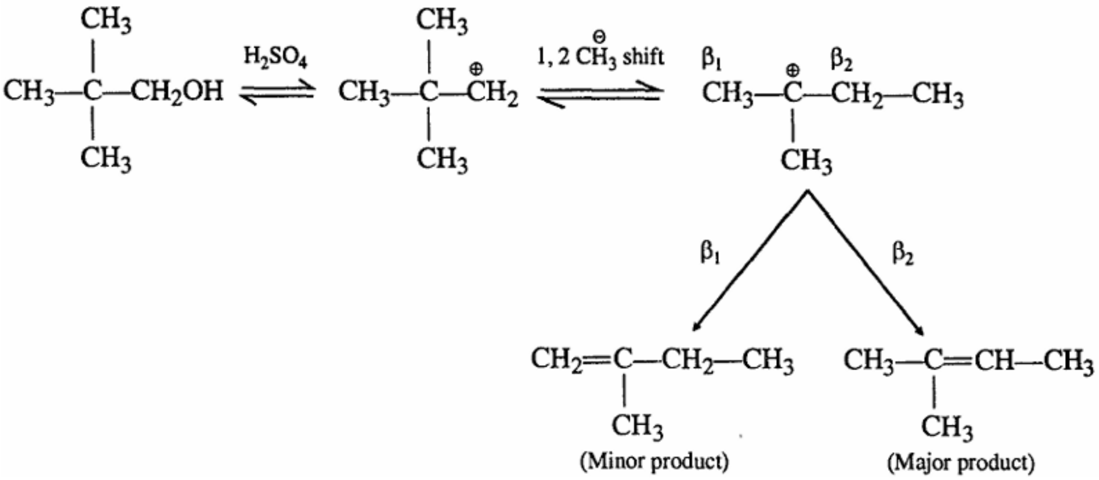
Solution: C > B > D > A.

Problem. Complete the following reaction :



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2OH \xrightarrow{\text{conc. } H_2SO_4/\Delta} ?$$

Solution: Compound will give E1 reaction because alcohol is *prim*-alcohol whose β-carbon is 4°.



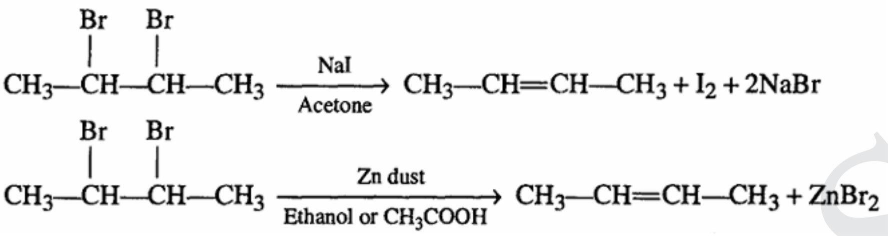
$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2OH \xrightleftharpoons{H_2SO_4} CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{\oplus}{C}H_2 \xrightleftharpoons{1,2\ \overset{\ominus}{C}H_3\text{ shift}} \overset{\beta_1}{C}H_3-\underset{CH_3}{\underset{|}{\overset{\oplus}{C}}}-\overset{\beta_2}{C}H_2-CH_3$$

$$\xrightarrow{\beta_1} CH_2=\underset{CH_3}{\underset{|}{C}}-CH_2-CH_3 \quad \text{(Minor product)}$$

$$\xrightarrow{\beta_2} CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH_3 \quad \text{(Major product)}$$

Dehalogenation (Dechlorination and Debromination)

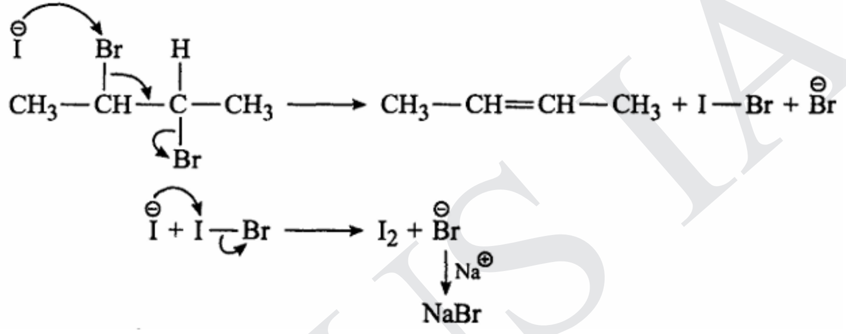
Vicinal (*Vic*) dihalides undergo dehalogenation when they are treated with solution of NaI in acetone or with Zn dust/ ethanol or Ag/ethanol.



$$CH_3-\overset{Br}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-CH_3 \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3-CH{=}CH-CH_3 + I_2 + 2NaBr$$

$$CH_3-\overset{Br}{\overset{|}{CH}}-\overset{Br}{\overset{|}{CH}}-CH_3 \xrightarrow[\text{Ethanol or } CH_3COOH]{\text{Zn dust}} CH_3-CH{=}CH-CH_3 + ZnBr_2$$

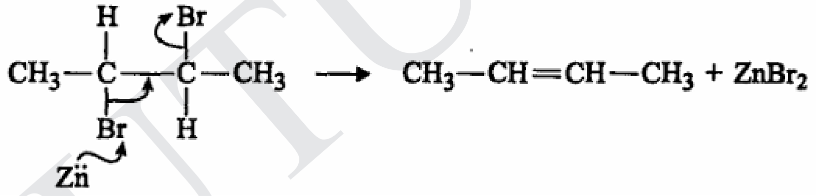
Dehalogenation by NaI takes place by an E2 mechanism



$$\overset{\ominus}{I} \quad CH_3-\overset{Br}{\overset{|}{CH}}-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3 \longrightarrow CH_3-CH{=}CH-CH_3 + I-Br + \overset{\ominus}{Br}$$

$$\overset{\ominus}{I} + I-Br \longrightarrow I_2 + \overset{\ominus}{Br} \xrightarrow{Na^{\oplus}} NaBr$$

Dehalogenation by Zn or Ag also takes place by E2 mechanism as follows :

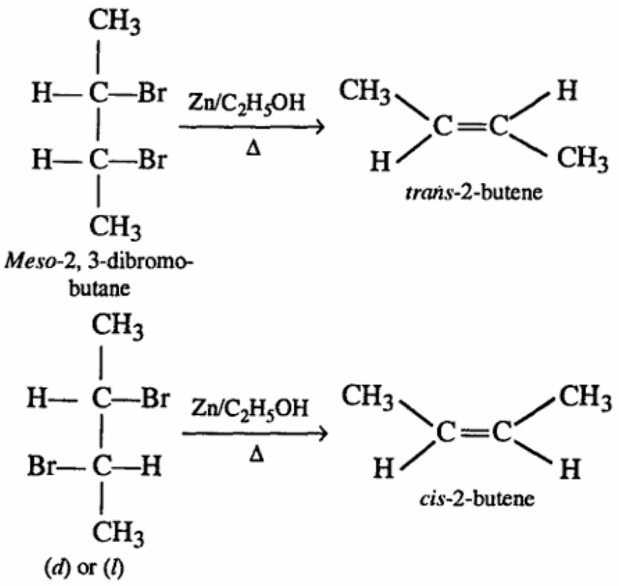


$$CH_3-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3 \longrightarrow CH_3-CH{=}CH-CH_3 + ZnBr_2$$

Stereochemistry of Dehalogenation Reactions: Dehalogenation reactions are *anti*-elimination reactions. These reactions are also stereoselective as well as stereospecific reactions. Geometry of alkenes depends on the configuration of the α, β-dihaloalkanes in which α and β-carbons are chiral.

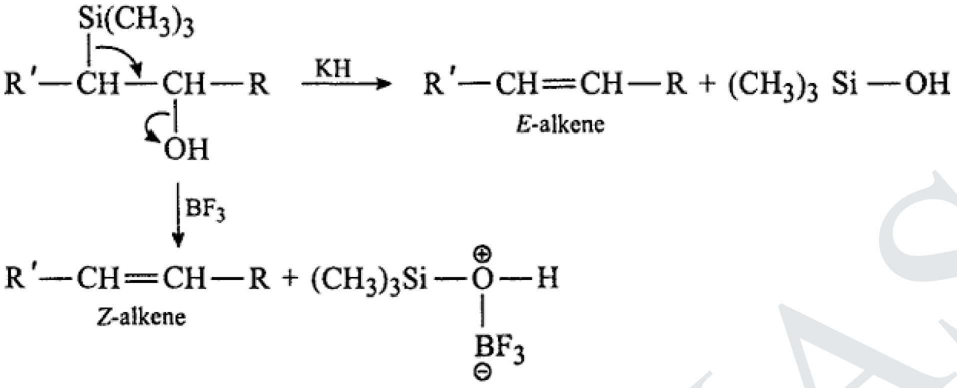
(i) *Meso* form gives *trans* alkene and (ii) *d* and *l* forms gives *cis* alkene.

Examples are :



Peterson Reaction

β-Hydroxy silane gives elimination reaction in the presence of acid as well as base and stereochemistry depends on the nature of the reagent.



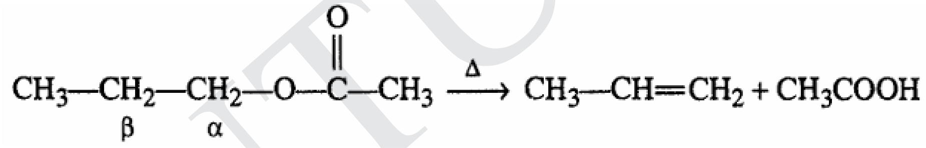
Thermal (Pyrolytic) Eliminations or Cyclic Eliminations

Thermal elimination is given by a small family of organic compounds like acetates, xanthates and amine oxides.

In this elimination, product formation takes place via formation of cyclic TS hence no carbon skeleton rearrangement occurs. Thus elimination is always syn elimination. This elimination takes place in gaseous state. This elimination does not involve acid or base as catalyst.

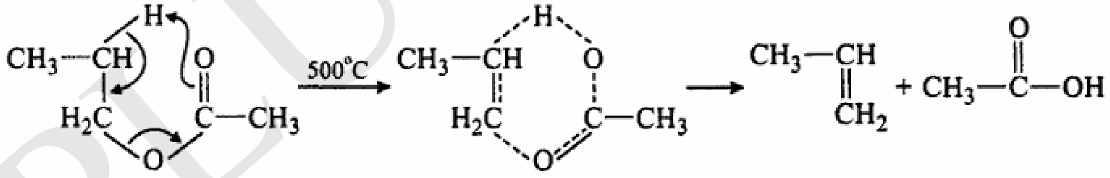
In thermal elimination, product formation always takes place by **Hofmann rule**.

(i) Thermal elimination of acetates :

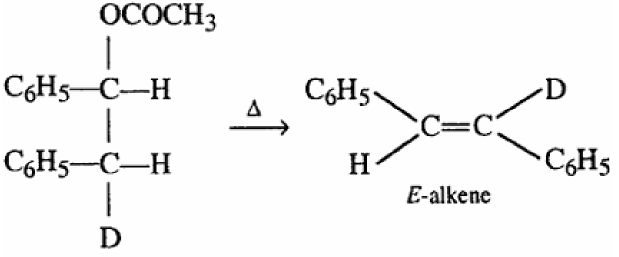


$$CH_3-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\Delta} CH_3-CH=CH_2+CH_3COOH$$

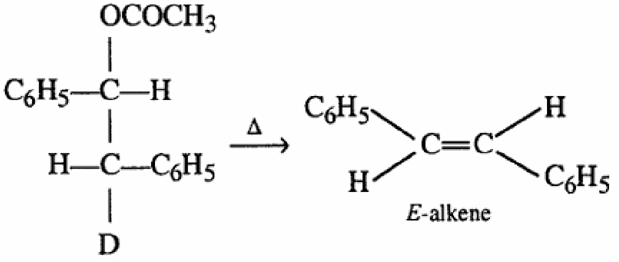
The reaction proceeds through a cyclic TS as shown below :



If substrate is optically active having two asymmetric carbons, then alkene is always *E*-alkene.

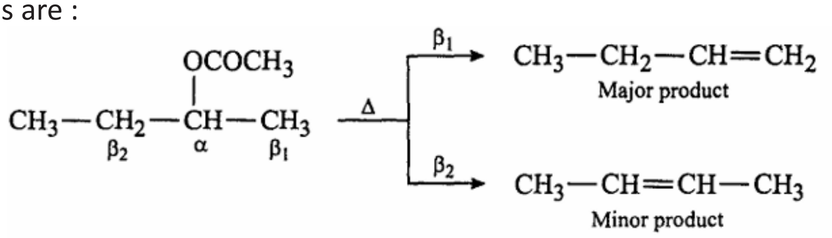


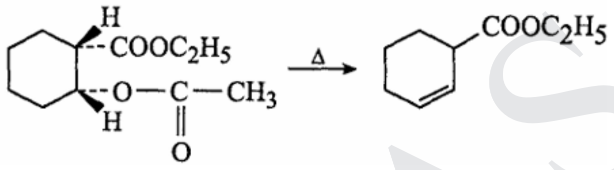
Erythro form



Threo form

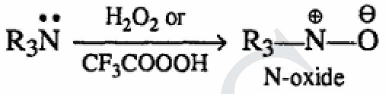
Some other examples are :





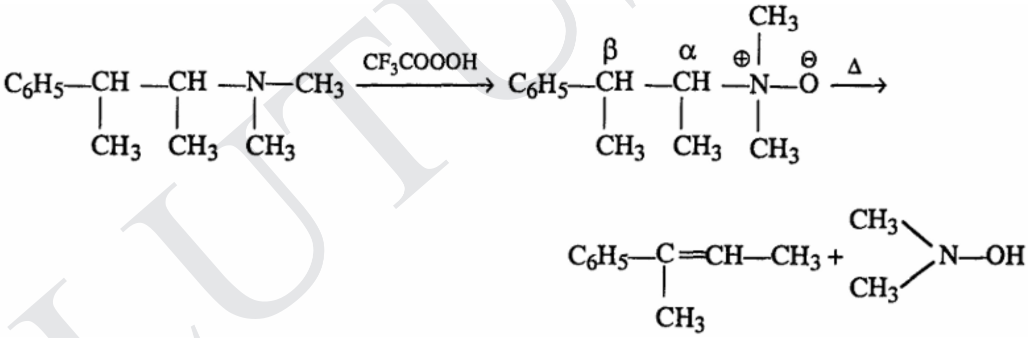
(ii) Thermal Elimination of Amine Oxides :
(COPE REACTION OR COPE ELIMINATION)

Tertiary amines are oxidised by hydrogen peroxide and per acids into amine oxides.



$$R_3\ddot{N} \xrightarrow[CF_3COOH]{H_2O_2 \text{ or}} \underset{\text{N-oxide}}{R_3-\overset{\oplus}{N}-\overset{\ominus}{O}}$$

When an amine oxide of 3°-amines containing at least one β-hydrogen is heated at about 150°C, it decomposes to form an alkene and a derivative of hydroxylamine. This elimination is an example of thermal elimination known as Cope elimination or Cope reaction.



The reaction proceeds through a cyclic TS as shown below :