

CHAPTER 10

Elimination Reactions

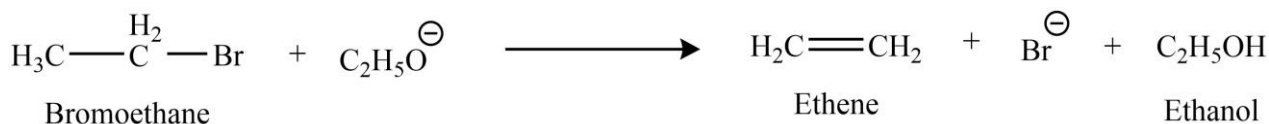
❖ The E₂, E₁ and E₁CB Mechanisms

No organic reaction is capable of giving 100% yield of a single product only, including nucleophilic substitutions. The reason for this type of behavior is the fact that nucleophilic substitution reactions are in direct competition with the elimination reactions; and if the reagent and substrate carefully with a fine-tuning of experimental conditions, elimination yield can even surpass the nucleophilic substitution product. In this section, we will discuss some important elimination mechanisms like E₂, E₁, and E₁CB-type.

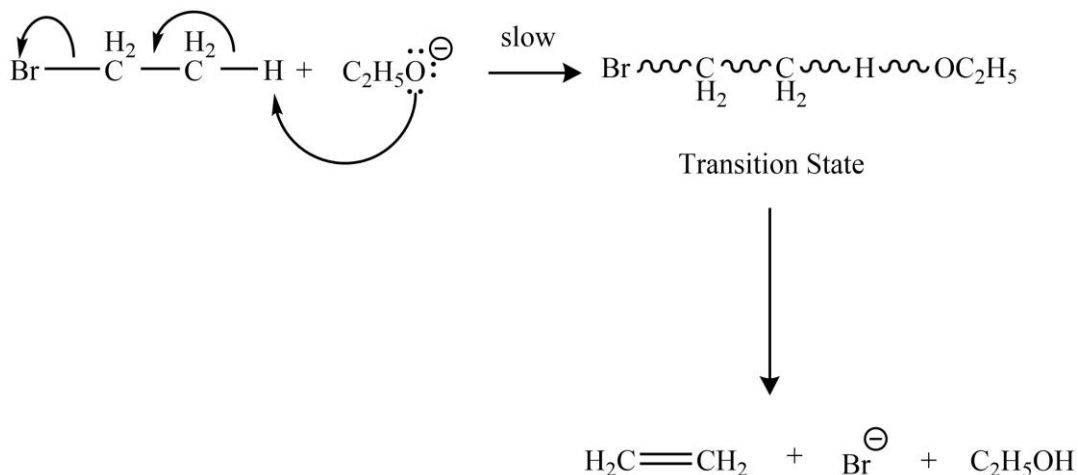
➤ E₂ (Bimolecular Elimination) Mechanism

An E₂ elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in a one-step concerted mechanism. The numbers refer not to the number of steps in the mechanism, but rather to the kinetics of the reaction which means that E₂ is a bimolecular (second-order) reaction.

Illustrative reaction: The reaction of ethoxide ion with ethyl bromide falls into this category because the rate of reaction depends only upon the concentration of the substrate as well as of reagent.



Mechanism involved: The proposed mechanism for the reaction given above involves one step which must be discussed before we give salient features of the same.



It is worthy to recall that even though the reaction is shown as a two-step process, it is actually concerted in nature where the bond breaking and bond-making occur simultaneously.

Salient Features: The main features of the mechanism involved in bimolecular elimination reactions are given below.

i) E₂ reactions follow second-order kinetics with the rate law

$$\text{Rate} = k[\text{RX}][\text{B}]$$

Where k is the rate constant. The symbol $[\text{RX}]$ and $[\text{B}]$ represent the molar concentration of the alkyl halide and base, respectively.

ii) E₂ typically takes place with primary alkyl halides but is possible with some secondary alkyl halides.

iii) Because of the formation of a π -bond in the course of the E₂ mechanism, the two leaving groups (often a halogen and hydrogen) must be antiperiplanar. The reason for this is the fact that the antiperiplanar transition state will have lower energy (staggered-conformation) than a synperiplanar transition state (eclipsed conformation). In other words, the E₂ reactions are favored by staggered conformation whereas the E₁ by eclipsed one.

iv) E₂ typically uses a strong base. It must be strong enough to remove the weakly acidic hydrogen.

v) E₂ competes with the S_N2 reaction mechanism if the base can also act as a nucleophile (true for many common bases).

➤ **E₁ (Unimolecular Elimination) Mechanism**

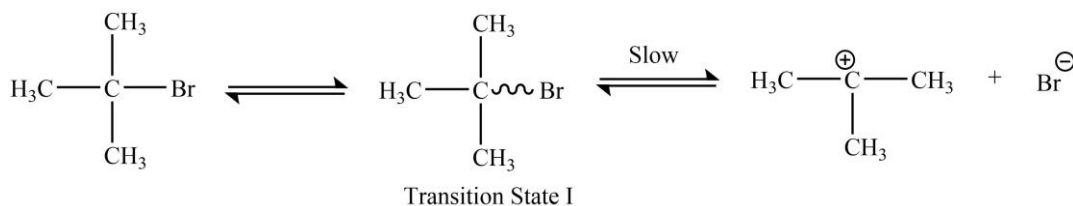
An E₁ elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in a two-step mechanism. The numbers refer not to the number of steps in the mechanism, but rather to the kinetics of the reaction which means that E₁ is a unimolecular (first-order) reaction.

Illustrative reaction: The reaction of NaOH with tert-butyl bromide falls into this category because the rate of reaction depends only upon the concentration of the substrate.

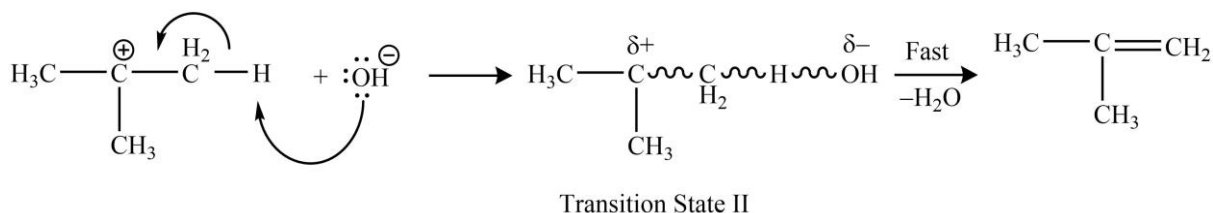


Mechanism involved: The proposed mechanism for the reaction given above involves two steps which must be discussed before we give salient features of the same.

i) *Generation of carbocation:* The alkyl halide accepts an electron from a radical initiator to form radical anion.



ii) Removal of proton:



Salient Features: The main features of the mechanism involved in unimolecular elimination reactions are:

i) E1 reactions follow first-order kinetics with the rate law

$$\text{Rate} = k[\text{RX}]$$

Where k is the rate constant. The symbol $[\text{RX}]$ represents the molar concentration of the substrate.

ii) The E₁ reactions generally occur with tertiary alkyl halides but are possible with some 2° alkyl halides.

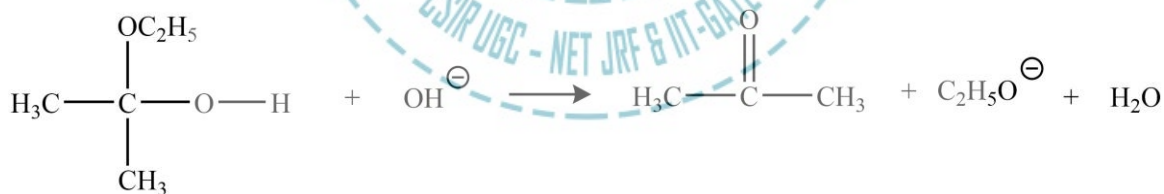
iii) The E₁ reaction typically takes place in the presence of a weak base or the base can be absent at all.

iv) E₁ reactions compete with S_N1 reactions because they share the same intermediate.

➤ **E₁CB (Conjugate Base Elimination) Mechanism**

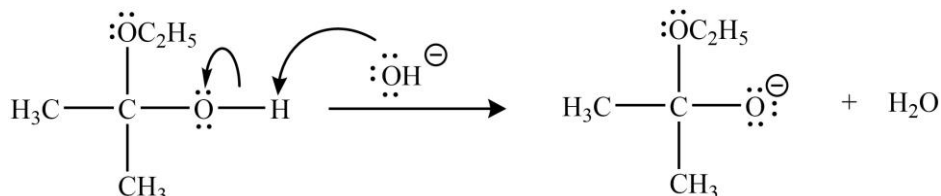
The E₁CB elimination reaction is a type of chemical transformation where the elimination occurs in the presence of a strong base, and the hydrogen to be removed is comparatively acidic, while the leaving group (such as -OH or -OR) is a relatively poor one.

Illustrative reaction: An example of the E₁CB reaction mechanism in the degradation of a hemiacetal under basic conditions.

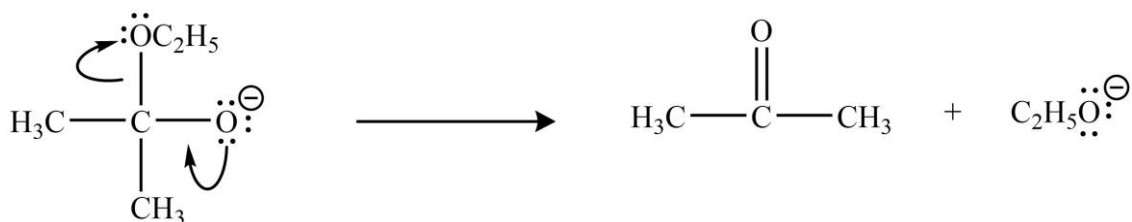


Mechanism involved: The proposed mechanism for the reaction given above involves two steps which must be discussed before we give salient features of the same.

i) *Proton abstraction:* The aryl halide accepts an electron from a radical initiator to form a radical anion.



ii) Detachment of leaving group:



Salient Features: The main features of the mechanism involved in unimolecular elimination conjugate-base reactions are:

i) E_1CB reactions follow first-order kinetics with the rate law

$$\text{Rate} = k[RX]$$

Where k is the rate constant. The symbol $[RX]$ represents the molar concentration of the substrate.

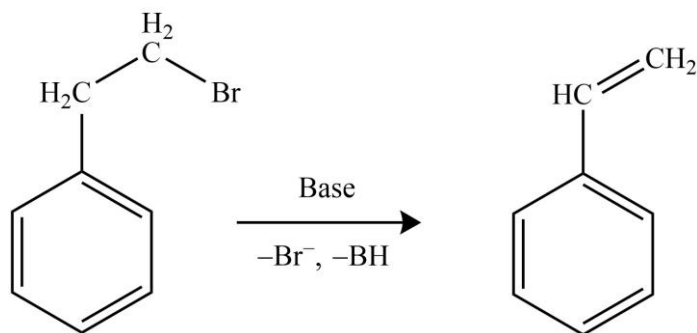
ii) The substrate must have acidic hydrogen on its β -carbon and a relatively poor leaving group on the α -carbon.

❖ Orientation of the Double Bond

In this section, we will discuss the effect of the orientation of the double bond (regio- and stereochemistry) on the reactivity of the elimination reaction.

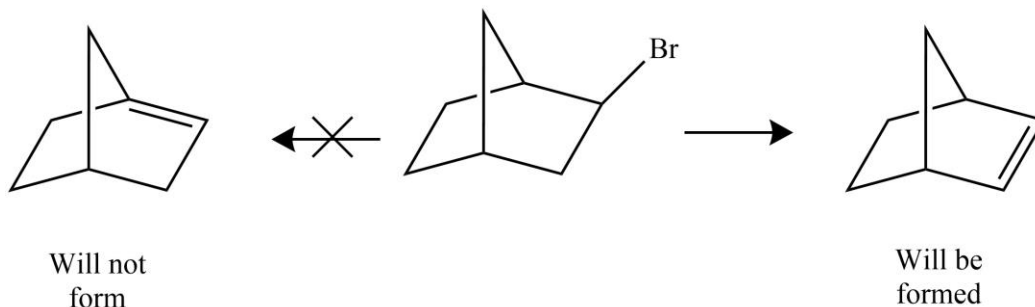
➤ Regiochemistry of the Double Bond

The possibility of regioselectivity in elimination reactions arises if more than one carbon have β -hydrogens. For instance, the sec-butyl halide (two types of β -hydrogen) can result in either 1- or 2-butene whereas $\text{PhCH}_2\text{CH}_2\text{Br}$ is not able to do so (only $\text{PhCH}=\text{CH}_2$).



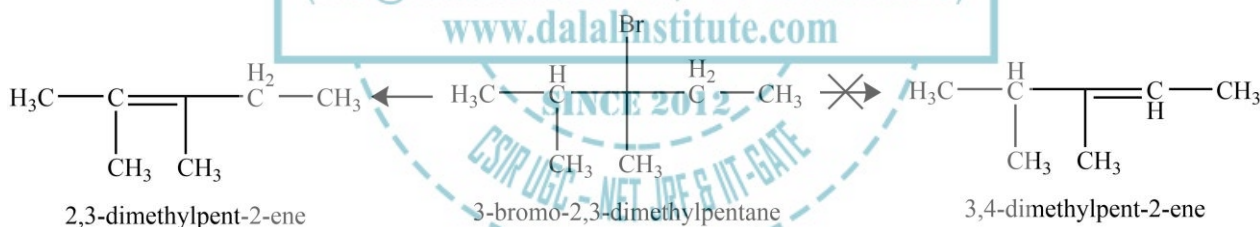
Therefore, the rules that dictate the major-minor products must be discussed for any stereochemical rationalization first.

Rule 1: The double bond will not shift to a bridgehead carbon irrespective of the mechanism-type until the ring size becomes quite big. This rule is also known as Bredt's rule because it was given Julius Bredt in 1902, and codification was completed in 1924.



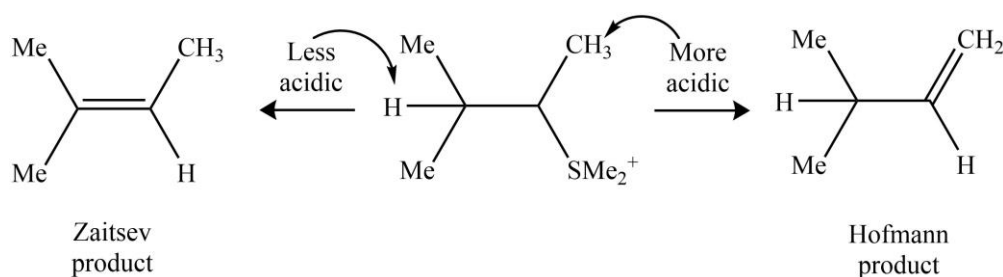
Rule 2: If there is a possibility of a newly formed double bond to get into conjugation with some previously present multiple bond or aromatic ring, it will always do so even if it leads to unfavorable stereochemistry.

Rule 3: The directional shift of the double bond in E_1 reactions is always decided by the relative stabilities of resulting products; which is because the initial departure of the leaving group leaves both possibilities open. In other words, the double bond moves primarily toward the more substituted carbon (Zaitsev's rule); which can be explained on the basis of the heat of hydration or hyper-conjugative structure. For instance, 2,3-dimethyl-2-pentene is formed from 3-bromo-2,3-dimethylpentane rather than either 3,4-dimethyl-2-pentene or 2-ethyl-3-methyl-1-butene.



Since the departure of the leaving group occurs first, the Zaitsev's rule dictates the orientation of double bond in E_1 reaction irrespective of the leaving group's nature (neutral or positive); however, in case it cannot be said for E_2 reactions, where the orientation of the double bond and the departure of the leaving group takes place simultaneously. Nevertheless, the non-Zaitsev product can also be the major product even in the case of E_1 eliminations because of reduced steric hindrance, or the formation of ion-pair.

Rule 4: It is quite a well-known fact that a trans β proton is required for the anti E_2 mechanism to be active; which is accessible only in one direction creating only one double-bond-shifting possibility. However, it is limited to the cyclic systems because the molecule may free rotation about carbon-carbon single bond (if the steric hindrance isn't very high). On the other hand, if two or more carbons have trans- β hydrogens, two types of products can be obtained; sometimes Zaitsev's product (double bond shifting toward the more substituted carbon), sometimes Hofmann's product (double bond shifting toward the least substituted carbon).



It has also been observed that Zaitsev's rule is followed in all substrates if the compound has uncharged nucleofuges (leaving as negative ions like Cl^-); whereas Hofmann's rule is followed if the compound has charged nucleofuges (leaving as neutral ions like NR_3^+) provided that the substrate is acyclic, otherwise Zaitsev's product (i.e., if the leaving group is connected to a benzene ring). Now because Zaitsev's rule gives rise to the thermodynamically stable product, its outranking by Hofmann's rule in some compounds should also be explained. This change of double bond orientation in acyclic systems can be rationalized in the terms of two different factors.



The first one is that the β -hydrogen becomes less acidic due to the presence of the alkyl group, which in turn favors Hoffman's rule. The second one is the fact that positively charged groups are generally larger in size than the neutral group, and therefore a CH_3 group (less substituted) is more prone to attack than a primary or secondary carbon; in other words, steric effects dictate the final product.

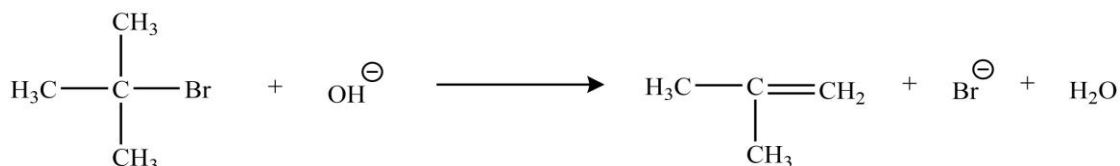
Rule 5: It has been observed that the Hofmann orientation is significantly favored over the Zaitsev product in syn- E_2 eliminations.

Rule 6: The regioselectivity is of less importance as far as the E_1CB -type reactions are concerned because this pathway is typically found in the systems with an electron-withdrawing group at β -site, attracting double bond movement towards itself.

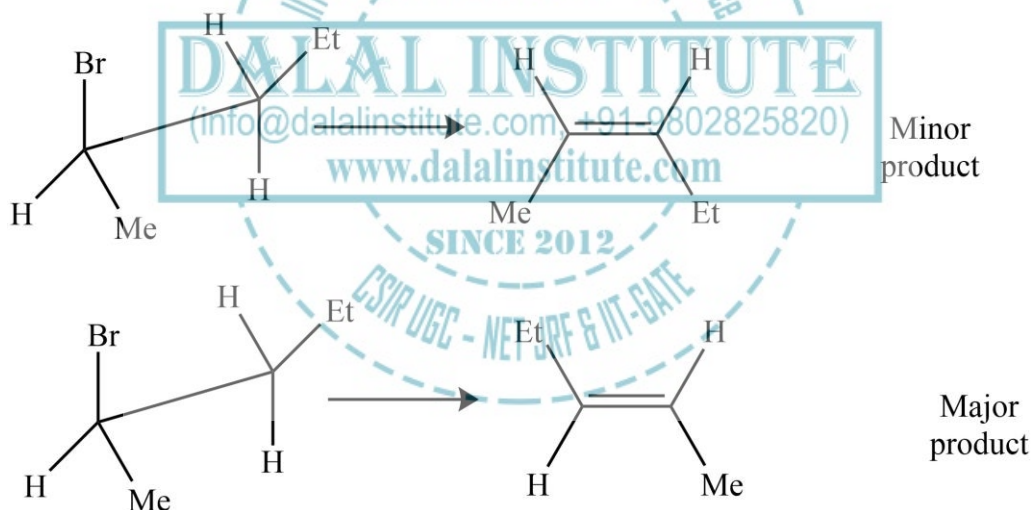
Rule 7: It is a well-known fact that E_2C reactions are susceptible to Zaitsev orientation, and this preference is of great importance as far as commercial production is concerned. However, the non-Zaitsev product is also obtained in some cases where conjugation with the aromatic ring is obtainable.

➤ **Stereochemistry of the Double Bond**

If CHAB–CGGX or CH₃–CABX type compounds undergo elimination, the resulting alkene cannot show cis-, trans-isomers. However, the CH₂E–CABX CHEG–CABX type compounds do have the ability to give rise to cis- and trans- isomers after undergoing elimination. For instance, consider the following transformation.



It has been observed that the threo- and erythro-compound gives rise to trans- and cis- alkene; respectively. Furthermore, two conformations can be obtained for the transition state in the case of compound II, where two isomers can be synthesized. Nevertheless, the eclipsing effects will dictate the major-minor one; like the Zaitsev elimination of 2-bromopentane leads to the trans-isomer as major. This because confirmation A (Et is in between H and Br) is more stable than conformation B (Et is in between Me and Br), and the effect becomes more dominating as the groups get bigger.



Moreover, the ratio of cis/trans isomers in the anti-E₂ reaction is also dictated by the solvent, nature of the leaving group, the substrate, and the attacking base. The complete picture of these effects is still not clear as far as the stereochemistry of the double bond is concerned. For instance, E₁-system with a bigger D-E pair opposite to the smaller AB pair is more stable if the carbocation free to rotate; and therefore, we should get the corresponding alkene. On the other hand, E₂-like products will be formed if the carbocation formed is not totally free; and the same is true for E₁CB reactions.

❖ Reactivity – Effects of Substrate Structures, Attacking Base, the Leaving Group and The Medium

In this section, we will discuss the effects of substrate structures, attacking base, the leaving group, and the nature of the medium on the reactivity of elimination reactions.

➤ *Effect of Substrate Structure on the Reactivity of Elimination Reactions*

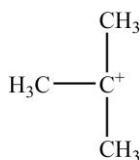
The effects of substrate structures on the reactivity of elimination reactions can be divided into the following categories.

1. Effect on the reaction Rate: Different Groups bonded to the α -carbon (C with nucleofuge i.e., C–X) or β -carbon (C that loses proton i.e., C–H) can primarily exercise four types of influences as discussed below.

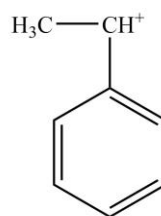
- The emerging double bond can be stabilized or destabilized by these groups.
- The groups attached at β -carbon can affect the acidity of β -proton by stabilizing or destabilizing the emerging negative charge.
- The groups attached at α -carbon can affect the stability of the emerging positive charge.
- The groups attached at α - and β -carbon can exert eclipsing effects (steric effects).

The first and fourth types of effects can affect all three kinds of elimination mechanisms, with steric effects as most dominant in E_2 reactions. Also, the second and third kinds of effects cannot be applied to E_1 and E_1CB , respectively. If the C=C bond formation is the rate-determining, the presence of C=C or aromatic ring enhances the reaction rate in all mechanisms. Finally, the presence of electron-withdrawing groups at β -position raises the acidity of leaving hydrogen but has little to no effect at α -sites provided that no multipole bond conjugation available; making CN, Br, Cl, NO_2 , Ts, SR, and CN suitable E_2 -kind reactions.

2. Effect on E_1 vs E_2 vs E_1CB : Since the presence of aryl or alkyl group at α -carbon can stabilize the carbocation via resonance or inductive effect, A shift towards the E_1 pathway should be observed in the same. Also, the same shift can also be carried out by Alkyl groups at β -position by decreasing the acidity of the hydrogen atom. Nevertheless, the presence of aryl groups at β -carbon will push the towards E_1CB pathway by carbanion's stabilization. Conclusively, it has been observed that the presence of any electron-withdrawing group at β -site always pushes the reaction E_1CB pathway. Finally, it should also be remembered that E_2C reactions are also favored by the presence of alkyl groups at α -sites.



Stablized via hyperconjugation
or inductive effect
(support E_1)



Stablized via Resonance
(support E_1)

3. Effect on elimination vs substitution: In bimolecular elimination reaction, the rate of reaction increases as the branching increases. This behavior can easily be rationalized in terms of statistical and steric factors. In other words, the increased α -branching leads to more base-attackable hydrogens, and increased steric hindrance opposes the attack at the carbon simultaneously. Moreover, the increased α -branching also supports unimolecular elimination over unimolecular nucleophilic substitution. The E_2 pathway is also favored over SN_2 when branching at the β -carbon is raised because of the suppression of the latter. Similarly, The E_1 pathway is also favored over SN_1 when the branching at the β -carbon is raised because of the steric factors. If the leaving group has a charge on it, the branching at the β -carbon will slow down the rate of E_2 reactions (Hofmann's rule). Also, the presence of electron-withdrawing groups at the β -site supports E_2 -pathway with the simultaneous shift towards the E_1CB route but (upsurging the elimination/substitution ratio).

➤ **Effect of Attacking Base on the Reactivity of Elimination Reactions**

The effects of attacking base on the reactivity of elimination reactions can be divided into the following two categories.

1. Effect on E_1 vs E_2 vs E_1CB : The outside base isn't required in E_1 reaction under typical conditions because itself can act as the base. Therefore, the reaction pathway shifts from E_1 to E_2 when the outside bases is mixed. Furthermore, adding more outside stronger base will shift the pathway even towards E_1CB . Nevertheless, weak bases are also capable of yielding elimination reactions with some particular substrate-types. Bases (besides organic) yielding normal E_2 reactions are given below.



It should also be noted that not all the bases are useful as far the practical synthetic route is concerned; for instance, NH_2^- , OR^- and OH^- are valuable for normal E_2 reaction; whereas the bases like OAc^- , Cl^- and RS^- are useful in preparing quaternary salts.

2. Effect on elimination vs substitution: Besides supporting E_2 over E_1 , strong bases also assist elimination over substitution reactions. The concentrated solution of strong bases in a nonionizing solvent not only favors E_2 but also helps them to outrank the SN_2 pathway. On the other hand, dilute basic solutions in ionizing solvents not only favor E_1 but also help them to outrank the SN_1 pathway. It was also deduced from the nucleophilic substitution studies that stronger bases aren't necessarily stronger nucleophile; and therefore, a weaker nucleophile but stronger base will prefer elimination over substitution. Nevertheless, weak bases can also lead to elimination if the solvent used is polar and aprotic.

➤ **Effect of Leaving Group on the Reactivity of Elimination Reactions**

The effects of leaving-group on the reactivity of elimination reactions can be divided into the following categories.

1. Effect on the general reactivity: Despite the different nature of the pathways, the leaving groups in both cases behave pretty much similar. Leaving groups in E_2 are NO_2 , F, Cl, Br, I, NR_3^+ , OHR^+ , SO_2R , PR_3^+ , SR_2^+ , OSO_2R , OOR , $OCOR$, OOH , and CN; leaving groups in E_1 are NR_3^+ , OSO_2R , SR_2^+ , OH_2^+ , OHR^+ , Br, I, $OCOR$, Cl, and N_2^+ .

2. Effect on E_1 vs E_2 vs E_1CB : Since the better leaving groups make the ionization easier, they will move the pathway towards E_1 reactions, which can be confirmed via ρ -values. Furthermore, positively charged or poor leaving groups will shift the pathway towards the E_1CB reactions, which can be attributed to the increased acidity β -protons that arises from the strong field effects of electron-withdrawing nature. Finally, it has also been observed that good leaving groups support E_2C reaction.

3. Effect on elimination vs substitution: Since the reaction pathway (elimination or substitution) is decided only after the departure of the leaving group in the reactions following first-order kinetics, the leaving group will not be able to prefer elimination over substitution, and vice-versa. Nevertheless, if ion-pair formation had taken place, the leaving group will affect the final product. Therefore, the elimination to substitution ratio (e/s) is largely independent of a halide as leaving group with only a minor raise in elimination to $Cl < Br < I$. On the other hand, the substitution pathway is strongly favored if the leaving group is like OTs. For instance, n - $C_{18}H_{37}Br$ treated with t -BuOK results in 85% elimination, whereas n - $C_{18}H_{37}OTs$ gives rise to 99% substitution under similar experimental conditions. Conversely, leaving groups with a positive charge will increase the elimination yield.

➤ **Effect of Medium on the Reactivity of Elimination Reactions**

The effects of the medium on the reactivity of elimination reactions can be divided into the following categories.

1. Effect on E_1 vs E_2 vs E_1CB : It is quite a well-known fact that reaction-rate increases with solvents polarity increases if the intermediates involved are ionic in nature. Furthermore, it has also been observed that the rate of E_1 and E_1CB pathways are also supported by increasing solvent's polarity and ionic strength, even if the leaving group is neutral in nature. Lastly, aprotic polar solvents encourage E_2C reactions with some particular substrates.

2. Effect on elimination vs substitution: The SN_2 pathway is favored at the cost of E_2 one if the solvent polarity is increased. For instance, KOH results in more elimination in alcohol but favors substitution in water as a solvent; which can partially be explained via the charge-dispersal phenomenon. On the other hand, the SN_1 pathway is encouraged over E_1 in most of the solvent mediums. Nevertheless, in the polar solvents with low nucleophilic character, the E_1 pathway become more prominent than the usual (like dipolar aprotic mediums). Finally, it has also been observed in the gas-phase studies (i.e., no medium) that when MeO^- reacts with 1-bromopropane exclusively via the elimination-route even if the substrate used in the process are only primarily substituted.

3. Effect of temperature: It has been proven again and again that raising the reaction temperature almost always supports the elimination over substitution despite the order of the reaction (first or second-order). This behavior can simply be attributed to the higher activation energies of eliminations than those of substitutions, arising from larger bonding-alteration.

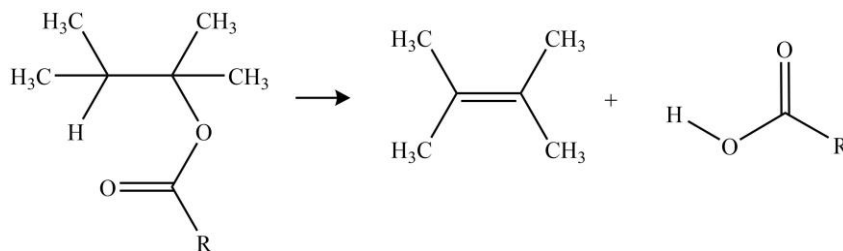
❖ Mechanism and Orientation in Pyrolytic Elimination

The pyrolytic elimination or E_i (elimination internal/intramolecular) mechanism is a special kind of elimination reaction where two vicinal groups on an alkane framework leave simultaneously through a cyclic transition state to form an alkene with a syn-elimination, and that is why they also called as pericyclic syn-or thermal syn elimination.

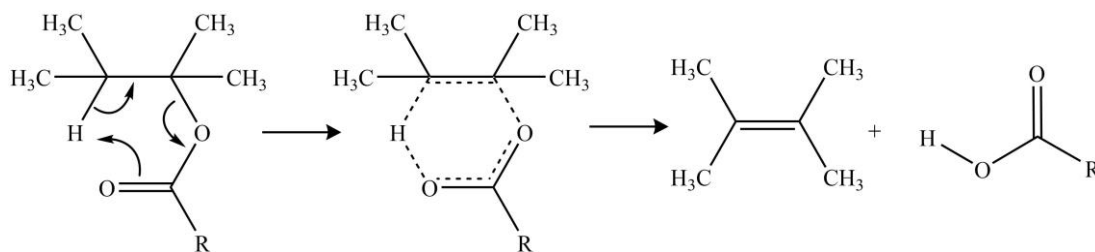
➤ Mechanism in Pyrolytic Elimination

The pyrolytic elimination is a unique type of elimination because it is activated thermally and does not need additional reagents unlike regular eliminations where an acid, a base, or charged intermediates is needed; and as the name suggests, it is often found in pyrolysis.

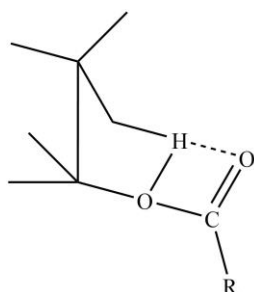
Illustrative reaction: one of the most common examples of pyrolytic elimination reaction is shown below for more clear understanding.



Mechanism involved: The proposed mechanism for the reaction given above involves one step which must be discussed before we give salient features of the same.



The elimination must be syn and the atoms coplanar for five and four-membered transition states, but coplanarity is not needed in the case where six-membered transition states are involved.



Coplanarity is not needed in 6-membered transition state

Salient Features: The main features of the mechanism involved in elimination internal (or intramolecular elimination) reactions are given below.

i) E_i reactions follow first-order kinetics with the rate law

$$\text{Rate} = k[RX]$$

Where k is the rate constant. The symbol $[RX]$ represents the molar concentration of the substrate.

ii) Elimination internal is thermally activated and does not need additional reagents unlike typical eliminations pathways where an acid or base is required, or sometimes involve charged intermediates.

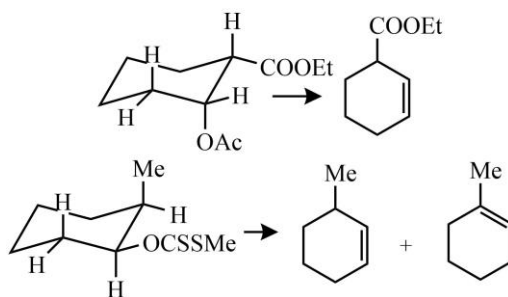
iii) The elimination mode must be syn and the atoms must be coplanar for five and four-membered transition states; nevertheless, the coplanarity is not necessary for six-membered transition states.

iv) The rate of the reactions is not affected by the use of free-radical inhibitors.

➤ **Orientation in Pyrolytic Elimination**

Just like in normal elimination reactions, Bredt's rule is also applicable in the case of pyrolytic elimination. Nevertheless, conjugated systems are preferred non-conjugated systems (if allowed sterically) if a double bond is available. Furthermore, some more conclusive remarks regarding orientation in pyrolytic elimination are also of great importance.

1. The pyrolytic elimination requires a β -hydrogen in cis position; and therefore, the double bond will have only one direction to move in cyclic systems with only cis-hydrogen. Nevertheless, the condition of the leaving groups to be cis isn't required in six-membered transition states (due to non-coplanarity). Consequently, the hydrogen must be at the equatorial site if the leaving group is present at the axial position because the transition state cannot be comprehended with both at the axial positions. On the other hand, the leaving group will become able to create a transition state with β -hydrogen if it occupies an equatorial site. Conclusively, we can say if the leaving group is at the axial site, the double bond formation will not take place in the carboxyl group's direction due to the lack of equatorial hydrogen. Therefore, compound A will result in 100% C; whereas 50% of each type of alkene will be obtained if an equatorial leaving group is present.



2. It has been observed that the more stable alkene product dominates (Zaitsev's rule) in many cases, particularly with cyclic reactants. For instance, more of Hofmann product was expected menthyl acetate due to the presence of cis- β hydrogen on both sides, but the experimental yield is opposite i.e., 65% Zaitsev and 35% Hofmann product.

3. In many cases, it has also been observed that steric effects also dictate the elimination's direction since minimum steric interactions are favorable in both transition state and ground state of the substrate.
4. If all the three effects mentioned above are absent, the orientation dictation will be statistical in nature, and therefore, will be controlled by the number of β -hydrogens (Hofmann's rule). For instance, 60% 1-butene and 40% 2-butene were obtained from sec-butyl acetate where the hydrogens present are also in the 3:2 ratio.



❖ Problems

- Q 1. Define elimination reactions.
- Q 2. Discuss E1 and E2 mechanisms. How they are different from SN₁ and SN₂ pathways?
- Q 3. State and explain E₁CB pathway of elimination reactions.
- Q 4. What is pyrolytic elimination? How would you explain the orientation effect in the same?
- Q 5. Discuss the reactivity of elimination reactions with special reference to substrate structure and attacking base.
- Q 6. How does a leaving group affect the rate of elimination reactions?
- Q 7. Write a short note on the reactivity of elimination reactions with special reference to reaction medium.

❖ Bibliography

1. M. B. Smith, *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, John Wiley & Sons, Inc., New Jersey, USA, 2013.
2. H. Zimmerman, *Quantum Mechanics for Organic Chemists*, Academic Press, New York, USA, 1975.
3. M.S. Singh, *Reactive Intermediates in Organic Chemistry*, John Wiley & Sons, Inc., New Jersey, USA, 2014.
4. D. Klein, *Organic Chemistry*, John Wiley & Sons, Inc., New Jersey, USA, 2015.
5. J. Clayden, N. Greeves, S. Warren, *Organic Chemistry*, Oxford University Press, Oxford, UK, 2012.
6. R. L. Madan, *Organic Chemistry*, Tata McGraw Hill, New Delhi India, 2013.
7. C. A. Coulson, B. O'Leary, R. B. Mallion, *Hückel Theory for Organic Chemists*, Academic Press, Massachusetts, USA, 1978.

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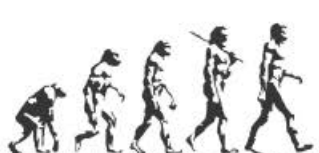
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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