

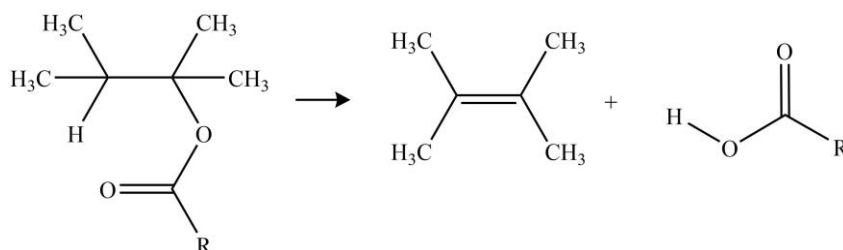
❖ Mechanism and Orientation in Pyrolytic Elimination

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.

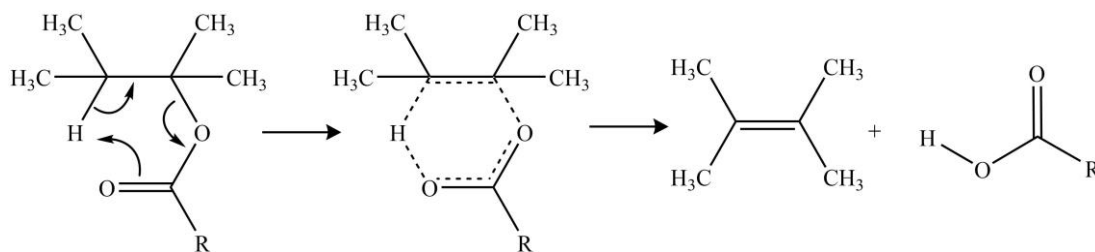
➤ Mechanism in Pyrolytic Elimination

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.

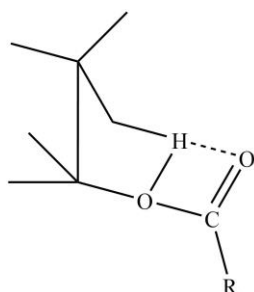
Illustrative reaction: one of the most common examples of pyrolytic elimination reaction is shown below for more clear understanding.



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.

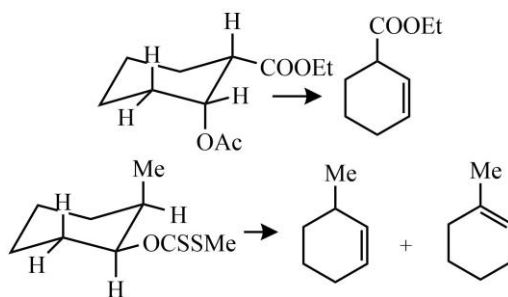
iii) The elimination mode must be syn and the atoms must be coplanar for five and four-membered transition states; nevertheless, the coplanarity is not necessary for six-membered transition states.

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.



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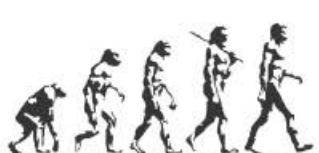
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

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