

STEREOCHEMISTRY

SEM-1, CC-1 / GE-1

PART-1, PPT-11

Part-1: Elimination Reactions

CONTENTS

- *Introduction*
- *Classification of Elimination reactions*
- *Mechanisms of Elimination Reactions*
 1. *Elimination Unimolecular (E1)*
 2. *Elimination Bimolecular (E2)*
- *Orientation in E2: Saytzeff and Hofmann Eliminations*

Dr. Kalyan Kumar Mandal

Associate Professor

St. Paul's C. M. College

Kolkata

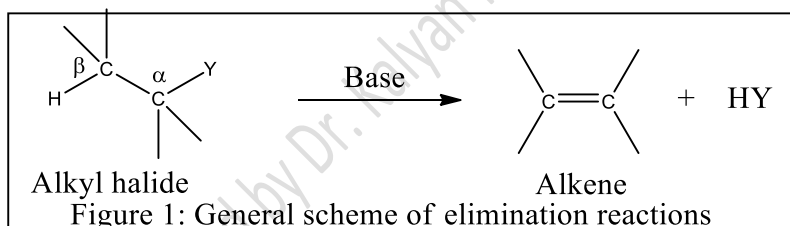
Elimination Reactions

(PART-1, PPT-11)

- *Introduction*
 - *Classification of Elimination reactions*
 - *Mechanisms of Elimination Reactions*
1. *Elimination Unimolecular (E1)*
 2. *Elimination Bimolecular (E2)*
- *Orientation in E2: Saytzeff and Hofmann Eliminations*

Elimination Reactions: Introduction

An **elimination reaction** is a type of organic reaction in which two atoms or groups are removed from a molecule, without their being replaced by other atoms or groups, resulting in the formation of a multiple bond. In the great majority of such reactions the atoms or groups are lost from adjacent carbon atoms, one of them very often being a proton and the other a good leaving group. A general scheme of elimination reactions is presented in **Figure 1**.

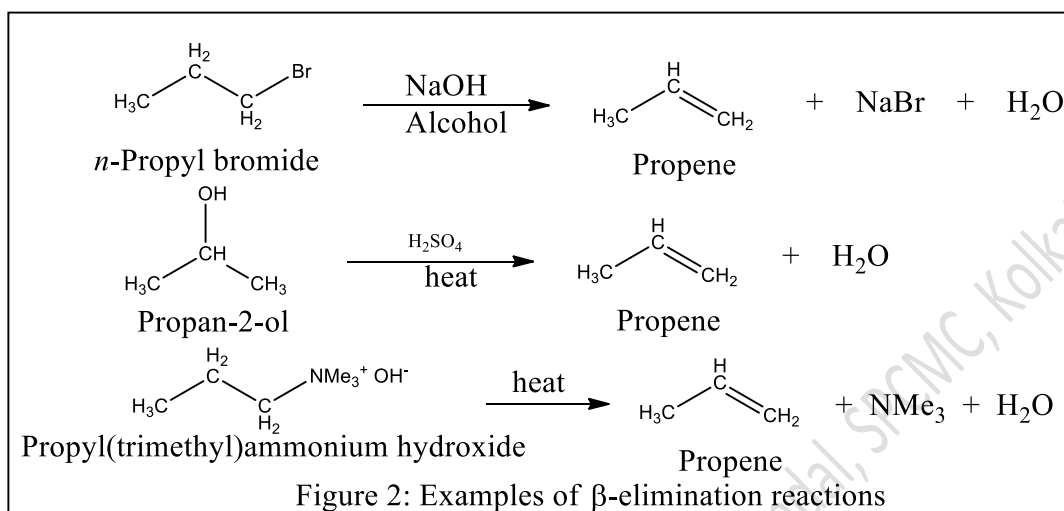


Elimination Reactions: Classification

The type of elimination reactions in which the carbon atom from which the leaving group is removed is generally designated as the α carbon and the adjacent carbon from which the hydrogen atom is removed is called the β carbon. So, these type of eliminations are known as the 1,2- (or α,β -) elimination or simple the β -elimination. Among the most familiar examples are base catalyzed elimination of hydrogen halides from an alkyl halide to the corresponding alkene. Propyl bromide gives propene in presence of alcoholic alkali (Example 1; **Figure 2**). Alcohols are dehydrated in presence of acid to give the alkenes. Propan-2-ol gives propene when heated with dilute mineral acid (e.g., dilute H_2SO_4) (Example 2).

Elimination Reactions

Quaternary alkylammonium hydroxides undergoes elimination on heating to give the corresponding alkene (**Example 3**). Examples are shown in **Figure 2**.



Elimination Reactions: Kinetics

Likewise, to substitution reactions, elimination reactions are also unimolecular and bimolecular. Kinetic measurement on reactions in which alkyl halides (R-X) react with a variety of different bases, B:, have revealed two essentially extreme types: one in which, rate of the reaction is dependent of [B:],

$$\text{Rate} = k_2[\text{R-X}][\text{B:}] \quad \text{----- I}$$

and another in which, the rate is independent of [B:],

$$\text{Rate} = k_1[\text{R-X}] \quad \text{-----II}$$

The reactions involve either a one- or two-step mechanism. The one-step mechanism is known as the **E2 reaction**, and the two-step mechanism is known as the **E1 reaction**. The numbers refer not to the number of steps in the mechanism, but rather to the kinetics of the reaction: **E2** is bimolecular (second-order) while **E1** is unimolecular (first-order).

Mechanism of Elimination Reaction

The elimination reaction consists of three fundamental events, and they are;

1. Proton removal.
2. C-C pi bond is formed.
3. There is a breakage in the bond of the leaving group.

Depending on the reaction kinetics, elimination reactions can occur mostly by two mechanisms namely **E1** or **E2** where **E** is referred to as elimination and the number represent the molecularity.

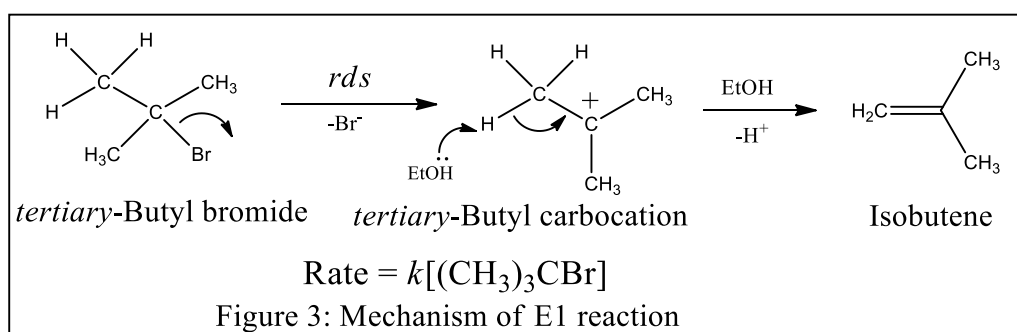
Elimination Unimolecular: E1 Mechanism

E1 is a model to explain a particular type of chemical elimination reaction. **E1** stands for **unimolecular elimination** and has the following specifications:

1. It is a **two-step process** of elimination: *ionization and deprotonation*.
 - **Ionization:** The carbon-halogen bond breaks to give a carbocation intermediate.
 - **Deprotonation:** Deprotonation of the carbocation gives the alkene.
2. **E1** reaction typically takes place with tertiary alkyl halides (R_3CX), but is possible with some secondary alkyl halides.
3. The reaction rate is influenced only by the concentration of the alkyl halide because carbocation formation is the **slowest step**, known as the rate-determining step. Therefore, first-order kinetics apply (unimolecular).
4. The reaction usually occurs in the complete absence of a base or the presence of only a weak base (acidic conditions and high temperature).
5. **E1** reactions are in competition with **S_N1** reactions because they share a common carbocationic intermediate.
6. There is no *antiperiplanar* requirement.

General Mechanism for E1 Elimination

E1 describes an elimination reaction (**E**) in which the rate-determining step is unimolecular (**1**) and does not involve the base. The leaving group leaves in this step, and the proton is removed in a separate second step. *Tertiary*-butyl bromide undergoes elimination reaction in presence of ethanol, a weak base to give isobutene. Mechanism of **E1** reaction is shown in **Figure 3**.



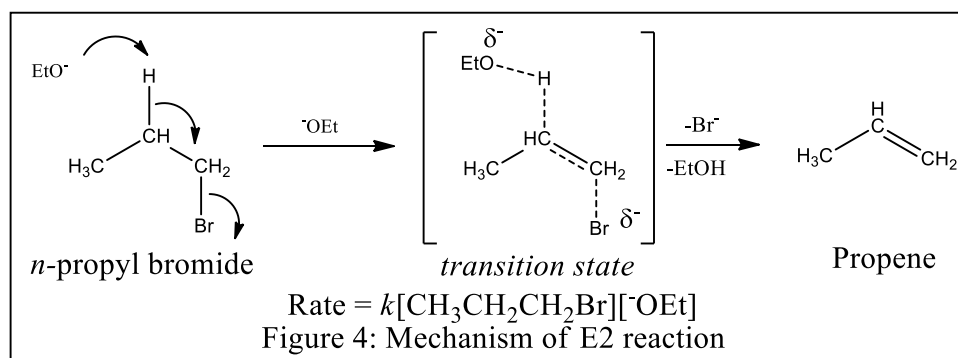
Elimination Bimolecular: E2 Mechanism

The **E2** mechanism (**E2** stands for **bimolecular elimination**) involves a one-step mechanism in which *carbon-hydrogen* and *carbon-halogen* bonds break to form a double bond ($C=C$ π -bond). The specifics of the reaction are as follows:

- **E2** is a single step elimination, with a single *transition state*.
- It is typically undergone by primary substituted alkyl halides, but is possible with some secondary alkyl halides and other compounds.
- The reaction rate is second order, because it's influenced by both the alkyl halide and the base (bimolecular).
- Because the **E2** mechanism results in the formation of a π -bond, the two leaving groups (often a hydrogen and a halogen) need to be *antiperiplanar*.
- An *antiperiplanar transition state* has *staggered* conformation with lower energy than a *synperiplanar transition state* which is in *eclipsed* conformation with higher energy. The reaction mechanism involving *staggered* conformation is more favorable for **E2** reactions (unlike **E1** reactions).
- **E2** typically uses a strong base. It must be strong enough to remove a weakly acidic hydrogen.
- In order for the π -bond to be created, the hybridization of carbons needs to be lowered from sp^3 to sp^2 .
- The C-H bond is weakened in the *rate determining step*.
- **E2** competes with the **S_N2** reaction mechanism if the base can also act as a nucleophile (true for many common bases).

General Mechanism for E2 Elimination

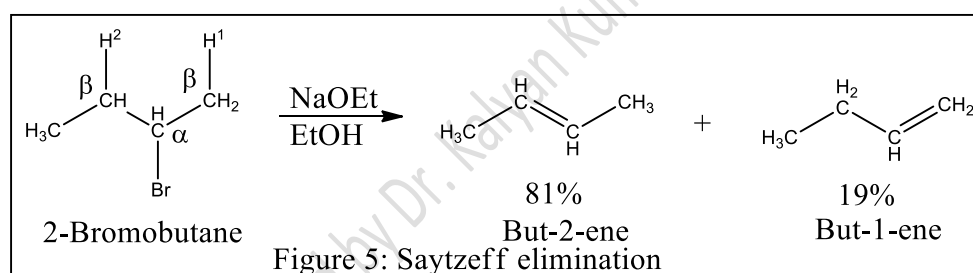
E2 describes an elimination reaction (**E**) in which the rate-determining step is bimolecular (**2**) and the base is involved in the rate equation. The eliminating groups, proton and the leaving groups leave in this step. *n*-Propyl bromide undergoes elimination reaction in presence of ethanol, a strong base than ethanol itself, to give propene. Mechanism of **E2** reaction is shown in **Figure 4**.



Orientation in E2: Saytzeff vs Hofmann

In substrates which have alternative β -hydrogen atoms available, it is possible to obtain more than one alkene on elimination. Here, there will be two possibilities:

Saytzeff (working on RBr compounds) states that hydrogen will be eliminated preferentially from that β -carbon atom which is attached with least number of hydrogen atom/s. Therefore, according to **Saytzeff** rule 'that alkene will predominate which has most alkyl substituents on the double bond carbons.' **Figure 5** illustrates the result.



Hofmann (working on RNMe_3^+ compounds) states that hydrogen will be eliminated preferentially from that β -carbon atom which is attached with most number of hydrogen atoms. Therefore, according to **Hofmann** rule 'that alkene will predominate which has least alkyl substituents on the double bond carbons.' **Figure 6** shows the result.

