ELIMINATION REACTIONS- 1

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Elimination Reactions

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**.

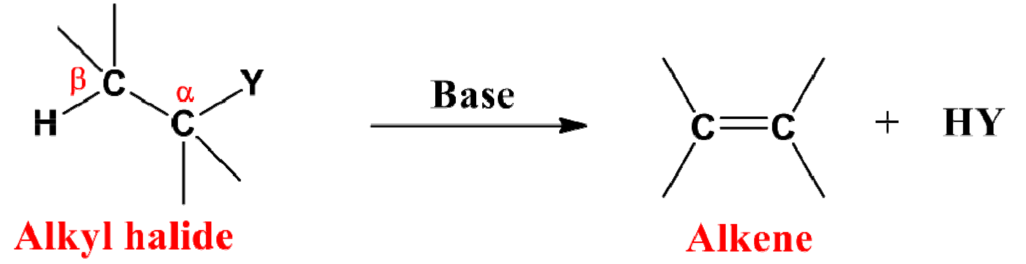


Figure 1: General scheme of elimination reactions

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**.

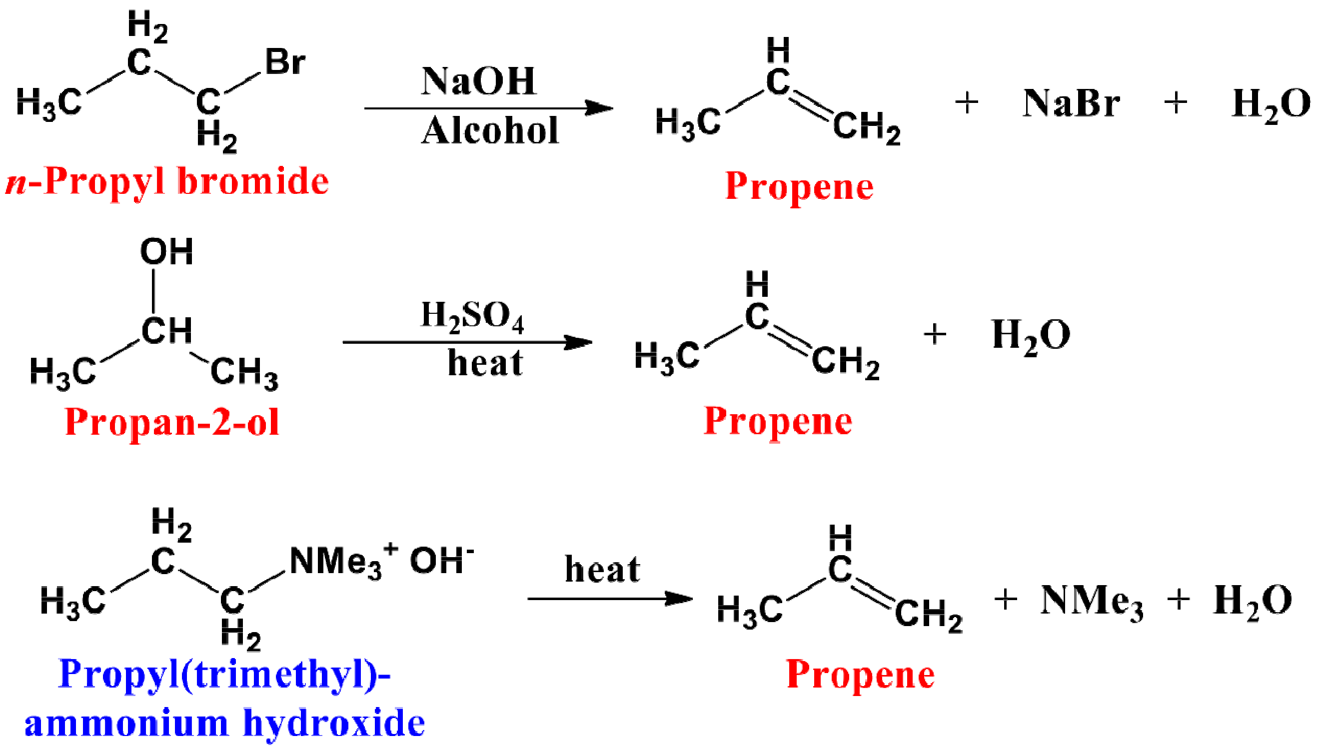


Figure 2: Examples of β-elimination reactions

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:],

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

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

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

- 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**.

Elimination Reactions

- 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.

1. **E1** reaction typically takes place with tertiary alkyl halides (R_3CX), but is possible with some secondary alkyl halides.

Elimination Unimolecular: E1 Mechanism

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).

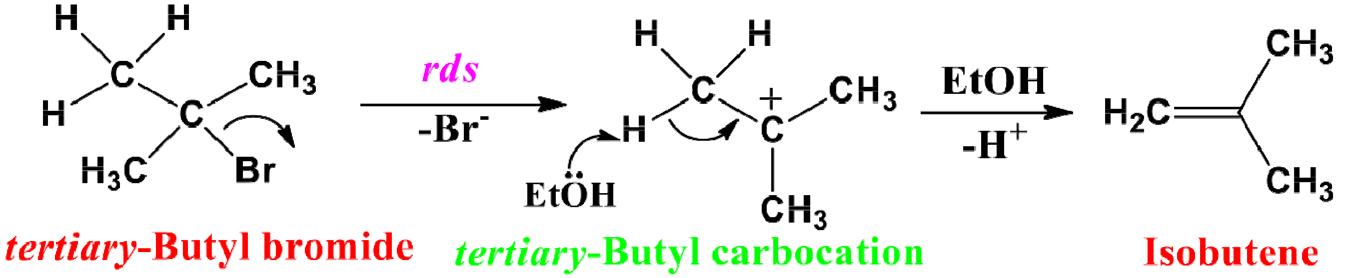
5. **E1** reactions are in competition with **S_N1** reactions because they share a common carbocationic intermediate.

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**.



Rate = $k[(CH_3)_3CBr]$

Figure 3: Mechanism of E1 reaction

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***.

Elimination Bimolecular: E2 Mechanism

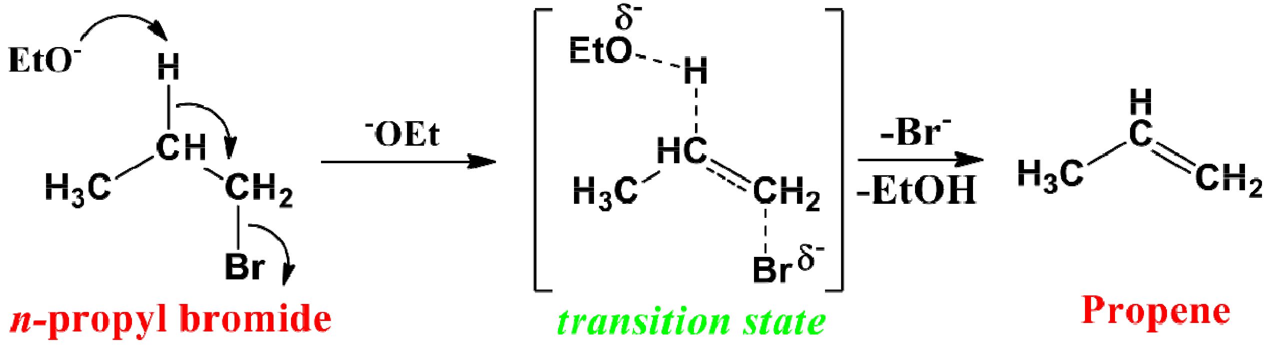
- An ***antiperiplanar transition state*** has ***staggered*** conformation with lower energy than a ***synperiplanar transition state*** which is in ***eclipsed*** conformation with higher energy. The reaction mechanism involving ***staggered*** conformation is more favorable for **E2** reactions (unlike **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 $\mathbf{sp^3}$ to $\mathbf{sp^2}$.
- The C-H bond is weakened in the ***rate determining step***.
- **E2** competes with the $\mathbf{S_N2}$ 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**.



$\text{Rate} = k[CH_3CH_2CH_2Br][^{-}OEt]$

Figure 4: Mechanism of E2 reaction

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 **Saytzeff** rule 'that alkene will predominate which has most alkyl substituents on the double bond carbons.' **Figure 5** illustrates the result.

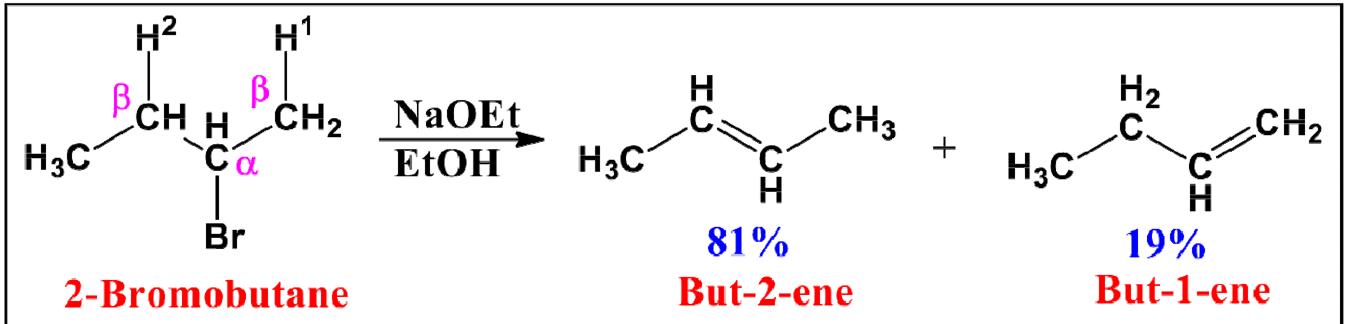


Figure 5: Saytzeff elimination

Orientation in E2: Saytzeff vs Hofmann

- **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.

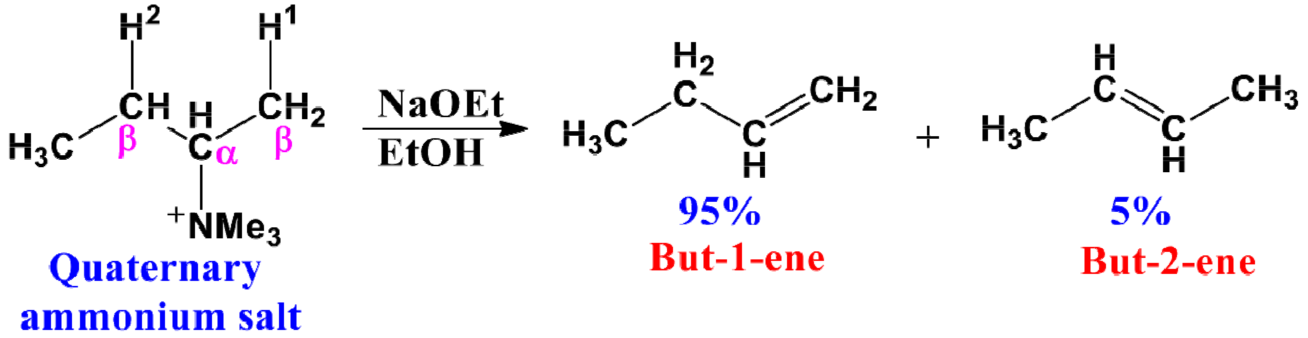


Figure 6: Hofmann elimination

THANK YOU