Unimolecular Elimination (E1) is a reaction in which the removal of an HX substituent results in the formation of a double bond. It is similar to a unimolecular nucleophilic substitution reaction (S_N1) in various ways. One being the formation of a carbocation intermediate. Also, the only rate determining (slow) step is the dissociation of the leaving group to form a carbocation, hence the name unimolecular. Thus, since these two reactions behave similarly, they compete against each other. Many times, both these reactions will occur simultaneously to form different products from a single reaction. However, one can be favored over another through thermodynamic control. Although Elimination entails two types of reactions, E1 and E2, we will focus mainly on E1 reactions with some reference to E2.

General Reaction

An E1 reaction involves the deprotonation of a hydrogen nearby (usually one carbon away, or the beta position) the carbocation resulting in the formation of an alkene product. In order to accomplish this, a Lewis base is required. For a simplified model, we’ll take B to be a Lewis base, and LG to be a halogen leaving group.

As can be seen above, the preliminary step is the leaving group (LG) leaving on its own. Because it takes the electrons in the bond along with it, the carbon that was attached to it loses its electron, making it a carbocation. Once it becomes a carbocation, a Lewis Base (\(B^-\)) deprotonates the intermediate carbocation at the beta position, which then donates its electrons to the neighboring C-C bond, forming a double bond. Unlike E2 reactions, which require the proton to be anti to the leaving group, E1 reactions only require a neighboring hydrogen. This is due to the fact that the leaving group has already left the molecule. The final product is an alkene along with the HB byproduct.

Reactivity

Due to the fact that E1 reactions create a carbocation intermediate, rules present in \(S_{N1}\) reactions still apply.

As expected, tertiary carbocations are favored over secondary, primary and methyl’s. This is due to the phenomena of hyperconjugation, which essentially allows a nearby C-C or C-H bond to interact with the p orbital of the carbon to bring the electrons down to a lower energy state. Thus, this has a stabilizing effect on the molecule as a whole. In general, primary and methyl carbocations do not proceed through the E1 pathway for this reason, unless there is a means of carbocation rearrangement to move the positive charge to a nearby carbon. Secondary and Tertiary carbons form more stable carbocations, thus this formation occurs quite rapidly.

Secondary carbocations can be subject to the E2 reaction pathway, but this generally occurs in the presence of a good / strong base. Adding a weak base to the reaction disfavors E2, essentially pushing towards the E1 pathway. In many instances, solvolysis occurs rather than using a base to deprotonate. This means heat is added to the solution, and the solvent itself deprotonates a hydrogen. The medium can effect the pathway of the reaction as well. Polar protic solvents may be used to hinder nucleophiles, thus disfavoring E2 / S_N2 from occurring.
Acid catalyzed dehydration of secondary / tertiary alcohols

We'll take a look at a mechanism involving solvolysis during an E1 reaction of Propanol in Sulfuric Acid.

[Image: E1 mechanism 2 hydration image.bmp]

- Step 1: The OH group on the pentanol is hydrated by H$_2$SO$_4$. This allows the OH to become an H$_2$O, which is a better leaving group.
- Step 2: Once the OH has been hydrated, the H$_2$O molecule leaves, taking its electrons with it. This creates a carbocation intermediate on the attached carbon.
- Step 3: Another H$_2$O molecule comes in to deprotonate the beta carbon, which then donates its electrons to the neighboring C-C bond. The carbons are rehybridized from sp$^3$ to sp$^2$, and thus a pi bond is formed between them.

Mechanism for Alkyl Halides

This mechanism is a common application of E1 reactions in the synthesis of an alkene.

[Image: alkyl halides.bmp]

Once again, we see the basic 2 steps of the E1 mechanism.

1. The leaving group leaves along with its electrons to form a carbocation intermediate.
2. A base deprotonates a beta carbon to form a pi bond.

In this case we see a mixture of products rather than one discrete one. This is the case because the carbocation has two nearby carbons that are capable of being deprotonated, but that only one forms a major product (more stable).
How are Regiochemistry & Stereochemistry involved?

In terms of regiochemistry, Zaitsev's rule states that although more than one product can be formed during alkene synthesis, the more substituted alkene is the major product. This infers that the hydrogen on the most substituted carbon is the most probable to be deprotonated, thus allowing for the most substituted alkene to be formed.

Unlike E2 reactions, E1 is not stereospecific. Thus, a hydrogen is not required to be anti-periplanar to the leaving group.

In this mechanism, we can see two possible pathways for the reaction. One in which the methyl on the right is deprotonated, and another in which the CH$_2$ on the left is deprotonated. Either one leads to a plausible resultant product, however, only one forms a major product. As stated by Zaitsev's rule, deprotonation of the most substituted carbon results in the most substituted alkene. This then becomes the most stable product due to hyperconjugation, and is also more common than the minor product.

Outside Sources


Problems

1) Which of these steps is the rate determining step (A or B)?

What is the major product formed (C or D)
2) In order to produce the most stable alkene product, from which carbon should the base deprotonate (A, B, or C)?

If the carbocation were to rearrange, on which carbon would the positive charge go onto without sacrificing stability (A, B, or C)?

3) Predict the major product of the following reaction.

4) (True or False) – There is no way of controlling the product ratio of E1 / S_n1 reactions.

5) Explain why the presence of a weak base / nucleophile favors E1 reactions over E2.

Answers

1. A, C
2. B, B
3. 

4. False - They can be thermodynamically controlled to favor a certain product over another.

5. By definition, an E1 reaction is a Unimolecular Elimination reaction. This means the only rate determining step is that of the dissociation of the leaving group to form a carbocation. Since E2 is bimolecular and the nucleophilic attack is part of
the rate determining step, a weak base/nucleophile disfavors it and ultimately allows E1 to dominate. (Don't forget about Sn1 which still pertains to this reaction simultaneously).

Contributors

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