11.7: ELIMINATION REACTIONS- ZAITSEV'S RULE

OBJECTIVE

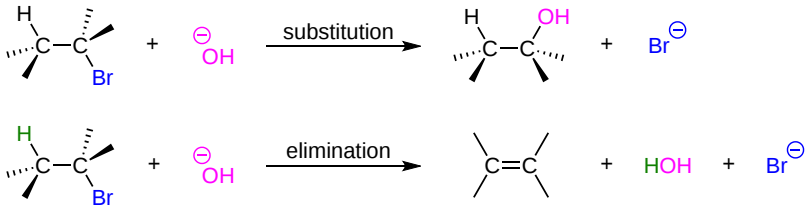
After completing this section, you should be able to apply Zaitsev's rule to predict the major product in a base-induced elimination of an unsymmetrical halide.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

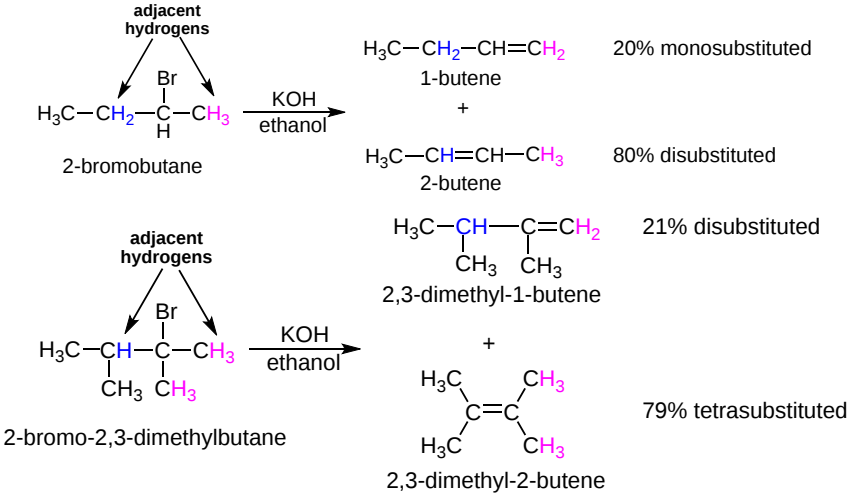
- Zaitsev's rule

When an alkyl halide is reacted with a nucleophile/Lewis base two major types of reaction can occur. Thus far in this chapter, we have discussed substitution reactions where a nucleophile displaces a leaving group at the electrophilic carbon of a substrate. Alternatively, the nucleophile could act as a Lewis base and cause an elimination reaction by removing a hydrogen adjacent to the leaving group. These reaction are similar and are often in competition with each other.



INTRODUCTION

The prefix "regio" indicates the interaction of reactants during bond making and/or bond breaking occurs preferentially by one orientation. If two or more structurally distinct groups of adjacent hydrogens are present in a given reactant, then multiple constitutionally isomeric alkenes may be formed by an elimination. **Zaitsev's rule** is an empirical rule used to predict the major products of elimination reactions. It states that in an elimination reaction the major product is the more stable alkene with the more highly substituted double bond. This situation is illustrated by the 2-bromobutane and 2-bromo-2,3-dimethylbutane elimination examples given below.



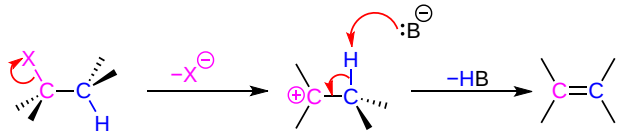
By using the strong base hydroxide, we direct these reactions toward elimination (rather than substitution). In both cases there are two different sets of adjacent hydrogens available to the elimination reaction (these are colored blue and magenta). If the rate of each possible elimination was the same, we might expect the amounts of the isomeric elimination products to reflect the number of hydrogens that could participate in that reaction. For example, since there are three 1°-hydrogens (magenta) and two 2°-hydrogens (blue) on beta-carbons in 2-bromobutane, statistics would suggest a 3:2 ratio of 1-butene and 2-butene in the products. This is not observed, and the latter predominates by 4:1. This departure from statistical expectation is even more pronounced in the second example, where there are six adjacent 1° hydrogens (magenta) compared with one 3°-hydrogen (blue). These results point to a strong favoring the more highly substituted product double bond predicted by **Zaitsev's Rule**.

THE E1, E2, AND E1CB REACTIONS

Elimination reaction take place by three common mechanism, E1, E2, and E1cB, all of which break the H-C and X-C bonds at different points of their mechanism. In addition, the different mechanisms will have subtle effects on the reaction products which will be discussed later in this chapter.

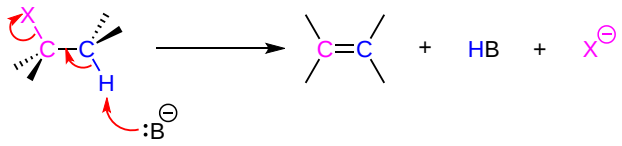
E1 MECHANISM

This mechanism starts the breaking of the C-X to provide a carbocation intermediate. A base removes a hydrogen adjacent to the original electrophilic carbon. The electrons from the broken H-C bond move to form the pi bond of the alkene. In much the same fashion as the S_N1 mechanism, the first step of the mechanism is slow making it the rate determining step. This means that the reaction kinetics are unimolecular and first-order with respect to the substrate.



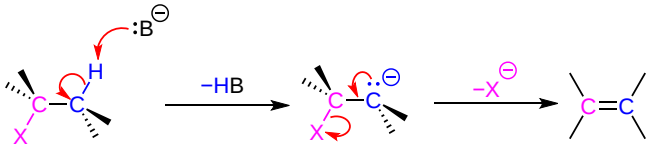
E2 MECHANISM

The E2 mechanism takes place in a single concerted step. The rate at which this mechanism occurs follows second order kinetics, and depends on the concentration of both the base and alkyl halide. The base removes a hydrogen from a carbon adjacent to the leaving group. The electrons of the broken H-C move to form the pi bond of the alkene. In doing this the C-X bond is broken causing the removal of the leaving group.



E1CB MECHANISM

The E1cB mechanism starts with the base deprotonating a hydrogen adjacent to the leaving to form a carbanion. In the second step of the mechanism the lone pair electrons of the carbanion move to become the pi bond of the alkene. This causes the C-X bond to break and the leaving group to be removed.



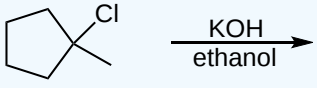
PREDICTING THE PRODUCTS OF AN ELIMINATION REACTION

For most elimination reactions, the formation of the product involves the breaking of a C-X bond from the electrophilic carbon, the breaking of a C-H bond from a carbon adjacent to the electrophilic carbon, and the formation of a pi bond between these two carbons. Which elimination mechanism is being followed has little effect on these steps. The limitations of each elimination mechanism will be discussed later in this chapter.

To determining the possible products, it is vital to first identify the electrophilic carbon in the substrate. Next identify all hydrogens on carbons directly adjacent to the electrophilic carbon. Each unique adjacent hydrogen has the possibility of forming a unique elimination product. Break a C-H bond from each unique group of adjacent hydrogens then break the C-X bond. Finally connect the adjacent carbon and the electrophilic carbon with a double bond. Repeat this process for each unique group of adjacent hydrogens. Finally, compare all of the possible elimination products. The product whose double bond has the most alkyl substituents will most likely be the preferred product.

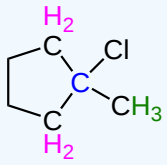
✔ WORKED EXAMPLE 11.7.1

What would be the expected products of the following reaction? Which would be expected to be the major product?



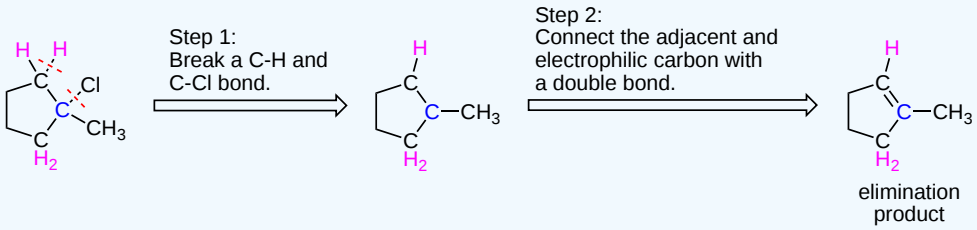
Solution

To solve this problem, first find the electrophilic carbon in the starting compound. This carbon is directly attached to the chlorine leaving groups and is shown in blue in the structure below. Next, identify all unique groups of hydrogens on carbons directly adjacent to the electrophilic carbon. In the starting compound, there are two distinct groups of hydrogens which can create a unique elimination product if removed. They are shown as magenta and green in the structure below.

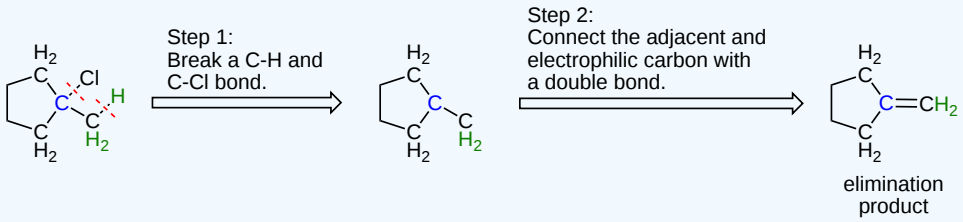


Create the possible elimination product by breaking a C-H bond from each unique group of adjacent hydrogens then breaking the C-Cl bond. Then connect the adjacent carbon and the electrophilic carbon with a double bond to create an alkene elimination product. Repeat this process for each unique group of adjacent hydrogens. Because the starting compound in this example has two unique groups of adjacent hydrogens, two elimination products can possibly be made.

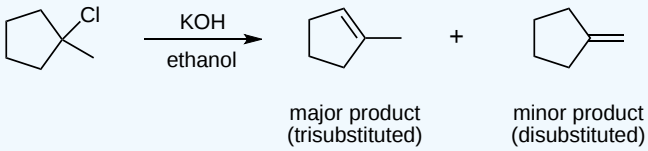
Product 1



Product 2



Finally, compare the possible elimination products to determine which has the most alkyl substituents. This product will most likely be the preferred. For this example product 1 has three alkyl substituents and product 2 has only two. This means product 1 will likely be the preferred product of the reaction.



? EXERCISE 11.7.1

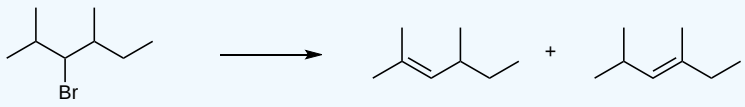
1) Ignoring the alkene stereochemistry show the elimination product(s) of the following compounds:

2) Predict the major products of the following reactions.

Answer

1)

a)



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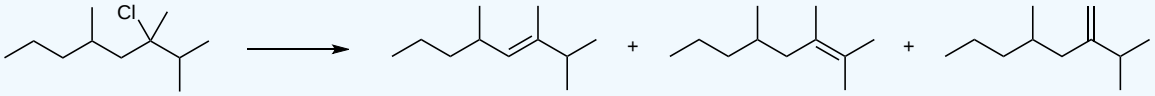

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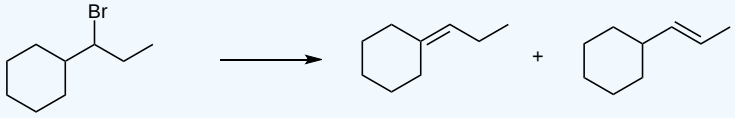
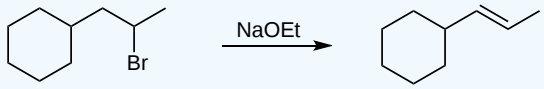
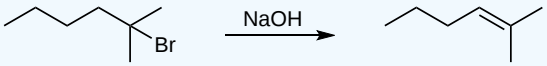


2)

a) 

b) 

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