Objectives

After completing this section, you should be able to

1. write an equation to describe the preparation of an alkyne by the dehydrohalogenation of a vicinal dihalide or vinylic halide.
2. identify the alkyne produced from the dehydrohalogenation of a given vicinal dihalide or vinylic halide.
3. write a reaction sequence to show how the double bond of an alkene can be transformed into a triple bond.
4. identify the vicinal dihalide (or vinylic halide) needed to synthesize a given alkyne by dehydrohalogenation.

Key Terms

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

- vicinal dihalide
- vinylic halide

Alkynes can be a useful functional group to synthesize due to some of their antibacterial, antiparasitic, and antifungal properties. One simple method for alkyne synthesis is by double elimination from a dihaloalkane.

Introduction

One case in which elimination can occur is when a haloalkane is put in contact with a nucleophile. The table below is used to determine which situations will result in elimination and the formation of a π bond.

<table>
<thead>
<tr>
<th>Type of Haloalkane</th>
<th>Weak Base, Poor Nucleophile</th>
<th>Weak Base, Good Nucleophile</th>
<th>Strong, Unhindered Base</th>
<th>Strong, Hindered Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unhindered</td>
<td></td>
<td></td>
<td>E2</td>
<td></td>
</tr>
<tr>
<td>Branched</td>
<td></td>
<td></td>
<td>E2</td>
<td>E2</td>
</tr>
<tr>
<td>Secondary</td>
<td>E1</td>
<td></td>
<td>E2</td>
<td>E2</td>
</tr>
<tr>
<td>Tertiary</td>
<td>E1</td>
<td>E1</td>
<td>E2</td>
<td>E2</td>
</tr>
</tbody>
</table>

* Empty Box means no elimination or π bond forms

To synthesize alkynes from dihaloalkanes we use dehydrohalogenation. The majority of these reactions take place using alkoxide bases (other strong bases can also be used) with high temperatures. This combination results in the majority of the product being from the E2 mechanism.
E2 Mechanism

Recall that the E2 mechanism is a concerted reaction (occurs in 1 step). However, in this 1 step there are 3 different changes in the molecule. This is the reaction between 2-Bromo-2-methylpropane and Sodium Hydroxide.

![E2 Mechanism Diagram]

1. The base will deprotonate the haloalkane.
2. The leaving group will depart from the molecule.
3. The deprotonated cation will recombine from each to salt.

This is a brief review of the E2 reaction. For further information on why the reaction proceeds as it does visit the E2 reaction page. Now, if we apply this concept using 2 halides on vicinal or geminal carbons, the E2 reaction will take place twice resulting in the formation of 2 π bonds and thus an Alkyne.

Dihaloalkane Elimination

This is a general picture of the reaction taking place without any of the mechanisms shown.

![Dihaloalkane Elimination Diagram]

or

* With a terminal haloalkane the equation above is modified in that 3 equivalents of base will be used instead of 2.

Lets look at the mechanism of a reaction between 2,3-Dibromopentane with sodium amide in liquid ammonia.
• Liquid ammonia is not part of the reaction, but is used as a solvent
• Notice the intermediate of the alkyne synthesis. It is stereospecifically in its anti form. Because the second proton and halogen are pulled off the molecule this is unimportant to the synthesis of alkynes. For more information on this see the page on preparation of alkenes from haloalkanes.

Preparation of Alkynes from Alkenes

Lastly, we will briefly look at how to prepare alkynes from alkenes. This is a simple process using first halogenation of the alkene bond to form the dihaloalkane, and next, using the double elimination process to protonate the alkane and from the 2 σ(π) bonds.

This first process is gone over in much greater detail in the page on halogenation of an alkene. In general, chlorine or bromine is used with an inert halogenated solvent like chloromethane to create a vicinal dihalide from an alkene. The vicinal dihalide formed is the reactant needed to produce the alkyne using double elimination, as covered previously on this page.

Terminal Alkynes

The acidity of terminal alkynes also plays a role in product determination when vicinal (or geminal) dihalides undergo base induced bis-elimination reactions. The following example illustrates eliminations of this kind starting from 1,2-dibromopentane, prepared from 1-pentene by addition of bromine. The initial elimination presumably forms 1-bromo-1-pentene, since base attack at the more acidic and less hindered 1 º-carbon should be favored. The second elimination then produces 1-pentyne. If the very strong base sodium amide is used, the terminal alkyne is trapped as its sodium salt, from which it may be released by mild acid treatment. (NB One cannot stop the reaction at the terminal alkyne with 2 equivalents of strong base.) However, if the weaker base KOH with heat is used for the elimination, the terminal alkyne salt is not formed, or is formed reversibly, and the initially generated 1-pentyne rearranges to the more stable 2-pentyne via an allene intermediate.
Questions

Question 1: Why would we need 3 bases for every terminal dihaloalkane instead of 2 in order to form an alkyne?

\[ \begin{array}{c}
\text{X} & \text{X} \\
\text{R}^-\text{C}^-\text{C}^-\text{H} & \rightarrow & \text{R}^-\text{C}^=\text{C}^-\text{H}
\end{array} \]

Question 2: What are the major products of the following reactions:

a.) 1,2-Dibromopentane with sodium amide in liquid ammonia

b.) 1-Pentene first with Br\textsubscript{2} and chloromethane, followed by sodium ethoxide (Na\textsuperscript{+} O-CH\textsubscript{2}CH\textsubscript{3})

Question 3: What would be good starting molecules for the synthesis of the following molecules:

a.) \[ \text{\underline{\text{\quad}}} \quad \text{from an alkene} \]

b.) \[ \text{\underline{\text{\quad}}} \quad \text{from a dihaloalkane} \]

Question 4: Use a 6 carbon diene to synthesize a 6 carbon molecule with 2 terminal alkynes.

Answers

Answer 1: Remember that hydrogen atoms on terminal alkynes make the alkyne acidic. One of the base molecules will pull off the terminal hydrogen instead of one of the halides like we want.

Answer 2:

a.) 1-Pentyne

b.) 1-Pentyne

Answer 3:
Answer 4: Bromine or chlorine can be used with different inert solvents for the halogenation. This can be done using many different bases. Liquid ammonia is used as a solvent and needs to be followed by an aqueous work-up.

![Diagram of halogenation process]

References


Exercises

1. Show, by means of equations, how you would convert
   a. $\ce{Ph-CH=CH2} \rightarrow \ce{Ph-CHBr-CH2Br} \rightarrow \ce{Ph-C#C-H}$
   b. 1-hexene into 1-hexyne.

2. Identify the vinyl halide or halides and the vicinal dihalide or dihalides that could be used in the synthesis of
   a. 2,2,5,5-tetramethyl-3-hexyne.
   b. 4-methyl-2-hexyne.

Answers

1. a. $\ce{Ph-CH=CH2 \rightarrow \text{Br}_2 \rightarrow \ce{CH}_2\text{Cl}_2 \rightarrow \ce{Ph-CHBr-CH2Br \rightarrow \text{1. NaNH}_2 \rightarrow \text{2. H}_3\text{O}^+ \rightarrow \ce{Ph-C#C-H}}}$

   b. $\ce{CH3(CH2)3CH=CH2 \rightarrow \text{Br}_2 \rightarrow \ce{CH}_2\text{Cl}_2 \rightarrow \ce{CH3(CH2)3CHBr-CH2Br \rightarrow \text{1. NaNH}_2 \rightarrow \text{2. H}_3\text{O}^+ \rightarrow \ce{CH3(CH2)3C#C-H}}}
\[ \text{CH}_3(\text{CH}_2)_3\text{C}#\text{C-H}]^+ \]

2. a. 3-bromo-2,2,5,5-tetramethyl-3-hexene and 3,4 bromo 2,2,5,5 tetramethylhexane
   b. 3-bromo-4-methyl-2-pentene or 2-bromo-4-methyl-2-pentene and 2,3-dibromo-4-methylpentane

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