Objectives

After completing this section, you should be able to

1. describe the bonding and geometry of the carbon-carbon triple bond in terms of the sp-hybridization of the carbon atoms involved.
2. explain the reactivity of alkynes based on the known strengths of carbon-carbon single, double and triple bonds.
3. write equations for the reaction of an alkyne with one or two equivalents of halogen (chlorine or bromine) or halogen acid (HCl, HBr or HI).
4. draw the structure of the product formed when an alkyne reacts with one equivalent of the halogens and halogen acids listed in Objective 3.
5. identify the alkyne which must have been used in an addition reaction with a halogen or halogen acid, given the product of such a reaction.

Study Notes

You might find it useful to review Section 1.9 before you begin work on this unit. If necessary, construct a molecular model of a simple alkyne. Notice the similarity between the behaviour of alkenes and that of alkynes. In the laboratory, you will observe that alkynes readily decolourize a solution of bromine in dichloromethane. Section 9.7 describes a test that allows you to distinguish between a terminal alkyne (i.e., one in which the triple bond occurs between the last two carbons in the chain) and nonterminal alkynes and alkenes. In Figure 9.2, on page 318 of the textbook, only the carbon carrying the positive charge is sp-hybridized—the carbon atom attached to two hydrogens is sp$^2$-hybridized.

Content

Reaction 1: Addition of Hydrogen Halide to an Alkyne

Summary: Reactivity order of hydrogen halides: HI > HBr > HCl > HF.

Follows Markovnikov’s rule:

- Hydrogen adds to the carbon with the greatest number of hydrogens, the halogen adds to the carbon with fewest hydrogens.
- Protination occurs on the more stable carbocation. With the addition of HX, haloalkenes form.
- With the addition of excess HX, you get anti addition forming a geminal dihaloalkane.

Addition of a HX to an Internal Alkyne

As described in Figure 1, the π electrons will attack the hydrogen of the HBr and because this is a symmetric molecule
it does not matter which carbon it adds to, but in an asymmetric molecule the hydrogen will covalently bond to the carbon with the most hydrogens. Once the hydrogen is covalently bonded to one of the carbons, you will get a carbocation intermediate (not shown, but will look the same as depicted in Figure 1) on the other carbon. Again, this is a symmetric molecule and if it were asymmetric, which carbon would have the positive charge?

The final step is the addition of the Bromine, which is a good nucleophile because it has electrons to donate or share. Bromine, therefore attacks the carbocation intermediate placing it on the highly substituted carbon. As a result, you get 2-bromobutene from your 2-butyne reactant, as shown below.

Figure2 (1).bmp

Now, what if you have excess HBr?

Addition due to excess HX present ? yields a geminal dihaloalkane

Figure3.bmp

Here, the electrophilic addition proceeds with the same steps used to achieve the product in Addition of a HX to an Internal Alkyne. The π electrons attacked the hydrogen, adding it to the carbon on the left (shown in blue). Why was hydrogen added to the carbon on left and the one on the right bonded to the Bromine?

Now, you will have your carbocation intermediate, which is followed by the attack of the Bromine to the carbon on the right resulting in a haloalkane product.

Addition of HX to Terminal Alkyne

- Here is an addition of HBr to an asymmetric molecule.
- First, try to make sense of how the reactant went to product and then take a look at the mechanism.
The $\pi$ electrons are attacking the hydrogen, depicted by the electron pushing arrows and the Bromine gains a negative charge. The carbocation intermediate forms a positive charge on the left carbon after the hydrogen was added to the carbon with the most hydrogen substituents.

The Bromine, which has a negative charge, attacks the positively charged carbocation forming the final product with the nucleophile on the more substituted carbon.

Most Hydrogen halide reactions with alkynes occur in a Markovnikov-manner in which the halide attaches to the most substituted carbon since it is the most positively polarized. A more substituted carbon has more bonds attached to 1) carbons or 2) electron-donating groups such as Fluorine and other halides. However, there are two specific reactions among alkynes where anti-Markovnikov reactions take place: the radical addition of HBr and Hydroboration Oxidation reactions. For alkynes, an anti-Markovnikov addition takes place on a terminal alkyne, an alkyne on the end of a chain.
HBr Addition With Radical Yields 1-bromoalkene

The Br of the Hydrogen Bromide (H-Br) attaches to the less substituted 1-carbon of the terminal alkyne shown below in an anti-Markovnikov manner while the Hydrogen proton attaches to the second carbon. As mentioned above, the first carbon is the less substituted carbon since it has fewer bonds attached to carbons and other substituents. The H-Br reagent must also be reacted with heat or some other radical initiator such as a peroxide in order for this reaction to proceed in this manner. This presence of the radical or heat leads to the anti-Markovnikov addition since it produces the most stable reaction. For more on Anti-Markovnikov additions: Radical Additions--Anti-Markovnikov Product Formation

\[
\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow{\text{H-Br}} \text{CH}_3\text{CH}_2\text{CH} \equiv \text{CH}_2\text{Br}
\]

A Peroxide

The product of a terminal alkyne that is reacted with a peroxide (or light) and H-Br is a 1-bromoalkene.

**Regioselectivity:** The Bromine can attach in a **syn** or **anti** manner which means the resulting alkene can be both **cis** and **trans.** **Syn** addition is when both Hydrogens attach to the same face or side of the double bond (i.e. **cis**) while the **anti** addition is when they attach on opposite sides of the bond (**trans**).

\[
\begin{align*}
\text{Cis-1-bromo-1-butene} & & \text{Trans-1-bromo-1-butene} \\
\text{H} & & \text{H} \\
\text{H} & & \text{Br} \\
\text{Br} & & \text{H}
\end{align*}
\]

**Reaction: Halogenation of Alkynes**

**Summary:**

- **Stereoslectivity:** anti addition
- **Reaction proceeds via cyclic halonium ion**
Addition of Br₂

- The addition of Br₂ to an alkyne is analogous to adding Br₂ to an alkene.
- Once Br₂ approaches the nucleophilic alkyne, it becomes polarized.
- The \(\pi\) electrons, from the triple bond, can now attack the polarized bromine forming a C-Br bond and displacing the bromine ion.
- Now, you will get an intermediate electrophilic carbocation, which will immediately react with the bromine ion giving you the dibromo product.

Figure6.bmp

First, you see the polarized Br₂ being attacked by the \(\pi\) electrons. Once you form the C-Br bond, the other bromine is released as a bromine ion. The intermediate here is a bromonium ion, which is electrophilic and reacts with the bromine ion giving you the dibromo product.

Exercise

1. Draw the structure, and give the IUPAC name, of the product formed in each of the reactions listed below.
   a. \(\text{CH}_3\text{C}≡\text{C}−\text{CH}_3\) → \(\text{CH}_3\text{C}≡\text{C}−\text{CH}_3\) 1 equiv HCl
   b. \(\text{CH}_3\text{C}≡\text{C}−\text{CH}_3\) excess HCl
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Objectives

After completing this section, you should be able to

1. write the equation for the reaction of water with an alkyne in the presence of sulfuric acid and mercury(II) sulfate.
2. describe keto-enol tautomerism.
3. predict the structure of the ketone formed when a given alkyne reacts with sulfuric acid in the presence of mercury(II) sulfate.

4. identify the reagents needed to convert a given alkyne to a given ketone.

5. identify the alkyne needed to prepare a given ketone by hydration of the triple bond.

6. write an equation for the reaction of an alkyne with borane.

7. write the equation for the reaction of a vinylic borane with basic hydrogen peroxide or hot acetic acid.

8. identify the reagents, the alkyne, or both, needed to prepare a given ketone or a given cis alkene through a vinylic borane intermediate.

9. identify the ketone produced when a given alkyne is reacted with borane followed by basic hydrogen peroxide.

10. identify the cis alkene produced when a given alkyne is reacted with borane followed by hot acetic acid.

11. explain why it is necessary to use a bulky, sterically hindered borane when preparing vinylic boranes from terminal alkynes.

12. predict the product formed when the vinylic borane produced from a terminal alkyne is treated with basic hydrogen peroxide.

13. identify the alkyne needed to prepare a given aldehyde by a vinylic borane.

Key Terms

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

- enol
- keto-enol tautomeric equilibrium
- tautomericism
- tautomers

Study Notes

Rapid interconversion between tautomers is called tautomericis; however, as the two tautomers are in equilibrium, the term tautomeric equilibrium may be used. This section demonstrates the equilibrium between a ketone and an enol; hence, the term keto-enol tautomeric equilibrium is appropriate. The term “enol” indicates the presence of a carbon-carbon double bond and a hydroxyl (i.e., alcohol) group. Later in the course, you will see the importance of keto-enol tautomerism in discussions of the reactions of ketones, carbohydrates and nucleic acids.

It is important to note that tautomerism is not restricted to keto-enol systems. Other examples include imine-enamine tautomerism

- imine-enamine tautomerism

and nitroso-oxime tautomerism

- nitroso-oxime tautomerism

However, at the moment you need only concern yourself with keto-enol tautomerism.

Notice how hydroboration complements hydration in the chemistry of both alkenes and alkynes.
hydroboration and hydration scheme of alkenes and alkynes

**Reaction: Hydration of Alkynes**

As with alkenes, hydration (addition of water) to alkynes requires a strong acid, usually sulfuric acid, and is facilitated by mercuric sulfate. However, unlike the additions to double bonds which give alcohol products, addition of water to alkynes gives ketone products (except for acetylene which yields acetaldehyde). The explanation for this deviation lies in **enol-keto tautomerization**, illustrated by the following equation. The initial product from the addition of water to an alkyne is an enol (a compound having a hydroxyl substituent attached to a double-bond), and this immediately rearranges to the more stable keto tautomer.

![Tautomerization Reaction]

Tautomers are defined as rapidly interconverted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom (colored red here) and a differently located double bond. The equilibrium between tautomers is not only rapid under normal conditions, but it often strongly favors one of the isomers (acetone, for example, is 99.999% keto tautomer). Even in such one-sided equilibria, evidence for the presence of the minor tautomer comes from the chemical behavior of the compound. Tautomeric equilibria are catalyzed by traces of acids or bases that are generally present in most chemical samples. The three examples shown below illustrate these reactions for different substitutions of the triple-bond. The tautomerization step is indicated by a red arrow. For terminal alkynes the addition of water follows the Markovnikov rule, as in the second example below, and the final product is a methyl ketone (except for acetylene, shown in the first example). For internal alkynes (the triple-bond is within a longer chain) the addition of water is not regioselective. If the triple-bond is not symmetrically located (i.e. if R & R’ in the third equation are not the same) two isomeric ketones will be formed.

\[
\text{HC\equiv CH} + \text{H}_2\text{O} + \text{HgSO}_4 \& \text{H}_2\text{SO}_4 \rightarrow \left[ \text{H}_2\text{C}=\text{CHOH} \right] \rightarrow \text{H}_3\text{C}-\text{CH}=\text{O}
\]

\[
\text{RC\equiv CH} + \text{H}_2\text{O} + \text{HgSO}_4 \& \text{H}_2\text{SO}_4 \rightarrow \left[ \text{RC(OH)}=\text{CH}_2 \right] \rightarrow \text{RC}(=\text{O})\text{CH}_3
\]

\[
\text{RC\equiv CR’} + \text{H}_2\text{O} + \text{HgSO}_4 \& \text{H}_2\text{SO}_4 \rightarrow \left[ \text{RHC}=(\text{OH})\text{R’} + \text{RC(OH)}=\text{CHR’} \right] \rightarrow \text{RCH}_2(=\text{O})\text{R’} + \text{RC}(=\text{O})-\text{CH}_2\text{R’}
\]

With the addition of water, alkynes can be hydrated to form enols that spontaneously tautomerize to ketones. Reaction is catalyzed by mercury ions. Follows Markovnikov’s Rule: Terminal alkynes give methyl ketones.
The first step is an acid/base reaction where the electrons of the triple bond acts as a Lewis base and attacks the proton therefore protinating the carbon with the most hydrogen substituents.

The second step is the attack of the nucleophilic water molecule on the electrophilic carbocation, which creates an oxonium ion.

Next you deprotonate by a base, generating an alcohol called an enol, which then tautomerizes into a ketone.

Tautomerism is a simultaneous proton and double bond shift, which goes from the enol form to the keto isomer form as shown above in Figure 7.

Now let's look at some Hydration Reactions.

**Hydration of Terminal Alkyne produces methyl ketones**

Just as described in Figure 7 the electrons will attack a proton, forming a carbocation, which then gets attacked by the nucleophilic water molecules. After deprotination, we generate an enol, which then tautomerizes into the ketone form shown.

**Hydration of Alkyne**
As you can see here, the electrons of the triple bond are attacking the proton, which forms a covalent bond on the carbon with the most hydrogen substituents. Once the hydrogen is bound you have a carbocation, which gets attacked by the water molecule. Now you have a positive charge on the oxygen which results in a base coming in and deprotinating the molecule. Once deprotinated, you have an enol, which then gets tautomerized.

Tautomerism is shown here when the proton gets attacked by the double bond electrons forming a covalent bond between the carbon and the hydrogen on the less substituted carbon. Electrons from the Oxygen end up moving to the carbon, forming a double bond with carbon and giving itself a positive charge, which then gets attacked by the base. The base deprotonates the Oxygen resulting in the more stable final product at equilibrium, which is a ketone.

### Exercises

1. Draw the structure of the product formed when each of the substances below is treated with H$_2$O/H$_2$SO$_4$ in the presence of HgSO$_4$.
   
   a. $\ce{CH3-CH2-C\#C-H}$
b. 3,3-dimethyl-1-alkyne

2. Draw the structure of the keto form of the compound shown below. Which form would you expect to be the most stable?

1-hydroxycyclohexene

Answers:

1. a. 2-butanone
   b. 3,3-dimethyl-2-butanone

2. cyclohexanone

   The keto form should be the most stable.

Questions

Q9.4.1

What alkyne would you start with to gain the following products, in an oxidation reaction? Keep in mind resonance.

A

\[
\begin{align*}
    &\text{O} \\
    &\text{Ar} \\
    &\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C} \text{CH}_3
\end{align*}
\]

B

\[
\begin{align*}
    &\text{O} \\
    &\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C} \text{CH}_3
\end{align*}
\]

Q9.4.2

Propose a reaction scheme for the following compound starting from the alkyne and showing required reagents and intermediates.
Solutions

S9.4.1

\[
\begin{align*}
A & \\
\text{\begin{tikzpicture}

\draw (0,0) circle (0.5cm);
\draw (0,0) -- (1.5,0);
\draw (1.5,0) -- (2.5,1);
\draw (2.5,1) -- (2.5,-1);
\draw (2.5,-1) -- (1.5,-2);
\draw (1.5,-2) -- (0,-3);
\draw (0,-3) -- (0,0);
\end{tikzpicture}}
\end{align*}
\]

\[
\begin{align*}
B & \\
\text{\begin{tikzpicture}

\draw (0,0) circle (0.5cm);
\draw (0,0) -- (1.5,0);
\draw (1.5,0) -- (2.5,1);
\draw (2.5,1) -- (2.5,-1);
\draw (2.5,-1) -- (1.5,-2);
\draw (1.5,-2) -- (0,-3);
\draw (0,-3) -- (0,0);
\end{tikzpicture}}
\end{align*}
\]

S9.4.2

\[
\begin{align*}
\text{\begin{tikzpicture}

\draw (0,0) circle (0.5cm);
\draw (0,0) -- (1.5,0);
\draw (1.5,0) -- (2.5,1);
\draw (2.5,1) -- (2.5,-1);
\draw (2.5,-1) -- (1.5,-2);
\draw (1.5,-2) -- (0,-3);
\draw (0,-3) -- (0,0);
\end{tikzpicture}}
\end{align*}
\]

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