Objectives

After completing this section, you should be able to

1. write an equation for the reaction that occurs between a terminal alkyne and a strong base, such as sodamide, NaNH₂.
2. rank a given list of compounds, including water, acetylene and ammonia, in order of increasing or decreasing acidity.
3. rank a given list of hydrocarbons, such as acetylene, ethylene and ethane, in order of increasing or decreasing acidity.
4. describe a general method for determining which of two given compounds is the stronger acid.
5. provide an acceptable explanation of why terminal alkynes are more acidic than alkanes or alkenes.

Key Terms

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

• acetylide anion
• acidity order

Study Notes

An acetylide anion is an anion formed by removing the proton from the end carbon of a terminal alkyne:

reaction of propyne with sodium to form sodium propylide

An acidity order is a list of compounds arranged in order of increasing or decreasing acidity.

The general ideas discussed in this section should already be familiar to you from your previous exposure to chemistry and from the review in Section 2.8. A slightly different account of why terminal alkynes are stronger acids than are alkenes or alkanes is given below. However, the argument is still based on the differences between sp-, sp²- and sp³-hybrid orbitals.

The carbons of a triple bond are sp-hybridized. An sp-hybrid orbital has a 50% s character and a 50% p character, whereas an sp²-hybrid orbital is 33% s and 67% p, and an sp³-hybrid orbital is 25% s and 75% p. The greater the s character of the orbital, the closer the electrons are to the nucleus. Thus in a C(sp)$\ce{-}$H bond, the bonding electrons are closer to the carbon nucleus than they are in a C(sp²)$\ce{-}$H bond. In other words, compared to a C(sp²)$\ce{-}$H bond (or a C(sp³)$\ce{-}$H bond), a C(sp)$\ce{-}$H bond is very slightly polar: C$^5-$H$^5^+$. This slight polarity makes it easier for a base to remove a proton from a terminal alkyne than from a less polar or non-polar alkene or alkane.

As you will appreciate, the reaction between sodium amide and a terminal alkyne is an acid-base reaction. The sodium acetylde product is, of course, a salt. Terminal alkynes can also form salts with certain heavy-metal cations, notably
silver(I) and copper(I). In the laboratory component of this course, you will use the formation of an insoluble silver acetylide as a method for distinguishing terminal alkynes from alkenes and non-terminal alkynes:

three reactions showing silver cation as test for terminal alkyne

Metal acetylides are explosive when dry. They should be destroyed while still wet by warming with dilute nitric acid:

silver propylide conversion to propyne with acid

Acidity of Terminal Alkynes: Formation of Acetylide Anions

Terminal alkynes are much more acidic than most other hydrocarbons. Removal of the proton leads to the formation of an acetylide anion, \(\text{RC} = \text{C}^–\). The origin of the enhanced acidity can be attributed to the stability of the acetylide anion, which has the unpaired electrons in an sp hybridized orbital. The stability results from occupying an orbital with a high degree of s-orbital character. There is a strong correlation between s-character in the orbital containing the non-bonding electrons in the anion and the acidity of hydrocarbons. The enhanced acidity with greater s-character occurs despite the fact that the homolytic \( \text{C-H BDE} \) is larger.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conjugate Base</th>
<th>Hybridization</th>
<th>“s Character”</th>
<th>pKa</th>
<th>C-H BDE (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{CH}_3)</td>
<td>(\text{CH}_3\text{CH}_2^–)</td>
<td>sp(^3)</td>
<td>25%</td>
<td>50</td>
<td>410</td>
</tr>
<tr>
<td>(\text{CH}_2\text{CH}_2)</td>
<td>(\text{CH}_2\text{CH}^–)</td>
<td>sp(^2)</td>
<td>33%</td>
<td>44</td>
<td>473</td>
</tr>
<tr>
<td>(\text{HCCH})</td>
<td>(\text{HCC}^–)</td>
<td>sp</td>
<td>50%</td>
<td>25</td>
<td>523</td>
</tr>
</tbody>
</table>

Consequently, acetylide anions can be readily formed by deprotonation using a sufficiently strong base. Amide anion \((\text{NH}_2)^–\), in the form of \(\text{NaNH}_2\) is commonly used for the formation of acetylide anions.

\[
\begin{align*}
\text{C≡C–H} & \quad \text{NaNH}_2 \quad \text{C≡C}^– \text{Na}^+ + \text{NH}_3 \\
\text{C≡C–H} & \quad \text{NaNH}_2 \quad \text{C≡C}^– \text{Na}^+ + \text{NH}_3
\end{align*}
\]

Exercise 9.7.1

1. Given that the pKa of water is 14.00, would you expect hydroxide ion to be capable of removing a proton from each of the substances listed below? Justify your answers, briefly.
   a. ethanol (pKa = 16)
   b. acetic acid (pKa = 4.72)
   c. acetylene (pKa = 25)
Answer

1.

a. No, not very well. The pKa of ethanol is greater than that of water, thus the equilibrium lies to the left rather than to the right. 

\[
\text{OH}^- + \overset{\text{H}}{\text{H}}\text{O} \rightleftharpoons \text{H}_2\text{O} + \overset{\text{O}}{\text{O}}^- 
\]

b. Yes, very well. There is a difference of 11 pKa units between the pKa of water and the pKa of acetic acid. The equilibrium lies well to the right. 

\[
\text{OH}^- + \overset{\text{O}}{\text{H}}\text{OH} \rightarrow \text{H}_2\text{O} + \overset{\text{O}}{\text{O}}^- 
\]

c. No, hardly at all. The hydroxide ion is too weak a base to remove a proton from acetylene. The equilibrium lies well to the left. 

\[
\text{OH}^- + \overset{\text{H}}{\text{C}}\overset{\text{H}}{\text{C}} \rightleftharpoons \text{H}_2\text{O} + \overset{\text{H}}{\text{C}}\overset{\text{C}}{\text{C}}^- 
\]

Questions

Q9.7.1

If OH\(^-\) has a pKa of 14.00 in water, what pKa be required to deprotonate OH\(^-\)?

Solutions

S9.7.1

Need a stronger base, or a compound with a pKa > 14.00 to deprotonate.

Contributors and Attributions

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Objectives
After completing this section, you should be able to

1. write an equation to describe the reaction of an acetylide ion with an alkyl halide.
2. discuss the importance of the reaction between acetylide ions and alkyl halides as a method of extending a carbon chain.
3. identify the alkyne (and hence the acetylide ion) and the alkyl halide needed to synthesize a given alkyne.
4. determine whether or not the reaction of an acetylide ion with a given alkyl halide will result in substitution or elimination, and draw the structure of the product formed in either case.

Key Terms

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

• alkylation

Study Notes

The alkylation of acetylide ions is important in organic synthesis because it is a reaction in which a new carbon-carbon bond is formed; hence, it can be used when an organic chemist is trying to build a complicated molecule from much simpler starting materials.

The alkyl halide used in this reaction must be primary. Thus, if you were asked for a suitable synthesis of 2,2-dimethyl-3-hexyne, you would choose to attack iodoethane with the anion of 3,3- dimethyl-1-butyne rather than to attack 2-iodo-2-methylpropane with the anion of 1-butyne.

The reasons will be made clear in Chapter 11.

---

**Nucleophilic Substitution Reactions of Acetylides**

*Edit section*

Acetylide anions are strong bases and strong nucleophiles. Therefore, they are able to displace halides and other leaving groups in substitution reactions. The product is a substituted alkyne.

\[
\text{R-}&\equiv\text{C}:+\overset{\text{SN}_2}\longrightarrow \text{R'-}&\equiv\text{C}+\text{X}^-\rightarrow \text{R-C}&\equiv\text{C-R'}+\text{X}^-
\]

Because the ion is a very strong base, the substitution reaction is most efficient with methyl or primary halides without substitution near the reaction center,
Secondary, tertiary or even bulky primary substrates will give elimination by the E2 mechanism.

Nucleophilic Addition of Acetylides to Carbonyls

Acetylide anions will add to aldehydes and ketones to form alkoxides, which, upon protonation, give propargyl alcohols.

With aldehydes and non-symmetric ketones, in the absence of chiral catalyst, the product will be a racemic mixture of the two enantiomers.

Exercises

1. The pK$_a$ of ammonia is 35. Estimate the equilibrium constant for the deprotonation of pent-1-yne by amide, as shown above.

Answers:

1. Assuming the pK$_a$ of pent-1-yne is about 25, then the difference in pK$_a$s is 10. Since pentyne is more acidic, the formation of the acetylide will be favored at equilibrium, so the equilibrium constant for the reaction is about $10^{10}$

Questions

Q9.8.1

Give the possible reactants for the following formations:
Q9.8.2

Propose a synthetic route to produce 2-pentene from propyne and an alkyl halide.

Solutions

S9.8.1

S9.8.2

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