**Alkynes: An Introduction to Organic Synthesis**

This presentation was created by
Professor Carl H. Snyder
Chemistry Department
University of Miami
Coral Gables, FL 33124
CSnyder@miami.edu

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**sp Hybridization**

- 2 unhybridized p orbitals
- 2 sp orbitals

[Diagram of sp hybridization]

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**Structure of Acetylene**

- sp hybridized carbons
- a linear molecule

[Diagram of acetylene structure]

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**Naming Alkynes**

Alkynes follow the general rules of hydrocarbon nomenclature discussed in Sections 5.4 and 6.5. The suffix -yne is used, and the position of the triple bond is indicated by giving the number of the first alkyne carbon in the chain. Numbering the main chain begins at the end nearer the triple bond so that the triple bond receives as low a number as possible.

- \( \text{CH}_3\text{CH}≡\text{CH}_2 \)
- \( \text{CH}_3\text{CH}≡\text{CHCH}_3 \)
- \( \text{CH}_3\text{CH}≡\text{C}_2\text{H}_5 \)

Begin numbering at the end nearer the triple bond.

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**Alkyl, Alkenyl, and Alkynyl Groups**

<table>
<thead>
<tr>
<th>Group</th>
<th>Molecular Formula</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl</td>
<td>( \text{CH}_3\text{CH}(_2)_3\text{CH}_3 )</td>
<td>1-Butyl</td>
</tr>
<tr>
<td>1-Butenyl</td>
<td>( \text{CH}_3\text{CH}(_2)_2\text{CH}≡\text{CH}_3 )</td>
<td>1-Butenyl (vinyl group)</td>
</tr>
<tr>
<td>1-Butynyl</td>
<td>( \text{CH}_3\text{CH}(_2)_2\text{CH}≡\text{C}_2\text{H}_5 )</td>
<td>1-Butynyl (a alkyne group)</td>
</tr>
</tbody>
</table>
Terminal And Internal Alkynes

**Terminal alkyne** -- Contains a triple bond between C-1 and C-2: \( \text{R-C}≡\text{CH} \)
A hydrogen is bonded to an sp carbon.

**Internal alkyne** -- Both sp carbons are bonded to carbon atoms: \( \text{R-C}=\text{C-R'} \)

Creation of Triple Bond
Elimination of two \( \text{HX} \) from vicinal dihalide

Additions To Alkynes - Addition of \( \text{HX} \)
Markovnikov orientation
Can occur either once or twice

Addition of \( \text{HX} \)
A vinyllic carboxylic is an intermediate.

Stereochemistry of Addition

Addition of \( \text{HX} \) to an internal alkyne produces a *trans* product.

Addition of \( \text{X}_2 \)

Addition of \( \text{X}_2 \) can occur either once or twice
Produces a *trans* product
Addition of $\text{H}_2\text{O} \rightarrow \text{H}^+$ and Hg
Catalyzed

Acid-catalyzed, as in acid-catalyzed hydration of alkenes
Also requires Hg catalysis
Involves enol intermediate

Aldehydes and Ketones

Keto-Enol Tautomerism

Keto-enol tautomerism usually favors the keto form

Terminal vs. Internal

Internal alkyne gives a mixture of two ketones.
Addition of $\text{H}_2\text{O}$

**Hydroboration/Oxidation - Terminal Alkynes**

Terminal alkynes produce only aldehydes on hydroboration/oxidation.

**Acidity of Terminal Alkynes**

The C=C-H of terminal alkynes is more acidic than any other hydrogen of alkanes, alkenes or alkynes.

Addition of $\text{H}_2$

**Lithium And Ammonia**

This method gives a trans alkene through *anti* addition of $\text{H}_2$.

For a cis alkene, through *syn* addition, use the *Lindlar catalyst*.

For an alkane, use $\text{H}_2$ and Pd/C.

**A Choice of Reagents**

For a ketone from a terminal alkyne, use $\text{H}^+$, HgSO$_4$, H$_2$O.

For an aldehyde from a terminal alkyne, use hydroboration/oxidation.

**Acidity of Simple Hydrocarbons**

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
<th>$K_a$</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkene</td>
<td>H=C=CH$^-$</td>
<td>$10^{-4}$</td>
<td>Strong acid</td>
</tr>
<tr>
<td>Alkene</td>
<td>HO-C=CH$^-$</td>
<td>$10^{-6}$</td>
<td>Medium acid</td>
</tr>
<tr>
<td>Alkane</td>
<td>CH$_3$</td>
<td>$10^{-10}$</td>
<td>Weak acid</td>
</tr>
</tbody>
</table>

The C=C-H of terminal alkynes is more acidic than any other hydrogen of alkanes, alkenes or alkynes.
Stability of the Acetylide Anion

The greater the $s$ character of the orbital, the closer to the nucleus it lies and the lower its energy.

Alkylation of The Acetylide Anion

The reaction of an acetylide anion and a methyl or a $1^o$ alkyl halide results in the alkylation of the acetylide anion. Here the anion is methylated.

Mechanism of The Alkylation

The nucleophilic acetylide anion uses its lone pair to form a bond to the partially positive, electrophilic cation to form an intermediate. As the new C-Br bond begins to form, the Br-C bond begins to break in the transition state.

The new C-C bond is finally formed and the old C-Br bond is fully broken at the end of the reaction.

Organic Synthesis: Challenge

Organic synthesis is the art of preparing substituted alkynes from simpler precursors. Terminal alkynes can be prepared by alkylation of acetylene itself, and internal alkynes can be prepared by further alkylation of a terminal alkyne.

Alkylation: Generality

Because of its generality, acetylide alkylation is the best method for preparing substituted alkynes from simpler precursors. Terminal alkynes can be prepared by alkylation of acetylene itself, and internal alkynes can be prepared by further alkylation of a terminal alkyne.

Alkylation: Limitation

Acetylide anion alkylation is limited to primary alkyl bromides and alkenes, including $1^o$ alkyl bromides, of which will be discussed in more detail in Chapter 11. The problem is that acetylide anions are sufficiently strong bases to cause dehydrobromination instead of substitution when they react with primary or tertiary alkyl halides. For example, reaction of bromoalkanes with propyne anion yields the elimination product cyclopropene rather than the substitution product 3-bromo-2-propyne.

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Organic Synthesis: Strategy

There's no secret to planning an organic synthesis. All it takes is knowledge of the different reactions, some discipline, and a lot of practice. The only real trick is to work backwards, in what is often referred to as a retrosynthetic direction. Don't look at the starting material and ask yourself what reactions it might undergo. Instead, look at the final product and ask, "What was the immediate precursor to that product?" For example, if the final product is an alkyl halide, the immediate precursor might be an allene (to which you could add HX). Having found an immediate precursor, work backwards again, one step at a time, until you get back to the starting material. You have to keep the starting material in mind, of course, so that you can work back to it, but you don't want that starting material to be your main focus.

Problem #1

Convert a 5-carbon, terminal alkyne into a 6-carbon, cis-2-alkene.
What's the final step?
Problem #1 - Solution

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{C} & \equiv \text{C}^- \text{Na}^+ + \text{CH}_3\text{I} & \overset{\text{THF}}{\text{1-Pentyne}} \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{C} & \equiv \text{C}^- \text{Na}^+ & \text{2-Hexyne} \\
\text{CH}_3\text{CH}_2\text{CH}_3 & \overset{\text{Li} \text{dil. etal.}}{\text{cis-2-Hexene}} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} & \equiv \text{C}^- \text{Na}^+ & \text{2-Hexyne} \\
\text{CH}_3\text{CH}_2\text{CH}_3 & \overset{\text{Li} \text{dil. etal.}}{\text{cis-2-Hexene}}
\end{align*}
\]

Problem #2

\[
\text{HC} \equiv \text{CH} \ + \ \text{RX} \quad \overset{\text{Br}}{\longrightarrow} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

Acetylene \quad \text{Alkyl halide} \quad \text{2-Bromopentane}

Convert a 2-carbon alkyne into a 5-carbon, \(2^\circ\) alkyl bromide.

Problem #2 - Solution

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{or} \quad \overset{\text{HBr, Ether}}{\text{Br}} & \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_3 & \quad \text{or} \quad \overset{\text{HBr, Ether}}{\text{Br}} & \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_3
\end{align*}
\]
Problem #2 - Solution

\[
\text{HC} \equiv \text{CH} + \text{NaNH}_2, \text{NH}_3 \xrightarrow{1} \text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow{2} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH}
\]

Acetylene \hspace{1cm} 1-Pentyne

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow{3b, \text{Lindlar catalyst}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2
\]

Problem #3

\[
\text{HC} \equiv \text{CH} + \text{RX} \xrightarrow{\text{THF}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

Acetylene \hspace{1cm} Alkyl halide \hspace{1cm} 1-Hexanol

Convert a 2-carbon alkyne into a terminal, 6-carbon, unbranched alcohol

Problem #3 - Solution

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow{3b, \text{Lindlar catalyst}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

Problem #3 - Solution

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow{3b, \text{Lindlar catalyst}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

Problem #3 - Solution

\[
\text{HC} \equiv \text{CH} + \text{NaNH}_2, \text{NH}_3 \xrightarrow{1} \text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow{1, \text{H} - \text{Br}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}
\]

1-Alkyne

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow{3b, \text{Lindlar catalyst}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

2-Alkyne

End

Alkynes