Learning Guide for Chapter 13 - Alkynes

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I. Introduction to Alkynes

Classifying Alkynes

Which of these is an alkyne? What is the other one called?

\[
\begin{align*}
\text{alkyne} & \quad \text{unsaturated ketone} \\
\text{hydrocarbon w/ a C--C} & \quad \text{not a hydrocarbon, so not an alkyne}
\end{align*}
\]

Which of these is a terminal alkyne? Which is an internal alkyne?

\[
\begin{align*}
\text{internal alkyne} & \quad \text{terminal alkyne} \\
\text{C--C between 2 C's} & \quad \text{C--C on the end}
\end{align*}
\]

Alkenes could also be labeled this way, but they usually aren't. Why not?

alkenes - no change in properties or behavior

alkynes - different IR, acid/base properties, reactivity
Hybridization and bond formation

What hybridization do each of the carbons in acetylene have?

\[
\text{H} - \text{C} \equiv \text{C} - \text{H}
\]

sp  sp

hybridized atomic orbitals: sp + sp + p + p

What kind of molecular orbital forms each bond?

\[
\text{H} - \text{H}
\]

\[
\text{sigma}
\]

\[
\text{py}
\]

\[
\text{sigma}
\]

Where do each of the bonds come from?

C-H bond  \( s + \text{sp} = \text{sigma} \)

C-C σ bond  \( \text{sp} + \text{sp} = \text{sigma} \)

C-C π bonds  \( \text{p} + \text{p} = \text{pi} \)

What orientation will the pi bonds have to each other?  \( 90° \)

show molecular model  from the side

90°

How do triple bonds compare to double and single bonds in length?

\[
\text{HC=CH} < \text{H}_2\text{C=CH}_2 < \text{H}_3\text{C} \equiv \text{CH}_3
\]

triple bonds are shorter

121 pm 134 pm 153 pm

Geometry

What geometry do carbons in triple bonds have?  \text{linear}

Draw a 6 carbon alkyne with the triple bond on the end. Then draw a 6 carbon alkyne with the alkyne in the middle.

\[
\begin{align*}
\text{wrong} & \quad \text{not linear} \\
\text{right} & \quad \text{linear}
\end{align*}
\]

How big does a ring have to before it can contain a triple bond (and be stable)?

at least 9 carbons

one more than trans C=C in a ring

unstable!

stable

cyclooctyne has been isolated by polymerizes at room temp
Stereochemistry

Can the carbon in a triple bond be a stereocenter?  no :)

- correct - linear geometry
- no cis/trans
- no up/down

Can alkynes be chiral?  yes

other C's in the molecule can be stereocenters

Molecular formula

How many units of unsaturation does a triple bond have?  2

What is the molecular formula for a simple alkyne?  \( \text{C}_n\text{H}_{2n-2} \)

What would be the formula of an alkyne with 10 carbons?

\[ \text{C}_{10}\text{H}_{18} \]

What would be the formula of a cyclic alkyne with 10 carbons?

\[ \text{C}_{10}\text{H}_{16} \]

Stabilization

Which is more stable, an internal alkyne or a terminal alkyne? Why?

\[ \text{C} = \text{C} \quad \text{terminal less stable} \]

\[ \text{C} = \text{C} \quad \text{internal more stable} \]

like C=C : more stable = more conjugated pi bonds overlap neighboring w/ C-H bonds (hyperconjugation)

we'll look at delta H's on p 15
Reactivity

Where are the two places that alkynes can react?

1. H (terminal alkynes)  
2. Pi bonds

How can a terminal alkyne react with a base?

1. Weak acid  
   
   \[
   \text{base} \quad \rightarrow \quad \text{strong} \quad \rightarrow \quad \text{used in } S_N2 \text{ and } E2 \text{ reactions as a strong } \text{Nu/base - acetylde ion}
   \]

How can an alkyne react with an acid? With an electrophile?

2. Weak base  
   strong E

Which is more reactive, an alkene or an alkyne? alkyne

- 264 kJ/mol to break pi bond
- 226 kJ/mol to break pi bond

How is the product of an alkyne reaction different from the product of an alkene reaction?

alkene:  

\[
\text{alkyne: } \quad \begin{array}{c}
\text{HCl} \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\end{array} \\
\text{still a C=C left can react again}
\]
II. Natural Occurrences and Uses of Alkynes

Alkynes are rarely found in nature. What is one exception?

\[
\text{diacetylene} \quad \equiv \equiv \quad \text{C}_4\text{H}_2
\]

found in carbon-rich atmospheres of Uranus, Neptune, Pluto, Titan, Triton

Unsaturated compounds with carbon-carbon triple bonds have been found. How many are known? What do they often have in common?

about 1000 known often toxic

Here are some examples:

- **capicillin**
  
  ![capicillin.png](attachment://capicillin.png)
  
  an oil found in chrysanthemums, exhibits fungicidal activity

- **tariric acid**
  
  ![tariric_acid.png](attachment://tariric_acid.png)
  
  fatty acid found in the seed of a plant native to Guatemala

- **cicutoxin**
  
  ![cicutoxin.png](attachment://cicutoxin.png)
  
  a neurotoxin found in hemlock

- **hystrionicotoxin**
  
  ![hystrionicotoxin.png](attachment://hystrionicotoxin.png)
  
  highly toxic compound isolated from "poison arrow" frogs in the lower Amazon basin

Unsaturated compounds with carbon-carbon triple bonds have also been isolated or synthesized for use as drugs. Here are some examples:

- **ethynyl estradiol**
  
  ![ethynyl_estradiol.png](attachment://ethynyl_estradiol.png)
  
  birth control agent Ortho-Novum, Loestrol, Ovral, etc

- **parsalmide**
  
  ![parsalmide.png](attachment://parsalmide.png)
  
  prescription analgesic Parsal, Sinovial
What is the most useful alkyne in industry?

acetylene \( \text{HC} \equiv \text{CH} \) used in cutting and welding torches

How is it made?

1) heat limestone and carbon to 2000° C, then add water

\[
\text{CaO} + 3 \text{C} \quad \rightarrow \quad \text{Ca}^{+2} \quad \text{HC} \equiv \text{CH} \quad + \quad \text{CO} \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{HC} \equiv \text{CH} \quad + \quad \text{Ca(OH)}_2
\]

2) heat methane to 1500° C for 0.01 sec

\[
\text{CH}_4 + \text{O}_2 \quad \rightarrow \quad \text{HC} \equiv \text{CH}
\]

How is it stored?

can't be stored as a liquid under pressure - heat or shock cause it to decompose to carbon and hydrogen and explode

stored dissolved in acetone under moderate pressure, absorbed onto firebrick

What happens when it burns?

\[
2 \text{HC} \equiv \text{CH} + 5 \text{O}_2 \quad \rightarrow \quad 4 \text{CO}_2 + 2 \text{H}_2\text{O}
\]

6000° F - hottest flame from a commonly available organic gas
yellow, smoky flame in air, clear blue flame in pure oxygen

What is polyacetylene? What is it used for?

long chain of single, double bonds \( \text{CH}_2 = \text{CH}_2 \) \( \text{HC} \equiv \text{CH} \) made from acetylene

used for foil packaging for computer parts (dissipates static charge), light-weight batteries

when treated with iodine, first polymer to conduct electricity - nearly as good as silver - 2000 Nobel Prize
III. Physical Properties of Alkynes

Give the following properties of alkynes:

- polarity: nonpolar
- water solubility: not soluble
- density: less dense than water - will float
- melting and boiling points: similar to alkenes and alkanes of the same MW
- flammability: highly flammable
- storage issues: polymerizes easily, sometimes explosively
- odor: strong, pungent odor
- state of matter: 2-4 C's - gas; 5-10 C's - liquid; 10+ C's - solid

IV. Spectroscopy of Alkynes

IR Spectroscopy

What two bonds do alkynes have that alkanes do not?

\[ \text{C} \equiv \text{C} \quad 2200-2100 \text{ cm}^{-1} \]

\[ \text{C} - \text{H} \text{ on } \text{C} \equiv \text{C} \quad \text{around } 3300 \text{ cm}^{-1} \]

How do the IR spectra of terminal alkynes differ from those of internal alkynes?

- internal - no C-H on C\(_{\text{---}}\)C, no C\(_{\text{---}}\)C (no dipole)
- looks like an alkane

small dipole
small peak

no dipole
no peak
How does the carbon-carbon triple bond band compare to a double bond band?

\[ \text{C--C 2200-2100} \quad \text{C=\text{C 1680-1620}} \quad \text{higher frequency - stronger bond} \]

How does the triple bond in an alkyne compare to the triple bond in a nitrile?

\[ \text{C--C vs C---N} \quad \text{C---N is much deeper, absorbs more light (more polar)} \]

How does the C-H on an alkyne compare to the C-H on an alkene?

\[ \text{C-H on C---C 3100-3000 higher frequency, separate from C-H deeper} \]
\[ \text{C-H on C=C \sim 3300 lower frequency, left side of C-H small} \]

\(^1\text{H NMR Spectroscopy}\)

Where do H's on terminal alkynes appear?

\[ 1.7 - 3.1 \text{ ppm (not very useful, too many other things show up there)} \]

Is the H on a terminal alkyne always a singlet?

\[ \text{no - can be split by H's farther away than one C because of the pi bonds (long range coupling), but the coupling constants are very small (two peaks of doublet very close together)} \]

\(^{13}\text{C NMR Spectroscopy}\)

Where do C's in the triple bond of an alkyne appear? \[ 65-85 \text{ ppm (not very useful either)} \]

**V. Nomenclature of Alkynes**

**Common names**

Give common names of the following compounds.

- methylacetylene
- cyclopentylacetylene
- ethylmethylacetylene
- phenylacetylene
- cyclopropylmethylacetylene
- diisopropylacetylene
IUPAC names

What steps should you follow when naming an alkyne?

1. determine stereochemistry, if any
2. choose the principle chain and name it
3. number the principle chain
4. name and order the substituents

What are the priorities for choosing the principle chain?

1. must contain the C---C, any C=C (all, if possible)
2. longest
3. most substituents

How are the names formed?

one C---C: change "ane" to "yne", put # in front

C---C and C=C: change "ane" to "en" then add "yne", put C=C # in front, C---C inside

What are the priorities for numbering the principle chain?

1. C---C or C=C, whichever comes first
2. if numbers are the same, C=C
3. first substituent
4. alphabet
C---C over substituent

lowest # to first C---C

lowest # to whichever comes first, double or triple bond

lowest # to C=C if the numbers are equal

lowest # to first substituent

lowest # to first in alphabet if #'s are the same

How do you name a substituent containing a carbon-carbon triple bond?

add "yn" before "yl"  (no common names like vinyl and allyl as there are in alkenes)

ethyl  ethynyl

Where do you number a substituent from?

where it is connected to the ring

2-propynyl  1-propynyl

4-(2-propynyl)-1-cyclohexene
Name the following compounds.

1-pentyne

4-methyl-2-pentyne

1,5-hexadiyne

1-penten-3-yne

3-propyl-1-hexyne

4-(2-propynyl)-1-cyclopentene

trans-3-penten-1-yne

or (E)-

(Z)-3-sec-butyl-3-penten-1-yne

or (Z)-3-(1-methylpropyl)-3-penten-1-yne

(S)-3-chloro-1-cyclooctyne

1-cyclopentyl-1,4-pentadiyne

Draw the following compounds, using the correct geometry!

5-methyl-3-octyne

cyclohexylacetylene

3-ethynyl-1-cyclohexene

"yne is a line"

(notice what a big difference that C=C makes)
VI. Acid-base Properties of Alkynes

How does the electronegativity of an atom affect the acidity of a H attached to it?

more EN - more acidic

How acidic would you expect a H attached to a C to be?

not very acidic at all - C has low EN

Why are alkynes more acidic than alkenes or alkanes?

hybridization: sp > sp² > sp³

alkanes ~50, alkenes ~44, alkynes 26

remember this number!

What is the conjugate base of an alkyne called?

acetylide ion

What kind of base would be required to successfully react with an alkyne?

to favor the products, pKa must be larger than 26

look on chart

NaH, Na⁺ H⁻ → H₂, pKa 35

NaNH₂, Na⁺ H⁻ N⁻ H → NH₃, pKa 36

What would happen if an acetylide ion came in contact with an acid with a pKa less than 26?

pKa 16

base → acid

products favored

How do alkyne anions react? Nu or base

strong Nu

strong base

What would happen with a 2°?

E2 and S_N2

Which is more useful? S_N2 - most common way of making alkynes

E2 is a waste of acetylide ion - better to use t-butoxide
How could an $S_N2$ reaction be used to synthesize 5-methyl-1-hexyne from acetylene?

2 steps: 1) deprotonate the alkyne to form the Nu
2) react with an alkyl halide - $S_N2$

What alkyl halide would be needed to make the following alkynes?

- benzyl bromide
- 2-bromoethylcyclopentane
- propyl bromide
- methyl bromide

How many steps would be needed to make an internal alkyne from acetylene? 4

Why can't you add both alkyl halides at the same time? you would get a mixture of products

symmetrical? use 2 eq base, 2 eq RX, only one anion forms at a time

What difficulties would you encounter in making the following alkynes?

- 2° alkyl halide - E2 products as well as $S_N2$
- 3° alkyl halide - E2 only
- aryl halide - no $S_N2$

ONLY USE 1° RX!
VII. Synthesis of Alkynes by Elimination

When alkynes can't be formed by a substitution reaction, what other method is available?

- substitution
- elimination

How can elimination be used to make C=C?

What is different about making a triple bond?

- need two halides; need 2 eq of base; base must be stronger - double elimination

Why is a stronger base needed?

- elimination from an sp² C is much more difficult

Why aren't cumulated dienes formed?

- H's on sp² C's are more acidic than H's on sp³ C's

When a terminal alkyne is formed, an addition step where water is added is necessary. Why is this?

- the H is deprotonated by the base

How can this reaction be used to make alkenes into alkynes?
VIII. Reduction of Alkynes to Form Alkenes and Alkanes

What kinds of compounds can be formed when alkynes undergo an addition reaction with hydrogen?

[Diagrams showing the formation of alkenes and alkanes from alkynes]

When an alkyne is reacted with $H_2$ and a metal catalyst, what kind of product results?

[Diagram showing the reaction of an alkyne with $H_2$, Pt/C to form an alkene]

**Why can't we isolate the product of the first stage of this reaction?**

*it reacts with the $H_2$, Pd/C to form an alkane*

**Why does the alkene intermediate have cis stereochemistry?**  *syn addition*

How can this reaction be used to determine the relative stability of terminal and internal alkynes?

[Diagram showing the comparison of terminal and internal alkynes]

How could you use this reaction to synthesize an alkane chain?

[Diagrams showing the synthesis of an alkane chain]
What can you do to stop the reaction at the alkene?

use a less reactive catalyst - often called a "poisoned" catalyst

Lindlar catalyst = Pd/CaCO₃, PbOAc, quinoline

What advantage does this have over E2 reactions to make alkenes?

no constitutional isomers, no stereoisomers

What this can you tell about the reactivity of alkenes and alkynes from this reaction?

alkynes are more reactive - they will react, alkenes won't

How can a trans alkene be formed?

can't use addition of H₂ - always syn addition
totally different reaction needed

How is the Na here different from NaH?

no charge - Na metal = Na⁺ still has valence e-

Why can this be called a dissolving metal reaction?
sodium metal dissolves in ammonia - deep blue color

Where do the H's come from?

from the ammonia

What is the mechanism of this reaction?

you do not need to be able to reproduce this mechanism
Synthesize the following compounds from an alkyne.

- \( \text{H}_2 \) with Pd/C
- Na with \( \text{NH}_3 \)
- H₂ with Lindlar

**IX. Addition of HX and \( X_2 \) to Alkynes**

**Addition of HX**

If HCl, HBr, or HI is added to an alkyne, what product will result?

1 eq of HBr

- terminal alkynes - halide goes to the more substituted side

What will happen if an internal alkyne is not symmetrical?

- two products

What will happen if a second equivalent of HX is added?

- geminal dihalide results
What happens if there is peroxide present in an HBr addition?

Addition of $X_2$

What products are formed when one or two equivalents of Br$_2$ are added to an alkyne?

X. Hydration of Alkynes

Acid- and mercury-catalyzed hydration

What reagents are required to add water across a carbon-carbon triple bond?

What kind of product results? What happens to it?

tautomerization - H and == change places

Which side is favored on a terminal alkyne?  more substituted side

What will happen if an internal alkyne is not symmetrical?  2 products
Hydroboration-oxidation of alkynes

What product results when an alkyne is treated with a borane reagent?

\[
\text{H} = \text{W} = \text{W} \quad \text{W} = \text{H} \quad \text{W}
\]

1. BH\textsubscript{3}-THF
2. H\textsubscript{2}O\textsubscript{2}, OH\textsuperscript{-}

What complication could occur? How do we prevent this?

C=C in the enol could react with the borane again

- internal alkynes - steric hindrance of alkyne is enough
- terminal alkynes - use sterically hindered borane reagent

\[
\begin{align*}
\text{disiamylborane} & \quad \text{dicyclohexylborane} \\
\end{align*}
\]

What regioselectivity is observed when an alkyne is treated with a borane reagent?

\[
\text{H} = \text{W} = \text{W} \quad \text{W} = \text{H} \quad \text{W}
\]

1. disiamylborane
2. H\textsubscript{2}O\textsubscript{2}, OH\textsuperscript{-}

\[
\text{OH goes to the less substituted side}
\]

How could the following compounds be synthesized from an alkyne?

\[
\begin{align*}
\text{H} = \text{W} = \text{W} \quad \text{W} = \text{H} \quad \text{W}
\end{align*}
\]

1. disiamylborane
2. H\textsubscript{2}O\textsubscript{2}, OH\textsuperscript{-}
XI. Oxidation of Alkynes

What happens when an alkyne reacts with KMnO₄?

What happens when an alkyne reacts with ozone?

Match the following reactions and products:
### Synthesis of alkynes

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetylene → terminal alkyne</td>
<td>$\text{HC}≡\text{CH}$ $\xrightarrow{\text{NaNH}_2, \text{CH}_3\text{Br}}$ $\equiv$</td>
</tr>
<tr>
<td>terminal alkyne → internal alkyne</td>
<td>$\equiv$ $\xrightarrow{\text{NaNH}_2, \text{CH}_3\text{Br}}$ $\equiv$</td>
</tr>
<tr>
<td>vicinal dihalide → alkyne</td>
<td>$\text{X}–\equiv–\text{X}$ $\xrightarrow{\text{NaNH}_2 \text{ or } \text{KOH, } 200^\circ\text{C}}$ $\text{HC}≡\text{CH}$</td>
</tr>
<tr>
<td>geminal dihalide → alkyne</td>
<td>$\text{X}–\equiv–\text{X}$ $\xrightarrow{\text{NaNH}_2 \text{ or } \text{KOH, } 200^\circ\text{C}}$ $\text{HC}≡\text{CH}$</td>
</tr>
</tbody>
</table>

### Reactions of alkynes

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkyne → alkane</td>
<td>$\equiv$ $\xrightarrow{\text{H}_2 \text{ Pd/C}}$ $\text{C}_2\text{H}_4$</td>
</tr>
<tr>
<td>alkyne → cis alkene</td>
<td>$\equiv$ $\xrightarrow{\text{H}_2 \text{ Lindlar}}$ $\text{C}_2\text{H}_4$</td>
</tr>
<tr>
<td>alkyne → trans alkene</td>
<td>$\equiv$ $\xrightarrow{\text{Na \text{ NH}_3}}$ $\text{C}_2\text{H}_4$</td>
</tr>
<tr>
<td>alkyne → vinyl halide or geminal dihalide</td>
<td>$\equiv$ $\xrightarrow{\text{HX}}$ $\text{C}_2\text{H}_4\text{X}$ $\xrightarrow{\text{HX}}$ $\text{C}_2\text{H}_4\text{X}$</td>
</tr>
<tr>
<td>alkyne → vicinal vinyl dihalide or tetrahalide</td>
<td>$\equiv$ $\xrightarrow{\text{X}_2}$ $\text{C}_2\text{H}_4\text{XX}$ $\xrightarrow{\text{X}_2}$ $\text{C}_2\text{H}_4\text{XX}$</td>
</tr>
<tr>
<td>alkyne → ketone</td>
<td>$\equiv$ $\xrightarrow{\text{Hg(OAc)}_2, \text{H}_2\text{SO}_4, \text{H}_2\text{O}}$ $\text{C}_2\text{H}_4\text{O} : \text{C} : \text{O} : \text{H}$</td>
</tr>
<tr>
<td>alkyne → aldehyde</td>
<td>$\equiv$ $\xrightarrow{1. \text{disiamyl borane} \ 2. \text{H}_2\text{O}_2, \text{NaOH}}$ $\text{C}_2\text{H}_4\text{O} : \text{C} : \text{O} : \text{H}$</td>
</tr>
<tr>
<td>alkyne → diketone</td>
<td>$\equiv$ $\xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}}$ $\text{C}_2\text{H}_4\text{O} : \text{C} : \text{O} : \text{H}$</td>
</tr>
<tr>
<td>alkyne → two carboxylic acids</td>
<td>$\equiv$ $\xrightarrow{\text{O}_3 \ \text{H}_2\text{O}}$ $\text{C}_2\text{H}_4\text{O} : \text{C} : \text{O} : \text{H}$</td>
</tr>
</tbody>
</table>