Hybridization and geometry

Alkynes are hydrocarbons which contain a carbon-carbon triple bond.

What hybridization are the carbons involved?

What geometry do these carbons have?

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

Label all bonds in the acetylene molecule shown below as σ or π, and give what orbitals they come from.

H——C——C——H

Draw a picture of what you think these orbitals might look like.

True or false: a triple bond is made up of two double bonds between the same carbons, at right angles to each other.
Reactivity
Which is more reactive, the σ bond or π bonds? Why?

Is either of the π bonds more reactive than the other?

Will alkynes react as nucleophiles or electrophiles? Why? How strong will they be?

Use your knowledge of how an alkene will react to predict the product of an alkyne reaction with bromine.

\[
\text{alkene: } \begin{array}{c} \ \\ \\ \\ \end{array} \xrightarrow{::Br—Br::} \begin{array}{c} \ \\ \\ \\ \end{array}
\]

\[
\text{alkyne: } \begin{array}{c} \ \\ \\ \\ \end{array} \xrightarrow{::Br—Br::} \begin{array}{c} \ \\ \\ \\ \end{array}
\]

How are the two products different?

What happened to the alkyne geometry?

(Incidentally, how come we can get away with using the same zig zag shape to represent tetrahedral and trigonal planar geometry?)
Types of alkenes

The following words are used to classify alkynes. What do these words mean in everyday usage? What do you think they mean in terms of alkynes?

internal

terminal

Could you talk about a terminal or internal alkene? Why do you think this might be a useful distinction to make with alkynes that wasn't important with alkenes?

Cyclic alkynes

Could a cyclic alkyne exist?

What would make it difficult to have a cyclic alkyne?

How big do you think a cyclic alkyne would need to be in order to be stable? (use models)

Physical properties of alkynes

Physical properties of alkanes, alkenes, and alkynes are very similar.

polarity

water solubility

solubility in organic solvents

density

flammable?

bp = 36°C  
d = 0.63

bp = 30°C  
d = 0.64
Spectroscopy of alkynes

What two bonds do alkynes have that alkanes do not?

Is the triple bond stretching frequency higher or lower than the double bond stretching frequency? Why?

How is the C-H stretching band different in an alkyne and alkene?

How would the spectrum of an internal compound be different from a terminal compound?

Would IR be a could way to characterize an internal alkyne? Why or why not?

Why is the double bond visible but not the triple bond in the compounds below? What about the third compound?
Acidity of alkynes

Which is the most acidic? Why?

In order to deprotonate an alkyne, what kind of base would we need to use?

Which acid should be stronger if you want the reaction to go forward?

What does that say about the pKa of the conjugate acid of the base?

Which bases will work? (look at your pKa chart!)

Deprotonated alkynes are called acetylide ions. Now that we know how to form them, what will they do?

What type of reaction would an acetylide ion undergo in the present of an acid with a pKa smaller than 26?

What type of reaction would an acetylide ion undergo in the presence of a compound with a leaving group?
Natural occurrence and uses of alkynes

Alkynes are not often found in nature, but some compounds which contain carbon-carbon triple bonds have been found. Some therapeutic compounds also contain triple bonds. 

- Capillin - an oil found in chrysanthemums, exhibits fungicidal activity
- Icthyothereol - poisonous substance used by Amazon native Americans to coat arrow heads; causes convulsions

17-ethynylestradiol - birth control agent

- Hystronicotoxin - highly toxic compound isolated from "poison arrow" frogs in the lower Amazon basin

By far the most useful alkyne is acetylene. It burns in air with a smoky yellow flame, but in pure oxygen it gives a very hot blue flame used for welding and cutting torches.

\[ 2 \text{H} - \text{C} \equiv \text{C} - \text{H} + 5 \text{O}_2 \rightarrow \]

Nomenclature of Alkynes (9-2)

Common names

Simple alkynes are often named as derivatives of acetylene.
Substitutive names
The steps in naming an alkyne are similar to naming alkenes.

1. **Choose the principle chain.**

   ![Structure](image1.png)
   root name?

   ![Structure](image2.png)
   root name?

   ![Structure](image3.png)
   root name?

2. **Number the principle chain.**

   ![Structure](image4.png)

   ![Structure](image5.png)

   ![Structure](image6.png)

   ![Structure](image7.png)

   ![Structure](image8.png)
3. Name and order the substituents.

- ethyl
- ethenyl (vinyl)
- ethynyl

4. Give the name of the compound. Specify stereochemistry of chiral compounds or C=C if needed.
Draw the following compounds, using the correct geometry!

5-methyl-3-octyne  
cyclohexylacetylene  
3-ethynyl-1-cyclohexene

**Synthesis of Alkynes (9-7, 9-8)**

There are two ways to make an alkyne.

1 - Start with acetylene, which contains a triple bond already present, and attach groups to one or both sides using substitution reactions.

\[
\text{\ce{H=C=H}} \quad \text{\ce{H-\text{R}_{\text{substitution}}}}
\]

2 - Start with the carbon skeleton already present, and create a two double bonds one top of each other by using two elimination reactions in a row.

\[
\text{\ce{H-\text{R}_{\text{top}}}} \quad \text{\ce{H-\text{R}_{\text{bottom}}}}
\]
Synthesis by substitution

What alkyl halide will be necessary to prepare 5-methyl-1-hexyne from acetylene?

\[
\text{HC}≡\text{CH} \xrightarrow{\text{+}} \text{HC}≡\text{CH} + \text{HC}≡\text{CH}
\]

How can you turn acetylene into a nucleophile?

\[
\text{HC}≡\text{CH} \xrightarrow{\text{HC}≡\text{C}^-\text{Na}^+} \text{HC}≡\text{C}^-\text{Na}^+
\]

Write a reaction sequence in which acetylene can be converted to 5-methyl-1-pentyne.

Write a reaction sequence in which acetylene can be converted to 3-phenyl-1-propylene.

What difficulty would you encounter attempting to synthesize isopropyl acetylene?

We can also make internal alkynes by substitution. What would happen in the following reaction? How can you solve the problem?

\[
\text{HC}≡\text{CH} + \text{CH}_3\text{Cl} + \text{CH}_3\text{Cl} \xrightarrow{2 \text{ eq NaH}}
\]
Synthesis by elimination

Alkynes can also be formed from vicinal or geminal dihalides using a double elimination reaction. A much stronger base or high temperatures are required to make the vinyl halide undergo the second elimination. Alkynes which cannot be made using acetylide ions can be formed in this way.

It is possible for cumulated alkenes to be formed, but these are less stable, and the alkyne will predominate. If a terminal alkyne is formed, a second step of water must be used to protonate the acetylide.

Since vicinal dihalides can be made from alkenes, a two step synthesis allows an alkene with only one substituent on both sides to be transformed into an alkyne.
Reduction of Alkynes (9-9A,B,C)

Alkynes undergo many of the same reactions as alkenes, with some variations in reagents and products. We will first look at the addition of H₂, or reduction reactions.

Alkynes can be reduced to form alkanes, cis alkenes, or trans alkenes, depending on the reagents used.

Reduction to alkanes

The reduction of an alkyne to an alkene is faster than the reduction of an alkene to an alkane. When palladium, platinum, or nickel catalysts are used with hydrogen gas, the alkyne goes to an alkene and then on to an alkane.

When combined with the synthesis of alkynes, this can be an effective way to build alkane chains.
Reduction to cis-alkenes

The hydrogenation may be stopped at the first stage by using "poisoned" or deactivated catalysts. The most common one is called the Lindlar catalyst - it contains palladium on barium sulfate with lead acetate and/or quinoline.

\[
\text{H}_2 \\ \text{Lindlar catalyst}
\]

As with the hydrogenation of alkenes, the reaction gives syn addition, so cis alkenes are formed. This is the most common method of forming cis alkenes.

Reduction to trans-alkenes

Trans alkenes are formed using a very different reaction. The alkyne is treated with sodium metal dissolved in liquid ammonia (which has a deep, rich blue color). [Note that this a much different from sodium amide, NaNH$_2$, although they look similar at first glance.]

\[
\text{Na} \\ \text{NH}_3
\]

Sodium metal has an extra electron that it donates to the alkyne. A radical anion results which has trans stereochemistry. It removes a hydrogen from NH$_3$, gets another electron from a different Na atom, and then picks up another proton.

\[
\cdot \text{Na} \\ \text{H}^+ \dot{\text{N}}-\text{H} \\ \text{H} \quad \text{H} \\
\cdot \text{Na} \\ \text{H}^+ \dot{\text{N}}-\text{H} \\ \text{H} \quad \text{H}
\]

Synthesize the following compounds from an alkyne.
Addition Reactions of Alkynes (9-9D,E,F)

Addition of HX

Either one or two equivalents of HCl, HBr, and HI can be added to alkynes - the intermediate product is less reactive than the starting alkyne, so the intermediate product can be obtained. The addition to terminal alkynes is regioselective - the halide goes to the substituted side. The addition to an internal alkyne shows anti addition when only one equivalent is added.
As with addition of HBr to alkenes, the presence of organic peroxides changes the mechanism to a radical reaction, and reverses the regioselectivity. A mixture of E and Z isomers results.

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

Either one or two equivalents of Cl\(_2\) or Br\(_2\) can be added to alkynes. With the addition of one equivalent, anti addition is most commonly observed.
Addition of water (hydration)

In the presence of mercury salts (usually mercuric acetate or mercuric sulfate), acid, and water, alkynes can be hydrated similarly to alkenes. No NaBH₄ is needed in the alkyne reaction.

Only one equivalent of water can be added, because the product of is an enol, which is in equilibrium with the more stable aldehyde or ketone form (depending on whether the alcohol is on the end). This type of reaction is called a tautomerization, and we will discuss it further in the chapter on aldehydes and ketones.

The regioselectivity favors the more substituted side of a terminal alkyne.

Practice:

\[ \text{HgSO}_4, \text{H}_2\text{O} \rightarrow \text{HgSO}_4 \]

\[ \text{Hg(OAc)}_2 \]

\[ \text{HgSO}_4, \text{H}_2\text{O} \rightarrow \text{HgSO}_4 \]

\[ \text{Hg(OAc)}_2 \]
**Addition of water (hydroboration)** - Alkynes will undergo hydroboration-oxidation to give enols, which also tautomerize to produce aldehydes and ketones. The OH (then =O) goes to the less substituted side.

```
\begin{align*}
\text{Alkyne} & \xrightarrow{\text{1. BH}_3-\text{THF}} \\
& \xrightarrow{\text{2. H}_2\text{O}_2, \text{OH}^-} \text{Enol} \\
& \xrightarrow{\text{OH}} \text{Aldehyde or Ketone}
\end{align*}
```

Remember that in the reaction with alkenes, the borane reagent reacts with three different C=C's. When using alkynes as the starting material, it is important to prevent the borane from reacting with the alkenes that came from alkynes.

With internal alkynes, there is enough steric hindrance to prevent this side reaction. With terminal alkynes, however, we must use borane reagents with large, bulky groups on them. The most common are disiamylborane and dicyclohexylborane.

![Disiamylborane and Dicyclohexylborane](image)

```
\begin{align*}
\text{Cycloalkyne} & \xrightarrow{\text{1. disiamylborane}} \\
& \xrightarrow{\text{2. H}_2\text{O}_2, \text{OH}^-} \text{Aldehyde or Ketone}
\end{align*}
```

Practice:

```
\begin{align*}
\text{Alkyne} & \xrightarrow{\text{1. 2 eq dicyclohexylborane}} \\
& \xrightarrow{\text{2. 2 eq H}_2\text{O}_2, \text{OH}^-} \text{Aldehyde or Ketone}
\end{align*}
```

```
\begin{align*}
\text{Alkyne} & \xrightarrow{\text{1. BH}_3} \\
& \xrightarrow{\text{2. H}_2\text{O}_2, \text{OH}^-} \text{Aldehyde or Ketone}
\end{align*}
```
Oxidations of Alkynes (9-10)

Alkynes react with potassium permanganate twice to give a species with four alcohols. Geminal diols, like enols, are not favored by the equilibrium, and react to form C=O compounds with loss of a water molecule. It is important to keep this reaction cool and neutral, or the diketone will react further.

Like alkenes, alkynes can be cleaved using ozonolysis. No dimethyl sulfide or hydrogen peroxide is needed; carboxylic acids always result.

<table>
<thead>
<tr>
<th>Summary of alkyne reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of alkyynes</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>reaction</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetylene → terminal alkyne</td>
<td>HC≡CH + NaNH₂ or CH₃Br</td>
</tr>
<tr>
<td>terminal alkyne → internal alkyne</td>
<td>NaNH₂ or CH₃Br</td>
</tr>
<tr>
<td>vicinal dihalide → alkyne</td>
<td>NaNH₂ or KOH, 200°C</td>
</tr>
<tr>
<td>geminal dihalide → alkyne</td>
<td>NaNH₂ or KOH, 200°C</td>
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</table>
Reactions of alkynes

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