

## 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?



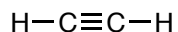
Which of these is a terminal alkyne? Which is an internal alkyne?



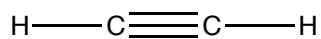
Alkenes could also be labeled this way, but they aren't. Why not?

Hybridization and bond formation

What hybridization do each of the carbons in acetylene have?

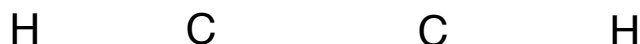


What kind of molecular orbital forms each bond?



Where do each of the bonds come from?

C-H bond

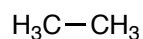
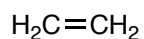


C-C  $\sigma$  bond

C-C  $\pi$  bonds

What orientation will the pi bonds have to each other?

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

Geometry

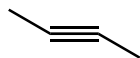
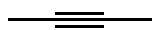
What geometry do carbons in triple bonds have?

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

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

## Stereochemistry

Can the carbon in a triple bond be a stereocenter?



Can alkynes be chiral?



## Molecular formula

How many units of unsaturation does a triple bond have?

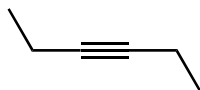
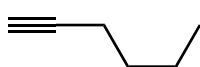
What is the molecular formula for a simple alkyne?

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

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

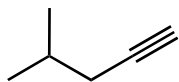
## Stabilization

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



Reactivity

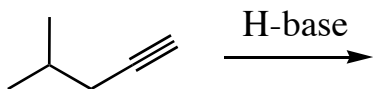
Where are the two places that alkynes can react?



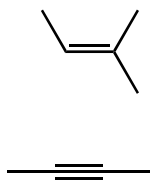
How can a terminal alkyne react with a base?



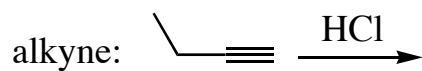
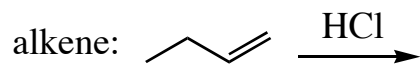
How can an alkyne react with an acid? With an electrophile?



Which is more reactive, an alkene or an alkyne?



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



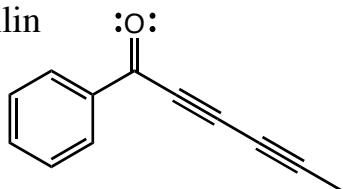
## II. Natural Occurrences and Uses of Alkynes

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

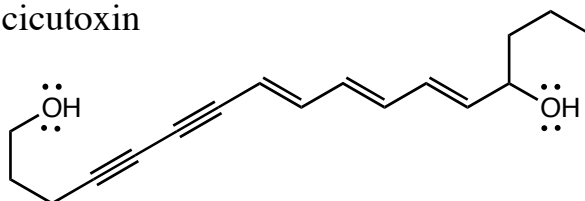
Unsaturated compounds with carbon-carbon triple bonds have been found. How many are known? What do they often have in common?

Here are some examples:

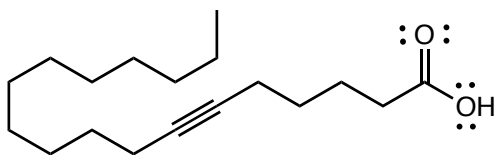
capicillin



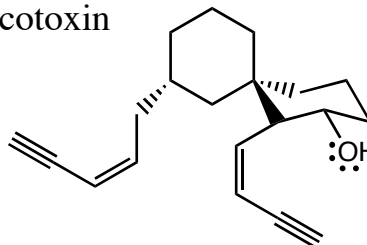
cicutoxin



tariric acid

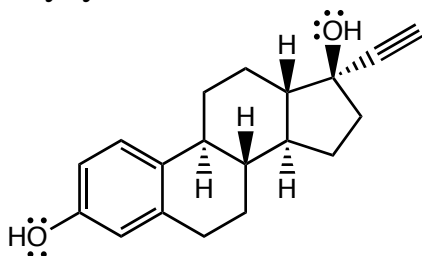


hystrioxicotin

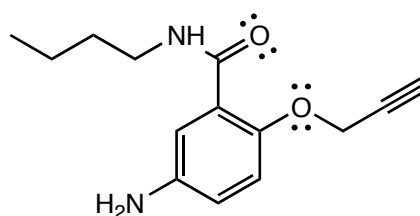


Unsaturated compounds with carbon-carbon triple bonds have also been isolated or synthesized for use as drugs. Here are some examples:

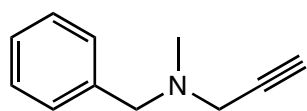
ethynyl estradiol



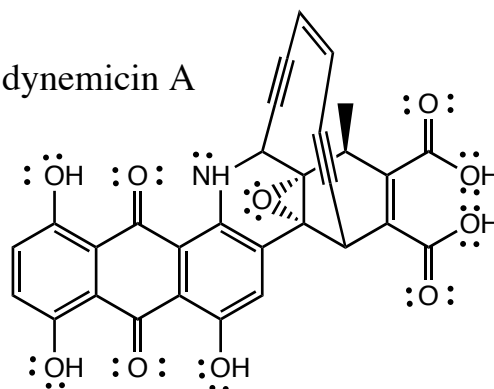
parsalimide



pargyline



dynemicin A



What is the most useful alkyne in industry?

How is it made?

How is it stored?

What happens when it burns?

What is polyacetylene? What is it used for?

### III. Physical Properties of Alkynes

Give the following properties of alkynes:

polarity

water solubility

density

melting and boiling points

flammability

storage issues

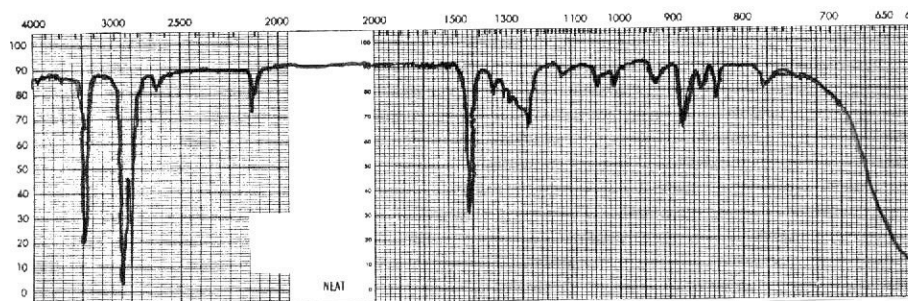
odor

state of matter

### IV. Spectroscopy of Alkynes

#### IR Spectroscopy

What two bonds do alkynes have that alkanes do not?



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

How does the carbon-carbon triple bond band compare to a double bond band?

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

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

### $^1\text{H}$ NMR Spectroscopy

Where do H's on terminal alkynes appear?

Is the H on a terminal alkyne always a singlet?

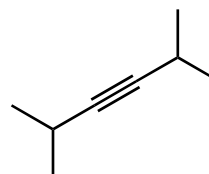
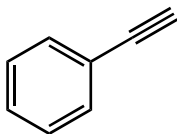
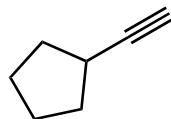
### $^{13}\text{C}$ NMR Spectroscopy

Where do C's in the triple bond of an alkyne appear?

## **V. Nomenclature of Alkynes**

### Common names

Give common names of the following compounds.





## IUPAC names

What steps should you follow when naming an alkyne?

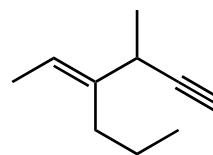
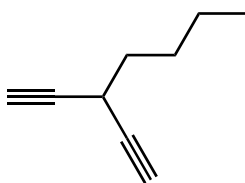
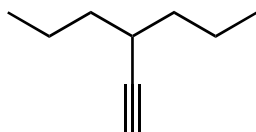
1.

2.

3.

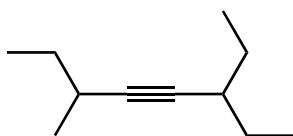
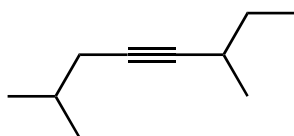
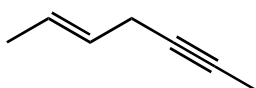
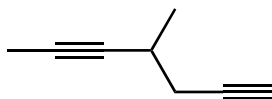
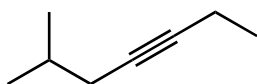
4.

What are the priorities for choosing the principle chain?

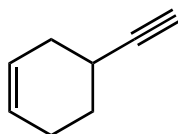
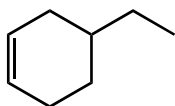


How are the names formed?

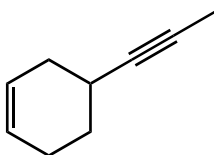
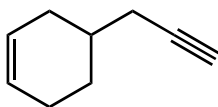
What are the priorities for numbering the principle chain?



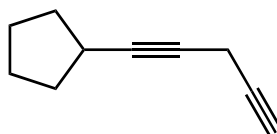
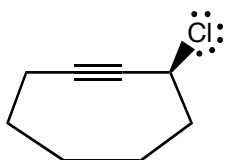
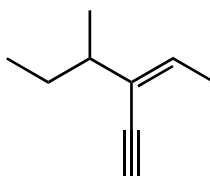
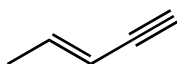
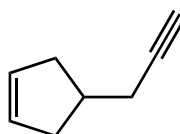
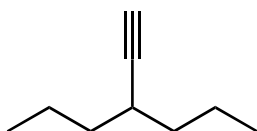
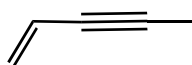
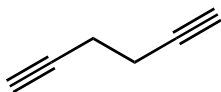
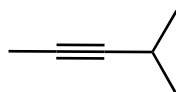
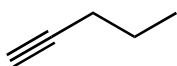
How do you name a substituent containing a carbon-carbon triple bond?



Where do you number a substituent from?



Name the following compounds.



Draw the following compounds, using the correct geometry!

5-methyl-3-octyne

cyclohexylacetylene

3-ethynyl-1-cyclohexene

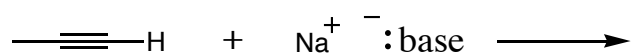
## VI. Acid-base Properties of Alkynes

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

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

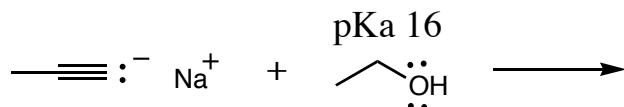
Why are alkynes more acidic than alkenes or alkanes?

What is the conjugate base of an alkyne called?

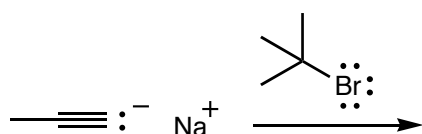
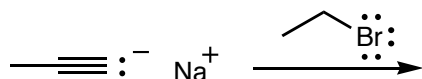


What kind of base would be required to successfully react with an alkyne?

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

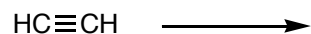


How do alkyne anions react?

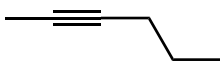
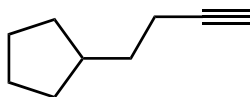
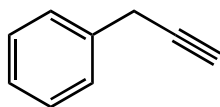


Which is more useful?

How could an S<sub>N</sub>2 reaction be used to synthesize 5-methyl-1-hexyne from acetylene?



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

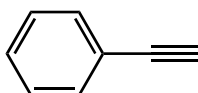
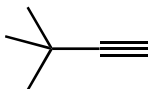
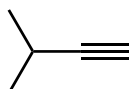


How many steps would be needed to make an internal alkyne from acetylene?



Why can't you add both alkyl halides at the same time?

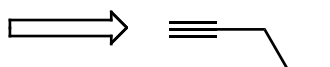
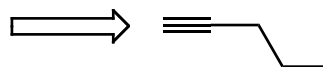
What difficulties would you encounter in making the following alkynes?



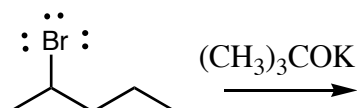
## VII. Synthesis of Alkynes by Elimination

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

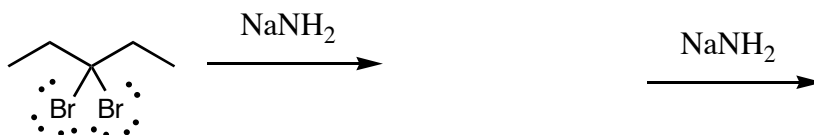
substitution



How can elimination be used to make C=C?



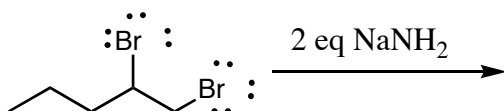
What is different about making a triple bond?



Why is a stronger base needed?

Why aren't cumulated dienes formed?

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

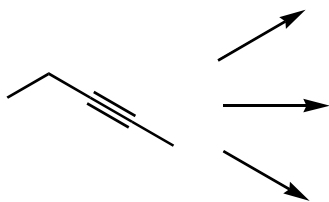


How can this reaction be used to make alkenes into alkynes?

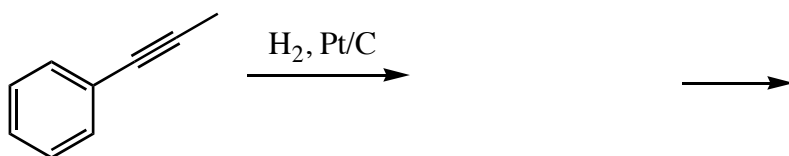


# VIII. Reduction of Alkynes to Form Alkenes and Alkanes

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



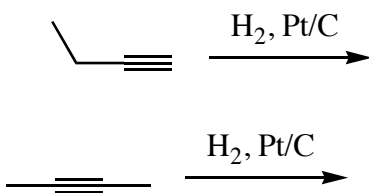
When an alkyne is reacted with  $H_2$  and a metal catalyst, what kind of product results?



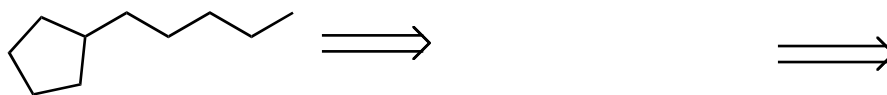
Why can't we isolate the product of the first stage of this reaction?

Why does the alkene intermediate have cis stereochemistry?

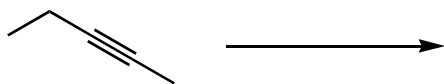
How can this reaction be used to determine the relative stability of terminal and internal alkynes?



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



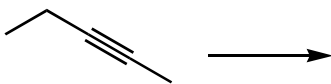
What can you do to stop the reaction at the alkene?



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

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

How can a trans alkene be formed?

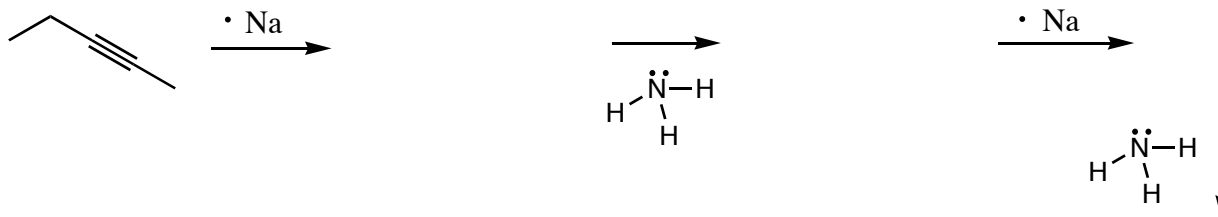


How is the Na here different from NaH?

Why can this be called a dissolving metal reaction?

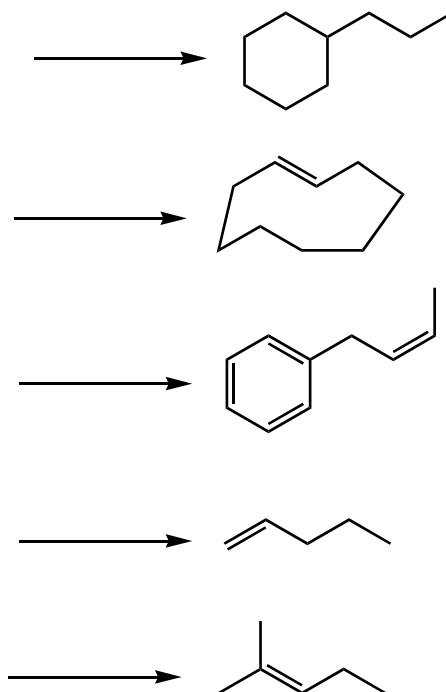
Where do the H's come from?

What is the mechanism of this reaction?





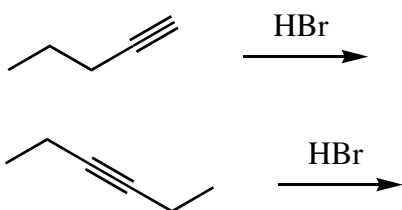
Synthesize the following compounds from an alkyne.



### IX. Addition of HX and X<sub>2</sub> to Alkynes

#### Addition of HX

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

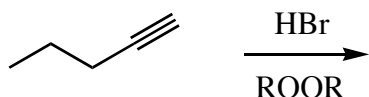


Which of these reactions demonstrates regioselectivity, and which side gets the halide?

What will happen if an internal alkyne is not symmetrical?

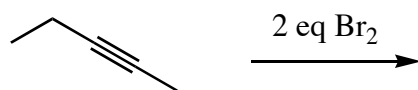
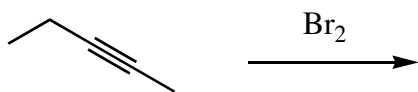
What will happen if a second equivalent of HX is added?

What happens if there is peroxide present in an HBr addition?



### Addition of X<sub>2</sub>

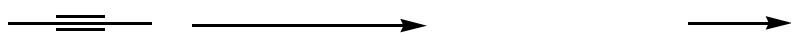
What products are formed when one or two equivalents of Br<sub>2</sub> are added to an alkyne?



## **X. Hydration of Alkynes**

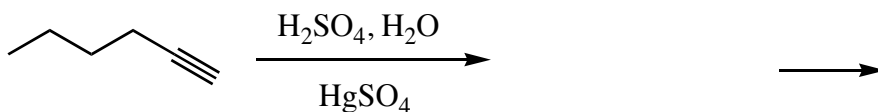
### Acid- and mercury-catalyzed hydration

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

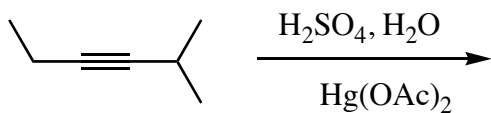


What kind of product results? What happens to it?

Which side is favored on a terminal alkyne?

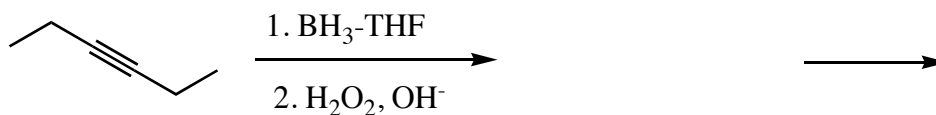


What will happen if an internal alkyne is not symmetrical?

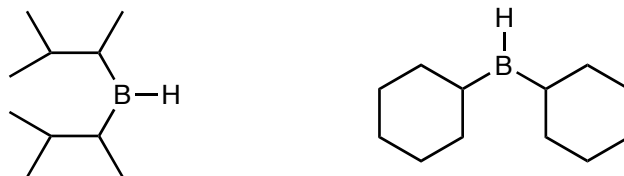


Hydroboration-oxidation of alkynes

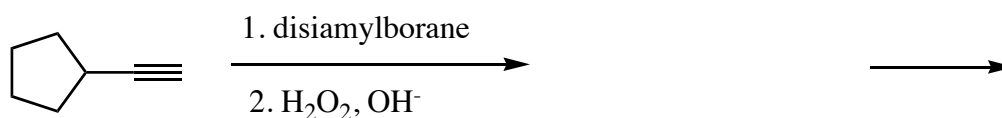
What product results when an alkyne is treated with a borane reagent?



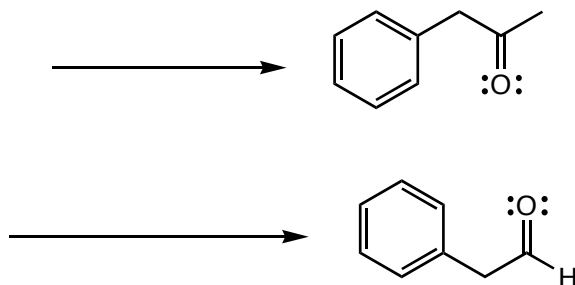
What complication could occur? How do we prevent this?



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

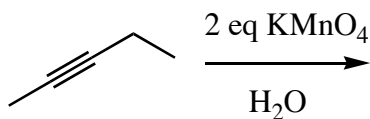


How could the following compounds be synthesized from an alkyne?

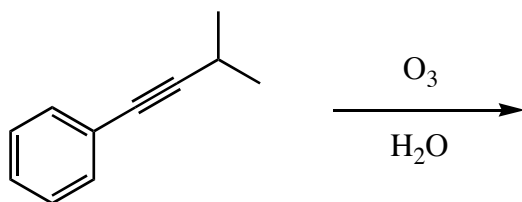


# XI. Oxidation of Alkynes

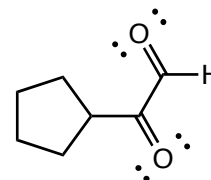
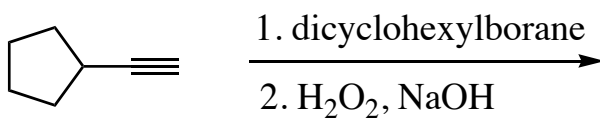
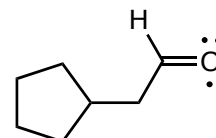
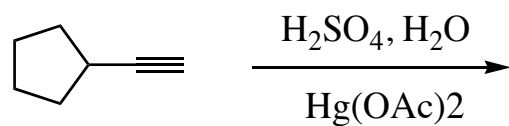
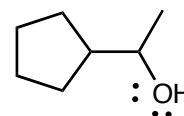
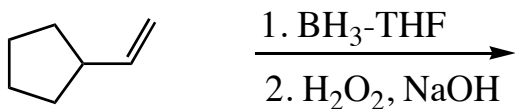
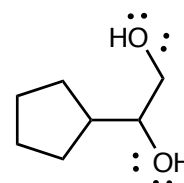
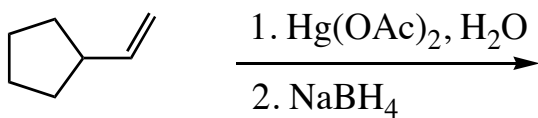
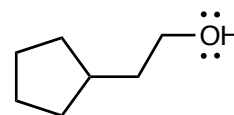
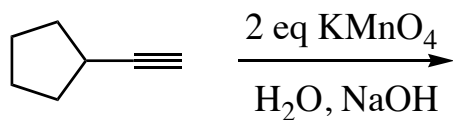
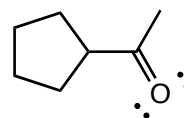
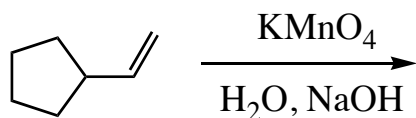
What happens when an alkyne reacts with  $\text{KMnO}_4$ ?



What happens when an alkyne reacts with ozone?



Match the following reactions and products:



## Summary of alkyne reactions

## Synthesis of alkynes

acetylene $\rightarrow$ terminal alkyne	$\text{HC}\equiv\text{CH} \xrightarrow[\text{CH}_3\text{Br}]{\text{NaNH}_2} \text{---}\equiv\text{---}$
terminal alkyne $\rightarrow$ internal alkyne	$\text{---}\equiv\text{---} \xrightarrow[\text{CH}_3\text{Br}]{\text{NaNH}_2} \text{---}\equiv\text{---}$
vicinal dihalide $\rightarrow$ alkyne	$\text{X}-\text{CH}_2-\text{CH}_2-\text{X} \xrightarrow[\text{KOH, 200}^\circ\text{C}]{\text{NaNH}_2 \text{ or}} \text{HC}\equiv\text{CH}$
geminal dihalide $\rightarrow$ alkyne	$\begin{array}{c} \text{X} \\   \\ \text{---C---} \\   \\ \text{X} \end{array} \xrightarrow[\text{KOH, 200}^\circ\text{C}]{\text{NaNH}_2 \text{ or}} \text{HC}\equiv\text{CH}$

## Reactions of alkynes

alkyne $\rightarrow$ alkane	$\text{---}\equiv\text{---} \xrightarrow[\text{Pd/C}]{\text{H}_2} \text{---CH}_2\text{---CH}_2\text{---}$
alkyne $\rightarrow$ cis alkene	$\text{---}\equiv\text{---} \xrightarrow[\text{Lindlar}]{\text{H}_2} \text{---CH=CH---}$
alkyne $\rightarrow$ trans alkene	$\text{---}\equiv\text{---} \xrightarrow[\text{NH}_3]{\text{Na}} \text{---CH=CH---}$
alkyne $\rightarrow$ vinyl halide or geminal dihalide	$\text{---}\equiv\text{---} \xrightarrow{\text{HX}} \begin{array}{c} \text{X} \\   \\ \text{---C=CH}_2 \end{array} \xrightarrow{\text{HX}} \begin{array}{c} \text{X} \quad \text{X} \\   \quad   \\ \text{---C---C---} \end{array}$
alkyne $\rightarrow$ vicinal vinyl dihalide or tetrahalide	$\text{---}\equiv\text{---} \xrightarrow{\text{X}_2} \begin{array}{c} \text{X} \quad \text{X} \\   \quad   \\ \text{---C=CH---} \end{array} \xrightarrow{\text{X}_2} \begin{array}{c} \text{X} \quad \text{X} \quad \text{X} \\   \quad   \quad   \\ \text{---C---C---C---} \end{array}$
alkyne $\rightarrow$ ketone	$\text{---}\equiv\text{---} \xrightarrow[\text{H}_2\text{SO}_4, \text{H}_2\text{O}]{\text{Hg}(\text{OAc})_2} \begin{array}{c} \text{:O:} \\    \\ \text{---C---} \end{array}$
alkyne $\rightarrow$ aldehyde	$\text{---}\equiv\text{---} \xrightarrow[2. \text{H}_2\text{O}_2, \text{NaOH}]{1. \text{disiamyl borane}} \begin{array}{c} \text{:O:} \\    \\ \text{---CH}_2\text{---CH}_2\text{---CH} \end{array} \text{H}$
alkyne $\rightarrow$ diketone	$\text{---}\equiv\text{---} \xrightarrow[\text{H}_2\text{O}]{\text{KMnO}_4} \begin{array}{c} \text{:O:} \quad \text{:O:} \\    \quad    \\ \text{---C---C---} \end{array}$
alkyne $\rightarrow$ two carboxylic acids	$\text{---}\equiv\text{---} \xrightarrow[\text{H}_2\text{O}]{\text{O}_3} 2 \begin{array}{c} \text{:O:} \\    \\ \text{---C---} \end{array} \text{:OH}$