

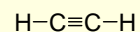
## Alkynes

- Hydrocarbons that contain carbon-carbon triple bonds
- Acetylene, the simplest alkyne is produced industrially from methane and steam at high temperature
- Our study of alkynes provides an introduction to organic synthesis, the preparation of organic molecules from simpler organic molecules

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## Electronic Structure of Alkynes

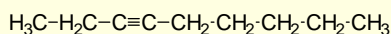
- Carbon-carbon triple bond result from sp orbital on each C forming a sigma bond and unhybridized p<sub>x</sub> and p<sub>y</sub> orbitals forming a π bond
- The remaining sp orbitals form bonds to other atoms at 180° to C-C triple bond.
- The bond is shorter and stronger than single or double
- Breaking a π bond in acetylene (HC≡CH) requires 318 kJ/mole (in ethylene it is 268 kJ/mole)



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## Naming Alkynes

- General hydrocarbon rules apply with “-yne” as a suffix indicating an alkyne.
- Numbering of chain with triple bond is set so that the smallest number possible include the triple bond.

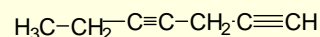


3-Nonyne

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## Diyines and Triynes

- A compound with two triple bonds is a diyne.
  - A triyne has three triple bonds.
- Number from chain that ends nearest a double or triple bond – double bonds is preferred if both are present in the same relative position.

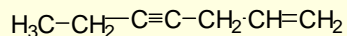


1,4-Heptydiyne

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## Enynes

- An enyne has a double bond and triple bond.
- Number for an Enynes starts at the multiple bond closest to the end (it does not matter whether it is a double or triple bond)

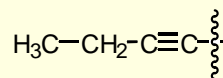


1-Hepten-4-yne

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## Alkynes as Substituents

Alkynes as substituents are called “alkynyl”.



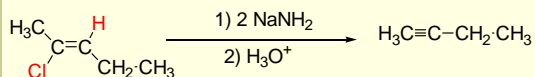
1-butynyl

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## Preparation of Alkynes:

### Elimination Reactions of Dihalides

- Treatment of a 1,2 dihaloalkane with KOH or NaOH (strong Base) produces a two-fold elimination of HX

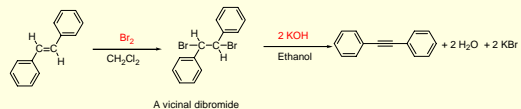


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## Preparation of Alkynes:

### Vicinal Dihalides

- Vicinal dihalides are available from addition of bromine or chlorine to an alkene.
- Intermediate is a vinyl halide.

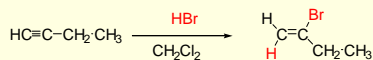


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## Reactions of Alkynes:

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

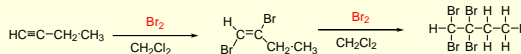
- Addition reactions of alkynes are similar to those of alkenes
- Intermediate alkene reacts further with excess reagent
- Regiospecificity according to Markovnikov



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## Addition of Bromine and Chlorine

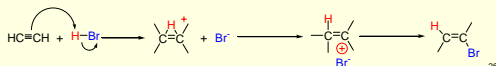
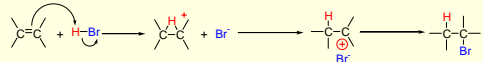
- Initial addition gives trans intermediate.
- Product with excess reagent is tetrahalide.



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## Addition of HX to Alkynes Involves Vinylic Carbocations

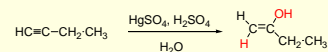
- Addition of H-X to alkyne should produce a vinylic carbocation intermediate
  - Secondary vinyl carbocations form less readily than primary alkyl carbocations
  - Primary vinyl carbocations probably do not form at all



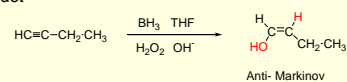
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## Hydration of Alkynes

- Addition of H-OH as in alkenes
  - Mercury (II) catalyzes Markovnikov oriented addition



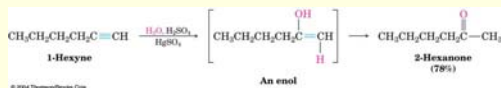
- Hydroboration-oxidation gives the non-Markovnikov product



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## Mercury(II)-Catalyzed Hydration

- Alkynes do not react with aqueous protic acids
- Mercuric ion (as the sulfate) is a Lewis acid catalyst that promotes addition of water in Markovnikov orientation
- The immediate product is a vinylic alcohol, or **enol**, which spontaneously transforms to a ketone

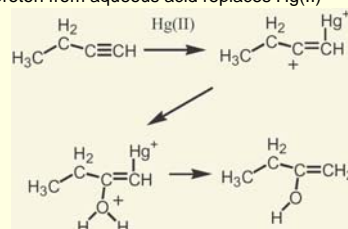


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## Mercury(II)-Catalyzed Hydration

### Mechanism

- Addition of Hg(II) to alkyne gives a vinylic cation
- Water adds and loses a proton
- A proton from aqueous acid replaces Hg(II)



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## Keto-enol Tautomerism

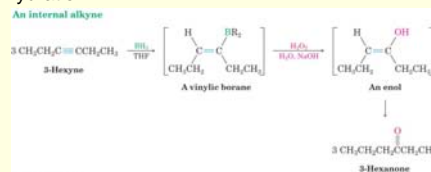
- Isomeric compounds that can rapidly interconvert by the movement of a proton are called **tautomers** and the phenomenon is called tautomerism
- Enols rearrange to the isomeric ketone by the rapid transfer of a proton from the hydroxyl to the alkene carbon
- The keto form is usually so stable compared to the enol that only the keto form can be observed



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## Hydroboration/Oxidation

- BH<sub>3</sub> (borane) adds to alkynes to give a vinylic borane
- Oxidation with H<sub>2</sub>O<sub>2</sub> produces an enol that converts to the ketone or aldehyde
- Process converts alkyne to ketone or aldehyde with orientation opposite to mercuric ion catalyzed hydration



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## Reduction of Alkynes

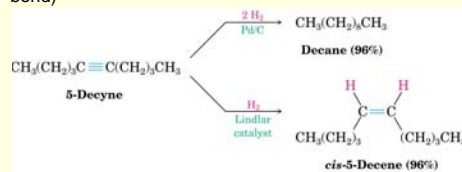
- Addition of H<sub>2</sub> over a metal catalyst (such as palladium on carbon, Pd/C) converts alkynes to alkanes (complete reduction)
- The addition of the first equivalent of H<sub>2</sub> produces an alkene, which is more reactive than the alkyne so the alkene is not observed



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## Conversion to cis-Alkenes

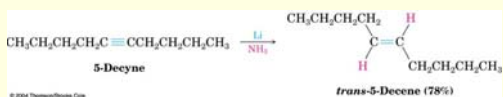
- Addition of H<sub>2</sub> using chemically deactivated palladium on calcium carbonate as a catalyst (the *Lindlar catalyst*) produces a cis alkene
- The two hydrogens add *syn* (from the same side of the triple bond)



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## Conversion to trans-Alkenes

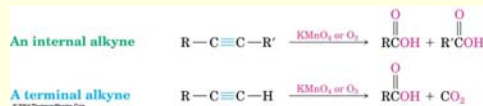
- Anhydrous ammonia (NH<sub>3</sub>) is a liquid below -33 °C
  - Alkali metals dissolve in liquid ammonia and function as reducing agents
- Alkynes are reduced to trans alkenes with sodium or lithium in liquid ammonia
- The reaction involves a *radical anion* intermediate



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## Oxidative Cleavage of Alkynes

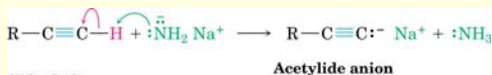
- Strong oxidizing reagents (O<sub>3</sub> or KMnO<sub>4</sub>) cleave internal alkynes, producing two carboxylic acids
- Terminal alkynes are oxidized to a carboxylic acid and carbon dioxide
- Neither process is useful in modern synthesis – were used to elucidate structures because the products indicate the structure of the alkyne precursor



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## Alkyne Acidity: Formation of Acetylide Anions

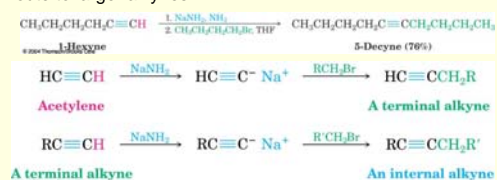
- Terminal alkynes are weak Brønsted acids (alkenes and alkanes are much less acidic, pK<sub>a</sub> ~ 25.)
- Reaction of strong anhydrous bases with a terminal acetylene produces an **acetylide ion**
- The sp-hybridization at carbon holds negative charge relatively close to the positive nucleus



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## Alkylation of Acetylide Anions

- Acetylide ions can react as nucleophiles as well as bases
- Reaction with a primary alkyl halide produces a hydrocarbon that contains carbons from both partners, providing a general route to larger alkynes



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