

Alkynes

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Introduction

- Alkynes contain a triple bond.
- General formula is C_nH_{2n-2} .
- Two elements of unsaturation for each triple bond.
- Some reactions are like alkenes: addition and oxidation.
- Some reactions are specific to alkynes.

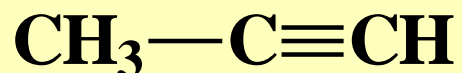
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Nomenclature: IUPAC

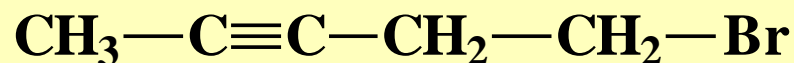
- Find the longest chain containing the triple bond.
- Change **-ane** ending to **-yne**.
- Number the chain, starting at the end closest to the triple bond.
- Give branches or other substituents a number to locate their position.

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Name these:

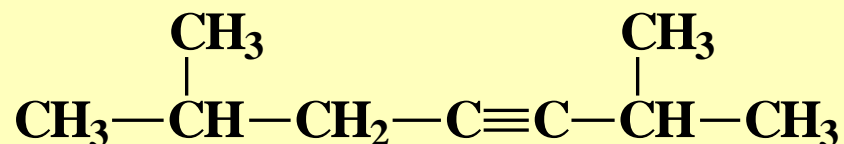


propyne



5-bromo-2-pentyne

5-bromopent-2-yne



2,6-dimethyl-3-heptyne

2,6-dimethylpept-3-yne

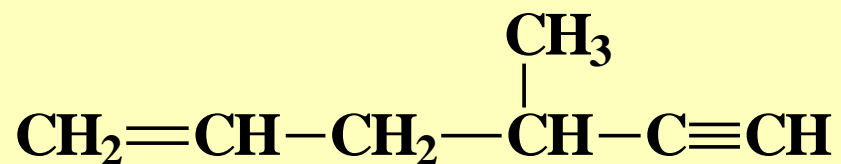
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Additional Functional Groups

- All other functional groups, except ethers and halides have a higher priority than alkynes.
- For a complete list of naming priorities, look inside the back cover of your text.

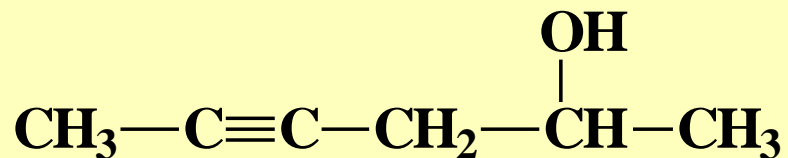
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Examples



4-methyl-1-hexen-5-yne

4-methylhex-1-en-5-yne



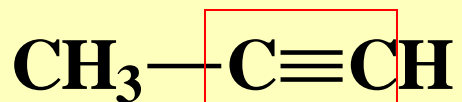
4-hexyn-2-ol

hex-4-yn-2-ol

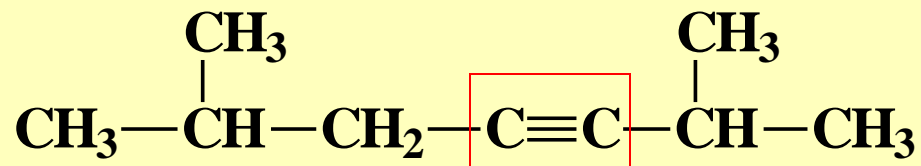
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Common Names

Named as substituted acetylene.



methylacetylene
(terminal alkyne)



isobutylisopropylacetylene
(internal alkyne)

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Physical Properties

- Nonpolar, insoluble in water.
- Soluble in most organic solvents.
- Boiling points similar to alkane of same size.
- Less dense than water.
- Up to 4 carbons, gas at room temperature.

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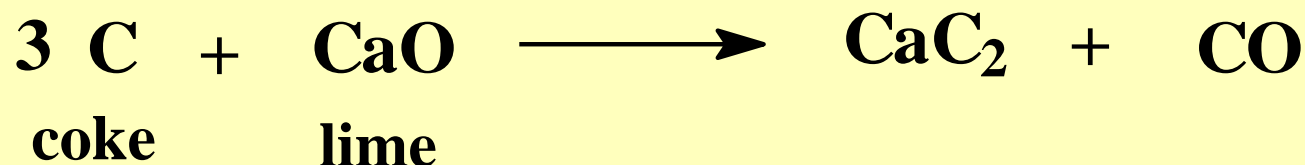
Acetylene

- Acetylene is used in welding torches.
- In pure oxygen, temperature of flame reaches 2800°C.
- It would violently decompose to its elements, but the cylinder on the torch contains crushed firebrick wet with acetone to moderate it.

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Synthesis of Acetylene

- Heat coke with lime in an electric furnace to form calcium carbide.
- Then drip water on the calcium carbide.

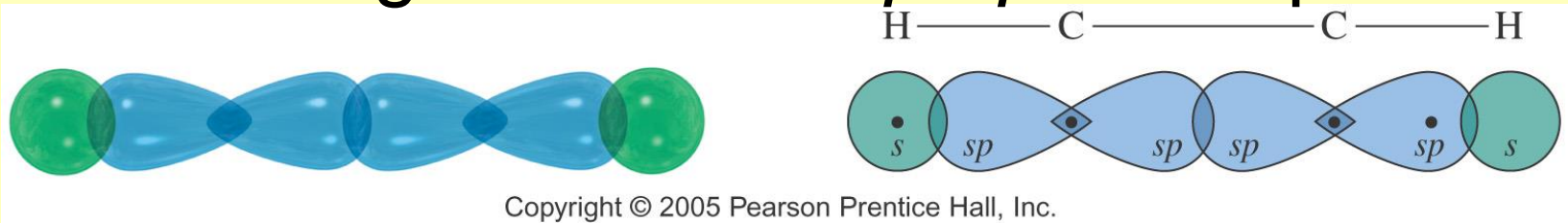


*This reaction was used to produce light for miners' lamps and for the stage.

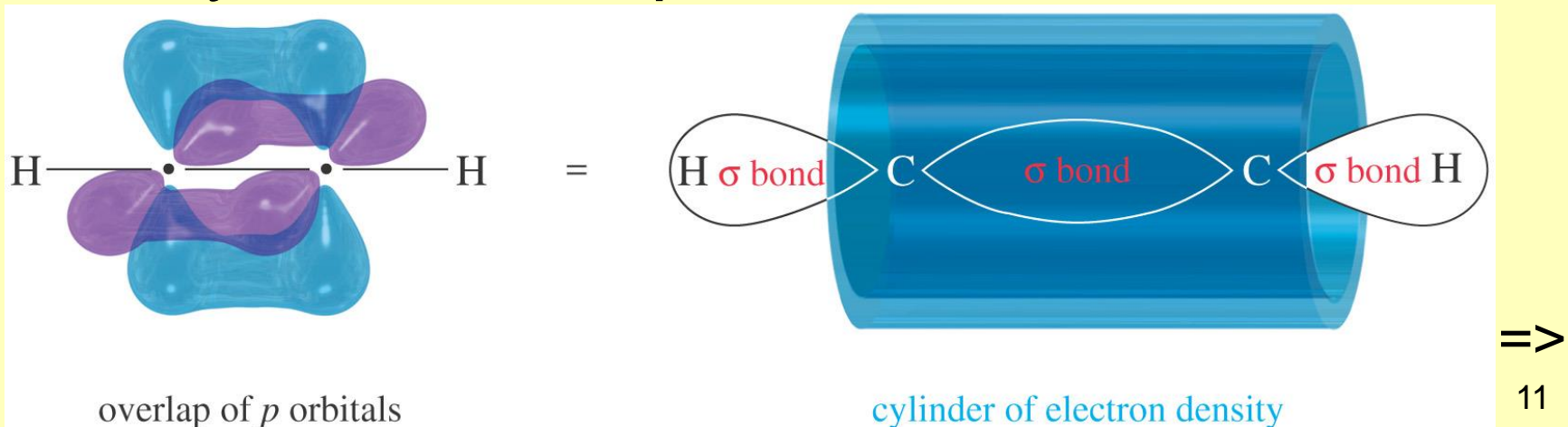
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Electronic Structure

- The sigma bond is sp - sp overlap.

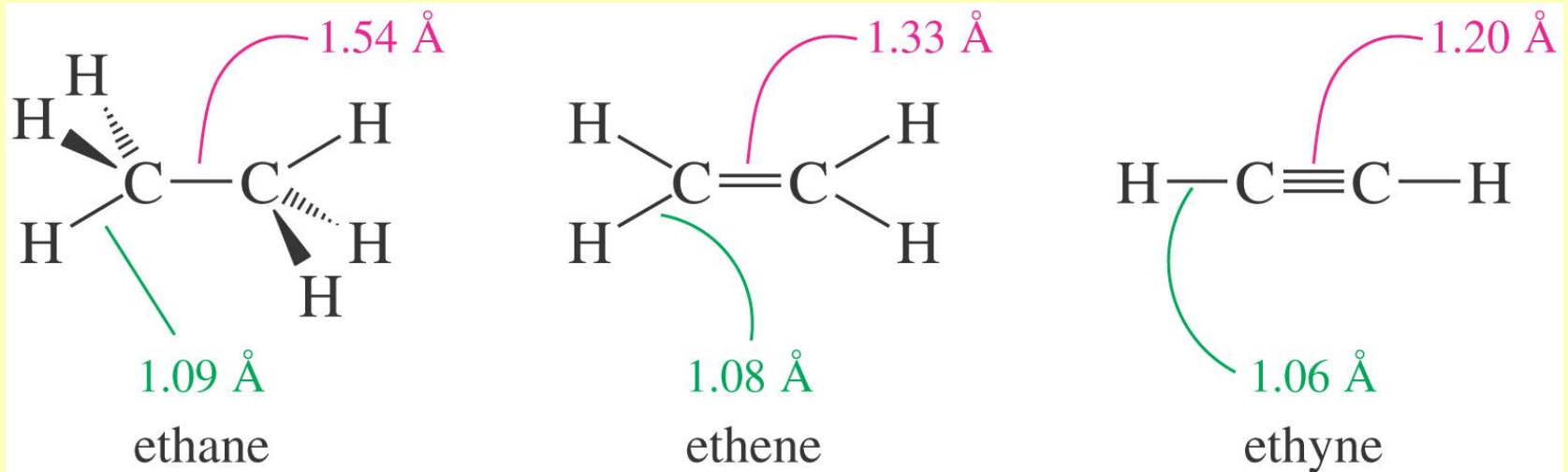


- The two pi bonds are unhybridized p overlaps at 90° , which blend into a cylindrical shape.



Bond Lengths

- More s character, so shorter length.
- Three bonding overlaps, so shorter.



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Bond angle is 180° , so linear geometry.

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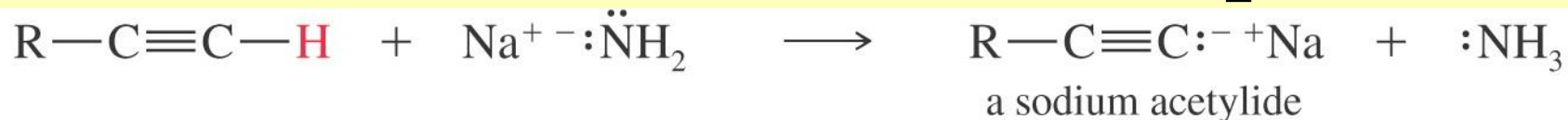
Acidity of Alkynes

- Terminal alkynes, $R-C\equiv C-H$, are more acidic than other hydrocarbons.
- Acetylene \rightarrow acetylide by NH_2^- , but not by OH^- or RO^- .
- More s character, so pair of electrons in anion is held more closely to the nucleus. Less charge separation, so more stable.

\Rightarrow

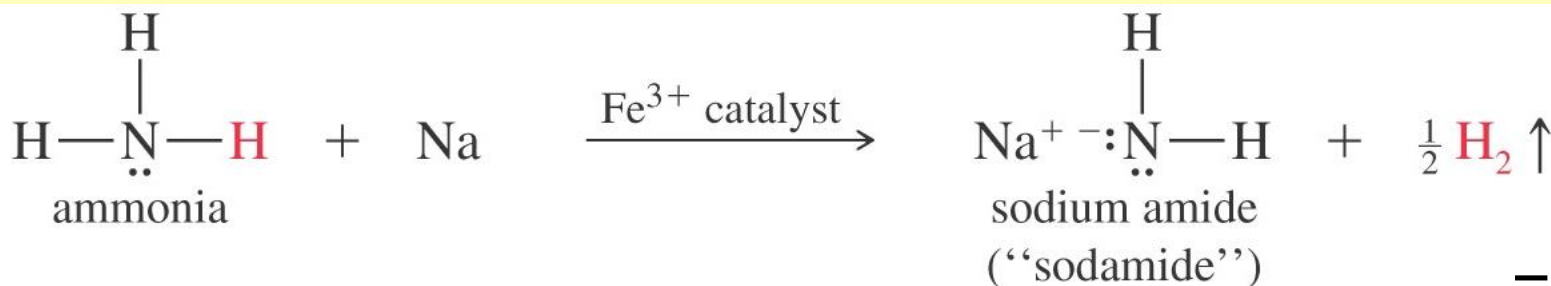
Forming Acetylide Ions

- H^+ can be removed from a terminal alkyne by sodium amide, NaNH_2 .



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- NaNH_2 is produced by the reaction of ammonia with sodium metal.



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Alkynes from Acetylides

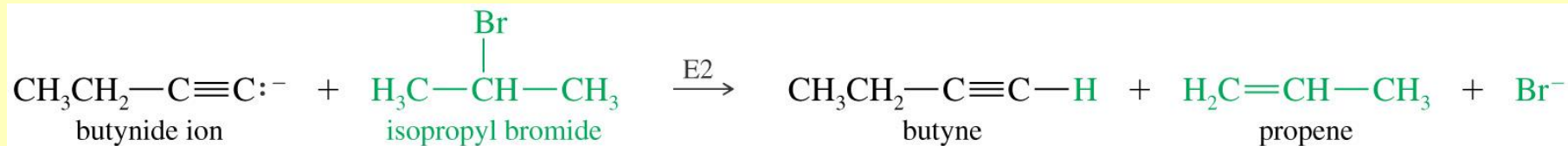
- Acetylide ions are good nucleophiles.
- S_N2 reaction with 1° alkyl halides lengthens the alkyne chain.



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Must be 1°

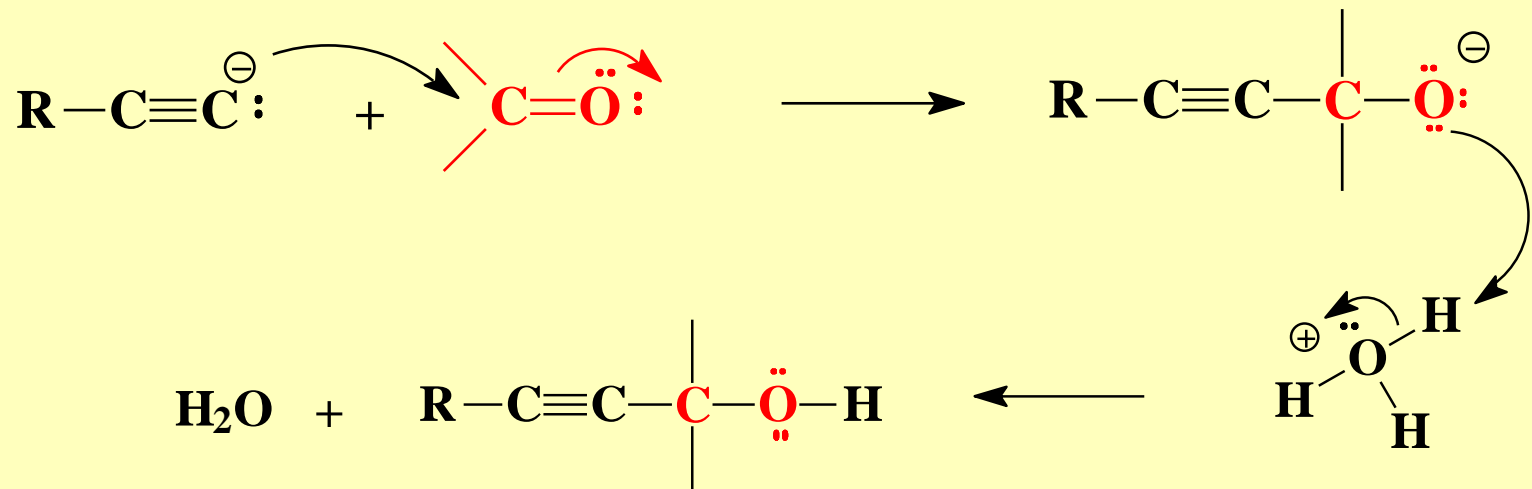
- Acetylide ions can also remove H⁺
- If back-side approach is hindered, elimination reaction happens via E2.



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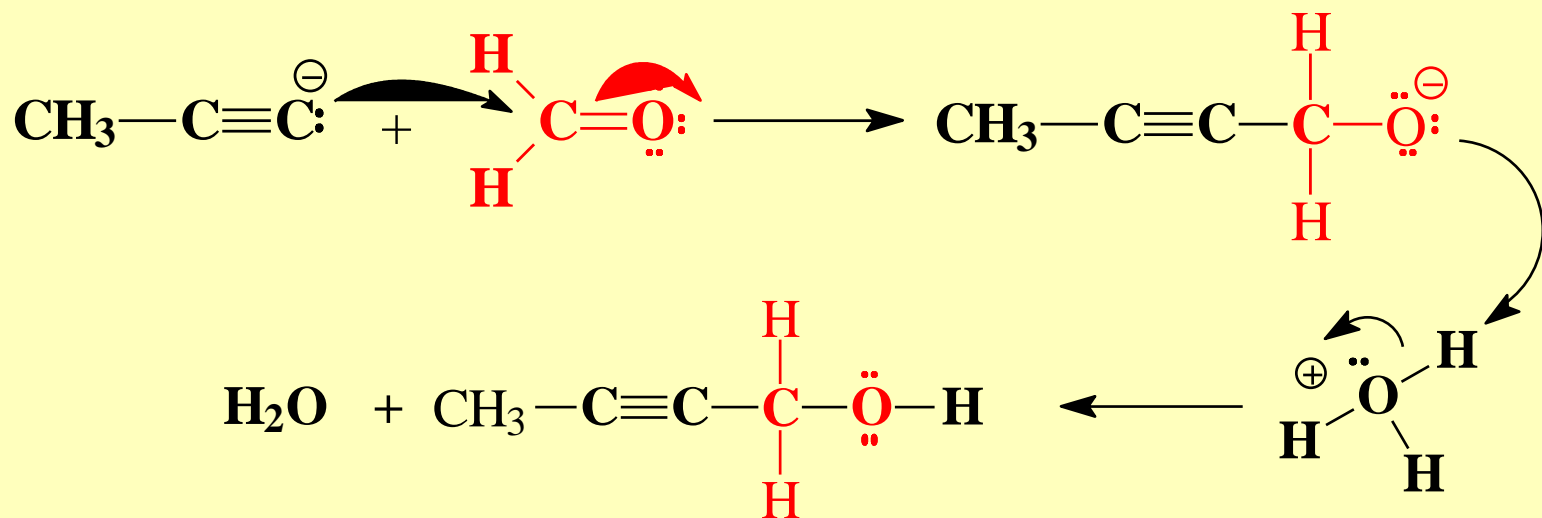
Addition to Carbonyl

Acetylide ion + carbonyl group yields an alkynol (alcohol on carbon adjacent to triple bond).



Add to Formaldehyde

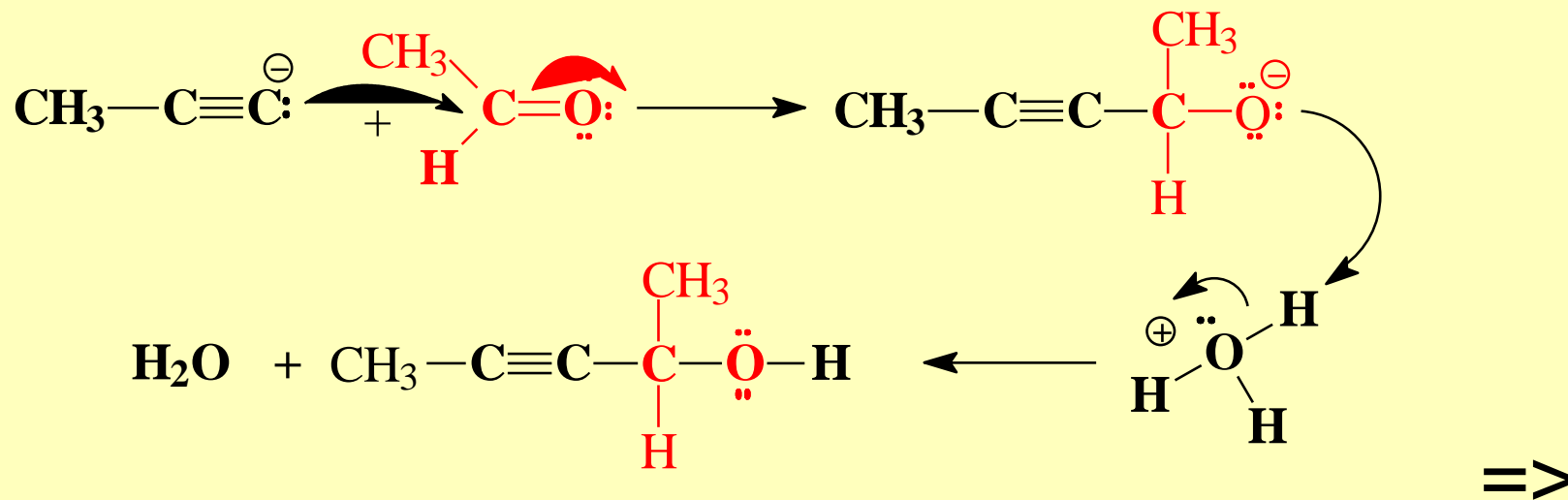
Product is a primary alcohol with one more carbon than the acetylide.



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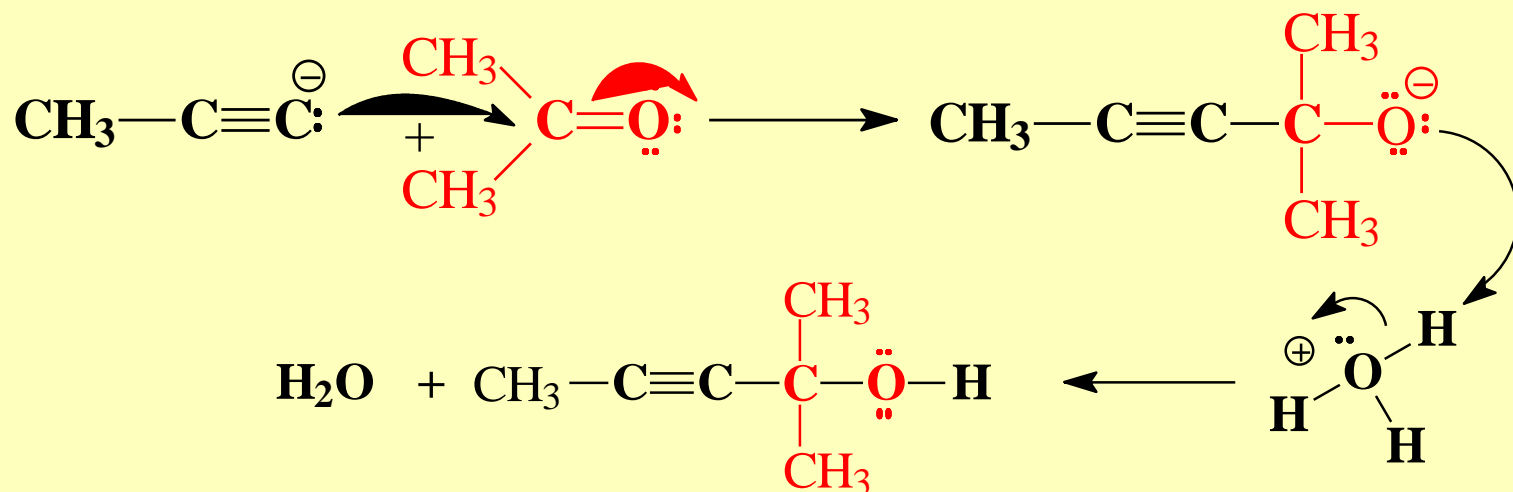
Add to Aldehyde

Product is a secondary alcohol, one R group from the acetylide ion, the other R group from the aldehyde.



Add to Ketone

Product is a tertiary alcohol.



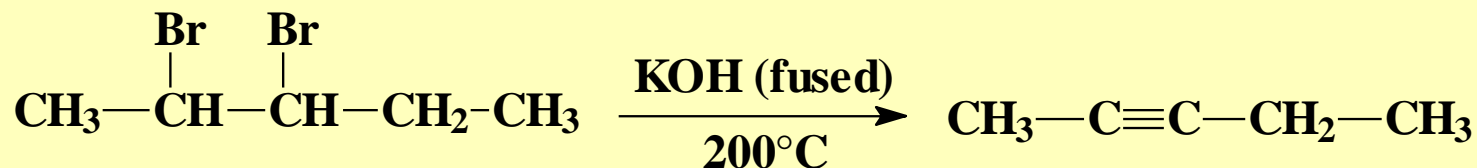
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Synthesis by Elimination

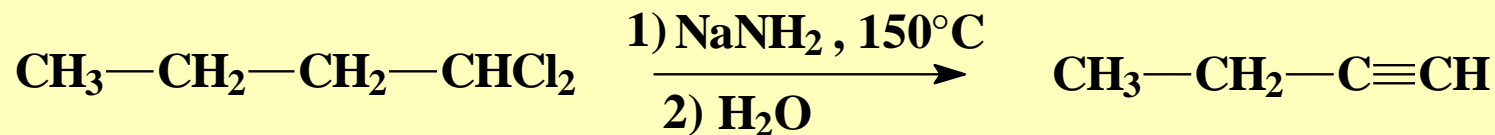
- Removal of two molecules of HX from a vicinal or geminal dihalide produces an alkyne.
- First step (-HX) is easy, forms vinyl halide.
- Second step, removal of HX from the vinyl halide requires very strong base and high temperatures.

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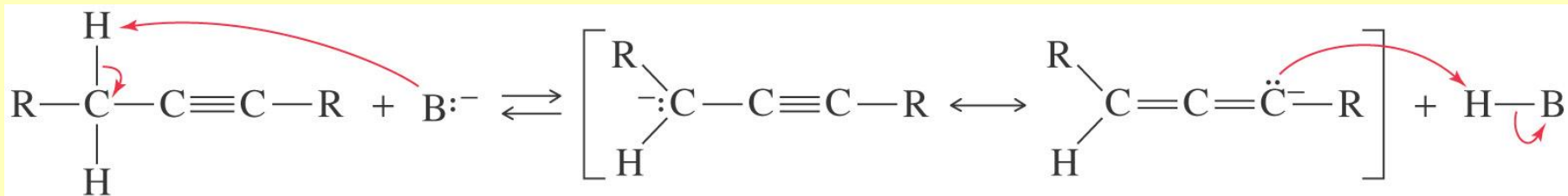
Reagents for Elimination



- Molten KOH or alcoholic KOH at 200°C favors an internal alkyne.
- Sodium amide, NaNH₂, at 150°C, followed by water, favors a terminal alkyne.

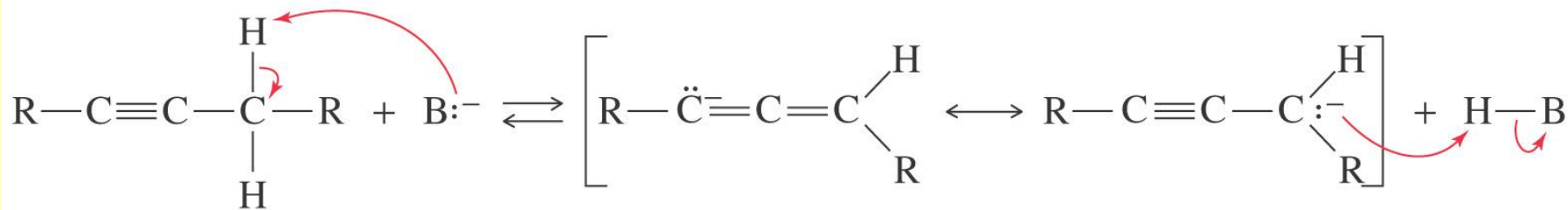
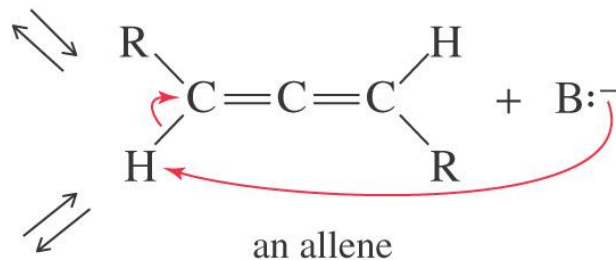


Migration of Triple Bond



an acetylene

resonance-stabilized carbanion



an isomerized acetylene

resonance-stabilized carbanion

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Addition Reactions

- Similar to addition to alkenes.
- Pi bond becomes two sigma bonds.
- Usually exothermic.
- One or two molecules may add.

TABLE 9-3 Approximate Bond Energies of Carbon–Carbon Bonds

Bond	Total Energy	Class of Bond	Approximate Energy
C—C	347 kJ (83 kcal)	alkane sigma bond	347 kJ (83 kcal)
C=C	611 kJ (146 kcal)	alkene pi bond	264 kJ (63 kcal)
C≡C	837 kJ (200 kcal)	second alkyne pi bond	226 kJ (54 kcal)

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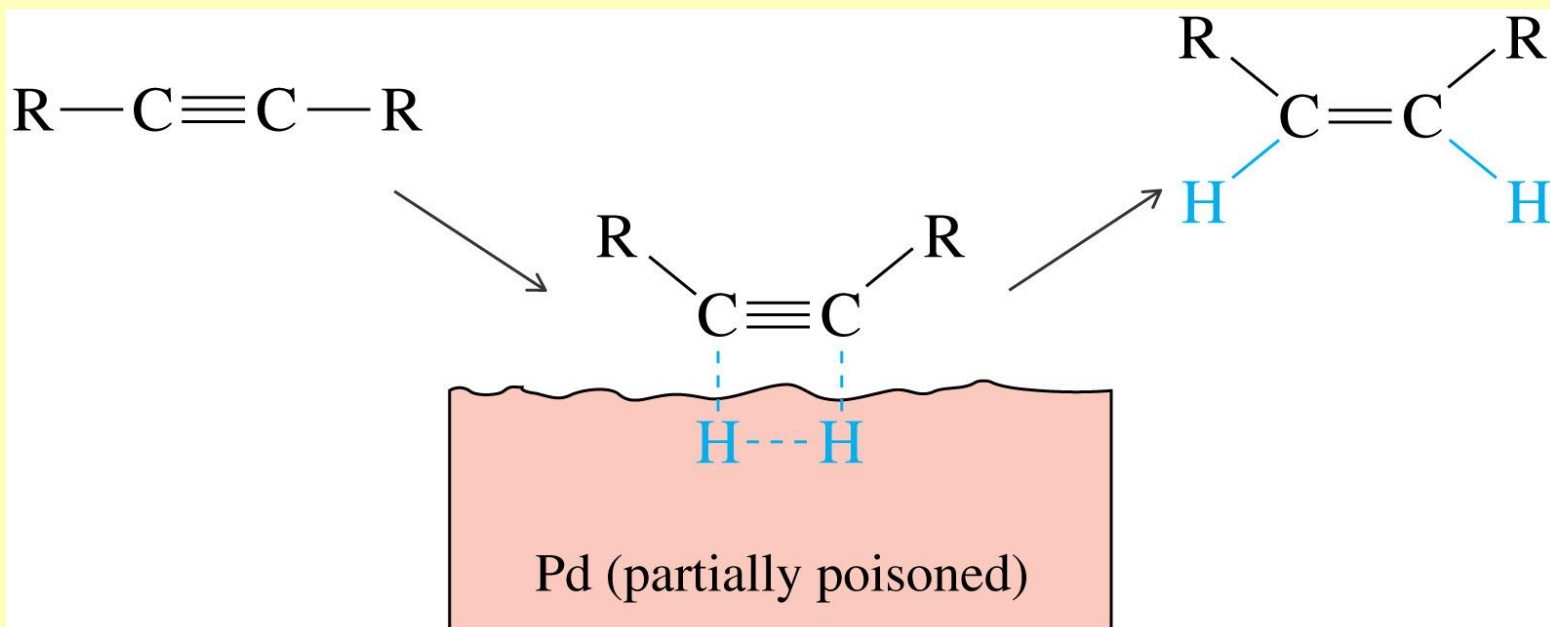
Addition of Hydrogen

- Three reactions:
- Add lots of H_2 with metal catalyst (Pd, Pt, or Ni) to reduce alkyne to alkane, completely saturated.
- Use a special catalyst, Lindlar's catalyst, to convert an alkyne to a **cis**-alkene.
- React the alkyne with sodium in liquid ammonia to form a **trans**-alkene.

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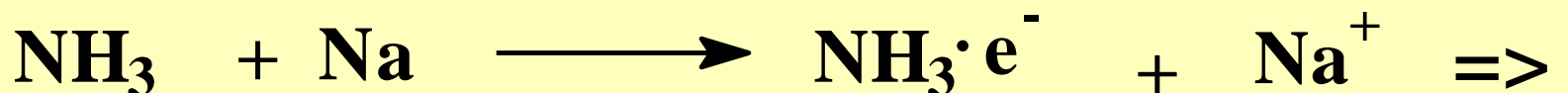
Lindlar's Catalyst

- Powdered BaSO_4 coated with Pd, poisoned with quinoline.
- H_2 adds syn, so **cis**-alkene is formed.



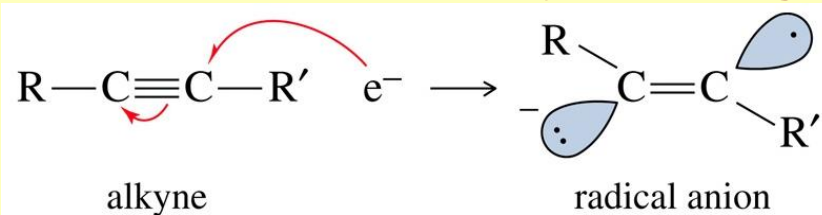
Na in Liquid Ammonia

- Use dry ice to keep ammonia liquid.
- As sodium metal dissolves in the ammonia, it loses an electron.
- The electron is solvated by the ammonia, creating a deep blue solution.

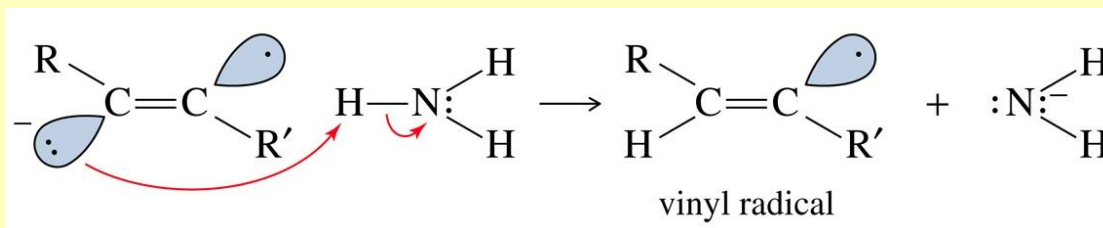


Mechanism

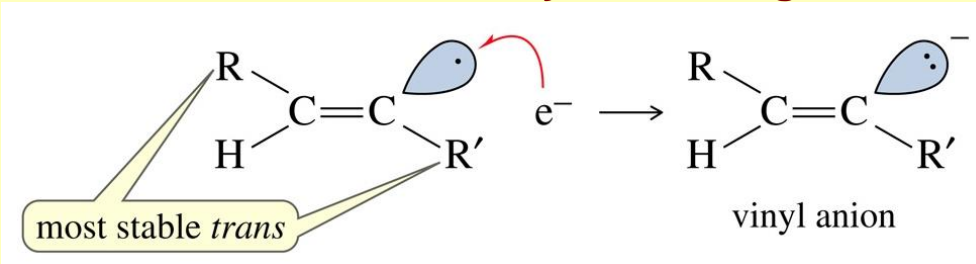
Step 1: An electron adds to the alkyne, forming a radical anion



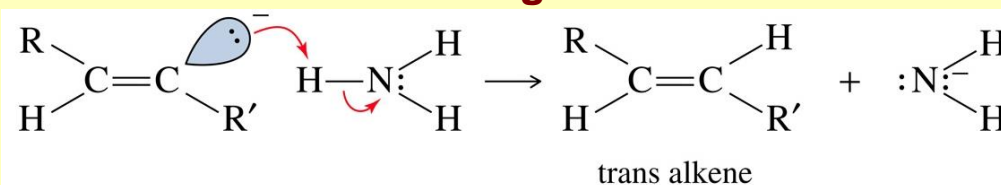
Step 2: The radical anion is protonated to give a radical



Step 3: An electron adds to the alkyne, forming an anion

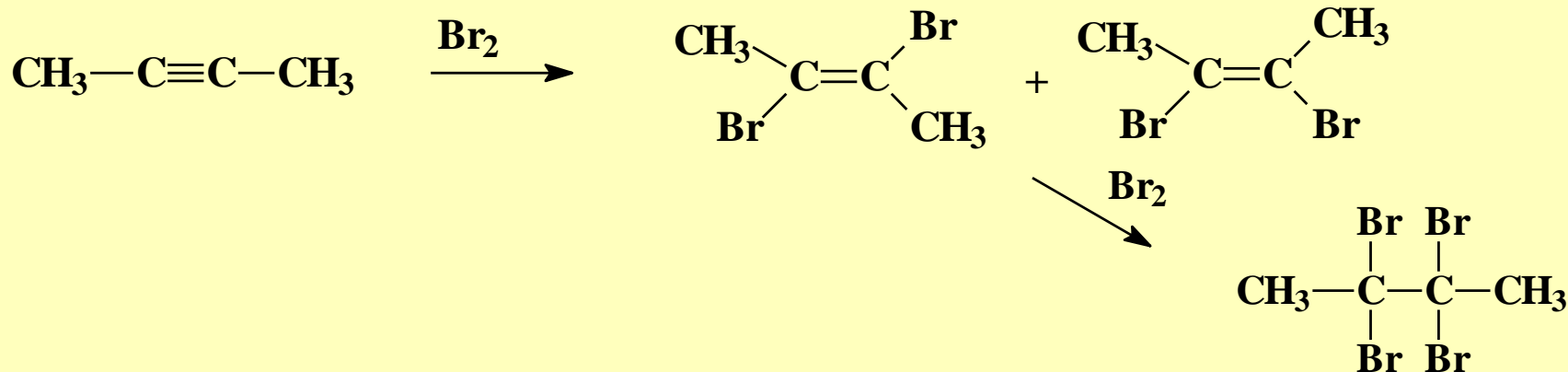


Step 4: Protonation of the anion gives an alkene



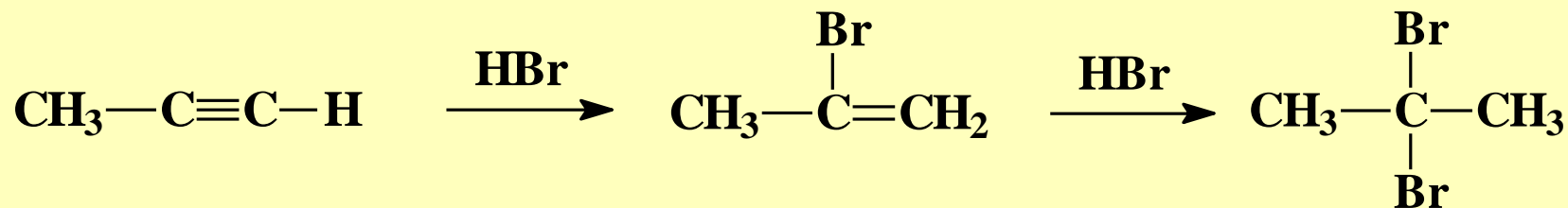
Addition of Halogens

- Cl_2 and Br_2 add to alkynes to form vinyl dihalides.
- May add syn or anti, so product is mixture of **cis** and **trans** isomers.
- Difficult to stop the reaction at dihalide.



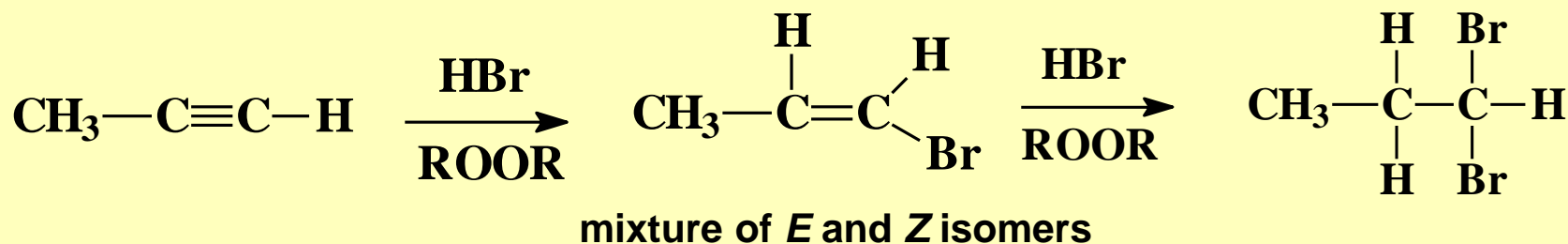
Addition of HX

- HCl, HBr, and HI add to alkynes to form vinyl halides.
- For terminal alkynes, Markovnikov product is formed.
- If two moles of HX is added, product is a geminal dihalide.



HBr with Peroxides

Anti-Markovnikov product is formed with a terminal alkyne.



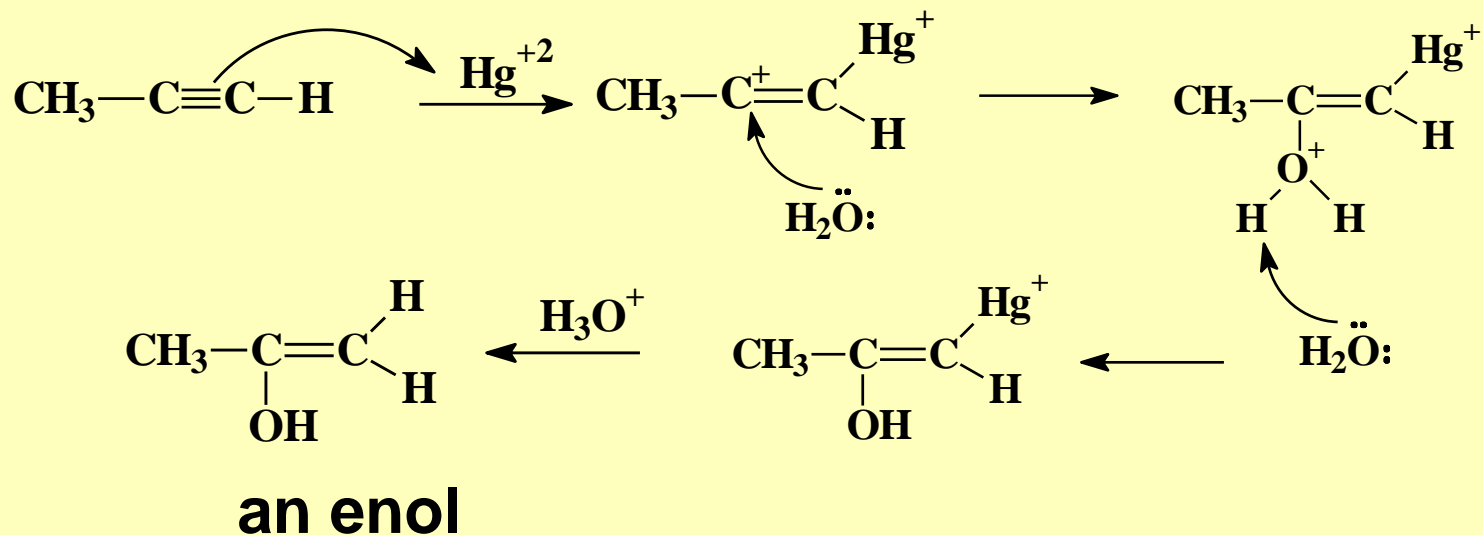
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Hydration of Alkynes

- Mercuric sulfate in aqueous sulfuric acid adds H-OH to one pi bond with a Markovnikov orientation, forming a vinyl alcohol (enol) that rearranges to a ketone.
- Hydroboration-oxidation adds H-OH with an anti-Markovnikov orientation, and rearranges to an aldehyde.

Mechanism for Mercuration

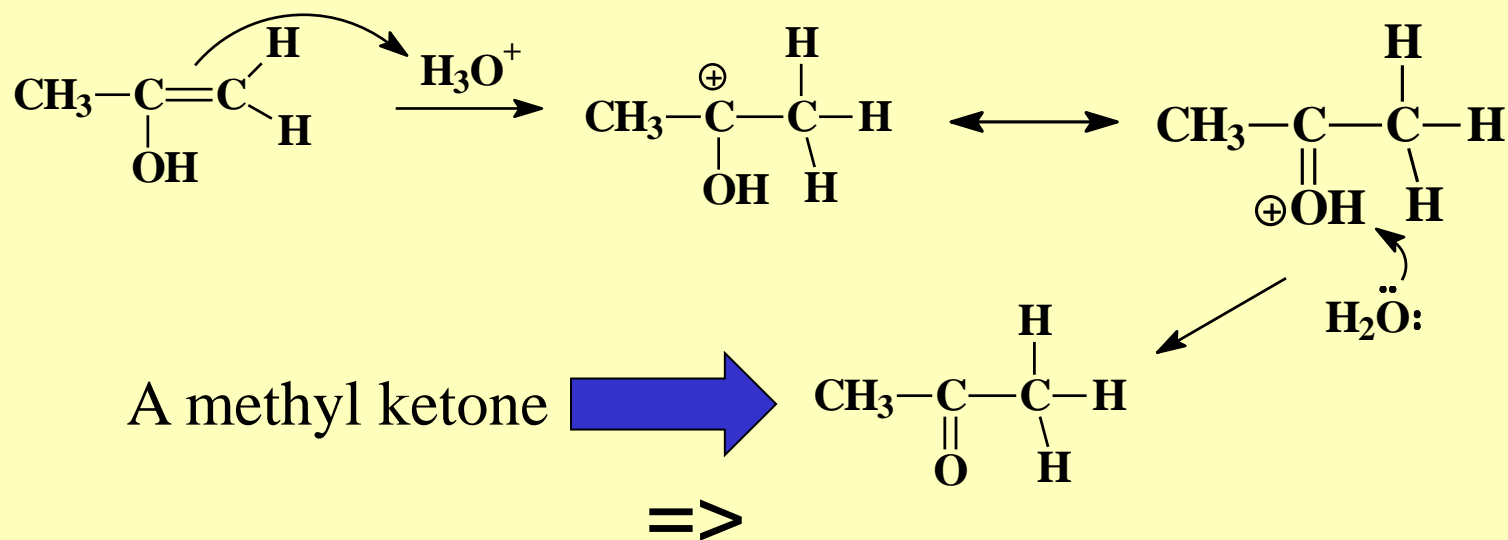
- Mercuric ion (Hg^{2+}) is electrophile.
- Vinyl carbocation forms on most-sub. C.
- Water is the nucleophile.



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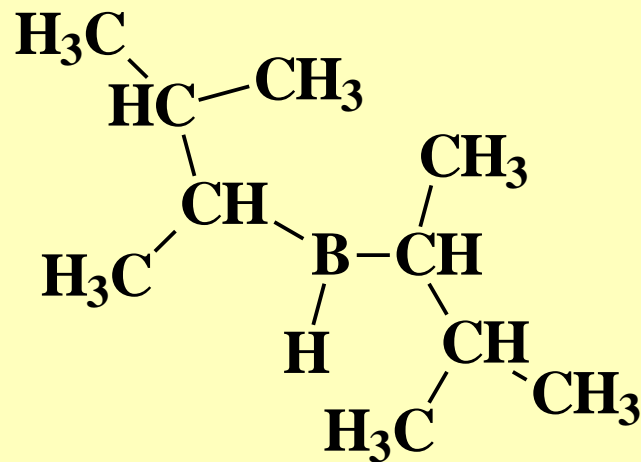
Enol to Keto (in Acid)

- Add H^+ to the $\text{C}=\text{C}$ double bond.
- Remove H^+ from OH of the enol.



Hydroboration Reagent

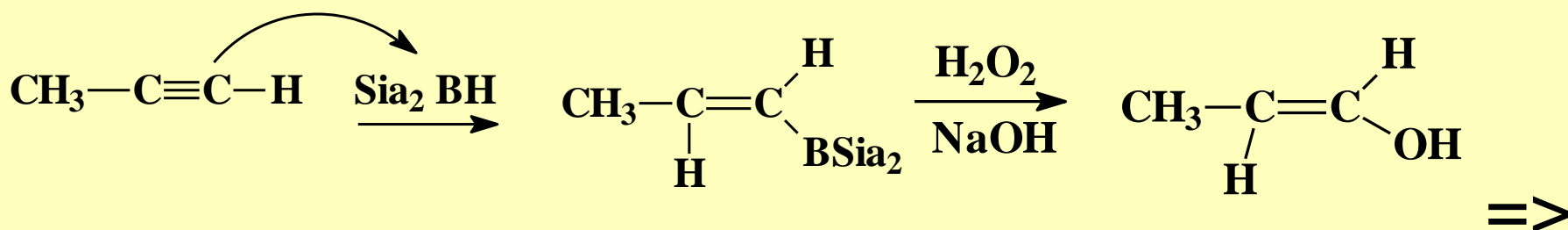
- Di(secondary isoamyl)borane, called disiamylborane.
- Bulky, branched reagent adds to the least hindered carbon.
- Only one mole can add.



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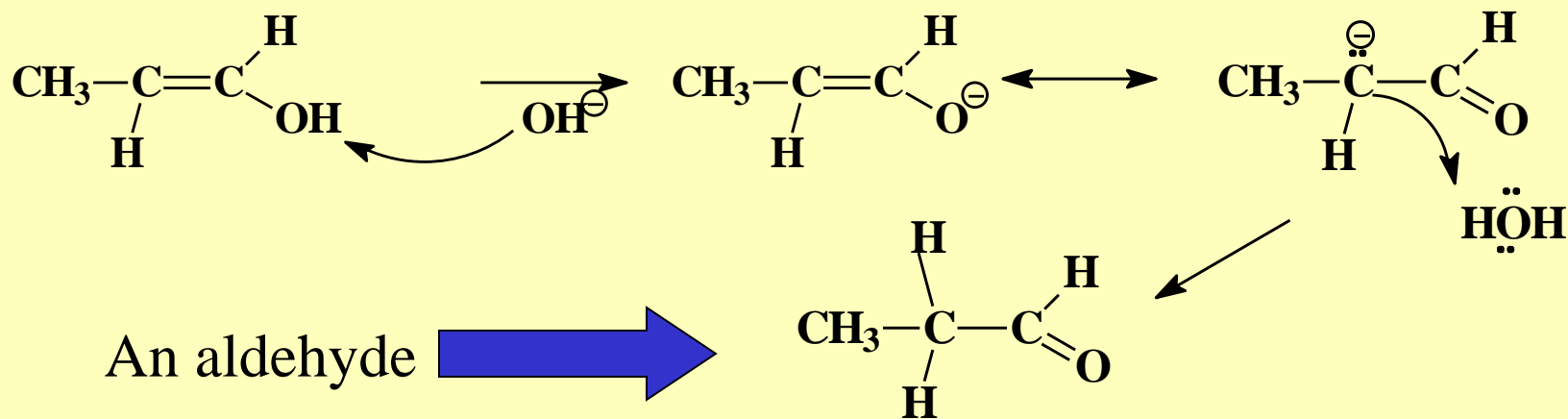
Hydroboration - Oxidation

- B and H add across the triple bond.
- Oxidation with basic H_2O_2 gives the enol.



Enol to Keto (in Base)

- H^+ is removed from OH of the enol.
- Then water gives H^+ to the adjacent carbon.



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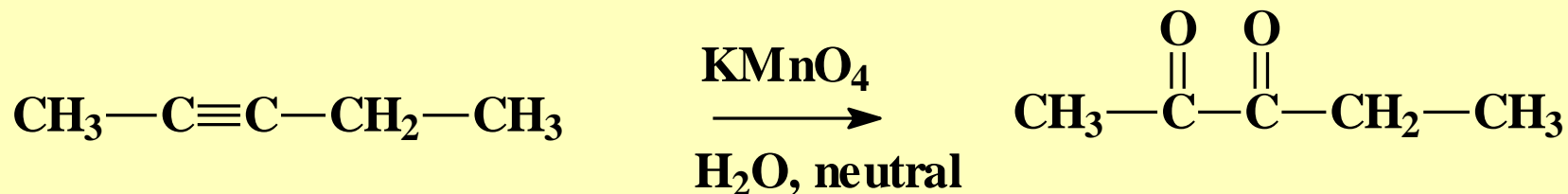
Oxidation of Alkynes

- Similar to oxidation of alkenes.
- Dilute, neutral solution of KMnO_4 oxidizes alkynes to a diketone.
- Warm, basic KMnO_4 cleaves the triple bond.
- Ozonolysis, followed by hydrolysis, cleaves the triple bond.

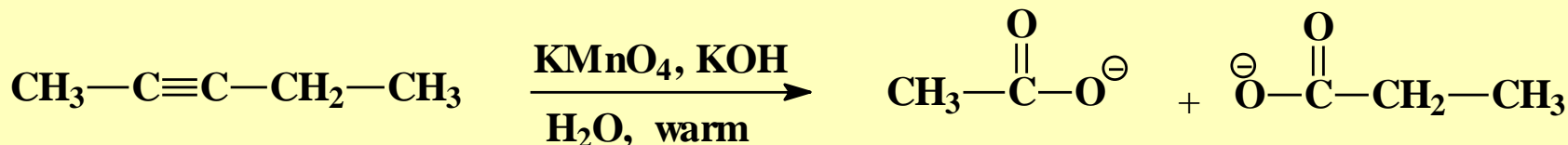
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Reaction with KMnO_4

- Mild conditions, dilute, neutral



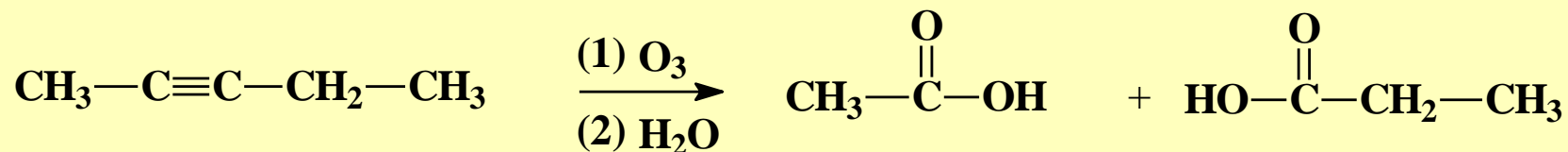
- Harsher conditions, warm, basic



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Ozonolysis

- Ozonolysis of alkynes produces carboxylic acids (alkenes gave aldehydes and ketones).



- Used to find location of triple bond in an unknown compound.

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