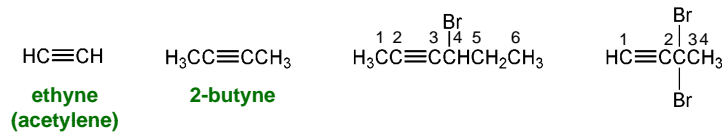


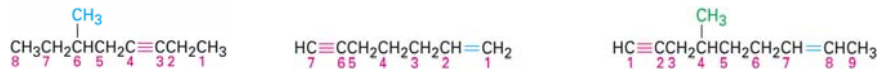
Naming the Alkynes

Alkynes: hydrocarbons that contain **carbon-carbon triple bonds**

General alkene nomenclature rules apply, with “-yne” replacing “-ene” as the suffix.

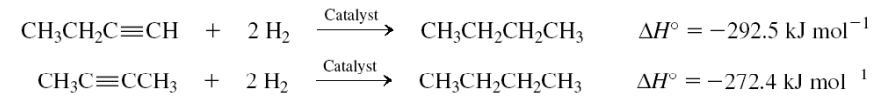
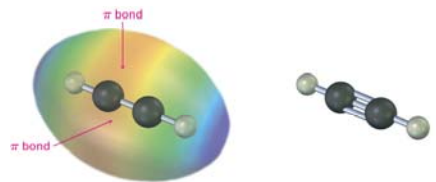
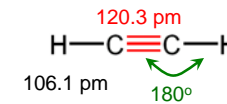
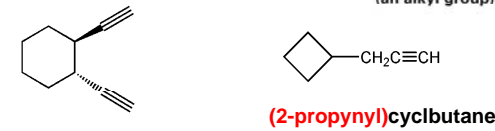
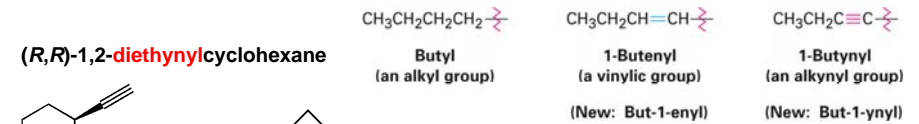


Compounds with more than one triple bond are called diynes, triynes, etc.; compounds containing both double and triple bonds are called enynes (not ynenes).



10-1

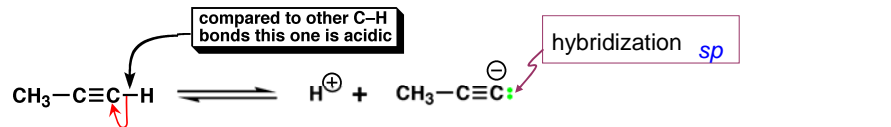
Nonmenclature (Cont'd) and Factoids of Alkynes



Relative stability: $\text{RC}\equiv\text{CH} < \text{RC}\equiv\text{CR}'$

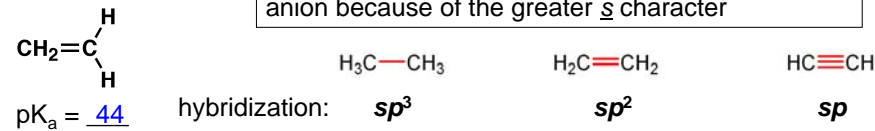
10-2

Acidity of Terminal Alkynes



$\text{pK}_a = 25$

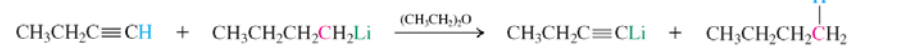
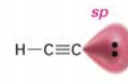
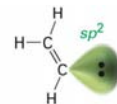
The acetylide anion is more stable than the vinylic anion because of the greater s character



$\text{pK}_a: 50$

44

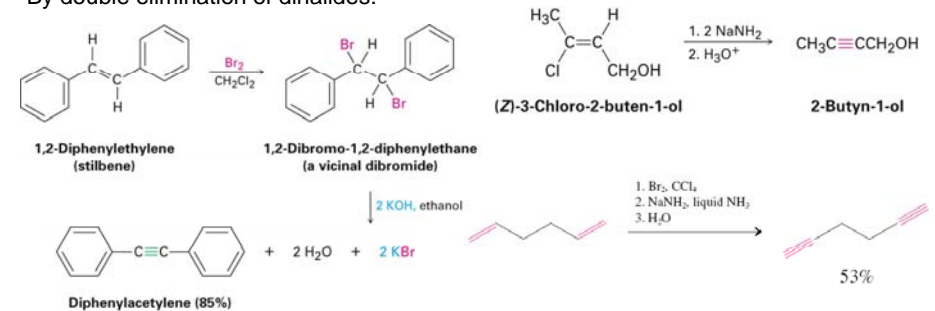
25



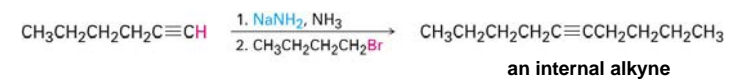
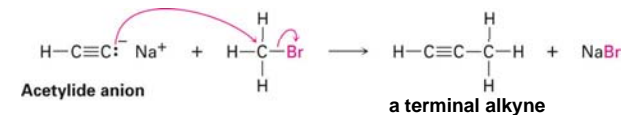
10-3

Preparation of Alkynes

By double elimination of dihalides:

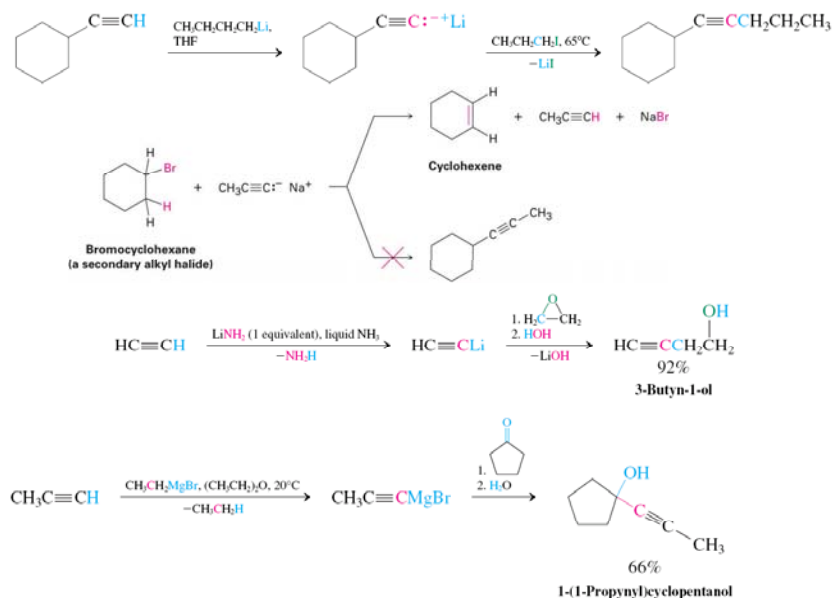


By acetylides and alkynyl anions: $\text{R}-\text{C}\equiv\text{C}-\text{H} + \text{:NH}_2^- \text{Na}^+ \rightarrow \text{R}-\text{C}\equiv\text{C}^- \text{Na}^+ + \text{:NH}_3$



10-4

Reactions of Alkynyl Anions

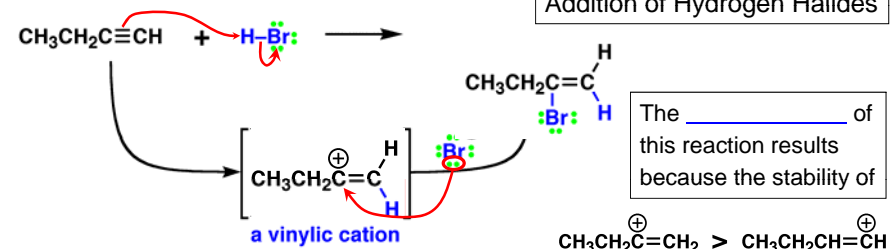


10-5

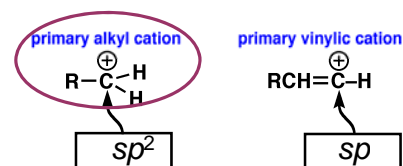
Reactions of Alkynes

Much of the chemistry of alkynes follows by analogy to alkenes

Addition of Hydrogen Halides



Which is more stable?



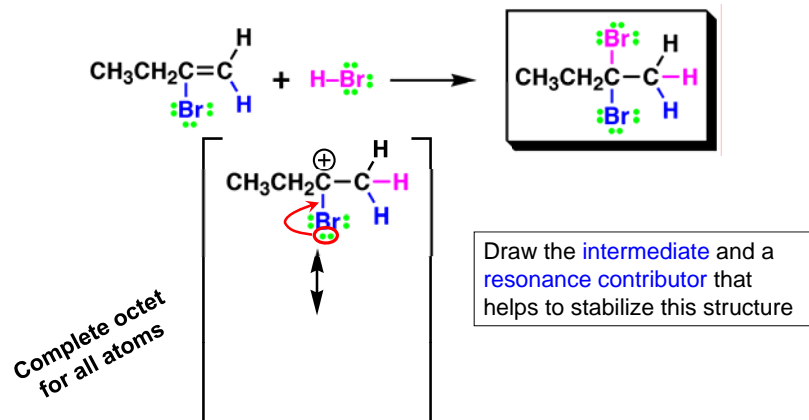
- The sp orbital has more "s" character than the sp^2 orbital (the sp is 55% s; the sp^2 is 33% s).
- The s orbital has a greater presence at the positively charged nucleus (**more electronegative**).
- Therefore, because of Coulombic (charge-charge) repulsion, the alkyl cation is more stable than the vinylic.

10-6

Successive Additions to Alkynes

It is usually difficult to limit the reaction to addition of a single HX.

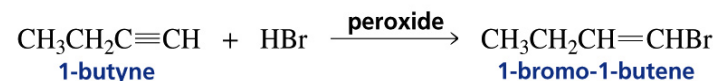
The resulting bromobutane can react with a second equivalent of HBr to produce a geminal dihalide.



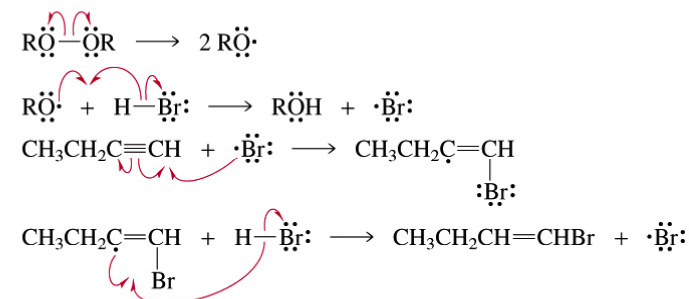
10-7

Radical Addition of H-Br to an Alkyne

Recall radical addition of HBr to alkenes gives anti-Markovnikov product.

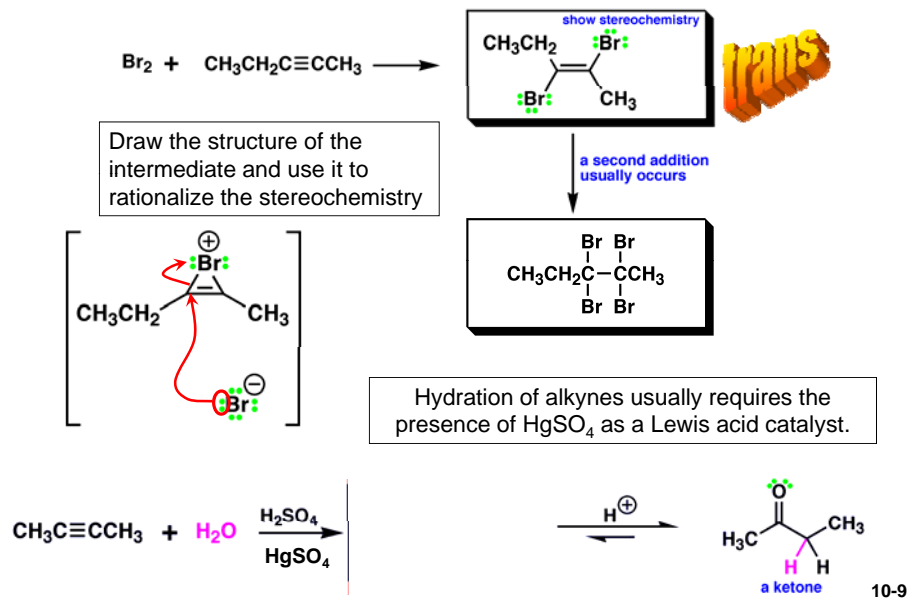


mechanism for the addition of HBr in the presence of peroxide



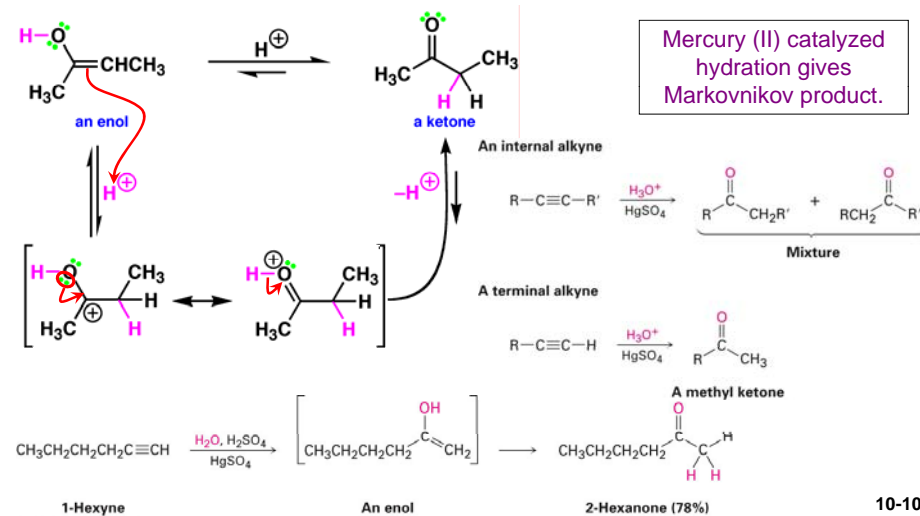
10-8

Addition of Br₂ or H₂O to an Alkyne

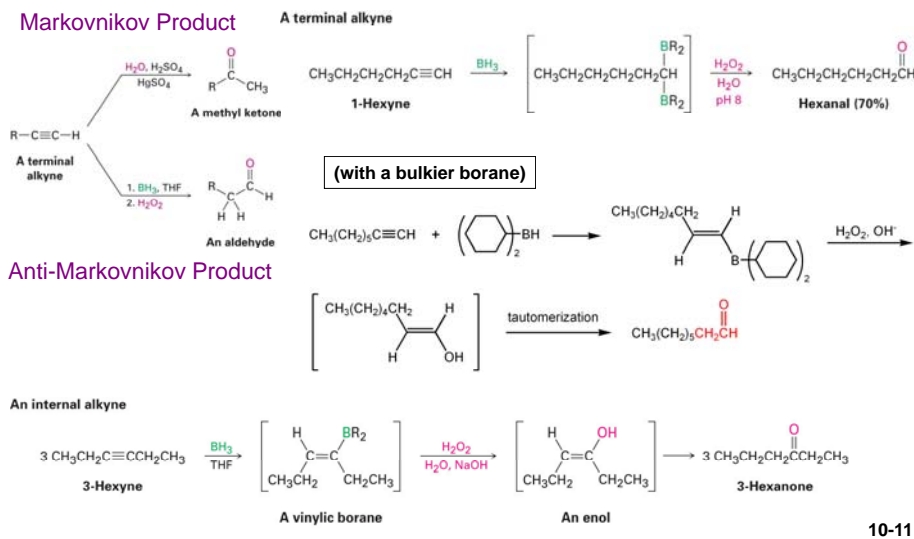


Mechanism of Enol Tautomerization

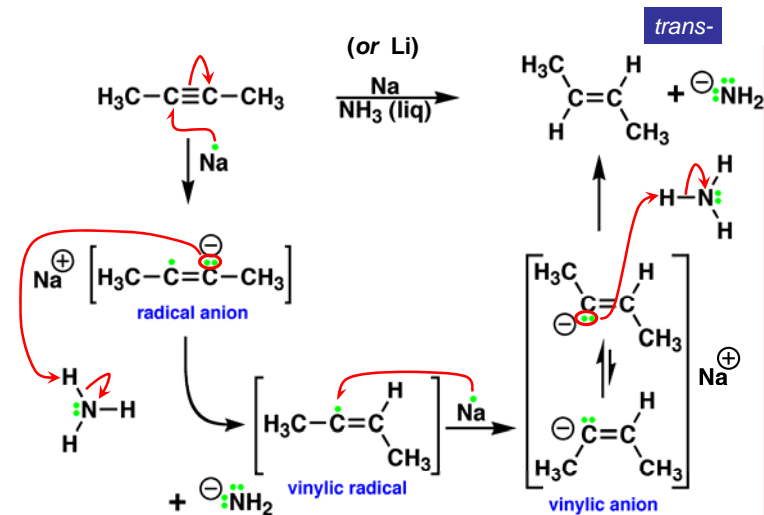
Enols are not stable to the reaction conditions (the name enol comes from alkene and alcohol). They are converted to carbonyl groups by a process called _____.



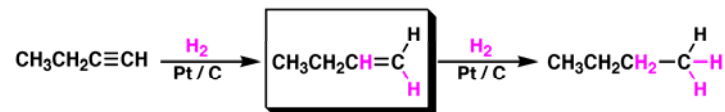
Hydroboration/Oxidation of Alkynes — Anti-Markovnikov Product



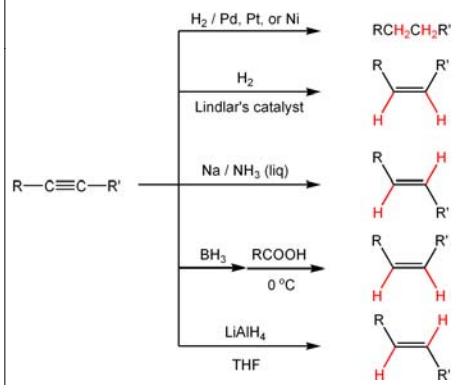
Formation of Trans Alkenes by Sodium Ammonia Reduction of Alkynes



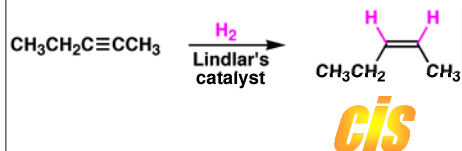
Reduction of Alkynes: Hydrogenation



Summary on Reduction of Alkynes



The reaction can be stopped after addition of one equivalent H_2 only if a **deactivated** catalyst is used

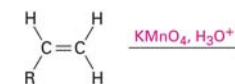
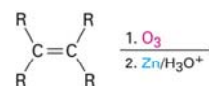


Lindlar's catalyst:
Pd-CaCO₃/Pb(OAc)₂/quinoline

10-13

Oxidative Cleavage of Alkynes

Recall:



An internal alkyne

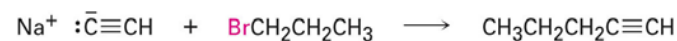
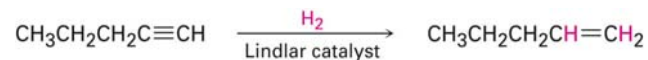
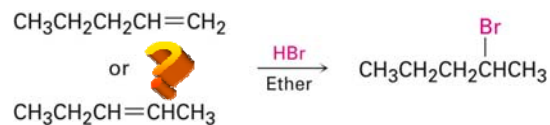


A terminal alkyne



10-14

An Introduction of Organic Synthesis



10-15