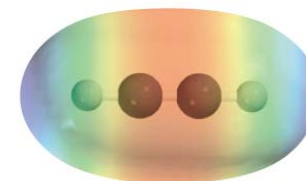
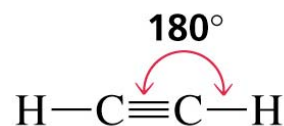
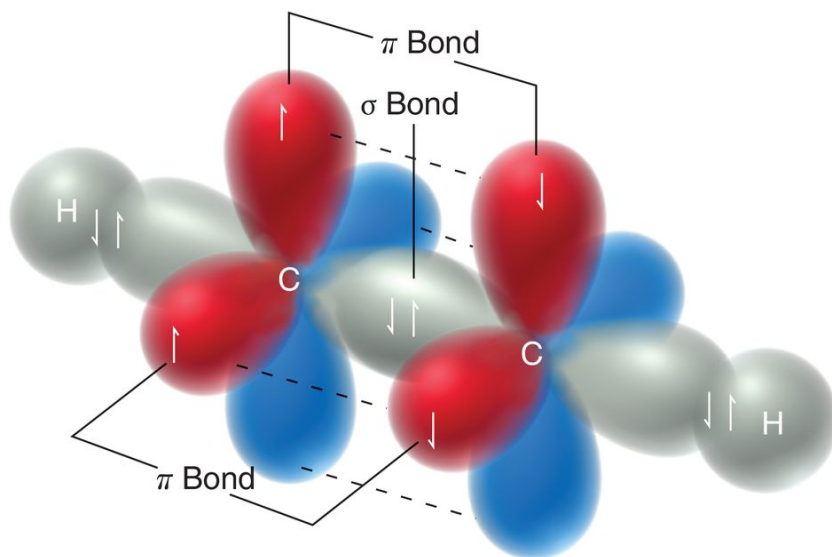


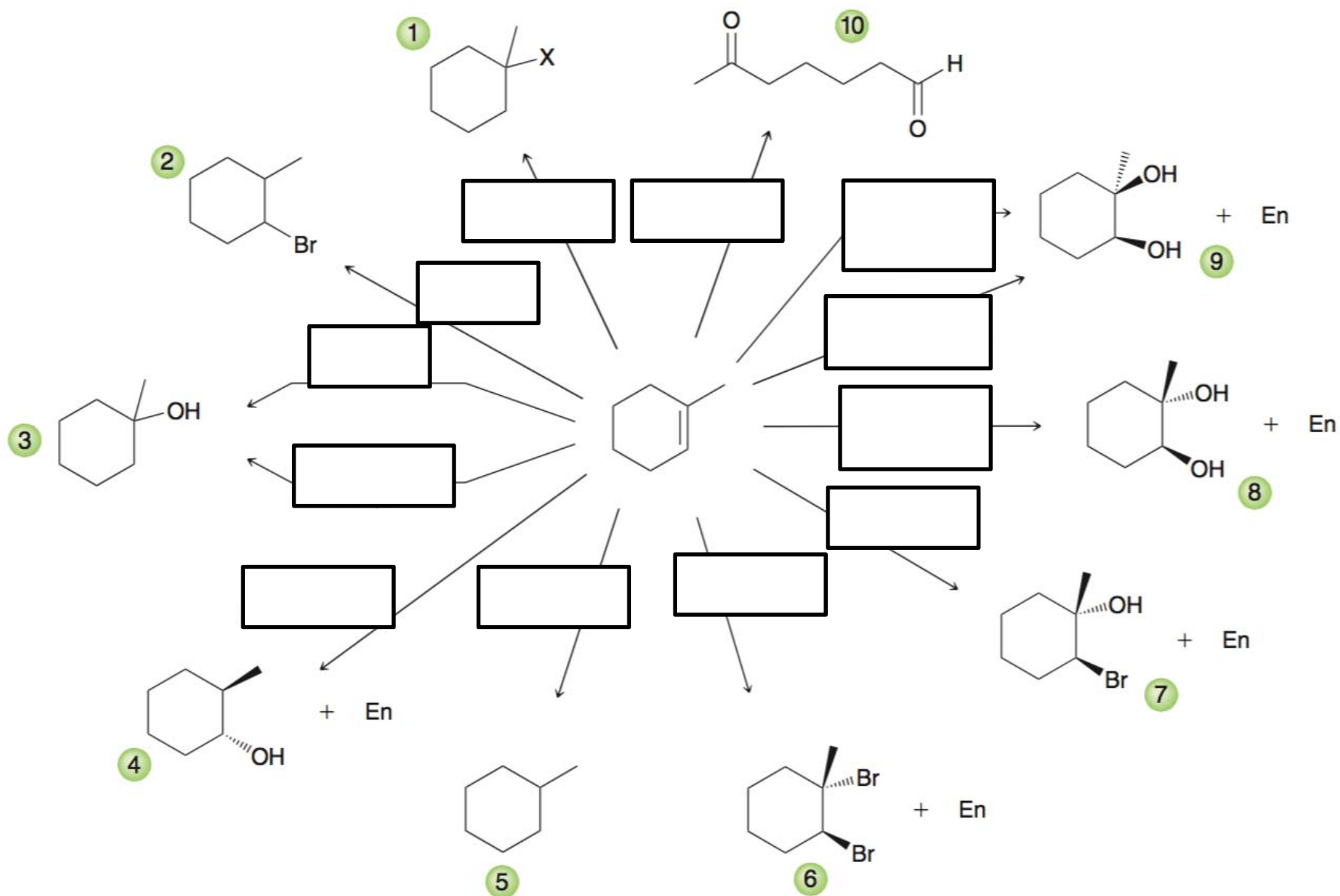
Chapter 9:

Alkynes and Reactions with Alkynes

- Today (9.1-9.4) Reactions with Alkynes
- Wednesday (9.4-9.8) Reactions with Alkynes
- Friday Finish Chapter 9 (9.8-9.11)

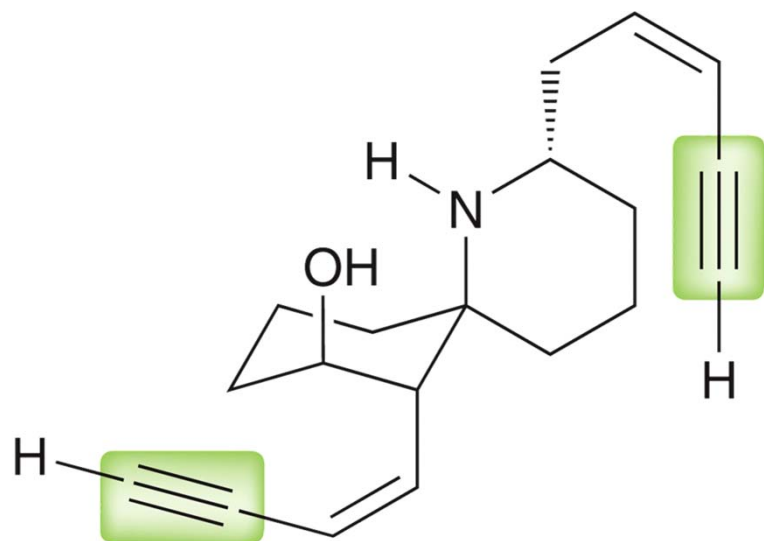


Electrophilic Addition Reactions:

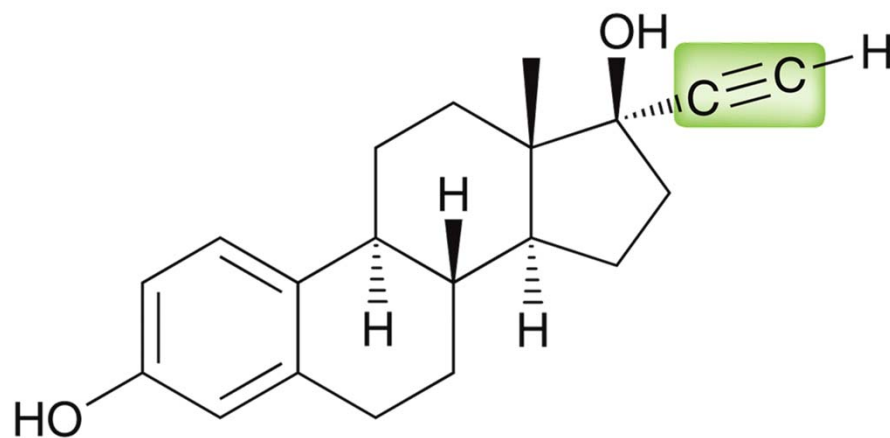


Alkynes in Industry and Nature

- Acetylene is the simplest alkyne
- It is used in blow torches and as a precursor for the synthesis of more complex alkynes
- More than 1000 different alkyne natural products have been isolated



Histrionicotoxin

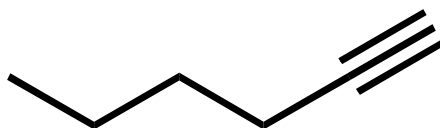


Ethynylestradiol

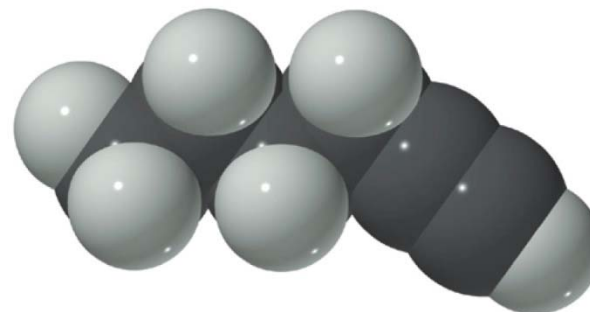
Ch. 9 - Alkynes – hydrocarbons that contain a carbon–carbon triple bond



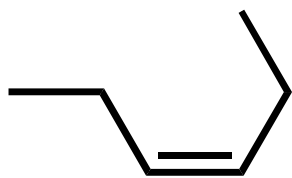
1-hexene



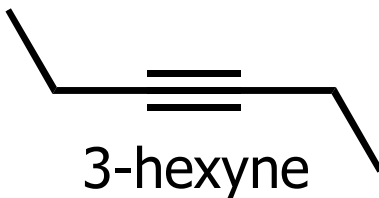
1-hexyne



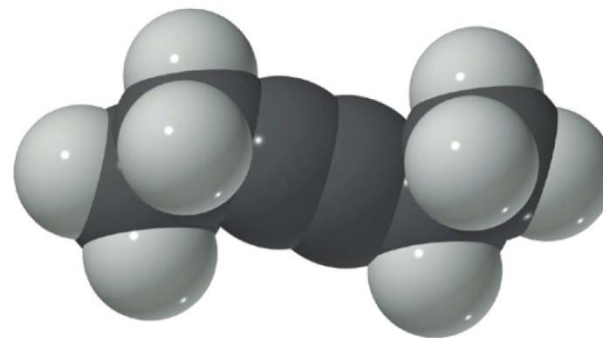
1-hexyne
a terminal alkyne



3-hexene

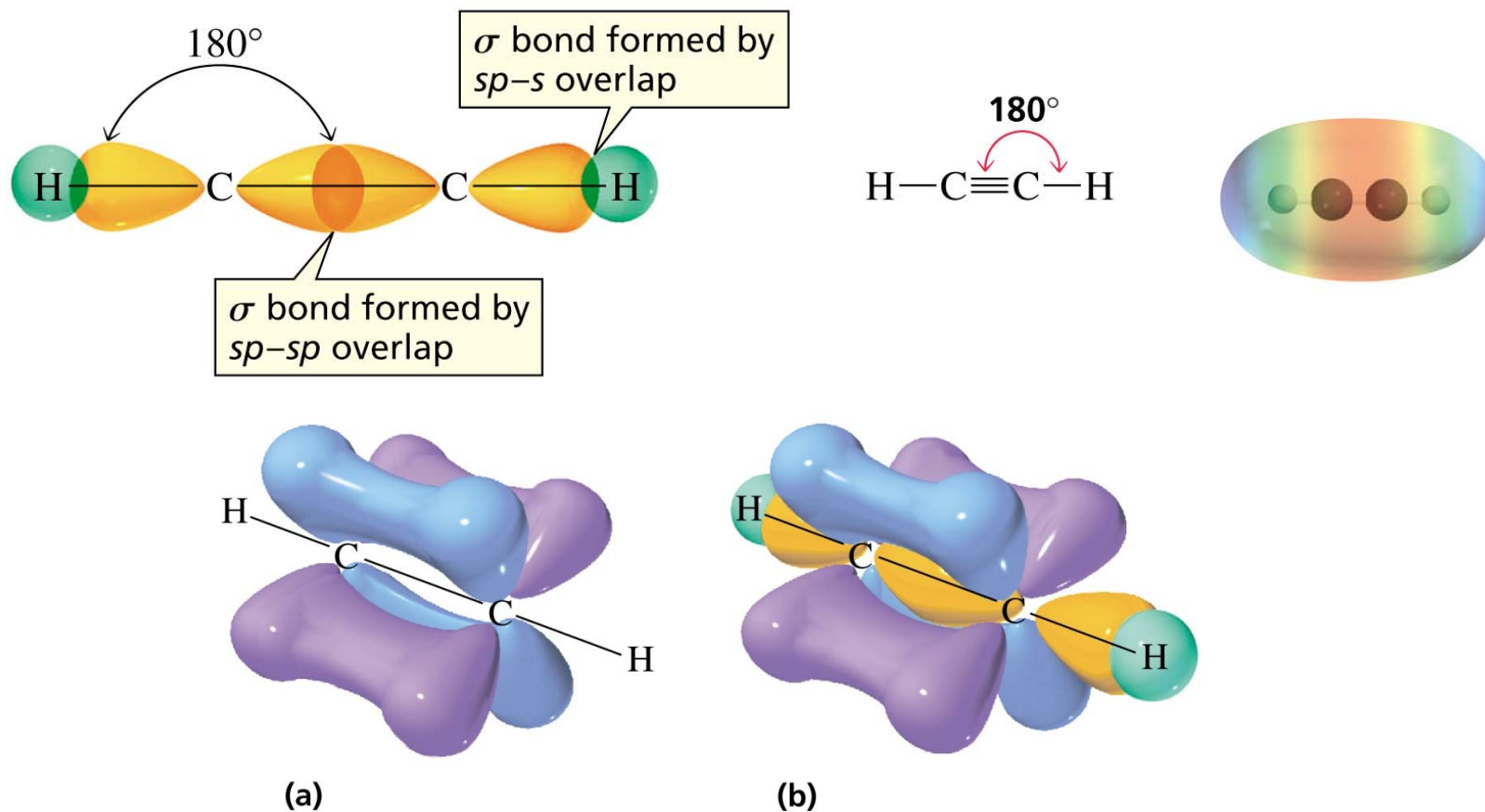


3-hexyne



3-hexyne
an internal alkyne

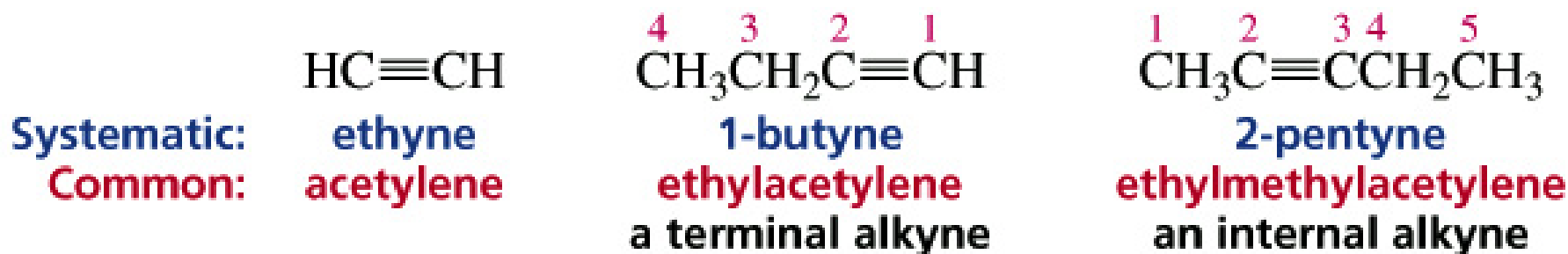
The Structure of Alkynes



- Given the presence of two pi bonds and their associated electron density, alkynes are similar to alkenes in their ability to act as a nucleophile.

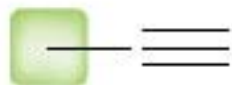
Nomenclature

In common nomenclature, alkynes are named as substituted acetylenes

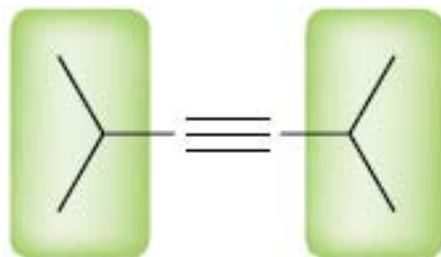


Alkyne Nomenclature

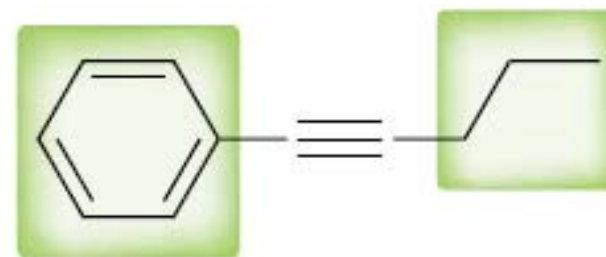
- In addition to the IUCAP naming system, chemists often use common names that are derived from the common parent name acetylene.



Methylacetylene

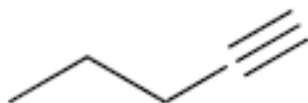


Diisopropylacetylene



Phenylpropylacetylene

- You should also be aware of the terminology below.

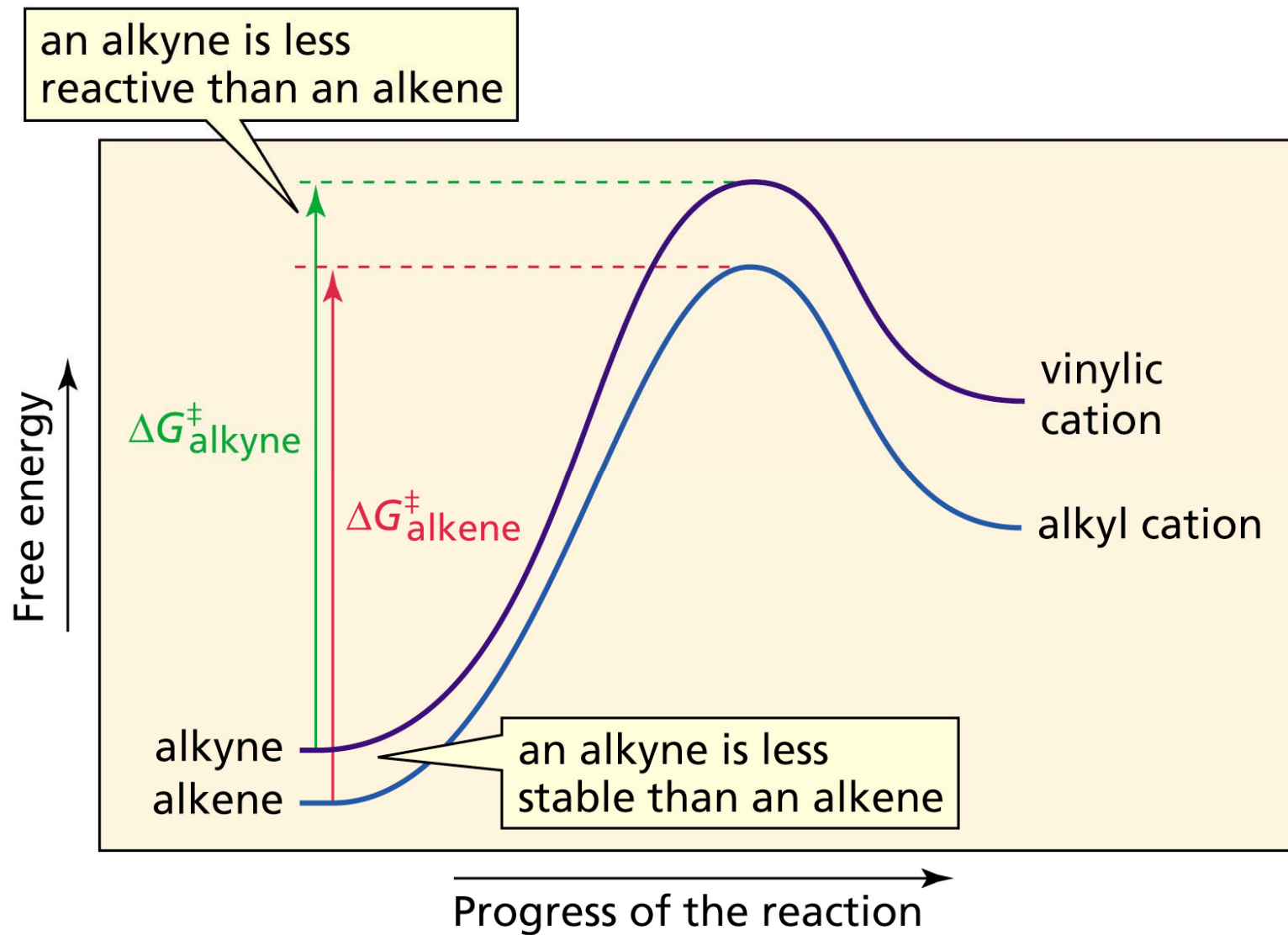


Terminal



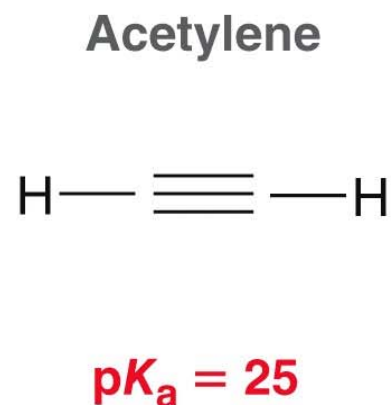
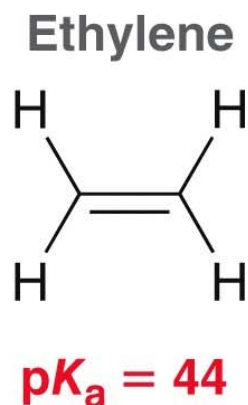
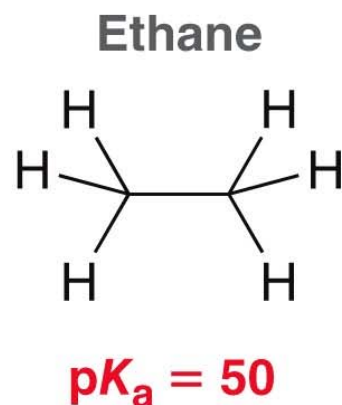
Internal

An alkyne is less reactive than an alkene



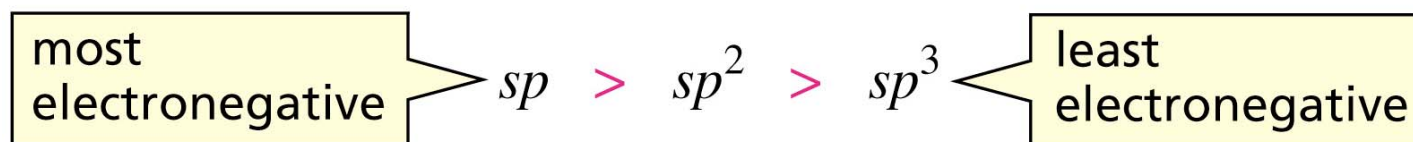
Acidity of Alkynes

- Recall that **terminal alkynes** have a lower pK_a (i.e. **more acidic**) than other hydrocarbons



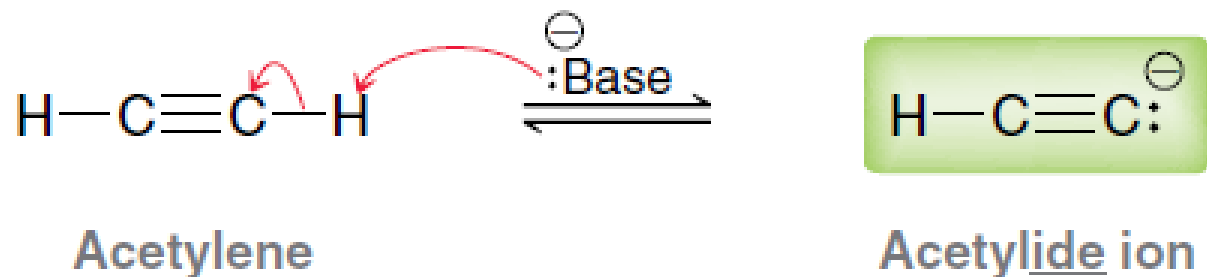
- Acetylene is 19 pK_a units more acidic than ethylene, which is 10^{19} times stronger

relative electronegativities of carbon atoms

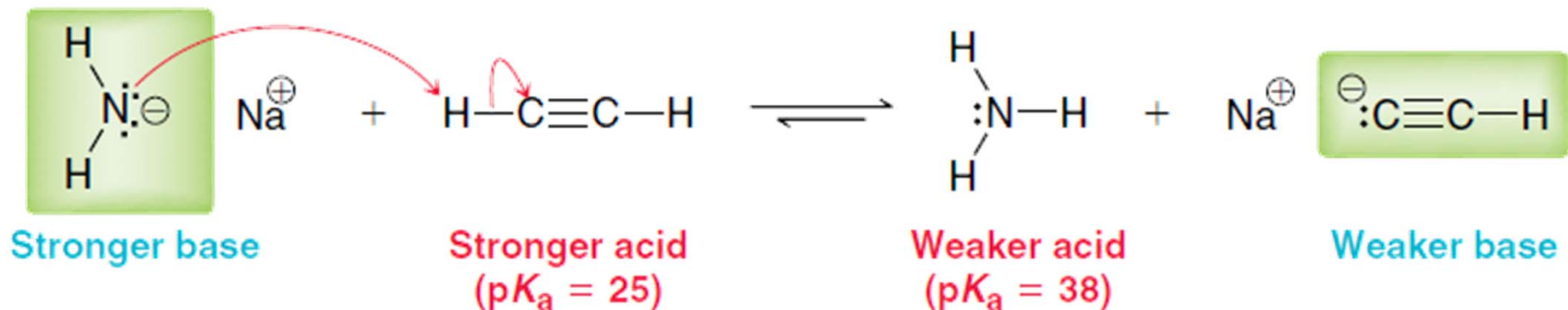


Alkyne Acidity

- Because acetylene ($pK_a=25$) is still much weaker than water ($pK_a=15.7$), a REALLY!! strong base is needed to make it react.

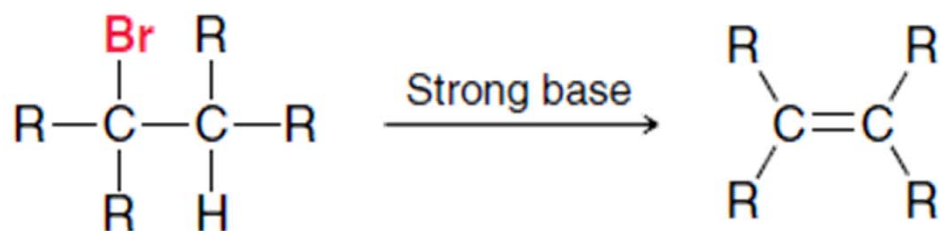


- A base's conjugate acid pK_a must be greater than 25 for it to be able to deprotonate a terminal alkyne.

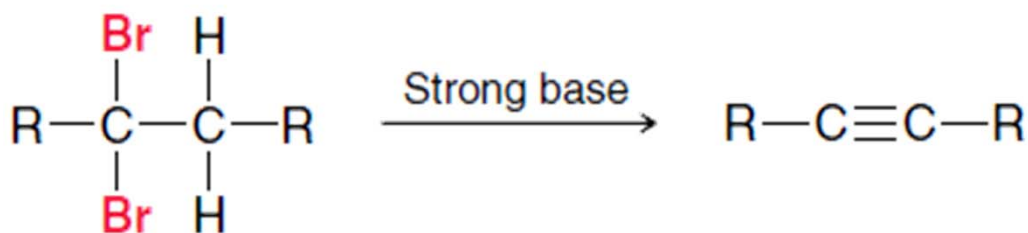


Preparation of Alkynes

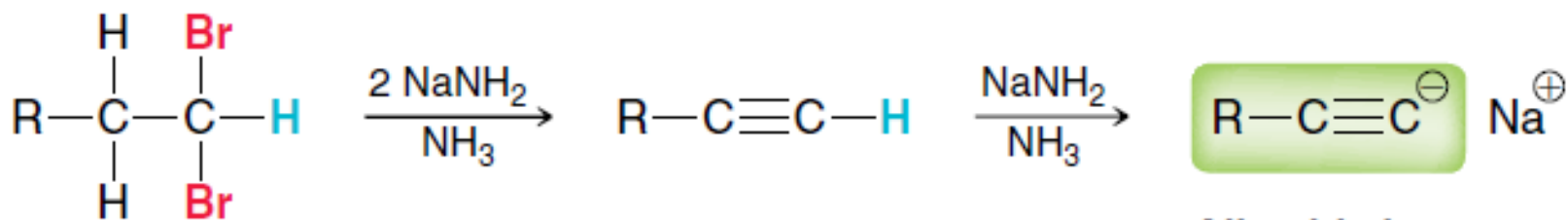
- Like alkenes, alkynes can also be prepared by elimination.



An alkyl halide



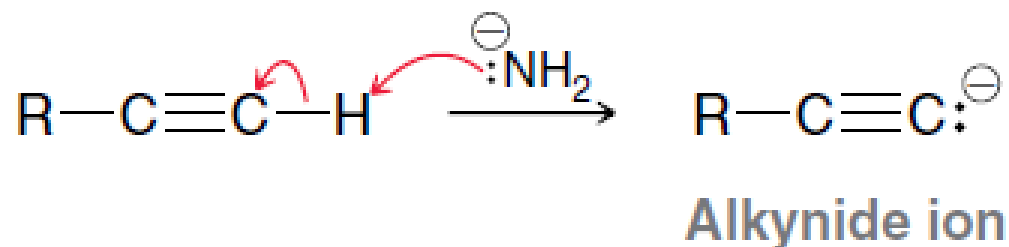
An alkyl dihalide



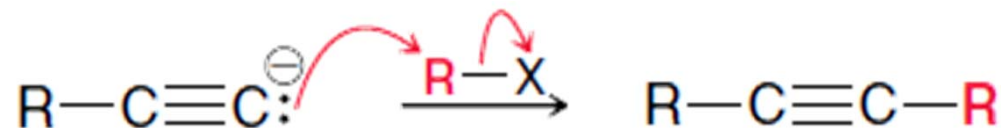
Alkynide ion

Alkylation of Terminal Alkynes

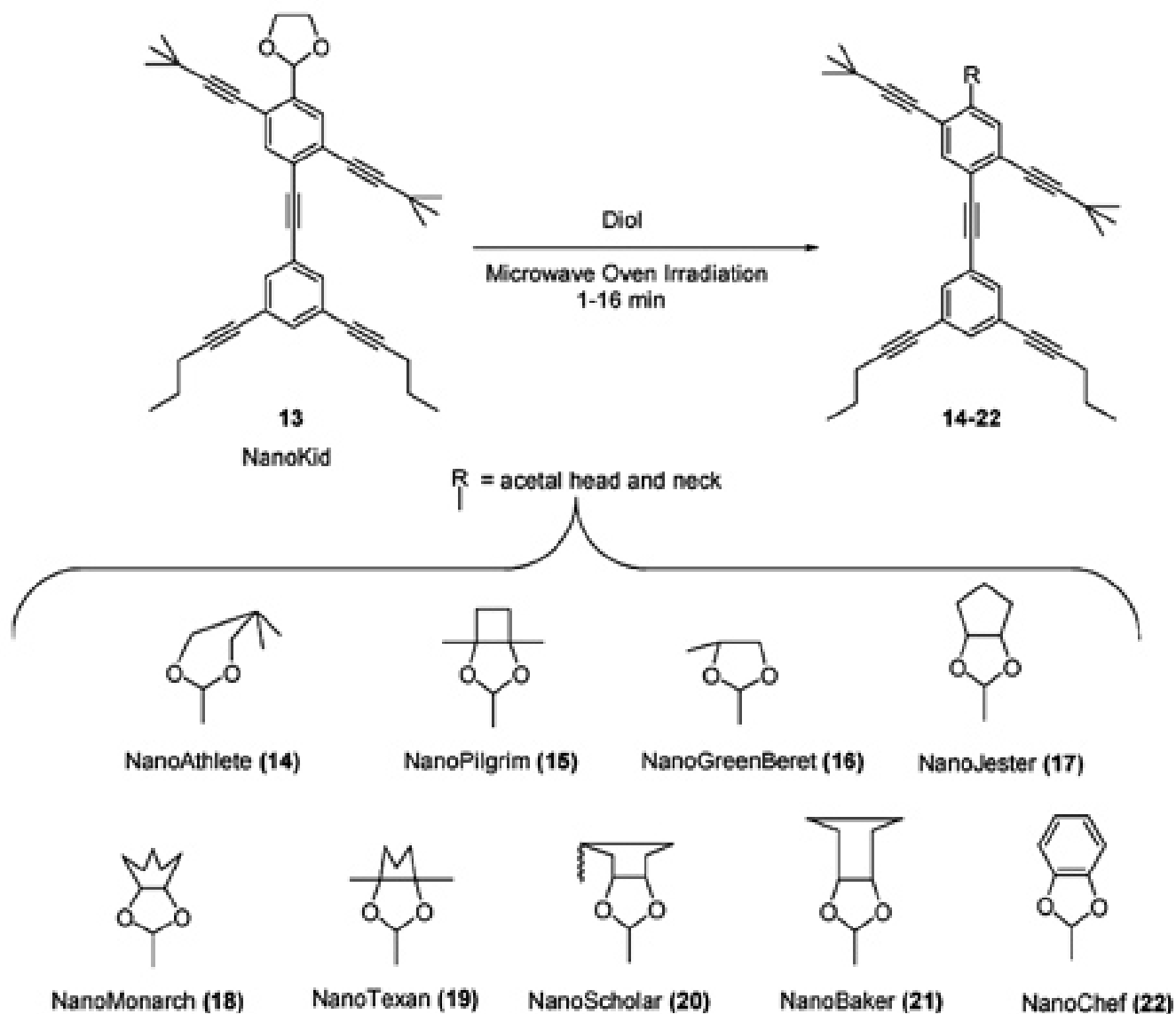
- As acids, terminal alkynes are quite weak.
- With a VERY strong base, a terminal alkyne can be deprotonated and converted into a good nucleophile.



- The alkynide ion can attack a methyl or 1° alkyl halide electrophile.



Synthesis of Anthropomorphic Molecules

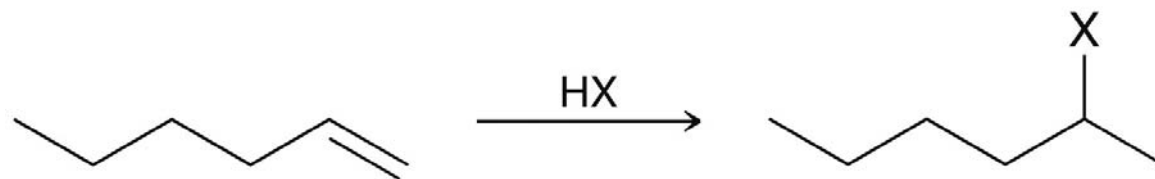


J. Org. Chem., **2003**, 68 (23), pp 8750–8766

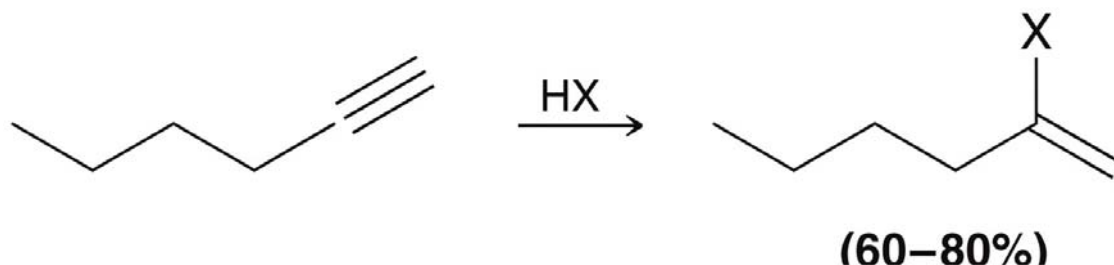
Hydrohalogenation of Alkynes

- **Hydrohalogenation** affords Markovnikov addition of **H** and **X** to an alkyne, same as with an alkene.

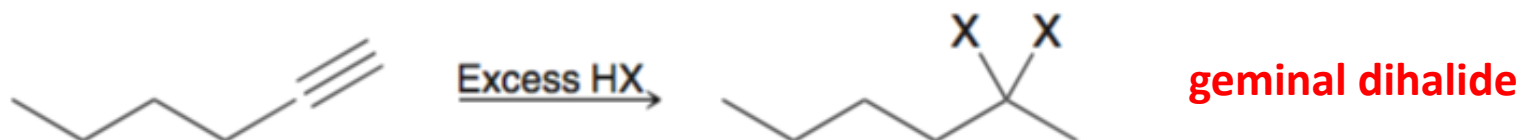
addition to an alkene



addition to an alkyne

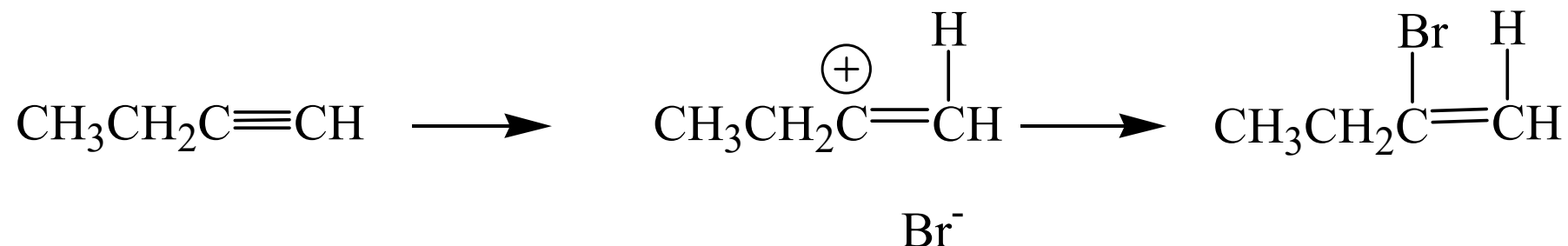


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Hydrohalogenation of Alkynes

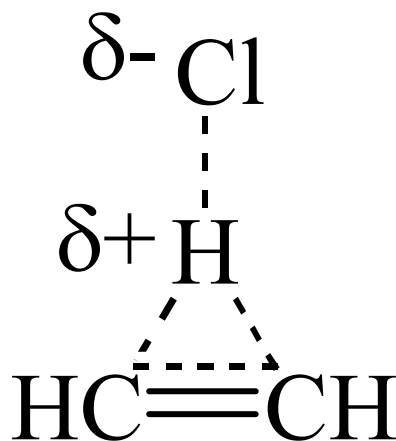
In the presence of 1 mole equivalent of HBr ->



The secondary vinyl cation is more stable

Hydrohalogenation of Alkynes

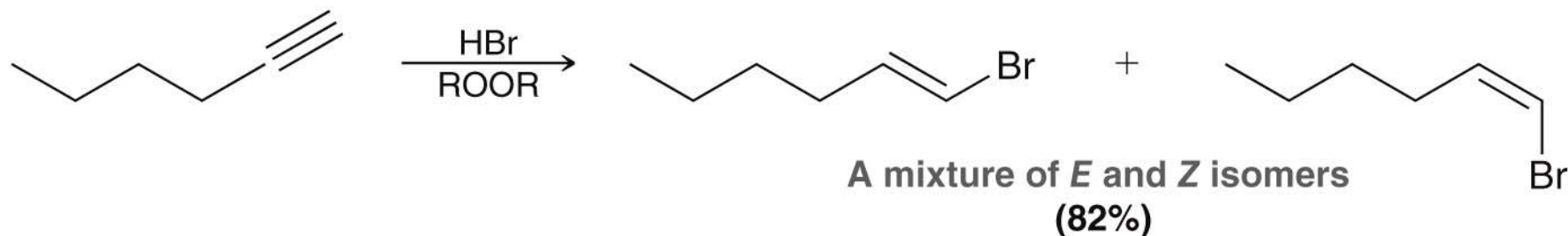
A secondary vinylic cation is about as stable as a primary cation, therefore a pi-complex may be the reaction intermediate.



Most alkyne addition reactions are stereoselective

Hydrohalogenation of Alkynes

- HBr with peroxides promotes *anti*-Markovnikov addition, just like with alkenes



- This only works with HBr (not with HCl or HI)

For Next Time....

Suggested Homework Problems Chapter 9

1,7,9,13,18,20,32-37, 41,44,52,57