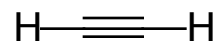


Alkynes

Compounds containing a carbon-carbon triple bond



Acetylene

-overall many reactions are similar to alkene reactions
therefore, electrophilic additions to multiple bonds and oxidation reactions

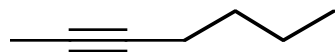
Nomenclature

Follow same rules as seen for alkenes

-find longest continuous chain containing the triple bond

-number the chain so that the lowest number is obtained for the triple bond

-use a -yne suffix with the correct root name



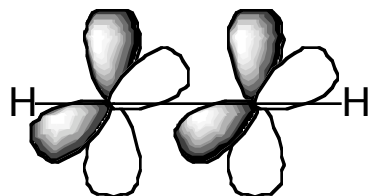
2-heptyne



6-bromo-3-heptyne

Electronic Structure

-remember the electronic structure for an alkyne



the triple bond refers to one σ and two π bonds

-the two π bonds are orthogonal to each other

as the number of bonds increases between two carbons the bond length decreases

C-C triple bond: bond length 1.20 Å

C-C double bond: bond length 1.33 Å

C-C single bond: bond length 1.54 Å

Acidity

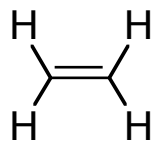
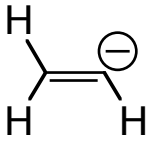
One effect of the increase in number of bonds (and bond length changes)
is the acidity of an sp hybridized C-H

As the resultant lone pair of electrons
(the pair remaining after the proton is abstracted in an acid-base reaction)
becomes closer to the positively charged nucleus the lone pair is MORE STABLE

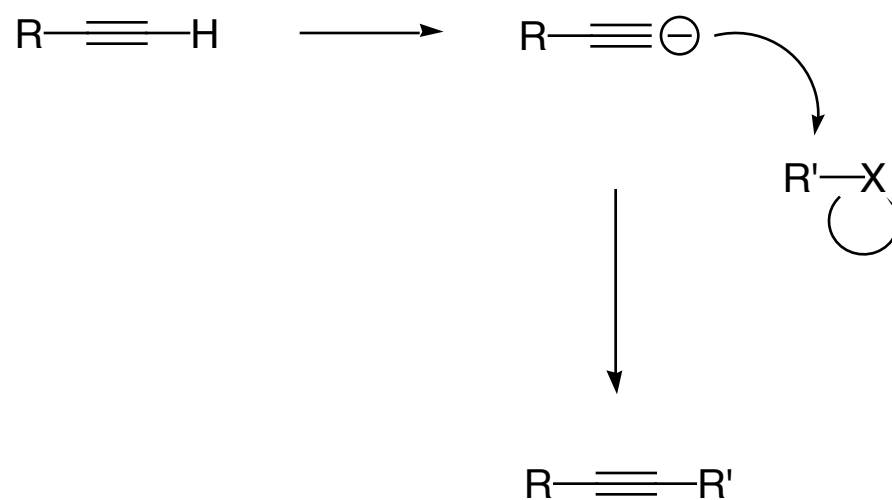
As the stability of the deprotonated form increases the compound is more acidic

Therefore an sp hybridized C-H bond is more acidic than an sp² hybridized bond which is
more acidic than an sp³ hybridized bond

Remember the Acidity Ranking

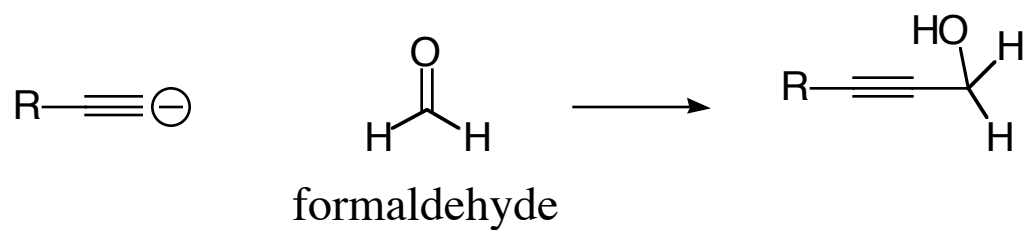
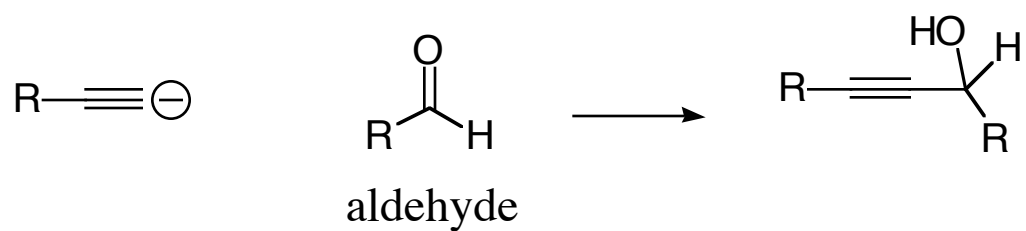
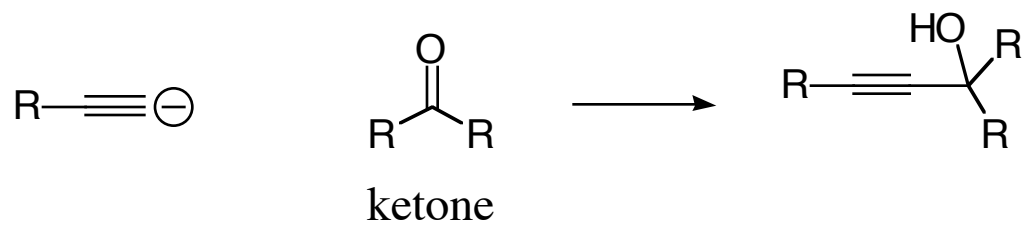
			pKa
CH_3CH_3	\longrightarrow	$\text{CH}_3\text{CH}_2^\ominus$	50
	\longrightarrow		44
NH_3	\longrightarrow	NH_2^\ominus	35
$\text{R}\text{---}\equiv\text{H}$	\longrightarrow	$\text{R}\text{---}\equiv^\ominus$	25
ROH	\longrightarrow	RO^\ominus	16

Acidity of sp hybridized C-H Allows Creation of Nucleophile

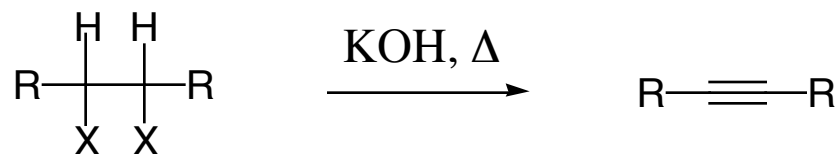


-hence an internal alkyne can be synthesized from a terminal alkyne

Can React Nucleophilic Acetylide with Other Electrophiles



Can Also Synthesize Alkynes by Elimination Route



-need very strong conditions for this reaction to occur

harder to eliminate the second H-X group than the first

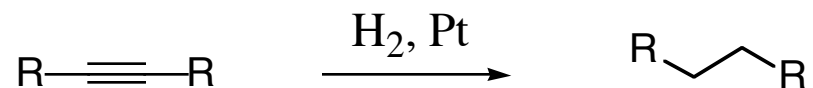
-with this route often obtain a mixture of rearranged products where the alkyne has shifted to another position

Reactions of Alkynes

-many reactions are similar to reactions of alkenes studied earlier

reduction of alkynes:

the multiple bonds can be reduced with hydrogen gas with a metal catalyst



-under these conditions it is very hard to stop at the alkene stage

the alkyne will be reduced fully to the alkane

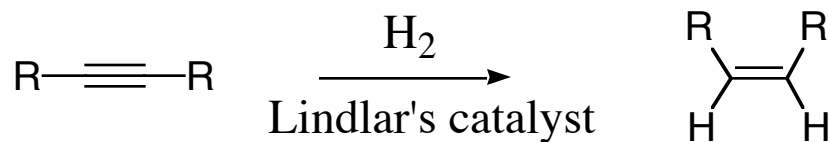
Alkyne to Alkene

-to stop at the alkene stage the alkyne needs to be reduced with a less effective catalyst

one approach is to use a "poisoned" catalyst (Lindlar's catalyst)

the catalyst has impurities added which lower the effectiveness of the metal surface

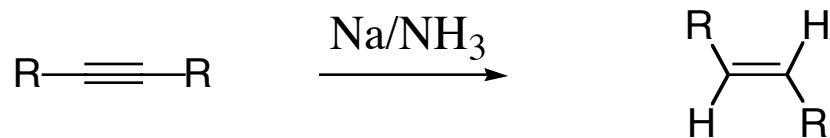
*obtain cis reduction because the alkyne must approach the metal surface from one direction, hence both hydrogens are added from the same side



Alkyne to trans-Alkene

-to obtain a trans alkene from reduction of alkyne a different mechanism is required

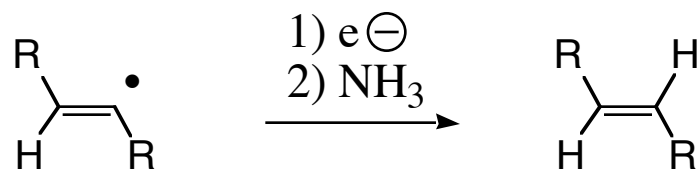
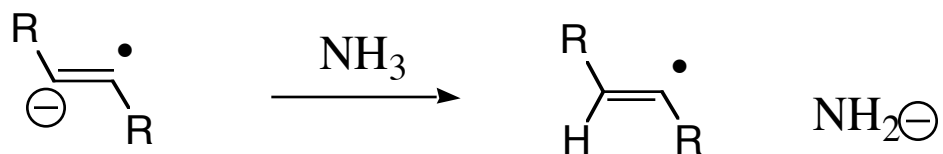
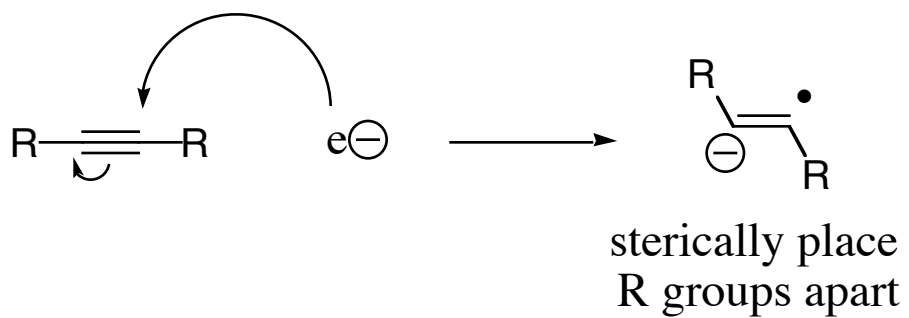
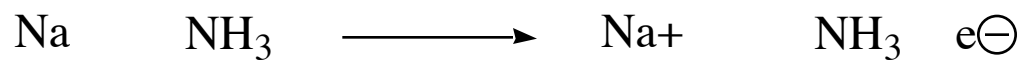
dissolving metal reduction yields trans product



reaction is run at low temperatures so that the ammonia is a liquid
(acts as solvent)

mechanism involves dissolved electrons reducing the alkyne

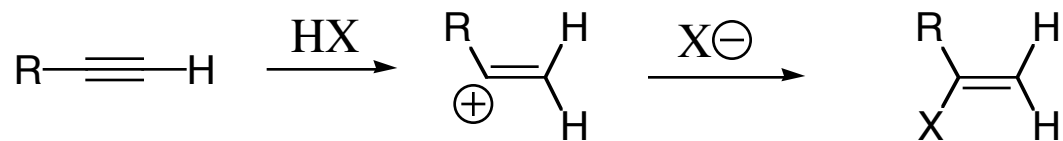
Mechanism of Dissolved Metal Reduction



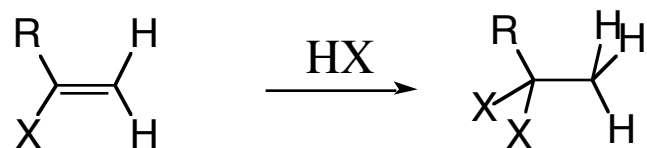
Hydrogen Halide Addition

-reaction occurs analogous to alkene additions

obtain mixture of trans and cis products with internal alkynes



obtain more stable
carbocation intermediate

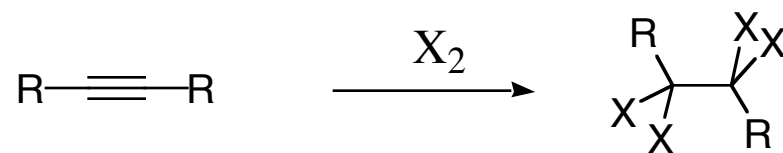


-with another equivalent of HX can get second addition to alkene

can stop at either stage

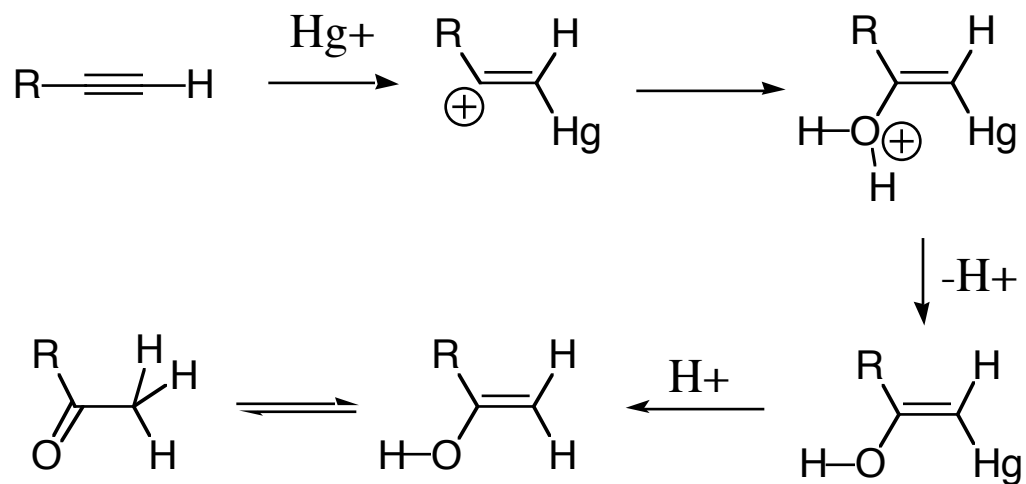
Halogen Addition

-in contrast to hydrogen halide addition it is very difficult to stop at only one addition of halogen to an alkyne, mainly obtain two molar additions



Hydration of Alkynes

To hydrate an alkyne a mercury catalyst is added
(in contrast to alkene reactions when acidic water alone is sufficient)

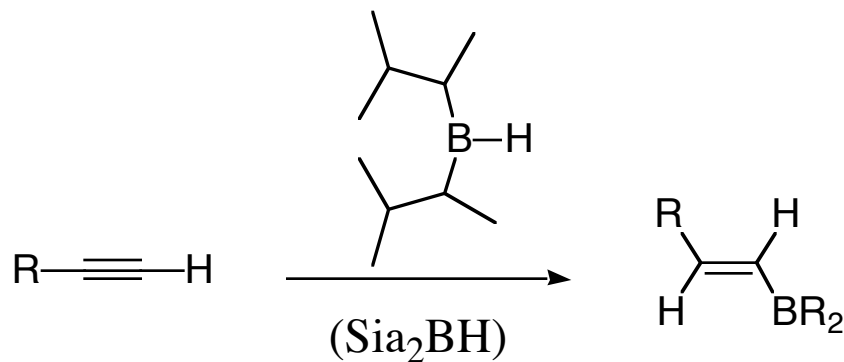


-the last step is a keto-enol equilibrium
(equilibrium NOT resonance)

Hydroboration

-hydroboration of alkynes can also occur

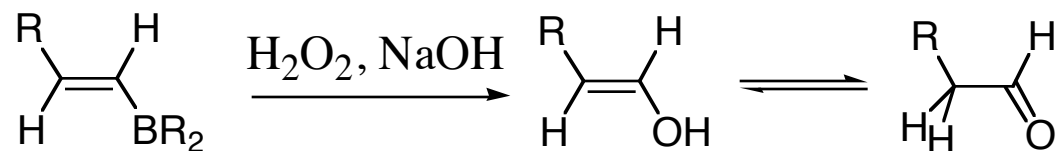
*need bulky borane reagent to eliminate side reactions from occurring



-notice hydroboration still occurs with syn addition and the regiochemistry is dictated by the stability of the initial carbocation intermediate

Oxidation of Borane Product

-the borane can be oxidatively removed
(analogous to alkene reactions)

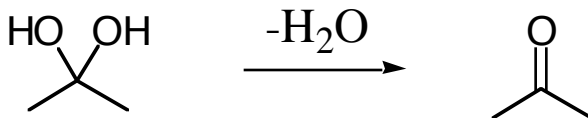
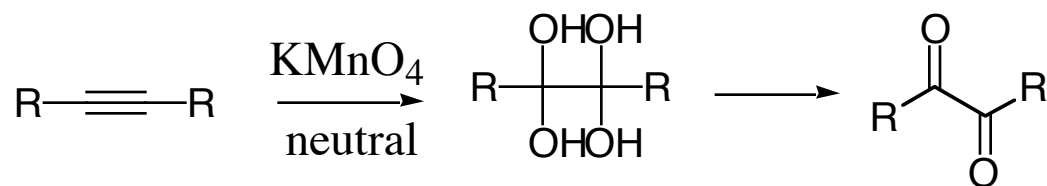


*if a terminal alkyne is used the product of this
reaction sequence is an aldehyde

Oxidation Reactions

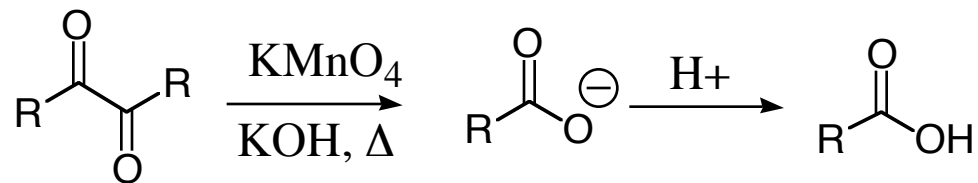
-the alkyne can also be oxidized similar to alkene reactions

**cannot stop at oxidizing only one unsaturated multiple bond



a geminol diol is equivalent to a carbonyl

the diketone can be overoxidized to create a carboxylic acid



Ozonolysis

-an ozonolysis can prevent this overoxidation step
(exactly similar to alkene reactions)

with ozonolysis both ends of the alkyne become oxidized to the carboxylic acid stage

