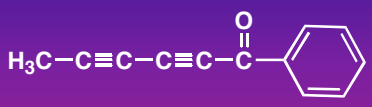
Alkynes

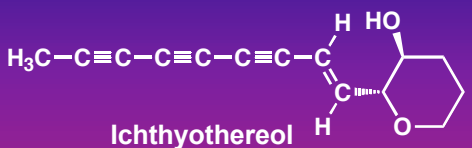
A. Structure
B. Nomenclature
C. Reactions
    1. Addition of HX (geminal dihalide)
    2. Addition of X_2 (tetrahalide)
    3. Hg^{2+} Catalyzed Hydration
    4. Hydroboration/Oxidation
    5. Reduction
        a. alkane
        b. *cis*-alkene
        c. *trans*-alkene
    6. Oxidative Cleavage
    7. Alkylation Reactions
D. Retrosynthetic Analysis

Suggested Reading: Chapter 8 in McMurry
Suggested Problems: 8.1, 8.3-8.14, 8.19-8.47

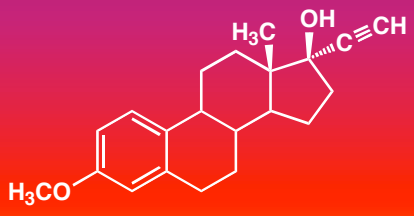
ALKYNES!



Capillin
(fungicidal activity)



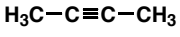
Ichthyothereol
(convulsant used by Amazon Indians for poisoned arrowheads)



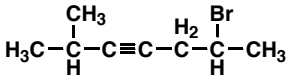
Norquen Ovastol
(in oral contraceptives)

Alkyne Nomenclature

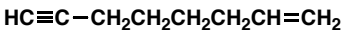
1. Follow alkene rules, but use -yne as suffix.
2. If more than one triple bond is present, use -diyne, -triyne, tetrayne . . .
3. If both double and triple bonds are present,
   - use -enyne as suffix
   - Number from side with nearest multiple bond (either double or triple)
   - If a double and triple bond is equidistant, make the double bond the lower number



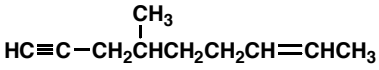
2-butyne



6-bromo-2-methyl-3-heptyne



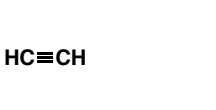
1-octen-7-yne



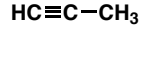
4-methyl-7-nonen-1-yne

Alkynes: Common Names and Groups

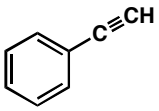
R−C≡C−H	R−C≡C−R
terminal alkyne	internal alkyne



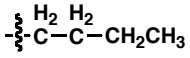
acetylene



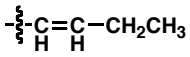
methylacetylene



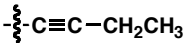
phenylacetylene



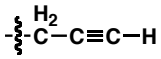
butyl



butenyl

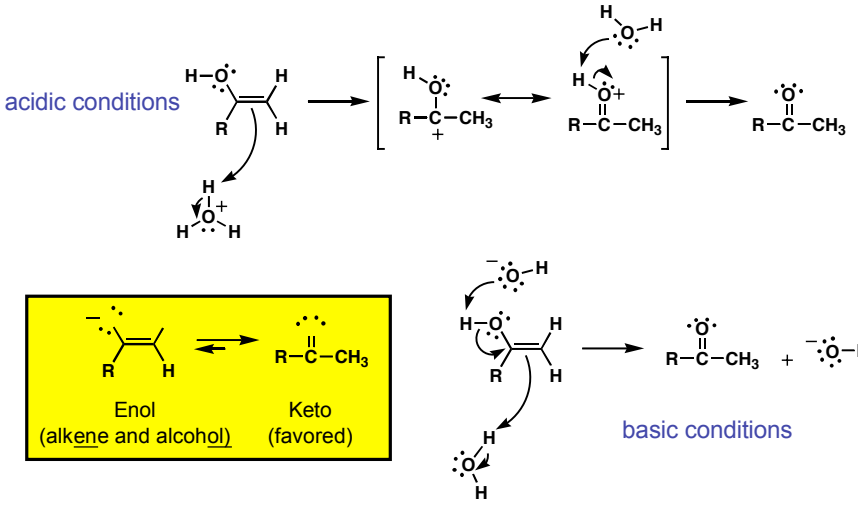


butynyl



propargyl

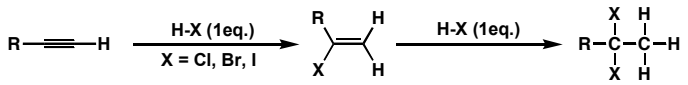
Tautomers - constitutional isomers that differ in the location of a H and a double bond
Tautomerization - conversion between two tautomers



Addition of Halogens to Alkynes

For Terminal Alkynes:

(internal alkynes result in a mixture of products)

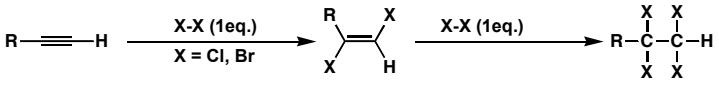


vinylic halide (E or Z)

Markovnikov
Carbocation intermediate

geminal dihalide

Markovnikov
syn + anti addition
Carbocation intermediate



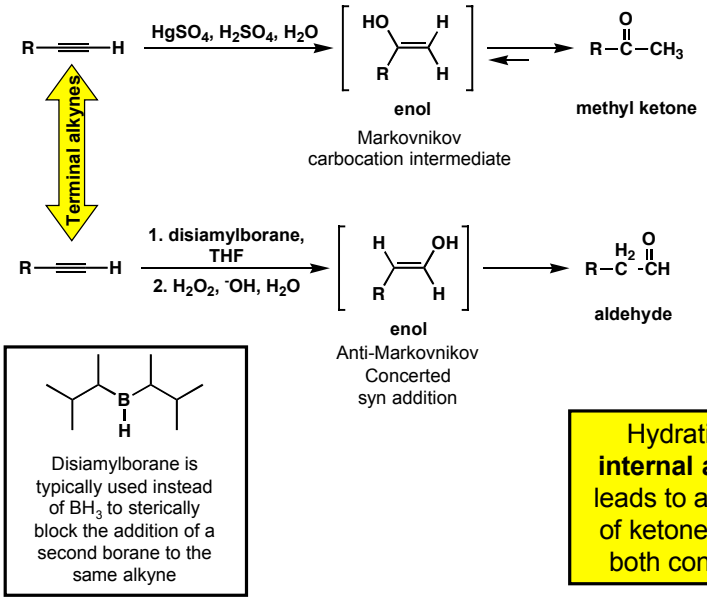
***trans*-dihalide**

Markovnikov

tetrahalide

Markovnikov
anti addition
halonium ion intermediate

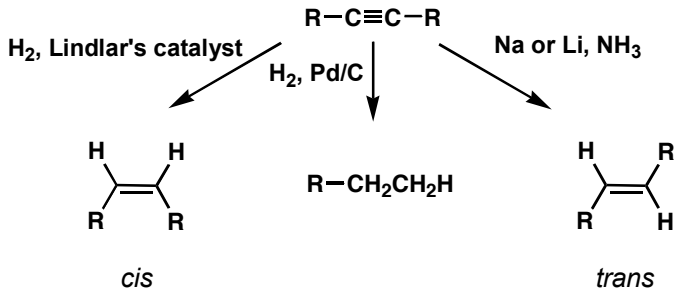
Hydration of Terminal Alkynes



Disiamylborane is typically used instead of BH_3 to sterically block the addition of a second borane to the same alkyne

Hydration of **internal alkynes** leads to a mixture of ketones under both conditions

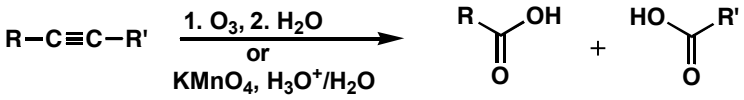
Reduction of Alkynes



Lindlar's catalyst
Deactivated (poisoned) catalyst
Pd, $CaCO_3$, lead acetate, quinoline

Oxidation of Alkynes

Internal Alkyne



Terminal Alkyne