Ch 9 Alkynes

C≡C Triple Bond
– A triple bond has two Π bonds and one σ bond.
– The two C's both have **sp** hybridization, so their geometry is **linear**.
– The σ bond is between two **sp** orbitals, which are shorter and rounder than sp^2 and sp^3 orbs.
– The triple bond is the shortest (120 pm) and strongest (835 kJ) of all known C/C bonds.

Naming Alkynes
– Use same general rules as alkanes and alkenes (sections 3.4 and 7.3)
– Parent is longest chain which has the C≡C.
– Parent name ends with the "-yne" suffix.
– Begin numbering at end closest to C≡C.
   For example, $CH_3CH_2CH_2C≡CCH_3$ is 2-hexyne.
– If two or three C≡C's are on the parent, the suffixes are -diyne and -triyne.
   For example, $HC≡CCH_2C≡CCH_3$ is 1,4-hexadiyne.
– If both C=C and C≡C are present, the molecule is an enyne.
   Start the numbering at the end nearest to the C=C, **not the C≡C**.
   The –ene number can go before either the full parent name or "–en".
   The –yne number goes before the –yne.
   For example, we can have Hept-1-en-6-yne for $H_2C=CHCH_2CH_2CH_2C≡CH$.
– A substituent with a triple bond is alkynyl. For example, HC≡C- is an ethynyl group.

Preparation
– Alkynes are generally prepared by (double) elimination of vicinal dihalides.
   Vicinal dihalides are the same as 1,2-dihaloalkanes.
– $BrCH_2CH_2Br$ treated with 2KOH (two equivalents) in EtOH creates HC≡CH.
– This is dehydrohalogenation, which we saw in chapter 7 creates alkenes from alkyl halides.
   The primary difference here is that we need two equivalents of base (to remove two HX's).
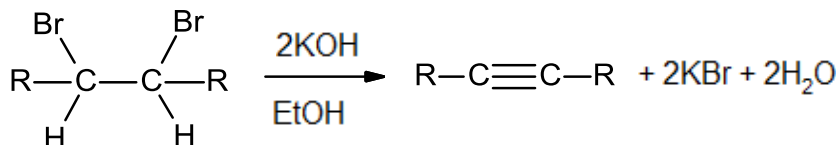
Addition of HX and X_2

- Similar to alkene addition reactions, but not identical.
- With HX addition, the reaction follows Markovnikov's rule,
  so that the H^{+1} adds to the less substituted C preferentially.
  This creates a $2°$ vinylic cation as the intermediate.
  The $1°$ vinylic cation is so unstable that it essentially does not exist.
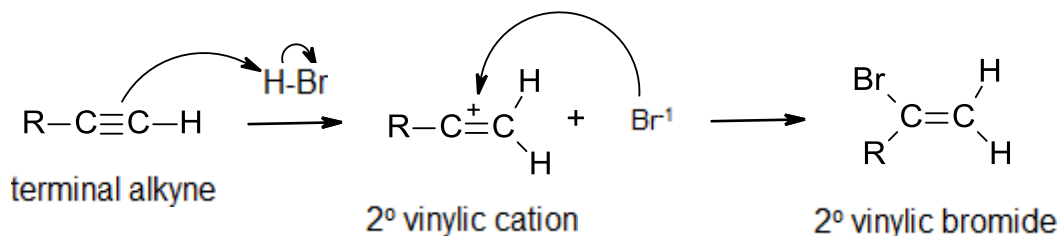
- Two equivalents of HX can be added to an alkyne to make a dihaloalkane.
  For this reaction, X can be Cl, Br, or I.
- Note that both of the halogens have added to the more substituted C.
 The halogens are never added to a terminal C.
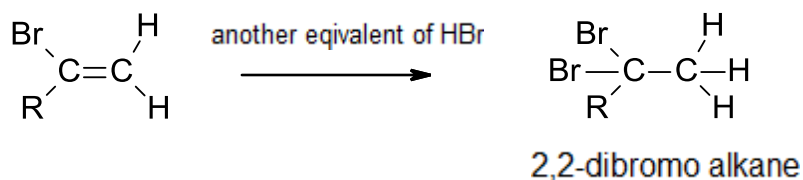
- Addition of the first Br_2 or Cl_2 equivalent puts one halogen on each of the two C's.
  The resulting stereochemistry is always trans.
- Also, two equivalents of X_2 can be added to the alkyne to make a tetrahaloalkane.
 So that two halogens will add to each C.
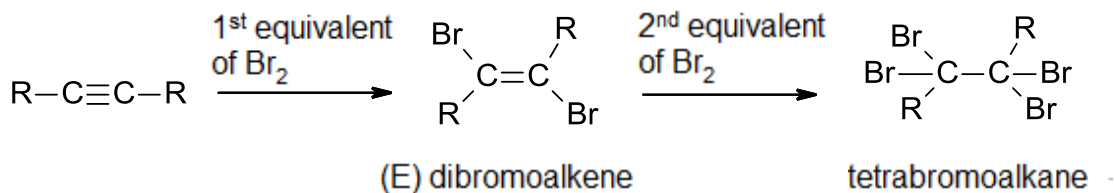
Hydration with Hg(II)
- Water is added to the alkyne triple bond with aqueous $HgSO_4$ and H_2SO_4.
- With a terminal alkyne ($RC{\equiv}CH$), an OH is added to the more substituted C.
  This is Markovnikov orientation, as is the case with oxymercuration of alkenes.
- The C's still have a double bond after the OH addition, which creates an enol ($H_2C{=}COHR$).
- The enol quickly rearranges to a methyl ketone ($H_3CC{=}OR$).
  This called the keto-enol tautomerization, where tautomers are constitutional isomers which interconvert rapidly. In this case, the two tautomers are the enol and the ketone.
- An unsymmetrical internal alkyne ($R'C{\equiv}CR$) will result in a mixture of two ketones.
  ($R'C{=}OCH_2R$ and $R'CH_2C{=}OR$)
- In contrast to oxymercuration of alkenes, $NaBH_4$ is not needed to obtain the product.
  The acid alone is sufficient to remove the Hg.
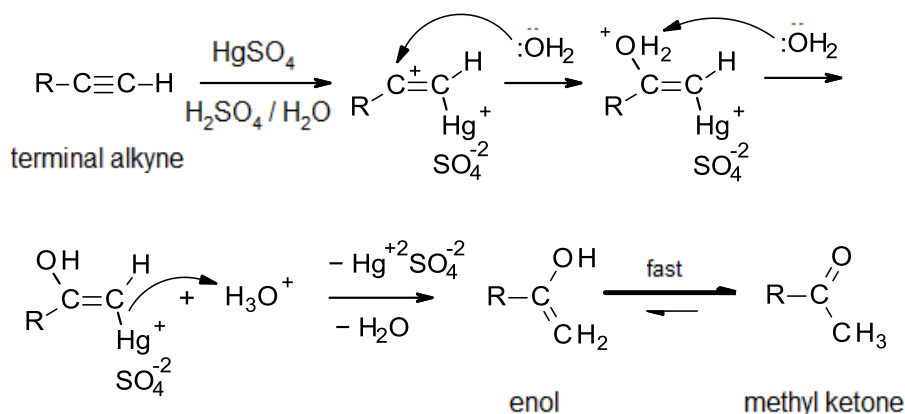
Hydration with Borane (Hydroboration/Oxidation)
- Treating an internal alkyne ($RC{\equiv}CR$) with BH_3 in THF will add BH_2 to one C
  and add H to the other C. This creates a vinylic borane ($RHC{=}CBH_2R$).
- The vinylic borane will be Z, with both alkyls on the same side.
- The vinylic borane is then treated with H_2O_2 and $NaOH_{(aq)}$ at pH 8.
  This creates an enol ($RHC{=}COHR$), which rearranges to a ketone ($RCH_2C{=}OR$).
- Overall, the reaction scheme is as follows:
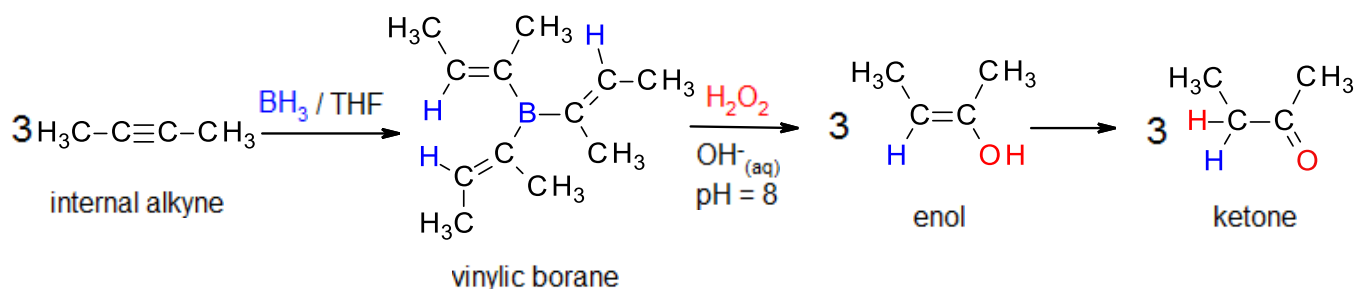
- Using BH_3 with a terminal alkene ($RC\equiv CH$) would simply not work!
  The terminal alkene is more reactive and adds a BH_3 across both Π bonds.
  The B will add to three alkyne molecules,
  which then add to more BH_3, and then more
 alkynes are added, eventually making...

$$3 \ H_3C-C\equiv C-H \xrightarrow{\ BH_3 \ / \ THF\ } \text{(a complete mess)}$$

terminal alkyne

a complete mess
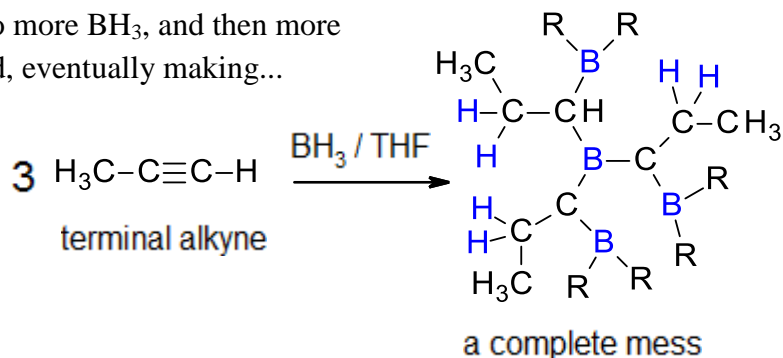
- For terminal alkynes ($R'C\equiv CH$), use R_2BH instead.
  A bulky alkyl group (R) will prevent a reaction with the second Π bond.
  R is typically a cyclohexyl or *sec*-isoamyl group.
- The $-BR_2$ unit adds to the terminal C to create $R'CHCH(BR_2)$.
  H_2O_2 at pH 8 is then added, but the result is an aldehyde ($R'CH_2CHO$) rather than a ketone.

$$H_3C-C\equiv C-H \xrightarrow[\text{THF}]{R_2BH} \text{organoborane} \xrightarrow[\substack{OH^-_{(aq)} \\ pH=8}]{H_2O_2} \text{aldehyde}$$

terminal alkyne   organoborane   aldehyde
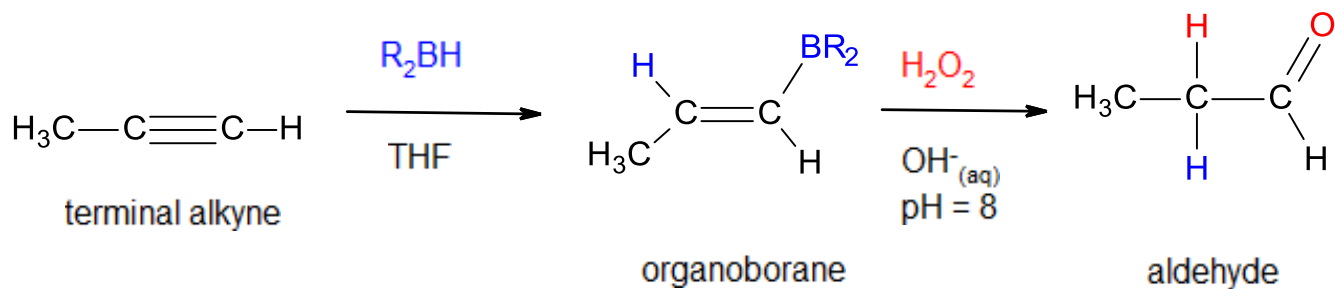
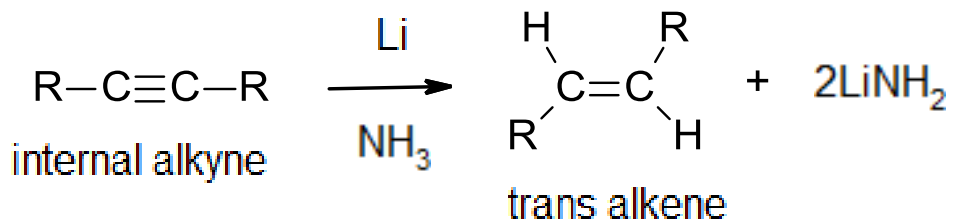Reduction of Alkynes (Cis Hydrogenation)
- As with alkenes, reduction with H_2 using Pd/C or PtO_2 as a catalyst will create an alkane.
- An alkyne can be converted to a cis-alkene using the Lindlar catalyst,
  which is partially-deactivated Pd on $CaCO_3$ support.

$$R-C\equiv C-R \xrightarrow[\text{Lindlar catalyst}]{H_2} \text{cis alkene}$$

internal alkyne   Lindlar catalyst
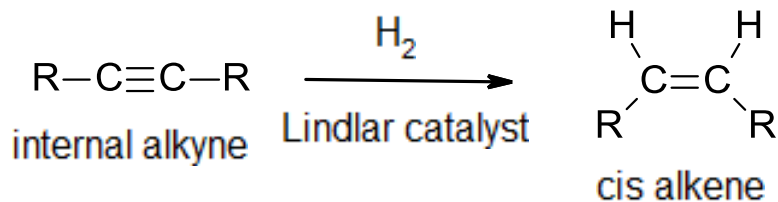
cis alkene

Reduction of Alkynes (Trans Hydrogenation)
- An alkyne can be converted to a trans-alkene using the Li metal and NH_3.
  The reaction is performed at $-33\ ^{\circ}C$, which is the normal BP of NH_3.

$$R-C\equiv C-R \xrightarrow[NH_3]{Li} \underset{\text{trans alkene}}{\overset{\displaystyle \overset{H}{\underset{R}{\diagdown}}C=C\overset{R}{\underset{H}{\diagup}}}{}} \;+\; 2LiNH_2$$

internal alkyne

Oxidative Cleavage
- Either $KMnO_4$ or O_3 can be used, but the results are slightly different than for alkenes.
- Using either reagent with an internal alkyne ($RC\equiv CR$) will create two carboxylic acids.

$$RC\equiv CR \text{ (with either } KMnO_4 \text{ or } O_3) \rightarrow 2RCOOH$$

- Using either reagent with a terminal alkyne ($RC\equiv CH$) will create
  one equivalent of carboxylic acid and one equivalent of O=C=O.

$$RC\equiv CH \text{ (with either } KMnO_4 \text{ or } O_3) \rightarrow RCOOH + CO_2$$

- These reactions have little use in synthesis, but have been
 commonly used in the past to determine alkyne structures.

Alkyne Acidity
- Terminal alkynes can be used to create acetylide anions ($\mathbf{RC{\equiv}C^{-1}}$).
- The shorter sp orbital on the terminal C can stabilize a negative charge,
  because the negative charge is closer to the positive carbon nucleus.
  So, the pKa of the terminal alkyne is ~ 25, which is much lower
  than the pKa of alkyl and alkenyl H's (~ 44 and ~ 60, respectively).
- This is not strongly acidic, but a terminal H can be removed from the alkyne
  with a very strong base, if its conjugate acid has pKa > 25.
- So, $RC{\equiv}CH$ will react with $NaNH_2$ (sodium amide), because NH_3 has pKa = 35.

$$RC{\equiv}CH + NaNH_2 \text{ (in } NH_3) \rightarrow RC{\equiv}C^{-1}Na^{+1} + NH_3$$

Alkylation of Acetylide Anions
- The acetylide anion can replace a halide of a 1° alkyl halide (RCH_2Br).
- The halide needs to be 1°, because 2° and 3° will undergo eliminations instead.

$$RC{\equiv}C^{-1}Na^{+1} + BrCH_2R' \rightarrow RC{\equiv}CCH_2R' + Na^{+1} + Br^{-1}$$
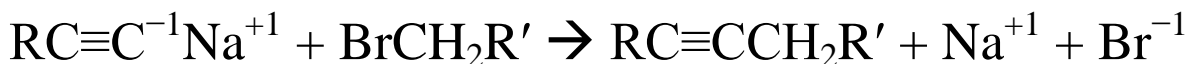
- The result is a longer internal alkyne, rather than the another terminal alkyne.
- The full scheme can be seen in this example:

$$CH_3C{\equiv}CH + NH_2^{-1} \text{ (in } NH_3) \rightarrow CH_3C{\equiv}C^{-1} + NH_3$$
$$CH_3C{\equiv}C^{-1} + BrCH_2CH_3 \rightarrow CH_3C{\equiv}CCH_2CH_3 + Br^{-1}$$