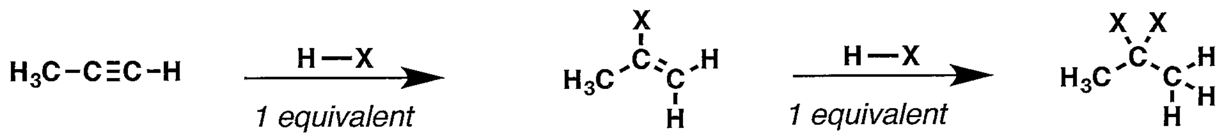
Chapter 5: Reactions of Alkynes
Addition of Hydrogen Halides To Alkynes

General Reaction:



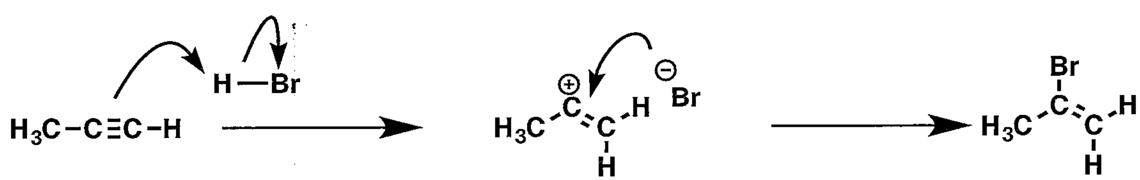
Vinyl halide *"Geminal" dihalide*

HX is a strong acid (e.g. HCl, HBr, HI) Addition of X to most substituted carbon ("Markovnikov")

Mechanism Basics Box:

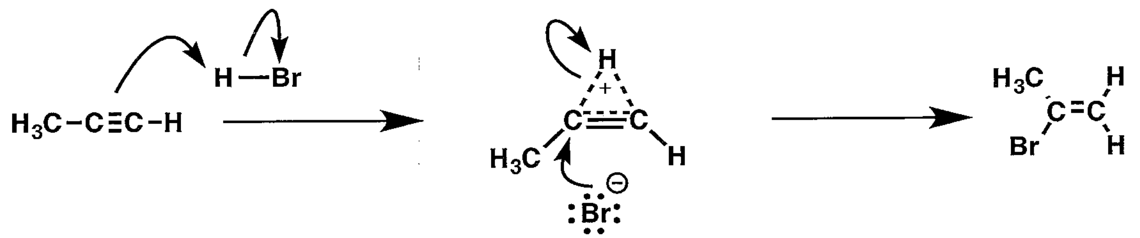
- Acids (HX) include HCl, HBr, and HI
- Mechanism is very similar to HX addition to an alkene
- Mechanism is not completely worked out! In one version, the first step is protonation of the alkyne to give a vinyl carbocation, which is trapped by the addition of X^-
An alternative mecahnism invokes a cyclic protonium ion, or alkyne complex with two molecules of H–Br
- The net effect is addition of HX across the triple bond with X at the "most substituted" position ("Markovnikov" selectivity)
- Addition of a second equivalent of HX will add to this product to give a "geminal dihalide". See mechanism for HX addition to an alkene.

General Mechanism:



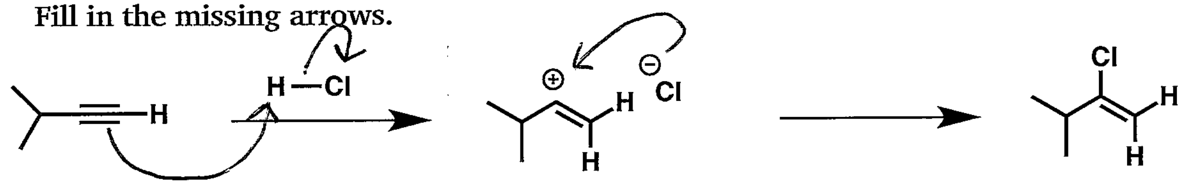
vinyl carbocation intermediate

A Possible Alternative Mechanism

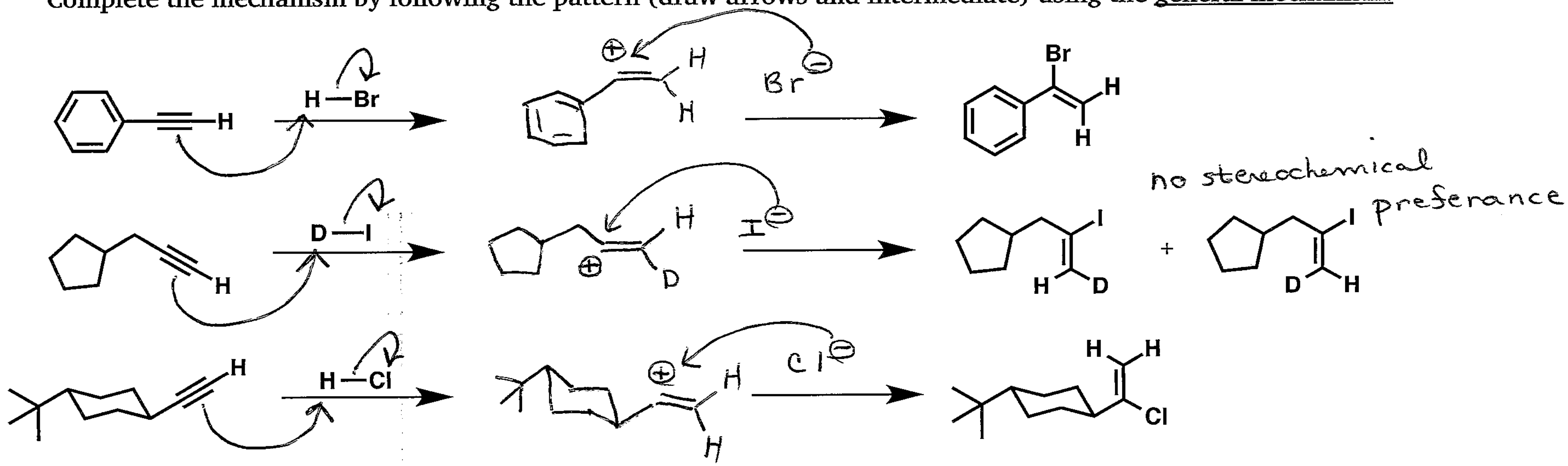


cyclic protonium ion

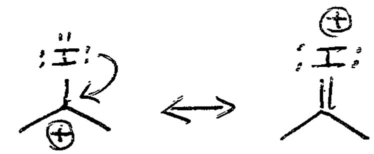
Fill in the missing arrows.



Complete the mechanism by following the pattern (draw arrows and intermediate) using the <u>general mechanism.</u>

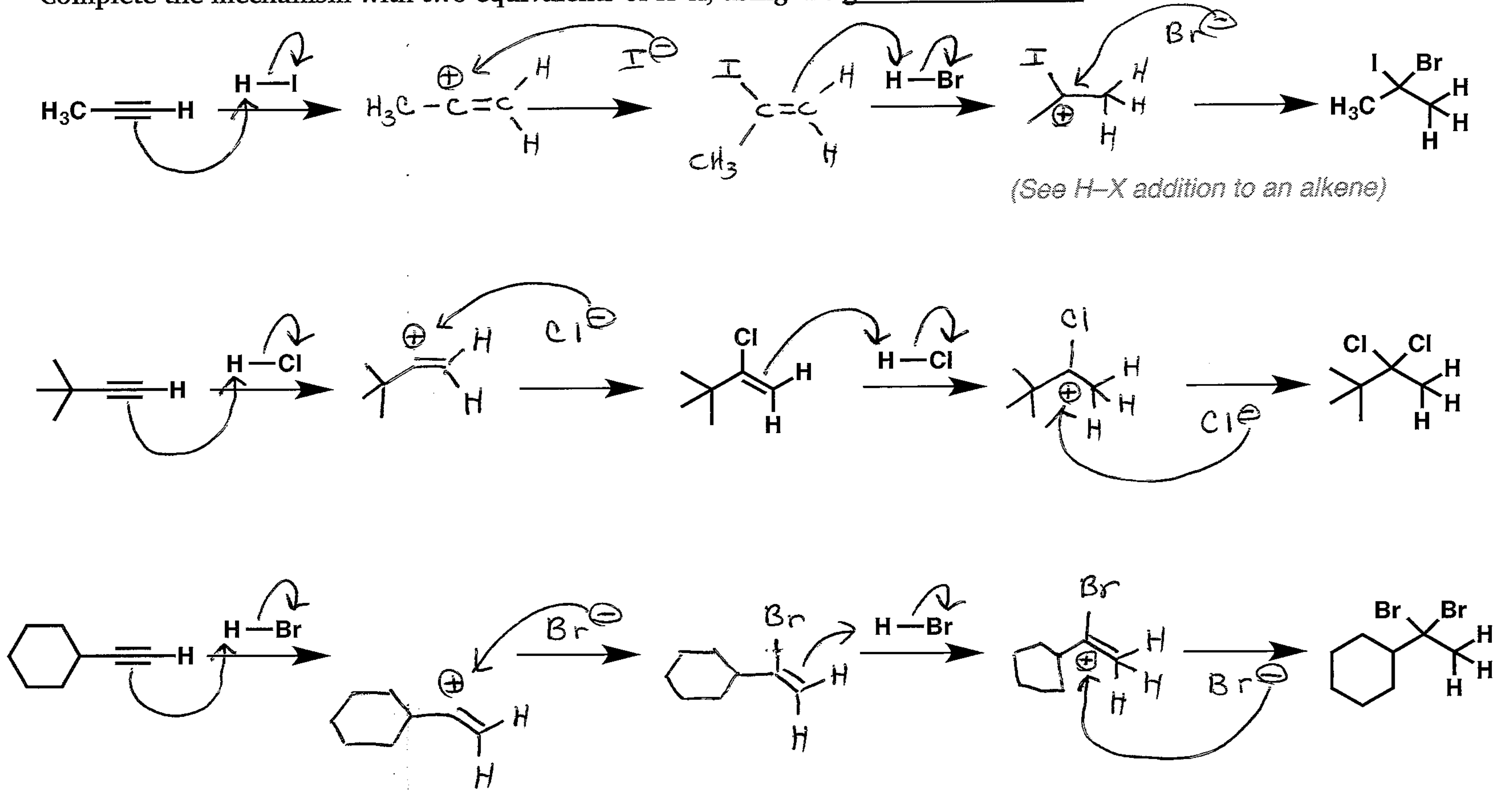


no stereochemical preferance



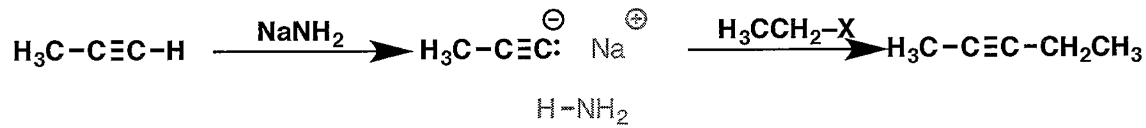
Stabilize the carbocation via resonance delocalization

Complete the mechanism with two equivalents of H–X, using the general mechanism



Alkylation of Acetylide Ions

General Reaction:



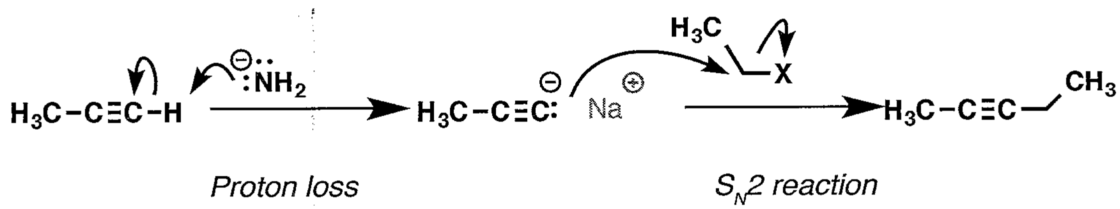
Most common base is $NaNH_2$ but can also use:

- *KNH_2*
- *Alkyl lithium reagents (e.g. BuLi)*
- *Grignard reagents (R–MgBr)*

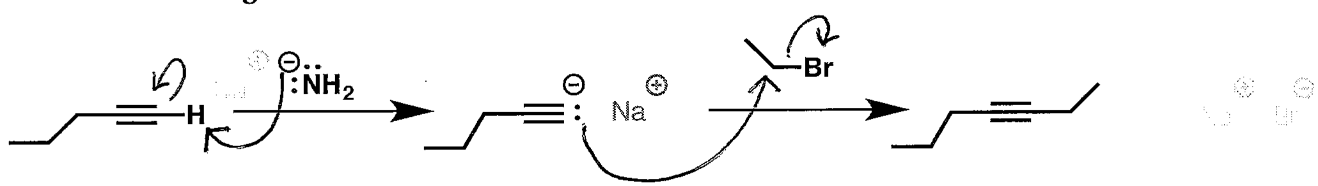
Mechanism Basics Box:

- Alkyne C–H is unusually acidic for a hydrocarbon (pKa = 25)
- First step is deprotonation of alkyne C–H by strong base (such as $NaNH_2$)
- Second step is S_N2 reaction of acetylide ion on the alkyl halide ("R–X")
- Works best if the alkyl group is methyl or primary; elimination (E2) occurs if "R" is secondary
- NaOH is not a strong enough base to deprotonate the alkyne

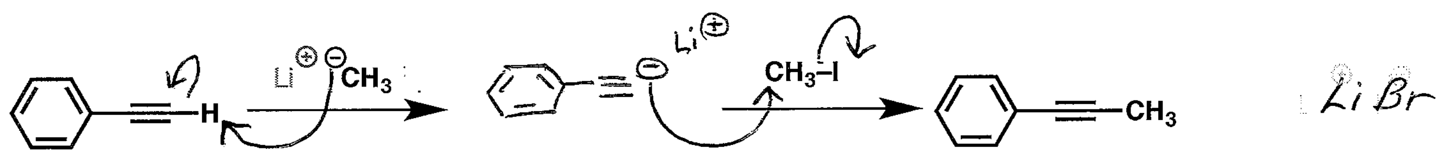
General Mechanism:

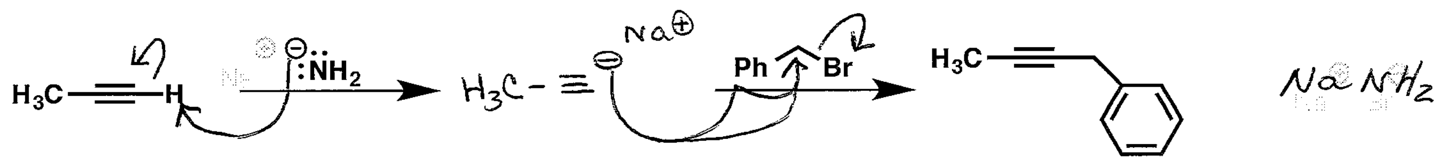


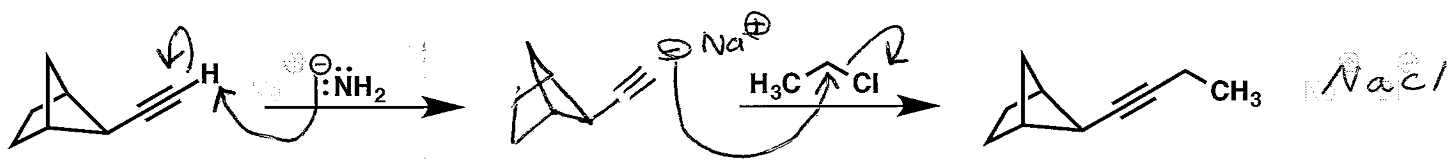
Fill in the missing arrows.



Complete the mechanism by following the pattern (draw arrows and intermediate)

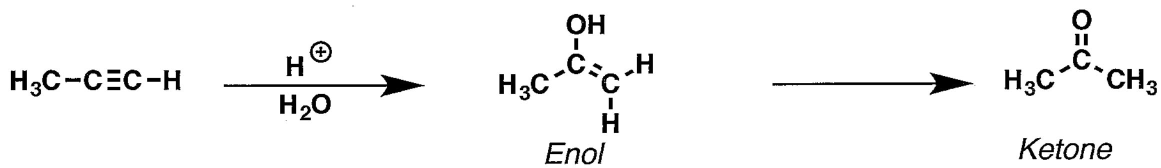






Hydration of Alkynes

General Reaction:

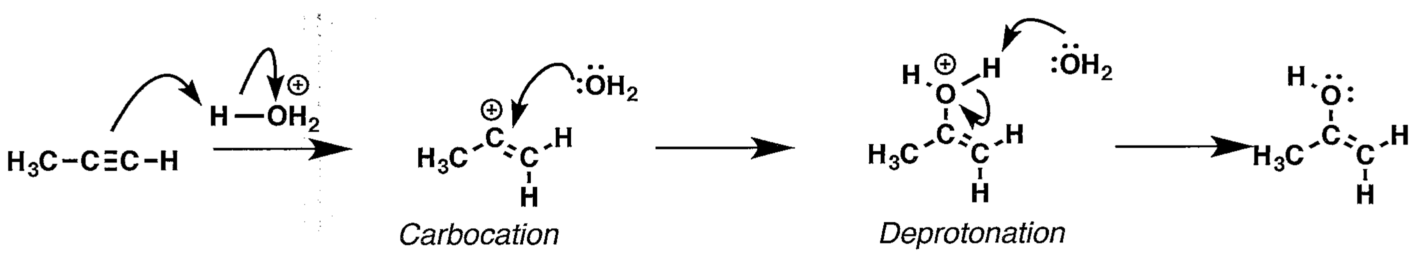


Can also be written H_3O^+ or H_2O/H_2SO_4

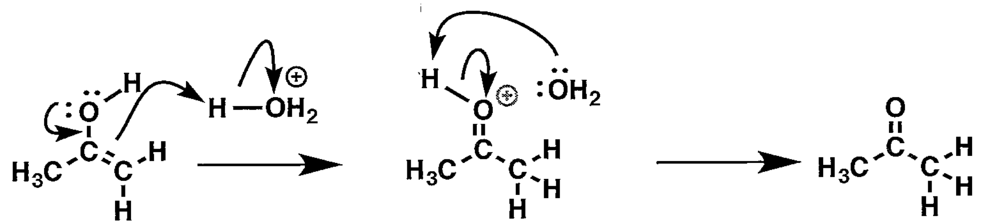
Mechanism Basics Box:

- Can also be written H_3O^+ or H_2SO_4/H_2O
- First step is protonation of alkyne to give carbocation
- Second step is attack of water (solvent) on carbocation to give an "enol"
- Third step is a rearrangement ("tautomerization") of the enol to give the ketone
- Note that addition of water is "Markovnikov" - the C–O bond is being formed on the most substituted carbon
- Rearrangement of the carbocation does not occur

General Mechanism, Part 1: Enol Formation

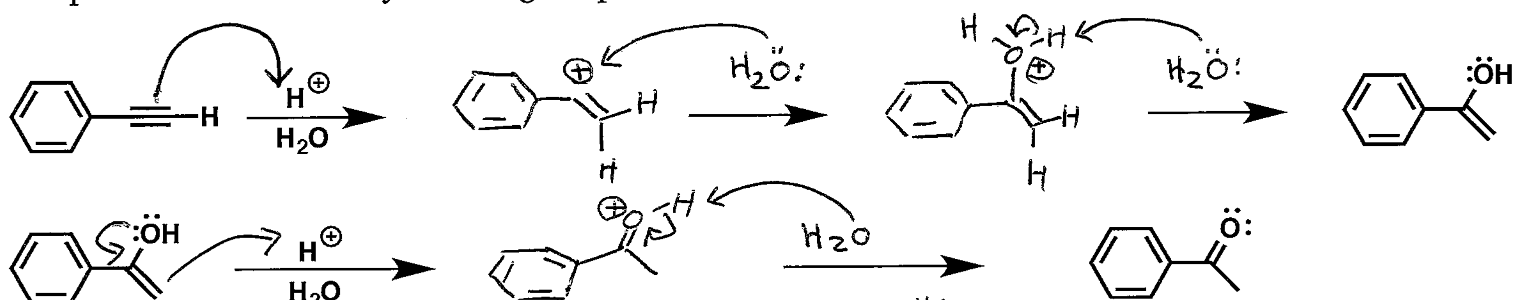


General Mechanism, Part 2: Keto-Enol Tautomerism

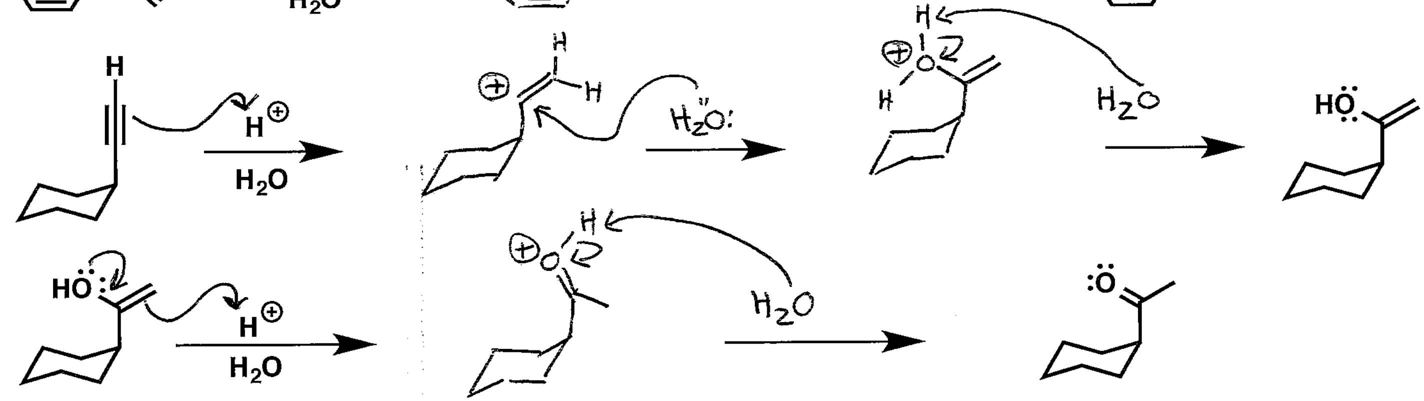


Complete the mechanism by following the pattern (draw arrows and intermediate)

a)

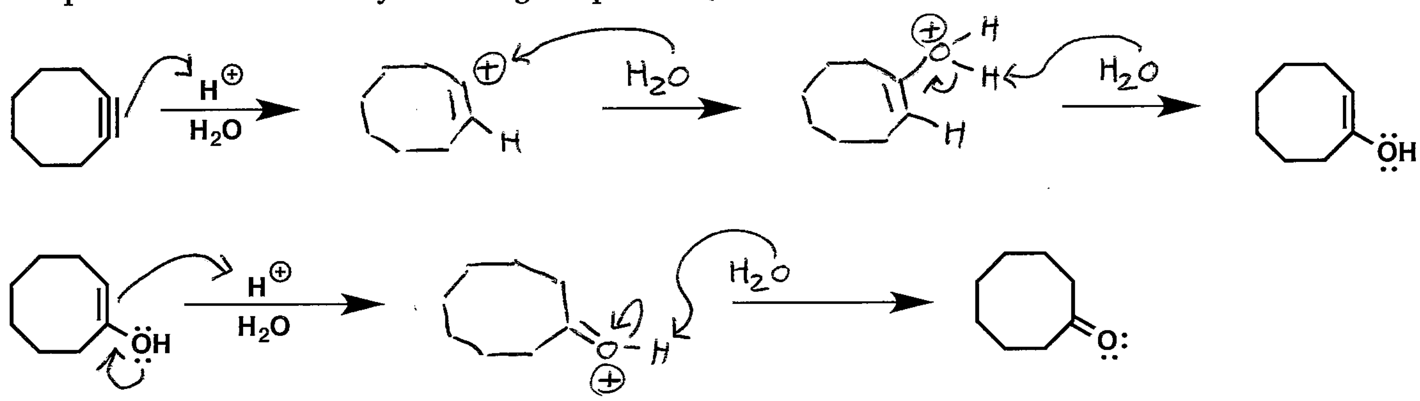


b)



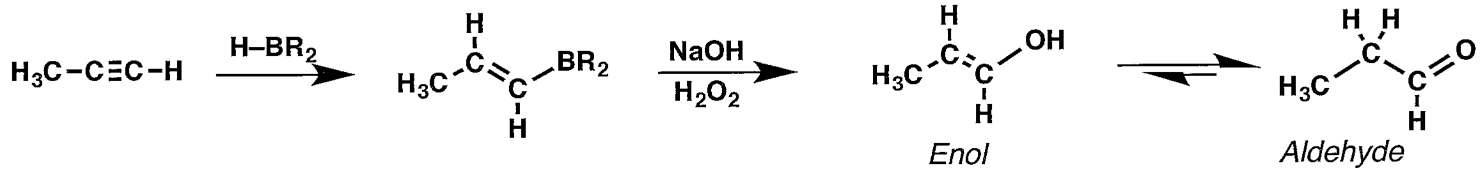
Complete the mechanism by following the pattern (draw arrows and intermediate)

c)



Hydroboration of Alkynes

General Reaction:



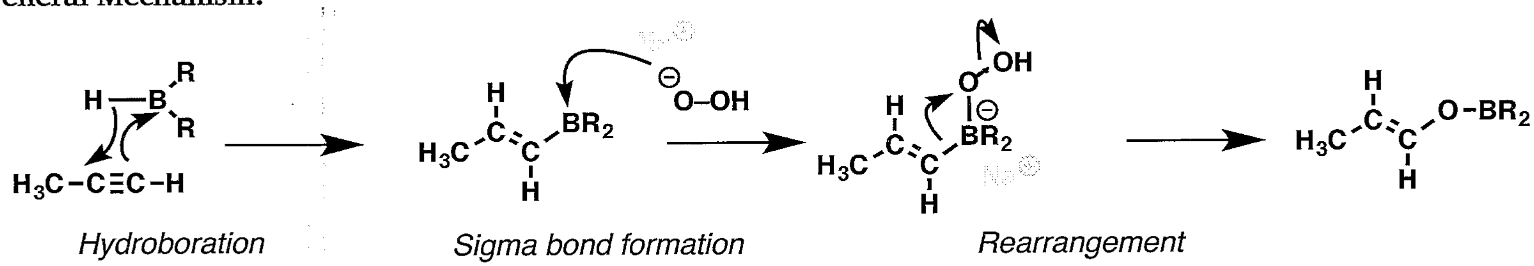
Note: anti-Markovnikov addition

Use of "bulkier" hydroboration reagents gives higher selectivity for anti-Markovnikov product
Examples of "H–BR_2" are 9-BBN, disiamylborane, catecholborane

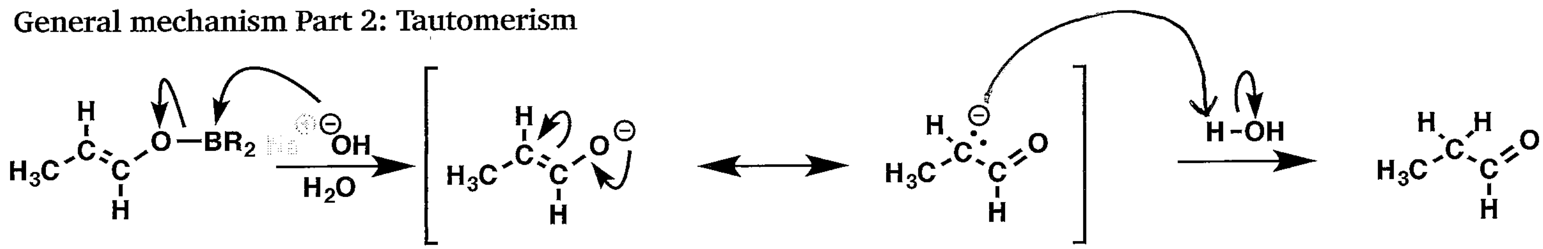
Mechanism Basics Box:

- First step is hydroboration - a concerted reaction that forms C–B and C–H
- Hydroboration is "anti-Markovnikov" - H ends up on the more substituted carbon, B on the less substituted carbon
- Second step (NaOH/H_2O_2) is oxidation - break C–B and form C–O with retention of configuration
- Next, O–B is cleaved to give an "enol" which rearranges ("tautomerism") to carbonyl
- Reaction on terminal alkynes gives aldehydes as the final product

General Mechanism:

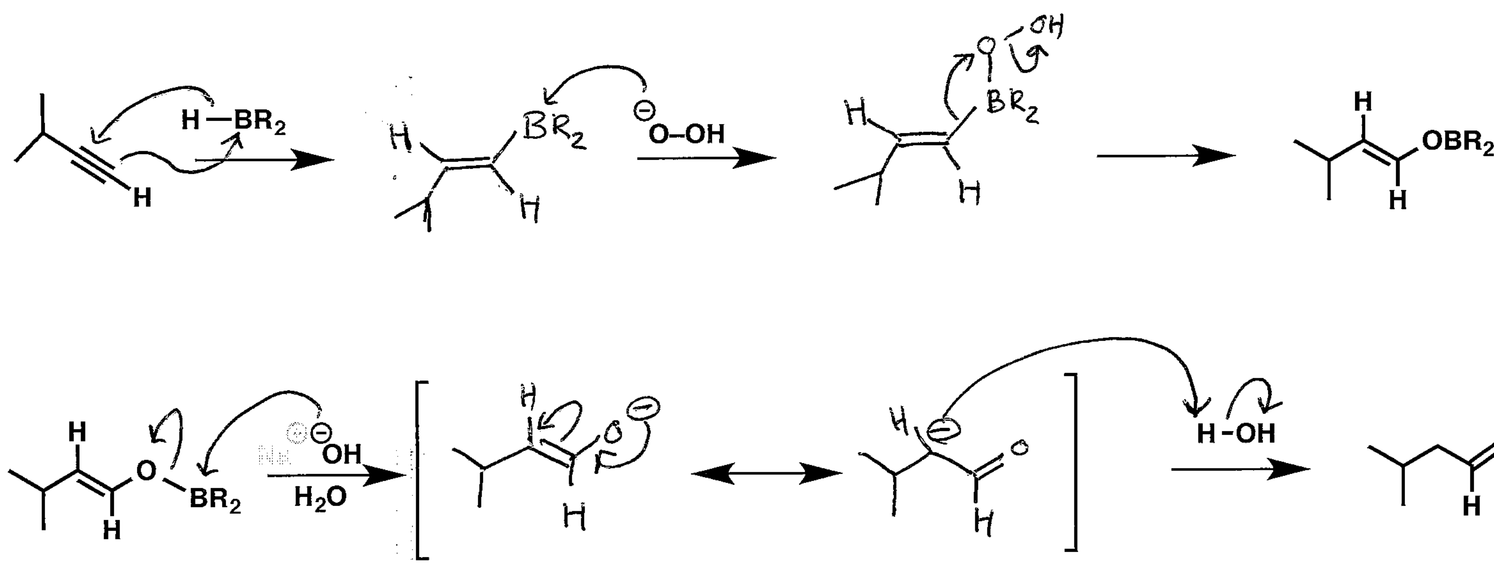


General mechanism Part 2: Tautomerism



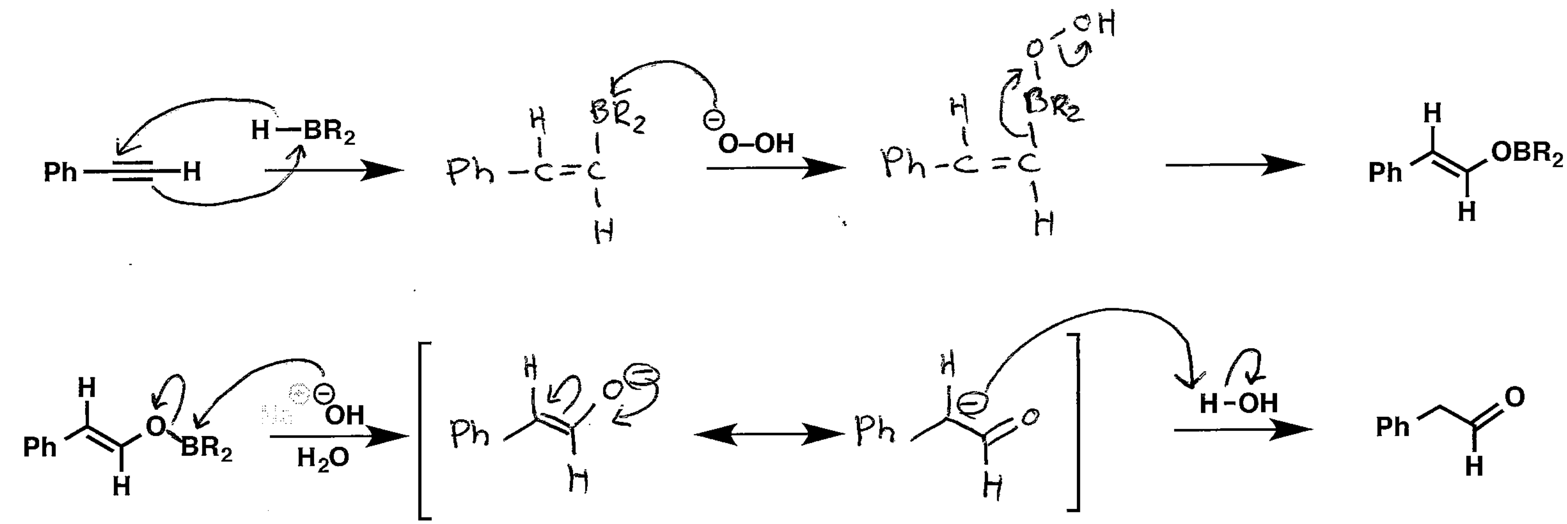
Complete the mechanism by following the pattern (draw arrows and intermediate)

a)

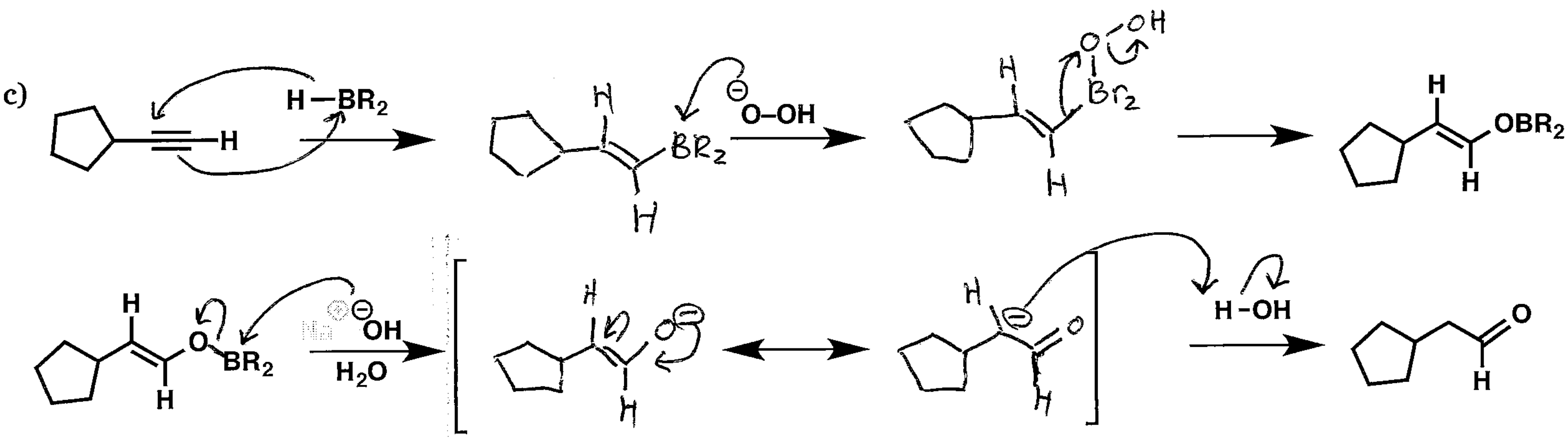


Complete the mechanism by following the pattern (draw arrows and intermediate)

b)

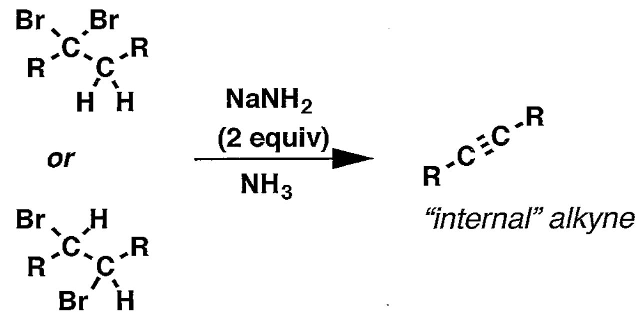


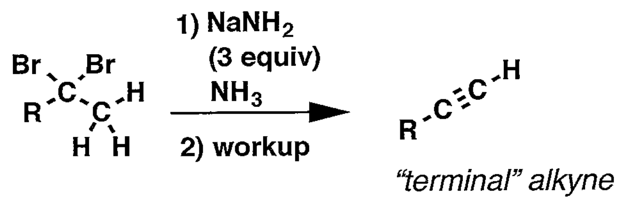
c)



Double Elimination To Form Alkynes

General Reaction:

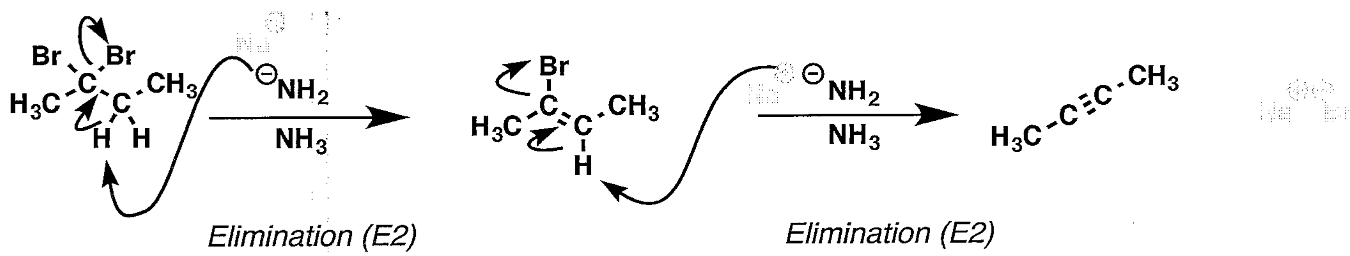




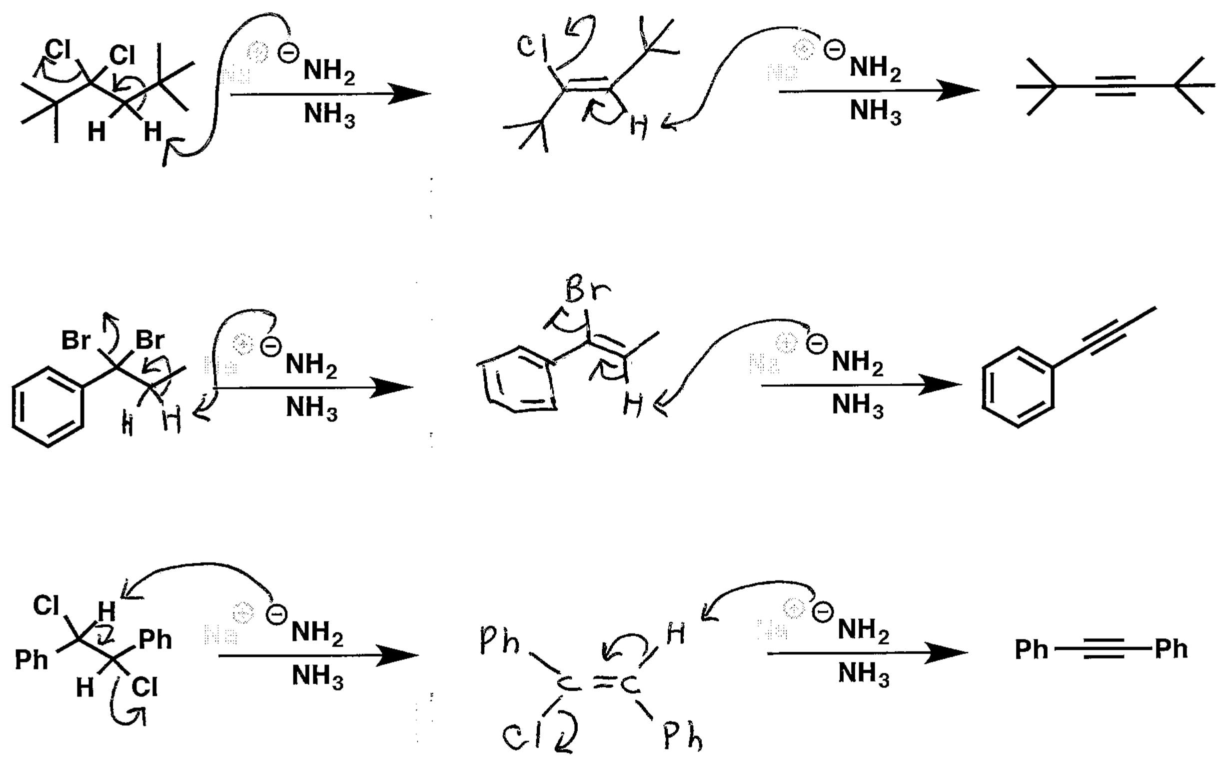
Mechanism Basics Box:

- Each elimination occurs anti (as with E2)
- Two equivalents of $NaNH_2$ used in formation of "internal" alkyne
- When terminal alkynes are used the alkyne ends up being deprotonated (3 equivalents)
- Rare case of elimination occuring on an sp^2 hybridized carbon

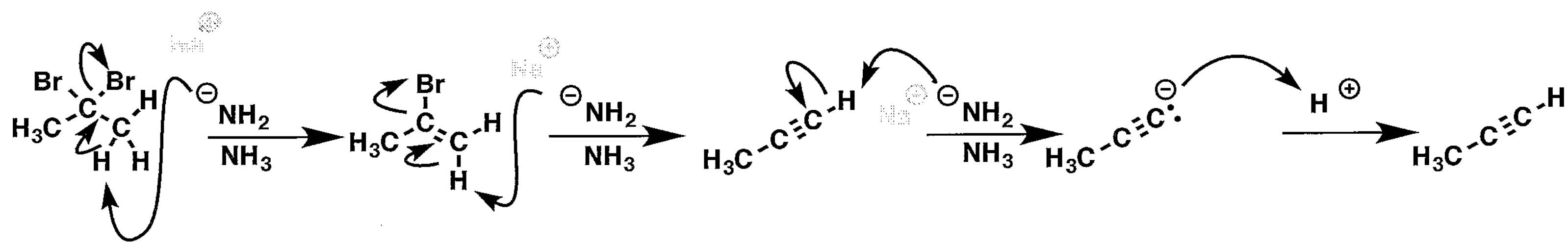
General Mechanism (internal alkynes)



Complete the mechanism by following the pattern (draw arrows and intermediate)



If you make a terminal alkyne, you need to use an extra equivalent of base. Here's why:



Complete the mechanism by following the pattern (draw arrows and intermediate)