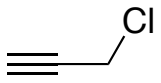
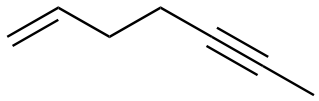
CHAPTER 9. ALKYNES: AN INTRODUCTION TO ORGANIC SYNTHESIS

Alkyne Nomenclature. Like alkenes, number so the alkyne gets the lowest number. Name the following two molecules:

$H_3C-C\equiv CCH_2CH_2CH(CH_3)_2$



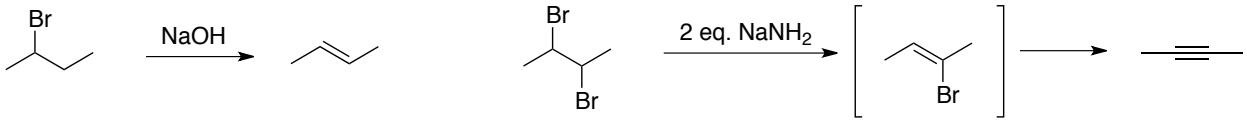
If, however, you have a molecule with both an alkene *and* an alkyne, the priority is determined by which gives you the lowest combination of numbers (1 and 5 versus 2 and 6):



1-hepten-5-yne

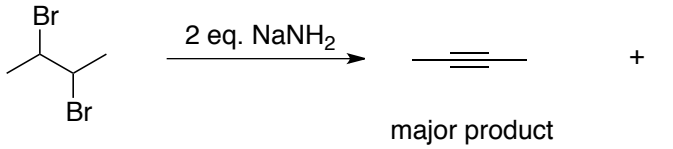
Draw 1-buten-3-yne:

Formation of Alkynes. Just like alkenes can be made through β-elimination, the same is true for alkynes… but twice.



It is important to note that the second β-elimination requires more energy than the first, and in part this is why a stronger base is used. Sodium amide, $NaNH_2$, is a common base used in alkyne synthesis.

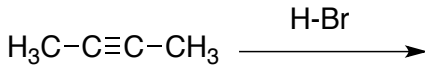
Although allenes are not typically formed in high yields, the two β-eliminations may generate a molecule that has one carbon having a double bond with each of its adjacent carbons. Can you draw the allene that may be formed by the following reaction?



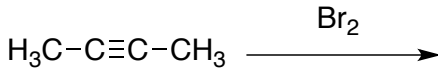
major product allene

Addition of HX and X_2. Electrophilic addition reactions occur nearly the same as their analogous alkene-versions. The primary difference is that there is ONE pi bonds in an alkene and TWO in an alkyne.

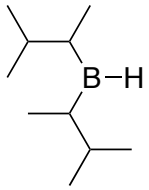
Try drawing the mechanism for the following - and predict the final product. Don't forget unless you are told otherwise, there is an excess of chemical reagents present.

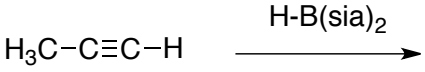


Let's try this one:



Hydration. The primary difference between hydration of alkenes and alkynes is that alkenes form alkyl alcohols and alkynes form vinyl alcohols (called enols). Most enols, however, are unstable and rapidly rearrange to give aldehydes and ketones.

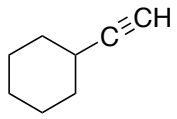
$H\text{-}B(sia)_2$ = 



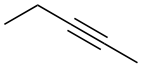
Draw the intermediate alkenylborane in the above space.

Now without concerning yourself with mechanism, draw the vinyl alcohol (enol) product after adding NaOH, H_2O and H_2O_2:

Some problems. Hydroboration leads to the least-substituted alkylborane, which ultimately leads to the least-substituted vinyl alcohol (enol). Depending on the molecule, this can lead to an aldehyde or ketone. Draw the final product(s) of these reactions:



1. $HB(sia)_2$
2. $NaOH, H_2O_2, H_2O$



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$H_3C-C\equiv CH$

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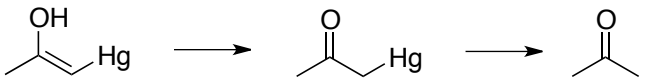
compare

Hydration by oxymercuration can also be applied to alkynes, but with slight modification. Here we see that acid-catalyzed hydration (we did this in chapter 8) is combined with oxymercuration to give a procedure unique to alkynes, but with a result that is not surprising:

$H_3C-C\equiv CH$ $\xrightarrow{HgSO_4,\ H_2SO_4}$ 

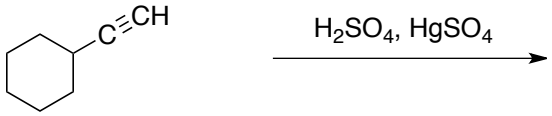
note that the alcohol is on the MOST substituted carbon, as we would expect for this reaction.

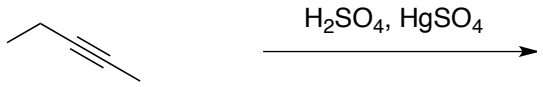
The first step is to recognize that $HgSO_4$ is a salt. Draw the mechanism and resulting reaction intermediate of 1-propyne with Hg^{2+} (forms a three-membered bridged intermediate):

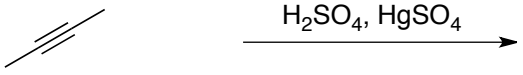
$H_3C-C\equiv CH \quad + \quad Hg^{2+}\ SO_4^{2-} \longrightarrow$

Here's the intermediate you should have drawn (the one on the left of the reaction arrow). Draw a mechanism showing water reacting with this to produce an enol (this ultimately forms the ketone):

Draw the final product(s):

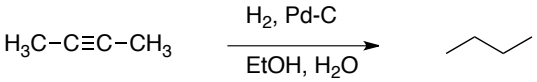




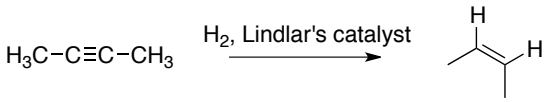


Oxidative Cleavage. Ozone, KMnO4… They tend not to work very well with alkynes. The reactions are low yielding and are sometimes unpredictable - so we won't take the time to discuss these reactions.

Reduction. Alkynes can be reduced in three ways.

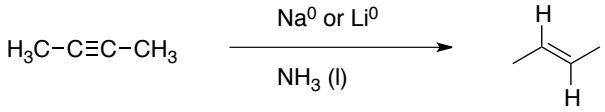


mechanism is same as before - syn addition (but twice)



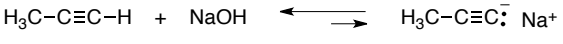
lindlar's catalyst = Pd-$CaCO_3$-PbO_2 or other variation

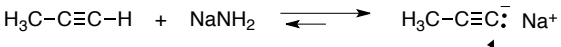
mechanism is same as before - syn addition



this is usually referred to as a"dissolving metal reduction"

Alkyne Acidity. The pKa of terminal alkene hydrogens is about 25, and by using a strong enough base ($NaNH_2$ or similar), we can remove the proton to give a nucleophilic carbon atom.

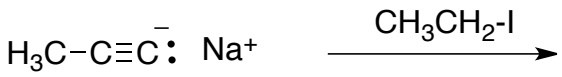




Carbon can be a strong nucleophile

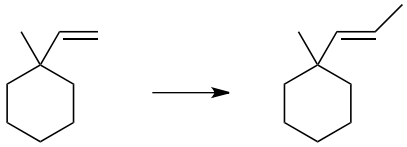
Draw the mechanism for this:

Negatively charged carbons make great nucleophiles. Draw the mechanism and product for the reaction below:

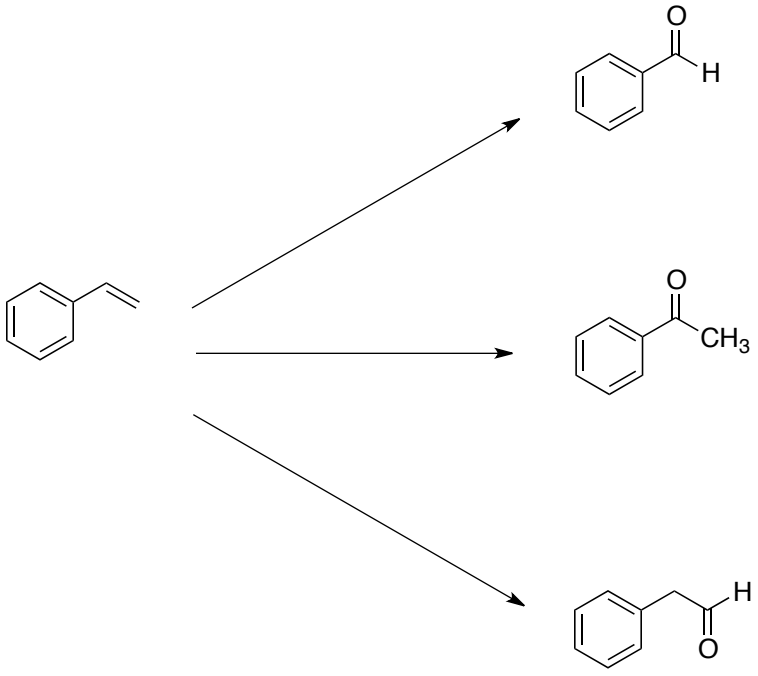


… and now let's tie it all together:

Provide chemical reagents (more than one step) that affect the following transformation:



Provide chemical reagents that affect the following transformations (may be more than one step):



Provide chemical reagents that affect the following transformations (some of these may be more than one step):