Objective 13: Apply reactivity principles to Electrophilic Addition reactions 2: alkynes - identify structural features (pi bond) and electrophiles, use curved arrows to predict product.

Quiz Practice problems

Key ideas:

Alkyne addition reactions are essentially the same as alkene addition reactions.

In an addition reaction, a carbon-carbon pi bond (nucleophile) reacts with an electrophile, which adds (forms a sigma bond) to each C in the triple bond.

Structural features: C=C pi bond, electrophile

In general, a carbocation intermediate forms. Stability of carbocations: $3^o > 2^o > 1^o$

The stability of the carbocation intermediate determines the product. See Markovnikov addition.

An addition reaction is the reverse of an elimination reaction.

Reaction to make a carbon-carbon bond: acetylene + strong base (see pK_a table) --> acetylide ion – RX --> HCCR + X^-.

This reaction is used to make bigger compounds from smaller compounds.

Skills:

Identify C=C pi bond in a compound.

Identify electrophile in addition reaction.

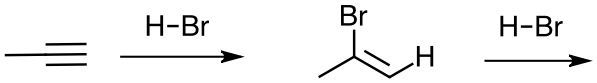
Given reactants, use curved arrows to show how nucleophile (C=C pi bond) reacts with electrophile to form addition product(s).

Identify the major product if more than one addition product forms.

Identify reaction conditions for Markovnikov addition.

Identify reaction conditions for non-Markovnikov addition.

1. Hydrohalogenation: Propyne reacts with HBr to form 2-bromopropene.



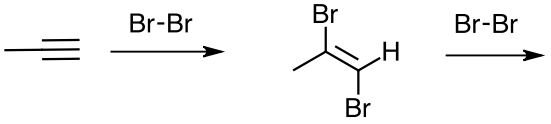
a. Use curved arrows to show how propyne reacts with HBr to form 2-bromopropene.

b. Why does 2-bromopropene form and not 1-bromopropene?

c. 2-bromopropene reacts with HBr. Draw the structure of the product(s).

d. Remember organic reactions are reversible. How would you make propyne?

2. Halogenation: Propyne reacts with Br_2 to form 1,2-dibromopropene.



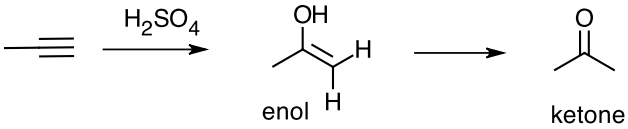
a. Use curved arrows to show how propyne reacts with Br_2 to form 1,2-dibromopropene.

b. 1,2-dibromopropene reacts with Br_2 to form _____. Draw the structure of the product(s).

c. Remember organic reactions are reversible. How would you make propyne?

3. Hydration: alkyne addition is like alkene addition with a “twist.”

Propyne reacts with H_2SO_4 (and a Hg^{2+} catalyst) to form an enol. The enol then forms (tautomerizes) to a ketone, which is more stable than the enol.



a. Use curved arrows to show how propyne reacts with H_2SO_4 to form the enol. (Hint: react the carbocation with water in the 2nd step.)

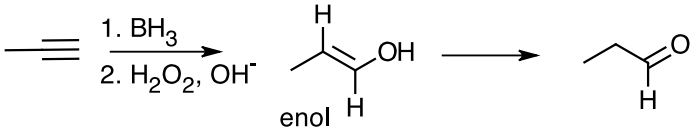
b. To convert the enol to the ketone:

(i) draw a resonance structure of the enol. Use curved arrows to show bonds breaking and forming. (You did this a few weeks ago in Objective 3.)

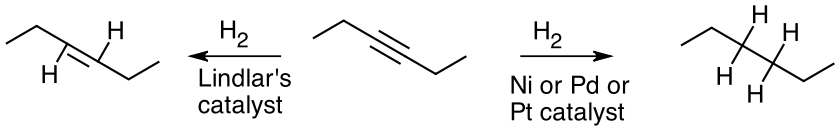
(ii) The less stable resonance structure reacts with H^+. Draw the product of this reaction. Use curved arrows to show bonds breaking and forming.

(iii) A base, $B:^-$, reacts with the product in (ii). Draw the product of this reaction. Use curved arrows to show bonds breaking and forming.

c. Propyne also undergoes hydroboration (1. BH_3 followed by 2. H_2O_2/OH^-) to form the enol on the less substituted C (anti-Markovnikov addition). The enol converts to an aldehyde. You want to know the reactants and products of the hydroboration reaction but you will not be responsible for knowing the hydroboration mechanism.

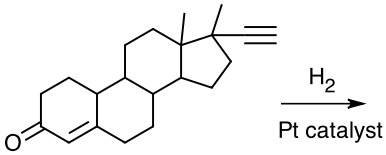


4. Hydrogenation: an alkyne reacts with H_2 with a Ni or Pd or Pt catalyst to make an alkene or alkane. The catalyst determines whether the alkene or alkane product forms.

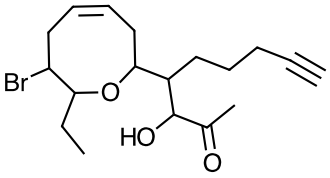


Predict the product of each reaction:

a. Norethindrone is an oral contraceptive. Draw the structure of the product of this reaction.



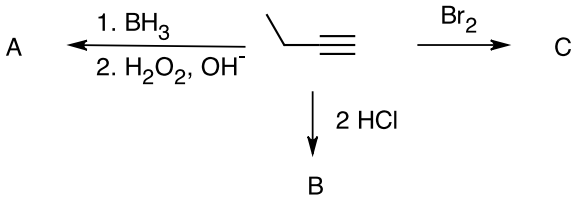
b. Which catalyst would you use that reacts at the alkyne only? Draw the product of this reaction.



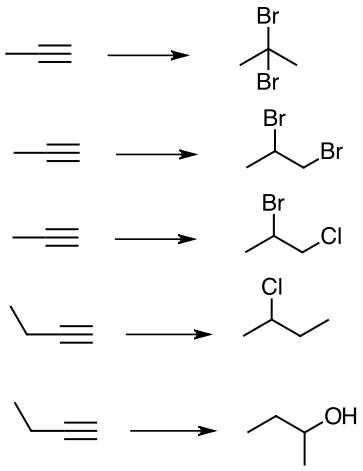
naturally occurring alkyne
isolated from red algae

(From http://chemistry.creighton.edu/~mhulce/ORGANIC/323/323%20slides/alkynes2.pdf)

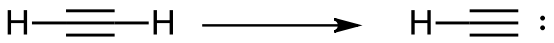
5. a. Predict the product of each reaction. Use curved arrows to show how each reaction occurs.



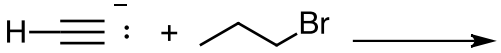
b. Determine the reaction conditions to make the product. Some reactions may take more than one step. Use curved arrows to show how each reaction occurs.



6. Review of proton transfer and substitution reactions.
Acetylene is a very weak acid and needs a very strong base to remove its acidic H:



a. See a pK_a table. What is the weakest base that can be used in this reaction?
b. The acetylide ion (conjugate base of acetylene) is a strong base and nucleophile. This ion can be used in a substitution reaction. Draw the structure of the substitution product. Use curved arrows to show how the reactant forms products.



Note: this is a good way to make a bigger molecule from a smaller one. So this reaction is very valuable in organic synthesis. See Objective 15.

c. Another organic product can form. Draw the structure of the other product. Use curved arrows to show how the reactant forms products.