

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:  $3^\circ > 2^\circ > 1^\circ$

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)  $\rightarrow$  acetylide ion - RX  $\rightarrow$  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.

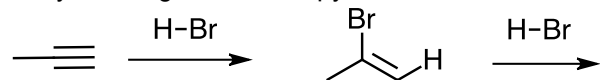
Given reactants, use curved arrows to show how nucleophile (C=C pi bond) reacts with electrophile to form addition product(s).

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.

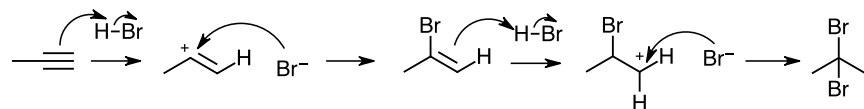
b. Why does 2-bromopropene form and not 1-bromopropene?

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

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

Answers:

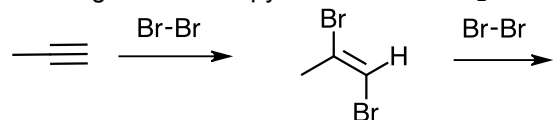
a and c.



b. Acetylene reacts with HBr to form the more stable  $2^\circ$  carbocation (shown) rather than the less stable  $1^\circ$  carbocation. 2-bromopropene forms from the more stable  $2^\circ$  carbocation. 1-bromopropene does not form because the less stable  $1^\circ$  carbocation does not form.

d. Do an elimination reaction: react the dihalide, e.g., 2,2-dibromopropane, with excess strong base, e.g.,  $C_2H_5O^-$ , to form 2-bromopropene (intermediate), which reacts with the strong base to form 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.

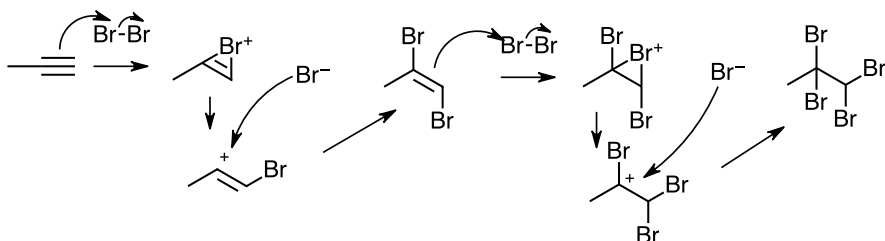
b. 1,2-dibromopropene reacts with  $Br_2$  to form \_\_\_\_\_. Draw the structure of the product(s).

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

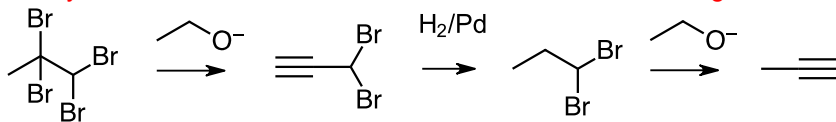
Answers:

a and b.

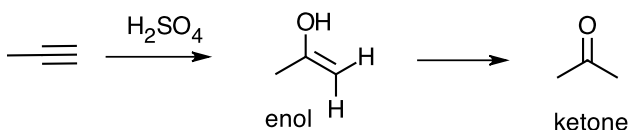
1,2-dibromopropene reacts with  $Br_2$  to form 1,1,2,2-tetrabromopropane.



c. Do an elimination reaction to eliminate 2 Br leaving groups. Then, do a hydrogenation (addition) reaction. Finally, do an elimination reaction to eliminate the 2 remaining Br leaving groups.



3. Hydration: alkyne addition is like alkene addition with a "twist." Propyne reacts with  $\text{H}_2\text{SO}_4$  (and a  $\text{Hg}^{2+}$  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  $\text{H}_2\text{SO}_4$  to form the enol. (Hint: react the carbocation with water in the 2<sup>nd</sup> step.)

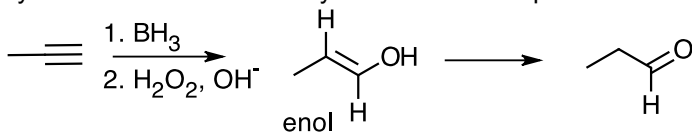
b. To convert the enol to the ketone:

(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.)

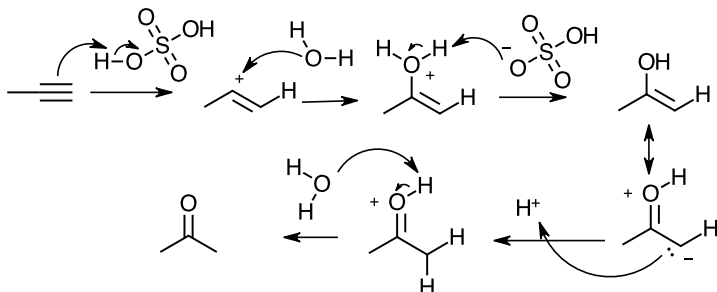
(ii) The **less** stable resonance structure reacts with  $\text{H}^+$ . Draw the product of this reaction. Use curved arrows to show bonds breaking and forming.

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

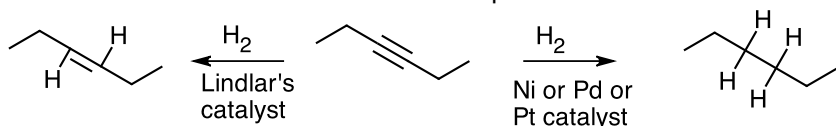
c. Propyne also undergoes hydroboration (1.  $\text{BH}_3$  followed by 2.  $\text{H}_2\text{O}_2/\text{OH}^-$ ) to form the enol on the less substituted C (anti-Markovnikov addition). The enol converts to an aldehyde. You want to know the reactants and products of the hydroboration reaction but you will not be responsible for knowing the hydroboration mechanism.



Answers:  
a and b.

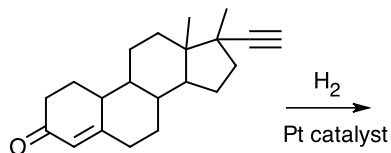


4. Hydrogenation: an alkyne reacts with  $\text{H}_2$  with a Ni or Pd or Pt catalyst to make an alkene or alkane. The catalyst determines whether the alkene or alkane product forms.

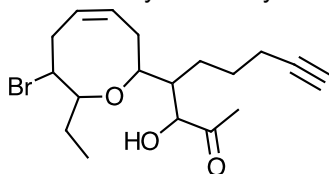


Predict the product of each reaction:

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.

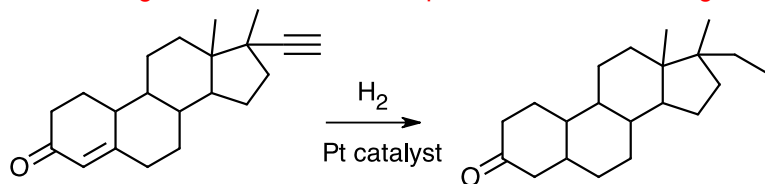


naturally occurring alkyne  
isolated from red algae

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

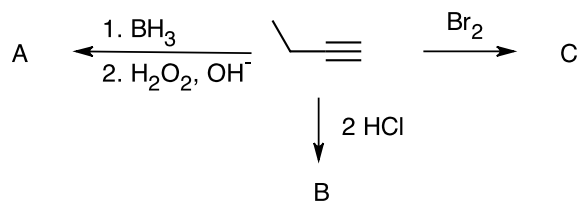
Answers:

a.  $H_2$  undergoes an addition to C-C pi bonds to form C-C sigma bond.

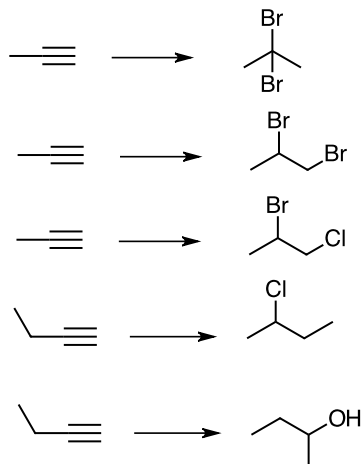


b. Use  $H_2$  and Lindlar's catalyst to react at alkyne only (alkyne  $\rightarrow$  alkene).

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

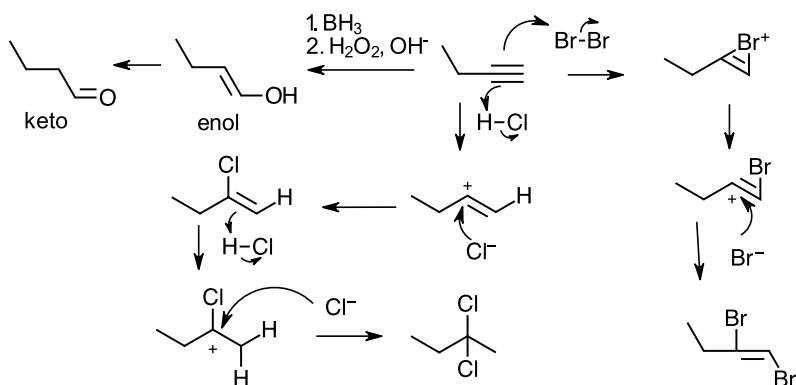


b. Determine the reaction conditions to make the product. Some reactions may take more than one step. Use curved arrows to show how each reaction occurs.

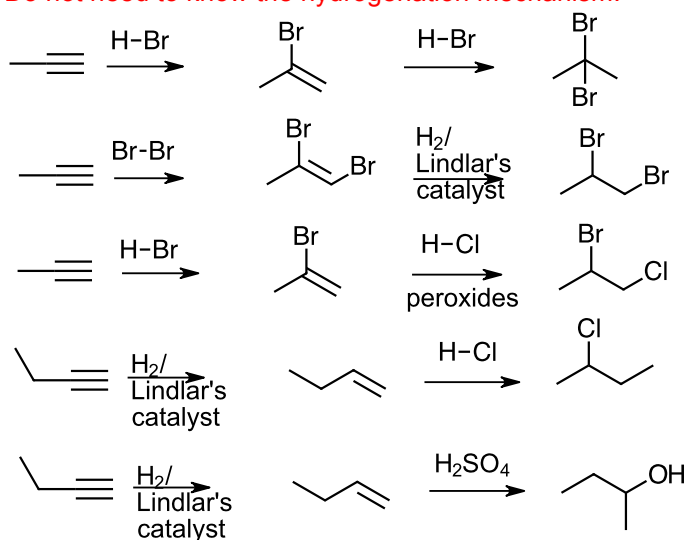


Answers:

a. Do not need to know the hydroboration mechanism. Keto product is more stable than enol

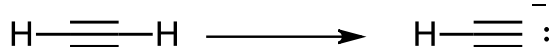


b. See previous problems for alkyne + HX, Br<sub>2</sub>, and H<sub>2</sub>SO<sub>4</sub> curved arrows. Alkyne pi bond = nucleophile, HX, Br<sub>2</sub>, and H<sub>2</sub>SO<sub>4</sub> = electrophiles. Carbocation intermediate forms in each reaction. Check stability of carbocation. Do not need to know the hydrogenation mechanism.



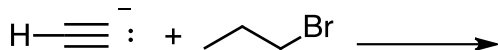
6. Review of proton transfer and substitution reactions.

Acetylene is a very weak acid and needs a very strong base to remove its acidic H:



a. See a pK<sub>a</sub> 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.



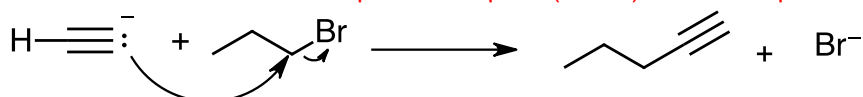
**Note:** this is a good way to make a bigger molecule from a smaller one. So this reaction is very valuable in organic synthesis. See Objective 15.

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

Answers:

a. The weakest base that can be used to remove the proton from acetylene is H<sup>-</sup>. This base is the first base below acetylene in the pK<sub>a</sub> table.

b. Substitution reaction. Lone pair nucleophile (HCC<sup>-</sup>) reacts at alpha C.



c. Elimination reaction. Lone pair nucleophile (HCC<sup>-</sup>) reacts at H on beta C.

