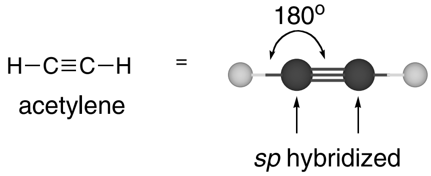
Chapter 11: Alkynes

♦ General facts about alkynes

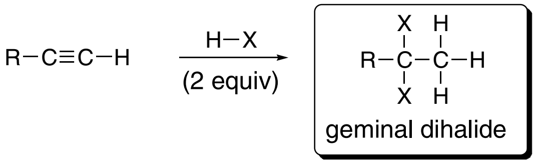
- Alkynes contain a carbon–carbon triple bond consisting of a strong σ bond and two weak π bonds. Each carbon is *sp* hybridized and linear (11.1).



- Alkynes are named using the suffix ***-yne*** (11.2).
- Alkynes have weak intermolecular forces, giving them low mp's and low bp's, and making them water insoluble (11.3).
- Since its weaker π bonds make an alkyne electron rich, alkynes undergo addition reactions with electrophiles (11.6).

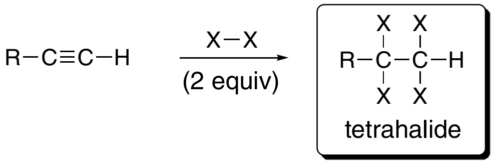
♦ Addition reactions of alkynes

[1] Hydrohalogenation—Addition of HX (X = Cl, Br, I) (11.7)



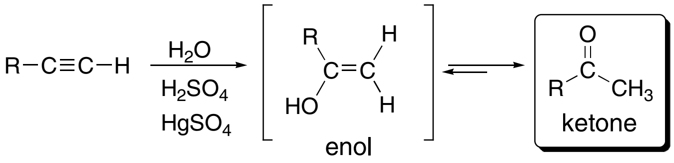
- Markovnikov's rule is followed. H bonds to the less substituted C in order to form the more stable carbocation.

[2] Halogenation—Addition of X_2 (X = Cl or Br) (11.8)



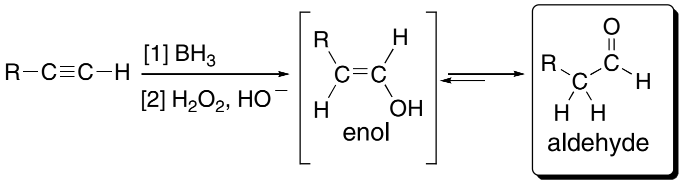
- Bridged halonium ions are formed as intermediates.
- Anti addition of X_2 occurs.

[3] Hydration—Addition of H_2O (11.9)



- Markovnikov's rule is followed. H bonds to the less substituted C in order to form the more stable carbocation.
- The unstable enol that is first formed rearranges to a carbonyl group.

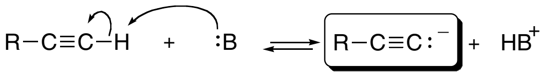
[4] Hydroboration–oxidation—Addition of H_2O (11.10)



- The unstable enol, first formed after oxidation, rearranges to a carbonyl group.

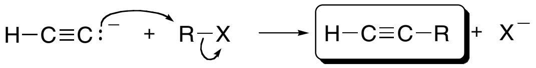
◆ Reactions involving acetylide anions

[1] Formation of acetylide anions from terminal alkynes (11.6B)



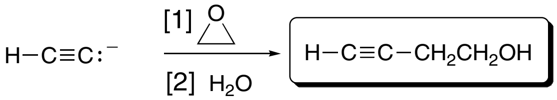
- Typical bases used for the reaction are $NaNH_2$ and NaH.

[2] Reaction of acetylide anions with alkyl halides (11.11A)



- The reaction follows an S_N2 mechanism.
- The reaction works best with CH_3X and RCH_2X.

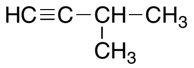
[3] Reaction of acetylide anions with epoxides (11.11B)



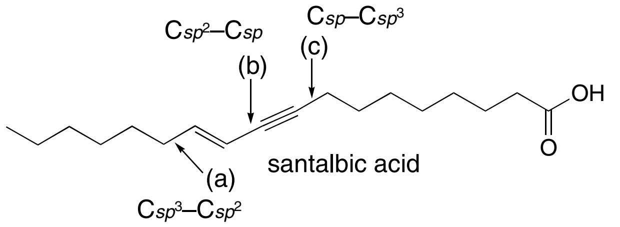
- The reaction follows an S_N2 mechanism.
- Ring opening occurs from the back side at the less substituted end of the epoxide.

Chapter 11: Answers to Problems

11.1 • An ***internal alkyne*** has the triple bond somewhere in the *middle* of the carbon chain.
• A ***terminal alkyne*** has the triple bond at the *end* of the carbon chain.

$HC\equiv C-CH_2CH_2CH_3$	$CH_3-C\equiv C-CH_2CH_3$	 $HC\equiv C-CH(CH_3)-CH_3$
terminal alkyne	internal alkyne	terminal alkyne

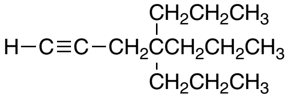
11.2



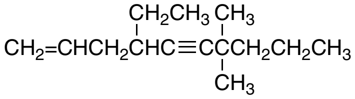
Increasing bond strength: a < c < b

11.3 Like alkenes, the larger the number of alkyl groups bonded to the *sp* hybridized C, the more stable the alkyne. This makes internal alkynes more stable than terminal alkynes.

11.4 To name an alkyne:
[1] Find the longest chain that contains both atoms of the triple bond, change the *-ane* ending of the parent name to *-yne*, and number the chain to give the first carbon of the triple bond the lower number.
[2] Name all substituents following the other rules of nomenclature.

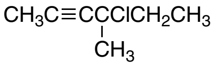
a. 
$H-C\equiv C-CH_2C(CH_2CH_2CH_3)_2CH_2CH_2CH_3$

4,4-dipropyl-1-heptyne

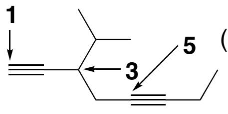
c. 
$CH_2{=}CHCH_2CH(CH_2CH_3)C\equiv CC(CH_3)_2CH_2CH_2CH_3$

(Number to give the lower number to the first site of unsaturation.)

4-ethyl-7,7-dimethyl-1-decen-5-yne

b. 
$CH_3C\equiv CCCl(CH_3)CH_2CH_3$

4-chloro-4-methyl-2-hexyne

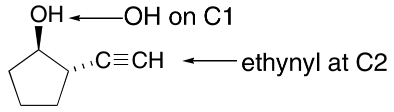
d. 

(The longest chain must contain both functional groups.)

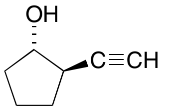
3-isopropyl-1,5-octadiyne

11.5 To work backwards from a name to a structure:
[1] Find the parent name and the functional group.
[2] Add the substituents to the appropriate carbon.

a. *trans*-2-ethynyl**cyclopentanol**
5 C ring with OH at C1

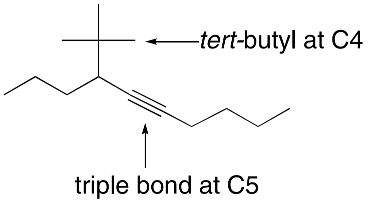


or



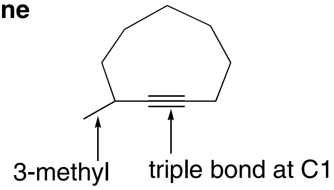
b. 4-*tert*-butyl-5-**decyne**

10 C chain with
a triple bond



c. 3-methyl**cyclononyne**

9 C ring with a
triple bond at C1



11.6 Two factors cause the boiling point increase. The linear *sp* hybridized C's of the alkyne allow for more van der Waals attraction between alkyne molecules. Also, since a triple bond is more polarizable than a double bond, this increases the van der Waals forces between two molecules as well.

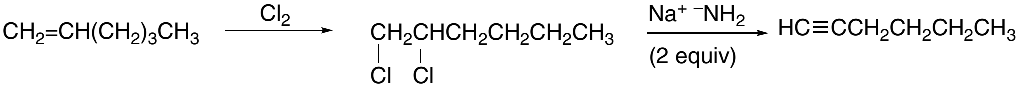
11.7 To convert an alkene to an alkyne:

[1] Make a vicinal dihalide from the alkene by addition of X_2.

[2] Add base to remove two equivalents of HX and form the alkyne.

a. $Br_2CH(CH_2)_4CH_3 \xrightarrow{Na^+\ ^-NH_2} \underset{\text{not isolated}}{\left[BrCH{=}CHCH_2CH_2CH_2CH_3 \right]} \xrightarrow{Na^+\ ^-NH_2} HC{\equiv}CCH_2CH_2CH_2CH_3$

b. $CH_2{=}CCl(CH_2)_3CH_3 \xrightarrow{Na^+\ ^-NH_2} HC{\equiv}CCH_2CH_2CH_2CH_3$

c. 

$$CH_2{=}CH(CH_2)_3CH_3 \xrightarrow{Cl_2} \underset{Cl\ \ \ \ Cl}{CH_2CHCH_2CH_2CH_2CH_3} \xrightarrow[\text{(2 equiv)}]{Na^+\ ^-NH_2} HC{\equiv}CCH_2CH_2CH_2CH_3$$

11.8 Acetylene has a pK_a of 25, so **bases having a conjugate acid with a pK_a *above* 25** will be able to deprotonate it.

a. CH_3NH^- [pK_a (CH_3NH_2) = 40]
pK_a > 25 = **Can deprotonate acetylene.**

b. CO_3^{2-} [pK_a (HCO_3^-) = 10.2]
pK_a < 25 = **Cannot deprotonate acetylene.**

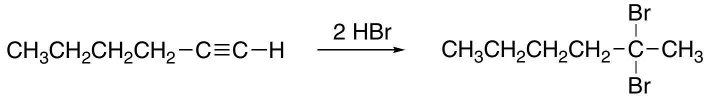
c. $CH_2{=}CH^-$ [pK_a ($CH_2{=}CH_2$) = 44]
pK_a > 25 = **Can deprotonate acetylene.**

d. $(CH_3)_3CO^-$ {pK_a [$(CH_3)_3COH$] = 18}
pK_a < 25 = **Cannot deprotonate acetylene.**

11.9 To draw the products of reactions with HX:

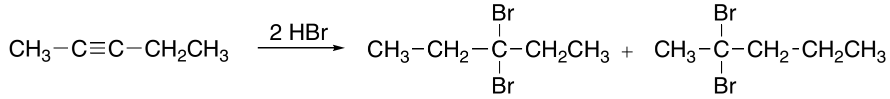
- Add two moles of HX to the triple bond, following Markovnikov's rule.
- Both X's end up on the more substituted C.

a.



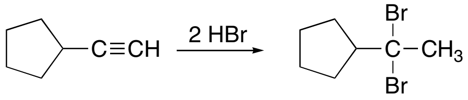
$$CH_3CH_2CH_2CH_2-C\equiv C-H \xrightarrow{2\ HBr} CH_3CH_2CH_2CH_2-\underset{Br}{\overset{Br}{C}}-CH_3$$

b.



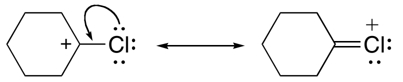
$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{2\ HBr} CH_3-CH_2-\underset{Br}{\overset{Br}{C}}-CH_2CH_3 + CH_3-\underset{Br}{\overset{Br}{C}}-CH_2-CH_2CH_3$$

c.

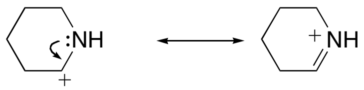


11.10

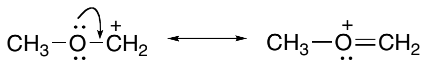
a.



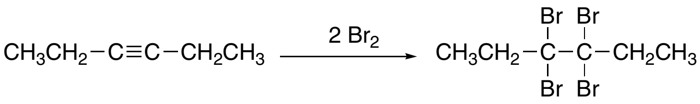
c.



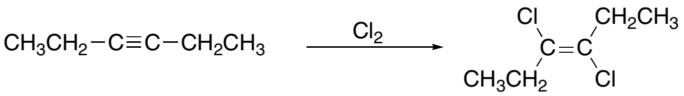
b.



11.11 Addition of one equivalent of X_2 to alkynes forms trans dihalides.
Addition of two equivalents of X_2 to alkynes forms tetrahalides.

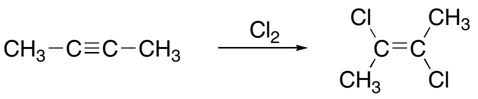


$$CH_3CH_2-C\equiv C-CH_2CH_3 \xrightarrow{2\ Br_2} CH_3CH_2-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-CH_2CH_3$$



trans dihalide

11.12



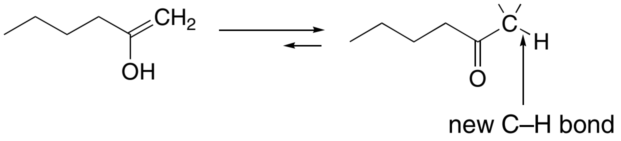
The two Cl atoms are electron withdrawing, making the π bond less electron rich and therefore less reactive with an electrophile.

11.13 To draw the keto form of each enol:

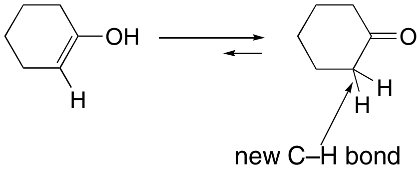
[1] Change the C–OH to a C=O at one end of the double bond.

[2] At the other end of the double bond, add a proton.

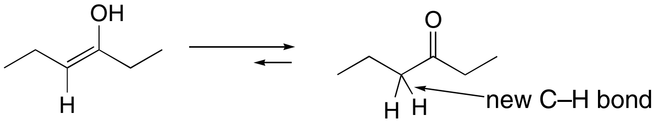
a.



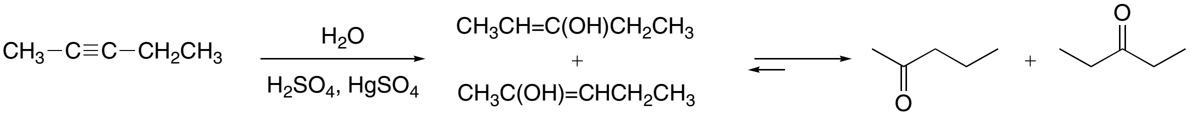
c.



b.



11.14 Treatment of alkynes with H_2O, H_2SO_4, and $HgSO_4$ yields ketones.

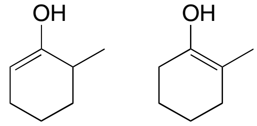


Two enols form.

two ketones after tautomerization

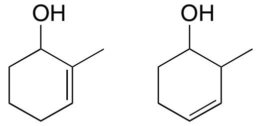
11.15

a.



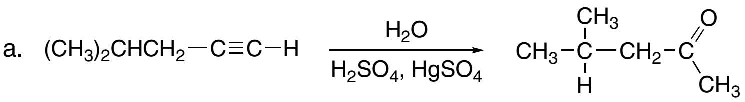
enol tautomers

b.

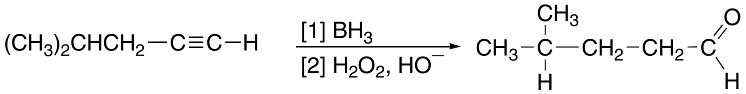


constitutional isomers, but not tautomers

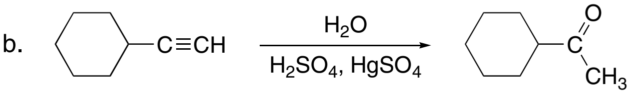
11.16 Reaction with H_2O, H_2SO_4, and $HgSO_4$ adds the oxygen to the *more* substituted carbon. Reaction with [1] BH_3, [2] H_2O_2, ^{-}OH adds the oxygen to the *less* substituted carbon.



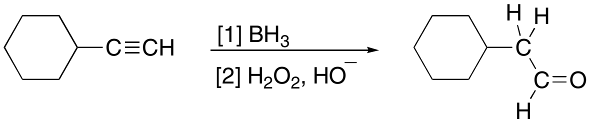
Forms a **ketone.** H_2O is added with the O atom on the *more* substituted carbon.



Forms an **aldehyde**. H_2O is added with the O atom on the *less* substituted carbon.

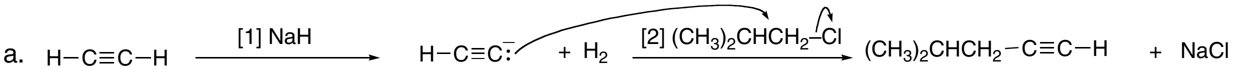


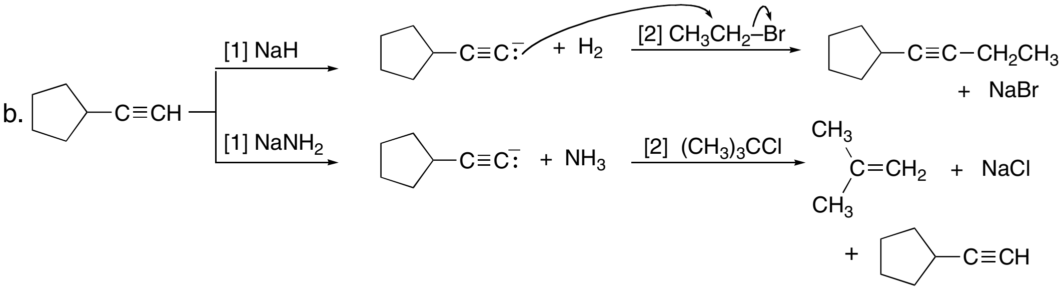
Forms a **ketone.** H_2O is added with the O atom on the *more* substituted carbon.



Forms an **aldehyde**. H_2O is added with the O atom on the *less* substituted carbon.

11.17



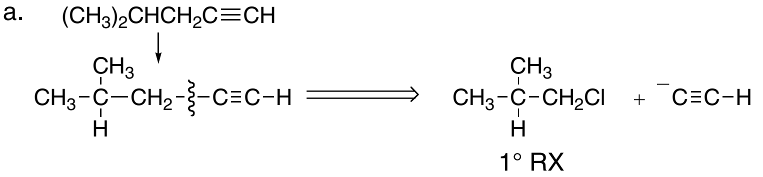


1° alkyl halide
substitution product

3° alkyl halide
elimination product

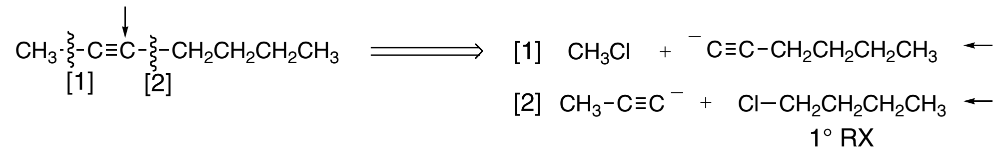
11.18

a. $(CH_3)_2CHCH_2C{\equiv}CH$



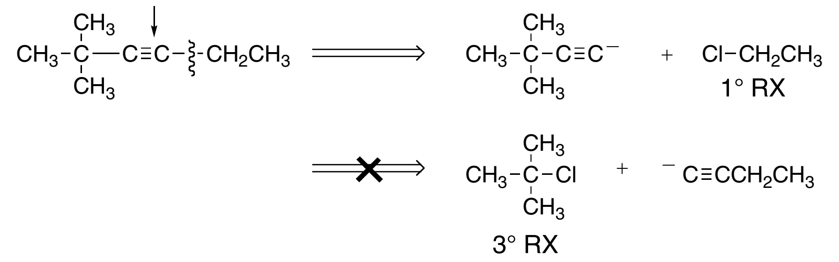
terminal alkyne
only one possibility

b. $CH_3C{\equiv}CCH_2CH_2CH_2CH_3$



internal alkyne
two possibilities

c. $(CH_3)_3CC{\equiv}CCH_2CH_3$

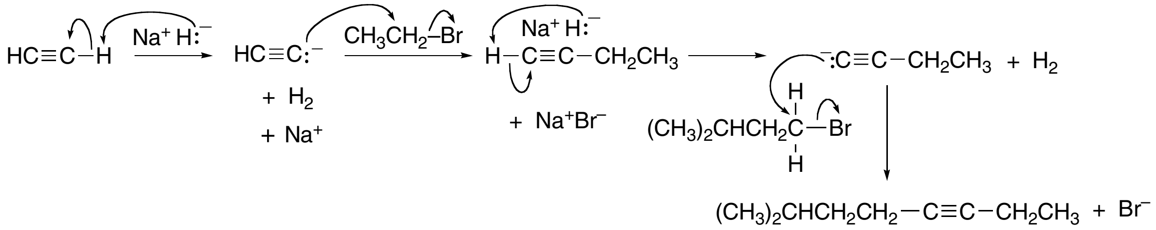


too crowded for S_N2 reaction

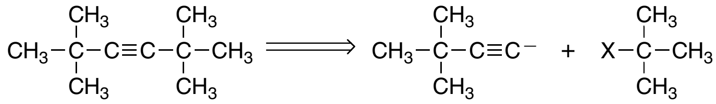
internal alkyne
only one possibility

The 3° alkyl halide
would undergo elimination.

11.19



11.20

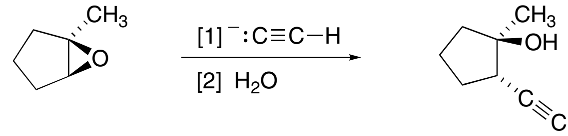


2,2,5,5-tetramethyl-3-hexyne

The 3° alkyl halide is too crowded for nucleophilic substitution. Instead, it would undergo elimination with the acetylide anion.

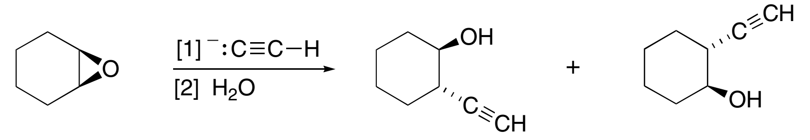
11.21

a.



Epoxide is drawn up, so the **acetylide anion attacks from *below* at *less* substituted C.**

b.



enantiomers

Backside attack of the nucleophile ($^-C{\equiv}CH$) at either C since both ends are equally substituted.

11.22

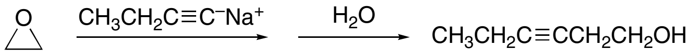
a. $CH_3CH_2CH_2Br \xrightarrow{CH_3CH_2C\equiv C^-Na^+} CH_3CH_2CH_2C\equiv CCH_2CH_3$

b. $(CH_3)_2CHCH_2CH_2Cl \xrightarrow{CH_3CH_2C\equiv C^-Na^+} (CH_3)_2CHCH_2CH_2C\equiv CCH_2CH_3$

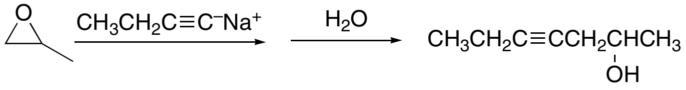
c. $(CH_3CH_2)_3CCl \xrightarrow{CH_3CH_2C\equiv C^-Na^+} (CH_3CH_2)_2C=CHCH_3 + CH_3CH_2C\equiv CH$

d. $BrCH_2CH_2CH_2CH_2OH \xrightarrow{CH_3CH_2C\equiv C^-Na^+} CH_3CH_2C\equiv CH + BrCH_2CH_2CH_2CH_2O^-Na^+$

e.



f.

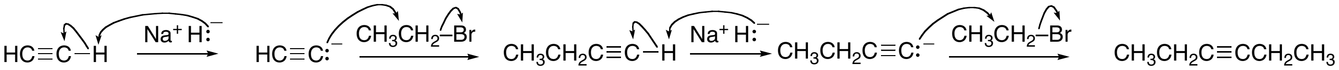


11.23 To use a retrosynthetic analysis:

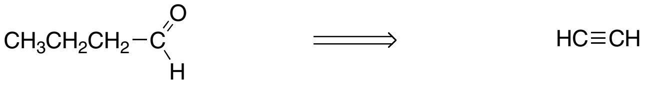
[1] **Count the number of carbon atoms** in the starting material and product.
[2] **Look at the functional groups** in the starting material and product.
Determine what types of reactions can form the product.
Determine what types of reactions the starting material can undergo.
[3] **Work backwards** from the product to make the starting material.
[4] Write out the synthesis in the synthetic direction.

$$\underset{\text{6 C's}}{CH_3CH_2C\equiv CCH_2CH_3} \overset{?}{\Longrightarrow} \underset{\text{2 C's}}{HC\equiv CH}$$

$$CH_3CH_2C\equiv CCH_2CH_3 \Longrightarrow CH_3CH_2C\equiv C^- + CH_3CH_2Br \Longrightarrow HC\equiv C^- + CH_3CH_2Br$$



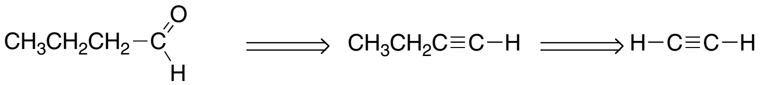
11.24



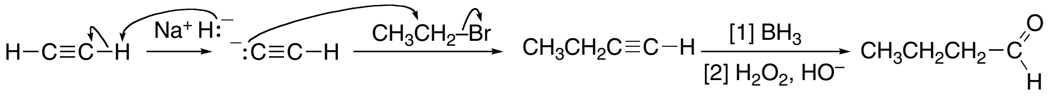
product:
4 carbons, aldehyde functional group
(can be made by hydroboration–oxidation of a terminal alkyne)

starting material:
2 carbons, C≡C functional group
(can form an acetylide anion by reaction with NaH)

Retrosynthetic analysis:

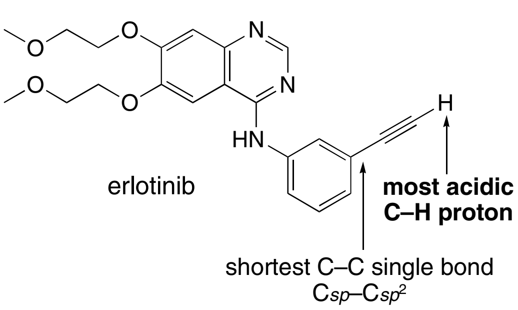


Forward direction:



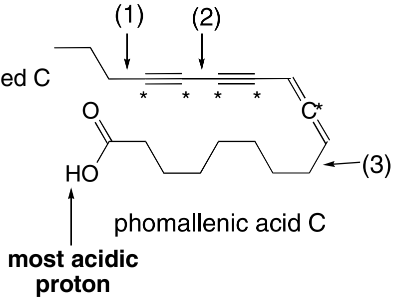
11.25

a., b.



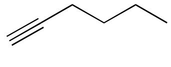
erlotinib

c.
d. * = *sp* hybridized C
e. 3 < 1 < 2

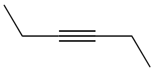


phomallenic acid C

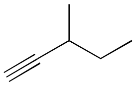
11.26 Use the rules from Answer 11.4 to name the alkynes.



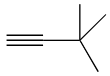
1-hexyne



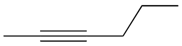
3-hexyne



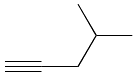
3-methyl-1-pentyne



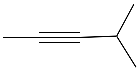
3,3-dimethyl-1-butyne



2-hexyne



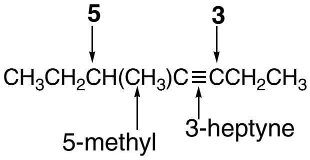
4-methyl-1-pentyne



4-methyl-2-pentyne

11.27 Use the rules from Answer 11.4 to name the alkynes.

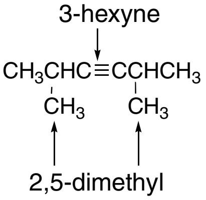
a.



$CH_3CH_2CH(CH_3)C\equiv CCH_2CH_3$

5-methyl-3-heptyne

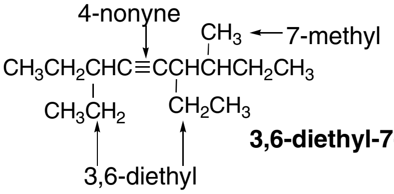
b.



$CH_3\underset{CH_3}{CH}C\equiv C\underset{CH_3}{CH}CH_3$

2,5-dimethyl-3-hexyne

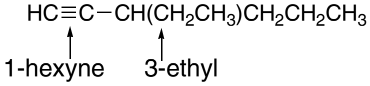
c.



$CH_3CH_2\underset{CH_3CH_2}{CH}C\equiv C\underset{CH_2CH_3}{CH}\overset{CH_3}{CH}CH_2CH_3$

3,6-diethyl-7-methyl-4-nonyne

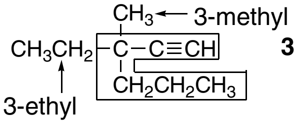
d.



$HC\equiv C-CH(CH_2CH_3)CH_2CH_2CH_3$

3-ethyl-1-hexyne

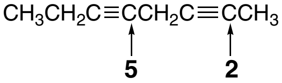
e.



$CH_3CH_2\underset{CH_2CH_2CH_3}{\overset{CH_3}{C}}-C\equiv CH$

3-ethyl-3-methyl-1-hexyne

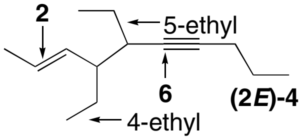
f.



$CH_3CH_2C\equiv CCH_2C\equiv CCH_3$

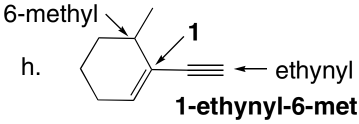
2,5-octadiyne

g.



(2*E*)-4,5-diethyl-2-decen-6-yne

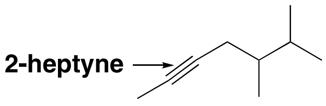
h.



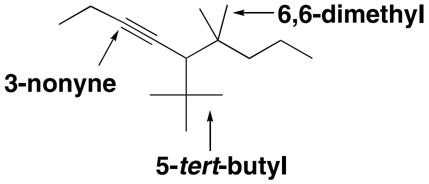
1-ethynyl-6-methylcyclohexene

11.28 Use the directions from Answer 11.5 to draw each structure.

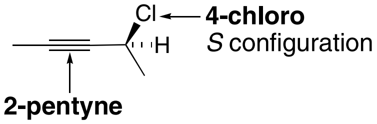
a. 5,6-dimethyl-2-**heptyne**



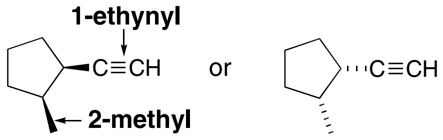
b. 5-*tert*-butyl-6,6-dimethyl-3-**nonyne**



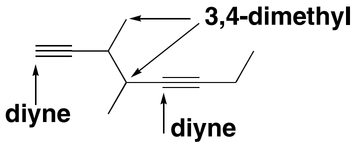
c. (4*S*)-4-chloro-2-**pentyne**



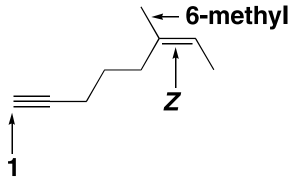
d. *cis*-1-ethynyl-2-methyl**cyclopentane**



e. 3,4-dimethyl-1,5-**octadiyne**

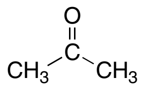


f. (6*Z*)-6-methyl-6-**octen-1-yne**



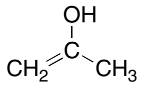
11.29 Keto–enol tautomers are constitutional isomers in equilibrium that differ in the location of a double bond and a hydrogen. The OH in an enol must be bonded to a C=C.

a.



CH_3COCH_3

and



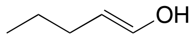
$CH_2=C(OH)CH_3$

- C=O
- one more CH bond

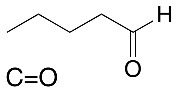
- C=C
- OH on C=C

keto–enol tautomers

c.



and

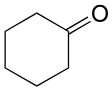


- C=C
- OH on C=C

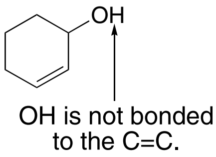
- C=O
- one more CH bond

keto–enol tautomers

b.

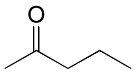


and

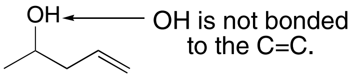


NOT keto–enol tautomers

d.



and



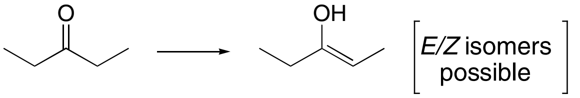
NOT keto–enol tautomers

11.30 To draw the enol form of each keto form:

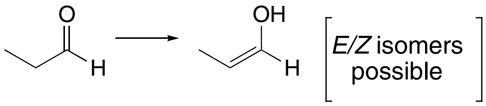
[1] Change the C=O to a C–OH.

[2] Change one single C–C bond to a double bond, making sure the OH group is bonded to the C=C.

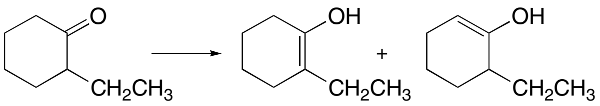
a.



b. CH_3CH_2CHO =

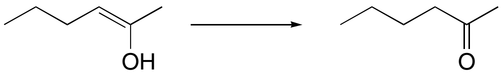


c.

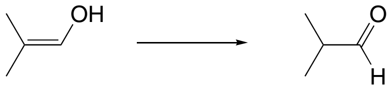


11.31 Use the directions from Answer 11.13 to draw each keto form.

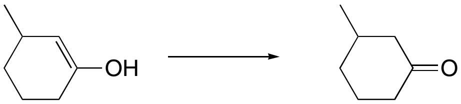
a.



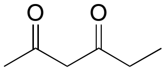
b.



c.

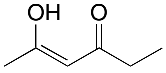


11.32 Tautomers are constitutional isomers that are in equilibrium and differ in the location of a double bond and a hydrogen atom.



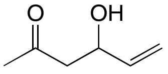
A

a.



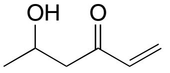
tautomer

b.



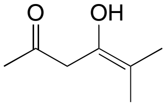
constitutional isomer

c.



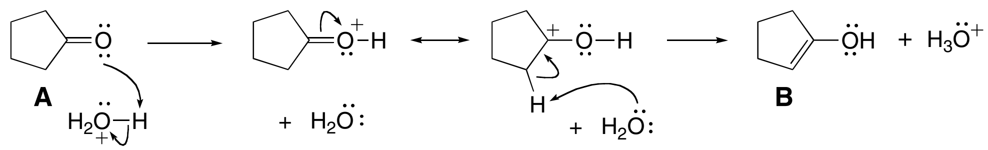
constitutional isomer

d.

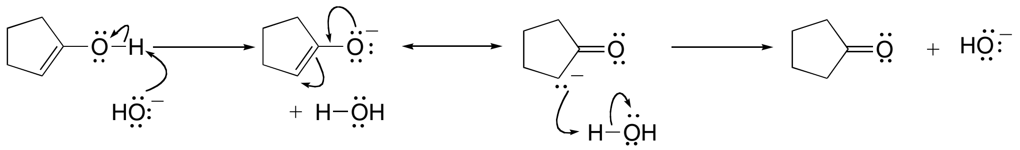


neither

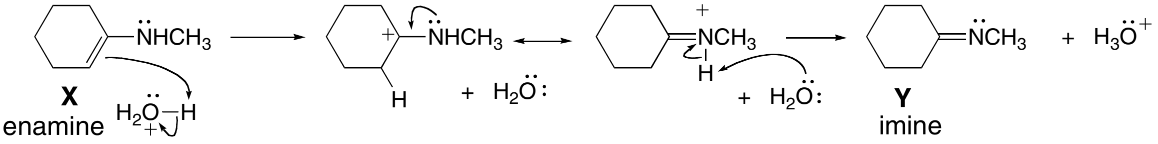
11.33



11.34



11.35



11.36 The equilibrium always favors the formation of the weaker acid and the weaker base.

a. $HC\equiv C^- + CH_3OH \rightleftharpoons HC\equiv CH + CH_3O^-$

$pK_a = 15.5$ $\quad$ $pK_a = 25$

weaker acid

Equilibrium favors products.

b. $CH_3C\equiv CH + CH_3^- \rightleftharpoons CH_3C\equiv C^- + CH_4$

$pK_a = 25$ $\quad$ $pK_a = 50$

weaker acid

Equilibrium favors products.

c. $HC\equiv CH + Na^+Br^- \rightleftharpoons HC\equiv C^-\ Na^+ + HBr$

$pK_a = 25$

weaker acid

Equilibrium favors starting materials.

$pK_a = -9$

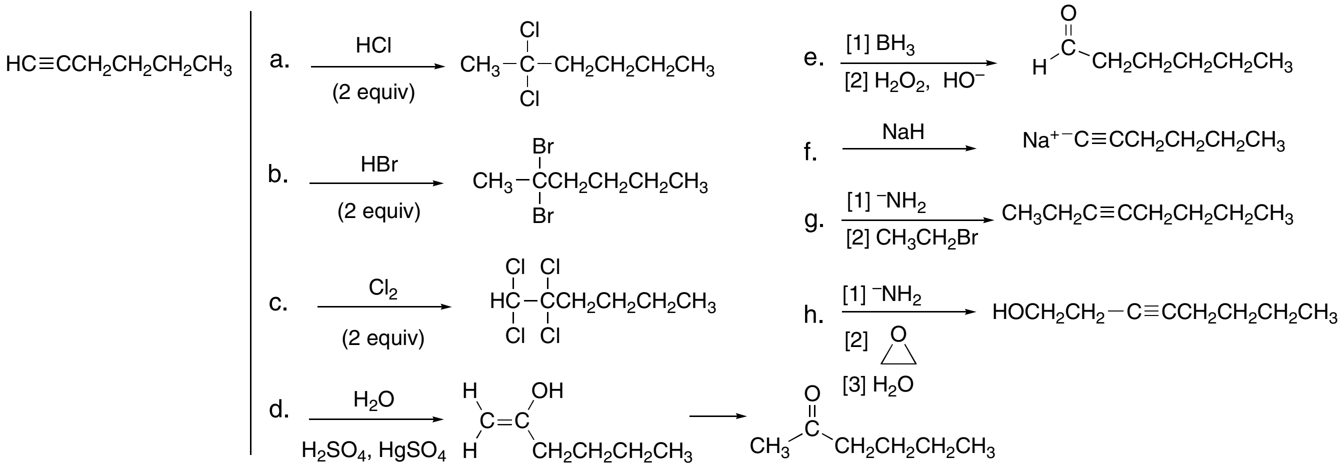
d. $CH_3CH_2C\equiv C^- + CH_3COOH \rightleftharpoons CH_3CH_2C\equiv CH + CH_3COO^-$

$pK_a = 4.8$ $\quad$ $pK_a = 25$

weaker acid

Equilibrium favors products.

11.37



$HC\equiv CCH_2CH_2CH_2CH_3$

a. $\xrightarrow[\text{(2 equiv)}]{HCl} CH_3{-}CCl_2{-}CH_2CH_2CH_2CH_3$

b. $\xrightarrow[\text{(2 equiv)}]{HBr} CH_3{-}CBr_2CH_2CH_2CH_2CH_3$

c. $\xrightarrow[\text{(2 equiv)}]{Cl_2} HCCl_2{-}CCl_2CH_2CH_2CH_2CH_3$

d. $\xrightarrow[H_2SO_4,\ HgSO_4]{H_2O} H_2C{=}C(OH)CH_2CH_2CH_2CH_3 \longrightarrow CH_3COCH_2CH_2CH_2CH_3$

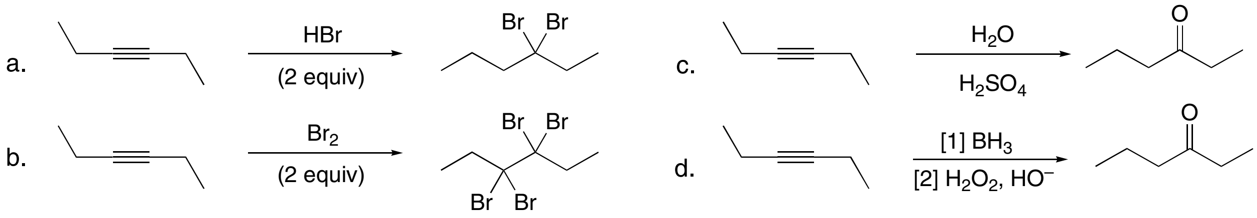
e. $\xrightarrow[\text{[2] } H_2O_2,\ HO^-]{\text{[1] } BH_3} HCOCH_2CH_2CH_2CH_2CH_3$

f. $\xrightarrow{NaH} Na^{+-}C\equiv CCH_2CH_2CH_2CH_3$

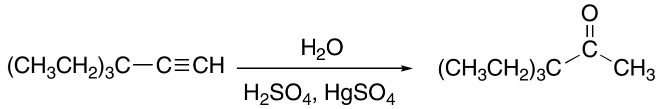
g. $\xrightarrow[\text{[2] } CH_3CH_2Br]{\text{[1] } {}^-NH_2} CH_3CH_2C\equiv CCH_2CH_2CH_2CH_3$

h. [1] $^-NH_2$, [2] ethylene oxide, [3] H_2O $\longrightarrow HOCH_2CH_2{-}C\equiv CCH_2CH_2CH_2CH_3$

11.38



11.39



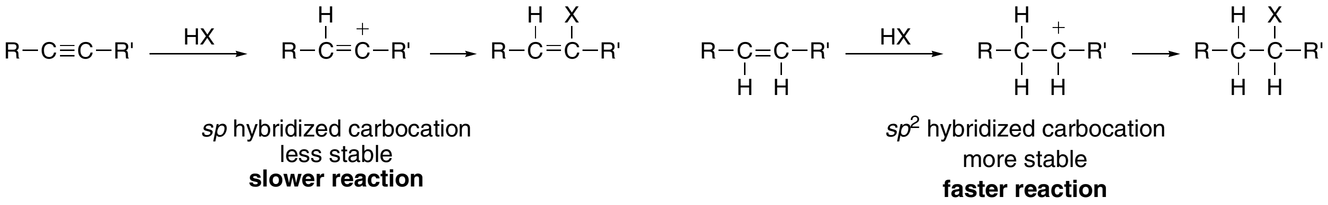
a. $(CH_3CH_2)_3C{-}C\equiv CH \xrightarrow[H_2SO_4,\ HgSO_4]{H_2O} (CH_3CH_2)_3CCOCH_3$

b. $(CH_3CH_2)_3C{-}C\equiv CH \xrightarrow[\text{[2] } H_2O_2,\ HO^-]{\text{[1] } BH_3} (CH_3CH_2)_3C{-}CH_2CHO$

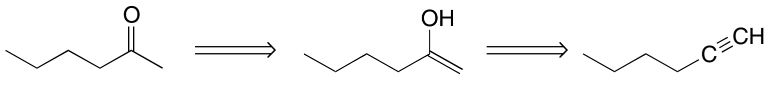
c. $(CH_3CH_2)_3C{-}C\equiv CH \xrightarrow[\text{(2 equiv)}]{HCl} (CH_3CH_2)_3CCCl_2CH_3$

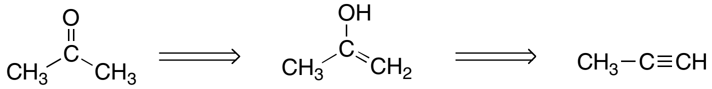
d. $(CH_3CH_2)_3C{-}C\equiv CH \xrightarrow[\text{[2] } CH_3CH_2Br]{\text{[1] } NaH} (CH_3CH_2)_3C{-}C\equiv CCH_2CH_3$

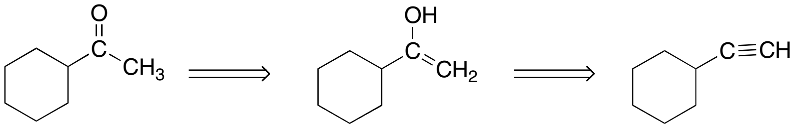
11.40 Reaction rate (which is determined by E_a) and enthalpy ($\Delta H°$) are not related. More exothermic reactions are not necessarily faster. Since the addition of HX to an alkene forms a more stable carbocation in an endothermic, rate-determining step, this carbocation is formed faster by the Hammond postulate.

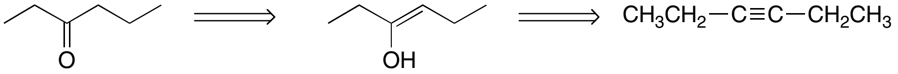


11.41

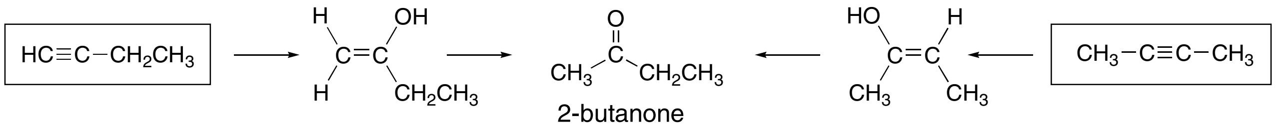
a. 

b. 

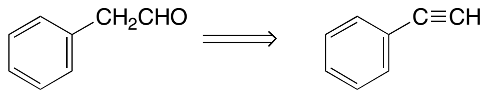
c. 

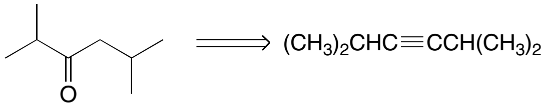
d. 

11.42 To determine what two alkynes could yield the given ketone, work backwards by drawing the enols and then the alkynes.

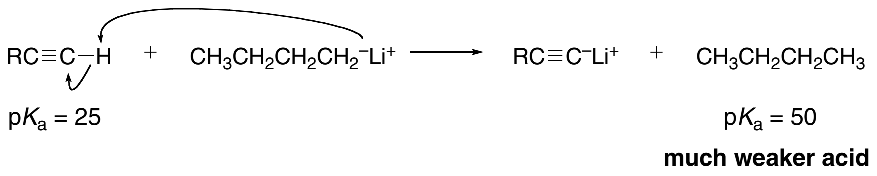


11.43

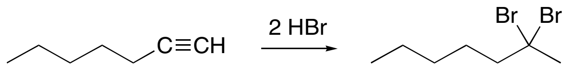
a. 

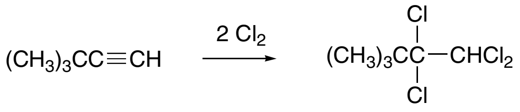
b. 

11.44 Equilibrium favors the weaker acid. $CH_3CH_2CH_2CH_2^-Li^+$ is a strong enough base to remove the proton of an alkyne because its conjugate acid, $CH_3CH_2CH_2CH_3$, is weaker than a terminal alkyne.

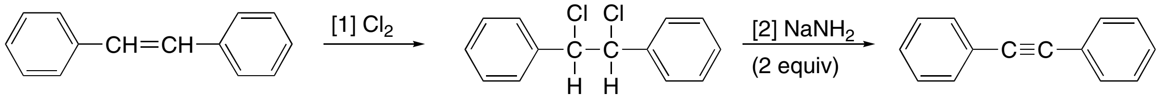


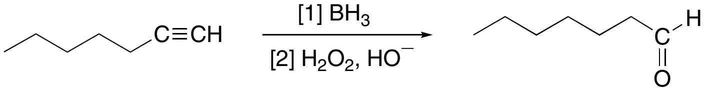
11.45

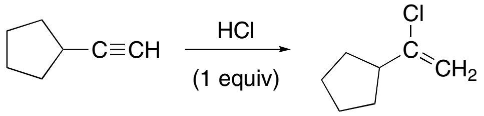
a. 

b.


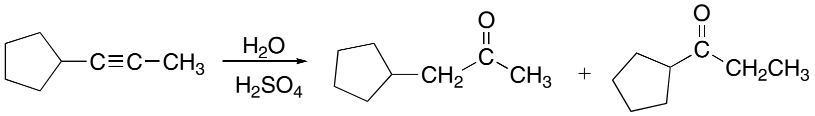
$(CH_3)_3CC\equiv CH \xrightarrow{2\ Cl_2} (CH_3)_3C\overset{Cl}{\underset{Cl}{C}}-CHCl_2$

c.


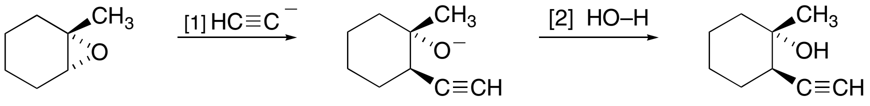
d.


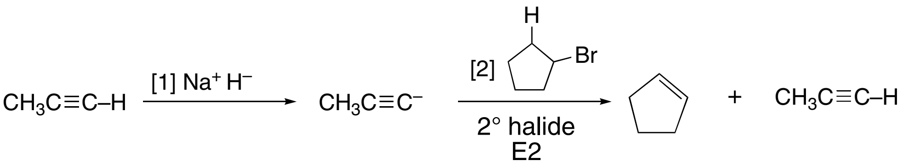
e.


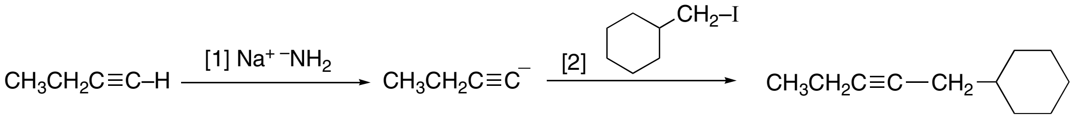
f. $HC\equiv C^- + D_2O \longrightarrow HC\equiv CD + DO^-$

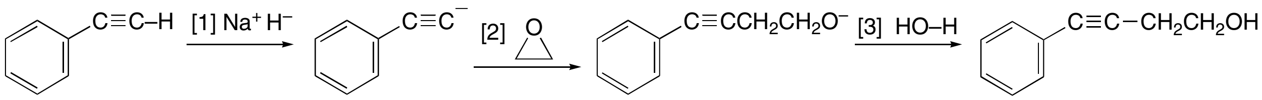
g.


h. $CH_3CH_2C\equiv C^- + CH_3CH_2CH_2\text{–}OTs \longrightarrow CH_3CH_2C\equiv CCH_2CH_2CH_3 + {}^-OTs$

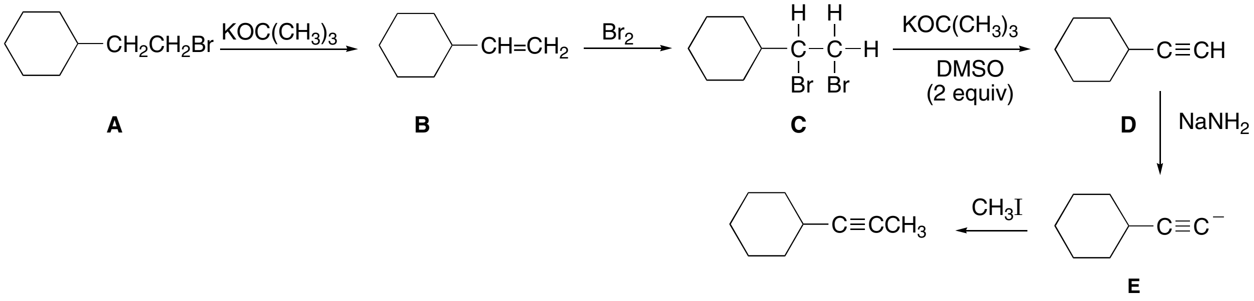
i.


j.


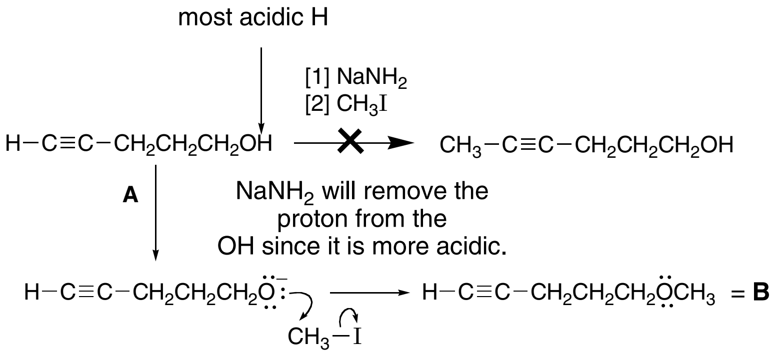
k.


l.


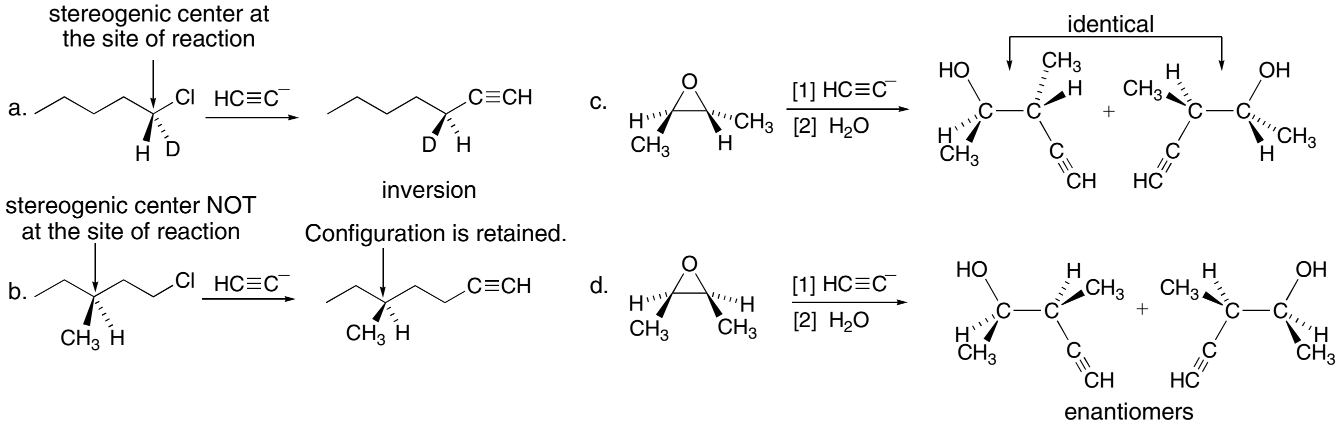
11.46



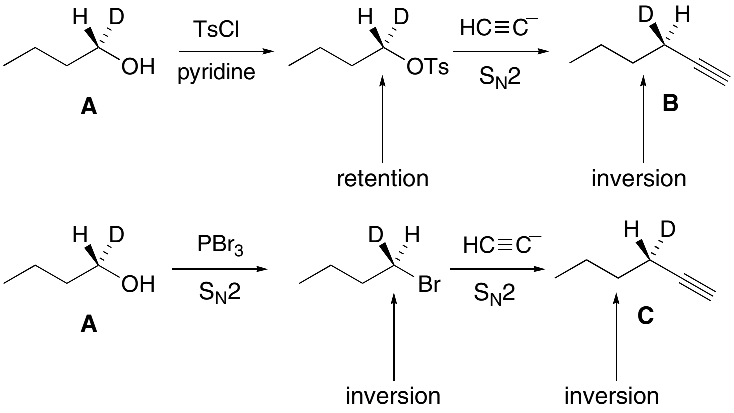
11.47



11.48

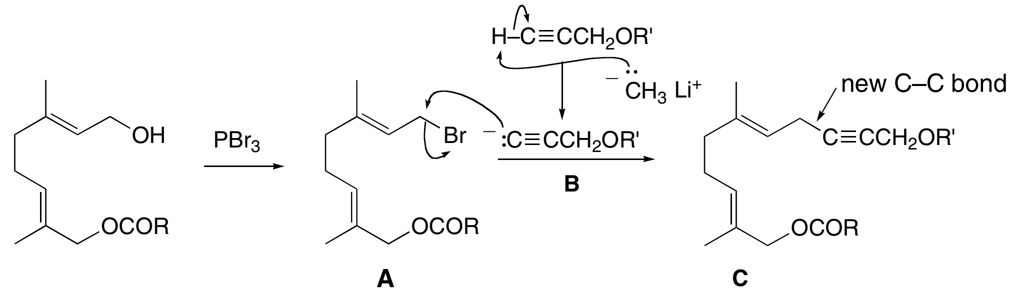


11.49

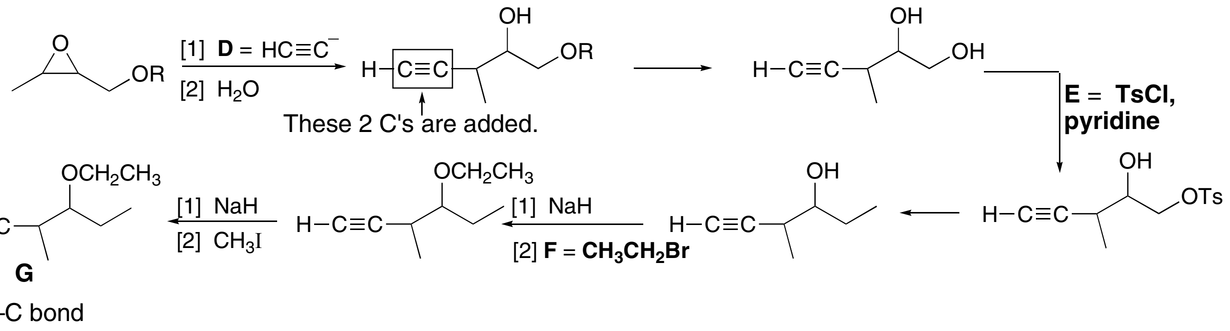


11.50

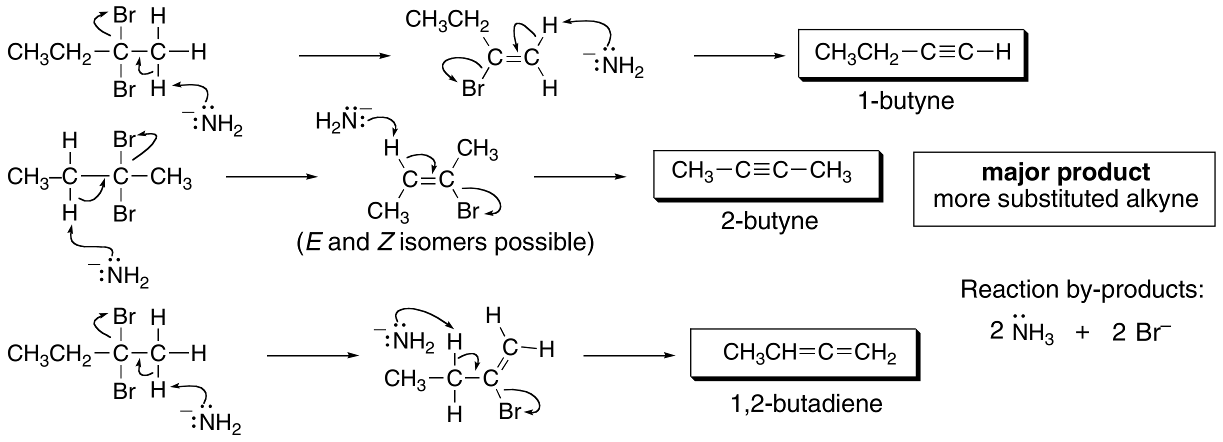
a.



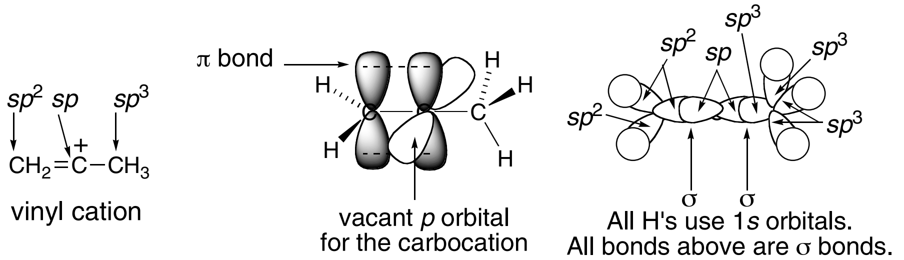
b.



11.51

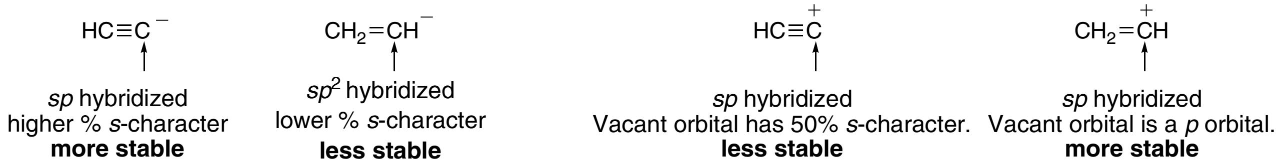


11.52 Draw two diagrams to show σ and π bonds.

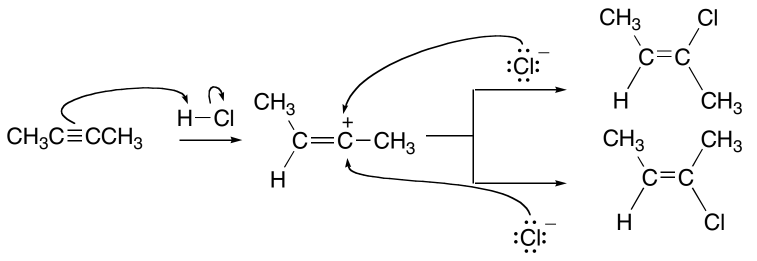


The positive charge in a vinyl carbocation resides on a carbon that is *sp* hybridized, while in $(CH_3)_2CH^+$, the positive charge is located on an sp^2 hybridized carbon. The higher percent *s*-character on carbon destabilizes the positive charge in the vinyl cation. Moreover, the positively charged carbocation is now bonded to an sp^2 hybridized carbon, which donates electrons less readily than an sp^3 hybridized carbon.

11.53 A carbanion is more stable when its lone pair is in an orbital with a higher percentage of the smaller *s* orbital. A carbocation is more stable when its positive charge is due to a vacant orbital with a lower percentage of the smaller *s* orbital. In $HC\equiv C^+$, the positively charged C uses two *p* orbitals to form two π bonds. If the σ bond is formed using an *sp* hybrid orbital, the second hybrid orbital would have to remain vacant, a highly unstable situation. See also Problem 11.52.



11.54

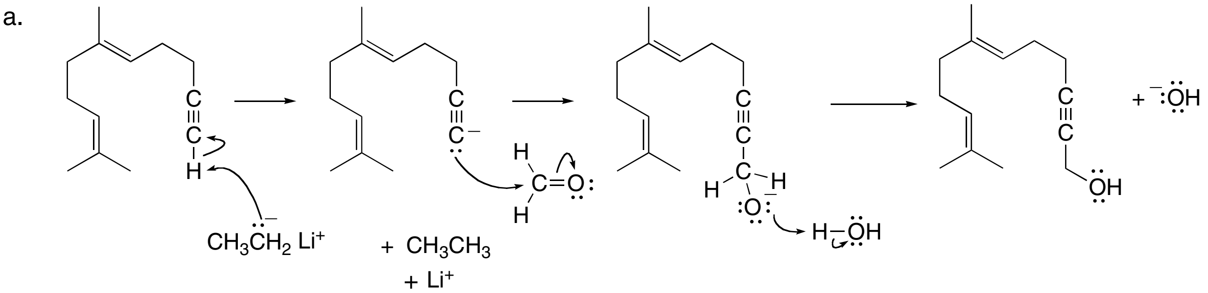


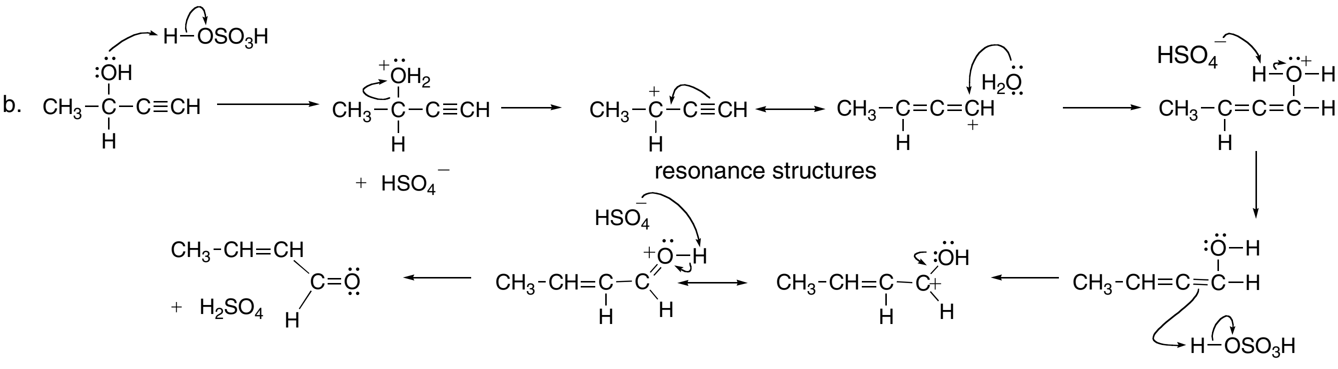
Cl⁻ attack on the opposite side to the H yields the ***Z*** isomer.

Cl⁻ attack on the same side as the H yields the ***E*** isomer.

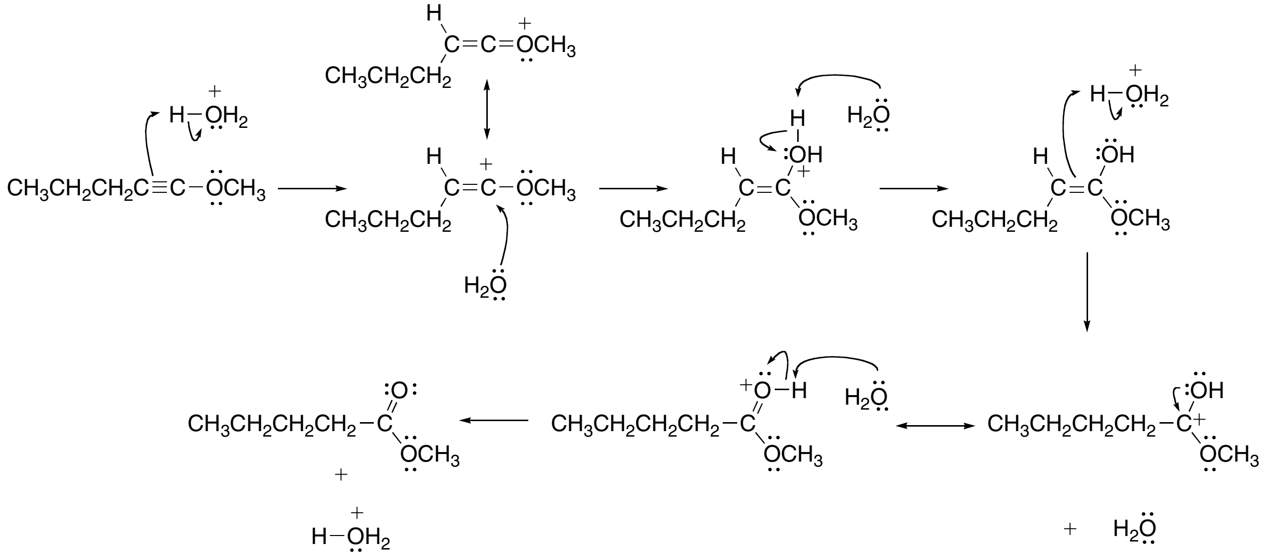
11.55

a.



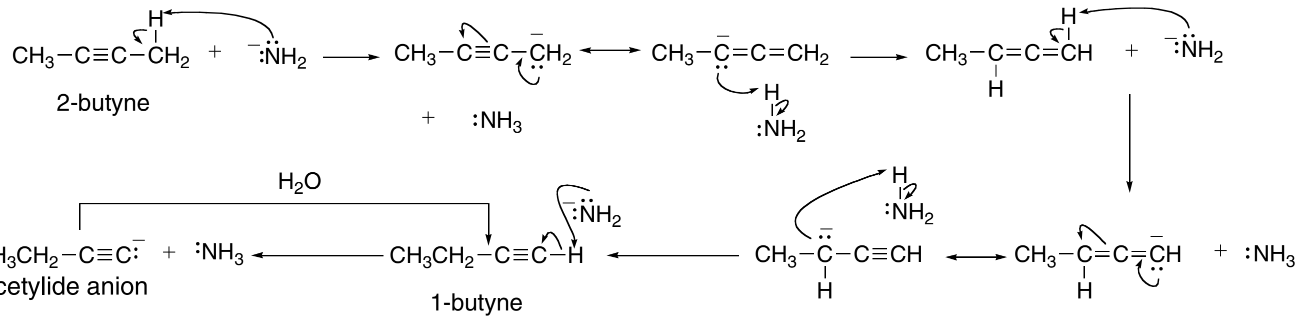


11.56



11.57

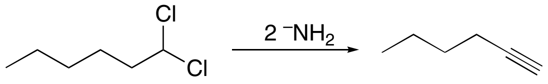
a.



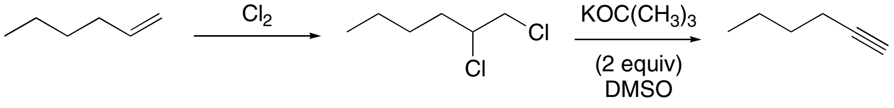
b. A more stable internal alkyne can be isomerized to a less stable terminal alkyne under these reaction conditions because when $CH_3CH_2C{\equiv}CH$ is first formed, it contains an *sp* hybridized C–H bond, which is more acidic than any proton in $CH_3–C{\equiv}C–CH_3$. Under the reaction conditions, this proton is removed with base. Formation of the resulting acetylide anion drives the equilibrium to favor its formation. Protonation of this acetylide anion gives the less stable terminal alkyne.

11.58

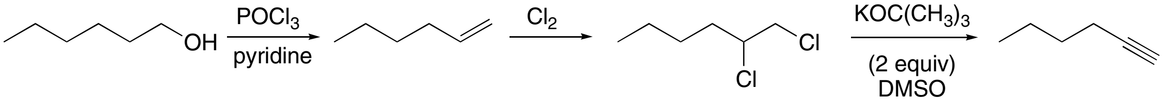
a.



b.



c.



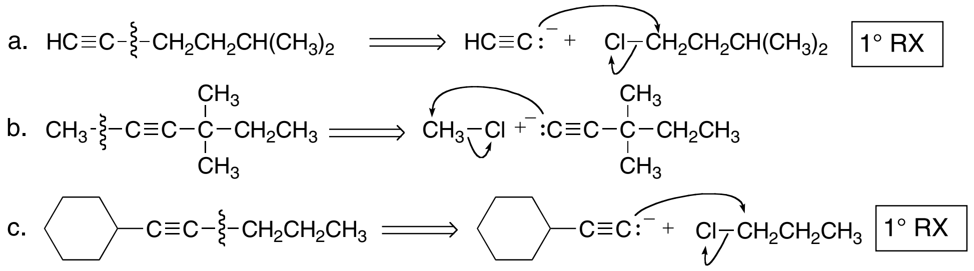
11.59

a. $C_6H_5CH_2CH_2Br \xrightarrow{KOC(CH_3)_3} C_6H_5CH{=}CH_2 \xrightarrow{Br_2} C_6H_5CHBrCH_2Br \xrightarrow[\text{excess}]{NaNH_2} C_6H_5C{\equiv}CH$

b. $C_6H_5CHBrCH_3 \xrightarrow{KOC(CH_3)_3} C_6H_5CH{=}CH_2 \xrightarrow{Br_2} C_6H_5CHBrCH_2Br \xrightarrow[\text{excess}]{NaNH_2} C_6H_5C{\equiv}CH$

c. $C_6H_5CH_2CH_2OH \xrightarrow{H_2SO_4} C_6H_5CH{=}CH_2 \xrightarrow{Br_2} C_6H_5CHBrCH_2Br \xrightarrow[\text{excess}]{NaNH_2} C_6H_5C{\equiv}CH$

11.60 The alkyl halides must be methyl or 1°.



11.61

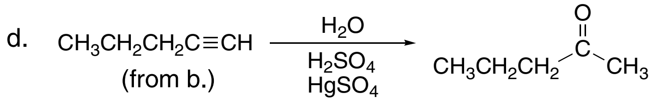
a. $HC{\equiv}C{-}H \xrightarrow{Na^+\,H^-} HC{\equiv}C^- \xrightarrow{(CH_3)_2CHCH_2{-}Cl} (CH_3)_2CHCH_2C{\equiv}CH$

b. $HC{\equiv}C{-}H \xrightarrow{Na^+\,H^-} HC{\equiv}C^- \xrightarrow{CH_3CH_2CH_2{-}Cl} \boxed{CH_3CH_2CH_2C{\equiv}CH} \xrightarrow{NaH} CH_3CH_2CH_2C{\equiv}C^-$

$\downarrow CH_3CH_2CH_2{-}Cl$

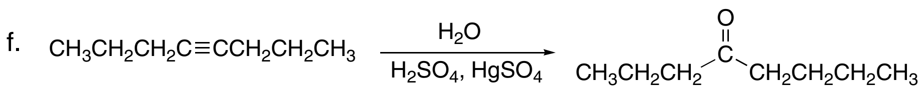
$CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$

c. $CH_3CH_2CH_2C{\equiv}CH \xrightarrow[\text{[2] } H_2O_2,\ HO^-]{\text{[1] } BH_3} CH_3CH_2CH_2CH_2CHO$
(from b.)



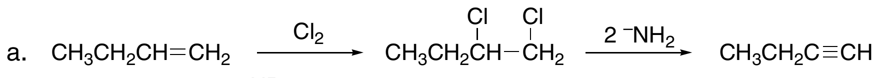
d. $CH_3CH_2CH_2C{\equiv}CH \xrightarrow[H_2SO_4,\ HgSO_4]{H_2O} CH_3CH_2CH_2C(=O)CH_3$
(from b.)

e. $CH_3CH_2CH_2C{\equiv}CH \xrightarrow{2\ HCl} CH_3CH_2CH_2CCl_2CH_3$
(from b.)



f. $CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3 \xrightarrow[H_2SO_4,\ HgSO_4]{H_2O} CH_3CH_2CH_2C(=O)CH_2CH_2CH_2CH_3$
(from b.)

11.62



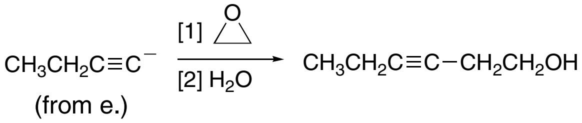
a. $CH_3CH_2CH{=}CH_2 \xrightarrow{Cl_2} CH_3CH_2CHCl{-}CH_2Cl \xrightarrow{2\ {}^-NH_2} CH_3CH_2C{\equiv}CH$

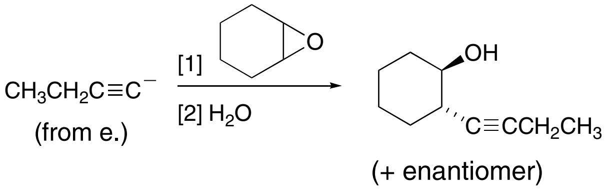
b. $CH_3CH_2C{\equiv}CH \xrightarrow[\text{(2 equiv)}]{HBr} CH_3CH_2CBr_2CH_3$
(from a.)

c. $CH_3CH_2C{\equiv}CH \xrightarrow[\text{(2 equiv)}]{Cl_2} CH_3CH_2CCl_2CHCl_2$
(from a.)

d. $CH_3CH_2CH{=}CH_2 \xrightarrow{Br_2} CH_3CH_2CHBrCH_2Br$

e. $CH_3CH_2C\equiv CH \xrightarrow{NaH} CH_3CH_2C\equiv C^- \xrightarrow{CH_3CH_2CH_2-Br} CH_3CH_2C\equiv C-CH_2CH_2CH_3$
(from a.)

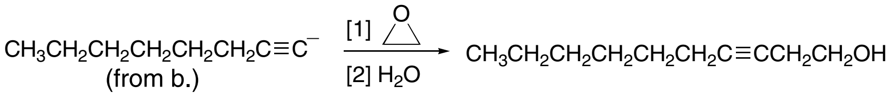
f.


g.


11.63

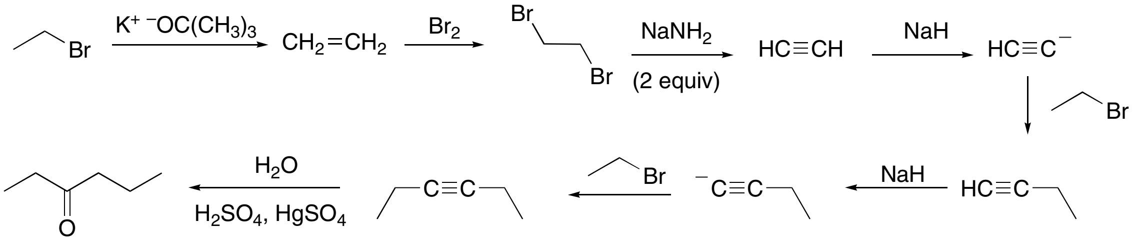
a. $HC\equiv CH \xrightarrow{NaH} HC\equiv C^- \xrightarrow{CH_3CH_2CH_2CH_2CH_2CH_2Br} CH_3CH_2CH_2CH_2CH_2CH_2C\equiv CH$

b. $CH_3CH_2CH_2CH_2CH_2CH_2C\equiv CH \xrightarrow{NaH} CH_3CH_2CH_2CH_2CH_2CH_2C\equiv C^- \xrightarrow{CH_3CH_2Br} CH_3CH_2CH_2CH_2CH_2CH_2C\equiv CCH_2CH_3$
(from a.)

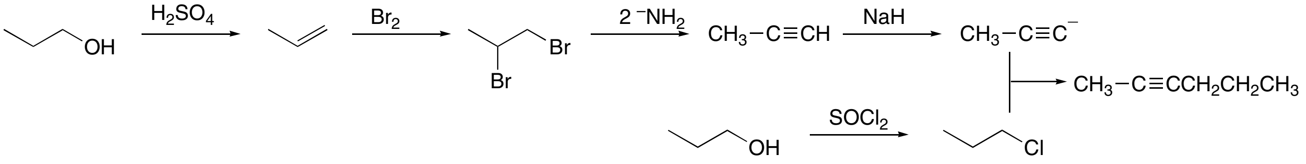
c.


d. $CH_3CH_2CH_2CH_2CH_2CH_2C\equiv CCH_2CH_2OH \xrightarrow[\text{[2] } CH_3CH_2Br]{\text{[1] NaH}} CH_3CH_2CH_2CH_2CH_2CH_2C\equiv CCH_2CH_2OCH_2CH_3$
(from c.)

11.64



11.65

a.


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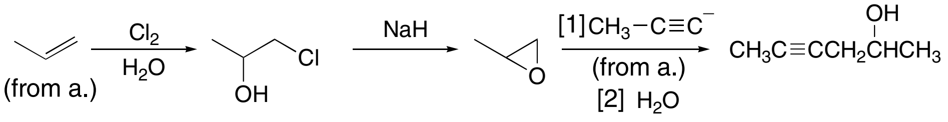
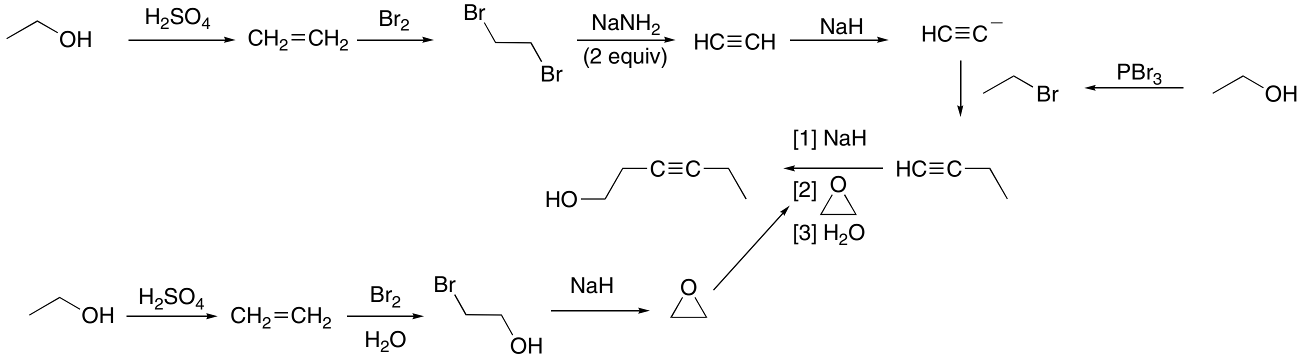
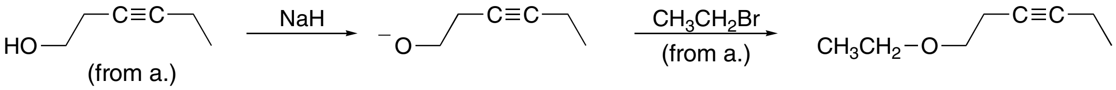


11.66

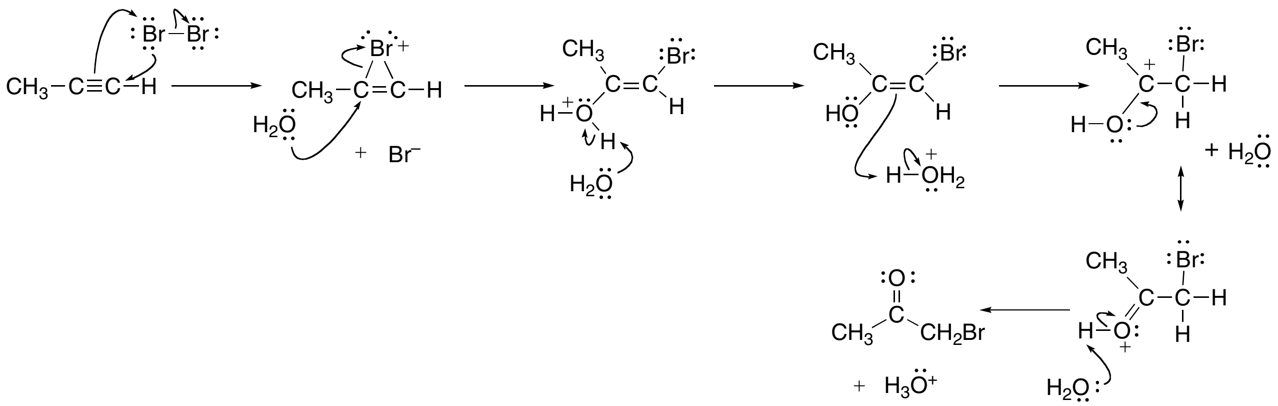
a.



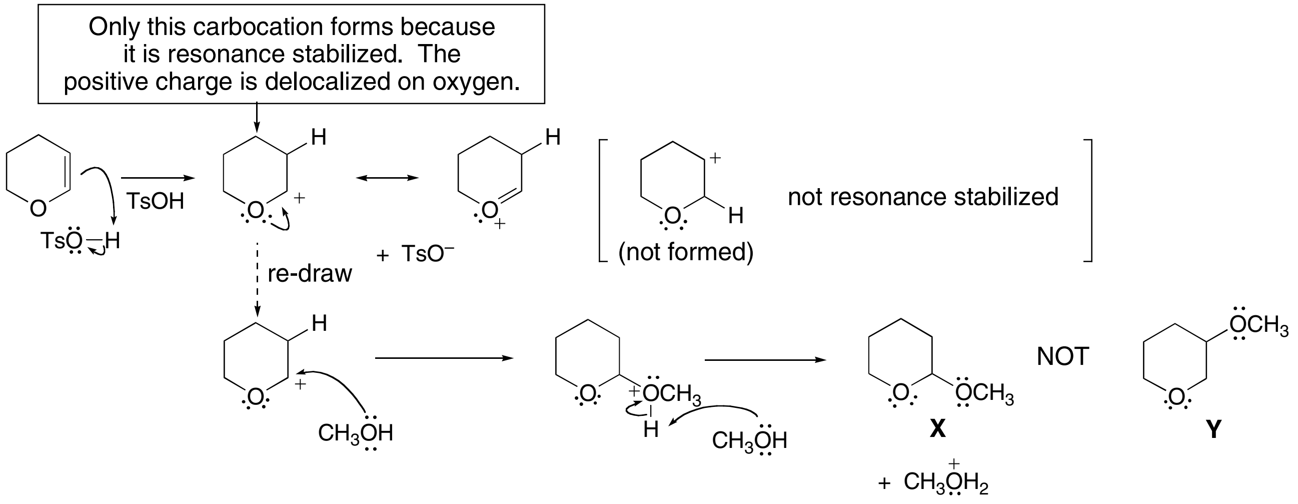
b.



11.67



11.68


Only this carbocation forms because it is resonance stabilized. The positive charge is delocalized on oxygen.

11.69