

CHAPTER 7

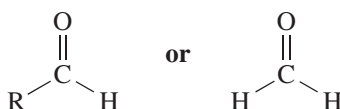
The Reactions of Alkynes • An Introduction to Multistep Synthesis

Important Terms

acetylide ion the conjugate base of a terminal alkyne.



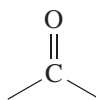
aldehyde a compound with a carbonyl group that is bonded to an alkyl group and to a hydrogen (or bonded to two hydrogens).



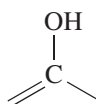
alkylation reaction a reaction that adds an alkyl group to a reactant.

alkyne a hydrocarbon that contains a triple bond.

carbonyl group a carbon doubly bonded to an oxygen.



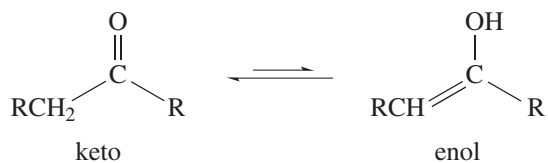
enol an alkene with an OH group bonded to one of the sp^2 carbons.



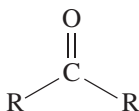
geminal dihalide a compound with two halogen atoms bonded to the same carbon.

internal alkyne an alkyne with its triple bond not at the end of the carbon chain.

keto-enol tautomers a ketone or an aldehyde and its isomeric enol. The keto and enol tautomers differ only in the location of a double bond and a hydrogen.



ketone a compound with a carbonyl group that is bonded to two alkyl groups.



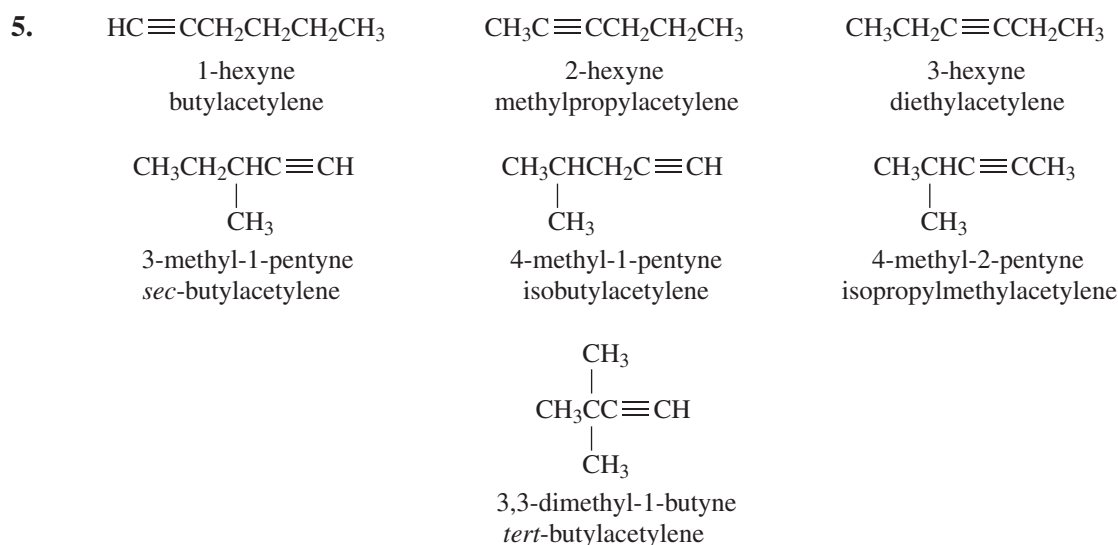
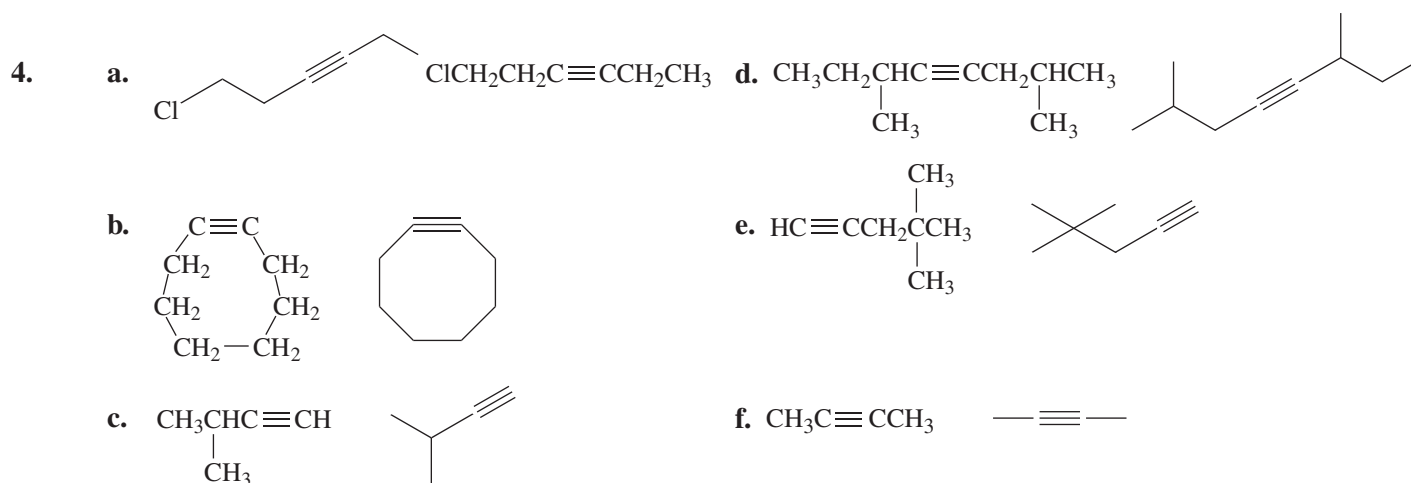
π -complex a complex formed between an electrophile and a triple bond.

radical anion	a species with an atom that has a negative charge and an unpaired electron.
retrosynthetic analysis or retrosynthesis	working backward (on paper) from a target molecule to available starting materials.
tautomerization	interconversion of keto–enol tautomers.
tautomers	constitutional isomers that are in rapid equilibrium; for example, keto and enol tautomers. The keto and enol tautomers differ only in the location of a double bond and a hydrogen.
terminal alkyne	an alkyne with its triple bond at the end of the carbon chain.
vinyllic cation	a species with a positive charge on a vinyllic carbon.
vinyllic radical	a species with an unpaired electron on a vinyllic carbon.

Solutions to Problems

- 5-bromo-2-pentyne
 - 6-bromo-2-chloro-4-octyne
 - 1-methoxy-2-pentyne
 - 3-ethyl-1-hexyne
- 6-methyl-2-octyne
 - 5-ethyl-4-methyl-1-heptyne
 - 2-bromo-4-octyne
- The general molecular formula of a noncyclic hydrocarbon is C_nH_{2n+2} . Therefore, the molecular formula for a noncyclic hydrocarbon with 14 carbons is $C_{14}H_{30}$.

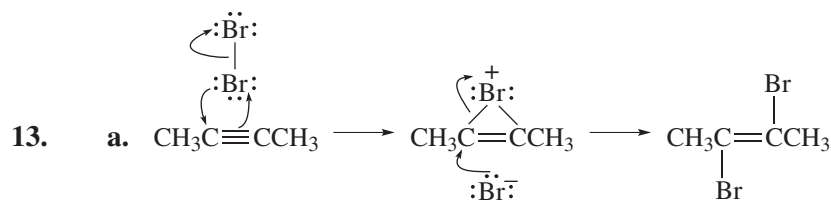
Because a compound has two fewer hydrogens for every ring and π bond, a compound with one ring and 4 π bonds (2 triple bonds) has 10 fewer hydrogens than the C_nH_{2n+2} formula. Therefore, the molecular formula is $C_{14}H_{20}$.



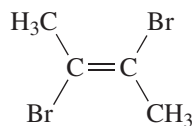
- 1-hepten-4-yne
 - 4-methyl-1,4-hexadiene
 - 5-vinyl-5-octen-1-yne
(One of the functional groups cannot be included in the parent hydrocarbon.)
 - 3-butyne-1-ol
 - 1,3,5-heptatriene
 - 2,4-dimethyl-4-hexen-1-ol

7. a. (*E*)-2-hepten-4-ol b. 1-hepten-5-yne c. (*E*)-4-hepten-1-yne
8. a. sp^2-sp^2 d. $sp-sp^3$ g. sp^2-sp^3
 b. sp^2-sp^3 e. $sp-sp$ h. $sp-sp^3$
 c. $sp-sp^2$ f. sp^2-sp^2 i. sp^2-sp
9. alkane = pentane alkene = 1-pentene alkyne = 1-pentyne
10. The *cis* isomer has a higher boiling point because it has a dipole moment, whereas the dipole moment of the *trans* isomer is zero.
11. Solved in the text.

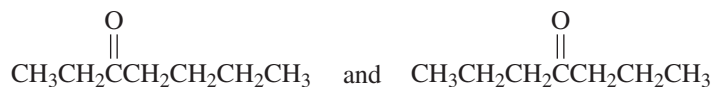
12. a. $\text{CH}_2=\underset{\text{Br}}{\text{C}}\text{CH}_3$ c. $\text{CH}_3\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}=\text{CCH}_3$ e. $\text{CH}_3\text{CH}_2\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}\text{CH}_3$
- b. $\text{CH}_3\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}\text{CH}_3$ d. $\text{HC}\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}-\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}\text{CH}_3$ f. $\text{CH}_3\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\overset{\text{Br}}{\underset{\text{Br}}{\text{C}}}\text{CH}_2\text{CH}_3$



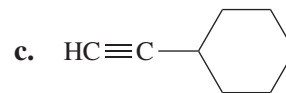
- b. Only anti addition occurs because the intermediate is a cyclic bromonium ion. Therefore, the product has the *E* configuration.



14. Because the alkyne is not symmetrical, two ketones are obtained.

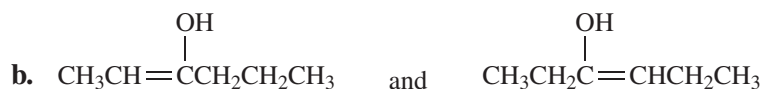


15. a. $\text{CH}_3\text{C}\equiv\text{CH}$ b. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$

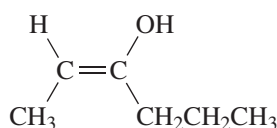
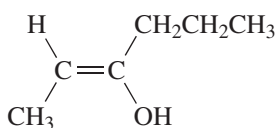
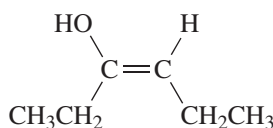
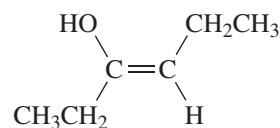
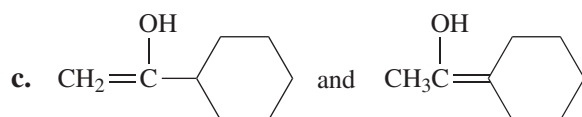


The best answer for **b** is 3-hexyne, because it would form only the desired ketone. 2-Hexyne would form two different ketones, so only half of the product would be the desired ketone.

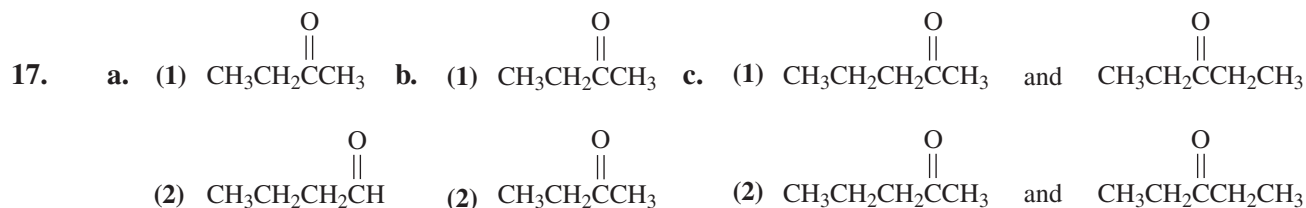
16. a. $\text{CH}_2=\overset{\text{OH}}{\text{C}}\text{CH}_3$ Because the ketone has identical substituents bonded to the carbonyl carbon, it has only one enol tautomer.



E and *Z* isomers are possible for each of these enols.

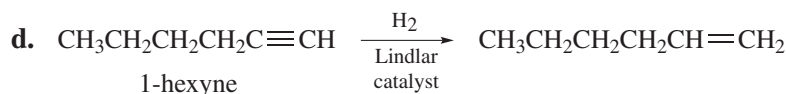
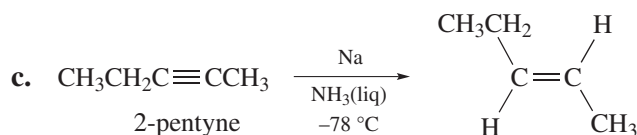
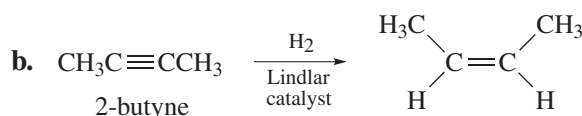
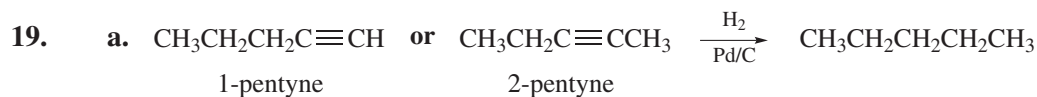
*E**Z**E**Z*

Because each enol has identical groups bonded to one of its sp^2 carbons, *E* and *Z* isomers are not possible for either enol.



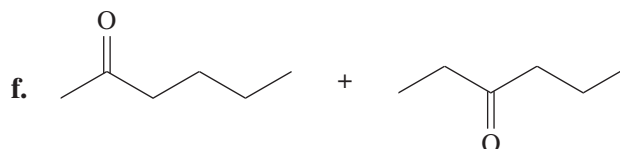
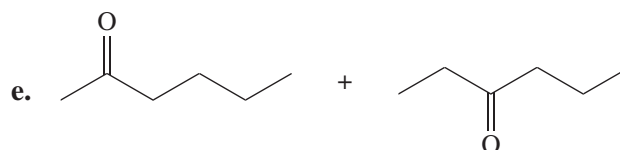
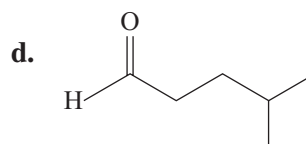
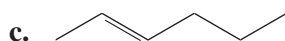
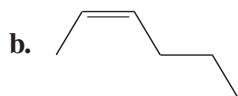
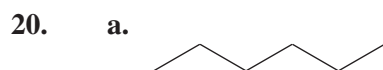
18. Ethyne (acetylene)

An alkyne can form an aldehyde only if the OH group adds to a terminal sp carbon. In the acid-catalyzed addition of water to a terminal alkyne, the proton adds to the terminal sp carbon. Therefore, the only way the OH group can add to a terminal sp carbon under these conditions is if there are two terminal sp carbons in the alkyne. In other words, the alkyne must be ethyne.



$\text{Na}/\text{NH}_3(\text{liq})$ cannot be used to reduce terminal alkynes because Na removes the hydrogen that is attached to the sp carbon of the terminal alkyne.



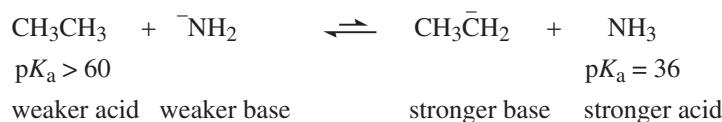


21. A terminal alkyne has a $pK_a = 25$. A base that removes a proton from a terminal alkyne in a reaction that favors products must have a conjugate acid that is a weaker acid than a terminal alkyne. That is, it must have a $pK_a > 25$. (Recall that the equilibrium favors formation of the weak acid.)

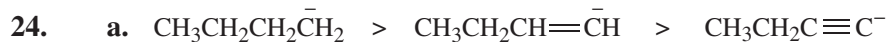
CH_3CH_2^- and $\text{H}_2\text{C}=\text{CH}^-$ because the pK_a values of their conjugate acids are > 60 and 44 , respectively.

The pK_a values of the conjugate acids of the other choices are all < 25 .

22. The reaction of sodium amide with an alkane does not favor products because the acid that would be formed is a stronger acid than the alkane (the reactant acid). Recall that the equilibrium favors reaction of the strong acid (or strong base) and formation of the weak acid (or weak base); Section 2.5.



23. The base used to remove a proton must be stronger than the base that is formed as a result of removing the proton. Therefore, the base used to remove a proton from a terminal alkyne must be a stronger base than the conjugate base of the terminal alkyne. A terminal alkyne has a $pK_a \sim 25$. In other words, any base whose conjugate acid has a pK_a greater than 25 can be used.

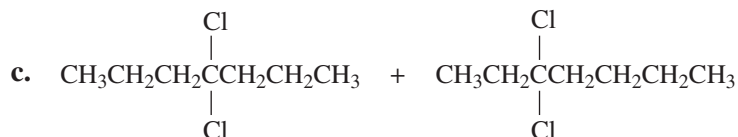
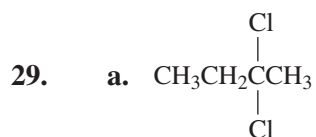
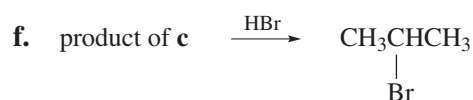
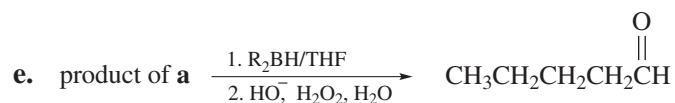
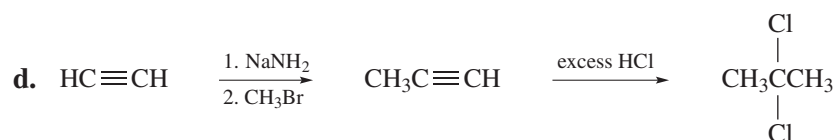
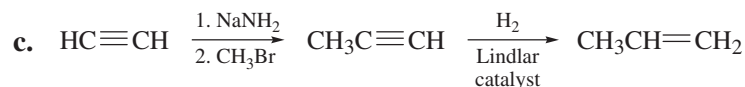
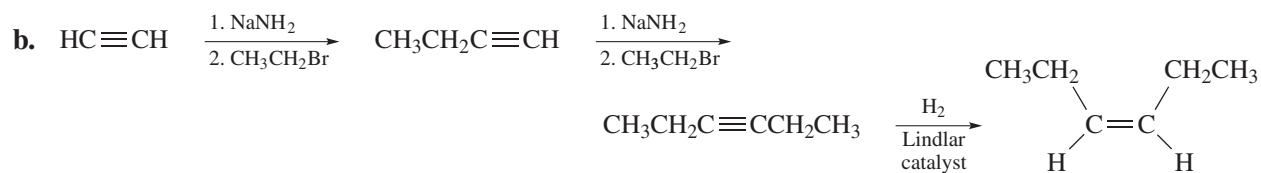
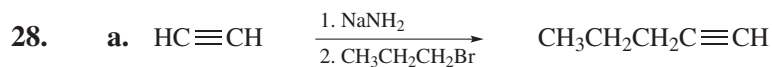


25. Solved in the text.

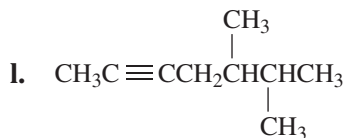
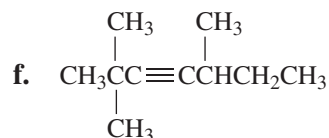
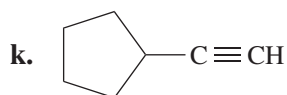
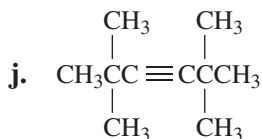
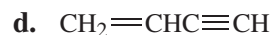
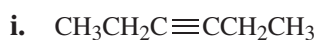
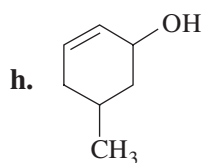
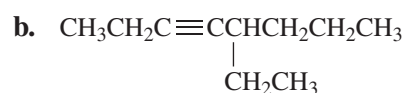
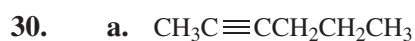
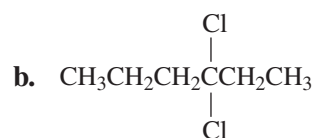


A triply bonded (sp) carbon is more electronegative than an sp^2 or sp^3 carbon. Therefore, a triply bonded carbon with a positive charge is less stable than a doubly bonded or singly bonded carbon with a positive charge. Thus, in **a**, the vinyl cation is more stable and in **b**, the ethyl cation is more stable.

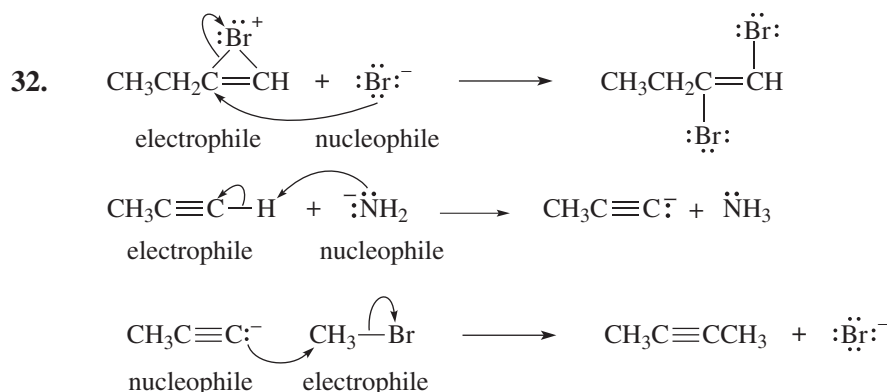
27. Solved in the text.



equal amounts

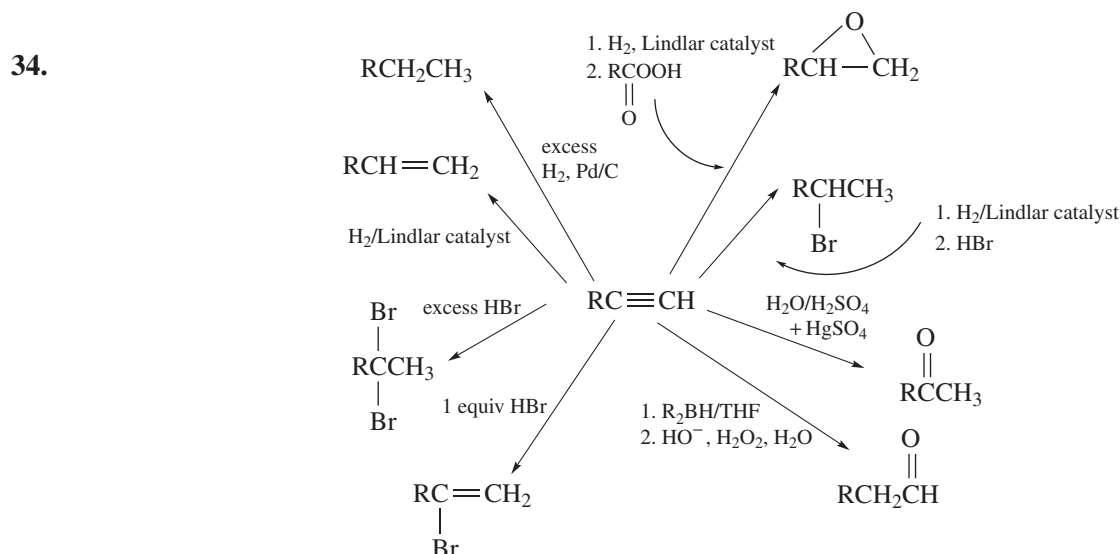


31. The student named only one correctly.
 a. 4-methyl-2-hexyne b. 7-bromo-3-heptyne c. correct d. 2-pentyne

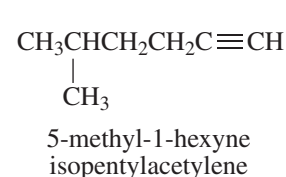
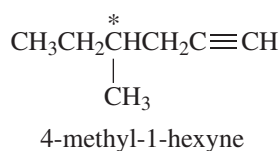
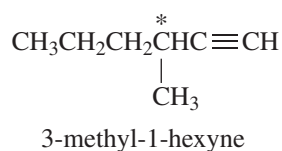
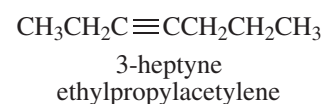
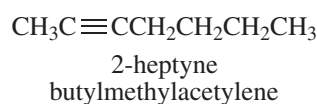
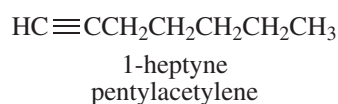


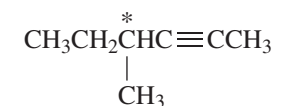
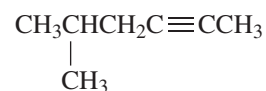
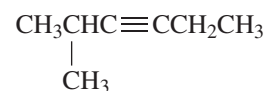
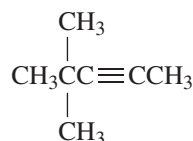
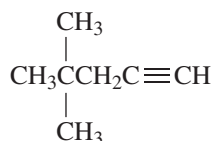
(Methyl bromide is an electrophile because the carbon has a partial positive charge since bromine is more electronegative than carbon.)

33. a. 5-bromo-2-hexyne c. 5,5-dimethyl-2-hexyne e. 1,5-cyclooctadiene
 b. 5-methyl-2-octyne d. 6-chloro-2-methyl-3-heptyne f. 1,6-dimethyl-1,3-cyclohexadiene

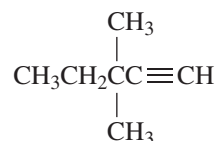
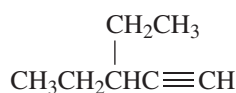


35. a. First draw the straight-chain compounds with seven carbons; then draw the straight-chain compounds with six carbons and one methyl group; then draw the straight-chain compounds with five carbons and two methyl groups (or with one ethyl group). Naming them will tell you if you have drawn one compound more than once because if two compounds have the same name, they are the same compound.

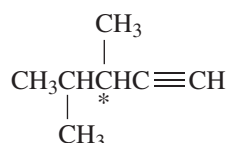


4-methyl-2-hexyne
sec-butylmethylacetylene5-methyl-2-hexyne
isobutylmethylacetylene2-methyl-3-hexyne
ethylisopropylacetylene4,4-dimethyl-2-pentyne
tert-butylmethylacetylene

4,4-dimethyl-1-pentyne

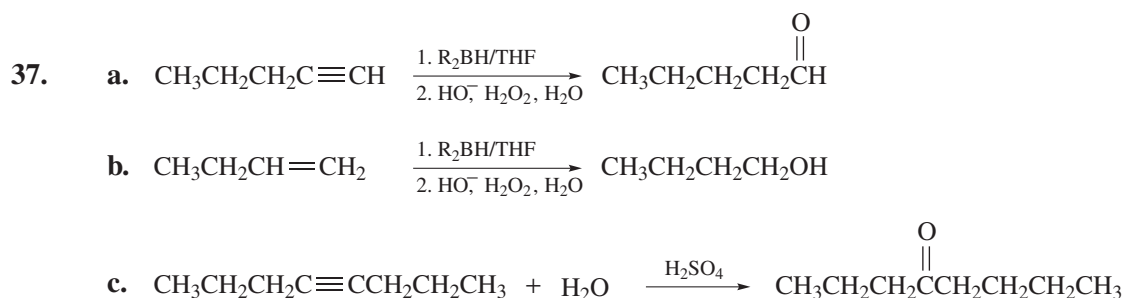
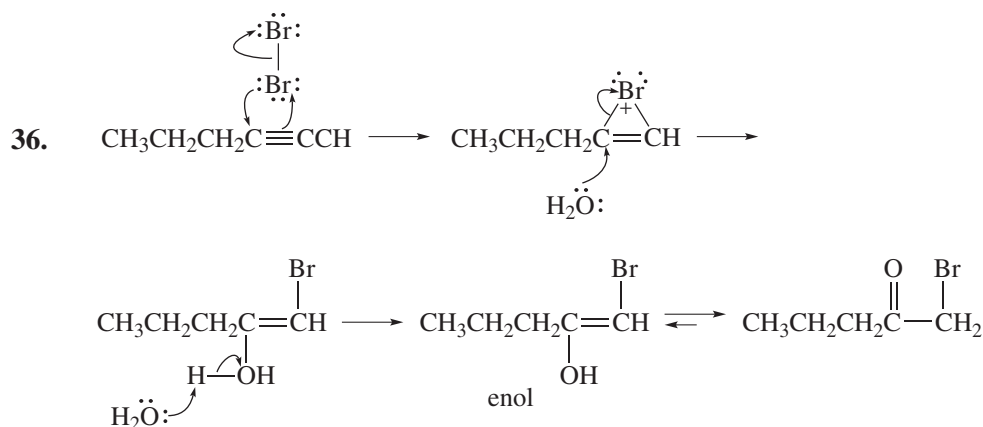
3,3-dimethyl-1-pentyne
tert-pentylacetylene

3-ethyl-1-pentyne



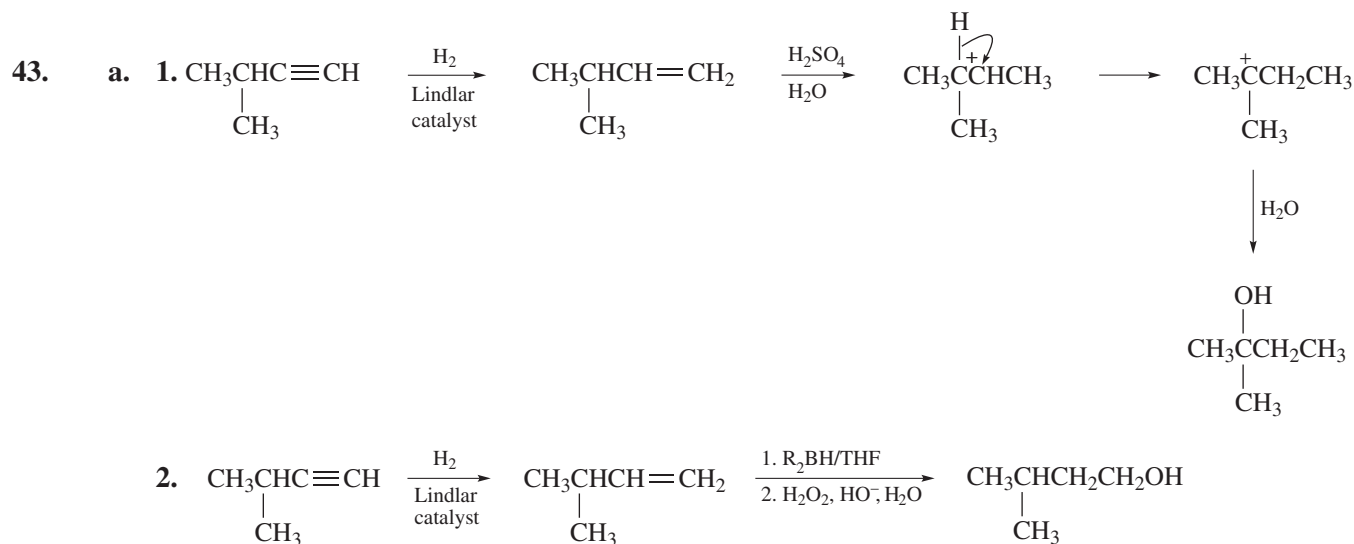
3,4-dimethyl-1-pentyne

- b. There are 14 alkynes if stereoisomers are ignored. Four of the 14 alkynes have an asymmetric center, so each of these can have either the *R* or *S* configuration. Therefore, if stereoisomers are included, there would be 18 alkynes.

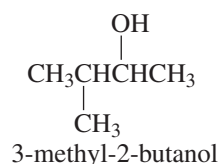


This symmetrical alkyne will give the greatest yield of the desired ketone. Because the reactant is not a terminal alkyne, the reaction can take place without the mercuric ion catalyst.

38. a. $\text{H}_2/\text{Lindlar catalyst}$ b. $\text{Na}, \text{NH}_3(\text{liq}), -78^\circ\text{C}$ c. excess $\text{H}_2, \text{Pd/C}$
39. a. $\text{CH}_2=\text{CCH}_3$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{Br}$
 b. CH_3CCH_3
 $\quad \quad \quad |$
 $\quad \quad \quad \text{Br}$
 c. $\begin{array}{c} \text{Br} \quad \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$
 d. $\begin{array}{c} \text{Br} \quad \text{Br} \\ | \quad | \\ \text{BrCHCCH}_3 \\ | \\ \text{Br} \end{array}$ g. $\text{CH}_3\text{CH}_2\text{CH}_3$ j. $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$
 e. $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CCH}_3 \end{array}$ h. $\text{CH}_3\text{CH}=\text{CH}_2$
 f. $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2\text{CH} \end{array}$ i. $\text{CH}_3\text{C}\equiv\text{C}^-$
40. a. $\text{CH}_3\text{CH}=\text{CCH}_3$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{Br}$
 b. $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3\text{CH}_2\text{CCH}_3 \\ | \\ \text{Br} \end{array}$
 c. $\begin{array}{c} \text{Br} \quad \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{Br} \end{array}$
 d. $\begin{array}{c} \text{Br} \quad \text{Br} \\ | \quad | \\ \text{CH}_3\text{C}-\text{CCH}_3 \\ | \quad | \\ \text{Br} \quad \text{Br} \end{array}$
 e. $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \end{array}$ i. no reaction
 f. $\begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \end{array}$ j. no reaction
 g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 h. $\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$
41. a. 1-octen-6-yne d. 5-chloro-1,3-cyclohexadiene
 b. *cis*-3-hexen-1-ol or (*Z*)-3-hexen-1-ol e. 1-methyl-1,3,5-cycloheptatriene
 c. 1,5-octadiyne f. 6-methyl-3-cyclohexenamine
42. The molecular formula of the hydrocarbon is $\text{C}_{32}\text{H}_{56}$.
 With one triple bond, two double bonds, and one ring, the degree of unsaturation is 5.
 Therefore, the compound is missing 10 hydrogens from $\text{C}_n\text{H}_{2n+2} = \text{C}_{32}\text{H}_{66}$.



b. 3-Methyl-2-butanol would be a minor product obtained from both **1** and **2**.



3-Methyl-2-butanol will be obtained from **1**, because occasionally water will attack the secondary carbocation before it has a chance to rearrange to the tertiary carbocation.

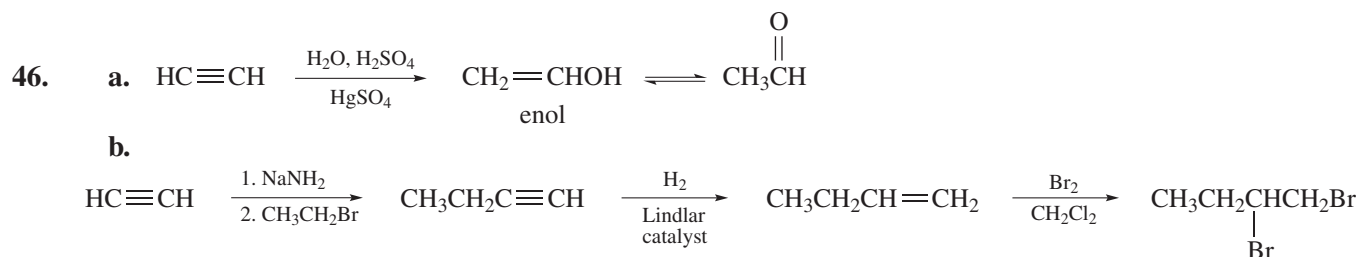
3-Methyl-2-butanol will be obtained from **2**, because in the second step of the synthesis, boron can also add to the other sp^2 carbon; it will be a minor product because the transition state for its formation is less stable than the transition state leading to the major product. Because a carbocation is not formed as an intermediate, a carbocation rearrangement cannot occur.

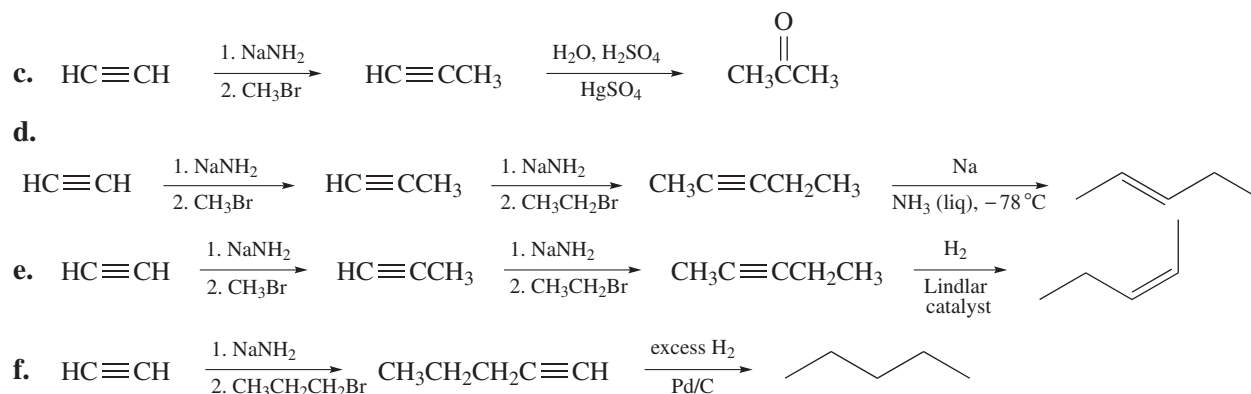
(The proton cannot add to the other sp^2 carbon in the second step of part **1** because that would form a primary carbocation. Primary carbocations are so unstable that they can never be formed.)

44. Three of the names are correct.

- a. 3-heptyne c. correct e. correct
b. 5-methyl-3-heptyne d. 6,7-dimethyl-3-octyne f. correct

45. Only **c** and **e** are keto-enol tautomers. Notice that an enol tautomer has an OH group bonded to an sp^2 carbon. The structures in **d** are not enol tautomers, because they do not have the oxygen on the same carbon.

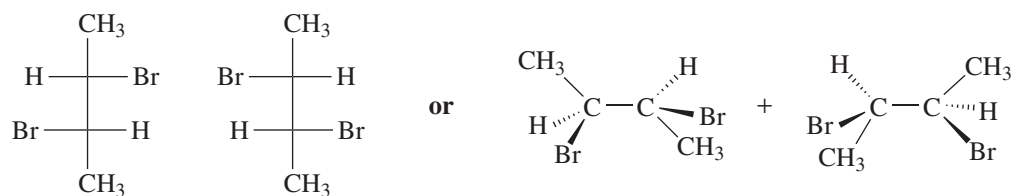




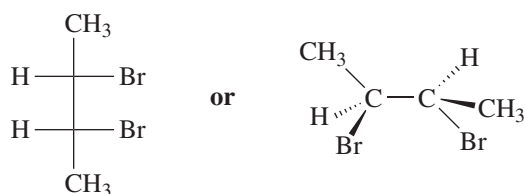
47. The first equilibrium lies to the right because HOOH ($\text{p}K_a = 11.6$) is a stronger acid than H_2O ($\text{p}K_a = 15.7$).
The second equilibrium lies to the left because the alkyne ($\text{p}K_a = 25$) is a weaker acid than HOOH ($\text{p}K_a = 11.6$).

48. a. (Z)-3,6-dimethyl-2-hepten-4-yne c. 4,4-dimethyl-1-nonen-6-yn-3-ol
b. 5-*tert*-butyl-2-methyl-3-octyne d. 4-(2-methylbutyl)-5-heptyn-3-amine

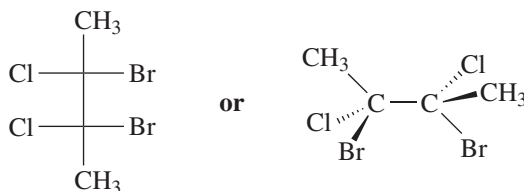
49. a. Syn addition of H_2 forms *cis*-2-butene; when Br_2 adds to *cis*-2-butene, the threo pair of enantiomers is formed.

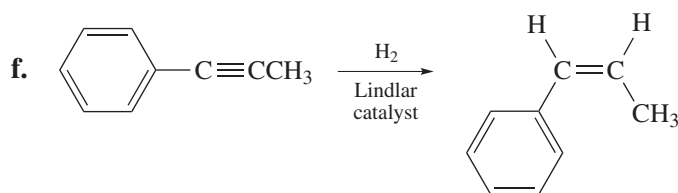
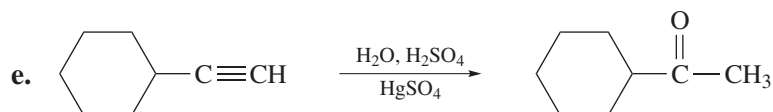
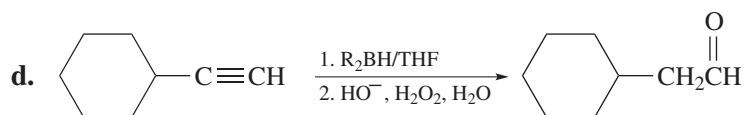
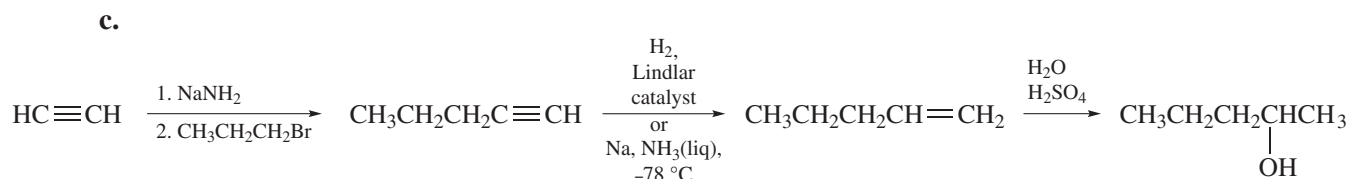
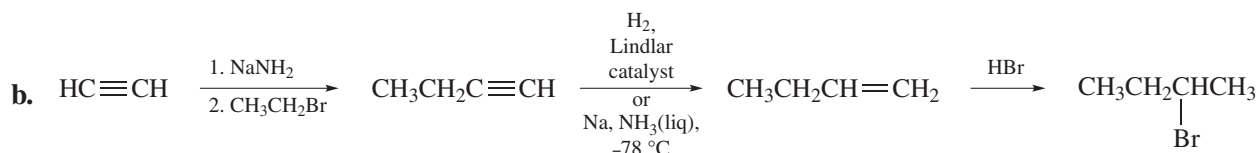
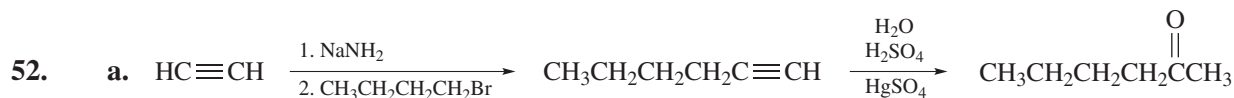
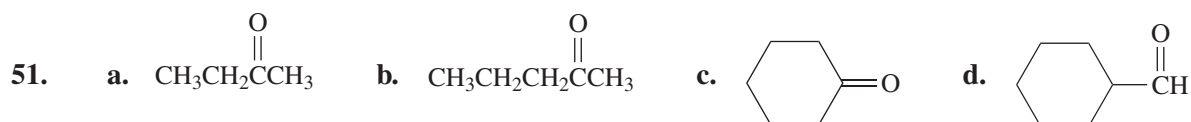
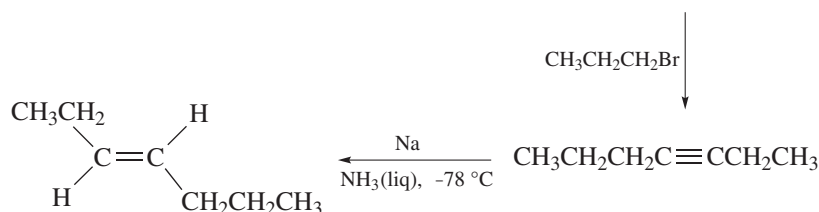
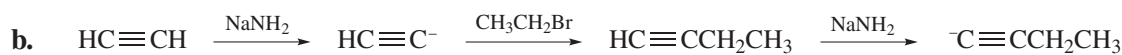
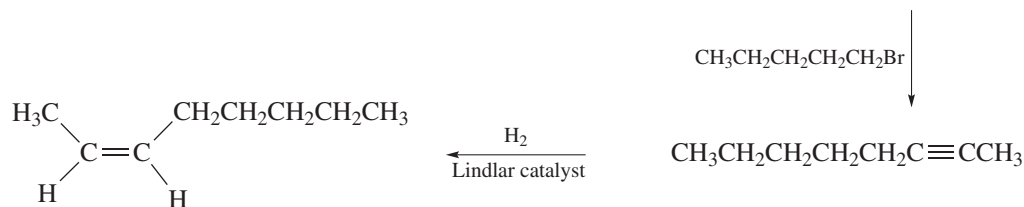
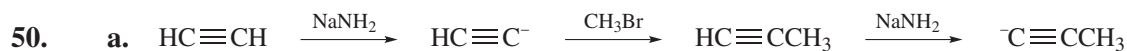


- b. Reaction with sodium and liquid ammonia forms *trans*-2-butene; when Br_2 adds to *trans*-2-butene, a meso compound is formed.

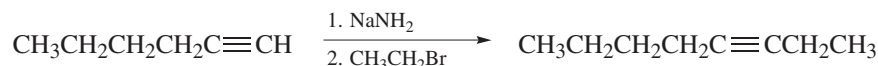


- c. Anti addition of Cl_2 forms *trans*-2,3-dichloro-2-butene; when Br_2 adds to *trans*-2,3-dichloro-2-butene, a meso compound is formed.

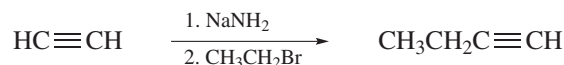




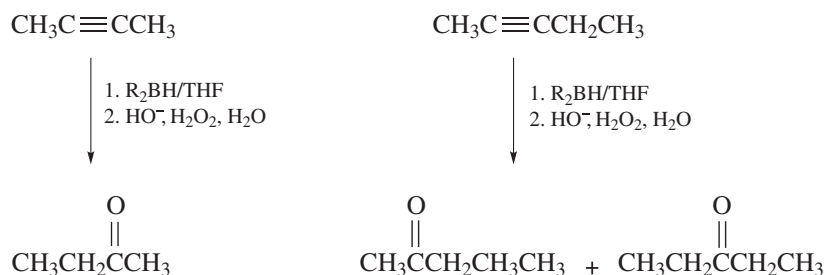
53. The chemist can make 3-octyne by using 1-hexyne instead of 1-butyne. He would then need to use ethyl bromide (instead of butyl bromide) for the alkylation step:



Or he could make the 1-butyne he needed by alkylating ethyne:



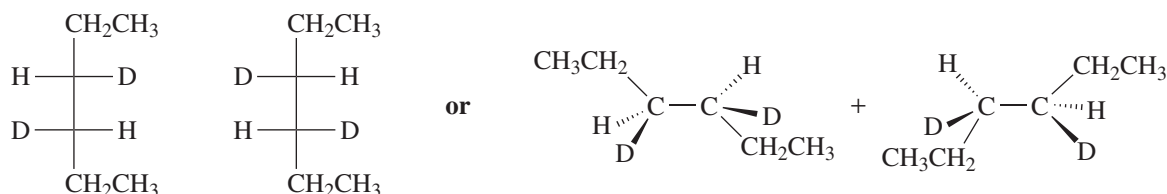
54. a. Only one product is obtained from hydroboration–oxidation of 2-butyne because the alkyne is symmetrical. Two different products can be obtained from hydroboration–oxidation of 2-pentyne because the alkyne is not symmetrical.



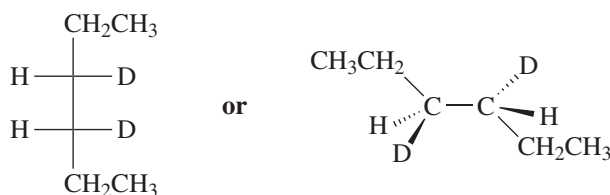
- b. Only one product is obtained from hydroboration–oxidation of a symmetrical alkyne such as 3-hexyne or 4-octyne.



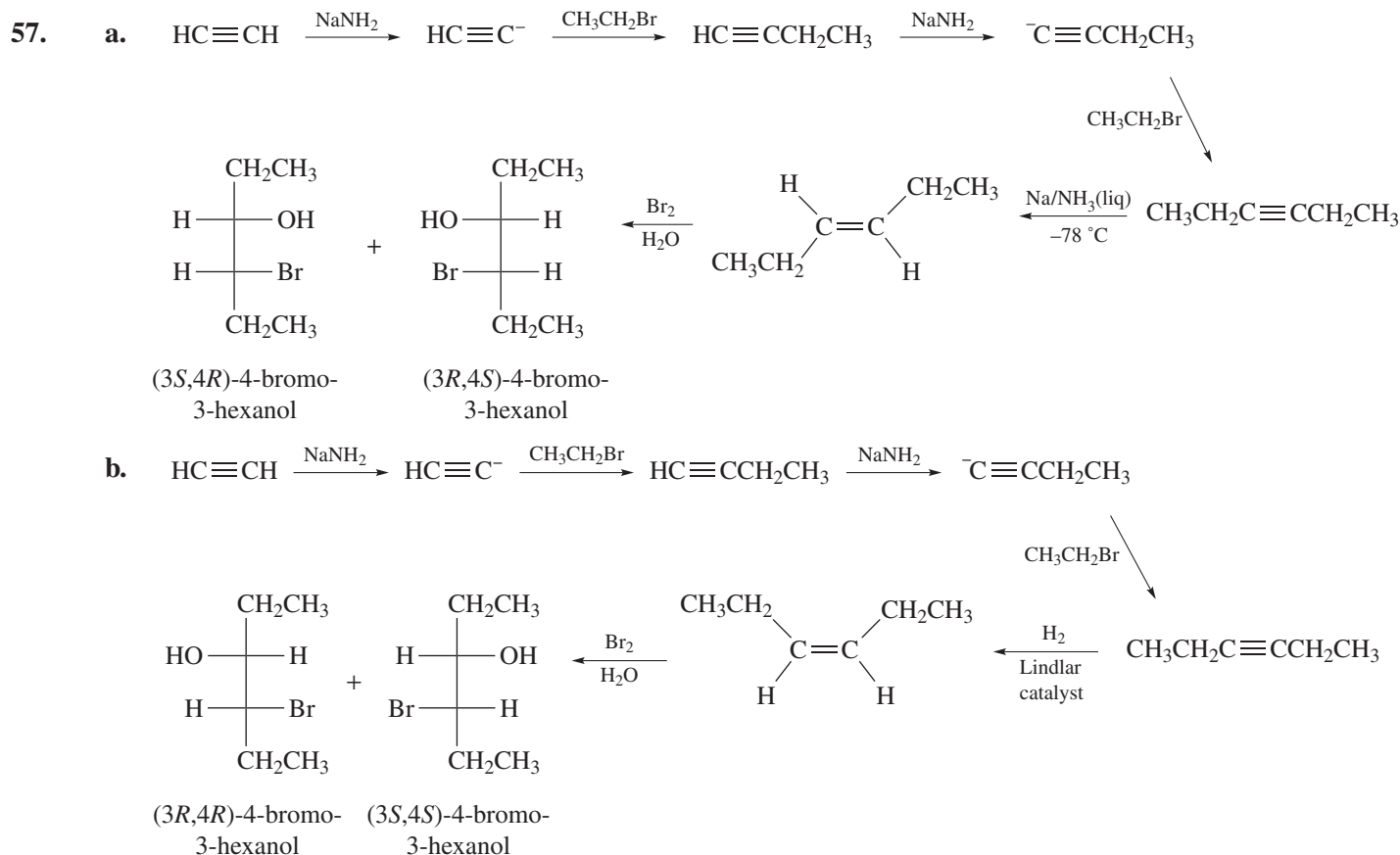
55. a. The first step forms a trans alkene. Syn addition to a trans alkene forms the threo pair of enantiomers.



- b. The first step forms a cis alkene. Syn addition to a cis alkene forms the erythro pair of enantiomers, but because each asymmetric carbon is bonded to the same four groups, the product is a meso compound.



56. If HO^- and HOOH are added at the same time as BH_3 (or R_2BH), HO^- is a better nucleophile than the alkyne (no bonds have to be broken when HO^- reacts with the electrophile), so BH_3 (or R_2BH) will react with HO^- instead of with the alkyne.

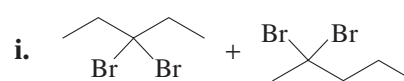
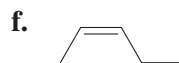
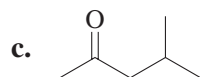
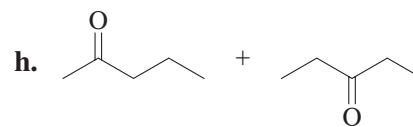
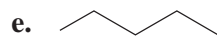
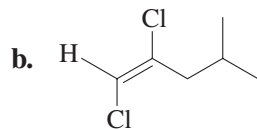
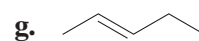
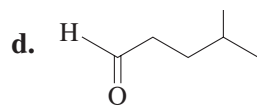
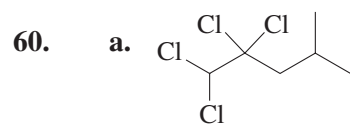
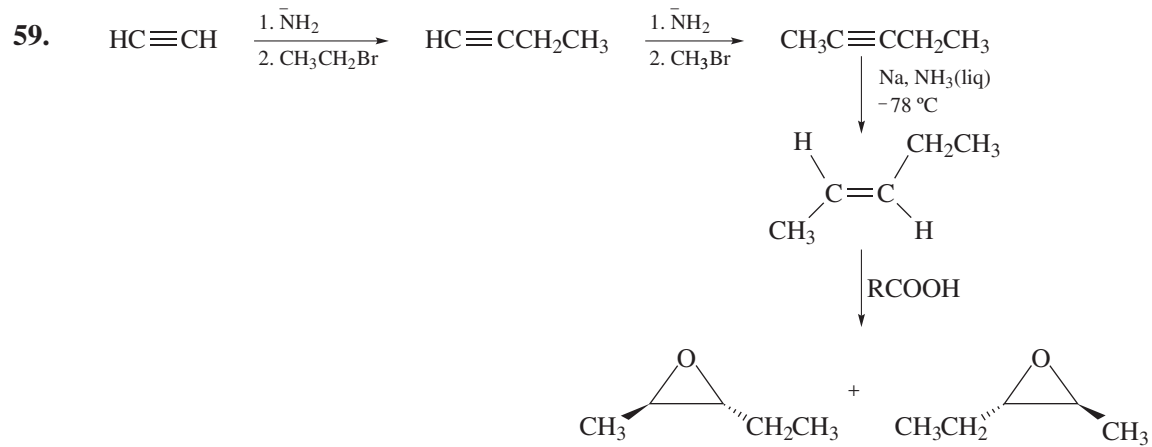


Because anti addition occurs in the last step, the threo enantiomers are formed.

If $\text{Na/NH}_3(\text{liq})/-78^\circ\text{C}$ is used instead of $\text{H}_2/\text{Lindlar catalyst}$ in the fifth step, the trans alkene will be formed. Reaction of Br_2 and H_2O with the trans alkene will form the erythro enantiomers.

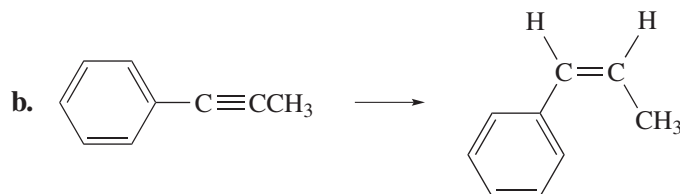
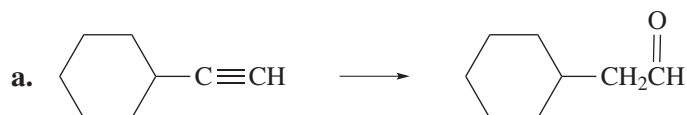
58. (3*E*,6*E*)-3,7,11-trimethyl-1,3,6,10-dodecatetraene

The configuration of the double bond at the 1-position and at the 10-position is not specified because isomers are not possible at those positions, because there are two hydrogens bonded to C-1 and two methyl groups bonded to C-11.

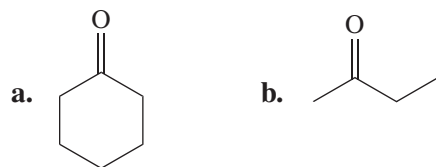


Chapter 7 Practice Test

1. What reagents can be used to convert the given starting material into the desired product?



2. Draw the enol tautomer(s) of the following ketones:



3. Draw the structure for each of the following:



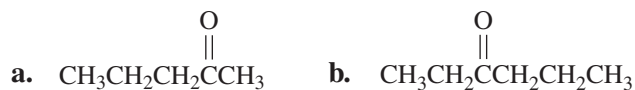
4. Indicate whether each of the following statements is true or false:

a. A terminal alkyne is more stable than an internal alkyne.	T	F
b. Propyne is more reactive than propene toward reaction with HBr.	T	F
c. 1-Butyne is more acidic than 1-butene.	T	F
d. An sp^2 carbon is more electronegative than an sp^3 carbon.	T	F
e. The reactions of internal alkynes are more regioselective than the reactions of terminal alkynes.	T	F
f. Alkenes are more reactive than alkynes.	T	F

5. What is each compound's systematic name?



6. What alkyne is the best reagent to use for the synthesis of each of the following ketones?



7. Rank the following compounds from most acidic to least acidic:



8. Give an example of a ketone that has two enol tautomers.

9. Show how the target molecules can be prepared from the given starting materials.

