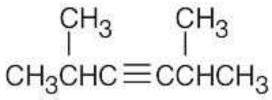
Chapter 9 – Alkynes: An Introduction to Organic Synthesis

Solutions to Problems

9.1 The rules for naming alkynes are almost the same as the rules for naming alkenes. The suffix -*yne* is used, and compounds containing both double bonds and triple bonds are -*enynes*, with the double bond taking numerical precedence.

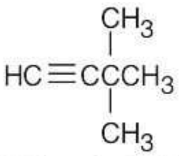
(a)



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

2,5-Dimethyl-3-hexyne

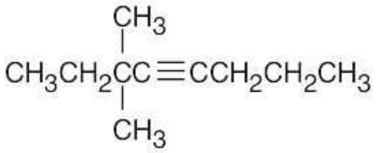
(b)



$HC\equiv C\underset{CH_3}{\overset{CH_3}{C}}CH_3$

3,3-Dimethyl-1-butyne

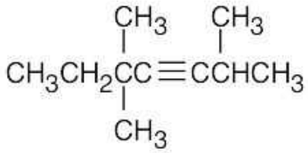
(c)



$CH_3CH_2\underset{CH_3}{\overset{CH_3}{C}}C\equiv CCH_2CH_2CH_3$

3,3-Dimethyl-4-octyne

(d)



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

2,5,5-Trimethyl-3-heptyne

(e) $CH_3CH=CHCH=CHC\equiv CCH_3$

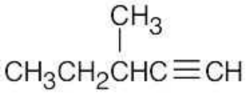
2,4-Octadien-6-yne
(not 4,6-Octadien-2-yne)

9.2

$CH_3CH_2CH_2CH_2C\equiv CH$
1-Hexyne

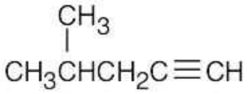
$CH_3CH_2CH_2C\equiv CCH_3$
2-Hexyne

$CH_3CH_2C\equiv CCH_2CH_3$
3-Hexyne



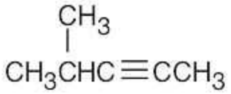
$CH_3CH_2\overset{CH_3}{CH}C\equiv CH$

3-Methyl-1-pentyne



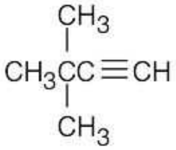
$CH_3\overset{CH_3}{CH}CH_2C\equiv CH$

4-Methyl-1-pentyne



$CH_3\overset{CH_3}{CH}C\equiv CCH_3$

4-Methyl-2-pentyne



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

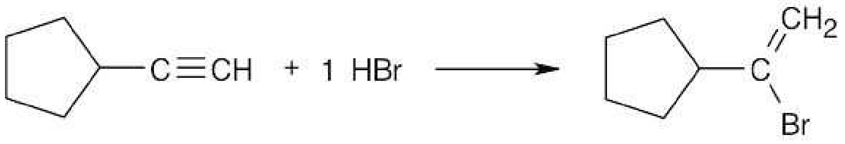
3,3-Dimethyl-1-butyne

9.3 Markovnikov addition is observed with alkynes as well as with alkenes.

(a)

$$CH_3CH_2CH_2C\equiv CH \quad + \quad 2\ Cl_2 \longrightarrow CH_3CH_2CH_2CCl_2CHCl_2$$

(b)



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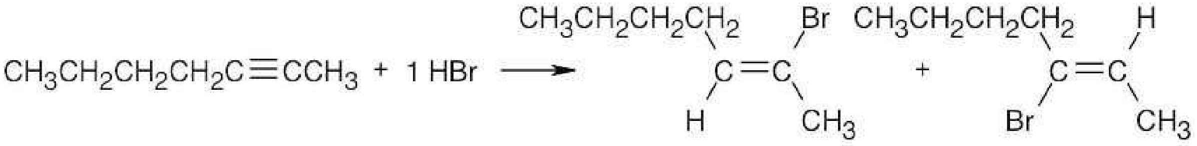
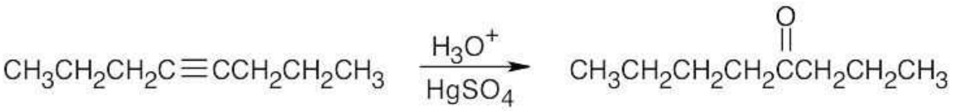


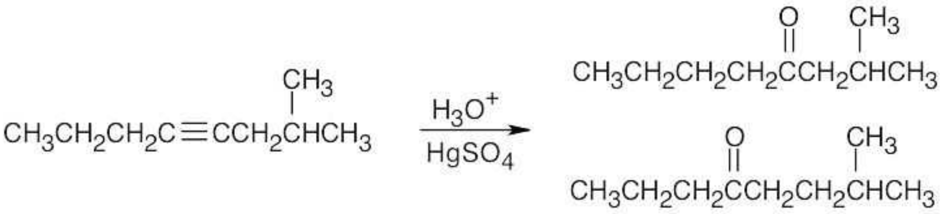
Two products result from addition to an internal alkyne.

9.4



$$CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3 \xrightarrow[HgSO_4]{H_3O^+} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$$

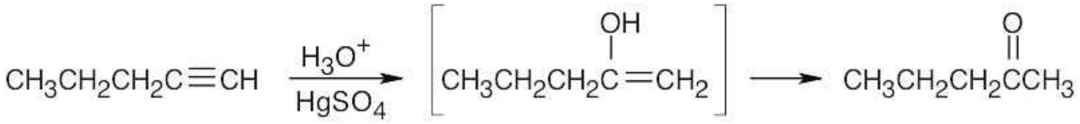
This symmetrical internal alkyne yields only one product.



$$CH_3CH_2CH_2C\equiv CCH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \xrightarrow[HgSO_4]{H_3O^+} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \quad CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$$

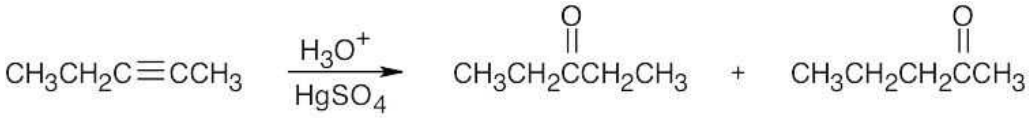
Two ketone products result from hydration of 2-methyl-4-octyne.

9.5 (a)



$$CH_3CH_2CH_2C\equiv CH \xrightarrow[HgSO_4]{H_3O^+} \left[CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}=CH_2\right] \longrightarrow CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$$

(b)

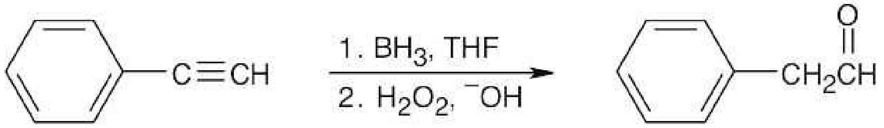


$$CH_3CH_2C\equiv CCH_3 \xrightarrow[HgSO_4]{H_3O^+} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 \quad + \quad CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$$

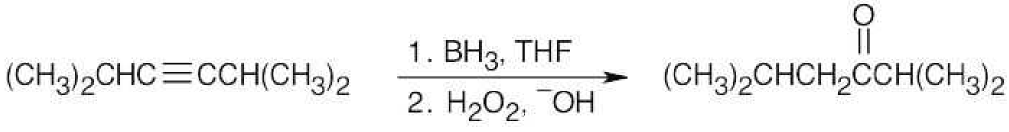
The desired ketone can be prepared only as part of a product mixture.

9.6 Remember that hydroboration yields aldehydes from terminal alkynes and ketones from internal alkynes.

(a)



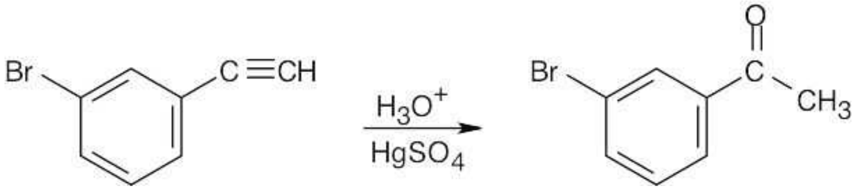
(b)



$$(CH_3)_2CHC{\equiv}CCH(CH_3)_2 \xrightarrow[\text{2. } H_2O_2,\ ^-OH]{\text{1. } BH_3,\ THF} (CH_3)_2CHCH_2\overset{O}{\overset{\|}{C}}CH(CH_3)_2$$

9.7

(a)



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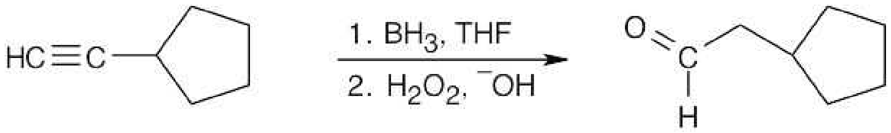
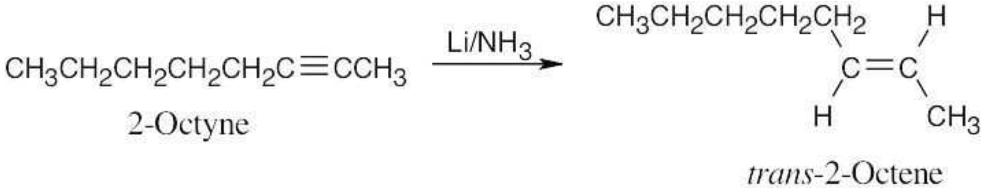
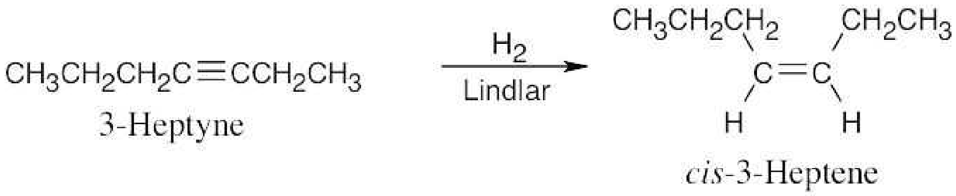


9.8 The correct reducing reagent gives a double bond with the desired geometry.

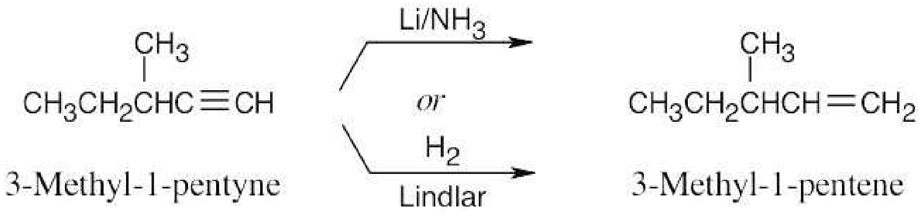
(a)



(b)

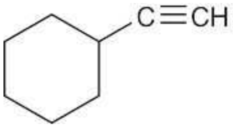
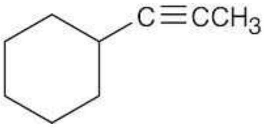


(c)



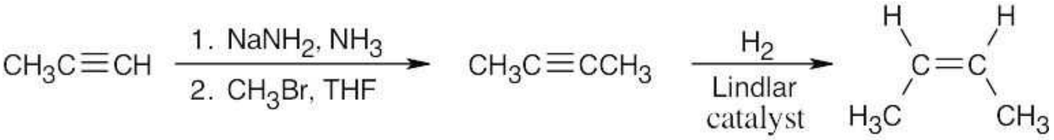
9.9 A base that is strong enough to deprotonate acetone must be the conjugate base of an acid weaker than acetone. In this problem, only $Na^+ \, ^-C\equiv CH$ is a base strong enough to deprotonate acetone.

9.10 Remember that the alkyne must be a terminal alkyne and the halide must be primary. More than one combination of terminal alkyne and halide may be possible.

	Alkyne		*R'X (X=Br or I)*	*Product*
(a)	$CH_3CH_2CH_2C\equiv CH$		CH_3X	$CH_3CH_2CH_2C\equiv CCH_3$ 2-Hexyne
	$HC\equiv CCH_3$	*or*	$CH_3CH_2CH_2X$	
(b)	$(CH_3)_2CHC\equiv CH$		CH_3CH_2X	$(CH_3)_2CHC\equiv CCH_2CH_3$ 2-Methyl-3-hexyne
(c)			CH_3X	

Products (b) and (c) can be synthesized by only one route because only primary halides can be used for acetylide alkylations.

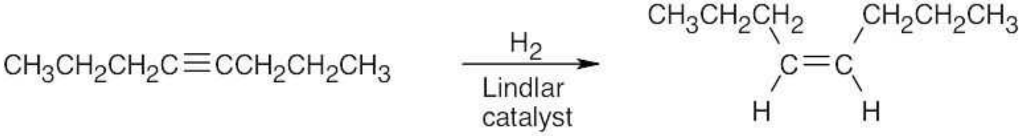
9.11 The cis double bond can be formed by hydrogenation of an alkyne, which can be synthesized by an alkylation reaction of a terminal alkyne.



cis-2-Butene

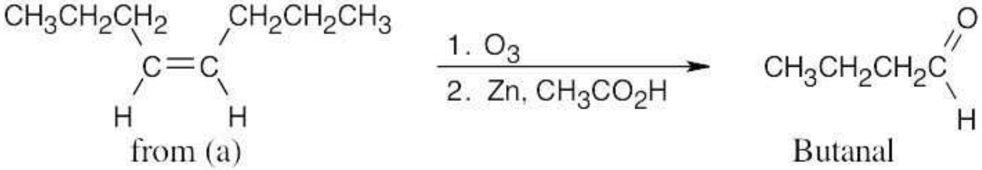
9.12 The starting material is $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3$. Look at the functional groups in the target molecule and work backward to 4-octyne.

(a) To reduce a triple bond to a double bond with *cis* stereochemistry use H_2 with Lindlar catalyst.

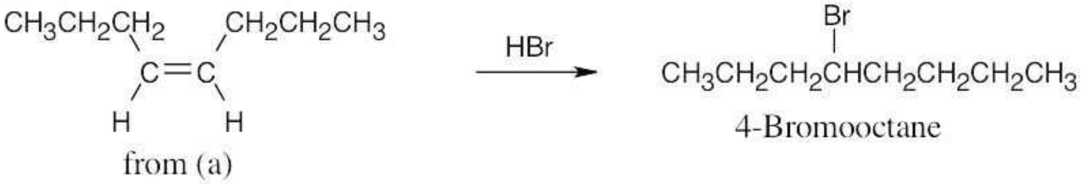


cis-4-Octene

(b) An aldehyde is the product of double-bond cleavage of an alkene with O_3. The starting material can be either *cis*-4-octene or *trans*-4-octene.

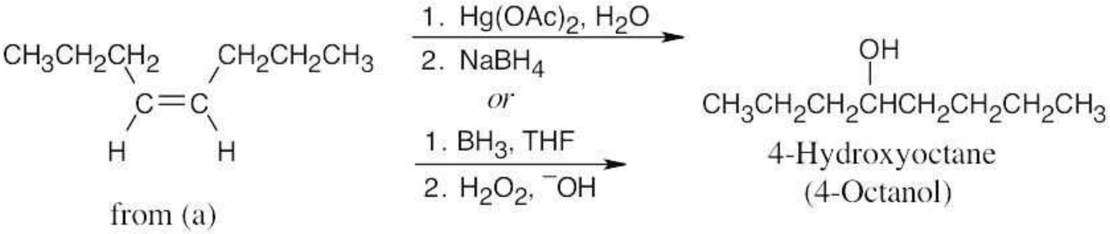


(c) Addition of HBr to *cis*-4-octene [part (a)] yields 4-bromooctane.

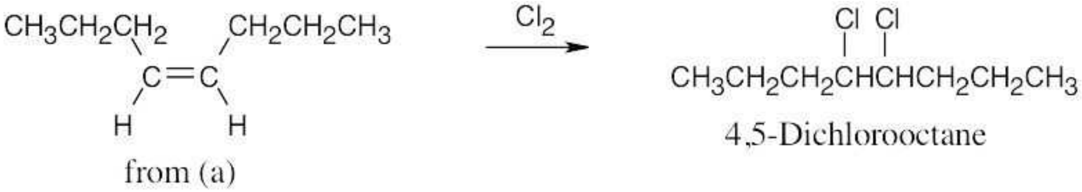


Alternatively, lithium/ammonia reduction of 4-octyne, followed by addition of HBr, gives 4-bromooctane.

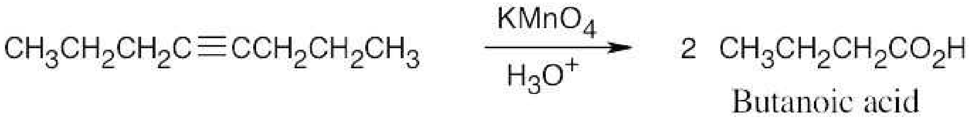
(d) Hydration or hydroboration/oxidation of *cis*-4-octene [part (a)] yields 4-hydroxyoctane (4-octanol).



(e) Addition of Cl_2 to 4-octene [part (a)] yields 4,5-dichlorooctane.



(f) $KMnO_4$ cleaves 4-octyne into two four-carbon fragments.

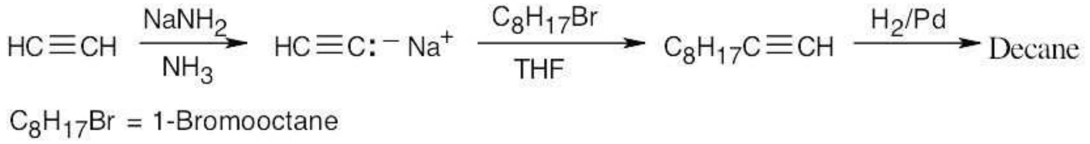


$$CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3 \xrightarrow[H_3O^+]{KMnO_4} 2\ CH_3CH_2CH_2CO_2H$$

9.13 The following syntheses are explained in detail in order to illustrate retrosynthetic logic – the system of planning syntheses by working backwards.

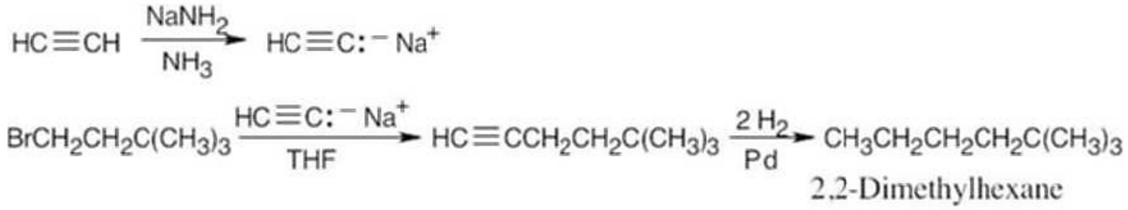
(a)

1. An immediate precursor to $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ might be an alkene or alkyne. Try $C_8H_{17}C{\equiv}CH$, which can be reduced to decane by H_2/Pd.
2. The alkyne $C_8H_{17}C{\equiv}CH$ can be formed by alkylation of $HC{\equiv}C{:}^-Na^+$ by $C_8H_{17}Br$, 1-bromooctane.
3. $HC{\equiv}C{:}^-\,Na^+$ can be formed by treatment of $HC{\equiv}CH$ with $NaNH_2$, NH_3.



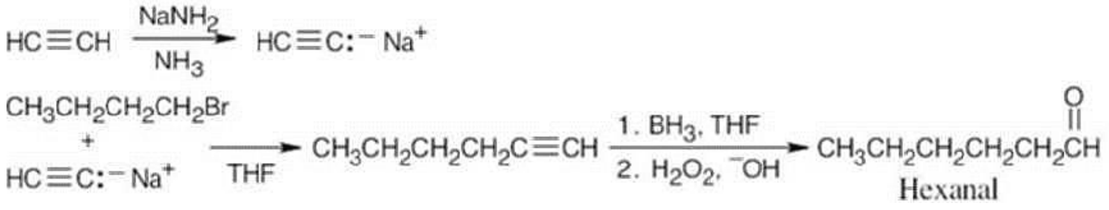
(b)

1. An immediate precursor to $CH_3CH_2CH_2CH_2C(CH_3)_3$ might be $HC{\equiv}CCH_2CH_2C(CH_3)_3$, which, when hydrogenated, yields 2,2-dimethylhexane.
2. $HC{\equiv}CCH_2CH_2C(CH_3)_3$ can be formed by alkylation of $HC{\equiv}C{:}^-\,Na^+$ (from a.) with $BrCH_2CH_2C(CH_3)_3$.



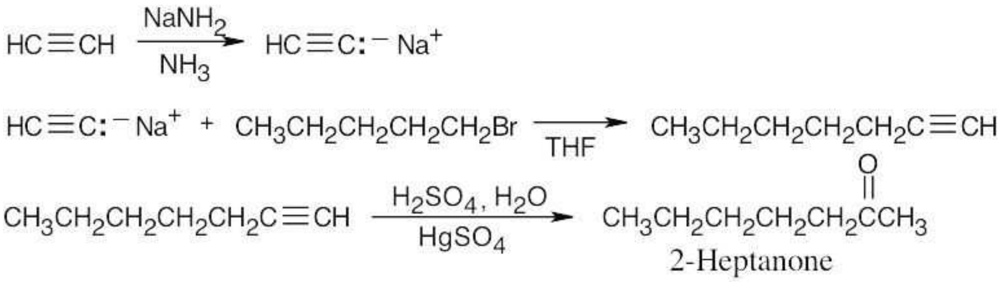
(c)

1. $CH_3CH_2CH_2CH_2CH_2CHO$ can be made by treating $CH_3CH_2CH_2CH_2C{\equiv}CH$ with borane, followed by H_2O_2.
2. $CH_3CH_2CH_2CH_2C{\equiv}CH$ can be synthesized from $CH_3CH_2CH_2CH_2Br$ and $HC{\equiv}C{:}^-\,Na^+$.



(d)

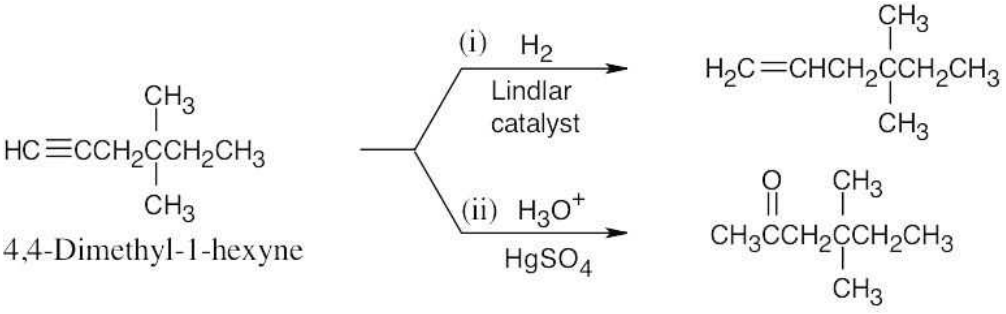
1. The desired ketone can be formed by mercuric-ion-catalyzed hydration of 1-heptyne.
2. 1-Heptyne can be synthesized by an alkylation of sodium acetylide by 1-bromopentane.



Additional Problems

Visualizing Chemistry

9.14 (a)



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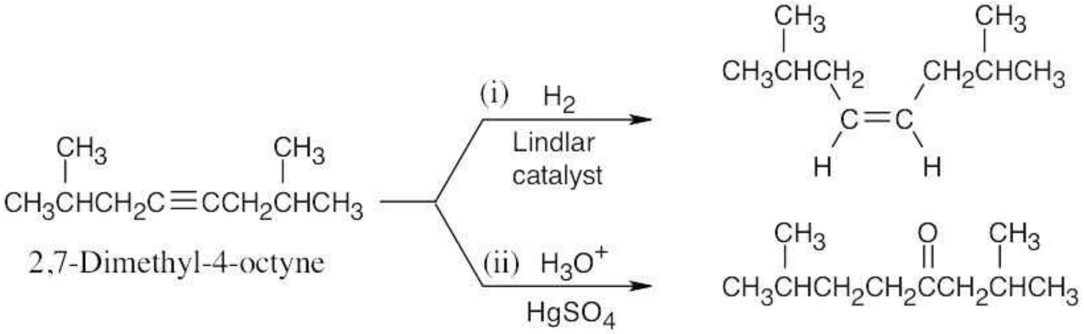
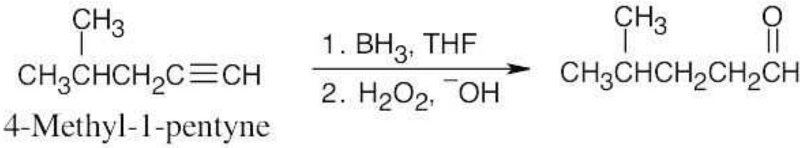
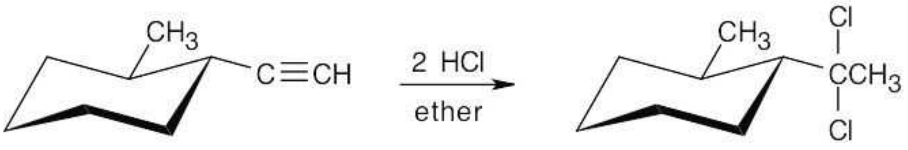


9.15 (a)



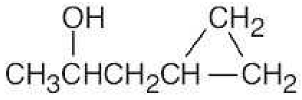
An aldehyde is formed by reacting a terminal alkyne with borane, followed by oxidation.

(b)



9.16 First, draw the structure of each target compound. Then, analyze the structures for a synthetic route.

(a)



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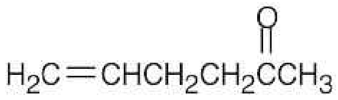
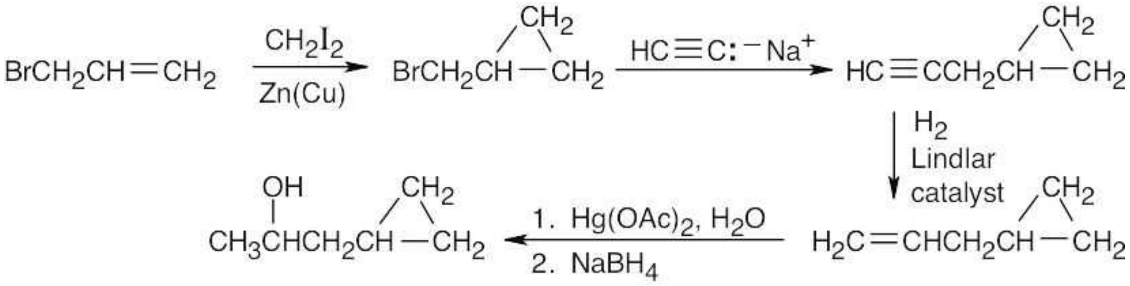
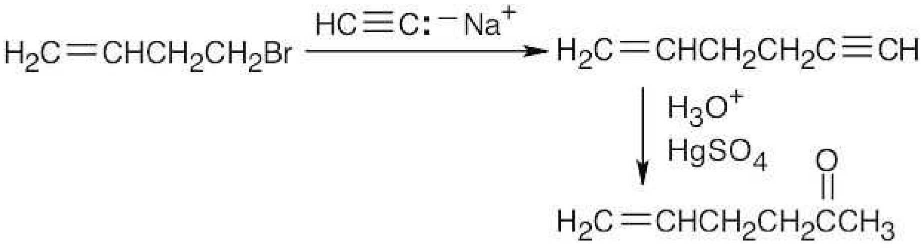


$H_2C{=}CHCH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$

(a) The left side and the right side might have double bonds as immediate precursors; the right side may result from a Simmons-Smith carbenoid addition to an alkene, and the left side may result from hydration of an alkene. Let's start with 3-bromo-1-propene.



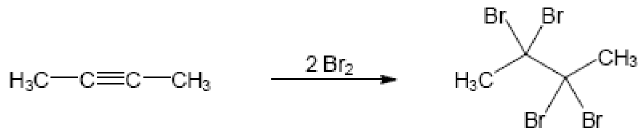
(b) The right side can result from Hg-catalyzed addition of H_2O to a terminal alkyne.



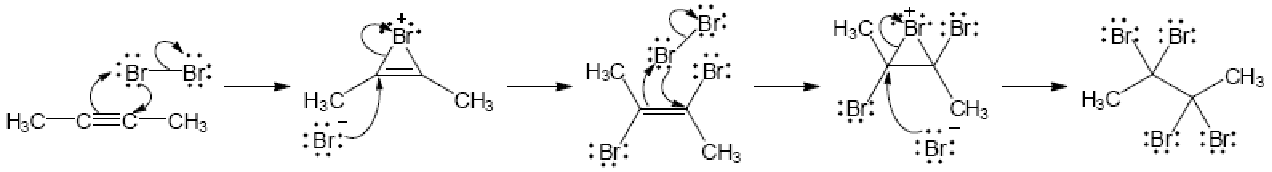
9.17 It's not possible to form a small ring containing a triple bond because the angle strain that would result from bending the bonds of an *sp*-hybridized carbon to form a small ring is too great.

Mechanism Problems

9.18 (a)



Mechanism:



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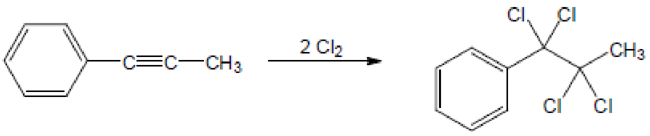
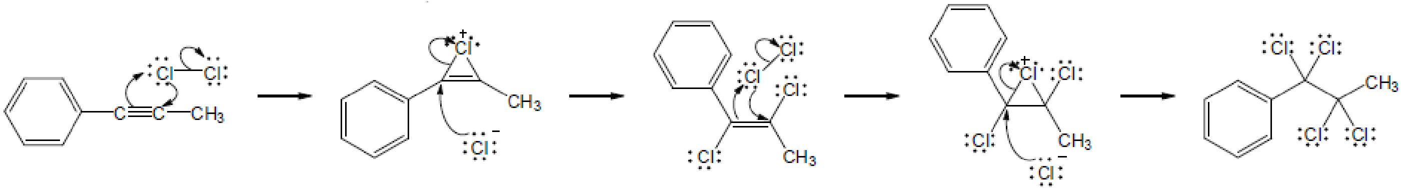


Mechanism:



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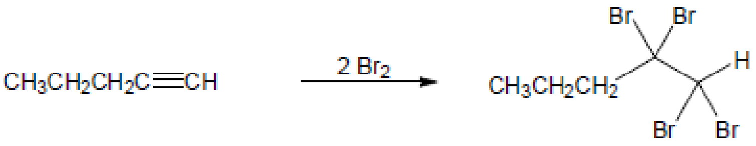
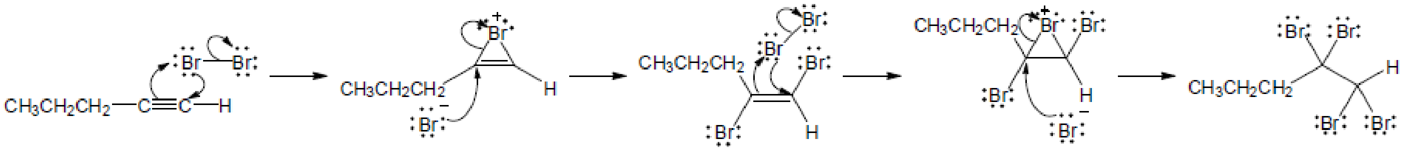
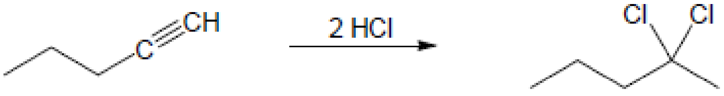


Mechanism:

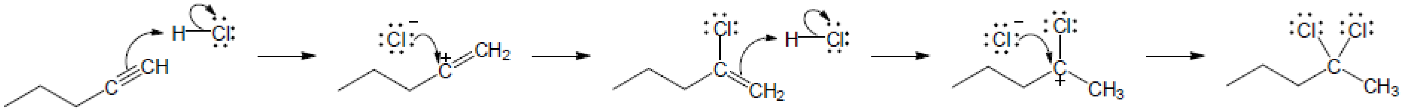


9.19 Assuming that strong acids add to akynes in the same manner that they add to alkenes, propose a mechanism for each reaction below.

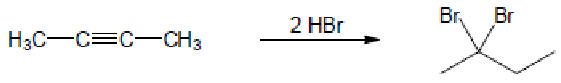
(a)



Mechanism:



(b)



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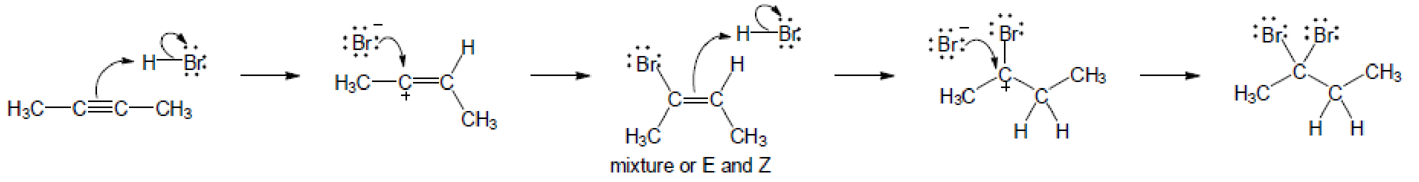
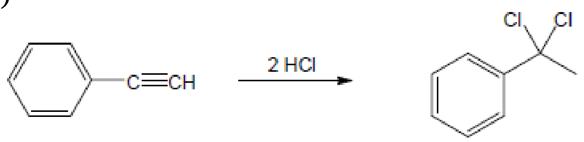
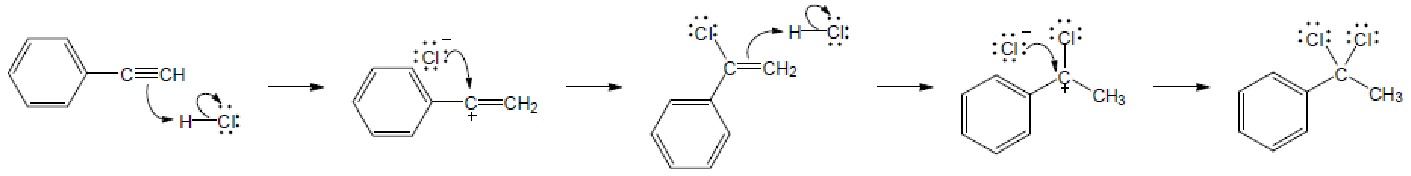


(c)

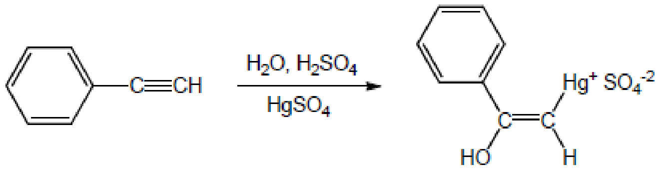


Mechanism:

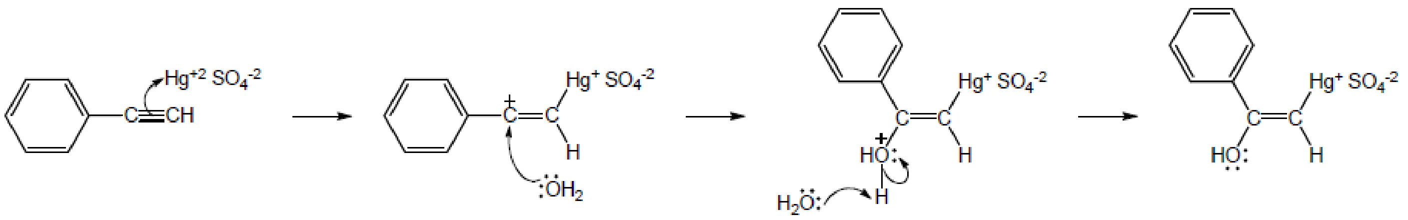


9.20 The mercury catalyzed hydration of alkynes involves the formation of an organomercury enol intermediate. Provide the electron pushing mechanism to show how each intermediate below is formed.

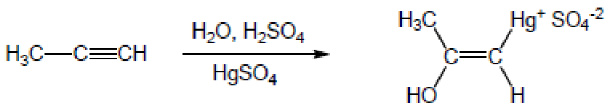
(a)



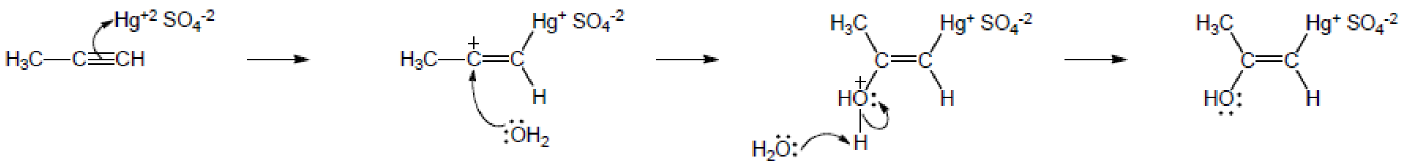
Mechanism:



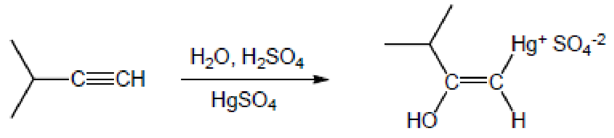
(b)



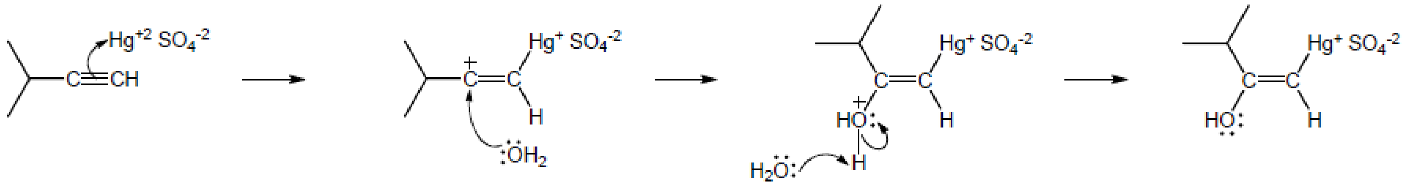
Mechanism:



(c)

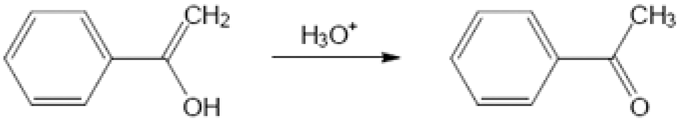


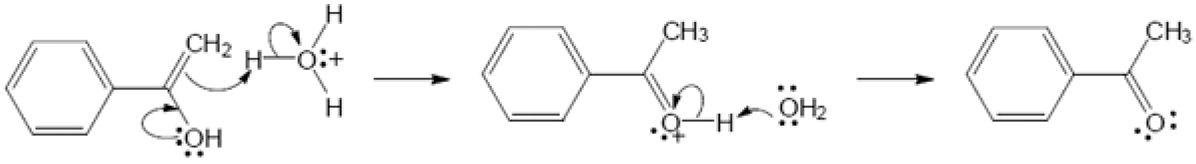
Mechanism:



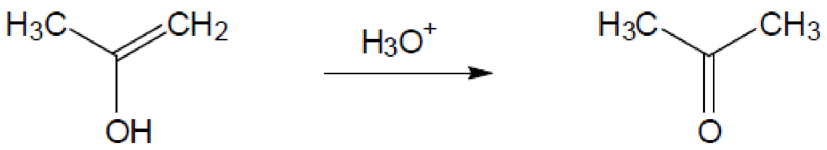
9.21 The final step in the hydration of an alkyne under acidic conditions is the tautomerism of an enol intermediate to the corresponding ketone. The mechanism involves a protonation followed by a deprotonation. Show the mechanism of each tautomerism below.

(a)

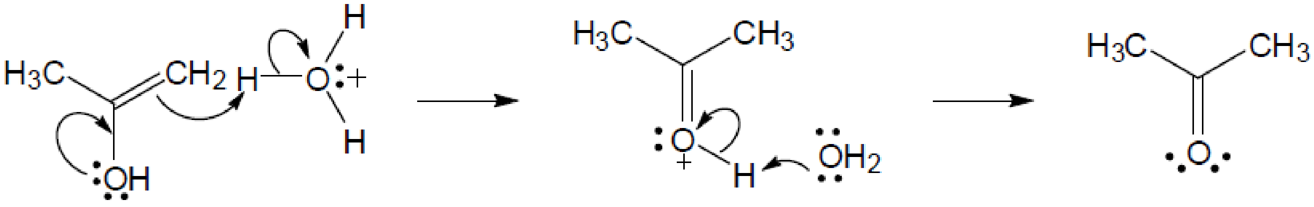




(b)



Mechanism:



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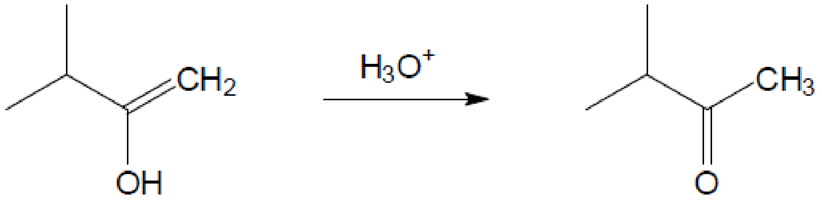
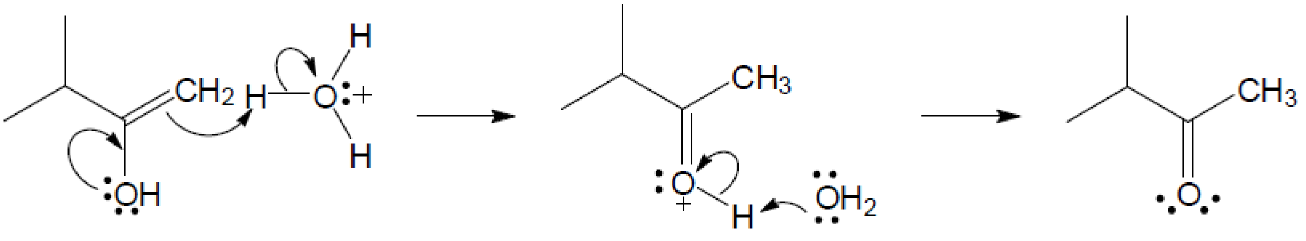
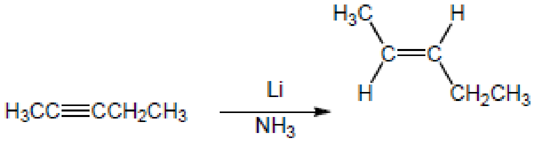


Mechanism:

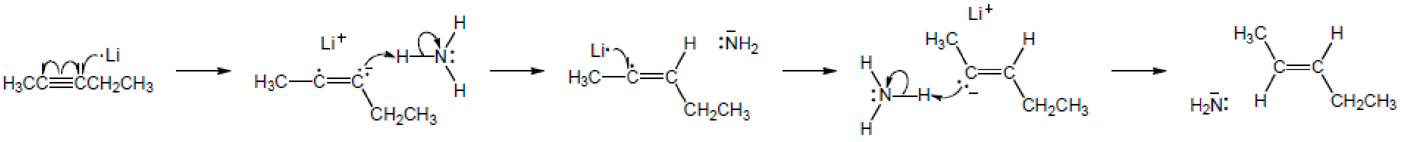


9.22 Predict the product(s) and show the complete electron pushing mechanism for each dissolving metal reduction below.

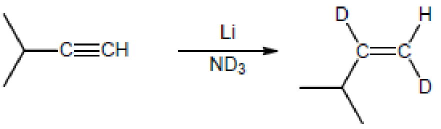
(a)



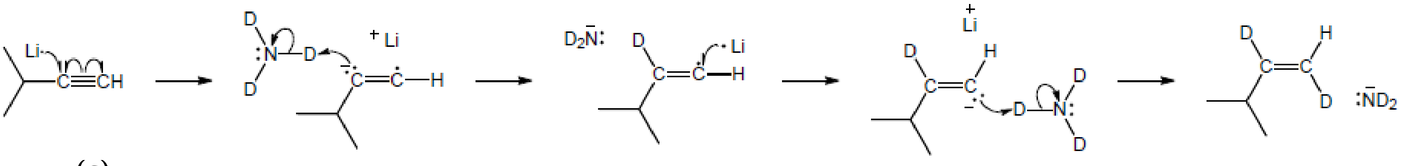
Mechanism:



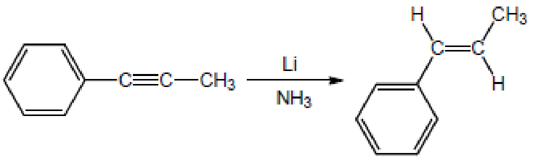
(b)



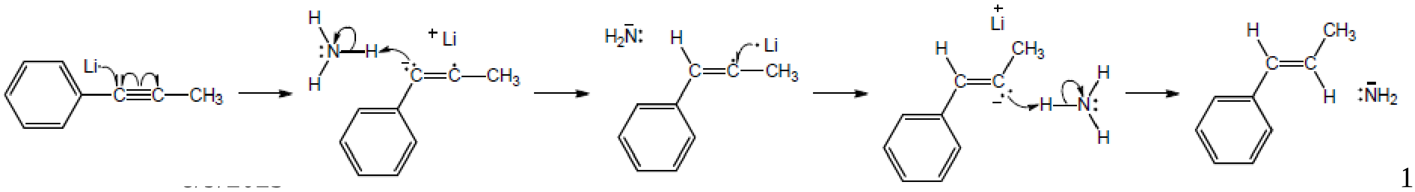
Mechanism:



(c)

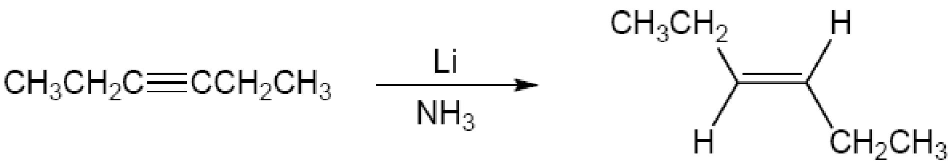


Mechanism:

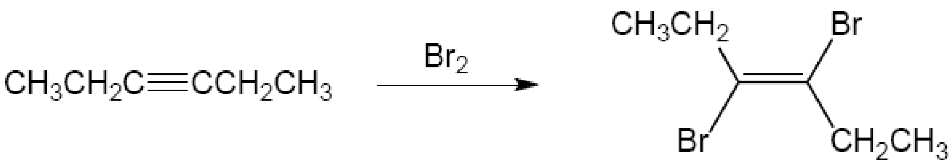


9.23 Identify the mechanisms for the reactions below as being either *polar*, *radical* or *both*.

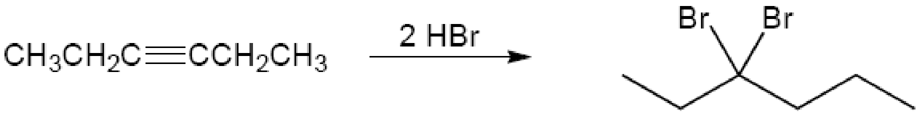
(a) *Both*. The addition of single electrons is a radical process, while adding protons is polar.



(b) Halogenation is a *polar* reaction.

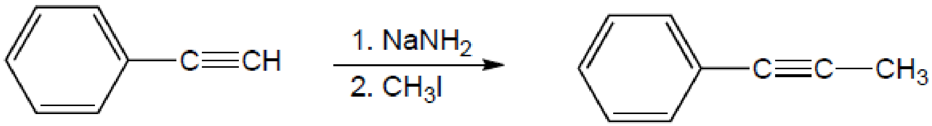


(c) Hydrohalogenation is a *polar* reaction.

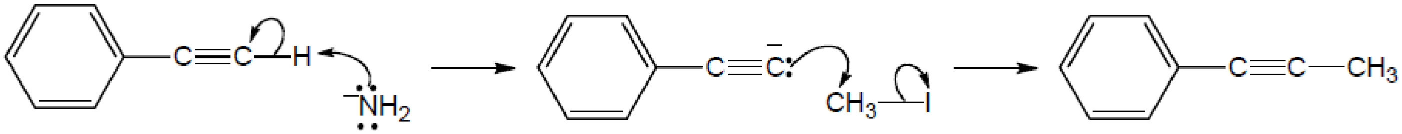


9.24 Predict the product and provide the complete electron pushing mechanism for the two-step synthetic processes below.

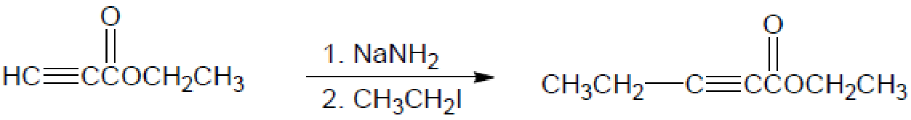
(a)



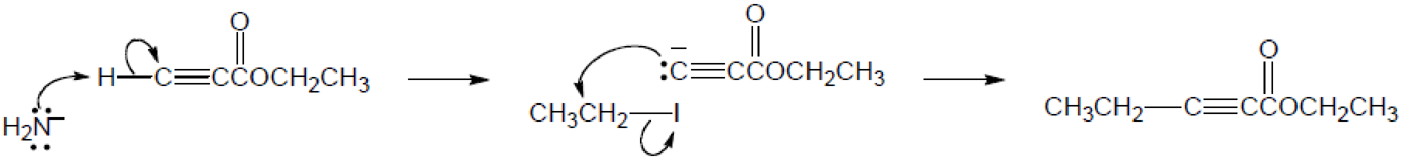
Mechanism:



(b)



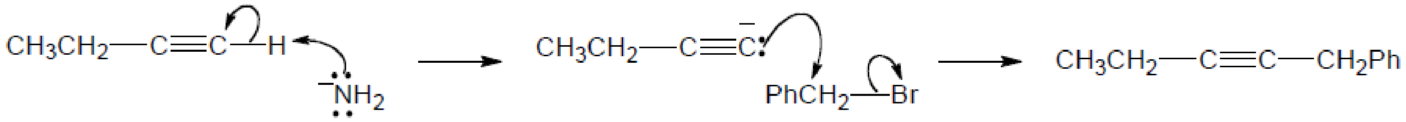
Mechanism:



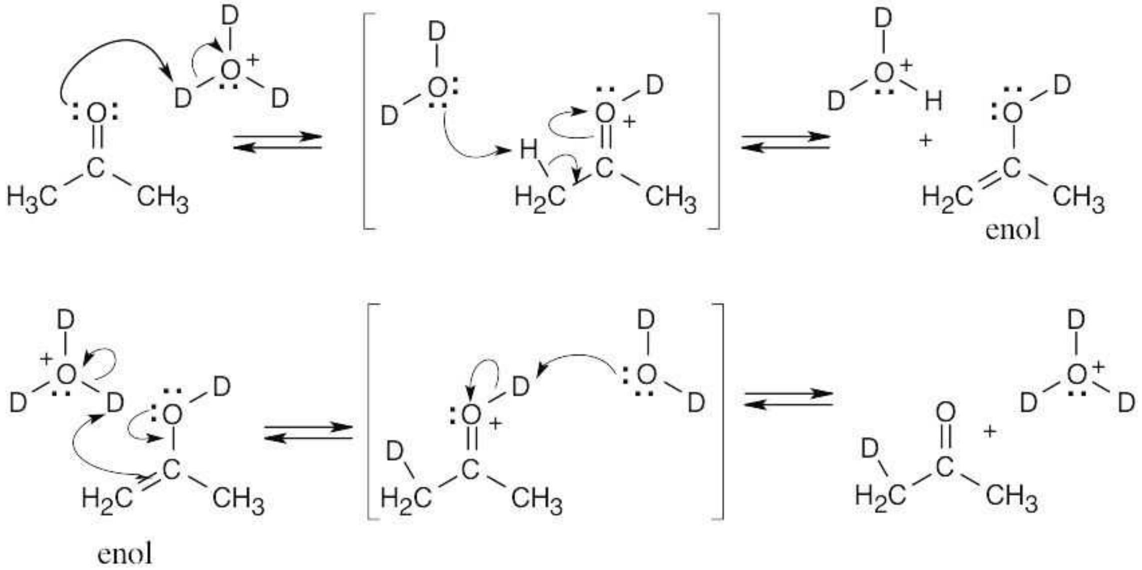
(c)

$$CH_3CH_2C{\equiv}CH \xrightarrow[2.\ PhCH_2Br]{1.\ NaNH_2} CH_3CH_2{-}C{\equiv}C{-}CH_2Ph$$

Mechanism:



9.25

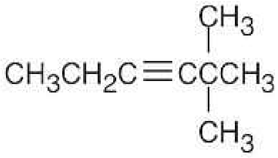


Repeating this process five more times replaces all hydrogen atoms with deuterium atoms. The first line represents the mechanism for acid-catalyzed tautomerization of a ketone.

Naming Alkynes

9.26

(a)



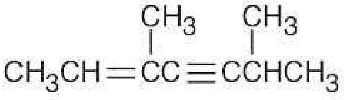
$CH_3CH_2C{\equiv}CC(CH_3)_2CH_3$

2,2-Dimethyl-3-hexyne

(b) $CH_3C{\equiv}CCH_2C{\equiv}CCH_2CH_3$

2,5-Octadiyne

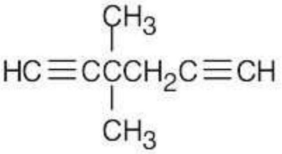
(c)



$CH_3CH{=}C(CH_3)C{\equiv}CCH(CH_3)CH_3$

3,6-Dimethyl-2-hepten-4-yne

(d)



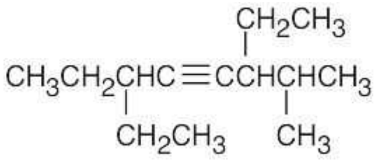
$HC{\equiv}CC(CH_3)_2CH_2C{\equiv}CH$

3,3-Dimethyl-1,5-hexadiyne

(e) $H_2C{=}CHCH{=}CHC{\equiv}CH$

1,3-Hexadien-5-yne

(f)

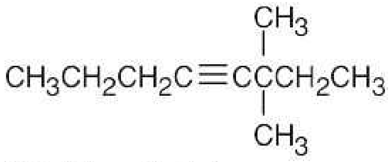


$CH_3CH_2\underset{CH_2CH_3}{CH}C{\equiv}C\overset{CH_2CH_3}{CH}\underset{CH_3}{CH}CH_3$

3,6-Diethyl-2-methyl-4-octyne

9.27

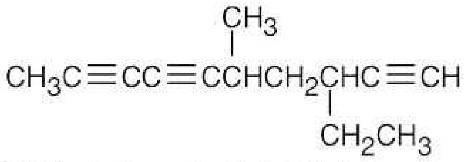
(a)



$CH_3CH_2CH_2C{\equiv}C\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_3$

3,3-Dimethyl-4-octyne

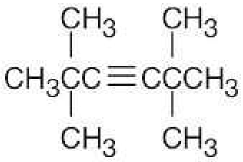
(b)



$CH_3C{\equiv}CC{\equiv}C\overset{CH_3}{CH}CH_2\underset{CH_2CH_3}{CH}C{\equiv}CH$

3-Ethyl-5-methyl-1,6,8-decatriyne

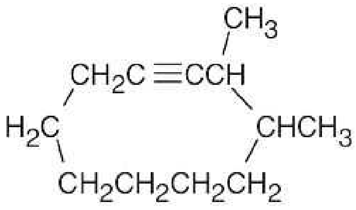
(c)



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

2,2,5,5-Tetramethyl-3-hexyne

(d)

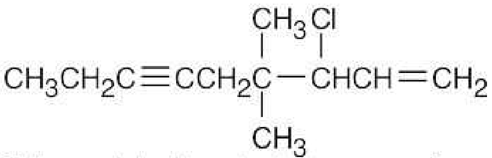


3,4-Dimethylcyclodecyne

(e) $CH_3CH{=}CHCH{=}CHC{\equiv}CH$

3,5-Heptadien-1-yne

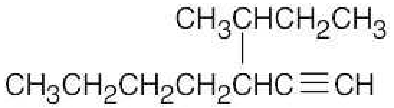
(f)



$CH_3CH_2C{\equiv}CCH_2\overset{CH_3}{\underset{CH_3}{C}}-\overset{Cl}{CH}CH{=}CH_2$

3-Chloro-4,4-dimethyl-1-nonen-6-yne

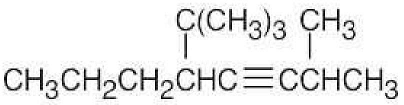
(g)



$CH_3CH_2CH_2CH_2\overset{CH_3CHCH_2CH_3}{CH}C{\equiv}CH$

3-*sec*-Butyl-1-heptyne

(h)



$CH_3CH_2CH_2\overset{C(CH_3)_3}{CH}C{\equiv}C\overset{CH_3}{CH}CH_3$

5-*tert*-Butyl-2-methyl-3-octyne

9.28 (a) $CH_3CH{=}CHC{\equiv}CC{\equiv}CCH{=}CHCH{=}CHCH{=}CH_2$.

1,3,5,11-Tridecatetraen-7,9-diyne

Using *E*–*Z* notation: (3*E*,5*E*,11*E*)-1,3,5,11-Tridecatetraen-7,9-diyne

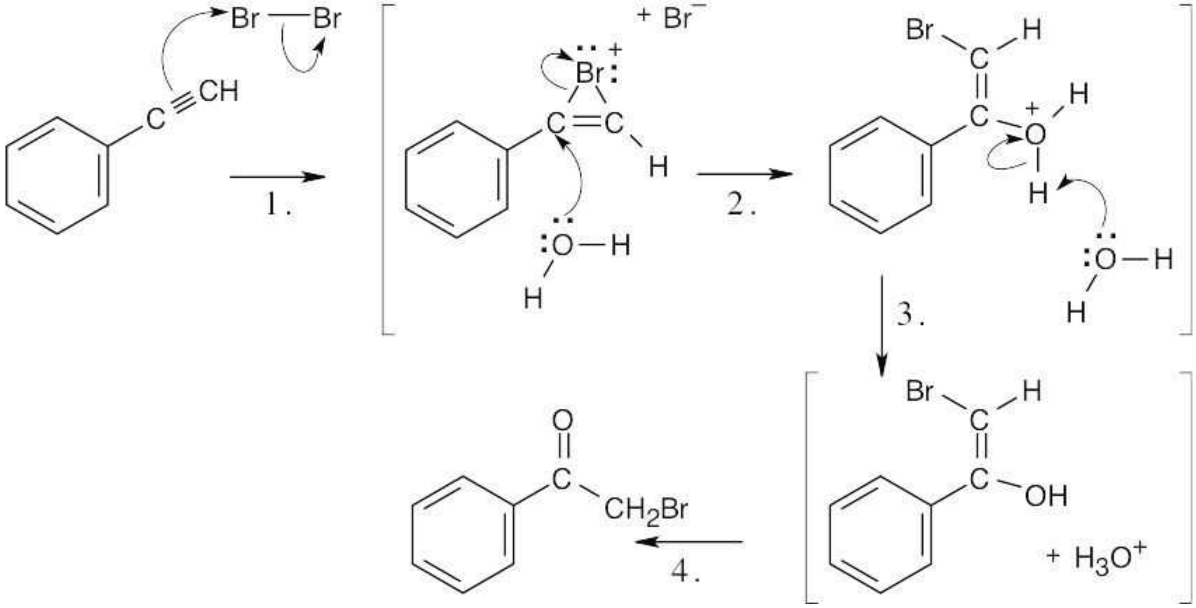
The parent alkane of this hydrocarbon is tridecane.

(b) $CH_3C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CCH{=}CH_2$. 1-Tridecen-3,5,7,9,11-pentayne

This hydrocarbon also belongs to the tridecane family.

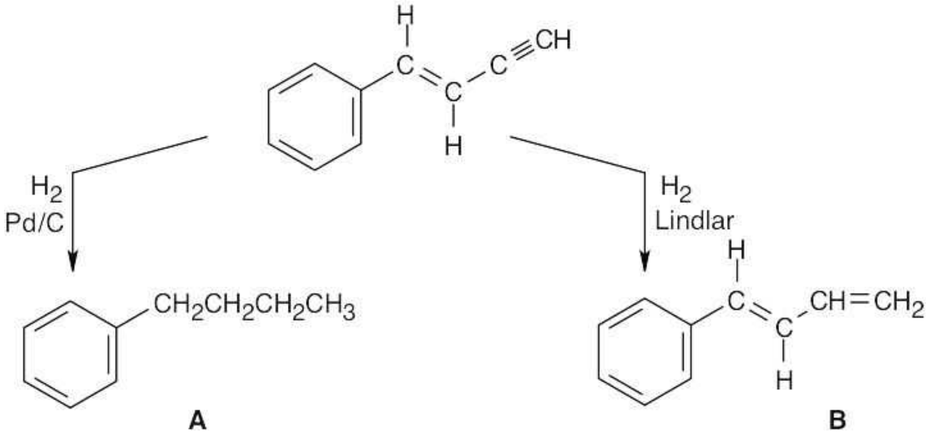
Reactions of Alkynes

9.29 This reaction mechanism is similar to the mechanism of halohydrin formation.



Step 1: Attack of π electrons on Br_2.
Step 2: Opening of cyclic cation by H_2O.
Step 3: Deprotonation.
Step 4: Tautomerization (for mechanism, see Problem 9.48 and Section 9.4).

9.30

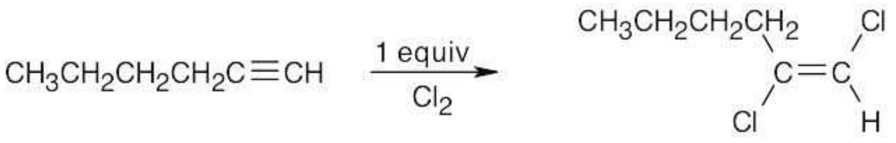


9.31

(a)

$$\mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[HBr]{1\ equiv} CH_3CH_2CH_2CH_2\overset{Br}{\overset{|}{C}}{=}CH_2}$$

(b)



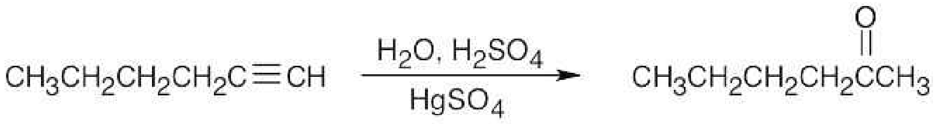
(c)

$$\mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[\substack{Lindlar\\ catalyst}]{H_2} CH_3CH_2CH_2CH_2CH{=}CH_2}$$

(d)

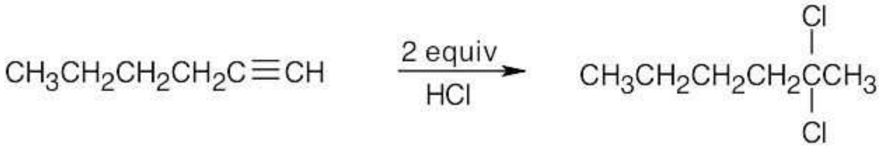
$$\mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[2.\ CH_3Br]{1.\ NaNH_2,\ NH_3} CH_3CH_2CH_2CH_2C{\equiv}CCH_3}$$

(e)



$$\mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3}$$

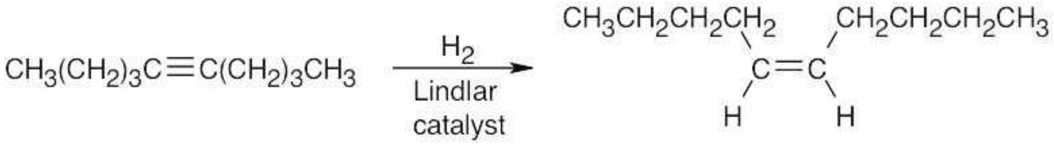
(f)



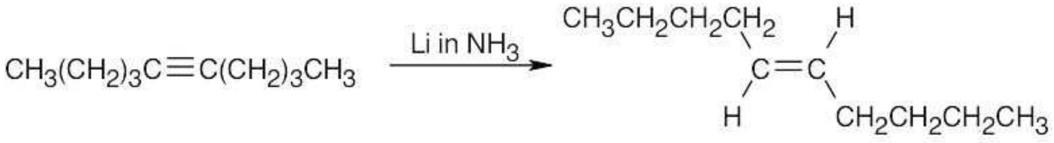
$$\mathrm{CH_3CH_2CH_2CH_2C{\equiv}CH \xrightarrow[HCl]{2\ equiv} CH_3CH_2CH_2CH_2\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}CH_3}$$

9.32

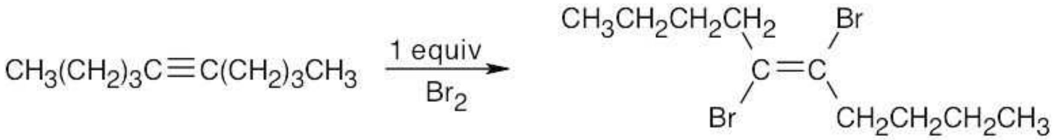
(a)



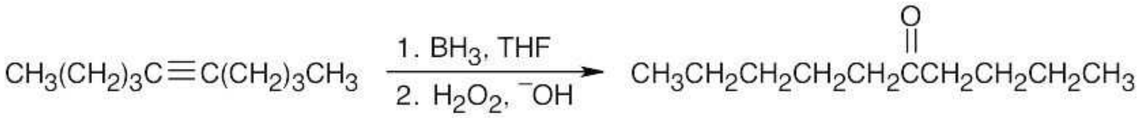
(b)



(c)

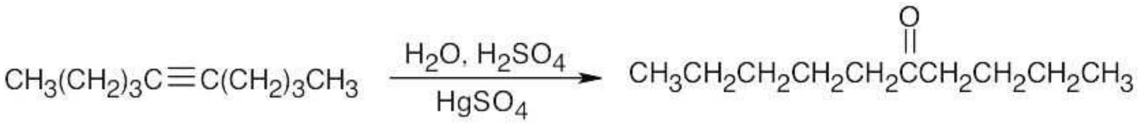


(d)



$$\mathrm{CH_3(CH_2)_3C{\equiv}C(CH_2)_3CH_3 \xrightarrow[2.\ H_2O_2,\ ^{-}OH]{1.\ BH_3,\ THF} CH_3CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3}$$

(e)



$$CH_3(CH_2)_3C\equiv C(CH_2)_3CH_3 \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3CH_2CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_3$$

(f)

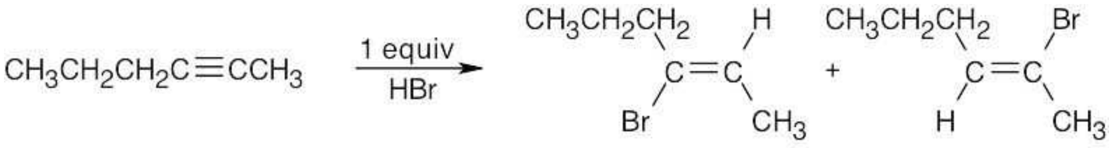
$$CH_3(CH_2)_3C\equiv C(CH_2)_3CH_3 \xrightarrow[Pd/C]{\text{excess } H_2} CH_3(CH_2)_8CH_3$$

9.33 Mixtures of products are sometimes formed since the alkynes are unsymmetrical.

(a)

$$CH_3CH_2CH_2C\equiv CCH_3 \xrightarrow[Br_2]{\text{2 equiv}} CH_3CH_2CH_2C(Br_2)C(Br_2)CH_3$$

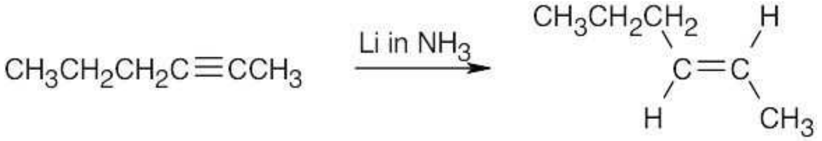
(b)



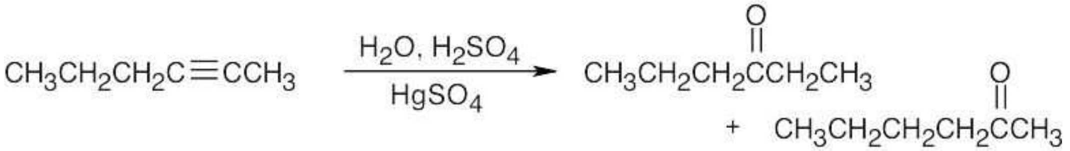
(c)

$$CH_3CH_2CH_2C\equiv CCH_3 \xrightarrow[HBr]{\text{excess}} CH_3CH_2CH_2C(Br_2)CH_2CH_3 + CH_3CH_2CH_2CH_2C(Br_2)CH_3$$

(d)



(e)



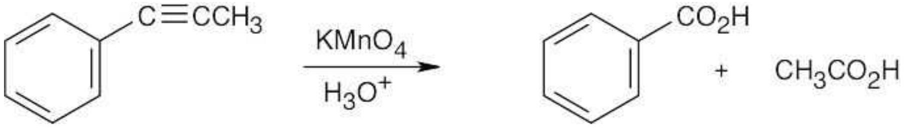
$$CH_3CH_2CH_2C\equiv CCH_3 \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3 + CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$$

9.34 Both $KMnO_4$ and O_3 oxidation of alkynes yield carboxylic acids; terminal alkynes give CO_2 also. In (a), (b), and (c), the observed products can also be formed by $KMnO_4$ oxidation of the corresponding alkenes.

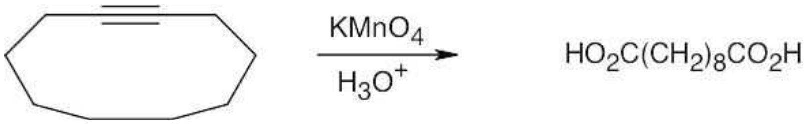
(a)

$$CH_3(CH_2)_5C\equiv CH \xrightarrow[H_3O^+]{KMnO_4} CH_3(CH_2)_5CO_2H + CO_2$$

(b)

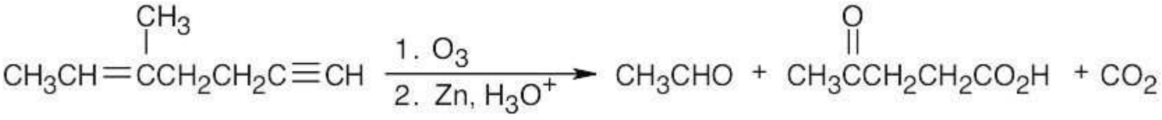


(c)



Since only one cleavage product is formed, the parent hydrocarbon must have contained a triple bond as part of a ring.

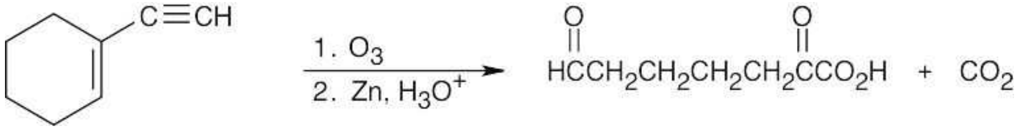
(d)



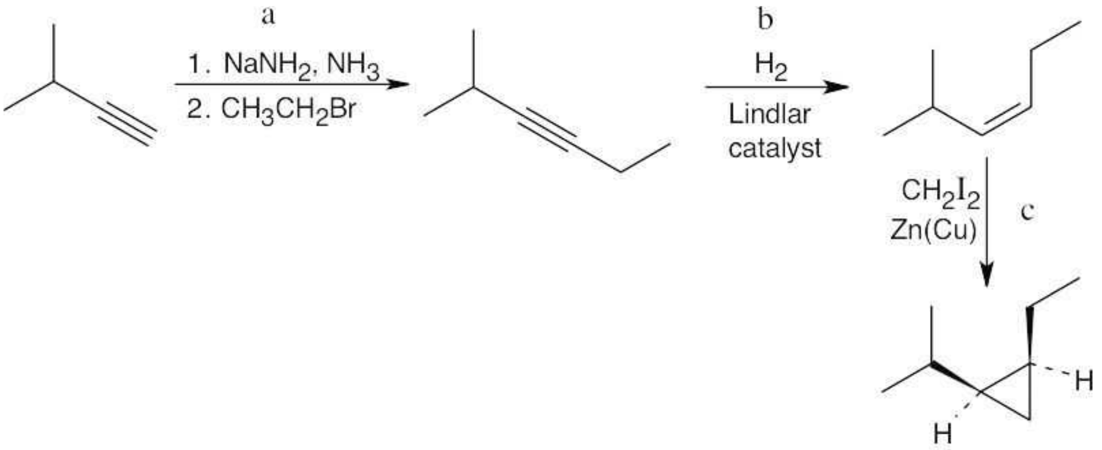
$$CH_3CH{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_2C{\equiv}CH \xrightarrow[2.\ Zn,\ H_3O^+]{1.\ O_3} CH_3CHO + CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CO_2H + CO_2$$

Notice that the products of this ozonolysis contain aldehyde and ketone functional groups, as well as a carboxylic acid and CO_2. The parent hydrocarbon must thus contain a double and a triple bond.

(e)

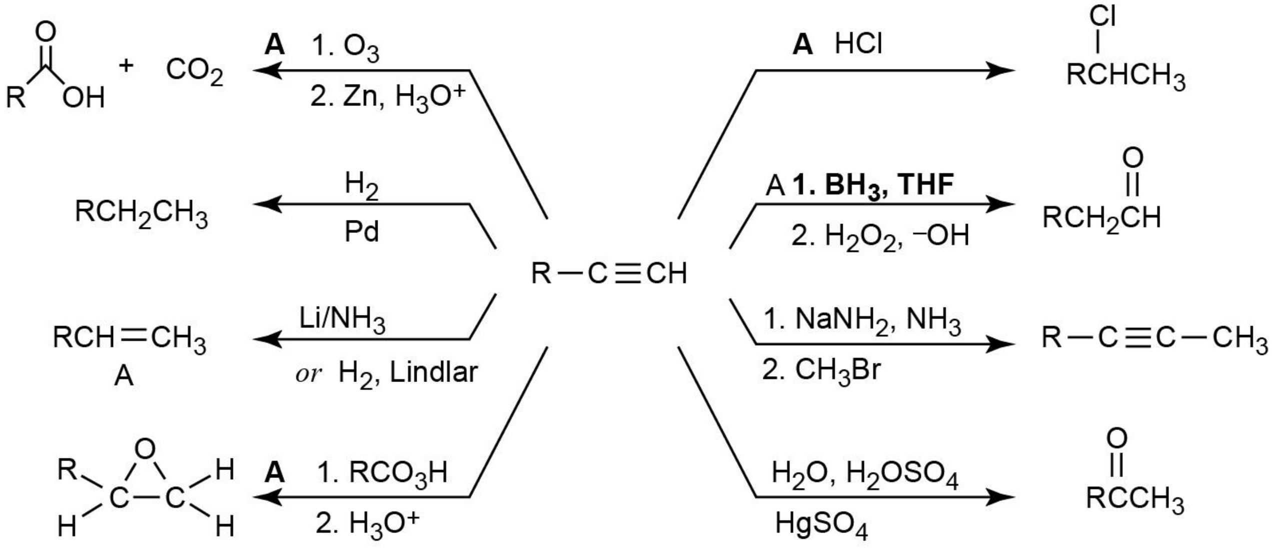


9.35



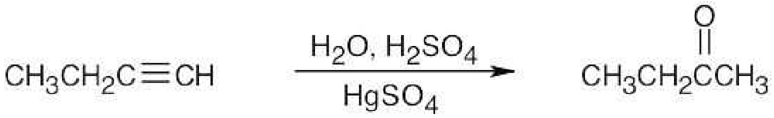
Organic Synthesis

9.36



9.37

(a)

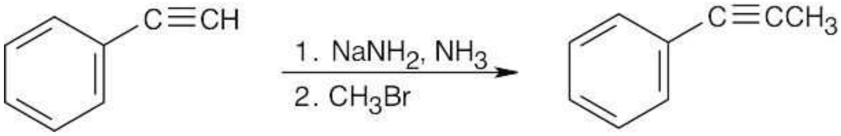


$$CH_3CH_2C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$$

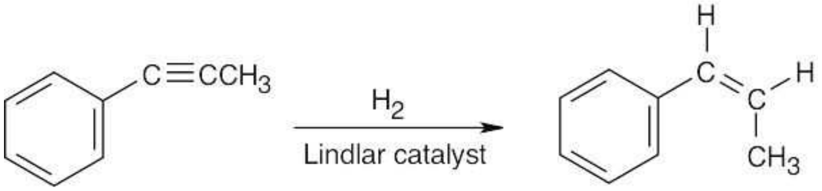
(b)

$$CH_3CH_2C\equiv CH \xrightarrow[2.\ H_2O_2,\ ^-OH]{1.\ BH_3,\ THF} CH_3CH_2CH_2CHO$$

(c)



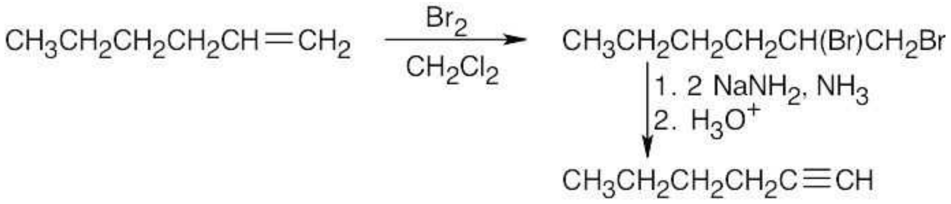
(d)



(e)

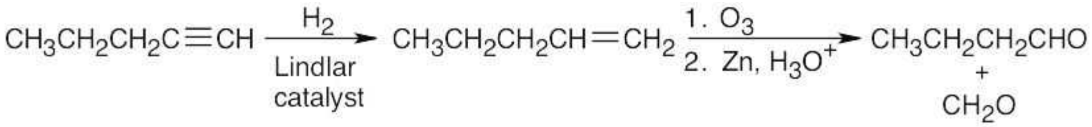
$$CH_3CH_2C\equiv CH \xrightarrow[H_3O^+]{KMnO_4} CH_3CH_2CO_2H \quad + \quad CO_2$$

(f)

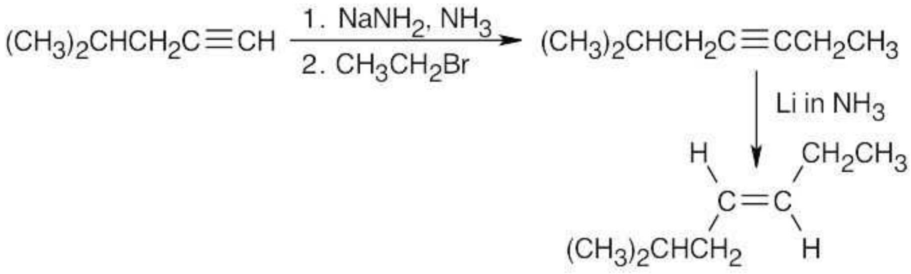


9.38

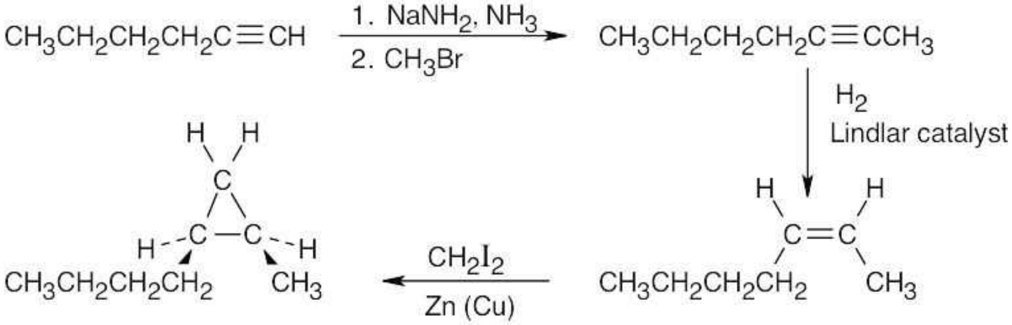
(a)



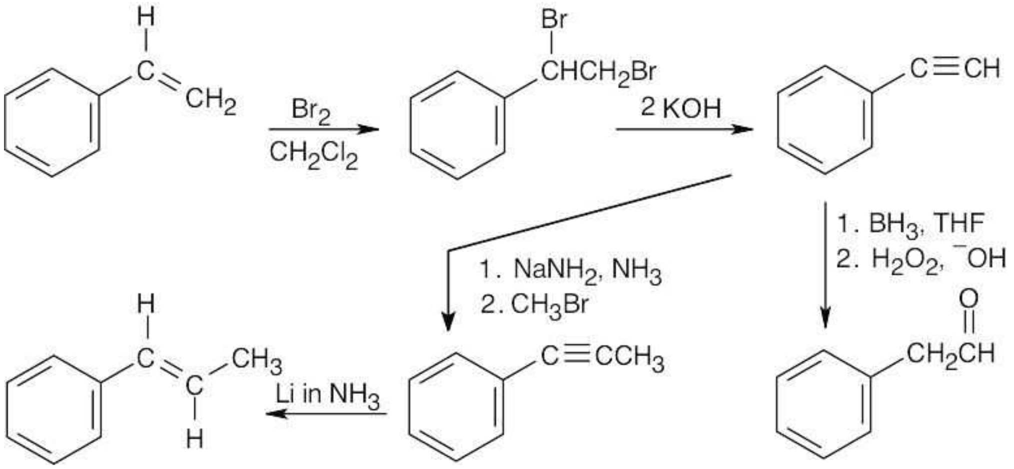
(b)



9.39 The product contains a cis-disubstituted cyclopropane ring, which can be formed from a Simmons–Smith reaction of CH_2I_2 with a cis alkene. The alkene with a cis bond can be produced from an alkyne by hydrogenation using a Lindlar catalyst. The needed alkyne can be formed from the starting material shown by an alkylation using bromomethane.



9.40



The trans double bond in the second target molecule is a product of reduction of a triple bond with Li in NH_3. The alkyne was formed by an alkylation of a terminal alkyne with bromomethane. The terminal alkyne was synthesized from the starting alkene by bromination, followed by dehydrohalogenation.

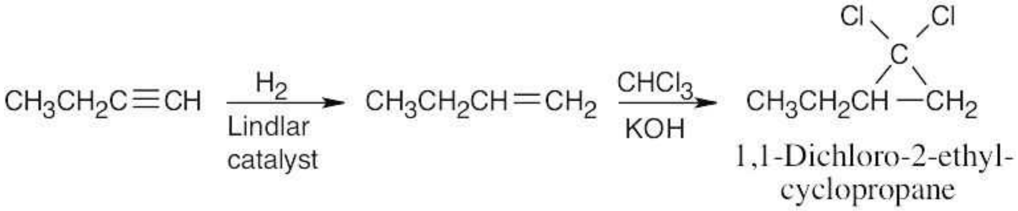
9.41

(a)

$$CH_3CH_2C\equiv CH \xrightarrow[CH_2Cl_2]{2\ Cl_2} CH_3CH_2C(Cl_2)CHCl_2$$

1,1,2,2-Tetrachlorobutane

(b)



1,1-Dichloro-2-ethylcyclopropane

9.42 In all of these problems, an acetylide ion (or an anion of a terminal alkyne) is alkylated by a haloalkane.

(a)

$$HC\equiv CH \xrightarrow[2.\ CH_3CH_2CH_2Br]{1.\ NaNH_2,\ NH_3} CH_3CH_2CH_2C\equiv CH$$

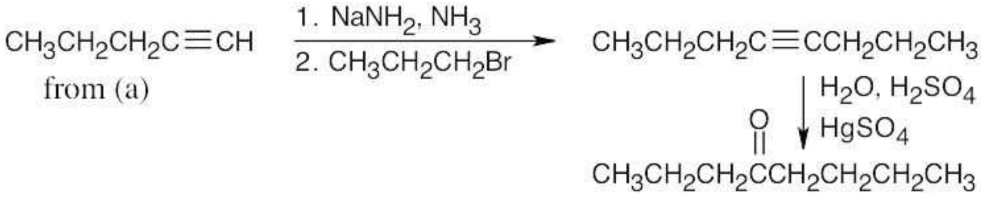
(b)

$$HC\equiv CH \xrightarrow[2.\ CH_3CH_2Br]{1.\ NaNH_2,\ NH_3} CH_3CH_2C\equiv CH \xrightarrow[2.\ CH_3CH_2Br]{1.\ NaNH_2,\ NH_3} CH_3CH_2C\equiv CCH_2CH_3$$

(c)

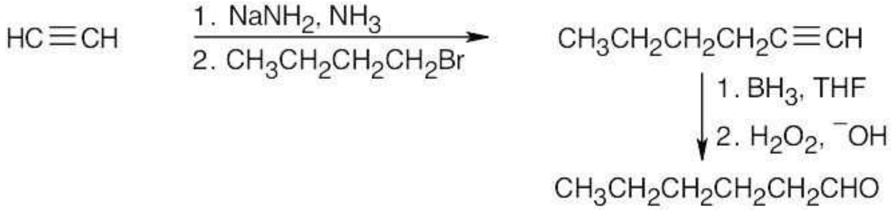
$$\begin{array}{ll} HC\equiv CH \xrightarrow[2.\ (CH_3)_2CHCH_2Br]{1.\ NaNH_2,\ NH_3} & (CH_3)_2CHCH_2C\equiv CH \\ & \downarrow \; H_2\text{, Lindlar catalyst } \textit{or} \text{ Li in } NH_3 \\ & (CH_3)_2CHCH_2CH=CH_2 \end{array}$$

(d)



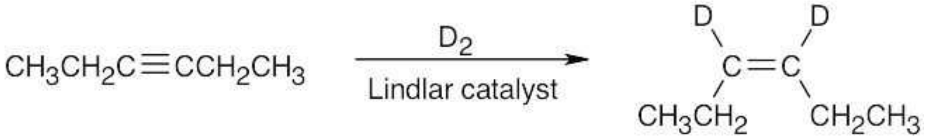
Hydroboration/oxidation can also be used to form the ketone from 4-octyne.

(e)

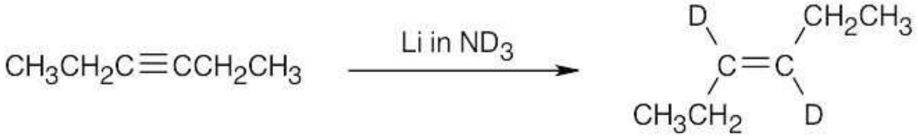


9.43

(a)



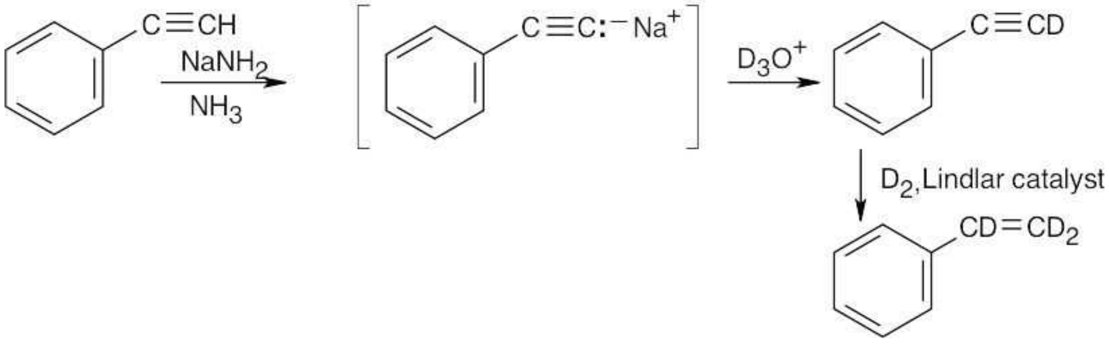
(b)



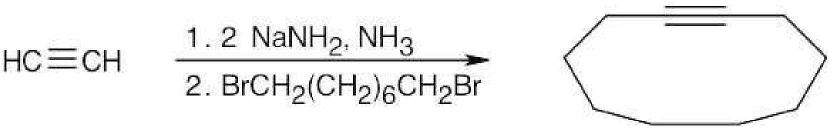
(c)

$$CH_3CH_2CH_2C\equiv CH \xrightarrow[NH_3]{NaNH_2} [CH_3CH_2CH_2C\equiv C{:}^-\ Na^+] \xrightarrow{D_3O^+} CH_3CH_2CH_2C\equiv CD$$

(d)

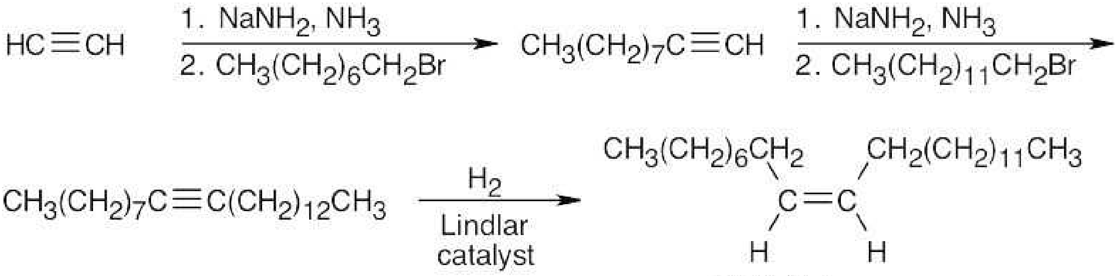


9.44



A dihalide is used to form the ring.

9.45 Muscalure is a C_{23} alkene. The only functional group present is the double bond between C_9 and C_{10}. Since our synthesis begins with acetylene, we can assume that the double bond can be produced by hydrogenation of a triple bond.



(Z)-9-Tricosene

General Problems

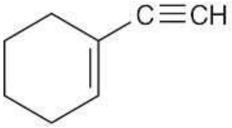
9.46 (a) An acyclic alkane with eight carbons has the formula C_8H_{18}. C_8H_{10} has eight fewer hydrogens, or four fewer pairs of hydrogens, than C_8H_{18}. Thus, C_8H_{10} contains four degrees of unsaturation (rings/double bonds/triple bonds).

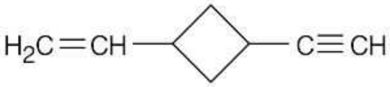
(b) Because only one equivalent of H_2 is absorbed over the Lindlar catalyst, *one* triple bond is present.

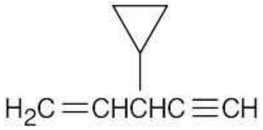
(c) Three equivalents of H_2 are absorbed when reduction is done over a palladium catalyst; two of them hydrogenate the triple bond already found to be present. Therefore, one *double* bond must also be present.

(d) C_8H_{10} must therefore contain one ring.

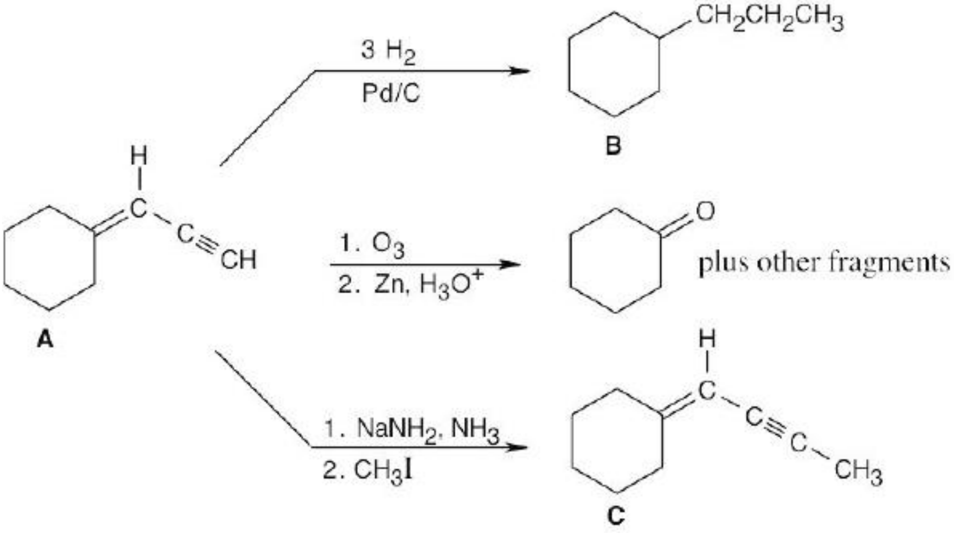
(e) Many structures are possible.



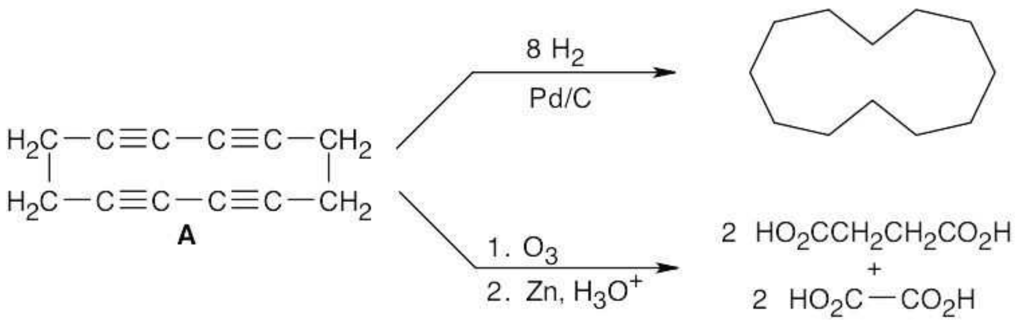




9.47

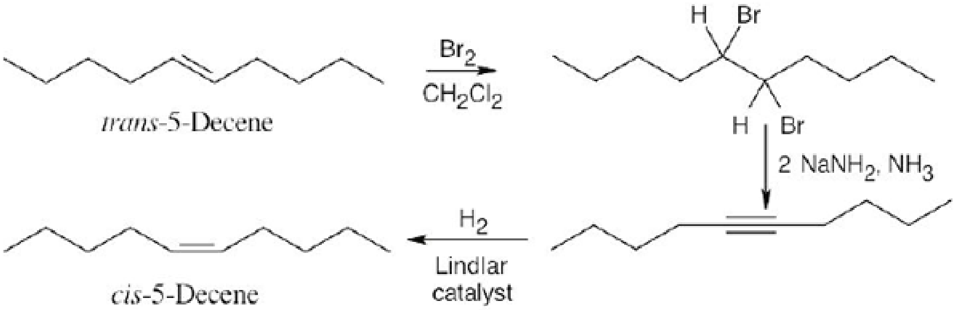


9.48

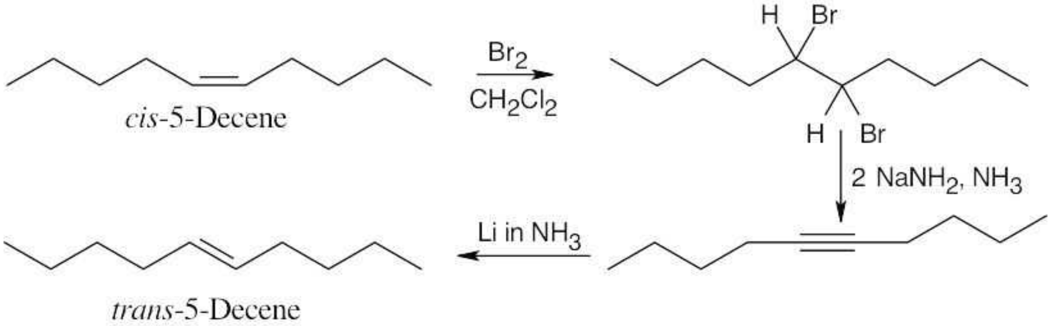


9.49

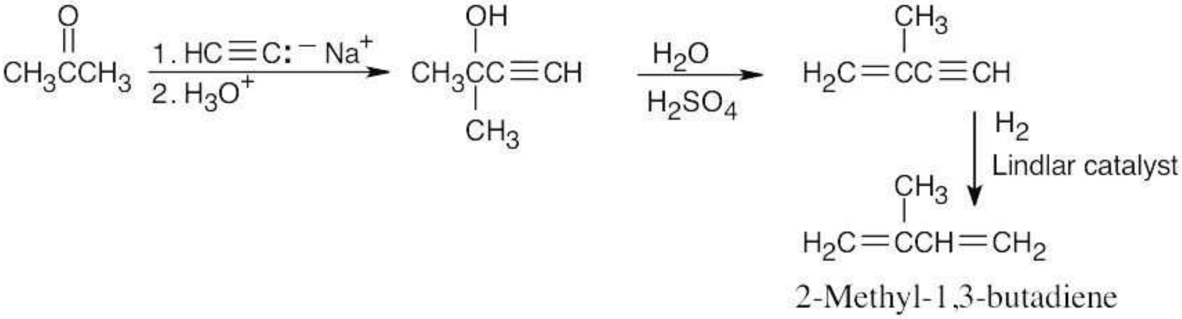
(a)



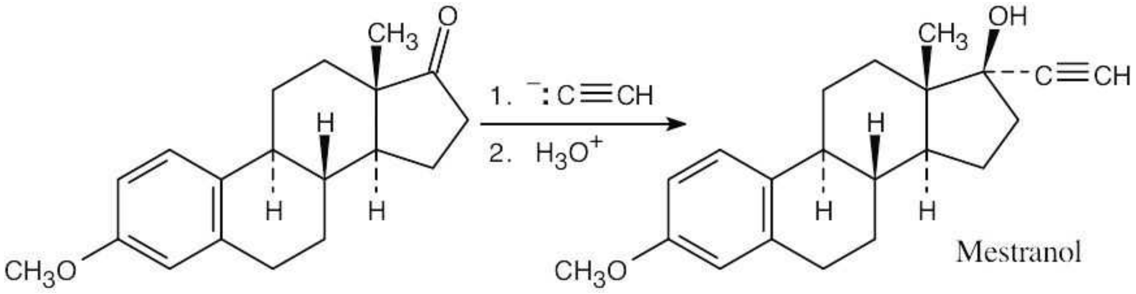
(b)



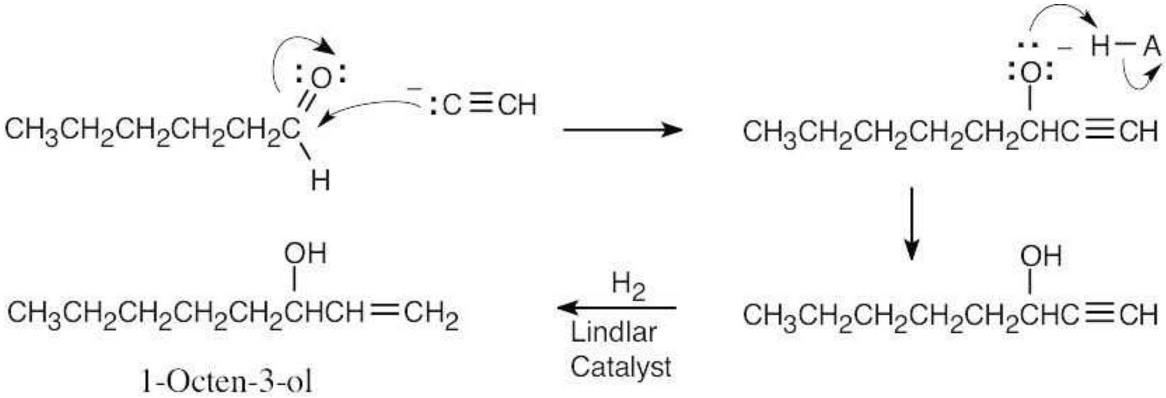
9.50



9.51



9.52



The addition of acetylide occurs by the same route as shown in Problem 9.41.

9.53 (1) Erythrogenic acid contains six degrees of unsaturation (see Sec. 7.2 for the method of calculating unsaturation equivalents for compounds containing elements other than C and H).

(2) One of these double bonds is contained in the carboxylic acid functional group $–CO_2H$; thus, five other degrees of unsaturation are present.

(3) Because five equivalents of H_2 are absorbed on catalytic hydrogenation, erythrogenic acid contains no rings.

(4) The presence of both aldehyde and carboxylic acid products of ozonolysis indicates that both double and triple bonds are present in erythrogenic acid.

(5) Only two ozonolysis products contain aldehyde functional groups; these fragments must have been double-bonded to each other in erythrogenic acid.
$H_2C{=}CH(CH_2)_4C{\equiv}$

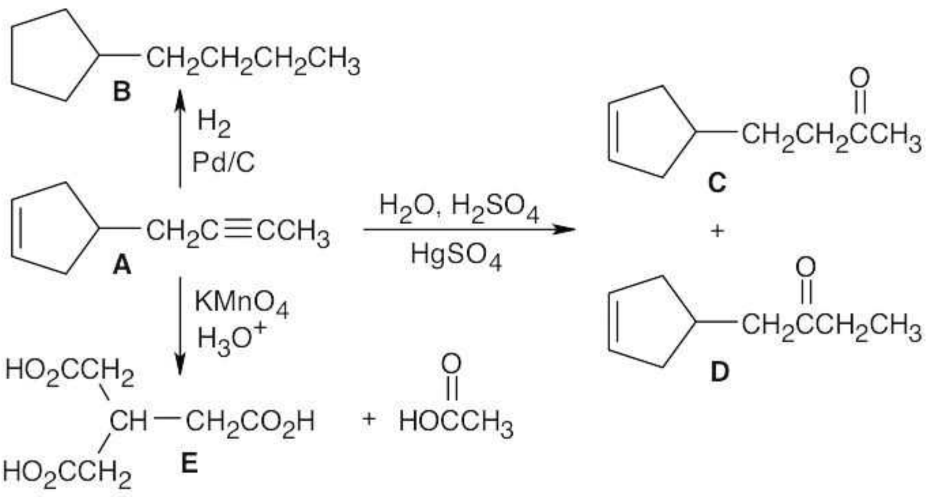
(6) The other ozonolysis products result from cleavage of triple bonds. However, not enough information is available to tell in which order the fragments were attached. The two possible structures are:

A $H_2C{=}CH(CH_2)_4C{\equiv}C{-}C{\equiv}C(CH_2)_7CO_2H$

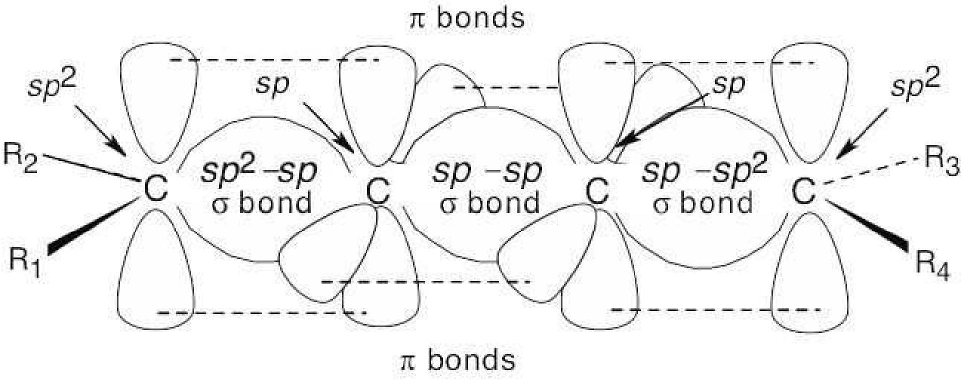
B $H_2C{=}CH(CH_2)_4C{\equiv}C(CH_2)_7C{\equiv}CCO_2H$

One method of distinguishing between the two possible structures is to treat erythrogenic acid with two equivalents of H_2, using a Lindlar catalyst. The resulting trialkene can then be ozonized. The fragment that originally contained the carboxylic acid can then be identified. (**A** is the structure of erythrogenic acid.)

9.54



9.55



This simplest cumulene is pictured above. The carbons at the end of the cumulated double bonds are sp^2-hybridized and form one π bond to the “interior” carbons. The interior carbons are *sp*-hybridized; each carbon forms two π bonds – one to an “exterior” carbon and one to the other interior carbon. If you build a model of this cumulene, you can see that the substituents all lie in the same plane. This cumulene can thus exhibit cis–trans isomerism, just as simple alkenes can.

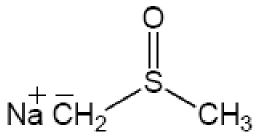
In general, the substituents of any compound with an odd number of adjacent double bonds lie in a plane; these compounds can exhibit cis–trans isomerism.

9.56 In order for a base to be strong enough to deprotonate an acid, the conjugate acid of the base must be a weaker acid (have a higher pK_a) than the acid being deprotonated. The pK_a of 1-butyne is 25.

(a) The pK_a of H_2O (the conjugate acid of hydroxide) is 15. Because water is a stronger acid than 1-butyne, hydroxide *will not deprotonate* 1-butyne.

KOH

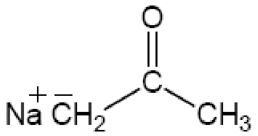
(b) The pK_a of dimethylsulfoxide (the conjugate acid of methylsulfinylmethylide ion, also called dimyslate ion) is 35. Because dimethylsulfoxide is a weaker acid than 1-butyne, methylsulfinylmethylide *will deprotonate* 1-butyne.



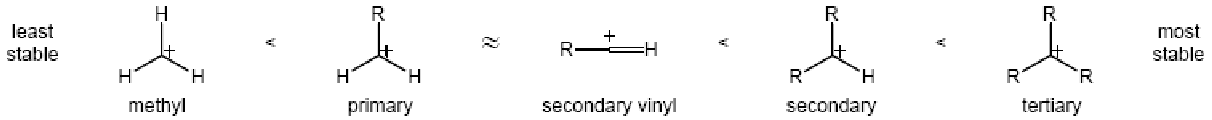
(c) The pK_a of butane (the conjugate acid of n-butyl lithium) is approximately 60. Because butane is a weaker acid than 1-butyne, n-butyl lithium *will deprotonate* 1-butyne.

$CH_3CH_2CH_2CH_2Li$

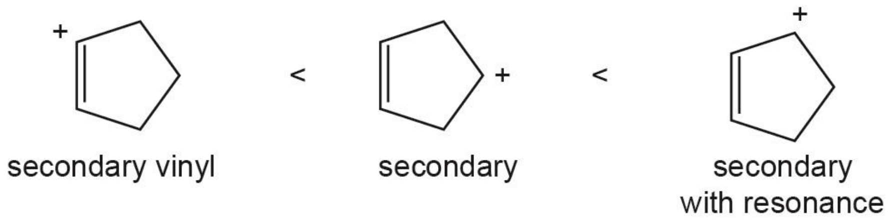
(d) The pK_a of acetone (the conjugate acid of acetone enolate) is 19. Because acetone is a stronger acid than 1-butyne, acetone enolate *will not deprotonate* 1-butyne.



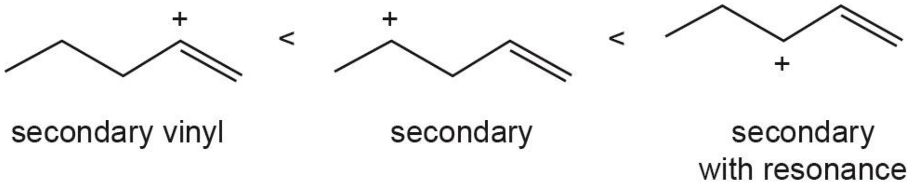
9.57 The overall trend for carbocation stability is shown below. Recall that resonance adds additional stability to carbocations.



(a)



(b)



(c)