

Chapter 8 – Alkynes: An Introduction to Organic Synthesis

Chapter Outline

I. Introduction to alkynes (Section 8.1 – 8.2).

A. Naming alkynes (Section 8.1).

The rules for naming alkynes are like the rules for alkenes (Sec. 6.3), with a few exceptions.

- The suffix *-yne* is used for an alkyne.
- Compounds with both double bonds and triple bonds are *enynes*.
- When there is a choice in numbering, double bonds receive lower numbers than triple bonds.
- Compounds can also contain alkynyl groups.

B. Preparation of alkynes (Section 8.2).

- Alkynes can be prepared by elimination reactions of 1,2-dihalides, using a strong base.
- The dihalides are formed by addition of X_2 to alkenes.
- Vinyl halides give alkynes when treated with a strong base.

II. Reactions of alkynes (Sections 8.3 – 8.6).

A. General principles (Section 8.3).

- Alkyne triple bonds result from the overlap of two *sp*-hybridized carbon atoms. One σ bond and two π bonds are formed.
- The length (120 pm) and strength (835 kJ/mol) of a $-C\equiv C-$ bond make it the strongest carbon-carbon bond.
- Alkynes are somewhat less reactive than alkenes in electrophilic addition reactions.

B. Addition of X_2 and HX.

- HX adds to alkynes by an electrophilic addition mechanism.
 - Addition of two equivalents of HX occurs if the acid is in excess.
 - Addition occurs with Markovnikov regiochemistry and with *trans* stereochemistry.
- X_2 also adds in the same manner, and *trans* stereochemistry is observed.
- The intermediate in addition reactions is a vinylic carbocation, which forms less readily than an alkyl carbocation.
- Mechanisms of some alkyne addition reactions are complex.

C. Hydration reactions of alkynes (Section 8.4).

- Hg(II)-catalyzed additions.
 - The $-OH$ group adds to the more substituted carbon to give Markovnikov product.
 - The intermediate enol product tautomerizes to a ketone.
 - The mechanism is similar to that of addition to alkenes, but no $NaBH_4$ is necessary for removal of Hg.
 - A mixture of products is formed from an internal alkyne, but a terminal alkyne yields a methyl ketone.
- Hydroboration/oxidation of alkynes.
 - Hydroboration/oxidation of alkynes gives an intermediate enol product that tautomerizes to a carbonyl product.
 - Hydroboration of a terminal alkyne gives an aldehyde.
 - Hydroboration of an internal alkyne gives a ketone.
 - Hydroboration/oxidation is complementary to Hg(II)-catalyzed hydration.

D. Reduction of alkynes (Section 8.5).

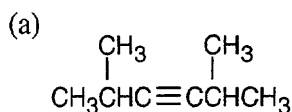
- Complete reduction to an alkane occurs when H_2/Pd is used.
- Partial reduction to a *cis* alkene occurs with H_2 and a Lindlar catalyst.

3. Partial reduction with Li in NH_3 produces a trans alkene.
 - a. The reaction proceeds through an anion radical \rightarrow vinylic radical \rightarrow vinylic anion.
 - b. The more stable trans vinylic anion is formed.
- E. Oxidative cleavage of alkynes (Section 8.6).
 1. O_3 or KMnO_4 cleave alkyne bonds to produce carboxylic acids or CO_2 (terminal alkyne).
 2. Oxidative cleavage reactions were formerly used for structure determinations.
- III. Alkyne acidity (Sections 8.7 – 8.8).
 - A. Formation of acetylide anions (Section 8.7).
 1. Terminal alkynes are weakly acidic ($\text{p}K_{\text{a}} = 25$).
 2. Very strong bases (NH_2^-) can deprotonate terminal alkynes.
 3. Acetylide anions are stabilized by the large amount of "s character" of the orbital that holds the electron.
 4. Acetylide anions are strongly nucleophilic.
 - B. Alkylation of acetylide anions (Section 8.8).
 1. Acetylide anions can react with haloalkanes to form substitution products.
 - a. The nucleophilic acetylide anion attacks the electrophilic carbon of a haloalkane to produce a new alkyne.
 - b. This reaction is called an alkylation reaction.
 - c. Any terminal alkyne can form an alkylation product.
 2. Acetylide alkylations are limited to primary alkyl bromides and iodides.
Acetylide ions cause dehydrohalogenation reactions with secondary and tertiary halides.
- IV. Organic synthesis (Section 8.9).
 - A. Reasons for the study of organic synthesis.
 1. In the pharmaceutical and chemical industries, synthesis produces new molecules, or better routes to important molecules.
 2. In academic laboratories, synthesis is done for creative reasons.
 3. In the classroom, synthesis is a tool for teaching the logic of organic chemistry.
 - B. Strategies for organic synthesis.
 1. Work backward, but –
 2. Keep the starting material in mind.

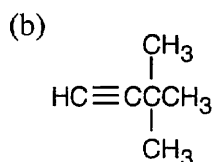
Solutions to Problems

- 8.1 Strategy:** 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*.

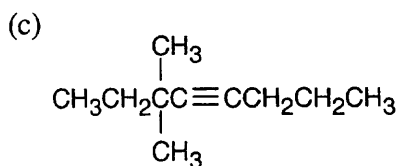
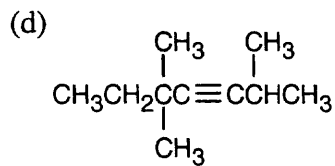
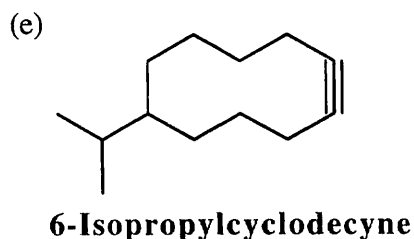
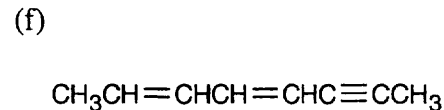
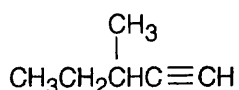
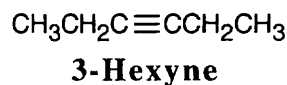
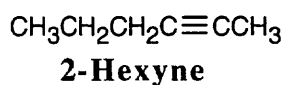
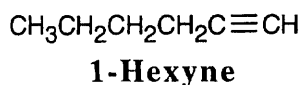
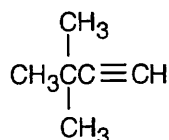
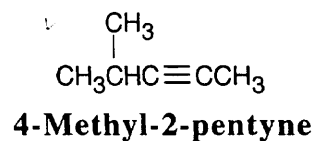
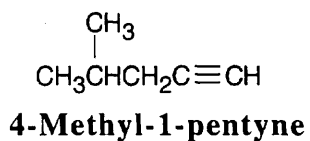
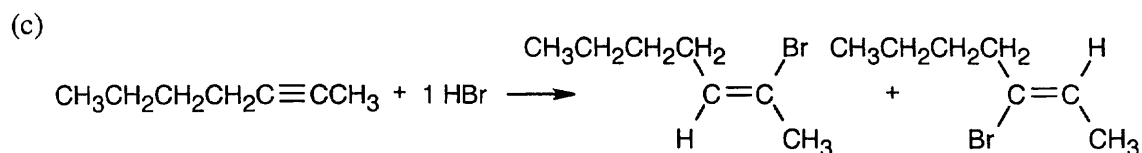
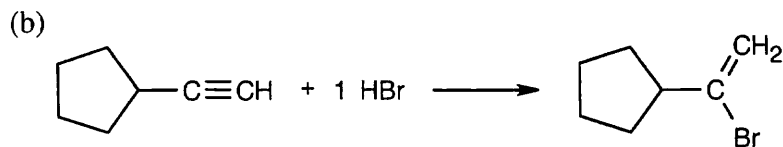
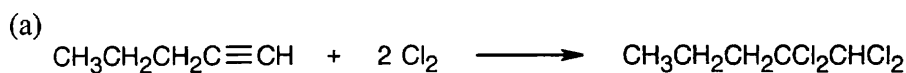
Solution:



2,5-Dimethyl-3-hexyne

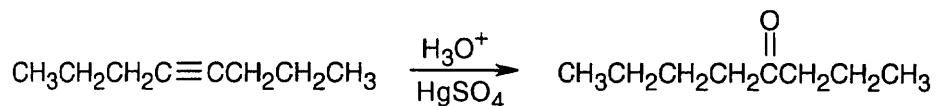


3,3-Dimethyl-1-butyne

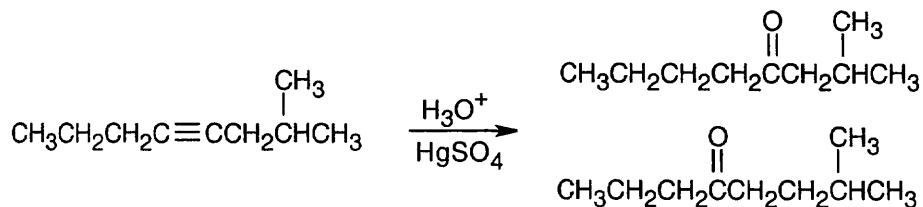
**3,3-Dimethyl-4-octyne****2,5,5-Trimethyl-3-heptyne****6-Isopropylcyclodecyne****2,4-Octadien-6-yne**
(not 4,6-Octadien-2-yne)**8.2****3-Methyl-1-pentyne****3,3-Dimethyl-1-butyne****8.3** Markovnikov addition is observed with alkynes as well as with alkenes.

Two products result from addition to an internal alkyne.

8.4

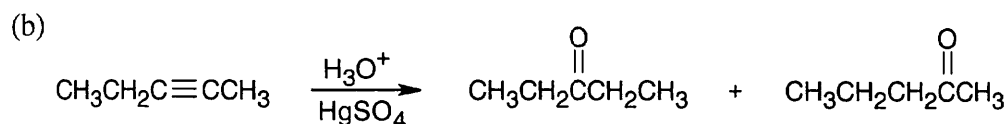
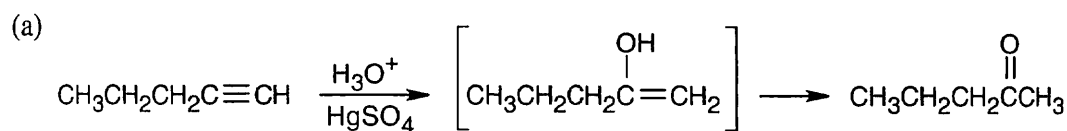


This symmetrical alkyne yields only one product.



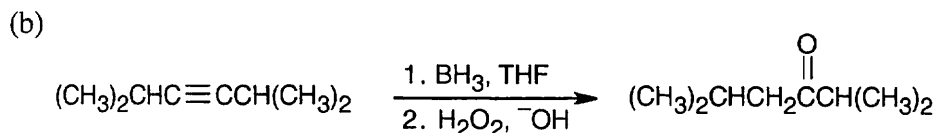
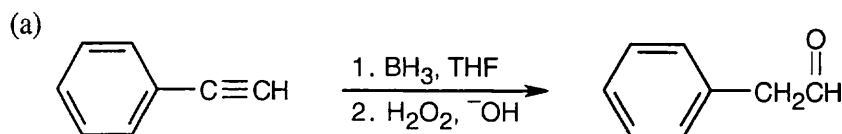
Two ketone products result from hydration of 2-methyl-4-octyne.

8.5

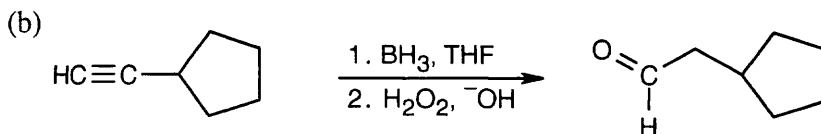
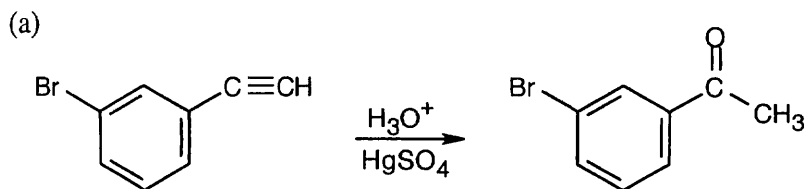


The desired ketone can be prepared only as part of a product mixture.

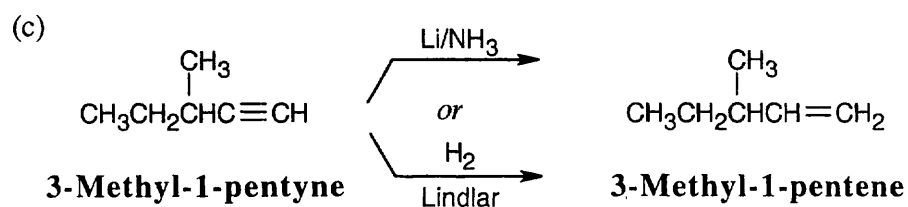
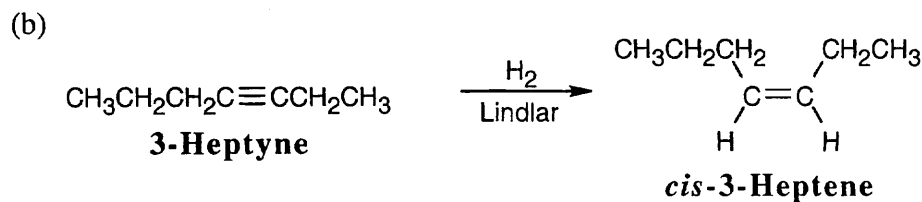
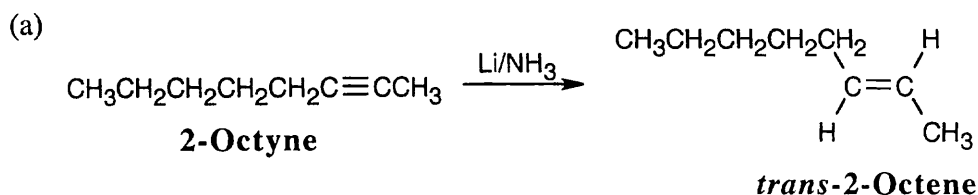
8.6 Remember that hydroboration yields aldehydes from terminal alkynes and ketones from internal alkynes.



8.7



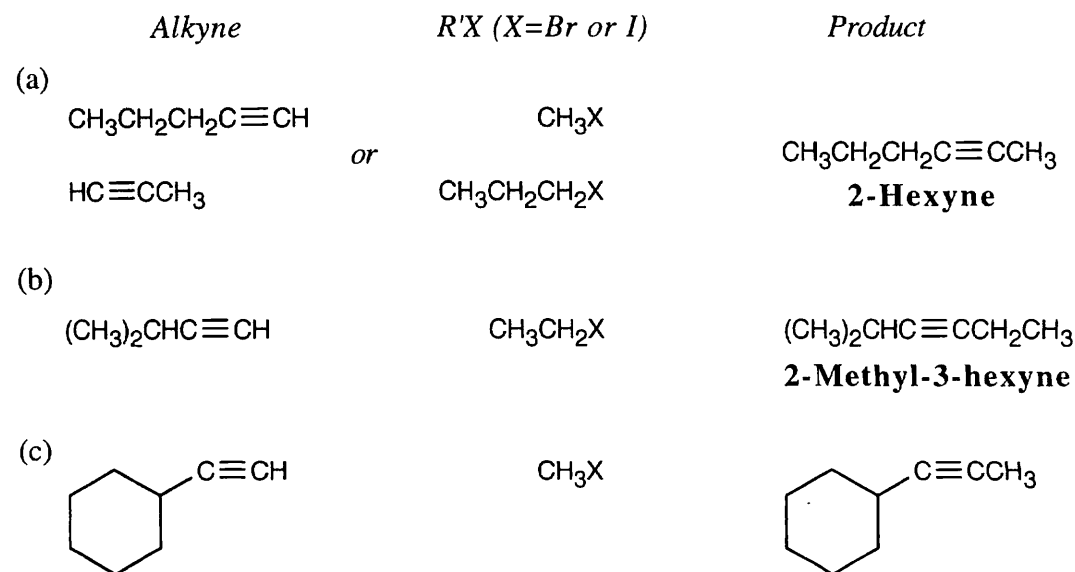
8.8 The correct reducing reagent gives a double bond with the desired geometry.



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

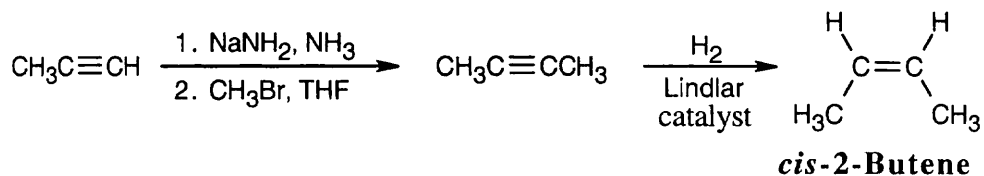
8.10 Strategy: Remember that the alkyne must be a terminal alkyne and the halide must be primary. More than one combination of terminal alkyne and halide may be possible.

Solution:



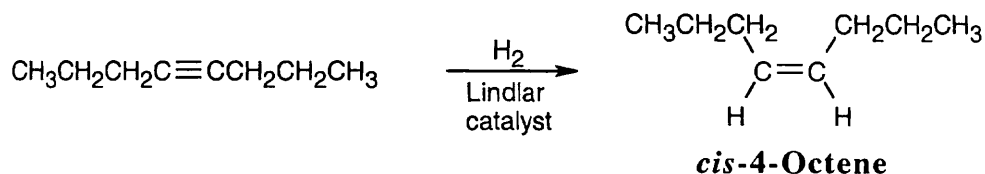
Products (b) and (c) can be synthesized by only one route because only primary halides can be used for acetylide alkylations.

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

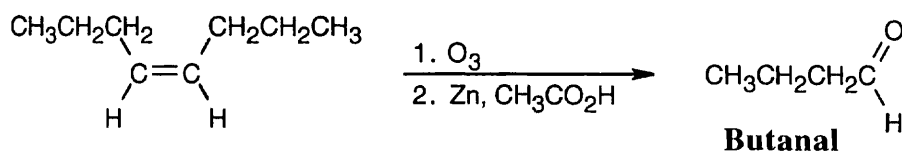


- 8.12 **Strategy:** The starting material is $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$. Look at the functional groups in the target molecule and work backward to 4-octyne.

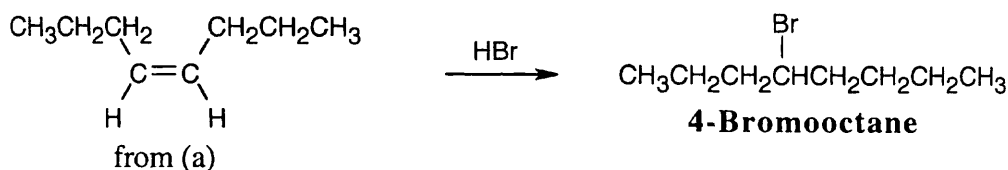
- (a) To reduce a triple bond to a double bond with *cis* stereochemistry use H_2 with Lindlar catalyst.



- (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.

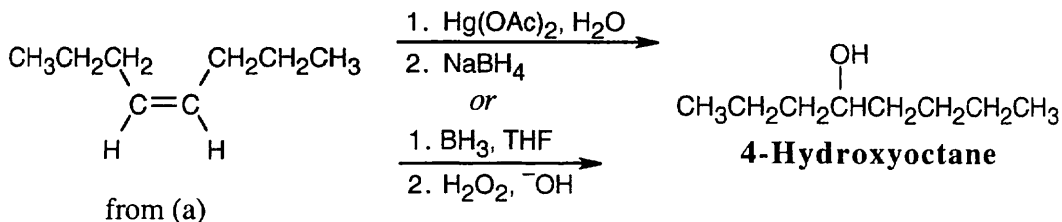


- (c) Addition of HBr to *cis*-4-octene [part (a)] yields 4-bromooctane.

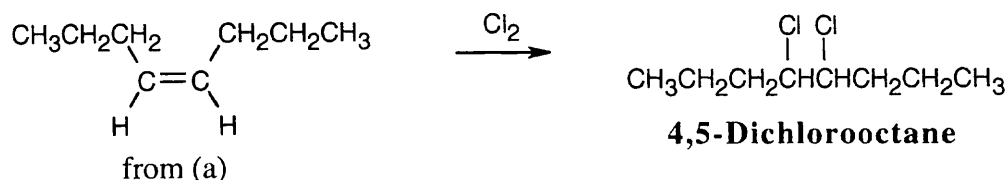


Alternatively, lithium/ammonia reduction of 4-octyne, followed by addition of HBr , gives 4-bromooctane.

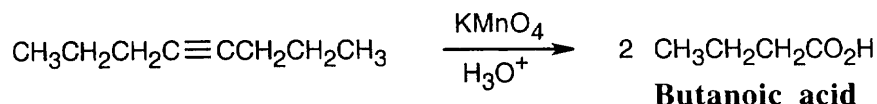
- (d) Hydration or hydroboration/oxidation of *cis*-4-octene [part (a)] yields 4-hydroxyoctane (4-octanol).



(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.

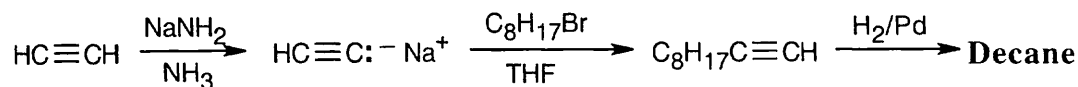


8.13 The following syntheses are explained in detail in order to illustrate retrosynthetic logic – the system of planning syntheses by working backwards.

(a) Strategy:

1. An immediate precursor to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ might be an alkene or alkyne. Try $\text{C}_8\text{H}_{17}\text{C}\equiv\text{CH}$, which can be reduced to decane by H_2/Pd .
2. The alkyne $\text{C}_8\text{H}_{17}\text{C}\equiv\text{CH}$ can be formed by alkylation of $\text{HC}\equiv\text{C}^- \text{Na}^+$ by $\text{C}_8\text{H}_{17}\text{Br}$, 1-bromooctane.
3. $\text{HC}\equiv\text{C}^- \text{Na}^+$ can be formed by treatment of $\text{HC}\equiv\text{CH}$ with NaNH_2 , NH_3 .

Solution:

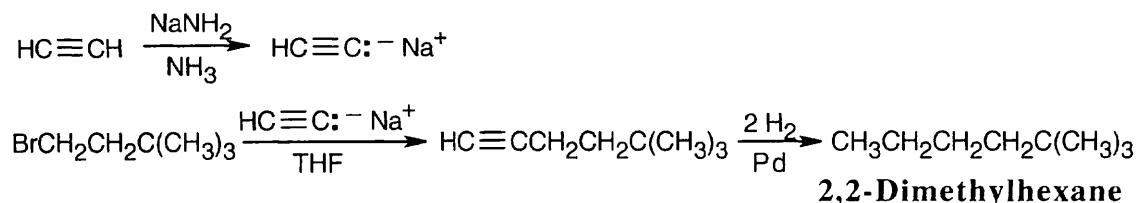


$\text{C}_8\text{H}_{17}\text{Br}$ = 1-Bromooctane

(b) Strategy:

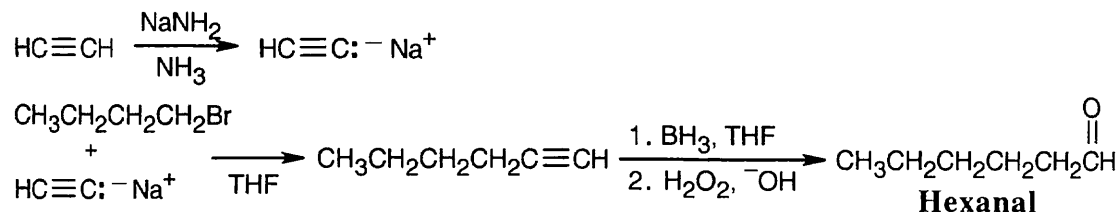
1. An immediate precursor to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ might be $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$, which, when hydrogenated, yields 2,2-dimethylhexane.
2. $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ can be formed by alkylation of $\text{HC}\equiv\text{C}^- \text{Na}^+$ with $\text{BrCH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$.

Solution:

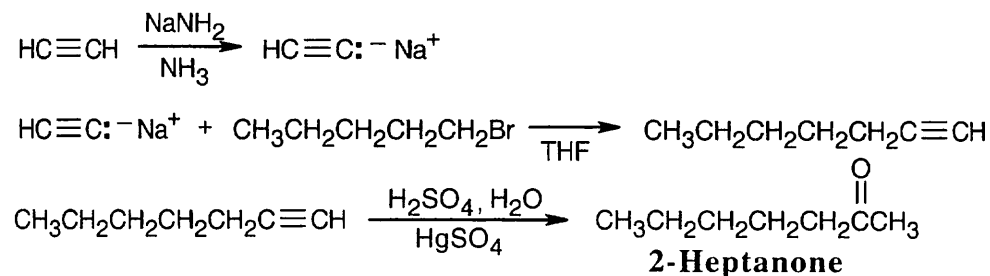


(c) **Strategy:**

1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$ can be made by treating $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ with borane, followed by H_2O_2 .
2. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ can be synthesized from $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ and $\text{HC}\equiv\text{C}^- \text{Na}^+$.

Solution:(d) **Strategy:**

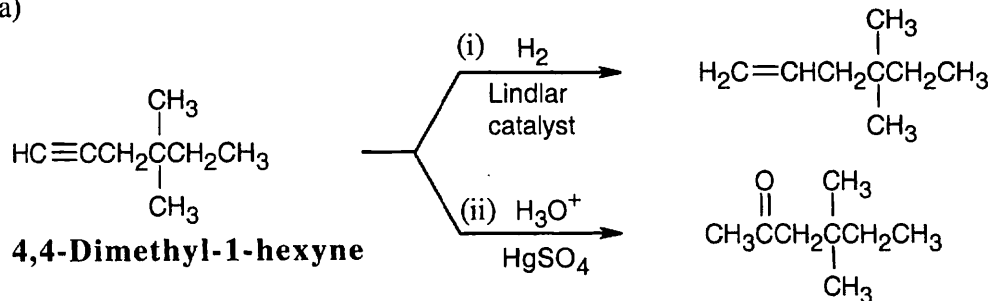
1. The desired ketone can be formed by mercuric-ion-catalyzed hydration of 1-heptyne.
2. 1-Heptyne can be synthesized by an alkylation of sodium acetylide by 1-bromopentane.

Solution:

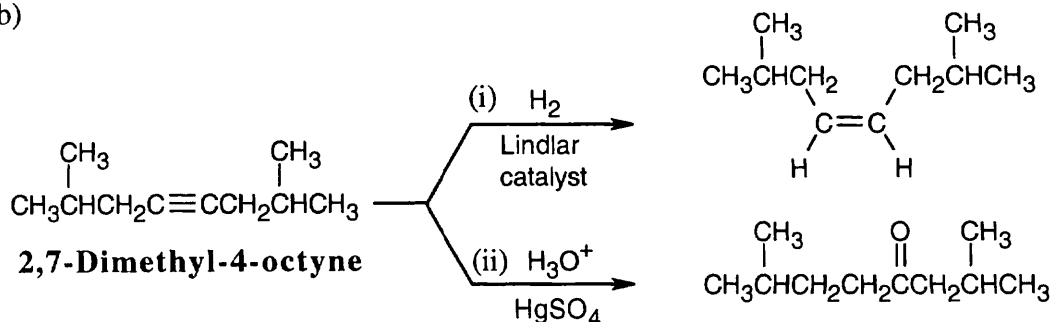
Visualizing Chemistry

8.14

(a)

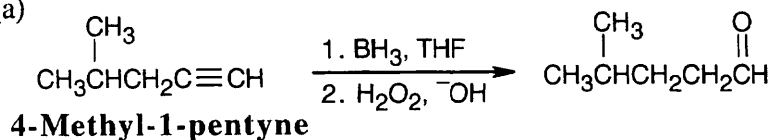


(b)



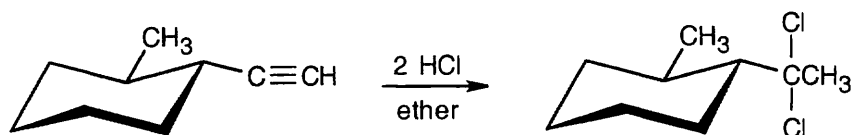
8.15

(a)



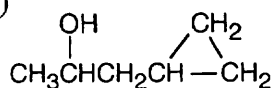
An aldehyde is formed by reacting a terminal alkyne with borane, followed by oxidation.

(b)

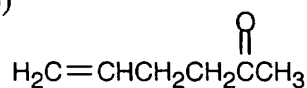


8.16 First, draw the structure of each target compound. Then, analyze the structures for a synthetic route.

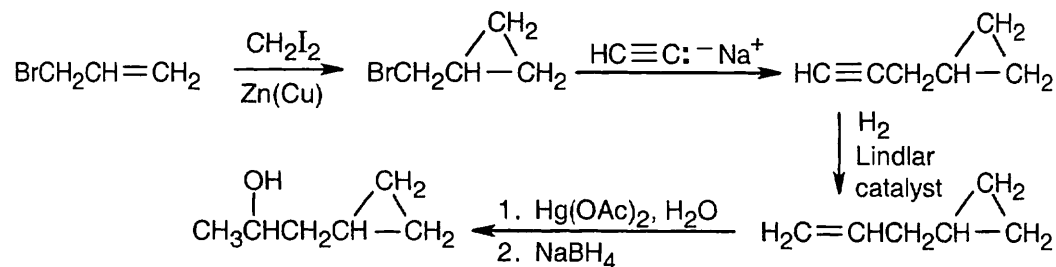
(a)



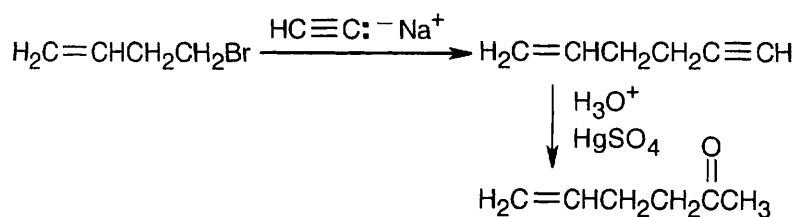
(b)



(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 alkyne. 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.

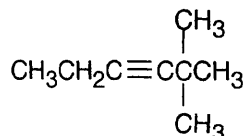


8.17 It's not possible to form a small ring containing a triple bond because the angle strain that would result from bending the bonds of an sp -hybridized carbon to form a small ring is too great.

Additional Problems

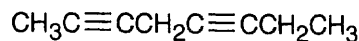
8.18

(a)



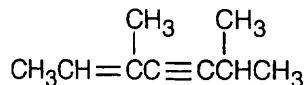
2,2-Dimethyl-3-hexyne

(b)



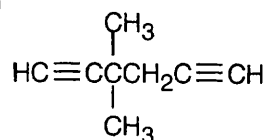
2,5-Octadiyne

(c)



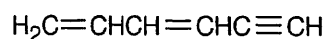
3,6-Dimethyl-2-hepten-4-yne

(d)



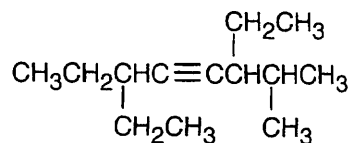
3,3-Dimethyl-1,5-hexadiyne

(e)



1,3-Hexadien-5-yne

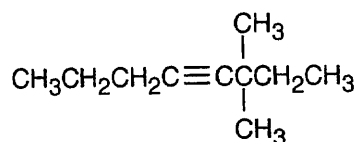
(f)



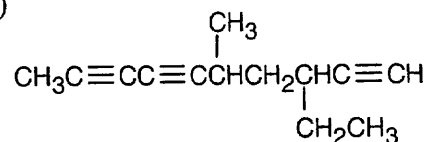
3,6-Diethyl-2-methyl-4-octyne

8.19

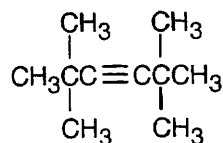
(a)

**3,3-Dimethyl-4-octyne**

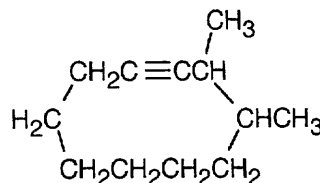
(b)

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

(c)

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

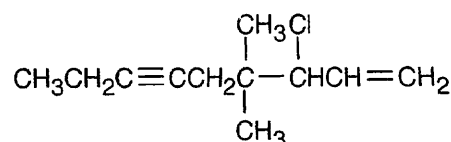
(d)

**3,4-Dimethylcyclodecyne**

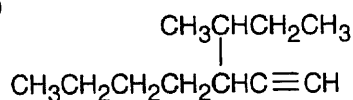
(e)

**3,5-Heptadien-1-yne**

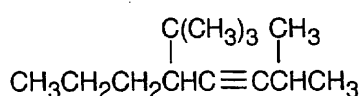
(f)

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

(g)

**3-sec-Butyl-1-heptyne**

(h)

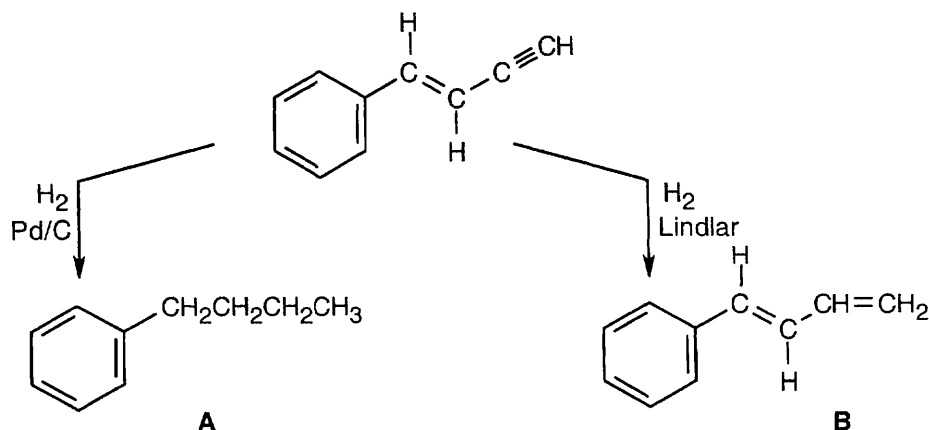
**5-tert-Butyl-2-methyl-3-octyne**

- 8.20 (a) $\text{CH}_3\text{CH}=\text{CHC}\equiv\text{CC}\equiv\text{CCH}=\text{CHCH}=\text{CHCH}=\text{CH}_2$.
1,3,5,11-Tridecatetraen-7,9-diyne

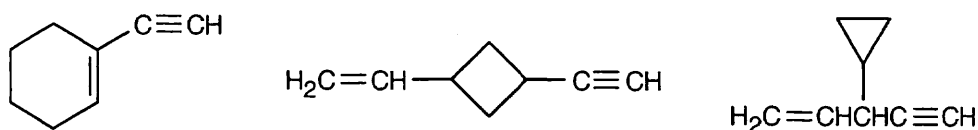
Using *E-Z* notation: **(3*E*,5*E*,11*E*)-1,3,5,11-Tridecatetraen-7,9-diyne**
 The parent alkane of this hydrocarbon is tridecane.

- (b) $\text{CH}_3\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{CCH}=\text{CH}_2$. **1-Tridecen-3,5,7,9,11-pentayne**
 This hydrocarbon also belongs to the tridecane family.

8.21



- 8.22 (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 contain one ring.
- (e) Many structures are possible.



8.23

- (a)
- $$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[1\text{ equiv}]{HBr} CH_3CH_2CH_2CH_2C(Br)=CH_2$$
- (b)
- $$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[1\text{ equiv}]{Cl_2} CH_3CH_2CH_2CH_2C(Cl)=C(H)Cl$$
- (c)
- $$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[\text{Lindlar catalyst}]{H_2} CH_3CH_2CH_2CH_2CH=CH_2$$
- (d)
- $$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[2. CH_3Br]{1. NaNH_2, NH_3} CH_3CH_2CH_2CH_2C\equiv CCH_3$$
- (e)
- $$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[HgSO_4]{H_2O, H_2SO_4} CH_3CH_2CH_2CH_2C(=O)CH_3$$
- (f)
- $$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[2\text{ equiv}]{HCl} CH_3CH_2CH_2CH_2C(Cl)(CH_3)_2$$

8.24

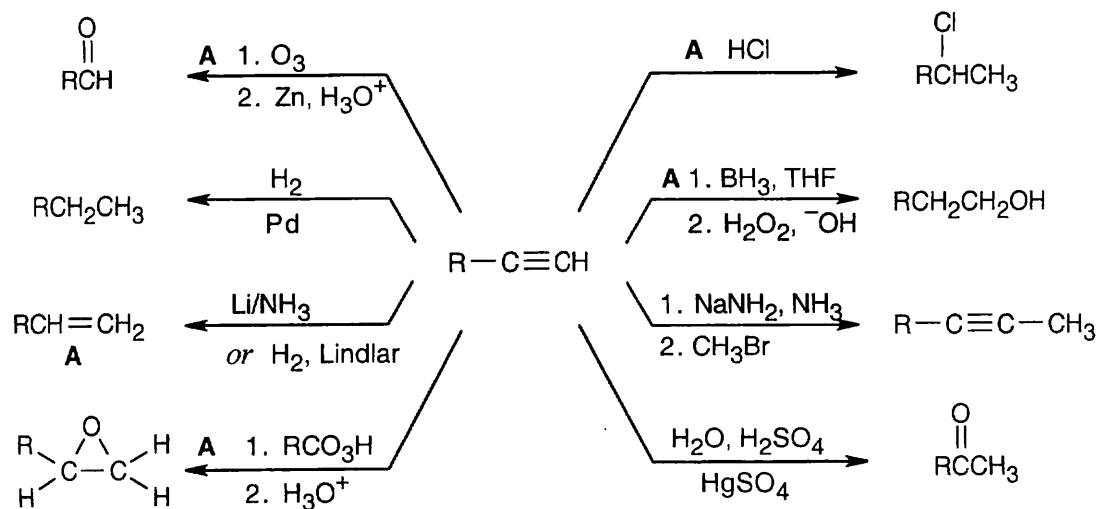
- (a)
- $$CH_3(CH_2)_3C\equiv C(CH_2)_3CH_3 \xrightarrow[\text{Lindlar catalyst}]{H_2} CH_3CH_2CH_2CH_2C(H)=C(H)CH_2CH_2CH_2CH_3$$

- (b) $\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3 \xrightarrow{\text{Li in NH}_3} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$
- (c) $\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3 \xrightarrow[\text{Br}_2]{1 \text{ equiv}} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \quad \text{Br} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Br} \quad \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$
- (d) $\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3 \xrightarrow[2. \text{H}_2\text{O}_2, ^-\text{OH}]{1. \text{BH}_3, \text{THF}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- (e) $\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3 \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{O}, \text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- (f) $\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3 \xrightarrow[\text{Pd/C}]{\text{excess H}_2} \text{CH}_3(\text{CH}_2)_8\text{CH}_3$

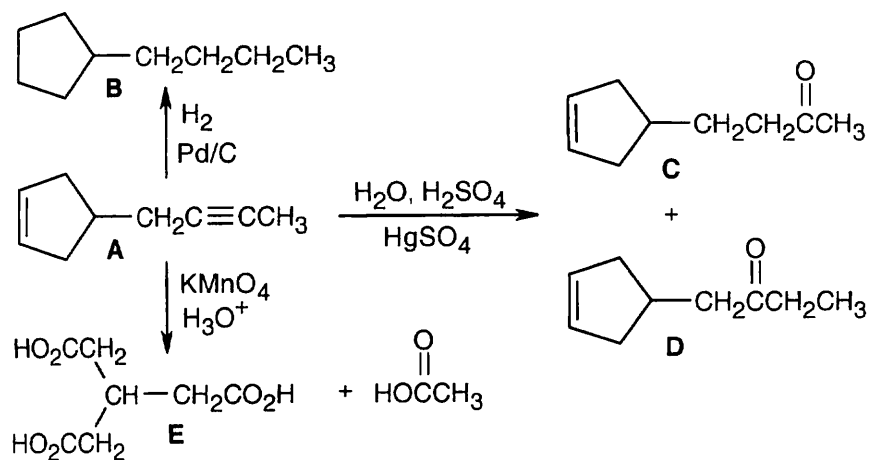
8.25

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3 \xrightarrow[\text{Br}_2]{2 \text{ equiv}} \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{Br}_2)\text{C}(\text{Br}_2)\text{CH}_3$
- (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3 \xrightarrow[\text{HBr}]{1 \text{ equiv}} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Br} \quad \text{CH}_3 \end{array} + \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2 \quad \text{Br} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_3 \end{array}$
- (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3 \xrightarrow[\text{HBr}]{\text{excess}} \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{Br}_2)\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{Br}_2)\text{CH}_3$
- (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3 \xrightarrow{\text{Li in NH}_3} \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_3 \end{array}$
- (e) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3 \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{O}, \text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_3$

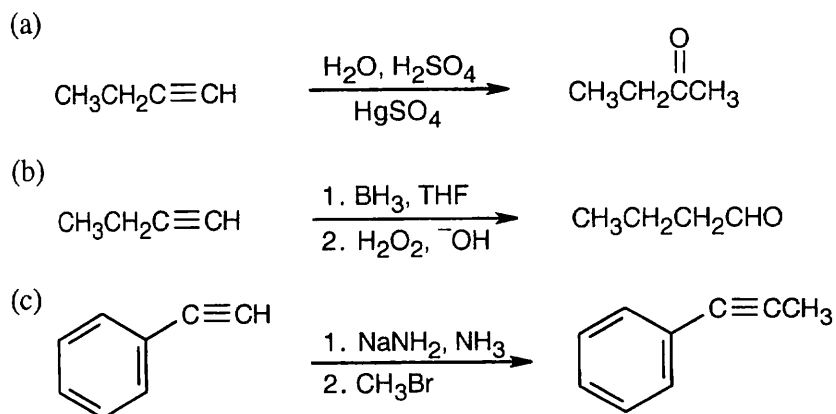
8.26



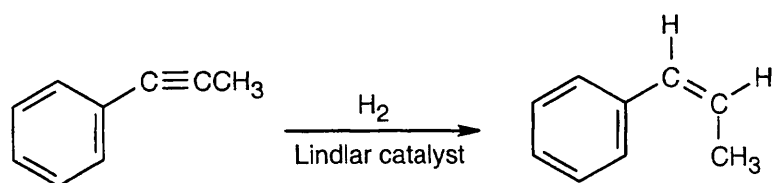
8.27



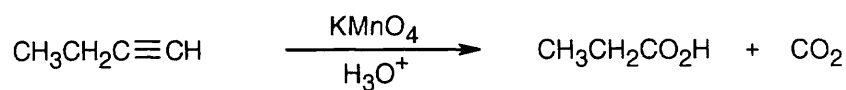
8.28



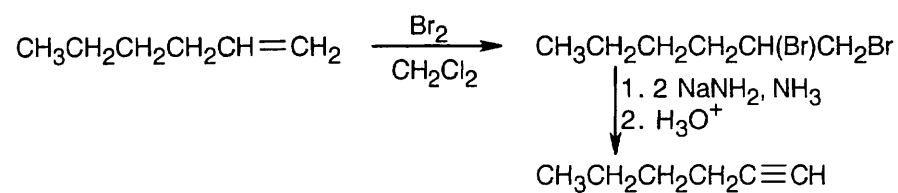
(d)



(e)

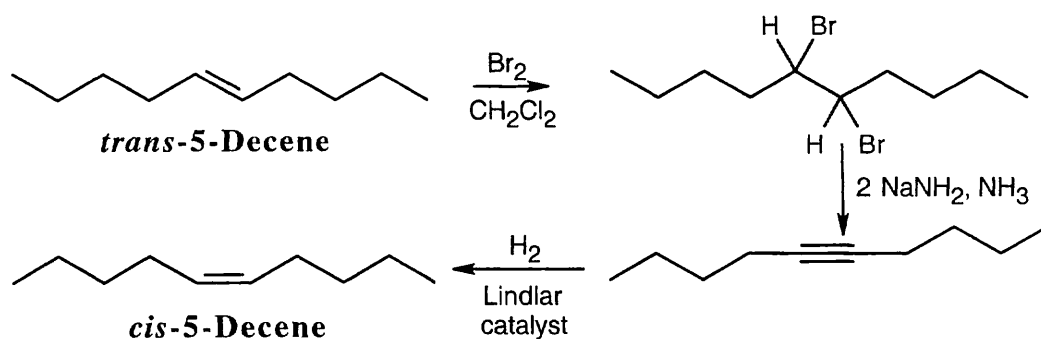


(f)

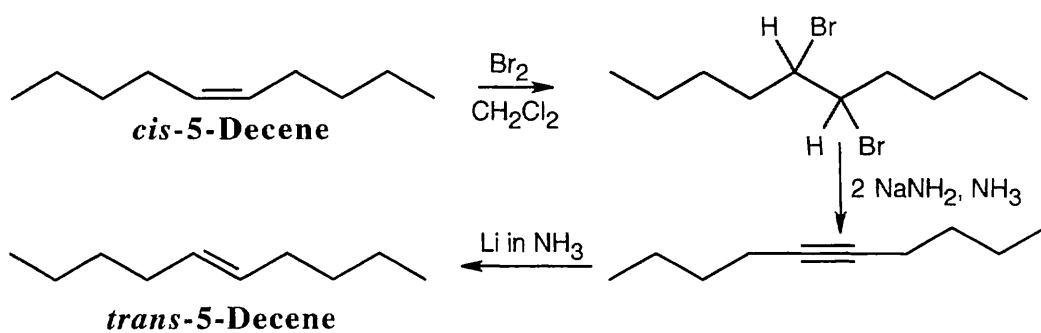


8.29

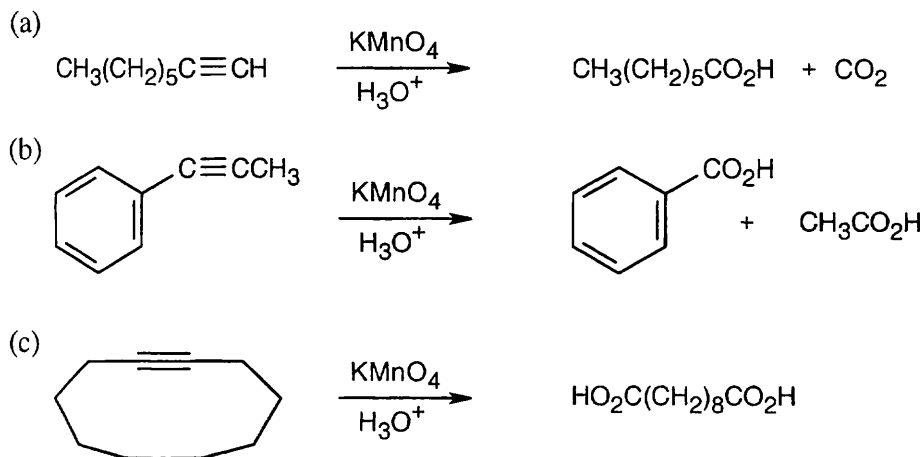
(a)



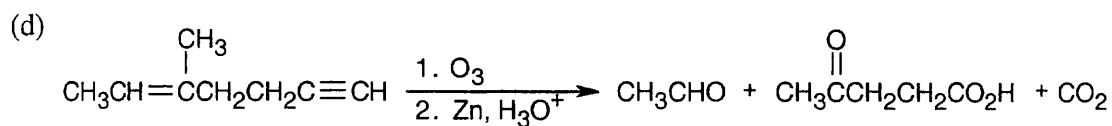
(b)



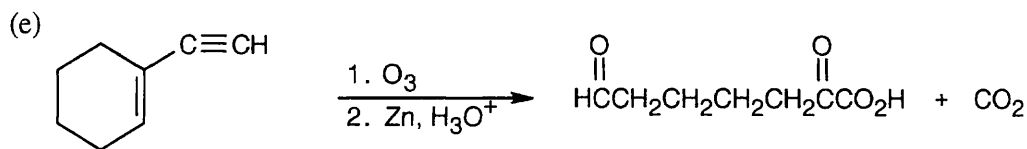
8.30 Both KMnO_4 and O_3 oxidation of alkynes yield carboxylic acids; terminal alkynes give CO_2 also. In (a), (b), and (c), the observed products can also be formed by KMnO_4 oxidation of the corresponding alkenes.



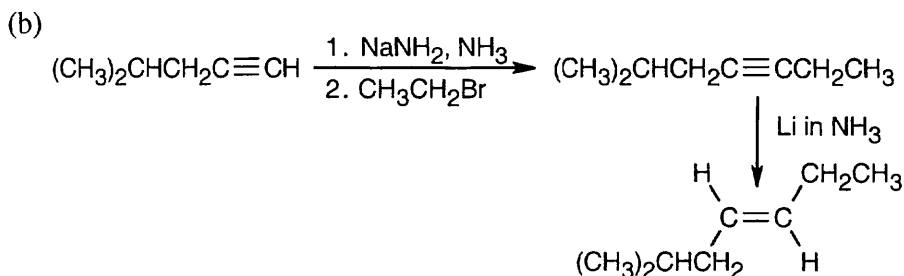
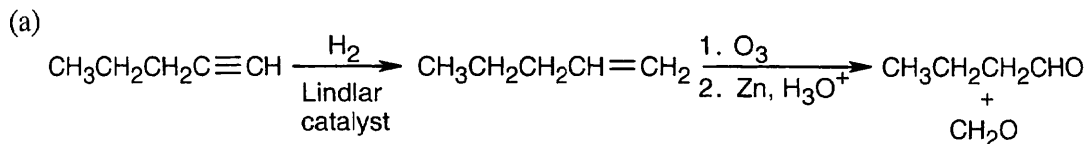
Since only one cleavage product is formed, the parent hydrocarbon must have contained a triple bond as part of a ring.



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.

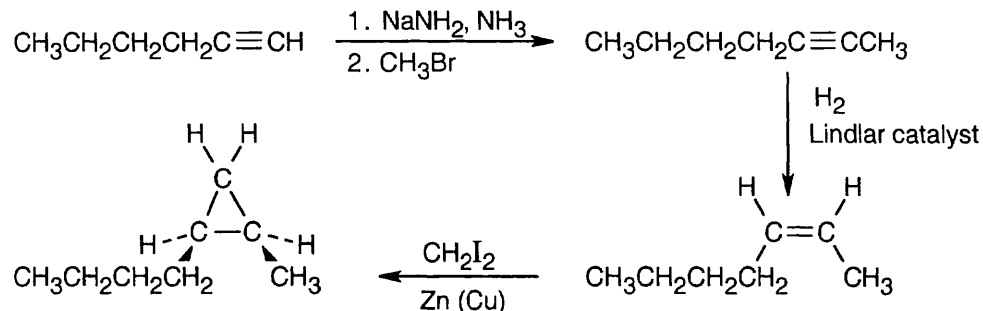


8.31

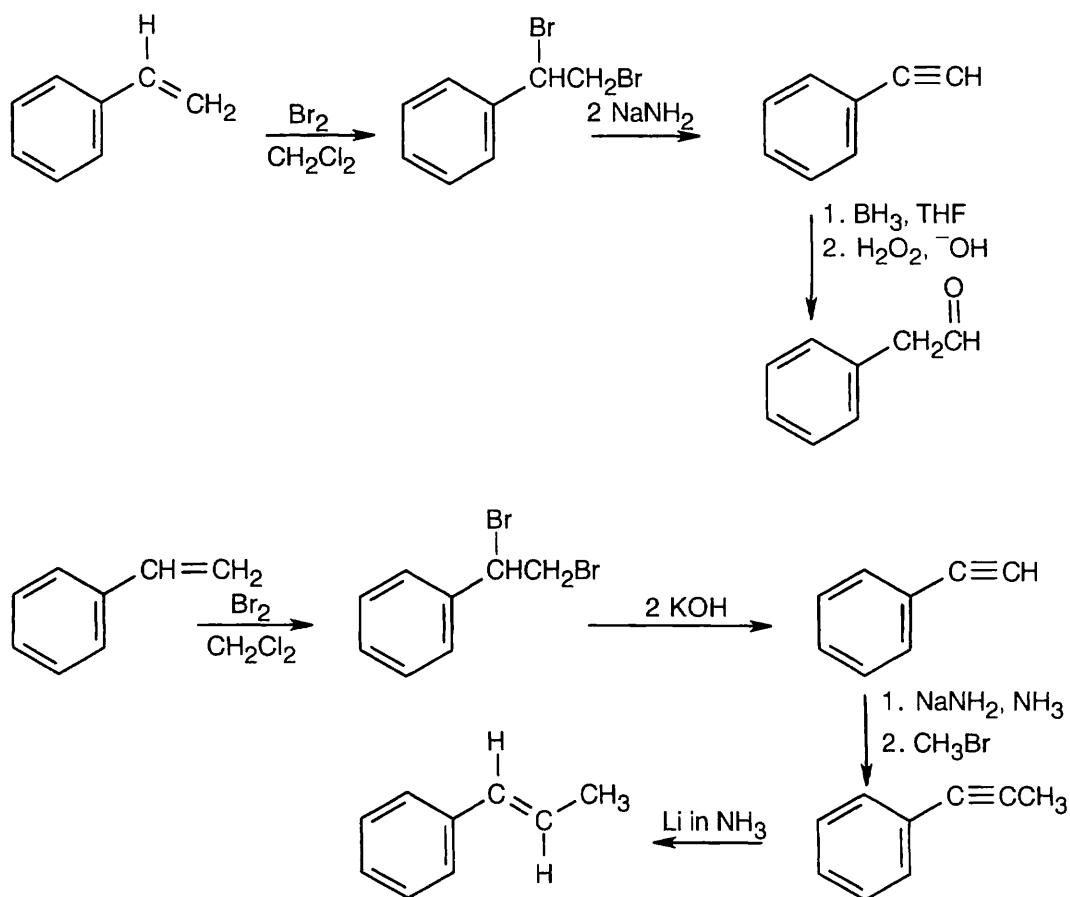


8.32 Strategy: The product contains a cis-disubstituted cyclopropane ring, which can be formed from a Simmons–Smith reaction of CH_2I_2 with a cis alkene. The alkene with a cis bond can be produced from an alkyne by hydrogenation using a Lindlar catalyst. The needed alkyne can be formed from the starting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

Solution:

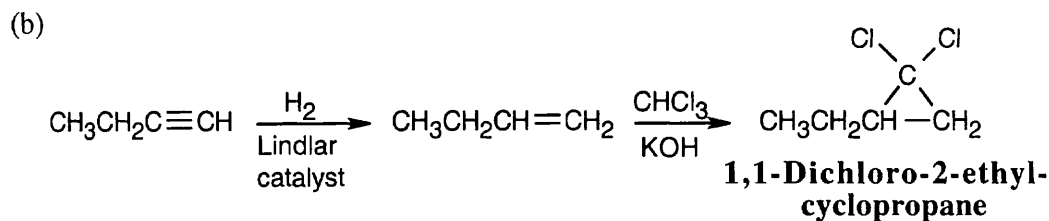
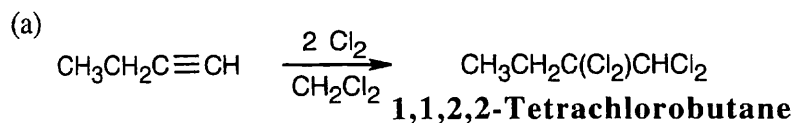


8.33

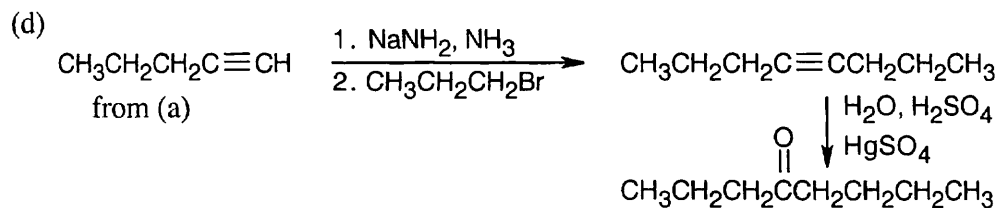
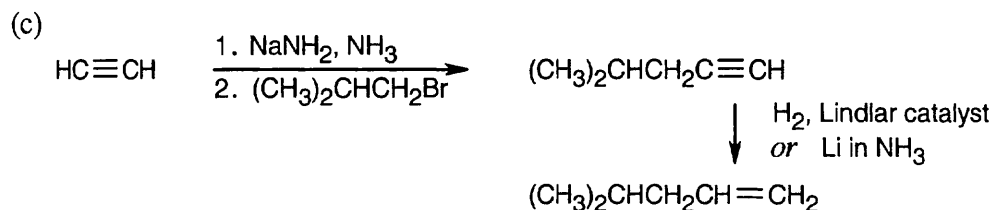
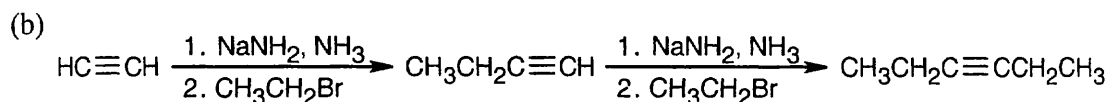
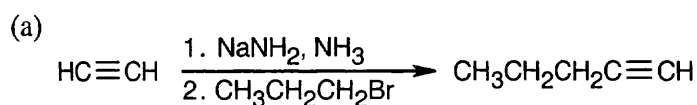


The trans double bond in the target molecule is a product of reduction of a triple bond with Li in NH_3 . The alkyne was formed by an alkylation of a terminal alkyne with bromomethane. The terminal alkyne was synthesized from the starting alkene by bromination, followed by dehydrohalogenation.

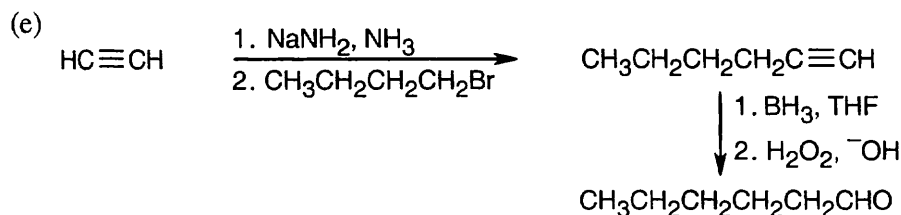
8.34



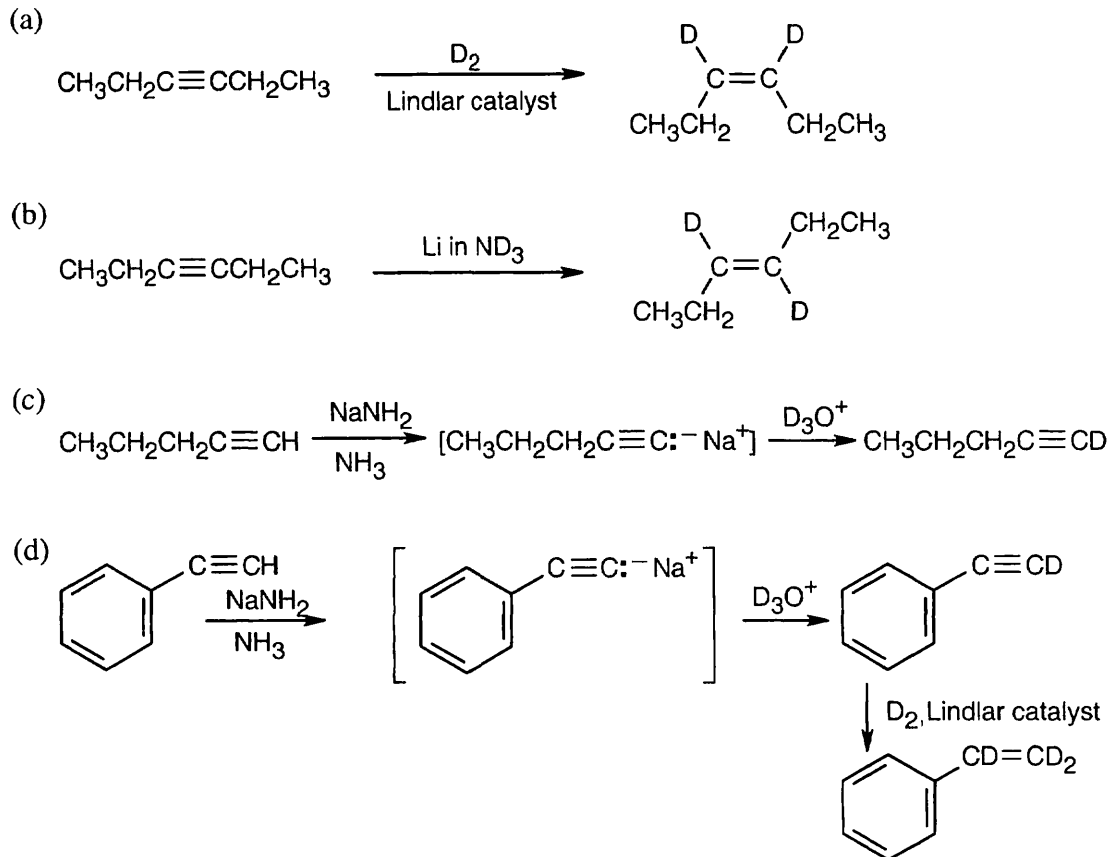
8.35 In all of these problems, an acetylide ion (or an anion of a terminal alkyne) is alkylated by a haloalkane.



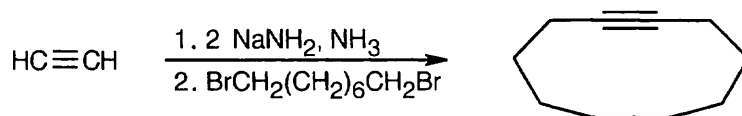
Hydroboration/oxidation can also be used to form the ketone from 4-octyne.



8.36

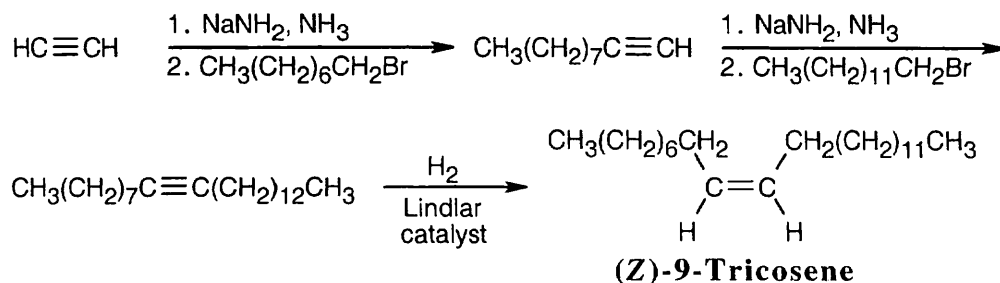


8.37

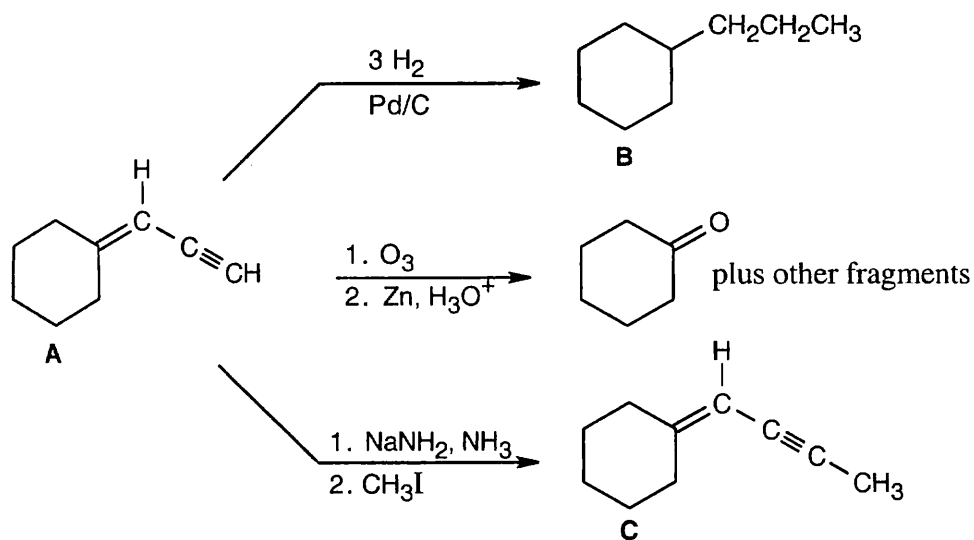


8.38 Strategy: Muscalure is a C₂₃ alkene. The only functional group present is the double bond between C₉ and C₁₀. Since our synthesis begins with acetylene, we can assume that the double bond can be produced by hydrogenation of a triple bond.

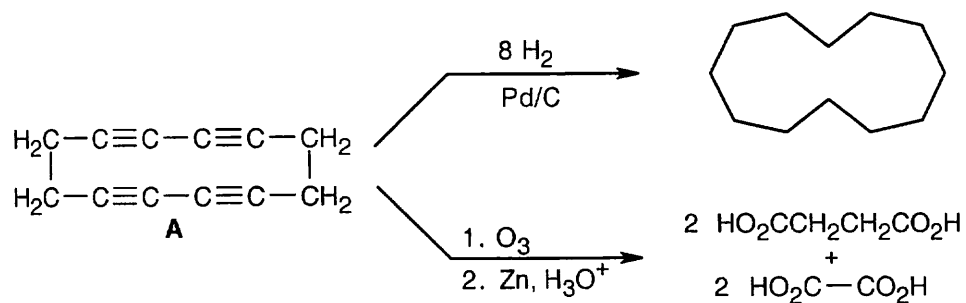
Solution:



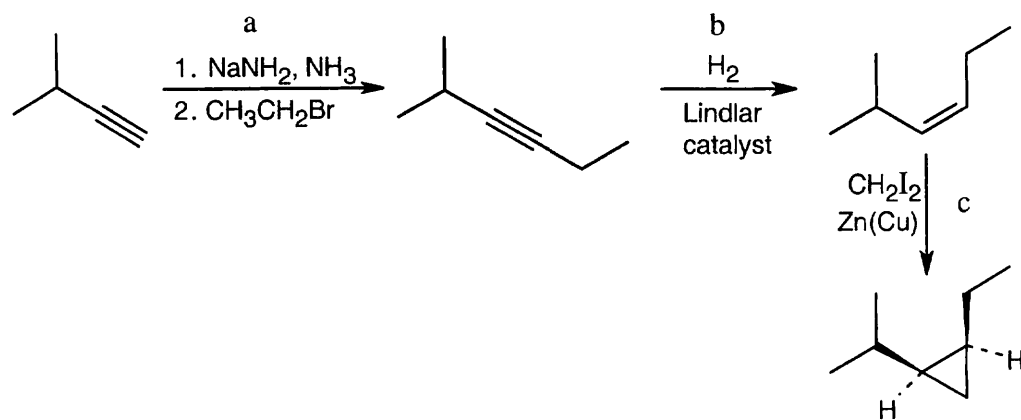
8.39



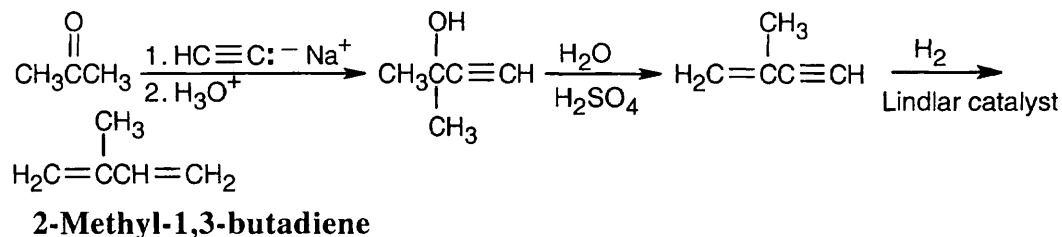
8.40



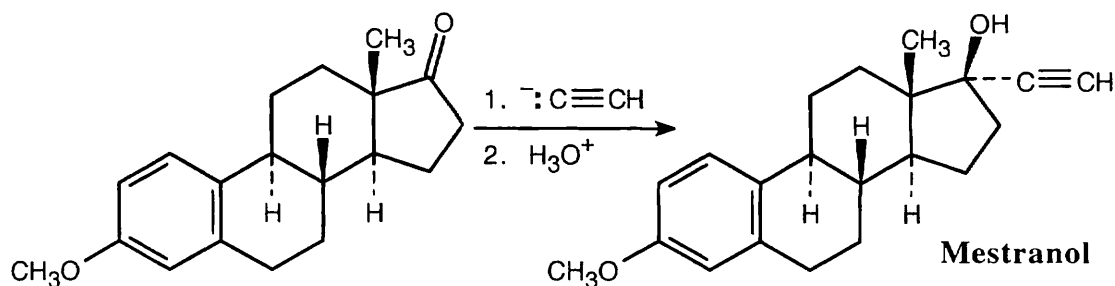
8.41



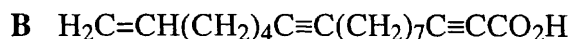
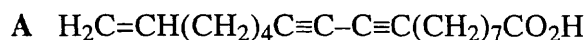
8.42



8.43

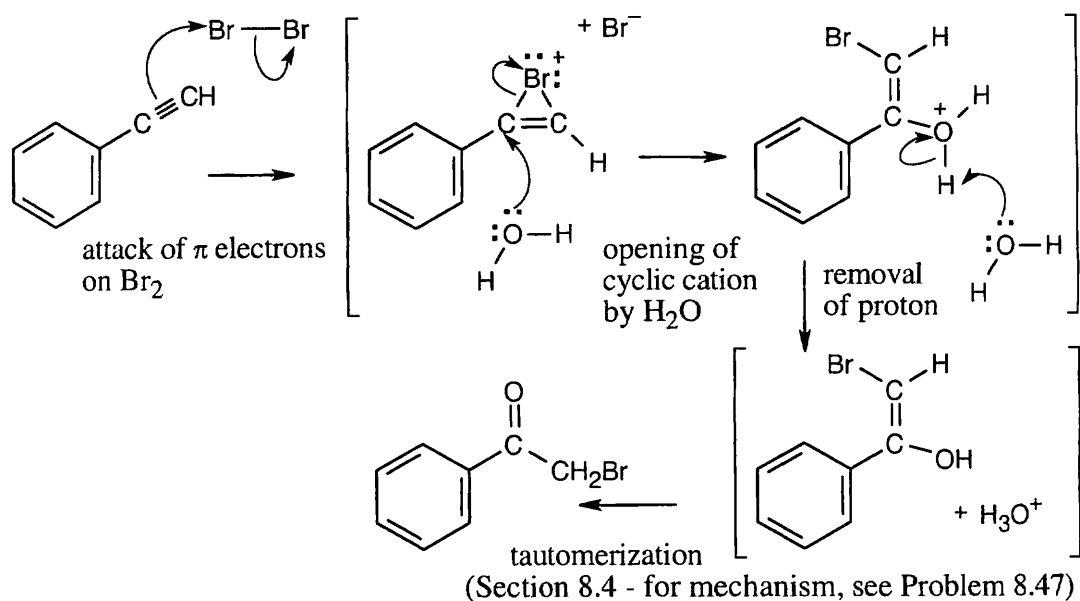


- 8.44** (1) Erythroenic acid contains six degrees of unsaturation (see Sec. 6.2 for the method of calculating unsaturation equivalents for compounds containing elements other than C and H).
- (2) One of these double bonds is contained in the carboxylic acid functional group $-\text{CO}_2\text{H}$; thus, five other degrees of unsaturation are present.
- (3) Because five equivalents of H_2 are absorbed on catalytic hydrogenation, erythroenic 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 erythroenic acid.
- (5) Only two ozonolysis products contain aldehyde functional groups; these fragments must have been double-bonded to each other in erythroenic acid.
- $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{C}\equiv$
- (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:

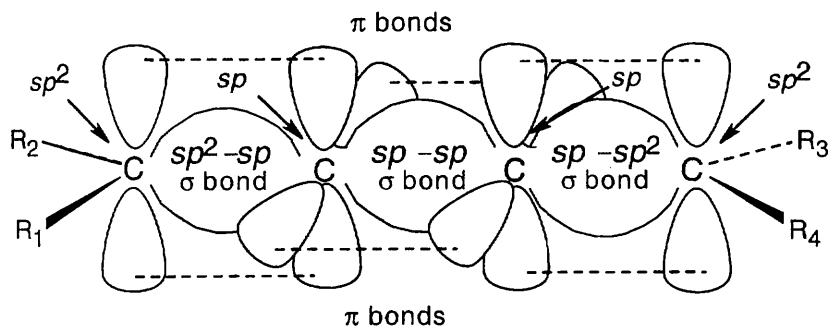


One method of distinguishing between the two possible structures is to treat erythroenic acid with two equivalents of H_2 , using Lindlar catalyst. The resulting trialkene can then be ozonized. The fragment that originally contained the carboxylic acid can then be identified.

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



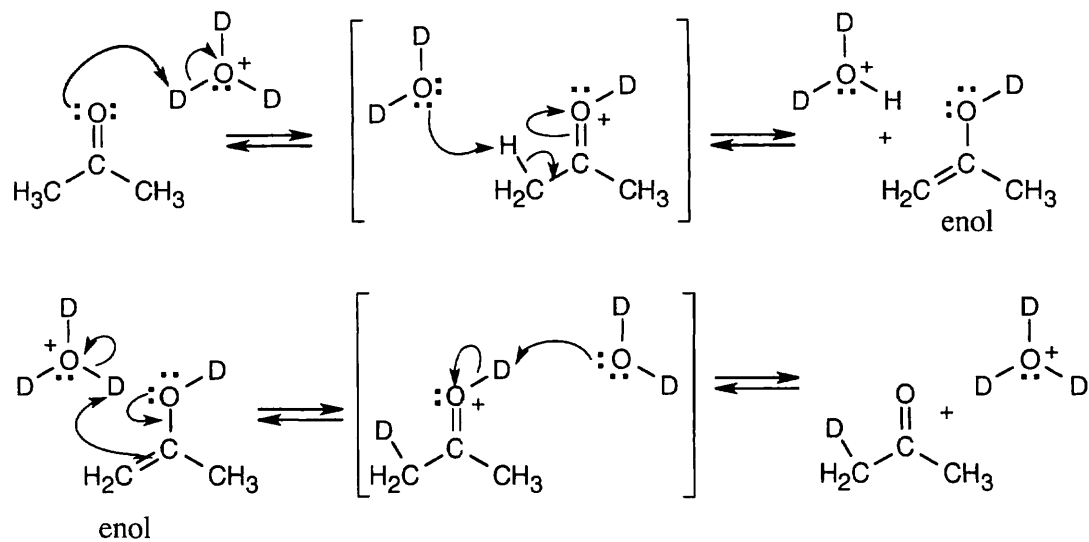
8.46



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. The relationship of substituents at the ends of any compound with an even number of adjacent double bonds will be explained in the next chapter.

8.47



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

Review Unit 3: Alkenes and Alkynes

Major Topics Covered (with vocabulary):

Introduction to alkenes:

degree of unsaturation methylene group vinyl group allyl group cis-trans isomerism
E,Z isomerism sequence rules heat of hydrogenation hyperconjugation

Electrophilic addition reactions:

electrophilic addition reaction regioselective Markovnikov's rule Hammond Postulate
carbocation rearrangement hydride shift

Other reactions of alkenes:

dehydrohalogenation dehydration anti stereochemistry bromonium ion halohydrin
hydration oxymercuration hydroboration syn stereochemistry carbene stereospecific
Simmons-Smith reaction hydrogenation hydroxylation diol osmate molybdenum oxide ozonide

Polymerization reactions:

polymer monomer chain branching radical polymerization cationic polymerization

Alkynes:

alkyne enyne vicinal tautomer Lindlar catalyst acetylide anion alkylation

Organic Synthesis.

Types of Problems:

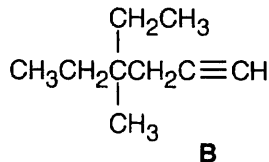
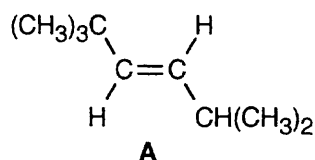
After studying these chapters you should be able to:

- Calculate the degree of unsaturation of any compound, including those containing N, O, and halogen.
- Name acyclic and cyclic alkenes and alkynes, and draw structures corresponding to names.
- Assign *E,Z* priorities to groups.
- Assign cis-trans and *E,Z* designations to double bonds.
- Predict the relative stability of alkene double bonds.
- Formulate mechanisms of electrophilic addition reactions.
- Predict the products of reactions involving alkenes and alkynes.
- Choose the correct alkene or alkyne starting material to yield a given product.
- Deduce the structure of an alkene or alkyne from its molecular formula and products of cleavage.
- Carry out syntheses involving alkenes and alkynes.

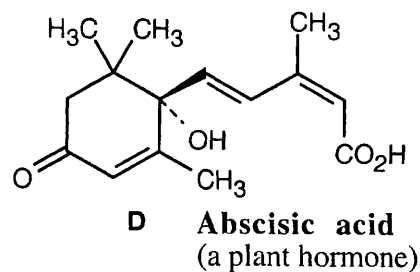
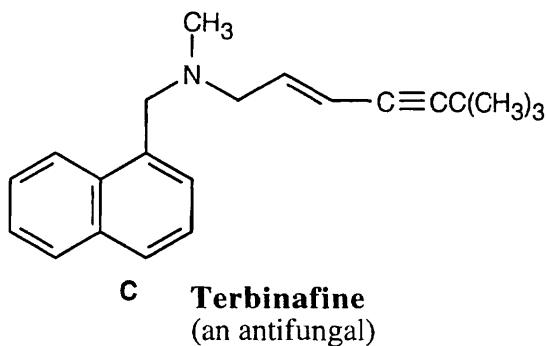
Points to Remember:

- * Calculating the degree of unsaturation is an absolutely essential technique in the structure determination of all organic compounds. It is the starting point for deciding which functional groups are or aren't present in a given compound, and eliminates many possibilities. When a structure determination problem is given, always calculate the degree of unsaturation first.

- * All *cis*–*trans* isomers can also be described by the *E,Z* designation, but not all *E,Z* isomers can be described by the *cis*–*trans* designation.
- * Bond dissociation energies, described in Chapter 5, measure the energy required to homolytically break a bond. They are not the same as dissociation enthalpies, which measure the ability of a compound to dissociate heterolytically. Bond dissociation energies can be used to calculate dissociation enthalpies in the gas phase if other quantities are also known.
- * Not all hydrogens bonded to carbons adjacent to a carbocation can take part in hyperconjugation at the same time. At any given instant, some of the hydrogens have C–H bonds that lie in the plane of the carbocation and are not suitably oriented for hyperconjugative overlap
- * Although it is very important to work backwards when planning an organic synthesis, don't forget to pay attention to the starting material, also. Planning a synthesis is like solving a maze from the middle outward: keeping your eye on the starting material can keep you from running into a dead end.
- * The reagent Li/NH_3 is used to reduce an alkyne to a *trans* alkene; the reagent $\text{NaNH}_2/\text{NH}_3$ is used to form an acetylide anion. It is easy to confuse the two reagents.

Self-Test:

Provide names for **A** and **B** (include bond stereochemistry). Predict the products of reaction of **A** and **B** with (a) 1 equiv HBr (b) H_2 , Pd/C (c) BH_3 , THF , then H_2O_2 , HO^- (d) O_3 , then Zn , H_3O^+ . Give a reagent that reacts with **A** but not **B**. Give a reagent that reacts with **B**, but not **A**.



What is the configuration of the double bond in the side chain of **C**? What products result from treatment of **C** with KMnO_4 , H_3O^+ (neither the aromatic ring nor the amine are affected)? How might the triple bond have been introduced?

Give *E,Z* configurations for the double bonds in **D**.

Multiple Choice:

1. What is the degree of unsaturation of a compound whose molecular formula is $C_{11}H_{13}N$?
(a) 4 (b) 5 (c) 6 (d) 7
2. Two equivalents of H_2 are needed to hydrogenate a hydrocarbon. It is also known that the compound contains two rings and has 15 carbons. What is its molecular formula?
(a) $C_{15}H_{22}$ (b) $C_{15}H_{24}$ (c) $C_{15}H_{28}$ (d) $C_{15}H_{32}$
3. Which group is of lower priority than $-CH=CH_2$?
(a) $-CH(CH_3)_2$ (b) $-CH=C(CH_3)_2$ (c) $-C\equiv CH$ (d) $-C(CH_3)_3$
4. What is the usual relationship between the heats of hydrogenation of a pair of cis/trans alkene isomers?
(a) Both have positive heats of hydrogenation (b) Both have negative heats of hydrogenation, and ΔH_{hydrog} for the cis isomer has a greater negative value (c) Both have negative heats of hydrogenation, and ΔH_{hydrog} for the trans isomer has a greater negative value (d) Both have negative heats of hydrogenation, but the relationship between the two values of ΔH_{hydrog} can't be predicted.
5. In a two-step exergonic reaction, what is the relationship of the two transition states?
(a) both resemble the intermediate (b) the first resembles the starting material, and the second resembles the product (c) the first resembles the intermediate and the second resembles the product (d) there is no predictable relationship between the two transition states
6. For synthesis of an alcohol, acid-catalyzed hydration of an alkene is useful in all of the following instances except:
(a) when an alkene has no acid-sensitive groups (b) when an alkene is symmetrical (c) when a large amount of the alcohol is needed (d) when two possible carbocation intermediates are of similar stability.
7. A reaction that produces a diol from an alcohol is a:
(a) hydration (b) hydrogenation (c) hydroboration (d) hydroxylation
8. Which of these cyclic intermediates is not part of an oxidative cleavage reaction?
(a) ozonide (b) molozonide (c) osmate (d) periodate
9. An enol is a tautomer of an:
(a) alcohol (b) alkyne (c) alkene (d) ketone
10. Which reaction proceeds through a vinylic radical?
(a) Hg-catalyzed hydration of an alkyne (b) Li/NH_3 reduction of an alkyne
(c) catalytic hydrogenation of an alkyne (d) treatment of an alkyne with a strong base