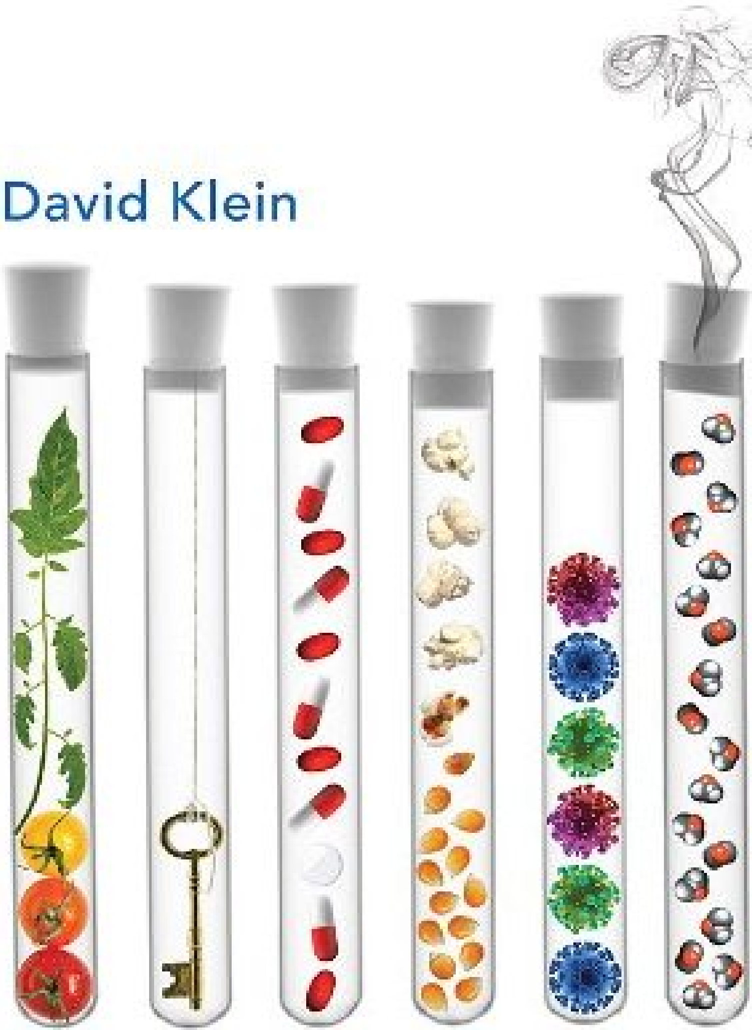
David Klein



STUDENT STUDY GUIDE & SOLUTIONS MANUAL

Organic Chemistry

Student Study Guide and Solutions Manual

for

Organic Chemistry

David R. Klein
Johns Hopkins University

WILEY

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PREFACE

This book contains more than just solutions to all of the problems in the textbook. Each chapter of this book also contains a series of exercises that will help you review the concepts, skills and reactions presented in the corresponding chapter of the textbook. These exercises are designed to serve as study tools that can help you identify your weak areas. Each chapter of this solutions manual/study guide has the following parts:

- ***Review of Concepts***. These exercises are designed to help you identify which concepts are the least familiar to you. Each section contains sentences with missing words (blanks). Your job is to fill in the blanks, demonstrating mastery of the concepts. To verify that your answers are correct, you can open your textbook to the end of the corresponding chapter, where you will find a section entitled *Review of Concepts and Vocabulary*. In that section, you will find each of the sentences, verbatim.
- ***Review of Skills***. These exercises are designed to help you identify which skills are the least familiar to you. Each section contains exercises in which you must demonstrate mastery of the skills developed in the *SkillBuilders* of the corresponding textbook chapter. To verify that your answers are correct, you can open your textbook to the end of the corresponding chapter, where you will find a section entitled *SkillBuilder Review*. In that section, you will find the answers to each of these exercises.
- ***Review of Reactions***. These exercises are designed to help you identify which reagents are not at your fingertips. Each section contains exercises in which you must demonstrate familiarity with the reactions covered in the textbook. Your job is to fill in the reagents necessary to achieve each reaction. To verify that your answers are correct, you can open your textbook to the end of the corresponding chapter, where you will find a section entitled *Review of Reactions*. In that section, you will find the answers to each of these exercises.
- ***Solutions***. At the end of each chapter, you'll find solutions to all problems in the textbook, including all Skillbuilders, conceptual checkpoints, additional problems, integrated problems, and challenge problems.

The sections described above have been designed to serve as useful tools as you study and learn organic chemistry. Good luck!

David Klein
Department of Chemistry
Johns Hopkins University

Chapter 1
Electrons, Bonds and Molecular Properties

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 1. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- _____________ **isomers** share the same molecular formula but have different connectivity of atoms and different physical properties.
- Second-row elements generally obey the _______ **rule**, bonding to achieve noble gas electron configuration.
- A pair of unshared electrons is called a ______________.
- A **formal charge** occurs when an atom does not exhibit the appropriate number of ____________________________.
- An **atomic orbital** is a region of space associated with ____________________, while a **molecular orbital** is a region of space associated with _______________.
- Methane’s tetrahedral geometry can be explained using four degenerate _____-**hybridized orbitals** to achieve its four single bonds.
- Ethylene’s planar geometry can be explained using three degenerate _____-**hybridized orbitals**.
- Acetylene’s linear geometry is achieved via _____-**hybridized** carbon atoms.
- The geometry of small compounds can be predicted using valence shell electron pair repulsion (**VSEPR**) theory, which focuses on the number of _______ bonds and _______________ exhibited by each atom.
- The physical properties of compounds are determined by __________________ forces, the attractive forces between molecules.
- **London dispersion forces** result from the interaction between transient __________________ and are stronger for larger alkanes due to their larger surface area and ability to accommodate more interactions.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 1. The answers appear in the section entitled *SkillBuilder Review*.

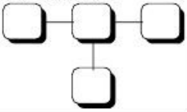
SkillBuilder 1.1 Determining the Constitution of Small Molecules

STEP 1 *- DETERMINE THE VALENCY (NUMBER OF EXPECTED BONDS) FOR EACH ATOM IN C_2H_5Cl* Each carbon atom is expected to form ___ bonds. Each hydrogen atom is expected to form ___ bonds. The chlorine atom is expected to form ___ bonds.	***STEP 2*** *- DRAW THE STRUCTURE OF C_2H_5Cl BY PLACING ATOMS WITH THE HIGHEST VALENCY AT THE CENTER, AND PLACING MONOVALENT ATOMS AT THE PERIPHERY*

SkillBuilder 1.2 Drawing the Lewis Dot Structure of an Atom

***STEP 1** - DETERMINE THE NUMBER OF VALENCE ELECTRONS*	***STEP 2** - PLACE ONE ELECTRON BY ITSELF ON EACH SIDE OF THE ATOM*	***STEP 3** - IF THE ATOM HAS MORE THAN FOUR VALENCE ELECTRONS, PAIR THE REMAINING ELECTRONS WITH THE ELECTRONS ALREADY DRAWN*
Nitrogen is in Group ___ of the periodic table, and is expected to have ___ valence electrons.		

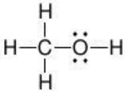
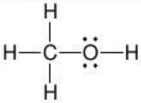
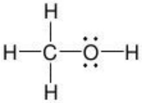
SkillBuilder 1.3 Drawing the Lewis Structure of a Small Molecule

***STEP 1** - DRAW THE LEWIS DOT STRUCTURE OF EACH ATOM IN CH_2O*	***STEP 2** - FIRST CONNECT ATOMS THAT FORM MORE THAN ONE BOND*	***STEP 3** - CONNECT THE HYDROGEN ATOMS*	***STEP 4** - PAIR ANY UNPAIRED ELECTRONS, SO THAT EACH ATOM ACHIEVES AN OCTET*
			

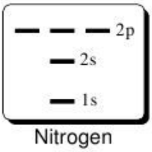
SkillBuilder 1.4 Calculating Formal Charge

***STEP 1** - DETERMINE THE APPROPRIATE NUMBER OF VALENCE ELECTRONS*	***STEP 2** - DETERMINE THE NUMBER OF VALENCE ELECTRONS IN THIS CASE*	***STEP 3** - ASSIGN A FORMAL CHARGE TO THE NITROGEN ATOM IN THIS CASE*
 Nitrogen is in Group ___ of the periodic table, and is expected to have ___ valence electrons.	 In this case, the nitrogen atom is using only ___ valence electrons.	

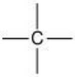
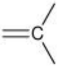
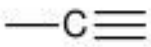
SkillBuilder 1.5 Locating Partial Charges

***STEP 1** - CIRCLE THE BONDS BELOW THAT ARE POLAR COVALENT*	***STEP 2** - FOR EACH POLAR COVALENT BOND, DRAW AN ARROW THAT SHOWS THE DIRECTION OF THE DIPOLE MOMENT*	***STEP 3** - INDICATE THE LOCATION OF ALL PARTIAL CHARGES ($\delta+$ and $\delta-$)*
		

SkillBuilder 1.6 Identifying Electron Configurations

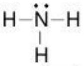
***STEP 1** - IN THE ENERGY DIAGRAM SHOWN HERE, DRAW THE ELECTRON CONFIGURATION OF NITROGEN (USING ARROWS TO REPRESENT ELECTRONS).*	***STEP 2** - FILL IN THE BOXES BELOW WITH THE NUMBERS THAT CORRECTLY DESCRIBE THE ELECTRON CONFIGURATION OF NITROGEN*
	$1s^{☐}2s^{☐}2p^{☐}$

SkillBuilder 1.7 Identifying Hybridization States

A CARBON ATOM WITH FOUR SINGLE BONDS WILL BE _____ HYBRIDIZED	*A CARBON ATOM WITH ONE DOUBLE BOND WILL BE _____ HYBRIDIZED*	*A CARBON ATOM WITH A TRIPLE BOND WILL BE _____ HYBRIDIZED*
		

SkillBuilder 1.8 Predicting Geometry

STEP 1 - *DETERMINE THE STERIC NUMBER OF THE NITROGEN ATOM BELOW BY ADDING THE NUMBER OF SINGLE BONDS AND LONE PAIRS*



# of single bonds =

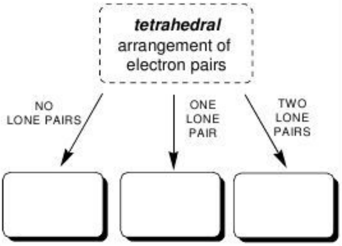
# of lone pairs =

Steric Number =

STEP 2 - *THE STERIC NUMBER DETERMINES THE HYBRIDIZATION STATE AND ELECTRONIC GEOMETRY. FILL IN THE CHART BELOW:*

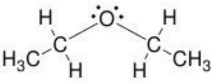
Steric #	Hybridization State	Electronic Geometry
4		
3		
2		

STEP 3 - *IGNORING LONE PAIRS, IDENTIFY THE GEOMETRY IN EACH CASE BELOW*



SkillBuilder 1.9 Identifying Molecular Dipole Moments

STEP 1 - *IDENTIFY THE GEOMETRY OF THE OXYGEN ATOM BELOW*



Geometry =

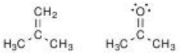
STEP 2 - *REDRAW THE COMPOUND. FOR EACH POLAR COVALENT BOND, DRAW AN ARROW THAT SHOWS THE DIRECTION OF THE DIPOLE MOMENT*

STEP 3 - *REDRAW THE COMPOUND, AND DRAW THE NET DIPOLE MOMENT*

SkillBuilder 1.10 Predicting Physical Properties

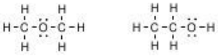
Dipole-Dipole Interactions

CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT



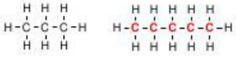
H-Bonding Interactions

CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT



Carbon Skeleton

CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT



Solutions

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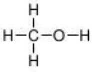
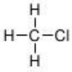
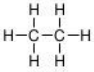
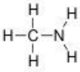
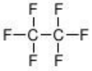
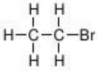
a) 

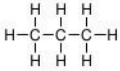
b) 

c) 

d) 

e) 

f) 

g) 

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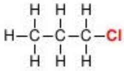

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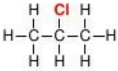

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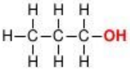
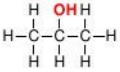
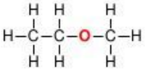
 or  or 

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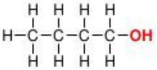
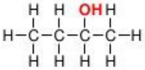
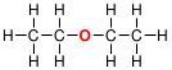
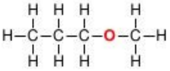
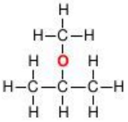
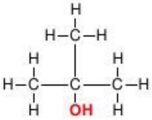


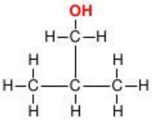












1.5.

a)  b)  c)  d) 

e)  f)  g)  h) 

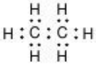
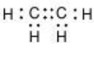
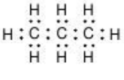
1.6. Both nitrogen and phosphorous belong to column 5A of the periodic table, and therefore, each of these atoms has five valence electrons. In order to achieve an octet, we expect each of these elements to form three bonds.

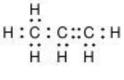
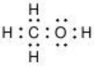
1.7. Aluminum is directly beneath boron on the periodic table (Column 3A), and therefore both elements exhibit three valence electrons.

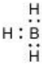
1.8.  resembles boron because it exhibits three valence electrons.

1.9.  resembles nitrogen because it exhibits five valence electrons.

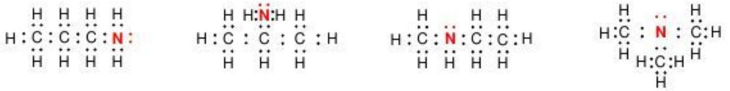
1.10.

a)  b)  c)  d) 

e)  f) 

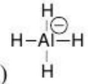
1.11  The central boron atom lacks an octet of electrons.

1.12



In all of the constitutional isomers above, the nitrogen atom has one lone pair.

1.13.

(a)


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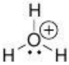

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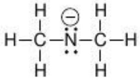

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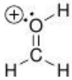

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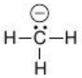

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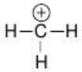

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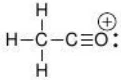
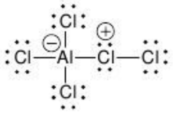


(h)


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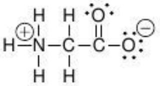
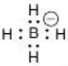
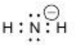


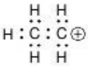
1.14.

a)


Boron has a formal charge

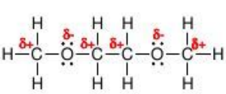
b)


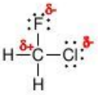
Nitrogen has a formal charge

c)


Carbon has a formal charge

1.15.

(a)


(b)


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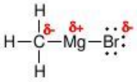

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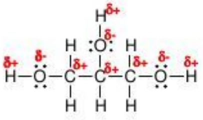
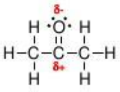
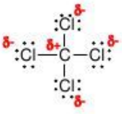
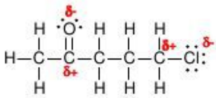


(e)


(f)


1.16.



1.17.

a) $1s^2 2s^2 2p^2$

b) $1s^2 2s^2 2p^4$

c) $1s^2 2s^2 2p^1$

d) $1s^2 2s^2 2p^5$

e) $1s^2 2s^2 2p^6 3s^1$

f) $1s^2 2s^2 2p^6 3s^2 3p^1$

1.18.

a) $\mathbf{1s^2 2s^2 2p^3}$ b) $\mathbf{1s^2 2s^2 2p^1}$ c) $\mathbf{1s^2 2s^2 2p^2}$ d) $\mathbf{1s^2 2s^2 2p^5}$

1.19. The bond angles of an equilateral triangle are 60º, but each bond angle of cyclopropane is supposed to be 109.5º. Therefore, each bond angle is severely strained, causing an increase in energy. This form of strain, called ring strain, will be discussed in Chapter 4. The ring strain associated with a three-membered ring is greater than the ring strain of larger rings, because larger rings do not require bond angles of 60º.

1.20

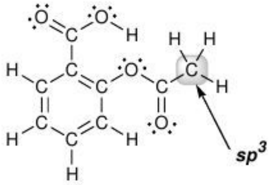
a) The C=O bond of formaldehyde is comprised of one sigma bond and one pi bond.

b) Each C-H bond is formed from the interaction between an sp^2 hybridized orbital from carbon and an *s* orbital from hydrogen.

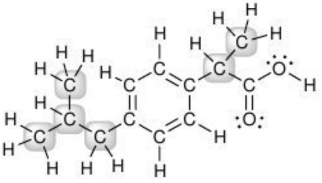
c) The oxygen atom is sp^2 hybridized, so the lone pairs occupy sp^2 hybridized orbitals.

1.21. Rotation of a single bond does not cause a reduction in the extent of orbital overlap, because the orbital overlap occurs on the bond axis. In contrast, rotation of a pi bond results in a reduction in the extent of orbital overlap, because the orbital overlap is NOT on the bond axis.

1.22.

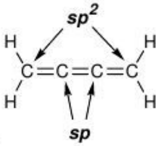


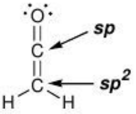
All carbon atoms in this molecule are sp^2 hybridized,
except for the carbon atom highlighted above,
a) which is sp^3 hybridized



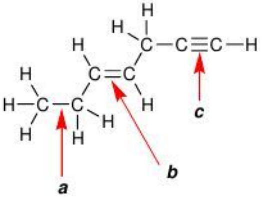
The carbon atoms highlighted above are sp^3 hybridized.
b) All other carbon atoms in this compound are sp^2 hybridized

1.23.

a) 

b) 

1.24.



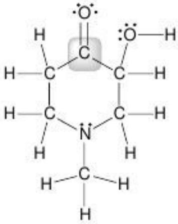
c < b < a

a is the longest bond and c is the shortest bond

1.25.

a) The nitrogen atom has three bonds and one lone pair, and is therefore trigonal pyramidal.
b) The oxygen atom has three bonds and one lone pair, and is therefore trigonal pyramidal.
c) The boron atom has four bonds and no lone pairs, and is therefore tetrahedral.
d) The boron atom has three bonds and no lone pairs, and is therefore trigonal planar.
e) The boron atom has four bonds and no lone pairs, and is therefore tetrahedral.
f) The carbon atom has four bonds and no lone pairs, and is therefore tetrahedral.
g) The carbon atom has four bonds and no lone pairs, and is therefore tetrahedral.
h) The carbon atom has four bonds and no lone pairs, and is therefore tetrahedral.

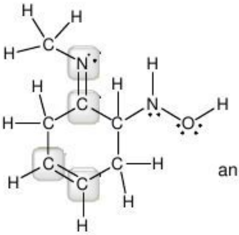
1.26.



(a)

All carbon atoms in this molecule are tetrahedral except for the highlighted carbon atom, which is trigonal planar.

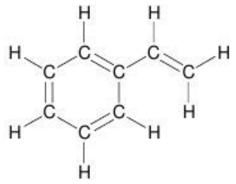
The oxygen atom (of the OH group) has bent geometry, and the nitrogen atom is trigonal pyramidal.



(b)

All carbon atoms are tetrahedral except for the carbon atoms highlighted, which are trigonal planar.

The oxygen atom and the highlighted nitrogen atom have bent geometry, and the other nitrogen atom is trigonal pyramidal.

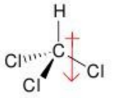
(c) 

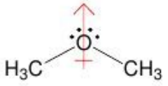
All carbon atoms are trigonal planar.

1.27. The carbon atom of the carbocation has three bonds and no lone pairs, and is therefore trigonal planar. The carbon atom of the carbanion has three bonds and one lone pair, and is therefore trigonal pyramidal.

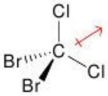
1.28. Every carbon atom in benzene is *sp*^{2} hybridized and trigonal planar. Therefore, the entire molecule is planar (all of the atoms in this molecule occupy the same plane).

1.29.

a) 

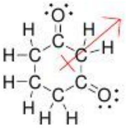
b) 

c) 

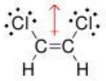
d) 

(e) 

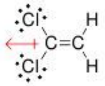
(f) none

(g) 

(h) none

(i) 

(j) none

(k) 

(l) none

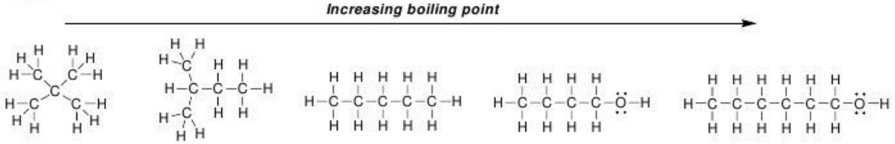
1.30. $CHCl_3$ is expected to have a larger dipole moment than $CBrCl_3$, because the bromine atom in the latter compound serves to nearly cancel out the effects of the other three chlorine atoms (as is the case in CCl_4).

1.31. The carbon atom of CO_2 has a steric number of two, and therefore has linear geometry. As a result, the individual dipole moments of each C=O bond cancel each other completely to give no overall molecular dipole moment. In contrast, the sulfur atom in SO_2 has a steric number of three (because it also has a lone pair, in addition to the two S=O bonds), which means that it has bent geometry. As a result, the individual dipole moments of each S=O bond do NOT cancel each other completely, and the molecule does have a molecular dipole moment.

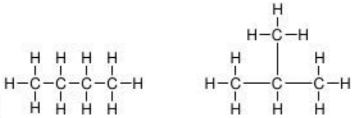
1.32.

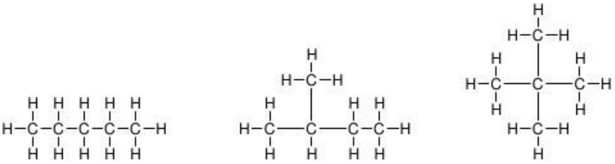
a) The latter, because it is less branched.
b) The latter, because it has more carbon atoms.
c) The latter, because it has an OH bond.
d) The former, because it is less branched.

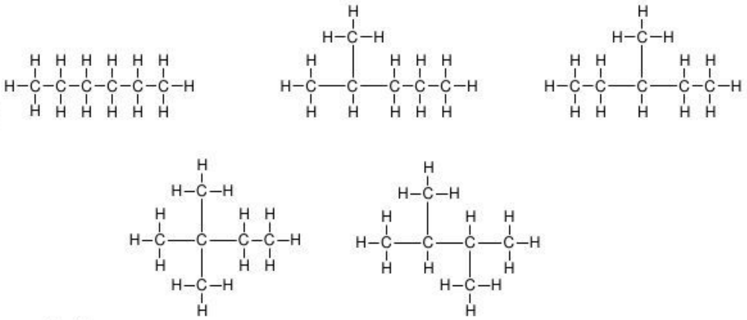
1.33.

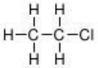


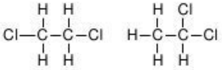
1.34.

a)


b)


c)


d)


e)


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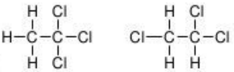
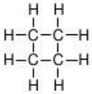
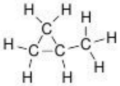


1.35.

a)





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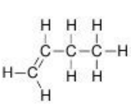
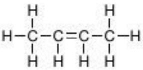
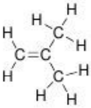
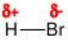






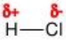
1.36.

a)



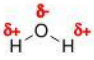
$\overset{\delta+}{H}—\overset{\delta-}{Br}$

b)

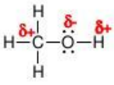


$\overset{\delta+}{H}—\overset{\delta-}{Cl}$

c)



d)



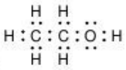
1.37.

a) NaBr, because the difference in electronegativity between Na and Br is greater than the difference in electronegativity between H and Br.

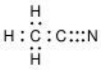
b) FCl, because the disparity in electronegativity between F and Cl is greater than the disparity in electronegativity Br and Cl.

1.38.

a)

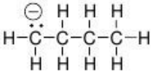


b)



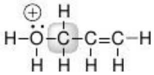
1.39.

a)



All carbon atoms in this molecule are tetrahedral except for the carbon atom bearing the negative charge, which is trigonal pyramidal.

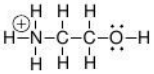
b)



The highlighted carbon atom is tetrahedral, and the other two carbon atoms are trigonal planar.

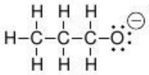
The oxygen atom is trigonal pyramidal.

c)



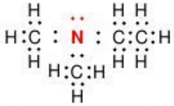
Both carbon atoms and the nitrogen atom are tetrahedral. The oxygen atom is bent.

d)

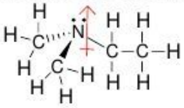


All three carbon atoms in this molecule are tetrahedral. The geometry of the oxygen atom is not relevant because it is only attached to one other group.

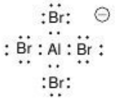
1.40.



The nitrogen atom has trigonal pyramidal geometry. The compound is expected to have the following molecular dipole moment:

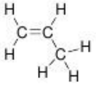


1.41.



The central aluminum has tetrahedral geometry.

1.42.



1.43.

a) No b) Yes c) Yes d) No 5) No 6)Yes

1.44.

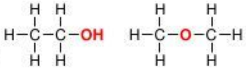
a) Oxygen b) Fluorine c) Carbon d) Nitrogen e) Chlorine

1.45.

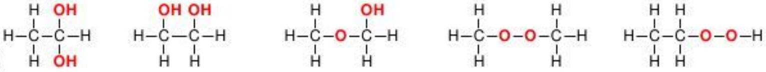
a) ionic
b) Na-O is ionic, and O-H is polar covalent
c) Na-O is ionic, O-C is polar covalent, and each C-H bond is covalent
d) The O-H and C-O bonds are polar covalent, and each C-H bond is covalent
e) The C=O bond is polar covalent, and each C-H bond is covalent

1.46.

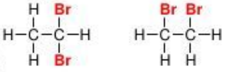
a)



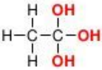
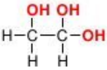
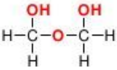
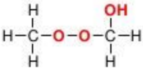
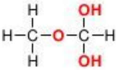
b)



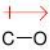
c)

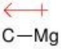


1.47.

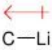






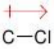
1.48.

a) 

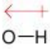
b) 

c) 

d) 

e) 

f) 

g) 

h) 

1.49.

a) All bond angles are approximately 109.5°, except for the C-O-H bond angle which is expected to be less than 109.5° as a result of the repulsion of the lone pairs on the oxygen.
b) All bond angles are approximately 120°.
c) All bond angles are approximately 120°.
d) All bond angles are 180°.
e) All bond angles are approximately 109.5°, except for the C-O-C bond angle which is expected to be less than 109.5° as a result of the repulsion of the lone pairs on the oxygen.
f) All bond angles are approximately 109.5°.
g) All bond angles are approximately 109.5°.
h) All bond angles are approximately 109.5° except for the C-C≡N bond angle which is 180°.

1.50.

a) sp^3, trigonal pyramidal
b) sp^2, trigonal planar
c) sp^2, trigonal planar
d) sp^3, trigonal pyramidal
e) sp^3, trigonal pyramidal

1.51. Sixteen sigma bonds and three pi bonds.

1.52.

a) the second, because it possesses an O-H bond.
b) the second, because it has more carbon atoms.
c) the first, because it has a polar bond.

1.53.

a) yes
b) no (this compound can serve as a hydrogen bond acceptor, but not a hydrogen bond donor)
c) no

d) no

e) no (this compound can serve as a hydrogen bond acceptor, but not a hydrogen bond donor)

f) yes

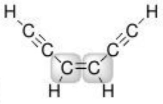
g) no

h) yes

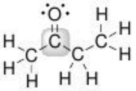
1.54.

a) 3 b) 4 c) 3 d) 2

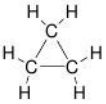
1.55.

a) 

The highlighted carbon atoms are sp^2 hybridized and trigonal planar. The remaining four carbon atoms are sp hybridized and linear.

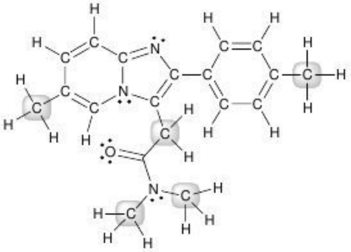
b) 

The highlighted carbon atom is sp^2 hybridized and trigonal planar. The remaining three carbon atoms are sp^3 hybridized and tetrahedral.

c) 

All carbon atoms are sp^3 hybridized and tetrahedral.

1.56.

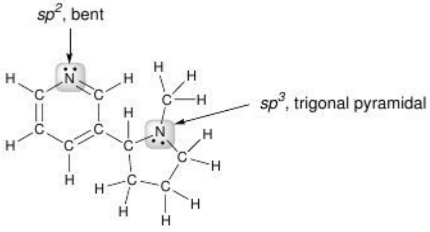


The highlighted carbon atoms are sp^3 hybridized and tetrahedral. The remaining carbon atoms are sp^2 hybridized and trigonal planar.

1.57.

a) oxygen b) fluorine c) carbon

1.58.

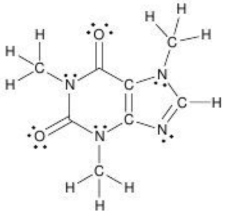


sp^2, bent

sp^3, trigonal pyramidal

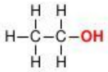
nicotine

1.59.

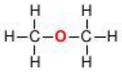


caffeine

1.60. The two isomers are:



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$$

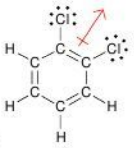


$$\mathrm{H-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-H}$$

The first will have a higher boiling point because it possesses an OH group which can form hydrogen bonds.

1.61.

a)



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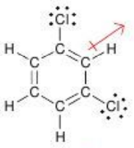

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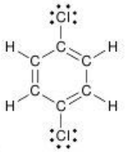
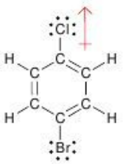


there is no molecular dipole moment

d)



Cl is more electronegative than Br

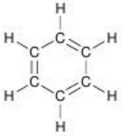
1.62. The third chlorine atom in chloroform partially cancels the effects of the other two chlorine atoms, thereby reducing the molecular dipole moment relative to methylene chloride.

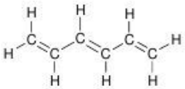
1.63.

a) Compound A and Compound B
b) Compound B
c) Compound B
d) Compound C
e) Compound C
f) Compound A
g) Compound B
h) Compound A is capable of hydrogen bonding

1.64.

a)





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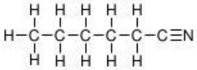

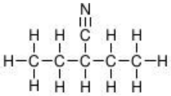

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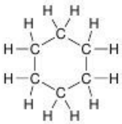
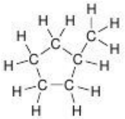
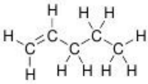


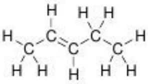


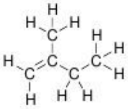
d)

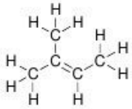
N≡C–C≡C–C≡C–C≡N   F–C≡C–C≡C–C≡C–F

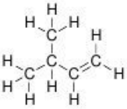
1.65.



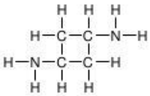


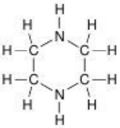




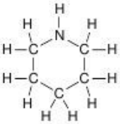


1.66.





1.67.



Chapter 2
Molecular Representations

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 2. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- In **bond-line structures**, _______atoms and most ________ atoms are not drawn.
- A ________________ is a characteristic group of atoms/bonds that show a predictable behavior.
- When a carbon atom bears either a positive charge or a negative charge, it will have ___________, rather than four, bonds.
- In bond-line structures, a **wedge** represents a group coming ______ the page, while a **dash** represents a group _________ the page.
- ___________ **arrows** are tools for drawing resonance structures.
- When drawing curved arrows for resonance structures, avoid breaking a _______ bond and never exceed _____________ for second-row elements.
- There are three rules for identifying significant resonance structures:
    1. Minimize ____________.
    2. Electronegative atoms can bear a positive charge, but only if they possess an ________ of electrons.
    3. Avoid drawing a resonance structure in which two carbon atoms bear _____________ charges.
- A ______________ lone pair participates in resonance and is said to occupy a ____ orbital.
- A _____________ lone pair does not participate in resonance.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 2. The answers appear in the section entitled *SkillBuilder Review*.

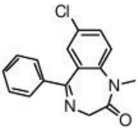
SkillBuilder 2.1 Converting Between Different Drawing Styles

DRAW THE LEWIS STRUCTURE OF THE FOLLOWING COMPOUND

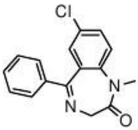
$(CH_3)_3COCH_3$ →

SkillBuilder 2.2 Reading Bond-Line Structures

CIRCLE ALL CARBON ATOMS IN THE COMPOUND BELOW

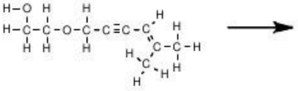


DRAW ALL HYDROGEN ATOMS IN THE COMPOUND BELOW



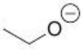
SkillBuilder 2.3 Drawing Bond-Line Structures

DRAW A BOND-LINE DRAWING OF THE FOLLOWING COMPOUND:

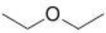


SkillBuilder 2.4 Identifying Lone Pairs on Oxygen Atoms

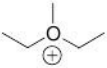
AN OXYGEN ATOM WITH A NEGATIVE CHARGE WILL HAVE ____ LONE PAIR(S)



AN OXYGEN ATOM WITH NO FORMAL CHARGE WILL HAVE ____ LONE PAIR(S)

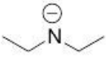


AN OXYGEN ATOM WITH A POSITIVE CHARGE WILL HAVE ____ LONE PAIR(S)

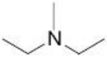


SkillBuilder 2.5 Identifying Lone Pairs on Nitrogen Atoms

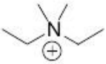
A NITROGEN ATOM WITH A NEGATIVE CHARGE WILL HAVE ____ LONE PAIR(S)



A NITROGEN ATOM WITH NO FORMAL CHARGE WILL HAVE ____ LONE PAIR(S)



A NITROGEN ATOM WITH A POSITIVE CHARGE WILL HAVE ____ LONE PAIR(S)



SkillBuilder 2.6 Identifying Valid Resonance Arrows

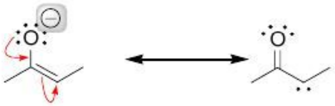
RULE 1: THE TAIL OF A CURVED ARROW CANNOT BE PLACED ON A ______________

RULE 2: THE HEAD OF A CURVED ARROW CANNOT RESULT IN ____________________

____

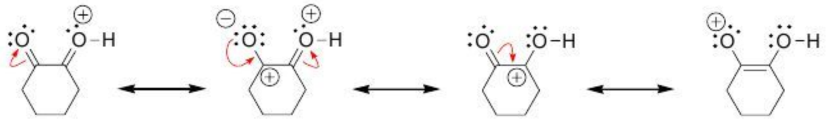
SkillBuilder 2.7 Assigning Formal Charges in Resonance Structures

INDICATE THE LOCATION OF THE NEGATIVE CHARGE IN THE SECOND RESONANCE STRUCTURE BELOW



SkillBuilder 2.8 Drawing Significant Resonance Structures

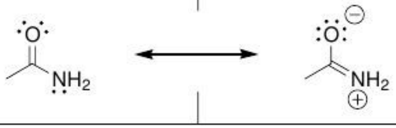
IDENTIFY WHICH RESONANCE STRUCTURES BELOW ARE SIGNIFICANT AND WHICH ARE INSIGNIFICANT



SkillBuilder 2.9 Identifying Localized and Delocalized Lone Pairs

IDENTIFY WHETHER THE LONE PAIR ON THE NITROGEN ATOM BELOW IS DELOCALIZED

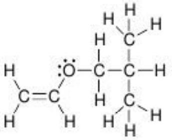
IDENTIFY THE HYBRIDIZATION STATE OF THE NITROGEN ATOM



Solutions

2.1.

a)



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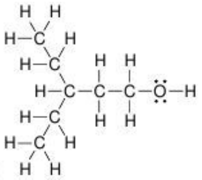

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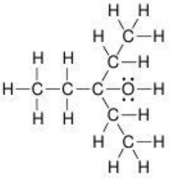

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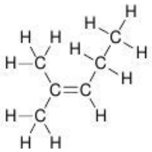

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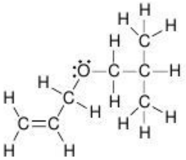

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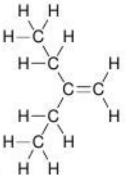

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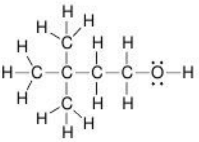

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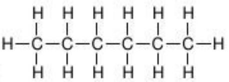
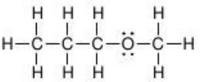
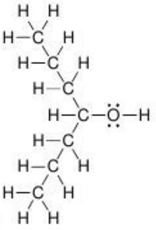


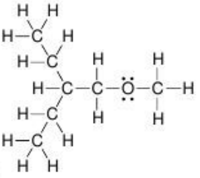
i)



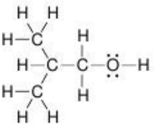
j)



k)



l)

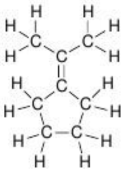


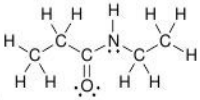
2.2 $(CH_3)_3C\ddot{\underset{\cdot\cdot}{O}}CH_3$ and $(CH_3)_2CH\ddot{\underset{\cdot\cdot}{O}}CH_2CH_3$

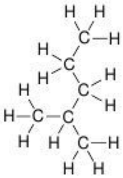
2.3 Six

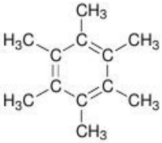
2.4 $H_2C{=}CHCH_3$

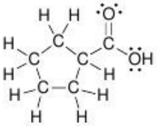
2.5.

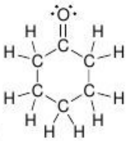
a) 

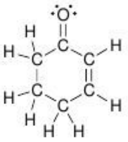
b) 

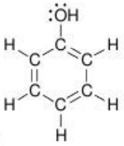
c) 

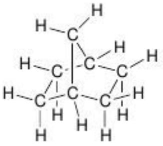
d) 

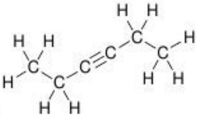
e) 

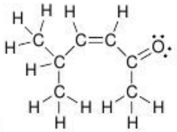
f) 

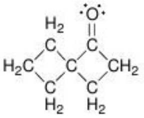
g) 

h) 

i) 

j) 

k) 

l) 

2.6

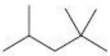
a) decrease (7→6) b) no change (8→8)

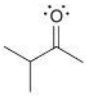
c) no change (8→8) d) increase (5→7)

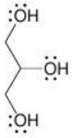
2.7

a) increase (12→14) b) decrease (8→6)

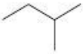
2.8.

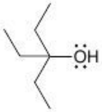
a) 

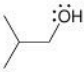
b) 

c) 

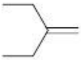
d) 

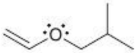
e) 

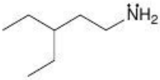
f) 

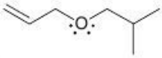
g) 

h) 

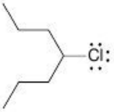
i) 

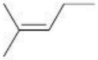
j) 

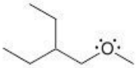
k) 

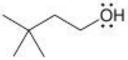
l) 

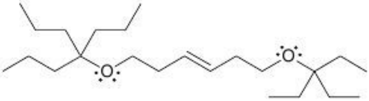
m) 

n) 

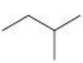
o) 

p) 

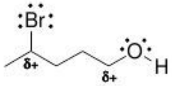
q) 

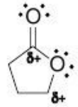
r) 

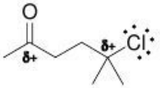
2.9.



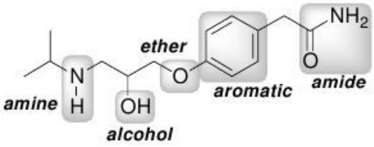
2.10.

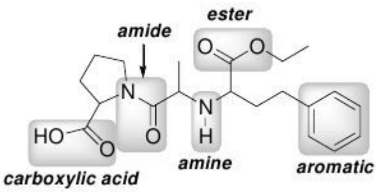
a) 

b) 

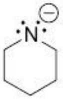
c) 

2.11.

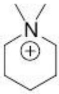




2.12.

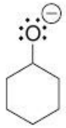
a) 

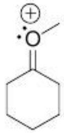
b) No charge

c) 

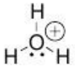
d) No charge

2.13.

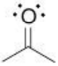
a)


b)


c) No charge

d)


2.14.

a)


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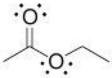

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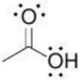

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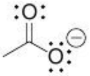

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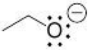

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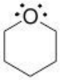
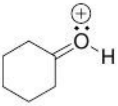
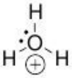
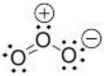


g)


h)


i)


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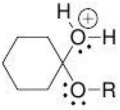
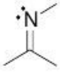


2.15. There are no hydrogen atoms attached to the central carbon atom. The carbon atom has four valence electron. Two valence electrons are being used to form bonds, and the remaining two electrons are a lone pair. This carbon atom is using the appropriate number of valence electrons.

2.16.

a)


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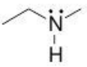

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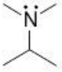
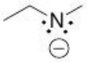
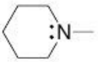
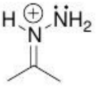


d) no lone pairs

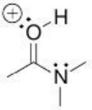
e)


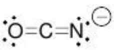
f)


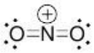
g) no lone pairs

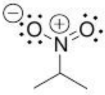
h)


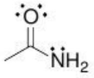
2.17.

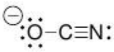
a)


b)


c)


d)


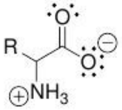
e)


f)


2.18.

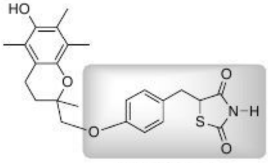
a) one b) zero c) one d) five

2.19 Five lone pairs:

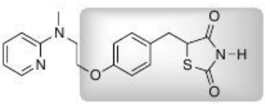


2.20

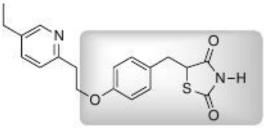
a)



Troglitazone



Rosiglitazone



Pioglitazone

b) Yes, it contains the likely pharmacophore highlighted above.

2.21

a) Violates second rule by giving a fifth bond to a nitrogen atom.

b) Does not violate either rule.

c) Violates second rule by giving five bonds to a carbon atom.

d) Violates second rule by giving three bonds and two lone pairs to an oxygen atom.

e) Violates second rule by giving five bonds to a carbon atom.

f) Violates second rule by giving five bonds to a carbon atom.

g) Violates second rule by giving five bonds to a carbon atom, and violates second rule by breaking a single bond.

h) Violates second rule by giving five bonds to a carbon atom, and violates second rule by breaking a single bond.

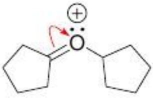
i) Does not violate either rule.

j) Does not violate either rule.

k) Violates second rule by giving five bonds to a carbon atom.

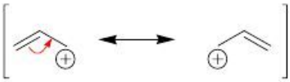
l) Violates second rule by giving five bonds to a carbon atom.

2.22.

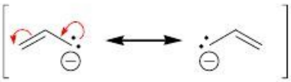


2.23.

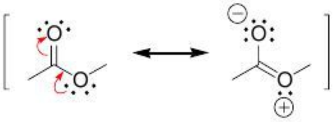
a)



b)



c)



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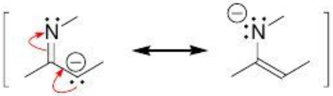
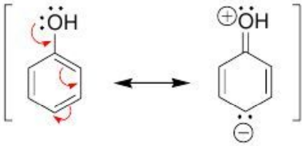
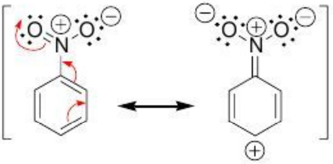


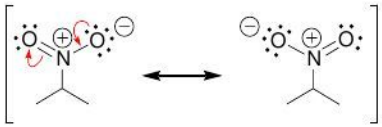
e)



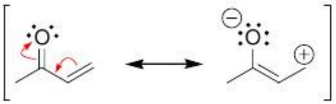
f)



g)

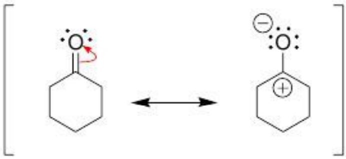


h)

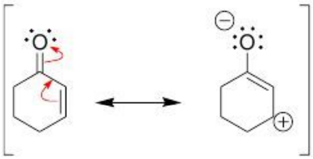


2.24.

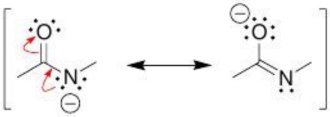
a)



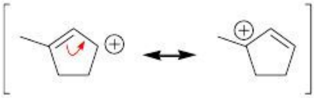
b)



c)

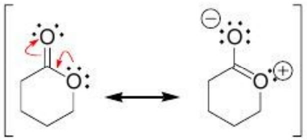


b)



2.25.

a)



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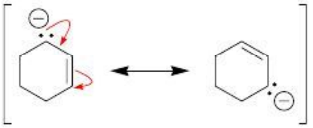

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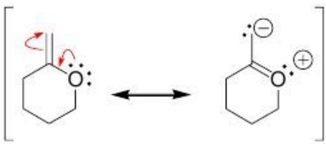

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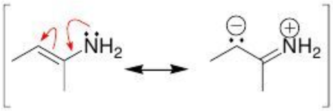
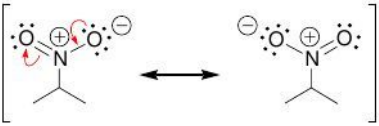


e)



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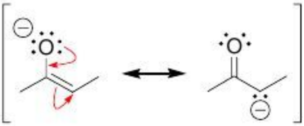

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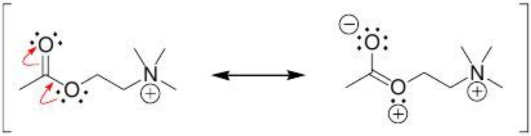
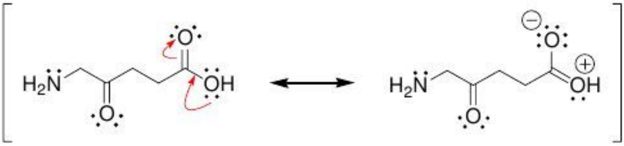
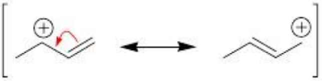


h)



2.26.

a)



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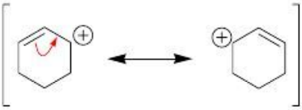

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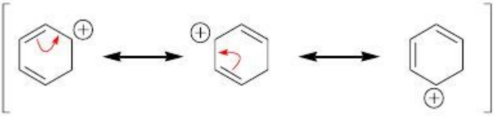

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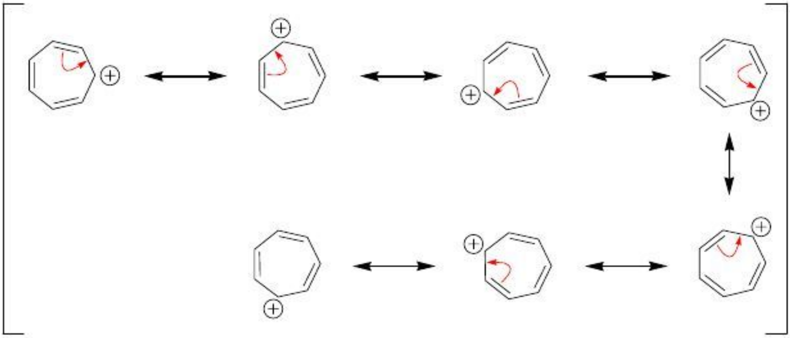
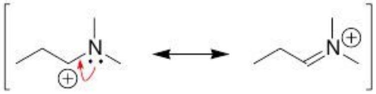
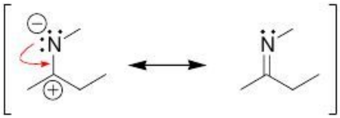
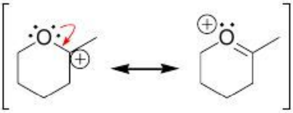


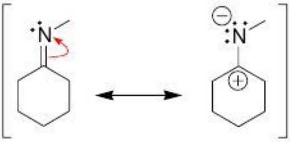
2.27.

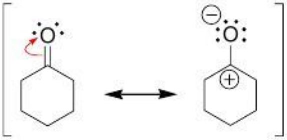
a) 

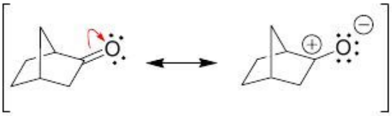
b) 

c) 

2.28.

a) 

b) 

c) 

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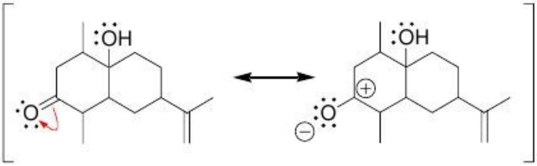
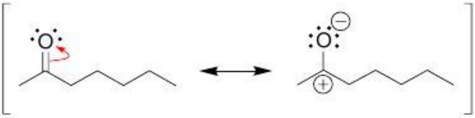


2.30.



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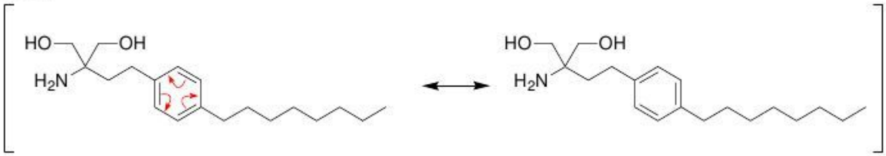
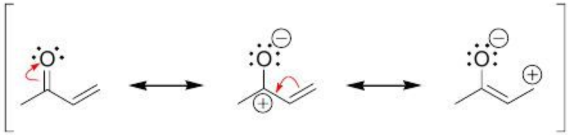


2.32.

a)



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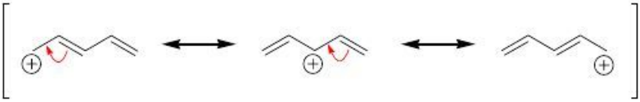

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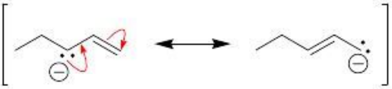
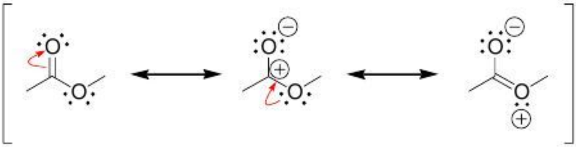
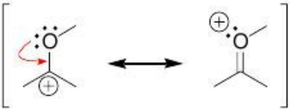


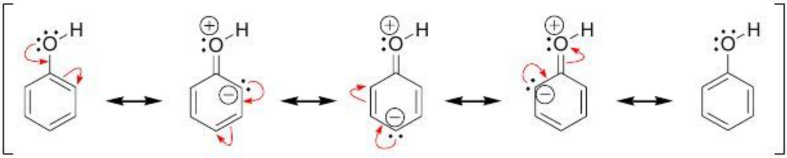
d)



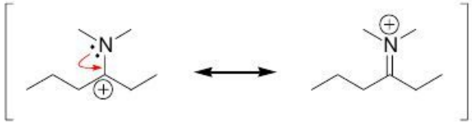
e)



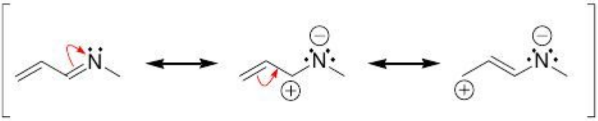
f)



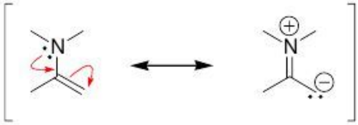
g)



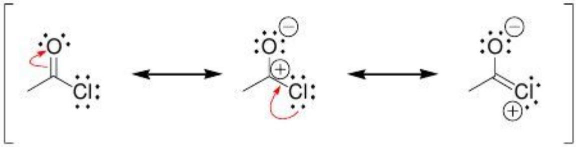
h)



i)

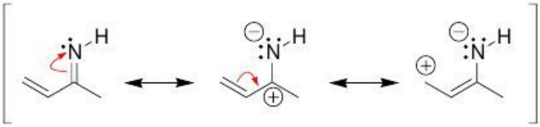


j)



2.33.

a)



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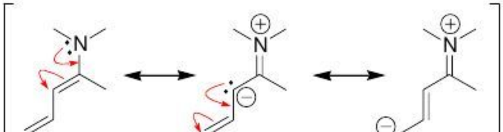

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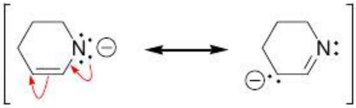

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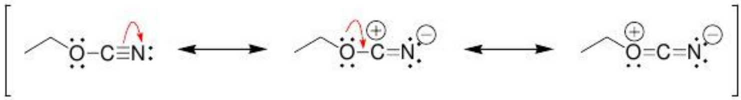
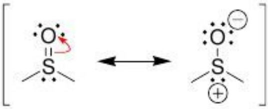
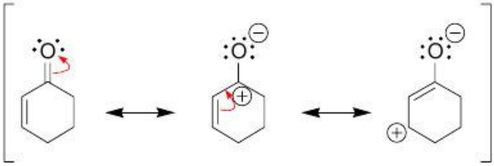


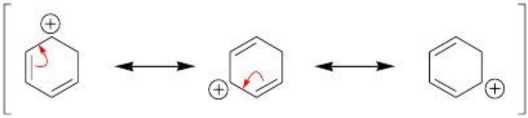


e)

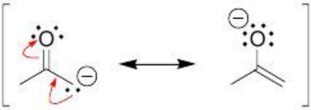
f)



g)



h)



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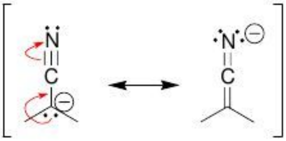
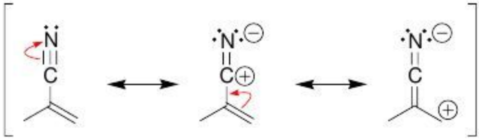


j)



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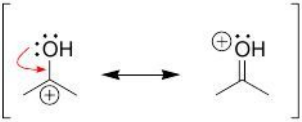
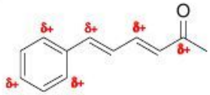
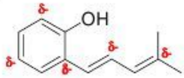


l)

2.34.

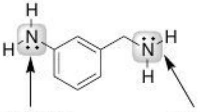


2.35.



2.36.

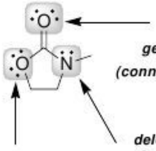
a)



delocalized
sp^2 hybridized
trigonal planar

localized
sp^3 hybridized
trigonal pyramidal

b)

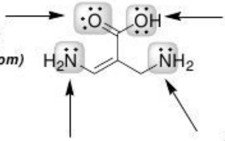


localized
sp^2 hybridized
geometry not relevant
(connected to only one atom)

One of these lone pairs is delocalized. The oxygen atom is therefore sp^2 hybridized and has bent geometry.

delocalized
sp^2 hybridized
trigonal planar

c)



localized
sp^2 hybridized
geometry not relevant
(connected to only one atom)

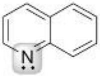
One of these lone pairs is delocalized. The oxygen atom is therefore sp^2 hybridized and has bent geometry.

delocalized
sp^2 hybridized
trigonal planar

localized
sp^3 hybridized
trigonal pyramidal

d)

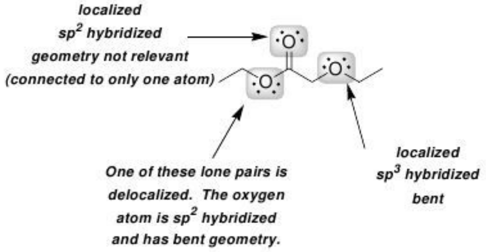
localized
sp^2 hybridized
bent



e)

delocalized
sp^2 hybridized
trigonal planar

f)



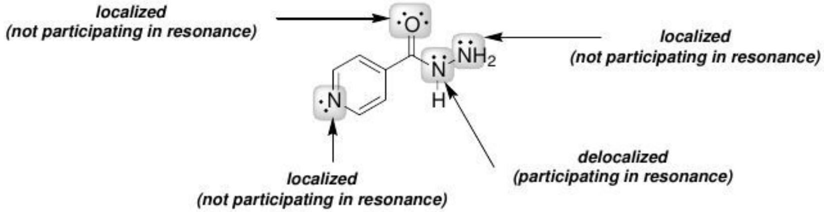
localized
sp^2 hybridized
geometry not relevant
(connected to only one atom)

One of these lone pairs is delocalized. The oxygen atom is sp^2 hybridized and has bent geometry.

localized
sp^3 hybridized
bent

2.37. Both lone pairs are localized and, therefore, both are expected to be reactive.

2.38.



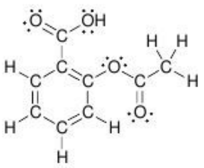
localized
(not participating in resonance)

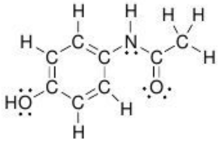
localized
(not participating in resonance)

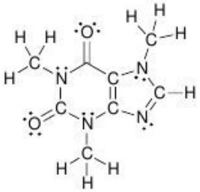
localized
(not participating in resonance)

delocalized
(participating in resonance)

2.39.

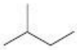




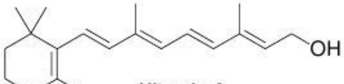


2.40.

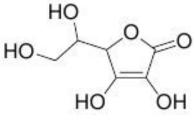
2.41.



2.42.



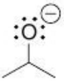
Vitamin A

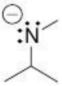


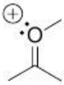
Vitamin C

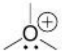
2.43. Twelve (each oxygen atom has two lone pairs)

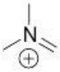
2.44.



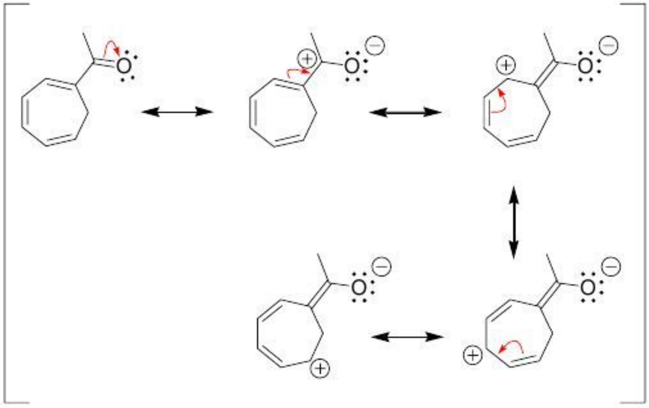








2.45.

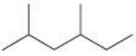


2.46.

a)

C_4H_{10}

C_6H_{14}



C_8H_{18}

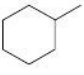
$C_{12}H_{26}$

In each of the compounds above, the number of hydrogen atoms is equal to two times the number of carbon atoms, plus two.

b)

C_4H_8

C_7H_{14}

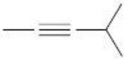


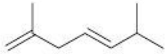
C_7H_{14}

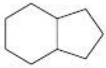
$C_{12}H_{24}$

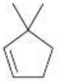
In each of the compounds above, the number of hydrogen atoms is two times the number of carbon atoms.

c)


C_6H_{10}


C_9H_{16}

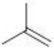

C_9H_{16}


C_7H_{12}

In each of the compounds above, the number of hydrogen atoms is two times the number carbon atoms, minus two.

d) A compound with molecular formula $C_{24}H_{48}$ must have either one double bond or one ring. It cannot have a triple bond, but it may have a double bond.

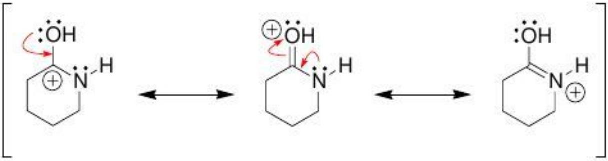
e)



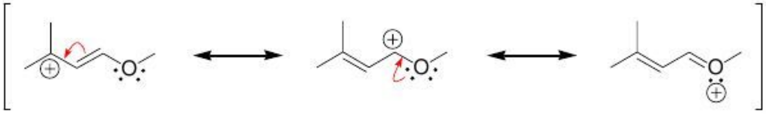
2.47.

a) an sp^2 hybridized atomic orbital
b) a p orbital
c) a p orbital

2.48.

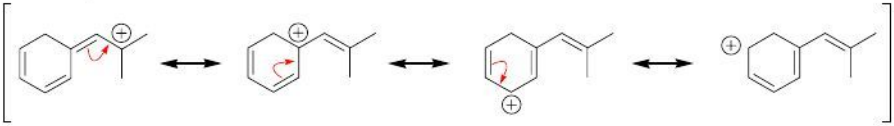


a)



b)

c)



2.49.

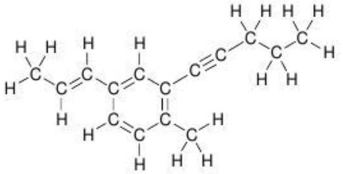
a) $(CH_3)_3CCH_2CH_2CH(CH_3)_2$
b) $(CH_3)_2CHCH_2CH_2CH_2OH$
c) $CH_3CH_2CH{=}C(CH_2CH_3)_2$

2.50.

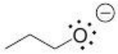
a) C_9H_{20}
b) $C_6H_{14}O$
c) C_8H_{16}

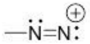
2.51.
(d) is not a valid resonance structure, because it violates the octet rule. The nitrogen atom has five bonds in this drawing, which is not possible, because the nitrogen atom only has four orbitals with which it can form bonds.

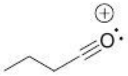
2.52. 15 carbon atoms and 18 hydrogen atoms:

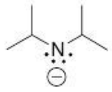


2.53.

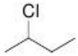
a) 

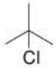
b) 

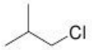
c) 

d) 

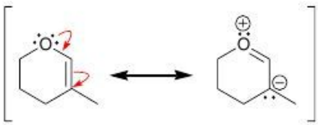
2.54.

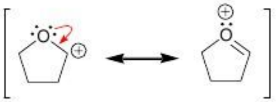


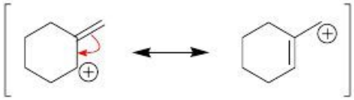


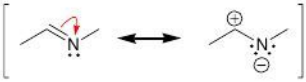


2.55.

a) 

b) 

c) 

d) 

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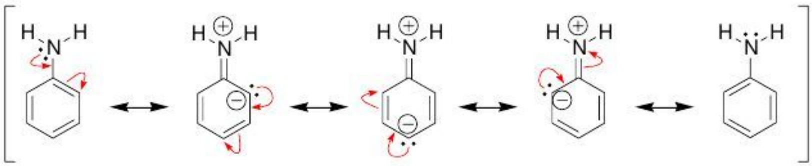

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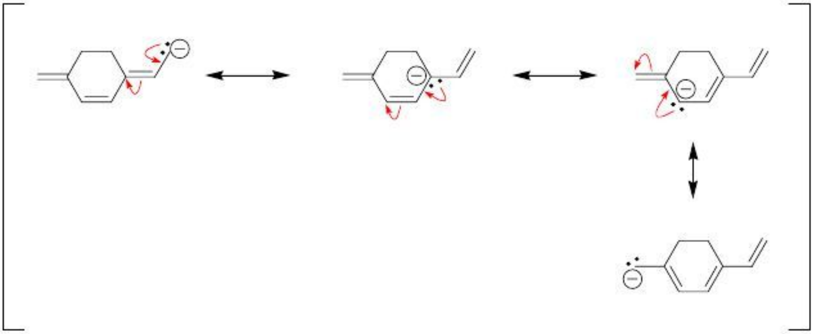

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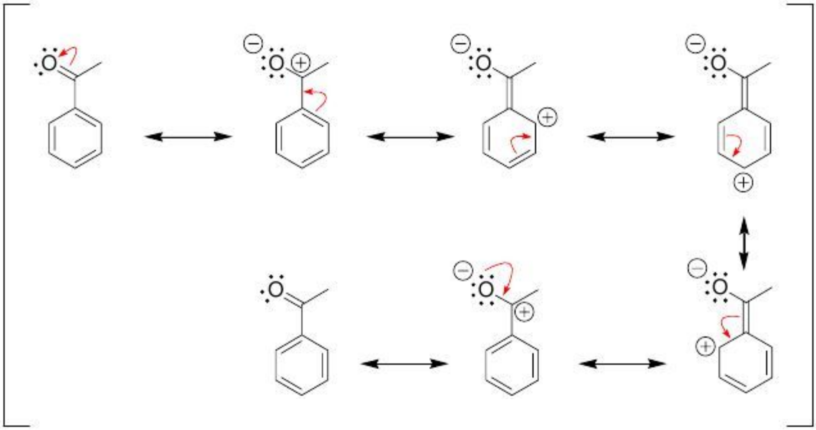
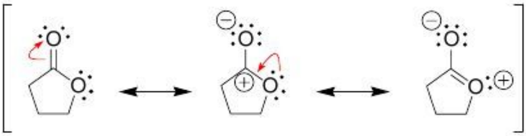
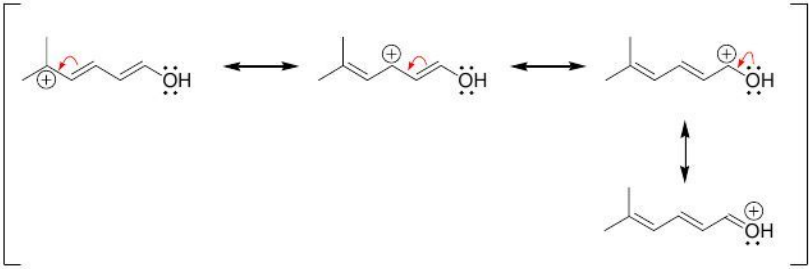




h)

i)



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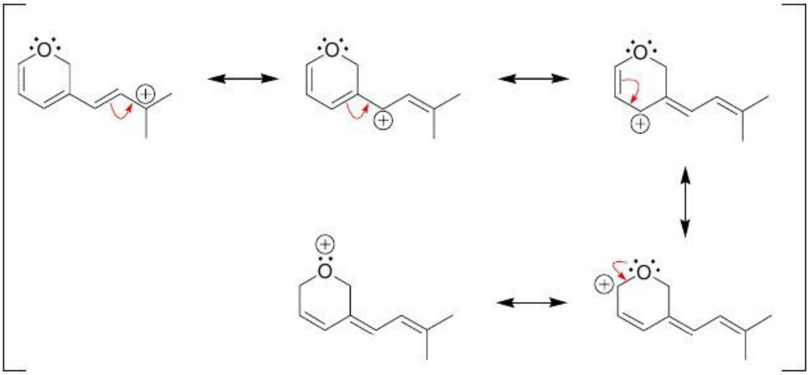


2.56. These structures do not differ in their connectivity of atoms. They differ only in the placement of electrons, and are therefore resonance structures.

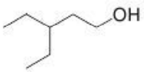
2.57.

a) constitutional isomers
b) same compound
c) different compounds that are not isomeric
d) constitutional isomers

2.58.

a)

b)



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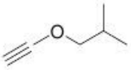
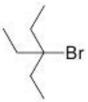


d)

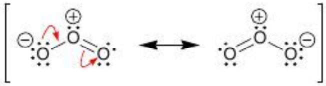
e)



f)

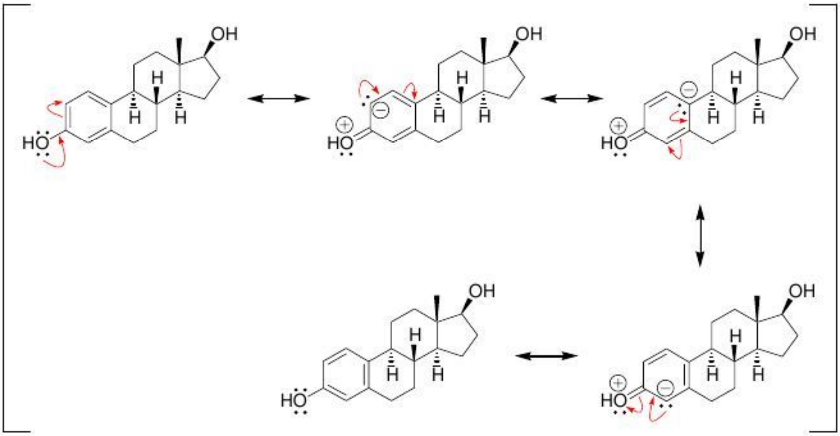
2.59. The nitronium ion does *not* have any significant resonance structures because any attempts to draw a resonance structure will either 1) exceed an octet for the nitrogen atom or 2) generate a nitrogen atom with less than an octet of electrons, or 3) generate a structure with three charges. The first of these would not be a valid resonance structure, and the latter two would not give significant resonance structures.

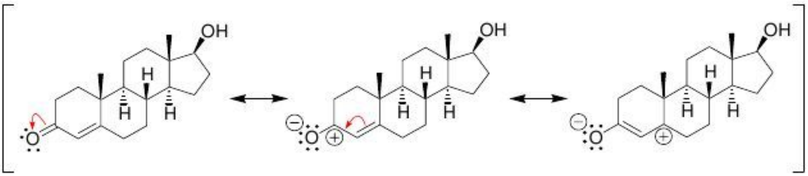
2.60.



2.61. Both nitrogen atoms are sp^2 hybridized and trigonal planar, because in each case, the lone pair participates in resonance.

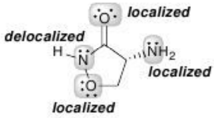
2.62.



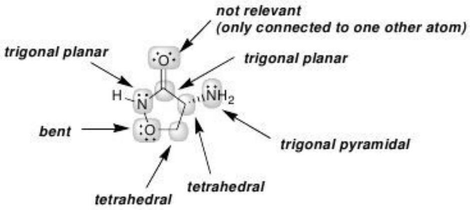


2.63.

a) The molecular formula is $C_3H_6N_2O_2$
b) There are two *sp*^{3} hybridized carbon atoms
c) There is one *sp*^{2} hybridized carbon atom
d) There are no *sp* hybridized carbon atoms
e) There are six lone pairs (each nitrogen atom has one lone pair and each oxygen atom has two lone pairs)
f)



g)



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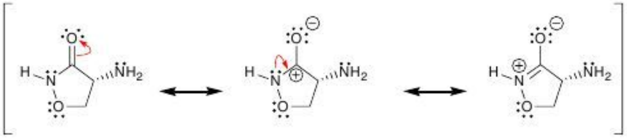
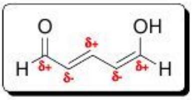
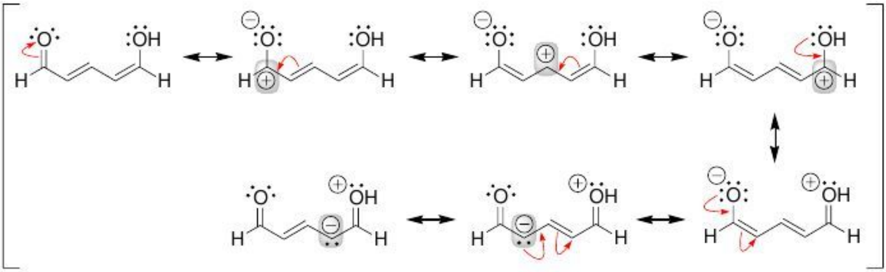


2.64.

a) The molecular formula is $C_{16}H_{21}NO_2$
b) There are nine *sp*^{3} hybridized carbon atoms
c) There is seven *sp*^{2} hybridized carbon atoms
d) There are no *sp* hybridized carbon atoms
e) There are five lone pairs (the nitrogen atom has one lone pair and each oxygen atom has two lone pairs)
f) The lone pairs on the oxygen of the C=O bond are localized. One of the lone pairs on the other oxygen atom is delocalized. The lone pair on the nitrogen atom is delocalized.
g) All *sp*^{2} hybridized carbon atoms are trigonal planar. All *sp*^{3} hybridized carbon atoms are tetrahedral. The nitrogen atom is trigonal planar. The oxygen atom of the C=O bond does not have a geometry because it is connected to only one other atom, and the other oxygen atom has bent geometry.

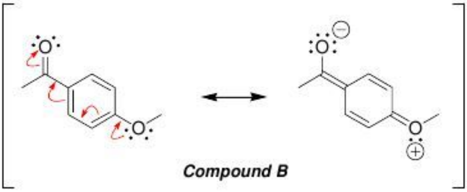
2.65.





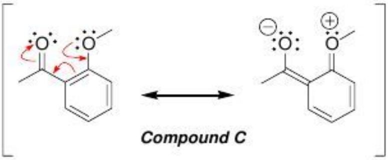
2.66.

a) Compound B has one additional resonance structure that Compound A lacks, because of the relative positions of the two groups on the aromatic ring. Specifically, Compound B has a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge:



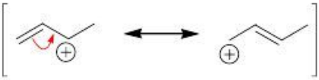
Compound A does *not* have a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge. That is, Compound A has fewer resonance structures than Compound B. Accordingly, Compound B has greater resonance stabilization.

b) Compound C is expected to have resonance stabilization similar to that of Compound B, because Compound C also has a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge:

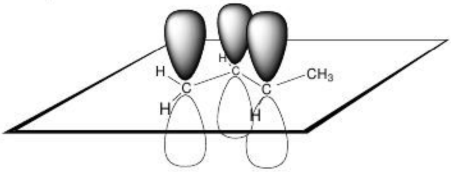


2.67.

The single bond mentioned in this problem has some double bond character, as a result of resonance:



Each of the carbon atoms of this single bond uses an atomic p orbital to form a conduit (as described in Section 2.7):



Rotation about this single bond will destroy the overlap of the p orbitals, thereby destroying the resonance stabilization. This single bond therefore exhibits a large barrier to rotation.

Chapter 3
Acids and Bases

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 3. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- A **Brønsted-Lowry acid** is a proton ________, while a **Brønsted-Lowry base** is a proton ________.
- The mechanism of **proton transfer** always involves at least _____ curved arrows.
- A strong acid has a _____ pK_a, while a weak acid has a _____ pK_a.
- There are four factors to consider when comparing the ___________ of conjugate bases.
- The equilibrium of an acid-base reaction always favors the more ____________ negative charge.
- A **Lewis acid** is an electron ___________, while a **Lewis base** is an electron ____________.

Review of Skills

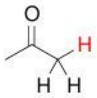
Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 3. The answers appear in the section entitled *SkillBuilder Review*.

SkillBuilder 3.1 Drawing the Mechanism of a Proton Transfer

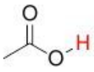
DRAW THE CURVED ARROWS FOR THE FOLLOWING ACID-BASE REACTION

SkillBuilder 3.2 Using pK_a Values to Compare Acids

CIRCLE THE COMPOUND BELOW THAT IS MORE ACIDIC



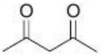
pKa = 19.2



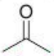
pKa = 4.75

SkillBuilder 3.3 Using pK_a Values to Compare Basicity

COMPARE THE FOLLOWING pK_a VALUES:

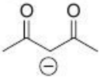


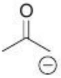
pKa = 9



pKa = 19

AND CIRCLE THE STRONGER BASE BELOW



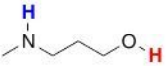


SkillBuilder 3.4 Using pK_a Values to Predict the Position of Equilibrium

CIRCLE THE SIDE OF THE EQUILIBRIUM THAT IS FAVORED:

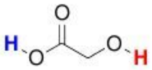
SkillBuilder 3.5 Assessing Relative Stability. Factor #1: Atom

COMPARE THE TWO PROTONS SHOWN IN THE FOLLOWING COMPOUND, AND CIRCLE THE ONE THAT IS MORE ACIDIC. USE THE EXTRA SPACE TO DRAW THE TWO POSSIBLE CONJUGATE BASES.



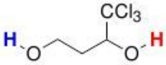
SkillBuilder 3.6 Assessing Relative Stability. Factor #2: Resonance

COMPARE THE TWO PROTONS SHOWN IN THE FOLLOWING COMPOUND, AND CIRCLE THE ONE THAT IS MORE ACIDIC. USE THE EXTRA SPACE TO DRAW THE TWO POSSIBLE CONJUGATE BASES.



SkillBuilder 3.7 Assessing Relative Stability. Factor #3: Induction

COMPARE THE TWO PROTONS SHOWN IN THE FOLLOWING COMPOUND, AND CIRCLE THE ONE THAT IS MORE ACIDIC. USE THE EXTRA SPACE TO DRAW THE TWO POSSIBLE CONJUGATE BASES.



SkillBuilder 3.8 Assessing Relative Stability. Factor #4: Orbital

COMPARE THE TWO PROTONS SHOWN IN THE FOLLOWING COMPOUND, AND CIRCLE THE ONE THAT IS MORE ACIDIC. USE THE EXTRA SPACE TO DRAW THE TWO POSSIBLE CONJUGATE BASES.

SkillBuilder 3.9 Assessing Relative Stability. Using all Four Factors

COMPARE THE TWO PROTONS SHOWN IN THE FOLLOWING COMPOUND, AND CIRCLE THE ONE THAT IS MORE ACIDIC. USE THE EXTRA SPACE TO DRAW THE TWO POSSIBLE CONJUGATE BASES.

SkillBuilder 3.10 Predicting the Position of Equilibrium Without the Use of pK_a Values

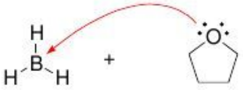
CIRCLE THE SIDE OF THE EQUILIBRIUM THAT IS FAVORED:

SkillBuilder 3.11 Choosing the appropriate reagent for a proton transfer reaction

DETERMINE WHETHER WATER IS A SUITABLE PROTON SOURCE TO PROTONATE THE ACETATE ION, AS SHOWN BELOW:

SkillBuilder 3.12 Identifying Lewis Acids and Lewis Bases

IDENTIFY THE LEWIS ACID
AND THE LEWIS BASE
IN THE FOLLOWING REACTION:



Solutions

3.1.

a)

b)

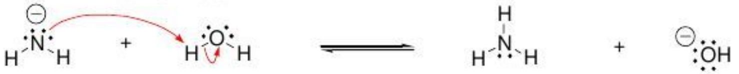
c)

d)

3.2.

a) There is only one arrow, and it is going in the wrong direction. The tail has been placed on the hydrogen atom, and this is incorrect. Curved arrows do not show the motion of atoms, but the motion of electrons. The tail of this curved arrow should be on the lone pair of the nitrogen atom, and the head of the curved arrow should be on the proton. In addition, a second curved arrow is also required. It should look like this:

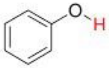
b) The first arrow (from the lone pair of nitrogen to the proton) is correct, but the second curved arrow is not correct. Specifically, the tail is placed on the proton, and instead should be placed on the bond between the proton and the oxygen atom. This bond must be drawn in order to properly place the second curved arrow:

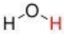


c) The second curved arrow is missing:

3.3.

3.4.

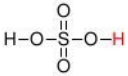
a) 

b) 

c) $H-C\equiv C-H$

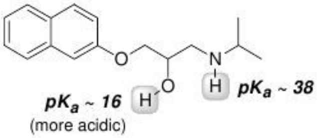
d) $Cl-H$

e) $H-C\equiv C-H$

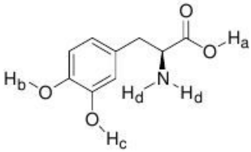
f) 

$H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H$

3.5.

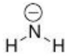


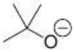
3.6.

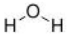


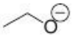
$H_d < H_b \sim H_c < H_a$

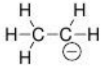
3.7.

a) 

b) 

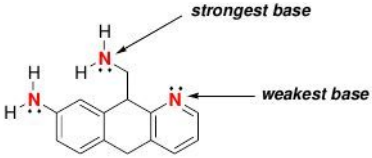
c) 

d) 

e) 

f) 

3.8.



3.9.

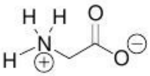
a) A lone pair on a nitrogen atom will be more basic than a lone pair on an oxygen atom.
b) The lone pair on the nitrogen atom is thirteen orders of magnitude more basic than the lone pair on the oxygen atom.

3.10.

a) left side
b) right side
c) right side
d) right side

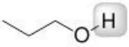
3.11. The equilibrium does not favor deprotonation of acetylene by hydroxide, because water is more acidic than acetylene. The equilibrium will favor the weaker acid (acetylene). A suitable base would be one whose conjugate acid is less acidic than acetylene. For example, H_2N^- would be a suitable base, because ammonia (NH_3) is less acidic than acetylene.

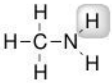
3.12.



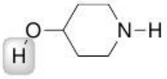
glycine

3.13.

a) 

b) 

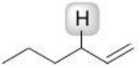
c) 

d) 

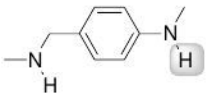
3.14. A proton connected to a sulfur atom will be more acidic than a proton connected to an oxygen atom, which will be more acidic than a proton connected to a nitrogen atom. Therefore, the proton on the sulfur atom will definitely be more acidic than the proton on the oxygen atom.

3.15.

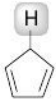
a)



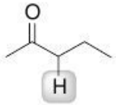
b)



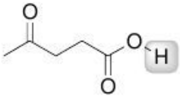
c)



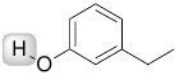
d)



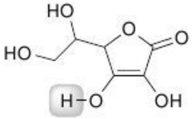
e)



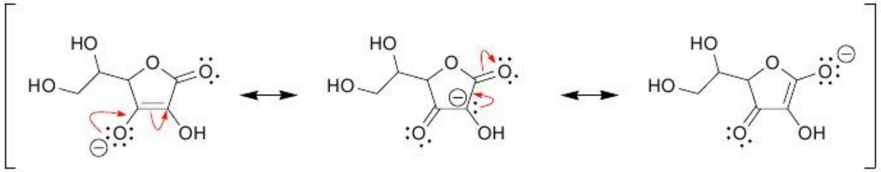
f)



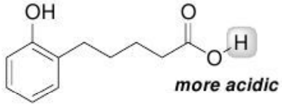
3.16.



The proton highlighted above is the most acidic proton in the structure, because deprotonation at that location generates a resonance-stabilized anion, in which the negative charge is spread over two oxygen atoms and one carbon atom:

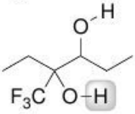


3.17.

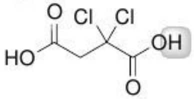


3.18.

a) The highlighted proton is more acidic. When this location is deprotonated, the conjugate base that is formed is stabilized by the electron-withdrawing effects of the electronegative fluorine atoms:

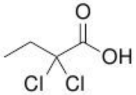


b) The highlighted proton is more acidic. When this location is deprotonated, the conjugate base that is formed is stabilized by the electron-withdrawing effects of the electronegative chlorine atoms, which are closer to this proton than the other proton:

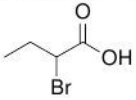


3.19.

a) The compound with two chlorine atoms is more acidic, because of the electron-withdrawing effects of the additional chlorine atom, which help stabilize the conjugate base that is formed when the proton is removed:

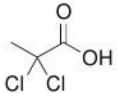


b) The more acidic compound is the one in which the bromine atom is closer to the acidic proton. The electron-withdrawing effects of the bromine atom stabilize the conjugate base that is formed when the proton is removed:

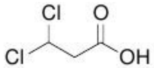


3.20.

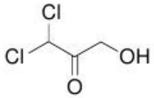
a) In the compound below, one of the chlorine atoms has been moved closer to the acidic proton, which further stabilizes the conjugate base that is formed when the proton is removed:



b) In the compound below, one of the chlorine atoms has been moved farther away from the acidic proton, which destabilizes the conjugate base that is formed when the proton is removed:



c) The compound below is less acidic than the compounds above, because this compound is not a carboxylic acid. That is, the conjugate base of this compound is NOT resonance stabilized:

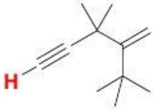


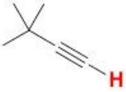
3.21. Both protons are the same distance from the fluorine atom, and both protons are the same distance from the chlorine atom. Accordingly, these protons are expected to be of equivalent acidity.

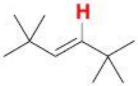
3.22. The compound below (acetylene) is more acidic. The conjugate base of this compound has a negative charge associated with a lone pair in an *sp* hybridized orbital, which is more stable than a negative charge associated with a lone pair in an sp^2 hybridized orbital.

$$H-C\equiv C-H$$

3.23.

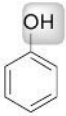


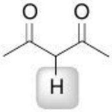


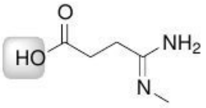


3.24. Most imines will have a pK_a below 35, because imines are expected to be more acidic than amines. This prediction derives from a comparison of the conjugate bases of amines and imines. The former has a negative charge in an sp^3 hybridized orbital, while the latter has a negative charge in an sp^2 hybridized orbital. The latter is expected to be more stable, and therefore, imines are expected to be more acidic.

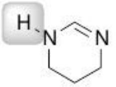
3.25.

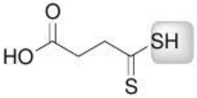
a) 

b) 

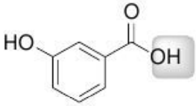
c) 

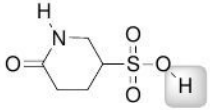
d) 

e) 

f) 

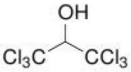
g) 

h) 

i) 

3.26.

a) HBr b) H_2S c) NH_3 d) H—≡—H e)

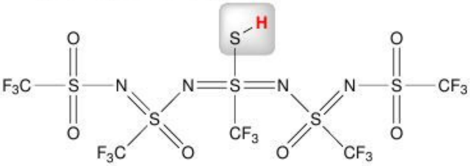


$\mathrm{Cl_3C}\overset{\mathrm{OH}}{\diagup\!\diagdown}\mathrm{CCl_3}$

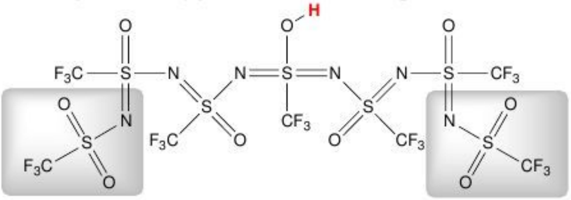
3.27.

a) When the proton is removed, the resulting conjugate base is highly resonance stabilized because the negative charge is spread over four nitrogen atoms and seven oxygen atoms. In addition, the inductive effects of the trifluoromethyl groups (-CF_3) further stabilize the negative charge.

b) The OH group can be replaced with an SH group. Sulfur is larger than oxygen and more capable of stabilizing a negative charge:

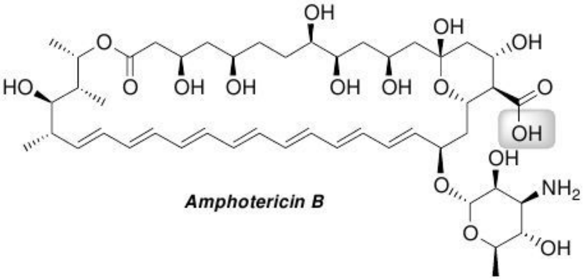


Alternatively, the conjugate base could be further stabilized by spreading the charge over a larger number of nitrogen and oxygen atoms, for example:



The additional structural units (highlighted above) would enable the conjugate base to spread its negative charge over six nitrogen atoms and nine oxygen atoms, which should be even more stable than being spread over four nitrogen atoms and seven oxygen atoms.

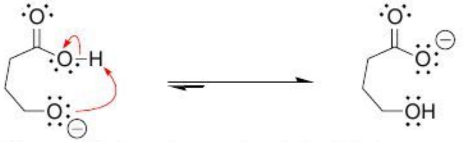
3.28.



3.29.

a) the right side
b) the left side
c) the right side

3.30.



The equilibrium favors the right side because the negative charge is resonance stabilized.

3.31.

a) Yes, because a negative charge on an oxygen atom will be more stable than a negative charge on a nitrogen atom.

b) Yes, because a negative charge on a nitrogen atom will be more stable than a negative charge on an *sp*^{3} hybridized carbon atom.

c) No, because a negative charge on an *sp*^{2} hybridized carbon atom will be less stable than a negative charge on a nitrogen atom.

d) No, because this base is resonance-stabilized, with the negative charge spread over two oxygen atoms and one carbon atom. Protonating this base with water would result in the formation of a hydroxide ion, which is less stable because the negative charge is localized on one oxygen atom.

e) Yes, because a negative charge on an oxygen atom will be more stable than a negative charge on a carbon atom.

f) Yes, because a negative charge on an *sp* hybridized carbon atom will be more stable than a negative charge on a nitrogen atom.

3.32.

a) Yes. This negative charge is less stable than hydroxide.

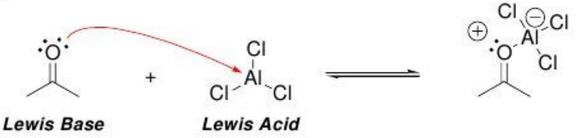
b) No. This negative charge is resonance stabilized and is more stable than hydroxide.

c) No. This negative charge is resonance stabilized and is more stable than hydroxide.

3.33. Water is more acidic than ethanol. Indeed, the pK_a of water (15.7) is lower than the pK_a of ethanol (16).

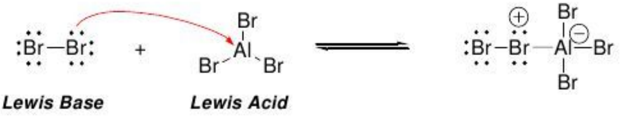
3.34.

a)

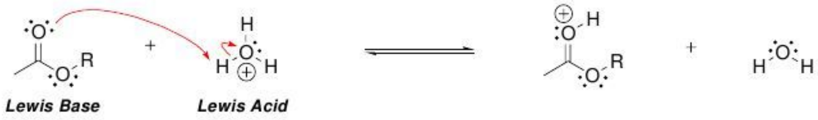


b)

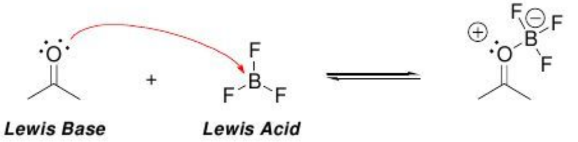
c)



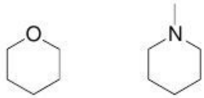
d)



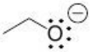
e)

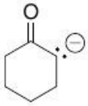


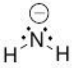
3.35.

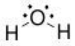


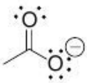
3.36.

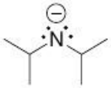
a) 

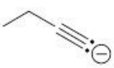
b) 

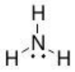
c) 

d) 

e) 

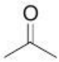
f) 

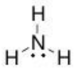
g) 

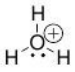
h) 

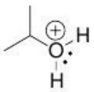
3.37.

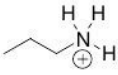
a) 

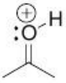
b) 

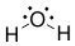
c) 

d) 

a) 

b) 

c) 

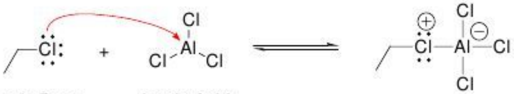
d) 

3.38. Compound A is 1000 times more acidic than compound B.

3.39. In each reaction below, identify the Lewis acid and the Lewis base:

a) ***Lewis Base*** ***Lewis Acid***

b) ***Lewis Base*** ***Lewis Acid***



c) ***Lewis Base*** ***Lewis Acid***

3.40.

3.41. No, because the leveling effect would cause the deprotonation of ethanol to form ethoxide ions, and the desired anion would not be formed under these conditions.

3.42. No, water would not be a suitable proton source in this case. This anion is the conjugate base of a carboxylic acid. The negative charge is resonance stabilized and is more stable than hydroxide.

3.43.

a)

b)

c)


d)


3.44.

a)


b)


c)


d)

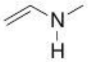

3.45.

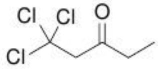
a) The second anion is more stable because it is resonance stabilized.

b) The second anion is more stable because the negative charge is on a nitrogen atom, rather than an sp^3 hybridized carbon atom.

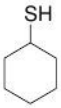
c) The second anion is more stable because the negative charge is on an *sp* hybridized carbon atom, rather than an sp^3 hybridized carbon atom.

3.46.

a)


b)


3.47.

a)


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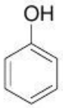

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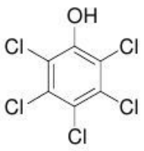

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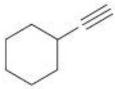

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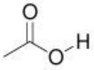

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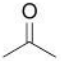

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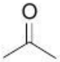

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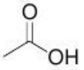


3.48.

The equilibrium will favor the weaker acid (the acid with the higher pK_a value). In this case, the equilibrium favors formation of HA.

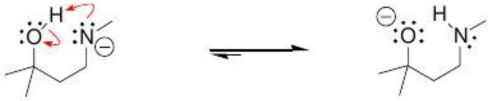
3.49.

a)

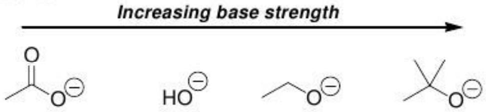
b)

c)

d)

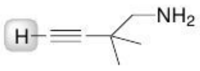


3.50.



3.51.

a)



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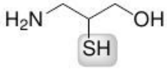

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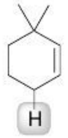

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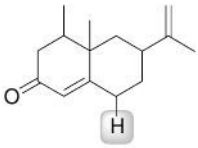

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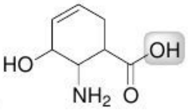

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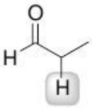

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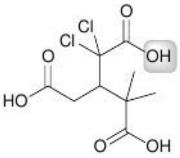


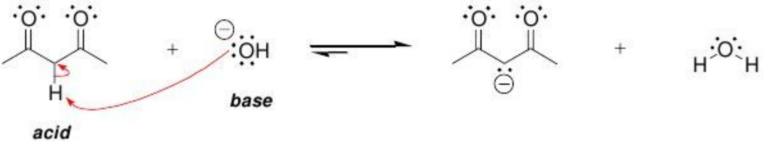
h)

3.52.

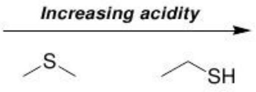
a)

b)

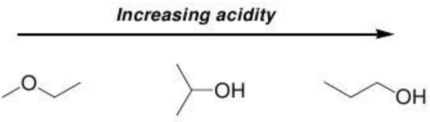
c)



3.53.



3.54.



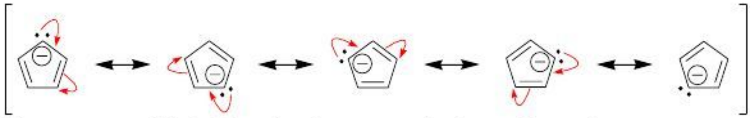
3.55.

a) There is only one sp^3 hybridized carbon atom in cyclopentadiene.

b) The most acidic proton in cyclopentadiene is highlighted below:

The corresponding conjugate base is highly resonance stabilized. In addition, the conjugate base is further stabilized by yet another factor that we will discuss in Chapter 18.

c)



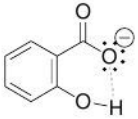
d) There are no sp^3 hybridized carbon atoms in the conjugate base.

e) All carbon atoms are sp^2 hybridized and trigonal planar. Therefore, the entire compound has planar geometry.

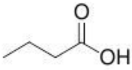
f) There are five hydrogen atoms in the conjugate base.

g) There is one lone pair in the conjugate base, and it is highly delocalized.

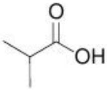
3.56. When salicylic acid is deprotonated, the resulting conjugate base is further stabilized by intramolecular hydrogen bonding:

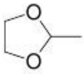


3.57.

a) 

or



b) 

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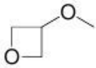
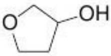


(there are other possibilities as well)

c) 

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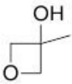
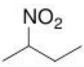
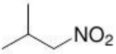
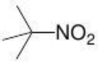


(there are other possibilities as well)

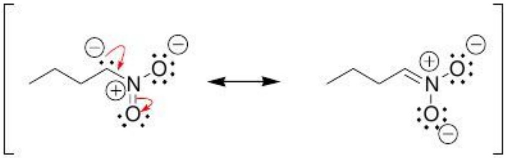
3.58. The four constitutional isomers are shown below.







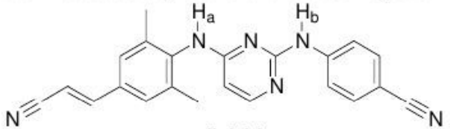
The last compound is expected to have the highest pK_a because its conjugate base is not resonance stabilized. The other three compounds have resonance-stabilized conjugate bases, for example:



3.59. Compare the conjugate bases. Both are resonance stabilized. But the conjugate base of the first compound has a negative charge spread over two nitrogen atoms and two carbon atoms, while the conjugate base of the second compound has a negative charge spread over one nitrogen atom and three carbon atoms. Since nitrogen is more electronegative than carbon, nitrogen is more capable of stabilizing a negative charge. Therefore, the conjugate base of the first compound is more stable than the conjugate base of the second compound. As a result, the first compound will be more acidic.

3.60.

a) The two most acidic protons are labeled H_a and H_b:

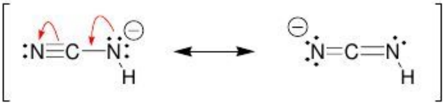


rilpivirine

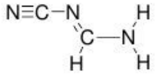
b) H_a is expected to be slightly more acidic than H_b, because removal of H_a produces a conjugate base that has one more resonance structure than the conjugate base formed from removal of H_b. The former has the negative charge spread over four nitrogen atoms and *five* carbon atoms, while the latter has the negative charge spread over four nitrogen atoms and *four* carbon atoms.

3.61.

a) When R is a cyano group, the conjugate base is resonance stabilized:



b) There are many possible answers. Here is one example, for which the conjugate base has the negative charge spread over three nitrogen atoms, rather than just two nitrogen atoms:



Chapter 4
Alkanes and Cycloalkanes

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 4. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

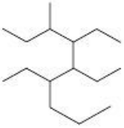
- Hydrocarbons that lack ____________ are called **saturated hydrocarbons**, or ___________.
- _________________ provide a systematic way for naming compounds.
- Rotation about C-C single bonds allows a compound to adopt a variety of ___________________.
- ___________ **projections** are often used to draw the various conformations of a compound.
- _____________ **conformations** are lower in energy, while ____________ **conformations** are higher in energy.
- The difference in energy between staggered and eclipsed conformations of ethane is referred to as _____________ **strain**.
- ________ **strain** occurs in cycloalkanes when bond angles deviate from the preferred _____°.
- The _______ conformation of cyclohexane has no torsional strain and very little angle strain.
- The term **ring flip** is used to describe the conversion of one ____________ conformation into the other. When a ring has one substituent…the equilibrium will favor the chair conformation with the substituent in the _____________ position.

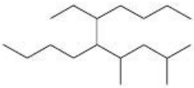
Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 4. The answers appear in the section entitled *SkillBuilder Review*.

SkillBuilder 4.1 Identifying the Parent

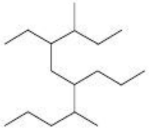
IDENTIFY THE PARENT IN EACH OF THE FOLLOWING COMPOUNDS.



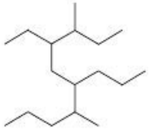


SkillBuilder 4.2 Identifying and Naming Substituents

STEP 1 *- IDENTIFY THE PARENT IN THE FOLLOWING COMPOUND*

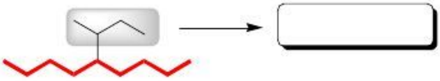


STEPS 2 AND 3 *- CIRCLE AND NAME ALL ALKYL SUBSTITUENTS CONNECTED TO THE PARENT*



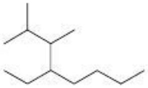
SkillBuilder 4.3 Identifying and Naming Complex Substituents

PROVIDE A NAME FOR THE FOLLOWING COMPLEX SUBSTITUENT (HIGHLIGHTED)



SkillBuilder 4.4 Assembling the Systematic Name of an Alkane

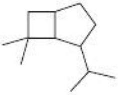
PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND



1) IDENTIFY THE PARENT
2) IDENTIFY AND NAME SUBSTITUENTS
3) ASSIGN LOCANTS TO EACH SUBSTITUENT
4) ALPHABETIZE

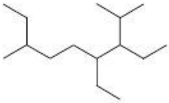
SkillBuilder 4.5 Assembling the Name of a Bicyclic Compound

PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND

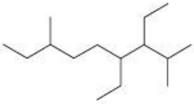


1) IDENTIFY THE PARENT
2) IDENTIFY AND NAME SUBSTITUENTS
3) ASSIGN LOCANTS TO EACH SUBSTITUENT
4) ALPHABETIZE

SkillBuilder 4.6 Identifying Constitutional Isomers

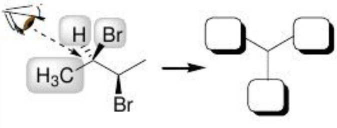


DETERMINE IF THESE TWO COMPOUNDS ARE THE SAME BY ASSIGNING A SYSTEMATIC NAME TO EACH AND THEN COMPARING THEM.

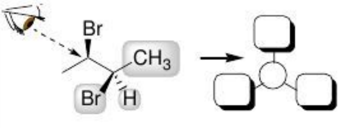


SkillBuilder 4.7 Drawing Newman Projections

STEP 1 *- IDENTIFY THE THREE GROUPS CONNECTED TO THE FRONT CARBON ATOM*



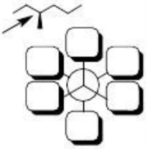
STEP 2 *- IDENTIFY THE THREE GROUPS CONNECTED TO THE BACK CARBON ATOM*



STEP 3 *- ASSEMBLE THE NEWMAN PROJECTION FROM THE TWO PIECES OBTAINED IN THE PREVIOUS STEPS*

SkillBuilder 4.8 Identifying Relative Energy of Conformations

STEP 1 - DRAW A NEWMAN PROJECTION LOOKING DOWN THE BOND INDICATED



STEP 2 - DRAW ALL THREE STAGGERED CONFORMATIONS AND DETERMINE WHICH ONE HAS THE FEWEST OR LEAST SEVERE GAUCHE INTERACTIONS

STEP 3 - DRAW ALL THREE ECLIPSED CONFORMATIONS AND DETERMINE WHICH ONE HAS THE HIGHEST ENERGY INTERACTIONS

SkillBuilder 4.9
Drawing a Chair Conformation

DRAW A CHAIR CONFORMATION

SkillBuilder 4.10
Drawing Axial and Equatorial Positions

DRAW A CHAIR CONFORMATION SHOWING ALL SIX AXIAL POSITIONS AND ALL SIX EQUATORIAL POSITIONS

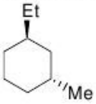
SkillBuilder 4.11 Drawing Both Chair Conformations of a Monosubstituted Cyclohexane

DRAW BOTH CHAIR CONFORMATIONS OF BROMOCYCLOHEXANE

$\rightleftharpoons$

SkillBuilder 4.12 Drawing Both Chair Conformations of Disubstituted Cyclohexanes

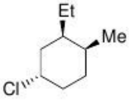
DRAW BOTH CHAIR CONFORMATIONS OF THE FOLLOWING COMPOUND



$\rightleftharpoons$

SkillBuilder 4.13 Drawing the More Stable Chair Conformation of Polysubstituted Cyclohexanes

DRAW BOTH CHAIR CONFORMATIONS OF THE FOLLOWING COMPOUND AND DETERMINE WHICH ONE IS MORE STABLE



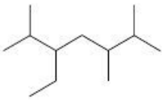
$\rightleftharpoons$

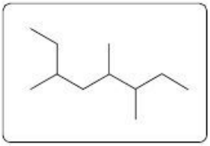
Solutions

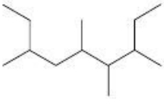
4.1.

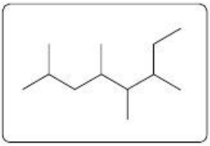
a) parent = hexane
b) parent = heptane
c) parent = heptanes
d) parent = nonane
e) parent = octane
f) parent = heptane
g) parent = cyclopentane
h) parent = cycloheptene
i) parent = cyclopropane

4.2.



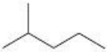






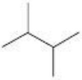
4.3.


parent = hexane

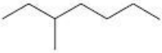

parent = pentane

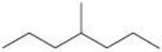

parent = pentane


parent = butane


parent = butane

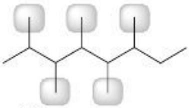
4.4. Only three of the isomers will have a parent name of heptane:



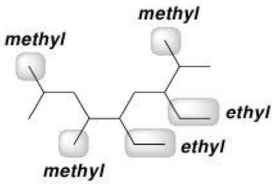


4.5.

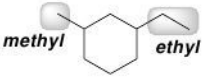
a)


All groups are methyl groups

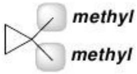
b)



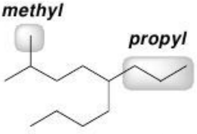
c)



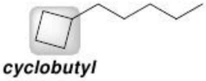
d)



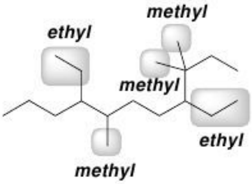
e)



f)

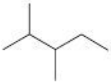


g)



4.6.

a)



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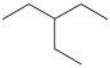
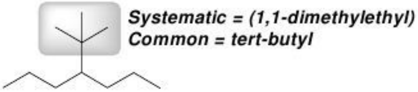
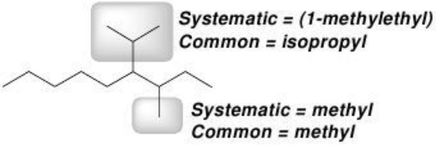


4.7.

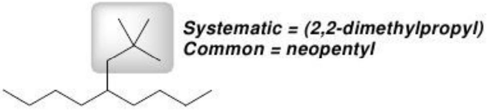
a)



b)



c)



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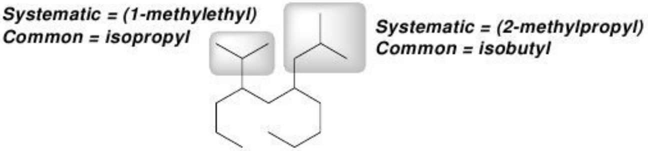
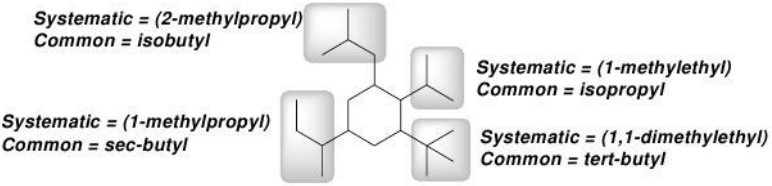
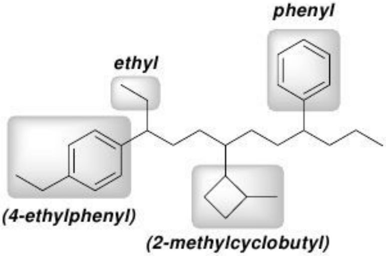


e)

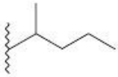


4.8.

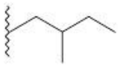


4.9.

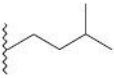
pentyl



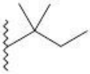
(1-methylbutyl)



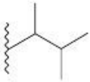
(2-methylbutyl)



(3-methylbutyl)

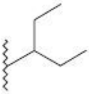


(1,1-dimethylpropyl)



(1,2-dimethylpropyl)

(2,2-dimethylpropyl)



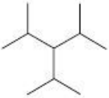
(1-ethylpropyl)

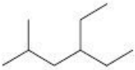
4.10.

a) 3,4,6-trimethyloctane
b) sec-butylcyclohexane
c) 3-ethyl-2-methylheptane
d) 3-isopropyl-2,4-dimethylpentane
e) 3-ethyl-2,2-dimethylhexane
f) 2-cyclohexyl-4-ethyl-5,6-dimethyloctane
g) 3-ethyl-2,5-dimethyl-4-propylheptane
h) 5-sec-butyl-4-ethyl-2-methyldecane
i) 2,2,6,6,7,7-hexamethylnonane
j) 4,5-dimethylnonane

k) 2,4,4,6-tetramethylheptane
l) 2,2,5-trimethylpentane
m) 4-tert-butylheptane
n) 3-ethyl-6-isopropyl-2,4-dimethyldecane
o) 3,5-diethyl-2-methyloctane
p) 1,3-diisopropylcyclopentane
q) 3-ethyl-2,5-dimethylheptane

4.11.

a) 

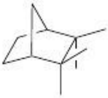
b) 

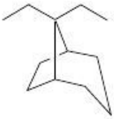
c) 

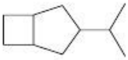
4.12.

a) 4-ethyl-1-methylbicyclo[3.2.1]octane
b) 2,2,5,7-tetramethylbicyclo[4.2.0]octane
c) 2,7,7-trimethylbicyclo[4.2.2]decane
d) 3-*sec*-butyl-2-methylbicyclo[3.1.0]hexane
e) 2,2-dimethylbicyclo[2.2.2]octane
f) 2,7-dimethylbicyclo[3.3.0]octane
g) bicyclo[1.1.0]butane
h) 5,5-dimethylbicyclo[2.1.1]hexane
i) 3-(3-methylbutyl)bicyclo[4.4.0]decane

4.13.

a) 

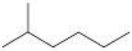
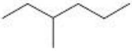
b) 

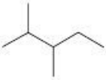
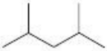
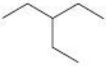
c) 

4.14.

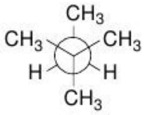
a) same compound
b) same compound
c) same compound
d) constitutional isomers

4.15.

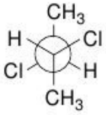





4.16.



a)



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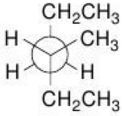
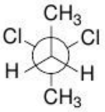
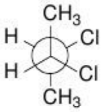


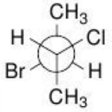
c)



d)



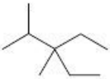
e)



f)

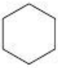
4.17.

a)



b)

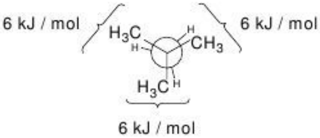
c)



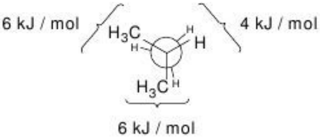
4.18. The compounds are not constitutional isomers. They are just two different representations of the same compound. They are both 2,3-dimethylbutane.

4.19.

a) The energy barrier is expected to be approximately 18 kJ / mol (calculation below):

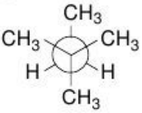


b) The energy barrier is expected to be approximately 16 kJ / mol (calculation below):

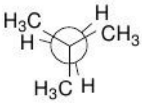


4.20.

a)

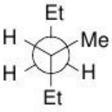


Lowest Energy

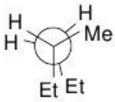


Highest Energy

b)

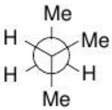


Lowest Energy

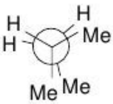


Highest Energy

c)

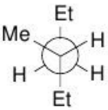


Lowest Energy

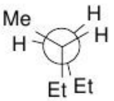


Highest Energy

d)

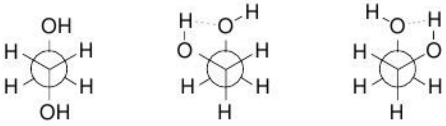


Lowest Energy



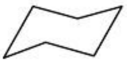
Highest Energy

4.21. The gauche conformations are capable of intramolecular hydrogen bonding, as shown below. The anti conformation lacks this stabilizing effect.



Anti ***Gauche*** ***Gauche***

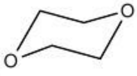
4.22.



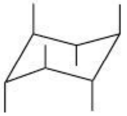
4.23.

a)

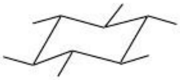
b)



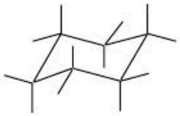
4.24.



4.25.



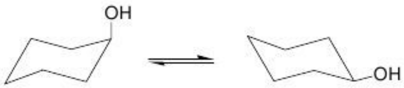
4.26.

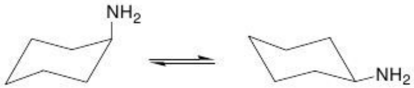


4.27. There are eight hydrogen atoms in axial positions and seven hydrogen atoms in equatorial positions.

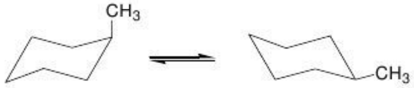
4.28.

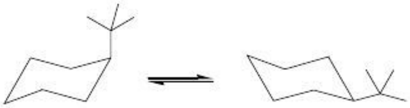
a)



b) 

c) 

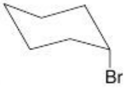
d) 

e) 

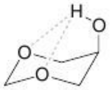
4.29.

a) The bromine atom occupies an equatorial position.

b) 

c) 

4.30. Although the OH group is in an axial position, nevertheless, this conformation is capable of intramolecular hydrogen bonding, which is a stabilizing effect:



4.31.

a) 

b) 

c)

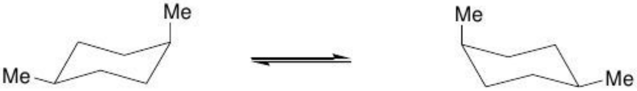
d)

e)

f)

g)

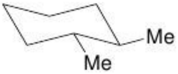
h)



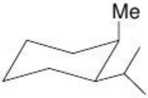
4.32.

4.33.

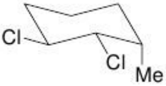
a)



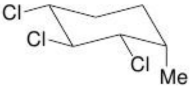
b)



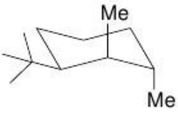
c)



d)



e)

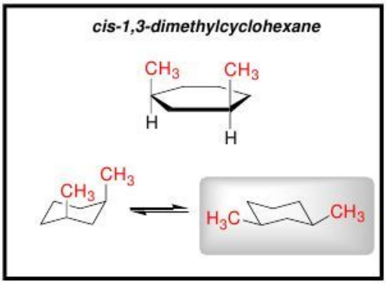


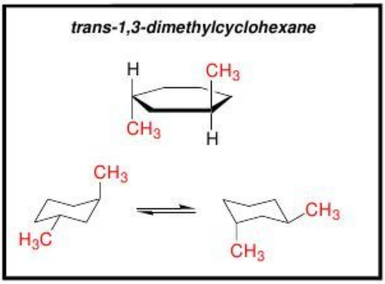
f)

4.34. The two chair conformations of lindane are degenerate. There is no difference in energy between them.

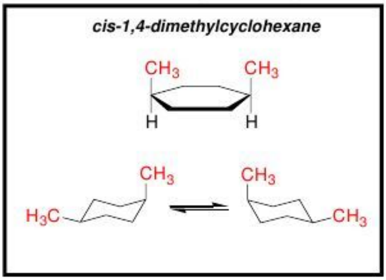
4.35. *trans*-1,4-di-*tert*-butylcyclohexane exists predominantly in a chair conformation, because both substituents can occupy equatorial positions. In contrast, *cis*-1,4-di-*tert*-butylcyclohexane cannot have both of its substituents in equatorial positions. Each chair conformation has one of the substituents in an axial position, which is too high in energy. The compound can achieve a lower energy state by adopting a twist boat conformation.

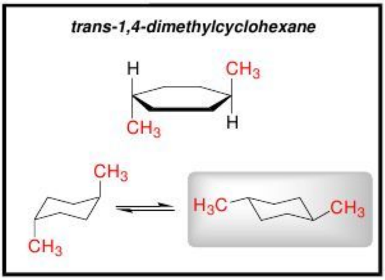
4.36. *cis*-1,3-dimethylcyclohexane is expected to be more stable than *trans*-1,3-dimethylcyclohexane because the former can adopt a chair conformation in which both substituents are in equatorial positions (highlighted below):



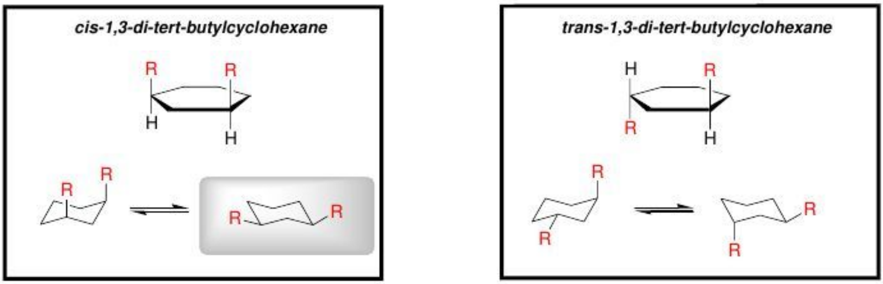


4.37. *trans*-1,4-dimethylcyclohexane is expected to be more stable than *cis*-1,4-dimethylcyclohexane because the latter can adopt a chair conformation in which both substituents are in equatorial positions (highlighted below):





4.38. *cis*-1,3-di-*tert*-butylcyclohexane can adopt a chair conformation in which both tert-butyl groups occupy equatorial positions (highlighted below), and as a result, it is expected to exist primarily in that conformation. In contrast, *trans*-1,3-di-*tert*-butylcyclohexane cannot adopt a chair conformation in which both tert-butyl groups occupy equatorial positions. In either chair conformation, one of the tert-butyl groups occupies an axial position. This compound can achieve a lower energy state by adopting a twist-boat conformation.



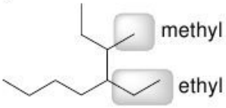
where R = tert-butyl group

4.39.

a) parent = octane
b) parent = nonane
c) parent = octane
d) parent = heptane

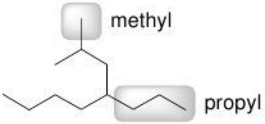
4.40.

a)



b) isopropyl or (1-methylethyl)

c)



d) *tert*-butyl or (1,1-dimethylethyl)

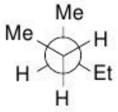
4.41.

a) 2,3,5-trimethyl-4-propylheptane
b) 1,2,4,5-tetramethyl-3-propylcyclohexane
c) 2,3,5,9-tetramethylbicyclo[4.4.0]decane
d) 1,4-dimethylbicyclo[2.2.2]octane

4.42.

a) same compound
b) constitutional isomers
c) same compound

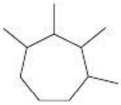
4.43.

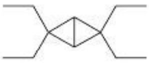


4.44. 

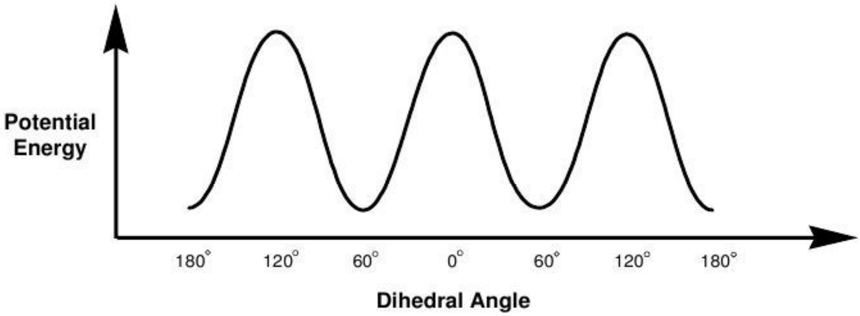
4.45.

a) 

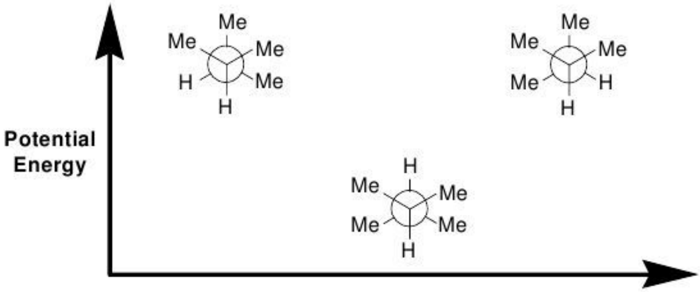
b) 

c) 

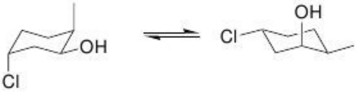
4.46. The energy diagram more closely resembles the shape of the energy diagram for the conformational analysis of ethane.



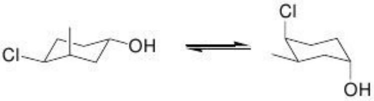
4.47. Two of the staggered conformations are degenerate. The remaining staggered conformation is lower in energy than the other two, as shown below:



4.48.

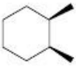
a) 

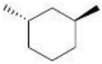
b) 

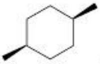
c) 

4.49.

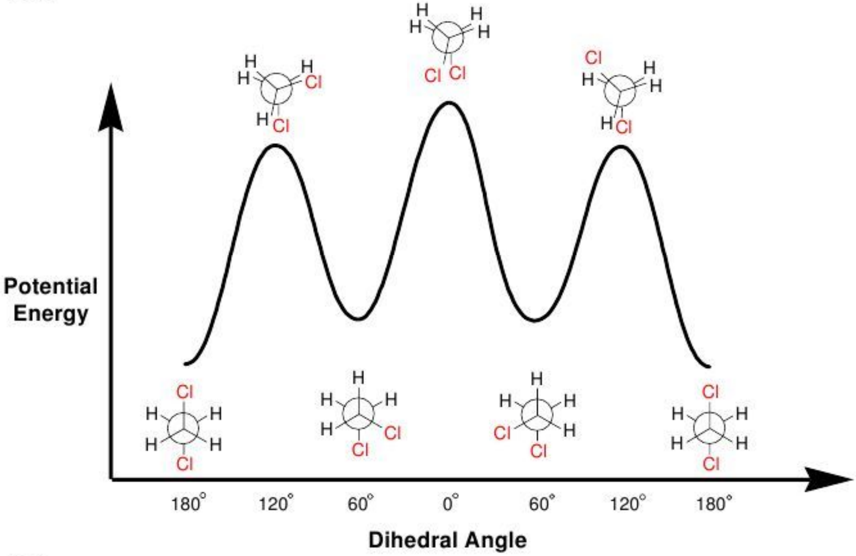
a)  has more CH_2 groups.

b)  cannot adopt a chair conformation in which both groups occupy equatorial positions.

c)  cannot adopt a chair conformation in which both groups occupy equatorial positions.

d)  cannot adopt a chair conformation in which both groups occupy equatorial positions.

4.50.



4.51.

a) hexane
b) methylcyclohexane
c) methylcyclopentane
d) *trans*-1,2-dimethylcyclopentane

4.52. Each H-H eclipsing interaction is 4 kJ / mol, and there are two of them (for a total of 8 kJ / mol). The remaining energy cost is associated with the Br-H eclipsing interaction: 15 – 8 = 7 kJ / mol.

4.53.

more stable
(all groups are equatorial)

4.54.

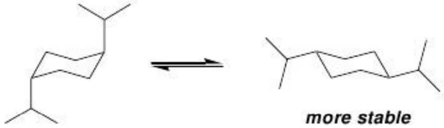
a) ***more stable***

b) ***more stable***

c)

more stable

d)



more stable

4.55.

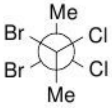
a) The second compound can adopt a chair conformation in which all three substituents occupy equatorial positions. Therefore, the second compound is expected to be more stable.

b) The first compound can adopt a chair conformation in which all three substituents occupy equatorial positions. Therefore, the first compound is expected to be more stable.

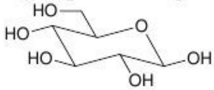
c) The first compound can adopt a chair conformation in which both substituents occupy equatorial positions. Therefore, the first compound is expected to be more stable.

d) The first compound can adopt a chair conformation in which all four substituents occupy equatorial positions. Therefore, the first compound is expected to be more stable.

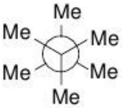
4.56.



4.57. All groups are in equatorial positions.

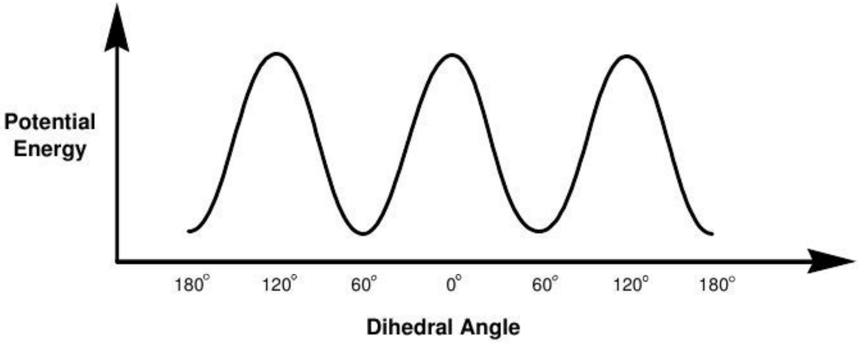


4.58.



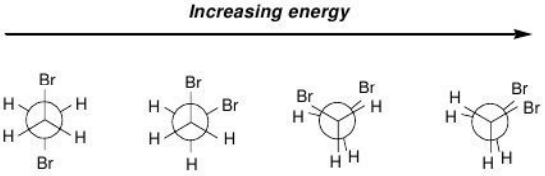
2,2,4,4-tetramethylbutane

All staggered conformations are degenerate, and the same is true for all eclipsed conformations. The energy diagram has a shape that is similar to the energy diagram for the conformational analysis of ethane:



The staggered conformations have six gauche interactions, each of which has an energy cost of 3.8 kJ / mol. Therefore, each staggered conformation has an energy cost of 22.8 kJ / mol. The eclipsed conformations have three methyl-methyl eclipsing interactions, each of which has an energy cost of 11 kJ / mol. Therefore, each eclipsed conformation has an energy cost of 33 kJ / mol. The difference in energy between staggered and eclipsed conformations is therefore expected to be approximately 10.2 kJ / mol.

4.59.

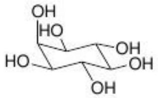


4.60.

a) This conformation has three gauche interactions, each of which has an energy cost of 3.8 kJ / mol. Therefore, this conformation has a total energy cost of 11.4 kJ / mol associated with torsional strain and steric strain.

b) This conformation has two methyl-H eclipsing interactions, each of which has an energy cost of 6 kJ / mol. In addition, it also has one methyl-methyl eclipsing interaction, which has an energy cost of 11 kJ / mol. Therefore, this conformation has a total energy cost of 23 kJ / mol associated with torsional strain and steric strain.

4.61.



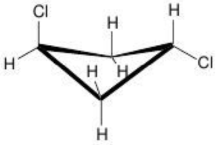
4.62.

a) equatorial	b) equatorial	c) axial
d) equatorial	e) equatorial	f) axial

4.63.

cyclopropane

4.64. As mentioned in Section 4.9, cyclobutene adopts a slightly puckered conformation in order to alleviate some of the torsional strain associated with the eclipsing hydrogen atoms:



In this non-planar conformation, the individual dipole moments of the C-Cl bonds in *trans*-1,3-dichlorocyclobutane do not fully cancel each other, giving rise to a small molecular dipole moment.

4.65. Cyclohexene cannot adopt a chair conformation because two of the carbon atoms are sp^2 hybridized and trigonal planar. A chair conformation can only be achieved when all six carbon atoms are sp^3 hybridized and tetrahedral (with bond angles of 109.5º).

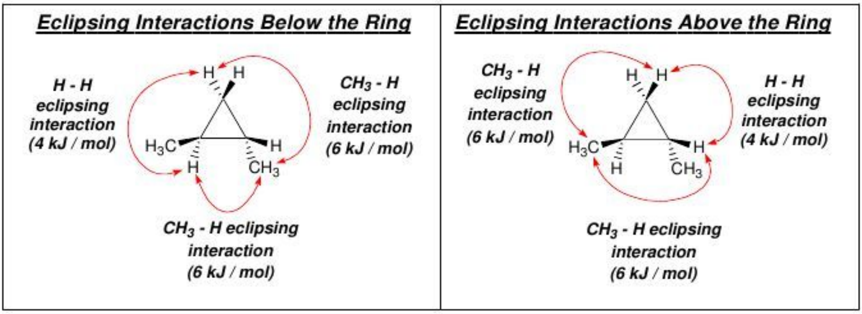
4.66.

a) identical compounds
b) constitutional isomers
c) identical compounds
d) constitutional isomers
e) identical compounds
f) stereoisomers
g) stereoisomers
h) stereoisomers
i) constitutional isomers
j) different conformations of the same compound
k) stereoisomers
l) constitutional isomers

4.67.

a) the trans isomer s expected to be more stable, because the *cis* isomer has a very high energy methyl-methyl eclipsing interaction (11 kJ / mol). See calculation below.

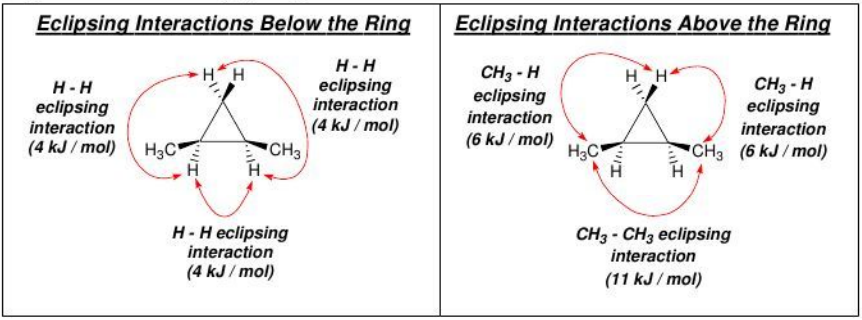
b) We calculate the energy cost associated with all eclipsing interactions in both compounds. Let's begin with the *trans* isomer. It has the following eclipsing interactions, below the ring and above the ring, giving a total of 32 kJ / mol:



Eclipsing Interactions Below the Ring

Eclipsing Interactions Above the Ring

Now let's focus on the *cis* isomer. It has the following eclipsing interactions, below the ring and above the ring, giving a total of 35 kJ / mol:



The difference between these two isomers is therefore predicted to be (35 kJ / mol) – (32 kJ / mol) = 3 kJ / mol.

4.68. With increasing halogen size, the bond length also increases. That is, the C-I bond is longer than the C-Br bond, which is longer than the C-Cl bond. So, although iodine is much larger than the other halogens, the longer bond length helps to accommodate the additional steric bulk. These two factors (increased steric bulk and increased bond length) mostly offset each other.

4.69.

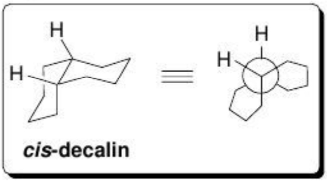
a)

b) Comparison of these chair conformations requires a comparison of the energy costs associated with all axial substituents (see Table 4.8). The first chair conformation has two axial substituents: an OH group (energy cost = 4.2 kJ / mol) and a Cl group (energy cost = 2.0 kJ / mol), giving a total of 6.2 kJ / mol. The second chair conformation has two axial substituents: an isopropyl group (energy cost = 9.2 kJ / mol) and an ethyl group (energy cost = 8.0 kJ / mol), giving a total of 17.2 kJ / mol. The first chair conformation has a lower energy cost, and is therefore more stable.

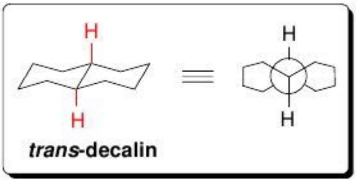
c) Using the numbers calculated in part b, the difference in energy between the these two chair conformations is expected to be (17.2 kJ / mol) – (6.2 kJ / mol) = 11 kJ / mol. Using the numbers in Table 4.8, we see that a difference of 9 kJ / mol corresponds with a ratio of 97:3 for the two conformations. In this case, the difference in energy is more than 9 kJ / mol, so the ratio should be even higher (more than 97%). Therefore, we do expect the compound to spend more than 95% of its time in the more stable chair conformation.

4.70.

a) *cis*-Decalin has three gauche interactions, while *trans*-decalin has only two gauche interactions.

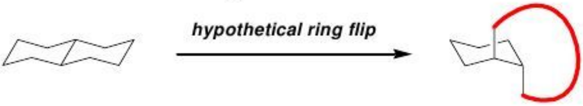


***cis*-decalin**



***trans*-decalin**

b) *trans*-Decalin is incapable of ring flipping, because a ring flip of one ring would cause its two alkyl substituents (which comprise the second ring) to be too far apart to accommodate the second ring.



cannot accomodate a six membered ring connecting these two substituents.

Chapter 5
Stereoisomerism

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 5. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

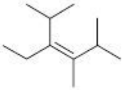
- ______**isomers** have the same connectivity of atoms but differ in their spatial arrangement.
- **Chiral** objects are not **superimposable** on their ______________________. The most common source of molecular chirality is the presence of a _________________, a carbon atom bearing ______ different groups.
- A compound with one chirality center will have one non-superimposable mirror image, called its ________________.
- The Cahn-Ingold-Prelog system is used to assign the _______________ of a chirality center.
- A **polarimeter** is a device used to measure the ability of chiral organic compounds to rotate the plane of _____________________ light. Such compounds are said to be ____________ **active**.
- A solution containing equal amounts of both enantiomers is called a __________ **mixture**. A solution containing a pair of enantiomers in unequal amounts is described in terms of **enantiomeric** _________ (*ee*).
- For a compound with multiple chirality centers, a family of stereoisomers exists. Each stereoisomer will have at most one enantiomer, with the remaining members of the family being ______________.
- A ______ **compound** contains multiple chirality centers but is nevertheless achiral because it possesses reflectional symmetry.
- __________ **projections** are drawings that convey the configuration of chirality centers, without the use of wedges and dashes.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 5. The answers appear in the section entitled *SkillBuilder Review*.

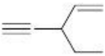
SkillBuilder 5.1 Identifying *cis-trans* Stereoisomerism

ASSIGN THE CONFIGURATION OF THE FOLLOWING DOUBLE BOND AS CIS OR TRANS



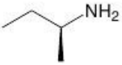
SkillBuilder 5.2 Locating Chirality Centers

CIRCLE THE CHIRALITY CENTER IN THE FOLLOWING COMPOUND



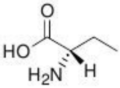
SkillBuilder 5.3 Drawing an Enantiomer

SHOW THREE WAYS TO DRAW THE ENANTIOMER OF THE FOLLOWING COMPOUND. PLACE YOUR ANSWERS IN THE BOXES SHOWN.



SkillBuilder 5.4 Assigning Configuration

ASSIGN THE CONFIGURATION OF THE CHIRALITY CENTER IN THE FOLLOWING COMPOUND



SkillBuilder 5.5 Calculating specific rotation

CALCULATE THE SPECIFIC ROTATION GIVEN THE FOLLOWING INFORMATION:

0.300 grams sucrose dissolved in 10.0 mL of water
sample cell = 10.0 cm
observed rotation = +1.99°

$$\text{specific rotation} = [\alpha] = \frac{\alpha}{c \times l} = \frac{\boxed{\quad}}{\boxed{\quad} \times \boxed{\quad}} = \boxed{\quad}$$

SkillBuilder 5.6 Calculating % *ee*

CALCULATE THE ENANTIOMERIC EXCESS GIVEN THE FOLLOWING INFORMATION:

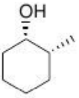
The specific rotation of optically pure adrenaline is -53 . A mixture of (*R*)- and (*S*)- adrenaline was found to have a specific rotation of - 45 . Calculate the % *ee* of the mixture

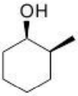
$$\%\,ee = \frac{\text{observed [ ]}}{\text{[ ] of pure enantiomer}} \times 100\,\%$$

$$= \frac{\boxed{\quad}}{\boxed{\quad}} \times 100\,\% = \boxed{\quad}$$

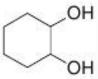
SkillBuilder 5.7 Determining Stereoisomeric Relationship

IDENTIFY THE STEREOISOMERIC RELATIONSHIP BETWEEN THE FOLLOWING TWO COMPOUNDS





SkillBuilder 5.8 Identifying Meso Compounds



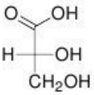
DRAW ALL POSSIBLE STEREOSIOMERS OF 1,2-CYCLOHEXANEDIOL (SHOWN LEFT), AND THEN LOOK FOR A PLANE OF SYMMETRY IN ANY OF THE DRAWINGS. THE PRESENCE OF A PLANE OF SYMMETRY INDICATES A MESO COMPOUND

$\boxed{\quad}$ + $\boxed{\quad}$ $\boxed{\quad}$ = $\boxed{\quad}$

ENANTIOMERS **MESO**

SkillBuilder 5.9 Assigning configuration from a Fischer projection

ASSIGN THE CONFIGURATION OF THE CHIRALITY CENTER IN THE FOLLOWING COMPOUND



Solutions

5.1.

a) *trans* b) not stereoisomeric

c) *trans* d) *trans*

e) *trans* f) not stereoisomeric

g) *cis*

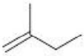
5.2. $H_2CCHCH_2CH_2CH_2CHCH_2$ =

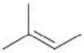
Neither double bond exhibits stereoisomerism, so this compound does not have any stereoisomers.

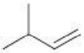
5.3.

a)

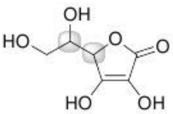
b)



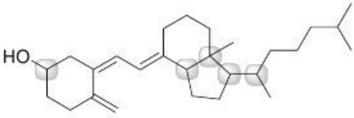




5.4. All chirality centers are highlighted below:



a)



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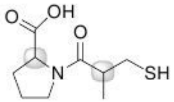
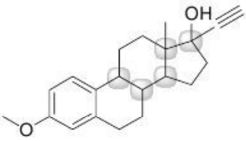
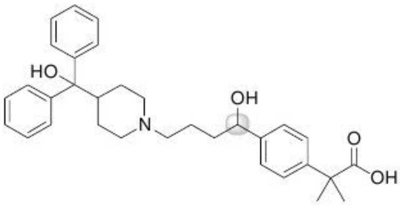


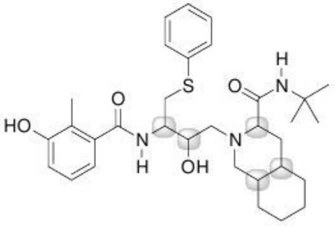
c)



d)

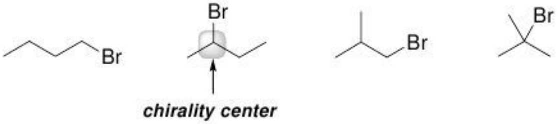


e)



f)

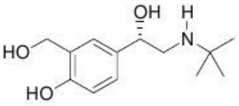
5.5.



5.6. The phosphorus atom has four different groups attached to it (a methyl group, an ethyl group, a phenyl group, and a lone pair). This phosphorous atom therefore represents a chirality center. This compound is not superimposable on its mirror image, as can be seen clearly by building and comparing molecular models.

5.7.

a)



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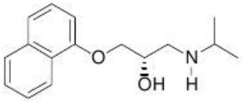

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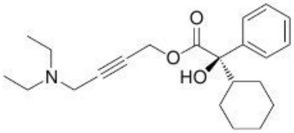

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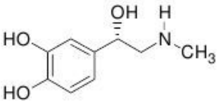

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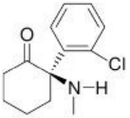
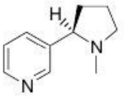
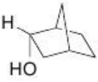


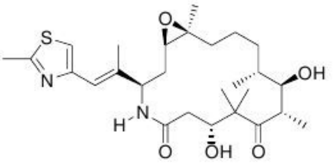
f)



g)

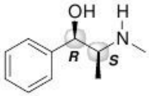


5.8.



5.9.

a)



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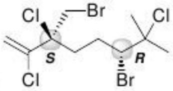

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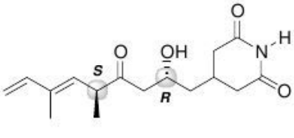

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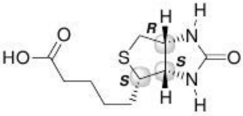

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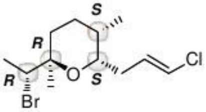
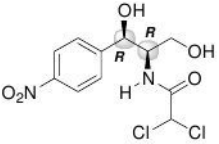
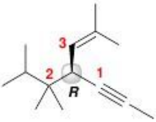


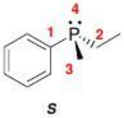
f)



5.10.



5.11.

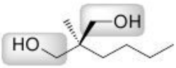


5.12. specific rotation $= [\alpha] = \dfrac{\alpha}{c\times l} = \dfrac{(+1.47^\circ)}{(0.0575\ \mathrm{g/mL})\times(1.00\ \mathrm{dm})} = \mathbf{+25.6}$

5.13. specific rotation $= [\alpha] = \dfrac{\alpha}{c\times l} = \dfrac{(-2.99^\circ)}{(0.095\ \mathrm{g/mL})\times(1.00\ \mathrm{dm})} = \mathbf{-31.5}$

5.14. specific rotation $= [\alpha] = \dfrac{\alpha}{c\times l} = \dfrac{(+0.57^\circ)}{(0.260\ \mathrm{g/mL})\times(1.00\ \mathrm{dm})} = \mathbf{+2.2}$

5.15. This compound does not have a chirality center, because two of the groups are identical:



Accordingly, the compound is achiral and is not optically active.

5.16.

$$[\alpha] = \frac{\alpha}{c \times l}$$

$$\alpha = [\alpha] \times c \times l = (+13.5)(0.100\ \text{g / mL})(1.00\ \text{dm}) = +1.35\,^{\circ}$$

5.17.

$$\%\ ee = \frac{\text{observed } [\alpha]}{[\alpha] \text{ of pure enantiomer}} \times 100\ \%$$

$$= \frac{(-37^{\circ})}{(-39.5^{\circ})} \times 100\ \%$$

$$= 94\ \%$$

5.18.

$$\%\ ee = \frac{\text{observed } [\alpha]}{[\alpha] \text{ of pure enantiomer}} \times 100\ \%$$

$$= \frac{(-6.0^{\circ})}{(-6.3^{\circ})} \times 100\ \%$$

$$= 95\ \%$$

5.19.

$$\%\ ee = \frac{\text{observed } [\alpha]}{[\alpha] \text{ of pure enantiomer}} \times 100\ \%$$

$$= \frac{(85^{\circ})}{(92^{\circ})} \times 100\ \%$$

$$= 92\ \%$$

5.20. Observed $[\alpha] = \dfrac{\alpha}{c \times l} = \dfrac{(+0.78^{\circ})}{(0.350\ \text{g / mL}) \times (1.00\ \text{dm})} = \mathbf{+2.2}$

$$\%\ ee = \frac{\text{observed } [\alpha]}{[\alpha] \text{ of pure enantiomer}} \times 100\ \%$$

$$= \frac{(2.2^{\circ})}{(2.8^{\circ})} \times 100\ \%$$

$$= 79\ \%$$

5.21.

- **a)** enantiomers
- **b)** diastereomers
- **c)** diastereomers
- **d)** diastereomers
- **e)** diastereomers
- **f)** enantiomers

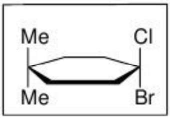
5.22. There are three chirality centers, and only one of these chirality centers has a different configuration in these two compounds. The other two chirality centers have the same configuration in both compounds. Therefore, these compounds are diastereomers.

5.23.

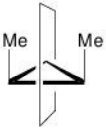
a) yes b) yes c) no d) yes e) yes f) no

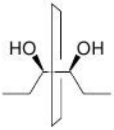
5.24. 5.23f has three planes of symmetry.

5.25.

a) 

b) 

c) 

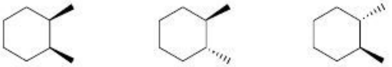
d) 

e) 

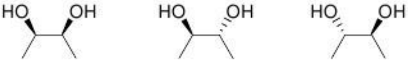
f) 

5.26.

a)



b)



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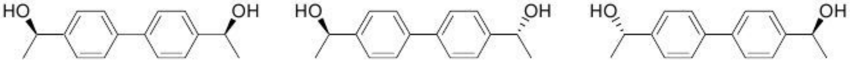

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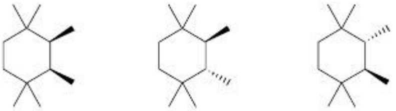
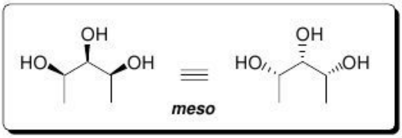
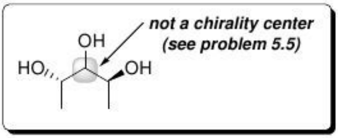
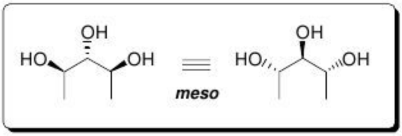


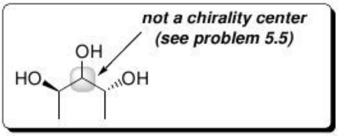
5.27. Each of these compounds is a meso compound and does not have an enantiomer.

5.28 There are only four stereoisomers:



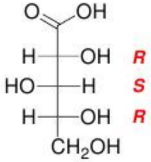


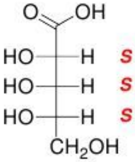


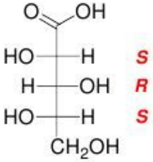


5.29. **a)** R **b)** S **c)** S **d)** S

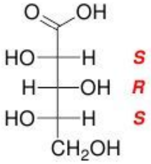
5.30.

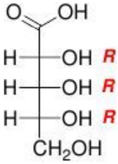
a) 

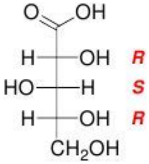
b) 

c) 

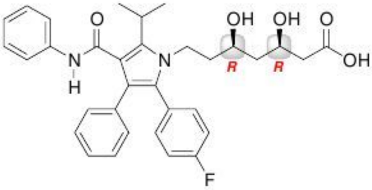
5.31.

a) 

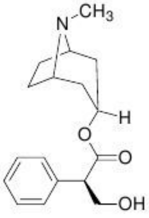
b) 

c) 

5.32.



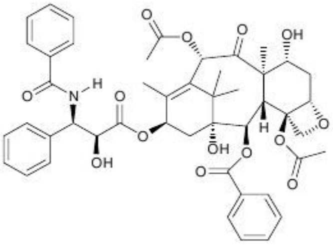
5.33.



5.34.

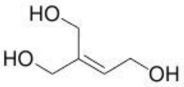
a) Paclitaxel has eleven chirality centers.

b) The enantiomer of paclitaxel is shown below:

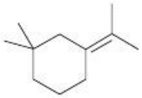


5.35.

trans



not stereoisomeric



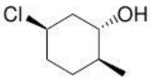
not stereoisomeric

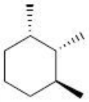
5.36.

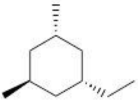
a) enantiomers
b) same compound
c) constitutional isomers
d) constitutional isomers
e) diastereomers
f) same compound
g) enantiomers
h) diastereomers
i) same compound
j) same compound
k) same compound
l) same compound

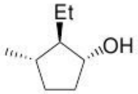
5.37. a) 8 b) 3 c) 16 d) 3 e) 3 f) 32

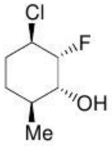
5.38.

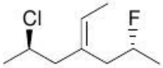
a) 

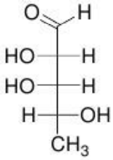
b) 

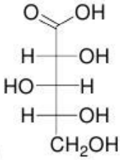
c) 

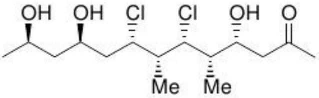
d) 

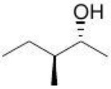
e) 

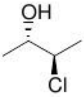
f) 

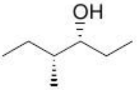
g) 

h) 

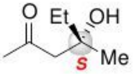
i) 

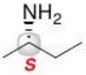
j) 

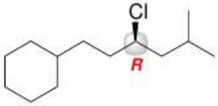
k) 

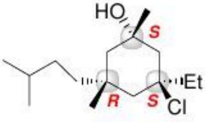
l) 

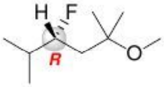
5.39.

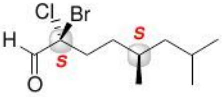
a)


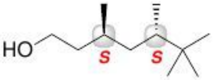
b)


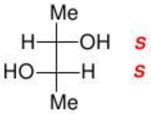
c)


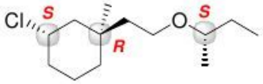
d)


e)


f)


g)


h)


i)


5.40. 96% *ee*

5.41.

a) diastereomers
b) diastereomers
c) enantiomers
d) same compound
e) enantiomers
f) diastereomers
g) enantiomers
h) diastereomers
i) enantiomers
j) same compound
k) enantiomer
l) diastereomers

5.42.

$$\%\ ee = \frac{\text{observed } [\alpha]}{[\alpha] \text{ of pure enantiomer}} \times 100\ \%$$

$$= \frac{(-55^\circ)}{(-61^\circ)} \times 100\ \%$$

$$= 90\ \%$$

5.43.

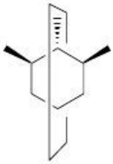
a) True.
b) False.
c) True.

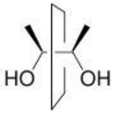
5.44. specific rotation = $[\alpha] = \dfrac{\alpha}{c \times 1} = \dfrac{(-0.47^\circ)}{(0.0075\ \text{g / mL}) \times (1.00\ \text{dm})} = \mathbf{-63}$

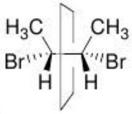
5.45.

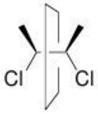
a) (*S*)-limonene b) (*R*)-limonene c) (*S*)-limonene d) (*R*)-limonene

5.46.

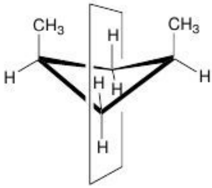
a) 

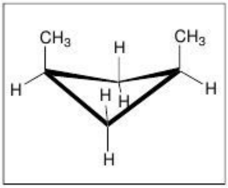
b) 

c) 

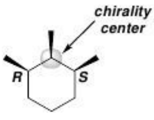
d) 

5.47.

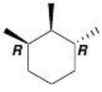




5.48. The first compound has three chirality centers:



three chirality centers



two chirality centers

This is apparent if we assign the configuration at C1 and C3 of the cyclohexane ring. In the first compound, the configuration at C1 is different than the configuration at C3. As a result, there are four different groups attached to the C2 position. That is, C1 and C3 represent two different groups: one with the R configuration and the other with the S configuration. In contrast, consider the configuration at C1 and C3 in the second compound. Both of these positions have the same configuration, and therefore, the C2 position in that compound does not have four different groups. Two of the groups are identical, so C2 is not a chirality center.

5.49.

a) enantiomers
b) diastereomers
c) enantiomers
d) same compound
e) enantiomers
f) diastereomers
g) same compound
h) constitutional isomers
i) diastereomers
j) diastereomers
k) same compound
l) enantiomers

5.50.

a) -61
b) 90 % *ee*
c) 95 % of the mixture is (*S*)-carvone

5.51.

a) chiral
b) chiral
c) achiral
d) achiral
e) chiral
f) achiral
g) achiral
h) chiral
i) chiral
j) achiral
k) chiral
l) chiral
l) achiral
m) chiral
n) achiral
o) achiral

5.52.

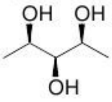
$$[\alpha] = \frac{\alpha}{c \times l}$$

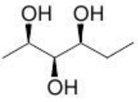
$$\alpha = [\alpha] \times c \times l = (+24)(0.0100 \text{ g / mL})(1.00 \text{ dm}) = +0.24\,°$$

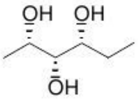
5.53.

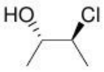
a) optically inactive (meso)
b) optically active
c) optically active
d) optically inactive
e) optically active
f) optically inactive (3-methylpentane has no chirality centers)
g) optically inactive (meso)
h) optically inactive

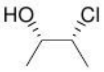
5.54.

a) 

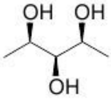
b) 

c) 

d) 

e) 

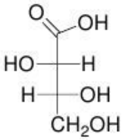
5.55.

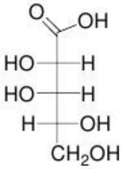
a) 

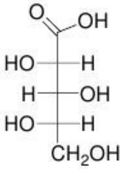
b) No. A racemic mixture is not optically active.

c) Yes, because d and e are not enantiomers. They are diastereomers, which are not expected to exhibit equal and opposite rotations.

5.56.

a) 

b) 

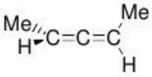
c) 

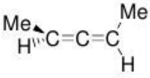
5.57.

a) 3-methylpentane and 2-methylpentane are constitutional isomers.

b) *trans*-1,2-dimethylcyclohexane and *cis*-1,2-dimethylcyclohexane are diastereomers.

5.58. The following two compounds are enantiomers because they are nonsuperimposable mirror images. You may find it helpful to construct molecular models to help visualize the mirror image relationship between these two compounds.





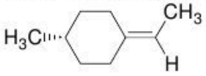
5.59. This compound will be achiral.

5.60.

a) This compound cannot be completely planar because steric hindrance prevents the two ring systems from rotating with respect to each other. The compound is locked in a particular conformation that is chiral.

b) This ring system cannot be planar because of steric hindrance, and must therefore adopt a spiral shape (like a spiral staircase). The spiral can be right handed or left handed, and the relationship between these two forms is enantiomeric.

5.61. The compound is chiral because it is not superimposable on its mirror image.



5.62. This compound has a center of inversion, which is a form of reflection symmetry. As a result, this compound is superimposable on its mirror image and is therefore optically inactive.

Chapter 6
Chemical Reactivity and Mechanisms

Review of Concepts

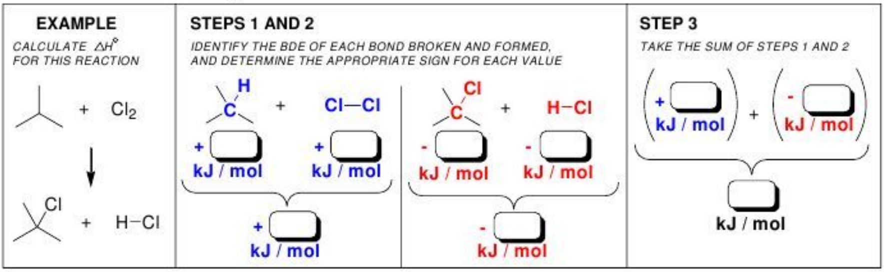
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 6. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- ________________ reactions involve a transfer of energy from the system to the surroundings, while ______________ reactions involve a transfer of energy from the surroundings to the system.
- Each type of bond has a unique ________________________ **energy**, which is the amount of energy necessary to accomplish **homolytic bond cleavage**.
- **Entropy** is loosely defined as the ___________ of a system.
- In order for a process to be spontaneous, the change in ____________________ must be negative.
- The study of relative energy levels and equilibrium concentrations is called ___________________.
- ____________ is the study of reaction rates.
- _____________ speed up the rate of a reaction by providing an alternate pathway with a lower **energy of activation**.
- On an energy diagram, each peak represents a ___________________, while each valley represents _________________________.
- A _________________ has an electron-rich atom that is capable of donating a pair of electrons.
- An __________________ has an electron-deficient atom that is capable of accepting a pair of electrons.
- For **ionic reactions**, there are four characteristic arrow-pushing patterns: 1) ___________________, 2) ___________________, 3) ___________________, and 4) ___________________.
- As a result of **hyperconjugation**, ___________ carbocations are more stable than secondary carbocations, which are more stable than ___________ carbocations.

Review of Skills

Fill in the empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 6. The answers appear in the section entitled *SkillBuilder Review*.

SkillBuilder 6.1 Predicting ΔH° of a Reaction



EXAMPLE

CALCULATE ΔH° FOR THIS REACTION

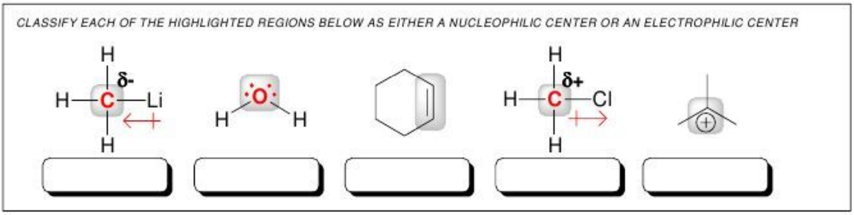
STEPS 1 AND 2

IDENTIFY THE BDE OF EACH BOND BROKEN AND FORMED, AND DETERMINE THE APPROPRIATE SIGN FOR EACH VALUE

STEP 3

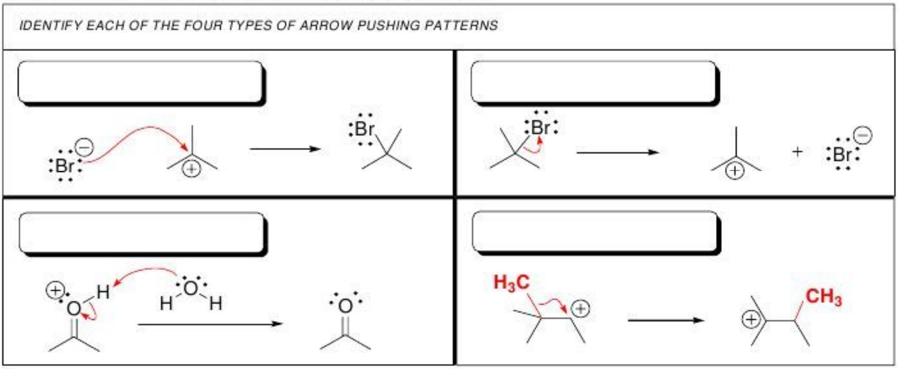
TAKE THE SUM OF STEPS 1 AND 2

SkillBuilder 6.2 Identifying Nucleophilic and Electrophilic Centers



CLASSIFY EACH OF THE HIGHLIGHTED REGIONS BELOW AS EITHER A NUCLEOPHILIC CENTER OR AN ELECTROPHILIC CENTER

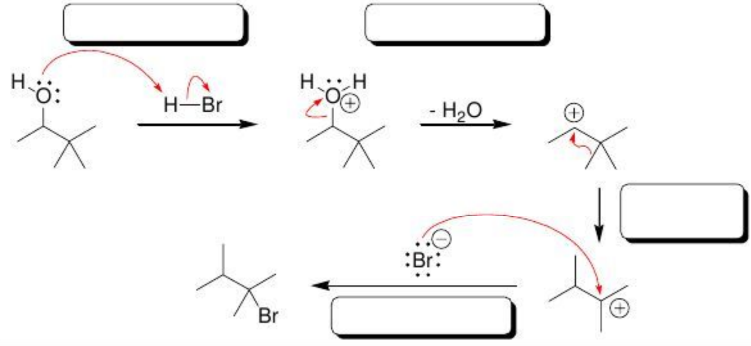
SkillBuilder 6.3 Identifying an Arrow Pushing Pattern



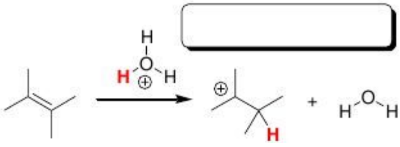
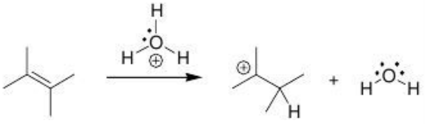
IDENTIFY EACH OF THE FOUR TYPES OF ARROW PUSHING PATTERNS

SkillBuilder 6.4 Identifying a Sequence of Arrow Pushing Patterns

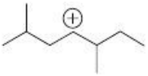
IDENTIFY EACH OF THE FOLLOWING ARROW PUSHING PATTERNS



SkillBuilder 6.5 Drawing Curved Arrows

STEP 1 *- IDENTIFY WHICH OF THE FOUR ARROW PUSHING PATTERNS TO USE IN THE FOLLOWING CASE:* 	***STEP 2*** *- DRAW THE CURVED ARROW, FOCUSING ON THE PROPER PLACEMENT OF THE TAIL AND HEAD OF EACH CURVED ARROW* 

SkillBuilder 6.6 Predicting Carbocation Rearrangements

STEP 1 *- CIRCLE THE CARBON ATOMS BELOW THAT ARE IMMEDIATELY ADJACENT TO THE C+* 	***STEP 2*** *- IDENTIFY ANY H OR CH_3 ATTACHED DIRECTLY TO THESE CARBON ATOMS*	***STEP 3****- FIND ANY GROUPS THAT CAN MIGRATE TO GENERATE A MORE STABLE C+*	***STEP 4*** *- DRAW A CURVED ARROW SHOWING THE C+ REARRANGEMENT AND THEN DRAW THE NEW CARBOCATION*

Solutions

6.1.

a)

Bonds Broken	**kJ/mol**	**Bonds Formed**	**kJ/mol**
H—$CH(CH_3)_2$	**+ 397**	$(CH_3)_2CH$—Br	**– 285**
Br—Br	**+ 192**	H—Br	**– 368**

Sum = – 64 kJ/mol.
ΔH° for this reaction is negative, which means that the system is losing energy. It is giving off energy to the environment, so the reaction is exothermic.

b)

Bonds Broken	**kJ/mol**	**Bonds Formed**	**kJ/mol**
$(CH_3)_3C$—Cl	**+ 331**	$(CH_3)_3C$—OH	**– 381**
H—OH	**+ 498**	H—Cl	**– 431**

Sum = + 17 kJ/mol.
ΔH° for this reaction is positive, which means that the system is gaining energy. It is receiving energy from the environment, so the reaction is endothermic.

c)

Bonds Broken	**kJ/mol**	**Bonds Formed**	**kJ/mol**
$(CH_3)_3C$—Br	**+ 272**	$(CH_3)_3C$—OH	**– 381**
H—OH	**+ 498**	H—Br	**– 368**

Sum = + 21 kJ/mol.
ΔH° for this reaction is positive, which means that the system is gaining energy. It is receiving energy from the environment, so the reaction is endothermic.

d)

Bonds Broken	**kJ/mol**	**Bonds Formed**	**kJ/mol**
$(CH_3)_3C$—I	**+ 209**	$(CH_3)_3C$—OH	**– 381**
H—OH	**+ 498**	H—I	**– 297**

Sum = + 29 kJ/mol.
ΔH° for this reaction is positive, which means that the system is gaining energy. It is receiving energy from the environment, so the reaction is endothermic.

6.2.

The C-C bond of CH_3—CH_3 has a bond dissociation energy of = +368 kJ/mol. If a C=C bond has a total bond dissociation energy of +632 kJ/mol, then the pi component of the double bond can be estimated to be (632 kJ/mol) – (368 kJ/mol) = 264 kJ/mol. In other words, the pi component of the C=C bond is not as strong as the sigma component of the C=C bond. In the reaction shown in this problem, the pi component of the C=C bond is broken but the sigma component remains intact. Accordingly, the calculation is as follows:

Bonds Broken	**kJ/mol**	**Bonds Formed**	**kJ/mol**
C=C (just the pi component)	**+ 264**	CH_3CH_2—OH	**– 381**
H—OH	**+ 498**	H—CH_2R	~ **– 410**

Sum = - 29 kJ/mol.
ΔH° for this reaction is predicted to be negative, which means that the system is losing energy. It is giving off energy to the environment, so the reaction is exothermic.

6.3.

a) ΔS_{sys} is expected to be negative (a decrease in entropy) because two molecules are converted into one molecule.
b) ΔS_{sys} is expected to be negative (a decrease in entropy) because an acylic compound is converted into a cyclic compound.
c) ΔS_{sys} is expected to be positive (an increase in entropy) because one molecule is converted into two molecules.
d) ΔS_{sys} is expected to be positive (an increase in entropy) because one molecule is converted into two ions.
e) ΔS_{sys} is expected to be negative (a decrease in entropy) because two chemical entities are converted into one.
f) ΔS_{sys} is expected to be positive (an increase in entropy) because a cyclic compound is converted into an acyclic compound.

6.4.

a) There is a competition between the two terms contributing to ΔG. In this case, the reaction is endothermic, which contributes to a positive value for ΔG, but the second term contributes to a negative value for ΔG:

$$\Delta G = \underset{\oplus}{\Delta H} + \underset{\ominus}{(-T\Delta S)}$$

The sign of ΔG will therefore depend on the competition between these two terms, which is affected by temperature. A high temperature will cause the second term to dominate, giving rise to a positive value of ΔG. A low temperature will render the second term insignificant, and the first term will dominate, giving rise to a negative value of ΔG.

b) In this case, both terms contribute to a negative value for ΔG, so ΔG will definitely be negative (the process will be spontaneous).

c) In this case, both terms contribute to a positive value for ΔG, so ΔG will definitely be positive (the process will not be spontaneous).

d) There is a competition between the two terms contributing to ΔG. In this case, the reaction is exothermic, which contributes to a negative value for ΔG, but the second term contributes to a positive value for ΔG:

$$\Delta G = \underset{\ominus}{\Delta H} + \underset{\oplus}{(-T\Delta S)}$$

The sign of ΔG will therefore depend on the competition between these two terms, which is affected by temperature. A high temperature will cause the second term to dominate, giving rise to a negative value of ΔG. A low temperature will render the second term insignificant, and the first term will dominate, giving rise to a positive value of ΔG.

6.5. A system can only achieve a lower energy state by transferring energy to its surroundings (conservation of energy). This increases the entropy of the surroundings, which more than offsets the decrease in entropy of the system. As a result, ΔS_{tot} increases.

6.6.

a) A positive value of ΔG favors reactants.
b) A reaction for which $K_{eq} < 1$ will favor reactants.
c) $\Delta G = \Delta H - T\Delta S = (33 \text{ kJ/mol}) - (298 \text{ K})(0.150 \text{ kJ/mol} \bullet \text{K}) = -11.7 \text{ kJ/mol}$
A negative value of ΔG favors products.
d) Both terms contribute to a negative value of ΔG, which favors products.
e) Both terms contribute to a positive value of ΔG, which favors reactants.

6.7.

a) Process D will occur more rapidly because it has a lower energy of activation than process A.
b) Process A will more greatly favor products at equilibrium than process B, because the former is exergonic (the products are lower in energy than the reactants) while the latter is not exergonic.
c) None of these processes exhibits an intermediate, because none of the energy diagrams has a local minimum (a valley). But all of the processes proceed via a transition state, because all of the energy diagrams have a local maximum (a peak).

d) In process A, the transition state resembles the reactants more than products because the transition state is closer in energy to the reactant than the products (the Hammond postulate).

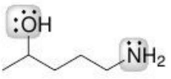
e) Process A will occur more rapidly because it has a lower energy of activation than process B.

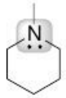
f) Process D will more greatly favor products at equilibrium than process B, because the former is exergonic (the products are lower in energy than the reactants) while the latter is not exergonic.

g) In process C, the transition state resembles the products more than reactants because the transition state is closer in energy to the products than the reactants (the Hammond postulate).

6.8.

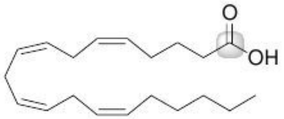
a) 

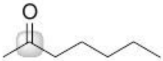
b) 

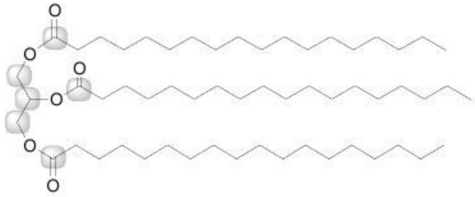
c) 

d) 

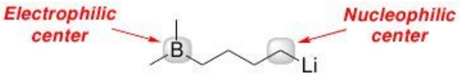
6.9.

a) 

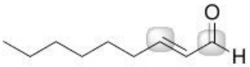
b) 

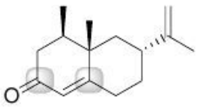
c) 

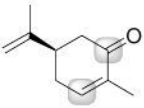
6.10.



6.11.

a) 

b) 

c) 

6.12.

a) loss of a leaving group

b) proton transfer

c) rearrangement

d) nucleophilic attack
e) proton transfer
f) nucleophilic attack
g) rearrangement
h) loss of a leaving group
i) nucleophilic attack

6.13. The pi bond functions as a nucleophile and attacks the electrophilic carbocation. This step is therefore a nucleophilic attack.

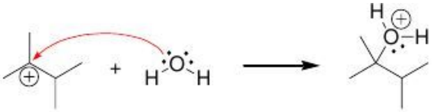
6.14.

a) proton transfer; nucleophilic attack; proton transfer
b) nucleophilic attack; proton transfer; proton transfer
c) proton transfer; nucleophilic attack; loss of a leaving group
d) proton transfer; loss of a leaving group; nucleophilic attack; proton transfer
e) proton transfer; nucleophilic attack; proton transfer

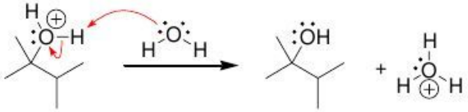
6.15. Both reactions have the same sequence: 1) nucleophilic attack, followed by 2) loss of a leaving group. In both cases, a hydroxide ion functions as a nucleophile and attacks a compound that can accept the negative charge and store it temporarily. The charge is then expelled as a chloride ion in both cases.

6.16.

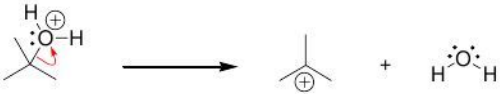
a)



b)

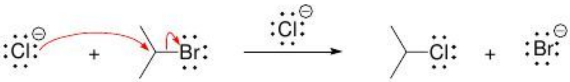


c)

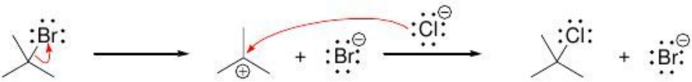


6.17.

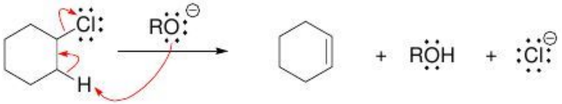
a)



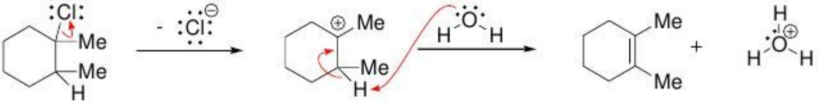
b)



c)

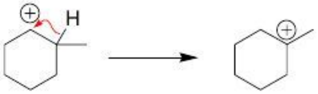


d)



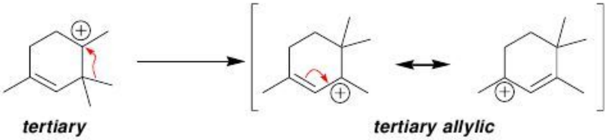
6.18.

a)



b) This carbocation is tertiary and will not rearrange

c)

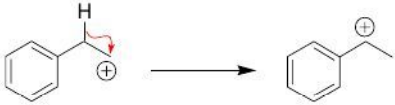


d) This carbocation is secondary, but it cannot rearrange to form a tertiary carbocation.

e)

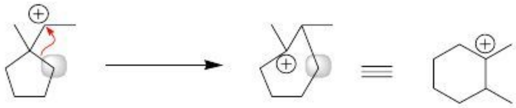
f)

g)



h) This carbocation is tertiary and it is resonance stabilized (we will see in Chapter 7 that this carbocation is called a benzylic carbocation). It will not rearrange.

6.19.



6.20.

a) a carbon-carbon triple bond is comprised of one sigma bond and two pi bonds, and is therefore stronger than a carbon-carbon double bond (one sigma and one pi bond) or a carbon-carbon single bond (only one sigma bond).

b) Using the data in Table 6.1, the C-F will have the largest bond dissociation energy.

6.21.

a)

Bonds Broken	**kJ/mol**	**Bonds Formed**	**kJ/mol**
RCH_2—Br	**+ 285**	RCH_2—OR	**– 381**
RCH_2O—H	**+ 435**	H—Br	**– 368**

Sum = – 29 kJ/mol.

ΔHº for this reaction is negative, which means that the system is losing energy. It is giving off energy to the environment, so the reaction is exothermic.

b) ΔS of this reaction is positive because one mole of reactant is converted into two moles of product.

c) Both terms (ΔH) and (-TΔS) contribute to a negative value of ΔG.

d) No.

e) Yes.

6.22.

a) A reaction for which $K_{eq} > 1$ will favor products.

b) A reaction for which $K_{eq} < 1$ will favor reactants.

c) A positive value of ΔG favors reactants.

d) Both terms contribute to a negative value of ΔG, which favors products.

e) Both terms contribute to a positive value of ΔG, which favors reactants.

6.23. $K_{eq} = 1$ when $\Delta G = 0$ kJ/mol (See Table 6.2).

6.24. $K_{eq} < 1$ when ΔG has a positive value. The answer is therefore “a” (+1 kJ/mol)

6.25.

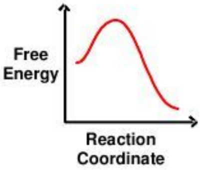
a) ΔS_{sys} is expected to be negative (a decrease in entropy) because two moles of reactant are converted into one mole of product.

b) ΔS_{sys} is expected to be positive (an increase in entropy) because one mole of reactant is converted into two moles of product.

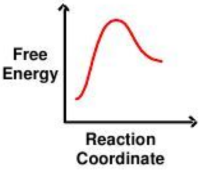
c) ΔS_{sys} is expected to be approximately zero, because two moles of reactant are converted into two moles of product.
d) ΔS_{sys} is expected to be negative (a decrease in entropy) because an acylic compound is converted into a cyclic compound.
e) ΔS_{sys} is expected to be approximately zero, because one mole of reactant is converted into one mole of product, and both the reactant and the product are acyclic.

6.26.

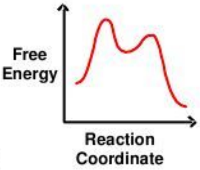
a)



b)

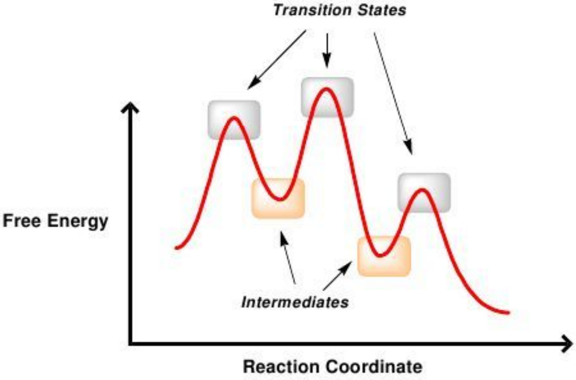


c)



6.27.
a) B and D
b) A and C
c) C
d) A
e) D
f) D
g) A and B
h) C

6.28. All local minima (valleys) represent intermediates, while all local maxima (peaks) represent transition states:



6.29.

a) Rate = k[nucleophile][substrate].

b) The rate will be tripled, because the rate is linearly dependent on the concentration of the nucleophile.

c) The rate will be tripled, because the rate is linearly dependent on the concentration of the substrate.

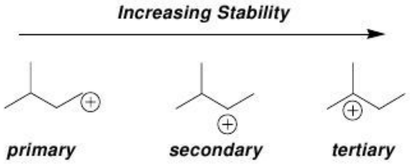
d) As a rule of thumb, the rate doubles for every increase of 10º C. Therefore an increase of 40º C will correspond to increase in rate of approximately 16-fold (2 x 2 x 2 x 2)

6.30.

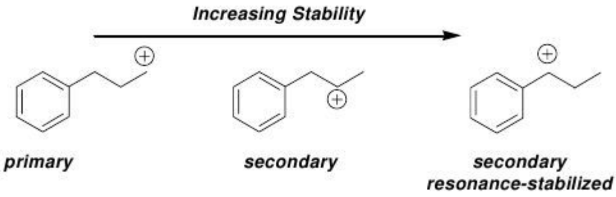
a) loss of a leaving group
b) carbocation rearrangement
c) nucleophilic attack
d) proton transfer

6.31.

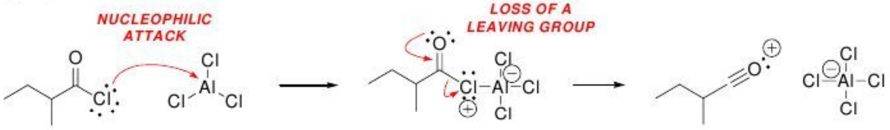
a)



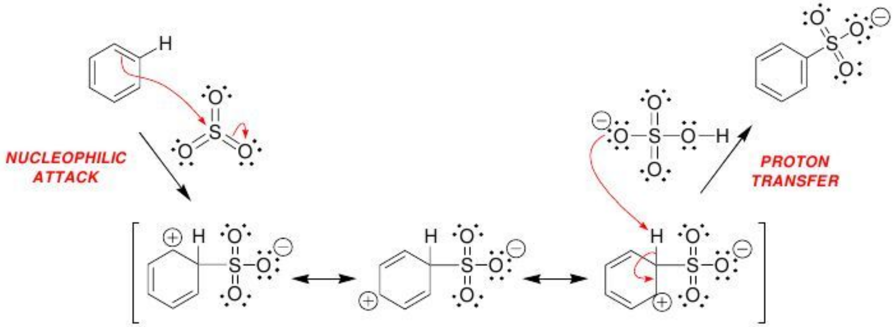
b)



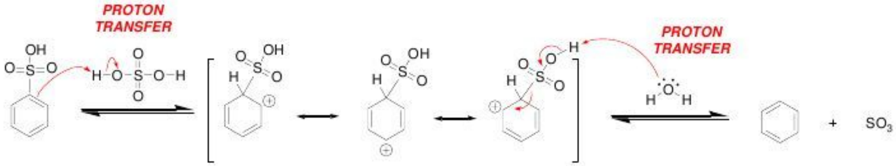
6.32.



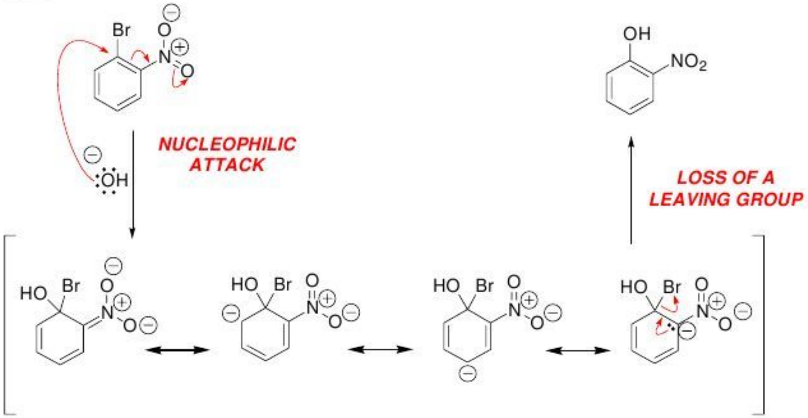
6.33.


NUCLEOPHILIC ATTACK
PROTON TRANSFER

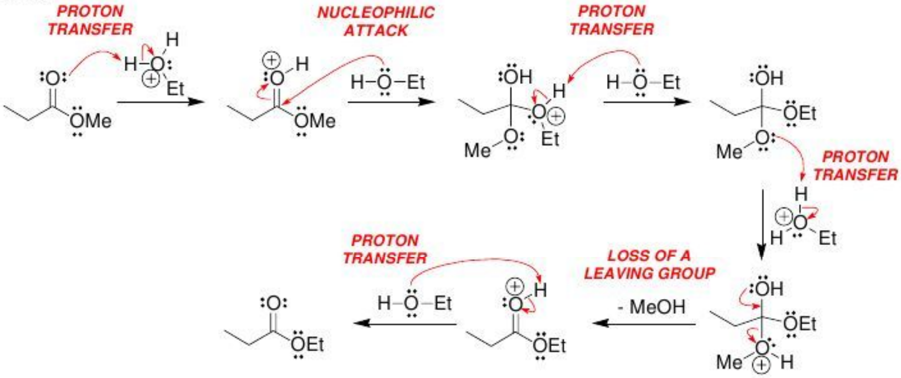
6.34.


PROTON TRANSFER
PROTON TRANSFER
SO3

6.35.


NUCLEOPHILIC ATTACK
LOSS OF A LEAVING GROUP
NO2

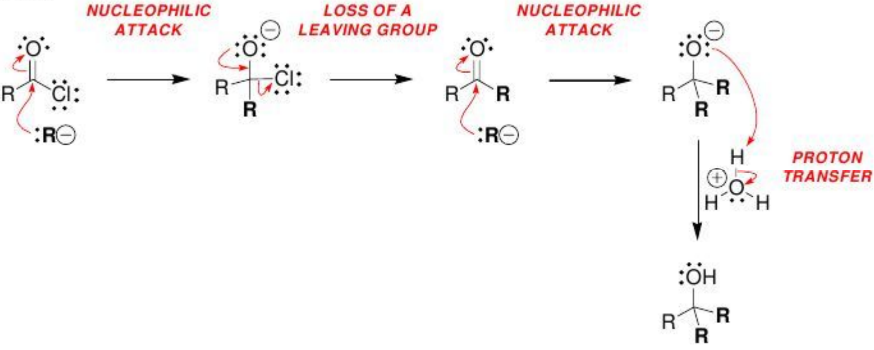
6.36.


PROTON TRANSFER
NUCLEOPHILIC ATTACK
H–O–Et
PROTON TRANSFER
H–O–Et
PROTON TRANSFER
LOSS OF A LEAVING GROUP
- MeOH
PROTON TRANSFER
H–O–Et

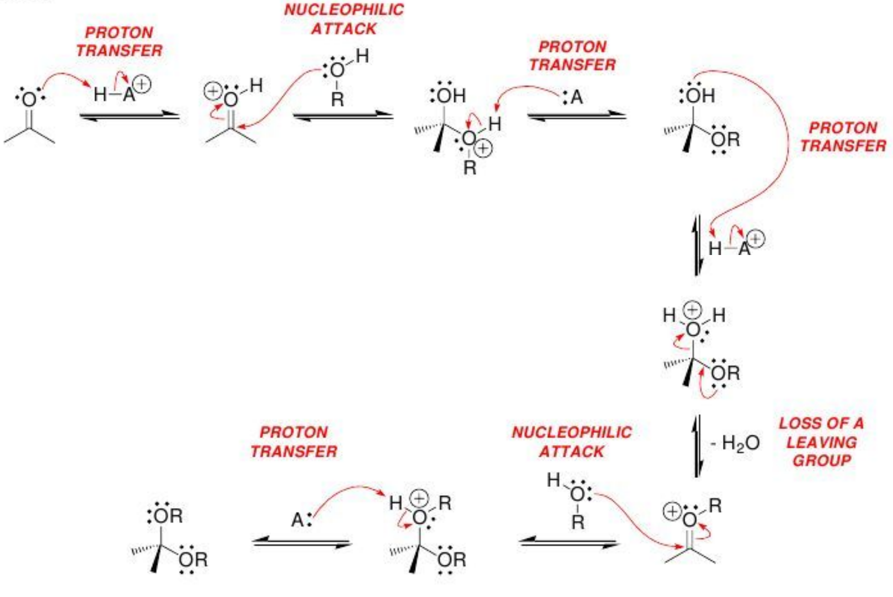
6.37.


NUCLEOPHILIC ATTACK
H–O–H
LOSS OF A LEAVING GROUP
- :Cl:
PROTON TRANSFER
H–O–H

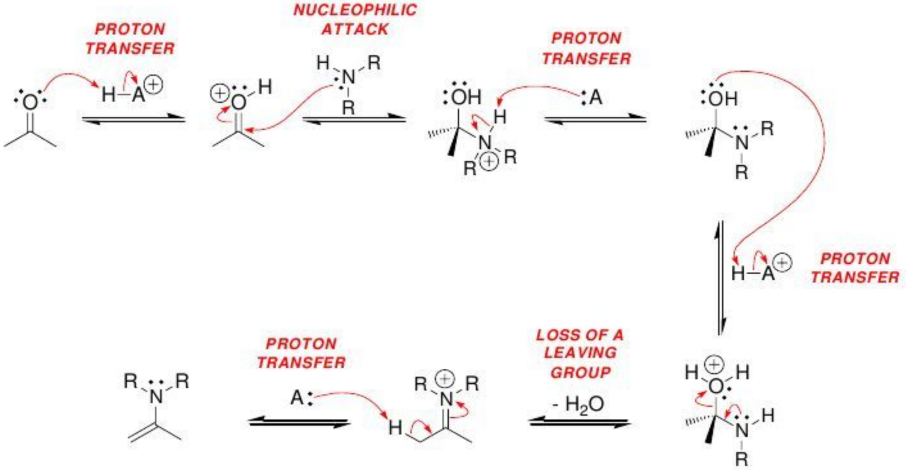
6.38.


NUCLEOPHILIC ATTACK
LOSS OF A LEAVING GROUP
NUCLEOPHILIC ATTACK
PROTON TRANSFER

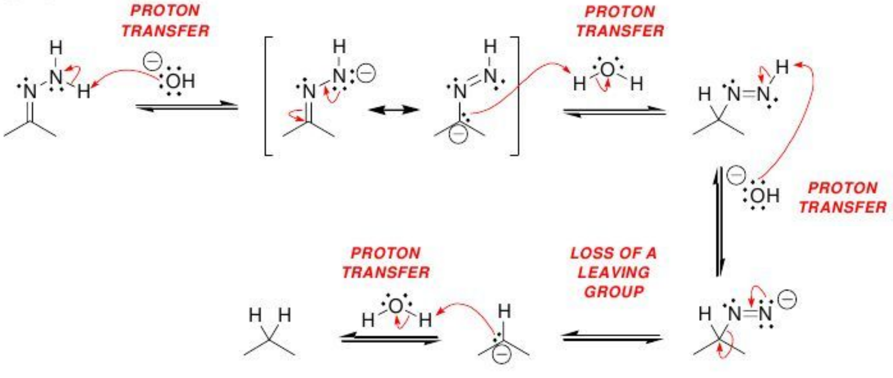
6.39.


PROTON TRANSFER
H–A⊕
NUCLEOPHILIC ATTACK
PROTON TRANSFER
:A
PROTON TRANSFER
H–A⊕
- H₂O
LOSS OF A LEAVING GROUP
NUCLEOPHILIC ATTACK
PROTON TRANSFER
A:

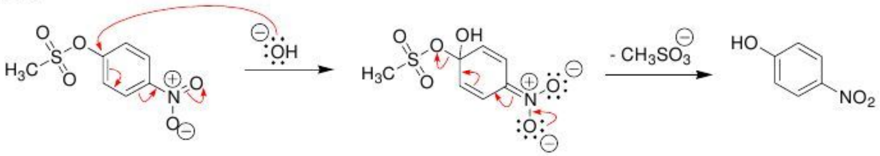
6.40.


PROTON TRANSFER
H–A⊕
NUCLEOPHILIC ATTACK
PROTON TRANSFER
:A
PROTON TRANSFER
H–A⊕
LOSS OF A LEAVING GROUP
- H₂O
PROTON TRANSFER
A:

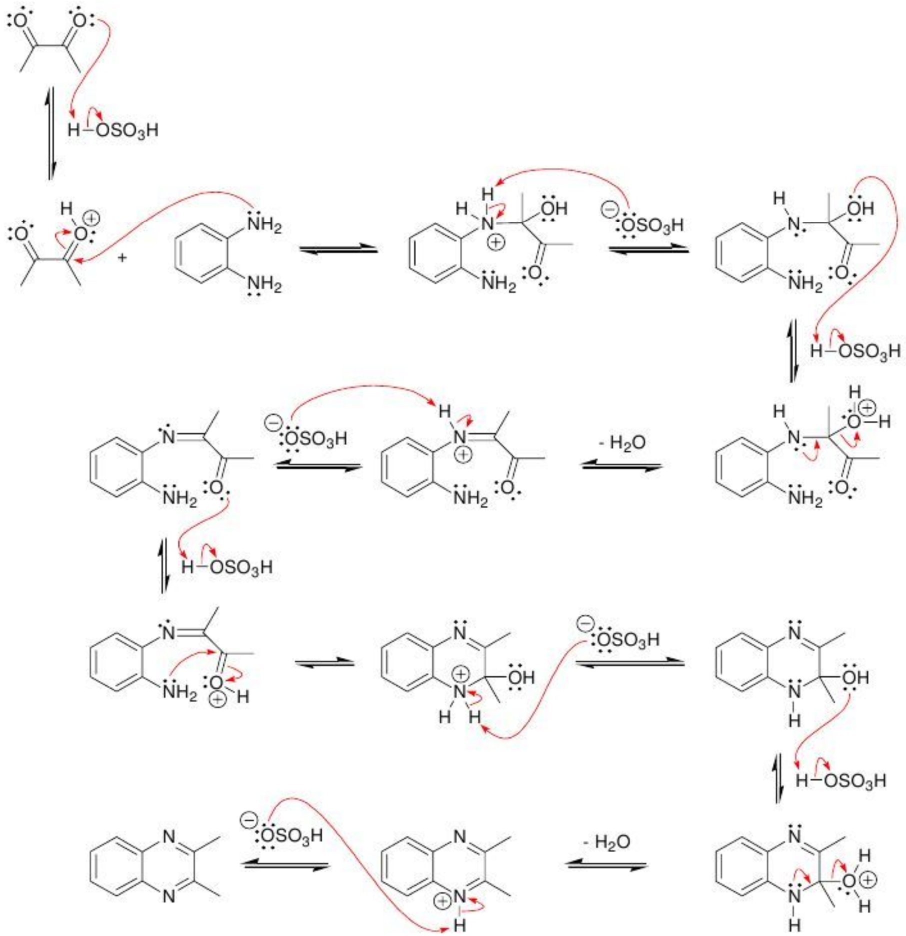
6.41.


PROTON TRANSFER
PROTON TRANSFER
PROTON TRANSFER
LOSS OF A LEAVING GROUP
PROTON TRANSFER

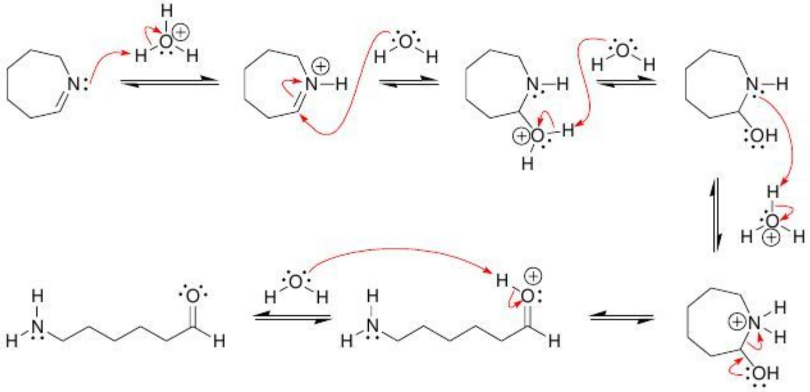
6.42.


- CH3SO3
NO2

6.43.



6.44.



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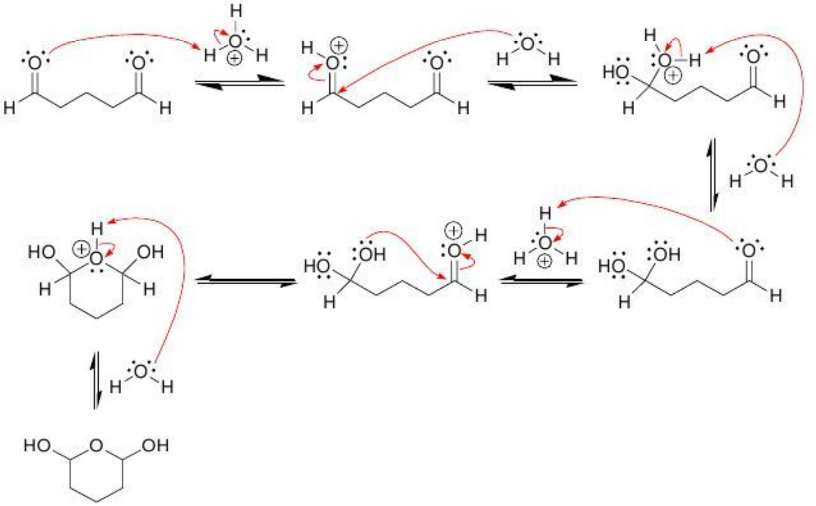

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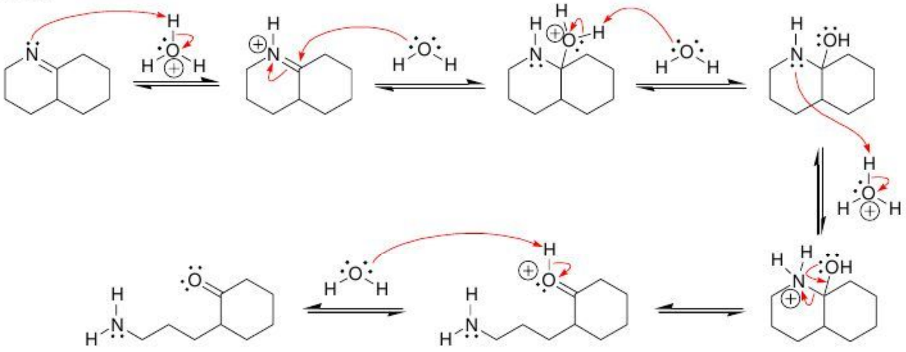
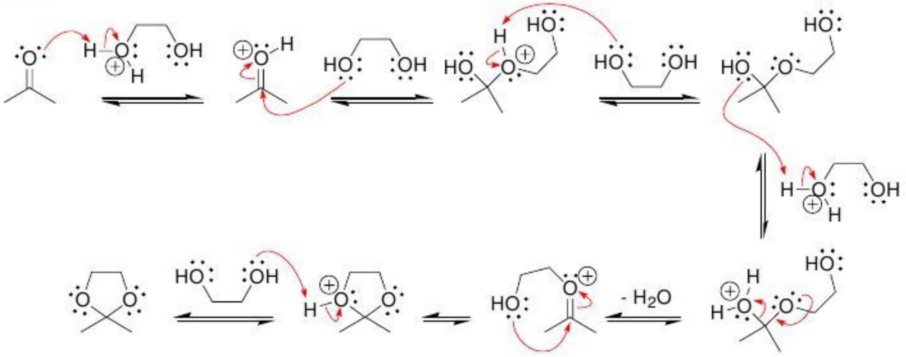
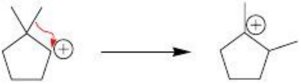


6.47.



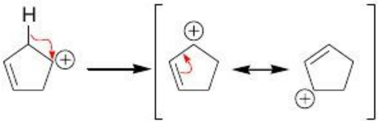
6.48.



a)

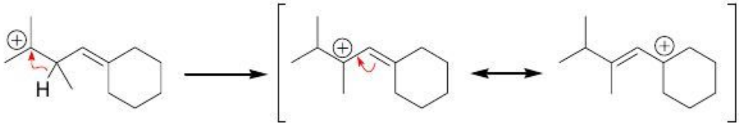
b)

c) This carbocation is secondary, but it cannot rearrange to generate a tertiary carbocation.

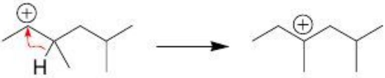


d)

e)



f)



g) This carbocation is tertiary and will not rearrange.

6.49.

a)

b) Nucleophilic attack and loss of a leaving group.

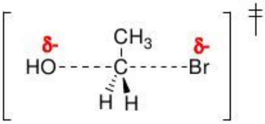
c) A CH_3CH_2—Br is broken, and a CH_3CH_2—OH is formed. Using the data in Table 6.1, ΔH for this reaction is expected to be approximately (285 kJ/mol) – (381 kJ/mol). The sign of ΔH is therefore predicted to be negative, which means that the reaction should be exothermic.

d) Two chemical entities are converted into two chemical entities. Both the reactants and products are acyclic. Therefore, ΔS for this process is expected to be approximately zero.

e) ΔG has two components: (ΔH) and (-TΔS). Based on the answers to the previous questions, the first term has a negative value and the second term is insignificant. Therefore, ΔG is expected to have a negative value. This is confirmed by the energy diagram, which shows the products having lower free energy than the reactants.

f) The position of equilibrium is dependent on the sign and value of ΔG. As mentioned in part e, ΔG is comprised of two terms. The effect of temperature appears in the second term (-TΔS), which is insignificant because ΔS is approximately zero. Therefore, an increase (or decrease) in temperature is not expected to have a significant impact on the position of equilibrium.

g) This transition state corresponds with the peak of the curve, and has the following structure:



h) The transition state in this case is closer in energy to the reactants than the products, and therefore, it is closer in structure to the reactants than the products (the Hammond postulate).

i) The reaction is second order.

j) According to the rate equation, the rate is linearly dependent on the concentration of hydroxide. Therefore, the rate will be doubled if the concentration of hydroxide is doubled.

k) Yes, the rate will increase with increasing temperature.

6.50.

a) K_{eq} does not affect the rate of the reaction. It only affects the equilibrium concentrations.

b) ΔG does not affect the rate of the reaction. It only affects the equilibrium concentrations.

c) Temperature does affect the rate of the reaction, by increasing the number of collisions that result in a reaction.

d) ΔH does not affect the rate of the reaction. It only affects the equilibrium concentrations.

e) E_a greatly affects the rate of the reaction. Lowering the E_a will increase the rate of reaction.

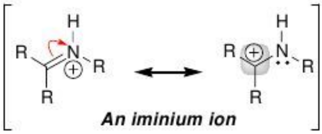
f) ΔS does not affect the rate of the reaction. It only affects the equilibrium concentrations.

6.51. In order to determine if reactants or products are favored at high temperature, we must consider the effect of temperature on the sign of ΔG. Recall that ΔG has two components: (ΔH) and (-TΔS). The reaction is exothermic, so the first term (ΔH) has a negative value, which contributes to a negative value of ΔG. This favors products. At low temperature, the second term will be insignificant and the first term will dominate. Therefore, the process will be thermodynamically favorable, and the reaction will favor the formation of products. However, at high temperature, the second term becomes more significant. In this case, two moles of reactants are converted into one mole of product. Therefore, ΔS for this process is negative, which means that (-TΔS) is positive. At high enough temperature, the second term (-TΔS) should dominate over the first term (ΔH), generating a positive value for ΔG. Therefore, the reaction will favor reactants at high temperature.

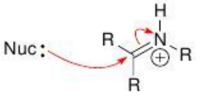
6.52. Recall that ΔG has two components: (ΔH) and (-TΔS). We must analyze each term separately. The first term is expected to have a negative value, because three pi bonds are being converted into one pi bond and two sigma bonds. A sigma bond is stronger (lower in energy) than the pi component of a double bond (see problems 6.2 and 6.20). Therefore, reaction is expected to release energy to the environment, which means the reaction should be exothermic. In other words, the first term (ΔH) has a negative value, which contributes to a negative value of ΔG. This favors products. Now let's consider the second term (-TΔS) contributing to ΔG. In this case, two moles of reactants are converted into one mole of product. Therefore, ΔS for this process is negative, which means that (-TΔS) is positive. At low temperature, the second term will be insignificant and the first term will dominate. Therefore, the process will be thermodynamically favorable, and the reaction will favor the formation of products. However, at high temperature, the second term becomes more significant. At high enough temperature, the second term (-TΔS) should dominate over the first term (ΔH), generating a positive value for ΔG. Therefore, the reaction will favor reactants at high temperature.

6.53. The nitrogen atom of an ammonium ion is positively charged, but that does not render it electrophilic. In order to be electrophilic, it must have an empty orbital that can be attacked by a nucleophile. The nitrogen atom in this case does not have an empty orbital, because nitrogen is a second row element and therefore only has four orbitals with which to form bonds. All four orbitals are being used for bonding, leaving none of the orbitals vacant. As a result, the nitrogen atom is not electrophilic, despite the fact that is positively charged.

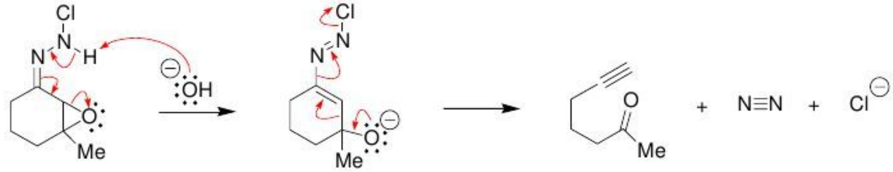
In contrast, an iminium ion is resonance stabilized:



The second resonance structure exhibits a positive charge on a carbon atom, which serves as an electrophilic center (a carbocation is an empty p orbital). Therefore, an iminium ion is an electrophile and is subject to attack by a nucleophile:



6.54.



Chapter 7
Substitution Reactions

Review of Concepts

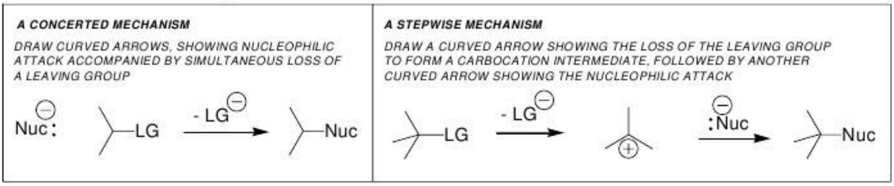
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 7. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- Substitution reactions exchange one _____________ for another.
- Evidence for the concerted mechanism, called **$\mathrm{S_N}$2**, includes the observation of a __________**-order** rate equation. The reaction proceeds with ____________ **of configuration**.
- $\mathrm{S_N}$2 reactions are said to be _________________ because the configuration of the product is determined by the configuration of the substrate.
- Evidence for the stepwise mechanism, called **$\mathrm{S_N}$1**, includes the observation of a __________**-order** rate equation.
- The __________ step of an $\mathrm{S_N}$1 process is the **rate-determining step**.
- An **$\mathrm{S_N}$1 reaction** is a stepwise process with a **first-order** rate equation.
- There are four factors that impact the competition between the $\mathrm{S_N}$2 mechanism and $\mathrm{S_N}$1: 1) the _____________, 2) the ________________, 3) the ___________ _______________, and 4) the ______________.
- ______________________ solvents favor $\mathrm{S_N}$2.

Review of Skills

Follow the instructions below. To verify that your answers are correct, look in your textbook at the end of Chapter 7. The answers appear in the section entitled *SkillBuilder Review*.

SkillBuilder 7.1 Drawing the Curved Arrows of a Substitution Reaction



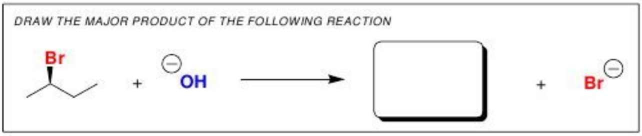
A CONCERTED MECHANISM

DRAW CURVED ARROWS, SHOWING NUCLEOPHILIC ATTACK ACCOMPANIED BY SIMULTANEOUS LOSS OF A LEAVING GROUP

A STEPWISE MECHANISM

DRAW A CURVED ARROW SHOWING THE LOSS OF THE LEAVING GROUP TO FORM A CARBOCATION INTERMEDIATE, FOLLOWED BY ANOTHER CURVED ARROW SHOWING THE NUCLEOPHILIC ATTACK

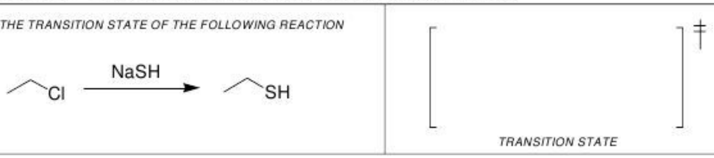
SkillBuilder 7.2 Drawing the Product of an $\mathrm{S_N}$2 Process



DRAW THE MAJOR PRODUCT OF THE FOLLOWING REACTION

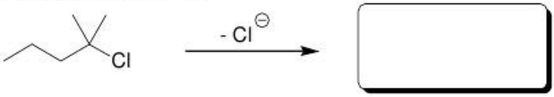
SkillBuilder 7.3 Drawing the Transition State of an S_N2 Process

DRAW THE TRANSITION STATE OF THE FOLLOWING REACTION



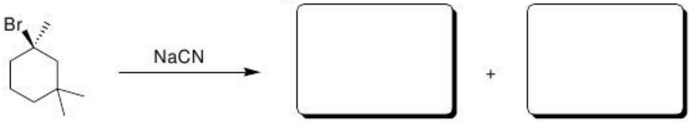
SkillBuilder 7.4 Drawing the Carbocation Intermediate of an S_N1 Process

DRAW THE CARBOCATION THAT WOULD BE FORMED IF A CHLORIDE ION IS EXPELLED FROM THE FOLLOWING COMPOUND



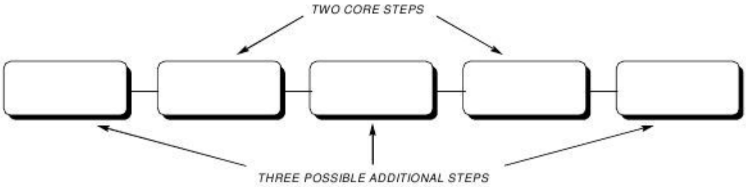
SkillBuilder 7.5 Drawing the Products of an S_N1 Process

PREDICT THE PRODUCTS OF THE FOLLOWING S_N1 REACTION



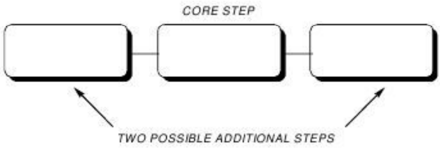
SkillBuilder 7.6 Drawing the Complete Mechanism of an S_N1 Process

IDENTIFY THE TWO CORE STEPS AND THREE POSSIBLE ADDITIONAL STEPS OF AN S_N1 PROCESS



SkillBuilder 7.7 Drawing the Complete Mechanism of an S_N2 Process

IDENTIFY THE ONE CORE STEP (CONCERTED) AND TWO POSSIBLE ADDITIONAL STEPS OF AN S_N2 PROCESS



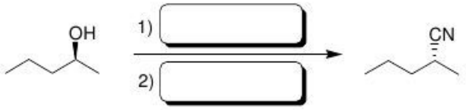
SkillBuilder 7.8 Determining whether a Reaction Proceeds via an S_N1 Mechanism or an S_N2 Mechanism

FILL IN THE TABLE BELOW, SHOWING THE FEATURES THAT FAVOR S_N2 OR S_N1 REACTIONS

	S_N2	S_N1
SUBSTRATE		
NUC		
LG		
SOLVENT		

SkillBuilder 7.9 Identifying the Reagents Necessary for a Substitution Reaction

IDENTIFY THE REAGENTS NECESSARY TO ACHIEVE THE FOLLOWING TRANSFORMATION

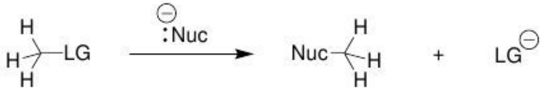


Review of Reactions

Follow the instructions below. To verify that your answers are correct, look in your textbook at the end of Chapter 7. The answers appear in the section entitled *Review of Reactions*.

S_N2

DRAW THE CURVED ARROWS THAT SHOW THE FLOW OF ELECTRON DENSITY DURING THE FOLLOWING S_N2 REACTION



S_N1

DRAW THE CURVED ARROWS THAT SHOW THE FLOW OF ELECTRON DENSITY DURING THE FOLLOWING S_N1 REACTION

Solutions

7.1.

a) 4-chloro-4-ethylheptane

b) 1-bromo-1-methylcyclohexane

c) 4,4-dibromo-1-chloropentane

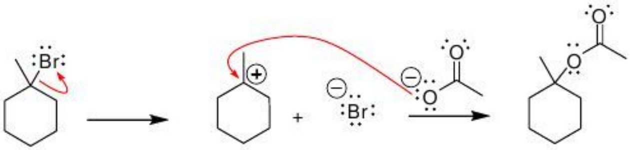
d) *(S)*-5-fluoro-2,2-dimethylhexane

7.2.

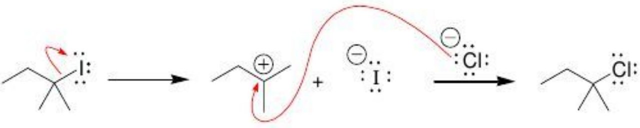
a)

b)

7.3.

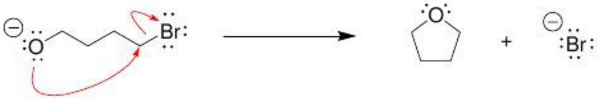


a)

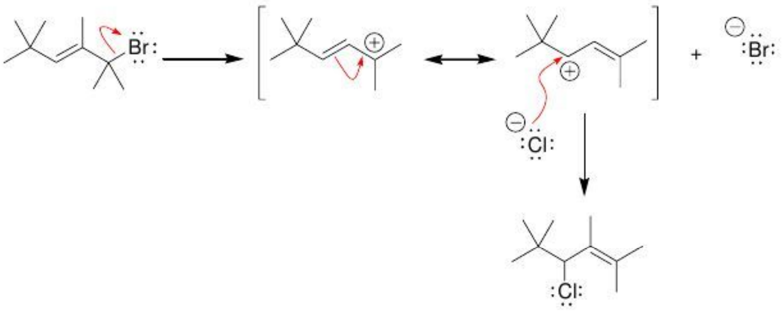


b)

7.4.



7.5.

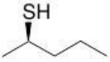


7.6.

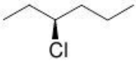
a) the rate of the reaction is tripled.
b) the rate of the reaction is doubled.
c) the rate of the reaction will be six times faster.

7.7.

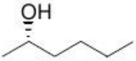
a)



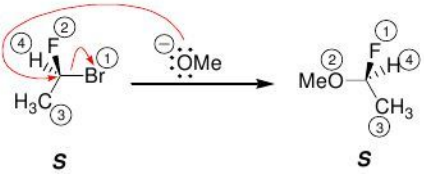
b)



c)



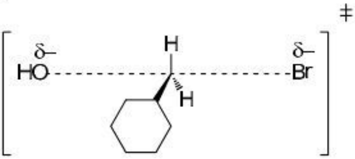
7.8.



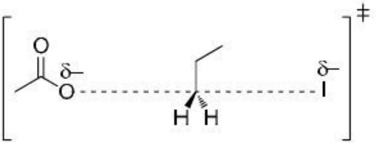
The reaction does proceed with inversion of configuration. However, the Cahn-Ingold-Prelog system for assigning a stereodescriptor (*R* or *S*) is based on a prioritization scheme. Specifically, the four groups connected to a chirality center are ranked (one through four). In the reactant (above left), the highest priority group is the leaving group (bromide) which is then replaced by a group that does not receive the highest priority. In the product, the fluorine atom has been promoted to the highest priority as a result of the reaction, and as such, the prioritization scheme has changed. In this way, the stereodescriptor (*S*) remains unchanged, despite the fact that chirality center undergoes inversion.

7.9.

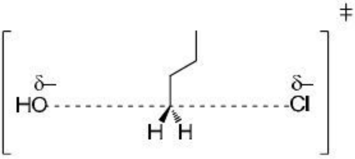
a)



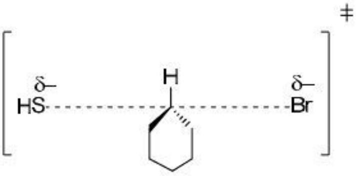
b)



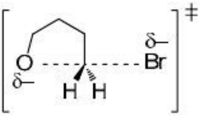
c)



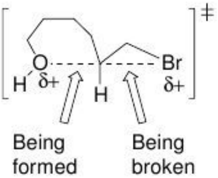
d)



7.10.

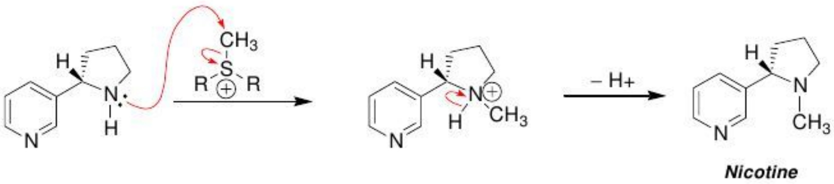


7.11.

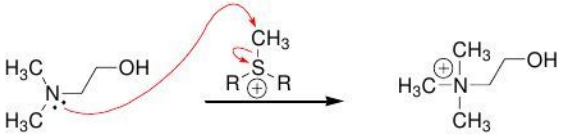


This step is favorable (downhill in energy) because ring strain is alleviated when the three-membered ring is opened.

7.12.



a)



b)

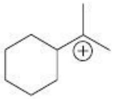
choline

7.13. a) The rate of the reaction will be doubled, because the change in concentration of sodium chloride will not affect the rate.

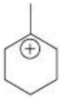
b) The rate of the reaction will remain the same, because the change in concentration of sodium chloride will not affect the rate.

7.14. Draw the carbocation intermediate generated by each of the following substrates in an S_N1 reaction:

(a)



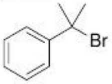
(b)



(c)

(d)

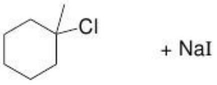
7.15.



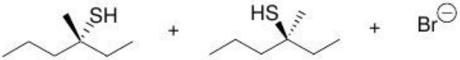
The first compound will generate a tertiary carbocation, while the second compound will generate a tertiary benzylic carbocation that is resonance stabilized. The second compound leads to a more stable carbocation, so that compound will lose its leaving group more rapidly than the first compound.

7.16.

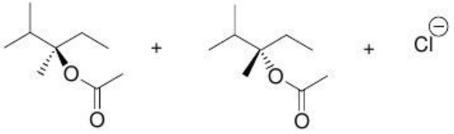
a)



b)

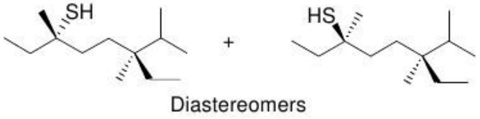


c)



d)

7.17.



7.18.

a) No b) Yes c) No d) Yes e) Yes f) No

7.19.

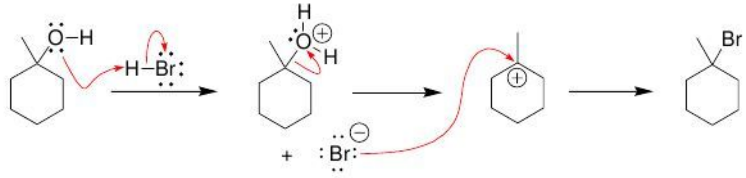
a) No b) Yes c) Yes d) Yes e) No f) No
g) No h) Yes i) No j) No k) Yes l) No

7.20.

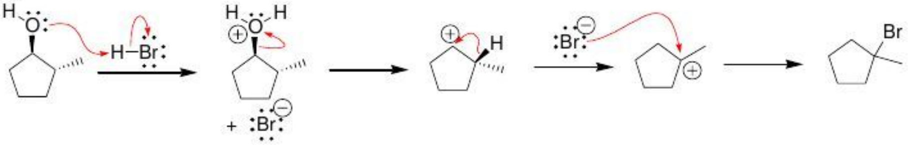
a) No b) Yes c) Yes d) No e) No f) No

7.21.

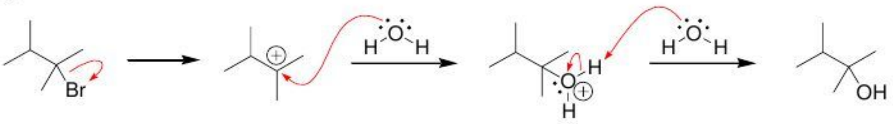
a)



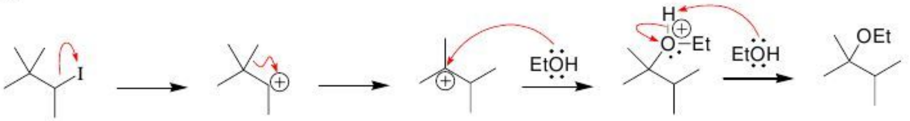
b)



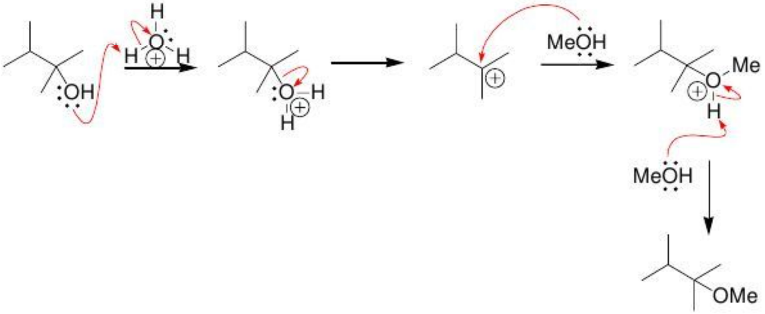
c)



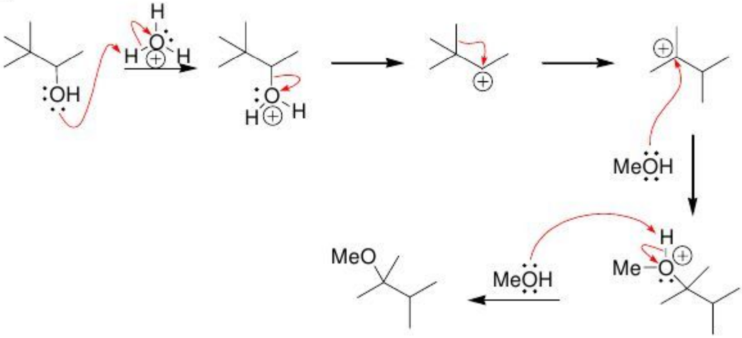
d)


I
EtOH
H
O
Et
EtOH
OEt

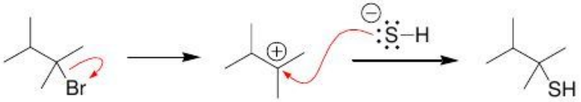
e)


H
O
H
H
OH
O
H
H
MeOH
O
Me
H
MeOH
OMe

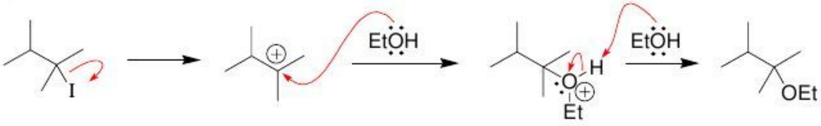
f)


H
O
H
H
OH
O
H
H
MeOH
H
Me
O
MeOH
MeO

g)


Br
S
H
SH

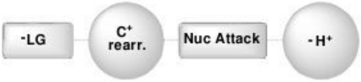
h)


I
EtOH
O
H
Et
EtOH
OEt

7.22.

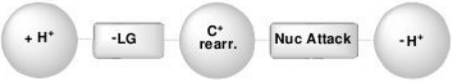
c)

d)



e)

f)

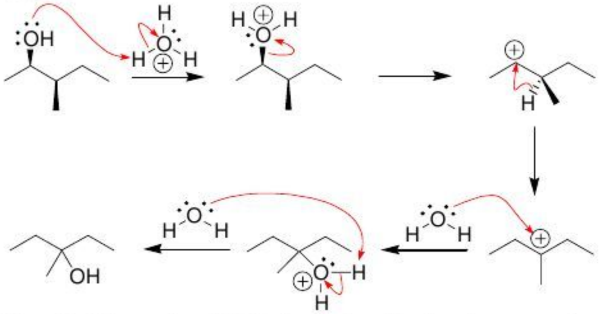


g)

h)

Problem 7.20c and 7.20h exhibit the same pattern. Both problems are characterized by three mechanistic steps: 1) loss of a leaving group, 2) nucleophilic attack, and 3) proton transfer.

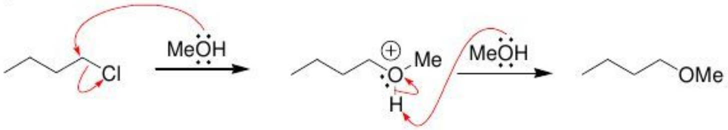
7.23.



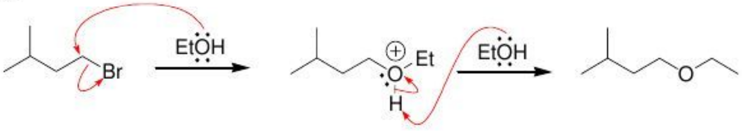
The chirality center at C2 is lost when the leaving group leaves to form a carbocation with trigonal planar geometry. The chirality center at C3 is lost during the hydride shift in the following step. Once again, the chirality center is converted into a trigonal planar sp^2 hybridized center (which is no longer a chirality center).

7.24.

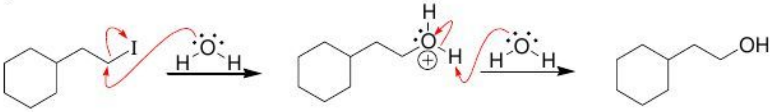
a)



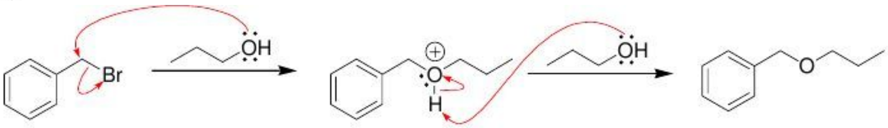
b)



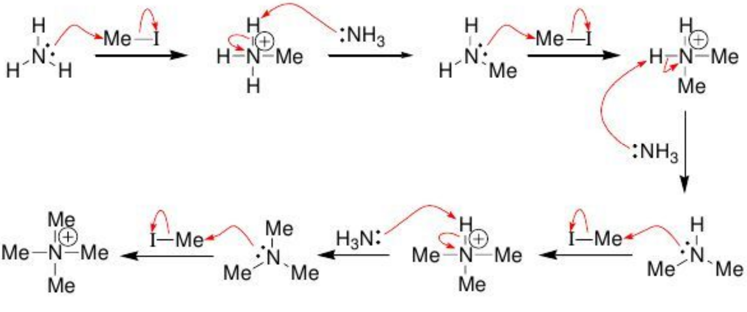
c)



d)



7.25.



7.26.

a) S_N1 b) S_N2 c) Neither d) S_N1

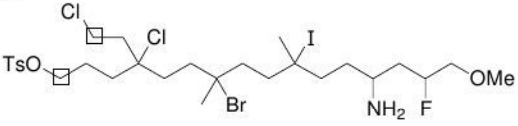
e) Both f) Neither g) Both

7.27.

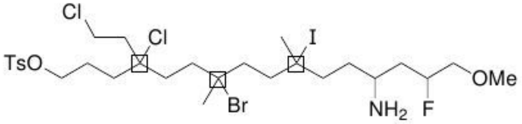
a) S_N1 b) S_N2 c) S_N2 d) S_N2 e) S_N2

7.28.

a)



b)



7.29.

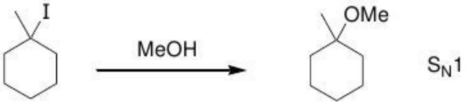
a) S_N1 b) S_N2 c) S_N1 d) S_N2
e) S_N1 f) S_N2 g) S_N2 h) S_N1

7.30.

Acetone is a polar aprotic solvent and will favor S_N2 by raising the energy of the nucleophile, giving a smaller E_a.

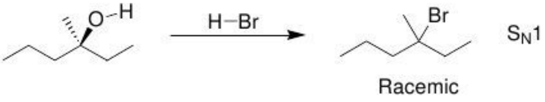
7.31.

a)

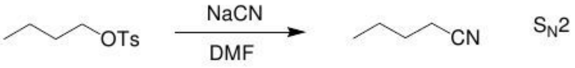


b)

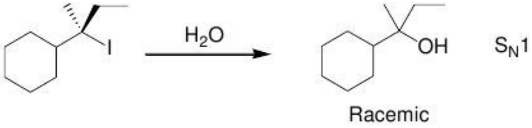
c)



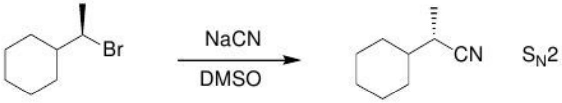
d)



e)



f)

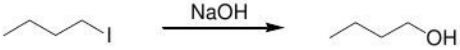


7.32.

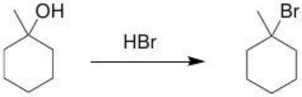
No. Preparation of this amine via the Gabriel synthesis would require the use of a tertiary alkyl halide, which will not undergo an S_N2 process.

7.33.

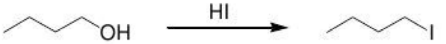
(a)



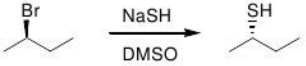
(b)



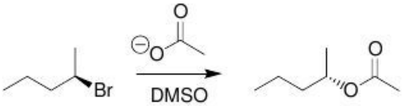
(c)



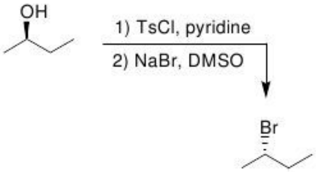
(d)



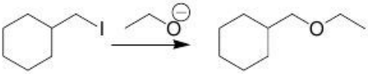
(e)



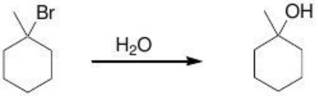
(f)



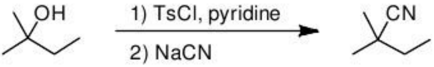
(g)



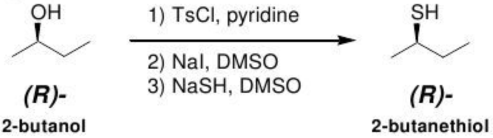
(h)



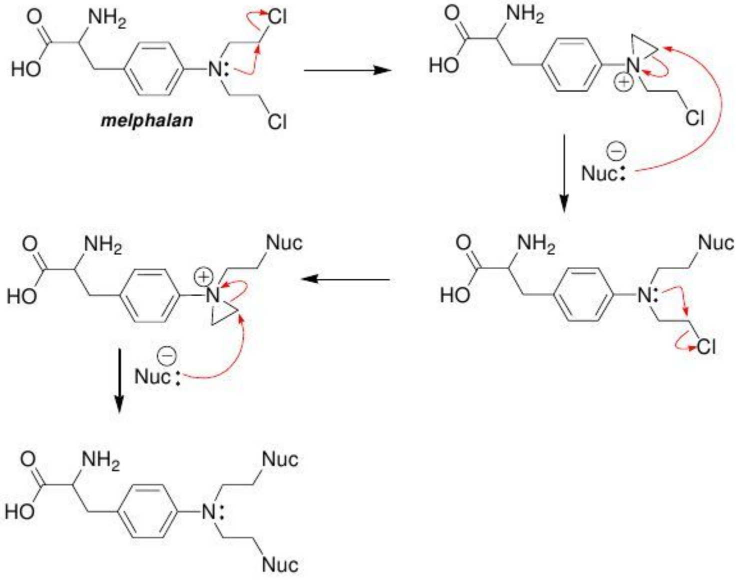
(i)



7.34.



7.35.



7.36.

a) Systematic Name = 2-chloropropane
Common Name = isopropyl chloride

b) Systematic Name = 2-bromo-2-methylpropane
Common Name = *tert*-butyl bromide

c) Systematic Name = 1-iodopropane
Common Name = propyl iodide

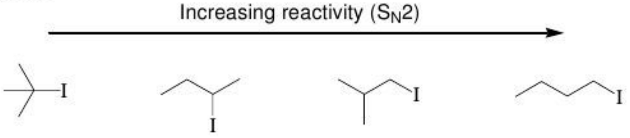
d) Systematic Name = 2-chlorobutane
Common Name = propyl iodide

d) Systematic Name = *(R)*-2-bromobutane
Common Name = *(R)*-*sec*-butyl bromide

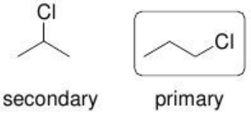
e) Systematic Name = 1-chloro-2,2-dimethylpropane
Common Name = neopentyl chloride

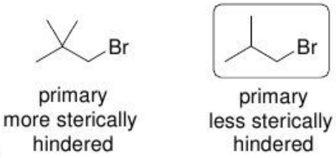
f) Systematic Name = chlorocyclohexane
Common Name = cyclohexyl chloride

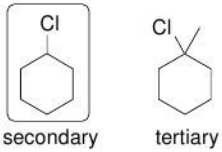
7.37.

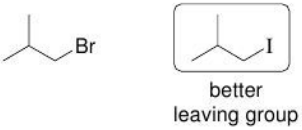


7.38.

a)


b)


c)


d)


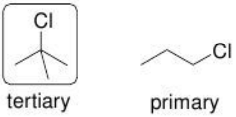
7.39.

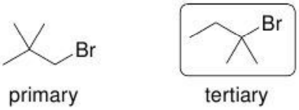
No. Preparation of this compound via the process above would require the use of a tertiary alkyl halide, which will not undergo an S_N2 process.

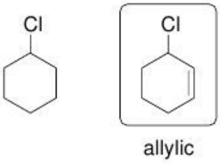
7.40.

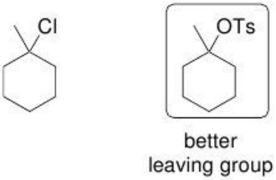
a) NaSH
b) sodium hydroxide
c) methoxide dissolved in DMSO

7.41.

a)


b)


c)


d)


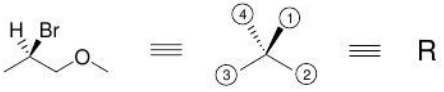
7.42. a) The rate of the reaction is doubled.
b) The rate of the reaction is doubled.

7.43. a) The rate of the reaction is doubled
b) The rate of the reaction will remain the same.

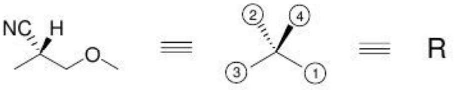
7.44. a) aprotic
b) protic
c) aprotic
d) protic
e) protic

7.45.

a)

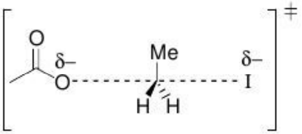


b)



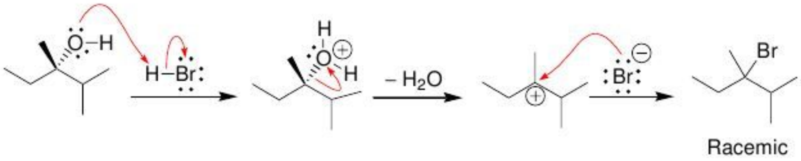
c) The reaction is an S_N2 process, and it does proceed with inversion of configuration. However, the prioritization scheme changes when bromide (#1) is replaced with a cyano group (#2). As a result, the Cahn-Ingold-Prelog system assigns the same configuration to the reactant and the product.

7.46.



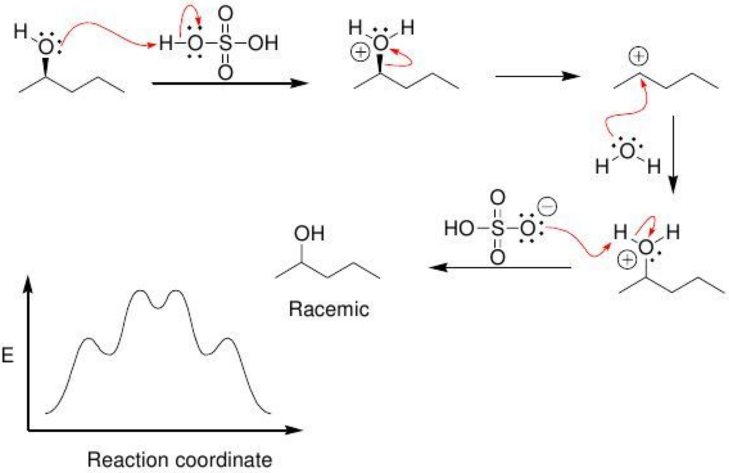
7.47.
Iodide functions as a nucleophile and attacks (*S*)-2-iodopentane, displacing iodide as a leaving group. The reaction is an S_N2 process, and therefore proceeds via inversion of configuration. The product is (*R*)-2-iodopentane. The reaction continues until a racemic mixture is obtained.

7.48.

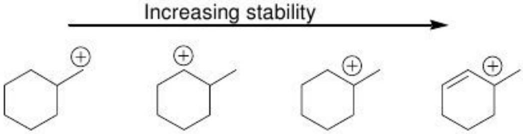


The chirality center is lost when the leaving group leaves to form a carbocation with trigonal planar geometry. The nucleophile can then attack either face of the planar carbocation, leading to a racemic mixture.

7.49.



7.50.

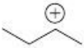


7.51.

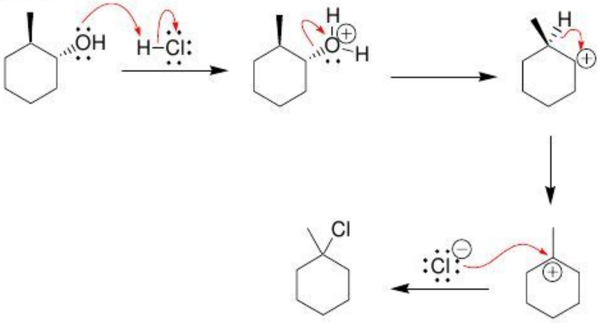

secondary


tertiary

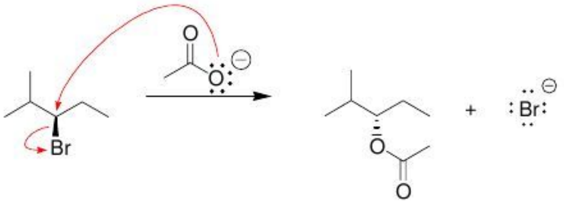

primary


secondary

7.52.

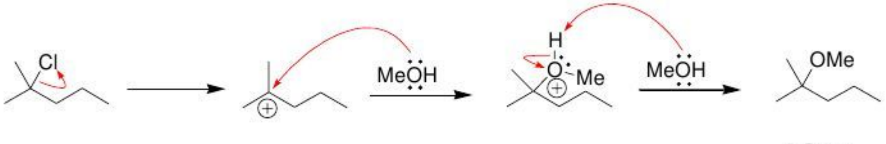


7.53.



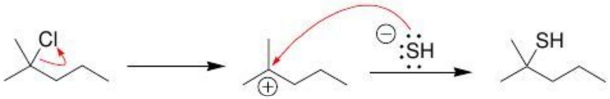
7.54.

a)



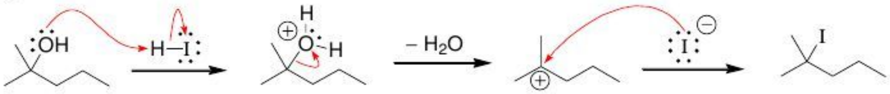
3 Steps

b)



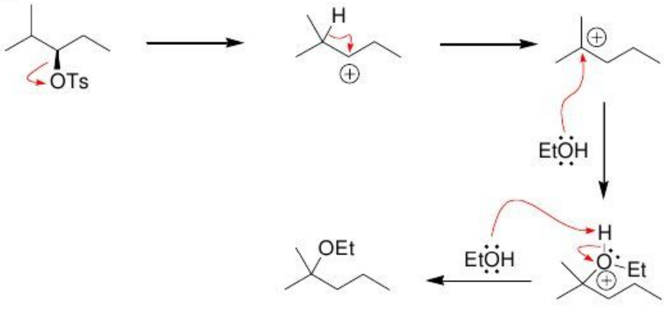
2 Steps

c)



3 Steps

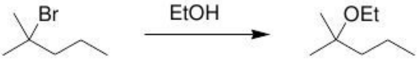
d)



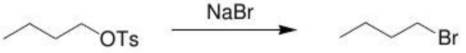
4 Steps

7.55.

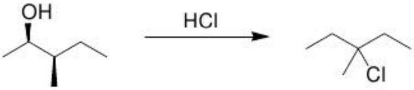
a)



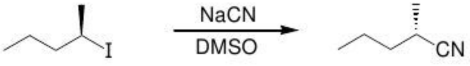
b)



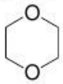
c)



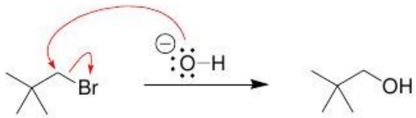
d)



7.56.



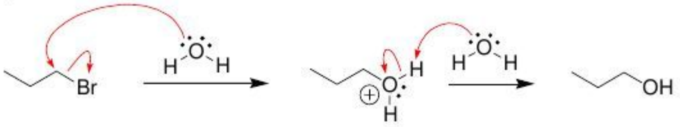
7.57.



Although the substrate is primary, it is still sterically hindered. As a result, S_N2 reactions at neopentyl halides do not occur at an appreciable rate.

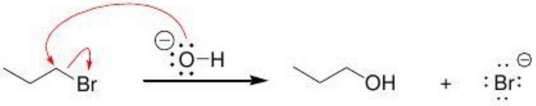
7.58.

a)



b) The substrate is primary, and therefore, the reaction must proceed via an S_N2 process. S_N2 reactions are highly sensitive to the strength of the nucleophile, and the nucleophile (water) is a weak nucleophile. As a result, the reaction occurs slowly.

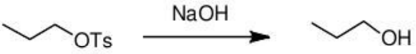
c)



Hydroxide is a strong nucleophile, which favors the S_N2 process.

7.59.

a)



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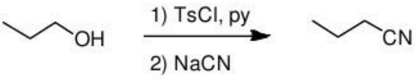
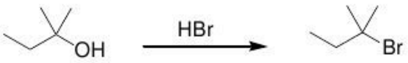
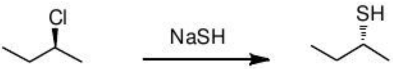


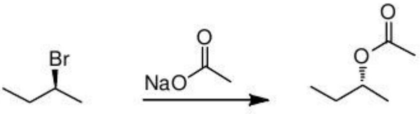
c)



d)

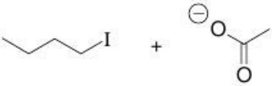


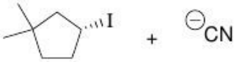
e)



7.60.

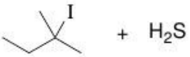
a)


b)


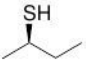
c)


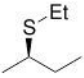
d)


e)


f)


7.61.

a)


b)


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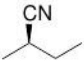
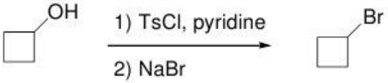


7.62.

The second method is more efficient because the alkyl halide (methyl iodide) is not sterically hindered. The first method is not efficient because it employs a tertiary alkyl halide, and S_N2 reactions do not occur at tertiary substrates.

7.63.

a)


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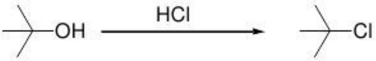

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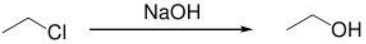
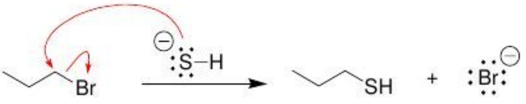
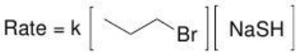


7.64.

a)

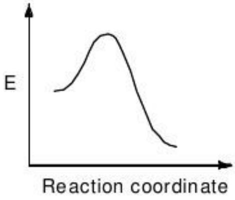


b)

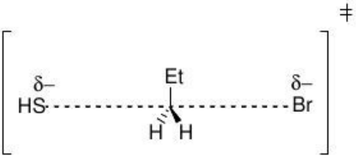


c) The rate would be slower.

d)



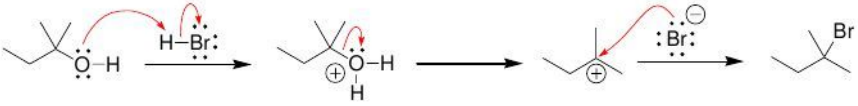
e)



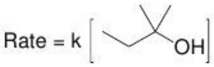
7.65.

a) S_N1 (tertiary substrate)

b)

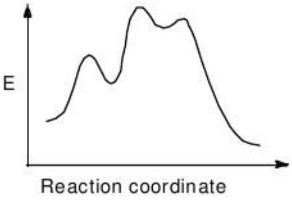


c)



d) No. The rate is not dependent on the concentration or strength of the nucleophile.

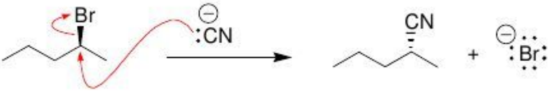
e)



7.66.

a) S_N2

b)



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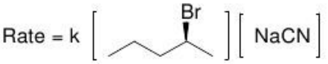
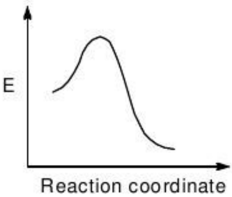
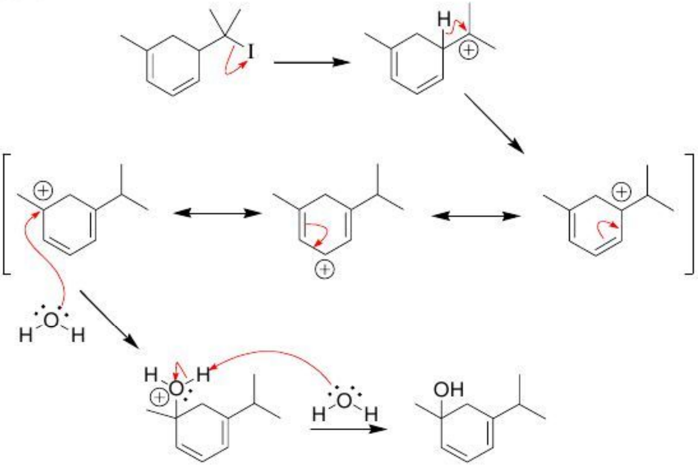


d) Yes. The reaction rate would double.

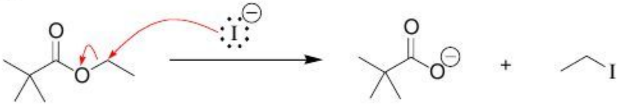
e)



7.67.

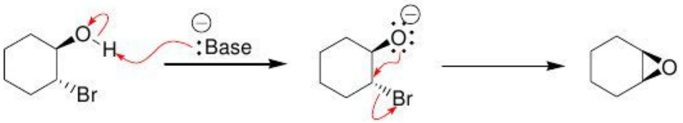


7.68.

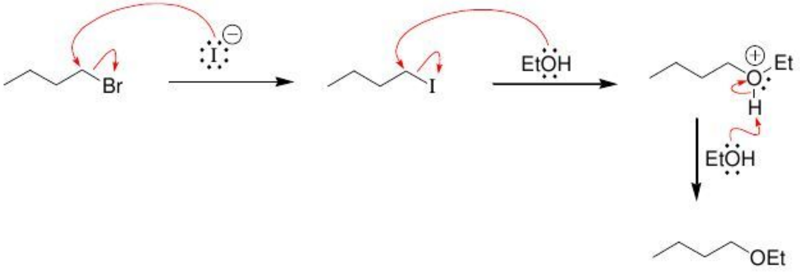
a) 

b) This reaction occurs via an S_N2 process. As such, the rate of the reaction is highly sensitive to the nature of the substrate. The reaction will be faster in this case, because the methyl ester is less sterically hindered than the ethyl ester.

7.69.

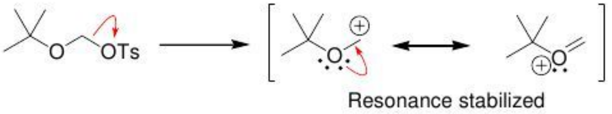


7.70.



7.71.

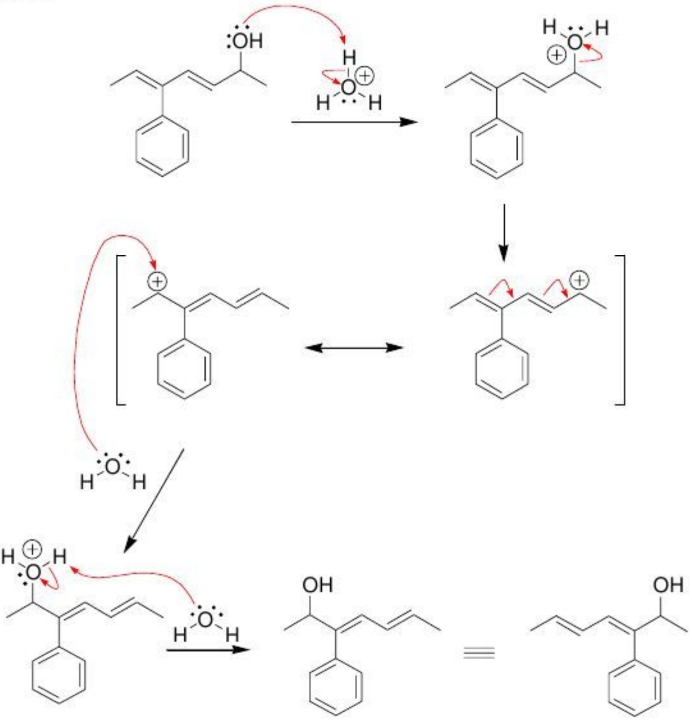
When the leaving group leaves, the carbocation formed is resonance stabilized:



7.72.

Iodide is a very good nucleophile (because it is polarizable), and it is also a very good leaving group (because it can stabilize the negative charge by spreading the charge over a large volume of space). As such, iodide will function as a nucleophile to displace the chloride ion. Once installed, the iodide group is a better leaving group than chloride, thereby increasing the rate of the reaction.

7.73.



Chapter 8
Alkenes: Structure and Preparation via Elimination Reactions

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 8. Each of the sentences below appears in the section entitled *Review of Concepts and Vocabulary*.

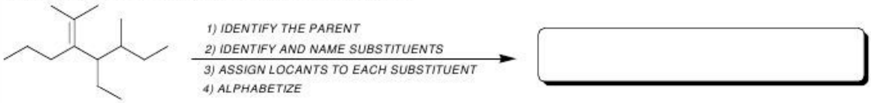
- Alkene stability increases with increasing degree of ________________.
- E2 reactions are said to be **regioselective**, because the more substituted alkene, called the ____________ **product**, is generally the major product.
- When both the substrate and the base are sterically hindered, the less substituted alkene, called the __________ **product,** is the major product.
- E2 reactions are **stereospecific** because they generally occur via the ____________________ conformation.
- Substituted cyclohexanes only undergo E2 reactions from the chair conformation in which the leaving group and the proton both occupy __________ positions.
- E1 reactions exhibit a regiochemical preference for the ____________ product.
- E1 reactions are not stereospecific, but they are stereo____________.
- Strong nucleophiles are compounds that contain a ______________ and/or are _________________.
- Strong bases are compounds whose conjugate acids are ________________.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 8. The answers appear in the section entitled *SkillBuilder Review*.

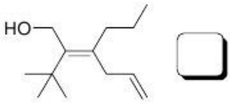
8.1 Assembling the Systematic Name of an Alkene

PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND



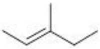
8.2 Assigning the Configuration of a double bond

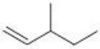
ASSIGN THE CONFIGURATION OF THE DOUBLE BOND IN THE FOLLOWING COMPOUND



8.3 Comparing the Stability of Isomeric Alkenes

CIRCLE THE MOST STABLE ALKENE BELOW





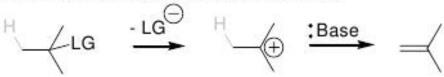
8.4 Drawing the Curved Arrows of an Elimination Reaction

A CONCERTED MECHANISM

DRAW THREE CURVED ARROWS, SHOWING A PROTON TRANSFER ACCOMPANIED BY SIMULTANEOUS LOSS OF A LEAVING GROUP

A STEPWISE MECHANISM

DRAW A CURVED ARROW SHOWING THE LOSS OF THE LEAVING GROUP TO FORM A CARBOCATION INTERMEDIATE, FOLLOWED BY ANOTHER TWO CURVED ARROWS SHOWING A PROTON TRANSFER

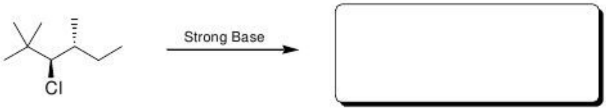


8.5 Predicting the Regiochemical Outcome of an E2 Reaction

DRAW THE ELIMINATION PRODUCTS OBTAINED WHEN THE COMPOUND BELOW IS TREATED WITH A STRONG BASE.

8.6 Predicting the Stereochemical Outcome of an E2 Reaction

PREDICT THE STEREOCHEMICAL OUTCOME OF THE FOLLOWING REACTION, AND DRAW THE PRODUCT.

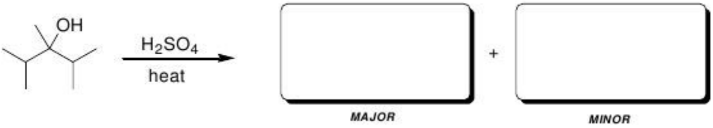


8.7 Drawing the Products of an E2 Reaction

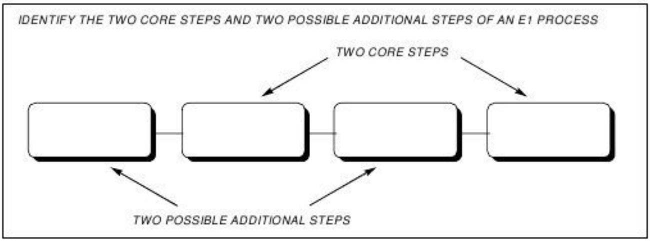
PREDICT THE MAJOR AND MINOR PRODUCTS OF THE FOLLOWING REACTION.

8.8 Predicting the Regiochemical Outcome of an E1 Reaction

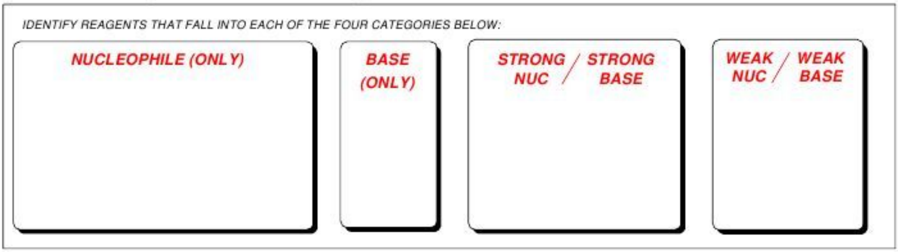
PREDICT THE MAJOR AND MINOR PRODUCTS OF THE FOLLOWING REACTION.



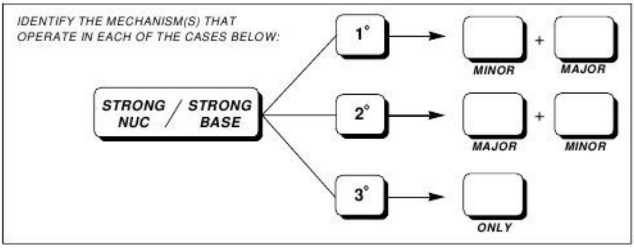
8.9 Drawing the Complete Mechanism of an E1 Reaction


IDENTIFY THE TWO CORE STEPS AND TWO POSSIBLE ADDITIONAL STEPS OF AN E1 PROCESS

8.10 Determining the Function of a Reagent


IDENTIFY REAGENTS THAT FALL INTO EACH OF THE FOUR CATEGORIES BELOW:

8.11 Identifying the Expected Mechanism(s)


IDENTIFY THE MECHANISM(S) THAT OPERATE IN EACH OF THE CASES BELOW:

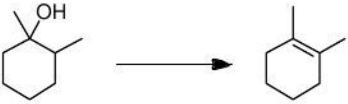
8.12 Predicting the Products of Substitution and Elimination Reactions

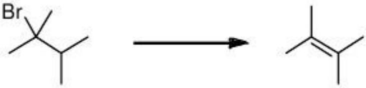
FILL IN THE BLANKS BELOW:

STEP 1	STEP 2	STEP 3
DETERMINE THE FUNCTION OF THE ________________	ANALYZE THE ________________ AND DETERMINE THE EXPECTED MECHANISM(S).	CONSIDER ANY RELEVANT REGIOCHEMICAL AND ____________________ REQUIREMENTS

Review of Synthetically Useful Elimination Reactions

Identify reagents that will achieve each of the transformations below. To verify that your answers are correct, look in your textbook at the end of Chapter 8. The answers appear in the section entitled *Review of Synthetically Useful Elimination Reactions*.



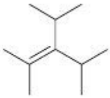


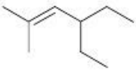
Solutions

8.1.

a) 2,3,5-trimethyl-2-heptene
b) 3-ethyl-2-methyl-2-heptene
c) 3-isopropyl-2,4-dimethyl-1-pentene
d) 4-*tert*-butyl-1-heptene

8.2.

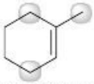
a) 

b) 

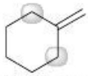
c) 

8.3. 2,3-dimethylbicyclo[2.2.1]hept-2-ene

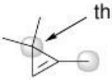
8.4.



a) ***trisubstituted***

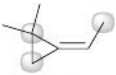


b) ***disubstituted***

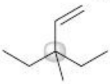


this substituent counts twice

c) ***trisubstituted***



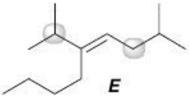
d) ***trisubstituted***



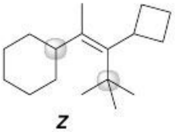
e) ***monosubstituted***

8.5.

a)



b)



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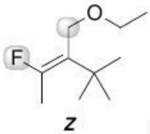
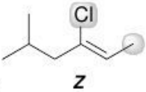
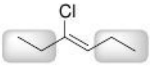


d)

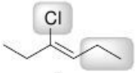


8.6. When using *cis-trans* terminology, we look for two identical groups. In this case, there are two ethyl groups that are in the *trans* configuration:



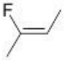
trans

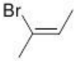
However, when using E-Z terminology, we look for the highest priority at each vinylic position. Chlorine receives a higher priority than ethyl, so in this case, the highest priority groups are on the same side of the pi bond:



Z

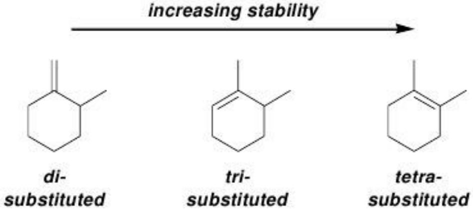
Below are two other examples of alkenes that have the trans configuration, but nevertheless have the Z configuration:



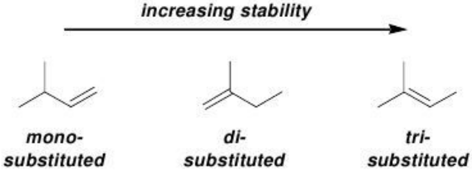


8.7.

a)



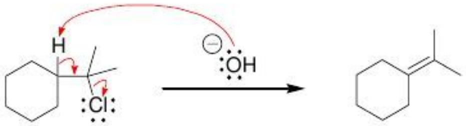
b)



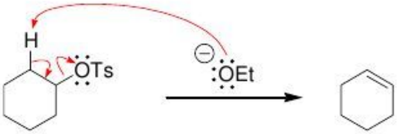
8.8. In the first compound, all of the carbon atoms of the ring are sp^3 hybridized and tetrahedral. As a result, they are supposed to have bond angles of approximately 109.5º, but their bond angles are compressed due to the ring (and are almost 90º). In other words, the compound exhibits angle strain characteristic of small rings. In the second compound, two of the carbon atoms are sp^2 hybridized and trigonal planar. As a result, they are supposed to have bond angles of approximately 120º, but their bond angles are compressed due to the ring (and are almost 90º). The resulting angle strain (120º → 90º) is greater than the angle strain in the first compound (109.5º → 90º). Therefore, the second compound is higher in energy, despite the fact that it has a more highly substituted double bond.

8.9.

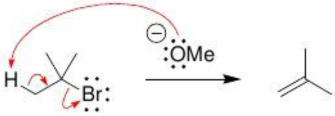
a)



b)

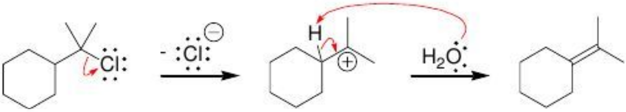


c)

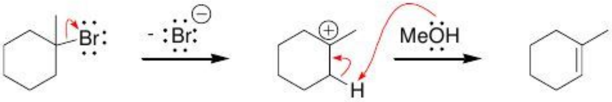


8.10.

a)



b)



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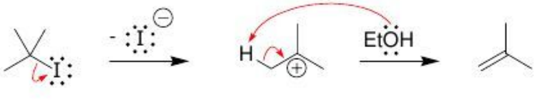
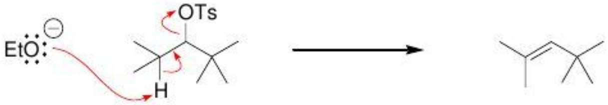
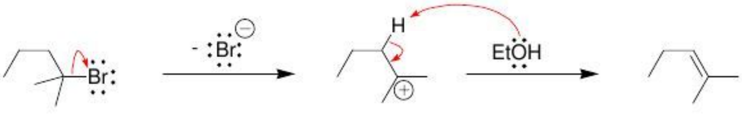


8.11. This mechanism is concerted:



8.12.

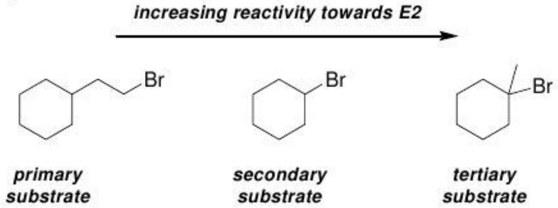


8.13.

a) 3x faster b) 2x faster c) 6x faster

8.14.

a)



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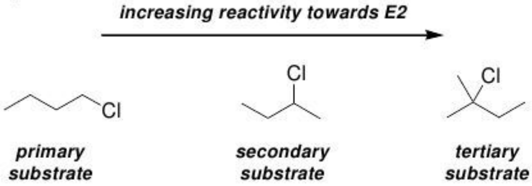
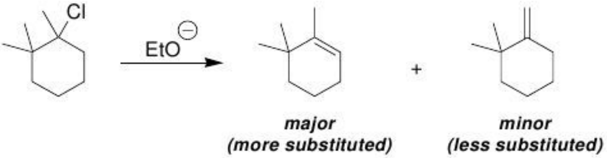
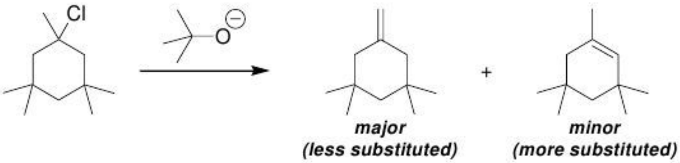


8.15.

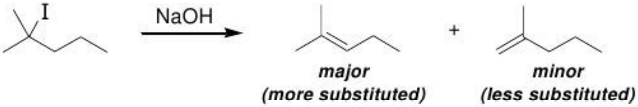


a)

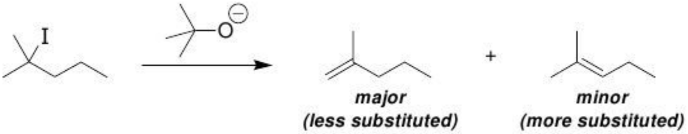
b)



c)



d)



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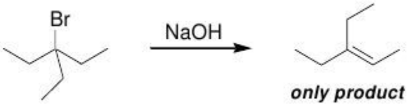

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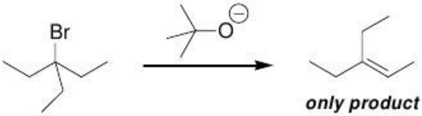


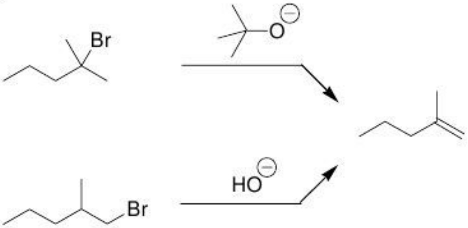
8.16.

a) The more substituted alkene is desired, so hydroxide should be used.

b) The less substituted alkene is desired, so *tert*-butoxide should be used.

8.17.

a)



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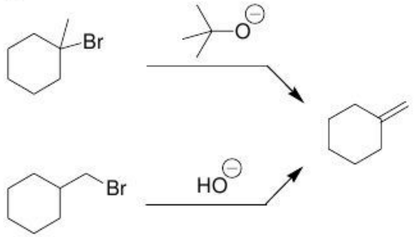
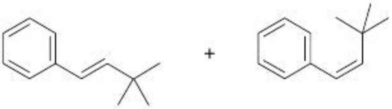
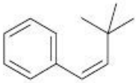


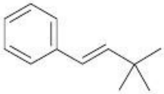
8.18.



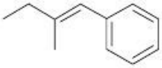
a) *major* *minor*



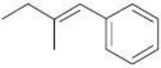
b) *the only E2 product*



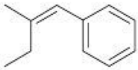
c) *the only E2 product*



d) *the only E2 product*



e) *the only E2 product*



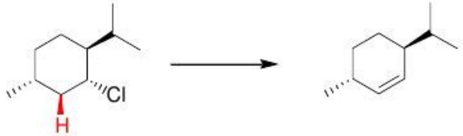
f) *the only E2 product*

g) *major* *minor*

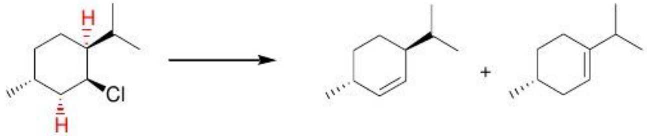
h) *major* *minor*

8.19.

8.20. The leaving group in menthyl chloride can only achieve antiperiplanarity with one beta proton, so only one elimination product is observed. In contrast, the leaving group in neomenthyl chloride can achieve antiperiplanarity with two beta protons, giving rise to two possible products:



menthyl chloride

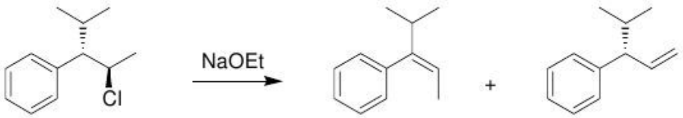


neomenthyl chloride

8.21. Because of the bulky *tert*-butyl group, the first compound is essentially locked in a chair conformation in which the chlorine occupies an equatorial position. This conformation cannot undergo an E2 reaction because the leaving group is not antiperiplanar to a proton. However, the second compound is locked in a chair conformation in which the chlorine occupies an axial position. This conformation rapidly undergoes an E2 reaction. Therefore, the second compound is expected to be more reactive towards an E2 process than the first compound.

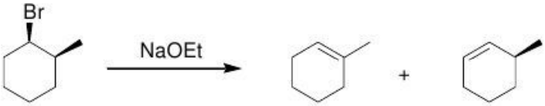
8.22.

a)



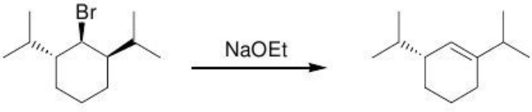
major ***minor***

b)

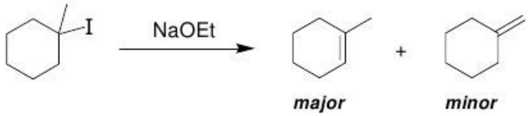


major ***minor***

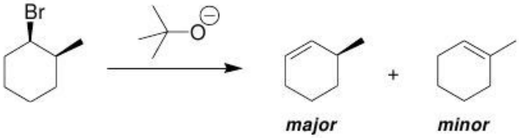
c)



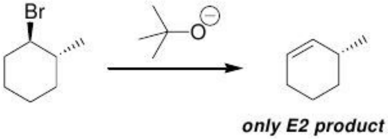
only E2 product



d)

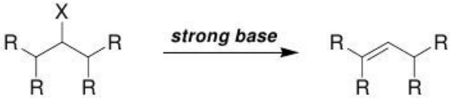


e)



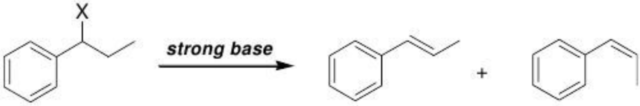
f)

8.23.

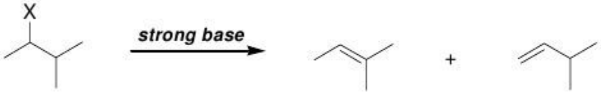


all R groups are identical

8.24.



8.25.

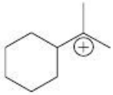


8.26.

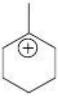
a) Only the concentration of *tert*-butyl iodide affects the rate, so the rate will double.
b) Only the concentration of *tert*-butyl iodide affects the rate, so the rate will remain the same.

8.27.

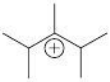
a)



b)

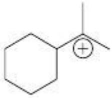


c)

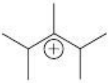


d)

8.28.

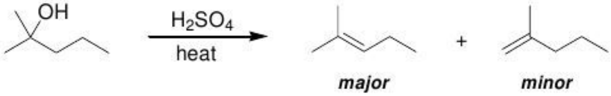
a) 

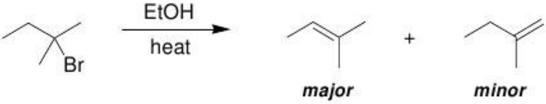
b) 

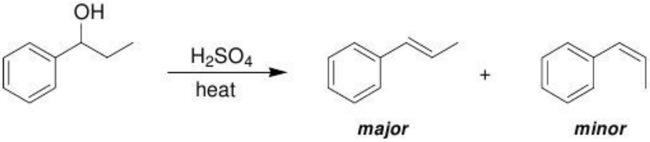
c) 

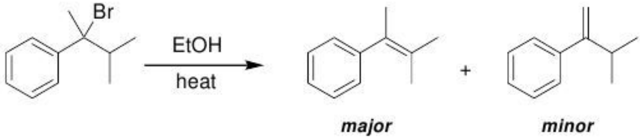
d) 

8.29.

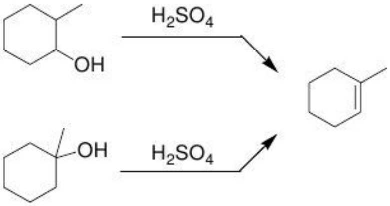
a) 

b) 

c) 

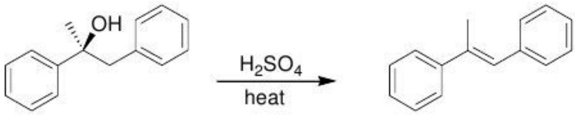
d) 

8.30. Both alcohols below can be used to form the product. The tertiary alcohol below will react more rapidly because the rate determining step involves formation of a tertiary carbocation rather than a secondary carbocation.

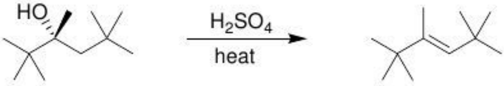


8.31.

a)



b)



8.32.

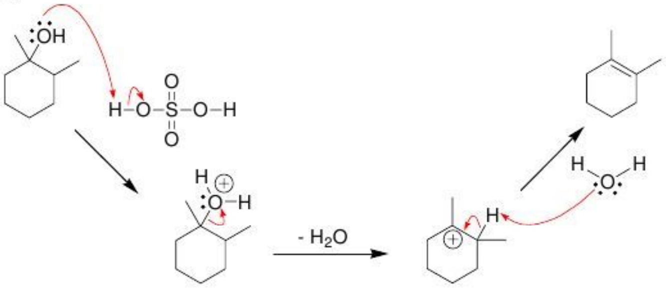
- **a)** No, the leaving group is not OH
- **b)** Yes, the leaving group is OH
- **c)** No, the leaving group is not OH
- **d)** Yes, the leaving group is OH
- **e)** No, the leaving group is not OH
- **f)** No, the leaving group is not OH

8.33.

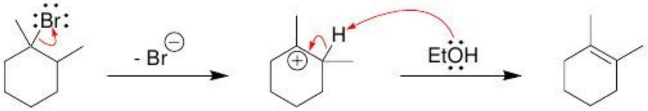
- **a)** No. Loss of the leaving group forms a tertiary carbocation, which will not rearrange.
- **b)** Yes. Loss of the leaving group forms a secondary carbocation, which can undergo a methyl shift to form a more stable tertiary carbocation.
- **c)** Yes. Loss of the leaving group forms a secondary carbocation, which can undergo a hydride shift to form a more stable tertiary carbocation.
- **d)** No. Loss of the leaving group forms a secondary carbocation, which cannot rearrange in this case to form a tertiary carbocation.
- **e)** No. Loss of the leaving group forms a tertiary carbocation, which will not rearrange.
- **f)** No. Loss of the leaving group forms a secondary carbocation, which cannot rearrange in this case to form a tertiary carbocation.

8.34.

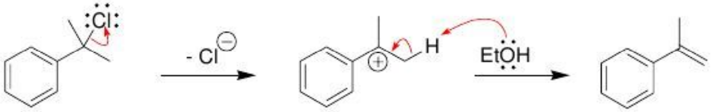
a)


OH
H–O–S–O–H
O
O
H
O–H
- H₂O
H
H
O
H

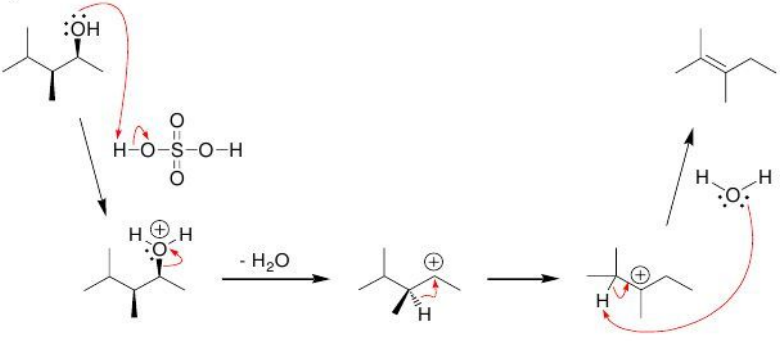
b)


Br
- Br
H
EtOH

c)

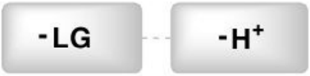

Cl
- Cl
H
EtOH

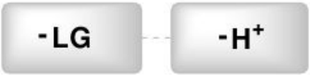
d)

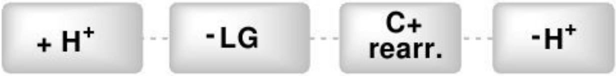

OH
H–O–S–O–H
O
O
H
O
H
- H₂O
H
H
H
O
H

8.35. Problem 8.34b and 8.34c exhibit the same pattern because both have leaving groups that can leave without being protonated, and both do not exhibit a carbocation rearrangement. As a result both mechanisms involve only two steps: 1) loss of a leaving group and 2) proton transfer.

a) 

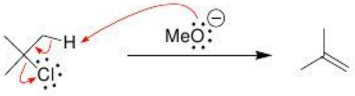
b) 

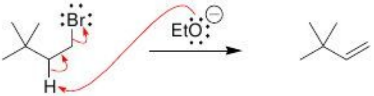
c) 

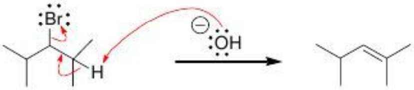
d) 

8.36. The first method is more efficient because it employs a strong base to promote an E2 process for a secondary substrate bearing a good leaving group. The second method relies on an E1 process occurring at a secondary substrate, which will be slow and will involve a carbocation rearrangement to produce a different product.

8.37.

a) 

b) 

c) 

8.38

8.39.

a) weak nucleophile, weak base
b) strong nucleophile, weak base
c) strong nucleophile, strong base
d) strong nucleophile, weak base
e) strong nucleophile, strong base
f) weak nucleophile, weak base
g) strong nucleophile, strong base
h) weak nucleophile, strong base

8.40. Aluminum is a larger atom and is polarizable. Therefore, the entire complex can function as a strong nucleophile, and can serve as a delivery agent of a hydride ion. In contrast, the hydride ion by itself is not polarizable and does not function as a nucleophile.

8.41.

a) NaOH is a strong nucleophile and strong base. The substrate in this case is primary. Therefore, we expect S_N2 (giving the major product) and E2 (giving the minor product).
b) NaSH is a strong nucleophile and weak base. The substrate in this case is primary. Therefore, we expect only S_N2.
c) When a primary alkyl halide is treated with *t*-BuOK, the predominant pathway is expected to be E2.
d) DBN is a weak nucleophile and a strong base. Therefore, we expect only E2.
e) NaOMe is a strong nucleophile and strong base. The substrate in this case is primary. Therefore, we expect S_N2 (giving the major product) and E2 (giving the minor product).

8.42.

a) NaOEt is a strong nucleophile and strong base. The substrate in this case is secondary. Therefore, we expect E2 (giving the major product) and S_N2 (giving the minor product).
b) NaI is a strong nucleophile and weak base. DMSO is a polar aprotic solvent. The substrate is secondary. Under these conditions, only S_N2 can occur.
c) DBU is a weak nucleophile and a strong base. Therefore, we expect only E2.
d) NaOH is a strong nucleophile and strong base. The substrate in this case is secondary. Therefore, we expect E2 (giving the major product) and S_N2 (giving the minor product).
e) *t*-BuOK is a strong, sterically hindered base. Therefore, we expect only E2.

8.43.

a) EtOH is a weak nucleophile and weak base. The substrate in this case is tertiary. Therefore, we expect both S_N1 and E1.

e) b) *t*-BuOK is a strong, sterically hindered base. Therefore, we expect only E2.
c) NaI is a strong nucleophile and weak base. The substrate in this case is tertiary. Therefore, we expect only S_N1.
d) NaOEt is a strong nucleophile and strong base. The substrate in this case is tertiary. Therefore, we expect only E2.
e) NaOH is a strong nucleophile and strong base. The substrate in this case is tertiary. Therefore, we expect only E2.

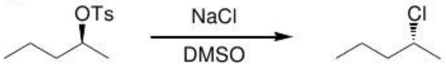
8.44.

a) An E2 reaction does not readily occur because the base is weak.
b) An E1 reaction does not readily occur because the substrate is primary.
c) Replacing the weak base (EtOH) with a strong base (such as NaOEt) would greatly enhance the rate of an E2 process.
d) Replacing the primary substrate with a tertiary substrate (such as 1-chloro-1,1-dimethylbutane) would greatly enhance the rate of an E1 process.

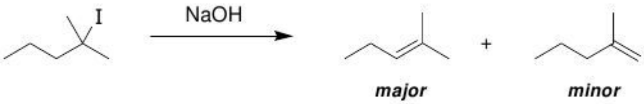
8.45. The substrate is tertiary, so S_N2 cannot occur at a reasonable rate. There are no beta protons, so E2 also cannot occur.

8.46.

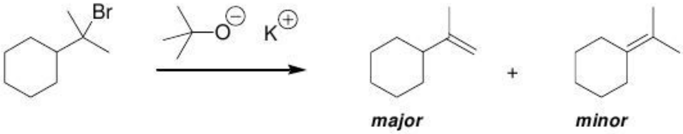
a)



b)

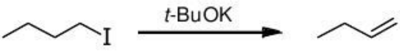


c)

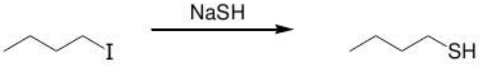


d)

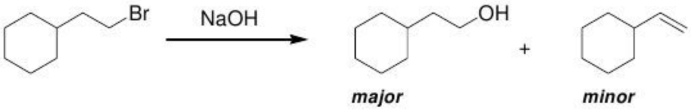
e)



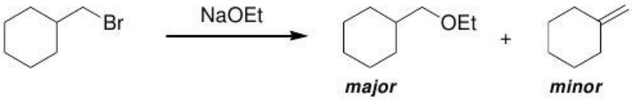
f)


I
NaSH
SH

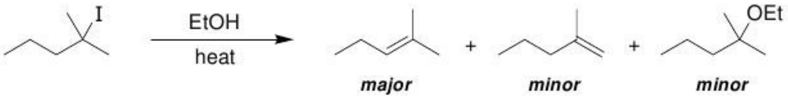
g)


Br
NaOH
OH
+
major
minor

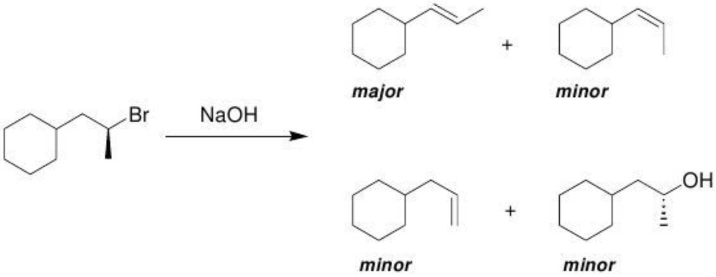
h)


Br
NaOEt
OEt
+
major
minor

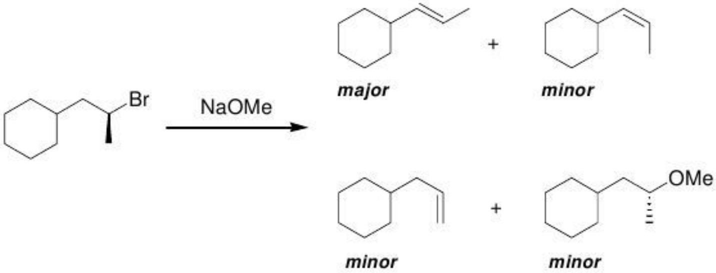
i)


I
EtOH
heat
+
+
major
minor
minor
OEt

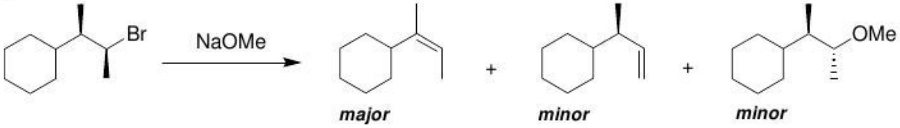
j)


Br
NaOH
+
major
minor
+
OH
minor
minor

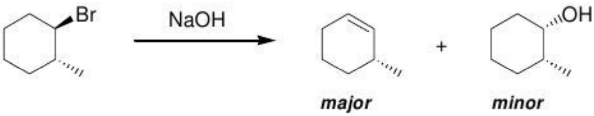
k)


Br
NaOMe
+
major
minor
+
OMe
minor
minor

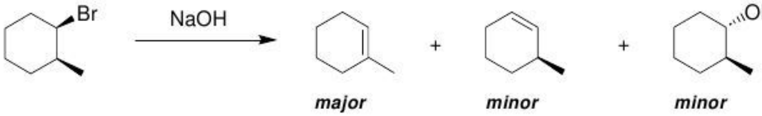
l)



m)

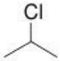


n)



8.47. There are only two constitutional isomers with molecular formula C_3H_7Cl:

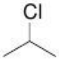
a primary alkyl halide



a secondary alkyl halide

Sodium methoxide is both a strong nucleophile and a strong base. When compound A is treated with sodium methoxide, a substitution reaction predominates. Therefore, compound A must be the primary alkyl chloride above. When compound B is treated with sodium methoxide, an elimination reaction predominates. Therefore, compound B must be the secondary alkyl chloride:

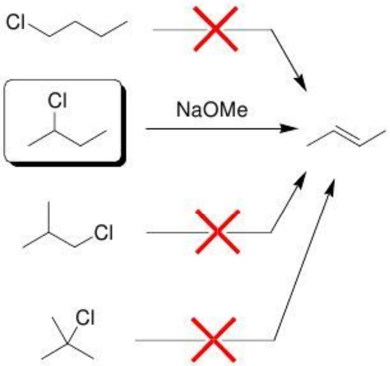
Compound A



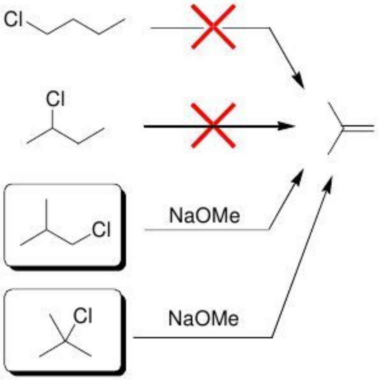
Compound B

8.48.

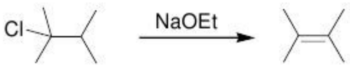
a)



b)



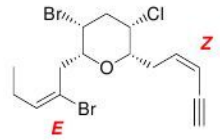
8.49.



8.50.

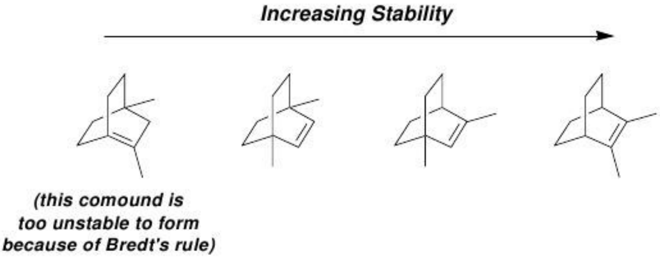
a) *trans*-3,4,5,5-tetramethyl-3-heptene
b) 1-ethylcyclohexene
c) 2-methylbicyclo[2.2.2]oct-2-ene

8.51.



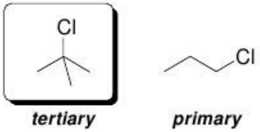
8.52. Because of the bulky *tert*-butyl group, the *trans* isomer is essentially locked in a chair conformation in which the chlorine occupies an equatorial position. This conformation cannot readily undergo an E2 reaction because the leaving group is not antiperiplanar to a proton. However, the *cis* isomer is locked in a chair conformation in which the chlorine occupies an axial position. This conformation rapidly undergoes an E2 reaction.

8.53.

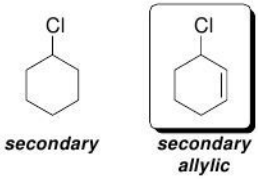


8.54.

a)



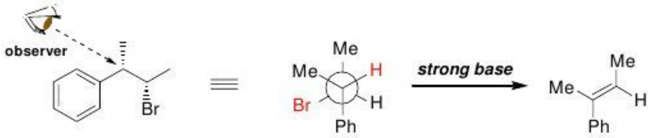
b)



8.55.

a) NaOH, because hydroxide bears a negative charge.
b) sodium ethoxide, because ethoxide bears a negative charge.
c) trimethylamine, because of the electron donating effects of the alkyl groups.

8.56.



8.57.

a) The rate of an E2 process is dependent on the concentrations of the substrate and the base. Therefore, the rate will be doubled if the concentration of *tert*-butyl bromide is doubled.

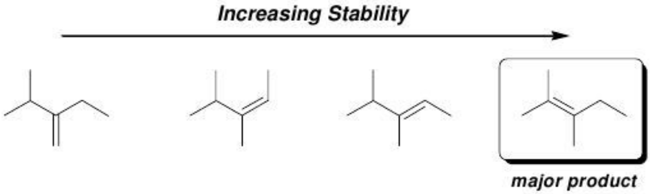
b) The rate of an E2 process is dependent on the concentrations of the substrate and the base. Therefore, the rate will be doubled if the concentration of sodium ethoxide is doubled.

8.58.

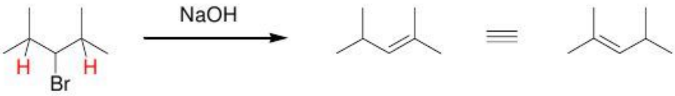
a) The rate of an E1 process is dependent only on the concentration of the substrate (not the base). Therefore, the rate will be doubled if the concentration of *tert*-butyl bromide is doubled.

b) The rate of an E1 process is dependent only on the concentration of the substrate (not the base). Therefore, the rate will remain the same if the concentration of ethanol is doubled.

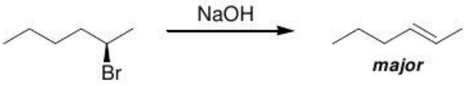
8.59.

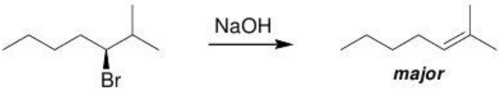


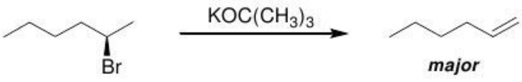
8.60. There are only two beta protons to abstract: one at C2 and the other at C4. Abstraction of either proton leads to the same product.

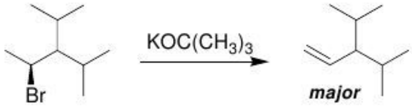


8.61.

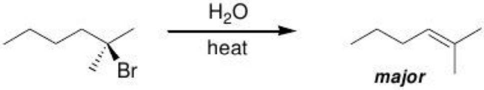
a) 

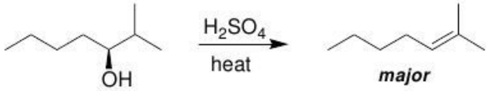
b) 

c) 

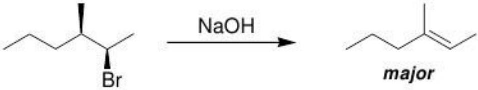
d) 

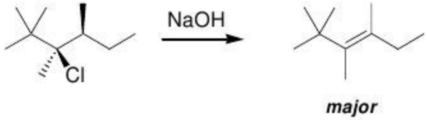
8.62.

a) 

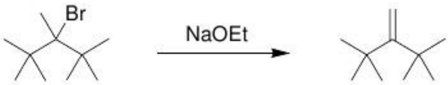
b) 

8.63.

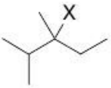
a) 

b) 

8.64. The reagent is a strong nucleophile and a strong base, so we expect a bimolecular reaction. The substrate is tertiary so only E2 can operate (S_N2 is too sterically hindered to occur). There is only one possible regiochemical outcome for the E2 process, because the other beta positions lack protons.



8.65.

a) 

b) 

c) 

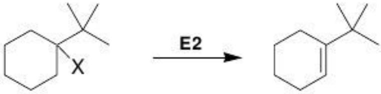
d) 

8.66.

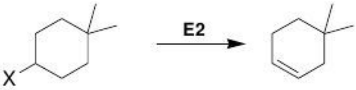
a) one
b) three
c) two
d) two
e) five

8.67.

a)

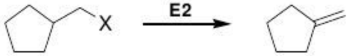


b)



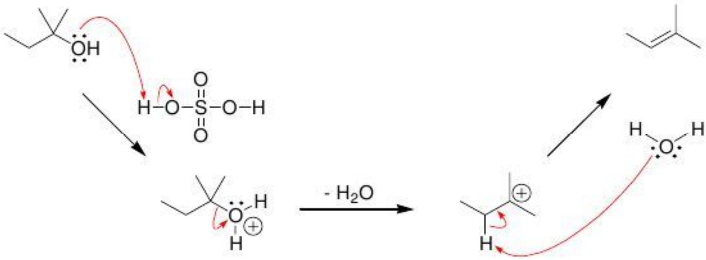
c)

d)



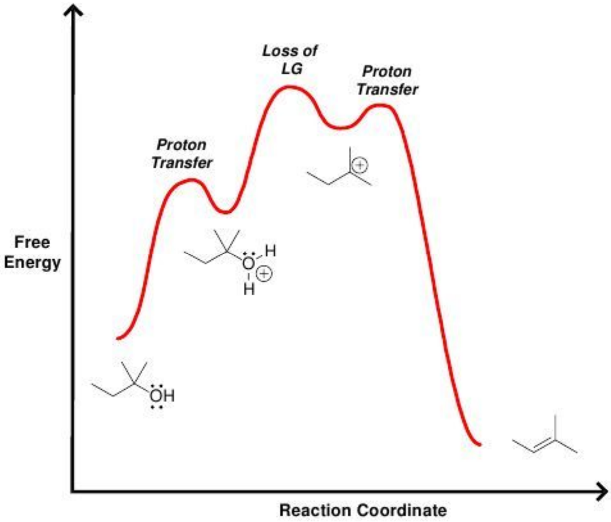
8.68.

a)



b) This is an E1 process, so the rate is dependent only on the substrate:
Rate = k[substrate]

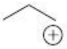
c)



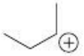
8.69. The primary substrate will not undergo an E1 reaction because primary carbocations are too high in energy to form readily.

a) ***secondary***

b) ***tertiary***

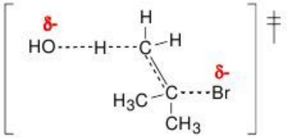


c) ***primary***



d) ***secondary***

8.70.



8.71. The first compound produces a trisubstituted alkene, while the second compound produces a monosubstituted alkene. As such, the transition state for the reaction of the first compound will be lower in energy than the transition state for the reaction of the second compound.

8.72. The first reaction is very slow, because the *tert*-butyl group effectively locks the ring in a chair conformation in which the leaving group (Br) occupies an equatorial position. In this conformation, the leaving group cannot be antiperiplanar to a beta proton. So the reaction can only occur from the other chair conformation, which the compound does not readily adopt. The second reaction is very rapid, because the *tert*-butyl group effectively locks the ring in a chair conformation in which the leaving group (Br) occupies an axial position. In this conformation, the leaving group is antiperiplanar to a beta proton. The third reaction does not occur at all because there are no beta protons that are antiperiplanar to the leaving group (on a cyclohexane ring, there must be at least one beta proton that is *trans* to the leaving group in order to be able to adopt an antiperiplanar conformation).

8.73. Pi bonds cannot be formed at the bridgehead of a bicyclic compound, unless one of the rings is large (at least eight carbon atoms). This rule is known as Bredt's rule.

8.74.

a) The first compound will react more rapidly because it is tertiary

b) The second compound will react more rapidly in an E2 reaction because the first compound does not have any beta protons (and therefore cannot undergo E2 at all).

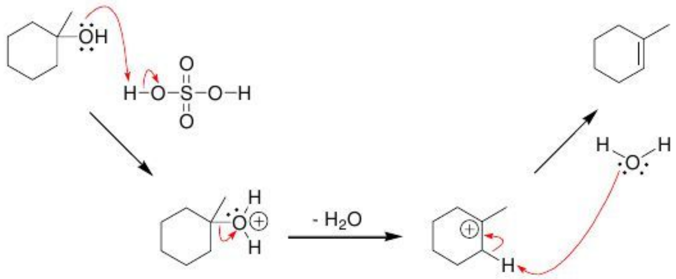
8.75.

a) The Zaitsev product is desired, so sodium hydroxide should be used.
b) The Hofmann product is desired, so potassium *tert*-butoxide should be used.
c) The Zaitsev product is desired, so sodium hydroxide should be used.
d) The Hofmann product is desired, so potassium *tert*-butoxide should be used.

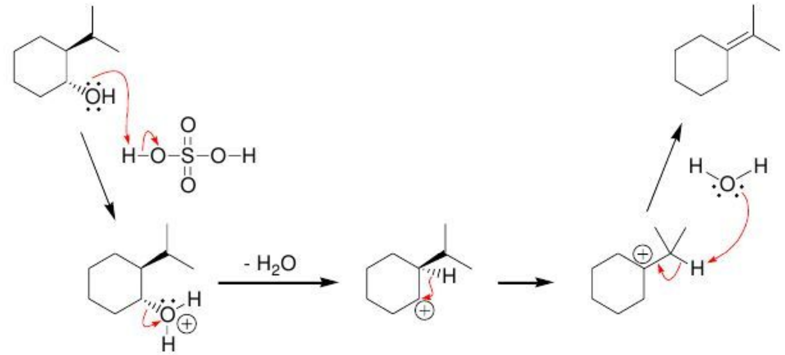
8.76. There is only one beta proton that can be abstracted so as to form the Zaitsev product. This proton is *cis* to the leaving group, and therefore, it cannot be antiperiplanar to the leaving group (not in either chair conformation). As a result, only the Hofmann product can be formed.

8.77.

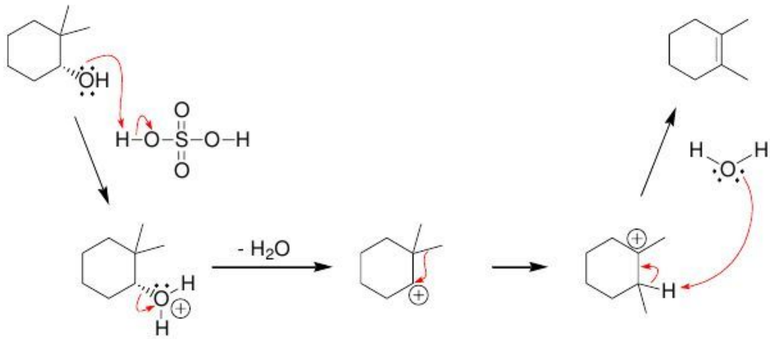
a)



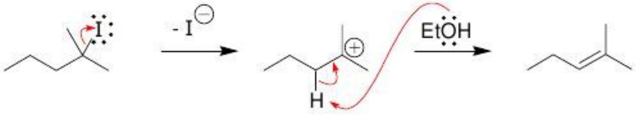
b)


OH
H–O–S–O–H
O
O
- H2O
H
O
H
H
H
H
H
O

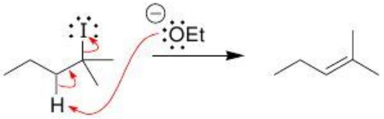
c)


OH
H–O–S–O–H
O
O
- H2O
H
O
H
H
H
O
H

d)

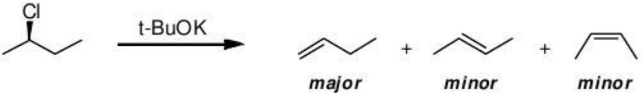

I
- I
EtOH
H

e)


I
OEt
H

8.78.

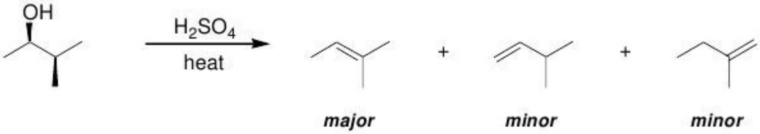
a)


Cl
t-BuOK
major
minor
minor

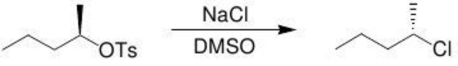
b)


OTs
NaOH
OH
major
minor

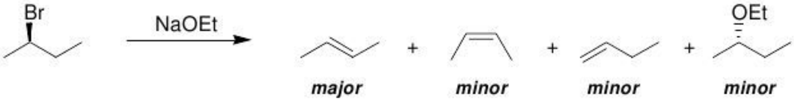
c)


OH
H_2SO_4
heat
major
minor
minor

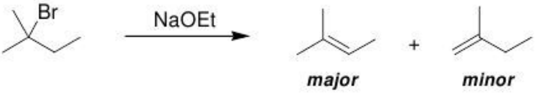
d)


OTs
NaCl
DMSO
Cl

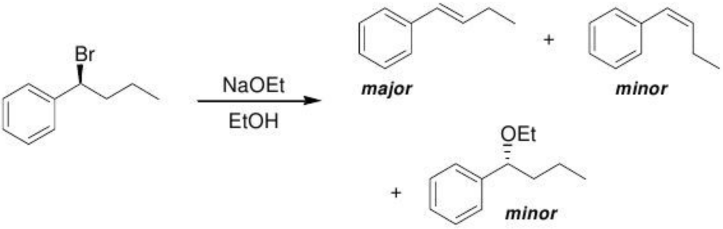
e)


Br
NaOEt
OEt
major
minor
minor
minor

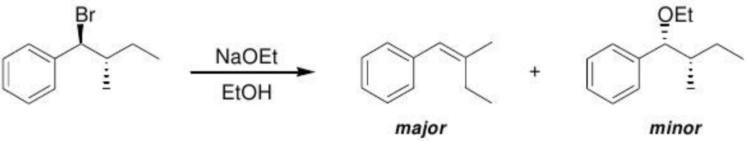
f)


Br
NaOEt
major
minor

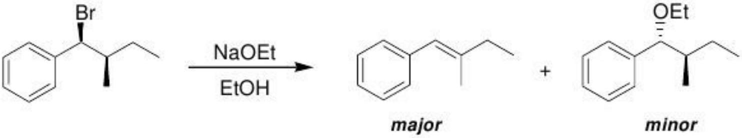
g)


Br
NaOEt
EtOH
major
minor
OEt
minor

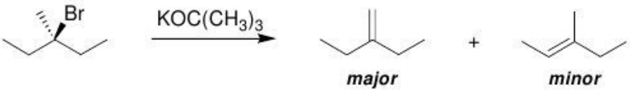
h)


Br
NaOEt
EtOH
OEt
major
minor

i)

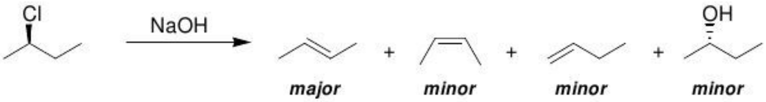

Br
NaOEt
EtOH
OEt
major
minor

j)



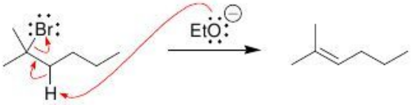
g)

h)



8.79.

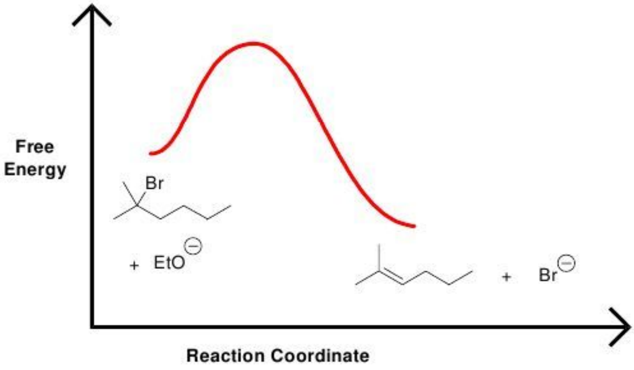
a)



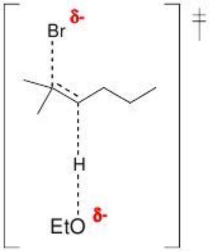
b) For an E2 process, the rate is dependent on the concentrations of the substrate and the nucleophile: Rate = k[substrate][base]

c) If the concentration of base is doubled, the rate will be doubled.

d)

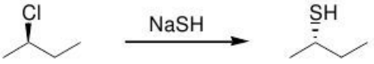


e)

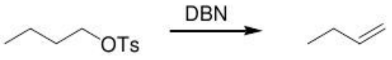


8.80.

a)



b)



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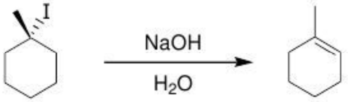

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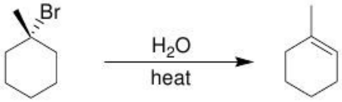

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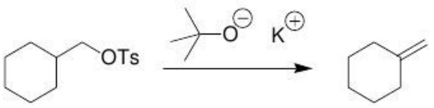

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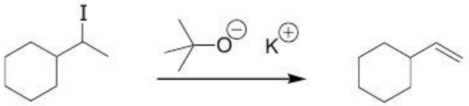

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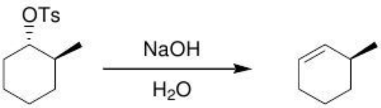

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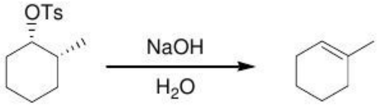
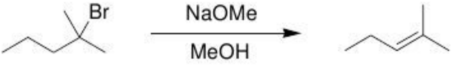
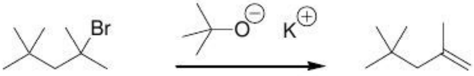

OTs
NaOH
H_2O

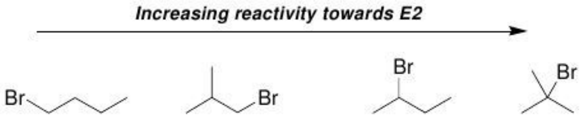
i)


Br
NaOMe
MeOH

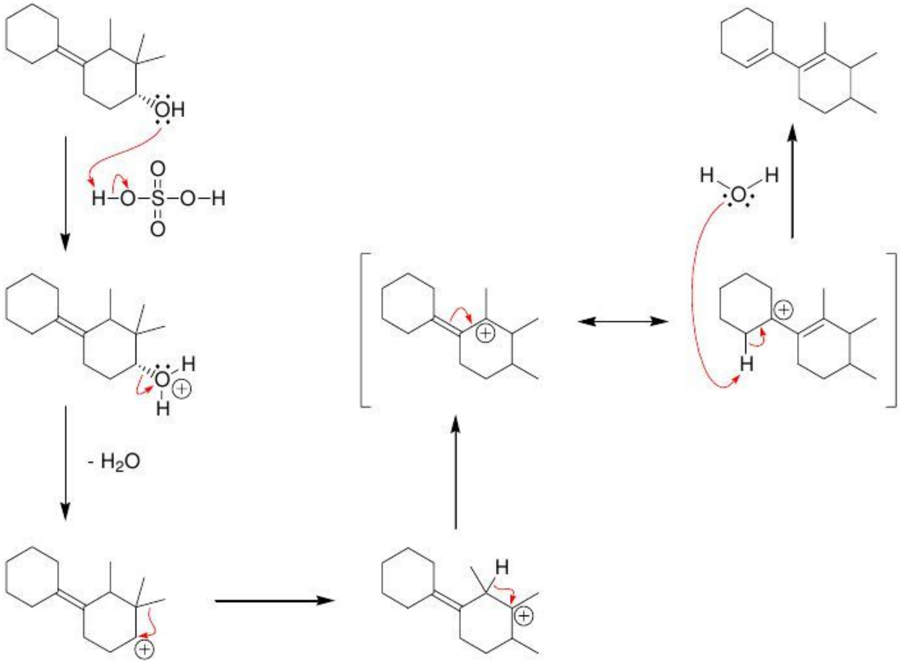
j)


Br
$O^{\ominus}$
$K^{\oplus}$

8.81.

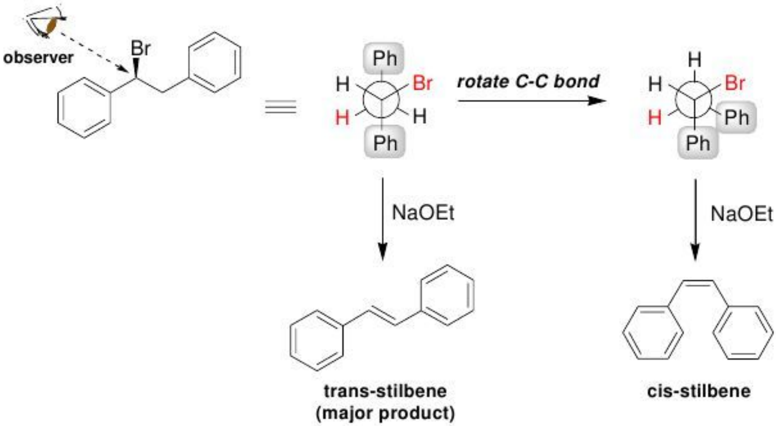

Increasing reactivity towards E2
Br
Br
Br
Br

8.82.


OH
H–O–S–O–H
O
O
H
H
- H_2O
H
H
H
O
H

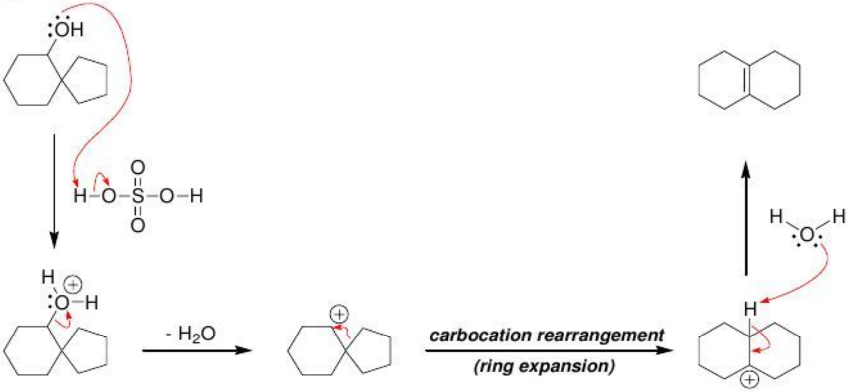
8.83.

a)

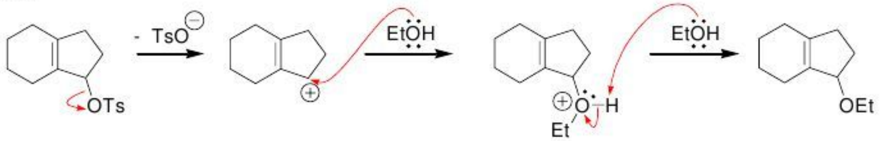


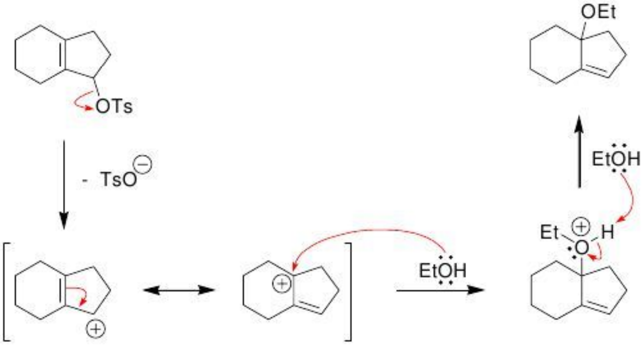
b) There are still two beta protons that can be abstracted in a beta elimination, and both products are still possible. The reaction will still proceed via the conformation with the least steric hinderance. That conformation will lead to the formation of *trans*-stilbene.

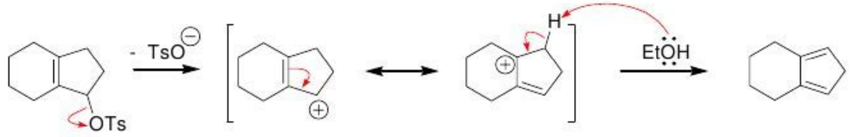
8.84.



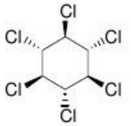
8.85.







8.86. The stereoisomer shown below does not readily undergo E2 elimination because none of the chlorine atoms can be antiperiplanar to a beta proton in a chair conformation. Recall that for substituted cyclohexanes, the leaving group must be *trans* to a beta proton in order to achieve antiperiplanarity. In the isomer below, none of the chlorine atoms are *trans* to a beta proton.



8.87. The first compound is a tertiary substrate. The second compound is a tertiary allylic substrate. The latter will undergo E1 more rapidly because a tertiary allylic carbocation is more highly stabilized than a tertiary carbocation. The rate-determining step (loss of the leaving group) will therefore occur more rapidly for the second compound.

Chapter 9
Addition Reactions of Alkenes

Review of Concepts

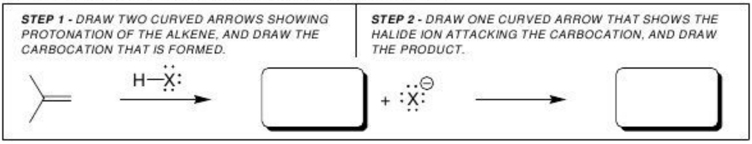
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 9. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- Addition reactions are thermodynamically favorable at ____ temperature and disfavored at _____ temperature.
- Hydrohalogenation reactions are **regioselective**, because the halogen is generally placed at the ______ substituted position, called _______________ **addition**.
- In the presence of _____________, addition of HBr proceeds via an ***anti*-Markovnikov addition**.
- The regioselectivity of an ionic addition reaction is determined by the preference for the reaction to proceed through _____________________________________.
- Acid-catalyzed hydration is inefficient when _____________________________ are possible. Dilute acid favors formation of the ___________ and while concentrated acid favors the ___________.
- **Oxymercuration-demercuration** achieves hydration of an alkene without ____.
- _____________-_______________ can be used to achieve an *anti*-Markovnikov addition of water across an alkene. The reaction is stereospecific and proceeds via a _____ **addition**.
- **Asymmetric hydrogenation** can be achieved with a ________ catalyst.
- Bromination proceeds through a bridged intermediate, called a ________________ ______, which is opened by an S_N2 process that produces an _____ **addition**.
- A two-step procedure for *anti* dihydroxylation involves conversion of an alkene to an _________, followed by acid-catalyzed ring opening.
- Ozonolysis can be used to cleave a double bond and produce two ______ groups.
- The position of a leaving group can be changed via ______________ followed by ________________.
- The position of a π bond can be changed via ______________ followed by ________________.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 9. The answers appear in the section entitled *SkillBuilder Review*.

9.1 Drawing a Mechanism for Hydrohalogenation



STEP 1 - DRAW TWO CURVED ARROWS SHOWING PROTONATION OF THE ALKENE, AND DRAW THE CARBOCATION THAT IS FORMED.

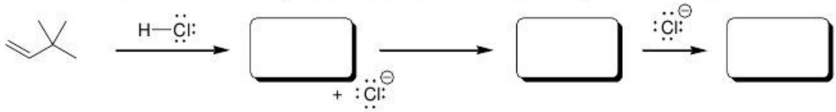
STEP 2 - DRAW ONE CURVED ARROW THAT SHOWS THE HALIDE ION ATTACKING THE CARBOCATION, AND DRAW THE PRODUCT.

9.2 Drawing a Mechanism for Hydrohalogenation with a Carbocation Rearrangement

***STEP 1** - DRAW TWO CURVED ARROWS SHOWING PROTONATION OF THE ALKENE AND DRAW THE CARBOCATION THAT IS INITIALLY FORMED.*

***STEP 2** - DRAW ONE CURVED ARROW SHOWING A CARBOCATION REARRANGEMENT AND DRAW THE RESULTING, MORE STABLE CARBOCATION.*

***STEP 3** - DRAW ONE CURVED ARROW SHOWING THE HALIDE ION ATTACKING THE CARBOCATION, AND DRAW THE PRODUCT.*

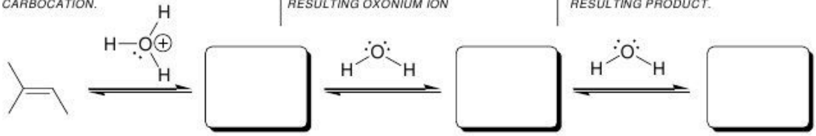


9.3 Drawing a Mechanism for an Acid-Catalyzed Hydration

***STEP 1** - DRAW TWO CURVED ARROWS SHOWING PROTONATION OF THE ALKENE, AND DRAW THE RESULTING CARBOCATION.*

***STEP 2** - DRAW ONE CURVED ARROW SHOWING WATER ATTACKING THE CARBOCATION, AND DRAW THE RESULTING OXONIUM ION*

***STEP 3** - DRAW TWO CURVED ARROWS SHOWING DEPROTONATION OF THE OXONIUM ION, AND DRAW THE RESULTING PRODUCT.*



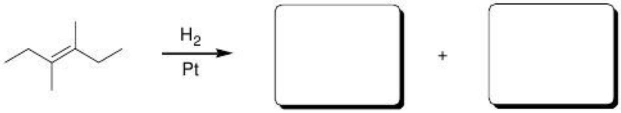
9.4 Predicting the Products of Hydroboration-Oxidation

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION, AND DETERMINE THEIR RELATIONSHIP

***RELATIONSHIP =** ____________________*

9.5 Predicting the Products of Catalytic Hydrogenation

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION, AND DETERMINE THEIR RELATIONSHIP



***RELATIONSHIP =** ____________________*

9.6 Predicting the Products of Halohydrin Formation

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION, AND DETERMINE THEIR RELATIONSHIP

***RELATIONSHIP =** ____________________*

9.7 Drawing the Products of *Anti* Dihydroxylation

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION, AND DETERMINE THEIR RELATIONSHIP

RELATIONSHIP = ______________

9.8 Predicting the Products of Ozonolysis

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION.

9.9 Predicting the Products of an Addition Reaction

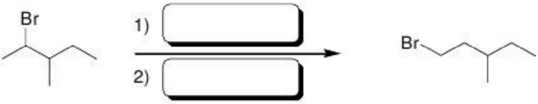
DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION.

9.10 Proposing a One-Step Synthesis

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:

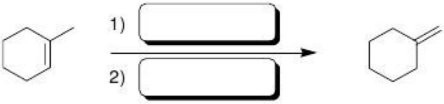
9.11 Changing the Position of a Leaving Group

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:



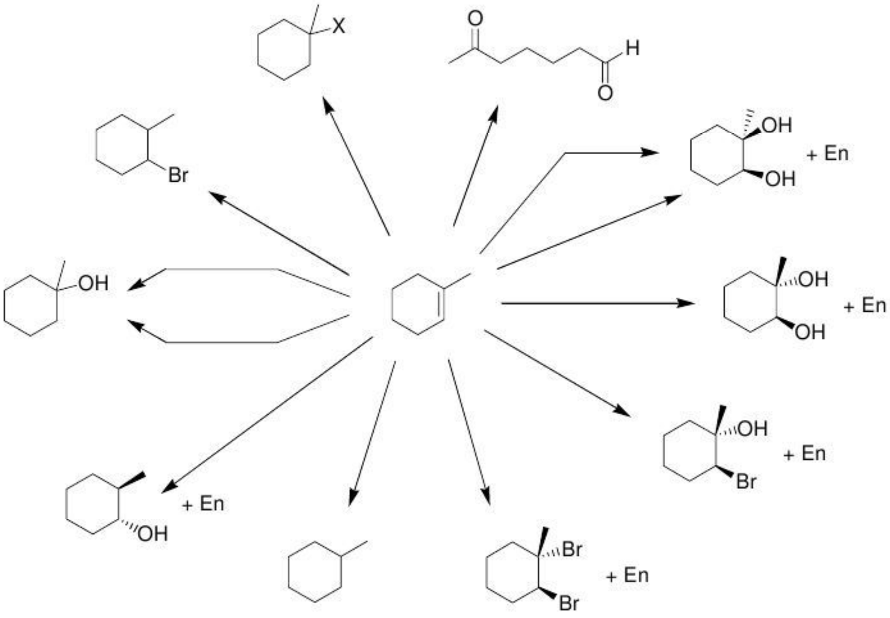
9.12 Changing the Position of a π Bond

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:



Review of Reactions

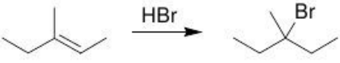
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 9. The answers appear in the section entitled *Review of Reactions*.



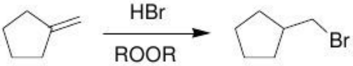
Solutions

9.1.

a)

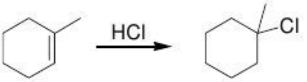


b)

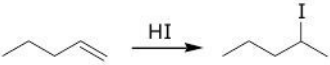


c)

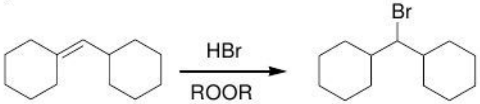
d)



e)

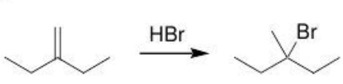


f)



9.2.

a)



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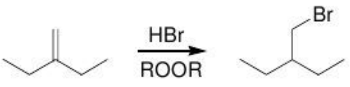
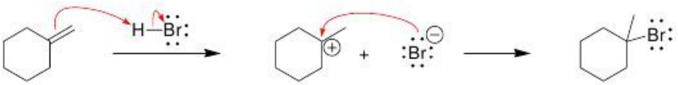
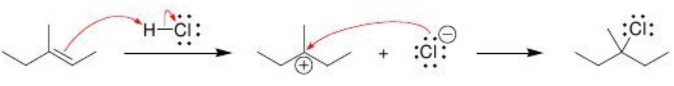


9.3.

a)



b)



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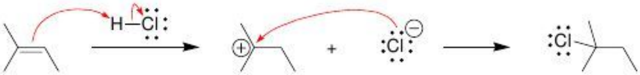
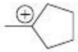


9.4.

a)

b)



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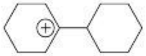

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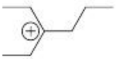
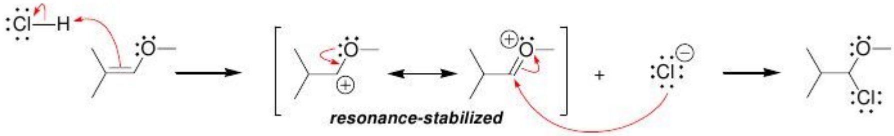
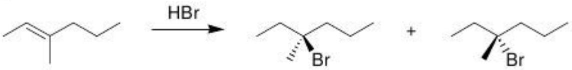


9.5. In this case, the less-substituted carbocation is more stable because it is resonance-stabilized:

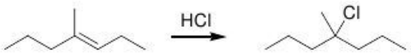


9.6.

a)



b)



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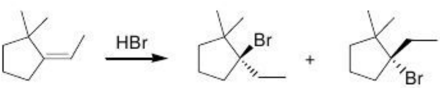
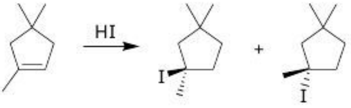
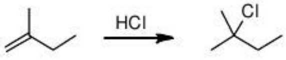


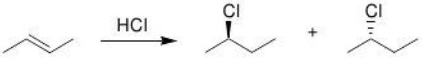
d)


HI
I
+
I

e)

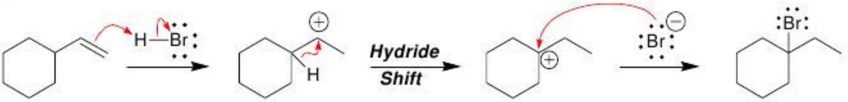

HCl
Cl

f)

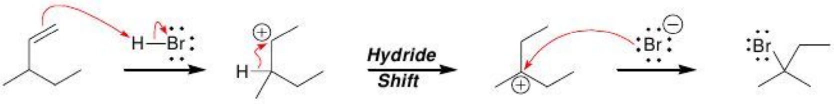

HCl
Cl
+
Cl

9.7.

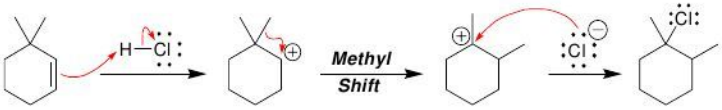
a)


H
Br
H
Hydride
Shift
Br
Br

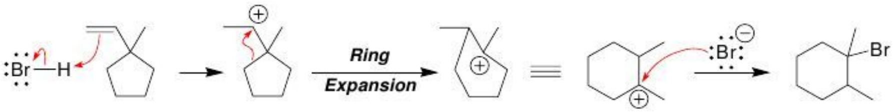
b)


H
Br
H
Hydride
Shift
Br
Br

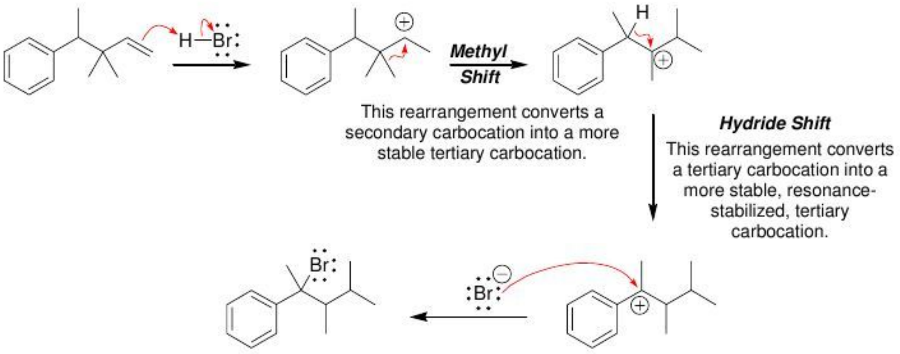
c)


H
Cl
Methyl
Shift
Cl
Cl

9.8.


Br
H
Ring
Expansion
Br
Br

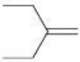
9.9.



This rearrangement converts a secondary carbocation into a more stable tertiary carbocation.

This rearrangement converts a tertiary carbocation into a more stable, resonance-stabilized, tertiary carbocation.

9.10.

a) , because the reaction proceeds via a tertiary carbocation, rather than a secondary carbocation.

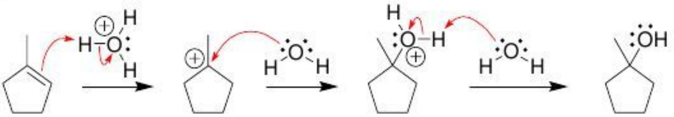
b) 2-methyl-2-butene, because the reaction proceeds via a tertiary carbocation, rather than a secondary carbocation.

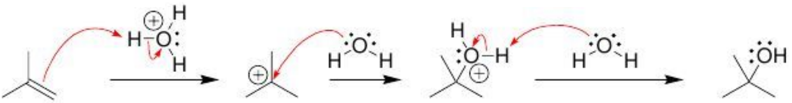
9.11.

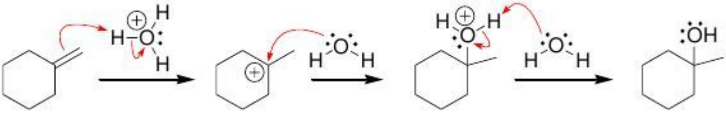
a) To favor the alcohol, dilute sulfuric acid (mostly water) is used. Having a high concentration of water favors the alcohol according to Le Chatelier's principle.

b) To favor the alkene, concentrated sulfuric acid (which has very little water) is used. Having a low concentration of water favors the alkene according to Le Chatelier's principle.

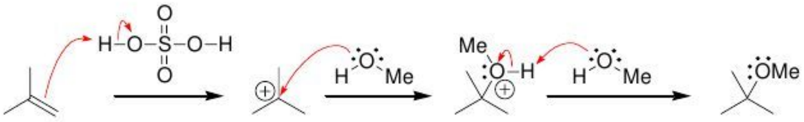
9.12.

a) 

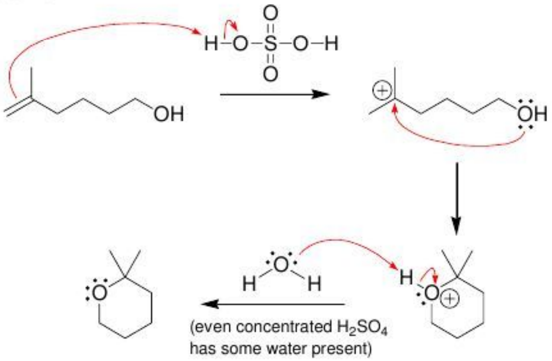
b) 

c) 

9.13.



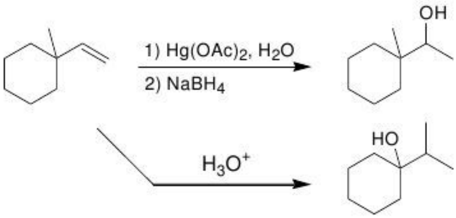
9.14.



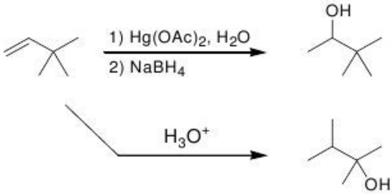
(even concentrated H_2SO_4 has some water present)

9.15.

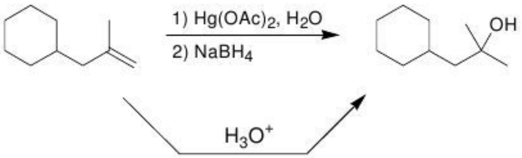
a)



b)

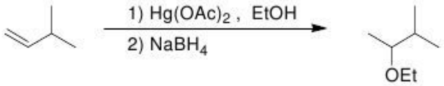


c)

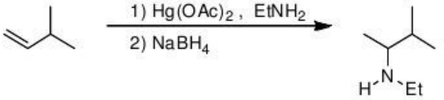


9.16.

a)

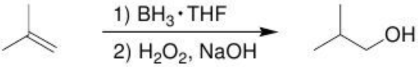


b)

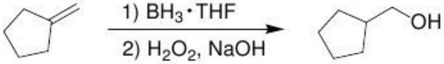


9.17.

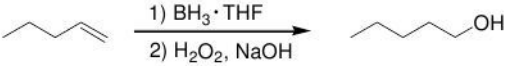
a)



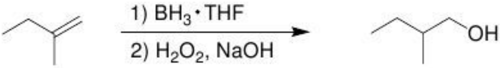
b)



c)

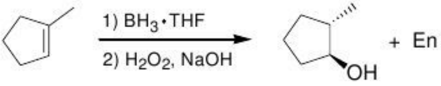


9.18.

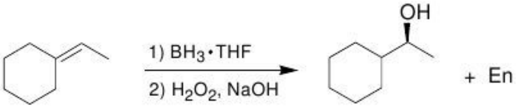


9.19.

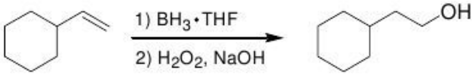
a)



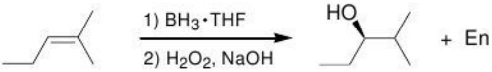
b)



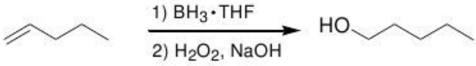
c)



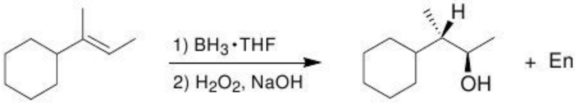
d)



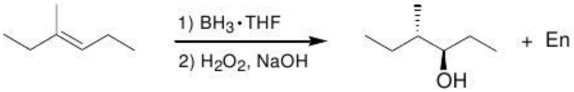
e)



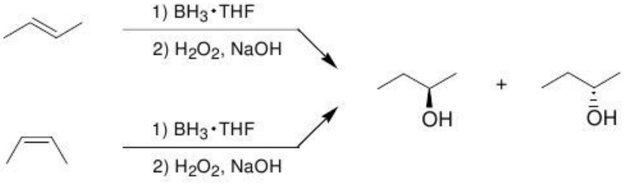
f)



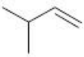
9.20.



9.21. Only one chirality center is formed, so both possible stereoisomers (enantiomers) are obtained, regardless of the configuration of the starting alkene:

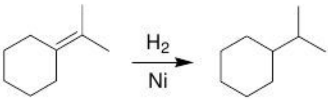


9.22.

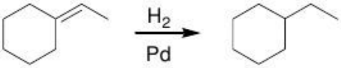


9.23.

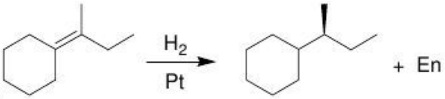
a)



b)

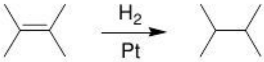


c)

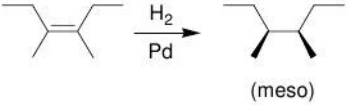


d)

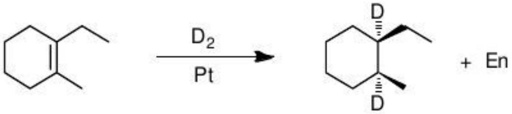
e)



f)

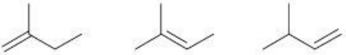


9.24.

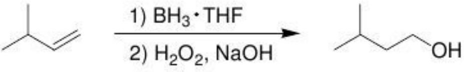


9.25.

a)

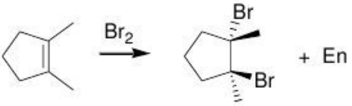


b)

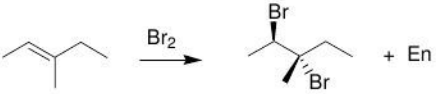


9.26.

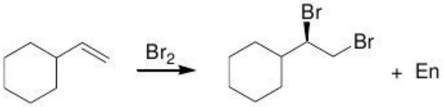
a)



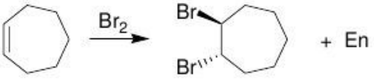
b)



c)

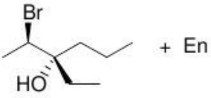


d)

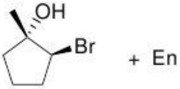


9.27.

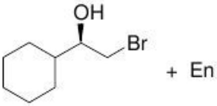
a)



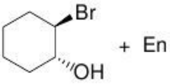
b)



c)

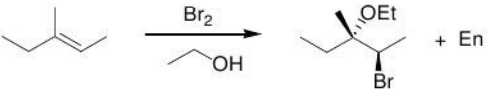


d)

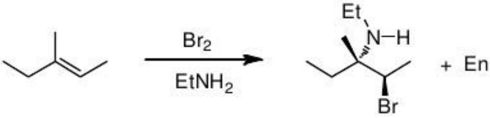


9.28.

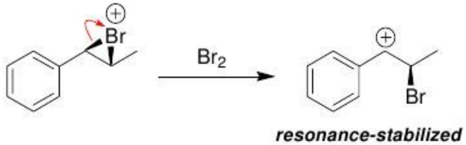
a)



b)

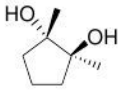


9.29. The bromonium ion can open (before a bromide ion attacks), forming a resonance stabilized carbocation. This carbocation is trigonal planar and can be attacked from either side:



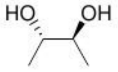
9.30.

a)



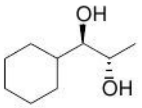
+ En

b)



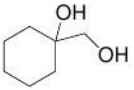
+ En

c)

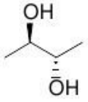


+ En

d)

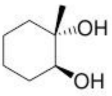


e)



(meso)

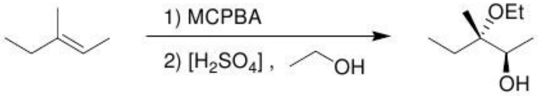
f)



+ En

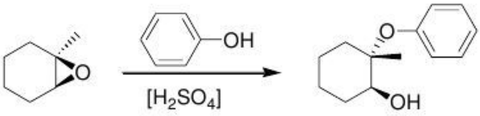
9.31.

a)



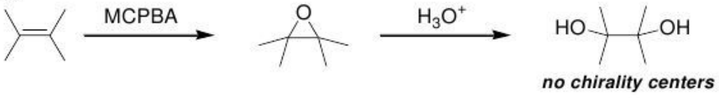
+ En

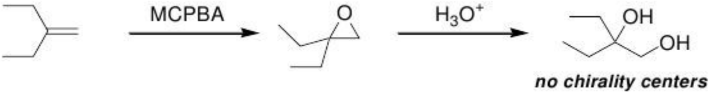
b)



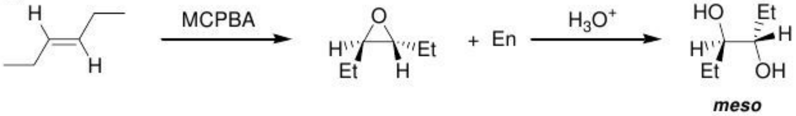
9.32.

a)



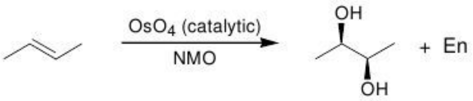


b)

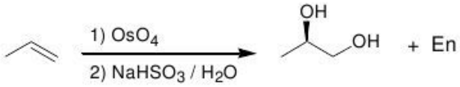

H
H
MCPBA
O
H
Et
Et
H
+ En
H_3O^+
HO
Et
H
H
Et
OH
meso

9.33.

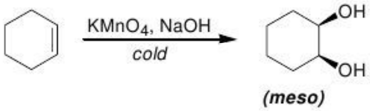
a)


OsO_4 (catalytic)
NMO
OH
OH
+ En

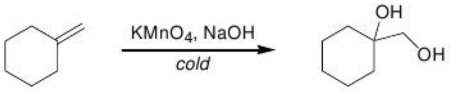
b)


1) OsO_4
2) $NaHSO_3$ / H_2O
OH
OH
+ En

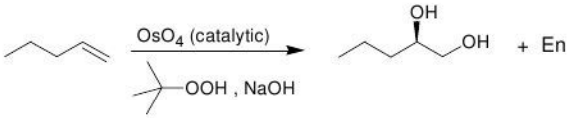
c)


$KMnO_4$, NaOH
cold
OH
OH
(meso)

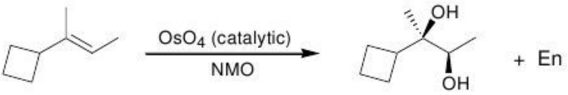
d)


$KMnO_4$, NaOH
cold
OH
OH

e)

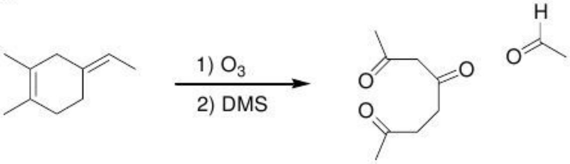

OsO_4 (catalytic)
OOH , NaOH
OH
OH
+ En

f)

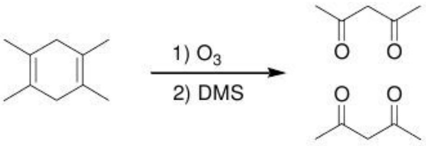

OsO_4 (catalytic)
NMO
OH
OH
+ En

9.34.

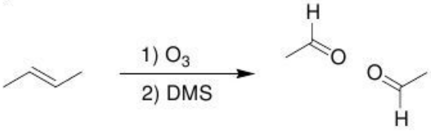
a)



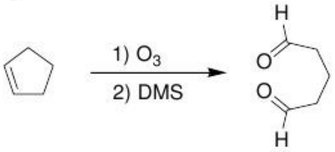
b)



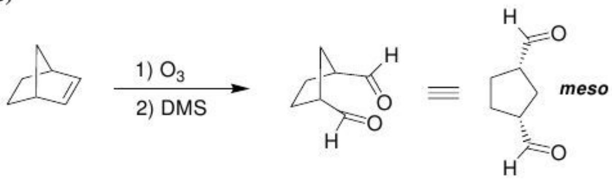
c)



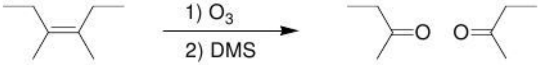
d)



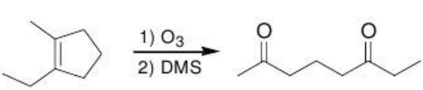
e)



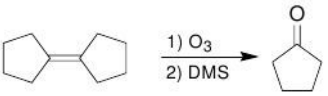
f)



9.35.

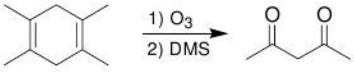


a)



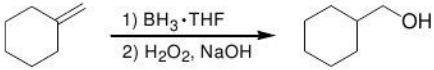
b)

c)

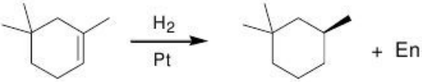


9.36.

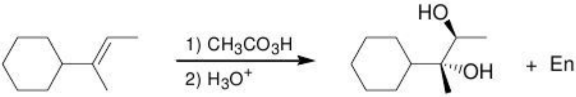
a)



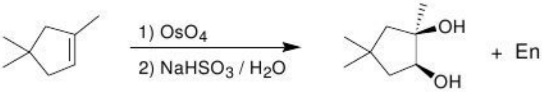
b)



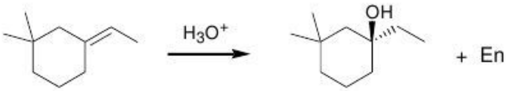
c)



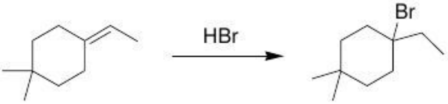
d)



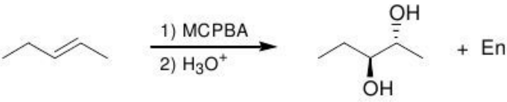
e)



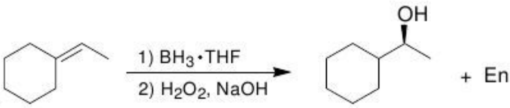
f)



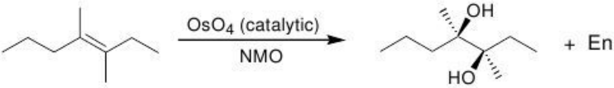
g)



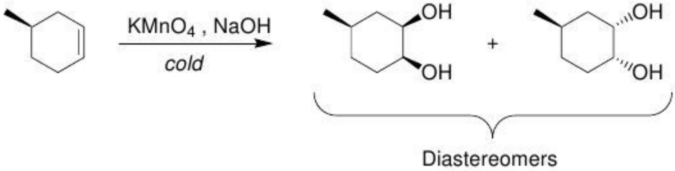
h)



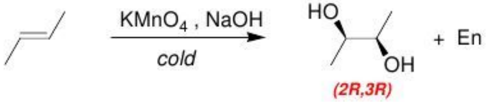
i)

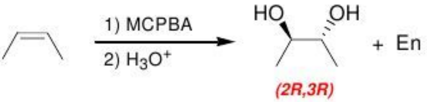


9.37.

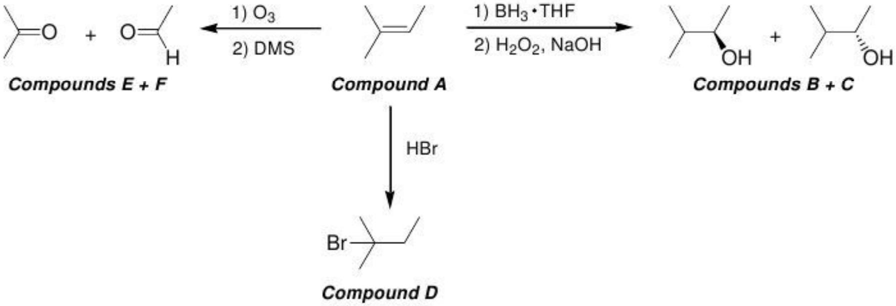


9.38. The products are the same:

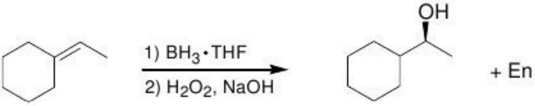




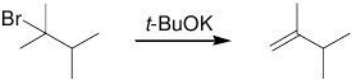
9.39.



9.40.



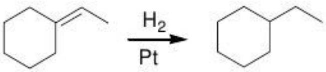
a)



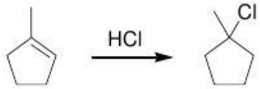
b)

c)

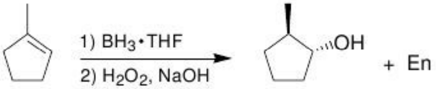
d)



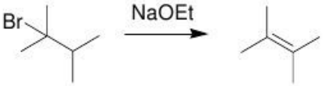
e)



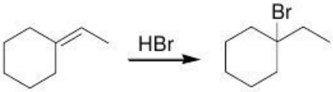
f)



g)

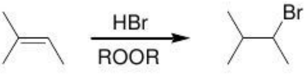


h)



9.41.

a)



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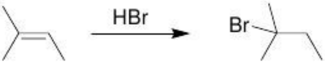

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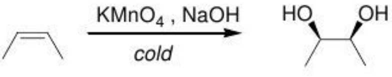
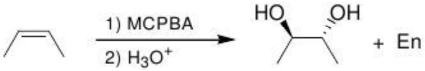
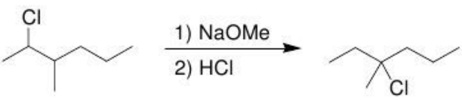


d)

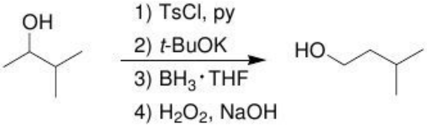


9.42.

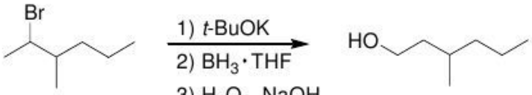
a)



b)



c)



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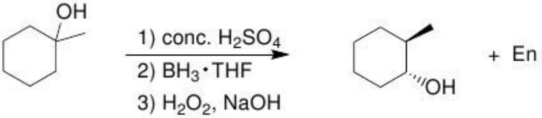
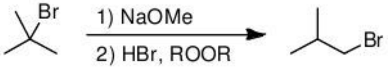
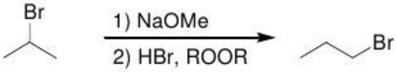


9.43.

a)



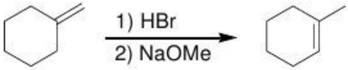
b)



9.44.

9.45.

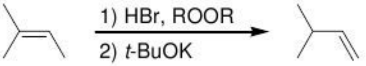
a)



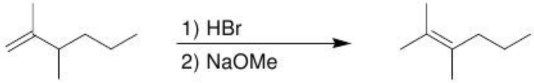
b)

9.46.

a)

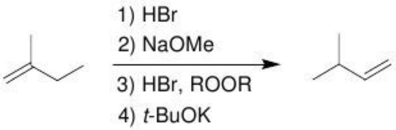


b)

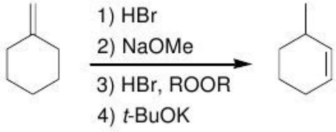


9.47.

a)

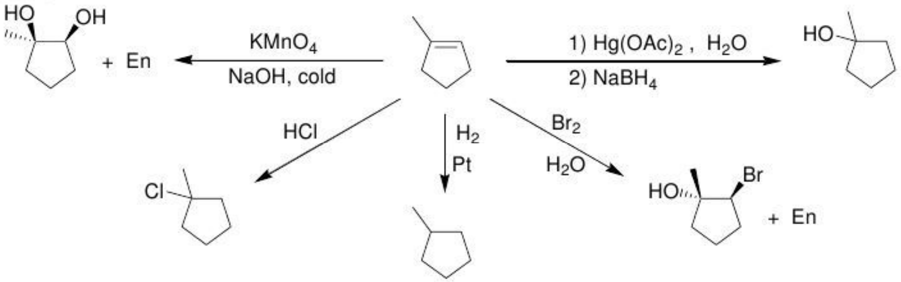


b)

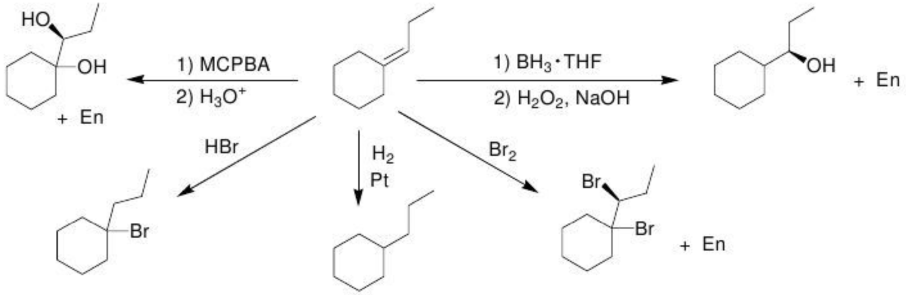


9.48. A reaction is only favorable if ΔG is negative. Recall that ΔG has two components: (ΔH) and (-TΔS). The first term (ΔH) is positive for this reaction (two sigma bonds are converted into one sigma bond and one pi bond). The second term (-TΔS) is negative because ΔS is positive (one molecule is converted into two molecules). Therefore, the reaction is only favorable if the second term is greater in magnitude than the first term. This only occurs at high temperature.

9.49.

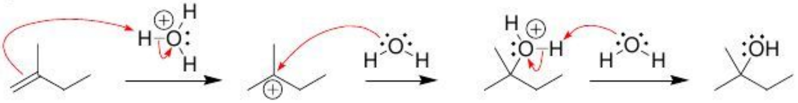


9.50.

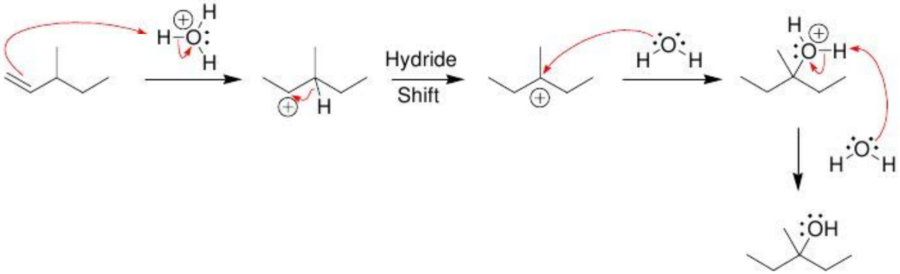

1) MCPBA
2) H_3O^+
+ En
1) $BH_3 \cdot THF$
2) H_2O_2, NaOH
+ En
HBr
H_2
Pt
Br_2
+ En

9.51.

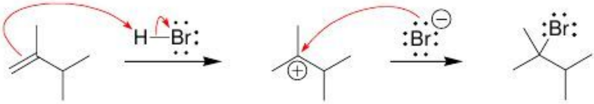
a)



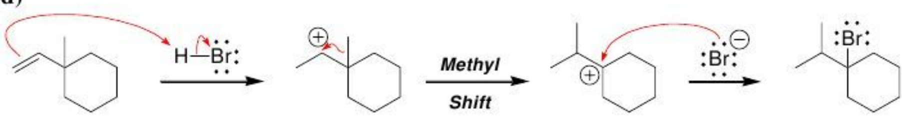
b)


Hydride
Shift

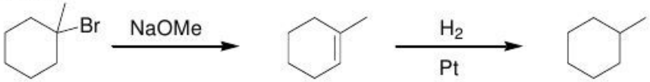
c)



d)


Methyl
Shift

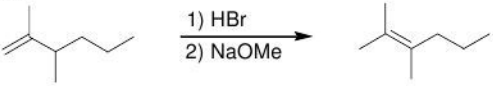
9.52.



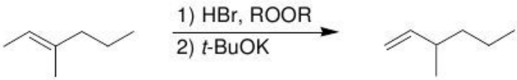
Compound A

9.53.

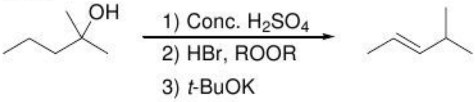
a)



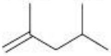
b)

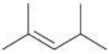


9.54.

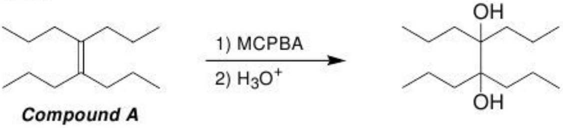


9.55. Two different alkenes will produce 2,4-dimethylpentane upon hydrogenation:





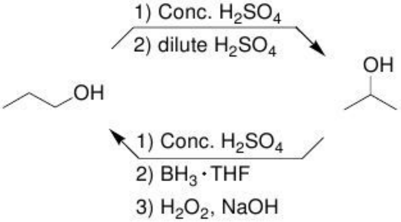
9.56.



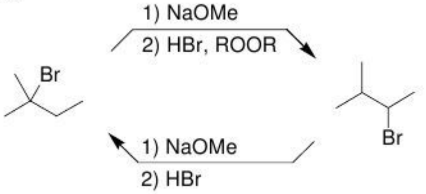
Compound A

9.57.

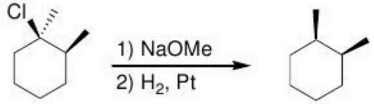
a)



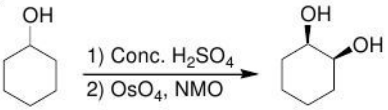
b)



c)

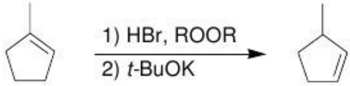


d)

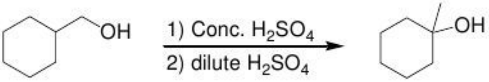


9.58.

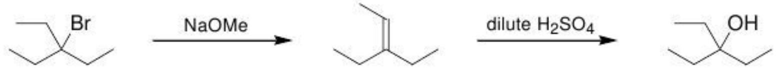
a)



b)

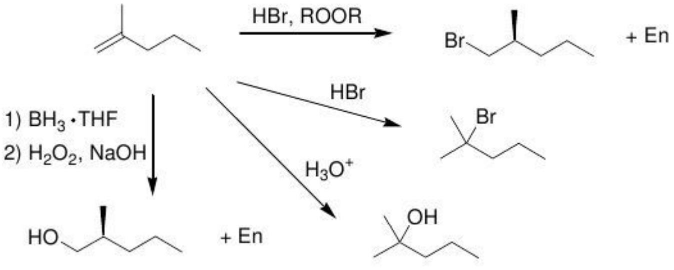


9.59.

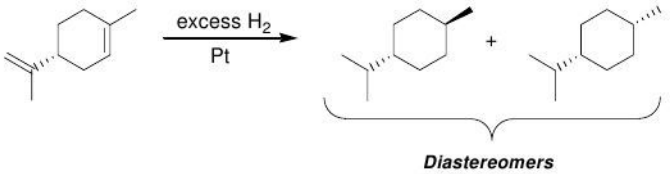


Compound A ***Compound B*** ***Compound C***

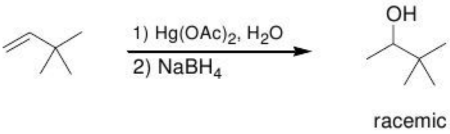
9.60.



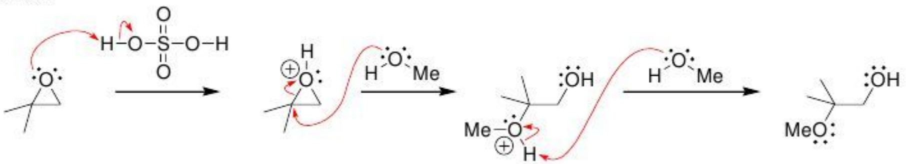
9.61.



9.62. Markovnikov addition of water without carbocation rearrangements can be achieved via oxymercuration-demercuration:

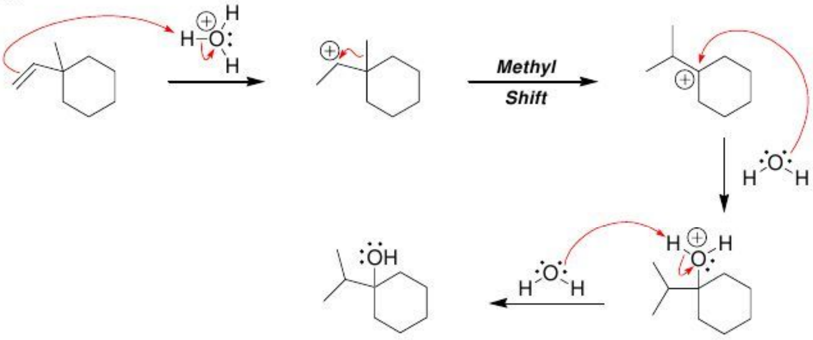


9.63.

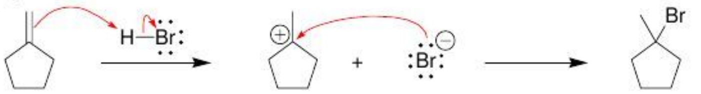


9.64.

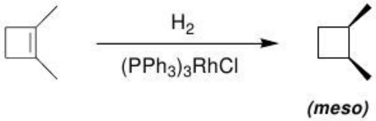
a)



b)

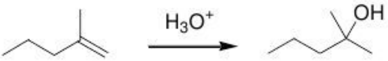


9.65.

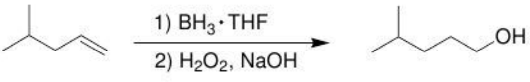


a)

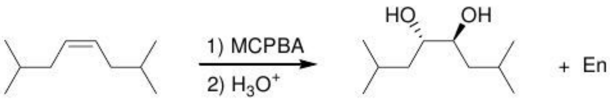
b)



c)



d)



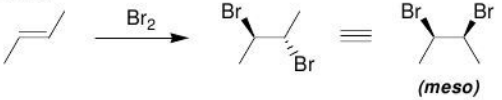
9.66.

a) Hydroboration-oxidation gives an anti-Markovnikov addition. If 1-propene is the starting material, the OH group will not be installed in the correct location. Acid-catalyzed hydration of 1-propene would give the desired product.

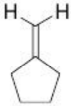
b) Hydroboration-oxidation gives a syn addition of H and OH across a double bond. This compound does not have a proton that is *cis* to the OH group, and therefore, hydroboration-oxidation cannot be used to make this compound.

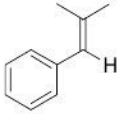
c) Hydroboration-oxidation gives an anti-Markovnikov addition. There is no starting alkene that would yield the desired product via an anti-Markovnikov addition.

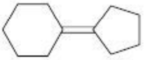
9.67.

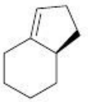


9.68.

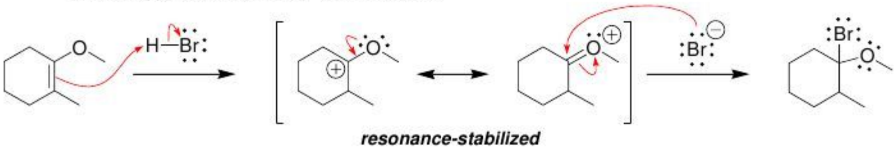
a)


b)


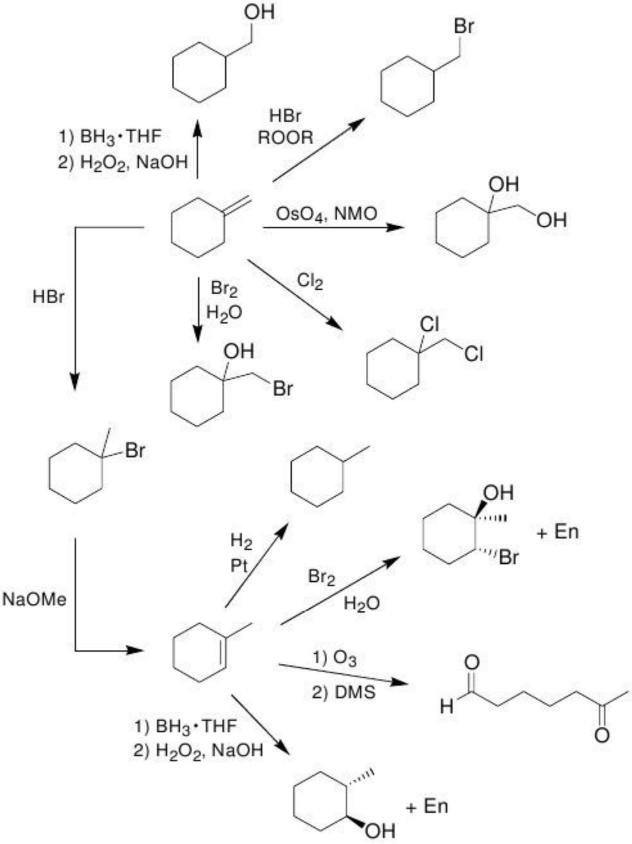
c)


d)


9.69. The reaction proceeds via a resonance-stabilized carbocation, which is even lower in energy than a tertiary carbocation:

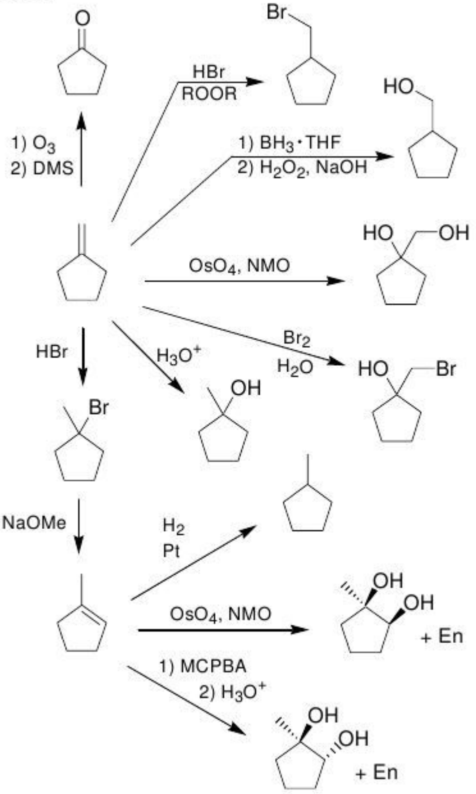


9.70.



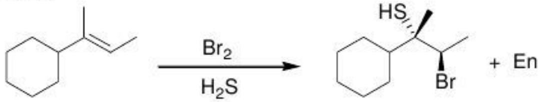
OH
Br
1) BH$_3$·THF
2) H$_2$O$_2$, NaOH
HBr
ROOR
OsO$_4$, NMO
OH
OH
HBr
Br$_2$
H$_2$O
Cl$_2$
Cl
Cl
OH
Br
Br
H$_2$
Pt
OH
+ En
Br
Br$_2$
H$_2$O
NaOMe
1) O$_3$
2) DMS
O
H
O
1) BH$_3$·THF
2) H$_2$O$_2$, NaOH
+ En
OH

9.71.



9.72. Addition of HBr to 2-methyl-2-pentene should be more rapid because the reaction can proceed via a tertiary carbocation. In contrast, addition of HBr to 4-methyl-1-pentene proceeds via a less stable, secondary carbocation.

9.73.



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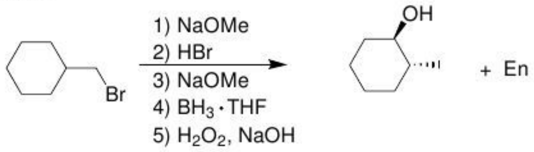

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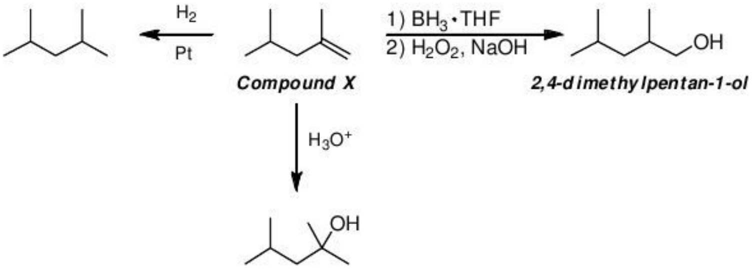

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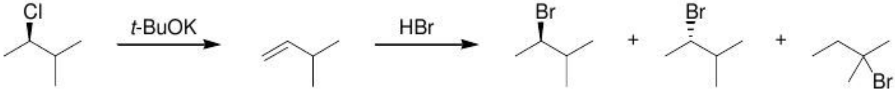

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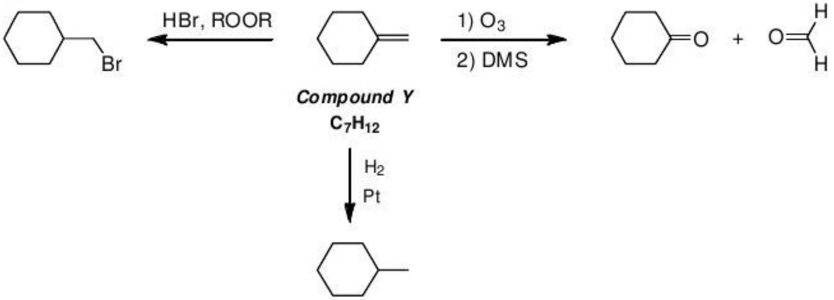

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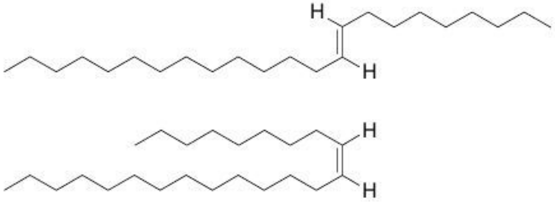
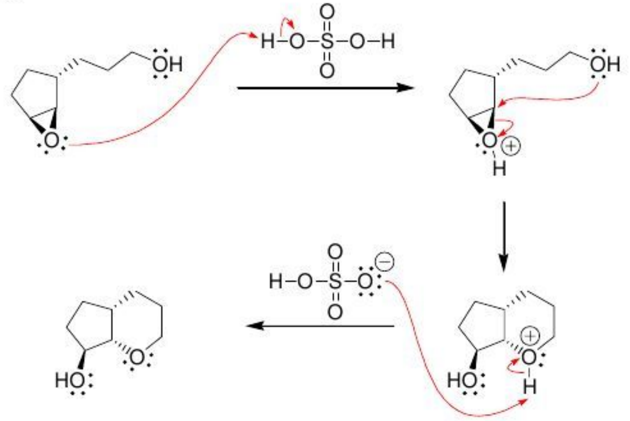


9.79.

a)



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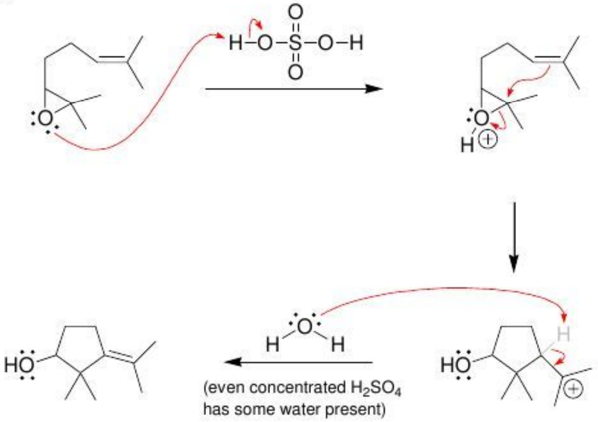
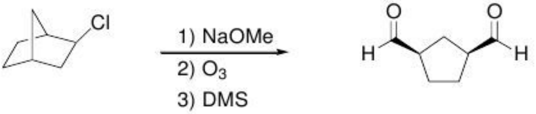


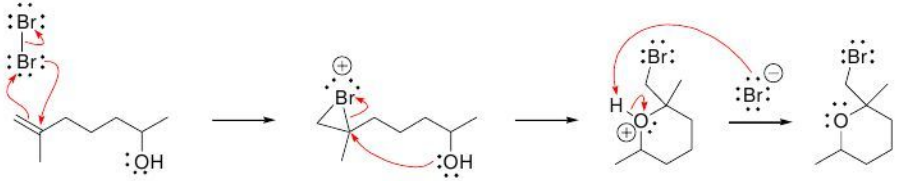
(even concentrated H_2SO_4 has some water present)

9.80.



9.81.

a)



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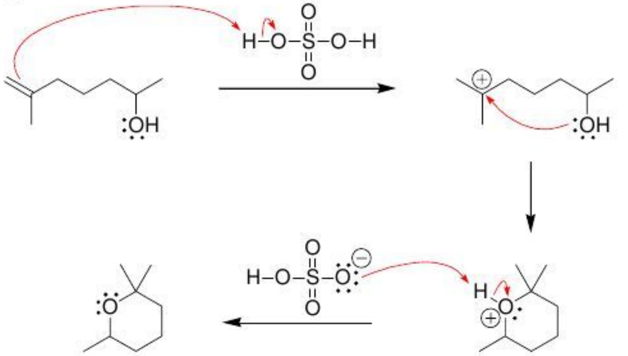

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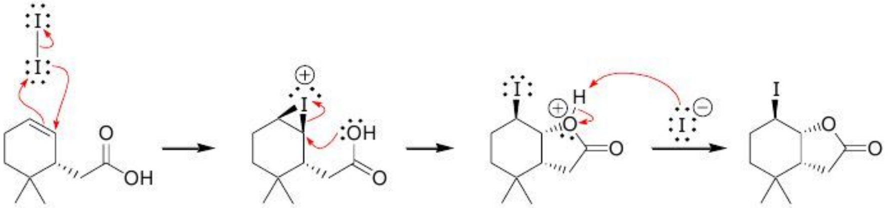
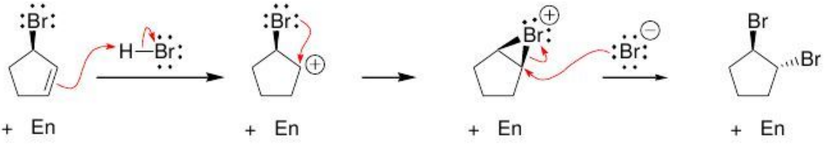


9.83.



Chapter 10
Alkynes

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 10. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

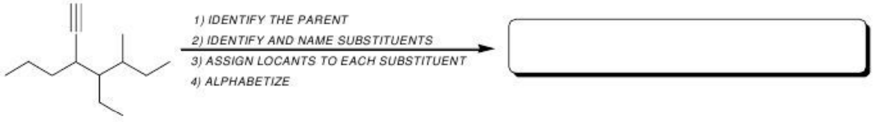
- A triple bond is comprised of three separate bonds: one ____ bond and two ____ bonds.
- Alkynes exhibit __________ geometry and can function either as bases or as ___________________.
- Monosubstituted alkynes are **terminal alkynes**, while disubstituted alkynes are _________ **alkynes**.
- Catalytic hydrogenation of an alkyne yields an __________.
- A **dissolving metal reduction** will convert an alkyne into a _______ alkene.
- Acid-catalyzed hydration of alkynes is catalyzed by mercuric sulfate to produce an ________ that cannot be isolated because it is rapidly converted into a ketone.
- Enols and ketones are ____________, which are constitutional isomers that rapidly interconvert via the migration of a proton.
- When treated with ozone, followed by water, internal alkynes undergo oxidative cleavage to produce ______________________.
- Alkynide ions undergo ______________ when treated with an alkyl halide (methyl or primary).

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 10. The answers appear in the section entitled *SkillBuilder Review*.

10.1 Assembling the Systematic Name of an Alkyne

PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND



10.2 Predicting the Position of Equilibrium for the Deprotonation of a Terminal Alkyne

CIRCLE THE SIDE OF THE EQUILIBRIUM THAT IS FAVORED IN THE FOLLOWING ACID-BASE REACTION

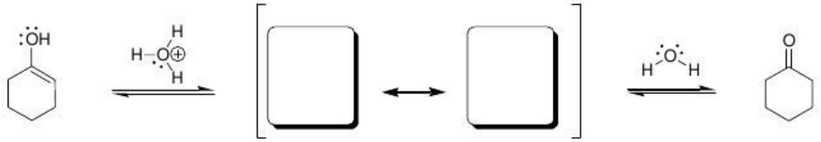
$$R-C\equiv C-H \quad + \quad {}^{\ominus}:\ddot{\underset{\cdot\cdot}{O}}H \quad \rightleftharpoons \quad R-C\equiv C:^{\ominus} \quad + \quad H_2O$$

10.3 Drawing the Mechanism of Acid-Catalyzed Keto-Enol Tautomerization

DRAW TWO CURVED ARROWS SHOWING PROTONATION OF THE π BOND

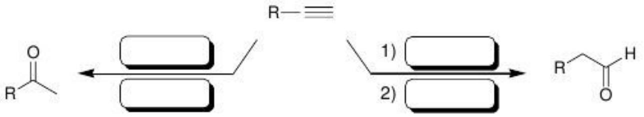
DRAW THE RESONANCE STRUCTURES OF THE INTERMEDIATE

DRAW TWO CURVED ARROWS SHOWING DEPROTONATION TO FORM THE KETONE



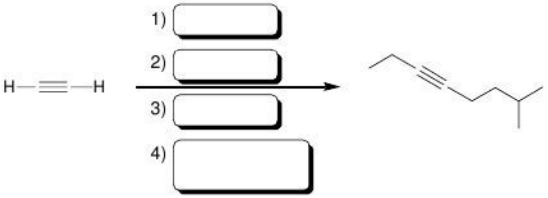
10.4 Choosing the Appropriate Reagents for the Hydration of an Alkyne

IDENTIFY REAGENTS THAT CAN ACHIEVE EACH OF THE FOLLOWING TRANSFORMATIONS



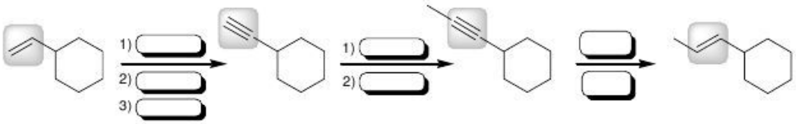
10.5 Alkylating Terminal Alkynes

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:



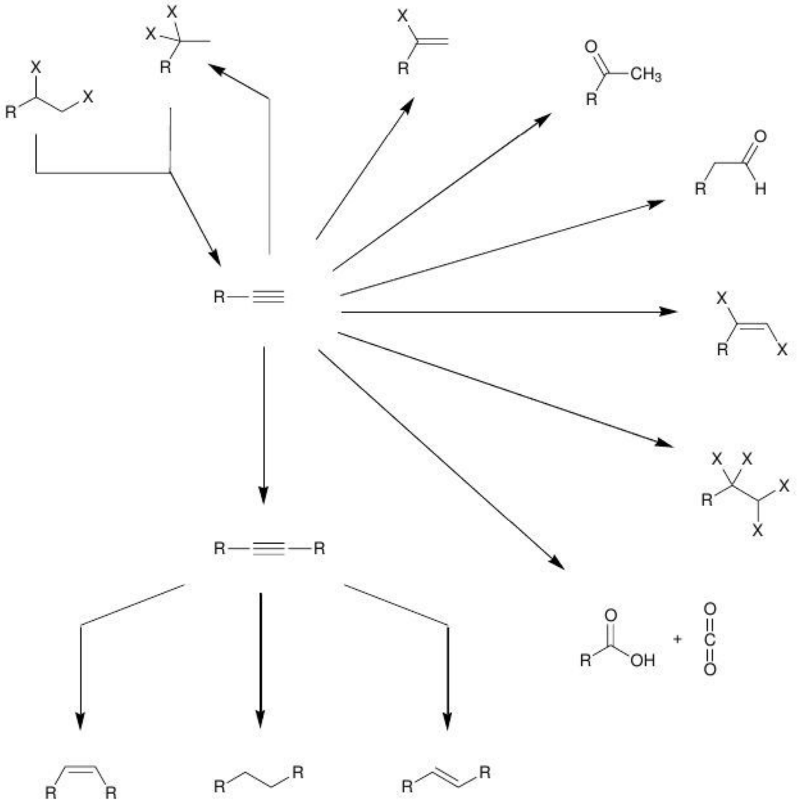
10.6 Interconverting Alkanes, Alkenes, and Alkyne

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATIONS:



Review of Reactions

Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 10. The answers appear in the section entitled *Review of Reactions*.



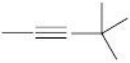
Solutions

10.1.

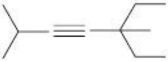
a) 3-hexyne
b) 2-methyl-3-hexyne
c) 3-octyne
d) 3,3-dimethyl-1-butyne

10.2.

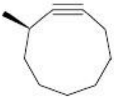
a)



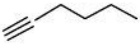
b)



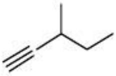
10.3.



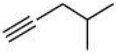
10.4.



1-hexyne



3-methyl-1-pentyne



4-methyl-1-pentyne

3,3-dimethyl-1-butyne

10.5.

a) Yes, $NaNH_2$ is strong enough of a base to deprotonate a terminal alkyne.
b) No, NaOEt is not strong enough of a base to deprotonate a terminal alkyne.
c) No, NaOH is not strong enough of a base to deprotonate a terminal alkyne.
d) Yes, BuLi is strong enough of a base to deprotonate a terminal alkyne.
e) Yes, NaH is strong enough of a base to deprotonate a terminal alkyne.
f) No, *t*-BuOK is not strong enough of a base to deprotonate a terminal alkyne.

10.6.

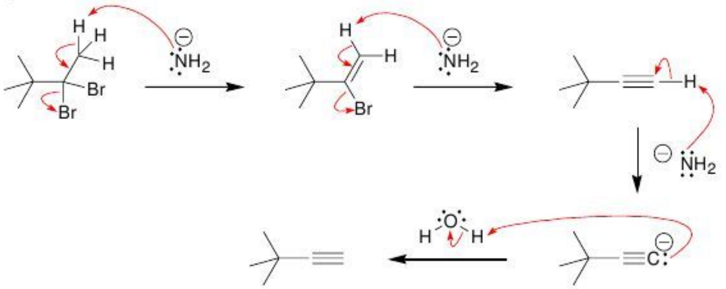
a) In the conjugate base of methyl amine (CH_3NH_2), the negative charge is associated with an sp^3 hybridized nitrogen atom. In the conjugate base of HCN, the negative charge is associated with an *sp* hybridized carbon atom. The latter is more stable, because the charge is closer to the positively charged nucleus. As a result, HCN is a stronger acid than methyl amine.

b) The pK_a of HCN is lower than the pK_a of a terminal alkyne. Therefore, cyanide cannot be used as a base to deprotonate a terminal alkyne, as it would involve the formation of a stronger acid.

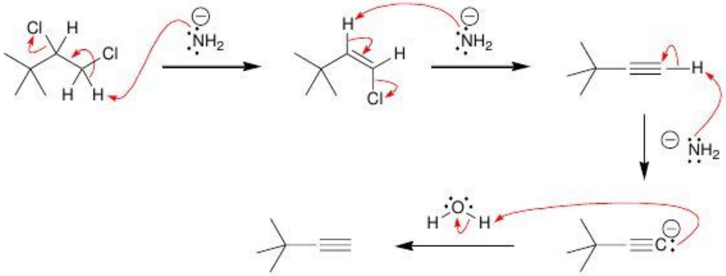
$$\underset{\textit{weaker acid}}{R{-}C{\equiv}C{-}H} \quad + \quad NaCN \quad \rightleftharpoons \quad R{-}C{\equiv}\overset{\ominus}{C}{:}\ \overset{\oplus}{Na} \quad + \quad \underset{\textit{stronger acid}}{HCN}$$

10.7.

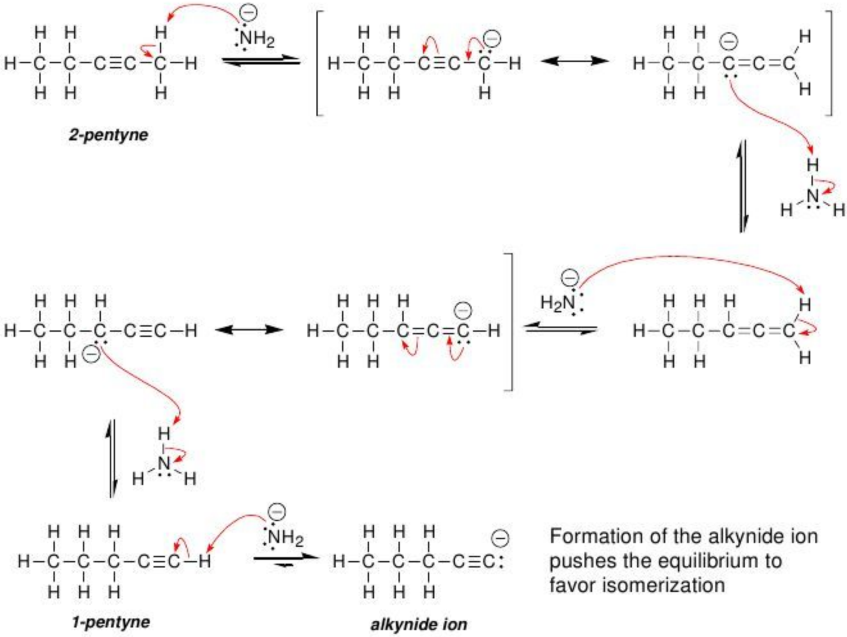
a)


H
H
H
Br
Br
NH2
H
H
Br
NH2
H
NH2
H
O
H
C

b)

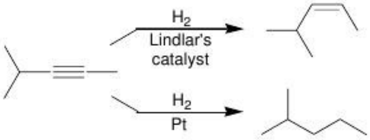

Cl
H
Cl
H
H
NH2
H
H
Cl
NH2
H
NH2
H
O
H
C

10.8.

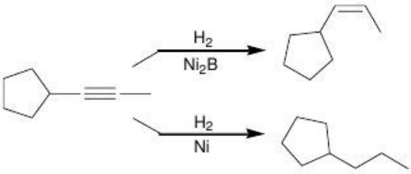


Formation of the alkynide ion pushes the equilibrium to favor isomerization

10.9.



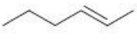
a)



b)

10.10.

a)



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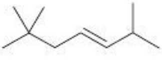
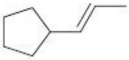
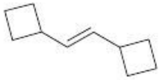


c)

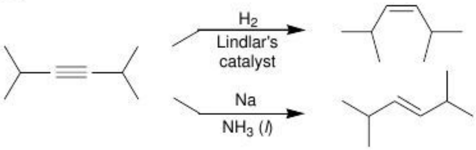


d)



10.11.

a)



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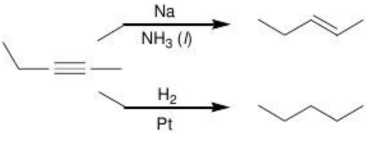
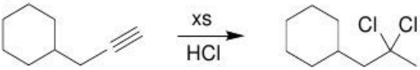


10.12.

10.13.

a)



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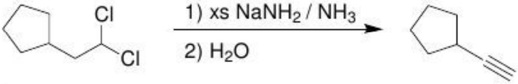

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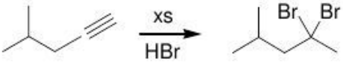

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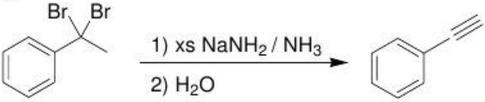
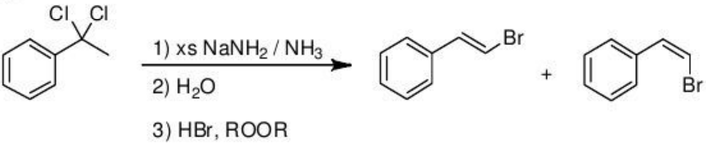


e)



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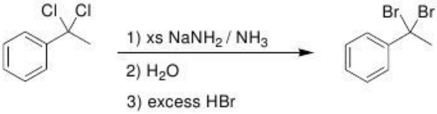
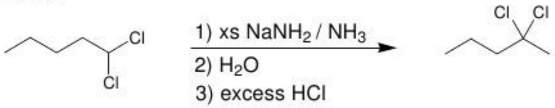


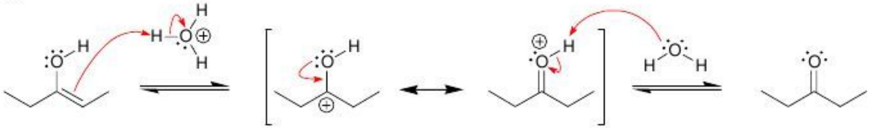
10.14.



10.15. If two products are obtained, then the alkyne must be internal and unsymmetrical. There is only one such alkyne with molecular formula C_5H_8:

10.16.

a)



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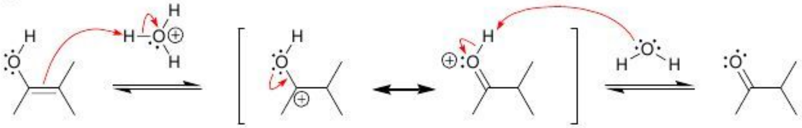

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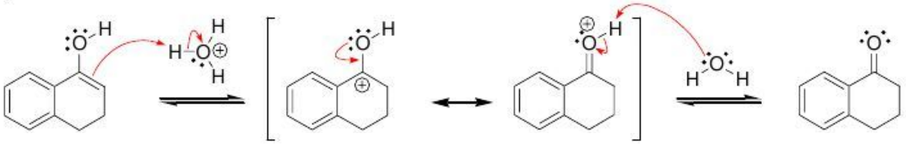

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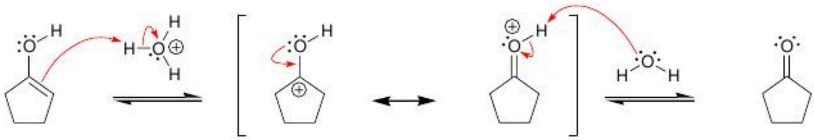
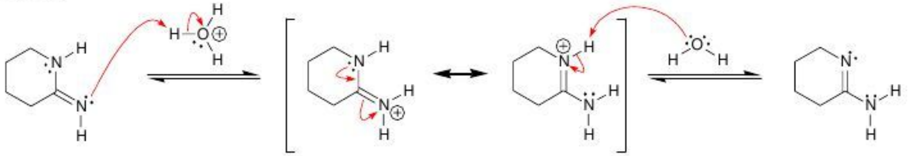
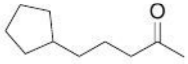


10.17.



10.18.

a)



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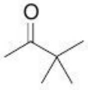

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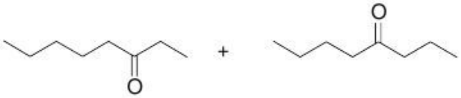

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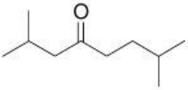

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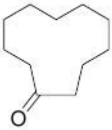
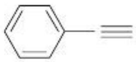


10.19.

a)

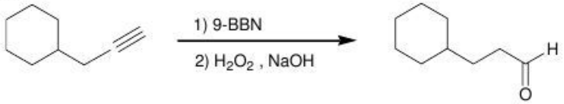
b)

c)

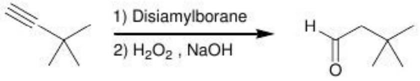


10.20.

a)



b)



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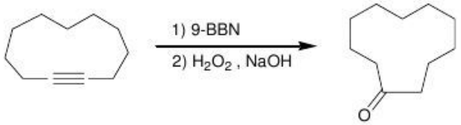
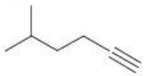


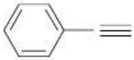
10.21.

a)



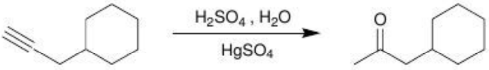
b)

c)

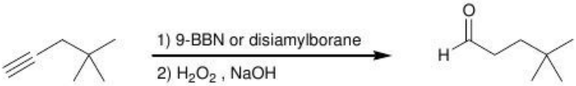


10.22.

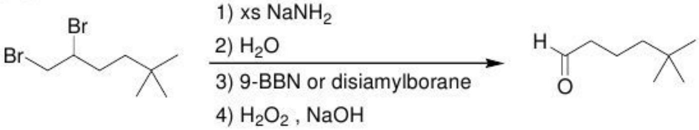
a)



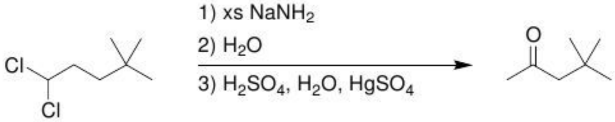
b)



10.23.

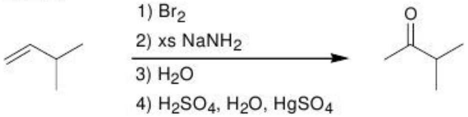


a)



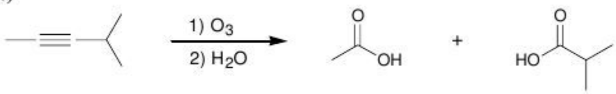
b)

10.24.

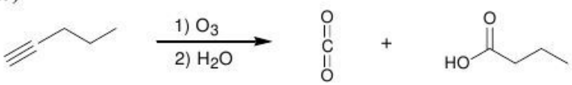


10.25.

a)

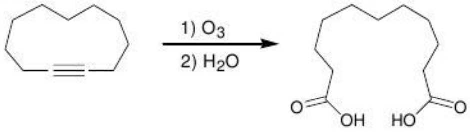


b)

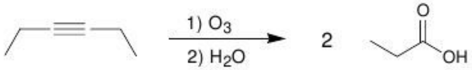


c)

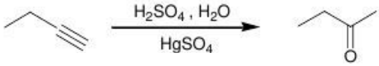
d)



10.26. If ozonolysis produces only one product, then the starting alkyne must be symmetrical. There is only one symmetrical alkyne with molecular formula C_6H_{10}:

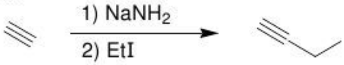


10.27.

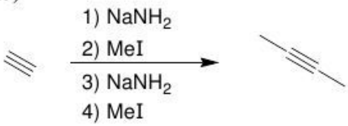


10.28.

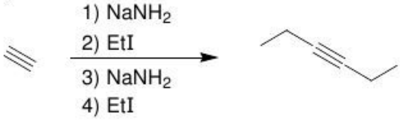
a)



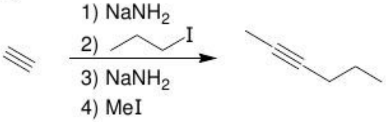
b)



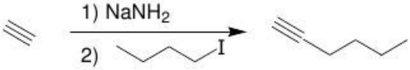
c)



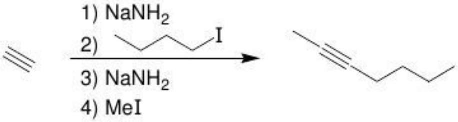
d)


1) NaNH2
2) I
3) NaNH2
4) MeI

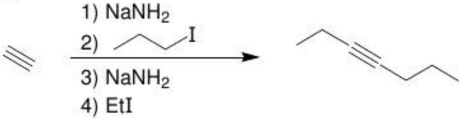
e)


1) NaNH2
2) I

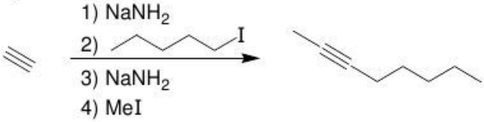
f)


1) NaNH2
2) I
3) NaNH2
4) MeI

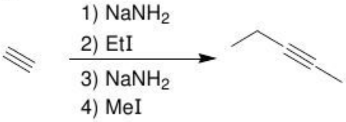
g)


1) NaNH2
2) I
3) NaNH2
4) EtI

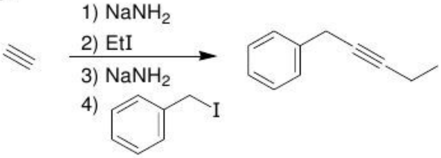
h)


1) NaNH2
2) I
3) NaNH2
4) MeI

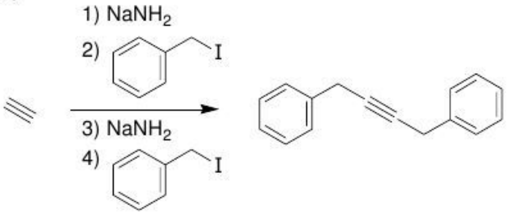
i)


1) NaNH2
2) EtI
3) NaNH2
4) MeI

j)


1) NaNH2
2) EtI
3) NaNH2
4) I

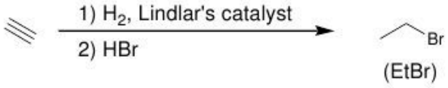
k)

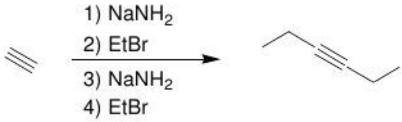


10.29. This process would require the used of a tertiary substrate, which is not reactive toward S_N2.

10.30. 4-octyne

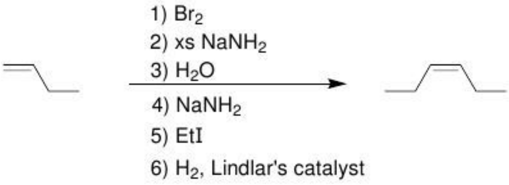
10.31.





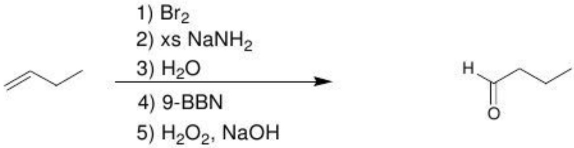
10.32.

a)

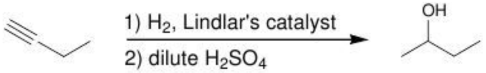


Note: The alkyne produced after step 3 does not need to be isolated and purified, and therefore, steps 3 and 4 can be omitted.

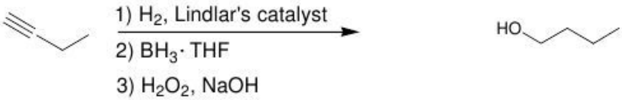
b)



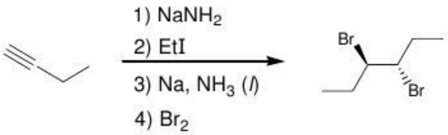
c)



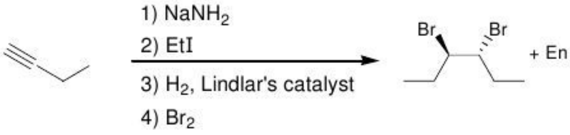
d)



e)

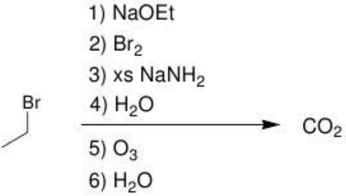


f)

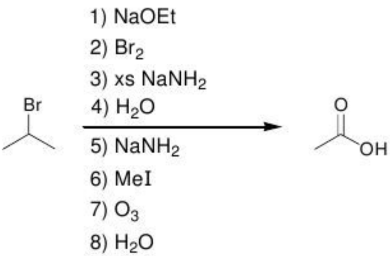


10.33.

a)

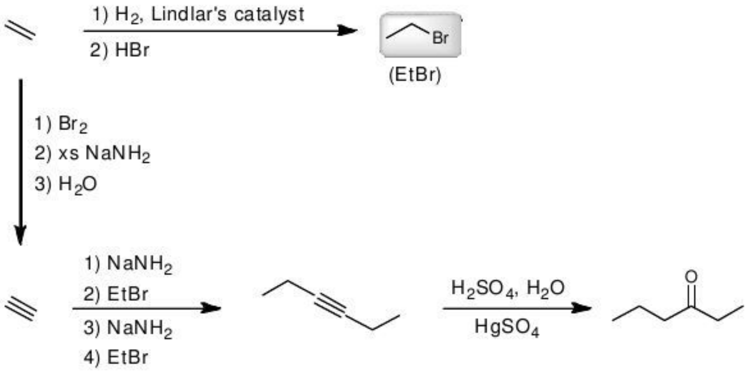


b)



Note: The alkyne produced after step 4 does not need to be isolated and purified, and therefore, steps 4 and 5 can be omitted.

10.34.

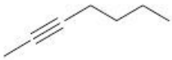


10.35.

a) 2,2,5-trimethyl-3-hexyne
b) 4,4-dichloro-2-hexyne
c) 1-hexyne
d) 3-bromo-3-methyl-1-butyne

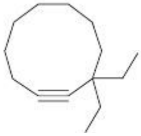
10.36.

a)



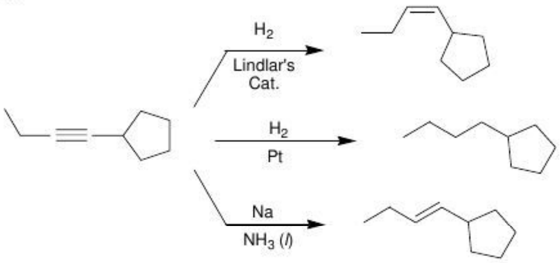
b)

c)

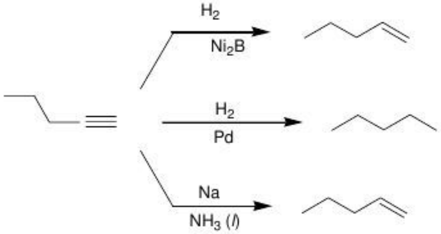


10.37.

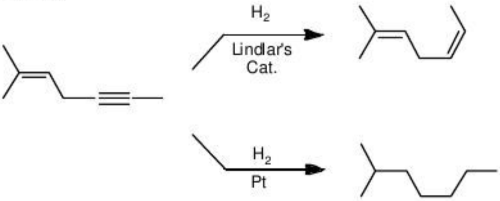
a)



b)



10.38.



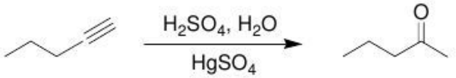
10.39.

a)

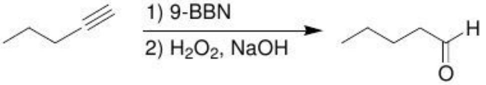
b)

10.40.

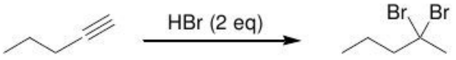
a)



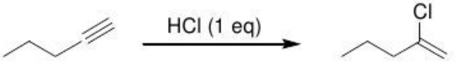
b)



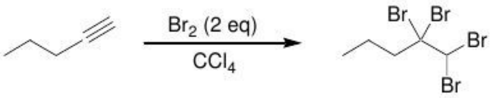
c)



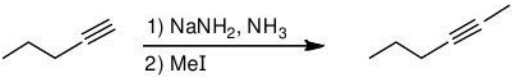
d)



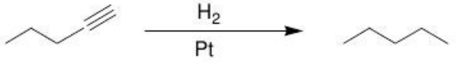
e)



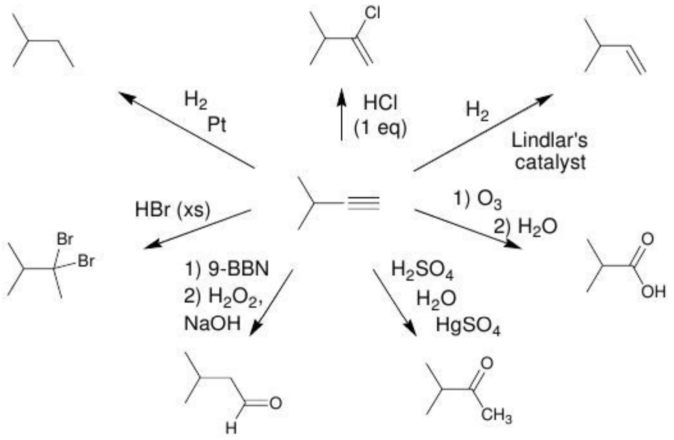
f)



g)



10.41.



10.42.

a) No **b)** Yes **c)** Yes **d)** No **e)** Yes

10.43.

a) No. These compounds are constitutional isomers, but they are not keto-enol tautomers because the pi bond is not adjacent to the OH group.

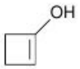
b) Yes

c) Yes

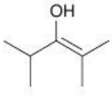
d) Yes

10.44.

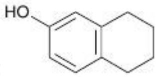
a)



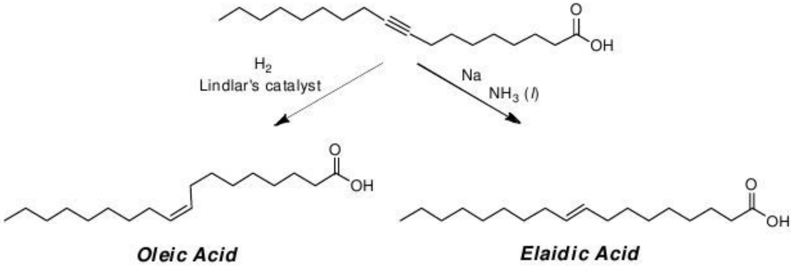
b)



c)

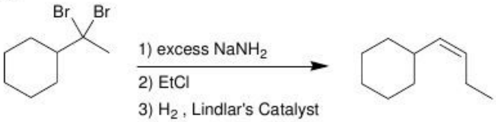


10.45.

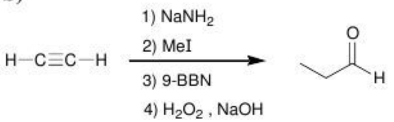


10.46.

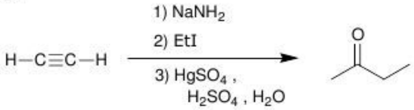
a)



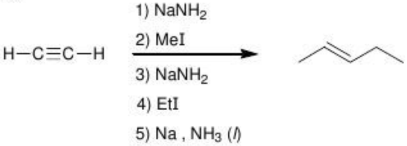
b)



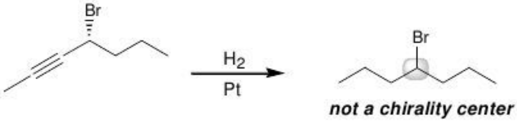
c)



d)

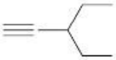


10.47. When *(R)*-4-bromohept-2-yne is treated with H_2 in the presence of Pt, the asymmetry is destroyed and C4 is no longer a chirality center:



This is not the case for *(R)*-4-bromohex-2-yne.

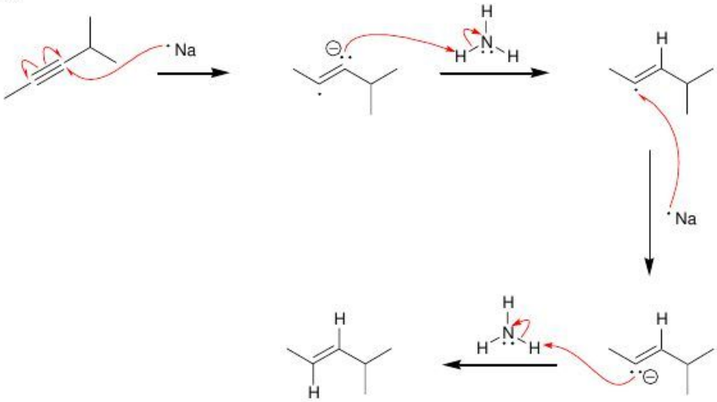
10.48.



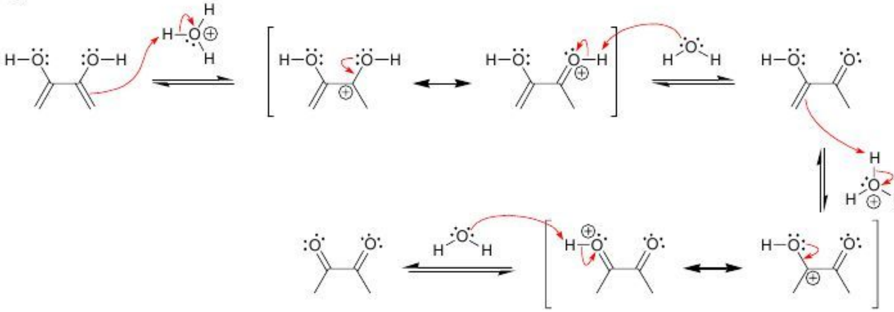
3-ethyl-1-pentyne

10.49.

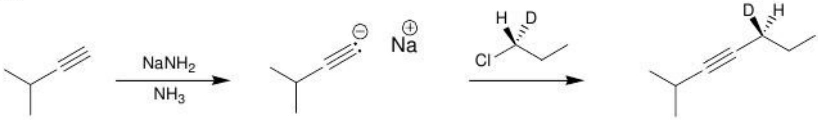
a)



b)

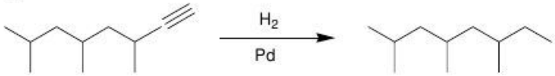


10.50.



10.51.

a)

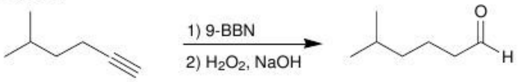


Compound A ***2,4,6-trimethyloctane***

b) Compound A has two chirality centers:

c) The locants for the methyl groups in Compound A are 3, 5, and 7, because locants are assigned in a way that gives the triple bond the lower possible number (1 rather than 7).

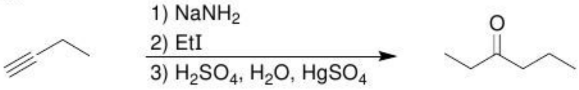
10.52.



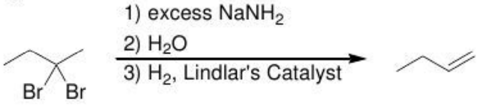
Compound A

10.53.

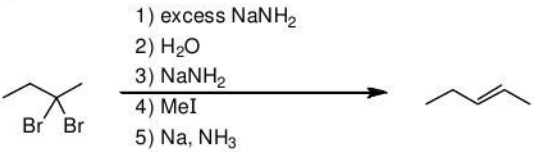
a)



b)

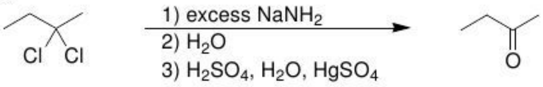


c)

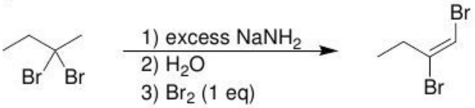


Note: The alkyne produced after step 2 does not need to be isolated and purified, and therefore, steps 2 and 3 can be omitted.

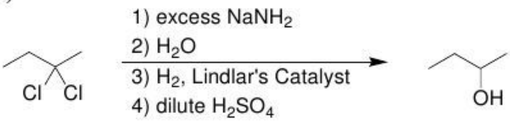
d)



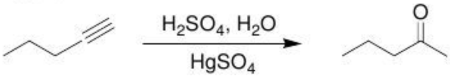
e)



f)

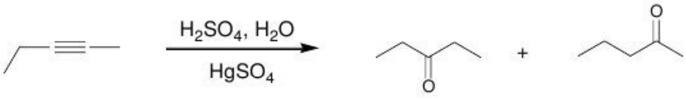


10.54.



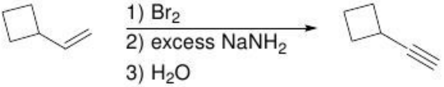
10.55. $H_3C-C\equiv C-H$

10.56. If two products are obtained, then the alkyne must be internal and unsymmetrical. There is only one such alkyne with molecular formula C_5H_8:



10.57.

a)



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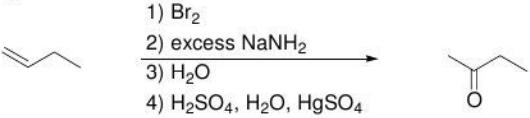

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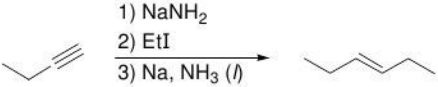

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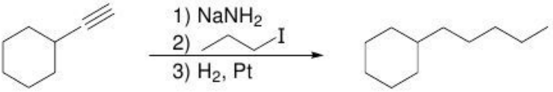

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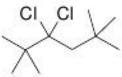

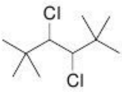

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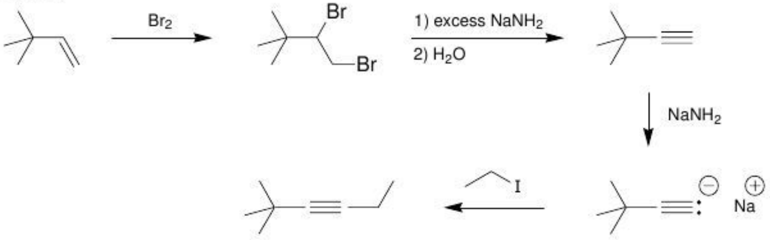
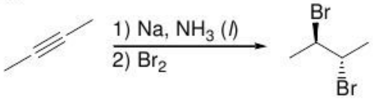


10.60.

a)



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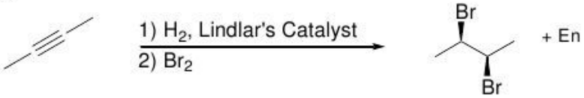
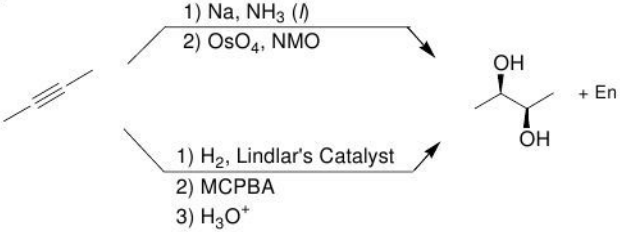


c)



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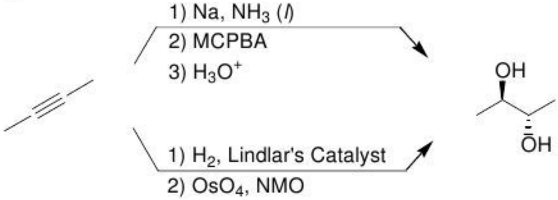
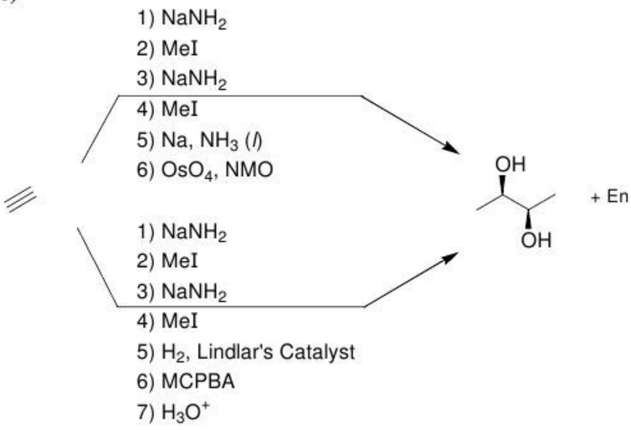
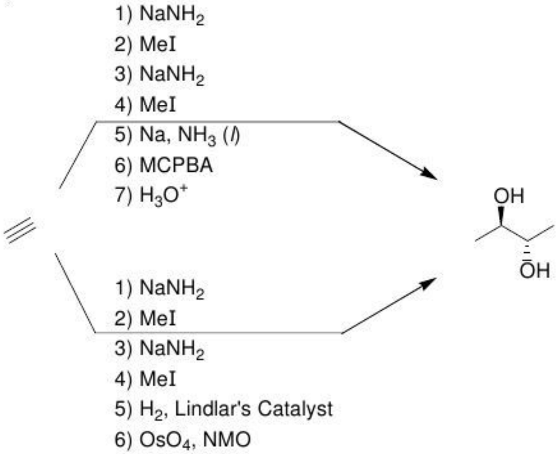


e)

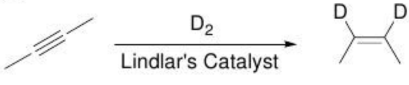

1) NaNH₂
2) MeI
3) NaNH₂
4) MeI
5) Na, NH₃ (l)
6) OsO₄, NMO
1) NaNH₂
2) MeI
3) NaNH₂
4) MeI
5) H₂, Lindlar's Catalyst
6) MCPBA
7) H₃O⁺
OH
OH
+ En

f)

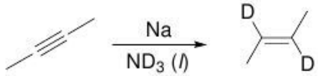

1) NaNH₂
2) MeI
3) NaNH₂
4) MeI
5) Na, NH₃ (l)
6) MCPBA
7) H₃O⁺
1) NaNH₂
2) MeI
3) NaNH₂
4) MeI
5) H₂, Lindlar's Catalyst
6) OsO₄, NMO
OH
OH

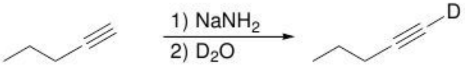
10.61.

a)

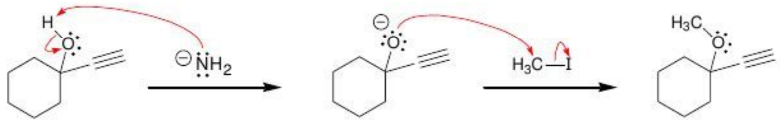

D₂
Lindlar's Catalyst
D
D

b)

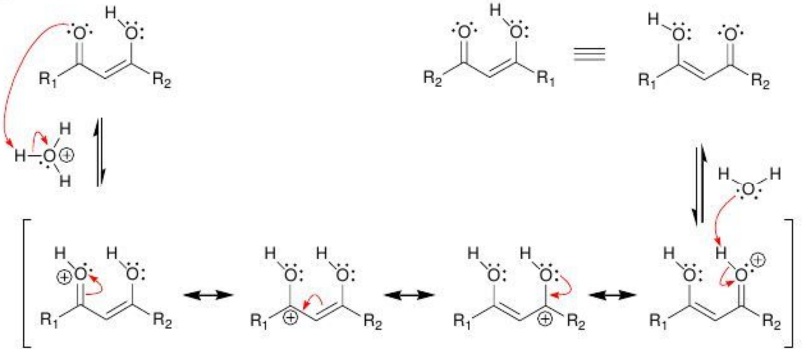

Na
ND₃ (l)
D
D

c) 

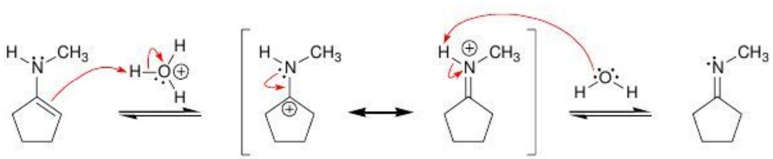
10.62.



10.63.

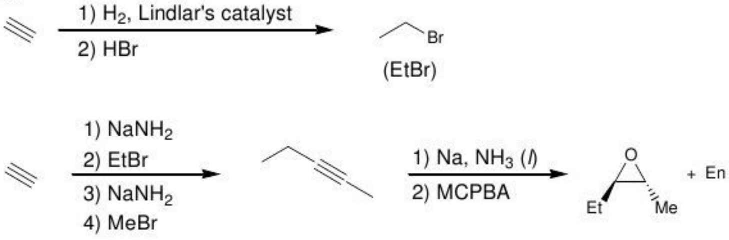


10.64.

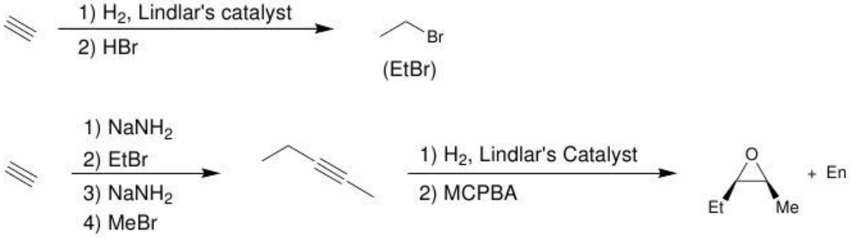


10.65.

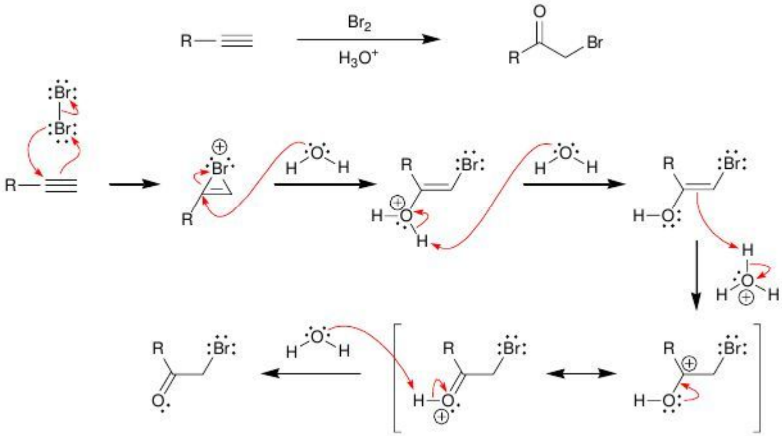
a)


1) H₂, Lindlar's catalyst
2) HBr
Br
(EtBr)
1) NaNH₂
2) EtBr
3) NaNH₂
4) MeBr
1) Na, NH₃ (l)
2) MCPBA
O
Et
Me
+ En

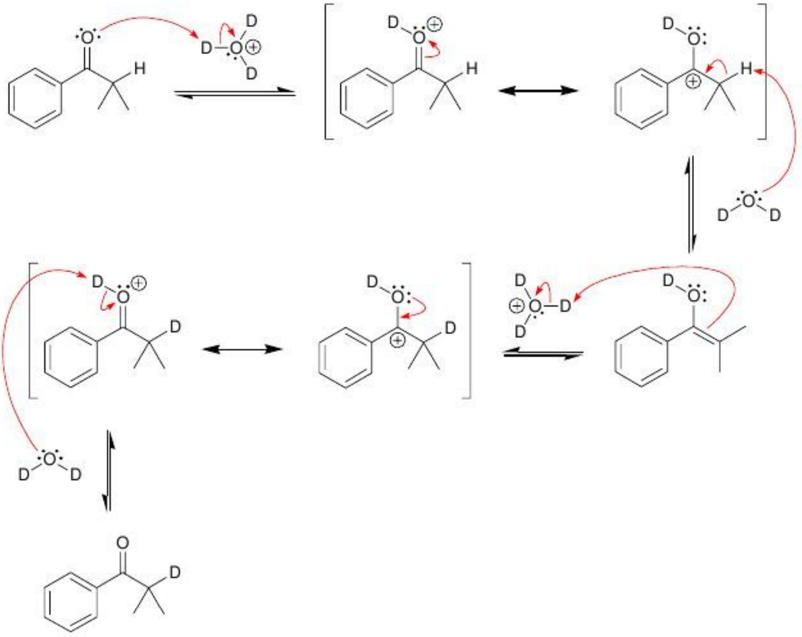
b)


1) H₂, Lindlar's catalyst
2) HBr
Br
(EtBr)
1) NaNH₂
2) EtBr
3) NaNH₂
4) MeBr
1) H₂, Lindlar's Catalyst
2) MCPBA
O
Et
Me
+ En

10.66.


R
Br₂
H₃O⁺
O
Br
Br
R
H
O
H
R
Br
H
O
H
R
Br
H
O
H
H
H
O
H
R
Br
H
O
R
Br
H
O
H
R
Br
H
O
R
Br
H
O

10.67.



Chapter 11
Radical Reactions

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 11. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- Radical mechanisms utilize **fishhook arrows**, each of which represents the flow of ______________________.
- Every step in a radical mechanism can be classified as **initiation**, ____________, or **termination**.
- A **radical initiator** is a compound with a weak bond that readily undergoes ___________________________.
- A ___________________, also called a radical scavenger, is a compound that prevents a chain process from either getting started or continuing.
- __________________ is more selective than chlorination.
- When a new chirality center is created during a radical halogenation process, a _____________ mixture is obtained.
- _________________ can undergo **allylic bromination**, in which bromination occurs at the allylic position.
- Organic compounds undergo oxidation in the presence of atmospheric oxygen to produce **hydroperoxides**. This process, called ___________________, is believed to proceed via a _____________ mechanism.
- **Antioxidants**, such as BHT and BHA, are used as food preservatives to prevent autooxidation of _________________ oils.
- When vinyl chloride is polymerized, _________________________ is obtained.
- Radical halogenation provides a method for introducing ________________ into an alkane.

Review of Skills

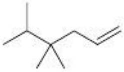
Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 11. The answers appear in the section entitled *SkillBuilder Review*.

11.1 Drawing Resonance Structures of Radicals

DRAW A RESONANCE STRUCTURE OF THE RADICAL BELOW:

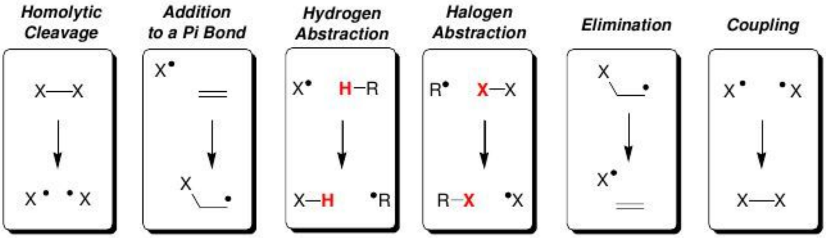
11.2 Identifying the Weakest C-H Bond in a Compound

IDENTIFY THE WEAKEST C-H BOND IN THE FOLLOWING COMPOUND:



11.3 Identifying a Radical Pattern and Drawing Fishhook Arrows

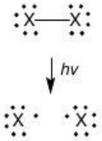
DRAW THE CURVED ARROWS FOR EACH OF THE SIX STEPS SHOWN BELOW:



11.4 Drawing a Mechanism for Radical Halogenation

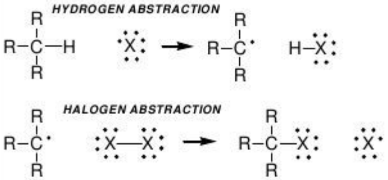
INITIATION

DRAW CURVED ARROWS FOR THE INITIATION STEP BELOW:



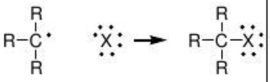
PROPAGATION

DRAW CURVED ARROWS FOR THE PROPAGATION STEPS BELOW:



TERMINATION

DRAW CURVED ARROWS FOR THE TERMINATION STEP BELOW:

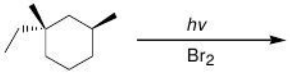


11.5 Predicting the Regiochemistry of Radical Bromination

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING MONOBROMINATION REACTION:

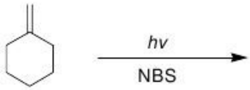
11.6 Predicting the Stereochemical Outcome of Radical Bromination

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION:



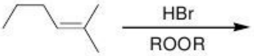
11.7 Predicting the Products of Allylic Bromination

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION:



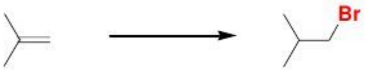
11.8 Predicting the Products for Radical Addition of HBr

DRAW THE EXPECTED PRODUCTS OF THE FOLLOWING REACTION:



Review of Reactions

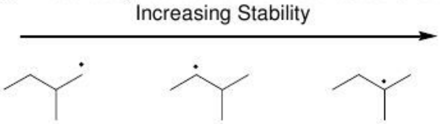
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 11. The answers appear in the section entitled *Review of Synthetically Useful Radical Reactions*.



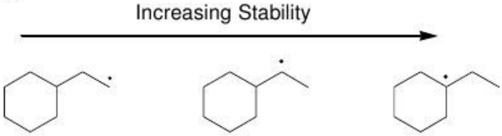
Solutions

11.1.

a) The tertiary radical is the most stable and the primary radical is the least stable.

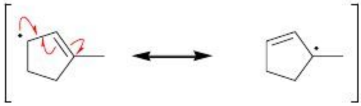


b)



11.2.

a)



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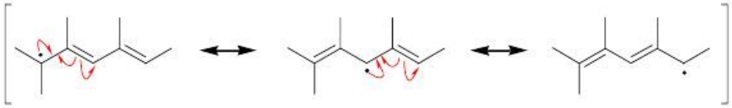

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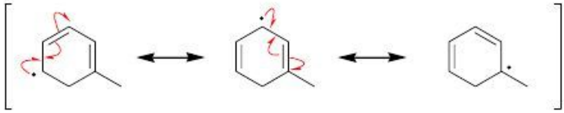

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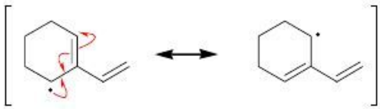
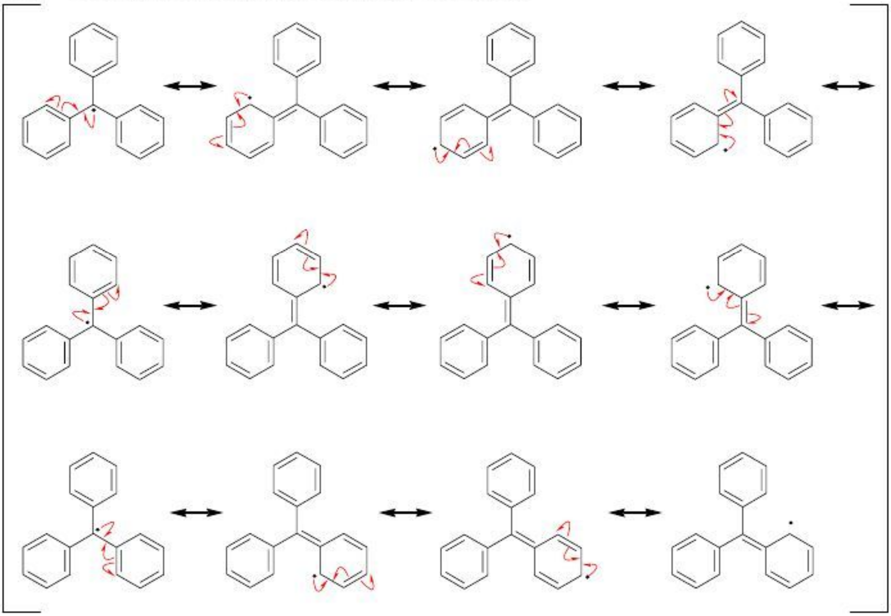
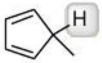


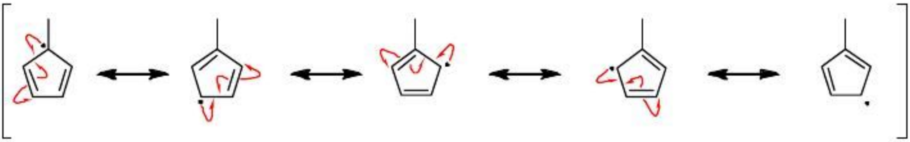
11.3. This radical is highly stabilized by resonance:



11.4.

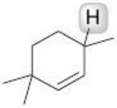


This hydrogen atom is removed

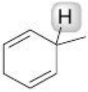


11.5.

a)



b)



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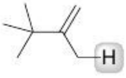

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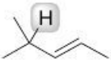
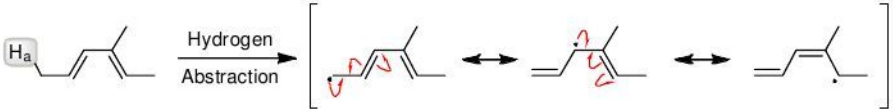
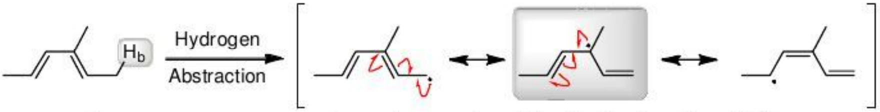


11.6. Draw the resonance structures of the radical that is formed when H_a is abstracted, and then draw the resonance structures of the radical that is formed when H_b is abstracted:

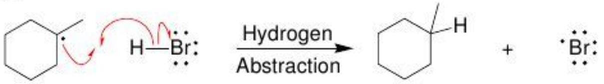




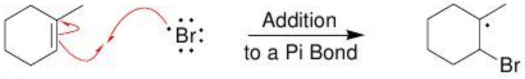
Compare the resonance structures in each case. Specifically, look at the middle resonance structure in each case. When H_b is abstracted, the middle resonance structure is tertiary, and the methyl group stabilizes the radical via electron donation. This stabilizing factor is not present when H_a is abstracted. Therefore, we expect the C-H_b bond to be slightly weaker than the C-H_a bond.

11.7.

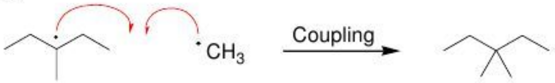
a)



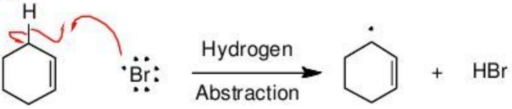
b)



c)

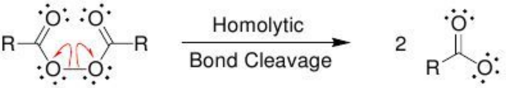


d)

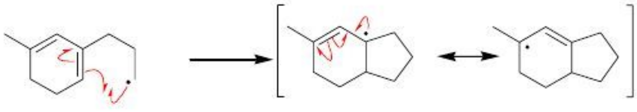


e)

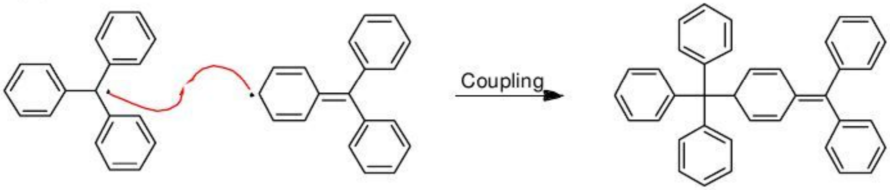
f)



11.8.

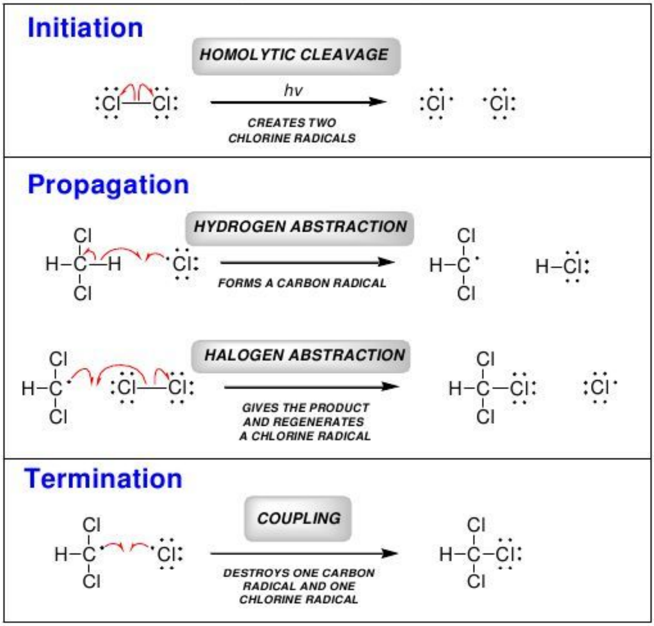


11.9.

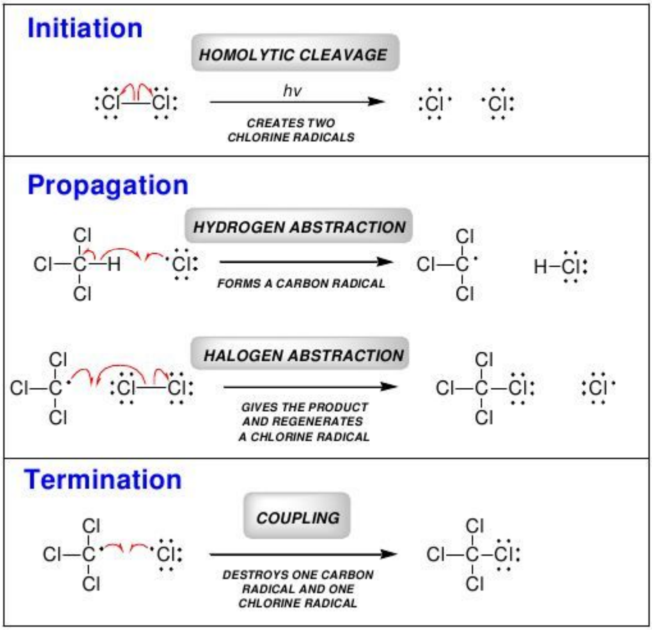


11.10.

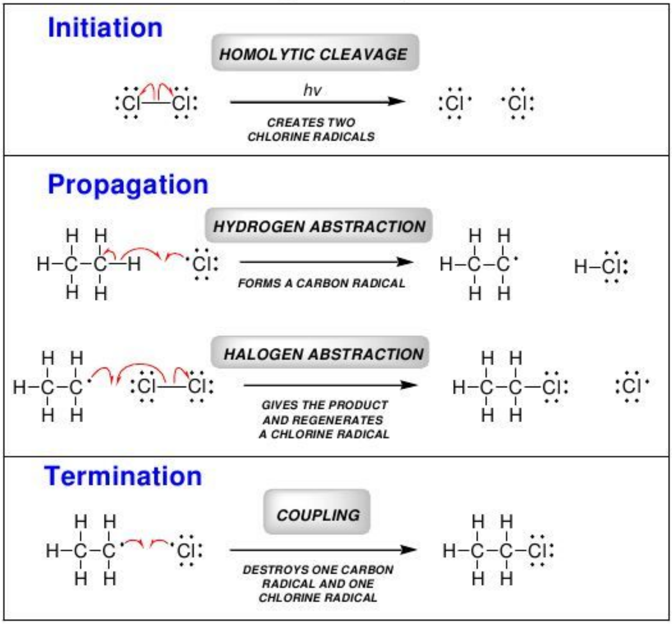
a) Chlorination of methylene chloride to produce chloroform:



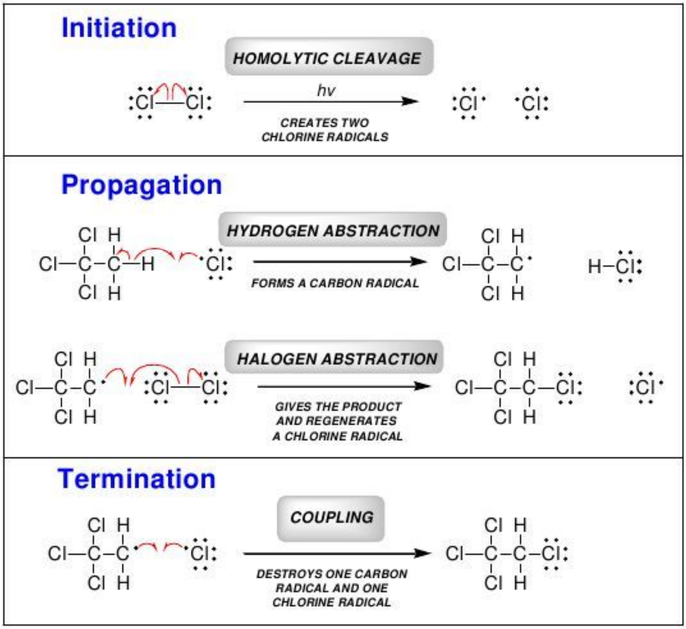
b) Chlorination of chloroform to produce carbon tetrachloride:



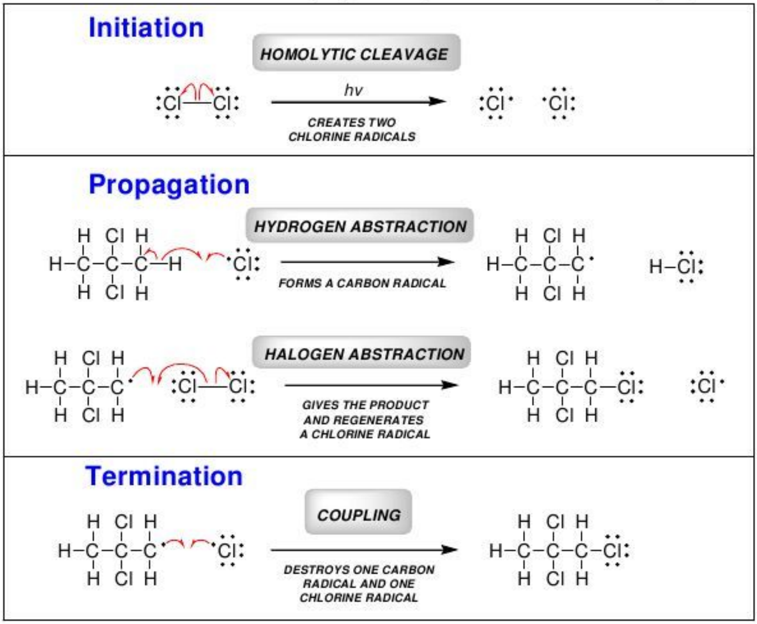
c) Chlorination of ethane to produce ethyl chloride



d) Chlorination of 1,1,1-trichloroethane to produce 1,1,1,2-tetrachloroethane:

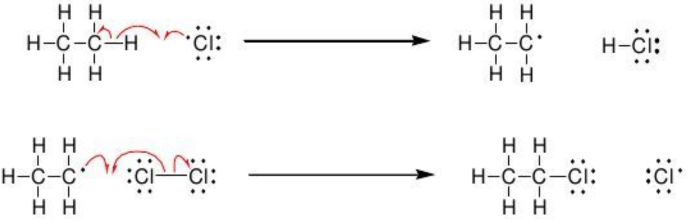


e) Chlorination of 2,2-dichloropropane to produce 1,2,2-trichloropropane:



11.11. During the chlorination of methane, methyl radicals are generated. Two of these methyl radicals can couple together to form ethane:

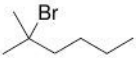
Ethane can then undergo hydrogen abstraction, followed by halogen abstraction to generate ethyl chloride:



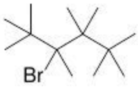
11.12.

a)

b)

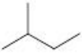


c)



11.13.

a)



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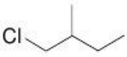

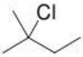

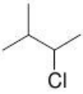

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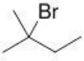
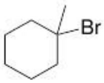


11.14.



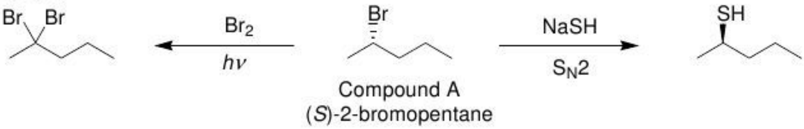
a) no chirality center

b)

c)

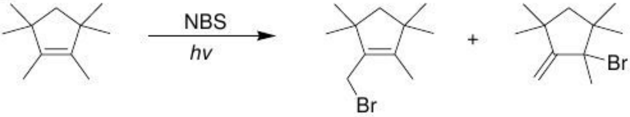
d)

11.15.

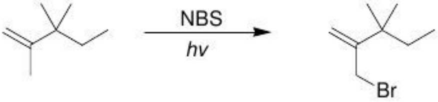


11.16.

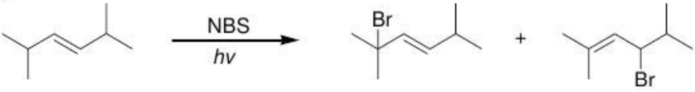
a)



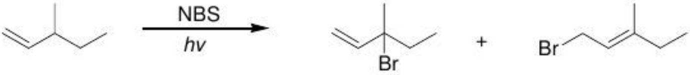
b)



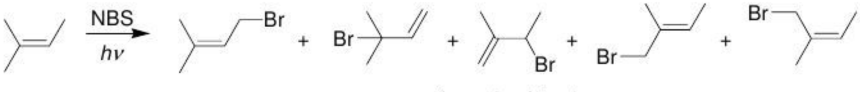
c)



d)

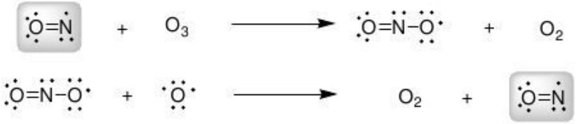


11.17.

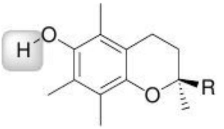


(racemic mixture)

11.18.



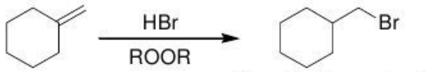
11.19.



Vitamin E

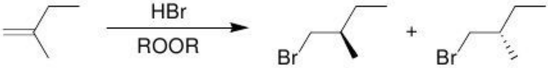
11.20.

a)



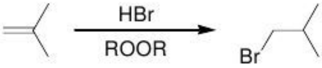
(no chirality centers)

b)



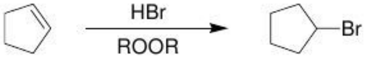
c)

d)



(no chirality centers)

e)



(no chirality centers)

f)

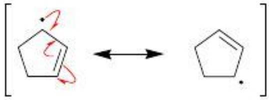
11.21.

a) One chemical entity is being converted into two chemical entities, which increases the entropy of the system.

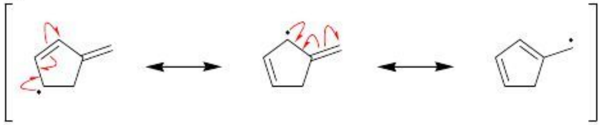
b) Recall that ΔG has two components: (ΔH) and (-TΔS). The magnitude of the latter term is dependent on the temperature. At high temperature, the latter term dominates over the former, and the reaction is thermodynamically favorable. However, at low temperature, the first term (enthalpy) dominates, and the reaction is no longer thermodynamically favored.

11.22.

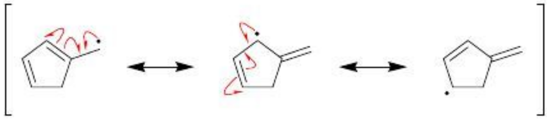
a)



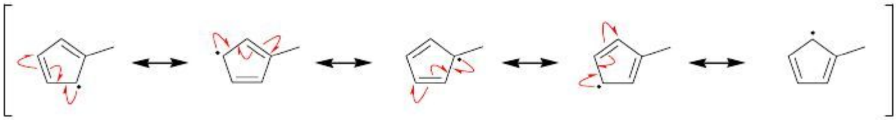
b)



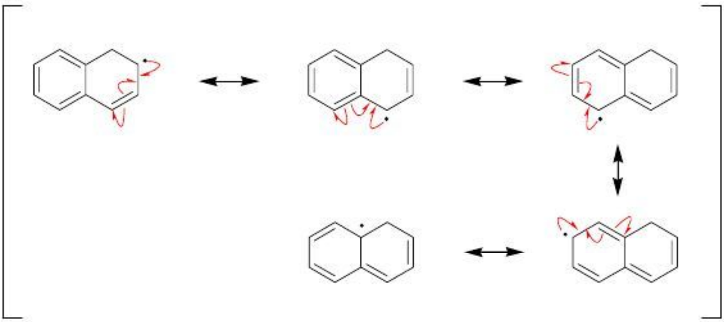
c)



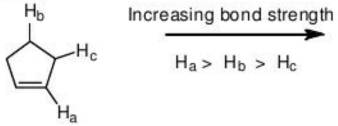
d)



e)



11.23.

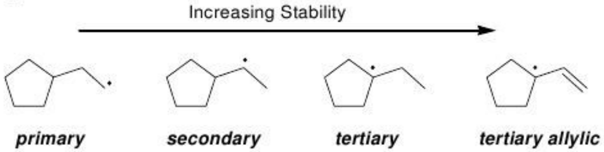


abstraction of H_a generates an unstable vinyl radical

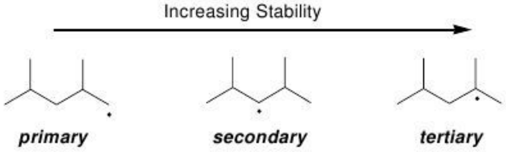
abstraction of H_c generates a resonance-stabilized radical

11.24.

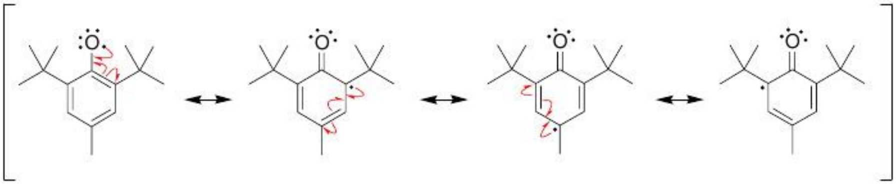
a)



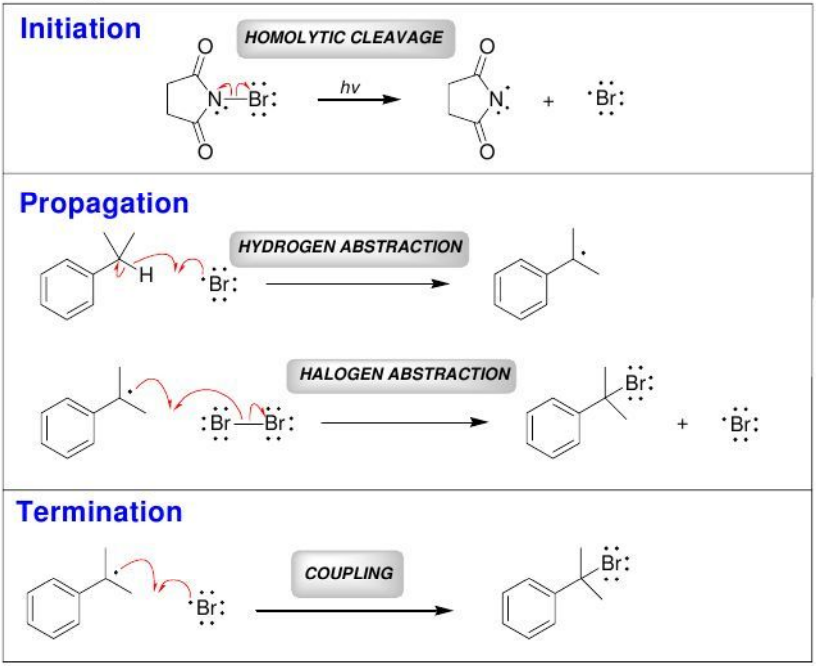
b)



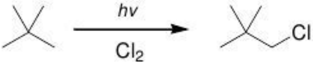
11.25.



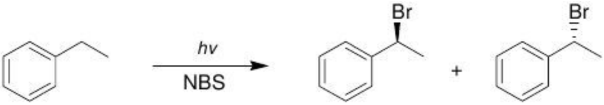
11.26. The benzylic position is selectively brominated because the benzylic C-H bond is the weakest bond. The benzylic hydrogen atom is the only hydrogen atom that can be abstracted to generate a resonance-stabilized radical.



11.27.



11.28. Selective bromination at the benzylic position generates a new chirality center. The intermediate benzylic radical is expected to be attacked from either face of the planar radical with equal likehood, giving rise to a racemic mixture of enantiomers:



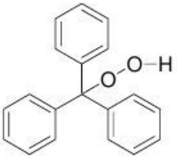
11.29.

a) These radicals are tertiary, and they are stabilized by resonance.

b) Loss of nitrogen gas would result in the formation of vinyl radicals, which are too unstable to form under normal conditions:

11.30.

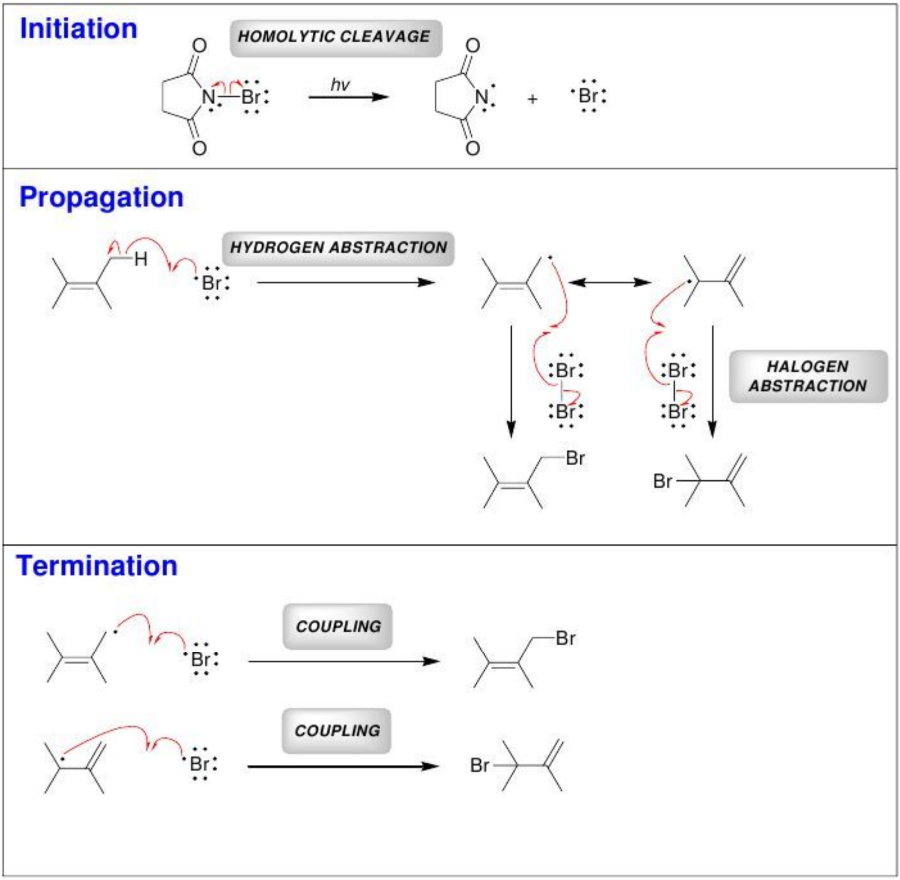
a)



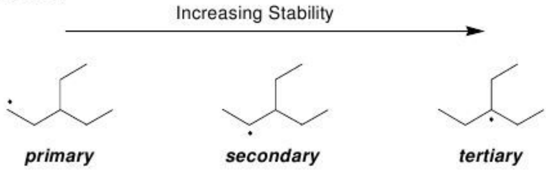
b) Hydrogen abstraction leads to an exceptionally stable radical, with many, many resonance structures (see problem 11.3).

c) Phenol acts as a radical scavenger, thereby preventing the chain process from taking off.

11.31.

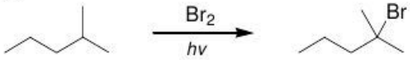


11.32.

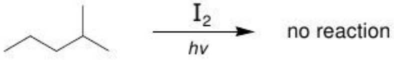


11.33.

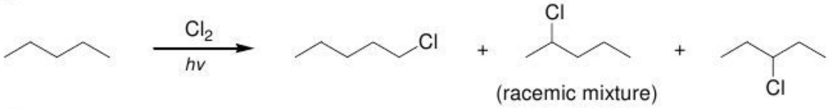
a)



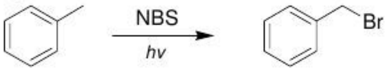
b)



c)

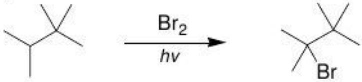


d)

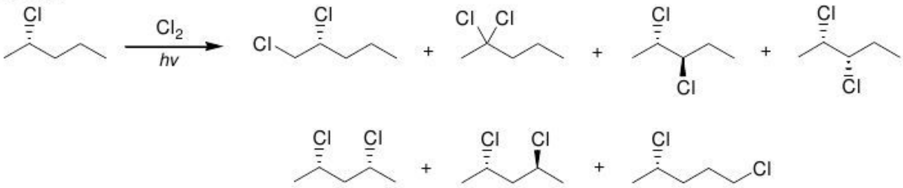


e)

f)



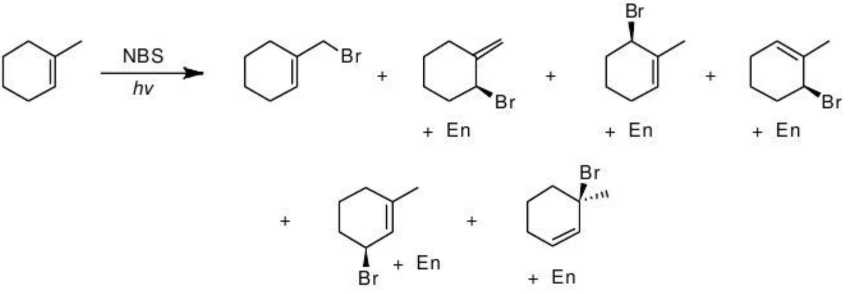
11.34.



11.35.

11.36.

a)



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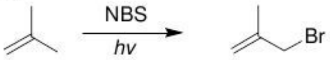

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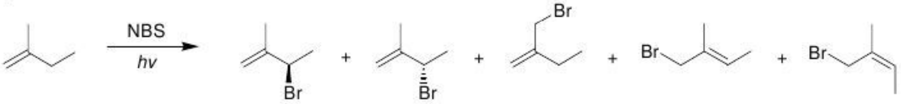

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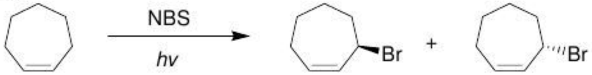
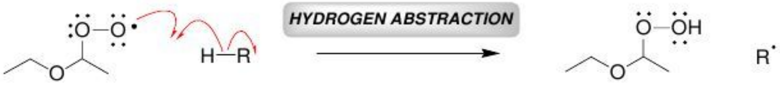
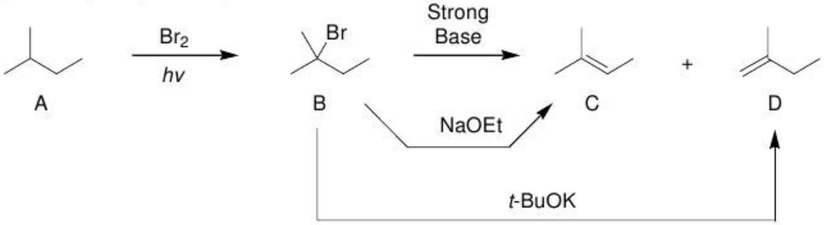


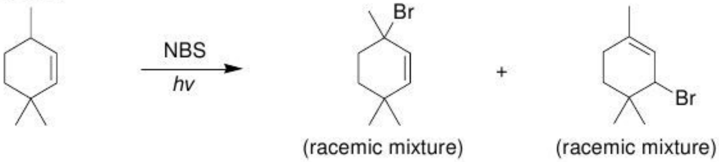
11.37.



11.38. When Compound B is treated with a sterically hindered base, the Hofmann product (Compound D) is favored. When treated with sodium ethoxide, the Zaitsev product (Compound B) is favored:

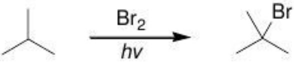


11.39.

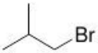


11.40.

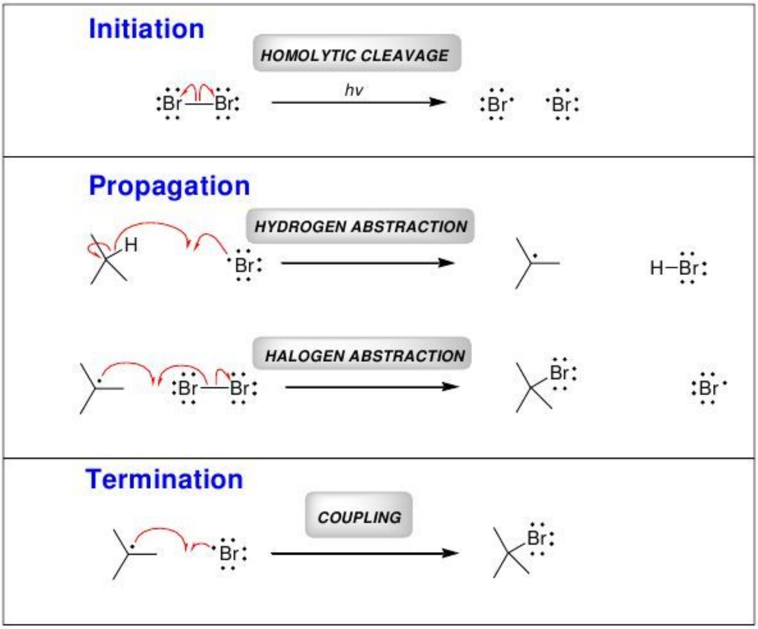
a)



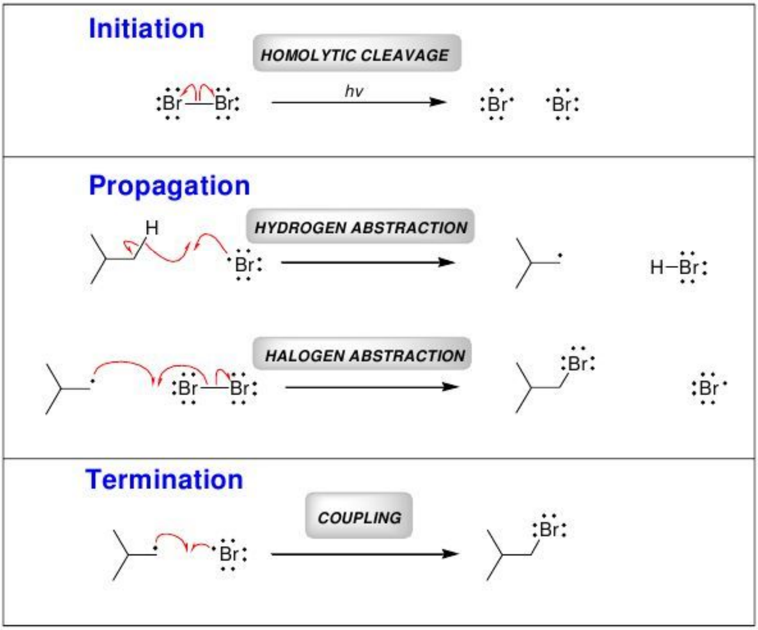
b)



c)



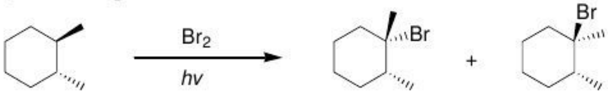
d)



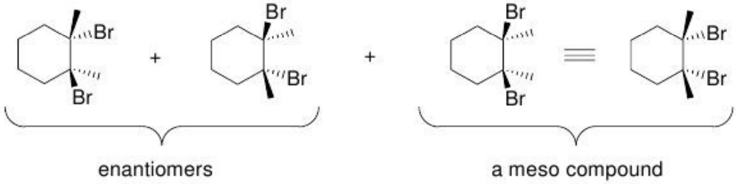
e) The minor product is only formed via a primary radical, which does not readily form under bromination conditions. The tertiary radical is selectively formed, which leads to the tertiary alkyl bromide as the major product.

11.41.

a) The two products are diastereomers



b)

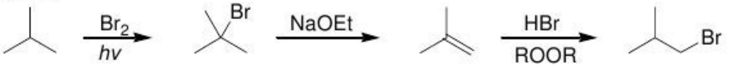


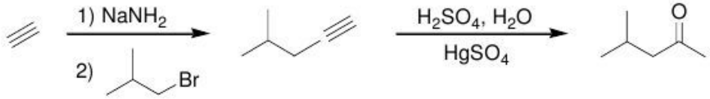
There are two chirality centers, so we might expect four products. However, one product is a meso compound, so there are only three products, rather than four. For a review of meso compounds, see Section 5.6.

11.42. Methyl radicals are less stable and less hindered than *tert*-butyl radicals.

11.43.
a) 1 **b)** 4 **c)** 3 **d)** 4 **e)** 2 **f)** 1 **g)** 5 **h)** 1 **i)** 3 **j)** 3

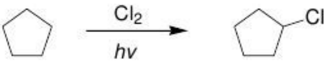
11.44.



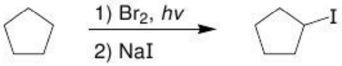


11.45.

a)



b)



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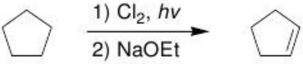

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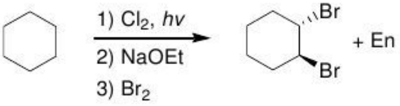
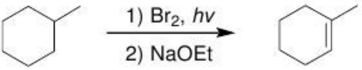
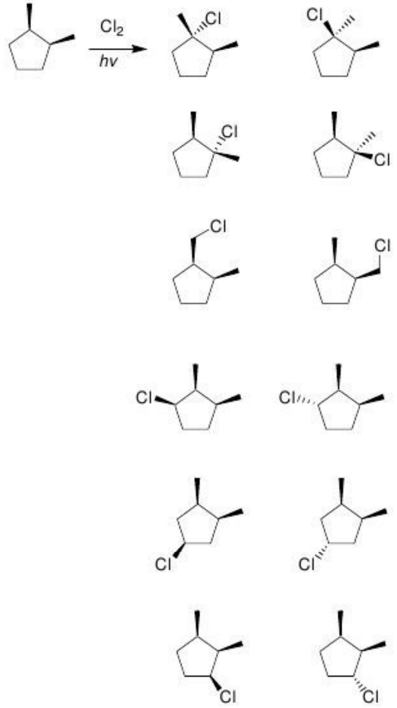
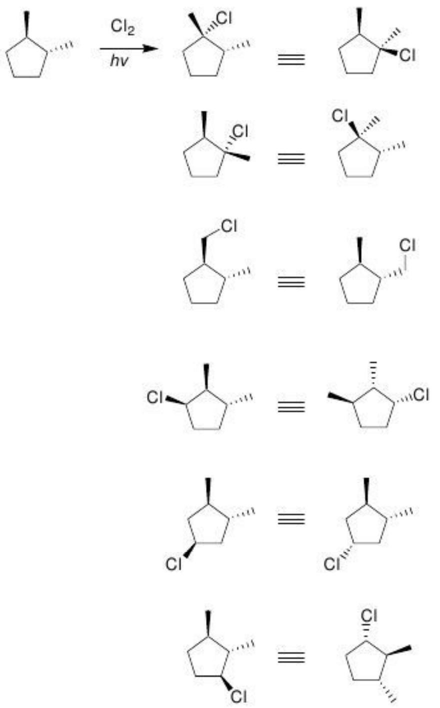


e)



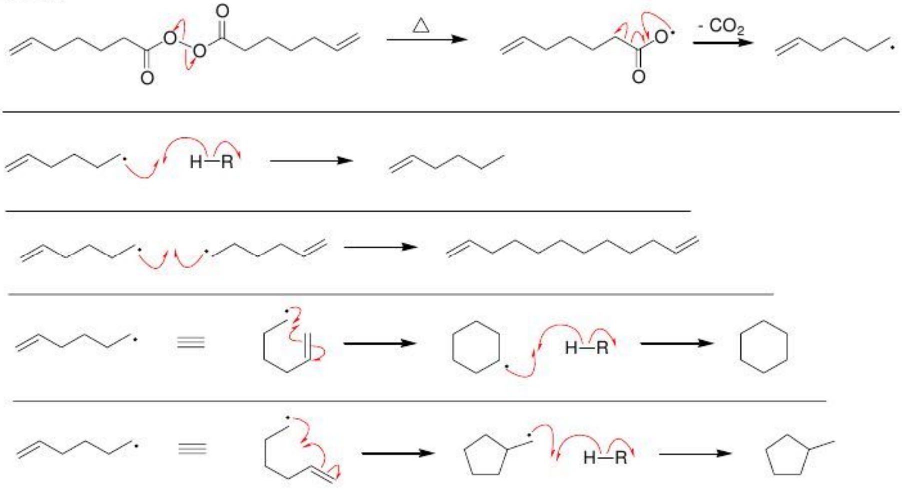
11.46. *cis*-1,2-Dimethylcyclopentane produces six pairs of compounds, where each pair have a diastereomeric relationship. In contrast, *trans*-dimethylcyclopentane produces only six different compounds, as shown below:





11.47. The first propagation step in a bromination process is generally slow and selective. In fact, this is the source of the regioselectivity for this reaction. A pathway via a tertiary radical will be significantly lower in energy than a pathway via a secondary or primary radical. As a result, bromination occurs predominantly at the more substituted position. However, when chlorine is present, chlorine radicals can perform the first propagation step (hydrogen abstraction) very rapidly, and with little selectivity. Under these conditions, secondary and primary radicals are formed almost as easily as tertiary radicals. The resulting radicals then react with bromine in the second propagation step to yield monobrominated products. Therefore, in the presence of chlorine, the selectivity normally observed for bromination is lost.

11.48.



Chapter 12
Synthesis

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 12. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

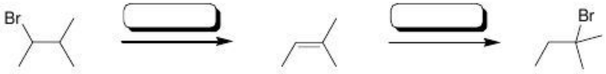
- The position of a halogen can be moved by performing __________ followed by ______________.
- The position of a π bond can be moved by performing ___________ followed by ______________.
- An alkane can be functionalized via radical _________________.
- Every synthesis problem should be approached by asking the following two questions:
    1. Is there any change in the ____________________?
    2. Is there any change in the identity or location of the _________________?
- In a _________________ **analysis**, the last step of the synthetic route is first established, and the remaining steps are determined, working backwards from the product.

Review of Skills

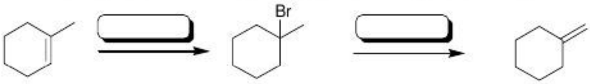
Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 12. The answers appear in the section entitled *SkillBuilder Review*.

12.1 Changing the Identity or Position of a Functional Group

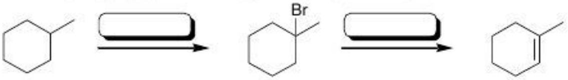
IDENTIFY THE TWO PROCESSES THAT ARE REQUIRED TO CHANGE THE POSITION OF A HALOGEN:



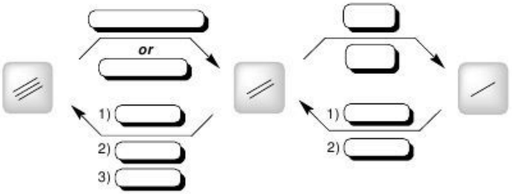
IDENTIFY THE TWO PROCESSES THAT ARE REQUIRED TO CHANGE THE POSITION OF A PI BOND:



IDENTIFY THE TWO PROCESSES THAT ARE REQUIRED TO INSTALL A PI BOND:

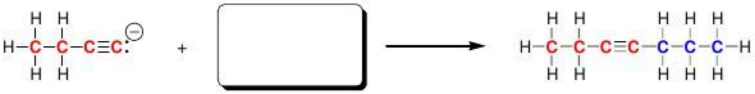


IDENTIFY THE REAGENTS NECESSARY TO ACHIEVE EACH OF THE FOLLOWING TRANSFORMATIONS



12.2 Changing the Carbon Skeleton

IDENTIFY THE REAGENT NECESSARY TO ACHIEVE THE FOLLOWING C-C BOND FORMING REACTION:



IDENTIFY THE REAGENTS NECESSARY TO ACHIEVE THE FOLLOWING C-C BOND BREAKING REACTION:

12.3 Approaching a Synthesis Problem by Asking Two Questions

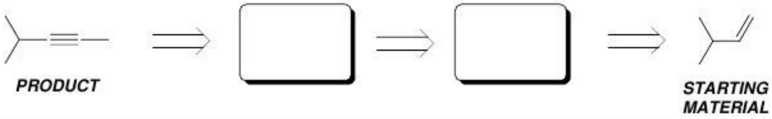
IDENTIFY THE TWO QUESTIONS TO ASK WHEN APPROACHING A SYNTHESIS PROBLEM:

1) ____?

2) ____?

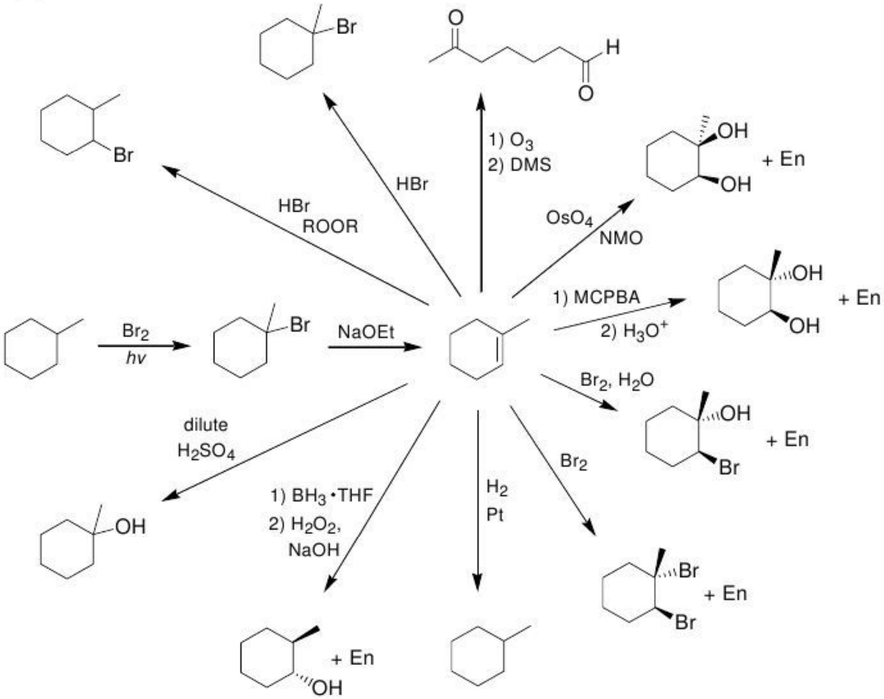
12.4 Retrosynthetic Analysis

COMPLETE THE FOLLOWING RETROSYNTHETIC ANALYSIS BY DRAWING THE APPROPRIATE STRUCTURES IN THE BOXES PROVIDED:

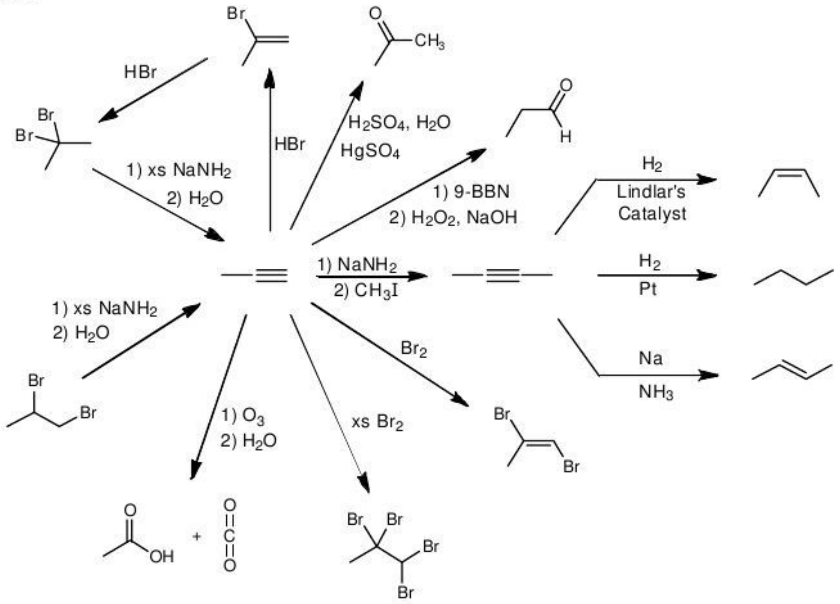


Solutions

12.1.

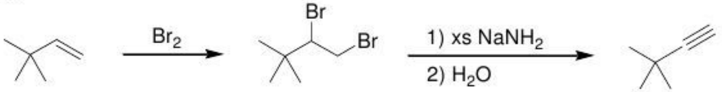


12.2.

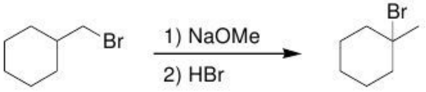

HBr
Br
Br
1) xs NaNH$_2$
2) H$_2$O
HBr
H$_2$SO$_4$, H$_2$O
HgSO$_4$
CH$_3$
O
1) 9-BBN
2) H$_2$O$_2$, NaOH
H
H$_2$
Lindlar's Catalyst
1) NaNH$_2$
2) CH$_3$I
H$_2$
Pt
1) xs NaNH$_2$
2) H$_2$O
Br$_2$
Na
NH$_3$
1) O$_3$
2) H$_2$O
xs Br$_2$
OH
+
O=C=O
Br

12.3.

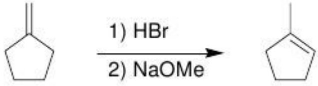
a)


Br$_2$
Br
Br
1) xs NaNH$_2$
2) H$_2$O

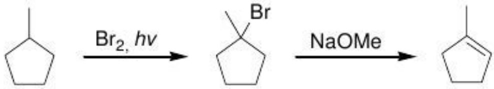
b)


Br
1) NaOMe
2) HBr
Br

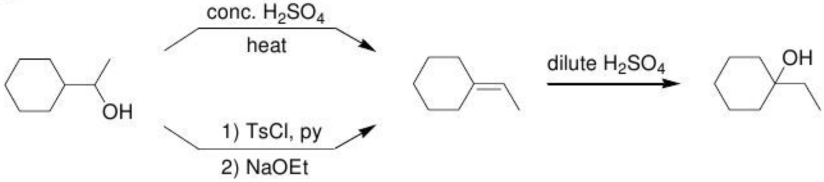
c)


1) HBr
2) NaOMe

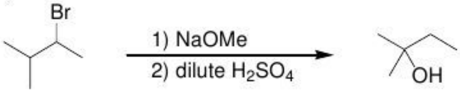
d)


Br$_2$, *hv*
Br
NaOMe

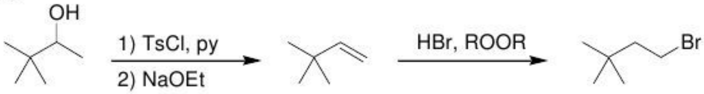
e)


conc. H_2SO_4
heat
1) TsCl, py
2) NaOEt
OH
dilute H_2SO_4
OH

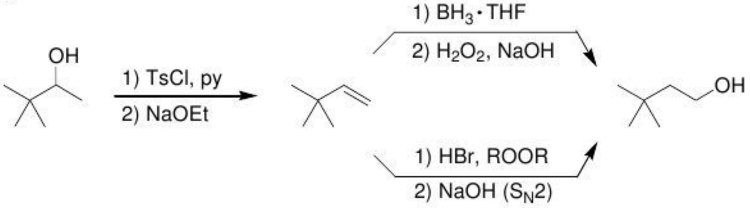
f)


Br
1) NaOMe
2) dilute H_2SO_4
OH

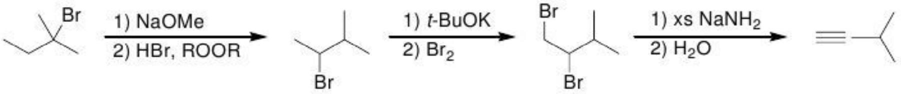
g)


OH
1) TsCl, py
2) NaOEt
HBr, ROOR
Br

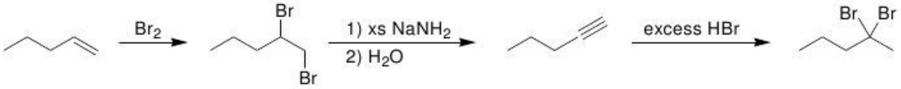
h)


OH
1) TsCl, py
2) NaOEt
1) $BH_3 \cdot THF$
2) H_2O_2, NaOH
1) HBr, ROOR
2) NaOH (S_N2)
OH

12.4.

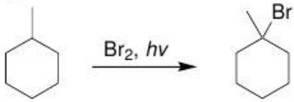

Br
1) NaOMe
2) HBr, ROOR
Br
1) *t*-BuOK
2) Br_2
Br
Br
1) xs $NaNH_2$
2) H_2O

12.5.

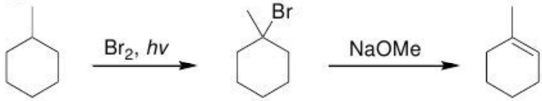

Br_2
Br
Br
1) xs $NaNH_2$
2) H_2O
excess HBr
Br
Br

12.6.

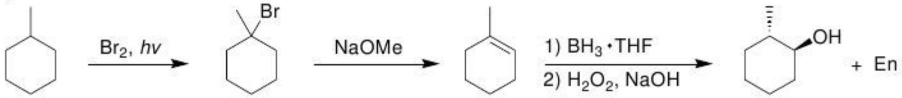
a)



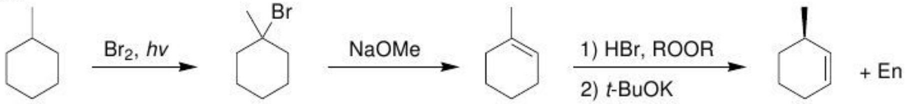
b)



c)

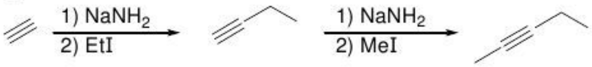


d)

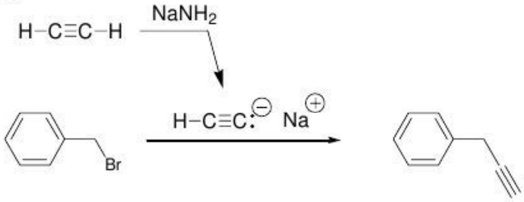


12.7.

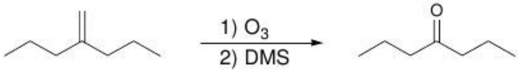
a)



b)

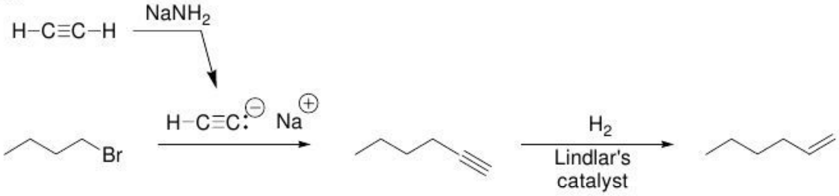


c)

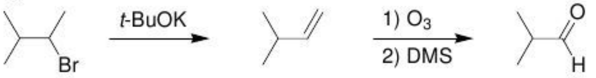


12.8.

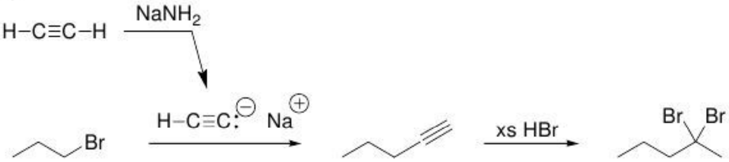
a)



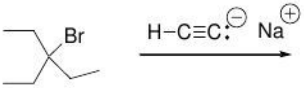
b)



c)

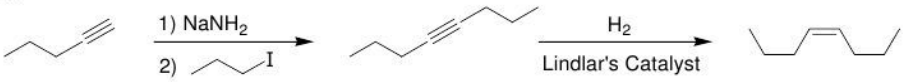


12.9. The alkyl halide is a tertiary substrate and does not readily undergo S_N2. Under these conditions, the acetylide ion functions as a base, rather than a nucleophile, giving an E2 reaction, instead of S_N2:

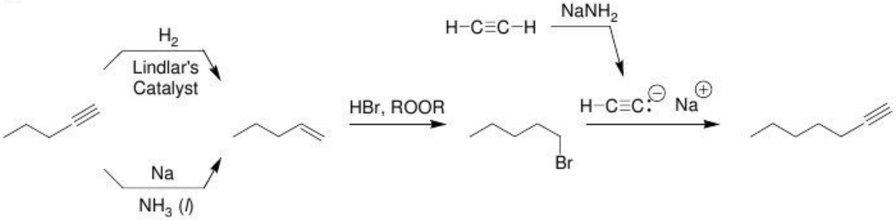


12.10.

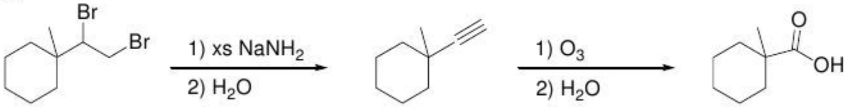
a)



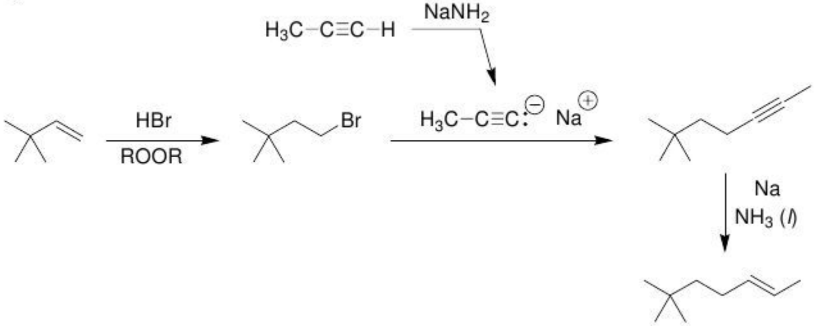
b)


H₂
Lindlar's Catalyst
Na
NH₃ (l)
HBr, ROOR
H−C≡C−H
NaNH₂
H−C≡C:⁻ Na⁺
Br

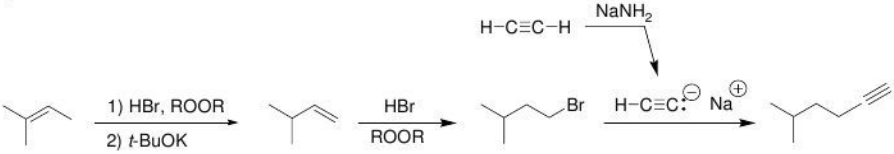
c)


Br
Br
1) xs NaNH₂
2) H₂O
1) O₃
2) H₂O
O
OH

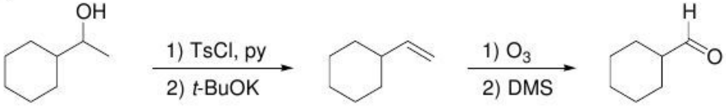
d)


HBr
ROOR
Br
H₃C−C≡C−H
NaNH₂
H₃C−C≡C:⁻ Na⁺
Na
NH₃ (l)

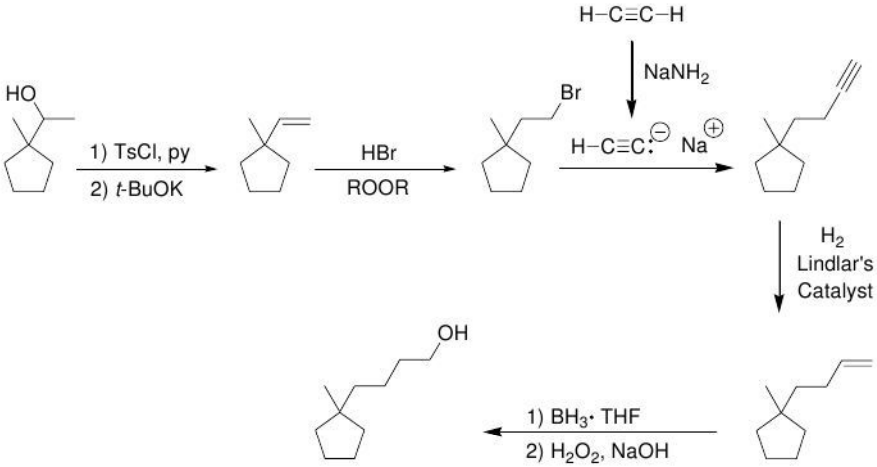
e)


1) HBr, ROOR
2) t-BuOK
HBr
ROOR
Br
H−C≡C−H
NaNH₂
H−C≡C:⁻ Na⁺

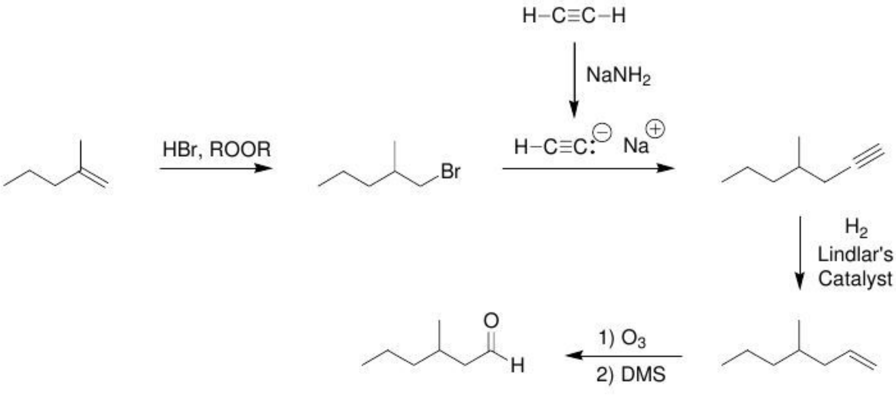
f)


OH
1) TsCl, py
2) t-BuOK
1) O3
2) DMS
H
O

12.11.

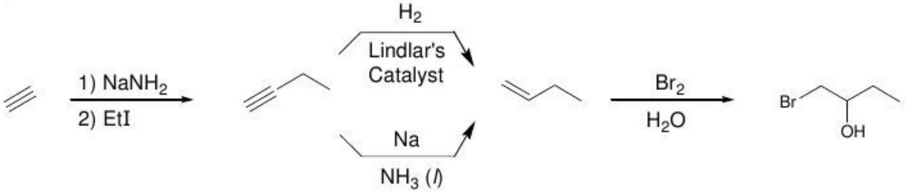

HO
1) TsCl, py
2) t-BuOK
HBr
ROOR
Br
H−C≡C−H
NaNH2
H−C≡C: Na
H2
Lindlar's
Catalyst
1) BH3· THF
2) H2O2, NaOH
OH

12.12.

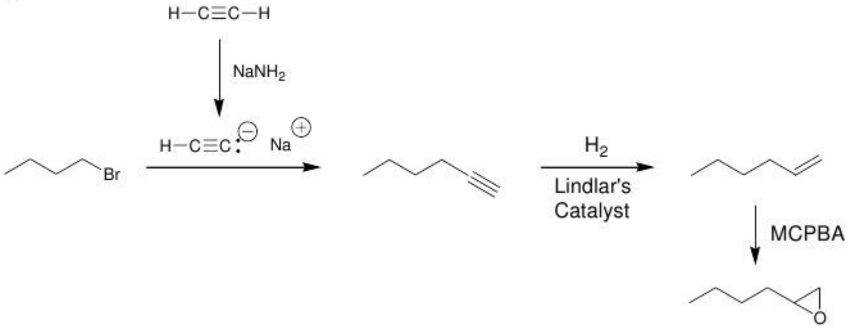

HBr, ROOR
Br
H−C≡C−H
NaNH2
H−C≡C: Na
H2
Lindlar's
Catalyst
1) O3
2) DMS
O
H

12.13.

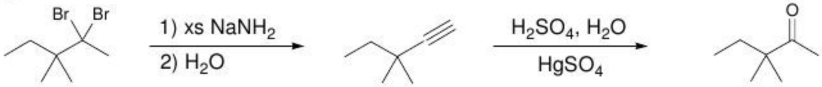
a)


1) NaNH$_2$
2) EtI
H$_2$
Lindlar's Catalyst
Na
NH$_3$ (*l*)
Br$_2$
H$_2$O
Br
OH

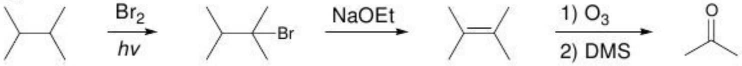
b)


H—C≡C—H
NaNH$_2$
H—C≡C:$^{\ominus}$ Na$^{\oplus}$
Br
H$_2$
Lindlar's Catalyst
MCPBA
O

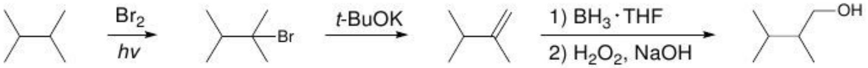
c)


Br Br
1) xs NaNH$_2$
2) H$_2$O
H$_2$SO$_4$, H$_2$O
HgSO$_4$
O

d)


Br$_2$
hv
Br
NaOEt
1) O$_3$
2) DMS
O

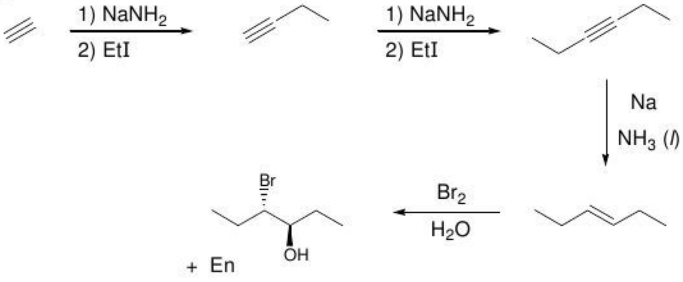
e)


Br$_2$
hv
Br
t-BuOK
1) BH$_3$·THF
2) H$_2$O$_2$, NaOH
OH

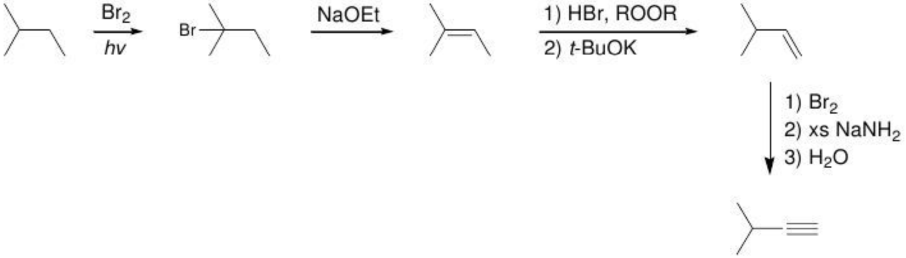
f)


Br
Br
1) xs NaNH$_2$
2) H$_2$O
1) O$_3$
2) H$_2$O
O
OH

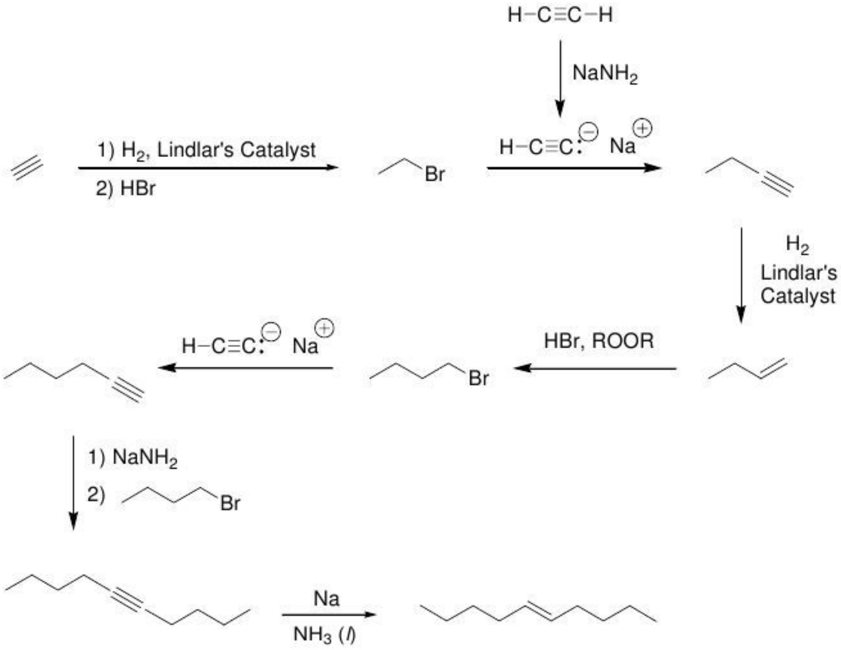
g)


1) NaNH$_2$
2) EtI
1) NaNH$_2$
2) EtI
Na
NH$_3$ (*l*)
Br$_2$
H$_2$O
Br
OH
+ En

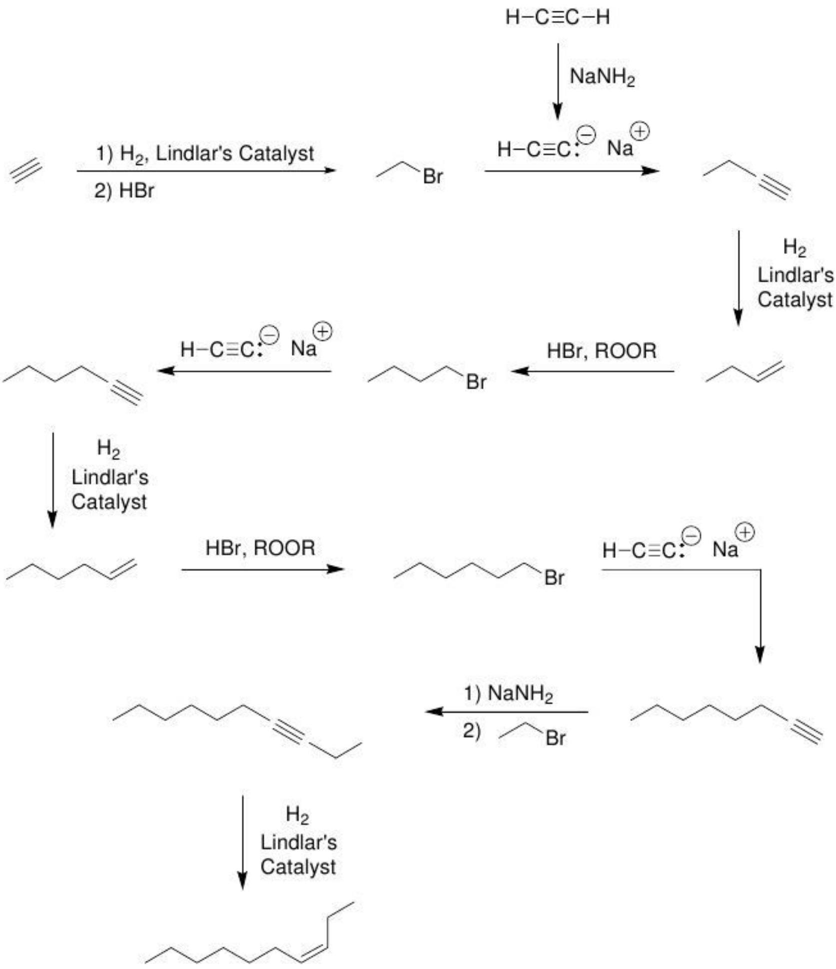
h)


Br$_2$
hv
Br
NaOEt
1) HBr, ROOR
2) *t*-BuOK
1) Br$_2$
2) xs NaNH$_2$
3) H$_2$O

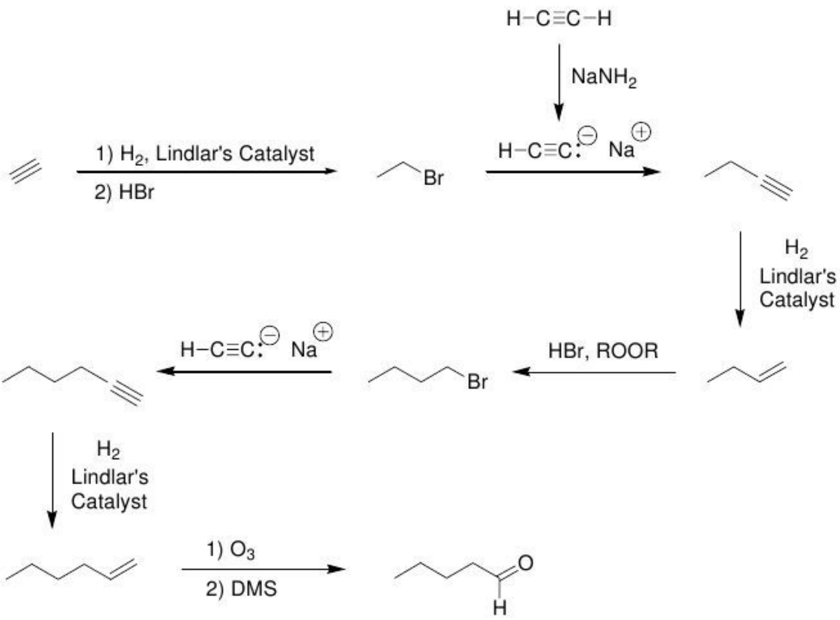
12.14.


H−C≡C−H
NaNH2
1) H2, Lindlar's Catalyst
2) HBr
Br
H−C≡C: Na
H2
Lindlar's
Catalyst
HBr, ROOR
Br
H−C≡C: Na
1) NaNH2
2)
Br
Na
NH3 (l)

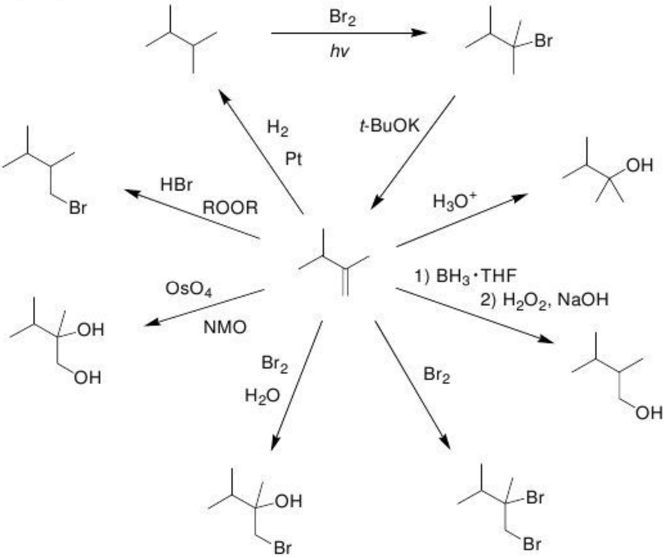
12.15.


H−C≡C−H
NaNH₂
1) H₂, Lindlar's Catalyst
2) HBr
Br
H−C≡C:⁻ Na⁺
H₂
Lindlar's
Catalyst
HBr, ROOR
Br
H−C≡C:⁻ Na⁺
H₂
Lindlar's
Catalyst
HBr, ROOR
Br
H−C≡C:⁻ Na⁺
1) NaNH₂
2) Br
H₂
Lindlar's
Catalyst

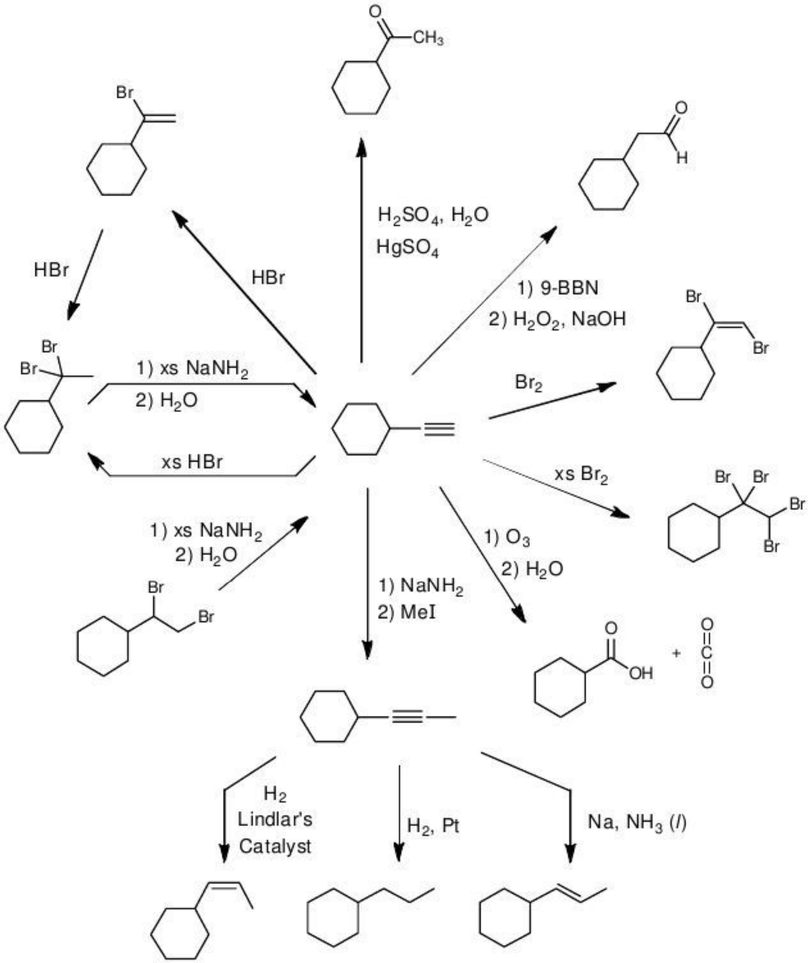
12.16.


H−C≡C−H
NaNH2
1) H2, Lindlar's Catalyst
2) HBr
Br
H−C≡C:⊖ Na⊕
H2
Lindlar's
Catalyst
HBr, ROOR
Br
H−C≡C:⊖ Na⊕
H2
Lindlar's
Catalyst
1) O3
2) DMS
O
H

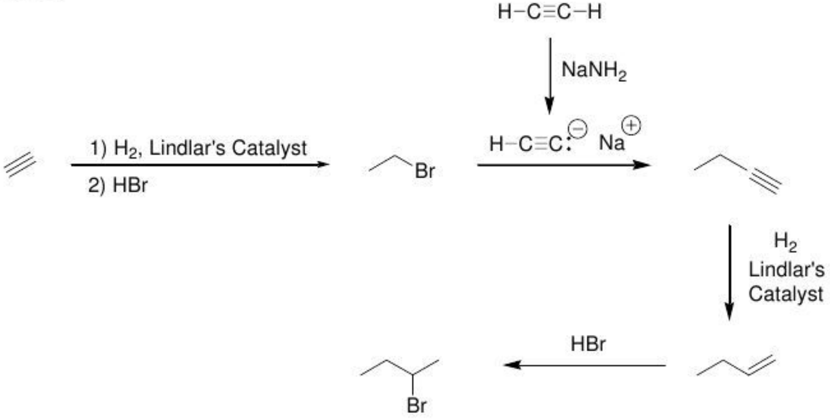
12.17.


Br2
hv
Br
t-BuOK
H2
Pt
HBr
ROOR
Br
H3O+
OH
OsO4
NMO
OH
OH
1) BH3·THF
2) H2O2, NaOH
OH
Br2
H2O
OH
Br
Br2
Br
Br

12.18.


HBr
HBr
H2SO4, H2O
HgSO4
1) 9-BBN
2) H2O2, NaOH
1) xs NaNH2
2) H2O
Br2
xs HBr
xs Br2
1) xs NaNH2
2) H2O
1) O3
2) H2O
1) NaNH2
2) MeI
+
H2
Lindlar's
Catalyst
H2, Pt
Na, NH3 (l)
Br
O
CH3
H
OH

12.19.



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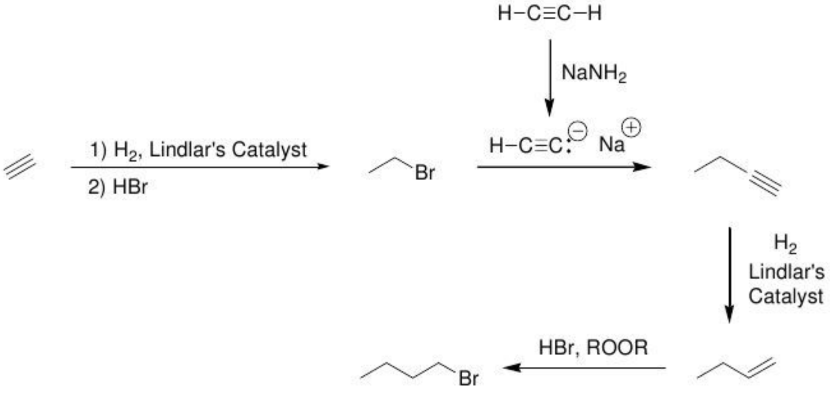

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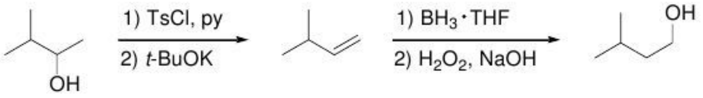
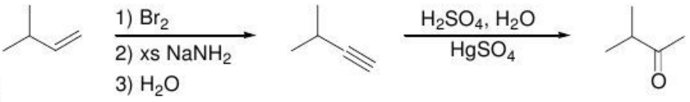
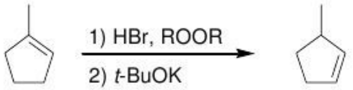


a)



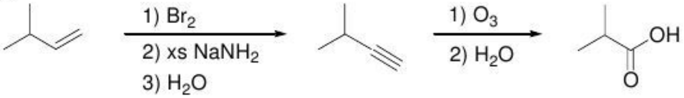
b)

12.22.

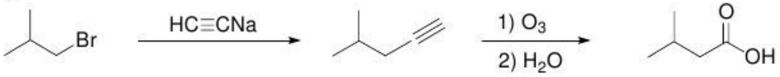


12.23.

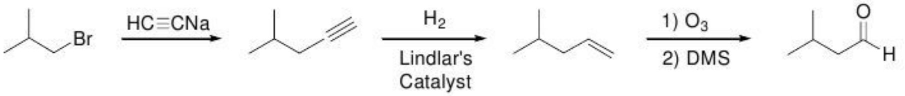
a)



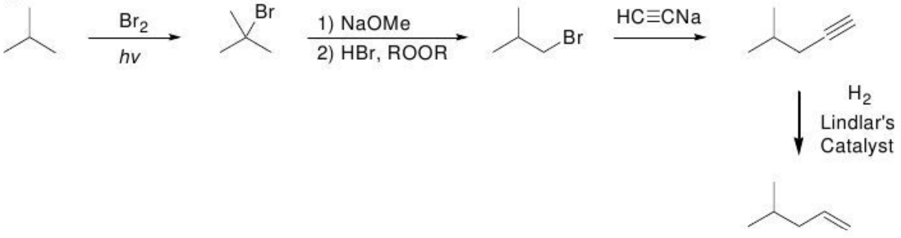
b)



c)



d)



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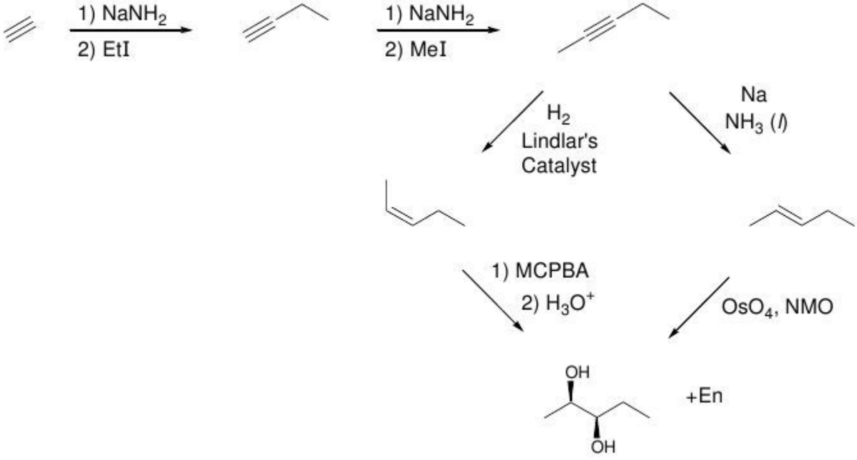

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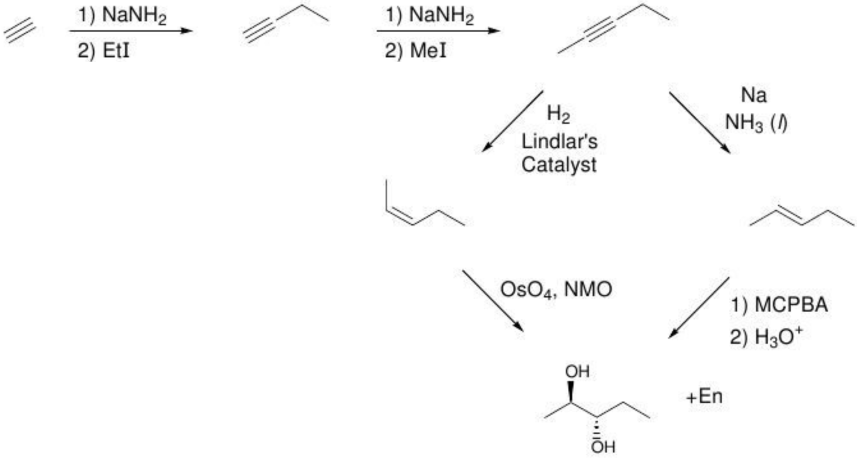
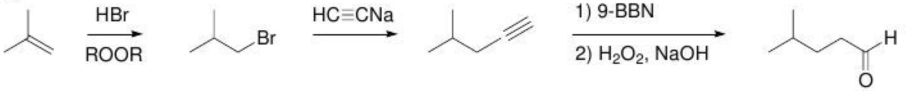


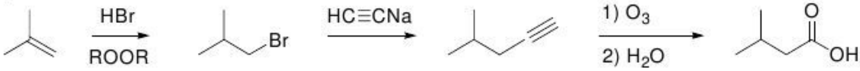
12.26.

a)

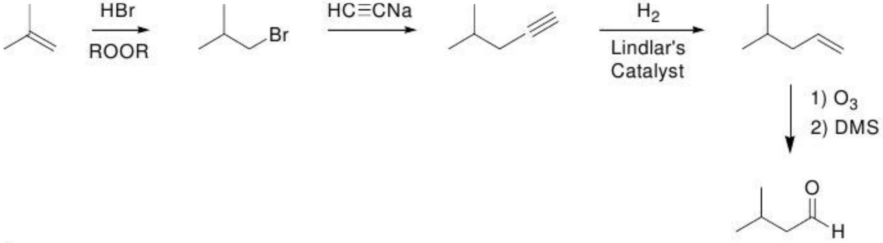
b)


HBr
ROOR
Br
HC≡CNa
1) 9-BBN
2) H₂O₂, NaOH
H
O

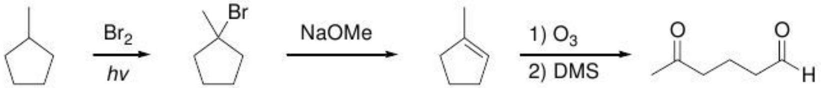
c)


HBr
ROOR
Br
HC≡CNa
1) O₃
2) H₂O
O
OH

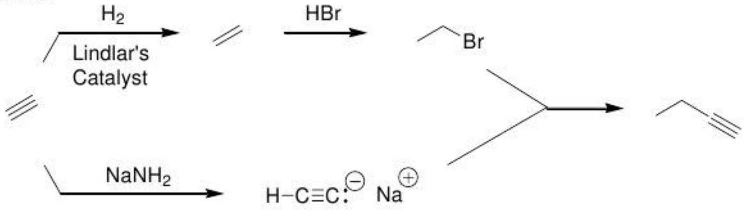
d)


HBr
ROOR
Br
HC≡CNa
H₂
Lindlar's
Catalyst
1) O₃
2) DMS
O
H

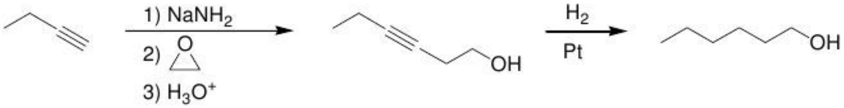
e)


Br₂
hv
Br
NaOMe
1) O₃
2) DMS
O
O
H

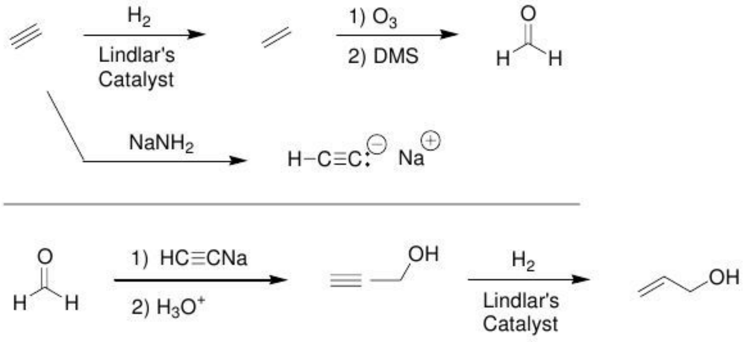
12.27.


H₂
Lindlar's
Catalyst
HBr
Br
NaNH₂
H−C≡C:⊖ Na⊕

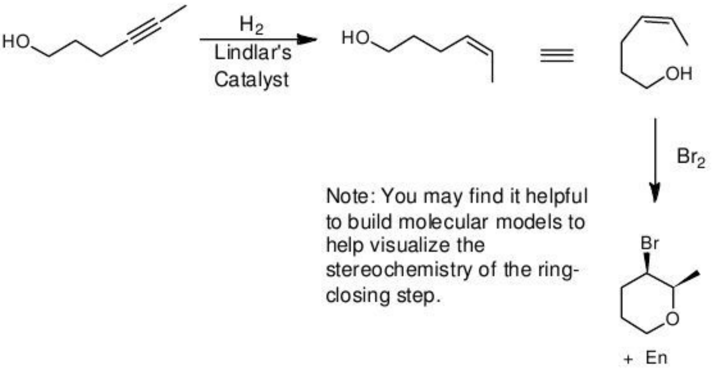

H₂
Lindlar's
Catalyst
MCPBA
O


1) NaNH₂
2) O
3) H₃O⁺
OH
H₂
Pt
OH

12.28.



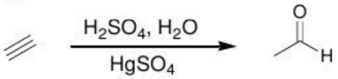
12.29.



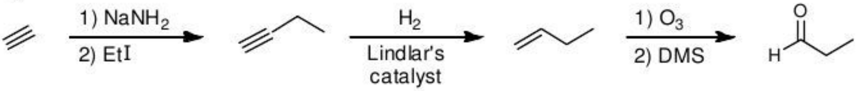
Note: You may find it helpful to build molecular models to help visualize the stereochemistry of the ring-closing step.

12.30.

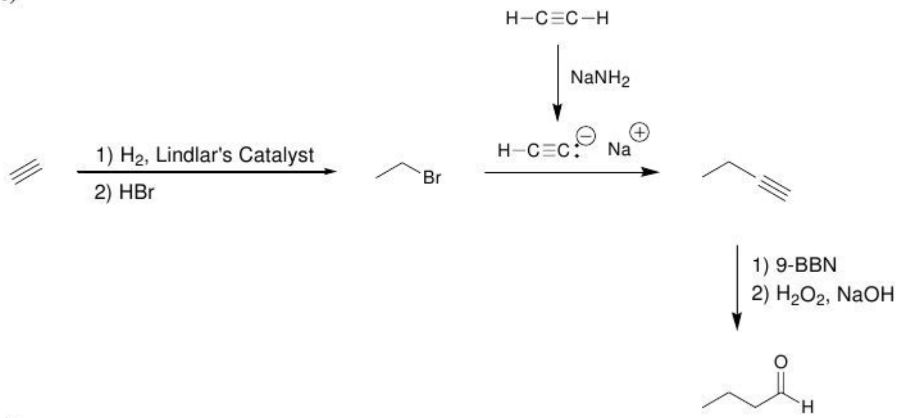
a)



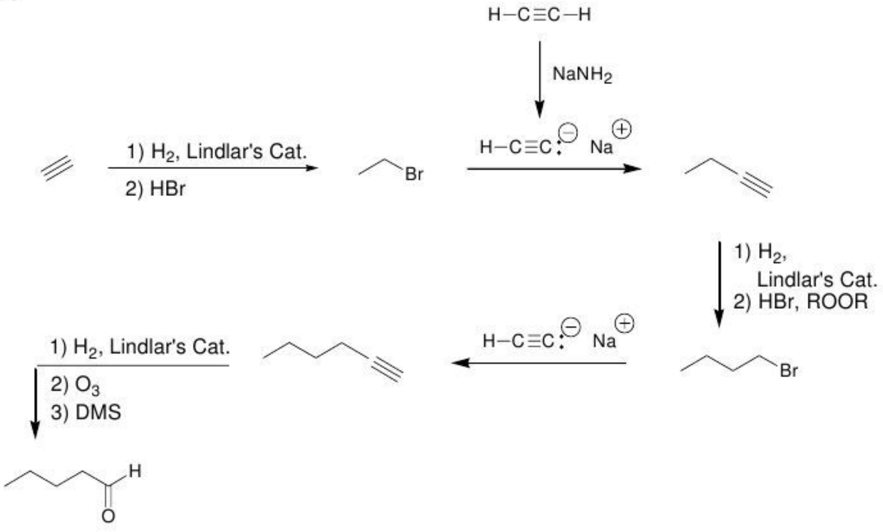
b)



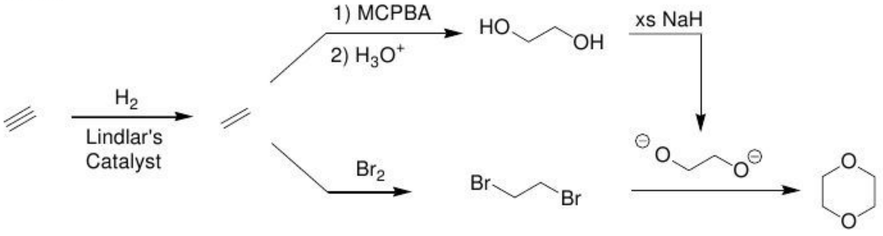
c)


H−C≡C−H
NaNH2
1) H2, Lindlar's Catalyst
2) HBr
Br
H−C≡C: Na
1) 9-BBN
2) H2O2, NaOH
O
H

d)


H−C≡C−H
NaNH2
1) H2, Lindlar's Cat.
2) HBr
Br
H−C≡C: Na
1) H2,
Lindlar's Cat.
2) HBr, ROOR
H−C≡C: Na
Br
1) H2, Lindlar's Cat.
2) O3
3) DMS
H
O

12.31.


1) MCPBA
2) H3O+
HO
OH
xs NaH
H2
Lindlar's
Catalyst
O
O
Br2
Br
Br
O
O

Chapter 13
Alcohols

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 13. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

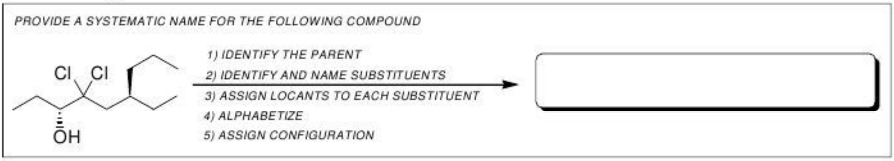
- When naming an alcohol, the parent is the longest chain containing the __________ group.
- The conjugate base of an alcohol is called an ___________ ion.
- Several factors determine the relative acidity of alcohols, including ___________, ____________, and _______________________.
- The conjugate base of phenol is called a ____________, or _____________ ion.

- When preparing an alcohol via a substitution reaction, primary substrates will require S_N___ conditions, while tertiary substrates will require S_N___ conditions.
- Alcohols can be formed by treating a **carbonyl group** (C=O bond) with a ______________ **agent**.
- **Grignard reagents** are carbon nucleophiles that are capable of attacking a wide range of _________________, including the carbonyl group of ketones or aldehydes, to produce an alcohol.
- _______________ **groups**, such as the trimethylsilyl group, can be used to circumvent the problem of Grignard incompatibility and can be easily removed after the desired Grignard reaction has been performed.
- Tertiary alcohols will undergo an S_N___ reaction when treated with a hydrogen halide.
- Primary and secondary alcohols will undergo an S_N___ process when treated with either HX, $SOCl_2$, PBr_3, or when the hydroxyl group is converted into a tosylate group followed by nucleophilic attack.
- Tertiary alcohols undergo E1 elimination when treated with __________.
- Primary alcohols undergo **oxidation** twice to give a ______________________.
- Secondary alcohols are oxidized only once to give a ___________
- PCC is used to convert a primary alcohol into an _____________.
- NADH is a biological reducing agent that functions as a ____________ delivery agent (very much like $NaBH_4$ or LAH), while NAD^+ is an _____________ agent.
- The are two key issues to consider when proposing a synthesis is whether there is:
  1. a change in the ___________________.
  2. a change in the ___________________.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 13. The answers appear in the section entitled *SkillBuilder Review*.

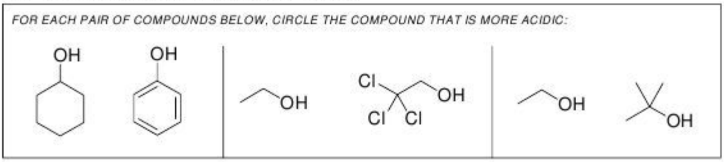
13.1 Naming an Alcohol



PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND

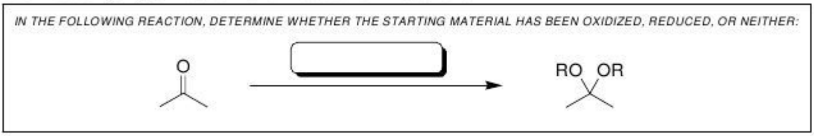
1) IDENTIFY THE PARENT
2) IDENTIFY AND NAME SUBSTITUENTS
3) ASSIGN LOCANTS TO EACH SUBSTITUENT
4) ALPHABETIZE
5) ASSIGN CONFIGURATION

13.2 Comparing the Acidity of Alcohols



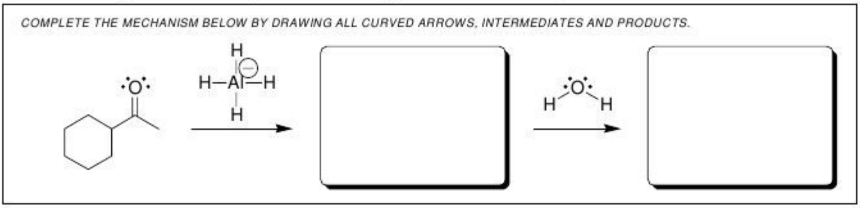
FOR EACH PAIR OF COMPOUNDS BELOW, CIRCLE THE COMPOUND THAT IS MORE ACIDIC:

13.3 Identifying Oxidation and Reduction Reactions



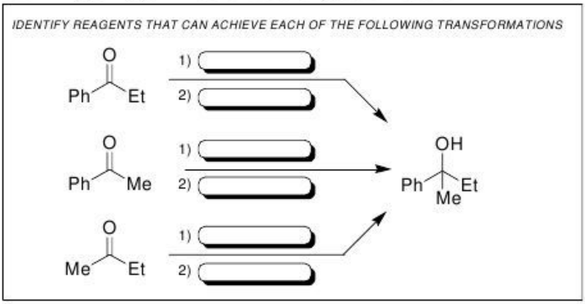
IN THE FOLLOWING REACTION, DETERMINE WHETHER THE STARTING MATERIAL HAS BEEN OXIDIZED, REDUCED, OR NEITHER:

13.4 Drawing a Mechanism, and Predicting the Products of Hydride Reductions



COMPLETE THE MECHANISM BELOW BY DRAWING ALL CURVED ARROWS, INTERMEDIATES AND PRODUCTS.

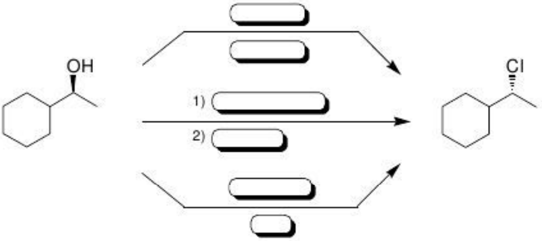
13.5 Preparing an Alcohol via a Grignard Reaction



IDENTIFY REAGENTS THAT CAN ACHIEVE EACH OF THE FOLLOWING TRANSFORMATIONS

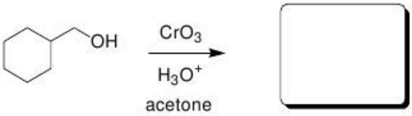
13.6 Proposing Reagents for the Conversion of an Alcohol into an Alkyl Halide

IDENTIFY REAGENTS THAT CAN ACHIEVE EACH OF THE FOLLOWING TRANSFORMATIONS



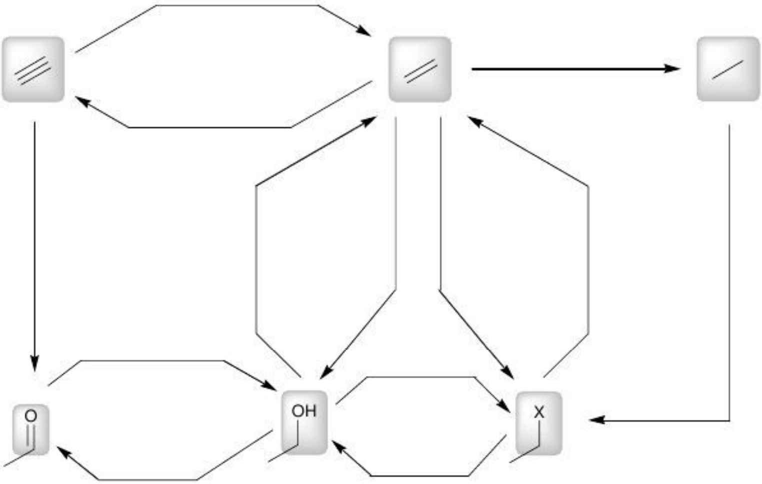
13.7 Predicting the Products of an Oxidation Reaction

DRAW THE EXPECTED PRODUCT OF THE FOLLOWING REACTION



13.8 Converting Functional Groups

IDENTIFY REAGENTS THAT CAN ACHIEVE EACH OF THE FOLLOWING FUNCTIONAL GROUP TRANSFORMATIONS



13.9 Proposing a Synthesis

AS A GUIDE FOR PROPOSING A SYNTHESIS, ASK THE FOLLOWING TWO QUESTIONS:

1) IS THERE A CHANGE IN THE ____________ SKELETON?

2) IS THERE A CHANGE IN THE LOCATION OR IDENTITY OF THE ______________________?

AFTER PROPOSING A SYNTHESIS, USE THE FOLLOWING TWO QUESTIONS TO ANALYZE YOUR ANSWER:

1) IS THE ______________________ OUTCOME OF EACH STEP CORRECT?

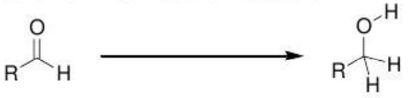
2) IS THE ______________________ OUTCOME OF EACH STEP CORRECT?

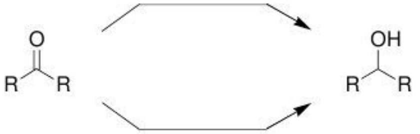
Review of Reactions

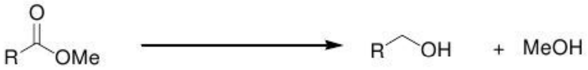
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 13. The answers appear in the section entitled *Review of Reactions*.

Preparation of Alkoxides

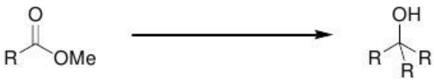
Preparation of Alcohols via Reduction



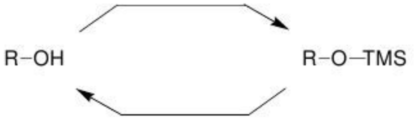




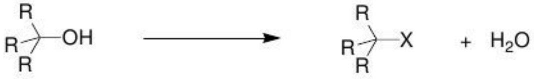
Preparation of Alcohols via Grignard Reagents



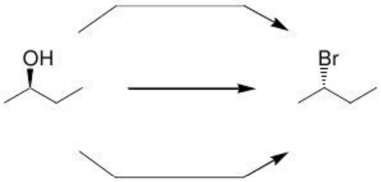
Protection and Deprotection of Alcohols

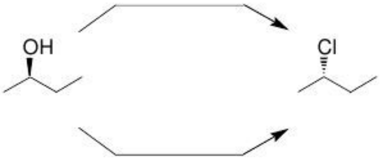


S_N1 Reactions with Alcohols

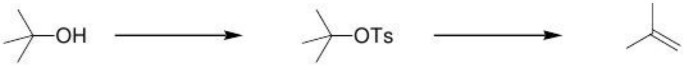


S_N2 Reactions with Alcohols

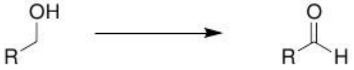




E1 and E2 Reactions with Alcohols



Oxidation of Alcohols and Phenols



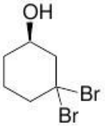
Solutions

13.1.

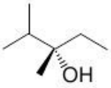
a) 5,5-dibromo-2-methylhexan-2-ol
b) (*2S,3R*)-2,3,4-trimethylpentan-1-ol
c) 2,2,5,5-tetramethylcyclopentanol
d) 2,6-diethylphenol
e) (*S*)-2,2,4,4-tetramethylcyclohexanol

13.2.

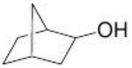
a)



b)



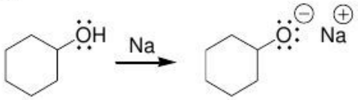
c)



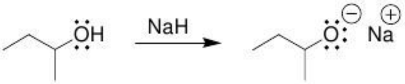
13.3. Nonyl mandelate has a longer alkyl chain than octyl mandelate and is therefore more effective at penetrating cell membranes, rendering it a more potent agent. Nonyl mandelate has a shorter alkyl chain than decyl mandelate and is therefore more water-soluble, enabling it to be transported through aqueous media and to reach its target destination more effectively.

13.4.

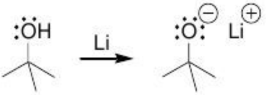
a)



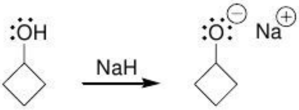
b)



c)

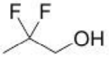


d)



13.5.

a)

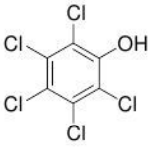


The electron-withdrawing effects of the fluorine atoms stabilize the conjugate base.

b)

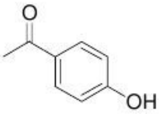
The conjugate base of a primary alcohol will be more easily solvated than the conjugate base of a tertiary alcohol.

c)



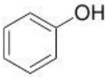
The electron-withdrawing effects of the chlorine atoms stabilize the conjugate base.

d)



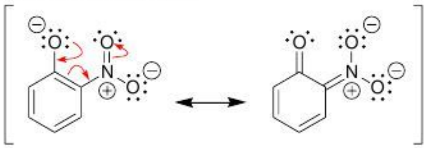
The conjugate base is more highly stabilized by resonance, with the negative charge spread over two oxygen atoms, rather than just one oxygen atom.

e)



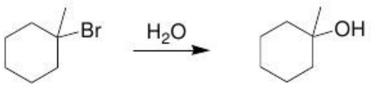
The conjugate base is stabilized by resonance.

13.6. 2-nitrophenol is expected to be more acidic (lower pK_a) because the conjugate base has a resonance structure in which the negative charge is spread onto an oxygen atom of the nitro group, shown below. In contrast, 3-nitrophenol does not have such a resonance structure:

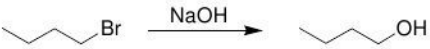


13.7.

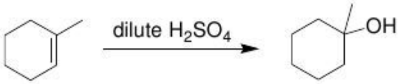
a)



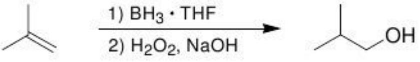
b)



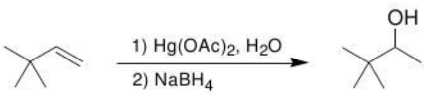
c)



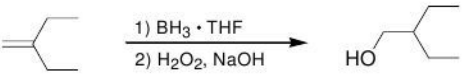
d)



e)

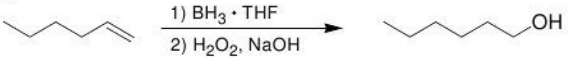


f)

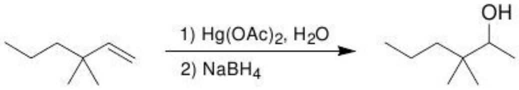


13.8

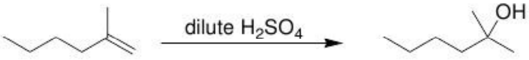
a)



b)



c)



13.9.

a) (+2) → (+2). The starting material is neither oxidized nor reduced.

b) (+1) → (+3). The starting material is oxidized.

c) (+3) → (-1). The starting material is reduced.

d) (+3) → (+3). The starting material is neither oxidized nor reduced.

e) (0) → (+2). The starting material is oxidized.

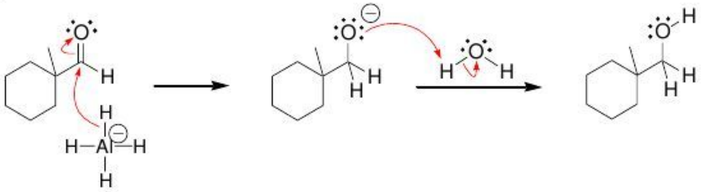
f) (+2) → (+3). The starting material is oxidized.

13.10. One carbon atom is reduced from an oxidation state of 0 to an oxidation state of -1, while the other carbon atom is oxidized from an oxidation state of 0 to an oxidation state of +1. Overall, the starting material does not undergo a net change in oxidation state and is, therefore, neither reduced nor oxidized.

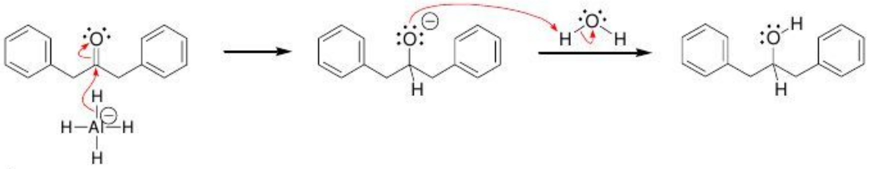
13.11. One carbon atom is reduced from an oxidation state of 0 to an oxidation state of -2, while the other carbon atom is oxidized from an oxidation state of 0 to an oxidation state of +2. Overall, the starting material does not undergo a net change in oxidation state and is, therefore, neither reduced nor oxidized.

13.12.

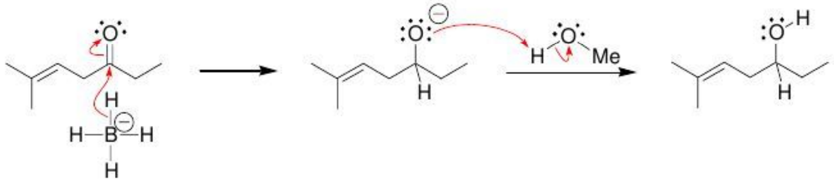
a)



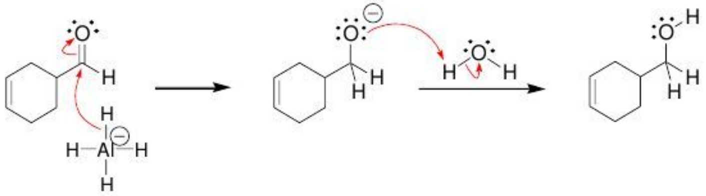
b)


O
H
H–Al–H
H
O
H
H O H
O H
H

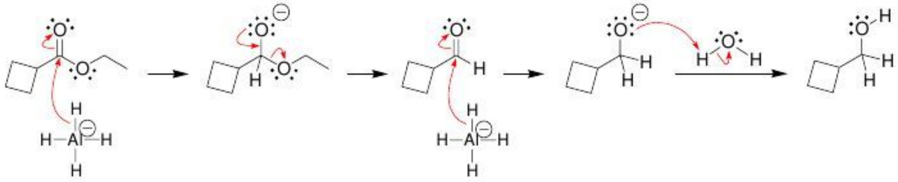
c)


O
H
H–B–H
H
O
H
H O Me
O H
H

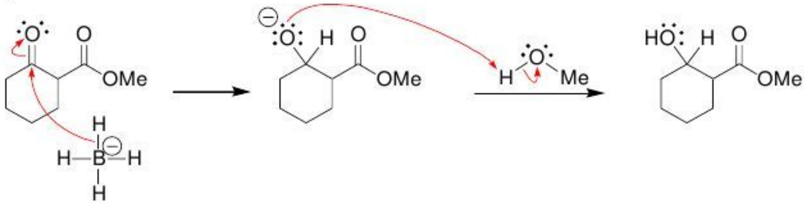
d)


O
H
H
H–Al–H
H
O
H
H
H O H
O H
H
H

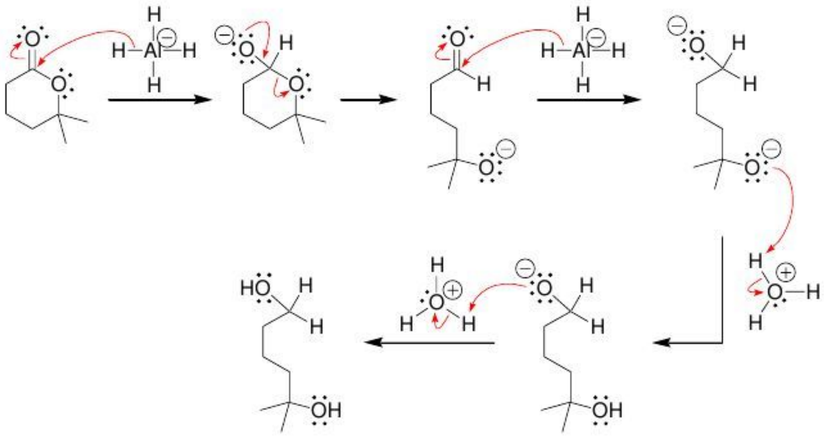
e)


O
O
H
H–Al–H
H
O
H
O
O
H
H
H–Al–H
H
O
H
H
H O H
O H
H
H

f)

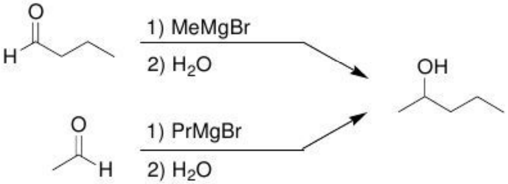

O
O
OMe
H
H–B–H
H
O
H
O
OMe
H O Me
HO
H
O
OMe

13.13.

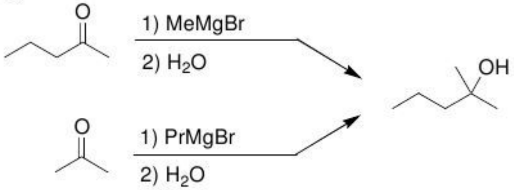


13.14.

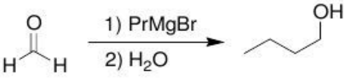
a)



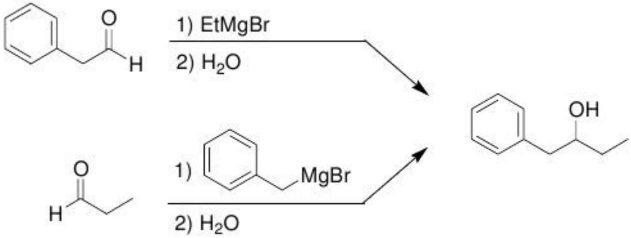
b)



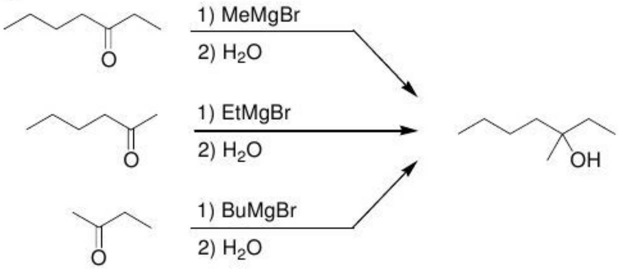
c)



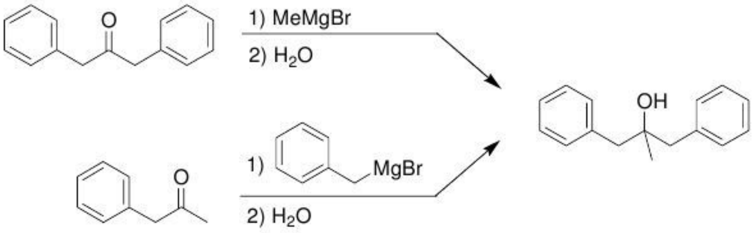
d)



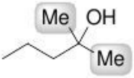
e)

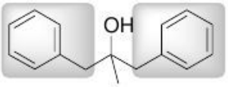


f)



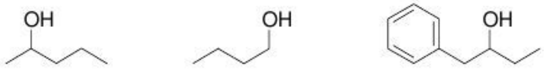
13.15 Each of the following two compounds can be prepared from the reaction between a Grignard reagent and an ester, because each of these compounds has two identical groups connected to the α position:





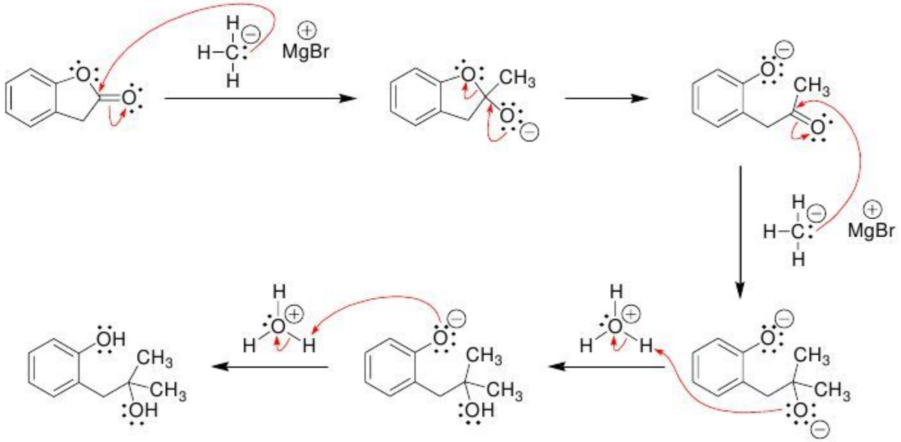
The other four compounds from Problem 13.14 do not contain two identical groups connected to the α position, and cannot be prepared from the reaction between an ester and a Grignard reagent.

13.16 Each of the following three compounds can be prepared from the reaction between a hydride reducing agent ($NaBH_4$ or LAH) and a ketone or aldehyde, because each of these compounds has a hydrogen atom connected to the α position:



The other three compounds from Problem 13.14 do not contain a hydrogen atom connected to the α position and, therefore, cannot be prepared from the reaction between a hydride reducing agent ($NaBH_4$ or LAH) and a ketone or aldehyde.

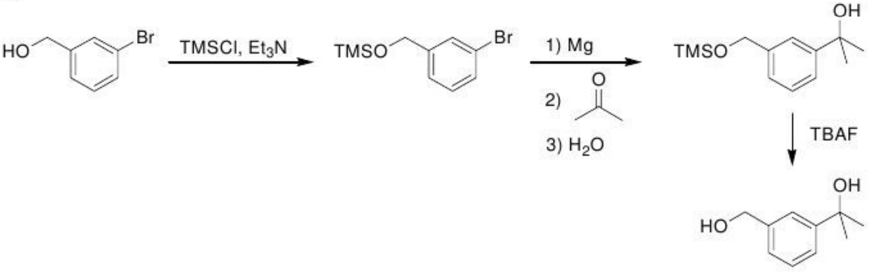
13.17.



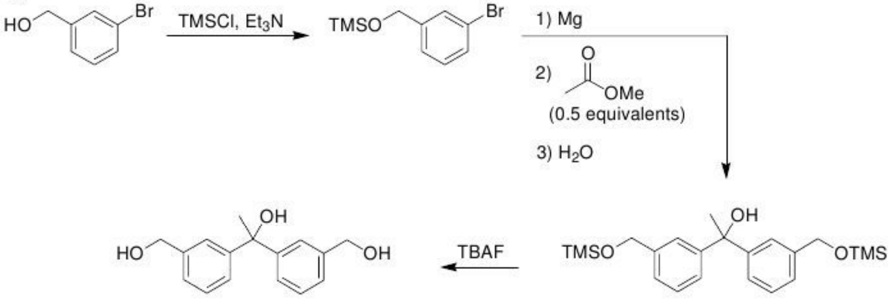
In this case, H_3O^+ must be used as a proton source because water is not sufficiently acidic to protonate a phenolate ion (see Section 13.2, Acidity of Alcohols and Phenols).

13.18.

a)

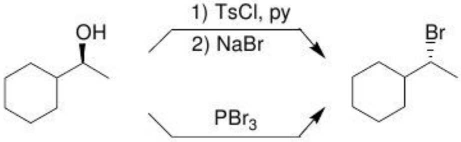


b)

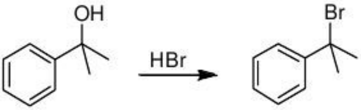

TMSCl, Et_3N
TMSO
Br
HO
1) Mg
2) OMe
(0.5 equivalents)
3) H_2O
OH
OTMS
TBAF
OH

13.19.

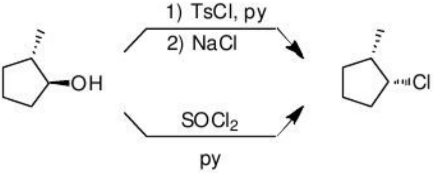
a)


OH
1) TsCl, py
2) NaBr
PBr_3
Br

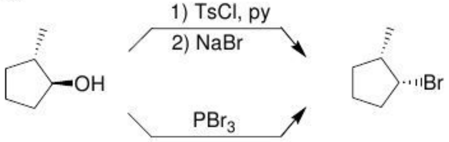
b)


OH
HBr
Br

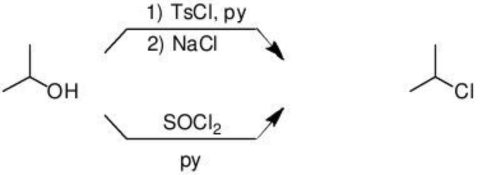
c)


OH
1) TsCl, py
2) NaCl
$SOCl_2$
py
Cl

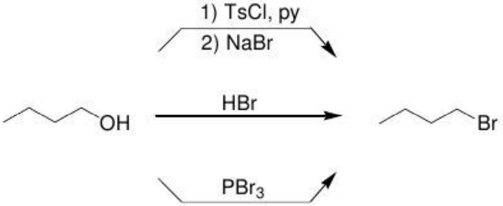
d)



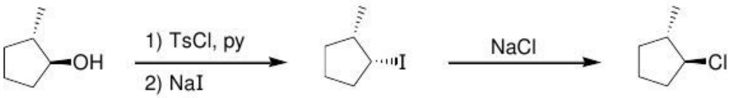
e)



f)

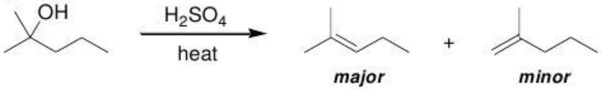


13.20.

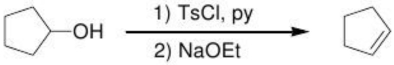


13.21.

a)

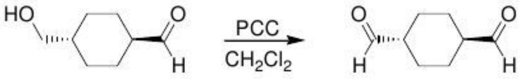


b)

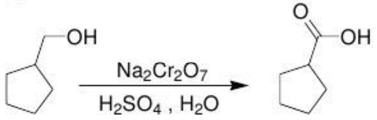


13.22.

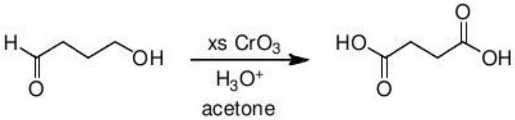
a)



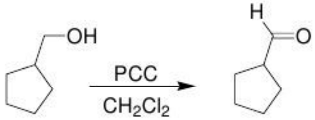
b)



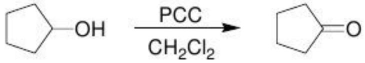
c)



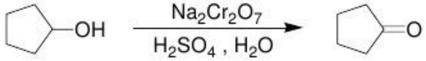
c)



e)

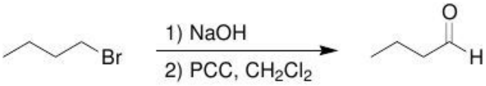


f)

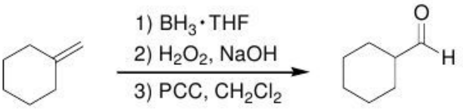


13.23.

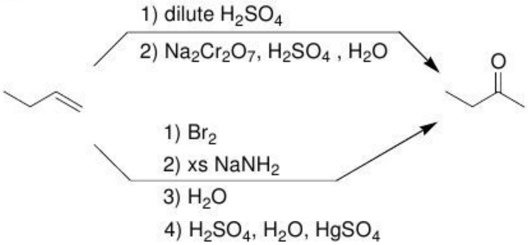
a)



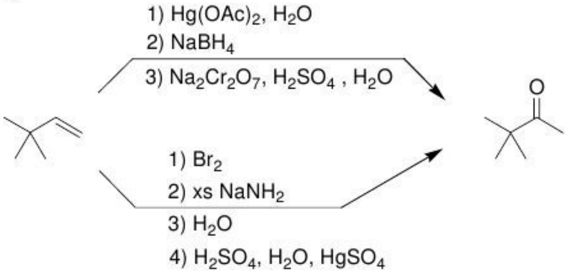
b)



c)

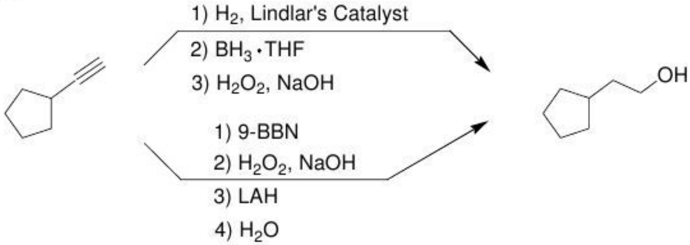

1) dilute H_2SO_4
2) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
O
1) Br_2
2) xs $NaNH_2$
3) H_2O
4) H_2SO_4, H_2O, $HgSO_4$

d)

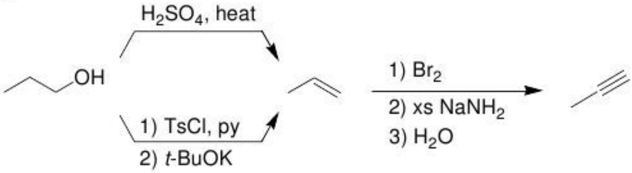

1) $Hg(OAc)_2$, H_2O
2) $NaBH_4$
3) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
O
1) Br_2
2) xs $NaNH_2$
3) H_2O
4) H_2SO_4, H_2O, $HgSO_4$

13.24.

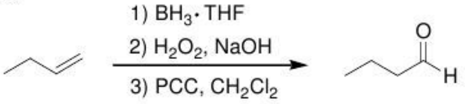
a)


1) H_2, Lindlar's Catalyst
2) $BH_3 \cdot THF$
3) H_2O_2, NaOH
OH
1) 9-BBN
2) H_2O_2, NaOH
3) LAH
4) H_2O

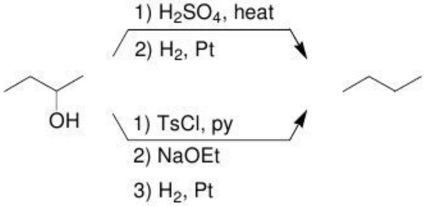
b)


H_2SO_4, heat
OH
1) TsCl, py
2) *t*-BuOK
1) Br_2
2) xs $NaNH_2$
3) H_2O

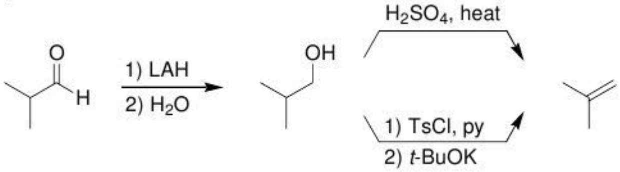
d)



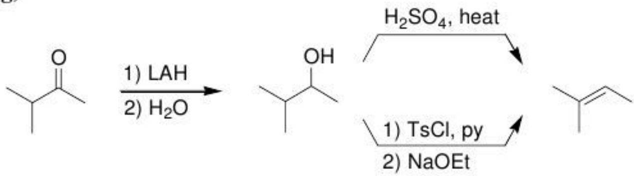
e)



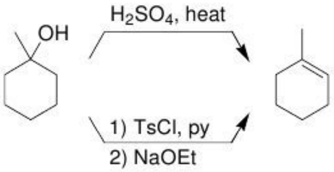
f)



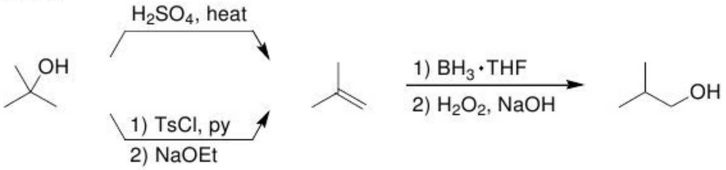
g)



13.25.

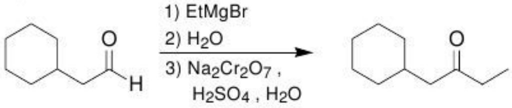


13.26.

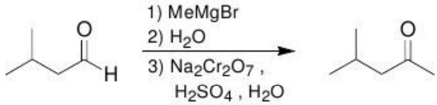


13.27.

a)

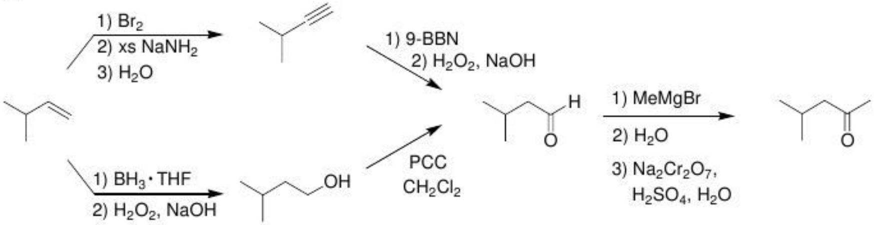


b)

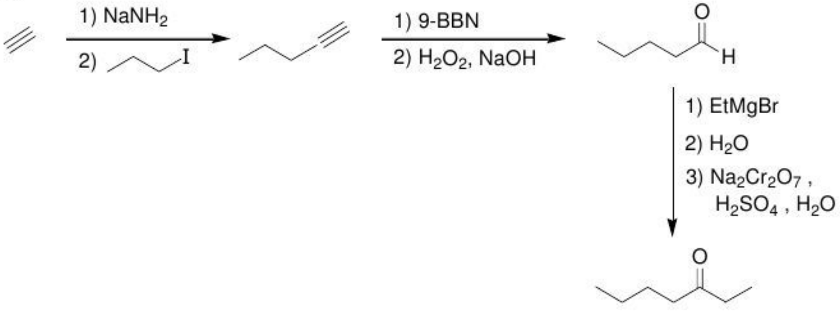


13.28.

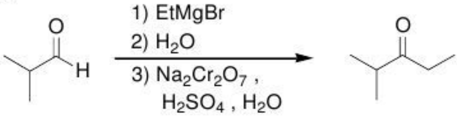
a)



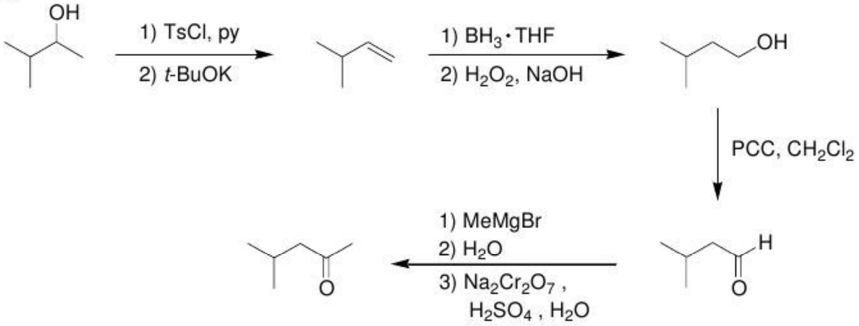
b)



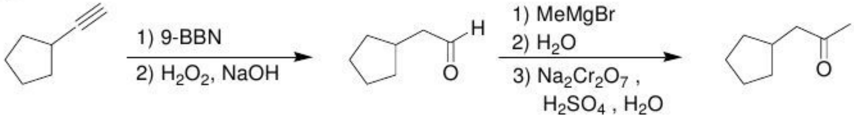
c)



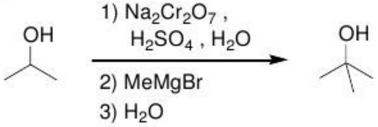
d)


OH
1) TsCl, py
2) t-BuOK
1) $BH_3 \cdot THF$
2) H_2O_2, NaOH
OH
PCC, CH_2Cl_2
H
O
1) MeMgBr
2) H_2O
3) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
O

e)

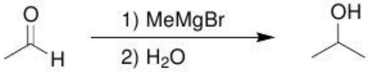

1) 9-BBN
2) H_2O_2, NaOH
H
O
1) MeMgBr
2) H_2O
3) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
O

f)

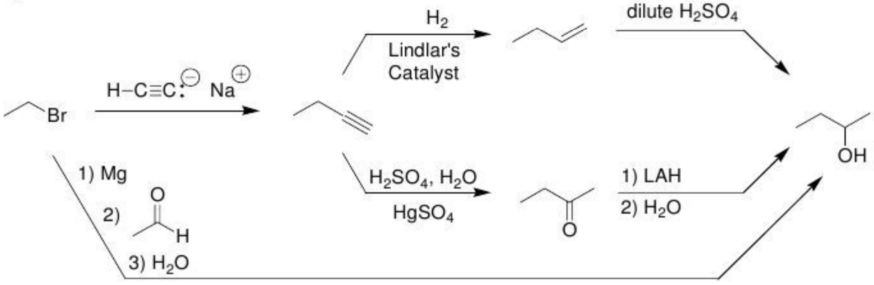

OH
1) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
2) MeMgBr
3) H_2O
OH

13.29.

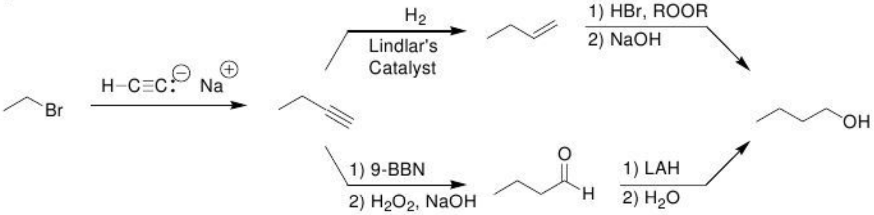
a)


O
H
1) MeMgBr
2) H_2O
OH

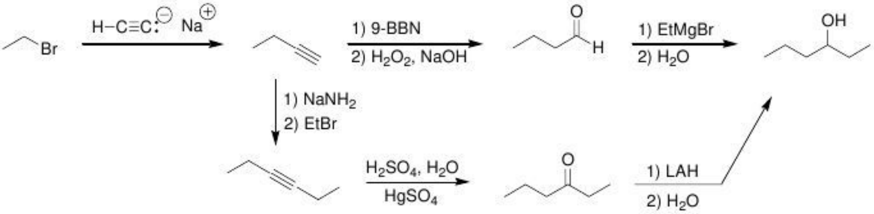
b)


Br
$H-C{\equiv}C\!:^{\ominus}$ $Na^{\oplus}$
H_2
Lindlar's Catalyst
dilute H_2SO_4
H_2SO_4, H_2O
$HgSO_4$
O
1) LAH
2) H_2O
OH
1) Mg
2)
O
H
3) H_2O

c)



d)

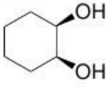


13.30.

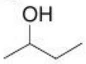
a) 2-propyl-1-pentanol
b) (*R*)-4-methyl-2-pentanol
c) 2-bromo-4-methylphenol
d) (*1R,2R*)-2-methylcyclohexanol

13.31.

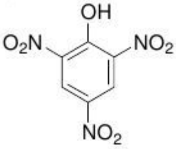
a)



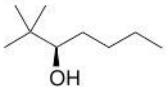
b)



c)

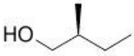


d)



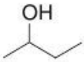
e)

f)

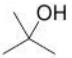


13.32.

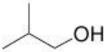
1-butanol



2-butanol



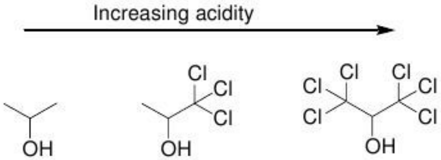
2-methyl-2-propanol



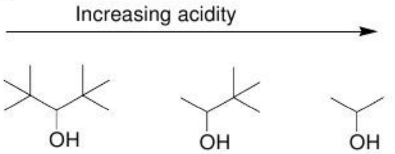
2-methyl-1-propanol

13.33.

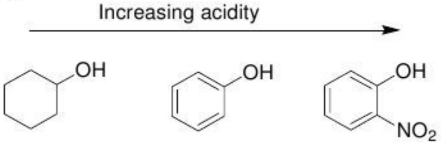
a)



b)

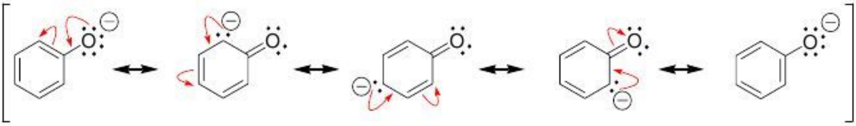


c)

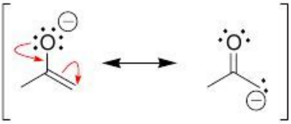


13.34.

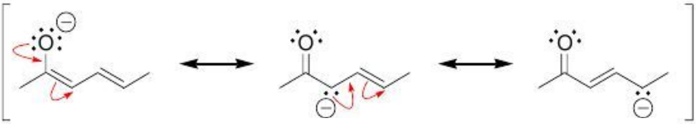
a)



b)



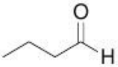
c)



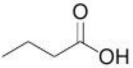
13.35.

a) 1-bromobutane b) 1-chlorobutane c) 1-chlorobutane d) *trans*-2-butene

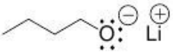
e)



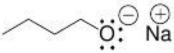
f)



g)



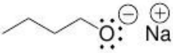
h)



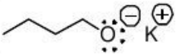
i)

j)

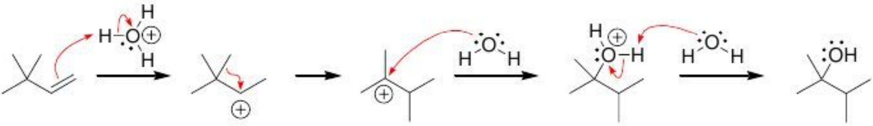
k)



l)

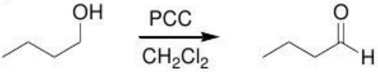


13.36.

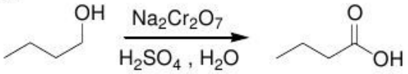


13.37.

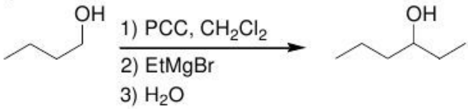
a)



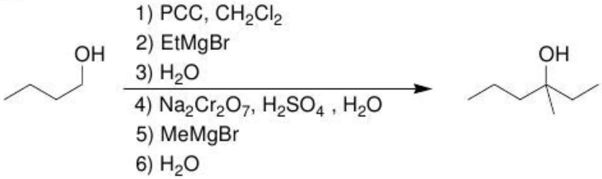
b)


OH
$Na_2Cr_2O_7$
H_2SO_4 , H_2O
O
OH

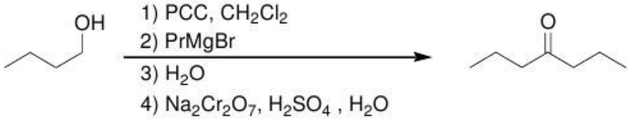
c)


OH
1) PCC, CH_2Cl_2
2) EtMgBr
3) H_2O
OH

d)

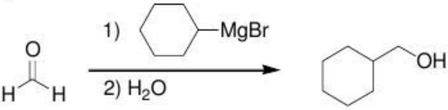

OH
1) PCC, CH_2Cl_2
2) EtMgBr
3) H_2O
4) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
5) MeMgBr
6) H_2O
OH

e)

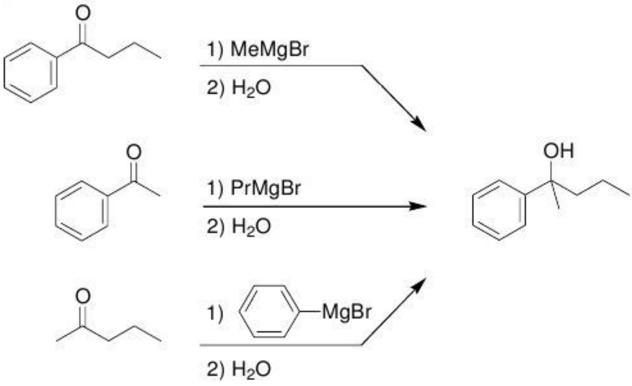

OH
1) PCC, CH_2Cl_2
2) PrMgBr
3) H_2O
4) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
O

13.38.

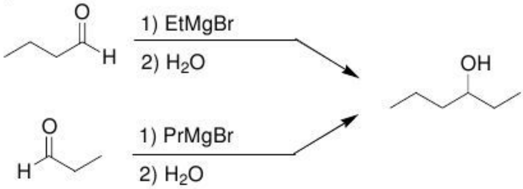
a)


O
H
H
1)
MgBr
2) H_2O
OH

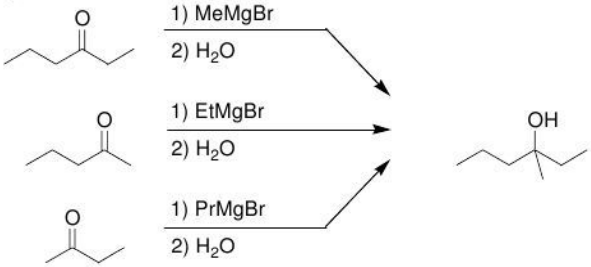
b)


O
1) MeMgBr
2) H_2O
O
1) PrMgBr
2) H_2O
OH
O
1)
MgBr
2) H_2O

c)

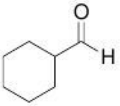


d)

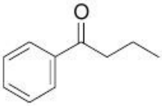


13.39.

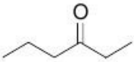
a)



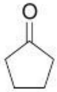
b)



c)

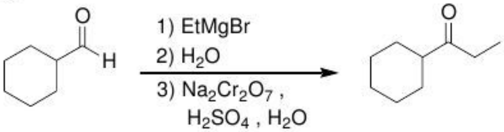


d)

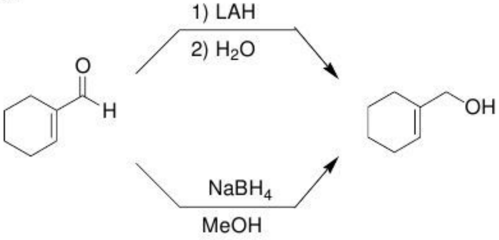


13.40.

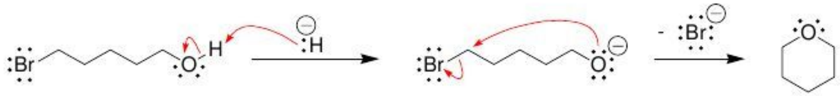
a)



b)

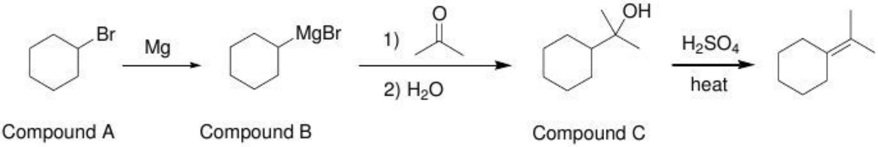


13.41.

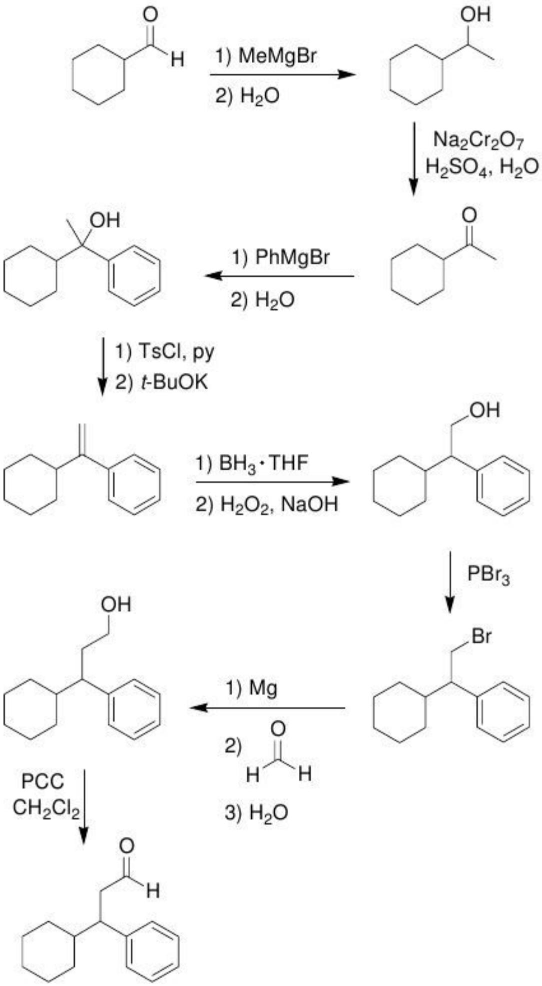


13.42. The major product is 1-methylcyclohexanol (resulting from Markvonikov addition), which is a tertiary alcohol. Tertiary alcohols do not generally undergo oxidation. The minor product (2-methylcyclohexanol) is a secondary alcohol and can undergo oxidation to yield a ketone.

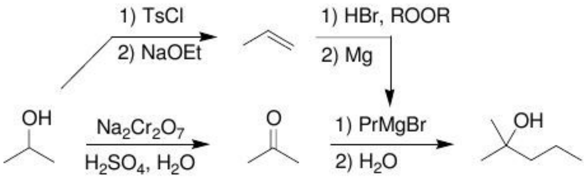
13.43.



13.44.

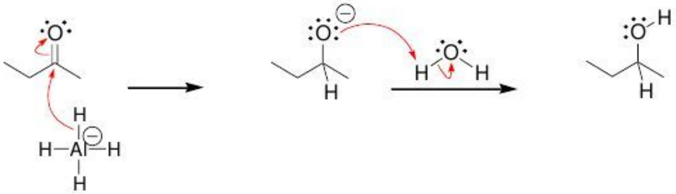

1) MeMgBr
2) H2O
Na2Cr2O7
H2SO4, H2O
1) PhMgBr
2) H2O
1) TsCl, py
2) t-BuOK
1) BH3·THF
2) H2O2, NaOH
PBr3
1) Mg
2) HCHO
3) H2O
PCC
CH2Cl2
OH
O
H
Br

13.45.

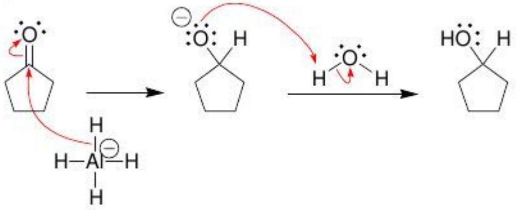

1) TsCl
2) NaOEt
1) HBr, ROOR
2) Mg
Na2Cr2O7
H2SO4, H2O
1) PrMgBr
2) H2O
OH
O

13.46.

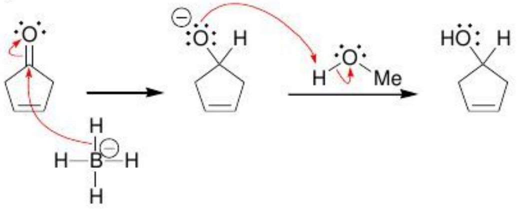
a)



b)

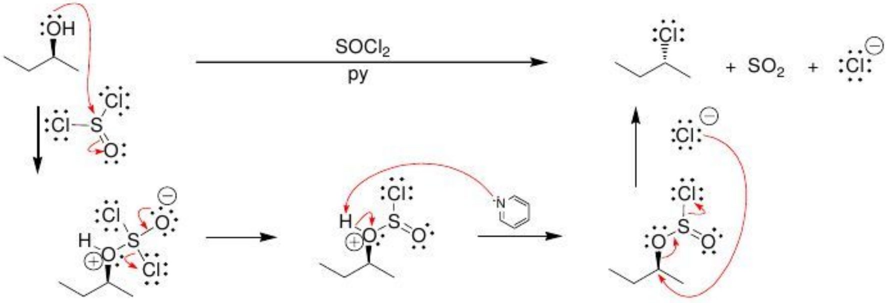


c)

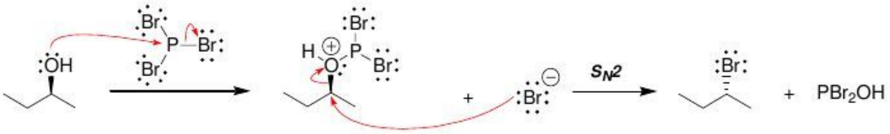


13.47.

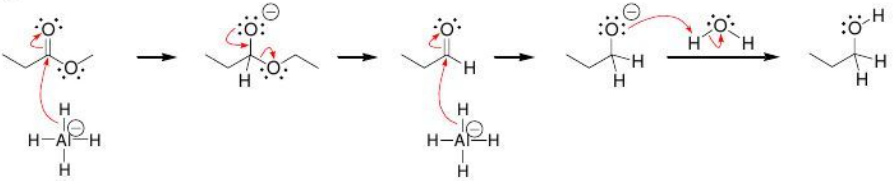
a)



b)

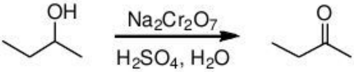


c)

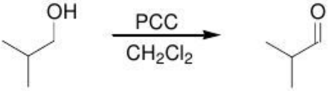


13.48.

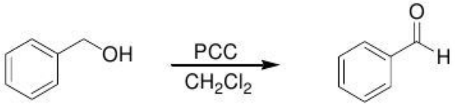
a)



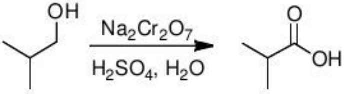
b)



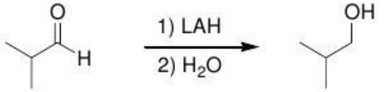
c)



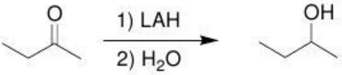
d)



e)

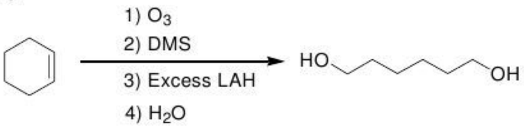


f)

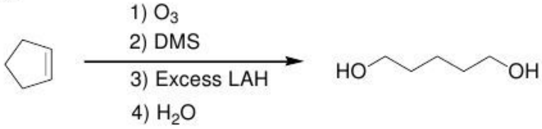


13.49

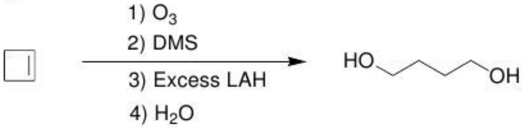
a)



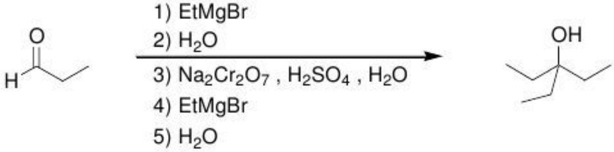
b)


1) O_3
2) DMS
3) Excess LAH
4) H_2O
HO
OH

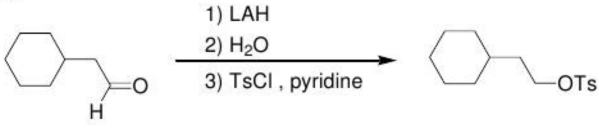
c)


1) O_3
2) DMS
3) Excess LAH
4) H_2O
HO
OH

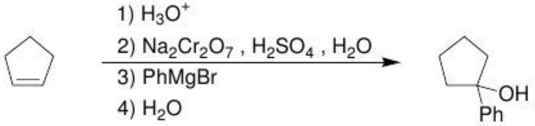
d)


O
H
1) EtMgBr
2) H_2O
3) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
4) EtMgBr
5) H_2O
OH

e)

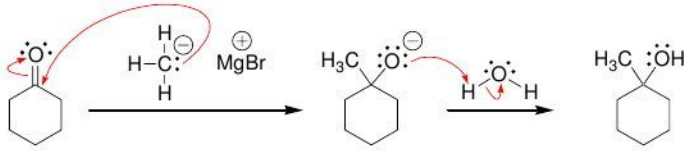

H
O
1) LAH
2) H_2O
3) TsCl , pyridine
OTs

f)

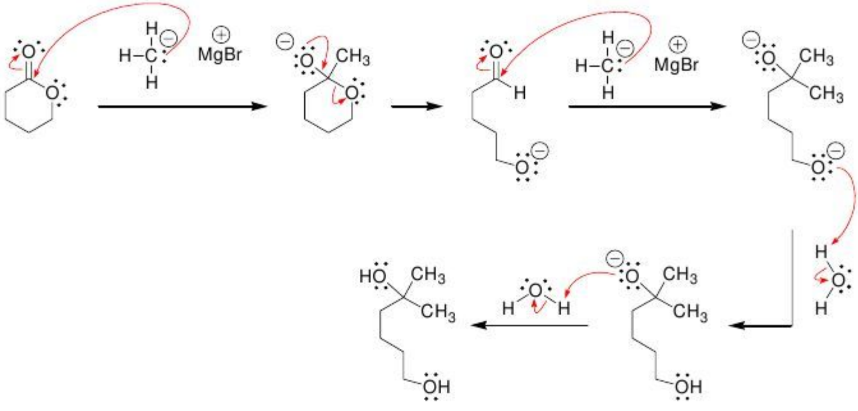

1) H_3O^+
2) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
3) PhMgBr
4) H_2O
OH
Ph

13.50.

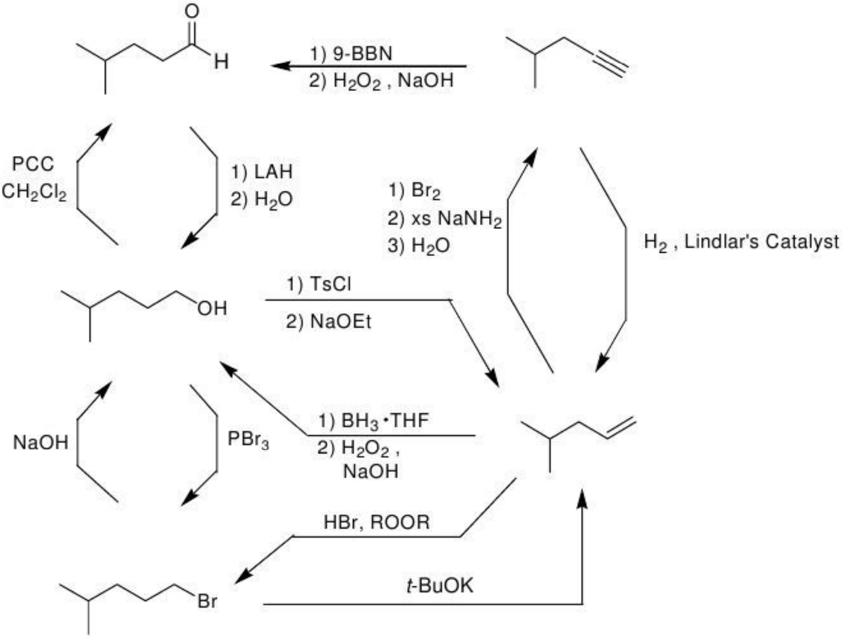
a)


O
H
H–C:
H
MgBr
H_3C
O
H
O
H
H_3C
OH

b)

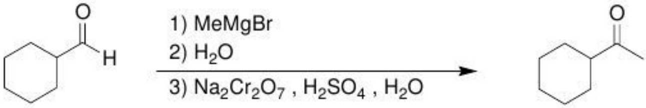

MgBr
CH3
H
OH

13.51.

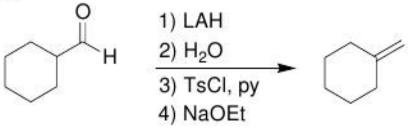

H
1) 9-BBN
2) H2O2 , NaOH
PCC
CH2Cl2
1) LAH
2) H2O
1) Br2
2) xs NaNH2
3) H2O
H2 , Lindlar's Catalyst
OH
1) TsCl
2) NaOEt
NaOH
PBr3
1) BH3 • THF
2) H2O2 ,
NaOH
HBr, ROOR
Br
t-BuOK

13.52.

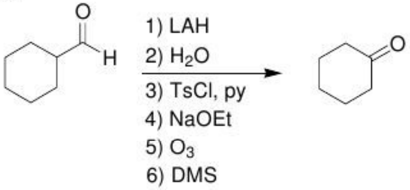
a)


O
H
1) MeMgBr
2) H_2O
3) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
O

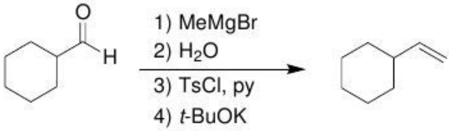
b)


O
H
1) LAH
2) H_2O
3) TsCl, py
4) NaOEt

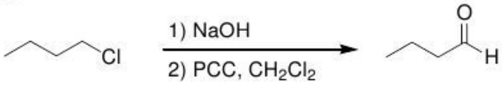
c)


O
H
1) LAH
2) H_2O
3) TsCl, py
4) NaOEt
5) O_3
6) DMS
O

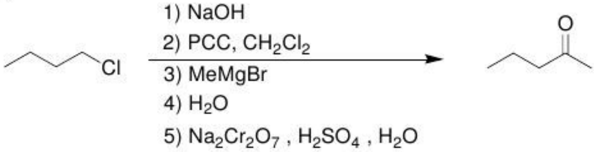
d)


O
H
1) MeMgBr
2) H_2O
3) TsCl, py
4) *t*-BuOK

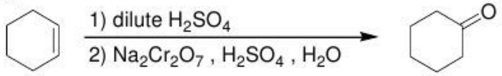
e)


Cl
1) NaOH
2) PCC, CH_2Cl_2
O
H

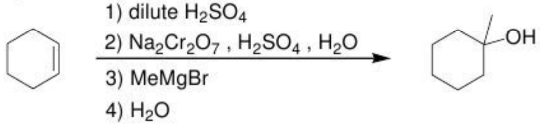
f)


Cl
1) NaOH
2) PCC, CH_2Cl_2
3) MeMgBr
4) H_2O
5) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
O

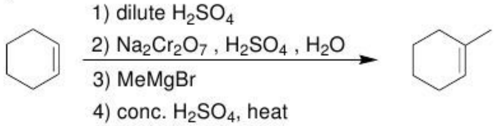
g)


1) dilute H_2SO_4
2) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
O

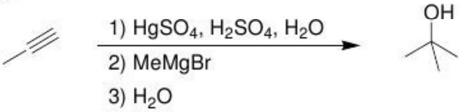
h)


1) dilute H_2SO_4
2) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
3) MeMgBr
4) H_2O
OH

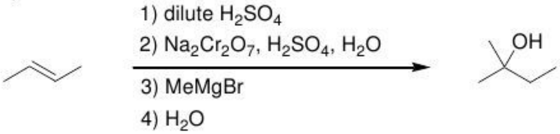
i)


1) dilute H_2SO_4
2) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
3) MeMgBr
4) conc. H_2SO_4, heat

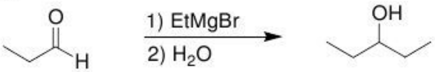
j)


1) $HgSO_4$, H_2SO_4, H_2O
2) MeMgBr
3) H_2O
OH

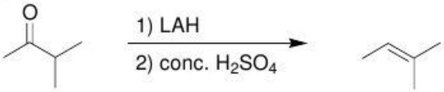
k)


1) dilute H_2SO_4
2) $Na_2Cr_2O_7$, H_2SO_4, H_2O
3) MeMgBr
4) H_2O
OH

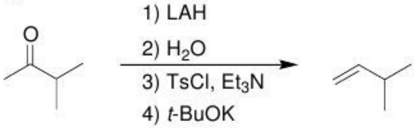
l)


O
H
1) EtMgBr
2) H_2O
OH

m)


O
1) LAH
2) conc. H_2SO_4

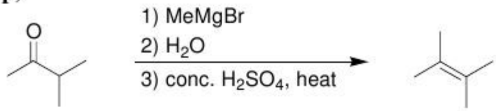
n)


1) LAH
2) H_2O
3) TsCl, Et_3N
4) *t*-BuOK

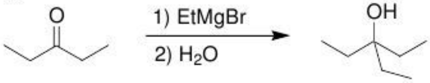
o)


1) LAH
2) H_2O
3) TsCl, Et_3N
4) *t*-BuOK
5) $BH_3 \cdot THF$
6) H_2O_2, NaOH
HO

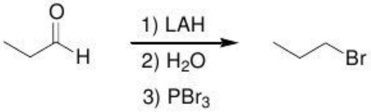
p)


1) MeMgBr
2) H_2O
3) conc. H_2SO_4, heat

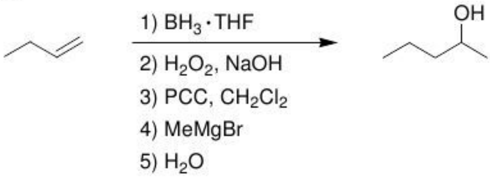
q)


1) EtMgBr
2) H_2O
OH

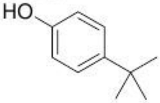
r)


H
1) LAH
2) H_2O
3) PBr_3
Br

s)

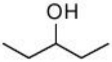

1) $BH_3 \cdot THF$
2) H_2O_2, NaOH
3) PCC, CH_2Cl_2
4) MeMgBr
5) H_2O
OH

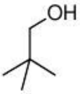
13.53.



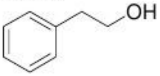
13.54.

13.55.

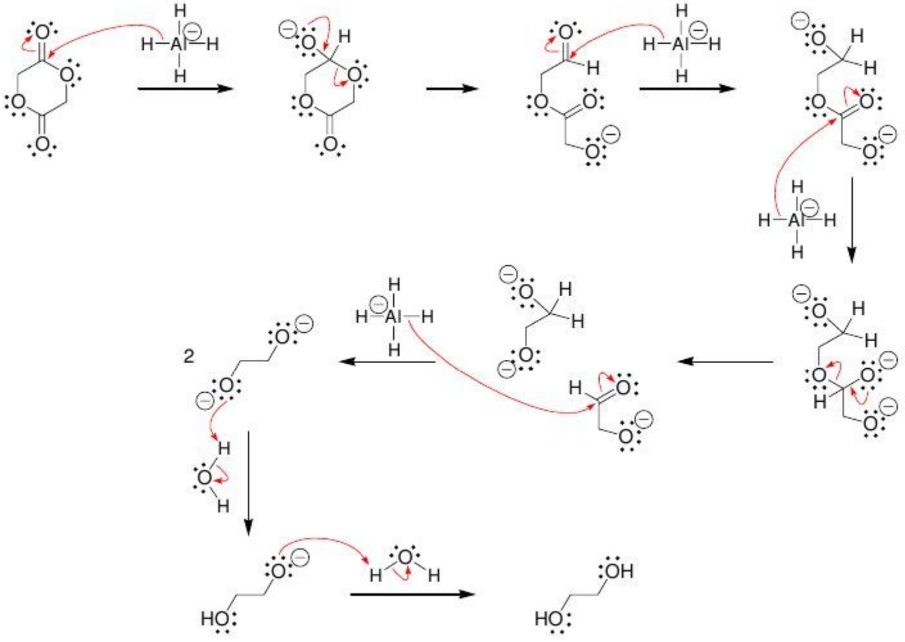




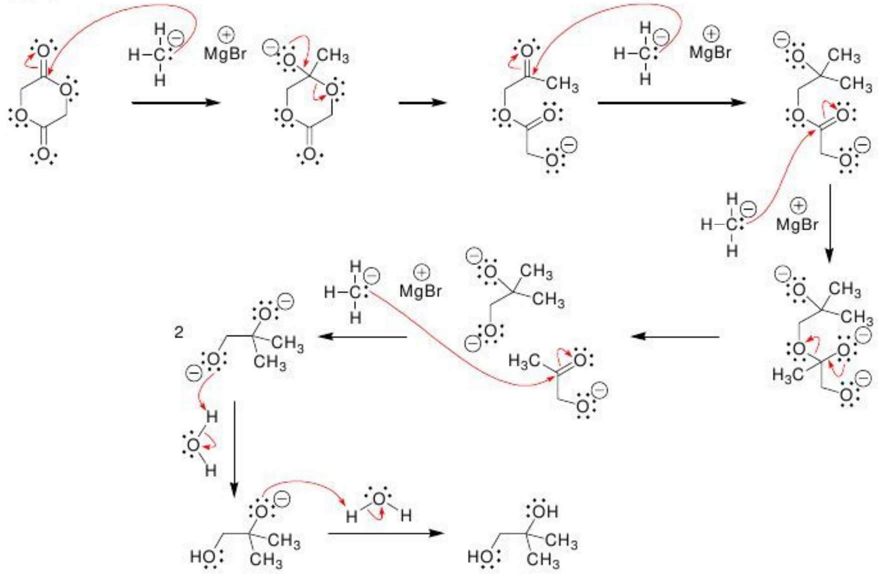
13.56.



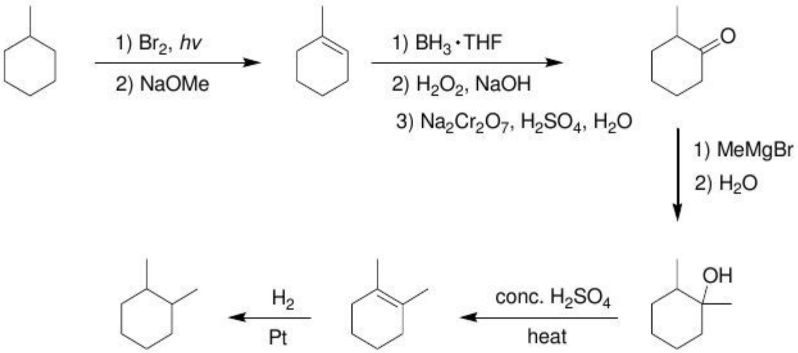
13.57



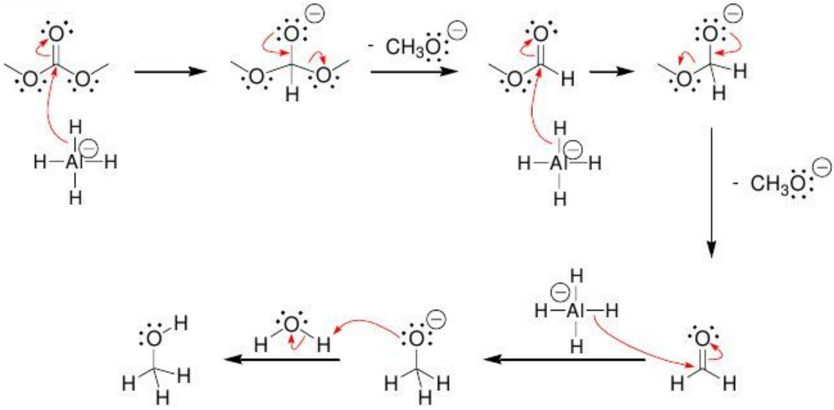
13.58


MgBr
2
CH3
H3C

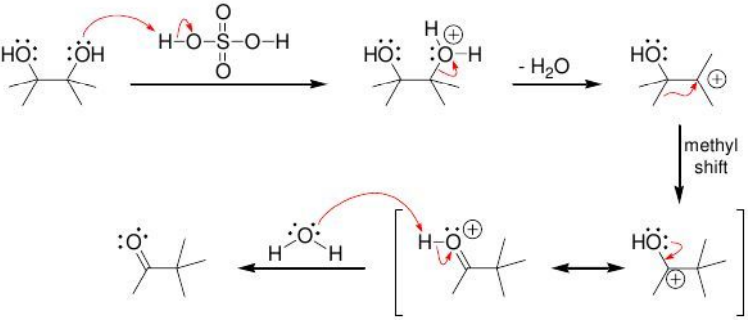
13.59


1) Br2, hv
2) NaOMe
1) BH3·THF
2) H2O2, NaOH
3) Na2Cr2O7, H2SO4, H2O
1) MeMgBr
2) H2O
OH
conc. H2SO4
heat
H2
Pt

13.60.



13.61.



13.62. One carbon atom is oxidized from an oxidation state of +1 to an oxidation state of +2, while the other carbon atom is reduced from an oxidation state of +1 to an oxidation state of 0. Overall, the starting material does not undergo a net change in oxidation state and is, therefore, neither reduced nor oxidized.

Chapter 14
Ethers and Epoxides;
Thiols and Sulfides

Review of Concepts

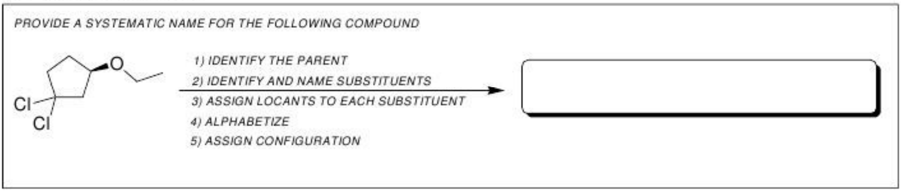
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 14. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- Ethers are often used as ____________ for organic reactions.
- Cyclic polyethers, or __________ **ethers**, are capable of solvating metal ions in organic (nonpolar) solvents.
- Ethers can be readily prepared from the reaction between an alkoxide ion and an ______________________, a process called a **Williamson ether synthesis**. This process works best for _________ or ______________ alkyl halides. _____________ alkyl halides are significantly less efficient, and ______________ alkyl halides cannot be used.
- When treated with a strong acid, an ether will undergo **acidic** _____________ in which it is converted into two alkyl halides.
- When a phenyl ether is cleaved under acidic conditions, the products are _____________ and an alkyl halide.
- Ethers undergo autooxidation in the presence of atmospheric oxygen to form _________________________.
- Substituted oxiranes are also called ________________.
- ______________ can be converted into epoxides by treatment with peroxy acids or via halohydrin formation and subsequent epoxidation.
- _____________ catalysts can be used to achieve the enantioselective epoxidation of allylic alcohols.
- Epoxides will undergo **ring-opening reactions** in: 1) conditions involving a strong nucleophile, or under 2) _____-catalyzed conditions. When a strong nucleophile is used, the nucleophile attacks at the ______-substituted position.
- Sulfur analogs of alcohols contain an SH group rather than an OH group, and are called ____________.
- Thiols can be prepared via an S_N2 reaction between sodium hydrosulfide (NaSH) and a suitable _________________________.
- The sulfur analogs of ethers (thioethers) are called _____________**.**
- Sulfides can be prepared from thiols in a process that is essentially the sulfur analog of the Williamson ether synthesis, involving a ____________ ion, rather than an alkoxide.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 14. The answers appear in the section entitled *SkillBuilder Review*.

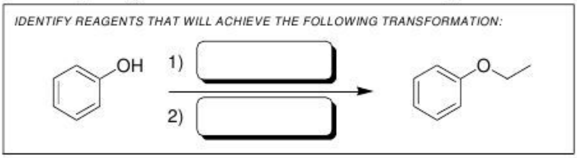
14.1 Naming an Ether



PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND

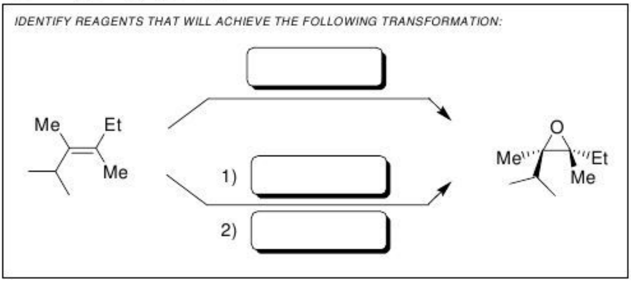
1) IDENTIFY THE PARENT
2) IDENTIFY AND NAME SUBSTITUENTS
3) ASSIGN LOCANTS TO EACH SUBSTITUENT
4) ALPHABETIZE
5) ASSIGN CONFIGURATION

14.2 Preparing an Ether via a Williamson Ether Synthesis



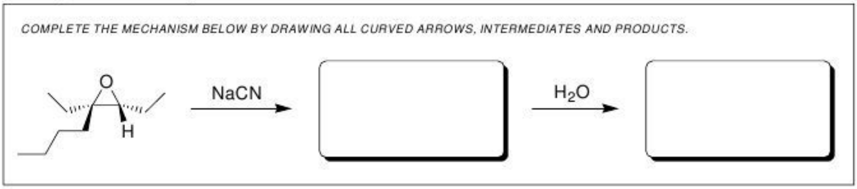
IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:

14.3 Preparing Epoxides



IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:

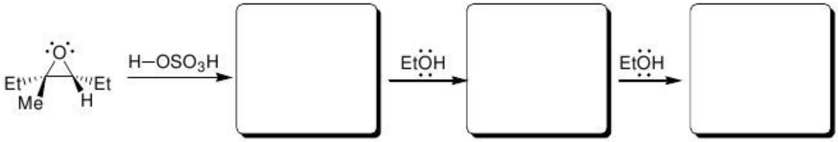
14.4 Drawing the Mechanism and Predicting the Product of the Reaction between a Strong Nucleophile and an Epoxide



COMPLETE THE MECHANISM BELOW BY DRAWING ALL CURVED ARROWS, INTERMEDIATES AND PRODUCTS.

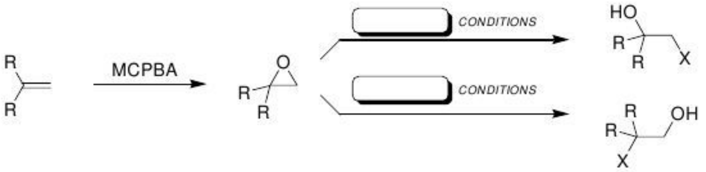
14.5 Drawing the Mechanism and Predicting the Product of Acid-Catalyzed Ring-Opening

COMPLETE THE MECHANISM BELOW BY DRAWING ALL CURVED ARROWS, INTERMEDIATES AND PRODUCTS.



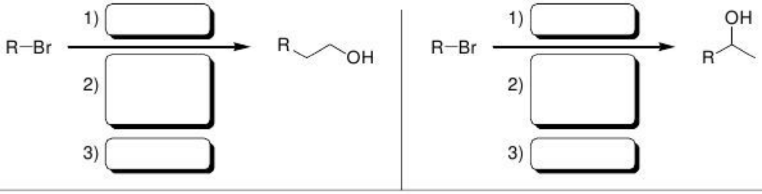
14.6 Installing Two Adjacent Functional Groups

IDENTIFY WHETHER EACH RING-OPENING REACTION BELOW REQUIRES ACIDIC CONDITIONS OR BASIC CONDITIONS:



14.7 Choosing the Appropriate Grignard Reaction

IDENTIFY REAGENTS THAT WILL ACHIEVE EACH OF THE FOLLOWING TRANSFORMATIONS:



Review of Reactions

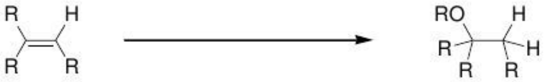
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 14. The answers appear in the section entitled *Review of Reactions*.

Preparation of Ethers

Williamson ether synthesis

$$\mathrm{R{-}OH} \longrightarrow \mathrm{R{-}O{-}R}$$

Alkoxymercuration-demercuration

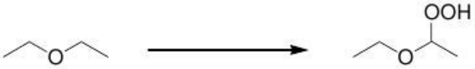


Reactions of Ethers

Acidic cleavage

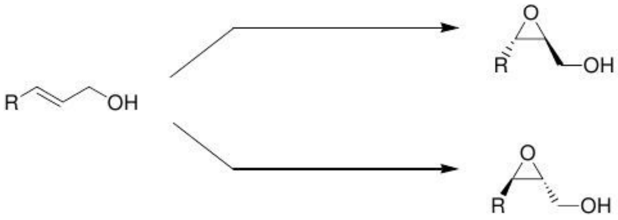
$$R{-}O{-}R \longrightarrow R{-}X \quad + \quad R{-}X \quad + \quad H_2O$$

Autooxidation

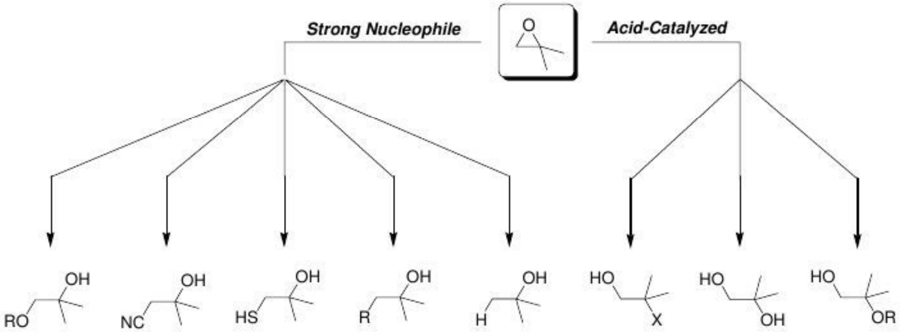


Preparation of Epoxides

Enantioselective Epoxidation

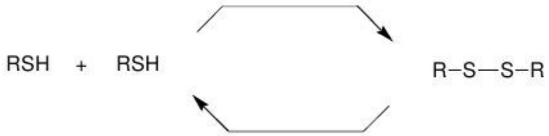


Ring-Opening Reactions of Epoxides



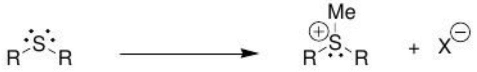
Thiols and Sulfides

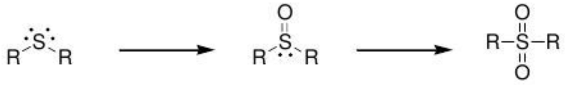
Thiols



Sulfides

$$R{-}SH \longrightarrow R{-}S{-}R$$





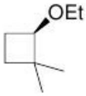
Solutions

14.1.

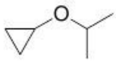
a) 2-ethoxypropane
b) (*S*)-2-chloro-1-ethoxypropane
c) 2,4-dichloro-1-ethoxybenzene
d) (*1R,2R*)-2-ethoxycyclohexanol
e) 1-ethoxycyclohexene

14.2.

a)



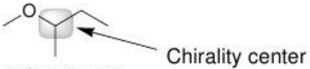
b)



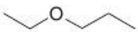
14.3.

Common names in parentheses:

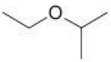
1-methoxybutane
(butyl methyl ether)



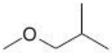
2-methoxybutane
(*sec*-butyl methyl ether)



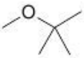
1-ethoxypropane
(ethyl propyl ether)



2-ethoxypropane
(ethyl isopropyl ether)



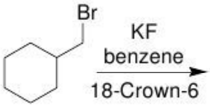
1-methoxy-2-methylpropane
(isobutyl methyl ether)



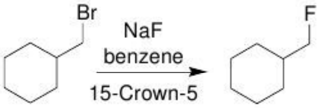
2-methoxy-2-methylpropane
(*tert*-butyl methyl ether)

14.4.

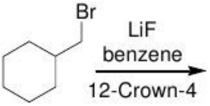
a)



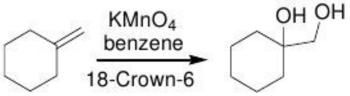
b)



c)

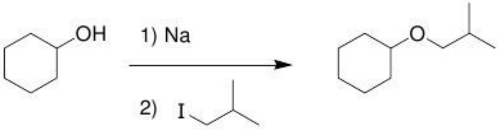


d)

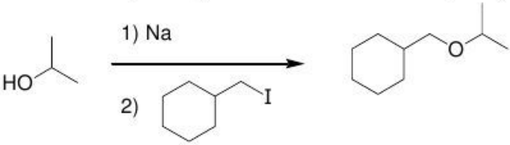


14.5.

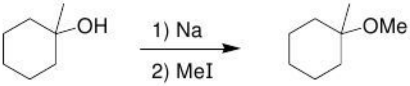
a) A Williamson ether synthesis will be more efficient with a less sterically hindered substrate, since the process involves an S_N2 reaction. Therefore, in this case, it is better to start with a secondary alcohol and a primary alkyl halide, rather than a primary alcohol and a secondary alkyl halide:



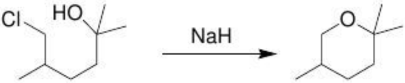
b) In this case, it is better to start with a secondary alcohol and a primary alkyl halide, rather than a primary alcohol and a secondary alkyl halide:



c) In this case, it is better to start with a tertiary alcohol and a methyl halide, rather than methanol and a tertiary alkyl halide:



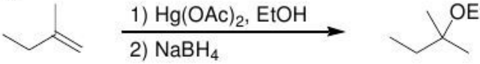
14.6.



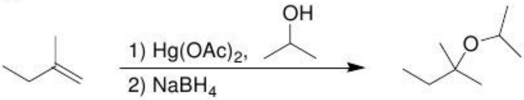
14.7. No. The Williamson ether synthesis employs an S_N2 process, which cannot occur readily at tertiary or vinylic positions. Making this ether would require at least one of these two processes, neither of which can be used.

14.8.

a)



b)



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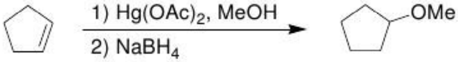

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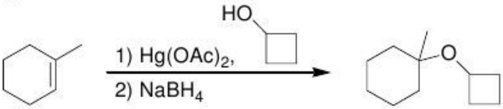
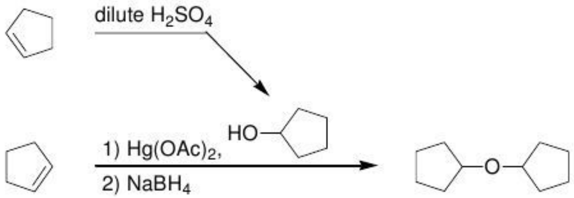
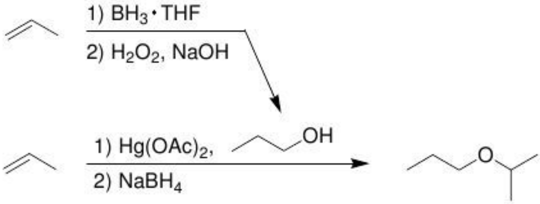


14.9.

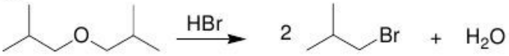


14.10.

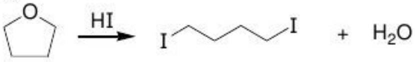


14.11.

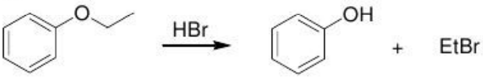
a)



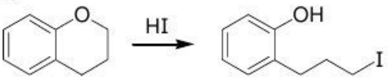
b)



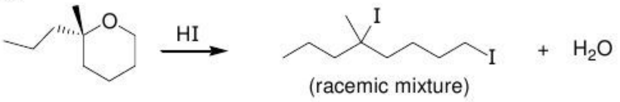
c)



d)



e)



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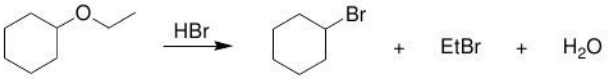


14.12.

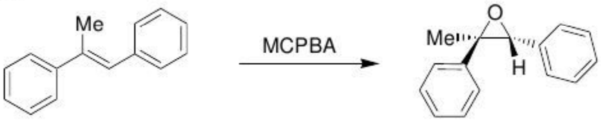
a) 2-methyl-1,2-epoxypropane or 1,1-dimethyloxirane
b) 1,1-diphenyl-1,2-epoxyethane or 1,1-diphenyloxirane
c) 1,2-epoxycyclohexane

14.13.

a) (*S*)-2-phenyl-1,2-epoxypropane or (*S*)-1-methyl-1-phenyloxirane
b) (*3R,4R*)-3,4-epoxyheptane or (*1R,2R*)-1-ethyl-2-propyloxirane
c) (*2R,3S*)-4-methyl-2,3-epoxypentane or (*1S,2R*)-1-isopropyl-2-methyloxirane

14.14.

a)



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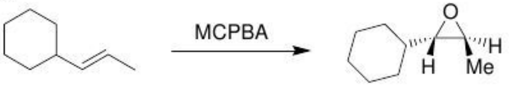

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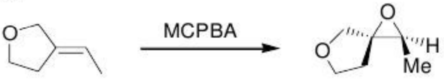
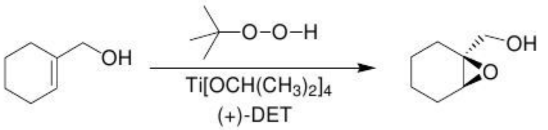


d)

14.15. This process for epoxide formation involves deprotonation of the hydroxyl group, followed by an intramolecular S_N2 attack. The S_N2 step requires back-side attack, which can only be achieved when both the hydroxyl group and the bromine occupy axial positions. Due to the steric bulk of a tert-butyl group, Compound A spends most of time in a chair conformation that has the tert-butyl group in an equatorial position. In this conformation, the OH and Br are indeed in axial positions, so the reaction can occur quite rapidly. In contrast, Compound B spends most of its time in a chair conformation in which the OH and Br occupy equatorial positions. The S_N2 process cannot occur from this conformation.

14.16.

a)



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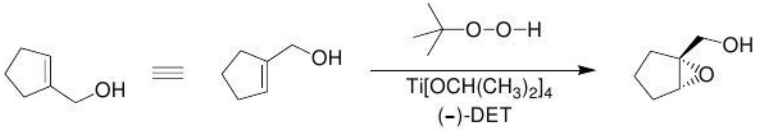

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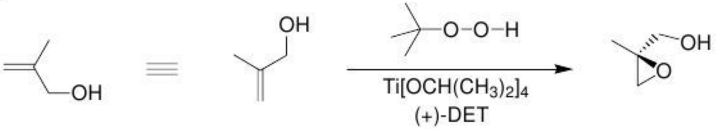

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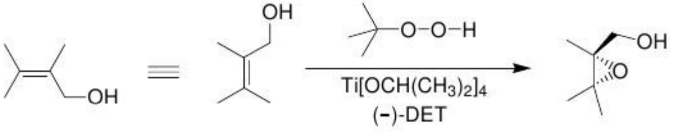
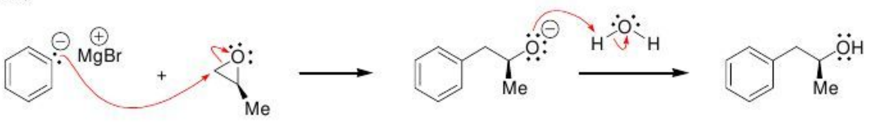


14.17.

a)



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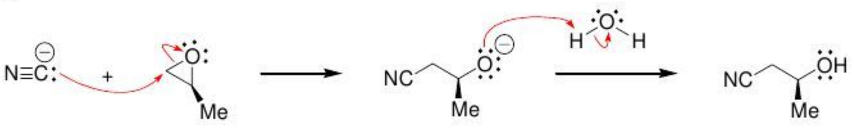

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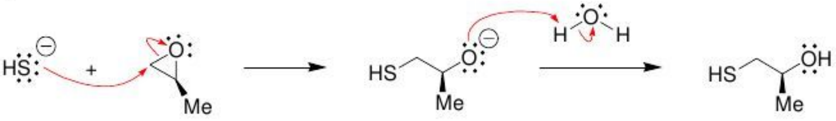

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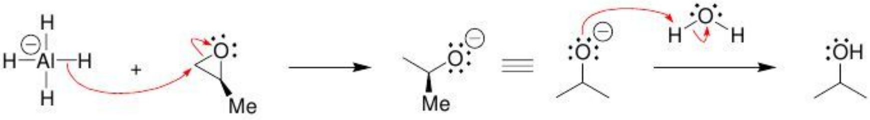

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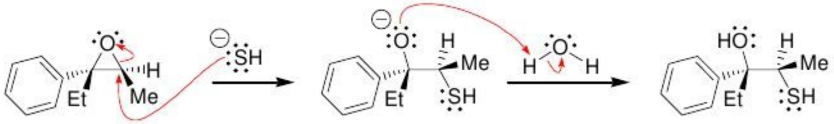

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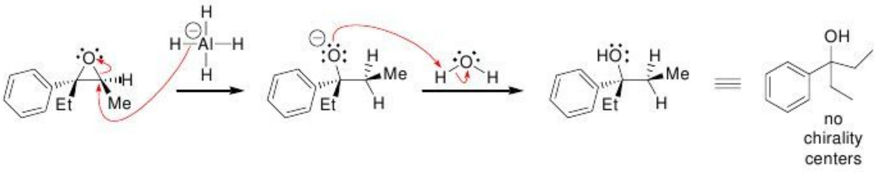
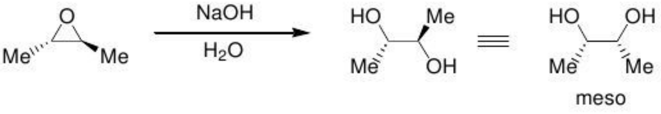
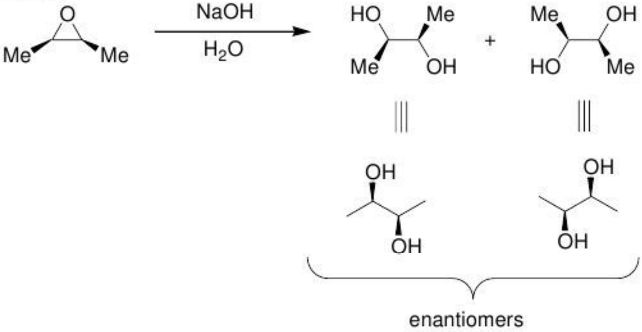


14.18. The reaction yields a meso compound, regardless of which electrophilic position is attacked by hydroxide.

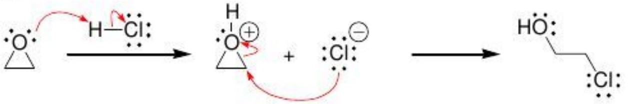


14.19.



14.20.

a)



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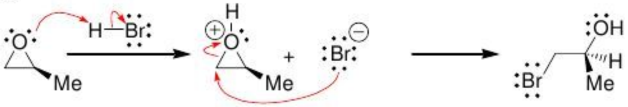

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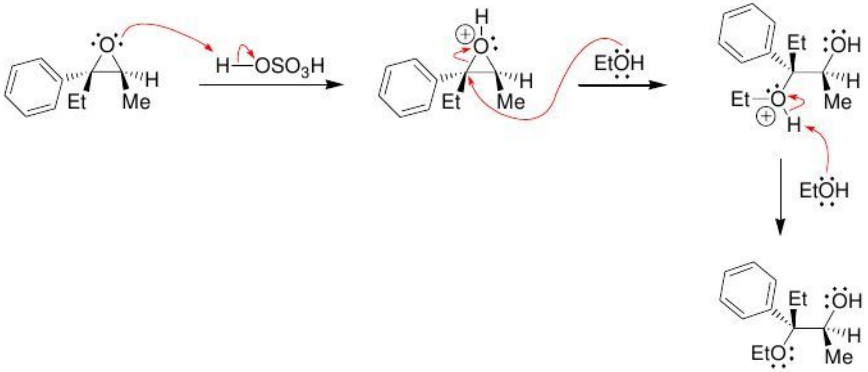
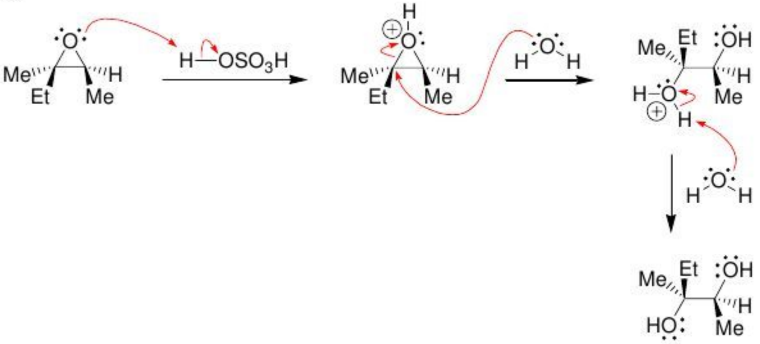
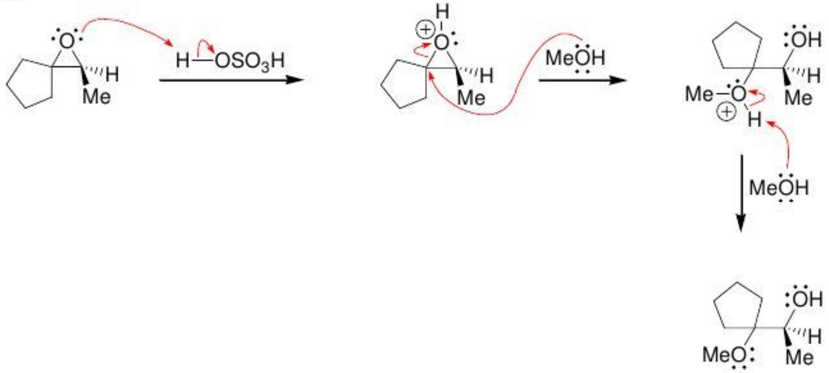


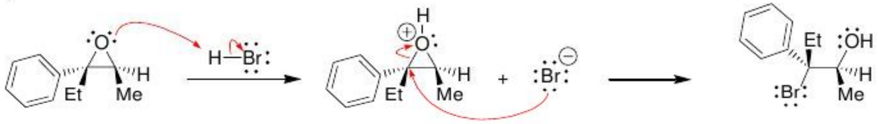
d)


Me
Et
Me
H
H—OSO$_3$H
H$_2$O
Et
OH
HO

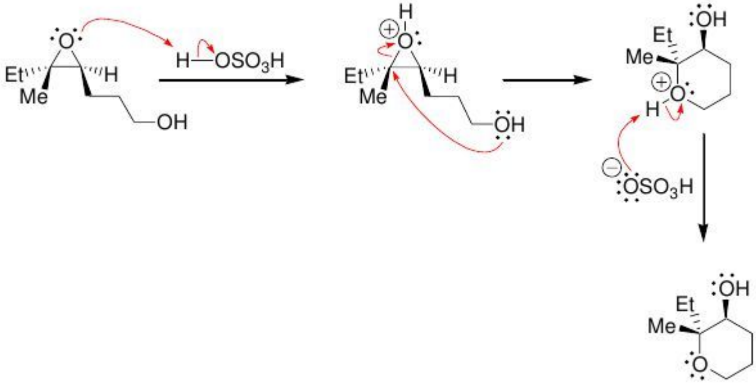
e)


H
Me
H—OSO$_3$H
MeOH
OH
MeO

f)

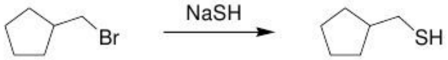

Et
Me
H
H—Br
Br
OH

14.21.



14.22.

a)



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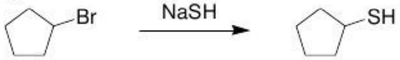

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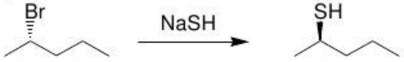
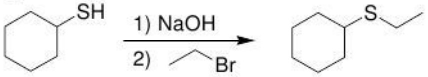


14.23.

a)



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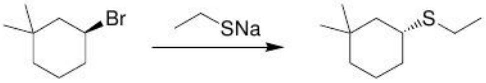

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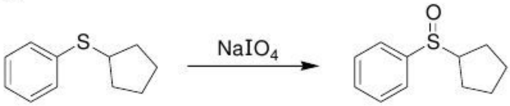

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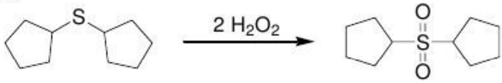
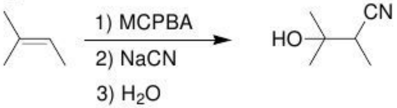


14.24.

a)



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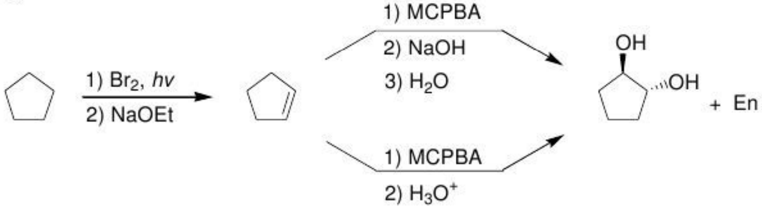

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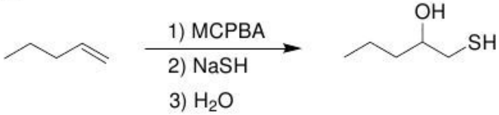

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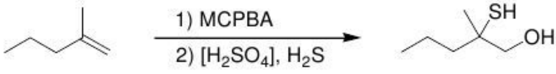

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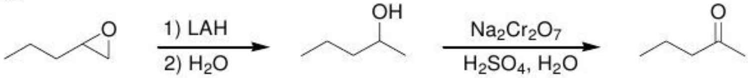
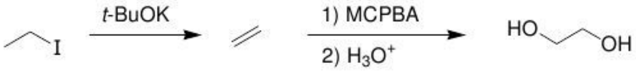
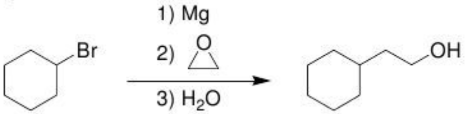


14.25.



14.26.

a)



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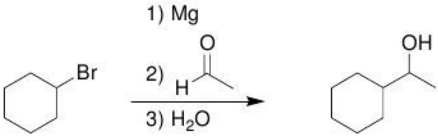

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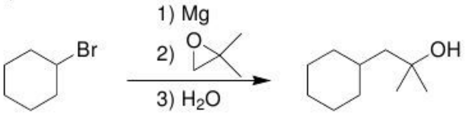

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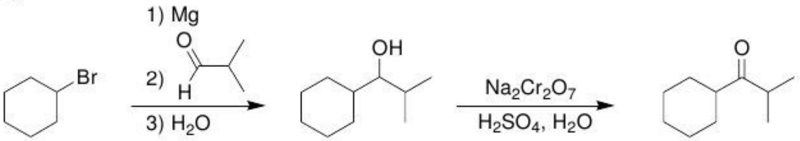

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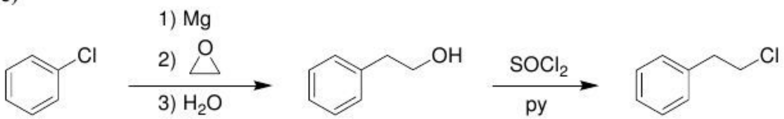

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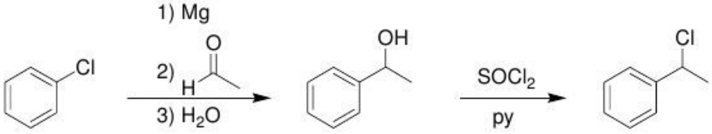
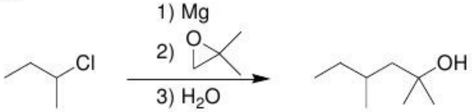
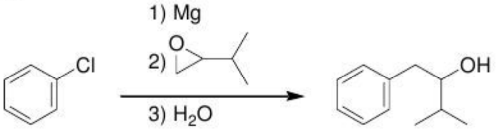

Cl
1) Mg
2) O H
3) H_2O
OH
$SOCl_2$
py
Cl

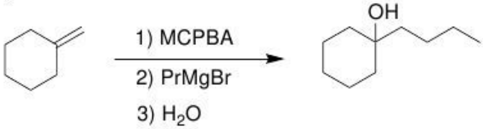
g)


Cl
1) Mg
2) O
3) H_2O
OH

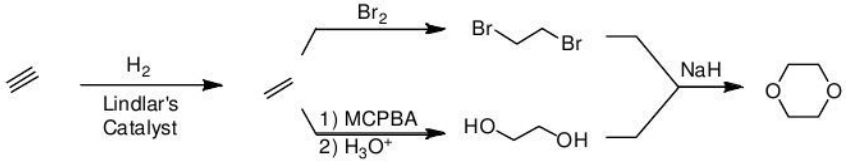
h)


Cl
1) Mg
2) O
3) H_2O
OH

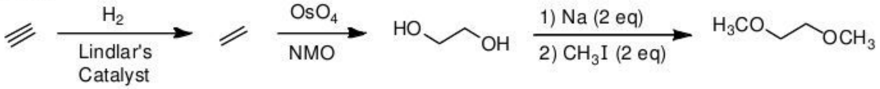
i)


1) MCPBA
2) PrMgBr
3) H_2O
OH

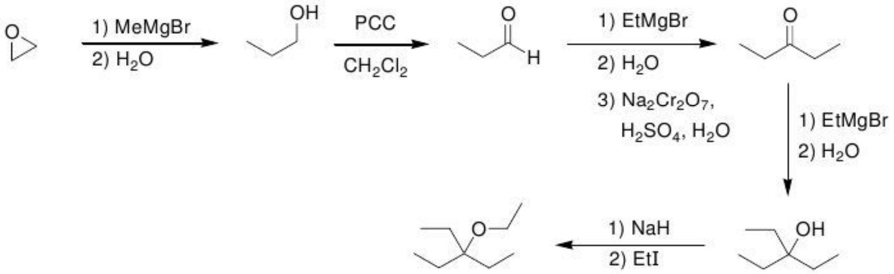
14.27.


H_2
Lindlar's Catalyst
Br_2
Br
Br
1) MCPBA
2) H_3O^+
HO
OH
NaH
O
O

14.28.



14.29.

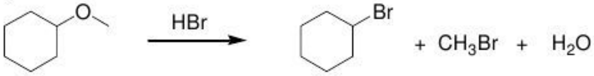


14.30

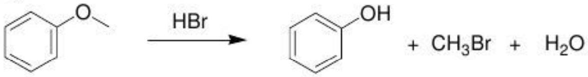
a) (*1S, 2S*)-1-ethoxy-2-methylcyclohexane
b) (*R*)-2-ethoxybutane
c) (S)-3-hexanethiol
d) ethyl propyl sulfoxide
e) (*E*)-2-ethoxy-3-methyl-2-pentene
f) 1,2-dimethoxybenzene
g) ethyl propyl sulfide

14.31

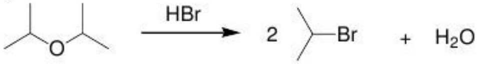
a)



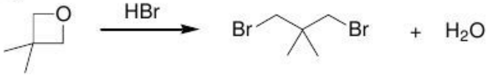
b)



c)

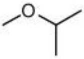


d)

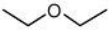


14.32

1-methoxypropane
(methyl propyl ether)



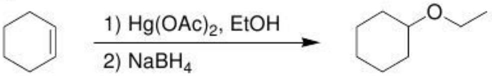
2-methoxypropane
(isopropyl methyl ether)



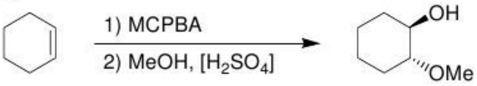
ethoxyethane
(diethyl ether)

14.33

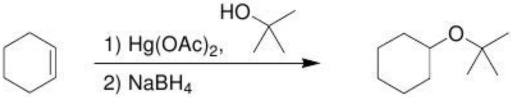
a)



b)



c)



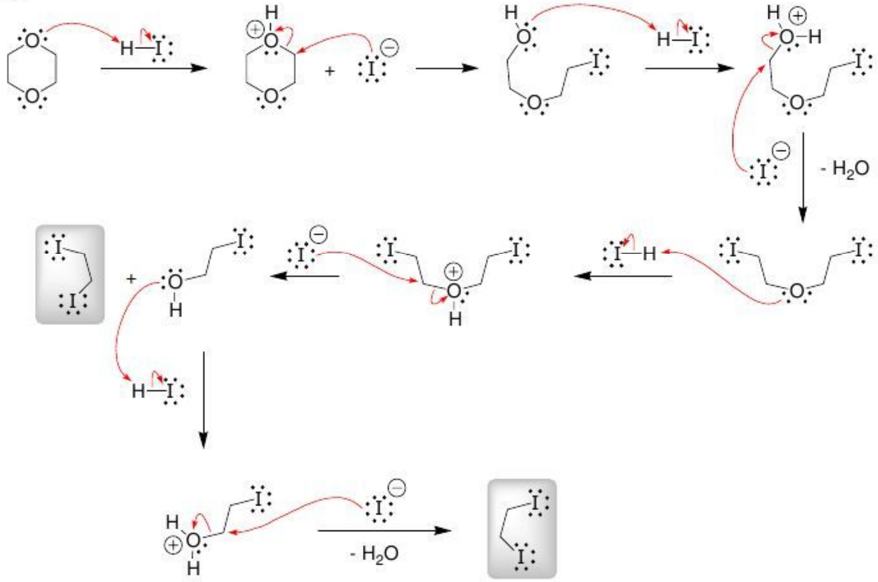
14.34

a)

Compound A

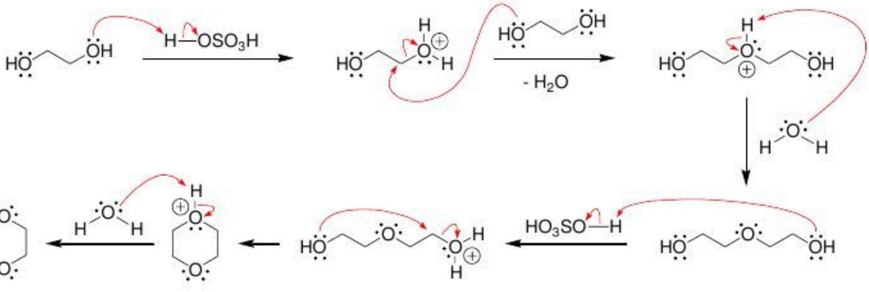
b) Two moles of Compound A are produced for every one mole of 1,4-dioxane.

c)



14.35

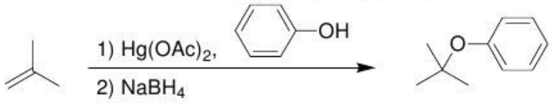
14.36



14.37

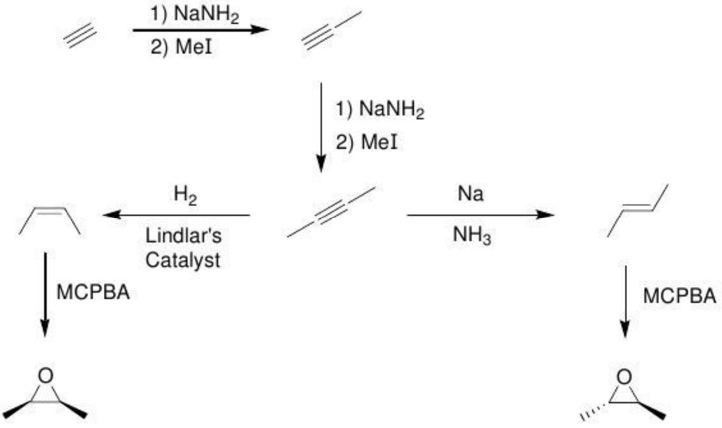
a) Neither alkyl group (on either side of the oxygen atom) can be installed via a Williamson ether synthesis. Installation of the *tert*-butyl group would require a tertiary alkyl halide, which is too sterically hindered to serve as an electrophile for an S_N2 process. Installation of the phenyl group would require an S_N2 reaction taking place at an sp^2 hybridized center, which does not readily occur.

b) Oxymercuration-demercuration can be used to prepare *tert*-butyl phenyl ether:

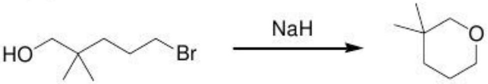


14.38 Ethylene oxide has a high degree of ring strain, and readily functions as an electrophile in an S_N2 reaction. The reaction opens the ring and alleviates the ring strain. Oxetane has less ring strain and is, therefore, less reactive as an electrophile towards S_N2. The reaction can still occur, albeit at a slower rate, to alleviate the ring strain associated with the four membered ring. THF has almost no ring strain (very little) and does not function as an electrophile in an S_N2 reaction.

14.39

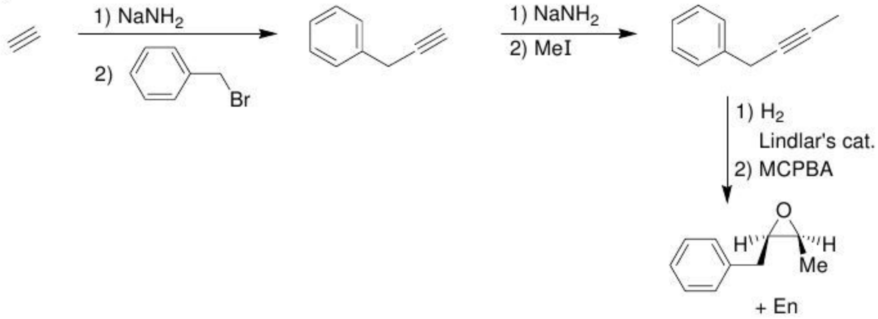


14.40

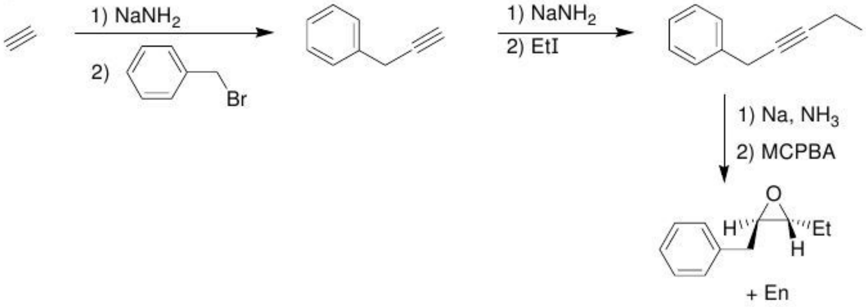


14.41

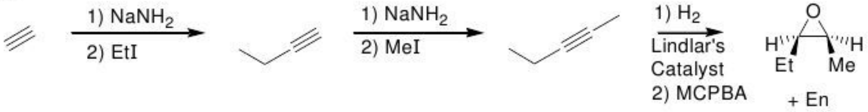
a)


1) NaNH$_2$
2)
Br
1) NaNH$_2$
2) MeI
1) H$_2$
Lindlar's cat.
2) MCPBA
O
H
H
Me
+ En

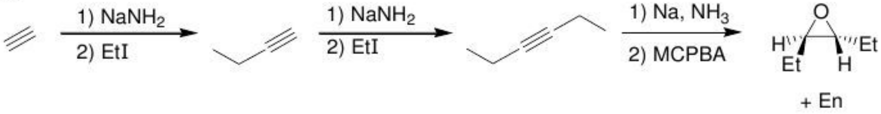
b)


1) NaNH$_2$
2)
Br
1) NaNH$_2$
2) EtI
1) Na, NH$_3$
2) MCPBA
O
H
Et
H
+ En

c)

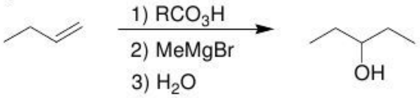

1) NaNH$_2$
2) EtI
1) NaNH$_2$
2) MeI
1) H$_2$
Lindlar's
Catalyst
2) MCPBA
O
H
H
Et
Me
+ En

d)

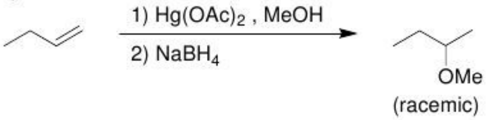

1) NaNH$_2$
2) EtI
1) NaNH$_2$
2) EtI
1) Na, NH$_3$
2) MCPBA
O
H
Et
Et
H
+ En

14.42

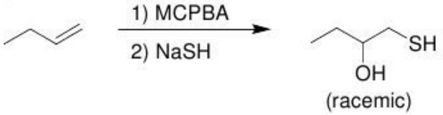
a)



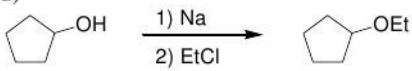
b)



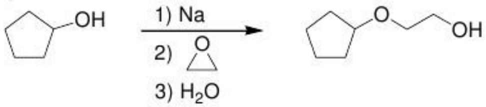
c)



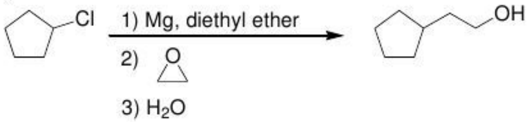
d)



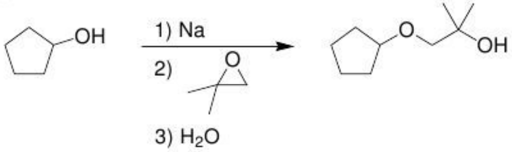
e)



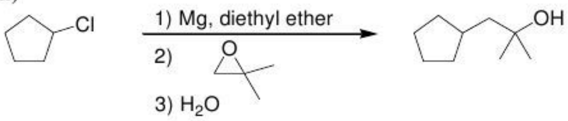
f)



g)

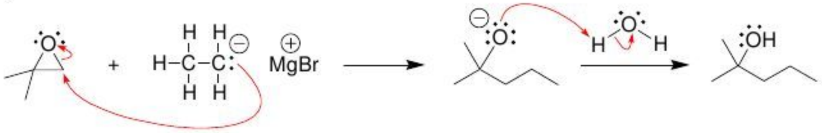


h)

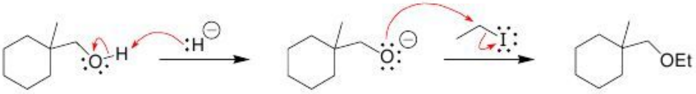


14.43

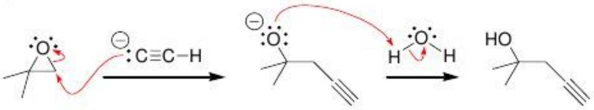
a)



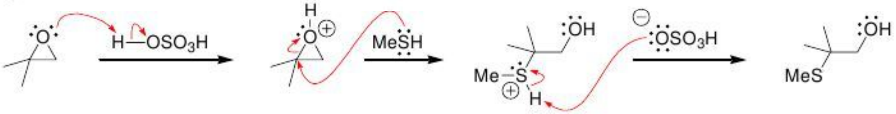
b)



c)

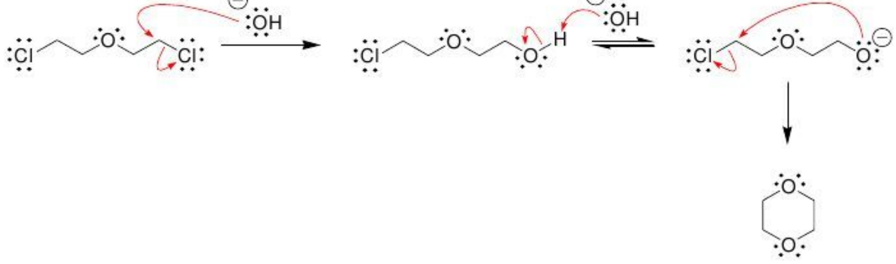


d)

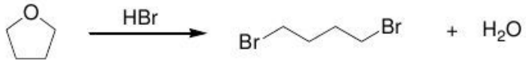


e)

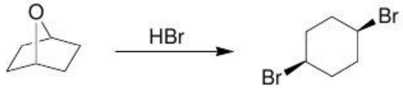
f)



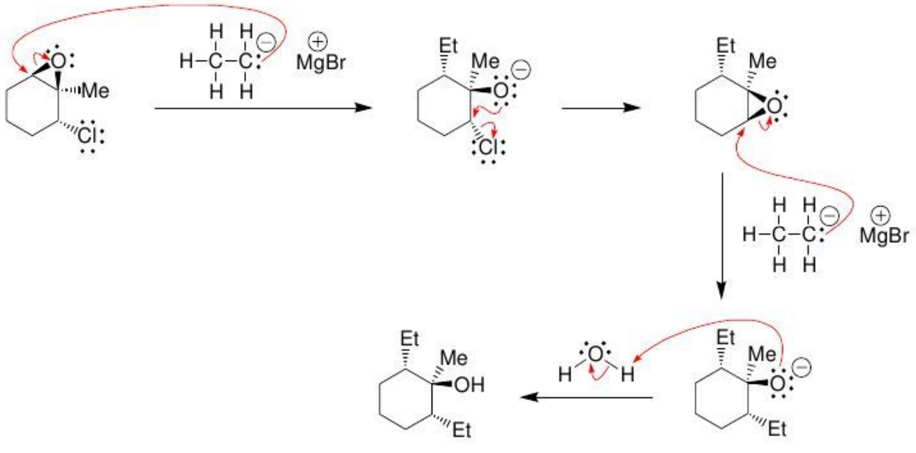
14.44



14.45

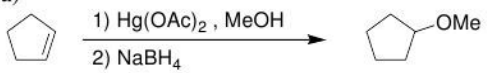


14.46

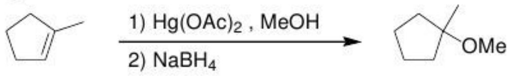


14.47

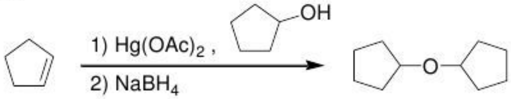
a)



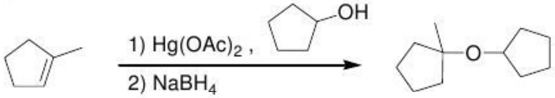
b)



c)

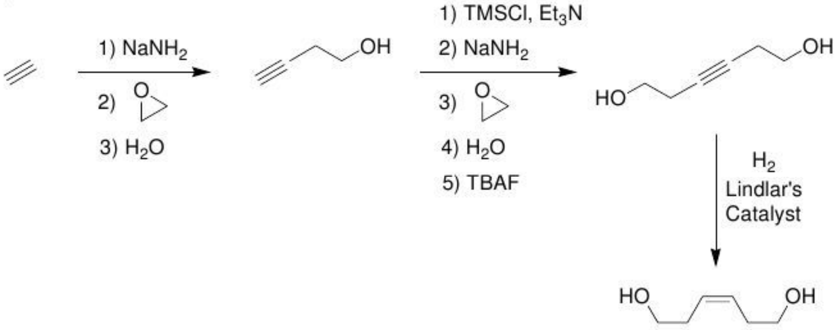

1) Hg(OAc)2 ,
OH
2) NaBH4
O

d)

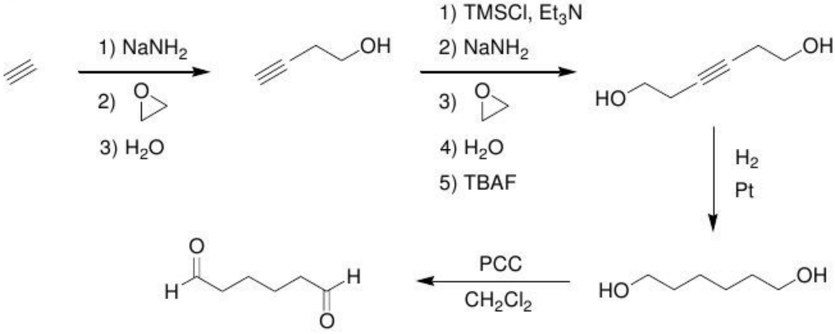

1) Hg(OAc)2 ,
OH
2) NaBH4
O

14.48

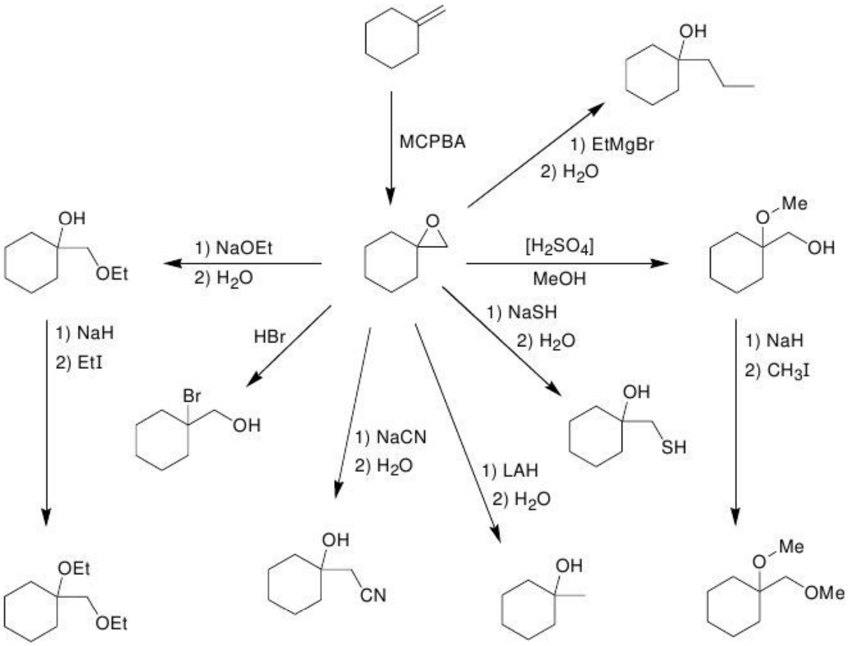
a)


1) NaNH2
2) O
3) H2O
OH
1) TMSCl, Et3N
2) NaNH2
3) O
4) H2O
5) TBAF
HO
OH
H2
Lindlar's
Catalyst
HO
OH

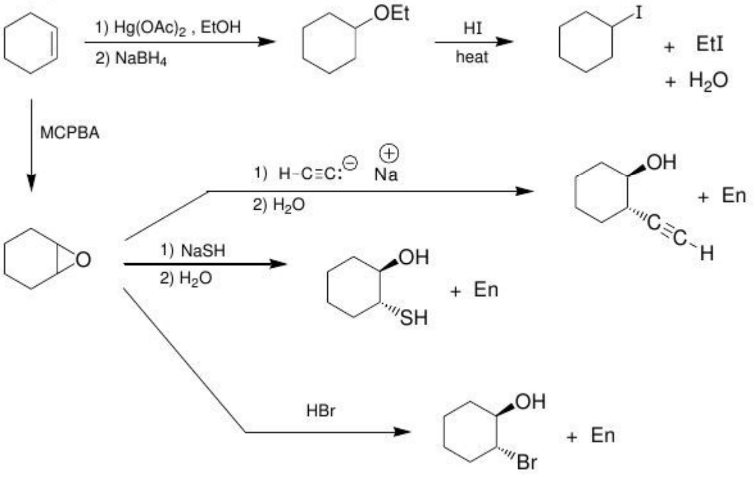
b)


1) NaNH2
2) O
3) H2O
OH
1) TMSCl, Et3N
2) NaNH2
3) O
4) H2O
5) TBAF
HO
OH
H2
Pt
HO
OH
PCC
CH2Cl2
O
H
H
O

14.49

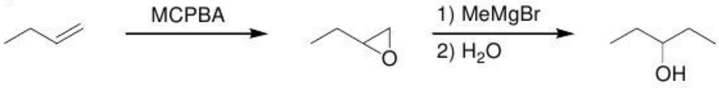

MCPBA
1) EtMgBr
2) H2O
OH
1) NaOEt
2) H2O
OEt
O
[H2SO4]
MeOH
O
Me
OH
1) NaSH
2) H2O
SH
HBr
Br
OH
1) NaCN
2) H2O
CN
1) LAH
2) H2O
1) NaH
2) EtI
OEt
OEt
1) NaH
2) CH3I
OMe

14.50

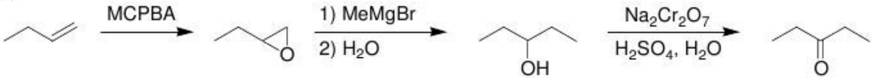

1) Hg(OAc)2 , EtOH
2) NaBH4
OEt
HI
heat
I
+ EtI
+ H2O
MCPBA
O
1) H−C≡C:⊖ ⊕Na
2) H2O
OH
C≡C−H
+ En
1) NaSH
2) H2O
OH
SH
+ En
HBr
OH
Br
+ En

14.51

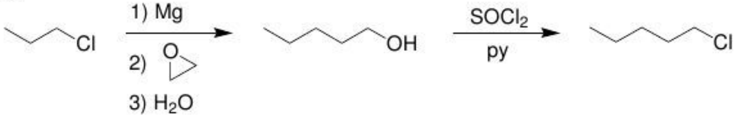
a)



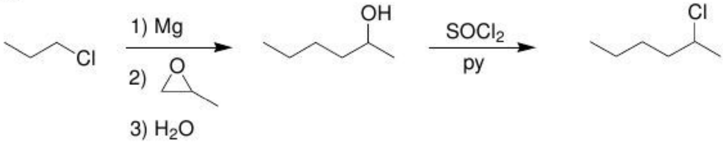
b)



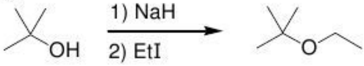
c)



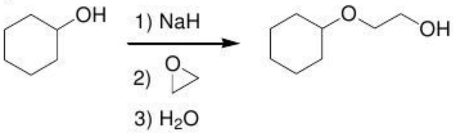
d)



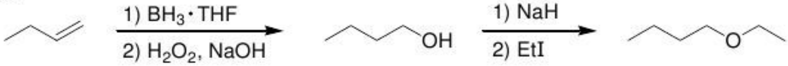
e)



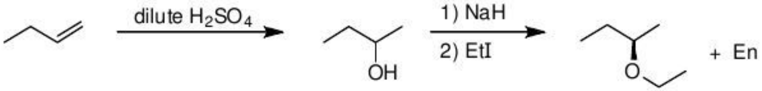
f)



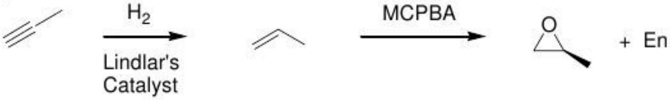
g)



h)


dilute H_2SO_4
OH
1) NaH
2) EtI
O
+ En

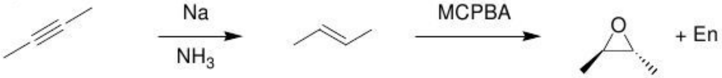
i)


H_2
Lindlar's Catalyst
MCPBA
O
+ En

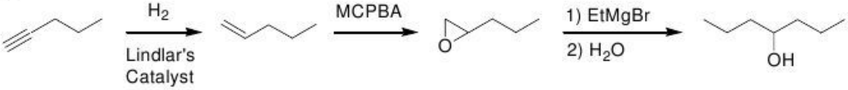
j)


H_2
Lindlar's Catalyst
MCPBA
O

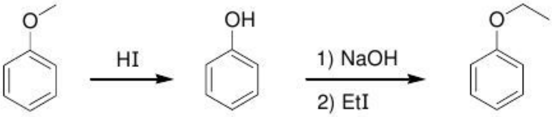
k)


Na
NH_3
MCPBA
O
+ En

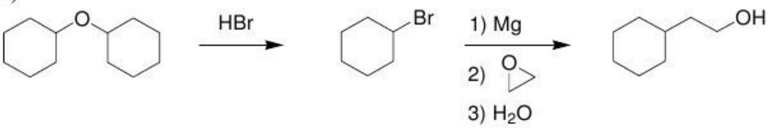
l)


H_2
Lindlar's Catalyst
MCPBA
O
1) EtMgBr
2) H_2O
OH

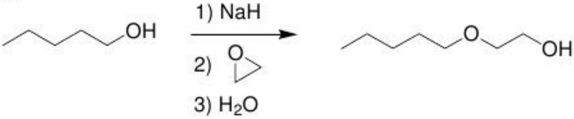
m)


O
HI
OH
1) NaOH
2) EtI
O

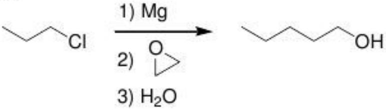
n)


O
HBr
Br
1) Mg
2) O
3) H_2O
OH

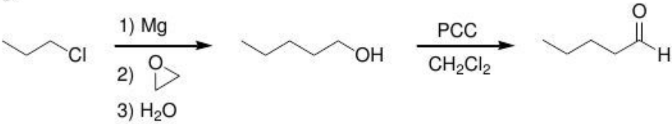
o)


OH
1) NaH
2) O
3) H_2O
O
OH

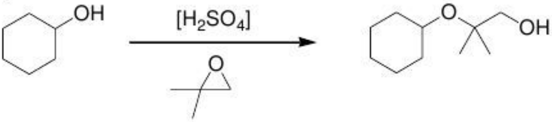
p)


Cl
1) Mg
2) O
3) H_2O
OH

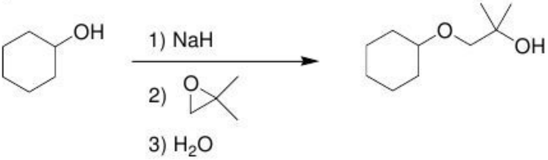
q)


Cl
1) Mg
2) O
3) H_2O
OH
PCC
CH_2Cl_2
O
H

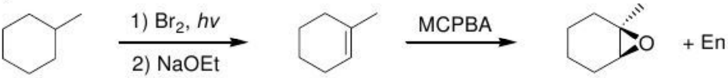
r)


OH
[H_2SO_4]
O
O
OH

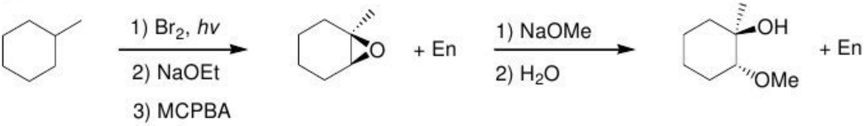
s)


OH
1) NaH
2) O
3) H_2O
O
OH

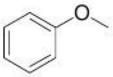
t)


1) Br_2, *hv*
2) NaOEt
MCPBA
O
+ En

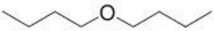
u)


1) Br_2, *hv*
2) NaOEt
3) MCPBA
O
+ En
1) NaOMe
2) H_2O
OH
OMe
+ En

14.52.

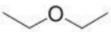


14.53.

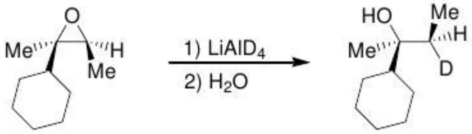


14.54.

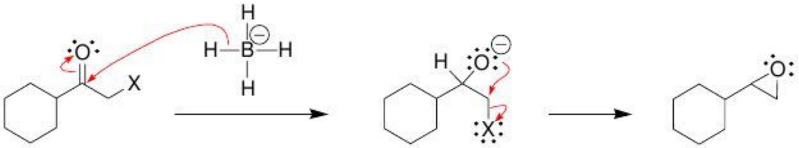
14.55.



14.56

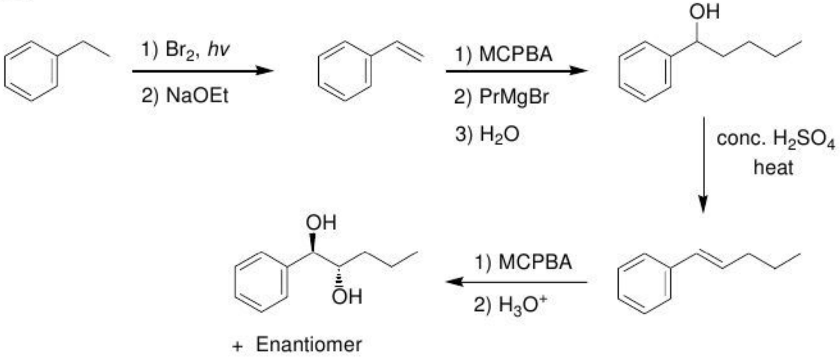


14.57

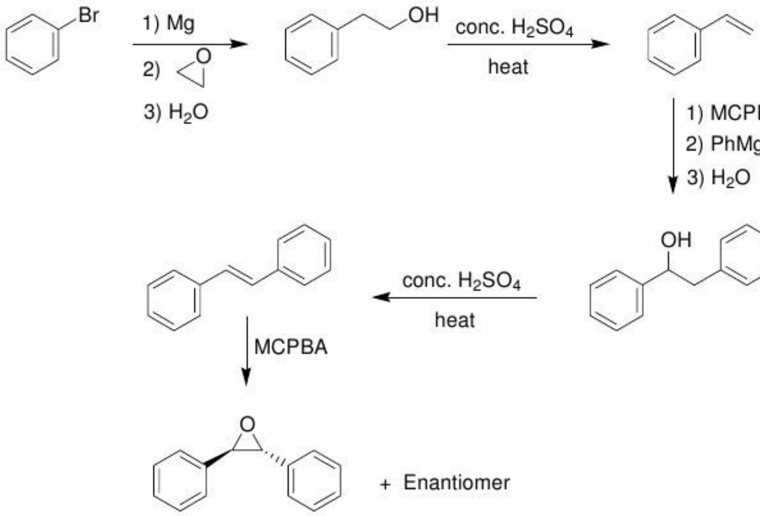


14.58 When methyloxirane is treated with HBr, the regiochemical outcome is determined by a competition between steric and electronic factors, with steric factors prevailing – the Br is positioned at the less substituted position. However, when phenyloxirane is treated with HBr, electronic factors prevail in controlling the regiochemical outcome. Specifically, the position next to the phenyl group is a benzylic position and can stabilize a large partial positive charge. In such a case, electronic factors are more powerful than steric factors, and the Br is positioned at the more substituted position.

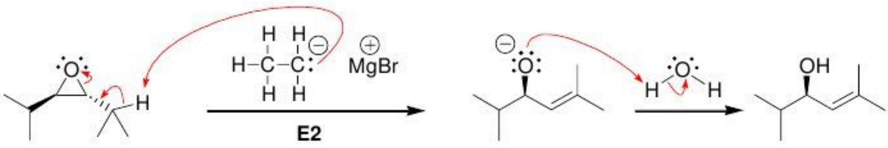
14.59.



14.60



14.61 Since the Grignard reagent is both a strong base and a strong nucleophile, substitution and elimination can both occur. Indeed, they compete with each other. As we discussed in Chapter 8, elimination will be favored when the substrate is secondary. Both electrophilic positions in this epoxide are secondary, and so, elimination predominates:



Chapter 15
Infrared Spectroscopy and Mass Spectrometry

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 15. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- **Spectroscopy** is the study of the interaction between _______ and ________.
- The difference in energy (ΔE) between vibrational energy levels is determined by the nature of the bond. If a photon of light possesses exactly this amount of energy, the bond can absorb the photon to promote a __________________ **excitation**.
- IR spectroscopy can be used to identify which _____________________ are present in a compound.
- The location of each signal in an IR spectrum is reported in terms of a frequency-related unit called _________________.
- The wavenumber of each signal is determined primarily by bond __________ and the __________ of the atoms sharing the bond.
- The intensity of a signal is dependent on the ______________ of the bond giving rise to the signal.
- __________________ C=C bonds do not produce signals.
- Primary amines exhibit two signals resulting from ___________ **stretching** and _____________ **stretching**.
- **Mass spectrometry** is used to determine the ___________________ and _________________________ of a compound.
- **Electron impact ionization** (**EI**) involves bombarding the compound with high energy ________________, generating a radical cation that is symbolized by (M)$^{+\bullet}$ and is called the **molecular ion**, or the __________ **ion**.
- Only the molecular ion and the cationic fragments are deflected, and they are then separated by their ____________________ (*m/z*).
- The tallest peak in a mass spectrum is assigned a relative value of 100% and is called the __________ **peak**.
- The relative heights of the (M)$^{+\bullet}$ peak and the (M+1)$^{+\bullet}$ peak indicates the number of ___________________.
- A signal at M-15 indicates the loss of a _________ group; a signal at M-29 indicates the loss of an _________ group.
- ______________ alkanes have a molecular formula of the form C_nH_{2n+2}.
- Each double bond and each ring represents one **degree of** _______________.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 15. The answers appear in the section entitled *SkillBuilder Review*.

15.1 Analyzing an IR Spectrum

STEP 1 *- LOOK FOR ____________ BONDS BETWEEN 1600 AND 1850* ***GUIDELINES:*** *C=O BONDS PRODUCE _______ SIGNALS* *C=C BONDS GENERALLY PRODUCE _____ SIGNALS. SYMMETRICAL C=C BONDS DO NOT APPEAR AT ALL*	***STEP 2*** *- LOOK FOR __________ BONDS BETWEEN 2100 AND 2300* ***GUIDELINES:*** *________________ TRIPLE BONDS DO NOT PRODUCE SIGNALS*	***STEP 3*** *- LOOK FOR ________ BONDS BETWEEN 2750 AND 4000* ***GUIDELINES:*** *DRAW A LINE AT 3000, AND LOOK FOR ________ OR __________ C-H BONDS TO THE LEFT OF THE LINE* *THE SHAPE OF AN O-H SIGNAL IS AFFECTED BY ____________________ (DUE TO H-BONDING)* *PRIMARY AMINES EXHIBIT TWO N-H SIGNALS (___________ AND ___________ STRETCHING)*

15.2 Distinguishing Two Compounds Using IR Spectroscopy

STEP 1 *- WORK METHODICALLY THROUGH THE EXPECTED ____________________ OF EACH COMPOUND*	***STEP 2*** *- DETERMINE IF ANY _________ WILL BE PRESENT FOR ONE COMPOUND BUT ABSENT FOR THE OTHER*	***STEP 3*** *- FOR EACH EXPECTED SIGNAL, COMPARE FOR ANY POSSIBLE DIFFERENCES IN __________, ______________, OR ______________.*

15.3 Using the Relative Abundance of the $(M+1)^{+\bullet}$ Peak to Propose a Molecular Formula

STEP 1 *- FILL IN THE BOXES BELOW TO COMPLETE THE FORMULA THAT CAN BE USED TO DETERMINE THE NUMBER OF CARBON ATOMS IN A COMPOUND USING MASS SPECTROMETRY:* $\dfrac{\left(\dfrac{\text{abundance of } \boxed{} \text{ Peak}}{\text{abundance of } \boxed{} \text{ Peak}}\right) \times 100\%}{1.1\ \%}$	***STEP 2*** *- ANALYZE THE MASS OF THE MOLECULAR ION TO DETERMINE IF ANY _______________ ARE PRESENT.*

15.4 Calculating HDI

STEP 1 *- REWRITE THE MOLECULAR FORMULA "AS IF" THE COMPOUND HAD NO ELEMENTS OTHER THAN C AND H, USING THE FOLLOWING RULES:* *- ADD ONE H FOR EACH ____________* *- IGNORE ALL ____________ ATOMS* *- SUBTRACT ONE H FOR EACH ______________*	***STEP 2*** *- DETERMINE WHETHER ANY H'S ARE MISSING. EVERY TWO H'S REPRESENTS ONE DEGREE OF UNSATURATION:* $C_4H_9Cl \longrightarrow$ *HDI = _____* $C_4H_8O \longrightarrow$ *HDI = _____* $C_4H_9N \longrightarrow$ *HDI = _____*

Solutions

15.1.

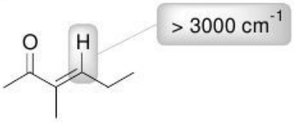
a) Increasing wavenumber ←

C−H C≡C C=C

b) Increasing wavenumber ←

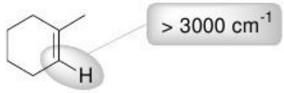
C−H C−C

15.2.

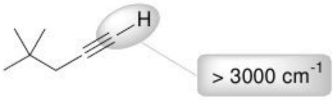
a) 

b) No

c) No

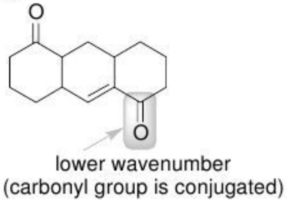
d) 

e) No

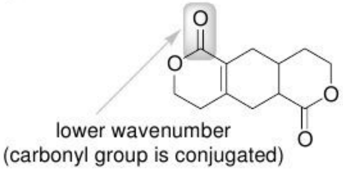
f) 

15.3.

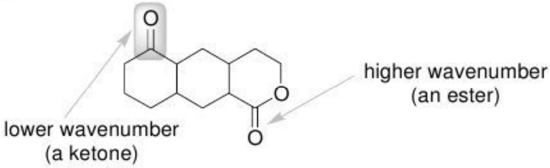
a)



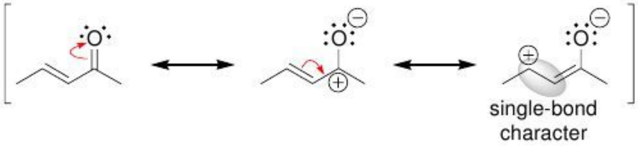
b)



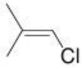
c)

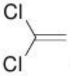


15.4. The C=C bond in the conjugated compound produces a signal at lower wavenumber because it has some single bond character, as seen in the third resonance structure below:

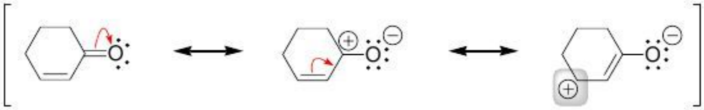


15.5.

a)  The presence of the Cl will cause the C=C bond in this compound to have a larger dipole moment than the C=C bond in the other compound.

b)  The C=C bond in this compound will have a larger dipole moment than the C=C bond in the other compound.

15.6. The C=C bond in 2-cyclohexenone has a large dipole moment, as can be rationalized with the third resonance structure below:



15.7. The vinylic C-H bond should produce a signal above 3000 cm^{-1}.

15.8. The narrow signal is produced by the O-H stretching in the absence of hydrogen bonding effect. The broad signal is produced by O-H stretching when hydrogen bonding is present. Hydrogen bonding effectively lowers the bond strength of the O-H bonds, because each hydrogen atom is slightly pulled away from the oxygen to which it is connected. A longer bond length (albeit temporary) corresponds with a weaker bond, which corresponds with a lower wavenumber.

15.9.

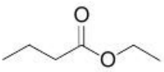
a) ROH b) neither c) RCO_2H d) neither e) ROH f) RCO_2H

15.10.
a) ketone b) RCO_2H c) R_2NH d) RNH_2 e) ROH f) ketone

15.11. The C_{sp^3}—H bonds can stretch symmetrically, asymmetrically, or in a variety of ways with respect to each other. Each one of these possible stretching modes is associated with a different wavenumber of absorption.

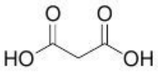
15.12.

a)


b)


c)


d)


e)


f)


15.13.
1) The O-H bond of the carboxylic acid moiety (expected to be 2200 - 3600 cm^{-1})
2) The vinylic C-H bond (expected to be ~ 3100 cm^{-1})
3) All other C-H bonds (expected to be <3000 cm^{-1})
4) The C=O bond of the carboxylic acid moiety (expected to be ~ 1720 cm^{-1})
5) The C=C bond (expected to be ~ 1650 cm^{-1})

15.14.
a) The starting material is an alcohol and is expected to produce a typical signal for an O-H stretch –a broad signal between 3200 - 3600 cm^{-1}. In contrast, the product is a carboxylic acid and is expected to produce an even broader O-H signal (2200 - 3600 cm^{-1}) as a result of more extensive hydrogen bonding. Alternatively, the product can be differentiated from the starting material by looking for a signal at around 1720 cm^{-1}. The product has a C=O bond and should exhibit this signal. The starting material lacks a C=O bond and will not show a signal at 1720 cm^{-1}.

b) The starting material is secondary amine and is expected to produce a typical signal for an N-H stretch at around 3400 cm^{-1}. In contrast, the product is a tertiary amine and is not expected to produce a signal above 3000 cm^{-1}.

c) The starting material is an unsymmetrical alkyne and is expected to produce a signal at around 2200 cm^{-1}. In contrast, the product is an unsymmetrical alkene and is expected to produce a signal at around 1600 cm^{-1}. Also, the product has vinylic C-H bonds that are absent in the starting material. The product is expected to have a signal at around 3100 cm^{-1}, and the starting material will have no signal in that region.

d) The C≡C bond in the starting material and the C=C bond in the product are both symmetrical and will not produce signals. However the product has vinylic C-H bonds that are absent in the starting material. The product is expected to have a signal at around 3100 cm^{-1}, and the starting material will have no signal in that region.

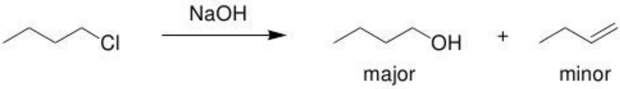
e) The starting material will have two signals in the double-bond region: one for the C=O bond and one for the C=C bond. The product only has one signal in the double-bond region. It only has the signal for the C=O bond, which is now at higher wavenumber because it is no longer in conjugation.

15.15. The starting material has a cyano group (C≡N) and is expected to produce a signal at around 2200 cm^{-1}. In contrast, the product is a carboxylic acid and is expected to produce a broad signal from 2200 – 3600 cm^{-1}, as well as a signal at 1720 cm^{-1} for the C=O bond.

15.16. The C≡C bond in the starting material (1-butyne) is unsymmetrical and produces a signal at 2200 cm^{-1}, corresponding with the C≡C stretch. In contrast, the C≡C bond in the product (3-hexyne) is symmetrical and does not produce a signal at 2200 cm^{-1}.

15.17. The starting material should have a C=O signal at 1720 cm^{-1}, while the product should have an O-H signal at 3200 – 3600 cm^{-1}.

15.18. 1-chlorobutane is primary substrate. When treated with sodium hydroxide, substitution is expected to dominate over elimination (see Chapter 8), but both products are expected to be obtained:



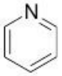
The substitution product is an alcohol and should have a broad signal from 3200 – 3600 cm^{-1}. The elimination product is an unsymmetrical alkene and is expected to give a C=C signal at approximately 1650 cm^{-1}, as well as a vinylic C-H signal at 3100 cm^{-1}.

15.19.

a) m/z = 68

m/z = 66

b) m/z = 78



m/z = 79

15.20.
a) This compound does not have any nitrogen atoms. According to the nitrogen rule, this compound should have an even molecular weight (*m/z* = 86).
b) This compound does not have any nitrogen atoms. According to the nitrogen rule, this compound should have an even molecular weight (*m/z* = 100).
c) This compound has one nitrogen atom. According to the nitrogen rule, this compound should have an odd molecular weight (*m/z* = 101).
d) This compound has two nitrogen atoms. According to the nitrogen rule, this compound should have an even molecular weight (*m/z* = 102).

15.21.
a) There must be four carbon atoms, and the molecular weight must be 72. The molecular formula could be C_4H_8O.

b) There must be four carbon atoms, and the molecular weight must be 68. The molecular formula could be C_4H_4O.

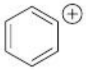
c) There must be four carbon atoms, and the molecular weight must be 54. The molecular formula could be C_4H_6.

d) There must be seven carbon atoms, and the molecular weight must be 96. The molecular formula could be C_7H_{12}.

15.22. Each nitrogen atom in the molecular formula of a compound should contribute 0.37% to the $(M+1)^{+\bullet}$ peak. Three nitrogen atoms therefore contribute the same amount (1.1%) as one carbon atom. A compound with molecular formula $C_8H_{11}N_3$ should have an $(M+1)^{+\bullet}$ peak that is 9.9% as tall as the molecular ion peak. If the molecular ion peak is 24% of the base peak, then the $(M+1)^{+\bullet}$ peak must be 2.4% of the base peak.

15.23.
a) This fragment is M – 79, which is formed by loss of a Br. So the fragment does not contain Br.

b)

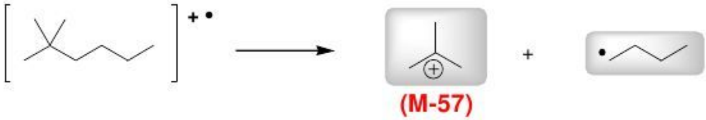


15.24.

a) There is not a significant $(M+2)^{+\bullet}$ peak, so neither bromine nor chlorine are present.
b) There is not a significant $(M+2)^{+\bullet}$ peak, so neither bromine nor chlorine are present.
c) The $(M+2)^{+\bullet}$ peak is approximately equivalent in height to the molecular ion peak, indicating the presence of a bromine atom.
d) The $(M+2)^{+\bullet}$ peak is approximately one-third as tall as the molecular ion peak, indicating the presence of a chlorine atom.

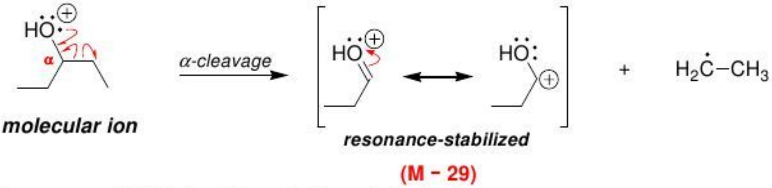
15.25.

a)

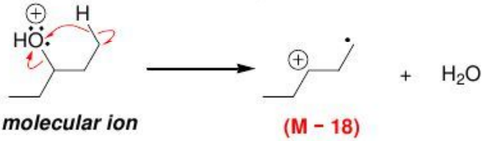


b) This carbocation is tertiary, and its formation is favored over the other possible secondary and primary carbocations.
c) They readily fragment to produce tertiary carbocations.
d) M-15 corresponds with loss of a methyl group. Indeed, loss of methyl group would also produce a tertiary carbocation, but at the expense of forming a methyl radical. That pathway is less favorable.

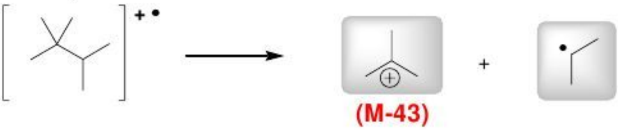
15.26. A fragment at M-29 should result from α cleavage:



and a fragment at M-18 should result from dehydration:

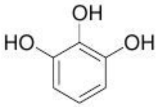


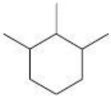
15.27. The fragment at M-43 is expected to be the base peak because it corresponds with formation of a tertiary carbocation:

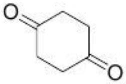


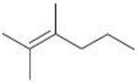
15.28. In the first spectrum, the base peak appears at M-29, signifying the loss of an ethyl group. This spectrum is likely the mass spectrum of ethylcyclohexane. The second spectrum has a base peak at M-15, signifying the loss of a methyl group. The second spectrum is likely the mass spectrum of 1,1-dimethylcyclohexane.

15.29.









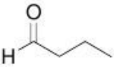
a) $m/z = 126.0315$ $m/z = 126.1404$ b) $m/z = 112.0522$ $m/z = 112.1248$

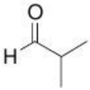
15.30.
a) The first compound should have a very broad signal between 3200 and 3600 cm^{-1}, corresponding with O-H stretching. The second compound will not have such a signal.
b) The first compound should have a pair of strong signals around 1720 cm^{-1}, corresponding with symmetric and asymmetric stretching of the C=O bonds. In contrast, the second compound will have a weak signal at around 1650cm^{-1}, corresponding to the C=C bond.

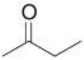
15.31.
a) 2 b) 1 c) 2 d) 1 e) 1
f) 1 g) 4 h) 0 i) 1 j) 0

15.32. Both $C_3H_5ClO_2$ and C_3H_6 have one degree of unsaturation.

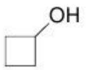
15.33. The compound has one degree and unsaturation, which is a C=O bond:. The following are all of the possible structures that have molecular formula C_4H_8O and contain a C=O bond:

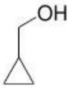


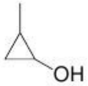




15.34. The compound must have one degree of unsaturation. The broad signal between 3200-3600 cm^{-1} indicates an OH group, and the absence of signals between 1600 and 1850 cm^{-1} indicates the absence of a double bond (either a C=O bond or an unsymmetrical C=C bond). This implies the presence of a ring (to achieve one degree of unsaturation). Below are possible structures:







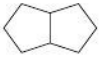
(Four possible stereoisomers)

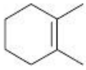
15.35. A signal at 2200cm^{-1} signifies the presence of a C≡C bond. There are only two possible constitutional isomers: 1-butyne or 2-butyne. The latter is symmetrical and would not produce a signal at 2200cm^{-1}. The compound must be 1-butyne.

15.36. The compound has exactly one degree of unsaturation, which means that it must contain either one ring or one double bond.

15.37.

a) HDI = 1 HDI = 1

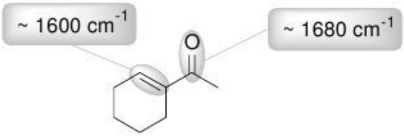


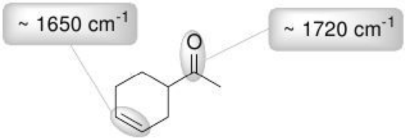


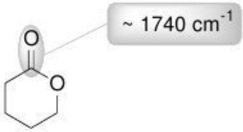
b) HDI = 2 HDI = 2

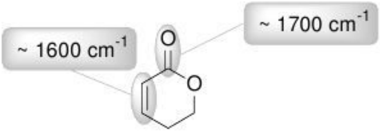
c) HDI = 2 HDI = 1

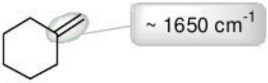
15.38.

a) 

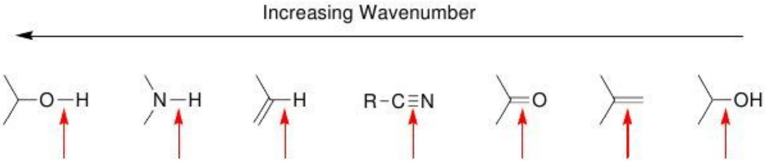
b) 

c) 

d) 

e) 

15.39.



15.40.

a) The C=N bond and the C=O bond should each produce a signal in the double bond region, 1600 - 1850 cm^{-1}

b) The C=C bond should produce a signal in the double bond region, 1600 - 1850 cm^{-1}

c) The C=C bond and the C=O bond should each produce a signal in the double bond region, 1600 - 1850 cm^{-1}, In addition, the two C≡C bonds should produce two signals around 2200 cm^{-1}, and the C*sp*-H bond should produce a signal around 3300 cm^{-1}.
d) The C=O bond should produce a signal in the double bond region, 1720 cm^{-1}, and the O-H of the carboxylic acid moiety should produce a very broad signal from 2200 – 3600 cm^{-1}.

15.41.
a) The reactant should have signals at 1650 cm^{-1} and 3100 cm^{-1}, while the product should not have either signals.

b) The reactant should have a broad signal from 3200 - 3600 cm^{-1}, while the product should lack this signal and instead should have a signal at ~ 1720 cm^{-1}.

c) The C=O bond of an ester should appear at higher wavenumber (~1740 cm^{-1}) than the C=O bond of a ketone (~1720 cm^{-1}).

d) The reactant should have signals at 1650 cm^{-1} and 3100 cm^{-1}, while the products should both have a signal at ~ 1720 cm^{-1}.

e) The reactant should not have signals at 1650 cm^{-1} or 3100 cm^{-1}, while the product should have such signals.

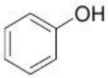
15.42.
a) a C=O signal at ~ 1720 cm^{-1}
b) a C=O signal at ~ 1680 cm^{-1} (conjugated) and a C=C signal at ~ 1600 cm^{-1} (conjugated) and a C*sp*^{2}-H signal at 3100 cm^{-1}.
c) a C=O signal at ~ 1720 cm^{-1} and a C=C signal at ~ 1650 cm^{-1} and a C*sp*^{2}-H signal at 3100 cm^{-1}.
d) a C=C signal at ~ 1650 cm^{-1} and an O-H signal at ~ 3200 – 3600 cm^{-1} and a C*sp*^{2}-H signal at 3100 cm^{-1}.
e) a C=O signal at ~ 1720 cm^{-1} and an O-H signal at ~ 2200 – 3600 cm^{-1}
f) a C=O signal at ~ 1720 cm^{-1} and an O-H signal at ~ 3200 – 3600 cm^{-1}

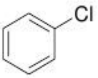
15.43.
a) C_7H_8 (m/z = 92)
b) C_6H_6O (m/z = 94)
c) $C_6H_{10}O$ (m/z = 98)
d) C_6H_8O (m/z = 96)
e) $C_6H_{15}N$ (m/z = 101)

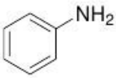
15.44. $C_5H_{10}O$

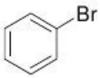
15.45. There are nine carbon atoms in the compound (10 / 1.1).

15.46.

a) 

b) 

c) 

d) 

15.47.

a) an OH group and double bonds.

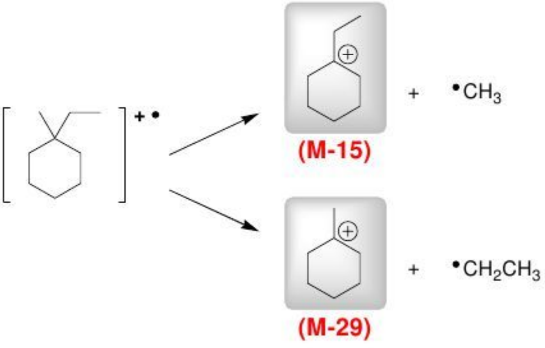
b) $$\frac{3.9\,\%}{27.2\,\%} \times 100\% = 14.3\%$$

$$\#\text{ of C} = \frac{14.3\,\%}{1.1\,\%} = 13$$

c) $C_{13}H_{24}O$ has thirteen carbon atoms and two degrees of unsaturation, consistent with the information that there are two double bonds.

15.48.
a) Both compounds are C_6H_{12}
b) Both compounds have an HDI of 1.
c) No, both compounds have exactly six carbon atoms and twelve hydrogen atoms, so they should have the same *m/z* even with high resolution mass spectrometry.
d) The IR spectrum of the alkene would have a signal at ~ 1650 cm^{-1} for the C=C bond and another signal at ~ 3100 cm^{-1} for the vinylic C-H bond. The IR spectrum of cyclohexane lacks both of these signals.

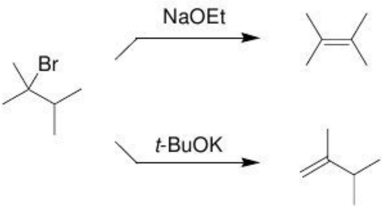
15.49. The signal at $m/z = 111$ is (M-15) which corresponds with loss of a methyl group. The signal at $m/z = 97$ is (M-29) which corresponds with loss of an ethyl group. Both fragmentations lead to a tertiary carbocation:



15.50.

a) No, because this fragment does not contain the bromine atom.
b) Yes, because this fragment still contains the bromine atom.
c) Yes, because this fragment still contains the bromine atom.

15.51. The more substituted alkene will not produce a signal at 1650 cm^{-1} nor will it produce a signal at 3100 cm^{-1}. The less substituted alkene will display both signals in its IR spectrum:

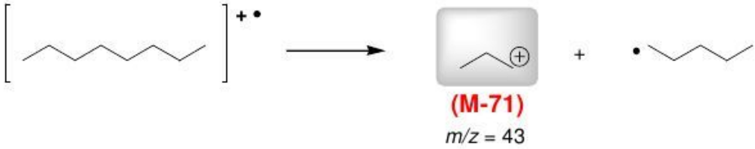


15.52.

a) C_5H_6
b) C_4H_6O

15.53.

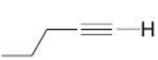
a) the molecular ion peak appears at m/z= 114
b) the base peak appears at m/z= 43
c)



15.54.

a) 2
b) 2
c) 2
d) 36
e) 4
f) 4
g) 5
h) 1
i) 4
j) 1

15.55

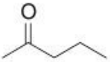


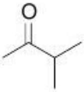
15.56. Limonene has three degrees of unsaturation and is comprised of only carbon and hydrogen atoms. The molecular weight is 136, so the molecular formula of limonene must be $C_{10}H_{16}$.

15.57. The IR spectrum of *trans*-3-hexene is expected to have a signal at 3100 cm^{-1} as a result of the vinylic C-H stretch. In contrast, 2,3-dimethyl-2-butene lacks a vinylic C-H group and does not exhibit that signal.

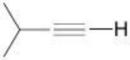
15.58. The compound exhibits intramolecular hydrogen bonding even in dilute solutions.

15.59. The IR spetrum indicates that the compound is a ketone. The mass spectrum indicates a molecular weight of 86. The base peak is at M-43, indicating the loss of a propyl group. The compound likely has a three carbon chain (either a propyl group or isopropyl group) on one side of the ketone:

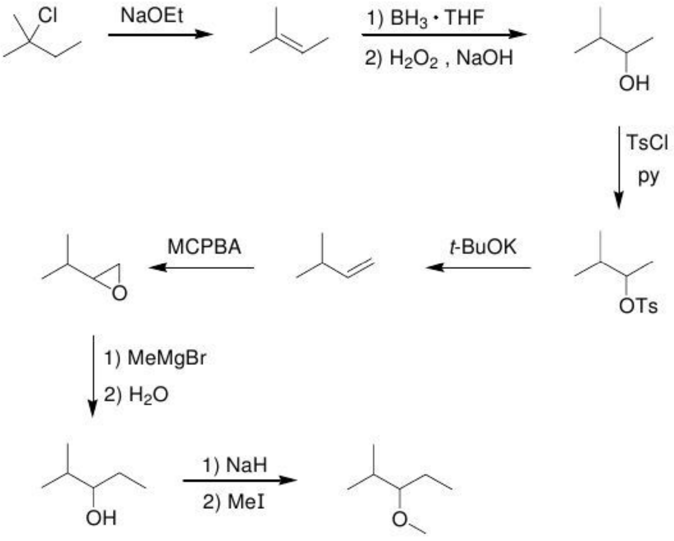




15.60. The IR spectrum indicates the presence of a triple bond as well as a C-H bond indicating that the triple bond is terminal. The mass spectrum indicates a molecular weight of 68. The following two structures are consistent with these data:



15.61.



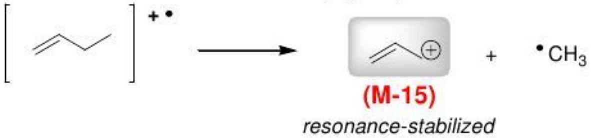
a) Compound F is an alcohol and its IR spectrum will exhibit a broad signal between 3200 and 3600 cm^{-1}. Compound G is an ether and its IR spectrum will not exhibit the same signal.

b) Compound D is an alkene and its IR spectrum will exhibit a signal at approximately 1650 cm^{-1} (for the C=C bond), as well as a signal at 3100 cm^{-1} (for vinylic C-H stretching). Compound E is an epoxide and its IR spectrum will not have these two signals.

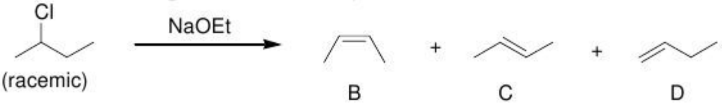
c) IR spectroscopy would not be helpful to distinguish these two compounds because they are both alcohols. Mass spectrometry could be used to differentiate these two compounds because they have different molecular weights.

d) No, they both have the same molecular formula, although a trained expert might be able to distinguish these compounds based on their fragmentation patterns.

15.62. 1-butene can lose a methyl group to form a resonance stabilized carbocation

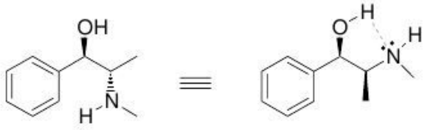


15.63. Yes, compound D is an unsymmetrical alkene:

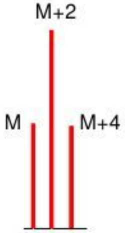


15.64.

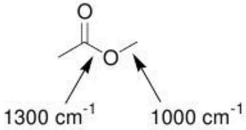
15.65. The OH group in ephedrine can engage in intramolecular hydrogen bonding, even in dilute solutions.



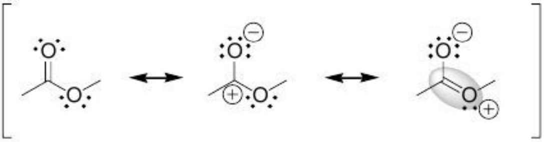
15.66.



15.67.



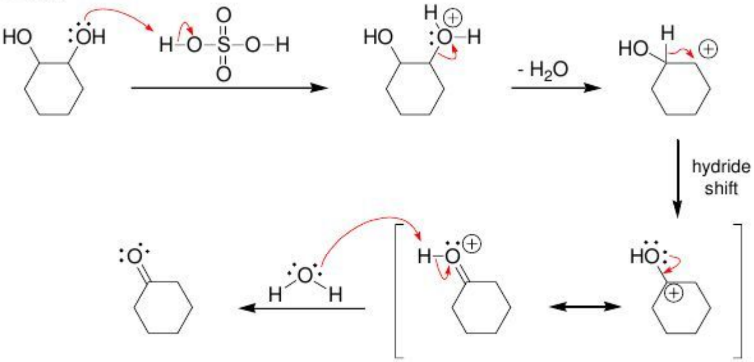
Explanation #1) One of the C-O bonds of the ester has some double bond character, as can be seen in the third resonance structure below:



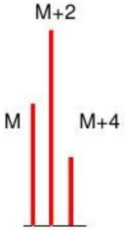
This C-O bond is a stronger bond than the other C-O single bond, which does not have any double bond character. As a result, the stronger C-O bond (highlighted above) appears at higher wavenumber.

Explanation #2) The C-O bond at 1300 cm^{-1} involves an sp^2 hybridized carbon atom, rather than an sp^3 hybridized carbon atom. The former has more *s*-character and holds its electrons closer to the positively charged nucleus. A $C_{sp^2}-O$ bond is therefore stronger than a $C_{sp^3}-O$ bond.

15.68.



15.69.



Chapter 16
Nuclear Magnetic Resonance Spectroscopy

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 16. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

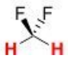
- A spinning proton generates a **magnetic** _____________, which must align either with or against an imposed external magnetic field.
- All protons do not absorb the same frequency because of ___________________, a weak magnetic effect due to the motion of surrounding electrons that either **shield** or **deshield** the proton.
- ________________ solvents are generally used for acquiring NMR spectra.
- In a ^{1}H NMR spectrum, each signal has three important characteristics: location, area and shape.
- When two protons are interchangeable by rotational symmetry, the protons are said to be ___________.
- When two protons are interchangeable by rotational symmetry, the protons are said to be ___________.
- The left side of an NMR spectrum is described as _____**field**, and the right side is described as _____**field**.
- In the absence of inductive effects, a methyl group (CH$_3$) will produce a signal near _____ppm, a **methylene group** (CH$_2$) will produce a signal near _____, and a __________ **group** (CH) will produce a signal near _____. The presence of nearby groups increases these values somewhat predictably.
- The _______________, or area under each signal, indicates the number of protons giving rise to the signal.
- _______________represents the number of peaks in a signal. A __________has one peak, a __________has two, a __________has three, a __________has four, and a __________has five.
- Multiplicity is the result of **spin-spin splitting**, also called __________, which follows **the n+1 rule**.
- When signal splitting occurs, the distance between the individual peaks of a signal is called the **coupling constant**, or _____ **value**, and is measured in Hz.
- Complex splitting occurs when a proton has two different kinds of neighbors, often producing a __________.
- ^{13}C is an __________of carbon, representing _____% of all carbon atoms.
- All ^{13}C-^{1}H splitting is suppressed with a technique called **broadband** ______________, causing all of the ^{13}C signals to collapse to ___________.

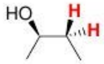
Review of Skills

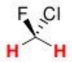
Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 16. The answers appear in the section entitled *SkillBuilder Review*.

16.1 Determining the Relationship between Two Protons in a Compound

FOR EACH OF THE FOLLOWING COMPOUNDS, IDENTIFY THE RELATIONSHIP BETWEEN THE TWO INDICATED PROTONS (ARE THEY HOMOTOPIC, ENANTIOPTOPIC OR DIASTEREOTOPIC?) AND DETERMINE WHETHER THEY ARE CHEMICALLY EQUIVALENT.





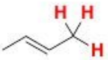


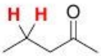
RELATIONSHIP

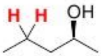
CHEMICALLY EQUIVALENT?

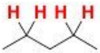
16.2 Identifying the Number of Expected Signals in a ^{1}H NMR Spectrum

FOR EACH OF THE FOLLOWING COMPOUNDS, DETERMINE WHETHER THE TWO INDICATED PROTONS ARE CHEMICALLY EQUIVALENT.





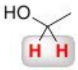




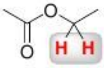
CHEMICALLY EQUIVALENT?

16.3 Predicting Chemical Shifts

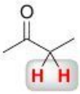
FOR EACH OF THE FOLLOWING COMPOUNDS, PREDICT THE EXPECTED CHEMICAL SHIFT OF THE INDICATED PROTONS.



ppm



ppm



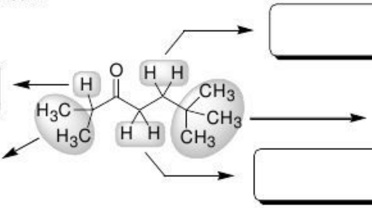
ppm

16.4 Determining the Number of Protons Giving Rise to a Signal

STEP 1 *- COMPARE THE RELATIVE ________________ VALUES, AND CHOOSE THE LOWEST NUMBER*	***STEP 2*** *- DIVIDE ALL INTEGRATION VALUES BY THE NUMBER FROM STEP #1, WHICH GIVES THE RATIO OF ____________*	***STEP 3*** *- IDENTIFY THE NUMBER OF PROTONS IN THE COMPOUND (FROM THE MOLECULAR FORMULA) AND THEN ADJUST THE RELATIVE INTEGRATION VALUES SO THAT THE SUM TOTAL EQUALS THE NUMBER OF ________________________________.*

16.5 Predicting the Multiplicity of a Signal

IDENTIFY THE EXPECTED MULTIPLICITY FOR EACH SIGNAL IN THE PROTON NMR SPECTRUM OF THE FOLLOWING COMPOUND.



16.6 Drawing the Expected ^{1}H NMR Spectrum of a Compound

STEP 1 *- IDENTIFY THE NUMBER OF ___________*	***STEP 2*** *- PREDICT THE __________ ___________ OF EACH SIGNAL*	***STEP 3*** *- DETERMINE THE ___________ OF EACH SIGNAL BY COUNTING THE NUMBER OF ________ GIVING RISE TO EACH SIGNAL*	***STEP 4*** *- PREDICT THE ________________ OF EACH SIGNAL*	***STEP 5*** *- DRAW EACH SIGNAL*

16.7 Using ^{1}H NMR Spectroscopy to Distinguish Between Compounds

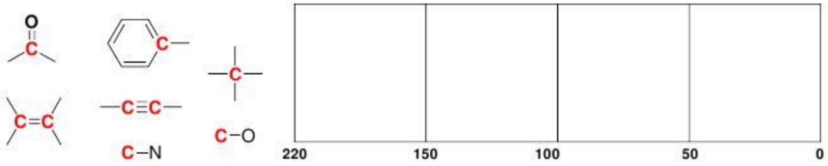
STEP 1 *- IDENTIFY THE NUMBER OF ______________ THAT EACH COMPOUND WILL PRODUCE.*	***STEP 2*** *- IF EACH COMPOUND IS EXPECTED TO PRODUCE THE SAME NUMBER OF SIGNALS, THEN DETERMINE THE ______________, ______________, AND ______________ OF EACH SIGNAL IN BOTH COMPOUNDS*	***STEP 3*** *- LOOK FOR DIFFERENCES IN THE CHEMICAL SHIFTS, MULTIPLICITIES OR INTEGRATION VALUES OF THE EXPECTED SIGNALS*

16.8 Analyzing a ^{1}H NMR Spectrum and Proposing the Structure of a Compound

STEP 1 *- USE THE __________ __________ TO DETERMINE THE HDI. AN HDI OF _____ INDICATES THE POSSIBILITY OF AN AROMATIC RING*	***STEP 2*** *- CONSIDER THE NUMBER OF SIGNALS AND INTEGRATION OF EACH SIGNAL (GIVES CLUES ABOUT THE ______________ OF THE COMPOUND)*	***STEP 3*** *- ANALYZE EACH SIGNAL (____, ____, AND ____), AND THEN DRAW FRAGMENTS CONSISTENT WITH EACH SIGNAL. THESE FRAGMENTS BECOME OUR PUZZLE PIECES THAT MUST BE ASSEMBLED TO PRODUCE A MOLECULAR STRUCTURE*	***STEP 4*** *- ASSEMBLE THE FRAGMENTS*

16.9 Predicting the Number of Signals and Approximate Location of Each Signal in a ^{13}C NMR Spectrum

BELOW ARE SEVEN DIFFERENT TYPES OF CARBON ATOMS. EACH OF THEM IS EXPECTED TO PRODUCE A SIGNAL IN ONE OF FOUR POSSIBLE REGIONS IN A CARBON NMR SPECTRUM. IDENITFY THE EXPECTED REGION FOR EACH TYPE OF CARBON ATOM.



16.10 Determining Molecular Structure using DEPT ^{13}C NMR Spectroscopy

COMPLETE THE FOLLOWING CHART BY DRAWING THE EXPECTED SHAPE OF EACH SIGNAL:

	CH_3	CH_2	CH	C
BROADBAND DECOUPLED				
DEPT-90				
DEPT-135				

Solutions

16.1.

a) homotopic
b) enantiotopic
c) diastereotopic
d) enantiotopic
e) homotopic

16.2.

a) All four protons can be interchanged either via rotation or reflection.
b) The three protons of a methyl group are always equivalent, and in this case, the two methyl groups are equivalent to each other because they can be interchanged by rotation. Therefore, all six protons are equivalent.
c) Three
d) Three
e) Six

16.3.

16.4.

a) 8 b) 4 c) 2 d) 3 e) 5 f) 3

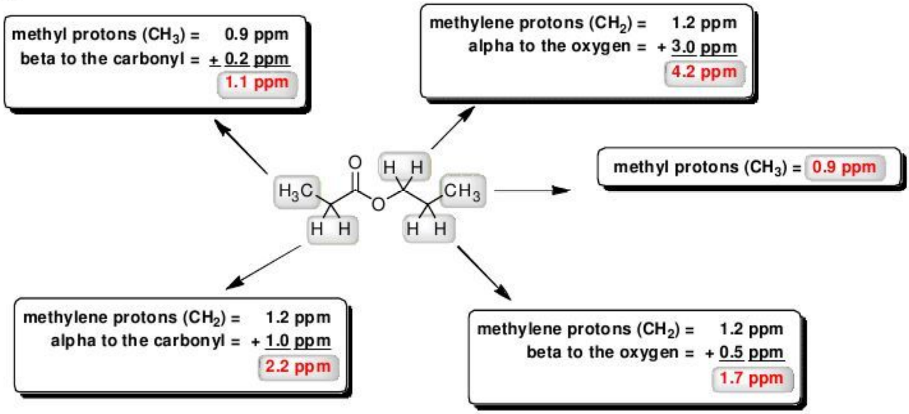
g) 4 h) 2 i) 4 j) 7 k) 4 l) 7

16.5. The presence of the bromine atom does not render C3 a chirality center because there are two ethyl groups connected to C3. Nevertheless, the presence of the bromine atom does prevent the two protons at C2 from being interchangeable by reflection. The replacement test gives a pair of diastereomers, so the protons are diastereotopic.

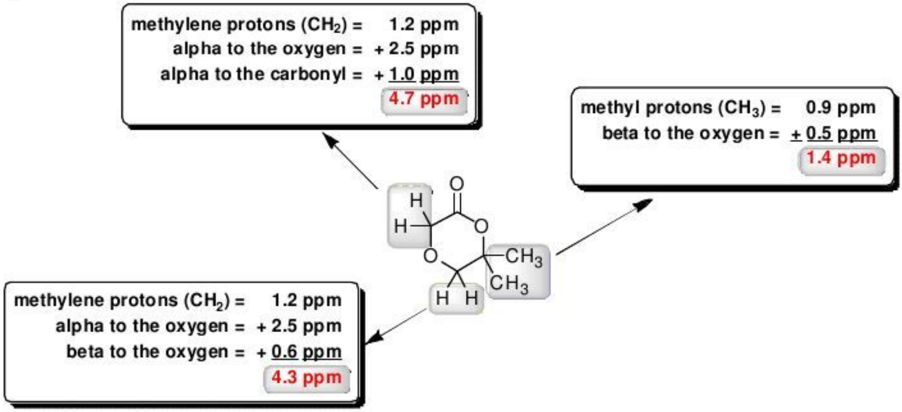
16.6. This compound will exhibit two signals in its ^{1}H NMR spectrum:

16.7.

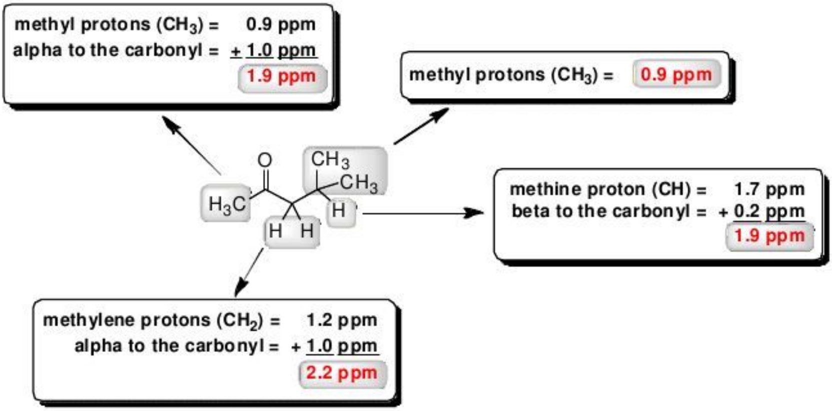
a)


methyl protons (CH_3) = 0.9 ppm
beta to the carbonyl = + 0.2 ppm
1.1 ppm
methylene protons (CH_2) = 1.2 ppm
alpha to the oxygen = + 3.0 ppm
4.2 ppm
methyl protons (CH_3) = 0.9 ppm
H_3C
O
H H
O
CH_3
H H
H H
methylene protons (CH_2) = 1.2 ppm
alpha to the carbonyl = + 1.0 ppm
2.2 ppm
methylene protons (CH_2) = 1.2 ppm
beta to the oxygen = + 0.5 ppm
1.7 ppm

b)


methylene protons (CH_2) = 1.2 ppm
alpha to the oxygen = + 2.5 ppm
alpha to the carbonyl = + 1.0 ppm
4.7 ppm
methyl protons (CH_3) = 0.9 ppm
beta to the oxygen = + 0.5 ppm
1.4 ppm
H
H
O
O
O
CH_3
CH_3
H H
methylene protons (CH_2) = 1.2 ppm
alpha to the oxygen = + 2.5 ppm
beta to the oxygen = + 0.6 ppm
4.3 ppm

c)



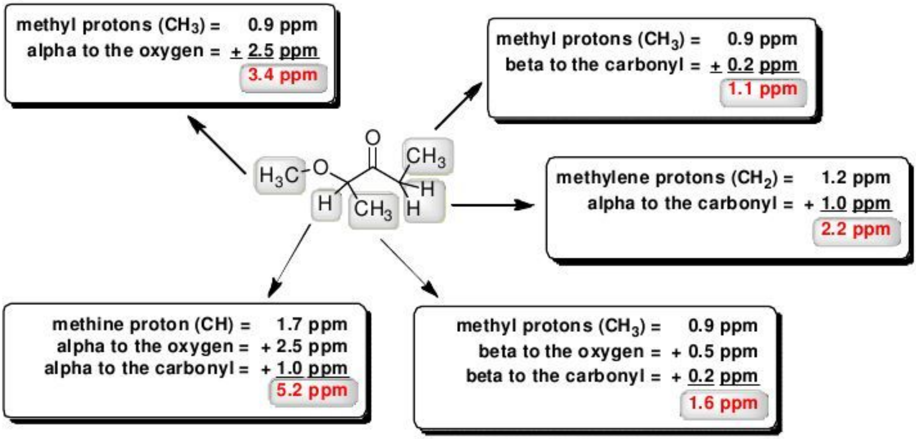
methyl protons (CH_3) = 0.9 ppm
alpha to the carbonyl = + 1.0 ppm
1.9 ppm

methyl protons (CH_3) = 0.9 ppm

methine proton (CH) = 1.7 ppm
beta to the carbonyl = + 0.2 ppm
1.9 ppm

methylene protons (CH_2) = 1.2 ppm
alpha to the carbonyl = + 1.0 ppm
2.2 ppm

d)



methyl protons (CH_3) = 0.9 ppm
alpha to the oxygen = + 2.5 ppm
3.4 ppm

methyl protons (CH_3) = 0.9 ppm
beta to the carbonyl = + 0.2 ppm
1.1 ppm

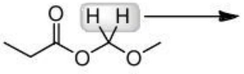
methylene protons (CH_2) = 1.2 ppm
alpha to the carbonyl = + 1.0 ppm
2.2 ppm

methine proton (CH) = 1.7 ppm
alpha to the oxygen = + 2.5 ppm
alpha to the carbonyl = + 1.0 ppm
5.2 ppm

methyl protons (CH_3) = 0.9 ppm
beta to the oxygen = + 0.5 ppm
beta to the carbonyl = + 0.2 ppm
1.6 ppm

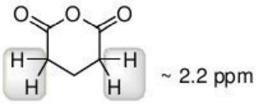
e) All four methylene groups are equivalent, so the compound will have only one signal in its ^1H NMR spectrum. That signal is expected to appear at approximately (1.2 + 2.5 + 0.5) = 4.2 ppm.

16.8.

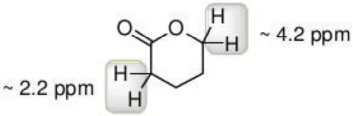


methylene protons (CH_2) = 1.2 ppm
alpha to the oxygen = + 3.0 ppm
alpha to the oxygen = + 2.5 ppm
6.7 ppm

16.9.



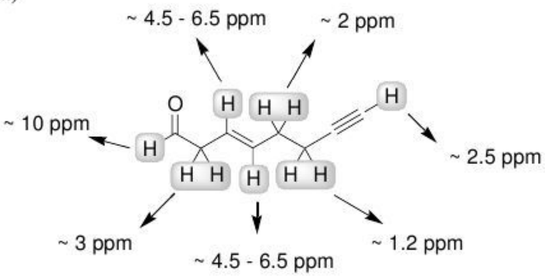
Only one signal downfield of 2.0 ppm
(the four highlighted protons are equivalent)



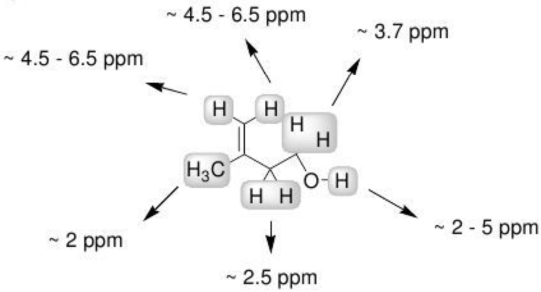
Two signals downfield of 2.0 ppm

16.10.

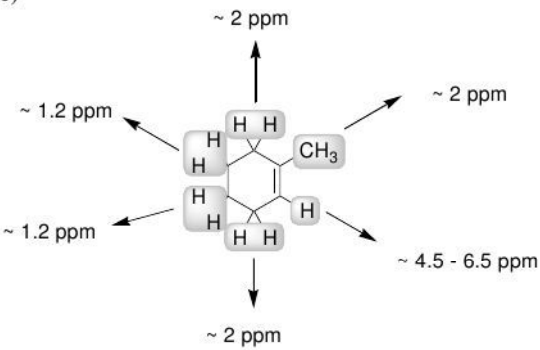
a)



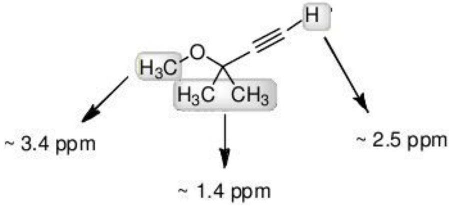
b)



c)



d)



16.11.

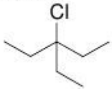
The signal at 4.0 ppm represents two protons.
The signal at 2.0 ppm represents three protons.
The signal at 1.6 ppm represents two protons.
The signal at 0.9 ppm represents three protons.

16.12.

The signal at 9.6 ppm represents one proton.
The signal at 7.5 ppm represents five protons.
The signal at 7.3 ppm represents one proton.
The signal at 2.1 ppm represents three protons.

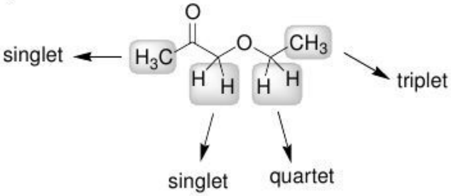
16.13. Each signal represents two protons.

16.14.

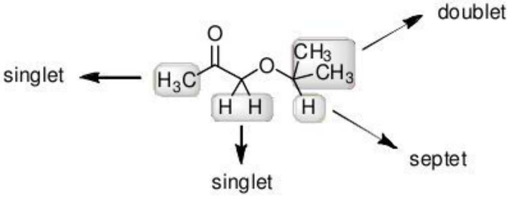


16.15.

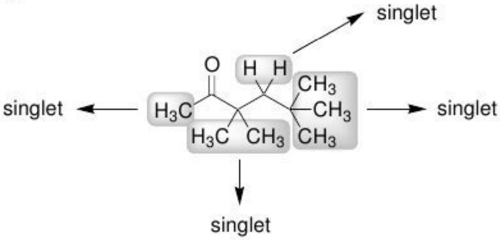
a)


singlet
triplet
singlet
quartet

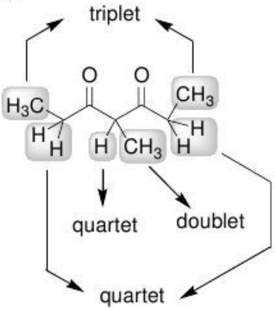
b)


doublet
singlet
septet
singlet

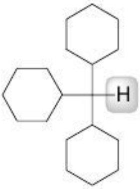
c)


singlet
singlet
singlet
singlet

d)


triplet
quartet
doublet
quartet

16.16.



16.17.

a) The spectrum exhibits the characteristic pattern of an isopropyl group.

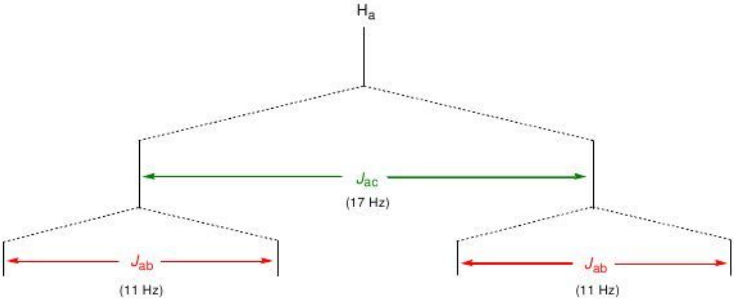
b) The spectrum exhibits the characteristic pattern of an isopropyl group as well as the characteristic pattern of an ethyl group.

c) The spectrum exhibits the characteristic pattern of a *tert*-butyl group.

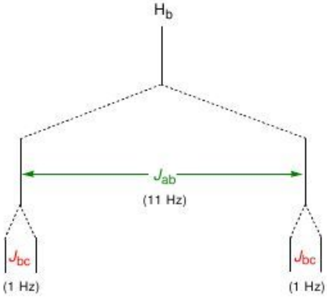
d) The spectrum does not exhibit the characteristic pattern of an ethyl group, an isopropyl group, or a *tert*-butyl group.

16.18.

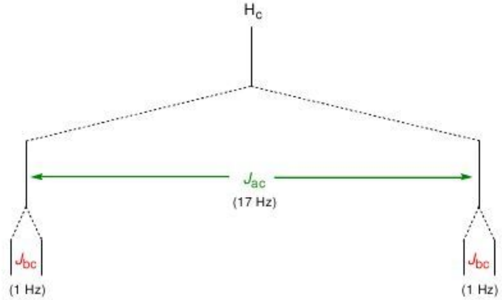
a)



b)

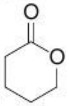


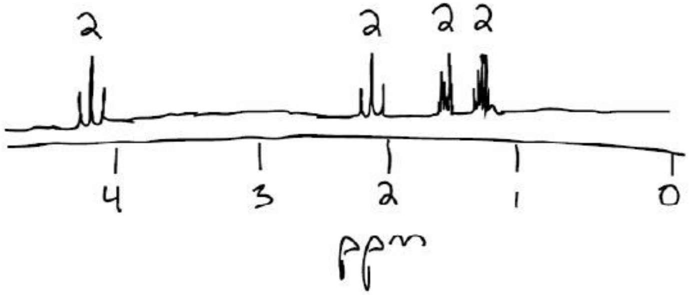
c)



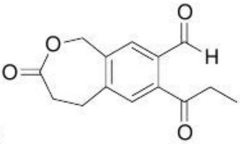
16.19. Draw the expected ^{1}H NMR spectrum for each of the following compounds

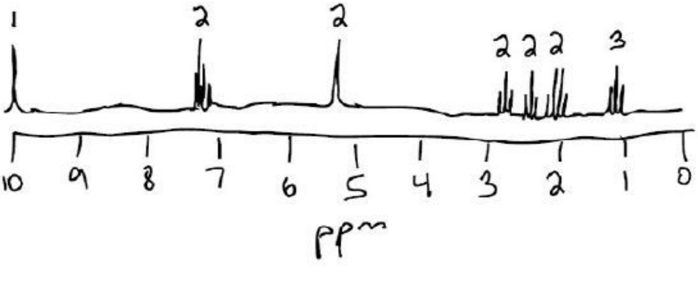
a)



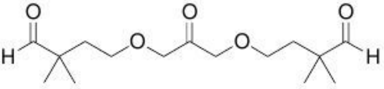


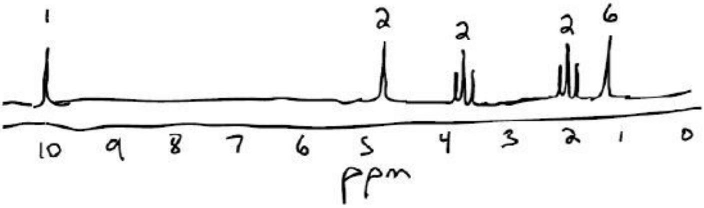
b)



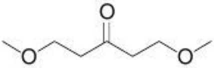


c)





16.20.



16.21.

a) The first compound will have only three signals in its ^{1}H NMR spectrum, while the second compound will have six signals.

b) Both compounds will exhibit ^{1}H NMR spectra with only two singlets. In each spectrum, the relative integration of the two singlets is 1:3. In the first compound, the singlet with the smaller integration value will be at approximately 2 ppm. In the second compound, the singlet with the smaller integration value will be at approximately 4 ppm.

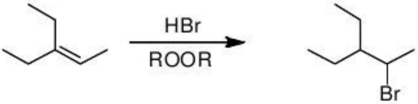
d) The first compound will have only two signals in its ^{1}H NMR spectrum, while the second compound will have three signals.

e) The first compound will have five signals in its ^{1}H NMR spectrum, while the second compound will have only three signals.

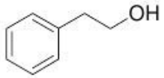
f) The first compound will have only four signals in its ^{1}H NMR spectrum, while the second compound will have five signals.

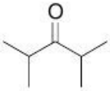
g) The first compound will have only one signal in its ^{1}H NMR spectrum, while the second compound will have two signals.

16.22. The presence of peroxides caused an *anti*-Markovnikov addition of HBr:

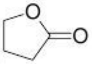


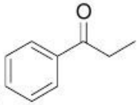
16.23.

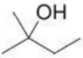
a)


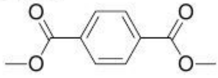
b)


c)


d)


e)


f)


16.24.


16.25.

a) Four signals. Three appear in the region 0 – 50 ppm, and the fourth signal (the C=O) appears in the region 150 – 220 ppm.

b) Five signals. All five appear in the region 0 – 50 ppm.

c) Six signals. Two appear in the region 0 – 50 ppm, and four signals appear in the region 100-150 ppm.

d) Nine signals. Two appear in the region 0 – 50 ppm, one appears in the region 50 – 100 ppm and six signals appear in the region 100 – 150 ppm.

e) Seven signals. Two appear in the region 0 – 50 ppm, one appears in the region 50 – 100 ppm and four signals appear in the region 100 – 150 ppm.

f) Five signals. Three appear in the region 0 – 50 ppm and two signals appear in the region 100 – 150 ppm.

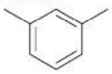
g) Seven signals. Five appear in the region 0 – 50 ppm and two signals appear in the region 100 – 150 ppm.

h) Two signals. One appears in the region 0 – 50 ppm and the other appears in the region 100 – 150 ppm.

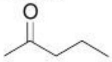
i) One signal appears in the region 50 – 100.
j) Five signals. One appears in the region 0 – 50 ppm, one appears in the region 50 – 100 ppm, two appear in the region 100-150, and one signal appears in the region 150 – 200 ppm.

16.26. The first compound lacks a chirality center. The two methyl groups are enantiotopic and are therefore chemically equivalent. The second compound has a chirality center (the position bearing the OH group). As such, the two methyl groups are diastereotopic and are therefore not chemically equivalent. For this reason, the ^{13}C NMR spectrum of the second compound exhibits six signals, rather than five.

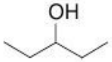
16.27.



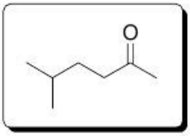
16.28.



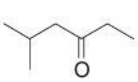
16.29.



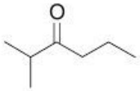
16.30.



Consistent with
^{1}H NMR and ^{13}C NMR spectra



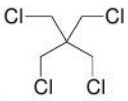
Consistent only with
^{13}C NMR spectrum

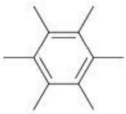


Consistent only with
^{13}C NMR spectrum

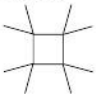
16.31.

a) 

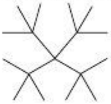
b) 

c) 

16.32.



16.33. This compound will exhibit three signals in its ^{13}C NMR spectrum:



16.34.

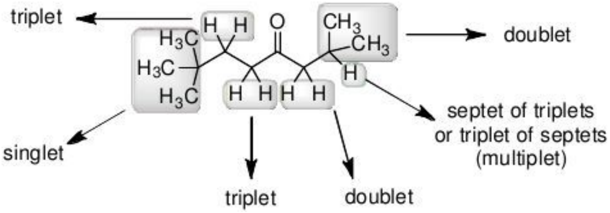
a) 2 b) 4 c) 4 d) 2 e) 2 f) 5

16.35.

a) 4 b) 6 c) 6 d) 4 e) 2 f) 4

16.36. The first compound will have five signals in its ^{13}C NMR spectrum, while the second compound will have seven signals.

16.37.



16.38.

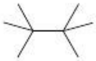
a) The first compound will have four signals in its ^{13}C NMR spectrum, while the second compound will have twelve signals.
The first compound will have two signals in its ^{1}H NMR spectrum, while the second compound will have eight signals.

b) The first compound is a meso compound. Two of the protons are enantiotopic (the protons that are alpha to the chlorine atoms) and are therefore chemically equivalent. The first compound will only have two signals in its ^{1}H NMR spectrum, while the second compound will have three signals. For a similar reason, first compound will only have two signals in its ^{13}C NMR spectrum, while the second compound will have three signals.

c) The ^{13}C NMR spectrum of the second compound will have one more signal than the ^{13}C NMR spectrum of the other first compound. The ^{1}H NMR spectra will differ in the following way: the first compound will have a singlet somewhere between 2 and 5 ppm with an integration of 1, while the second compound will have a singlet at approximately 3.4 ppm with an integration of 3.

d) The first compound will have three signals in its ^{13}C NMR spectrum, while the second compound will have five signals.
The first compound will have two signals in its ^{1}H NMR spectrum, while the second compound will have four signals.

16.39. This compound will exhibit two signals in its ^{13}C NMR spectrum:



16.40.

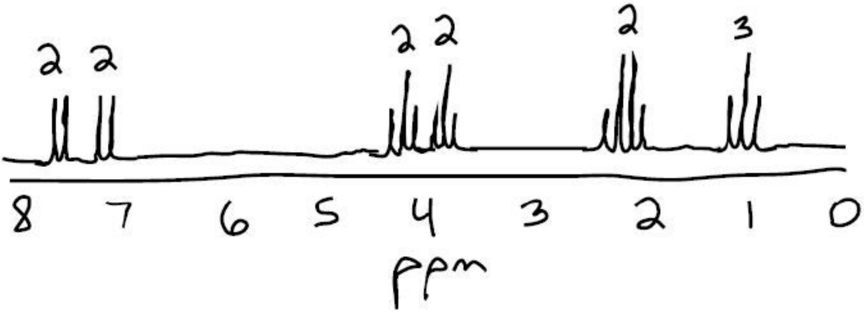
a) homotopic b) enantiotopic c) enantiotopic d) homotopic

e) diastereotopic f) homotopic g) diastereotopic h) diastereotopic

i) homotopic j) homotopic k) homotopic l) diastereotopic

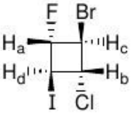
m) enantiotopic n) diastereotopic o) homotopic

16.41.



16.42.

a) Four signals are expected in the ^{1}H NMR spectrum of this compound.



b) $\xleftarrow{\text{Increasing chemical shift}}$

$H_a > H_b > H_c > H_d$

c) Four signals are expected in the ^{13}C NMR spectrum of this compound.

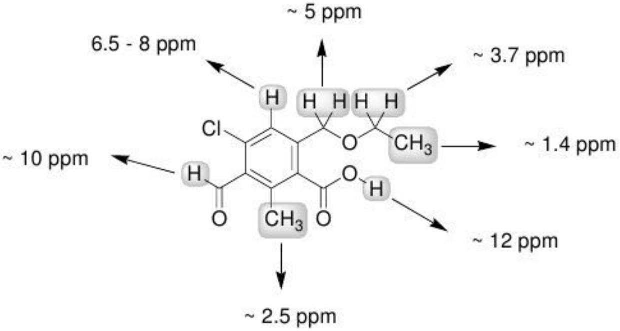
d) The carbon atoms follow the same trend exhibited by the protons.

16.43.

16.44.

a) Nine b) Eight c) Six

16.45.



16.46.

a) Six signals, all of which appear in the region 100 – 150 ppm.

b) Seven signals. One appears in the region 150 – 220 ppm, and the remaining six signals appear in the region 0 – 50 ppm.

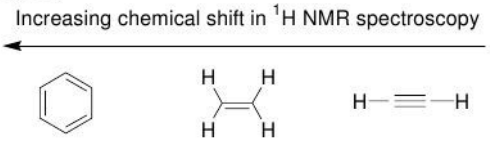
c) Four signals. One appears in the region 0 – 50 ppm, two appear in the region 50 – 100 ppm, and one signal appears in the region 150 – 200 ppm.

16.47. The ^{1}H NMR spectrum of the Markovnikov product should have only four signals, while the anti-Markovnikov product should have many more signals in its ^{1}H NMR spectrum.

16.48.

a) 2 b) 8 c) 4 d) 2 e) 3 f) 6 g) 2 h) 3

16.49.

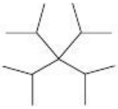


16.50.

$$\delta = \frac{(\text{observed shift from TMS in hertz}) \times 10^6}{(\text{operating frequency of the instrument in hertz})}$$

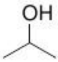
(Observed shift from TMS in hertz) = (δ)(operating frequency) / 10^6

16.51.

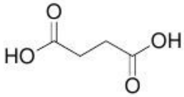


16.52.

16.53.

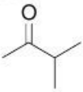


16.54.

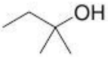


16.55.

a)



b)



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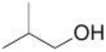
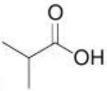
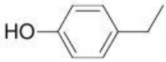


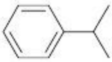
d)



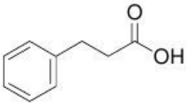
16.56.



16.57.

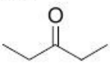


16.58.

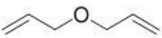


16.59.

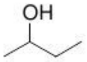
a)



b)

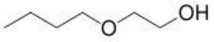


16.60.

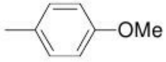


16.61.

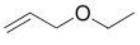
16.62.



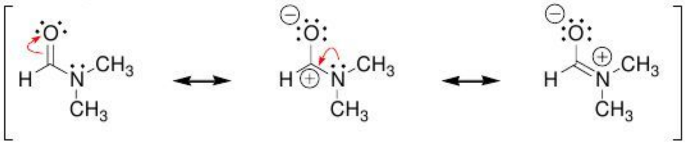
16.63.



16.64.



16.65. N,N-dimethylformamide (DMF) has several resonance structures:



Consider the third resonance structure shown above, in which the C-N bond is a double bond. This indicates that this bond is expected to have some double bond character. As such, there is an energy barrier associated with rotation about this bond, such that rotation of this bond occurs at a rate that it slower than the timescale of the NMR spectrometer. At high temperature, more molecules will have the requisite energy to undergo free rotation about the C-N bond, so the process can occur on a time scale that is faster than the timescale of the NMR spectrometer. For this reason, the signals are expected to collapse into one signal at high temperature.

16.66. In a concentrated solution of phenol, the OH groups are engaged in extensive, intermolecular hydrogen-bonding interactions. These interactions cause the average distance to increase between the O and H of each OH group. This effectively deshields the protons of the hydroxyl groups. These protons therefore show up downfield. In a dilute solution, there are fewer hydrogen bonding interactions, and the effect described above is not observed.

16.67. The methyl group on the right side is located in the shielding region of the π bond, so the signal for this proton is moved upfield to 0.8 ppm.

16.68. Bromine is significantly larger than chlorine, and the electron density of a bromine atom partially surrounds any carbon atom attached directly to the bromine, thereby shielding it. In CBr_4, the carbon atom in the center of the compound is significantly shielded because it is positioned within the electron clouds of the four bromine atoms. In fact, it is so strongly shielded that it produces a signal even higher upfield than TMS.

Chapter 17

Conjugated Pi Systems and Pericyclic Reactions

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 17. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

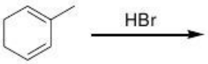
- Conjugated dienes experience free-rotation about the C2-C3 bond, giving rise to two important conformations: *s*-_____ and *s*-_____. The *s-trans* conformation is lower in energy.
- The HOMO and LUMO are referred to as ___________ **orbitals**, and the reactivity of conjugated polyenes can be explained with **frontier orbital theory**.
- An _________ **state** is produced when a π electron in the HOMO absorbs a photon of light bearing the appropriate energy necessary to promote the electron to a higher energy orbital.
- Reactions induced by light are called _______________ **reactions**.
- When butadiene is treated with HBr, two major products are observed, resulting from ______**-addition** and ______**-addition**.
- Conjugated dienes that undergo addition at low temperature are said to be under ____________ **control.** Conjugated dienes that undergo addition at elevated temperature are said to be under _________________ **control**.
- _______________ **reactions** proceed via a concerted process with a cyclic transition state, and they are classified as **cycloaddition reactions**, ______________ **reactions**, and **sigmatropic rearrangements.**
- The Diels–Alder reaction is a **[** _______ **] cycloaddition** in which two C-C bonds are formed simultaneously.
- High temperatures can often be used to achieve the reverse of a Diels–Alder reaction, called a _________ **Diels–Alder**.
- The starting materials for a Diels–Alder reaction are a diene, and a ___________.
- The Diels–Alder reaction only occurs when the diene is in an ____ conformation.
- When cyclopentadiene is used as the starting diene, a bridged bicyclic compound is obtained, and the _____ cycloadduct is favored over the _____ cycloadduct.
- Conservation of orbital symmetry determines whether an electrocyclic reaction occurs in a ___________ fashion or a ____________ fashion.
- A [_________] sigmatropic rearrangement is called a **Cope rearrangement** when all six atoms of the cyclic transition state are carbon atoms.
- Compounds that possess a conjugated π system will absorb UV or visible light to promote an electronic excitation called a __________ transition.
- The most important feature of the absorption spectrum is the _________, which indicates the wavelength of maximum absorption.
- When a compound exhibits a λ_{max} above 400 nm, the compound will absorb __________ light, rather than UV light.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 17. The answers appear in the section entitled *SkillBuilder Review*.

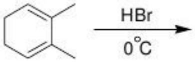
17.1 Proposing the Mechanism and Predicting the Products of Electrophilic Addition to Conjugated Dienes

IN THE SPACE PROVIDED, DRAW THE MECHANISM OF THE REACTION THAT IS EXPECTED TO OCCUR WHEN THE FOLLOWING COMPOUND IS TREATED WITH HBr. MAKE SURE TO DRAW ALL POSSIBLE PRODUCTS.



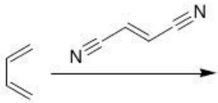
17.2 Predicting the Major Product of an Electrophilic Addition to Conjugated Dienes

DRAW THE MAJOR PRODUCTS OF THE FOLLOWING REACTION:



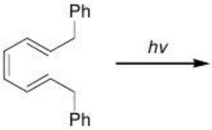
17.3 Predicting the Product of a Diels–Alder Reaction

DRAW THE MAJOR PRODUCTS OF THE FOLLOWING REACTION:



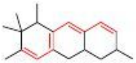
17.4 Predicting the Product of an Electrocyclic Reaction

DRAW THE MAJOR PRODUCTS OF THE FOLLOWING REACTION:



17.5 Using Woodward–Fieser Rules to Estimate λ_{max}

USE WOODWARD-FIESER RULES TO ESTIMATE λ_{max} FOR THE FOLLOWING COMPOUND:



BASE VALUE =

ADDITIONAL DOUBLE BONDS =

AUXOCHROMIC ALKYL GROUPS =

EXOCYCLIC DOUBLE BOND =

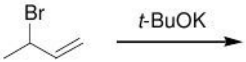
HOMOANNULAR DIENE =

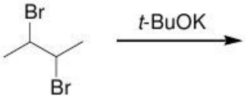
TOTAL =

Review of Reactions

Predict the Products for each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 17. The answers appear in the section entitled *Review of Reactions*.

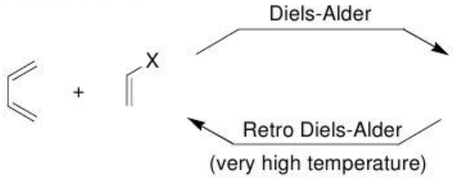
Preparation of Dienes

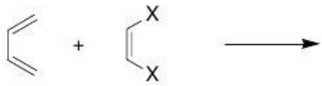


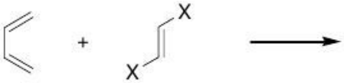


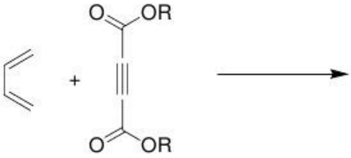
Electrophilic Addition

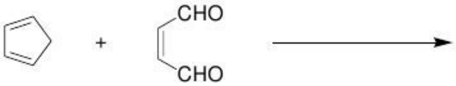
Diels–Alder Reaction



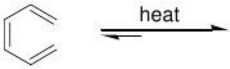


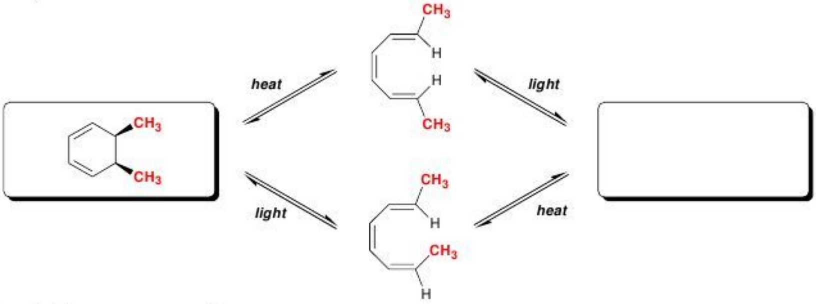






Electrocyclic Reactions





Sigmatropic Rearrangements

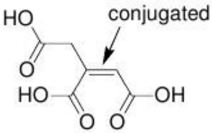
Cope Rearrangement

Claisen Rearrangement

Solutions

17.1.

a)



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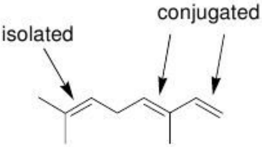

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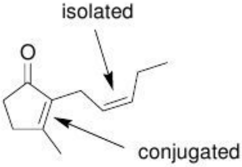

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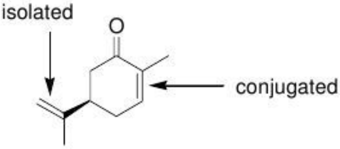
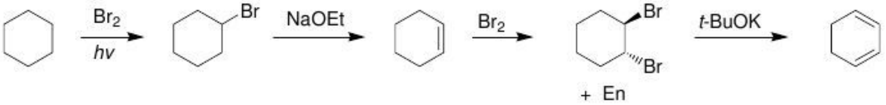
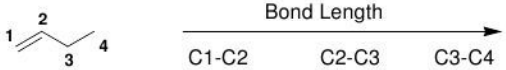


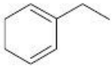
17.2.



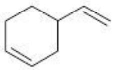
17.3.



17.4.

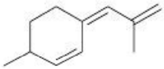
a) 

The conjugated diene will liberate the least heat because it is the most stable of the three compounds.

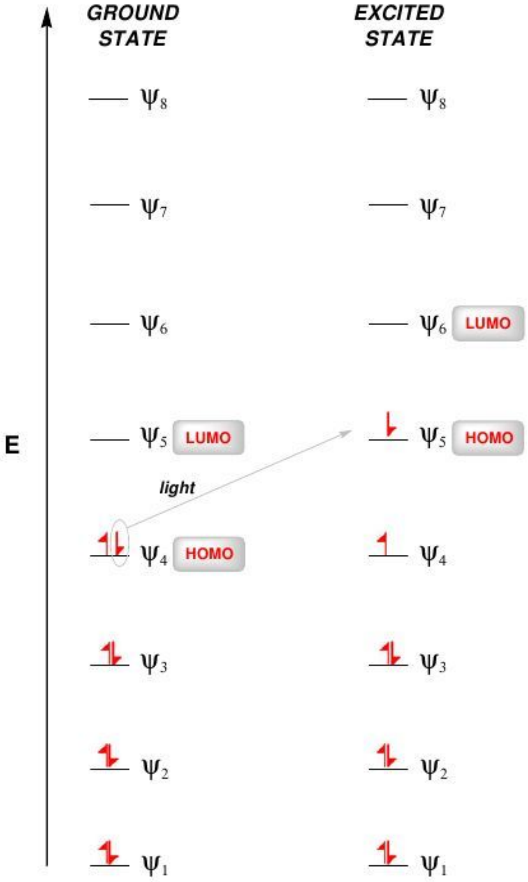
b) 

This isolated diene will liberate more heat than the other isolated diene, because the π bonds in this compound are not highly substituted (one π bond is monosubstituted and the other is disubstituted). In the other isolated diene, the π bonds are disubstituted and trisubstituted (and therefore more stable).

17.5. In the compound below, all three π bonds are conjugated:

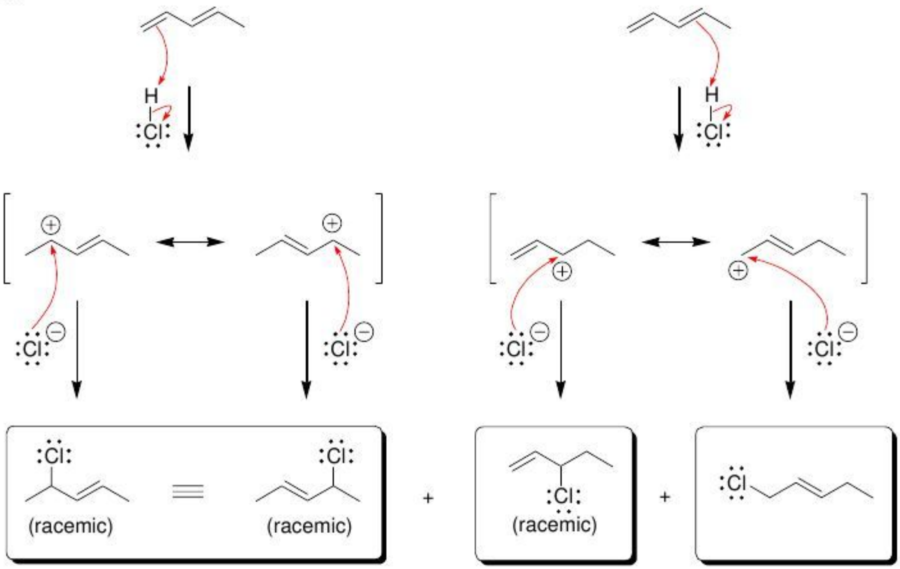


17.6.

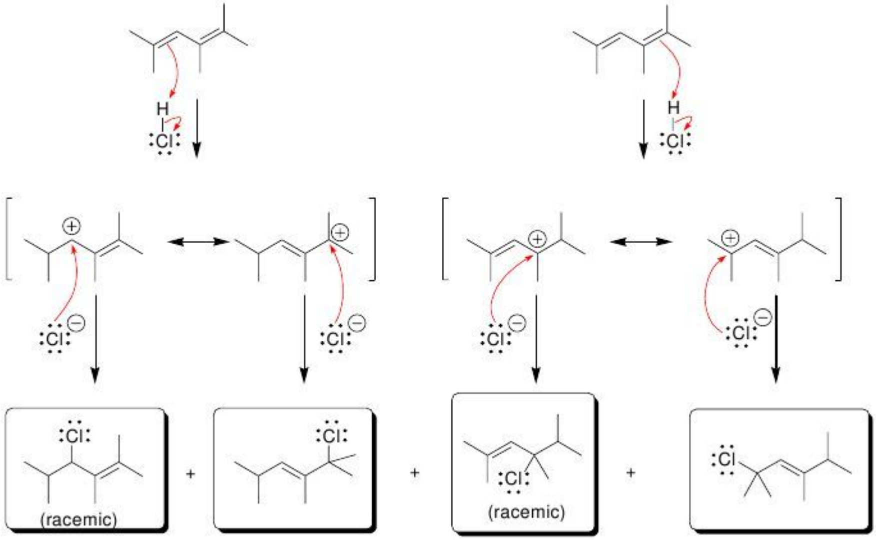

GROUND STATE
EXCITED STATE
E
ψ8
ψ7
ψ6
ψ5
LUMO
light
ψ4
HOMO
ψ3
ψ2
ψ1
ψ8
ψ7
ψ6
LUMO
ψ5
HOMO
ψ4
ψ3
ψ2
ψ1

17.7.

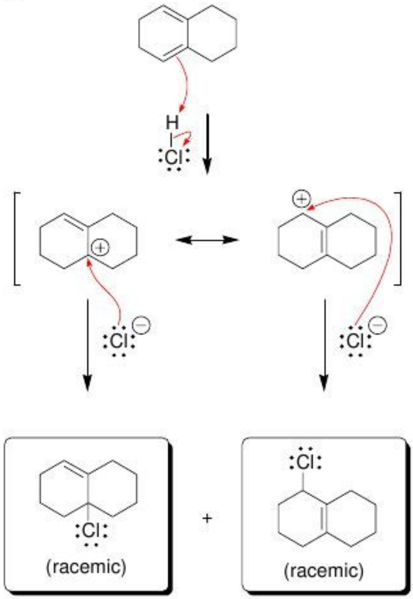
a)



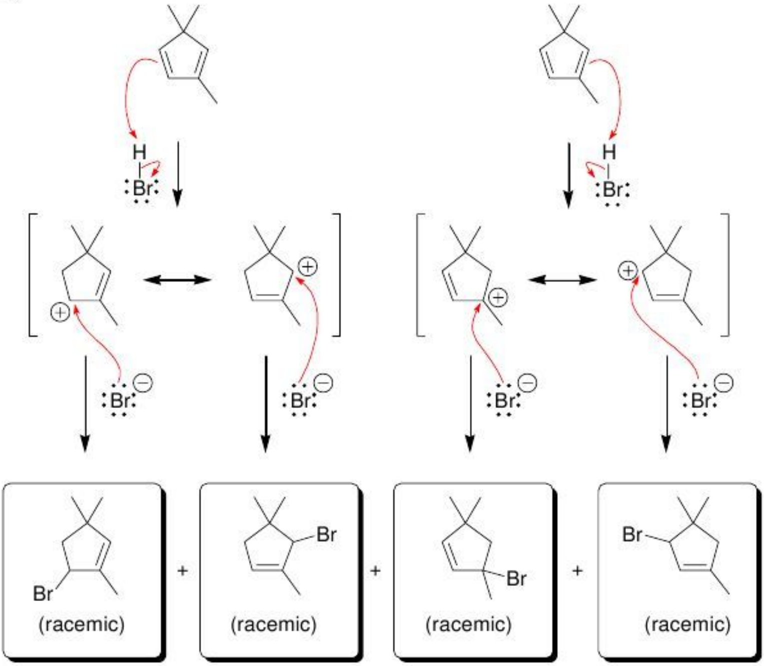
b)



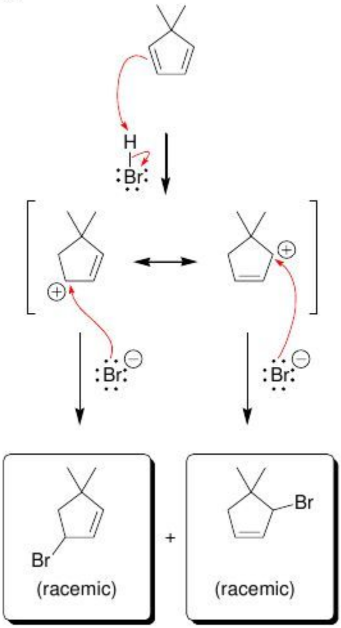
c)


H
:Cl:
:Cl:
:Cl:
:Cl:
(racemic)
+
:Cl:
(racemic)

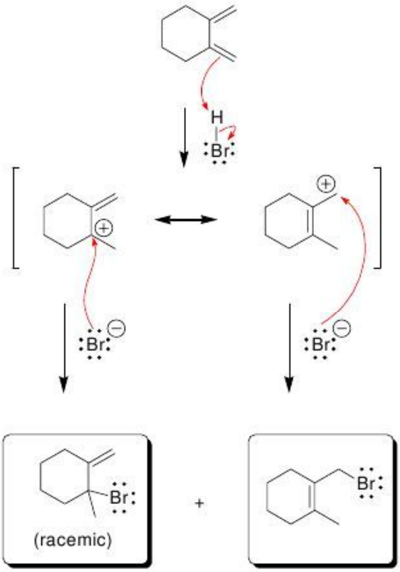
d)


H
:Br:
H
:Br:
:Br:
:Br:
:Br:
:Br:
Br
(racemic)
+
Br
(racemic)
+
Br
(racemic)
+
Br
(racemic)

e)

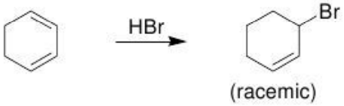


f)



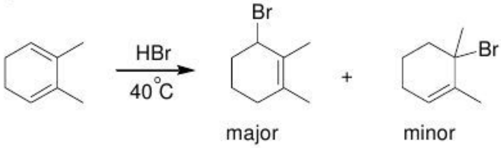
17.8. The first diene can be protonated either at C1 or at C4. Each of these pathways produces a resonance stabilized carbocation. And each of these carbocations can be attacked in two positions, giving rise to four possible products. In contrast, the second diene yields the same carbocation regardless of whether protonation occurs at C1 or at C4. This resonance-stabilized carbocation can be attacked in two positions, giving rise to two products.

17.9.

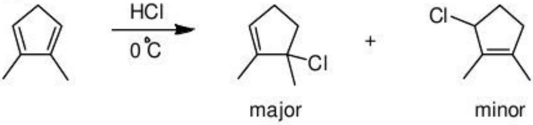


17.10.

a)



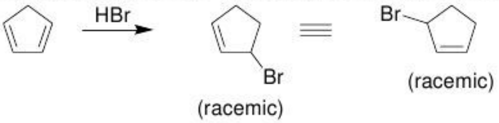
b)



c)

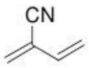
17.11. In this case, the π bond in the 1,2-adduct is more substituted than the π bond in the 1,4-adduct (trisubstituted rather than disubstituted). As a result, the 1,2-adduct predominates at either low temperature or high temperature.

17.12. In this case, 1,2-addition and 1,4-addition yield the same product.



17.13.

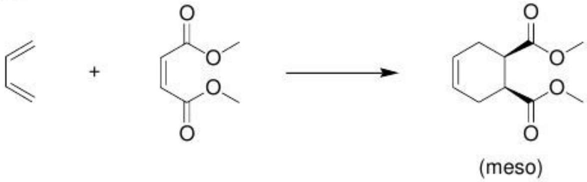
a)



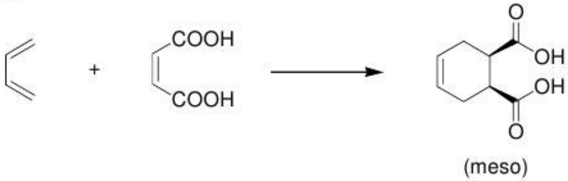
b)

17.14.

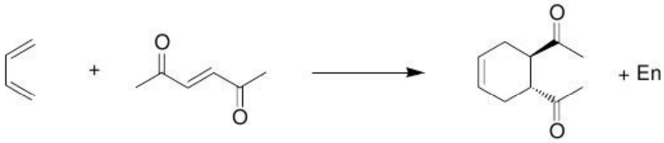
a)



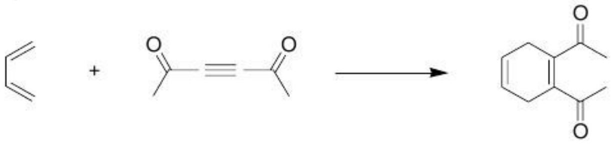
b)



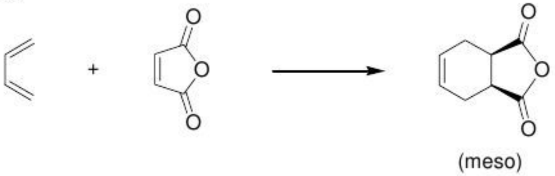
c)



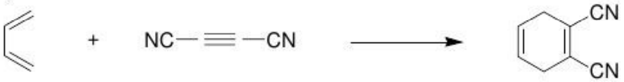
d)



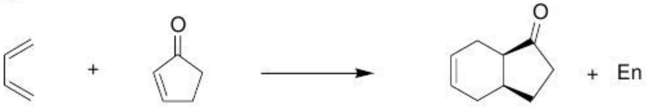
e)


+
O
O
O
O
O
O
(meso)

f)


+
NC
CN
CN
CN

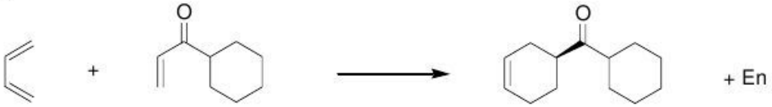
g)


+
O
O
+ En

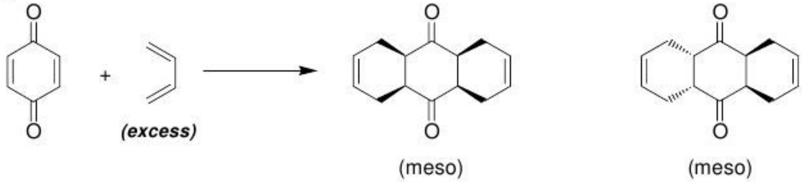
h)


+
O
OH
O
OH

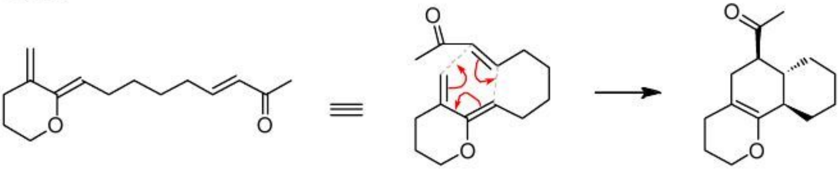
i)


+
O
O
+ En

17.15.


O
O
+
(excess)
O
O
(meso)
O
O
(meso)

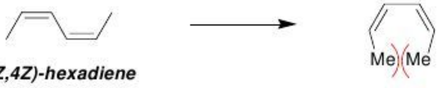
17.16.



17.17. The *2E,4E* isomer is expected to react more rapidly as a diene in a Diels–Alder reaction, because it can readily adopt an *s-trans* conformation.

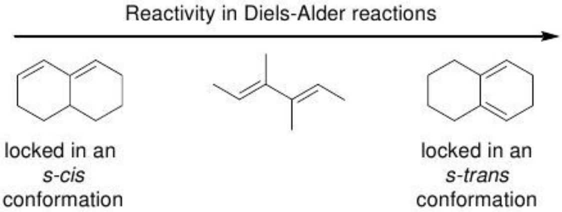
(2E,4E)-hexadiene

In contrast, the *2Z,4Z* isomer is expected to react more slowly as a diene in a Diels–Alder reaction, because it cannot readily adopt an *s-trans* conformation, as a result of steric hinderance.



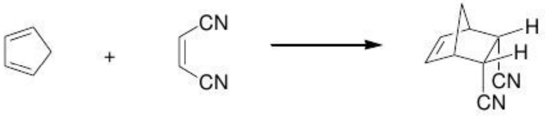
(2Z,4Z)-hexadiene

17.18.



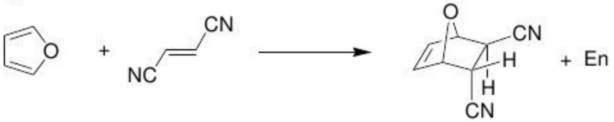
17.19.

a)

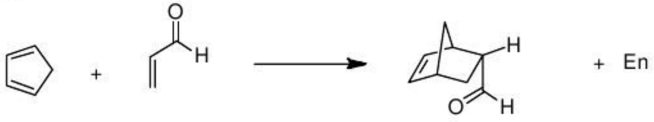


(meso)

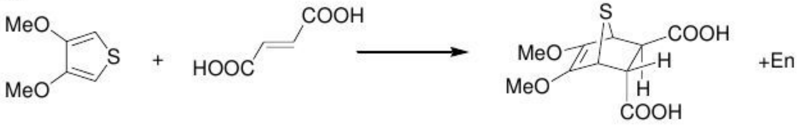
b)



c)

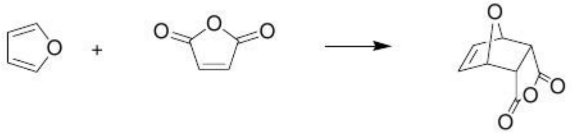


d)



e)

f)

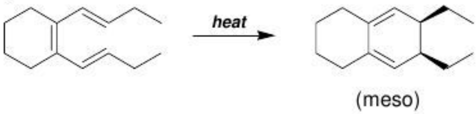


(meso)

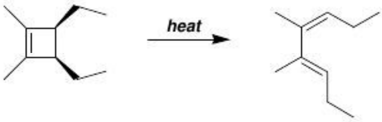
17.20. We first consider the HOMO of one molecule of butadiene and the LUMO of another molecule of butadiene. The phases of these MOs do not align, so a thermal reaction is symmetry-forbidden. However, if one molecule is photochemically excited, the HOMO and LUMO of that molecule are redefined. The phases of the frontier orbitals will align under these conditions, so the reaction is expected to occur photochemically.

17.21.

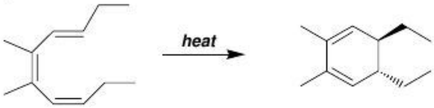
a)



b)



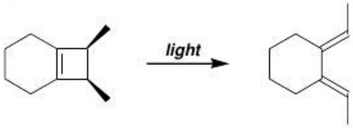
c)



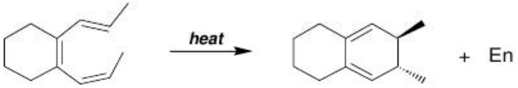
17.22.

a)

b)

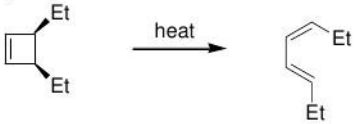


c)

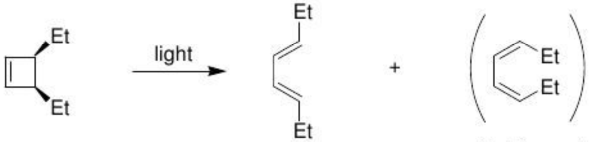


17.23.

a)



b)



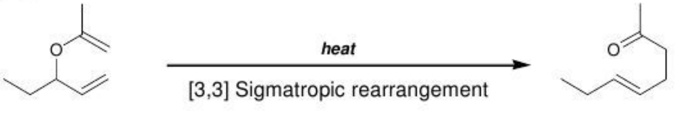
Not formed
Ethyl groups are too crowded

17.24.

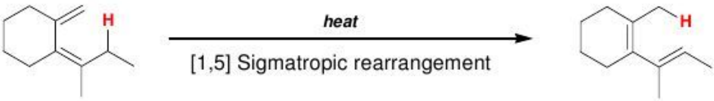
a) a meso compound
b) a pair of enantiomers
c) a pair of enantiomers

17.25.

a)

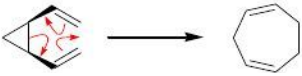


b)



17.26.

a)

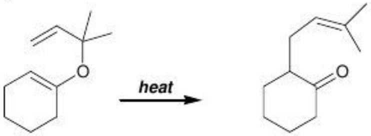


b) [3,3] Sigmatropic rearrangement

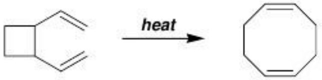
c) The ring strain associated with the three-membered ring is alleviated. The reverse process would involve forming a high-energy, three-membered ring. The equilibrium disfavors the reverse process.

17.27.

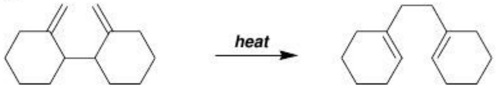
a)



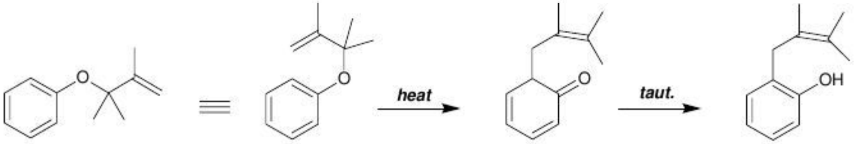
b)



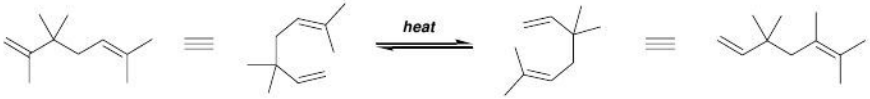
c)



d)



17.28.



17.29.

a)

Base = 217
Additional double bonds = 0
Auxochromic alkyl groups = +25
Exocyclic double bond = +5
Homoannular diene = 0
Total = 247 nm

b)

Base = 217
Additional double bonds = +30
Auxochromic alkyl groups = +25
Exocyclic double bond = +5
Homoannular diene = 0
Total = 277 nm

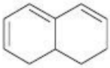
c)

Base = 217
Additional double bonds = +30
Auxochromic alkyl groups = +30
Exocyclic double bonds = +15
Homoannular diene = 0
Total = 292 nm

d)

Base = 217
Additional double bonds = +30
Auxochromic alkyl groups = +35
Exocyclic double bonds = +5
Homoannular diene = +39
Total = 326 nm

17.30



17.31.

a) Blue.
b) Red-Orange.
c) Blue-violet.

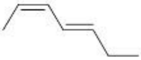
17.32.

a)

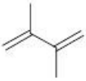
b)

c)

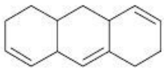
d)

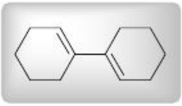


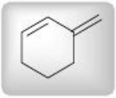
e)

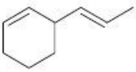


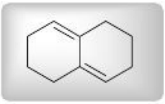
17.33.

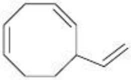


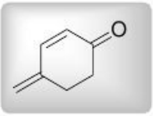












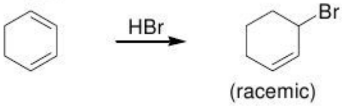
17.34.

a) These drawings represent two different conformations of the same compound: the *s-cis* conformation and the *s-trans* conformation. These two conformations are in equilibrium at room temperature.

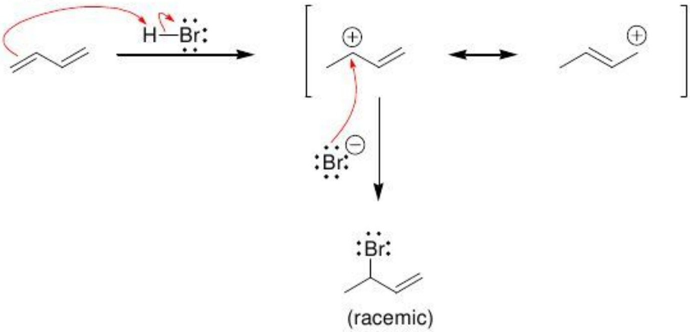
b) These drawings represent two different compounds: (*Z*)-1,3,5-hexatriene and (*E*)-1,3,5-hexatriene. These compounds are diastereomers and can be isolated from one another.

c) These drawings represent two different conformations of the same compound: the *s-cis* conformation and the *s-trans* conformation. These two conformations are in equilibrium at room temperature.

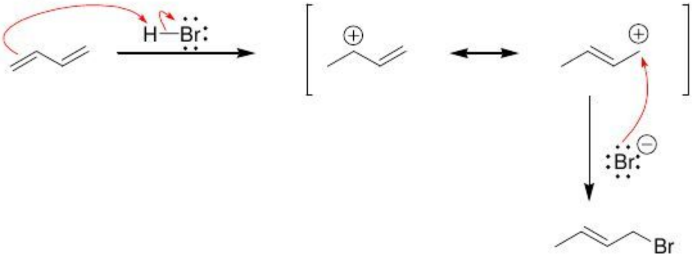
17.35.



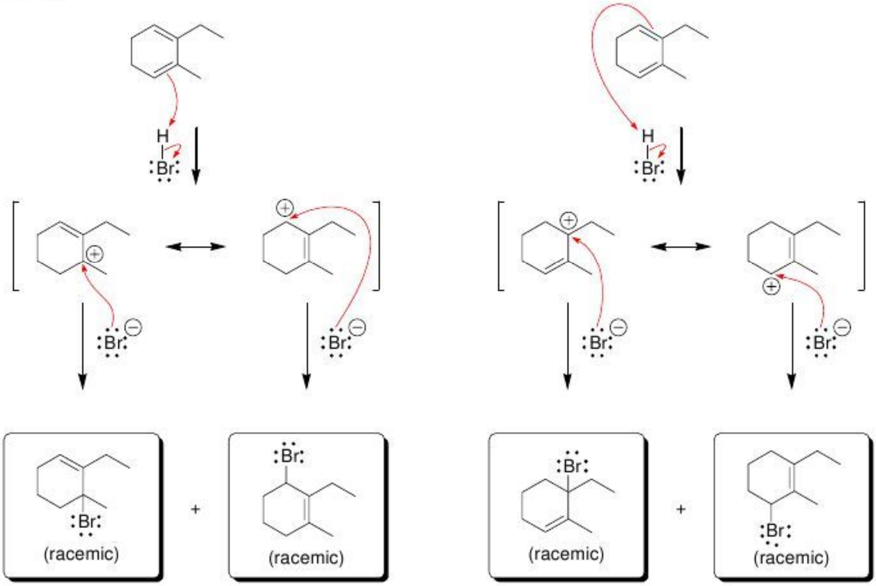
17.36.



17.37.



17.38.



17.39. An increase in temperature allowed the system to reach equilibrium concentrations, which are determined by the relative stability of each product. Under these conditions, the 1,4-adducts predominate. Once at equilibrium, lowering the temperature will not cause a decrease in the concentration of the 1,4-adducts.

17.40.

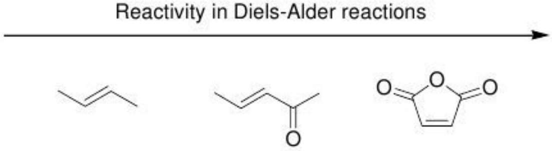
a) The *tert*-butyl groups provide significant steric hinderance that prevents the compound from adopting an *s-cis* conformation.

b) This diene is not conjugated.

c) The methyl groups provide significant steric hinderance that prevents the compound from adopting an *s-cis* conformation.

d) This diene cannot adopt an *s-cis* conformation

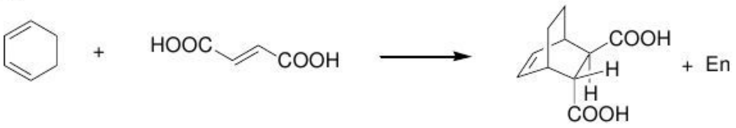
17.41.



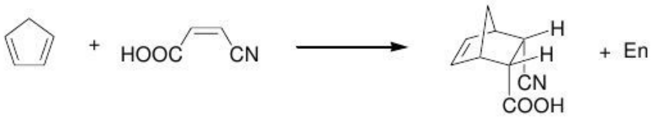
17.42. The π bonds in 1,2-butadiene are not conjugated, and λ_{max} is therefore lower than 217 nm. In fact, it is below 200 nm, which is beyond the range used by most UV-VIS spectrometers.

17.43.

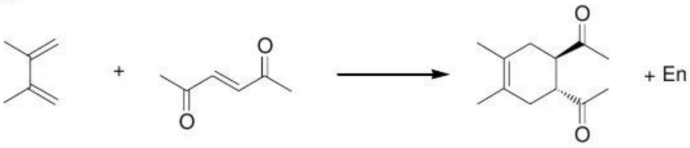
a)



b)



c)



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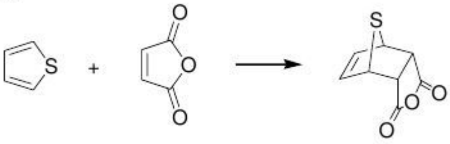
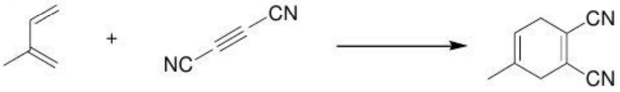


(meso)

e)



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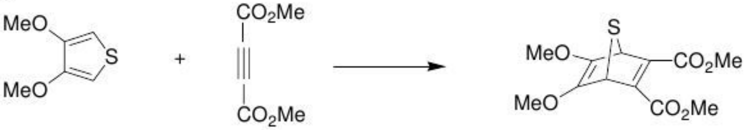
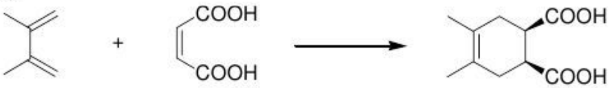


17.44.

a)



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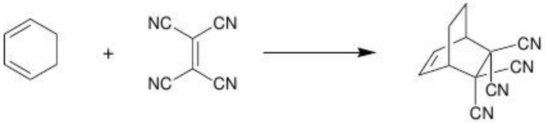
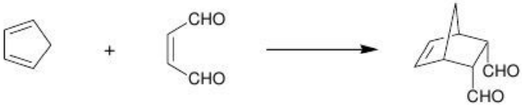


c)



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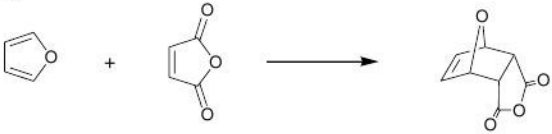

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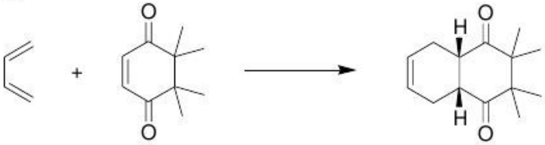

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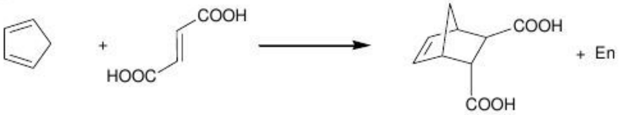

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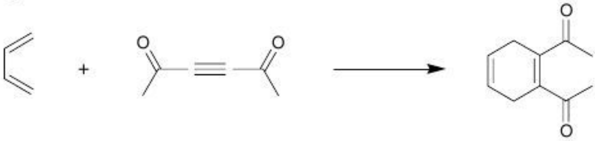

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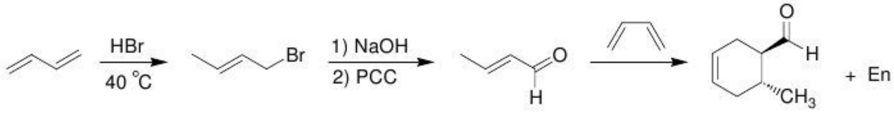

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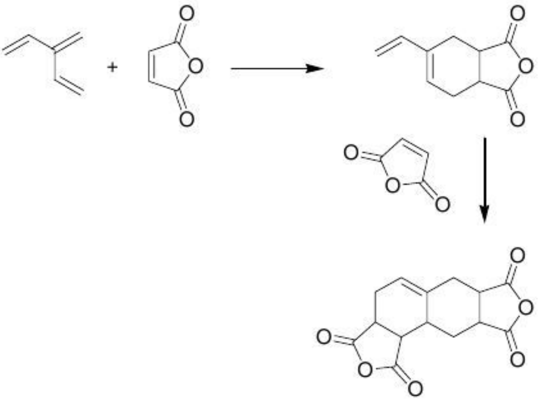
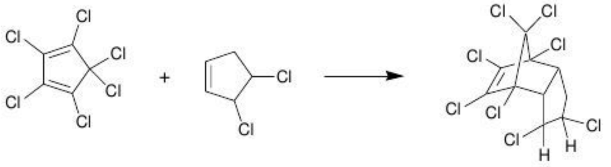


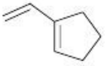
17.47.

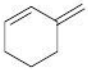


chlordane

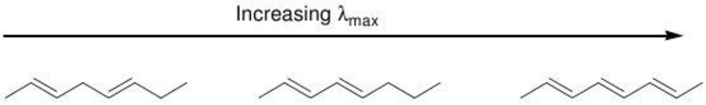
17.48. The two ends of the conjugated system are much farther apart in a seven-membered ring than they are in a five-membered ring.

17.49.

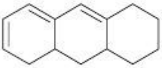




17.50.



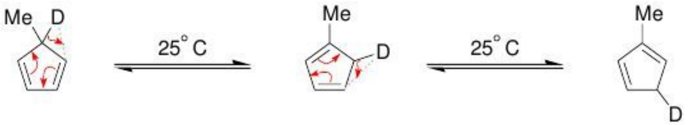
17.51. Two of the π bonds are homoannular in this compound, which adds +39 nm according to Woodward-Fieser rules.



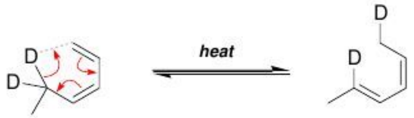
17.52.

Base = 217
Additional double bonds = +60
Auxochromic alkyl groups = +35
Exocyclic double bonds = +5
Homoannular diene = +39
Total = 356 nm

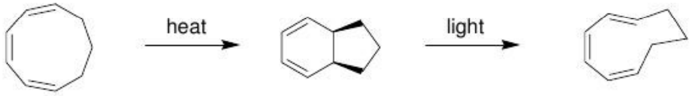
17.53. Each of these transformations can be explained with a [1,5] sigmatropic rearrangement:



17.54. This transformation can be explained with a [1,5] sigmatropic rearrangement:

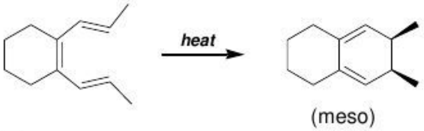


17.55.

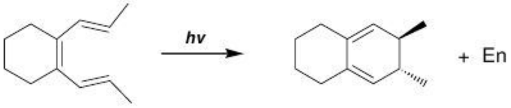


17.56.

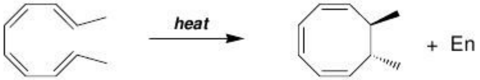
a)



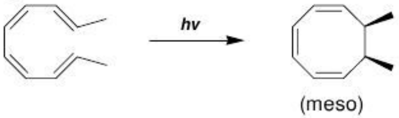
b)



c)

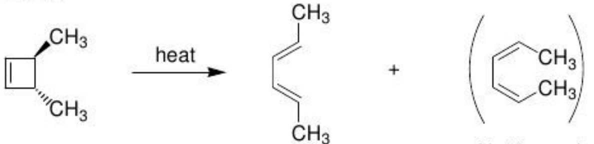


d)



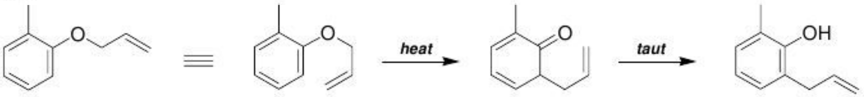
17.57. The compound on the right has a π bond in conjugation with the aromatic ring, while the compound on the left does not. Therefore, the compound on the right side of the equilibrium is expected to be more stable, and the equilibrium will favor the compound that is lower in energy.

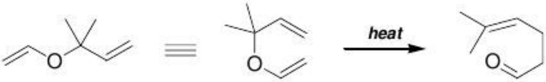
17.58.

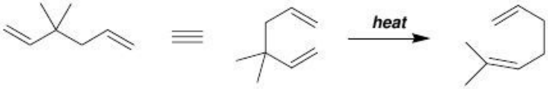


Not formed
Methyl groups are too crowded

17.59.

a)


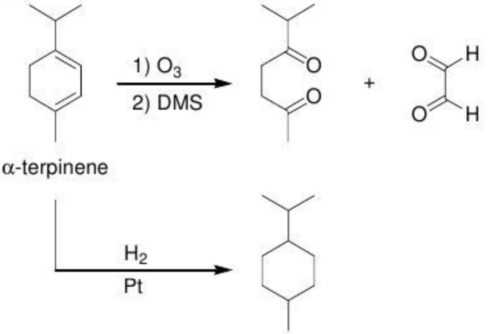
b)


c)


17.60.

a) α-Terpinene has two double bonds.

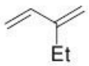
b)

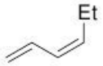


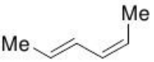
c)

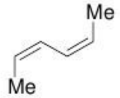
Base = 217
Additional double bonds = 0
Auxochromic alkyl groups = +20
Exocyclic double bonds = 0
Homoannular diene = +39
Total = 276 nm

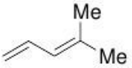
17.61.

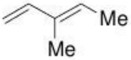


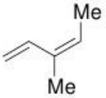


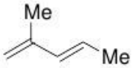


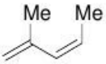


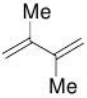




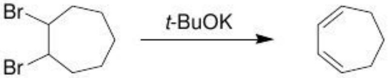






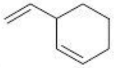


17.62.

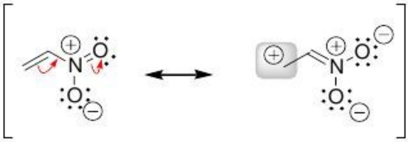


17.63. In each case, the non-conjugated isomer will be higher in energy:

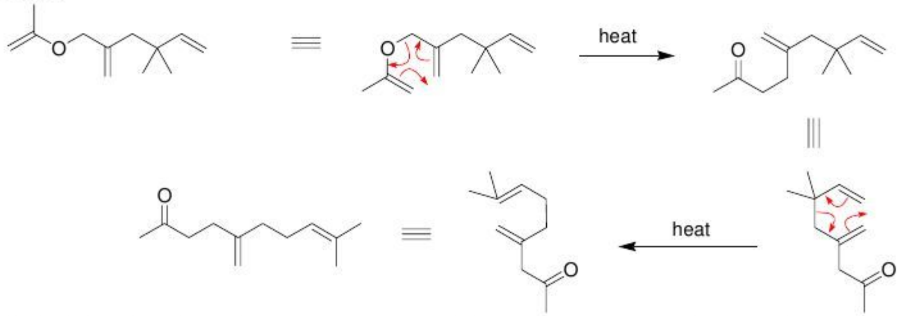
a) 

b) 

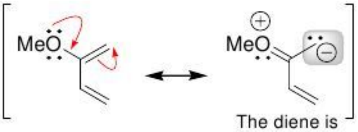
17.64. Nitroethylene should be more reactive than ethylene in a Diels–Alder reaction, because the nitro group is electron-withdrawing, via resonance:



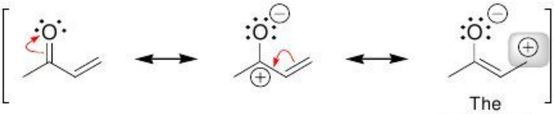
17.65.



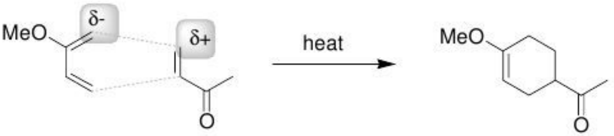
17.66. The diene is electron-rich in one specific location, as seen in the second resonance structure below:


The diene is electron rich in this location

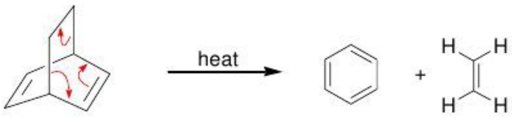
The dienophile is electron-poor in one specific location, as seen in the third resonance structure below:


The dienophile is electron poor in this location

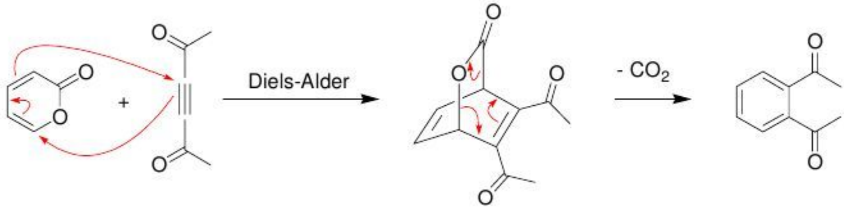
These two compounds will join in such a way that the electron-poor center lines up with the electron-rich center:



17.67.



17.68.



17.69. The nitrogen atom in divinyl amine is *sp*^{2} hybridized. The lone pair is delocalized, and joins the two neighboring π bonds into one conjugated system. As such, the compound absorbs light above 200 nm (UV light). In contrast, 1,4-pentadiene has two isolated double bonds and therefore does not absorb UV light in the region between 200 and 400 nm.

Chapter 18
Aromatic Compounds

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 18. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

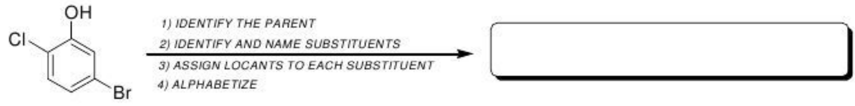
- When a benzene ring is a substituent, it is called a _________ **group**.
- Dimethyl derivatives of benzene can be differentiated by the use of the descriptors _______, ***meta*** and _______, or by the use of locants
- Benzene is comprised of a ring of six identical C-C bonds, each of which has a bond order of _____.
- The **stabilization energy** of benzene can be measured by comparing ________ of hydrogenation.
- The stability of benzene can be explained with MO theory. The six π electrons all occupy ___________ MOs.
- The presence of a fully conjugated ring of π electrons is not the sole requirement for aromaticity. The requirement for an odd number of electron pairs is called ___________ **rule**.
- **Frost circles** accurately predict the relative energy levels of the ________ in a conjugated ring system.
- A compound is aromatic if it contains a ring comprised of __________________ __________________________ and if it has a ________ number π electrons in the ring.
- Compounds that fail the first criterion are called _______________.
- Compounds that satisfy the first criterion, but have 4n electrons (rather than 4n+2) are _______________.
- Cyclic compounds containing hetereoatoms, such as S, N, O are called _____________________.
- Any carbon atom attached directly to a benzene ring is called a _____________ **position**.
- Alkyl benzenes are oxidized at the benzylic position by _____________ or ________________________.
- In a **Birch reduction**, the aromatic moiety is reduced to give a nonconjugated diene. The carbon atom connected to ___________ is not reduced, while the carbon atom connected to __________________________ is reduced.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 18. The answers appear in the section entitled *SkillBuilder Review*.

18.1 Naming a Polysubstituted Benzene

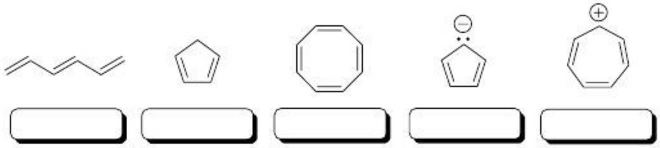
PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND



1) IDENTIFY THE PARENT
2) IDENTIFY AND NAME SUBSTITUENTS
3) ASSIGN LOCANTS TO EACH SUBSTITUENT
4) ALPHABETIZE

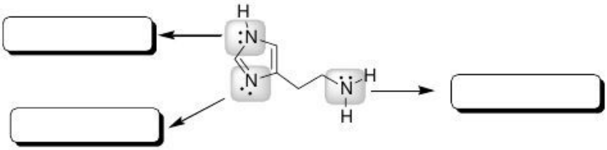
18.2 Determining Whether a Compound is Aromatic, Nonaromatic, or Antiaromatic

IDENTIFY EACH COMPOUND OR ION BELOW AS AROMATIC, ANTIAROMATIC, OR NONAROMATIC:



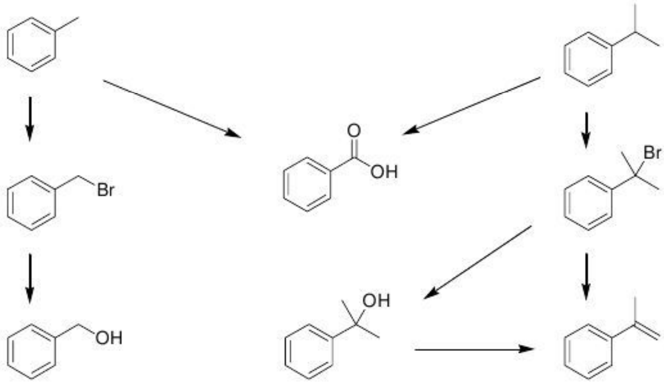
18.3 Determining Whether a Lone Pair Participates in Aromaticity

IN THE FOLLOWING COMPOUND, IDENTIFY WETHER EACH LONE PAIR PARTICPATES IN AROMATICITY:



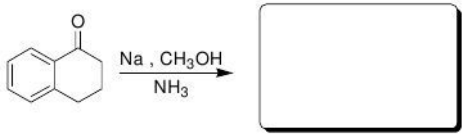
18.4 Manipulating the Side Chain of an Aromatic Compound

FOR EACH TRANSFORMATION BELOW, IDENTIFY THE TYPE OF REACTION THAT COULD BE USED (S_N2, S_N1, E2, ETC.)



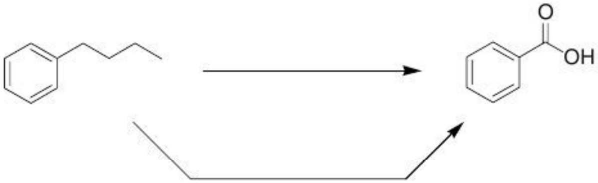
18.5 Predicting the Product of a Birch Reduction

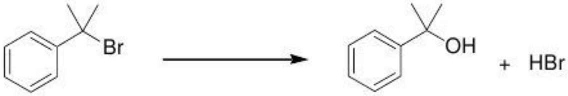
PREDICT THE MAJOR PRODUCT OF THE FOLLOWING REACTION:

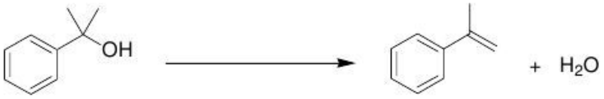


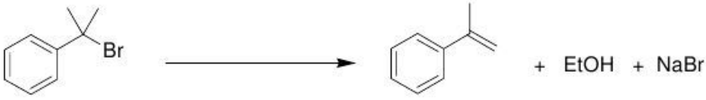
Review of Reactions

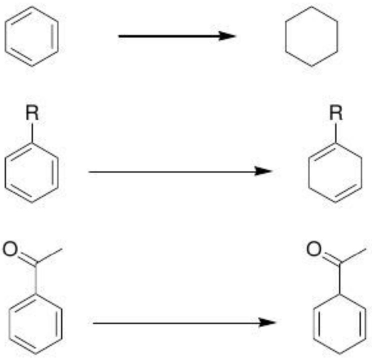
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 18. The answers appear in the section entitled *Review of Reactions*.











Solutions

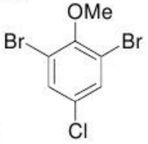
18.1.

a) 3-isopropylbenzaldehyde or *meta*-isopropylbenzaldehyde
b) 2-bromotoluene or *ortho*-bromotoluene
c) 2,4-dinitrophenol
d) 2-ethyl-1,4-diisopropylbenzene
f) 2,6-dibromo-4-chloro-3-ethyl-5-isopropylphenol

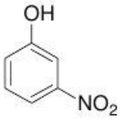
18.2.
a) 4-bromo-2-methylphenol
b) 2-hydroxy-5-bromotoluene
c) 4-bromo-1-hydroxy-2-methylbenzene

18.3.

a)

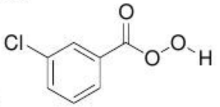


b)



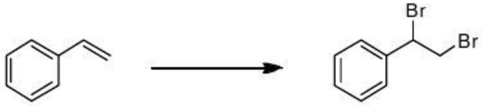
18.4.
a) meta-xylene
b) 1,3-dimethylbenzene
c) meta-dimethylbenzene
d) meta-methyltoluene
e) 3-methyltoluene

18.5.

a) 

b) 3-methylperbenzoic acid or *meta*-methylperbenzoic acid.

18.6.



Compound A
(C_8H_8)

Compound B
($C_8H_8Br_2$)

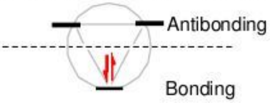
18.7.

a) ΔH has a positive value
b) ΔH has a positive value
c) ΔH has a negative value

18.8.

a) No, 12 is not a Hückel number.
b) Yes, 14 is a Hückel number.
c) No, 16 is not a Hückel number.

18.9. The cyclopropenyl cation is expected to exhibit aromatic stabilization.



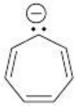
18.10. The compound will be aromatic because there are 22 π electron, and 22 is a Hückel number.

18.11.

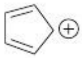
a) antiaromatic b) aromatic c) antiaromatic d) aromatic

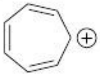
18.12. Cyclopentadiene is more acidic because its conjugate base is highly stabilized. Deprotonation of cyclopentadiene generates an anion that is aromatic, because it is a continuous system of overlapping p orbitals containing 6 π electrons. In contrast, deprotonation of cycloheptatriene gives an anion with 8 π electrons.

more stable



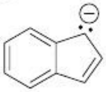
18.13. The first step of an S_N1 process is loss of a leaving group, forming a carbocation, so we compare the carbocations that would be formed.

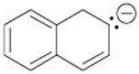




The second carbocation is more stable, because it is aromatic, and is therefore lower in energy than the first carbocation. The transition state leading to the second carbocation will be lower in energy than the transition state leading to the first carbocation, and therefore, the second carbocation will be formed more rapidly than the first.

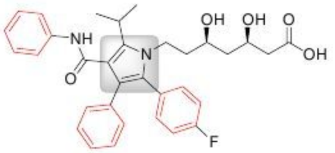
18.14. The first compound is more acidic because deprotonation of the first compound generates a new (second) aromatic ring. Deprotonation of the second compound does not introduce a new aromatic ring:



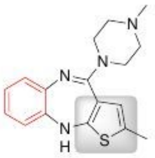


18.15.
a) One of the lone pairs on oxygen
b) One of the lone pairs on sulfur
c) The lone pair on nitrogen is NOT participating in aromaticity (8 pi electrons).
d) One of the lone pairs on sulfur
e) There is only one pair (on oxygen) and it is not participating in aromaticity.
f) Each nitrogen has one lone pair, and neither is participating in aromaticity.
g) The compound is not aromatic. In order to achieve a continuous system of overlapping *p* orbitals, each oxygen atom would need to contribute a lone pair in a *p* orbital, and that would give 8 π electrons (not a Hückel number).
h) One of the lone pairs on oxygen (not the lone pair on the nitrogen)

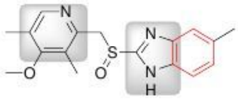
18.16.



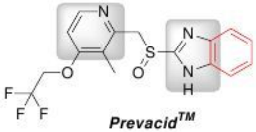
Lipitor^{TM}



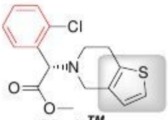
Zyprexa^{TM}



Nexium^{TM}

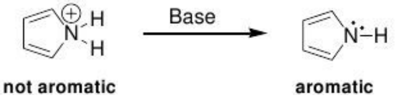


Prevacid^{TM}



Plavix^{TM}

18.17. The first compound is expected to be more acidic (has a lower pK_a), because deprotonation restores aromaticity to the ring. The second compound is already aromatic, even before deprotonation.



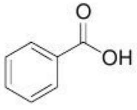
18.18.

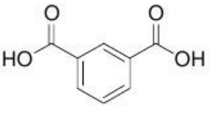
a) Yes, it has the required pharmacophore (two aromatic rings separated by one carbon atom, and a tertiary amine.

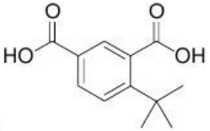
b) Meclizine crosses the blood-brain barrier and binds with receptors in the central nervous system, causing sedation.

c) Introduce polar functional groups that reduce the ability of the compound to cross the blood-brain barrier.

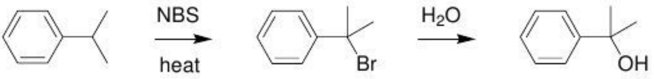
18.19.

a) 

b) 

c) 

18.20.

a) 

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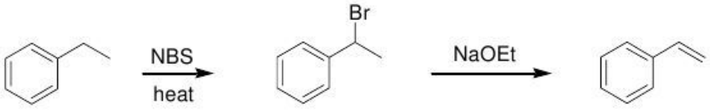

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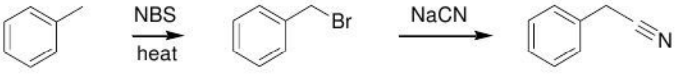
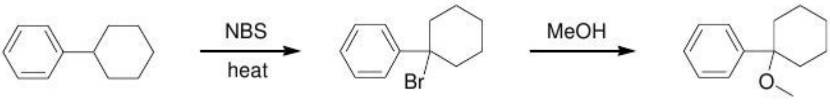
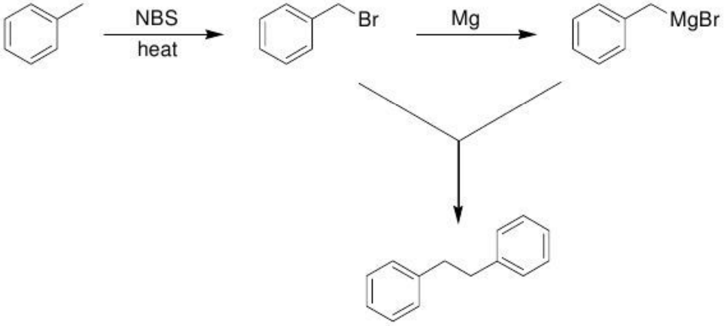


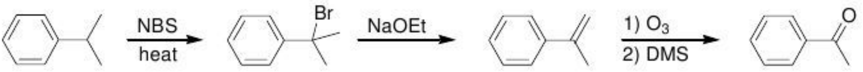
d)



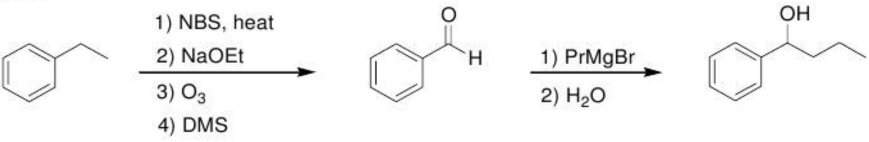
18.21.



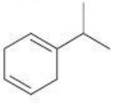
18.22.

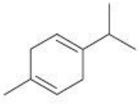


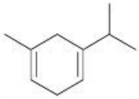
18.23.

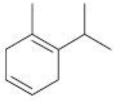


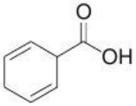
18.24.

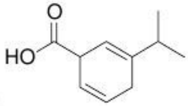
a) 

b) 

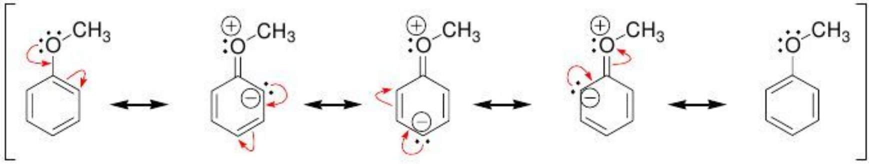
c) 

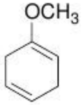
d) 

e) 

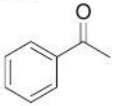
f) 

18.25.

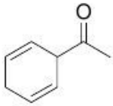
a) 

b) 

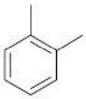
18.26.

a) 

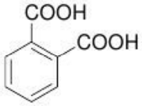
b) acetophenone

c) 

18.27.

a) 

b) *ortho*-xylene

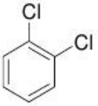
c) 

18.28.

a) 4-ethylbenzoic acid or *para*-ethylbenzoic acid
b) 2-bromophenol or *ortho*-bromophenol
c) 2-chloro-4-nitrophenol
d) 2-bromo-5-nitrobenzaldehyde
e) 1,4-diisopropyl benzene or *para*-diisopropyl benzene

18.29.

a)



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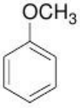

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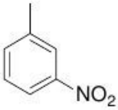

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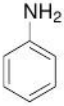
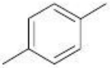
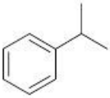


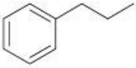
e)

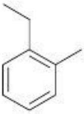
f)

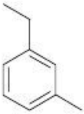


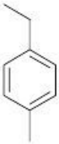
18.30.

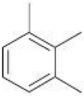


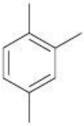


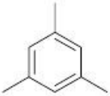












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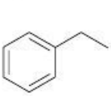
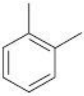
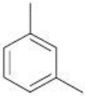
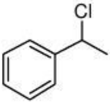
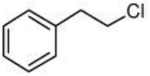


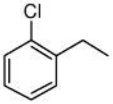


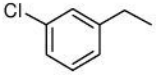


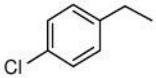
18.32.

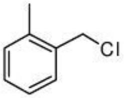


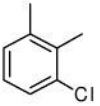


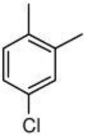


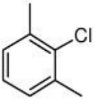


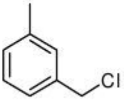


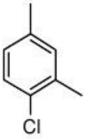


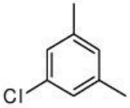


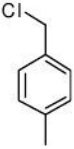


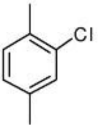




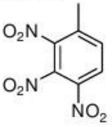




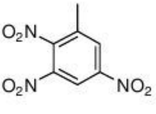




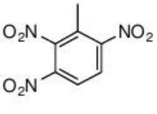
18.33.



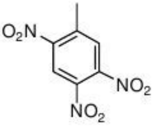
2,3,4-trinitrotoluene



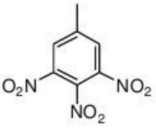
2,3,5-trinitrotoluene



2,3,6-trinitrotoluene



2,4,5-trinitrotoluene



3,4,5-trinitrotoluene

18.34.

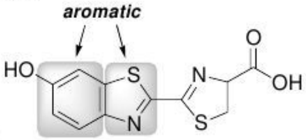
a) 10 b) 6 c) 10 d) 4 e) 6

18.35.

a) benzene b) benzene c) benzene
d) cyclohexane e) benzene f) cyclohexane
g) benzene h) benzene i) benzene
j) cyclohexane k) cyclohexane

18.36. a) Yes b) No c) No d) Yes e) No

18.37.

a) 

b) One of the lone pairs on the sulfur atom in the five-membered aromatic ring

18.38.

a) Nonaromatic. The lone pairs on the oxygen atom will remain in sp^3 hybridized orbitals in order to avoid anti-aromaticity.

b) Nonaromatic. The lone pair on the nitrogen atom will remain in an sp^3 hybridized orbital in order to avoid anti-aromaticity.

c) Aromatic. One of the lone pairs of the sulfur atom occupies a *p* orbital, thereby establishing a continuous system of overlapping *p* orbitals, containing six π electrons.

d) Aromatic. Both lone pairs occupy sp^2 hybridized orbitals and do not participate in establishing aromaticity.

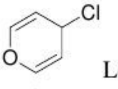
e) Aromatic. A continuous system of overlapping *p* orbitals, containing six π electrons.

f) Non aromatic. The nitrogen atom does not have a *p* orbital, so there is not a continuous system of overlapping *p* orbitals.

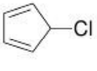
g) Aromatic. The lone pair of the oxygen atom occupies a *p* orbital, thereby establishing a continuous system of overlapping *p* orbitals, containing six π electrons.

h) Aromatic. Both lone pairs occupy *p* orbitals, thereby establishing a continuous system of overlapping *p* orbitals, containing six π electrons.

18.39.

a) 

Loss of the leaving group generates an aromatic cation.

b) 

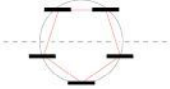
Loss of the leaving group generates an antiaromatic cation.

18.40.

Deprotonation of cyclopentadiene generates an aromatic anion.

18.41. The second compound is a stronger base, because the lone pair on the nitrogen atom is localized and available to function as a base. However, the nitrogen atom in the first compound is delocalized and is participating in aromaticity. This lone pair is unavailable to function as a base, because that would cause a loss of aromaticity.

18.42. Six π electrons are required in order to achieve aromaticity. This cation only has four electrons.



18.43. If both lone pairs occupy *p* orbitals, then there is a continuous system of overlapping *p* orbitals. There are 10 π electrons, so the dianion is aromatic.

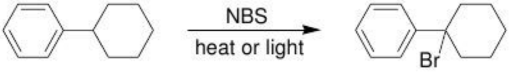
18.44. Yes. The lone pairs on the nitrogen atoms do not contribute to aromaticity. They occupy sp^2 hybridized orbitals. One of the lone pairs on the oxygen atom (in the ring) occupies a *p* orbital, giving a continuous system of overlapping *p* orbitals containing six π electrons.

18.45. Steric hindrance forces the rings out of coplanarity.

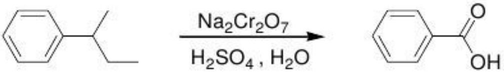
18.46. Benzene does not have three C-C single bond and three C-C double bonds. In fact, all six C-C bonds of the ring have the same bond order are the same length. However, cyclooctatetraene has four isolated π bonds. The molecule adopts a tub shape to avoid antiaromaticity. Some of the C-C bonds are double bonds (shorter in length), and some of the C-C bonds are single bonds (longer in length). Therefore, the two methyl groups can be separated by a C-C single bond or a C=C double bond. And those two possibilities represent different compounds.

18.47.

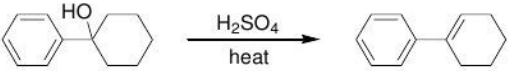
a)



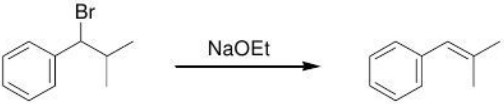
b)



c)



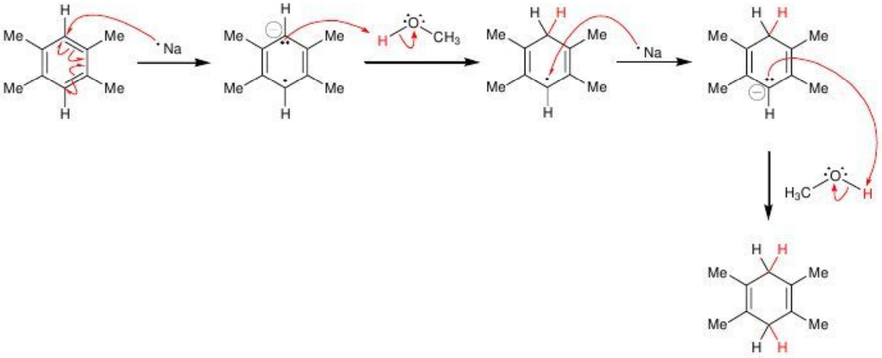
d)



18.48.

a) 6 b) 5 c) 3 d) 9

18.49.



18.50. *meta*-Xylene.

18.51.

a) The first compound would lack C-H stretching signals just above 3000 cm^{-1}, while the second compound will have C-H stretching signals just above 3000 cm^{-1}.

b) The ^{1}H NMR spectrum of the first compound will have only one signal, while the ^{1}H NMR spectrum of the second compound will have two signals.

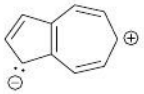
c) The ^{13}C NMR spectrum of the first compound will have only two signals, while the ^{13}C NMR spectrum of the second compound will have three signals.

18.52. When either compound is deprotonated, an aromatic anion is generated, which can be drawn with five resonance structures. The resulting anion is the same in either case.

18.53. In cycloheptatrienone, the resonance structures with C+ and O- contribute significant character to the overall resonance hybrid, because these forms are aromatic. Therefore, the oxygen atom of this C=O bond is particularly electron rich. A similar analysis of cyclopentadienone reveals resonance structures with antiaromatic character. These resonance structures contribute very little character to the overall resonance hybrid, and as a result, the oxygen atom of this C=O bond is not as electron rich when compared with most C=O bonds.

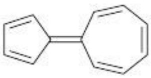
18.54.

a) Each of the rings in the following resonance structure is aromatic.

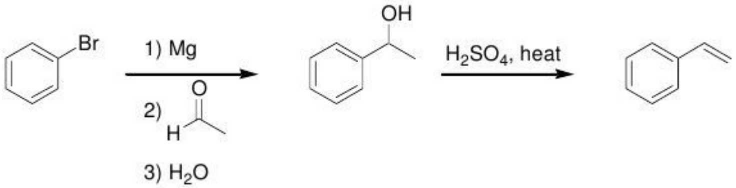


Therefore, this resonance structure contributes significant character to the overall resonance hybrid, which gives the azulene a considerable dipole moment.

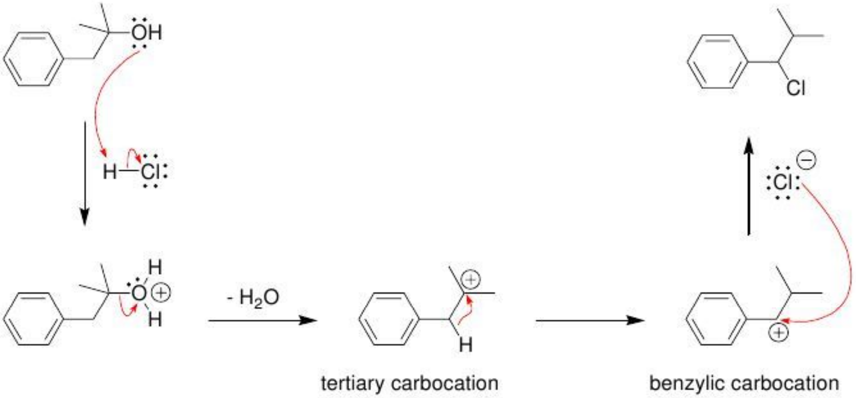
b)



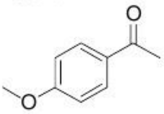
18.55.



18.56.

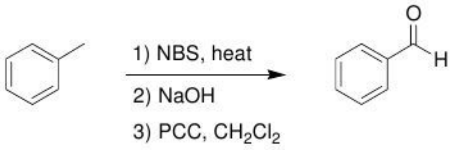


18.57.

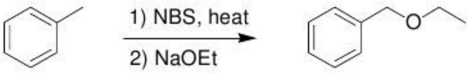


18.58.

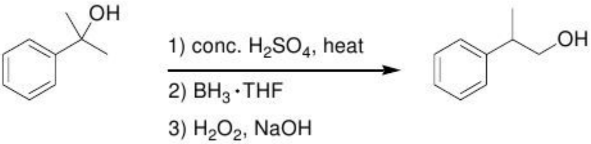
a)



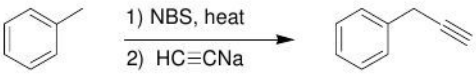
b)



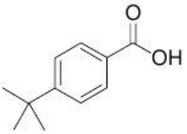
c)



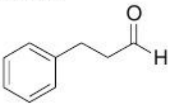
d)



18.59.



18.60.



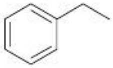
18.61.

a) The second compound holds greater promise as a potential antihistamine, because it possesses two planar aromatic rings separated from each other by one carbon atom. The first compound has only one aromatic ring. The ring with sulfur and oxygen is not aromatic and not planar.

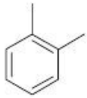
b) Yes, because it lacks polar functional groups that would prevent it from crossing the blood-brain barrier.

18.62. No, this compound possesses an allene moiety (C=C=C). The *p* orbitals of one C=C bond of the allene moiety do not overlap with the *p* orbitals of the other C=C bond. This prevents the compound from having one continuous system of overlapping *p* orbitals.

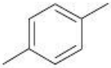
18.63.



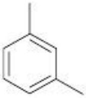
Compound A



Compound B



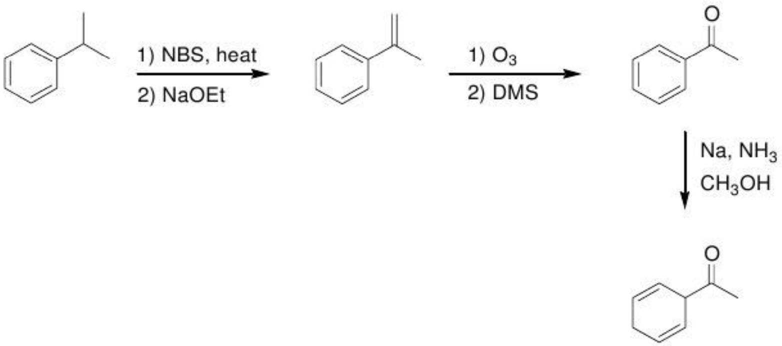
Compound C



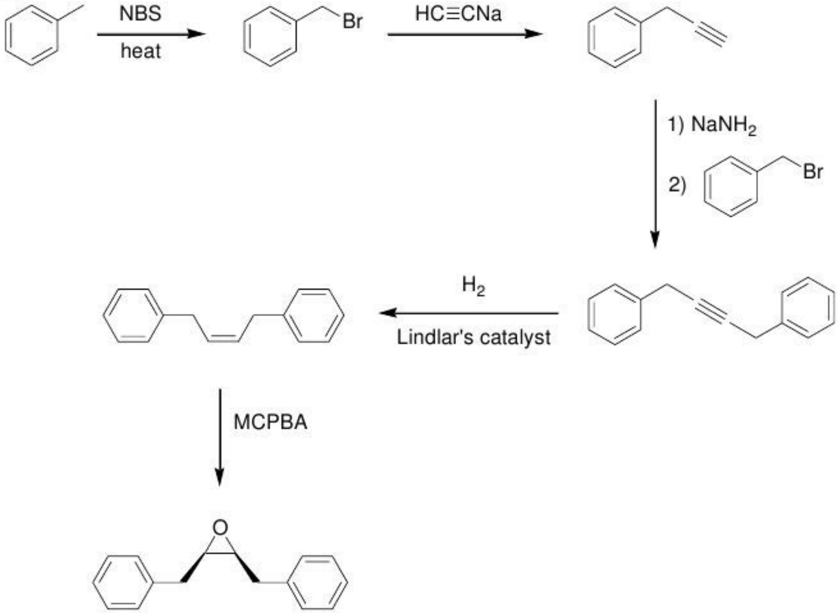
Compound D

18.64. The nitrogen atom in compound A is localized and is not participating in resonance. The nitrogen atom in compound B is delocalized, and some of the resonance structures are aromatic. These resonance structures contribute significant character to the overall resonance hybrid. The nitrogen atom in compound B is not available to function as a base.

18.65.



18.66.



Chapter 19
Aromatic Substitution Reactions

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 19. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

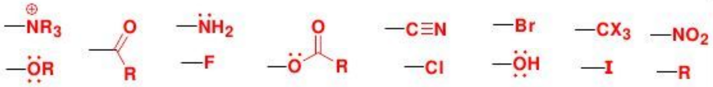
- In the presence of iron, an _____________ **aromatic substitution** reaction is observed between benzene and bromine.
- Iron tribromide is a __________ acid that interacts with Br_2 and generates Br^+, which is sufficiently electrophilic to be attacked by benzene.
- Electrophilic aromatic substitution involves two steps:
  - Formation of the __________ **complex**, or **arenium ion.**
  - Deprotonation, which restores _________________.
- Sulfur trioxide (SO_3) is a very powerful ____________ that is present in fuming sulfuric acid. Benzene reacts with SO_3 in a reversible process called __________.
- A mixture of sulfuric acid and nitric acid produces the **nitronium ion** (NO_2^+). Benzene reacts with the nitronium ion in a process called ____________.
- A nitro group can be reduced to an ______group.
- **Friedel–Crafts alkylation** enables the installation of an alkyl group on _______________________. When choosing an alkyl halide, the carbon atom connected to the halogen must be ______hybridized.
- When treated with a Lewis acid, an acyl chloride will generate an _________ **ion**, which is resonance stabilized and not susceptible to __________ rearrangements.
- When a Friedel–Crafts acylation is followed by a **Clemmensen reduction**, the net result is the installation of an ______ group.
- An aromatic ring is **activated** by a methyl group, which is an ______**-**______ **director**.
- All activators are ______-______directors
- A nitro group **deactivates** an aromatic ring and is a ______director.
- Most deactivators are ______directors.
- **Strong activators** are characterized by the presence of a __________________ immediately adjacent to the aromatic ring.
- **Strong deactivators** are powerfully electron-withdrawing, either by ____________or ____________.
- When multiple substituents are present, the more powerful __________________ dominates the directing effects.
- In a **nucleophilic aromatic substitution** reaction, the aromatic ring is attacked by a ____________. This reaction has three requirements: 1) the ring must contain a powerful electron-withdrawing group (typically a ______group) 2) the ring must contain a ____________, and 3) the leaving group must be either ______or ______to the electron-withdrawing group.
- An **elimination-addition** reaction occurs via a ____________intermediate.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 19. The answers appear in the section entitled *SkillBuilder Review*.

19.1 Identifying the Effects of a Substituent

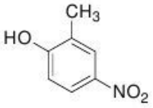
PLACE EACH OF THE FOLLOWING GROUPS IN THE CORRECT CATEGORY BELOW.



ACTIVATORS			DEACTIVATORS		
STRONG	**MODERATE**	**WEAK**	**WEAK**	**MODERATE**	**STRONG**

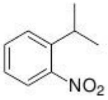
19.2 Identifying Directing Effects for Disubstituted and Polysubstituted Benzene Rings

IN THE FOLLOWING COMPOUND, IDENTIFY THE POSITION THAT IS MOST REACTIVE TOWARDS ELECTROPHILIC AROMATIC SUBSTITUTION.



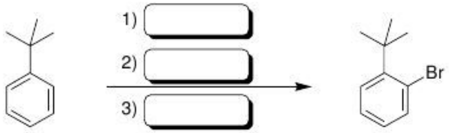
19.3 Identifying Steric Effects for Disubstituted and Polysubstituted Aromatic Benzene Rings

IN THE FOLLOWING COMPOUND, IDENTIFY THE POSITION THAT IS MOST REACTIVE TOWARDS ELECTROPHILIC AROMATIC SUBSTITUTION.



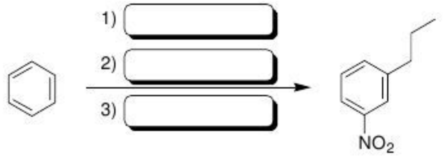
19.4 Using Blocking Groups to Control the Regiochemical Outcome of an Electrophilic Aromatic Substitution Reaction

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:



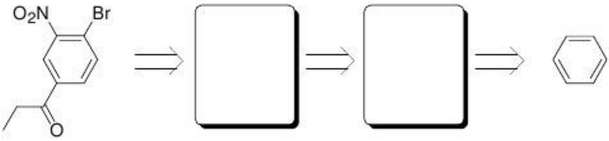
19.5 Proposing a Synthesis for a Disubstituted Benzene Ring

IDENTIFY A THREE-STEP PROCESS FOR ACHIEVING THE FOLLOWING TRANSFORMATION:



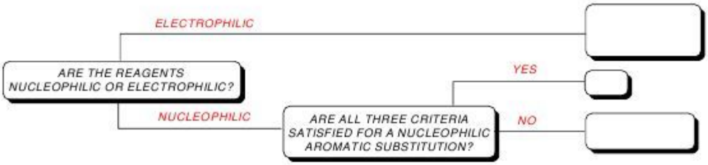
19.6 Proposing a Synthesis for a Polysubstituted Benzene Ring

COMPLETE THE FOLLOWING RETROSYNTHETIC ANALYSIS:



19.7 Determining the Mechanism of an Aromatic Substitution Reaction

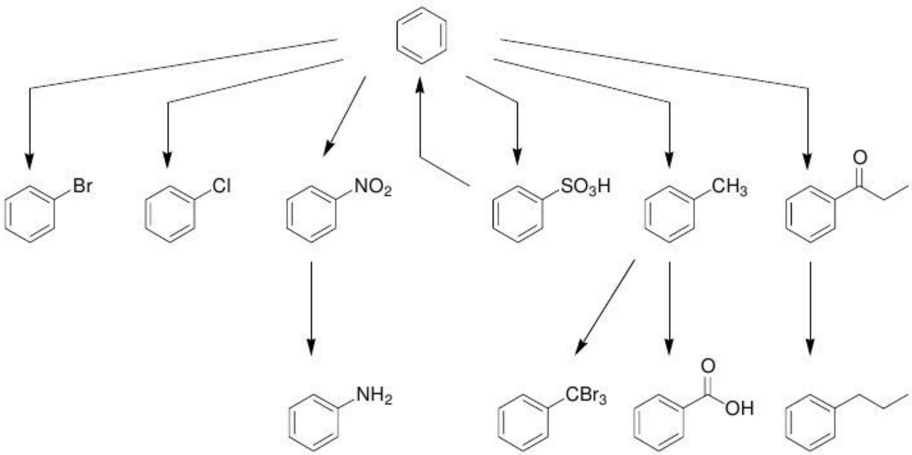
INDICATE THE MECHANISM THAT OPERATES IN EACH OF THE THREE SCENARIOS SHOWN IN THE FOLLOWING DECISION TREE:



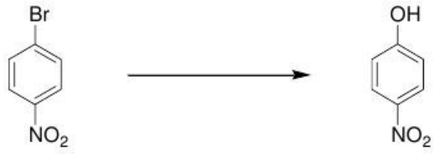
Review of Reactions

Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 19. The answers appear in the section entitled *Review of Reactions*.

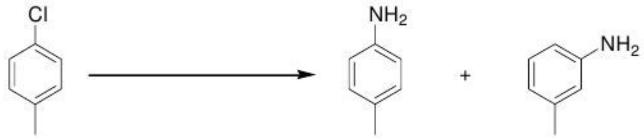
Electrophilic Aromatic Substitution



Nucleophilic Aromatic Substitution

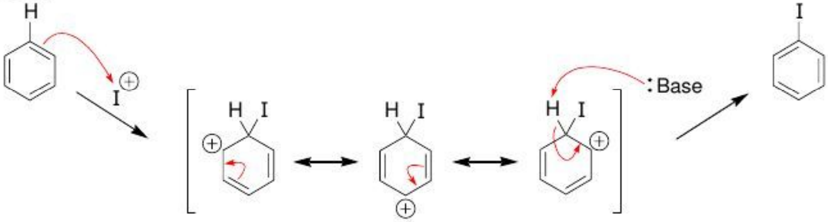


Elimination-Addition

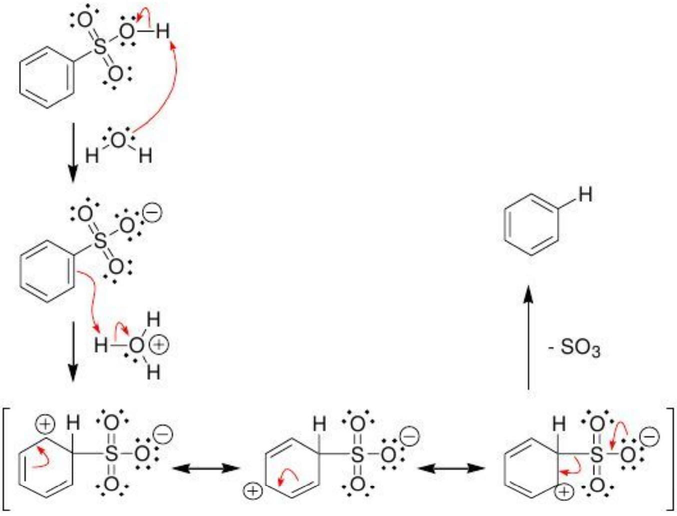


Solutions

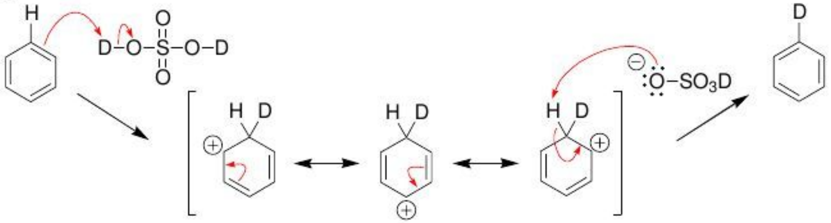
19.1.



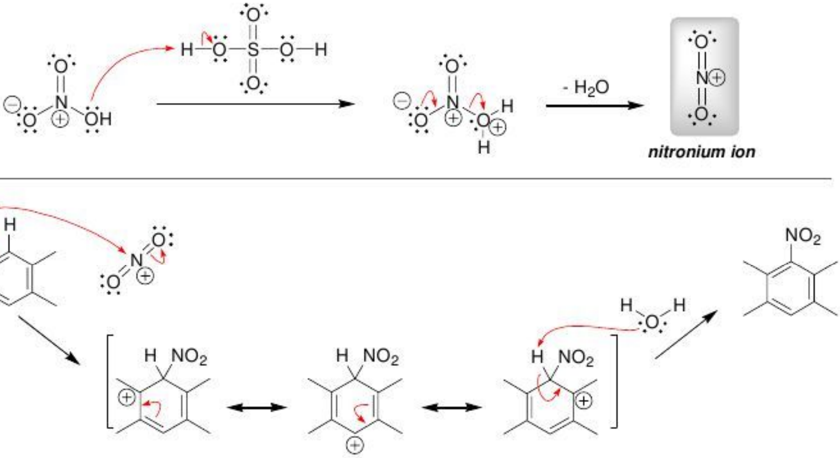
19.2.



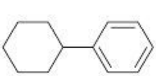
19.3.

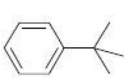


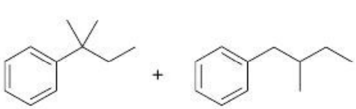
19.4.



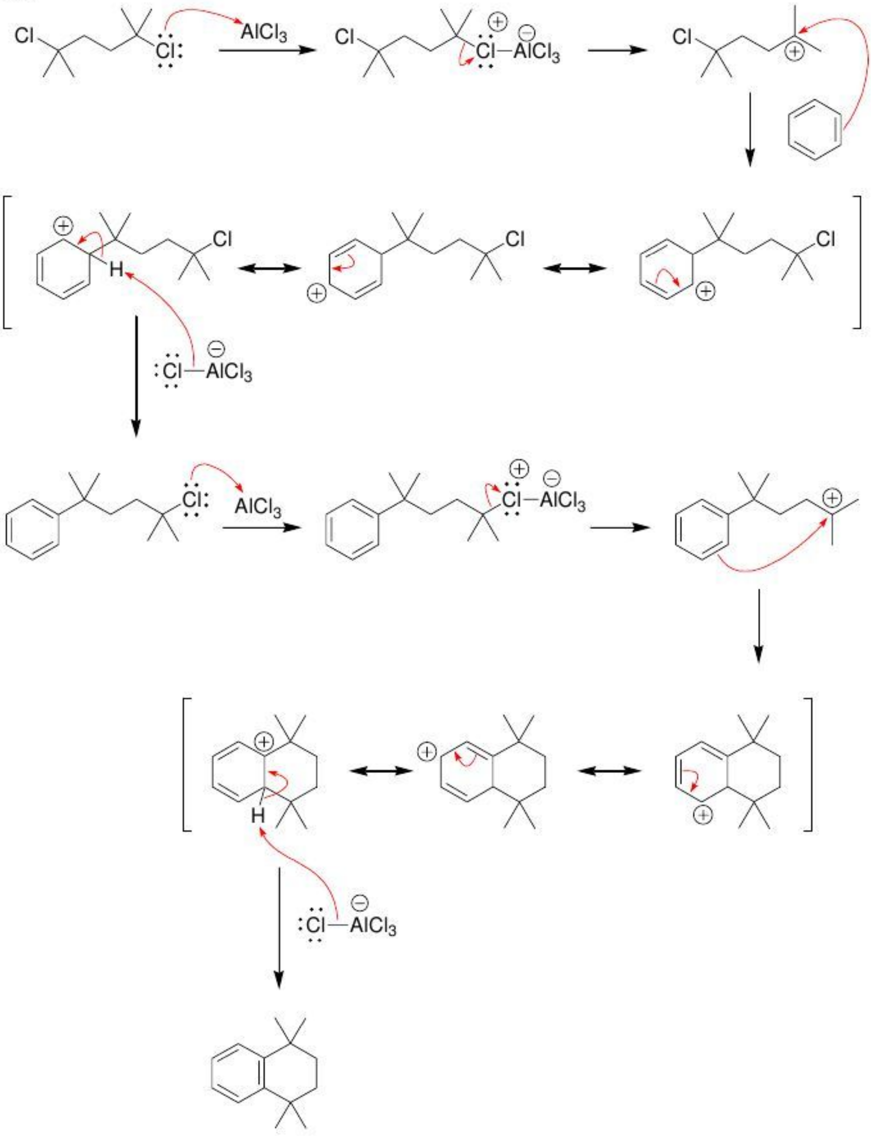
19.5.

a) 

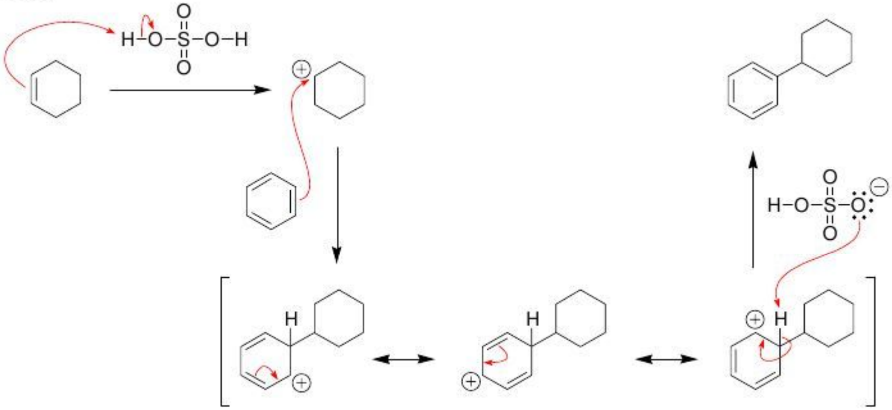
b) 

c) 

19.6.


Cl
:Cl:
AlCl$_3$
Cl
Cl
AlCl$_3$
Cl
H
Cl
Cl
:Cl—AlCl$_3$
:Cl:
AlCl$_3$
Cl
AlCl$_3$
H
:Cl—AlCl$_3$

19.7.



19.8.

a) It is necessary to perform an acylation followed by a Clemmensen reduction to avoid carbocation rearrangements.

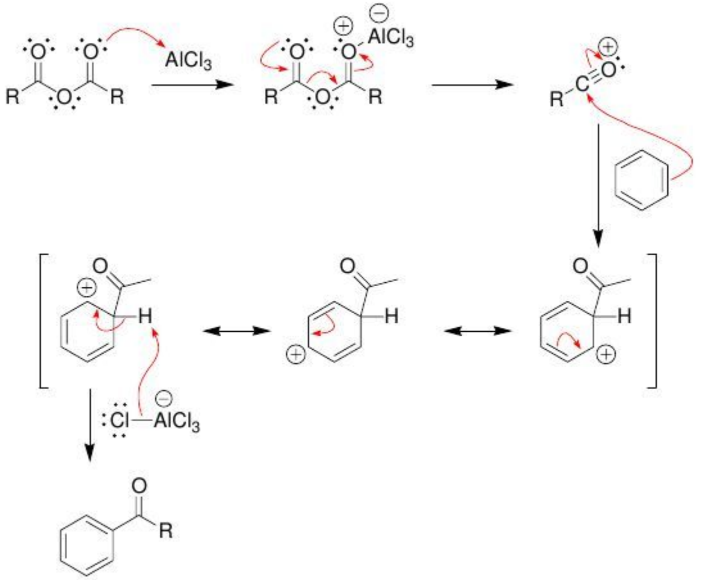
b) It is necessary to perform an acylation followed by a Clemmensen reduction to avoid carbocation rearrangements.

c) It is necessary to perform an acylation followed by a Clemmensen reduction to avoid carbocation rearrangements.

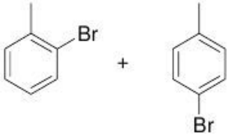
d) The compounds can be made using a direct Friedel–Crafts alkylation.

19.9. It cannot be made via alkylation because the carbocation required would undergo a methyl shift to give a tertiary carbocation. It cannot be made via acylation followed by a Clemmensen reduction, because the product of a Clemmensen reduction has two benzylic protons. This compound has only one benzylic proton, which means that it cannot be made via a Clemmensen reduction.

19.10.

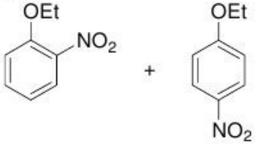


19.11.

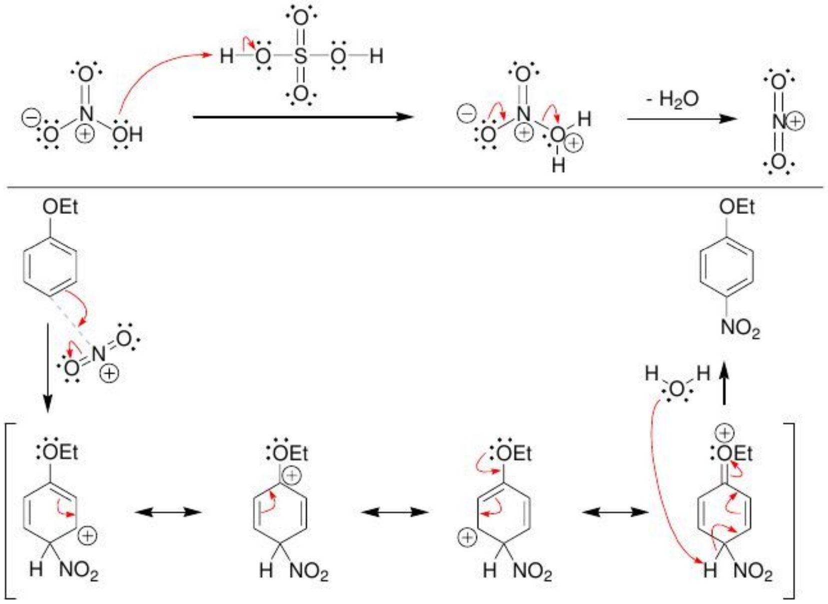


19.12.

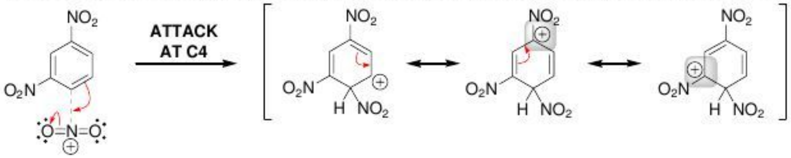
a)

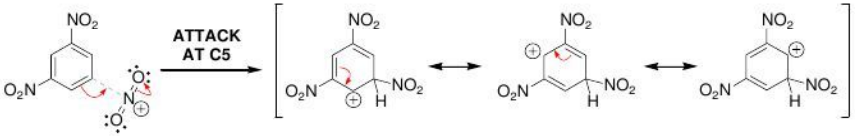


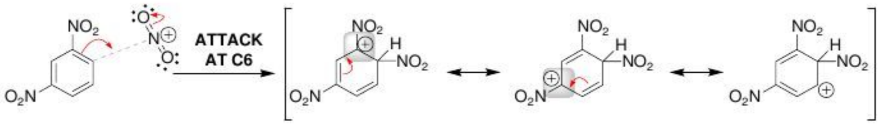
b)



19.13. As show below, attack at C4 or C6 produces a sigma complex in which two of the resonance structures have a positive charge next to an electron-withdrawing group (NO_2). These resonance structures are less contributing to the resonance hybrid, thereby destabilizing the sigma complex. In contrast, attack at C5 produces a sigma complex for which none of the resonance structures have a positive charge next to a nitro group.

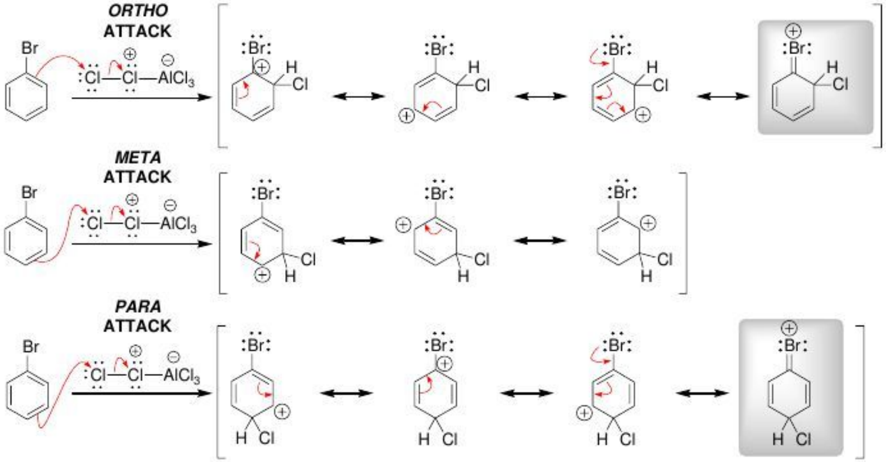






19.14. The chlorine atom in chlorobenzene deactivates the ring relative to benzene. If benzene requires a Lewis acid for chlorination, than chlorobenzene should certainly require a Lewis acid for chlorination.

19.15. *Ortho* attack and *para* attack are preferred because each of these pathways involves a sigma complex with four resonance structures (shown below). Attack at the *meta* position involves formation of a sigma complex with only three resonance structures, which is not as stable as a sigma complex with four resonance structures. The reaction will proceed more rapidly via the lower energy sigma complex, so attack takes place at the *ortho* and *para* positions in preference to the *meta* position.



19.16.

a) The nitro is strongly deactivating and *meta*-directing.

b) An acyl group is moderately deactivating and *meta*-directing.

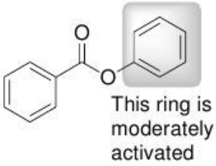
c) A bromine atom weakly deactivating and *ortho, para*-directing.

d) This group is moderately deactivating and *meta*-directing.

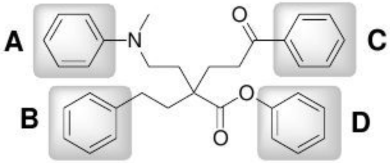
e) This group is moderately deactivating and *meta*-directing.

f) This group is moderately activating and *ortho, para* -directing.

19.17.



19.18.



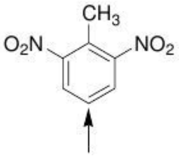
Increasing reactivity toward electrophilic aromatic substitution

$\xrightarrow{\hspace{4cm}}$

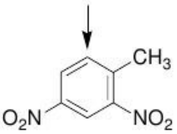
C **B** **D** **A**

19.19.

a)



b)



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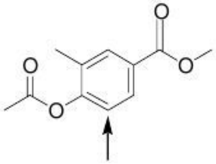
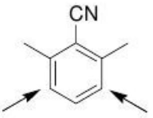


d)



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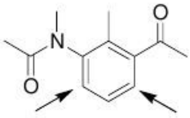
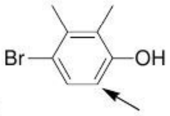
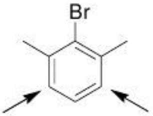


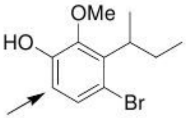
f)



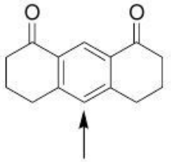
g)



h)

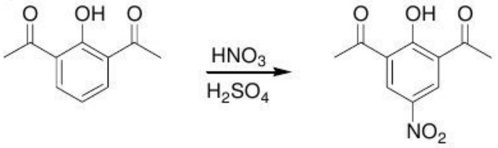


i)

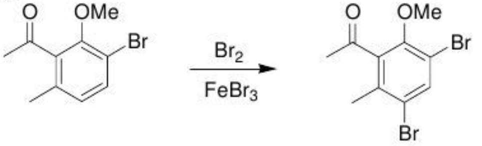


19.20.

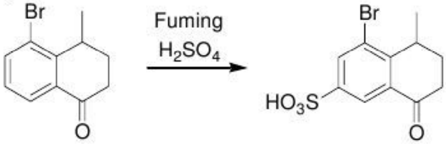
a)



b)



c)



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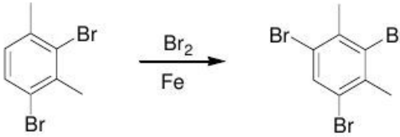
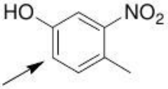
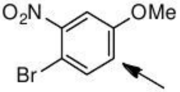


19.22.

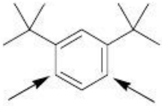
a)



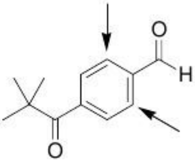
b)



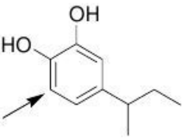
c)



d)

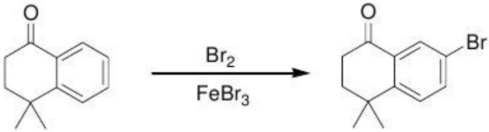


e)



19.23. All three available positions are sterically hindered.

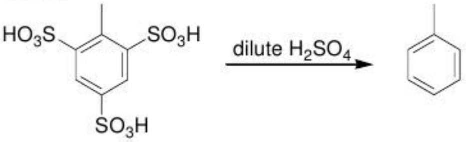
19.24.



19.25.

a) Yes b) No c) Yes d) No

19.26.



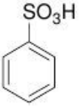
19.27.

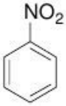
a) The nitro group must be installed in a position that is *meta* to each of the OH groups. Even with a blocking group, *meta* attack cannot be achieved on a highly activated ring.
b) The position that must undergo bromination is too sterically hindered because of the presence of the *tert*-butyl groups.

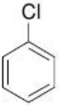
19.28.

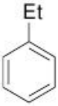
a) Cl_2, $AlCl_3$
b) HNO_3, H_2SO_4
c) Br_2, $FeBr_3$
d) CH_3CH_2Cl, $AlCl_3$
e) CH_3CH_2COCl, followed by HCl, Zn[Hg], heat
f) $(CH_3)_2CHCl$, $AlCl_3$
g) HNO_3, H_2SO_4, followed by followed by HCl, Zn
h) CH_3Cl, $AlCl_3$, followed by $KMnO_4$, NaOH, heat, followed by H_3O^+
i) CH_3Cl, $AlCl_3$

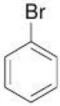
19.29.

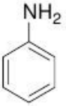
a) 

b) 

c) 

d) 

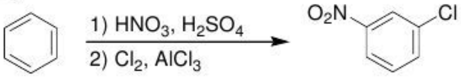
e) 

f) 

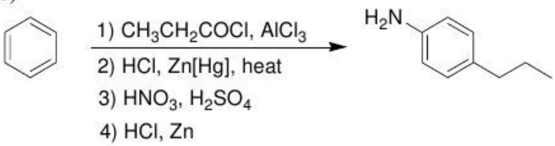
19.30.

a)

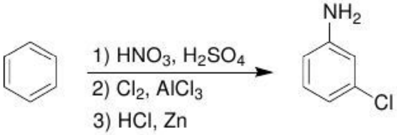
b)



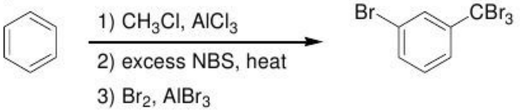
c)


1) CH_3CH_2COCl, $AlCl_3$
2) HCl, Zn[Hg], heat
3) HNO_3, H_2SO_4
4) HCl, Zn
H_2N

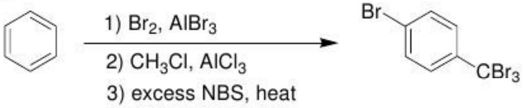
d)


1) HNO_3, H_2SO_4
2) Cl_2, $AlCl_3$
3) HCl, Zn
NH_2
Cl

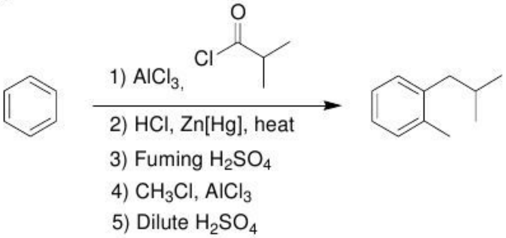
e)


1) CH_3Cl, $AlCl_3$
2) excess NBS, heat
3) Br_2, $AlBr_3$
Br
CBr_3

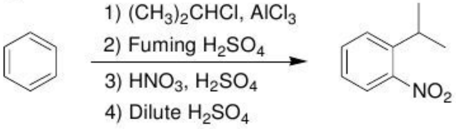
f)


1) Br_2, $AlBr_3$
2) CH_3Cl, $AlCl_3$
3) excess NBS, heat
Br
CBr_3

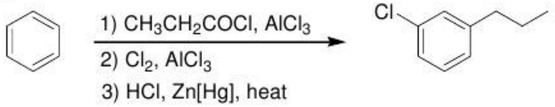
g)


O
Cl
1) $AlCl_3$,
2) HCl, Zn[Hg], heat
3) Fuming H_2SO_4
4) CH_3Cl, $AlCl_3$
5) Dilute H_2SO_4

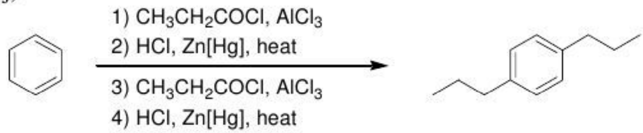
h)


1) $(CH_3)_2CHCl$, $AlCl_3$
2) Fuming H_2SO_4
3) HNO_3, H_2SO_4
4) Dilute H_2SO_4
NO_2

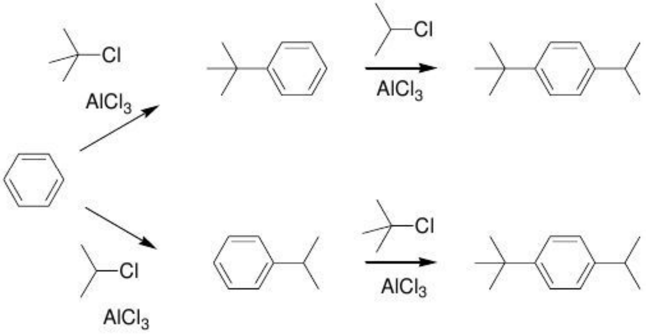
i)



j)



19.31. The *para* product will be more strongly favored over the *ortho* product if the *tert*-butyl group is installed first. The steric hindrance provided by a *tert*-butyl group is greater than the steric hindrance provided by an isopropyl group. Of the following two possible pathways, the first should provide a greater yield of the desired product.



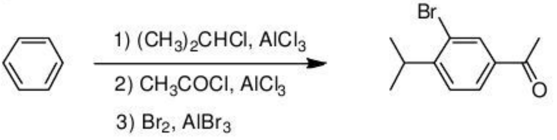
19.32.

a) Nitration cannot be achieved effectively in the presence of an amino group.

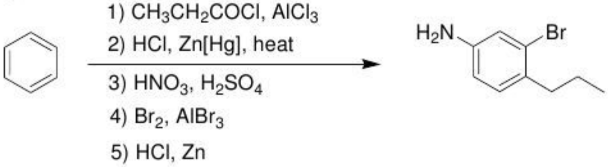
b) Each of the two alkyl groups is *ortho-para* directing, but the two groups are *meta* to each other. A Friedel-Crafts acylation will not work in this case (see solution to problem 19.9)

19.33.

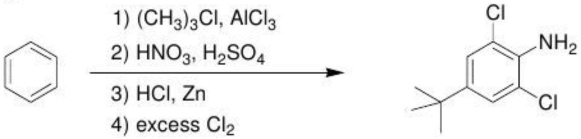
a)



b)

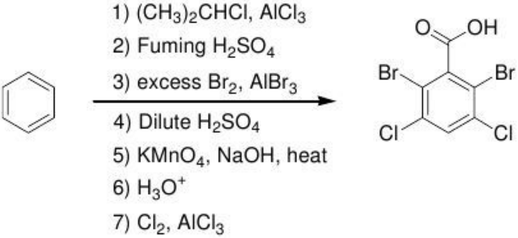


c)



d)

19.34.

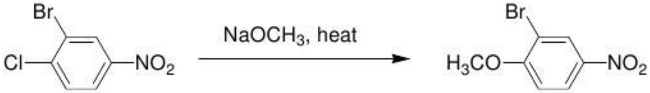


a)

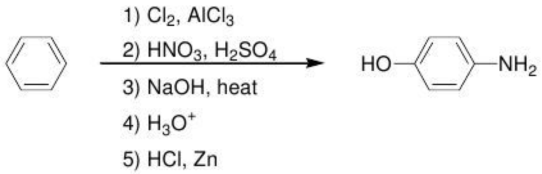
b) The sixth position is sterically hindered by the presence of the Cl atoms.

c) The ring is deactivated because all five groups are deactivators.

19.35.



19.36.

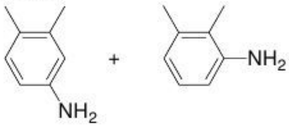


19.37.

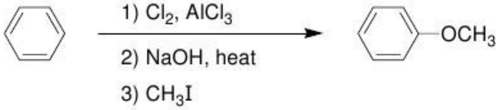
a) Each additional nitro group serves as a reservoir of electron density and provides for an additional resonance structure in the sigma complex, thereby stabilizing the sigma complex and lowering the energy of activation for the reaction.

b) No, a fourth nitro group would not be *ortho* or *para* to the leaving group, and therefore cannot function as a reservoir.

19.38.

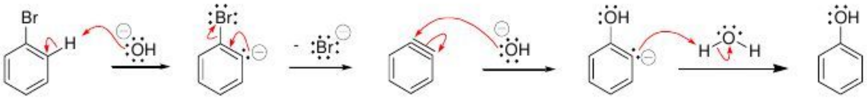


19.39.

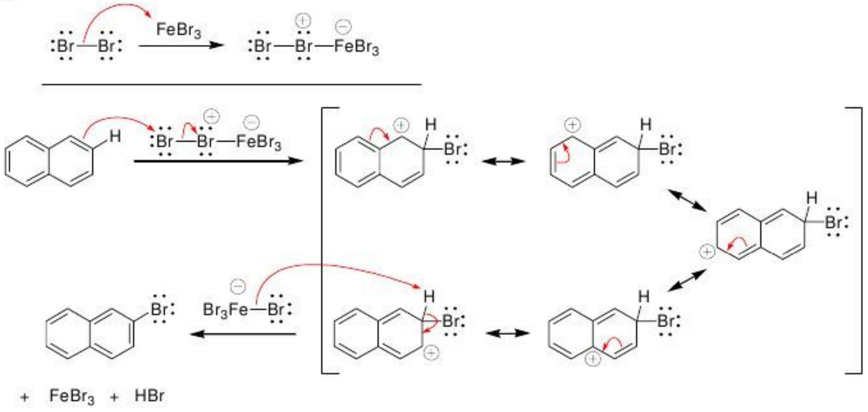


19.40.

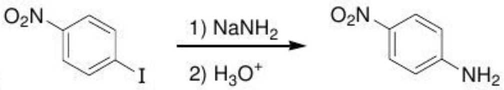
a)

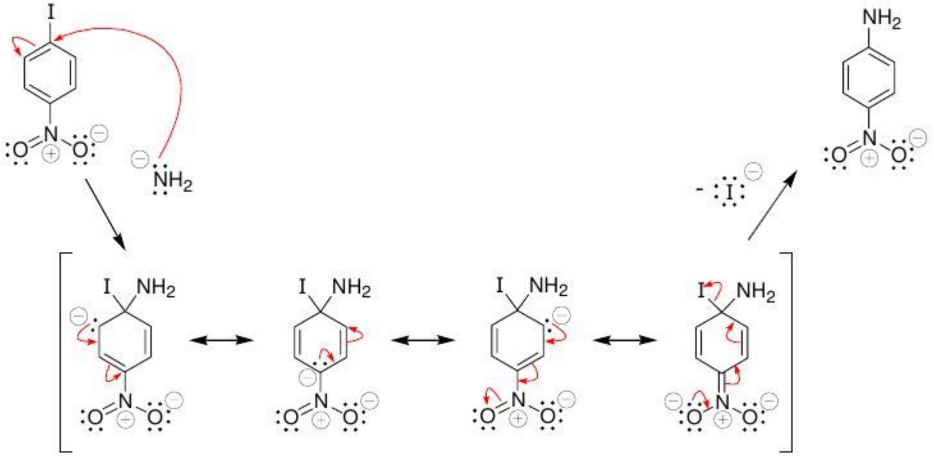


b)

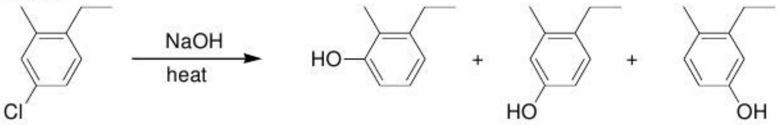

FeBr$_3$
Br
Br
FeBr$_3$
H
Br
+ FeBr$_3$ + HBr
Br$_3$Fe

c)


O$_2$N
I
1) NaNH$_2$
2) H$_3$O$^+$
O$_2$N
NH$_2$

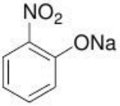

I
NH$_2$
N
O
- I

19.41.

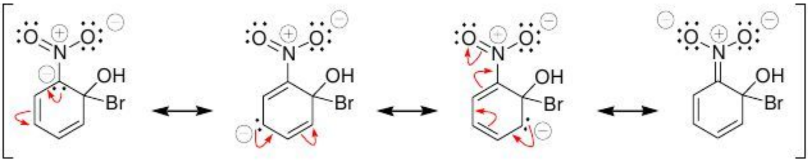


19.42.

a)



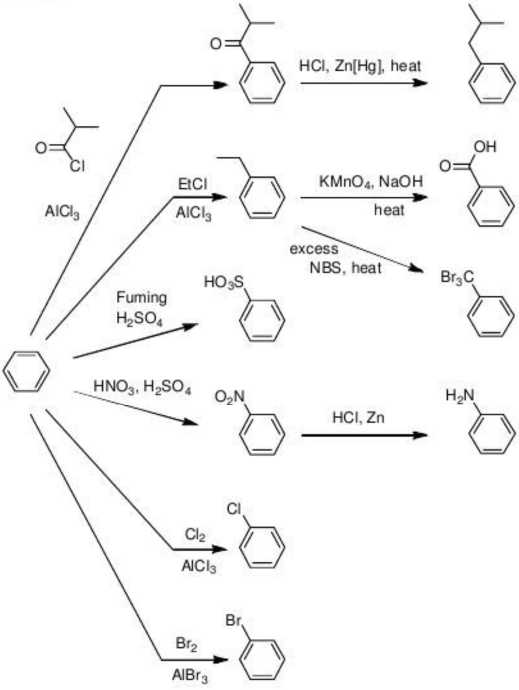
b)



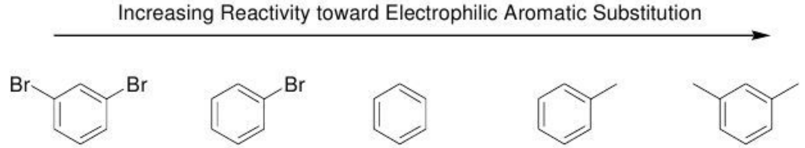
c) No

d) Yes

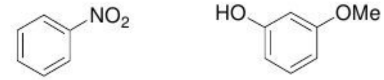
19.43.



19.44.

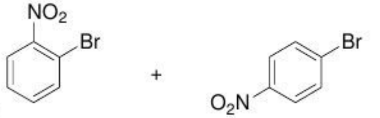


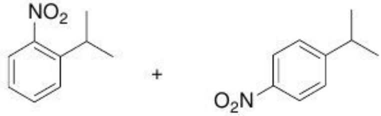
19.45.

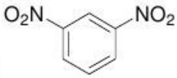


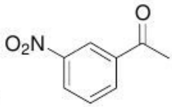
least activated most activated

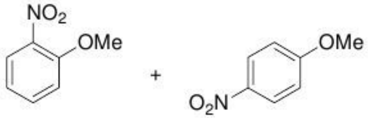
19.46.

a) 

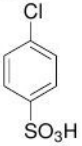
b) 

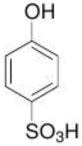
c) 

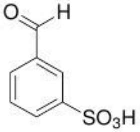
d) 

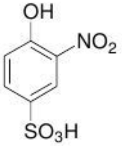
e) 

19.47.

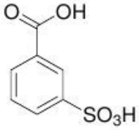
a) 

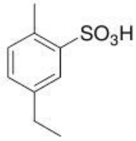
b) 

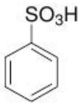
c) 

d) 

e) 

f) 

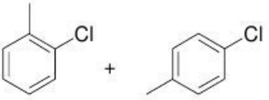
g) 

h) 

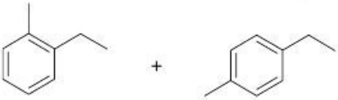
19.48.

a) This group is an activator and an *ortho*,*para*-director.
b) This group is an activator and an *ortho*,*para*-director.
c) This group is an activator and an *ortho*,*para*-director.
d) This group is a deactivator and an *ortho*,*para*-director.
e) This group is a deactivator and a *meta*-director.
f) This group is a deactivator and a *meta*-director.
g) This group is a deactivator and a *meta*-director.
h) This group is a deactivator and a *meta*-director.
i) This group is a deactivator and an *ortho*,*para*-director.
j) This group is a deactivator and a *meta*-director.

19.49.

a)


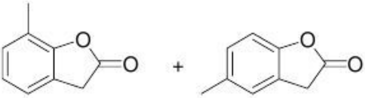
b) unreactive c) unreactive

d)


e)

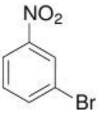

f)

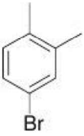

g) unreactive

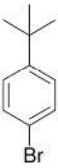
h)


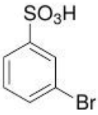
19.50.

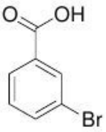
a)

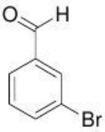

b)


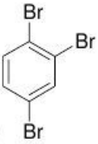
c)


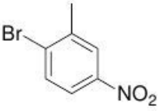
d)


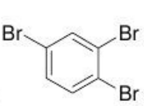
e)


f)


g)


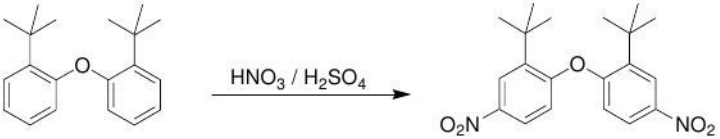
h)


i)


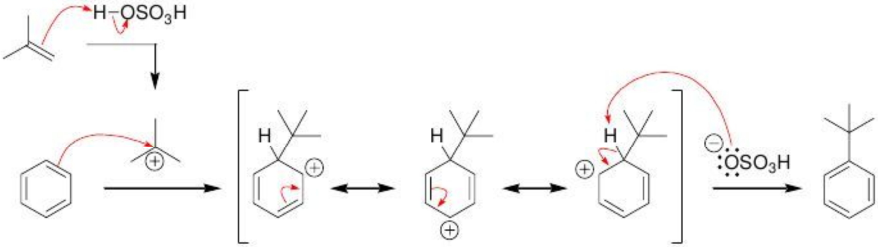
j) 

k) 

19.51.

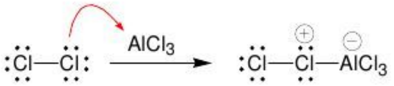


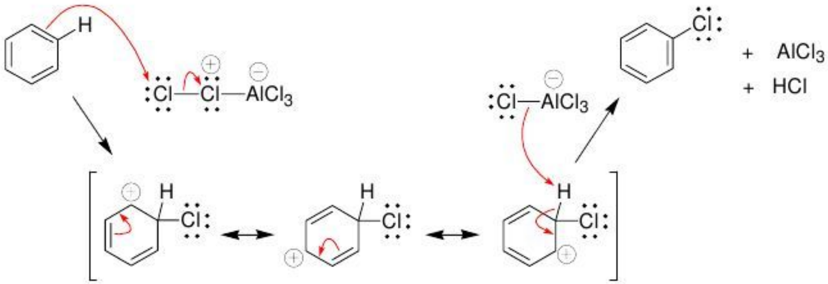
19.52.



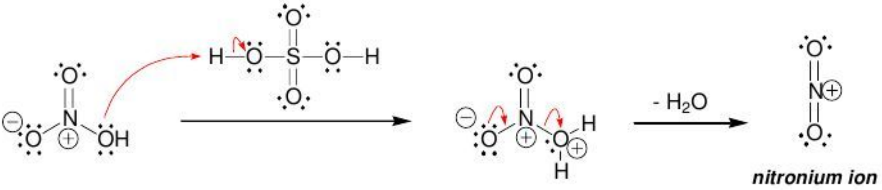
19.53.

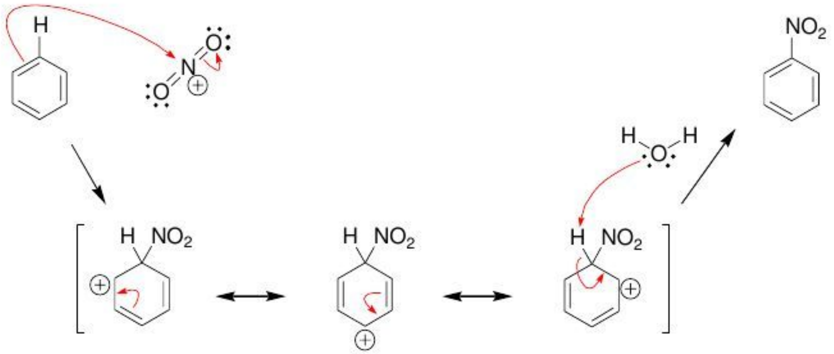
a)



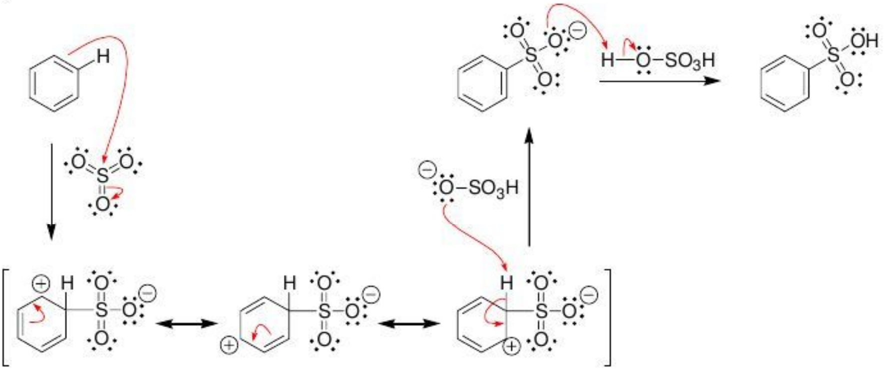


b)

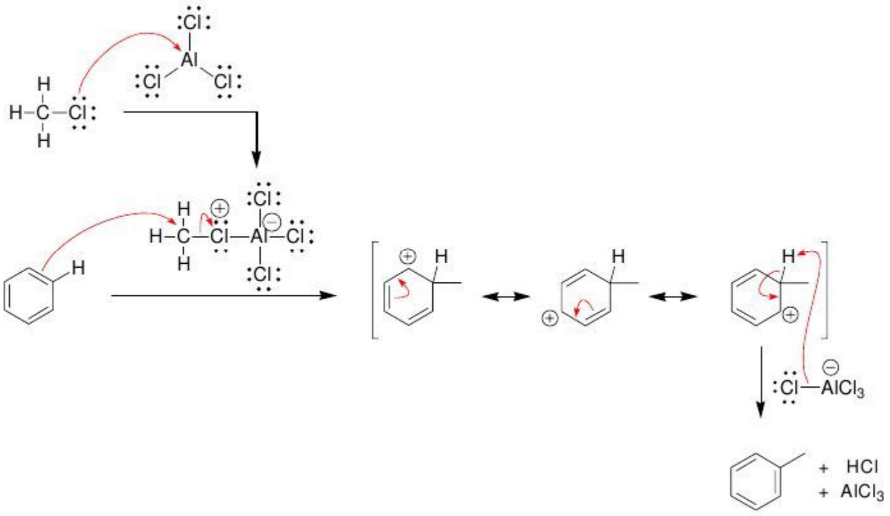




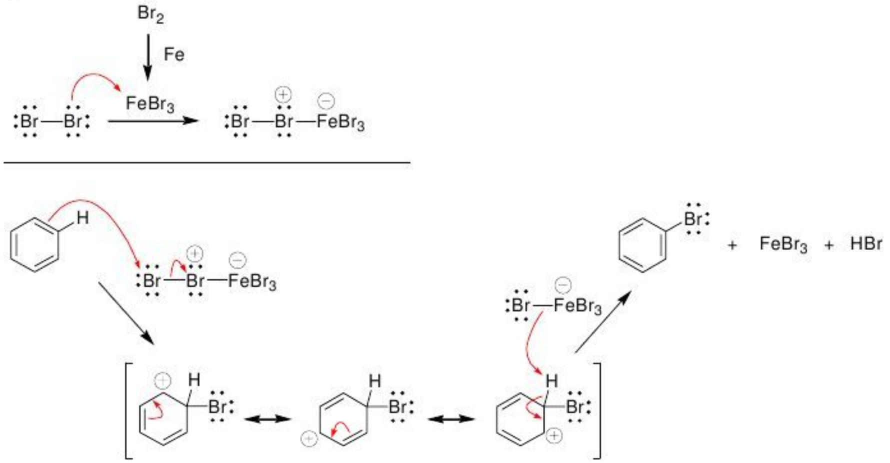
c)



d)

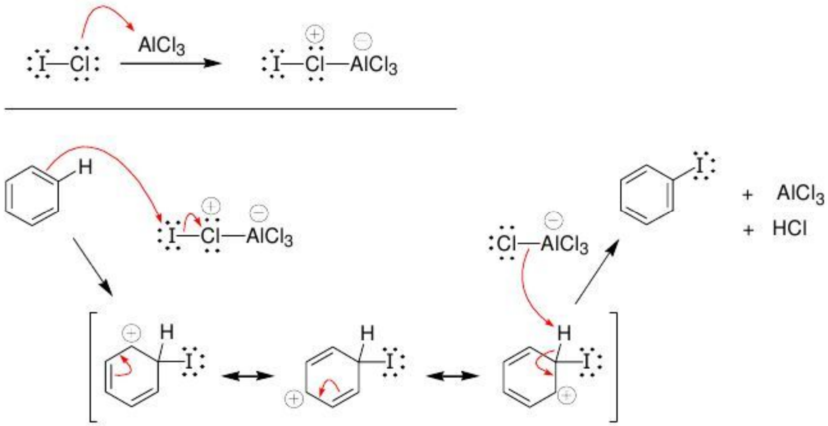

H
H–C–Cl
H
Cl
Al
Cl
Cl
H
H–C–Cl–Al–Cl
H
Cl
Cl
H
H
H
H
Cl–AlCl3
+ HCl
+ AlCl3

e)

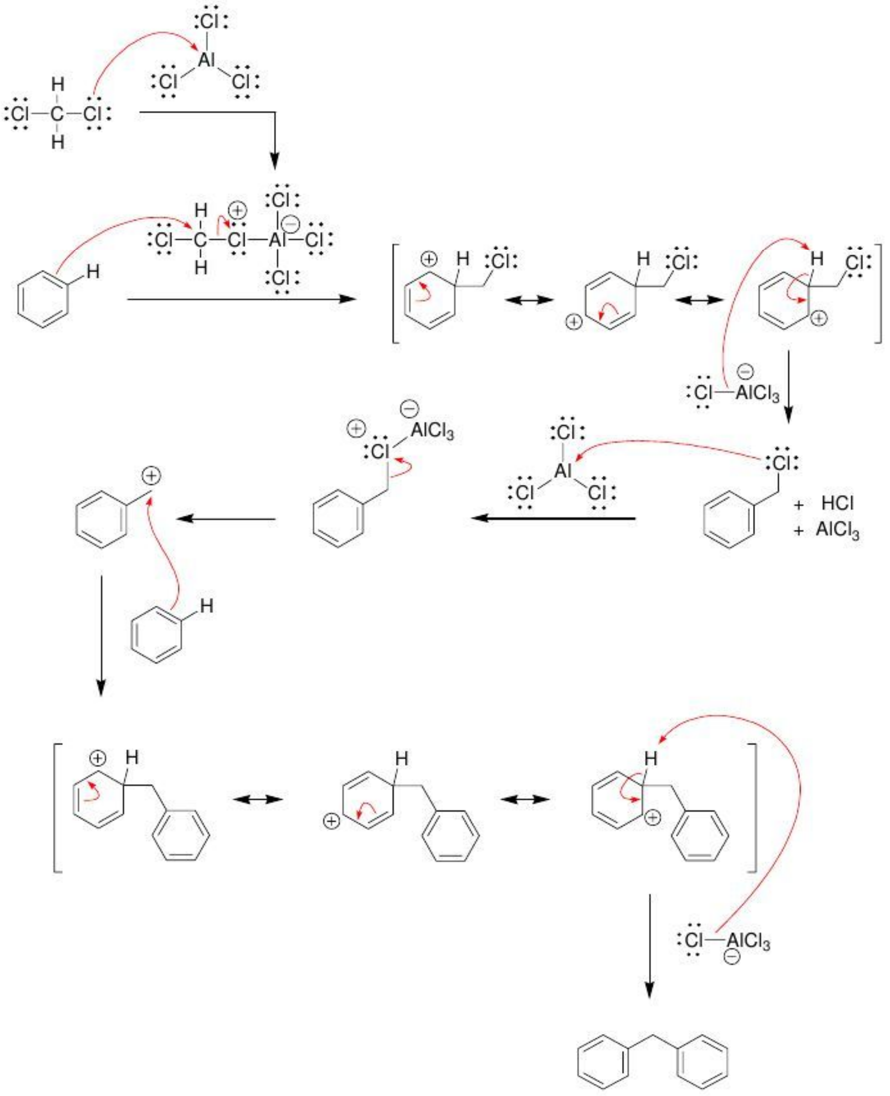

Br2
Fe
FeBr3
Br–Br
Br–Br–FeBr3
H
Br–Br–FeBr3
Br–FeBr3
Br
+ FeBr3 + HBr
H
Br
H
Br
H
Br

19.54.

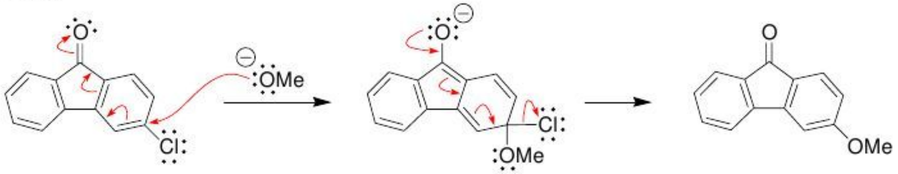
a)



b)

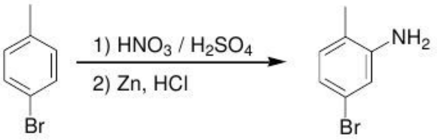


19.55.

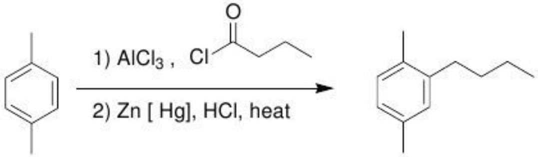


19.56.

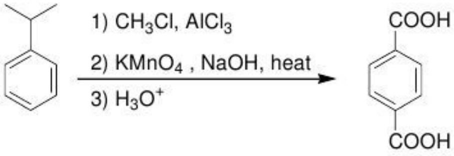
a)



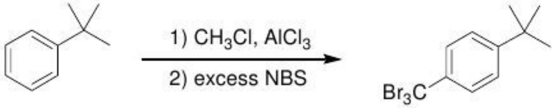
b)



c)

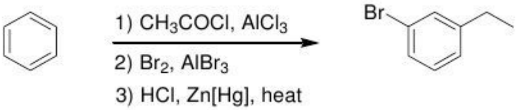


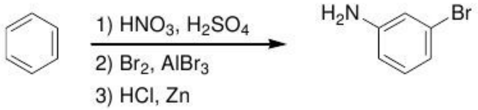
d)



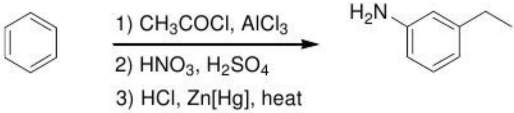
19.57.

a)





b)



c)

19.58.

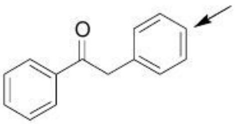
a) The second step of the synthesis will not work, because a strongly deactivated ring will not undergo a Friedel-Crafts alkylation. The product of the first step, nitrobenzene, will be unreactive in the second step.

b) The second step of the synthesis will not efficiently install a propyl group, because a carbocation rearrangement can occur, which will result in the installation of an isopropyl group.

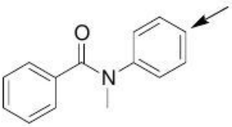
c) The second step of the synthesis will not install the acyl group in the *meta* position. It will be installed in a position that is either *ortho* or *para* to the bromine atom.

d) The second step of the synthesis will not install the bromine atom in the *ortho* position, because of steric hindrance from the *tert*-butyl group. Bromination will occur primarily at the *para* position.

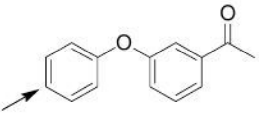
19.59.



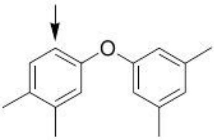
a)



b)

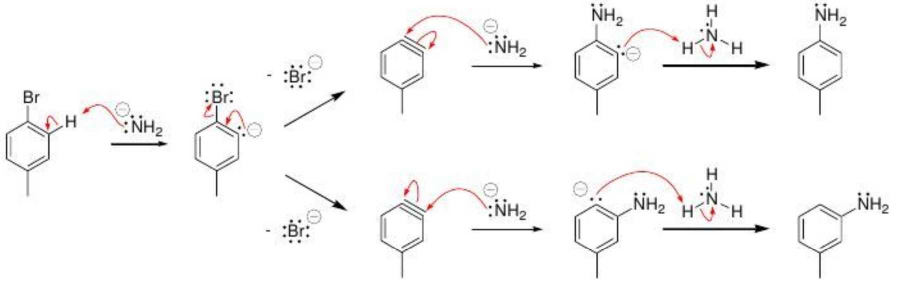


c)

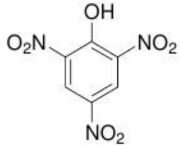


d)

19.60.

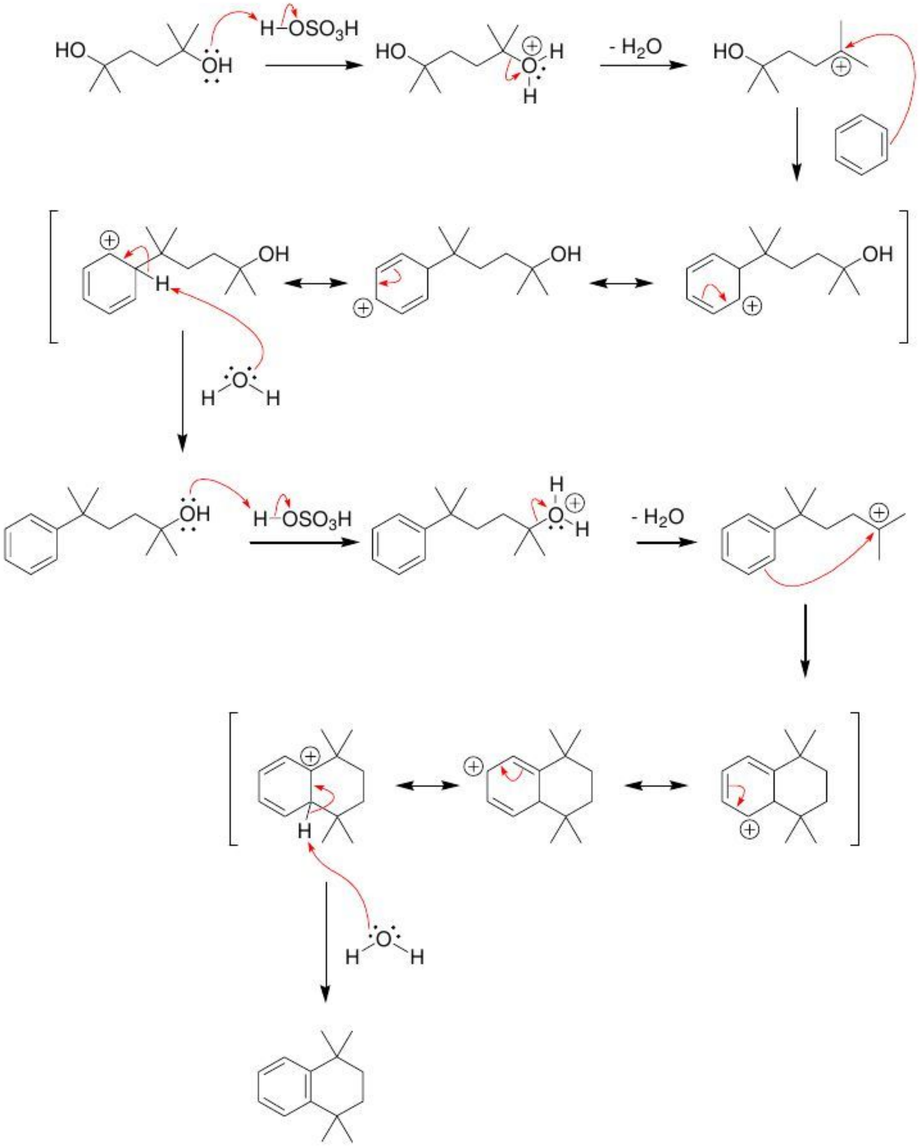


19.61.



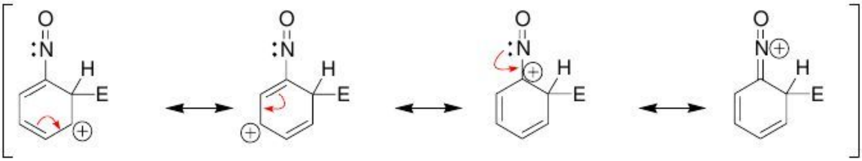
2,4,6-trinitrophenol
(picric acid)

19.62.

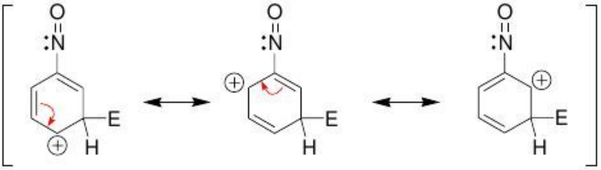


19.63.

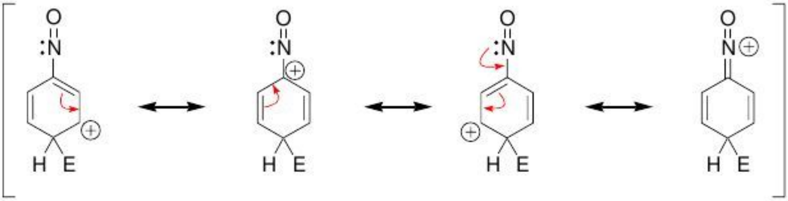
19.64.



a)



b)

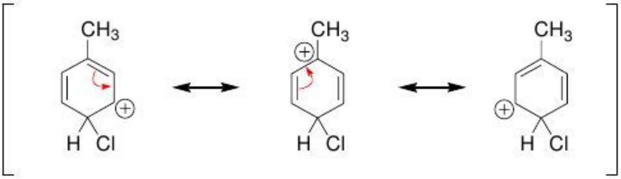


c)

d) The nitroso group should be *ortho-para* directing, because attack at the *ortho* or *para* position generates a sigma complex with an additional resonance structure.

e) The nitroso group is a deactivator, yet it is an *ortho-para* director, just like a chlorine atom.

19.65.

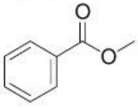


19.66.

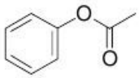
a) Toluene is the only compound containing an activated ring, and it is expected to undergo a Friedel-Crafts reaction most rapidly to give *ortho*-ethyltoluene and *para*-ethyltoluene.

b) Anisole is the most activated compound (among the three compounds), and is expected to undergo a Friedel-Crafts reaction most rapidly to give *ortho*-ethylanisole and *para*-ethylanisole.

19.67.



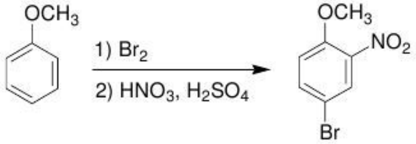
Compound A



Compound B

19.68.

a)



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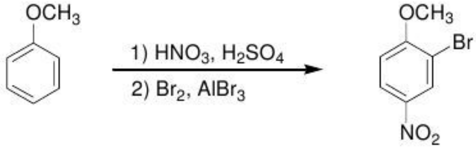

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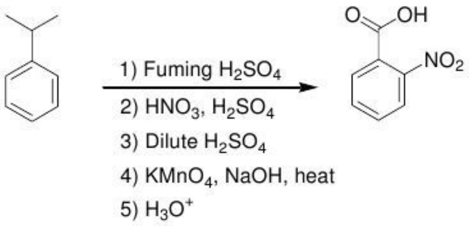

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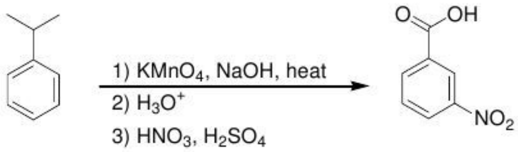
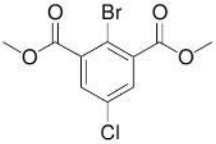


19.69.

a)



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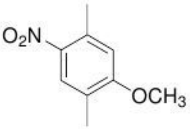

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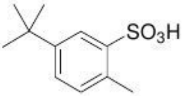

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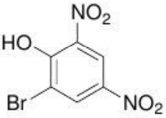
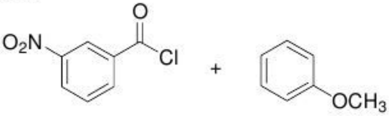
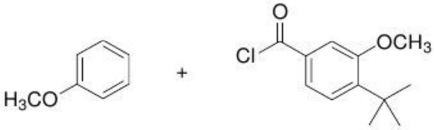


19.70.

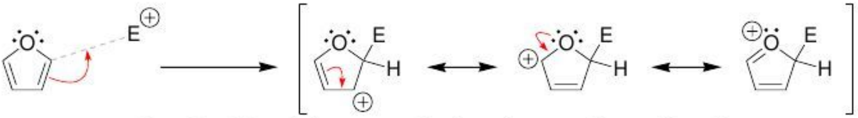
a)



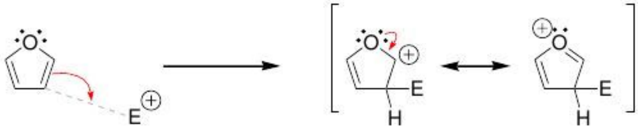
b)



19.71. Attack at the C2 position proceeds via an intermediate with three resonance structures:



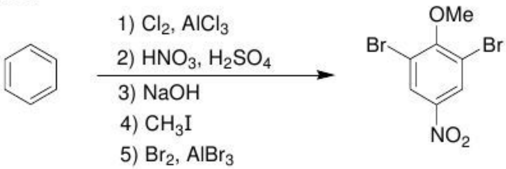
In contrast, attack at the C3 position proceeds via an intermediate with only two resonance structures:



The intermediate for C2 attack is lower in energy than the intermediate for C3 attack. The transition state leading to the intermediate of C2 attack will therefore be lower in energy than the transition state leading to the intermediate of C3 attack. As a result, C2 attack occurs more rapidly.

19.72.

a)



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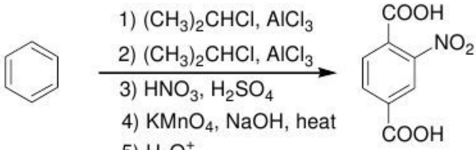

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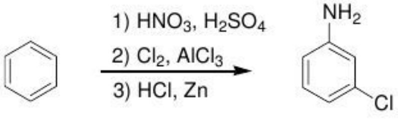
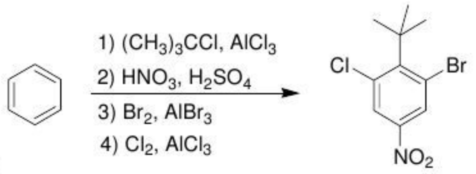
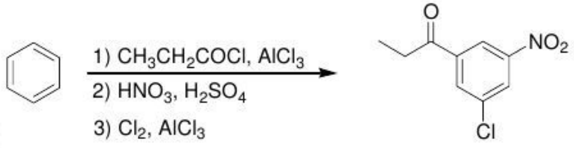


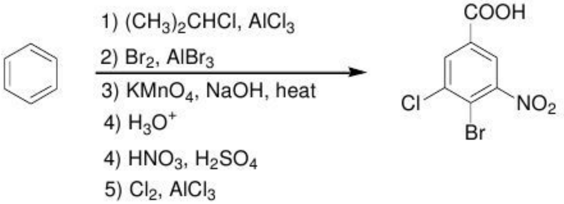
d)


1) (CH3)3CCl, AlCl3
2) HNO3, H2SO4
3) Br2, AlBr3
4) Cl2, AlCl3
Cl
Br
NO2

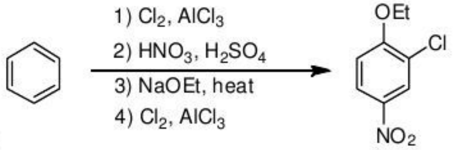
e)


1) CH3CH2COCl, AlCl3
2) HNO3, H2SO4
3) Cl2, AlCl3
O
NO2
Cl

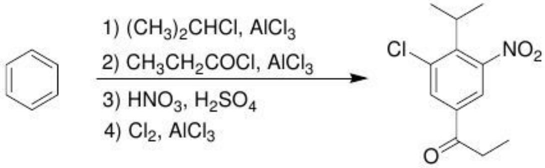
f)


1) (CH3)2CHCl, AlCl3
2) Br2, AlBr3
3) KMnO4, NaOH, heat
4) H3O+
4) HNO3, H2SO4
5) Cl2, AlCl3
COOH
Cl
NO2
Br

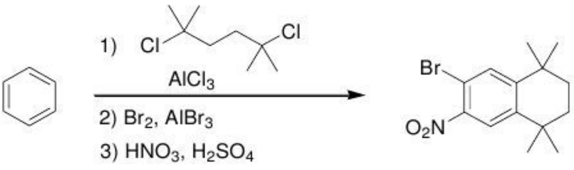
g)


1) Cl2, AlCl3
2) HNO3, H2SO4
3) NaOEt, heat
4) Cl2, AlCl3
OEt
Cl
NO2

h)


1) (CH3)2CHCl, AlCl3
2) CH3CH2COCl, AlCl3
3) HNO3, H2SO4
4) Cl2, AlCl3
Cl
NO2
O

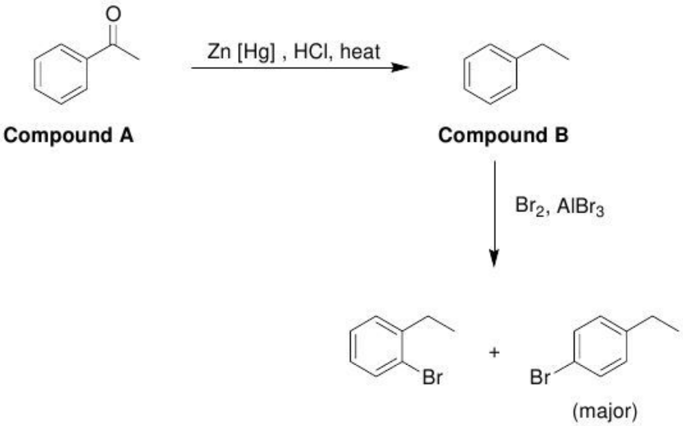
i)


1)
Cl
Cl
AlCl3
2) Br2, AlBr3
3) HNO3, H2SO4
Br
O2N

19.73.

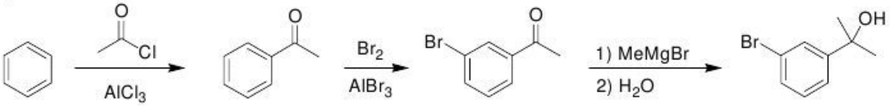
1,2,4-trimethylbenzene

19.74. Bromination at the para position occurs more rapidly because ortho attack is sterically hindered by the ethyl group:

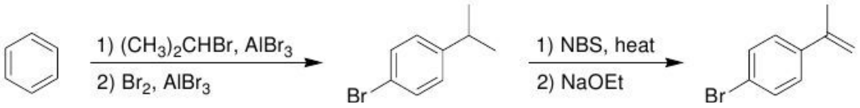


19.75.

a)

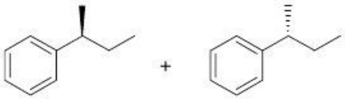


b)



19.76.

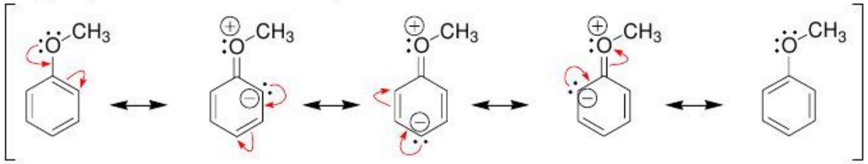
a)



b) The reaction proceeds via a carbocation intermediate, which can be attacked from either face, leading to a racemic mixture.

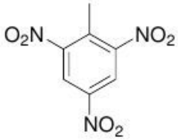
19.77.

The OH group activates the ring toward electrophilic aromatic substitution because the OH group donates electron density via resonance.



This effect gives electron density primarily to the *ortho* and *para* positions, as seen in the resonance structures above. These positions are shielded, and the protons at these positions are expected to produce signals farther upfield than protons at the *meta* position. According to this reasoning, the *meta* protons correspond with the signal at 7.2ppm.

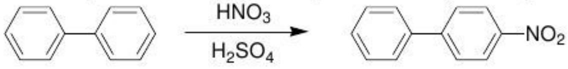
19.78.



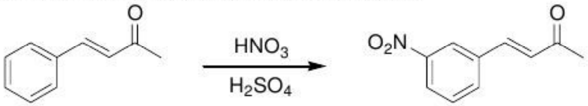
2,4,6-trinitrotoluene

19.79.

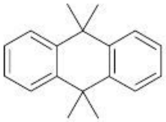
a) A phenyl group is an *ortho-para* director, because the sigma complex formed from *ortho* attack or *para* attack is highly stabilized by resonance (the positive charge is spread over both rings). The *ortho* position is sterically hindered while the *para* position is not, so we expect nitration to occur predominantly at the *para* position:



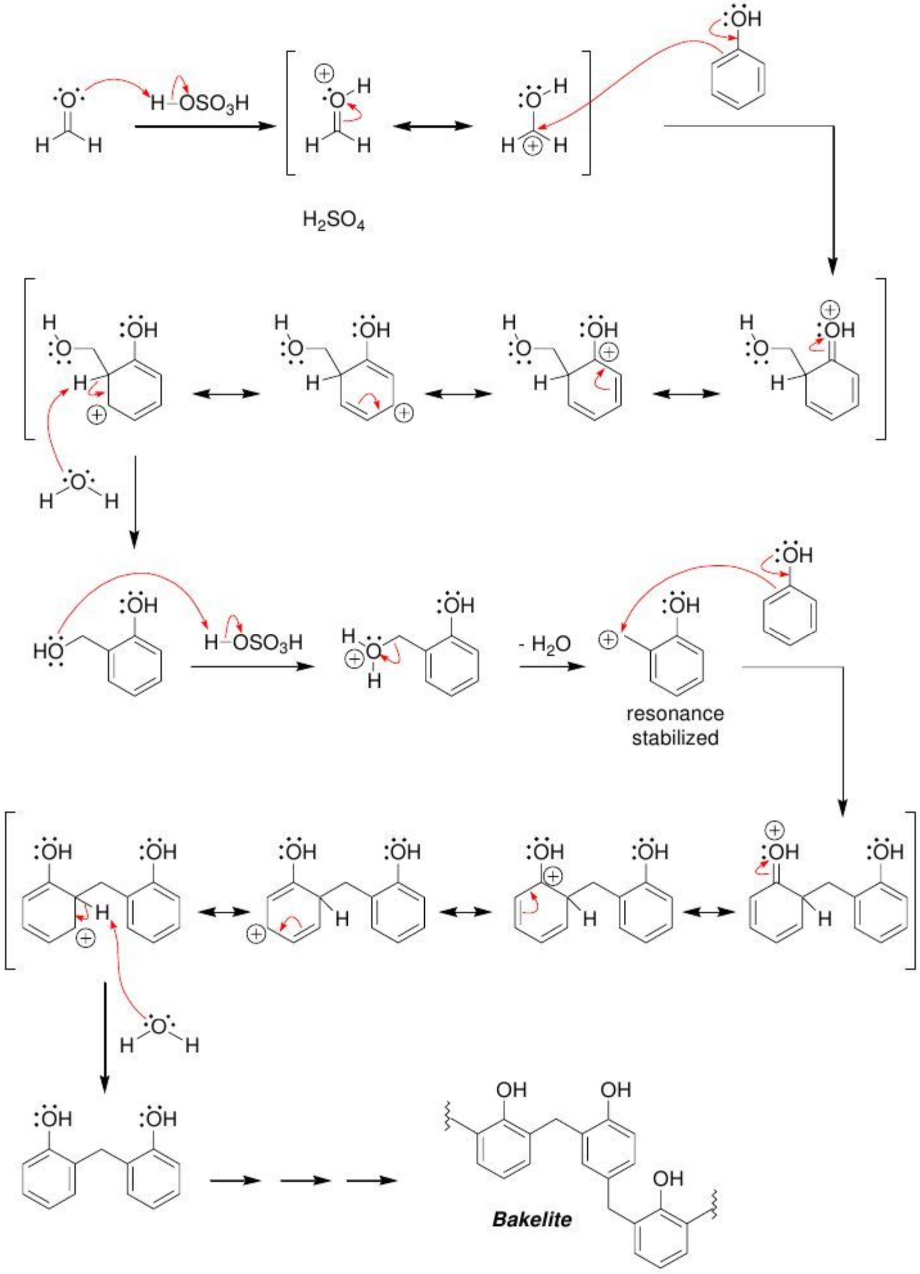
b) This group withdraws electron density form the ring via resonance (the resonance structures have a positive charge in the ring). As a result, this group is a moderate deactivator, and therefore a *meta*-director:



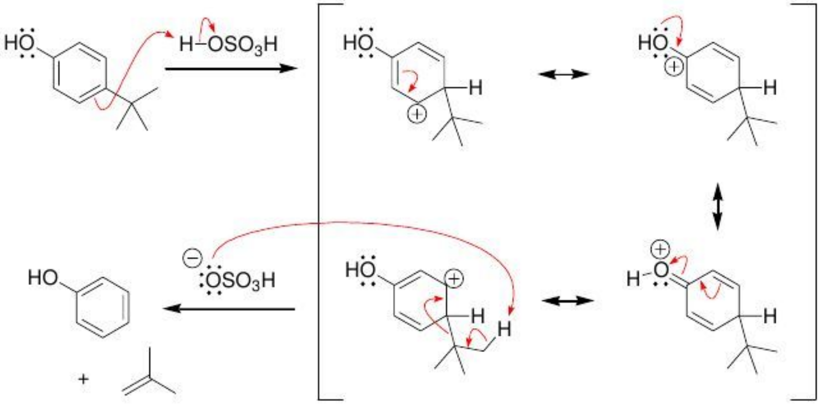
19.80.



19.81.



19.82.



19.83. The amino group in *N,N*-dimethylaniline is a strong activator, and therefore, an *ortho-para* director. For this reason, bromination occurs at the *ortho* and *para* positions. However, in acidic conditions, the amino group is protonated to give an ammonium ion. Unlike the amino group, an ammonium ion is a strong deactivator and a *meta* director. Under these conditions, nitration occurs primarily at the *meta* position.

Chapter 20
Ketones and Aldehydes

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 20. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- The suffix "_____" indicates an aldehydic group, and the suffix "_____" is used for ketones.
- The electrophilicity of a carbonyl group derives from _____________ effects, as well as __________ effects.
- A general mechanism for nucleophilic addition under basic conditions involves two steps
  1) nucleophilic attack to generate a _____________ **intermediate**.
  2) _____________________
- The position of equilibrium is dependent on the ability of the nucleophile to function as a _______________.
- In acidic conditions, an aldehyde or ketone will react with two molecules of alcohol to form an __________.
- The reversibility of acetal formation enables acetals to function as _______________ groups for ketones. Acetals are stable under strongly _______ conditions.
- In acidic conditions, an aldehyde or ketone will react with a primary amine to form an _________.
- In acidic conditions, an aldehyde or ketone will react with a secondary amine to form an __________.
- In the **Wolff-Kishner reduction**, a hydrazone is reduced to an _________ under strongly basic conditions.
- In acidic conditions, all reagents, intermediates, and leaving groups either should be ____________ or should bear one ___________ charge.
- _________________ of acetals, imines, and enamines under acidic conditions produces ketones or aldehydes.
- In acidic conditions, an aldehyde or ketone will react with two equivalents of a thiol to form a ______________.
- When treated with Raney nickel, thioacetals undergo **desulfurization** to yield a ______________ group.
- When treated with a hydride reducing agent, such as lithium aluminum hydride (LAH) or sodium borohydride ($NaBH_4$), aldehydes and ketones are reduced to _______________.
- The reduction of a carbonyl group with LAH or $NaBH_4$ is not a reversible process, because hydride does not function as a ____________________.
- When treated with a Grignard agent, aldehydes and ketones are converted into alcohols, accompanied by the formation of a new ___________ bond.

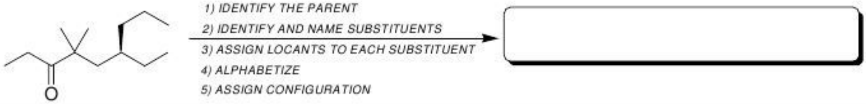
- Grignard reactions are not reversible, because carbanions do not function as ___________________.
- When treated with hydrogen cyanide (HCN), aldehydes and ketones are converted into _______________. For most aldehydes and unhindered ketones, the equilibrium favors formation of the ___________________.
- The **Wittig reaction** can be used to convert a ketone to an __________.
- A **Baeyer-Villiger oxidation** converts a ketone to an ___________ by inserting ______________________ next to the carbonyl group. Cyclic ketones produce cyclic esters called ________________.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 20. The answers appear in the section entitled *SkillBuilder Review*.

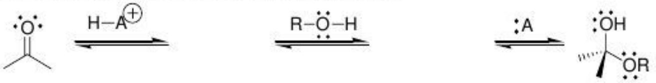
20.1: Naming Aldehydes and Ketones

PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND



20.2: Drawing the Mechanism of Acetal Formation

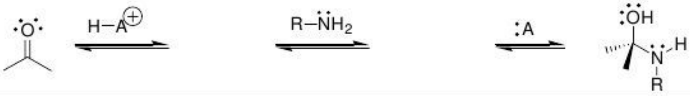
DRAW A MECHANISM FOR THE ACID-CATALYZED CONVERSION OF A KETONE TO A HEMIACETAL.
MAKE SURE TO DRAW ALL CURVED ARROWS AND INTERMEDIATES.



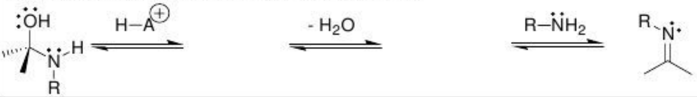
DRAW A MECHANISM FOR THE ACID-CATALYZED CONVERSION OF A HEMIACETAL TO AN ACETAL.
MAKE SURE TO DRAW ALL CURVED ARROWS AND INTERMEDIATES.

20.3: Drawing the Mechanism of Imine Formation

DRAW A MECHANISM FOR THE ACID-CATALYZED CONVERSION OF A KETONE TO A CARBINOLAMINE.
MAKE SURE TO DRAW ALL CURVED ARROWS AND INTERMEDIATES.

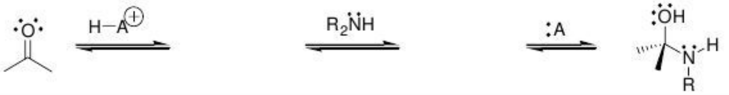


DRAW A MECHANISM FOR THE ACID-CATALYZED CONVERSION OF A CARBINOLAMINE TO AN IMINE.
MAKE SURE TO DRAW ALL CURVED ARROWS AND INTERMEDIATES.

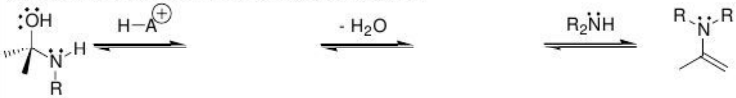


20.4: Drawing the Mechanism of Enamine Formation

DRAW A MECHANISM FOR THE ACID-CATALYZED CONVERSION OF A KETONE TO A CARBINOLAMINE. MAKE SURE TO DRAW ALL CURVED ARROWS AND INTERMEDIATES.



DRAW A MECHANISM FOR THE ACID-CATALYZED CONVERSION OF A CARBINOLAMINE TO AN ENAMINE. MAKE SURE TO DRAW ALL CURVED ARROWS AND INTERMEDIATES.



20.5: Drawing the Mechanism of a Hydrolysis Reaction

STEP 1 *- WORKING BACKWARDS, DRAW ALL ____________________.*	***STEP 2*** *- DRAW ALL ____________ AND ____________________________________, USING THE FOLLOWING RULES:* *IN ACIDIC CONDITIONS, ALL REAGENTS, ____________________, AND ____________________ SHOULD EITHER BE NEUTRAL OR SHOULD BEAR ONE POSITIVE CHARGE.*

20.6: Planning an Alkene Synthesis with a Wittig Reaction

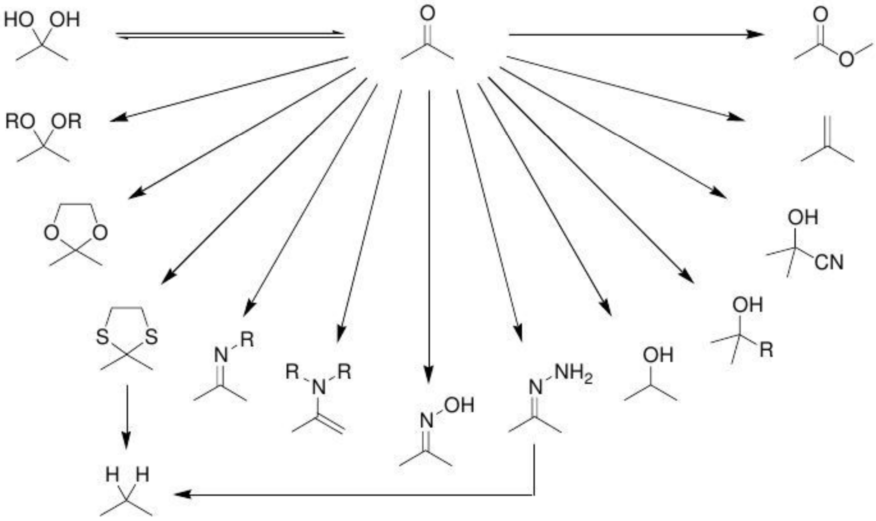
IDENTIFY THE REACTANTS YOU WOULD USE TO PREPARE THE FOLLOWING COMPOUND VIA A WITTIG REACTION:

20.7: Proposing a Synthesis

BEGIN BY ASKING THE FOLLOWING TWO QUESTIONS: *1) IS THE THERE A CHANGE IN THE ____________________?* *2) IS THERE A CHANGE IN THE ____________________?*	*IF THERE IS A CHANGE IN THE CARBON SKELETON, CONSIDER ALL OF THE C-C BOND FORMING REACTIONS AND ALL OF THE C-C BOND BREAKING REACTIONS THAT YOU HAVE LEARNED SO FAR.* *C-C BOND-FORMING REACTIONS IN THIS CHAPTER:* - ________________ - ________________________ - ________________ *C-C BOND-BREAKING REACTIONS IN THIS CHAPTER:* - ________________________

Review of Reactions

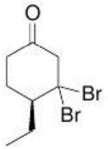
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 20. The answers appear in the section entitled *Review of Reactions*.



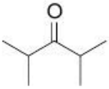
Solutions

20.1. a) 5,5-dibromo-2,2-dimethylhexanal
b) (*3R,4S*)-3,4,5-trimethyl-2-hexanone
c) 2,2,5,5-tetramethylcyclopentanone
d) 2-propylpentanal
e) cyclobutanecarbaldehyde

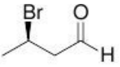
20.2. a)



b)



c)

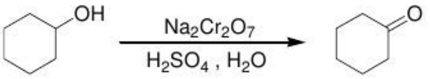


20.3. (*1S,4R*)bicyclo[2.2.1]heptan-2-one

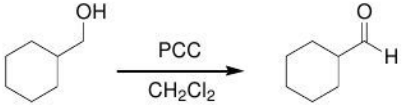
20.4. a) 1,3-cyclohexanedione b) 1,4-cyclohexanedione c) 2,5,8-nonanetrione

20.5.

a)



b)



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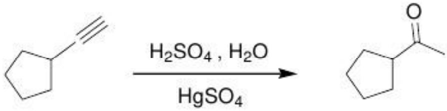

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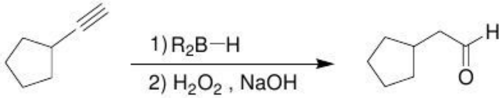
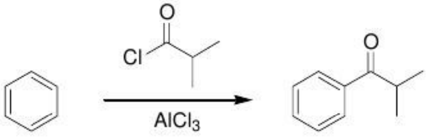


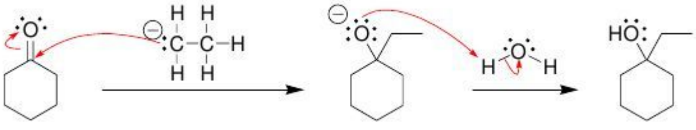
e)

f)

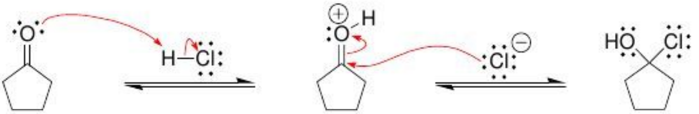


20.6.

a)



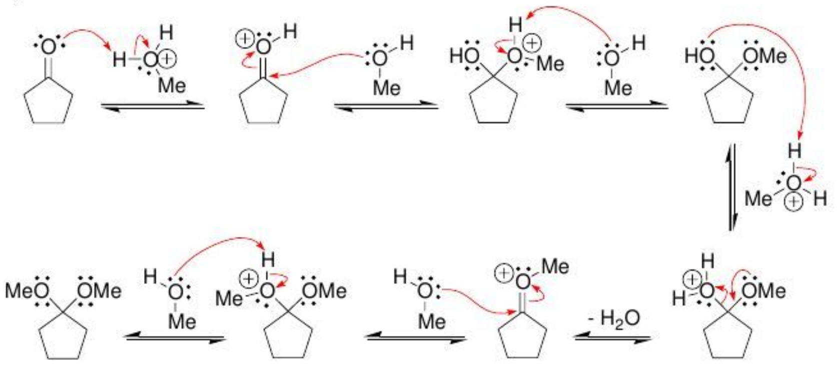
b)



20.7. The carbonyl group in hexafluoroacetone is flanked by two very powerful electron-withdrawing groups (CF_3). These groups withdraw electron density from the carbonyl group, thereby increasing the electrophilicity of the carbonyl group. The resulting increase in energy of the reactant causes the equilibrium to favor the product (the hydrate).

20.8.

a)



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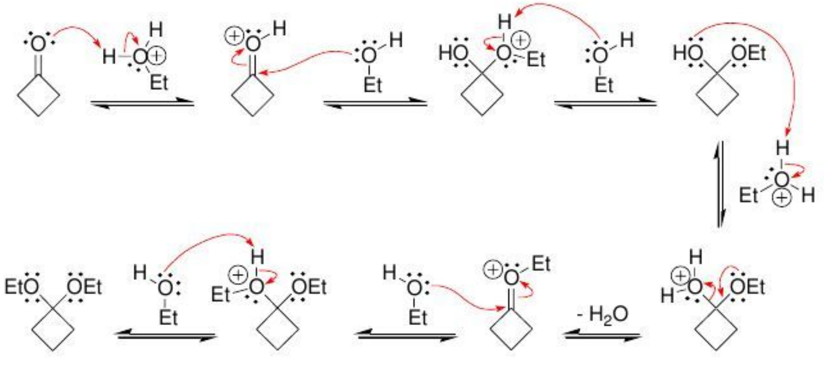
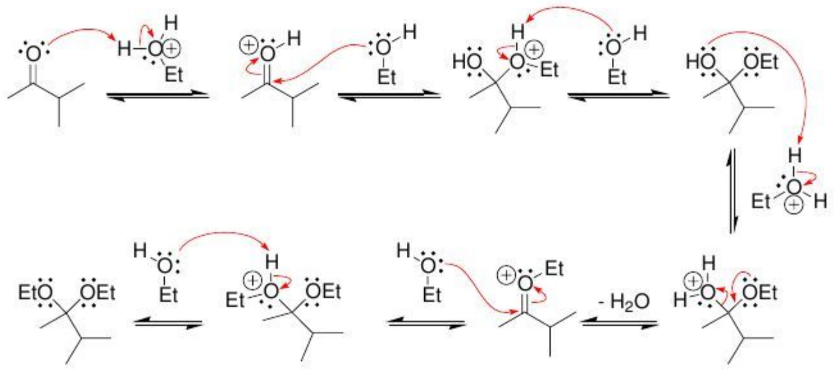
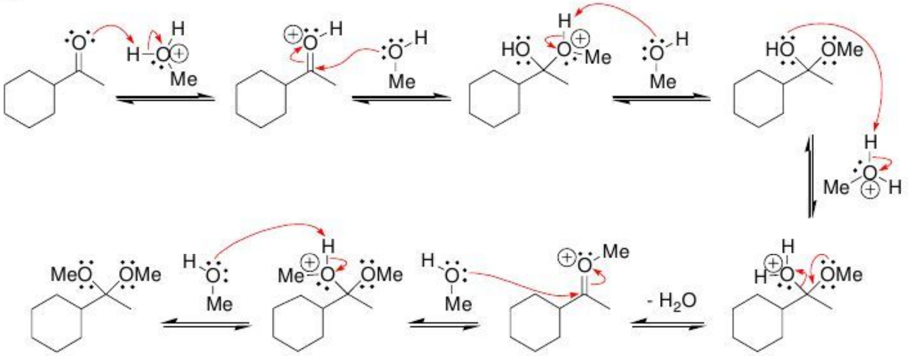


c)

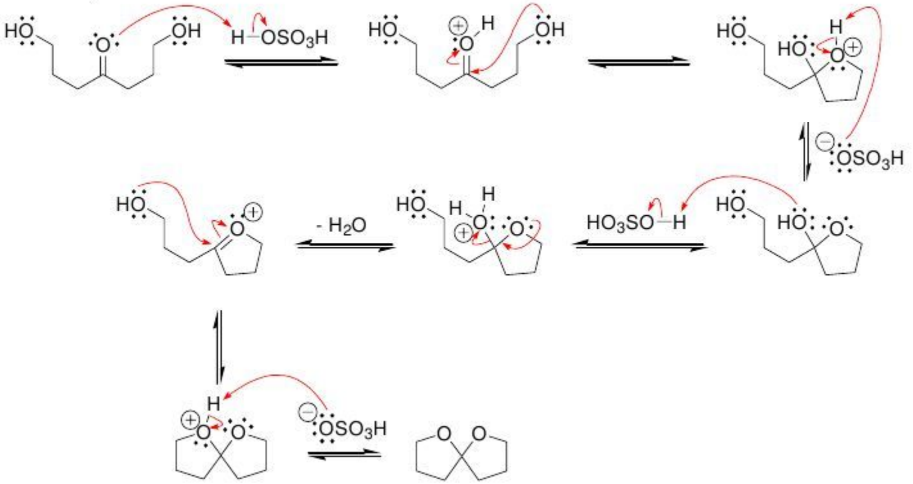


d)

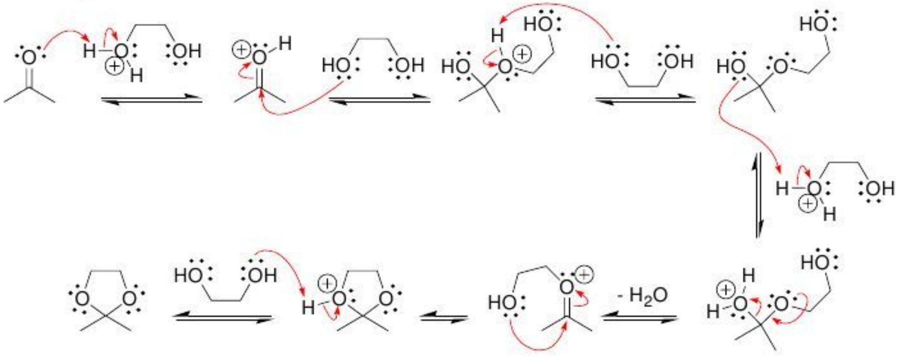


20.9.

a)

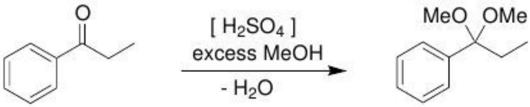


b)



20.10.

a)



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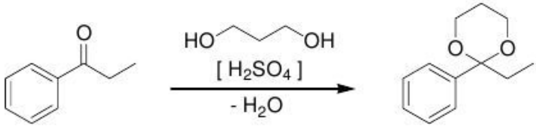
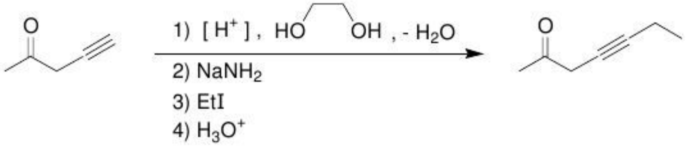


20.11.

a)



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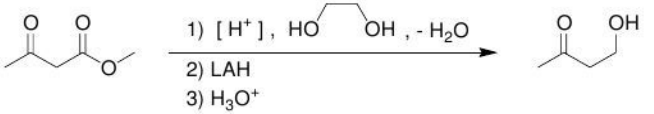

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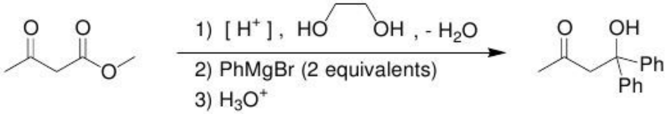
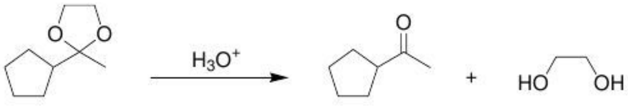


20.12. a)



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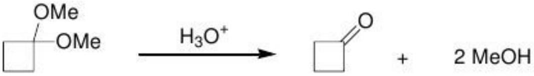

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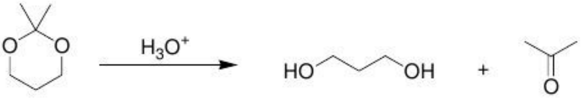
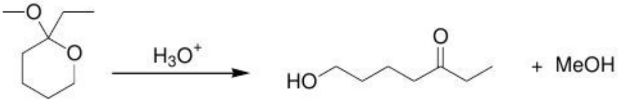
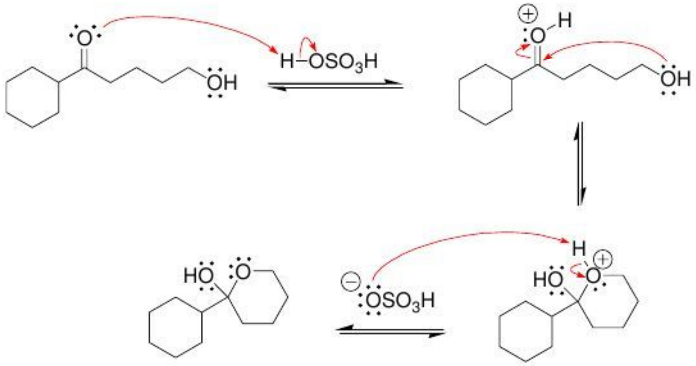


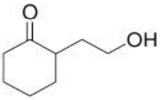
d)



20.13.

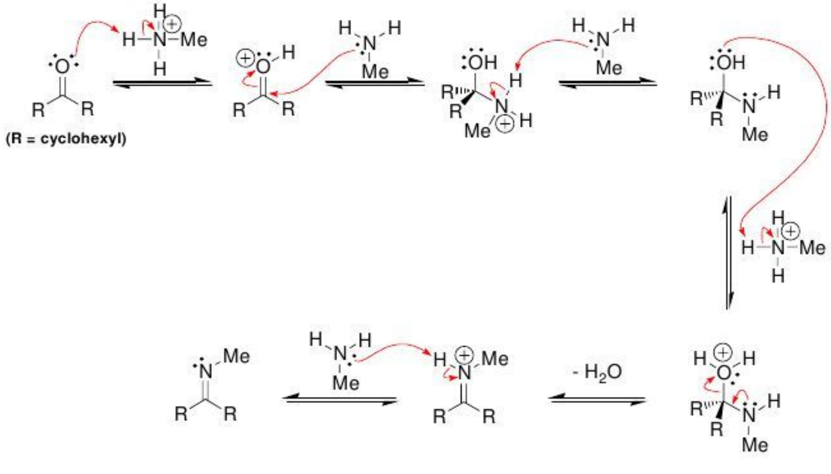


20.14.



20.15. Note: ***For each of the mechanisms shown below, the first two steps can be reversed (first the amine attacks the carbonyl group, and then the tetrahedral intermediate is protonated). It would be wise to check your lecture notes to determine if you instructor has a strong preference for this alternate sequence of steps.***

a)



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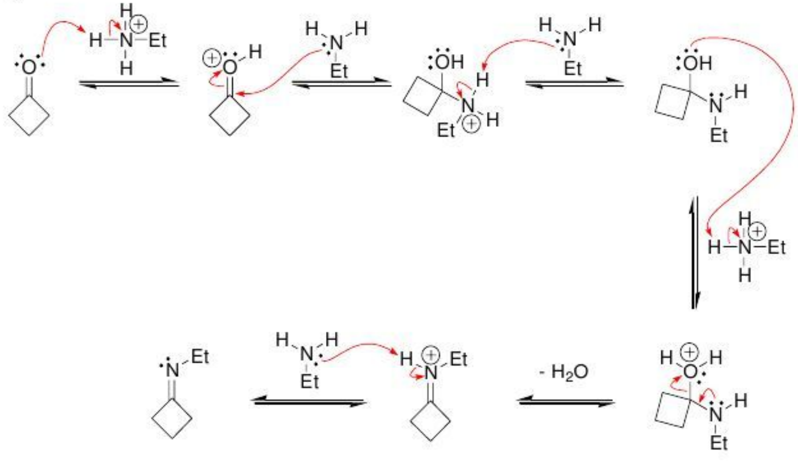
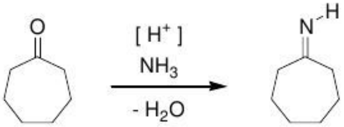


20.16.

a)



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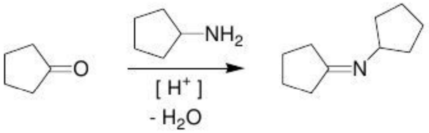
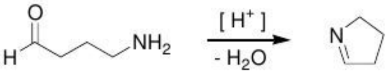


20.17.

a)



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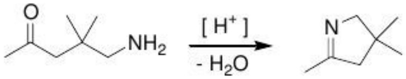
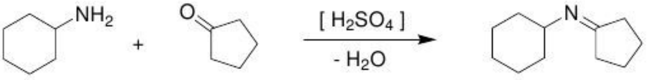
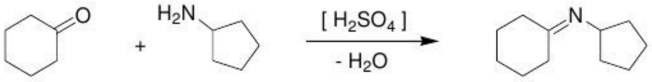


20.18.

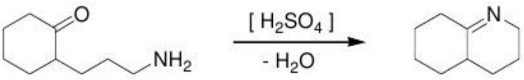
a)



b)

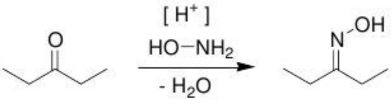


c)

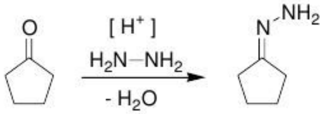


20.19.

a)

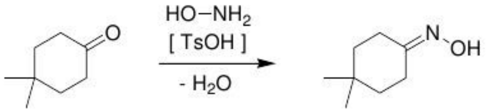


b)



20.20.

a)



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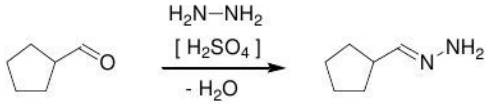
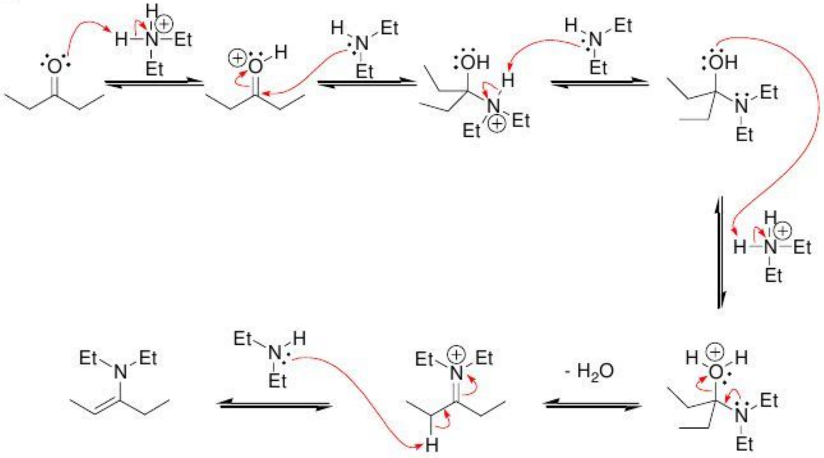


20.21. **Note**: ***For each of the mechanisms shown below, the first two steps can be reversed (first the amine attacks the carbonyl group, and then the tetrahedral intermediate is protonated). It would be wise to check your lecture notes to determine if you instructor has a strong preference for this alternate sequence of steps.***

a)



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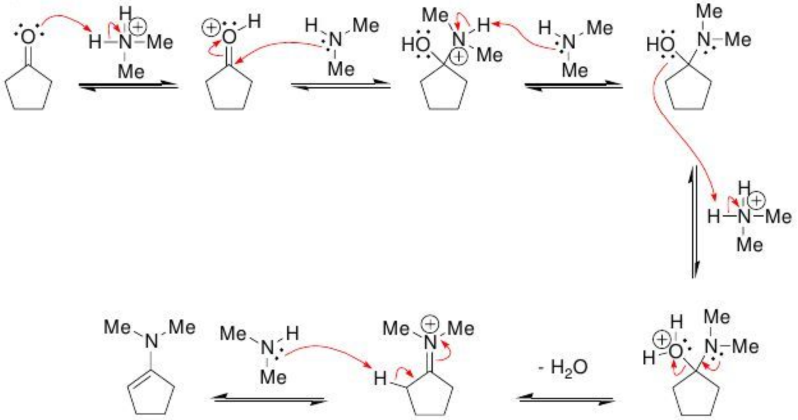
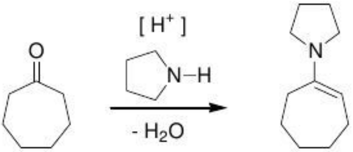
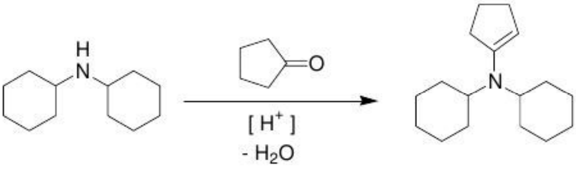
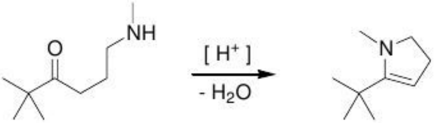


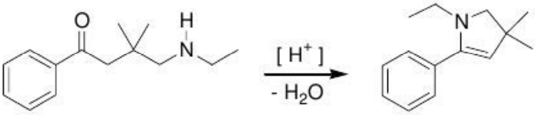
20.22.

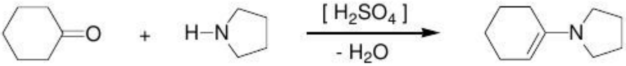
a) 

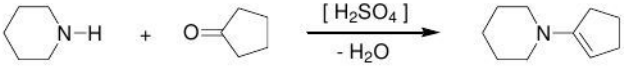
b) 

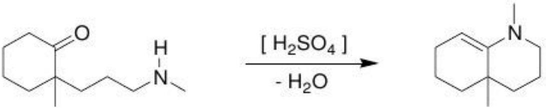
20.23.

a) 

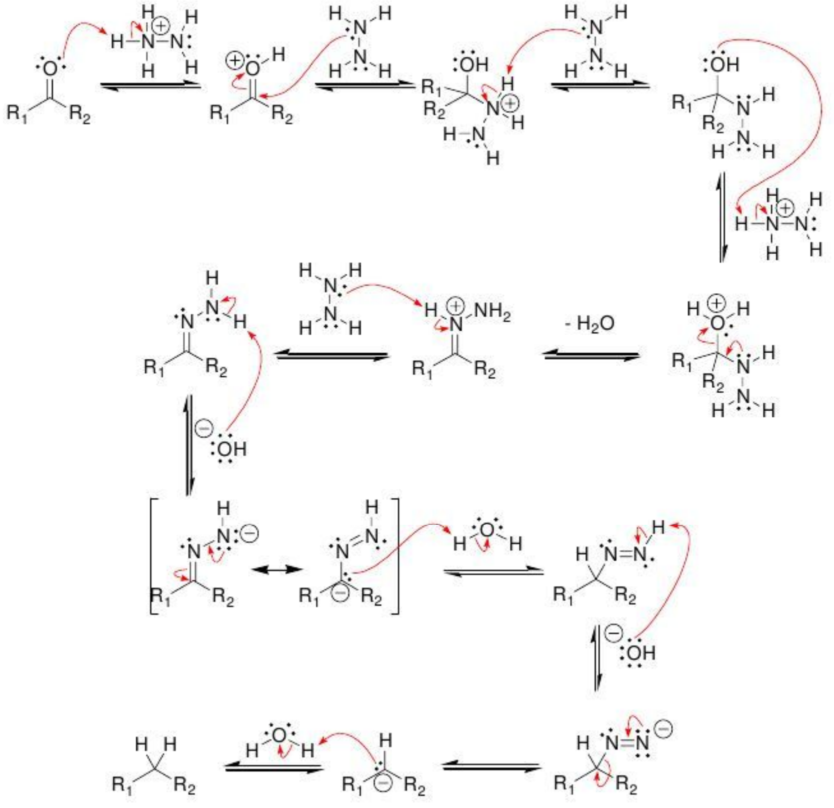
b) 

20.24. a) 

b) 

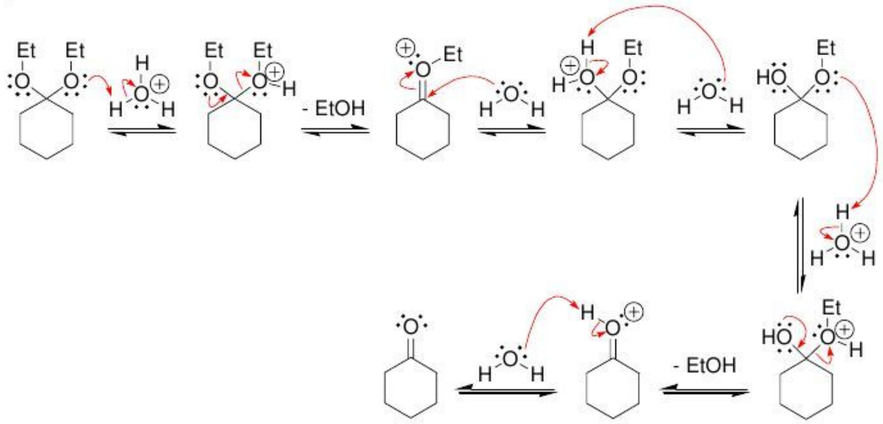
c) 

20.25. **Note**: ***The first two steps of this mechanism can be reversed (first the amine attacks the carbonyl group, and then the tetrahedral intermediate is protonated). It would be wise to check your lecture notes to determine if you instructor has a strong preference for this alternate sequence of steps.***

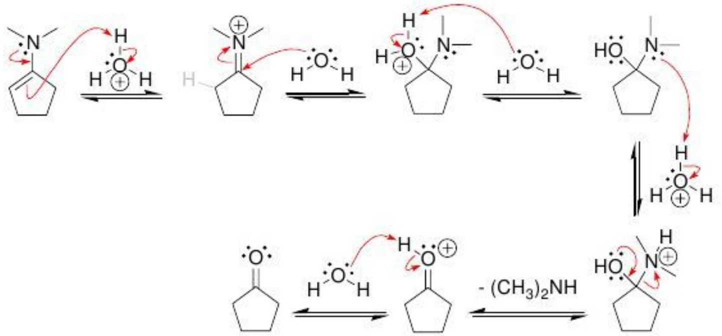


20.26.

a)



b)



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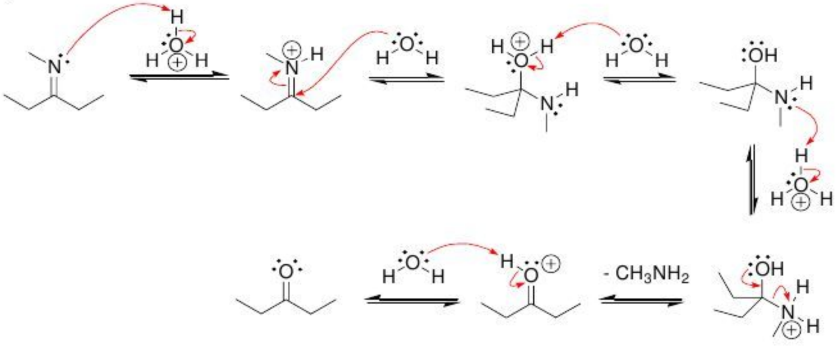
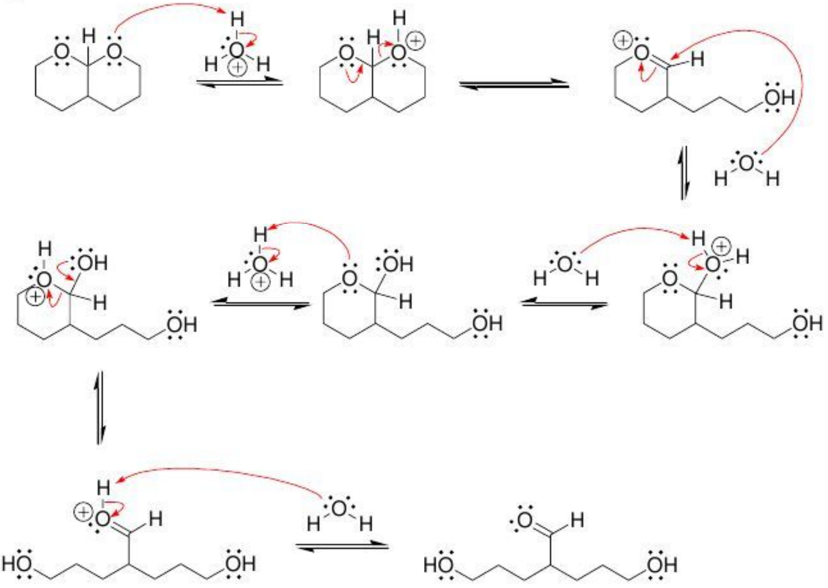
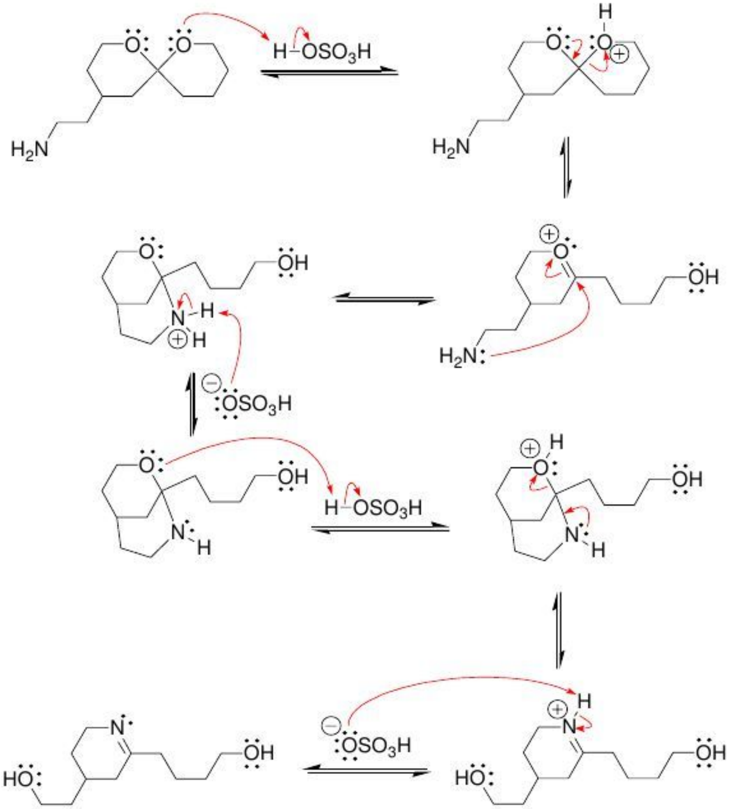


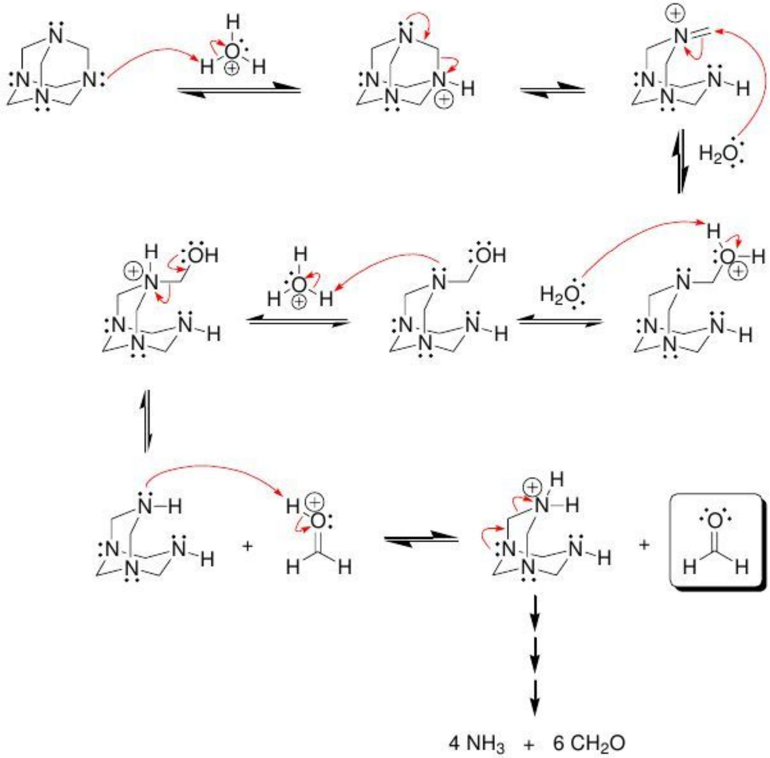
d)



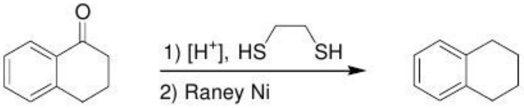
20.27.



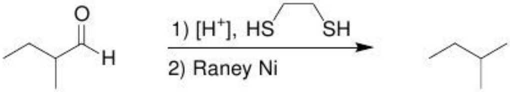
20.28.



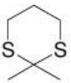
20.29. a)



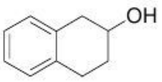
b)

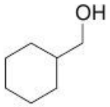


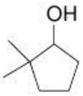
20.30.

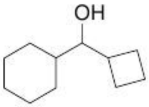


20.31.

a) 

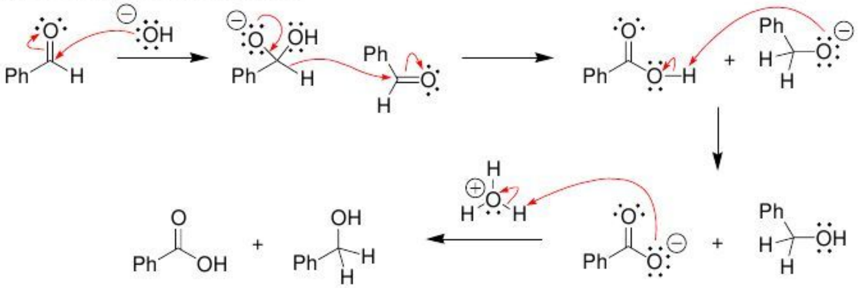
b) 

c) 

d) 

20.32.

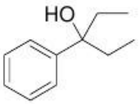
a) Below is a mechanism for the Cannizzaro reaction. After a hydroxide ion attacks one molecule of benzaldehyde, the resulting tetrahedral intermediate functions as a hydride delivery agent to attack another molecule of benzaldehyde, giving a carboxylic acid and an alkoxide ion. The alkoxide ion then deprotonates the carboxylic acid, generating a more stable carboxylate ion. This carboxylate ion is then protonated when an acid is added to the reaction mixture.

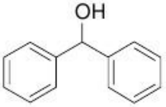


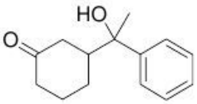
b) The function of H_3O^+ in the second step is to serve as a proton source to protonate the resulting carboxylate ion.

c) Water is only a weak acid (pK_a = 15.74), and is not sufficiently strong to serve as a proton source for a carboxylate ion (pK_a of PhCOOH is 4.21). See section 3.5 for a discussion of this topic.

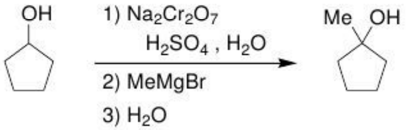
20.33.

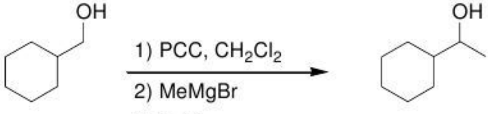
a) 

b) 

c) 

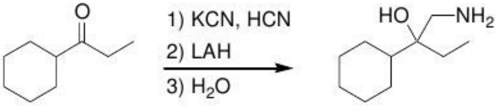
20.34.

a) 

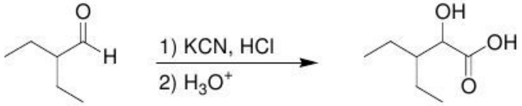
b) 

20.35.

a)

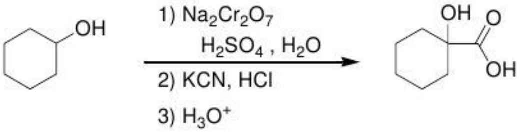


b)

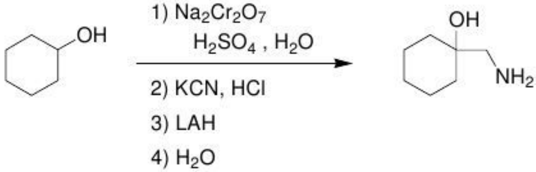


20.36.

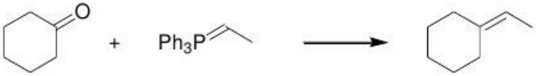
a)



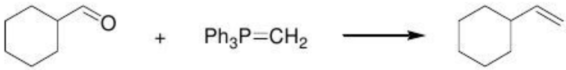
b)



20.37. a)



b)



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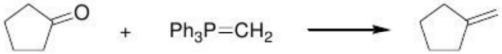
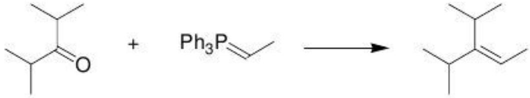
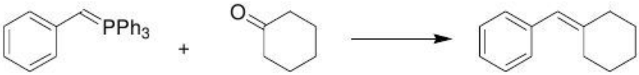


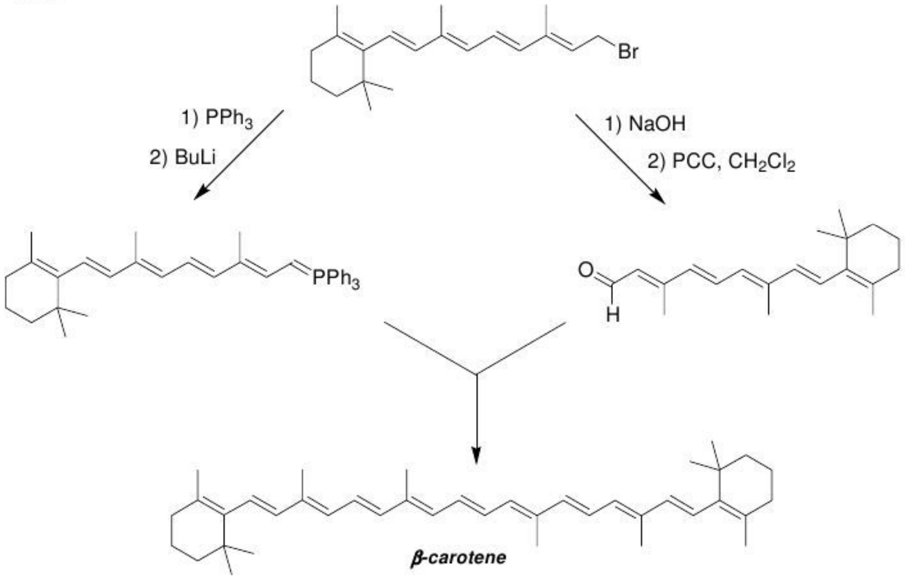
d)



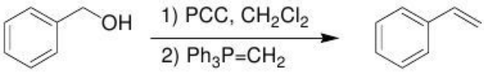
e)



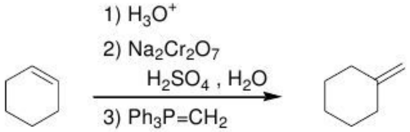
20.38.



20.39. a)

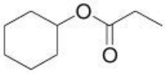


b)

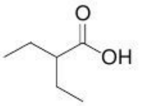


20.40.

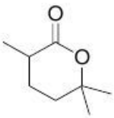
a)



b)

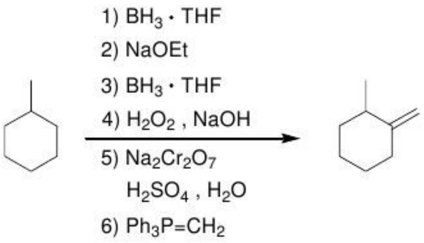


c)

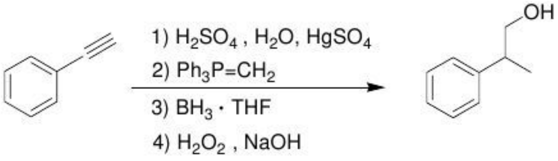


20.41.

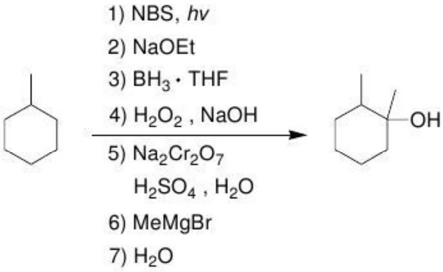
a)


1) $BH_3 \cdot THF$
2) NaOEt
3) $BH_3 \cdot THF$
4) H_2O_2 , NaOH
5) $Na_2Cr_2O_7$
H_2SO_4 , H_2O
6) $Ph_3P{=}CH_2$

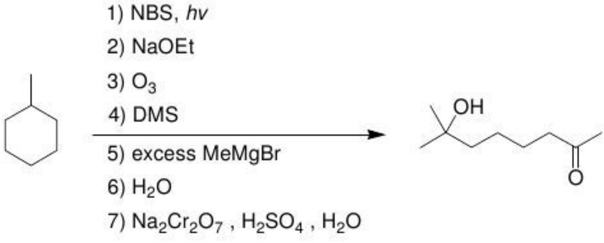
b)


OH
1) H_2SO_4 , H_2O, $HgSO_4$
2) $Ph_3P{=}CH_2$
3) $BH_3 \cdot THF$
4) H_2O_2 , NaOH

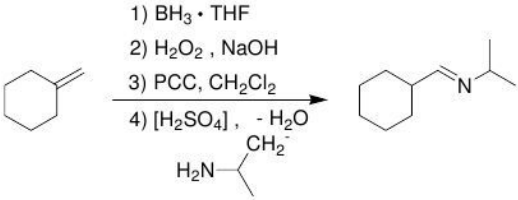
c)


1) NBS, *hv*
2) NaOEt
3) $BH_3 \cdot THF$
4) H_2O_2 , NaOH
5) $Na_2Cr_2O_7$
H_2SO_4 , H_2O
6) MeMgBr
7) H_2O
OH

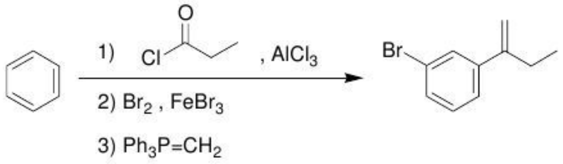
d)


1) NBS, *hv*
2) NaOEt
3) O_3
4) DMS
5) excess MeMgBr
6) H_2O
7) $Na_2Cr_2O_7$, H_2SO_4 , H_2O
OH
O

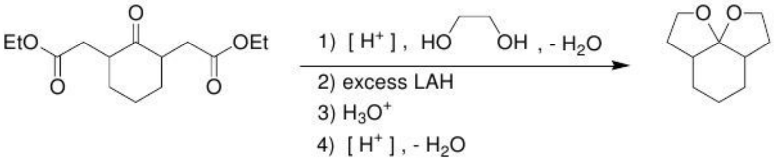
e)


1) $BH_3 \cdot THF$
2) H_2O_2 , NaOH
3) PCC, CH_2Cl_2
4) $[H_2SO_4]$, $- H_2O$
CH_2^-
H_2N
N

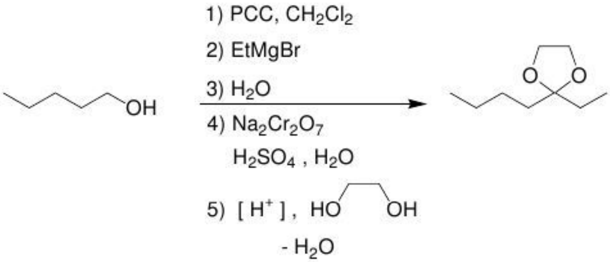
f)


1)
O
Cl
, $AlCl_3$
2) Br_2 , $FeBr_3$
3) $Ph_3P{=}CH_2$
Br

g)

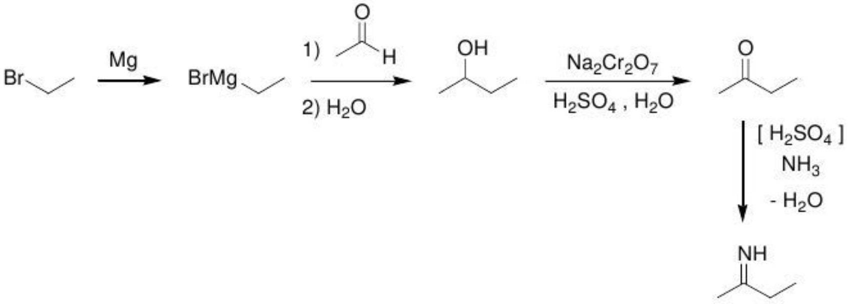

O
EtO
O
OEt
O
1) [H^+], HO OH , - H_2O
2) excess LAH
3) H_3O^+
4) [H^+], - H_2O
O O

h)

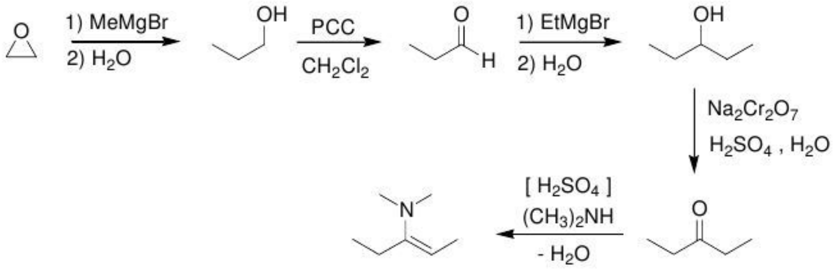

OH
1) PCC, CH_2Cl_2
2) EtMgBr
3) H_2O
4) $Na_2Cr_2O_7$
H_2SO_4 , H_2O
5) [H^+], HO OH
- H_2O
O O

20.42.

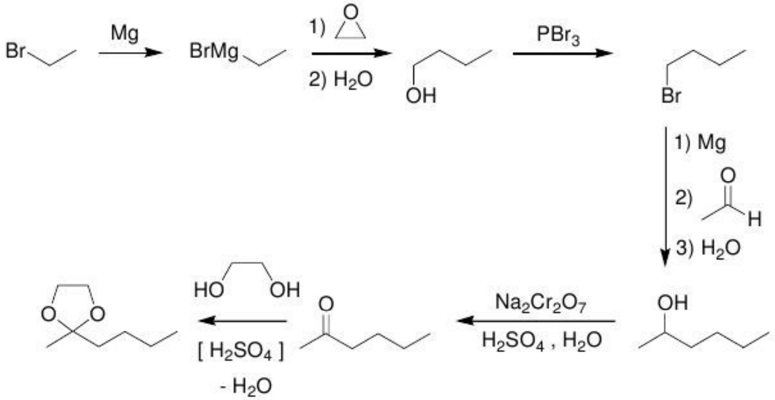
a)


Br
Mg
BrMg
1) O H
2) H_2O
OH
$Na_2Cr_2O_7$
H_2SO_4 , H_2O
O
[H_2SO_4]
NH_3
- H_2O
NH

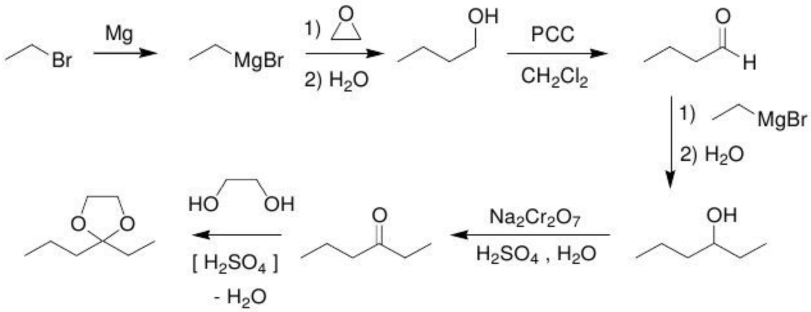
b)


1) MeMgBr
2) H_2O
OH
PCC
CH_2Cl_2
O
H
1) EtMgBr
2) H_2O
OH
$Na_2Cr_2O_7$
H_2SO_4 , H_2O
O
[H_2SO_4]
$(CH_3)_2NH$
- H_2O
N

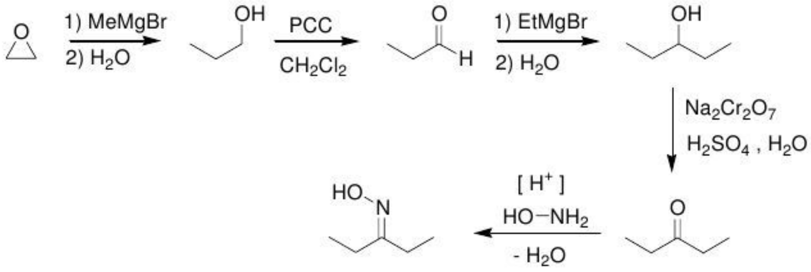
c)


Br
Mg
BrMg
1)
O
2) H_2O
OH
PBr_3
Br
1) Mg
2)
O
H
3) H_2O
OH
$Na_2Cr_2O_7$
H_2SO_4 , H_2O
O
HO
OH
[H_2SO_4]
- H_2O
O
O

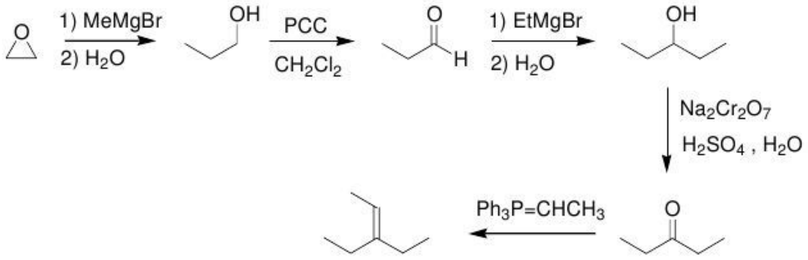
d)


Br
Mg
MgBr
1)
O
2) H_2O
OH
PCC
CH_2Cl_2
O
H
1)
MgBr
2) H_2O
OH
$Na_2Cr_2O_7$
H_2SO_4 , H_2O
O
HO
OH
[H_2SO_4]
- H_2O
O
O

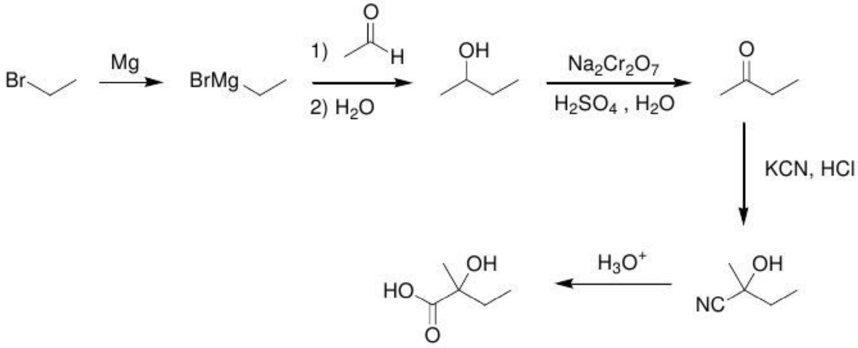
e)


1) MeMgBr
2) H_2O
OH
PCC
CH_2Cl_2
O
H
1) EtMgBr
2) H_2O
OH
$Na_2Cr_2O_7$
H_2SO_4 , H_2O
O
[H^+]
HO−NH_2
- H_2O
HO
N

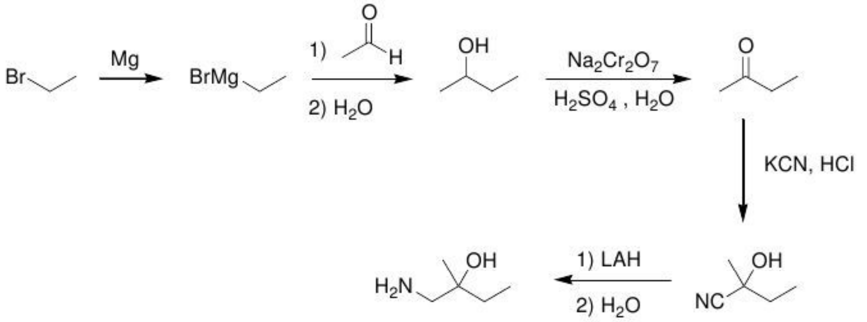
f)


1) MeMgBr
2) H_2O
OH
PCC
CH_2Cl_2
O
H
1) EtMgBr
2) H_2O
OH
$Na_2Cr_2O_7$
H_2SO_4 , H_2O
O
$Ph_3P=CHCH_3$

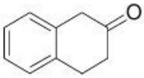
g)


Br
Mg
BrMg
1)
O
H
2) H_2O
OH
$Na_2Cr_2O_7$
H_2SO_4 , H_2O
O
KCN, HCl
OH
NC
H_3O^+
HO
OH
O

h)



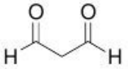
20.43.



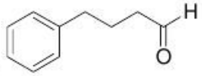
(because this carbonyl group is not conjugated)

20.44. a) (*2S,3R*)-3-methyl-2-propylcyclopentanone
b) cyclohexanecarbaldehyde
c) 3-methyl-2-butenal
d) (*S*)-4-methyl-3-hexanone

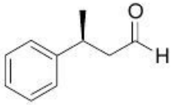
20.45. a)



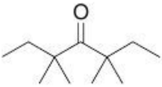
b)



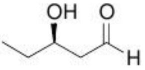
c)



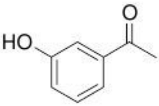
d)



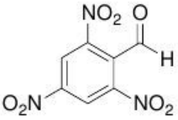
e)



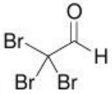
f)



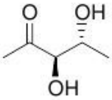
g)



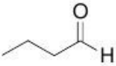
h)



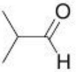
i)



20.46.

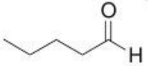


butanal

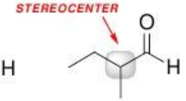


2-methylpropanal

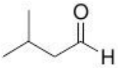
20.47.



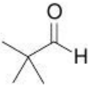
pentanal



2-methylbutanal

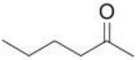


3-methylbutanal

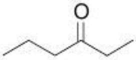


2,2-dimethylpropanal

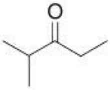
20.48.



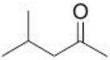
2-hexanone



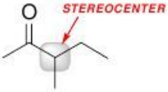
3-hexanone



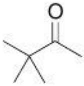
2-methyl-3-pentanone



4-methyl-2-pentanone



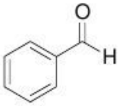
3-methyl-2-pentanone



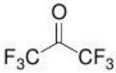
3,3-dimethyl-2-butanone

20.49. The carbonyl group of a ketone will never appear at C-1 because if it would did, the compound would be called an aldehyde rather than a ketone.

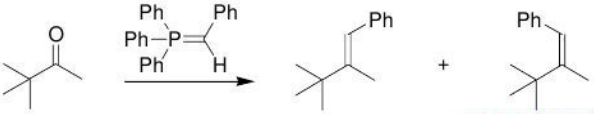
20.50. a)



b)

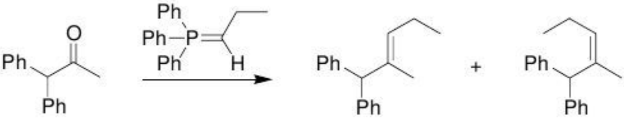


20.51



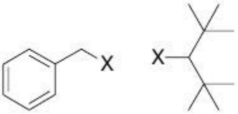
PROBABLY A MINOR PRODUCT BECAUSE STERIC INTERACTIONS RENDER THE COMPOUND HIGH IN ENERGY

a)



b)

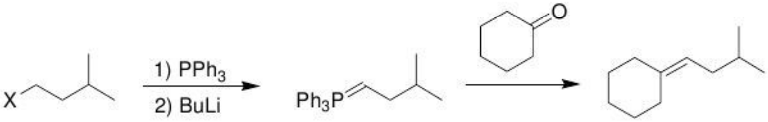
20.52.



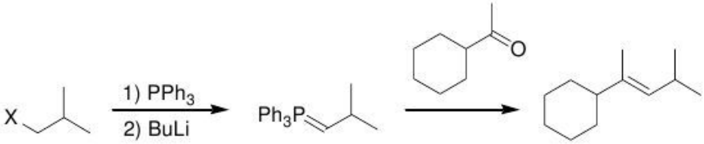
The latter alkyl halide above will be more difficult to convert into a Wittig reagent, because it is too sterically hindered to undergo S_N2 attack.

20.53.

a)

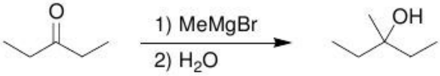


b)

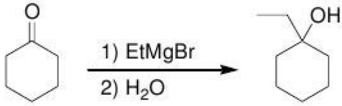


20.54.

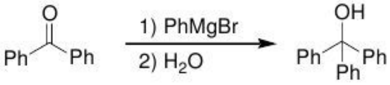
a)



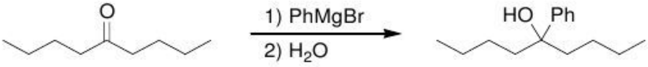
b)



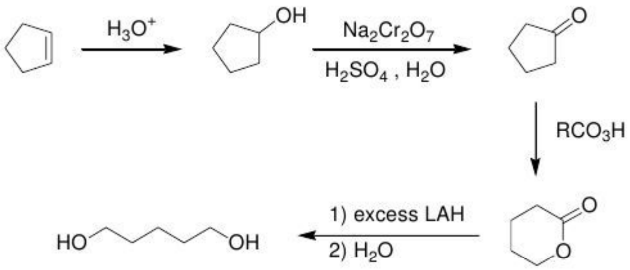
c)

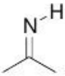


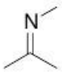
d)

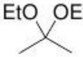


20.55.



20.56. a)


b)


c)


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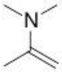
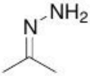
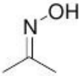
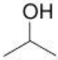
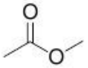
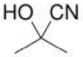


e)


f)


g)


h)


i)


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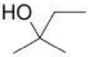

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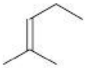

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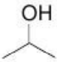
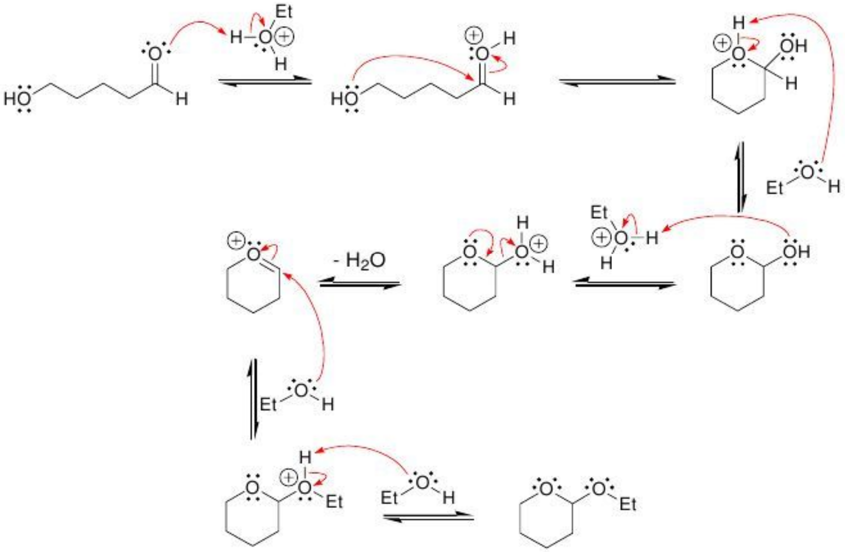
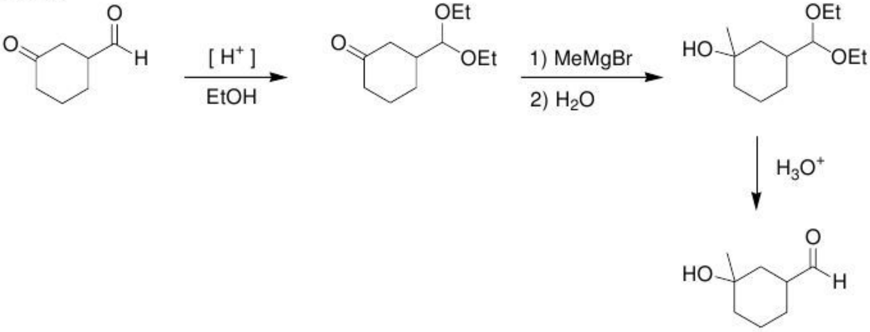


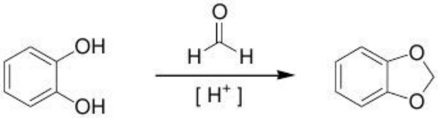
20.57.



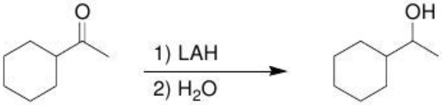
20.58.



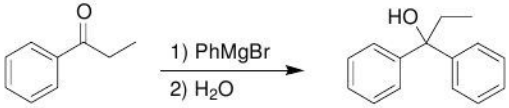
20.59.



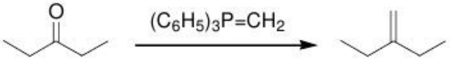
20.60. a)



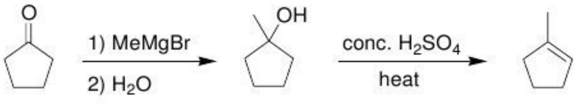
b)



c)



20.61. a)



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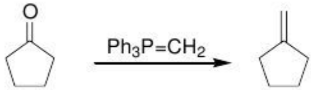
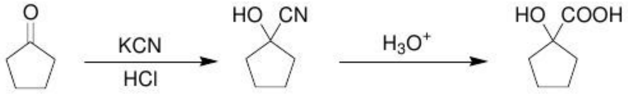


c)



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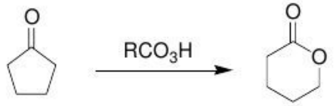
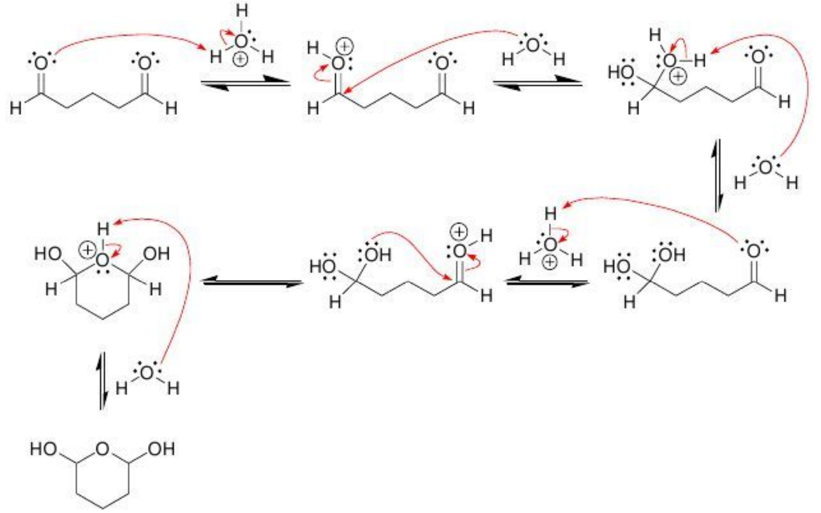
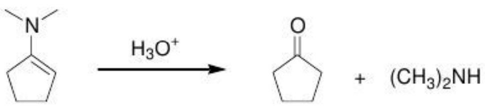


20.62.

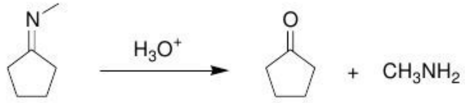


20.63.

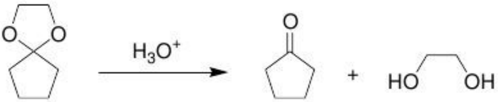
a)



b)



c)



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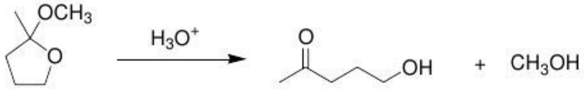
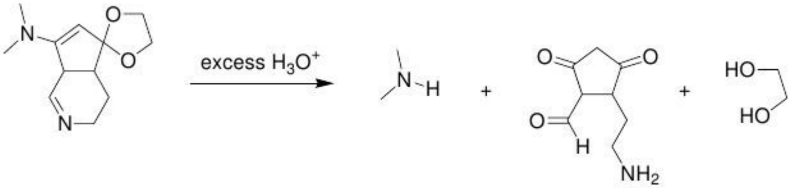
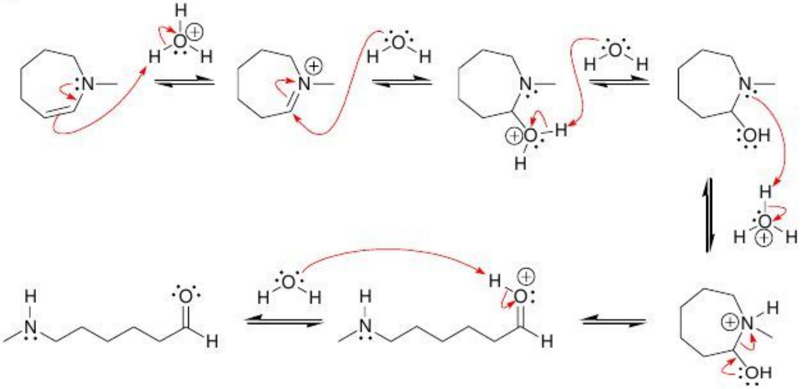


20.64.



20.65.

a)



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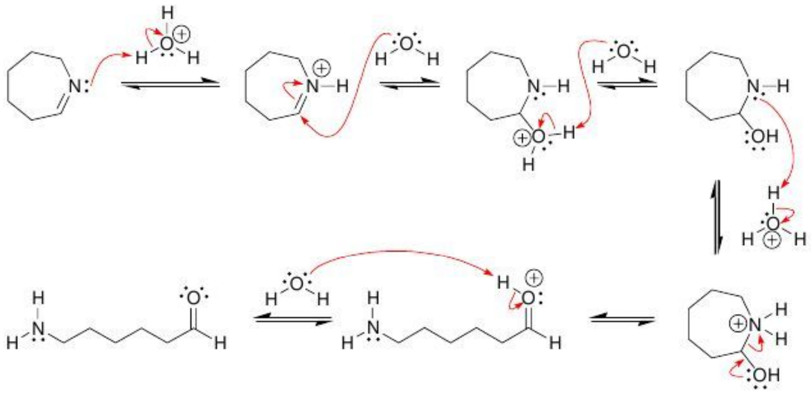
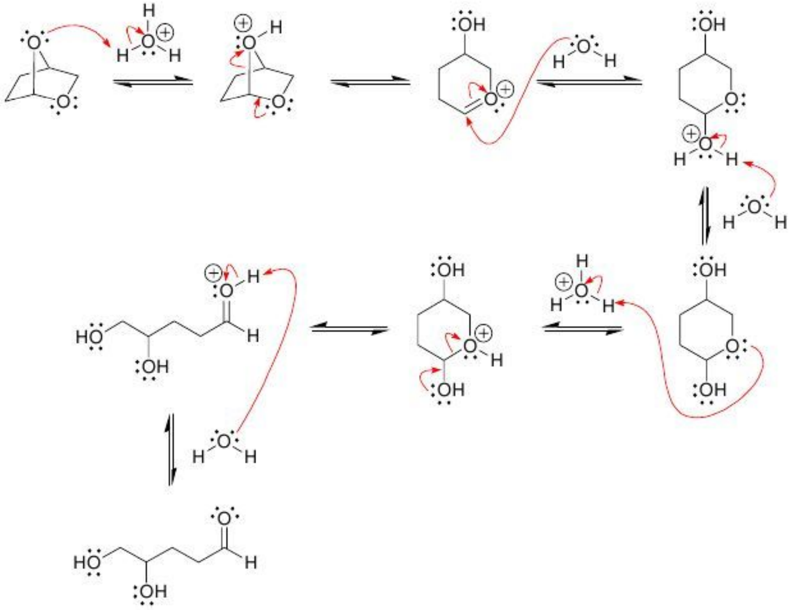
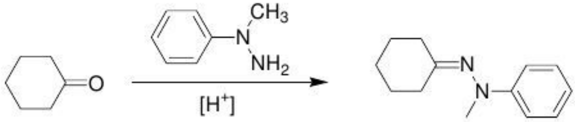


c)

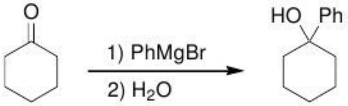


20.66.

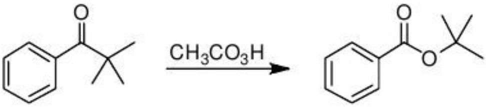
a)



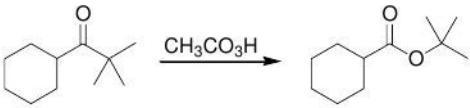
b)



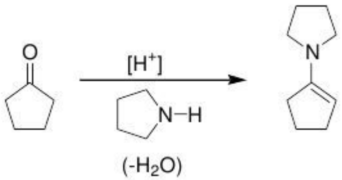
c)



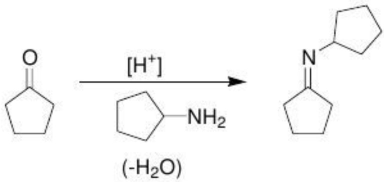
d)



e)

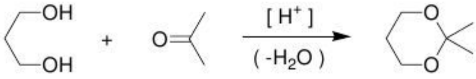


f)

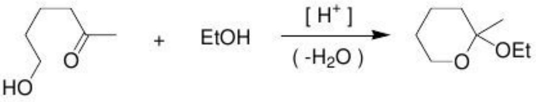


20.67.

a)



b)



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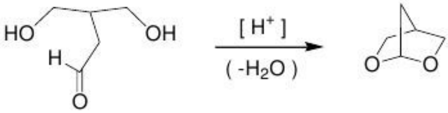
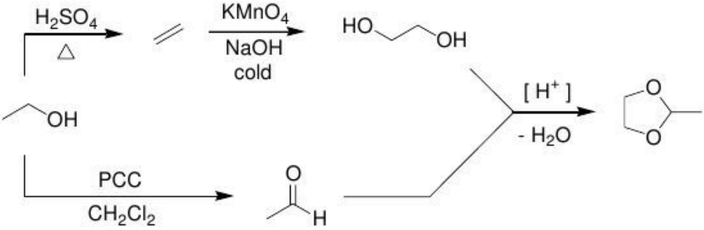
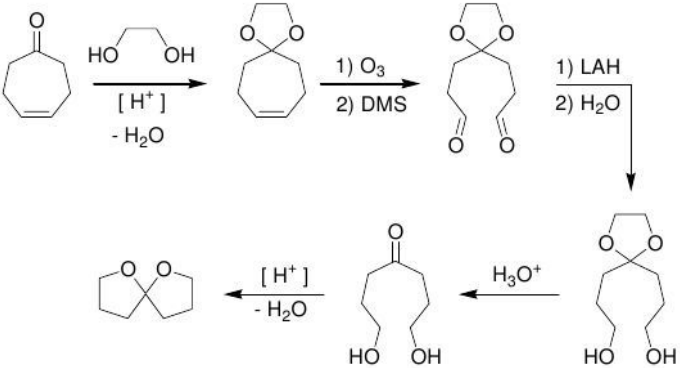


20.68.

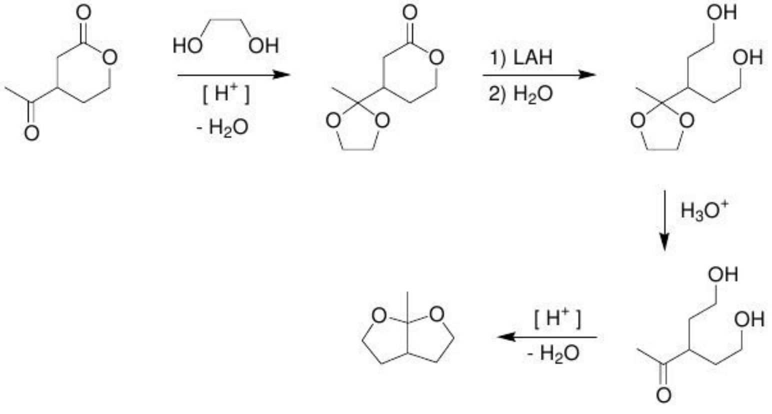


20.69.

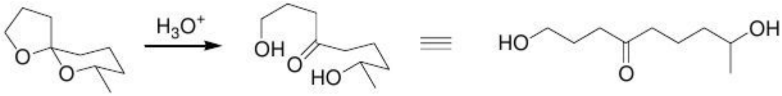
a)



b)

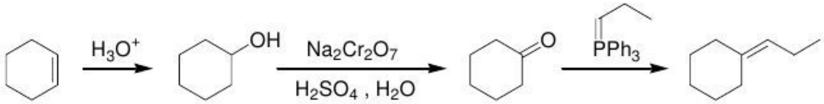


20.70.

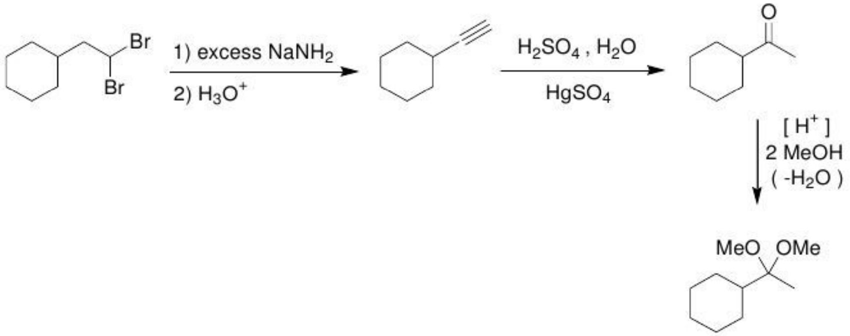


20.71.

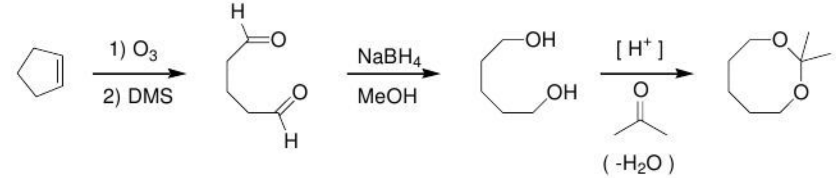
a)



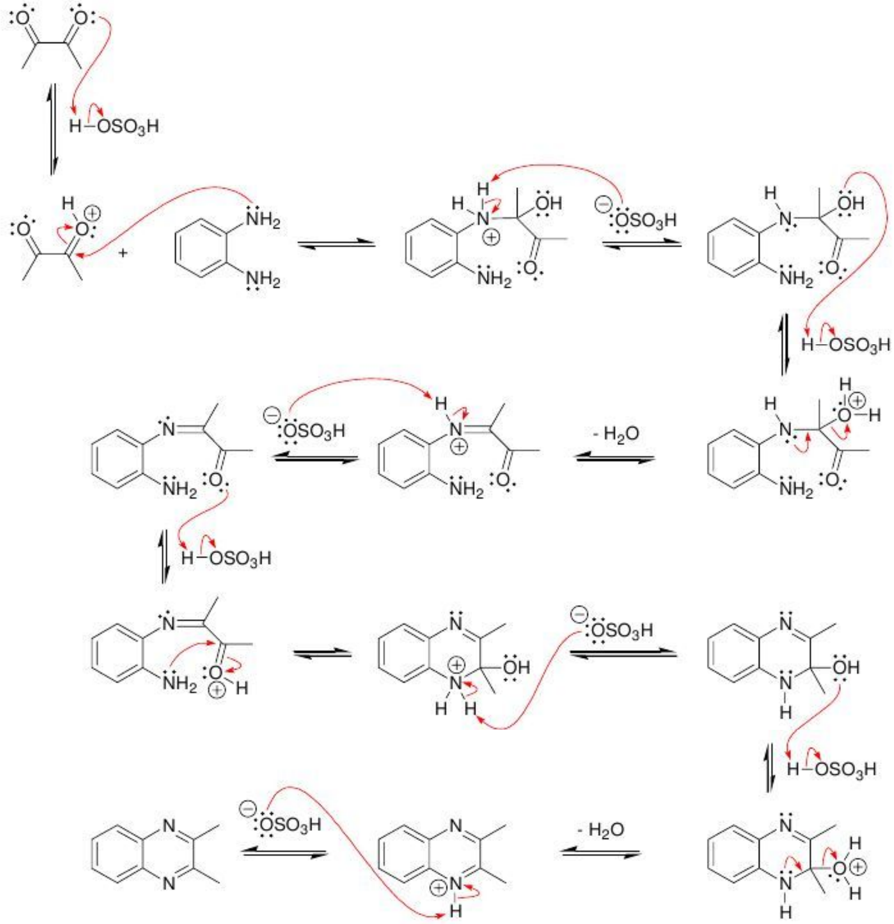
b)



c)


1) O$_3$
2) DMS
H
O
O
H
NaBH$_4$
MeOH
OH
OH
[H$^+$]
O
(-H$_2$O)
O
O

20.72.

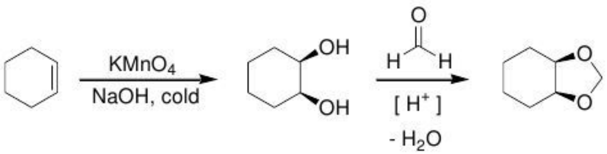

H–OSO$_3$H
+
NH$_2$
NH$_2$
⊖ OSO$_3$H
H–OSO$_3$H
- H$_2$O
⊖ OSO$_3$H
H–OSO$_3$H
⊖ OSO$_3$H
H–OSO$_3$H
- H$_2$O
⊖ OSO$_3$H
N
N

20.73. Cyclopropanone exhibits significant ring strain, with bond angles of approximately 60º. Some of this ring strain is relieved upon conversion to the hydrate, because an *sp*^{2}-hybridized carbon atom (that must be 120º to be strain free) is replaced by an *sp*^{3}-hybridized carbon atom (that must be only 109.5º to be strain free). In contrast, cyclohexanone is a larger ring and exhibits only minimal ring strain. Conversion of cyclohexanone to its corresponding hydrate does not alleviate a significant amount of ring strain.

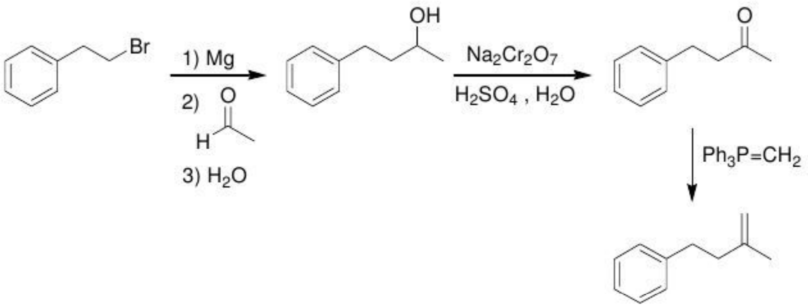
20.74. 1,2-dioxane has two adjacent oxygen atoms and is therefore a peroxide. Like other peroxides, it is extremely unstable and potentially explosive.
1,3-dioxane has two oxygen atoms separated by one carbon atom. This compound is therefore an acetal. Like other acetals, it is only stable under basic conditions, but undergoes hydrolysis under mildly acidic conditions.
1,4-dioxane is stable under basic conditions as well as mildly acidic conditions, and is therefore used as a common solvent.

20.75.

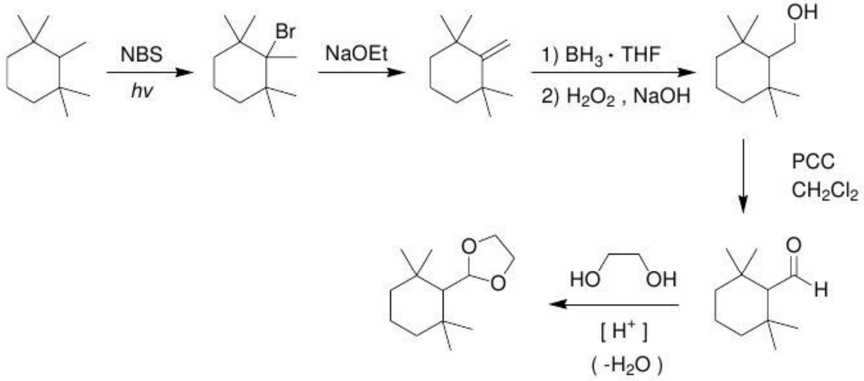
a)



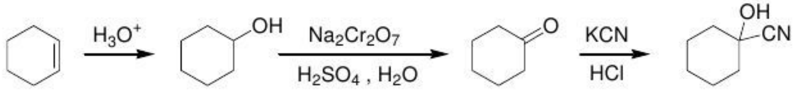
b)



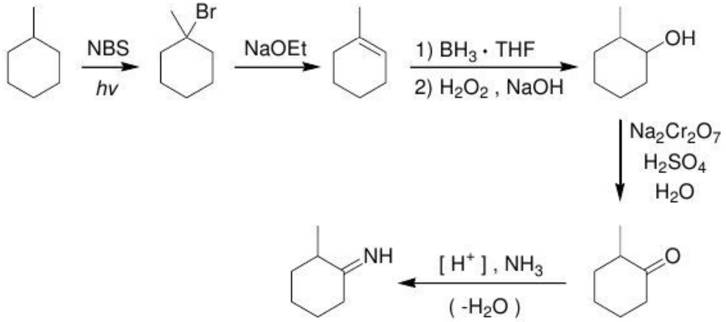
c)


NBS
hv
Br
NaOEt
1) BH3 · THF
2) H2O2 , NaOH
OH
PCC
CH2Cl2
O
H
HO
OH
[H+]
(-H2O)
O
O

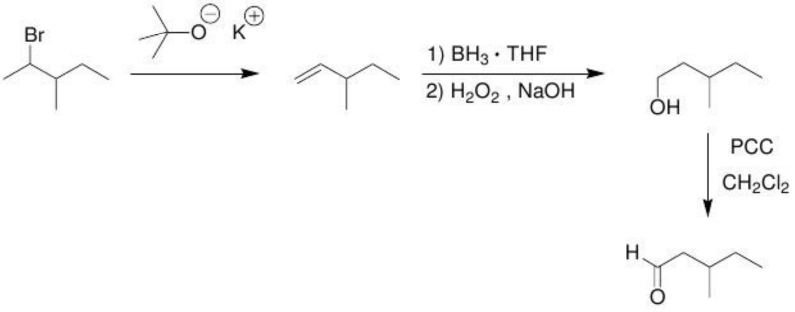
d)


H3O+
OH
Na2Cr2O7
H2SO4 , H2O
O
KCN
HCl
OH
CN

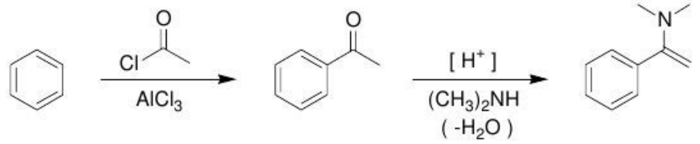
e)


NBS
hv
Br
NaOEt
1) BH3 · THF
2) H2O2 , NaOH
OH
Na2Cr2O7
H2SO4
H2O
O
[H+] , NH3
(-H2O)
NH

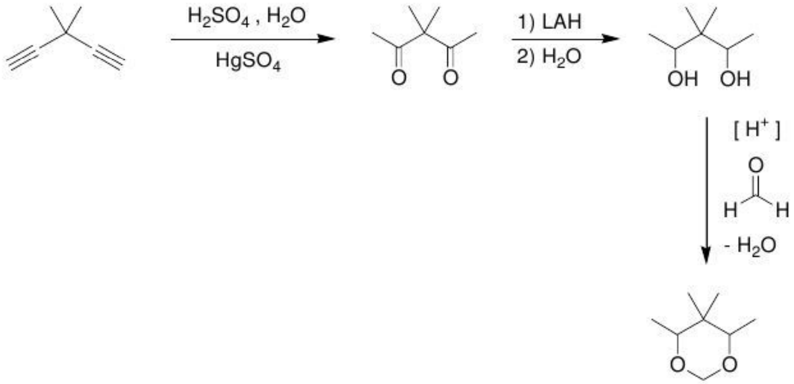
f)


Br
O
K
1) BH3 · THF
2) H2O2 , NaOH
OH
PCC
CH2Cl2
H
O

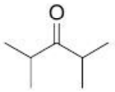
g)



h)



20.76.

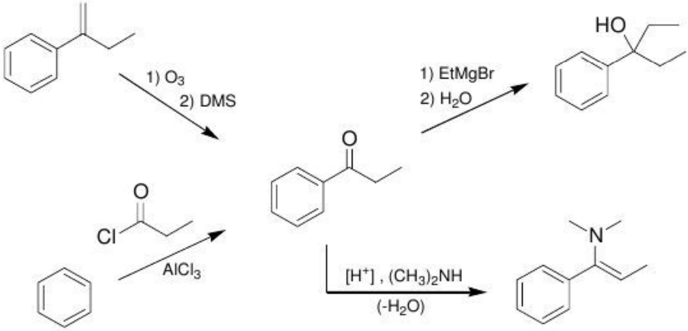


Compound A

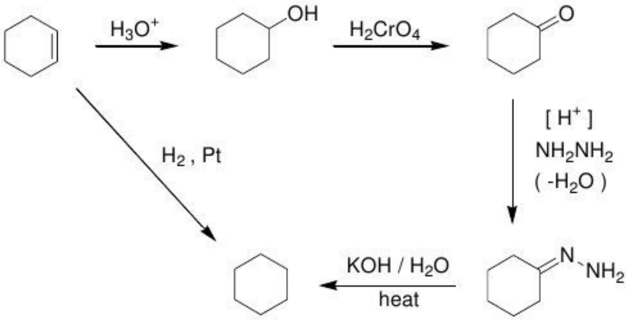
Compound B

a) Three
b) Three
c) Compound A is a ketone, while Compound B is an alkane. Therefore, Compound A will exhibit a signal at approximately 1715 cm^{-1}, while Compound B will not exhibit a signal in the same region.

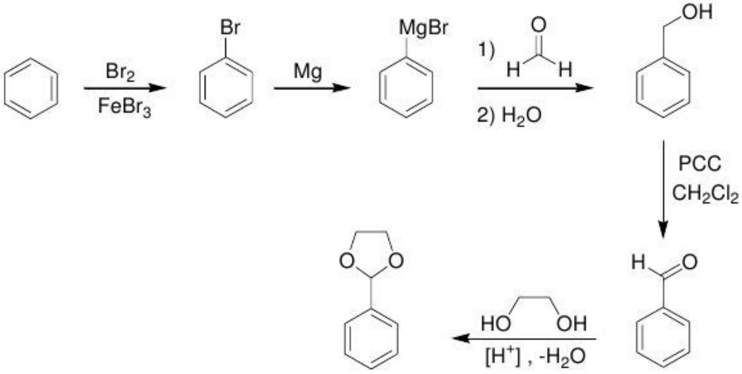
20.77.

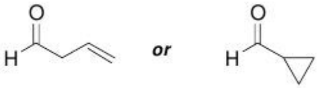


20.78.



20.79.

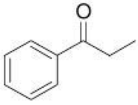




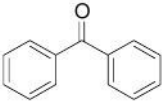
20.80. a)

b) The first compound above would exhibit four signals in its ^{13}C NMR spectrum, while the second compound would exhibit only three signals in its ^{13}C NMR spectrum.

20.81.



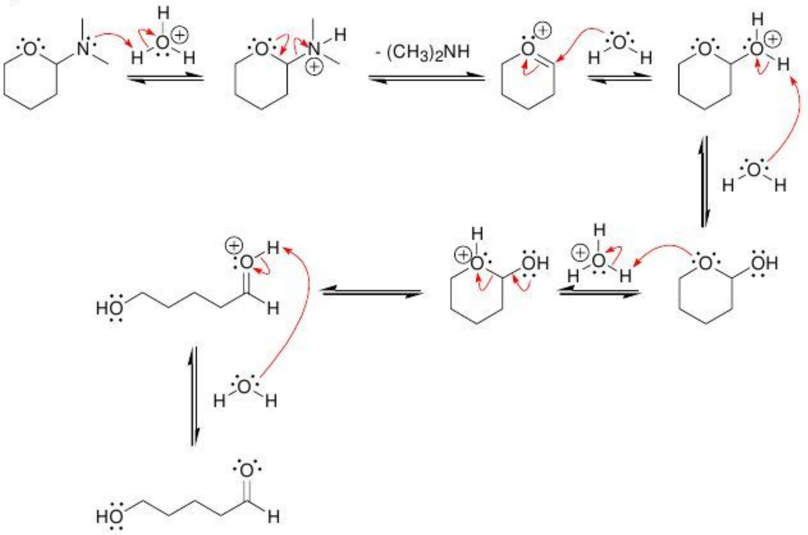
20.82.



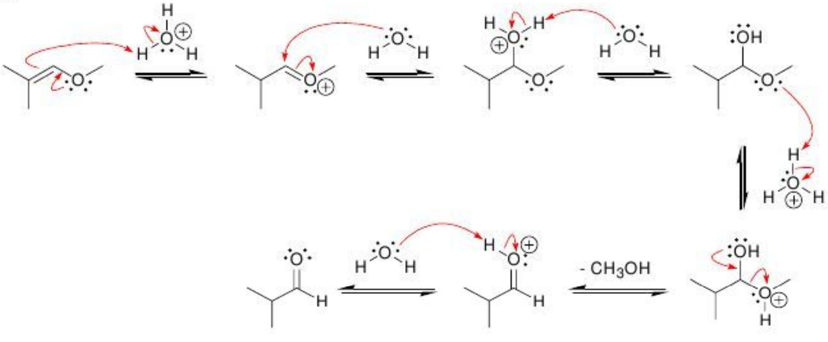
20.83. 2,2,4,4-Tetramethyl-3-pentanone

20.84.

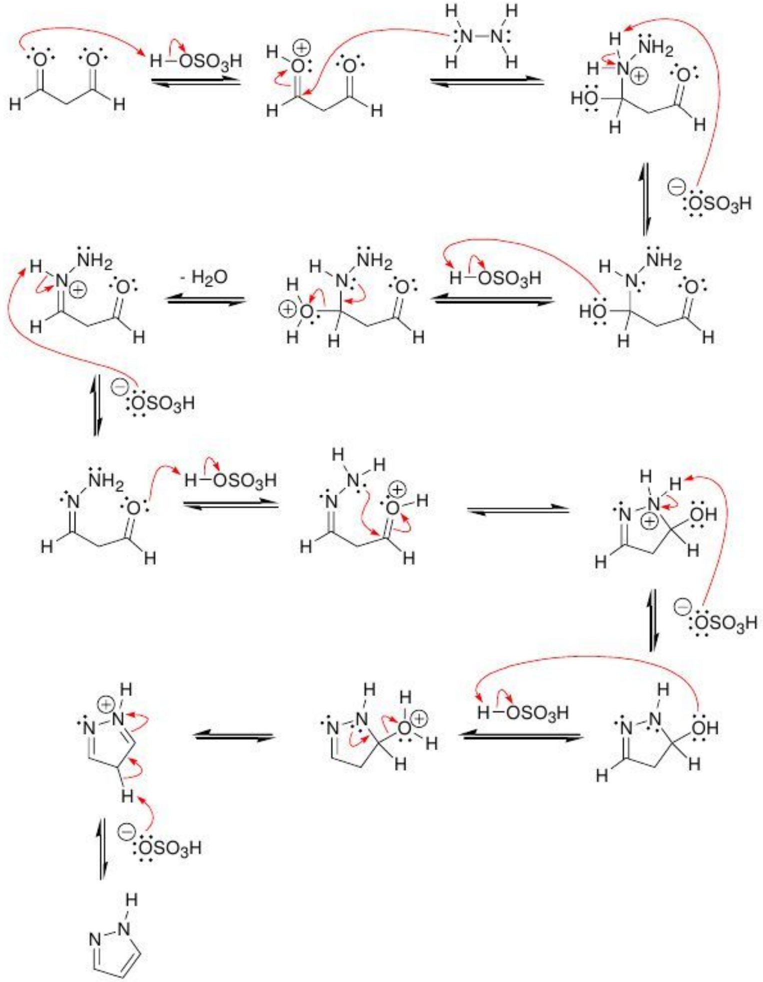
a)



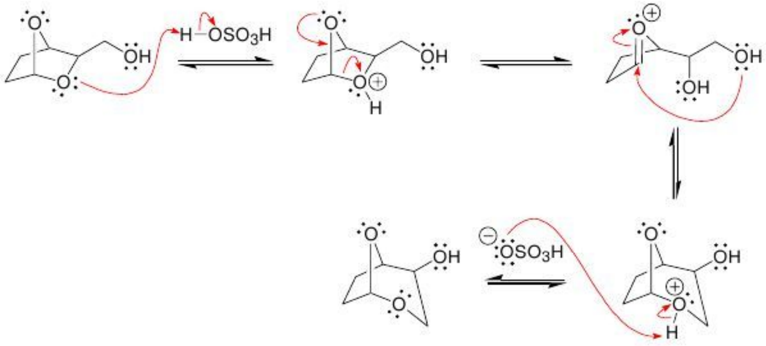
b)



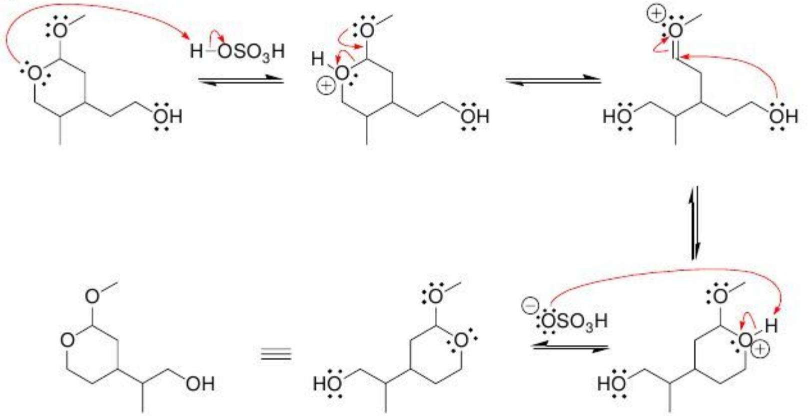
c) **Note**: ***The first two steps of the mechanism below can be reversed (first the amine attacks the carbonyl group, and then the tetrahedral intermediate is protonated). The same is true for attack of the second carbonyl group (half-way through the mechanism). It would be wise to check your lecture notes to determine if you instructor has a strong preference for this alternate sequence of steps.***



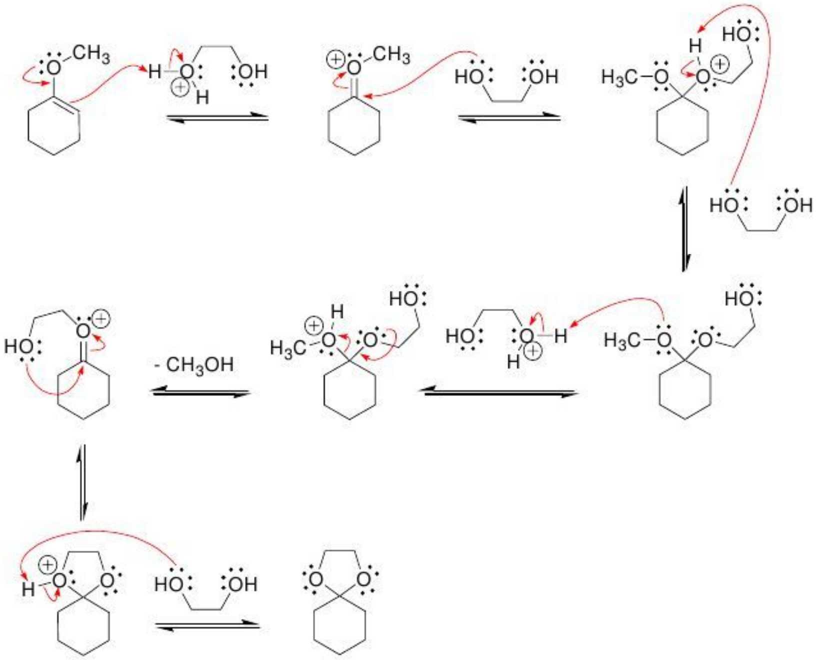
d)


H–OSO3H
OH
OH
OH
OH
OSO3H
OH
OH

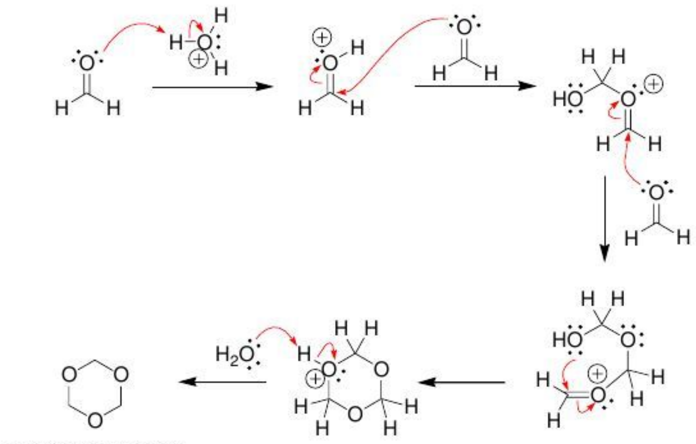
e)


H–OSO3H
OH
H
OH
HO
OH
OSO3H
H
HO
HO
O
O
OH

f)



20.85.



paraformaldehyde

Chapter 21
Carboxylic Acids and Their Derivatives

Review of Concepts

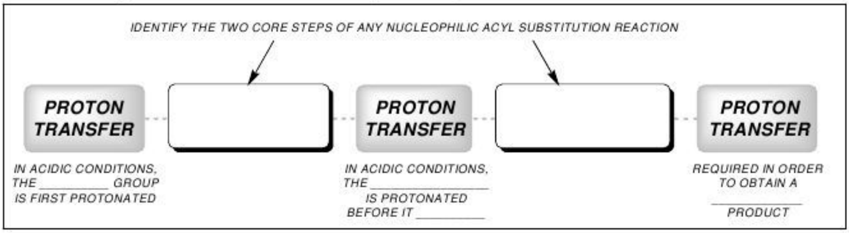
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 21. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- Treatment of a carboxylic acid with a strong base yields a _____________ salt.
- The pK_a of most carboxylic acids is between ____ and _____.
- Using the **Henderson-Hasselbalch equation**, it can be shown that carboxylic acids exist primarily ______________________ at **physiological pH**.
- Electron-____________ substituents can increase the acidity of a carboxylic acid.
- When treated with aqueous acid, a nitrile will undergo ___________, yielding a carboxylic acid.
- Carboxylic acids are reduced to ________ upon treatment with lithium aluminum hydride or borane.
- **Carboxylic acid derivatives** exhibit the same ________ state as carboxylic acids.
- Carboxylic acid derivatives differ in reactivity, with _____________ being the most reactive and __________ the least reactive.
- When drawing a mechanism, avoid formation of ___________ charges in acidic conditions, and avoid formation of ____________ charges in alkaline conditions.
- When a nucleophile attacks a carbonyl group to form a tetrahedral intermediate, always reform the carbonyl if possible, but never expel _____ or ______.
- When treated with an alcohol, acid chlorides are converted into _________.
- When treated with ammonia, acid chlorides are converted into _________.
- When treated with a __________ reagent, acid chlorides are converted into alcohols with the introduction of two alkyl groups.
- The reactions of anhydrides are the same as the reactions of ________________ except for the identity of the leaving group.
- When treated with a strong base followed by an alkyl halide, carboxylic acids are converted into __________.
- In a process called the **Fischer esterification**, carboxylic acids are converted into esters when treated with an ____________ in the presence of ________________.
- Esters can be hydrolyzed to yield carboxylic acids by treatment with either aqueous base or aqueous _______. Hydrolysis under basic conditions is also called ________________.
- When treated with lithium aluminum hydride, esters are reduced to yield ___________. If the desired product is an aldehyde, then ________ is used as a reducing agent instead of LAH.
- When treated with a ____________ reagent, esters are reduced to yield alcohols, with the introduction of two alkyl groups.
- When treated with excess LAH, amides are converted into __________.
- Nitriles are converted to amines when treated with _______.

Review of Skills

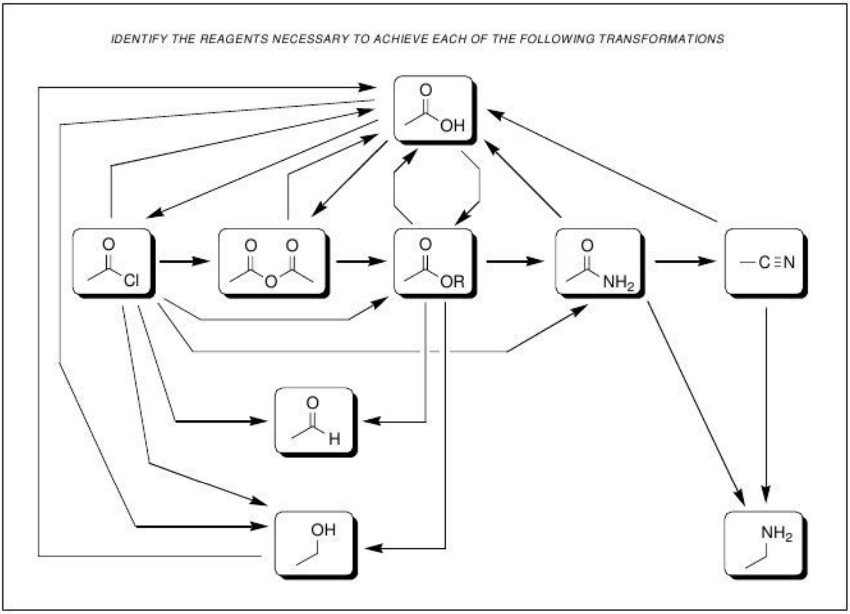
Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 21. The answers appear in the section entitled *SkillBuilder Review*.

21.1 Drawing the Mechanism of a Nucleophilic Acyl Substitution Reaction



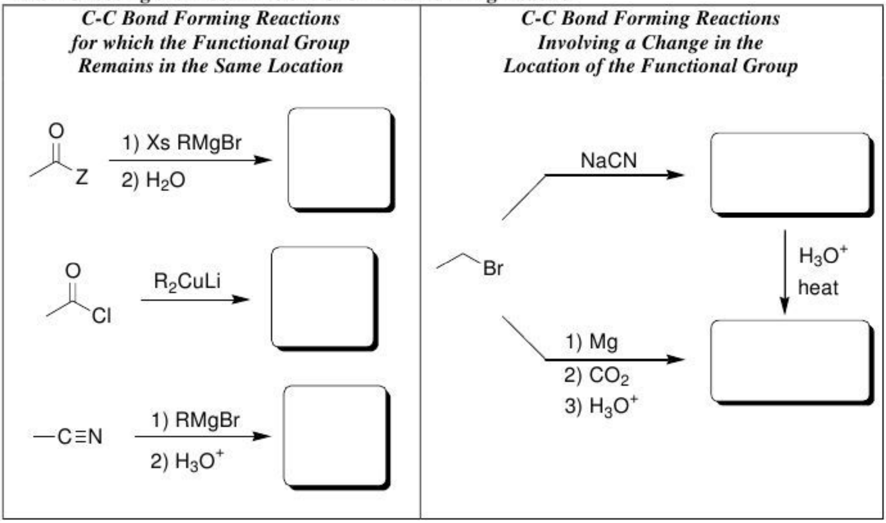
IDENTIFY THE TWO CORE STEPS OF ANY NUCLEOPHILIC ACYL SUBSTITUTION REACTION

21.2 Interconverting Functional Groups



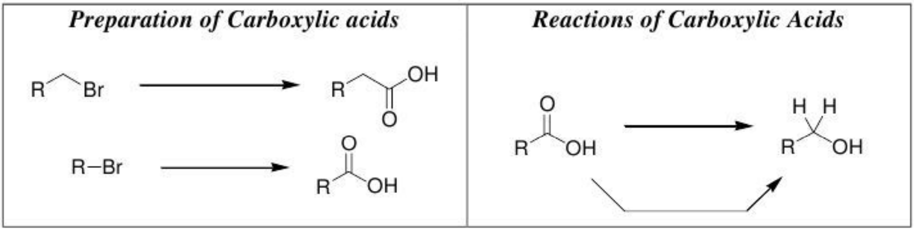
IDENTIFY THE REAGENTS NECESSARY TO ACHIEVE EACH OF THE FOLLOWING TRANSFORMATIONS

21.3 Choosing the Most Efficient C-C Bond-Forming Reaction

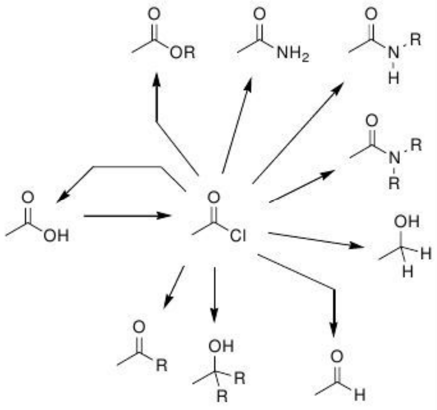


Review of Reactions

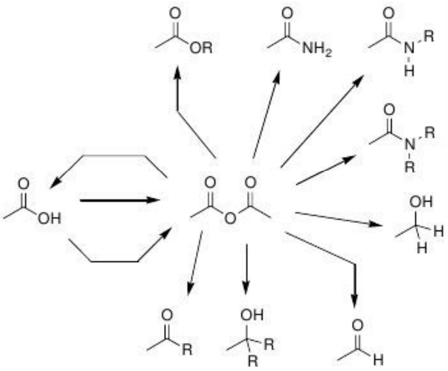
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 21. The answers appear in the section entitled *Review of Reactions*.



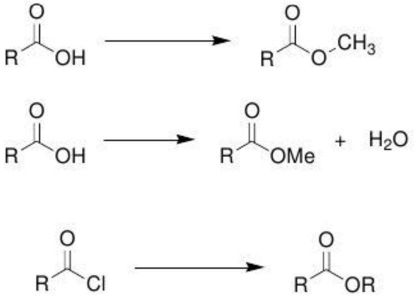
Preparation and Reactions of Acid Chlorides



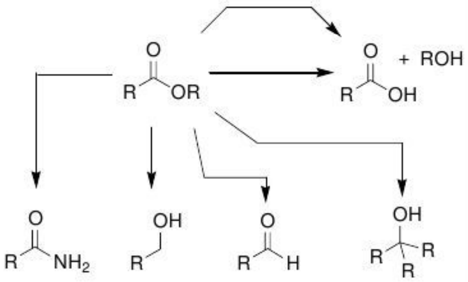
Preparation and Reactions of Acid Anhydrides



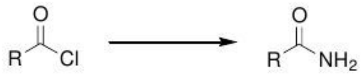
Preparation of Esters



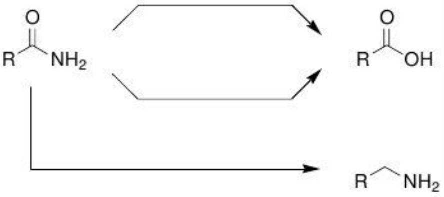
Reactions of Esters

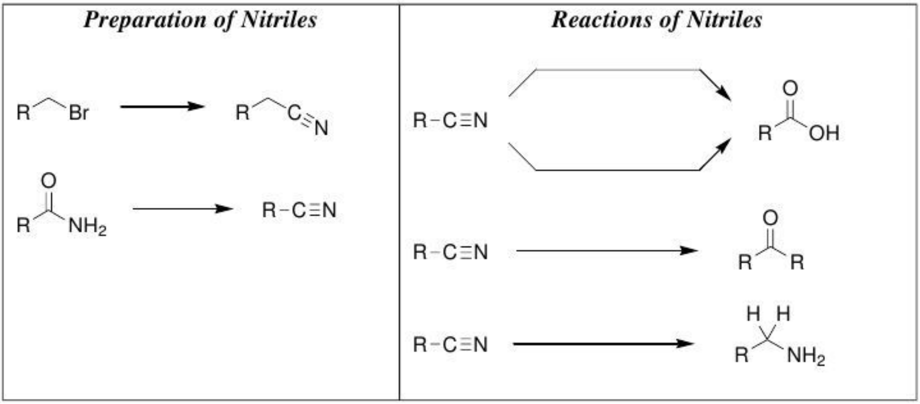


Preparation of Amides



Reactions of Amides




Preparation of Nitriles

Reactions of Nitriles

Solutions

21.1.
a) IUPAC name = pentanedioic acid
Common name = glutaric acid

b) IUPAC name = butanoic acid
Common name = butyric acid

c) IUPAC name = benzene carboxylic acid
Common name = benzoic acid

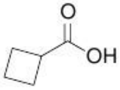
d) IUPAC name = butanedioic acid
Common name = succinic acid

e) IUPAC name = ethanoic acid
Common name = acetic acid

f) IUPAC name = methanoic acid
Common name = formic acid

21.2.

a)



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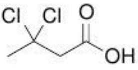
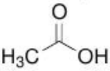


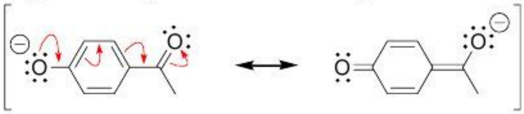
c)

21.3.
a) 3,3,4,4-tetramethylhexanoic acid
b) 2-propylpentanoic acid
c) (*S*)-2-amino-3-phenylpropanoic acid

21.4. The compound below is more acidic because its conjugate base is resonance stabilized. The conjugate base of the other compound is not resonance stabilized.

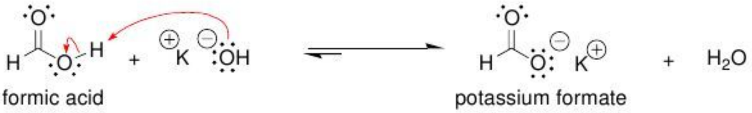


21.5.
The conjugate base is resonance stabilized, with the negative charge spread over two oxygen atoms, just like with carboxylic acids:



21.6. *meta*-Hydroxyacetophenone should be less acidic than *para*-hydroxyacetophenone, because in the conjugate base of the former, the negative charge is spread over only one oxygen atoms (and three carbon atoms). In contrast, the conjugate base of *para*-hydroxyacetophenone has the negative charge spread over two oxygen atoms (more stable).

21.7.



21.8. The conjugate base predominates under these conditions:

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = 10^{(\text{pH} - \text{p}K_a)} = 10^{(5.76 - 4.76)} = 10^{1} = 10$$

21.9.
a) 2,3-dichlorobutyric acid is the most acidic and 3,4-dimethylbutyric acid is the least acidic.
b) 2,2-dibromopropionic acid is the most acidic and 3-bromopropionic acid is the least acidic.

21.10.

a) $Na_2Cr_2O_7$, H_2SO_4, H_2O

b) $Na_2Cr_2O_7$, H_2SO_4, H_2O

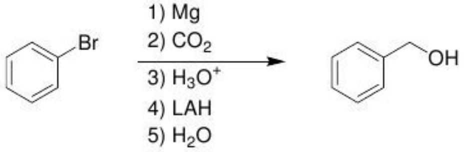
c) CH_3Cl, $AlCl_3$ followed by $Na_2Cr_2O_7$, H_2SO_4, H_2O

d) NaCN, followed by H_3O^+, heat
  or Mg, followed by CO_2, followed by H_3O^+

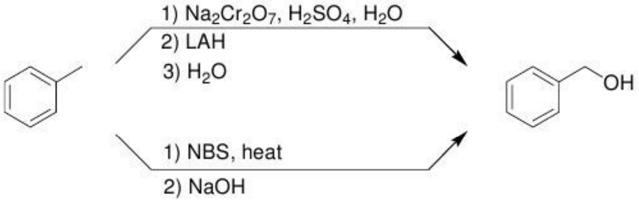
e) $Na_2Cr_2O_7$, H_2SO_4, H_2O

f) Mg, followed by CO_2, followed by H_3O^+

21.11.



a)



b)

21.12.

a) propionic anhydride

b) *N,N*-diphenyl-propionamide

c) dimethylsuccinate

d) *N*-ethyl-*N*-methylcyclobutanecarboxamide

e) butyronitrile

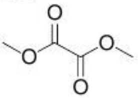
f) propyl butyrate

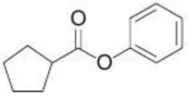
g) succinic anhydride

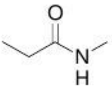
h) methyl benzoate

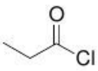
i) phenyl acetate

21.13.

a) 

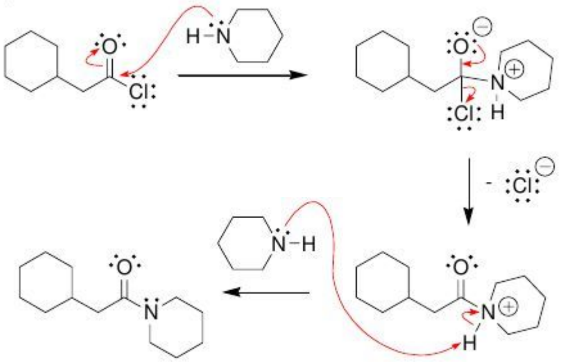
b) 

c) 

d) 

21.14.

a)



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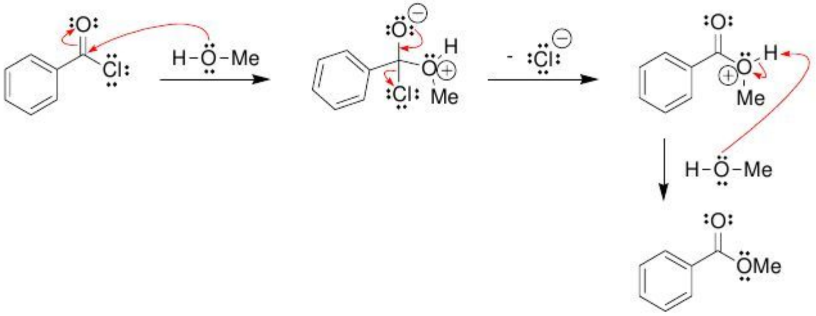

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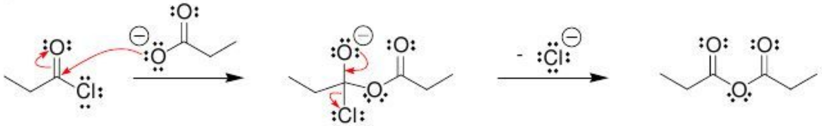

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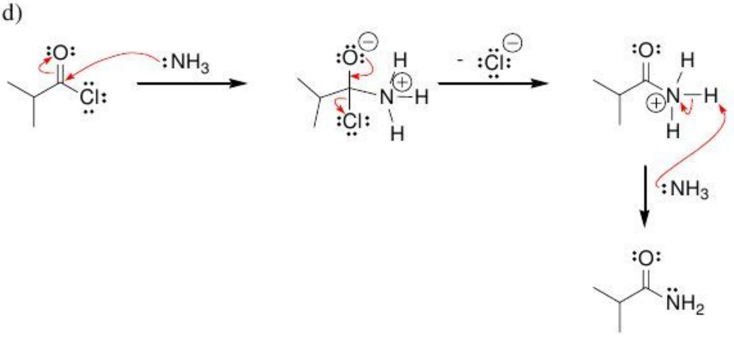

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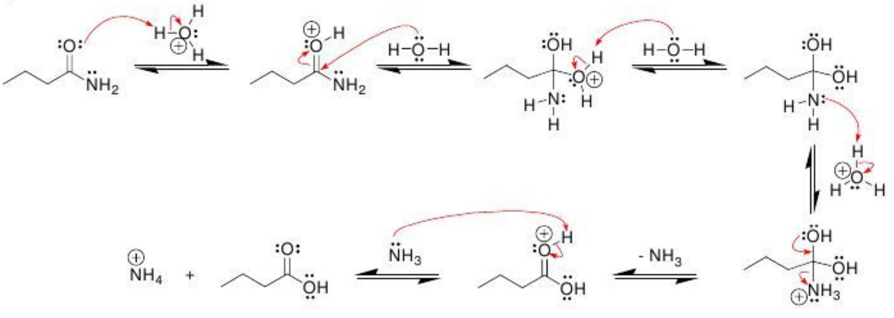

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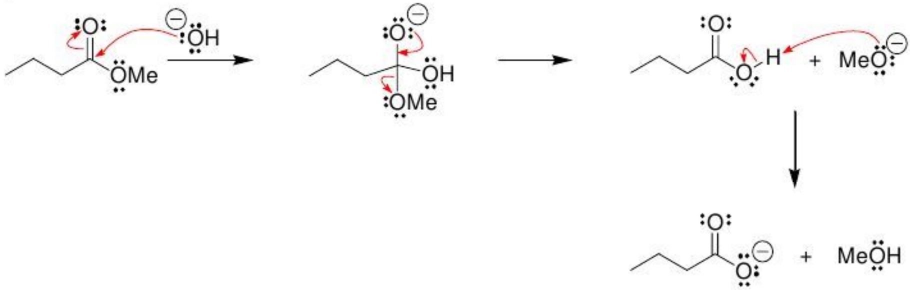

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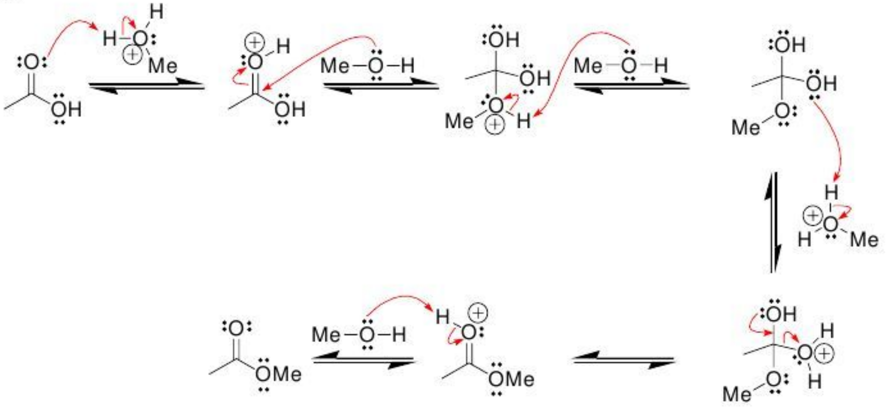

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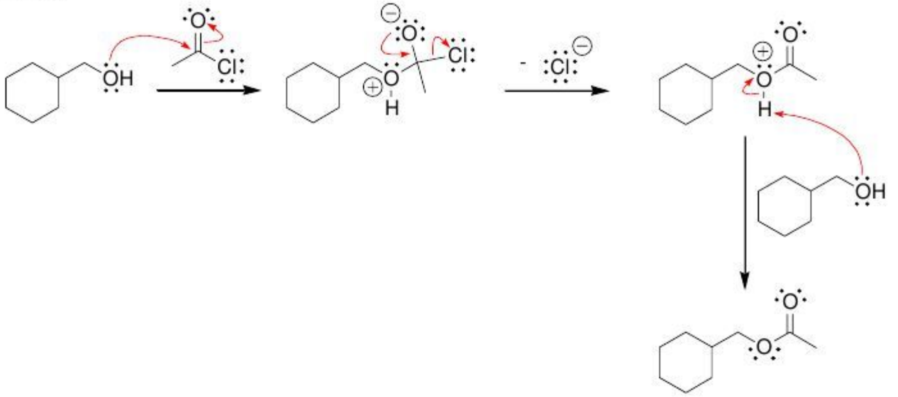
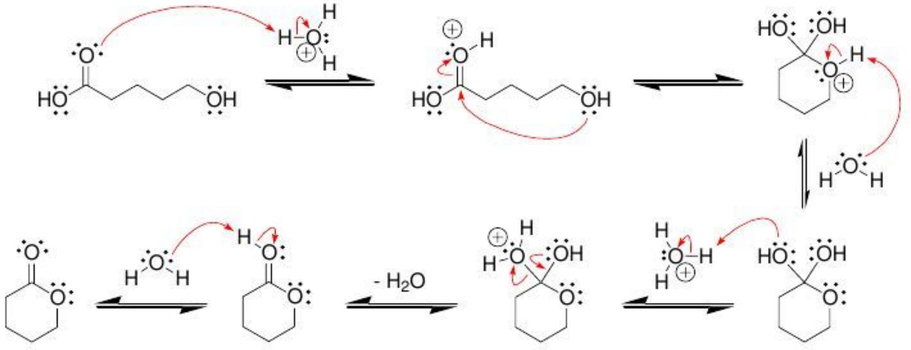
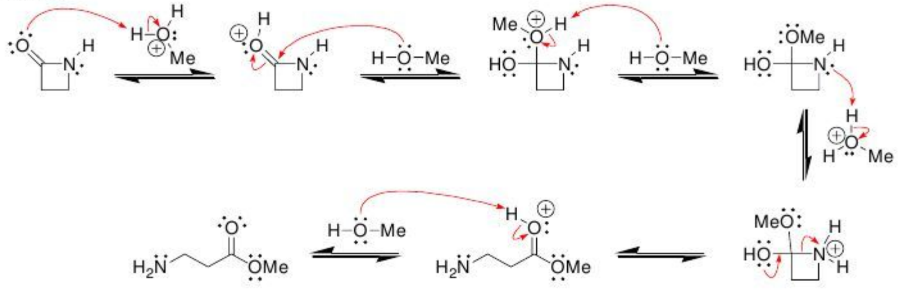


21.16.

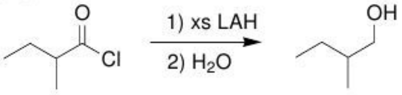


21.17.



21.18.

a)



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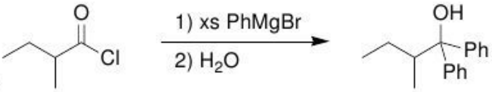

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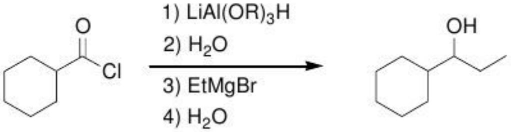

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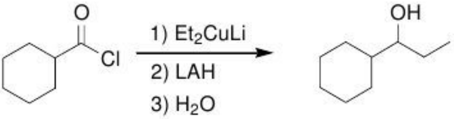

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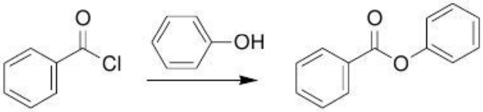

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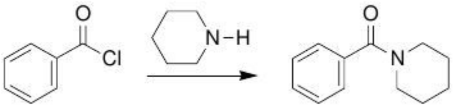

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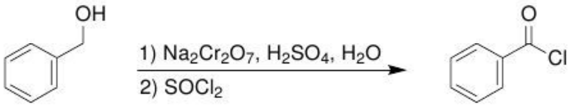

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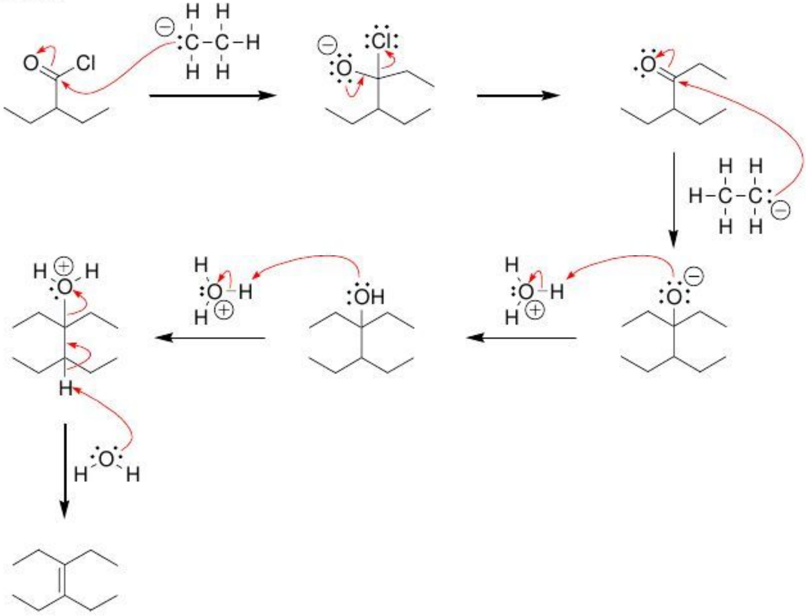
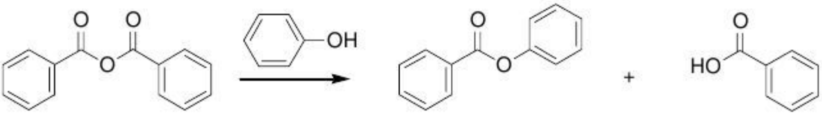


21.21.

a)



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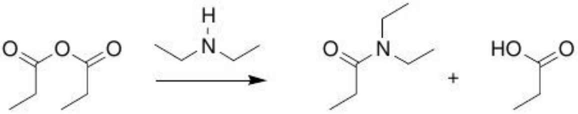

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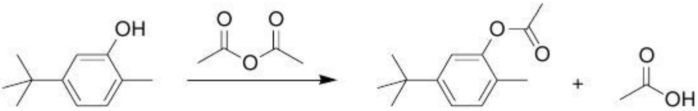

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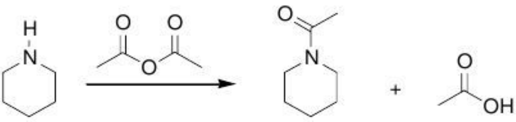

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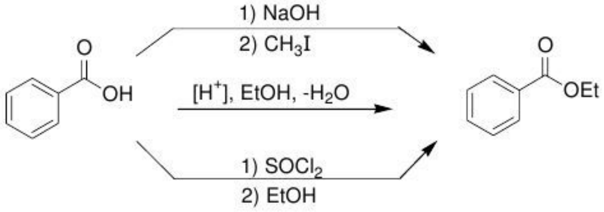
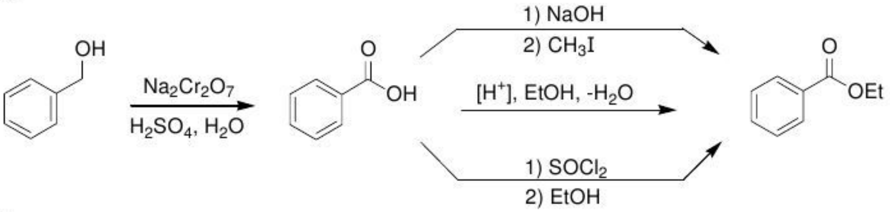


21.23.

a)



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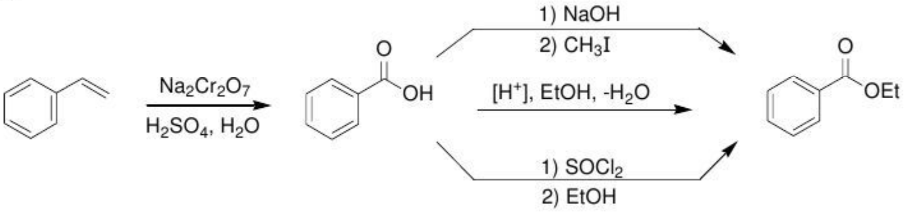
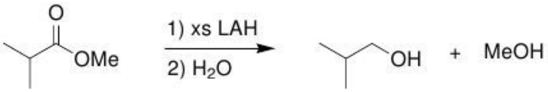


21.24.

a)



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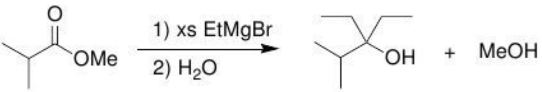

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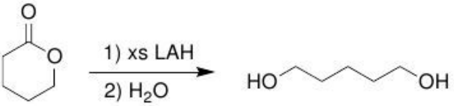

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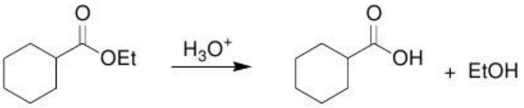

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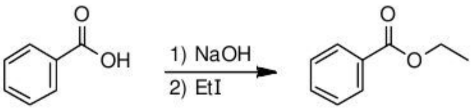

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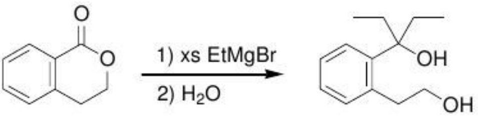
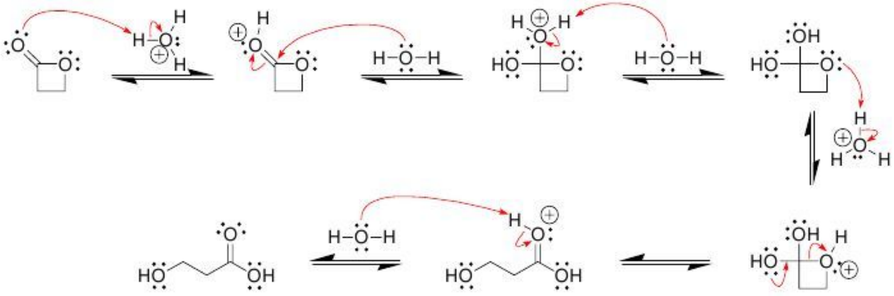
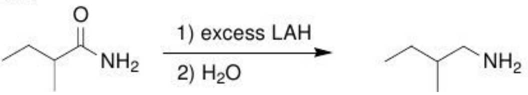


21.25.

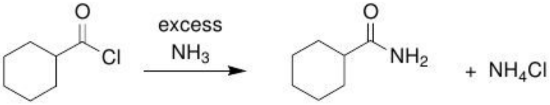


21.26.

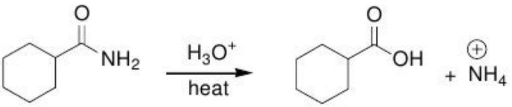
a)



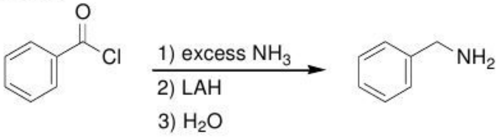
b)



c)

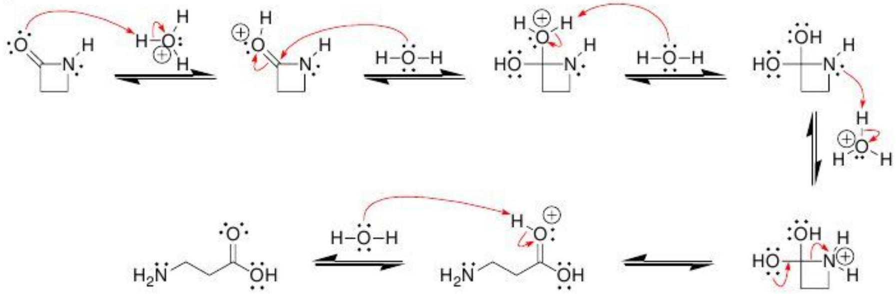


21.27.

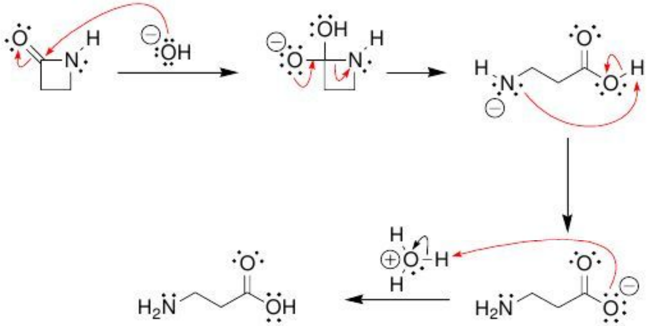


21.28.

a)

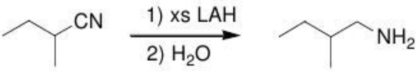


b)

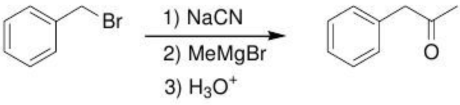


21.29.

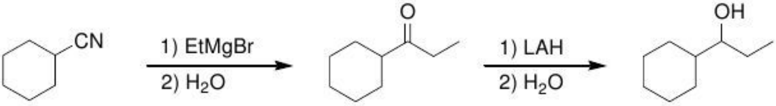
a)



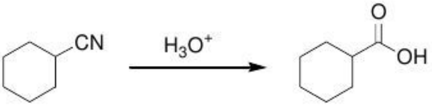
b)



c)

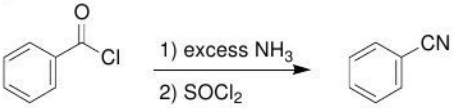


d)

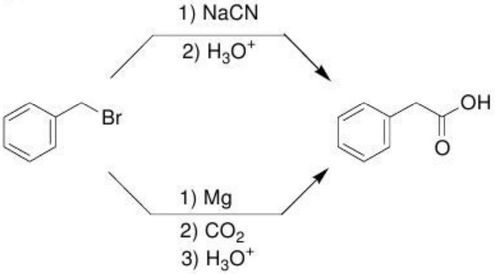


21.30.

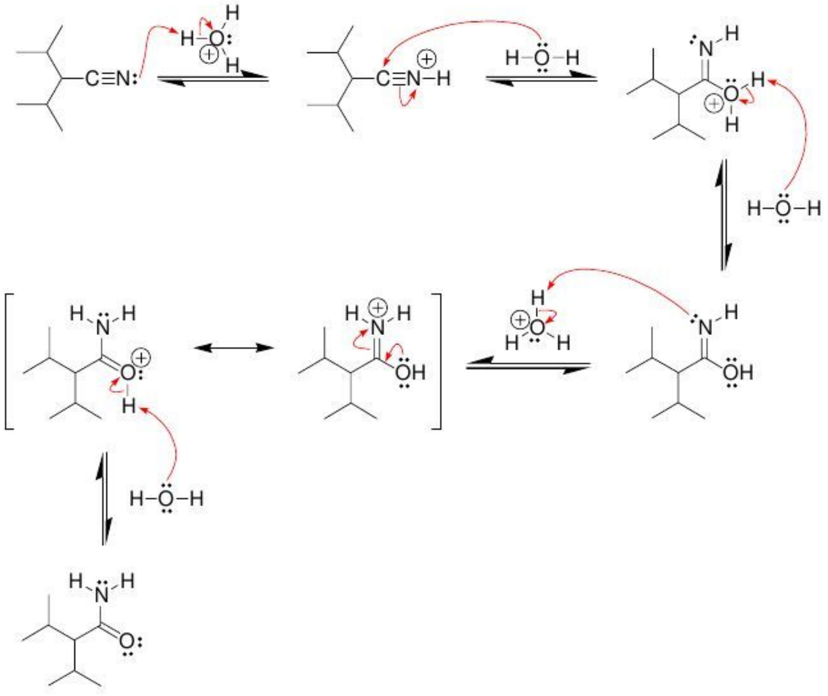
a)



b)

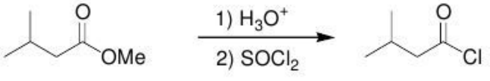


21.31.

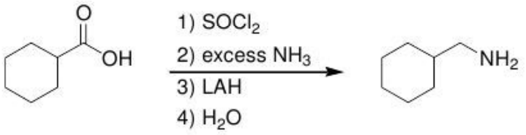


21.32.

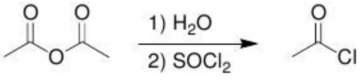
a)

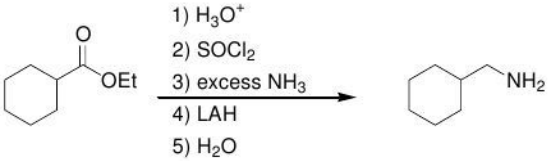


b)

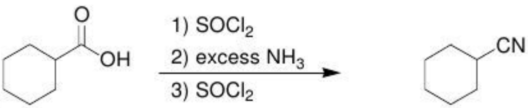


c)

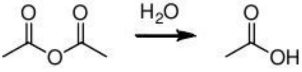




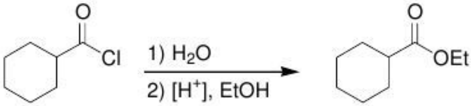
d)



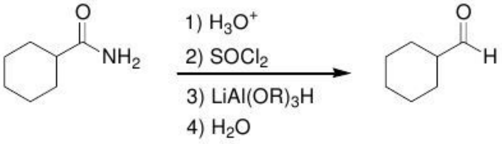
e)



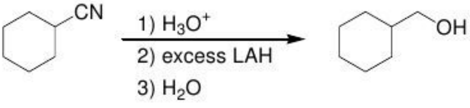
f)



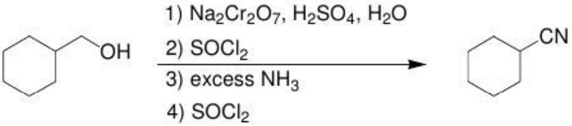
g)



h)



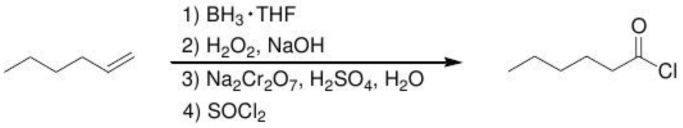
i)



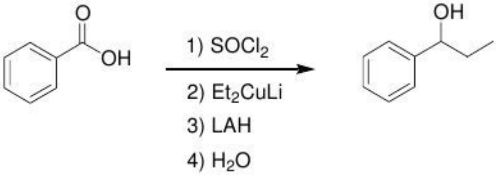
j)

21.33. Four steps: 1) oxidize to a carboxylic acid, 2) convert into an acid halide, 3) convert into an amide, and 4) reduce to give an amine.

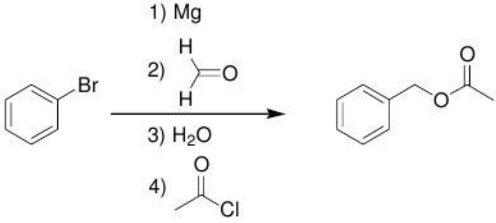
21.34.



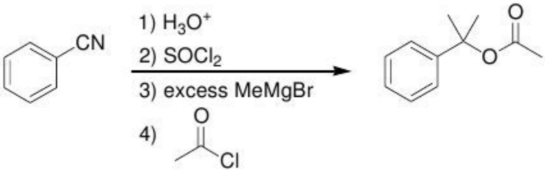
21.35.



a)

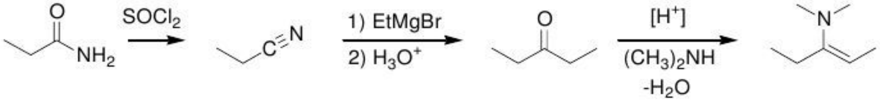


b)



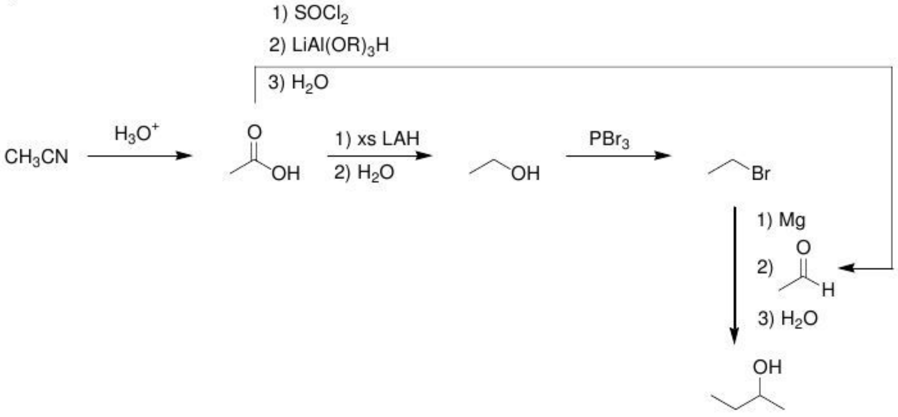
c)

21.36.



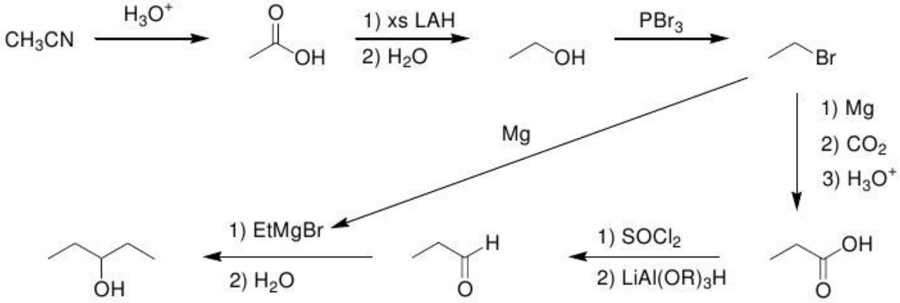
21.37.

a)



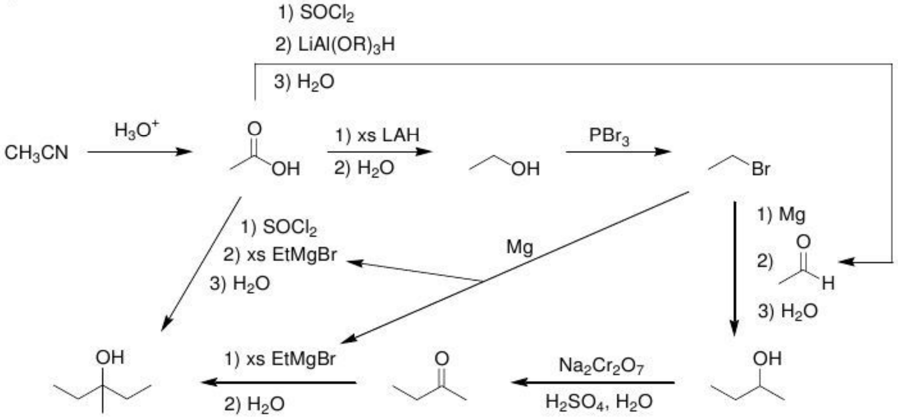
1) $SOCl_2$
2) $LiAl(OR)_3H$
3) H_2O
CH_3CN
H_3O^+
OH
1) xs LAH
2) H_2O
OH
PBr_3
Br
1) Mg
2)
H
3) H_2O
OH

b)



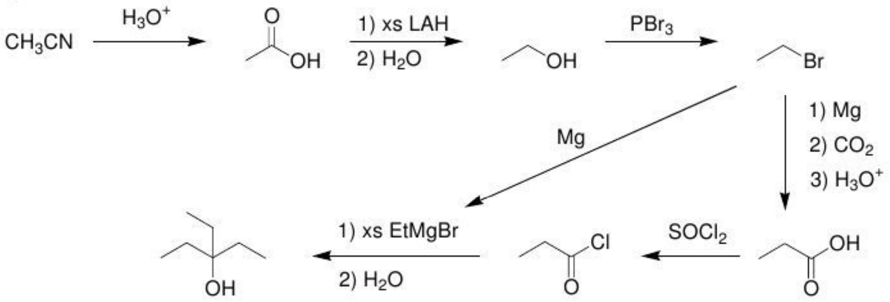
CH_3CN
H_3O^+
OH
1) xs LAH
2) H_2O
OH
PBr_3
Br
Mg
1) Mg
2) CO_2
3) H_3O^+
1) EtMgBr
2) H_2O
H
1) $SOCl_2$
2) $LiAl(OR)_3H$
OH
OH

c)

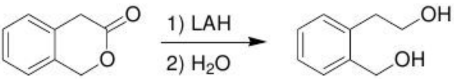


1) $SOCl_2$
2) $LiAl(OR)_3H$
3) H_2O
CH_3CN
H_3O^+
OH
1) xs LAH
2) H_2O
OH
PBr_3
Br
1) $SOCl_2$
2) xs EtMgBr
3) H_2O
Mg
1) Mg
2)
H
3) H_2O
OH
1) xs EtMgBr
2) H_2O
$Na_2Cr_2O_7$
H_2SO_4, H_2O
OH

d)

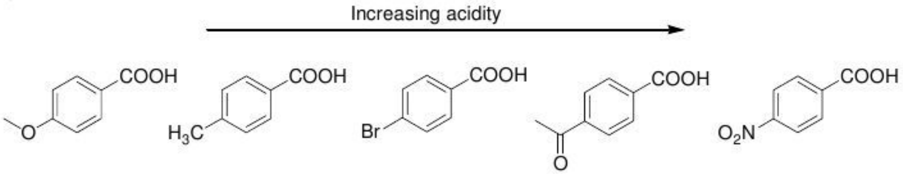


21.38. The signal at 1740 cm^{-1} indicates that the carbonyl group is not conjugated with the aromatic ring (it would be at a lower wavenumber if it was conjugated),

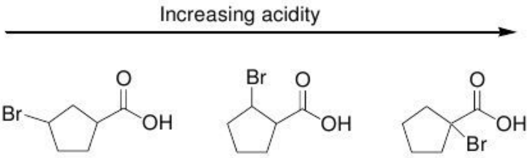


21.39.

a)



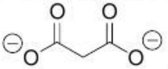
b)



21.40.

a) The second carboxylic acid moiety is electron withdrawing, and stabilizes the conjugate base that is formed when the first proton is removed.

b) The carboxylate ion is electron rich and it destabilizes the conjugate base that is formed when the second proton is removed.

c)  .

d) The number of methylene groups (CH_2) separating the carboxylic acid moieties is greater in succinic acid than in malonic acid. Therefore, the inductive effects are not as strong.

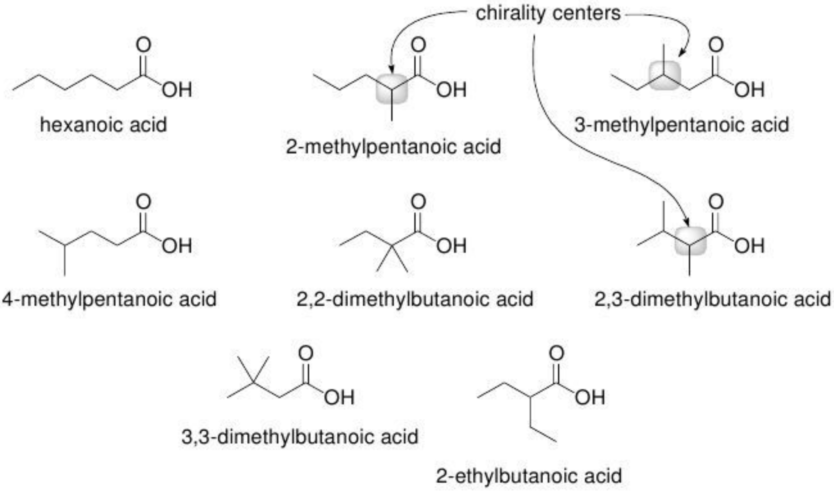
21.41.

a) cyclopentanecarboxylic acid
b) cyclopentanecarboxamide
c) benzoyl chloride
d) ethyl acetate
e) hexanoic acid
f) pentanoyl chloride
g) hexanamide

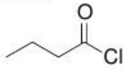
21.42.

a) acetic anhydride
b) benzoic acid
c) formic acid
d) oxalic acid

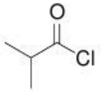
21.43.



21.44.

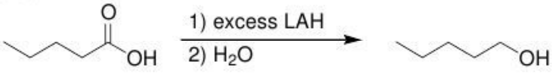


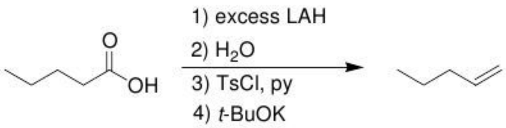
butanoyl chloride

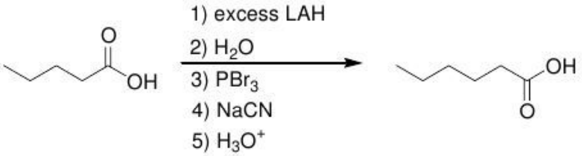


2-methylpropanoyl chloride

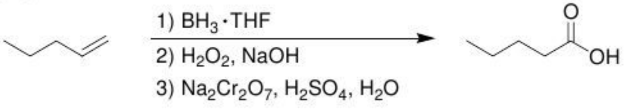
21.45.

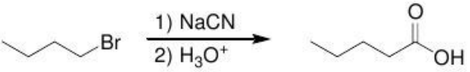
a) 

b) 

c) 

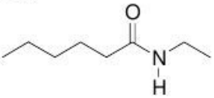
21.46.

a) 

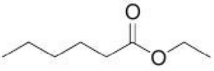
b) 

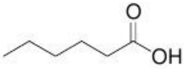
21.47. As discussed in Chapter 19, the methoxy group is electron donating via resonance, but electron withdrawing via induction. The resonance effect is stronger, but only occurs when the methoxy group is in an *ortho* or *para* position.

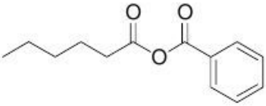
21.48.

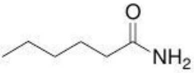
a) 

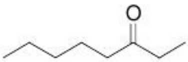
b) 

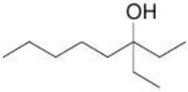
c) 

d) 

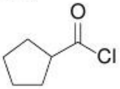
e) 

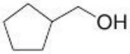
f) 

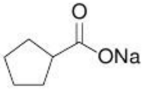
g) 

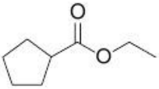
h) 

21.49.

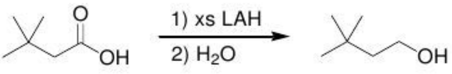
a) 

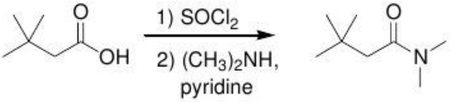
b) 

c) 

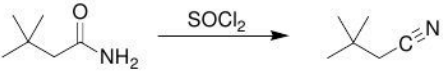
d) 

21.50.

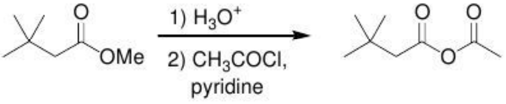
a) 


OH
1) $SOCl_2$
2) $(CH_3)_2NH$, pyridine
O
N

b)


O
NH_2
$SOCl_2$
C≡N

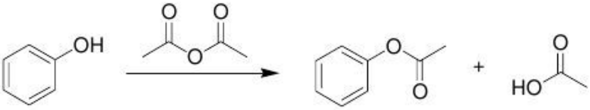
c)


O
OMe
1) H_3O^+
2) CH_3COCl, pyridine
O
O
O

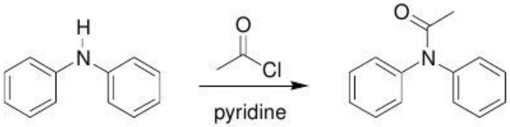
d)


O
OMe
DIBAH
O
H

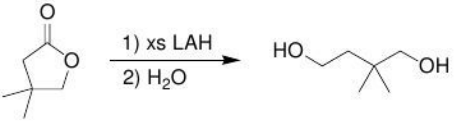
e)


OH
O
O
O
O
O
+
O
HO

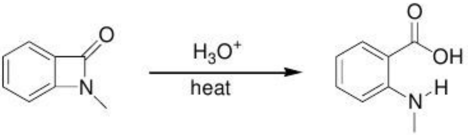
f)


H
N
O
Cl
pyridine
O
N

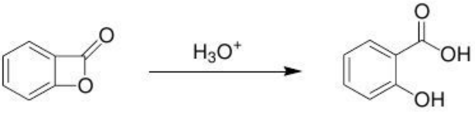
g)


O
O
1) xs LAH
2) H_2O
HO
OH

h)

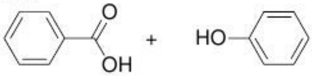

O
N
H_3O^+
heat
O
OH
N
H

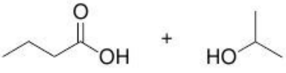
i)


O
O
H_3O^+
O
OH
OH

j)

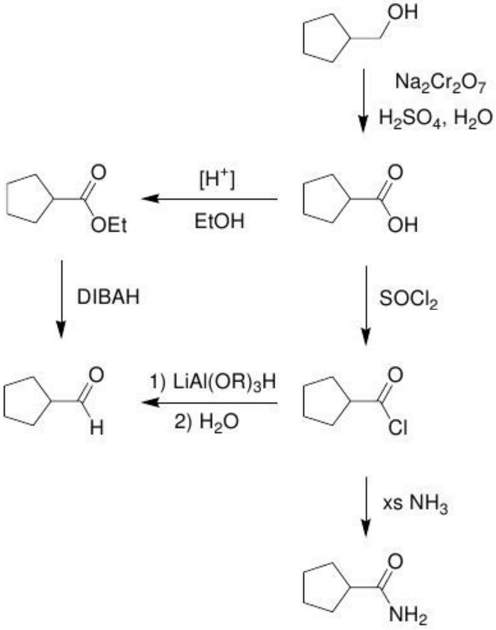
21.51.

a) 

b) 

c) $CH_3CH_2CO_2H$ + $(CH_3)_3COH$

21.52.



21.53.

a) NaOH, followed by $Na_2Cr_2O_7$, H_2SO_4, H_2O

b) NaCN followed by H_3O^+

c) NaOH, followed by $Na_2Cr_2O_7$, H_2SO_4, H_2O, followed by $SOCl_2$

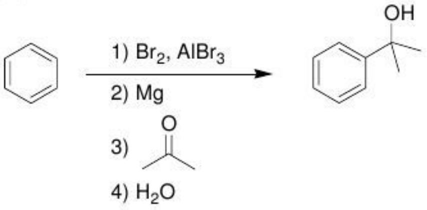
d) NaCN, followed by H_3O^+, followed by $SOCl_2$, followed by xs NH_3

e) NaOH, followed by $Na_2Cr_2O_7$, H_2SO_4, H_2O, followed by $SOCl_2$, followed by xs NH_3

f) NaCN followed by H_3O^+, followed by $[H^+]$, EtOH (with removal of water)

21.54.

a)



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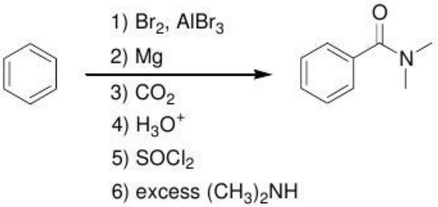

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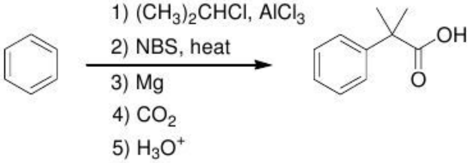
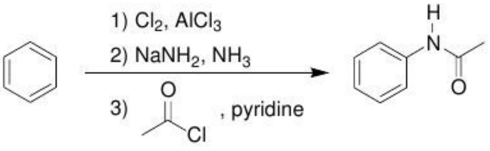
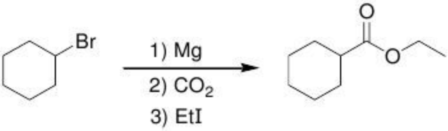


d)



21.55.

a)



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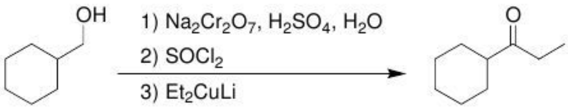

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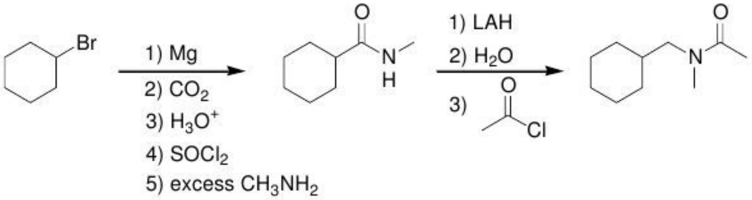

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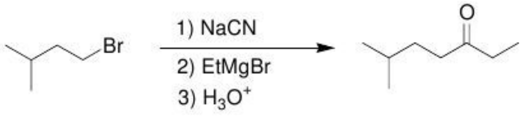
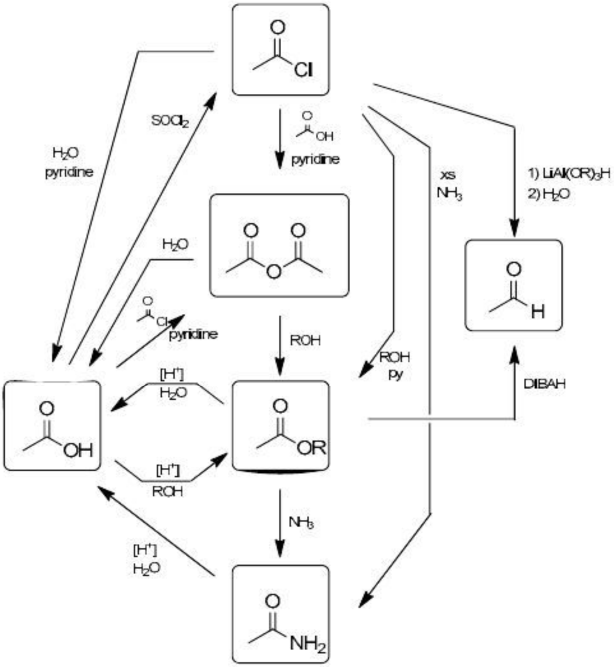
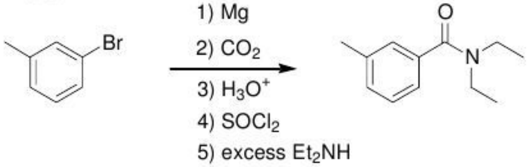


21.56. A methoxy group is electron donating, thereby decreasing the electrophilicity of the ester moiety. A nitro group is electron withdrawing, thereby increasing the electrophilicity of the ester group.

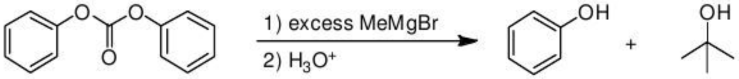
21.57.



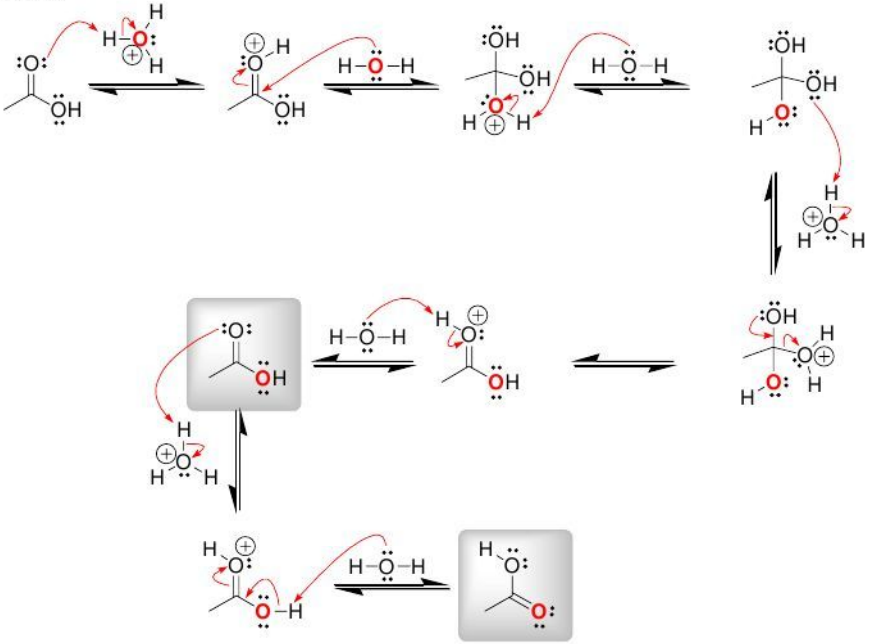
21.58.



21.59.

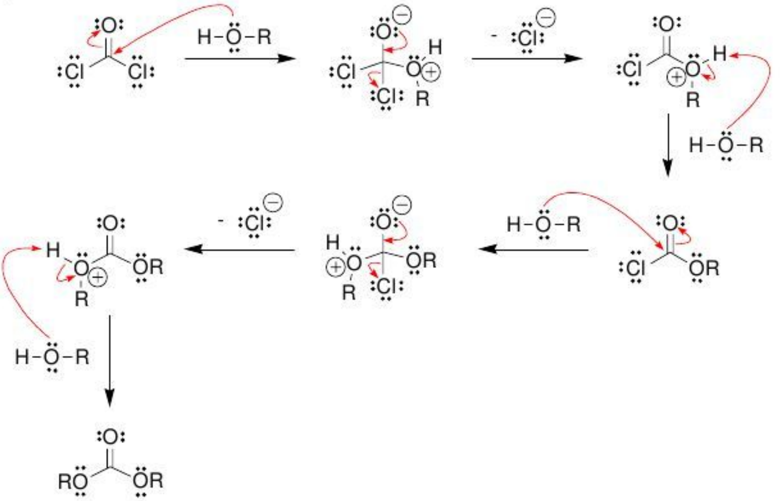


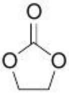
21.60.

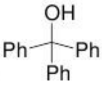


21.61.

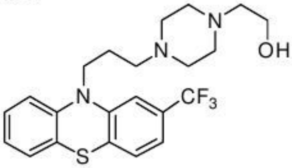
a)



b) 

c) 

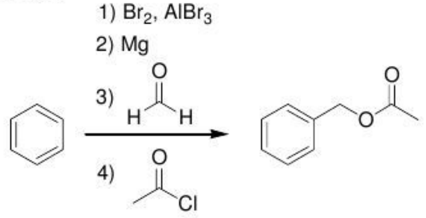
21.62.

a) 

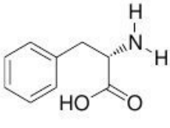
b) 

decanoic acid

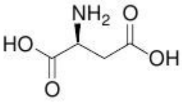
21.63.



21.64.



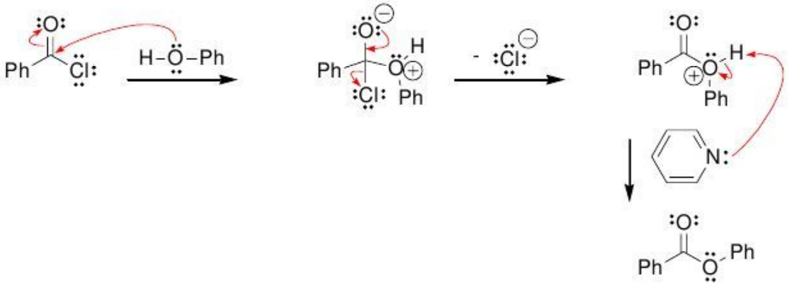
phenylalanine



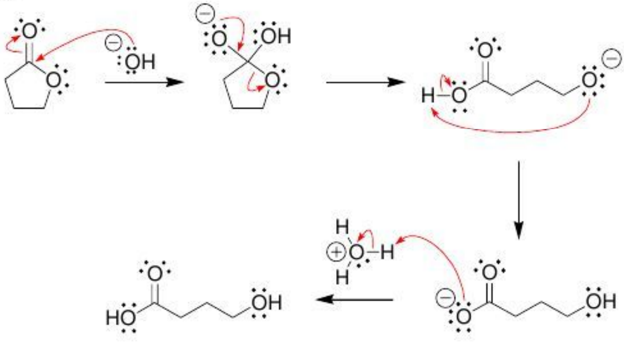
aspartic acid

21.65.

a)



b)



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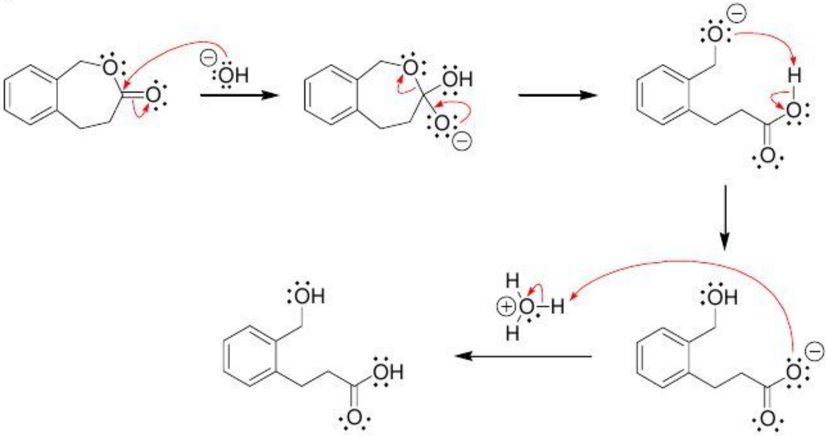

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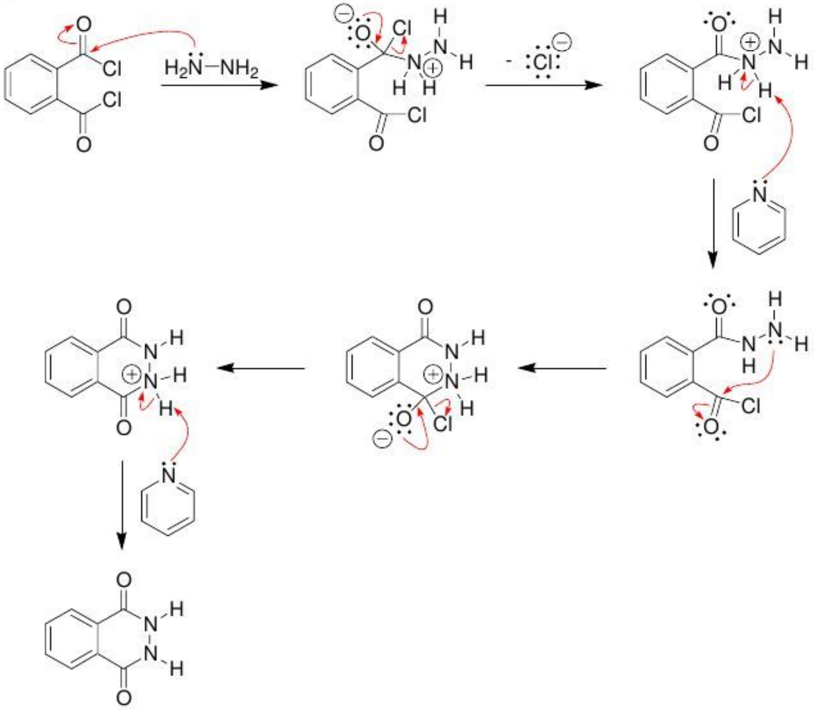
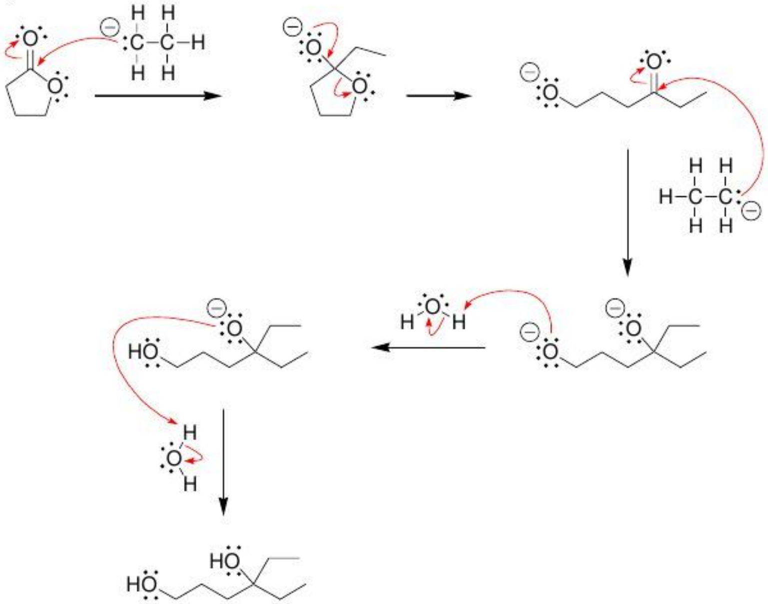
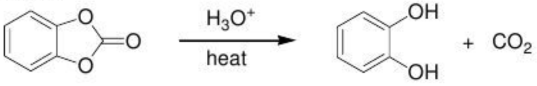


e)

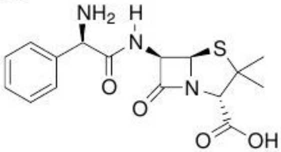


21.66. The three chlorine atoms withdraw electron density via induction. This effect renders the carbonyl group more electrophilic.

21.67.



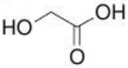
21.68



a)

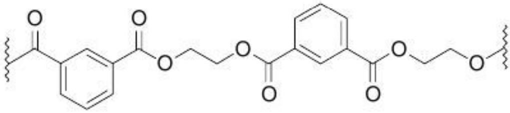
b) Ampicillin

21.69.

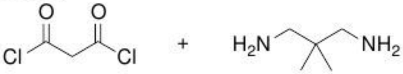


(glycolic acid)
hydroxyacetic acid

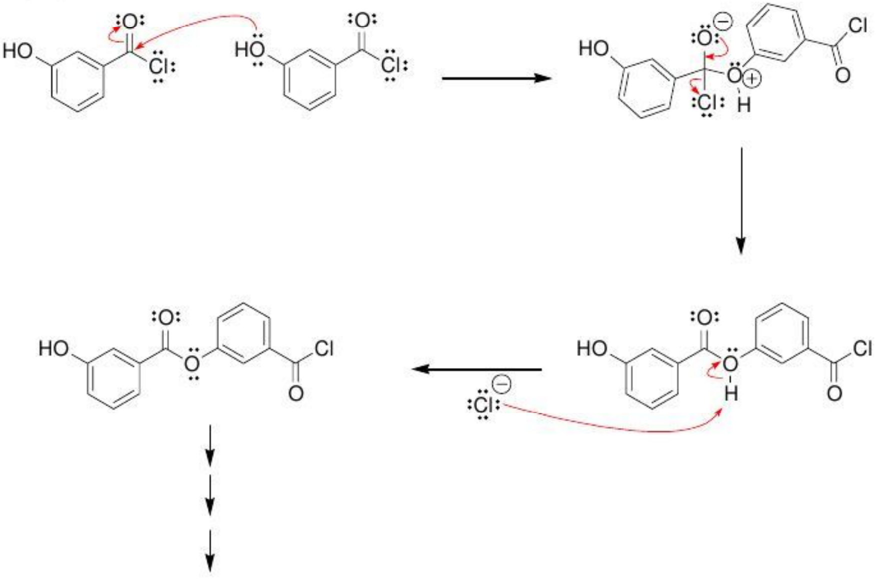
21.70.



21.71.

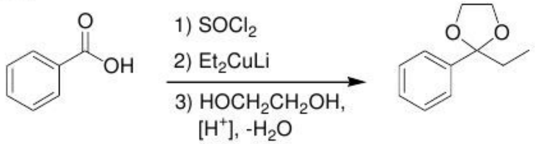


21.72.

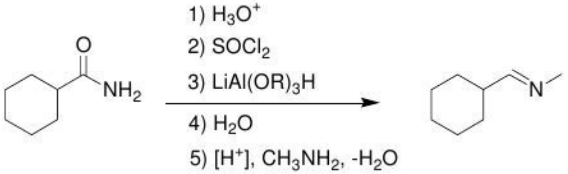


21.73.

a)



b)



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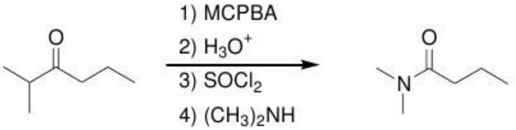
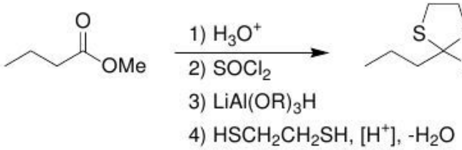
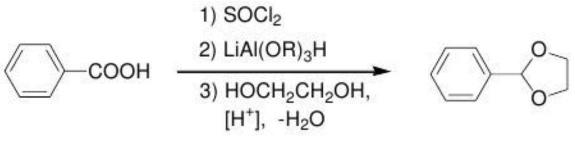


d)



e)



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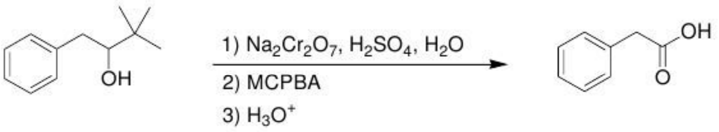
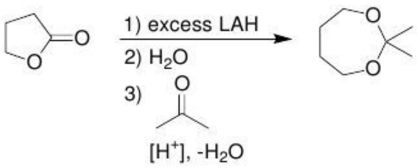
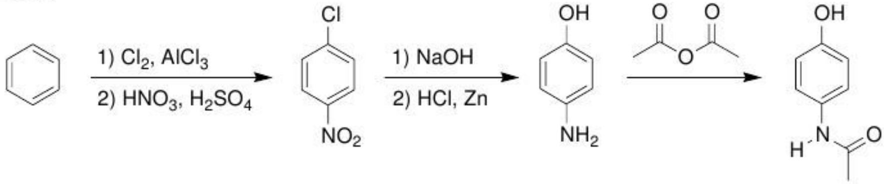


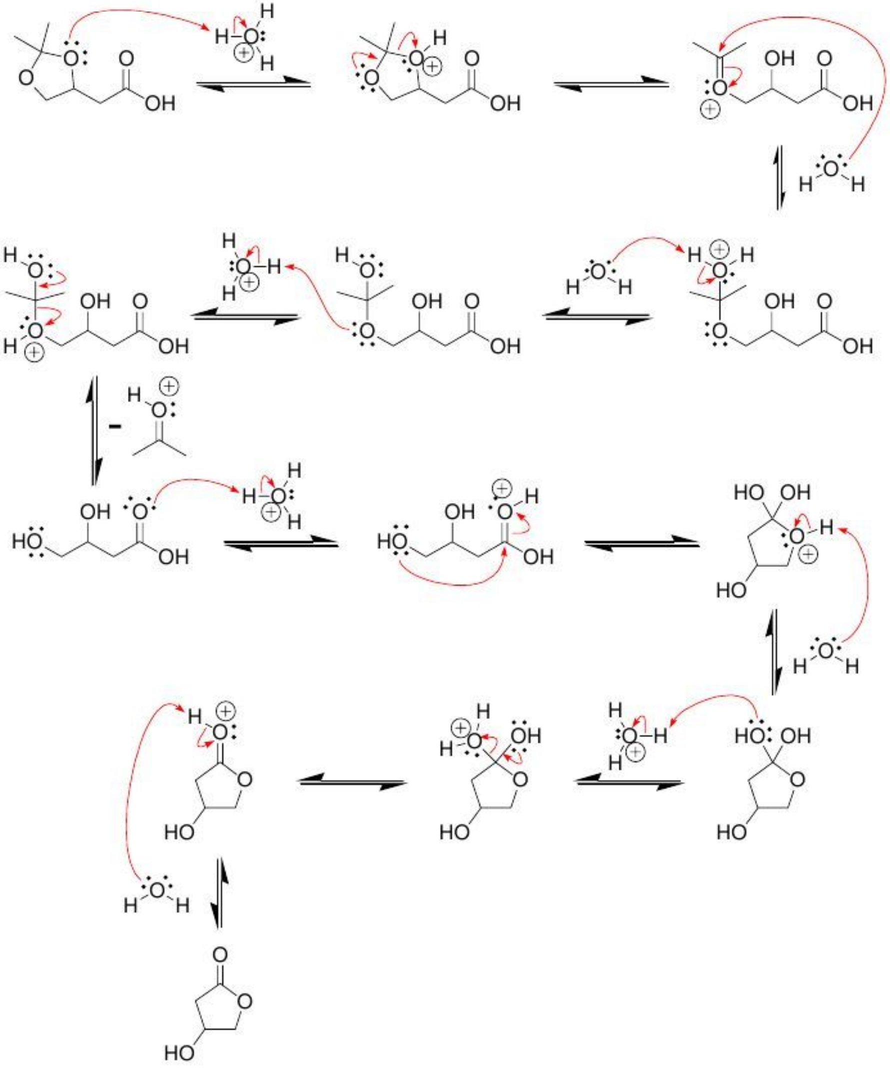
g)



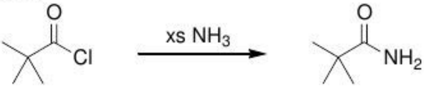
21.74.



21.75.

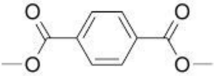


21.76.



Compound A

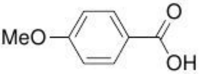
21.77.



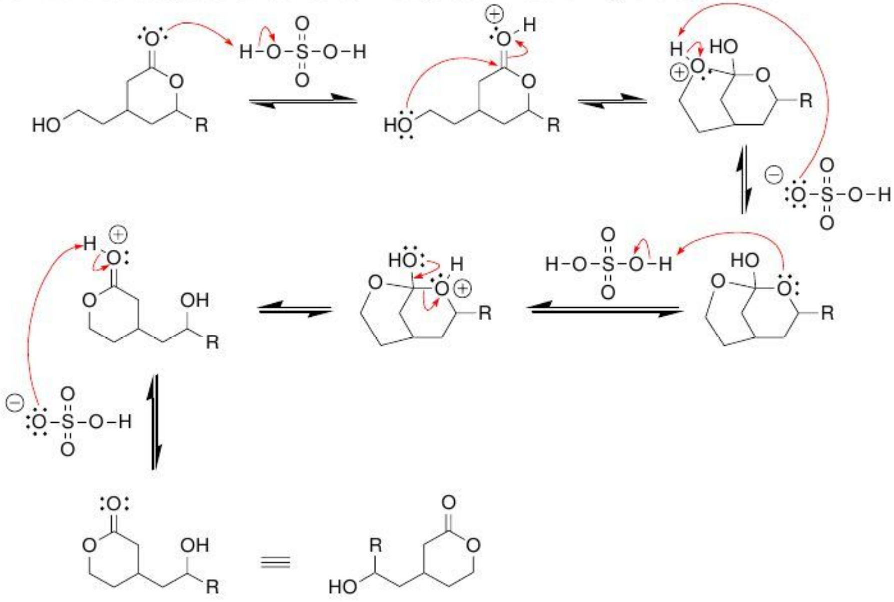
21.78. An IR spectrum of butyric acid should have a broad signal between 2500 cm^{-1} and 3600 cm^{-1}. An IR spectrum of ethyl acetate will not have this signal.

21.79. The ^{1}H NMR spectrum of *para*-chlorobenzaldehyde should have a signal at approximately 10 ppm corresponding to the aldehydic proton. The ^{1}H NMR spectrum of benzoyl chloride should not have a signal near 10 ppm.

21.80.



21.81. If the oxygen atom of the OH group in the starting material is an isotopic label, then we would expect the label to be incorporated into the ring of the product:



21.82. The lone pair of the nitrogen atom in this case is participating in resonance and is less available to donate electron density to the carbonyl group. As a result, the carbonyl group is more electrophilic than the carbonyl group of a regular amide (where the lone pair contributes significant electron density to the carbonyl group). Also, when this compound functions as an electrophile in a nucleophilic acyl substitution reaction, the leaving group is particularly stable because it is an aromatic anion. With a good leaving group, this compound more closely resembles the reactivity of an acid halide than an amide.

21.83.

a) DMF, like most amides, exhibits restricted rotation about the bond between the carbonyl group and the nitrogen atom. This restricted rotation causes the methyl groups to be in different electronic environments. They are not chemically equivalent, and will therefore produce two different signals (in addition to the signal from the other proton in the compound). Upon treatment with excess LAH followed by water, DMF is reduced to an amine that does not exhibit restricted rotation. As such, the methyl groups are now chemically equivalent and will together produce only one signal.

b) Restricted rotation causes the methyl groups to be in different electronic environments. As a result, the ^{13}C NMR spectrum of DMF should have three signals.

Chapter 22

Alpha Carbon Chemistry: Enols and Enolates

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 22. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- In the presence of catalytic acid or base, a ketone will exist in equilibrium with an _____. In general, the equilibrium position will significantly favor the ________.
- When treated with a strong base, the α position of a ketone is deprotonated to give an ___________.
- __________________ or _____ will irreversibly and completely convert an aldehyde or ketone into an enolate.
- In the **haloform reaction**, a _______ ketone is converted into a carboxylic acid upon treatment with excess base and excess halogen followed by acid workup.
- When an aldehyde is treated with sodium hydroxide, an **aldol addition reaction** occurs, and the product is a ________________________________.
- For most simple aldehydes, the position of equilibrium favors the aldol product. For most ketones, the reverse process, called a ______**-aldol reaction** is favored.
- When an aldehyde is heated in aqueous sodium hydroxide, an **aldol** ___________ **reaction** occurs, and the product is an ____________________________. Elimination of water occurs via an ______ **mechanism**.
- **Crossed aldol,** or **mixed aldol reactions** are aldol reactions that occur between different partners, and are only efficient if one partner lacks __________ or if a **directed aldol addition** is performed.
- Intramolecular aldol reactions show a preference for formation of ______ and ____-membered rings.
- When an ester is treated with an alkoxide base, a **Claisen condensation reaction** occurs, and the product is a ________________.
- The α position of a ketone can be alkylated by forming an enolate and treating it with an _________________.
- For unsymmetrical ketones, reactions with _____ at low temperature favor formation of the kinetic enolate, while reactions with ______ at room temperature favor the thermodynamic enolate.
- When LDA is used with an unsymmetrical ketone, alkylation occurs at the __________________ position.
- The ______________________ **synthesis** enables the conversion of an alkyl halide into a carboxylic acid with the introduction of two new carbon atoms.
- The ______________________ **synthesis** enables the conversion of an alkyl halide into a methyl ketone with the introduction of two new carbon atoms.
- Aldehydes and ketones that possess _____-unsaturation are susceptible to nucleophilic attack at the β position. This reaction is called a ____________ **addition, 1,4-addition,** or a **Michael reaction**.

Review of Skills

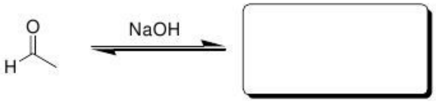
Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 22. The answers appear in the section entitled *SkillBuilder Review*.

22.1 Drawing Enolates

DRAW THE RESONANCE STRUCTURES OF THE ENOLATE THAT IS FORMED WHEN THE KETONE BELOW IS TREATED WITH A STRONG BASE:

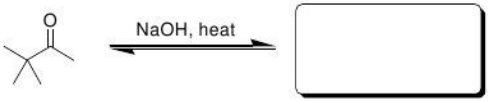
22.2 Predicting the Products of an Aldol Addition Reaction

PREDICT THE PRODUCT OF THE ALDOL ADDITION REACTION THAT OCCURS WHEN THE FOLLOWING ALDEHYDE IS TREATED WITH SODIUM HYDROXIDE:



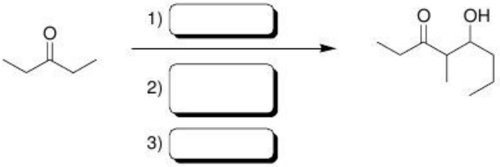
22.3 Drawing the Product of an Aldol Condensation

DRAW THE PRODUCT OF THE ALDOL CONDENSATION REACTION THAT OCCURS WHEN THE FOLLOWING COMPOUND IS HEATED WITH SODIUM HYDROXIDE:



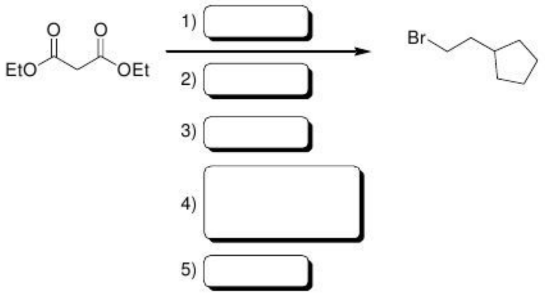
22.4 Identifying the Reagents Necessary for a Crossed Aldol Reaction

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:



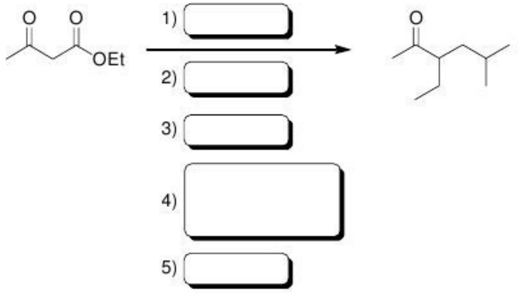
22.5 Using the Malonic Ester Synthesis

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:



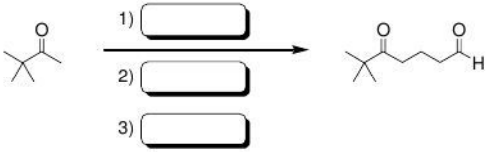
22.6 Using the Acetoacetic Ester Synthesis

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:

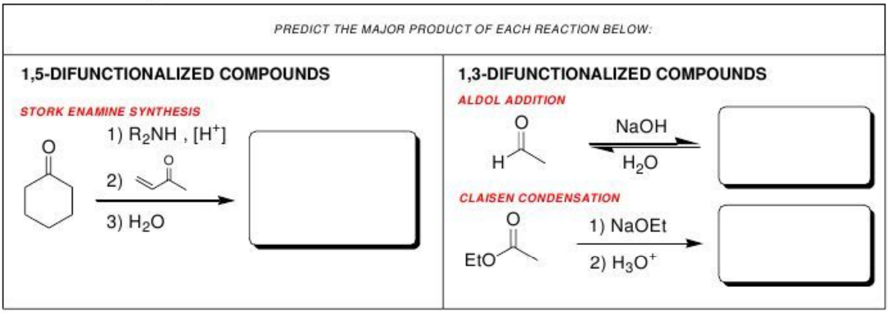


22.7 Determining When to Use a Stork Enamine Synthesis

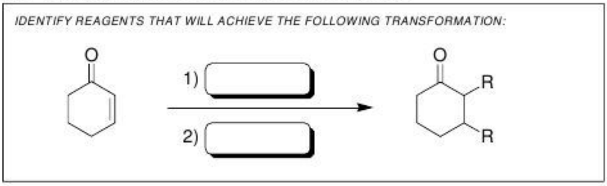
IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:



22.8 Determining which Addition or Condensation Reaction to Use



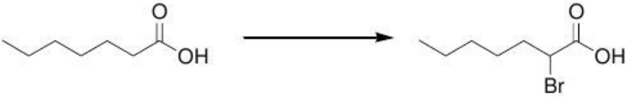
22.9 Alkylating the Alpha and Beta Positions

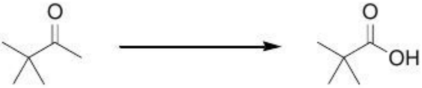


Review of Reactions

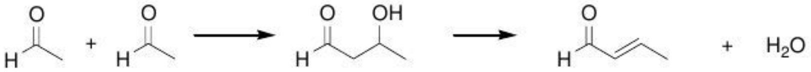
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 22. The answers appear in the section entitled *Review of Reactions*.

Alpha Halogenation

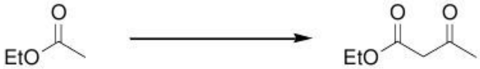




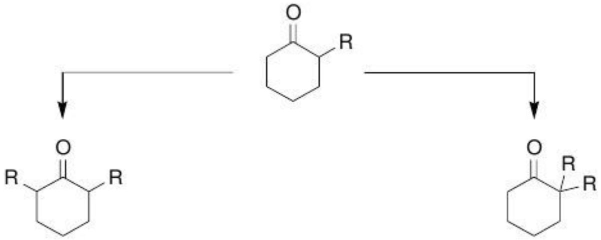
Aldol Reactions

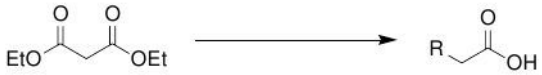


Claisen Condensation

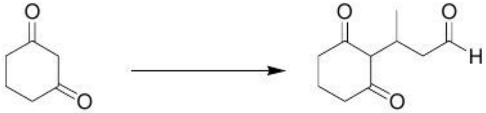


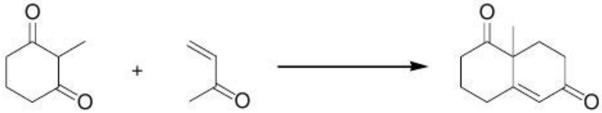
Alkylation





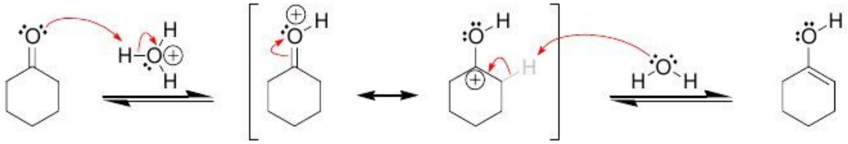
Michael Additions



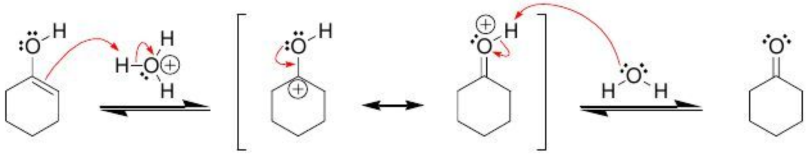


Solutions

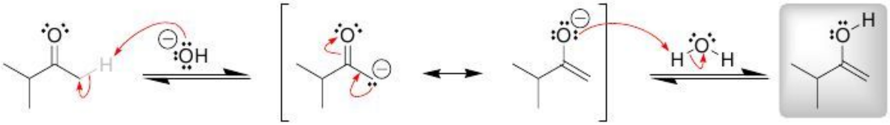
22.1.

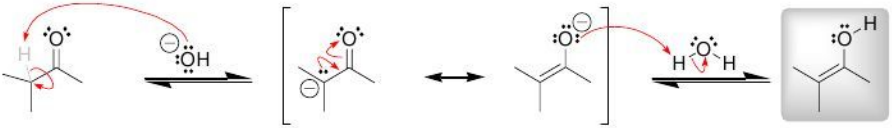


22.2.



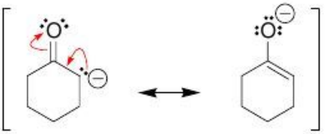
22.3.



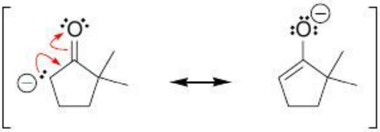


22.4.

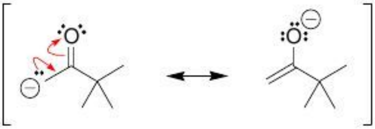
a)



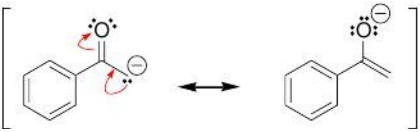
b)



c)

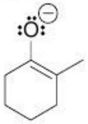


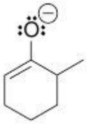
d)



e)

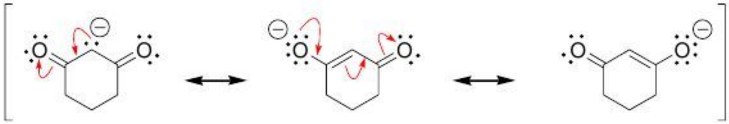
22.5.



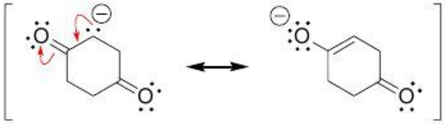


22.6.

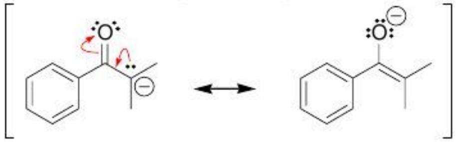
a) This anion is a doubly stabilized enolate ion, so there will not be a substantial amount of ketone present together with the enolate at equilibrium:



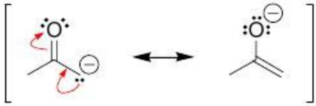
b) This anion is a regular enolate ion (not doubly stabilized), so there will be a substantial amount of ketone present together with the enolate at equilibrium:



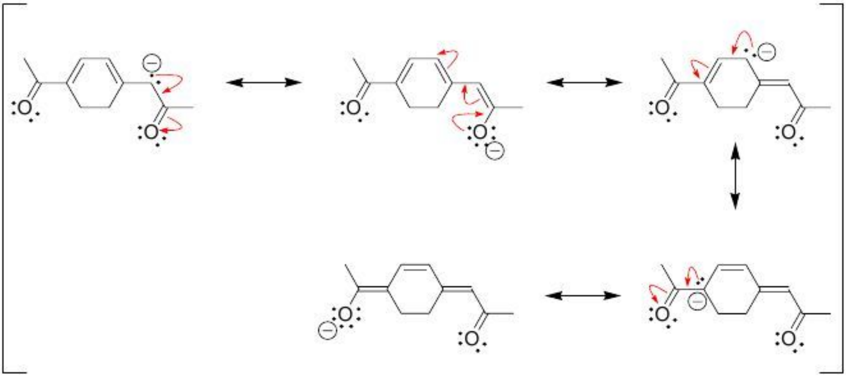
c) This anion is a regular enolate ion (not doubly stabilized), so there will be a substantial amount of ketone present together with the enolate at equilibrium:



d) This anion is a regular enolate ion (not doubly stabilized), so there will be a substantial amount of ketone present together with the enolate at equilibrium:



22.7. This anion is highly stabilized by resonance. The negative charge is spread over two oxygen atoms (just like a doubly stabilized enolate) and three carbon atoms:



22.8.

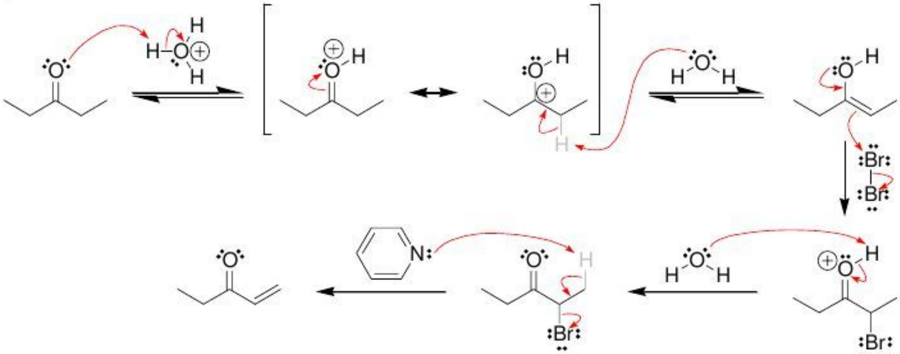
a) 2,4-dimethyl-3,5-heptanedione is more acidic because its conjugate base is a doubly stabilized enolate. The other compound (4,4-dimethyl-3,5-heptanedione) cannot form a doubly stabilized enolate because there are no protons connected to the carbon atom that is in between both carbonyl groups.

b) 1,3-cyclopentanedione is more acidic because its conjugate base is a doubly stabilized enolate. The other compound (1,2-cyclopentanedione) cannot form a doubly stabilized enolate because the carbonyl groups are adjacent to each other.

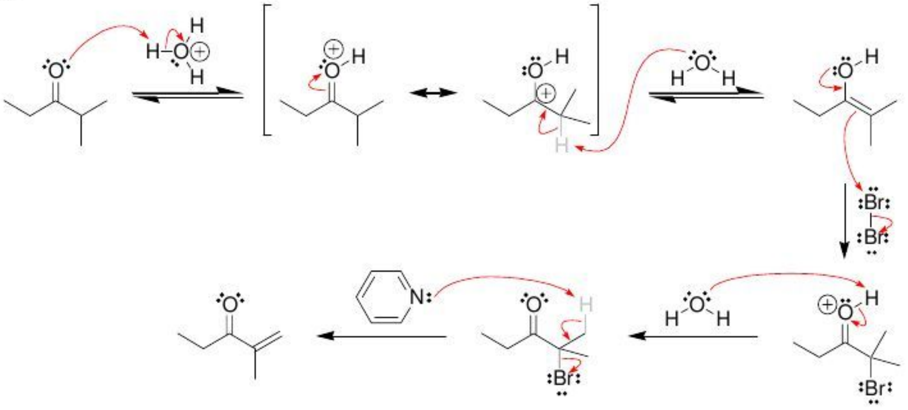
c) Acetophenone is more acidic than benzaldehyde because the former has alpha protons and the latter does not.

22.9.

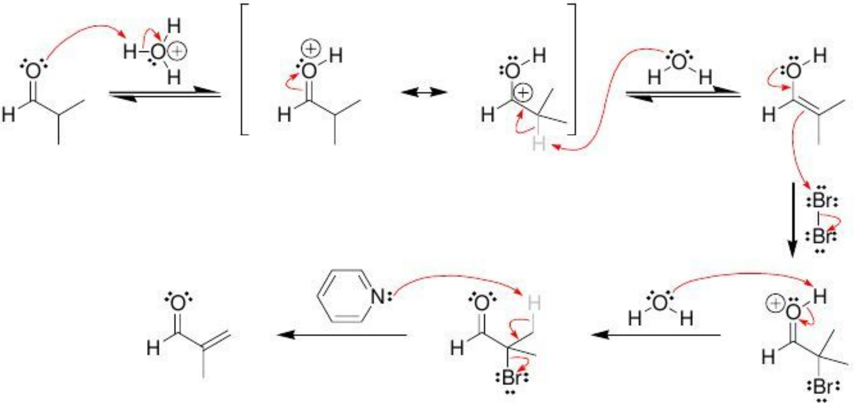
a)



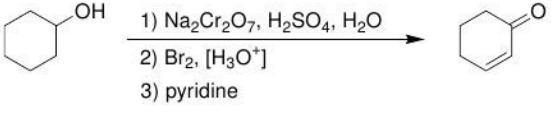
b)



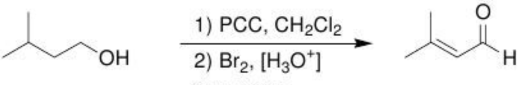
c)



22.10.


1) $Na_2Cr_2O_7$, H_2SO_4, H_2O
2) Br_2, $[H_3O^+]$
3) pyridine

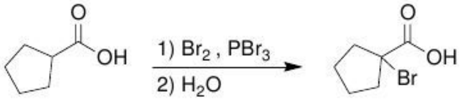
a)


1) PCC, CH_2Cl_2
2) Br_2, $[H_3O^+]$
3) pyridine

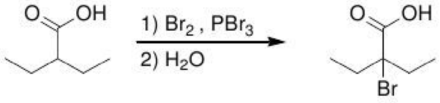
b)

22.11.

a)

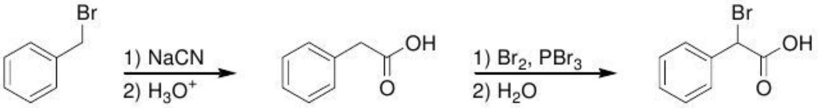


b)

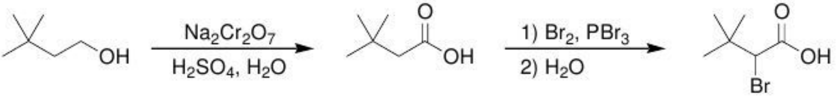


22.12.

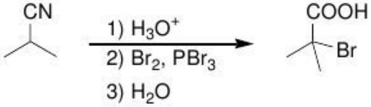
a)



b)

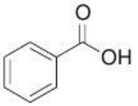


c)

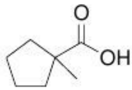


22.13.

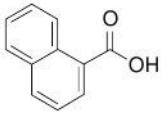
a)



b)

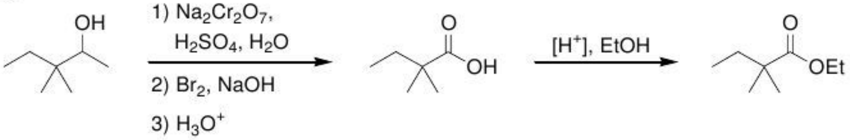


c)



22.14.

a)



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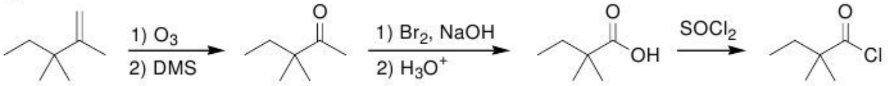
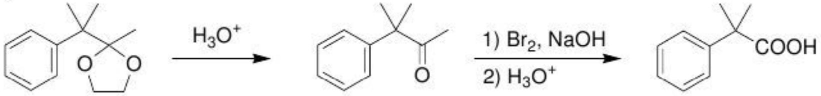
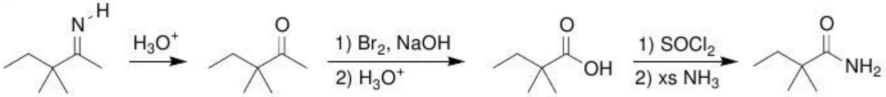


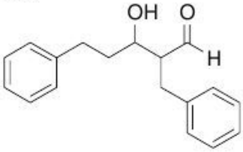
c)



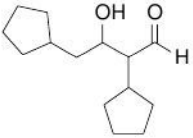
d)



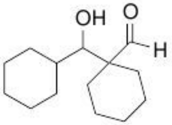
22.15.



a)



b)



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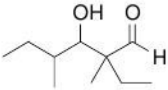
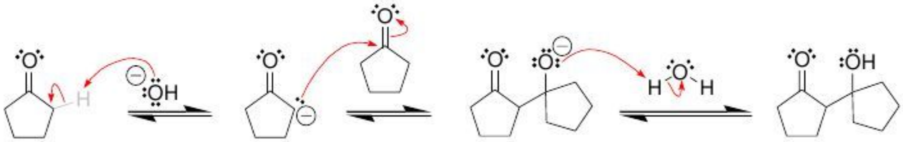


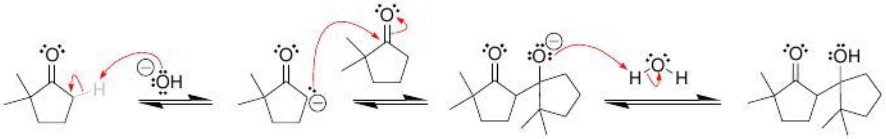
d)

22.16.

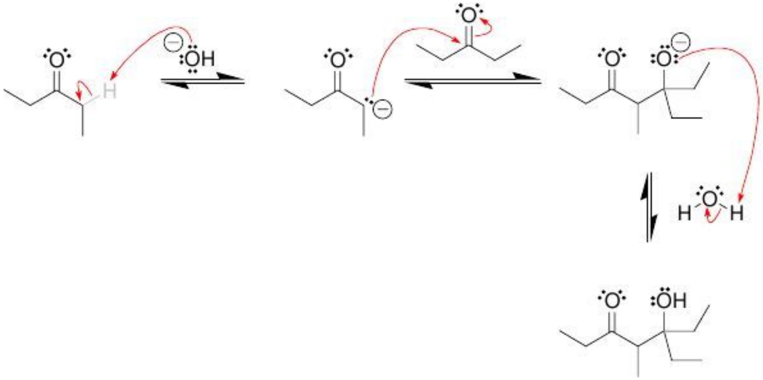
a)



b)



c)



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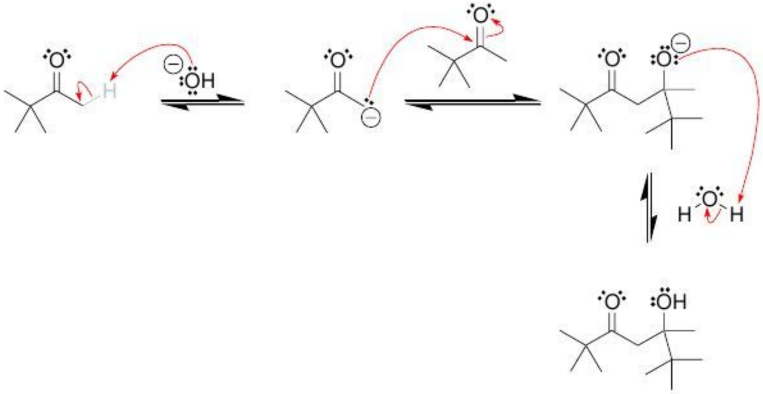
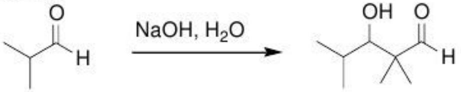
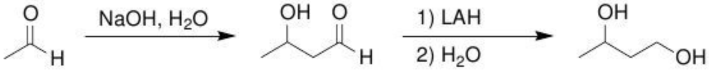


22.17. The first step of an aldol addition reaction is deprotonation at the alpha position, but this compound has no alpha protons.

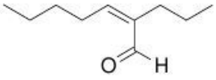
22.18.

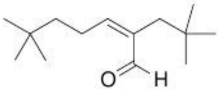


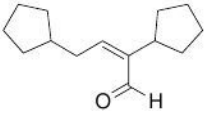
22.19.

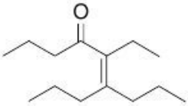


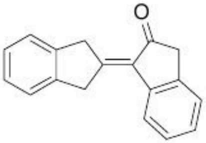
22.20.

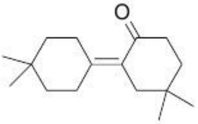
a) 

b) 

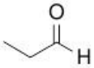
c) 

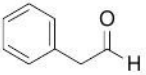
d) 

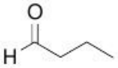
e) 

f) 

22.21.

a) 

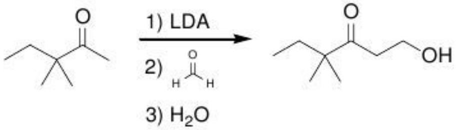
b) 

c) 

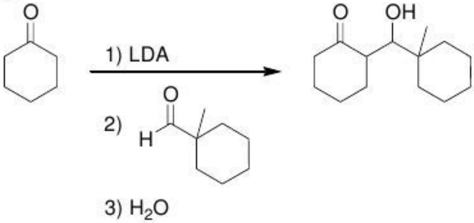
22.22.

22.23.

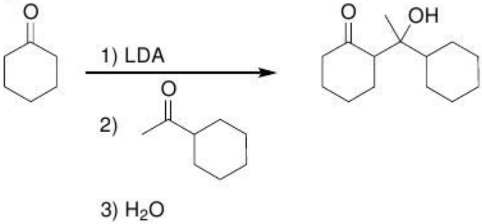
a)



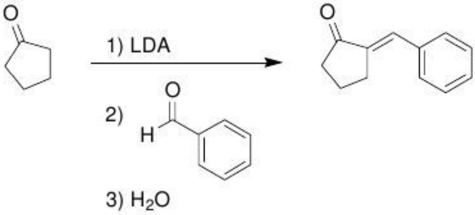
b)


1) LDA
2)
3) H2O

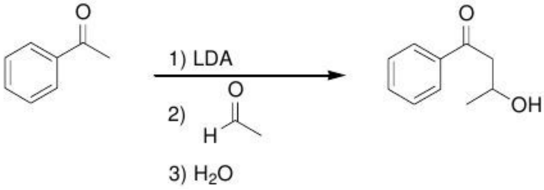
c)


1) LDA
2)
3) H2O

d)

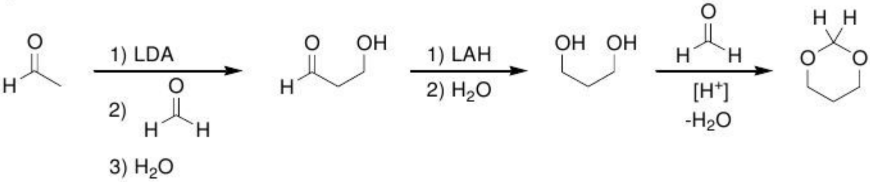

1) LDA
2)
3) H2O

e)

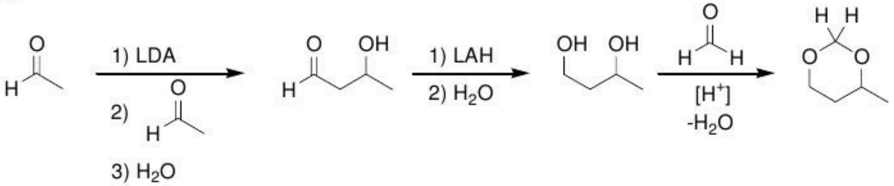

1) LDA
2)
3) H2O

22.24.

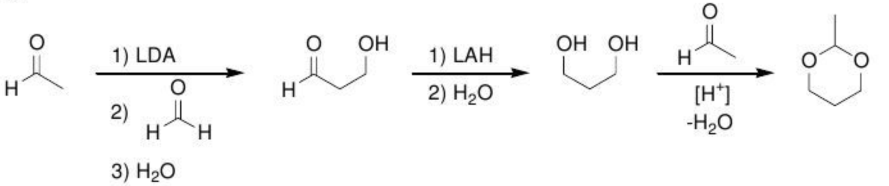
a)


1) LDA
2)
3) H2O
1) LAH
2) H2O
[H+]
-H2O

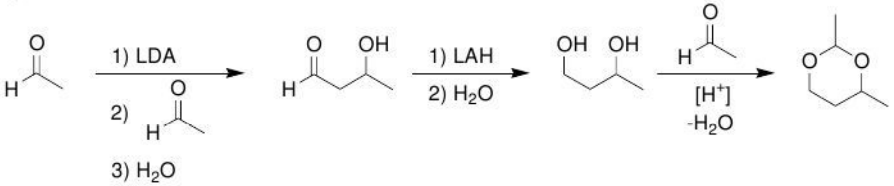
b)


1) LDA
2)
3) H2O
1) LAH
2) H2O
[H+]
-H2O

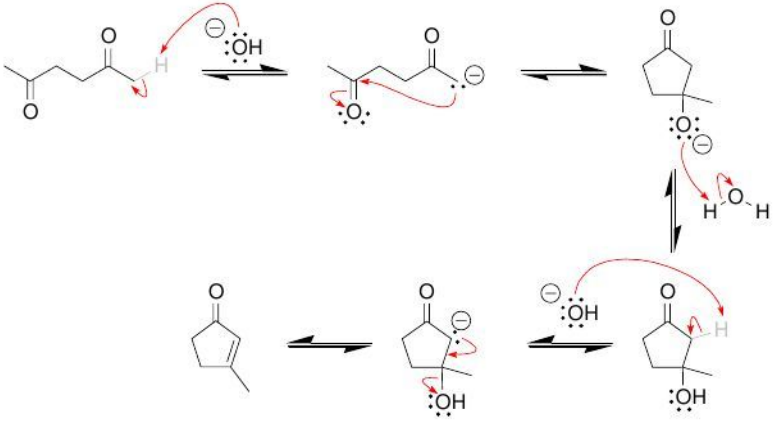
c)


1) LDA
2)
3) H2O
1) LAH
2) H2O
[H+]
-H2O

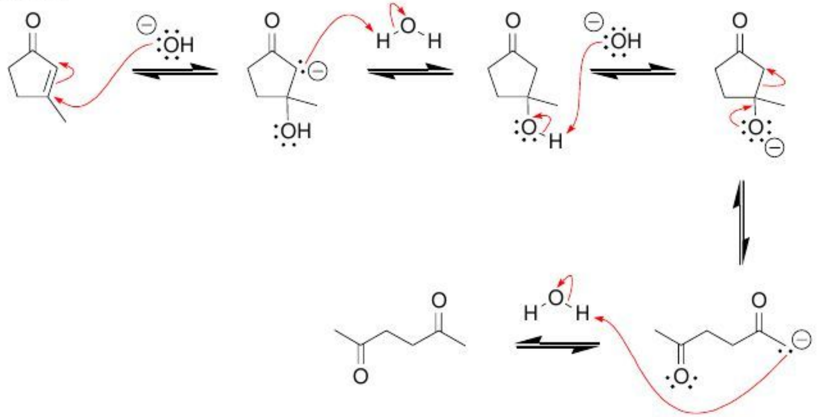
d)


1) LDA
2)
3) H2O
1) LAH
2) H2O
[H+]
-H2O

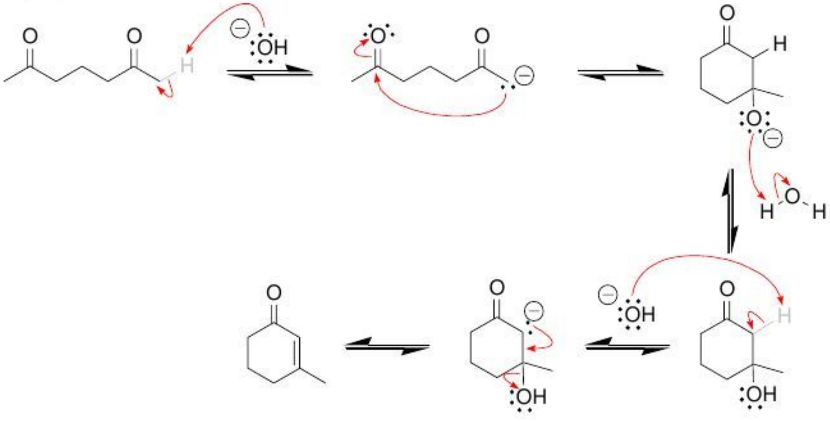
22.25.


OH
H
H O H
OH
OH

22.26.



22.27.

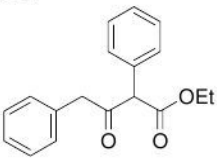


22.28.

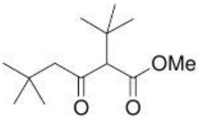
a) NaOEt b) *t*-BuOK

22.29.

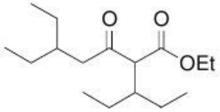
a)



b)

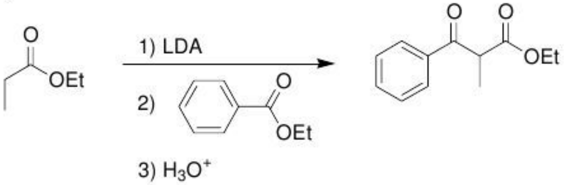


c)



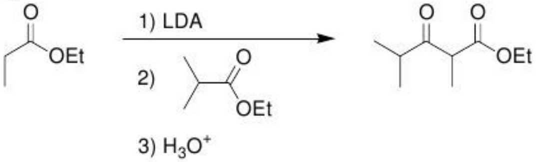
22.30.

a)



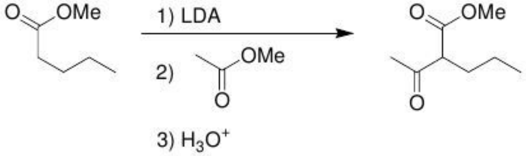
O
OEt
1) LDA
2)
O
OEt
3) H_3O^+
O
O
OEt

b)



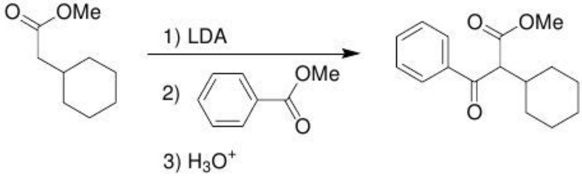
O
OEt
1) LDA
2)
O
OEt
3) H_3O^+
O
O
OEt

c)



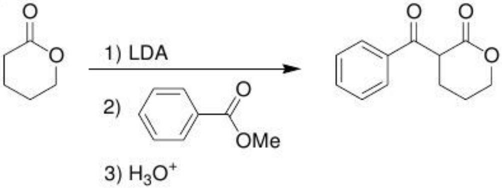
O
OMe
1) LDA
2)
OMe
O
3) H_3O^+
O
OMe
O

d)



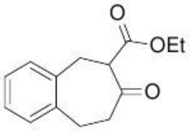
O
OMe
1) LDA
2)
OMe
O
3) H_3O^+
O
OMe
O

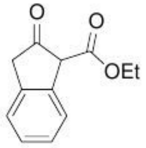
e)

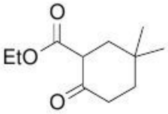


O
O
1) LDA
2)
O
OMe
3) H_3O^+
O
O
O

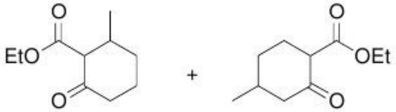
22.31.

a) 

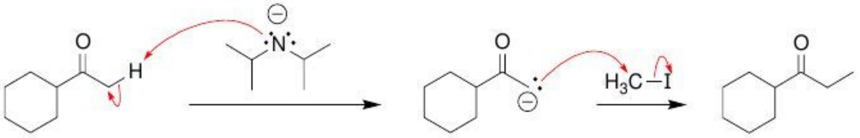
b) 

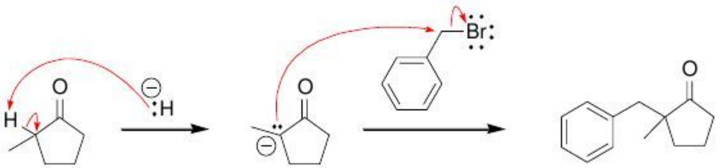
c) 

22.32.

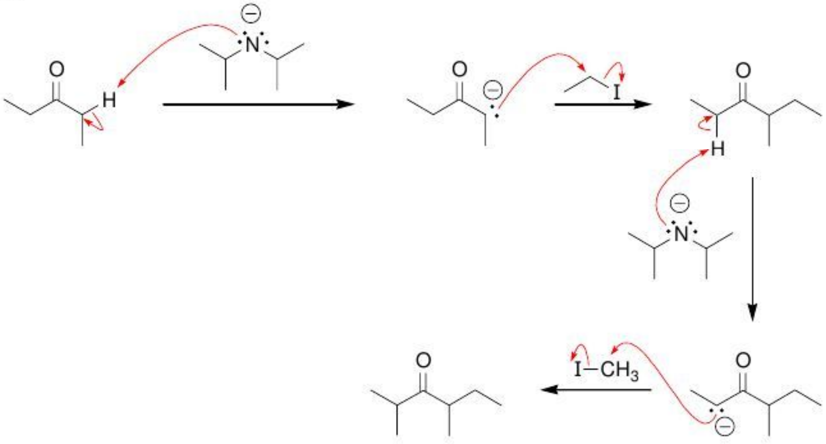


22.33.

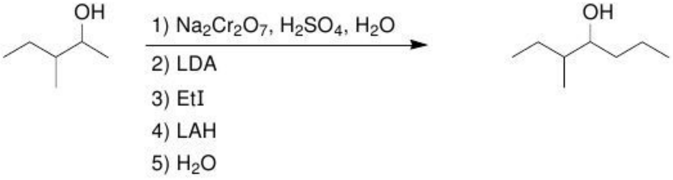
a) 

b) 

c)

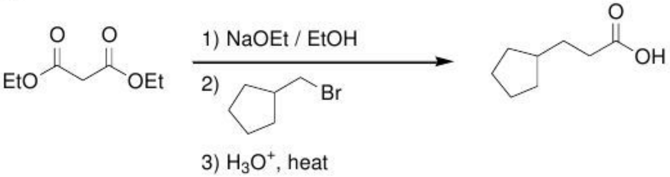


22.34.

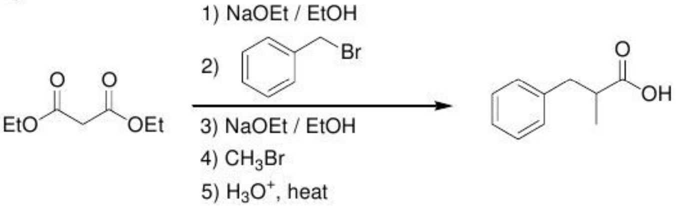


22.35.

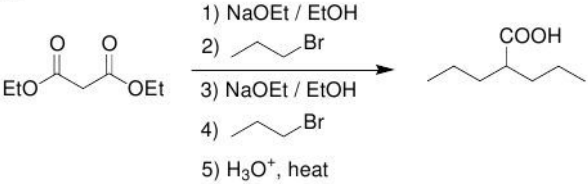
a)



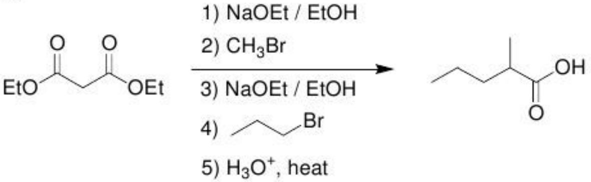
b)



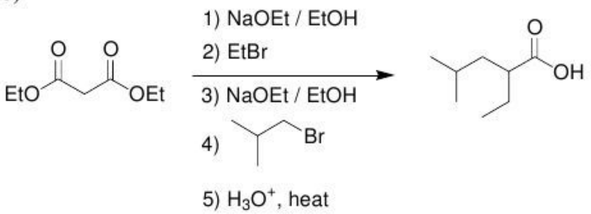
c)



d)

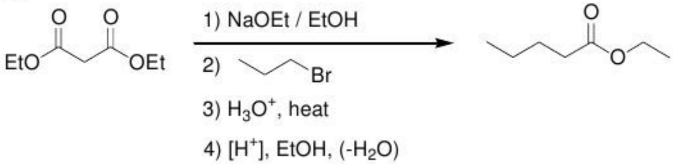


e)

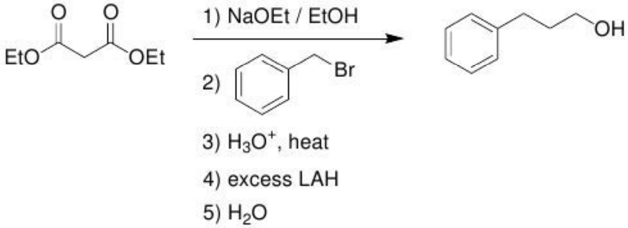


22.36.

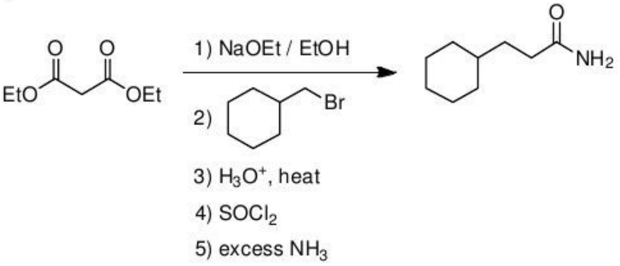
a)



b)

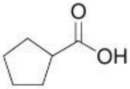


c)



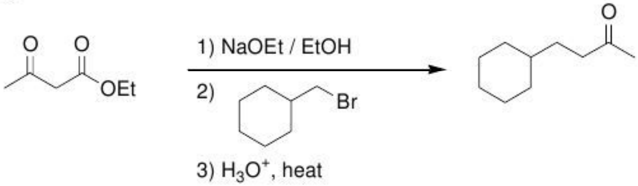
22.37. Preparation of the desired compound requires the installation of three alkyl groups at the alpha position. The malonic ester synthesis can only be used to install two alkyl groups because the starting material (diethyl malonate) has only two alpha protons.

22.38.

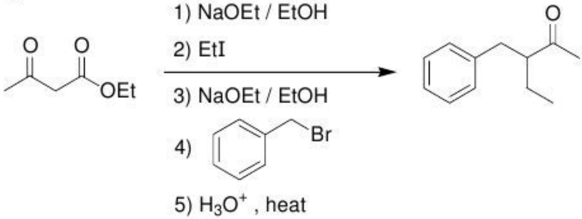


22.39.

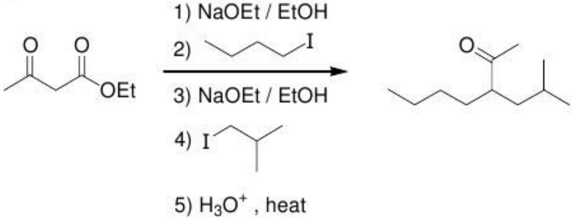
a)



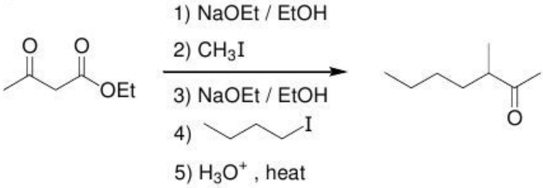
b)



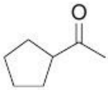
c)



d)

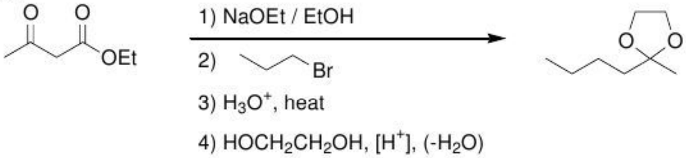


22.40.

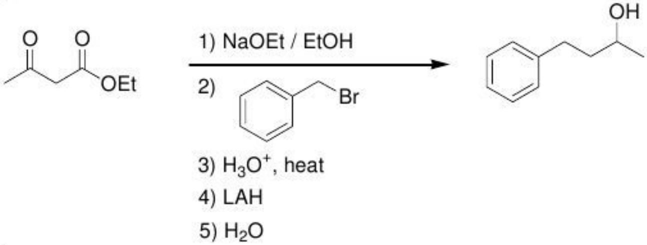


22.41.

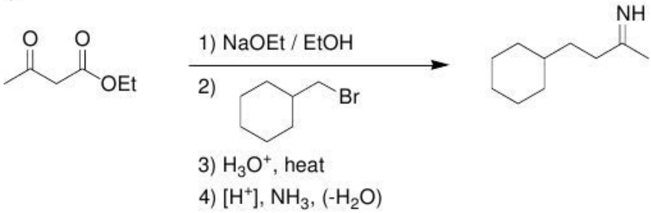
a)



b)

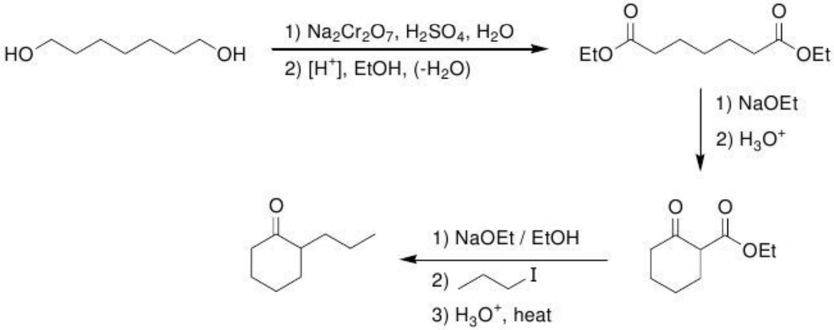


c)

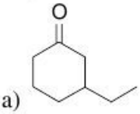


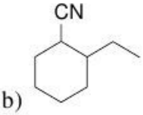
22.42. Preparation of the desired compound requires the installation of three alkyl groups at the alpha position. The acetoacetic ester synthesis can only be used to install two alkyl groups because the starting material (diethyl malonate) has only two alpha protons.

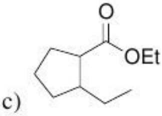
22.43.



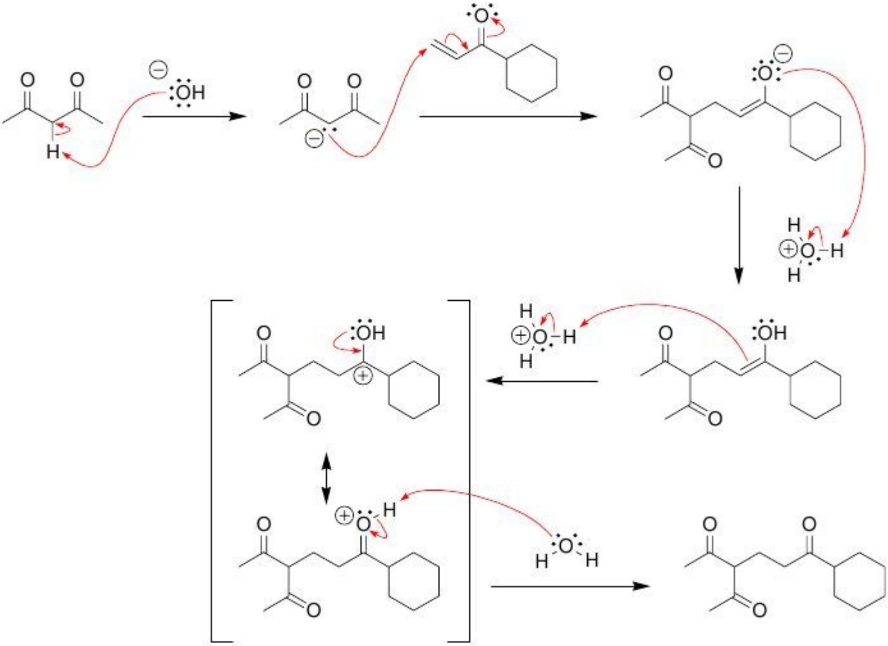
22.44.





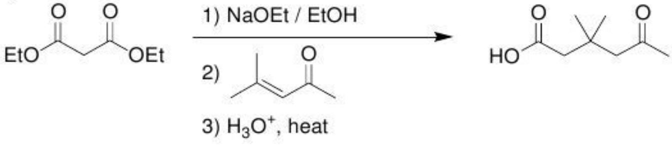


22.45.

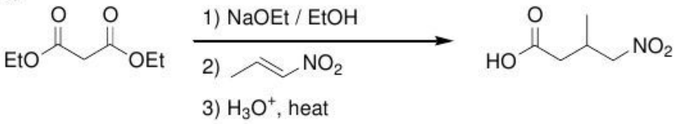


22.46.

a)

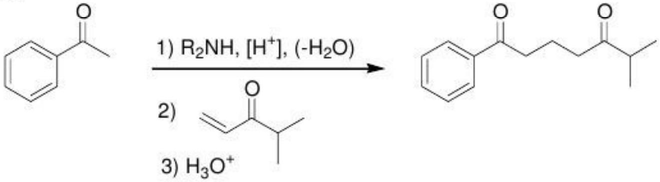


b)

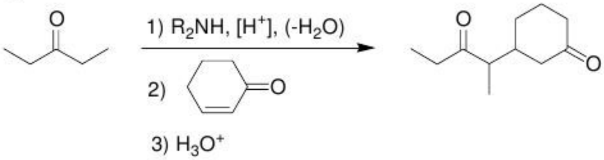

EtO
OEt
1) NaOEt / EtOH
2) NO_2
3) H_3O^+, heat
HO
NO_2

22.47.

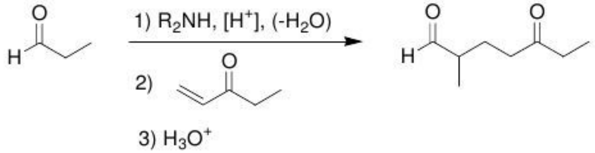
a)


1) R_2NH, [H^+], (-H_2O)
2)
3) H_3O^+

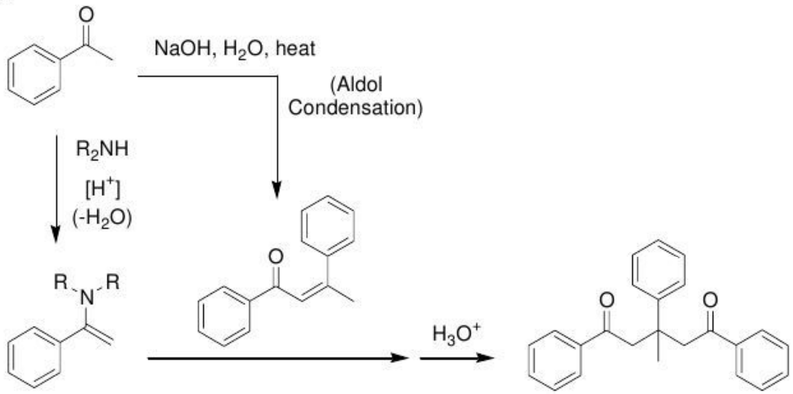
b)


1) R_2NH, [H^+], (-H_2O)
2)
3) H_3O^+

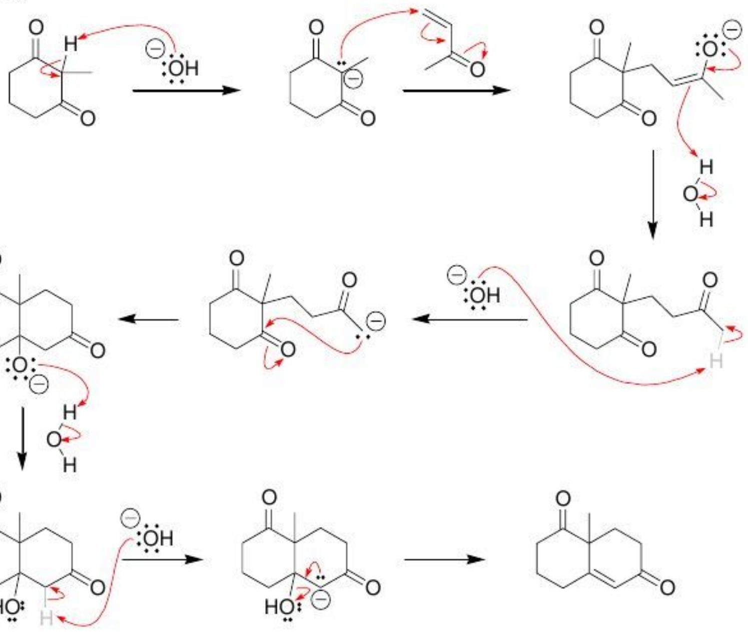
c)


H
1) R_2NH, [H^+], (-H_2O)
2)
3) H_3O^+
H

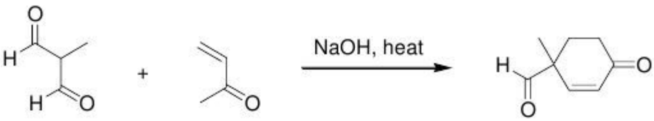
22.48.



22.49.

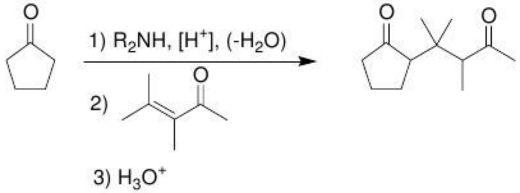


22.50.

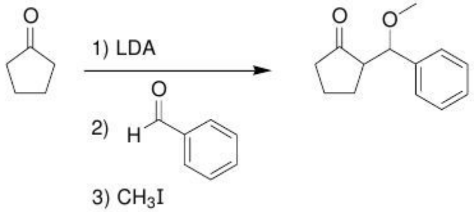


22.51.

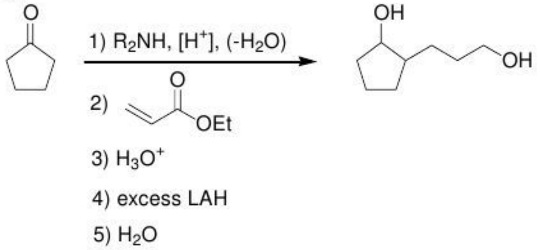
a)



b)

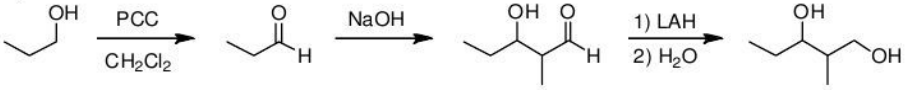


c)

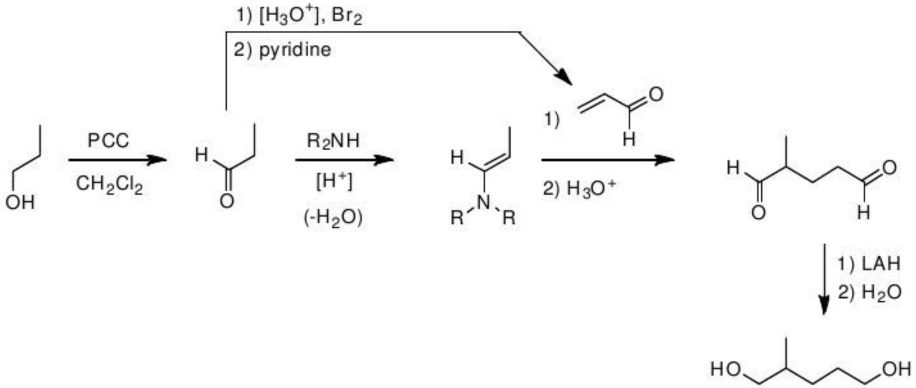


22.52.

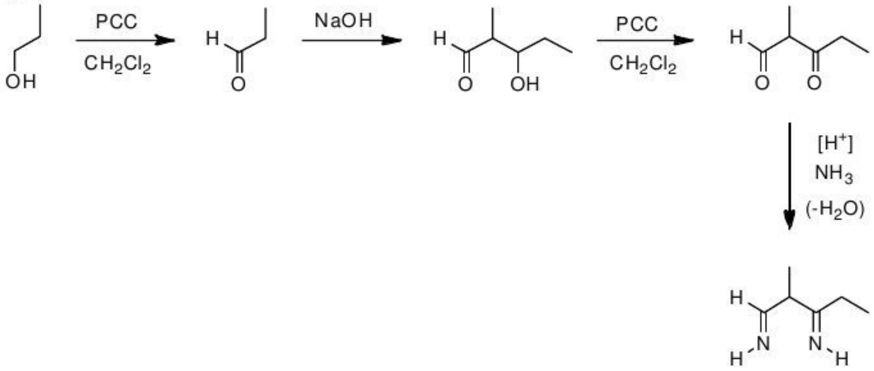
a)



b)

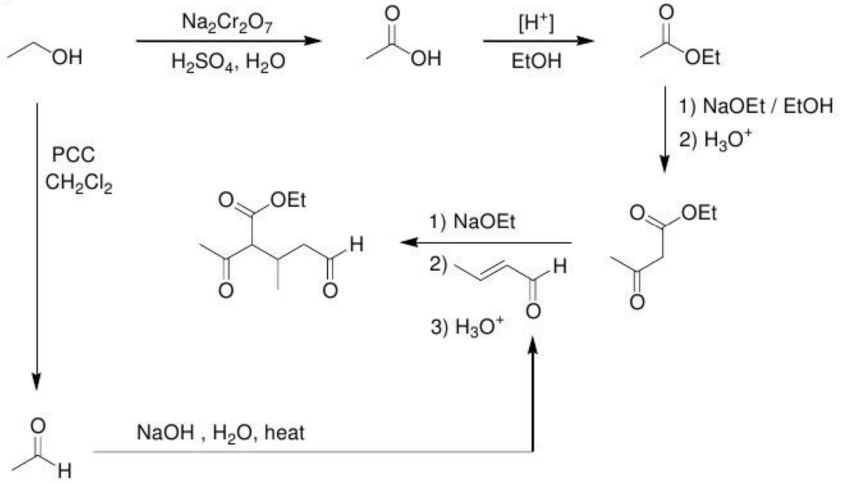

1) [H3O+], Br2
2) pyridine
PCC
CH2Cl2
R2NH
[H+]
(-H2O)
1)
2) H3O+
1) LAH
2) H2O

c)

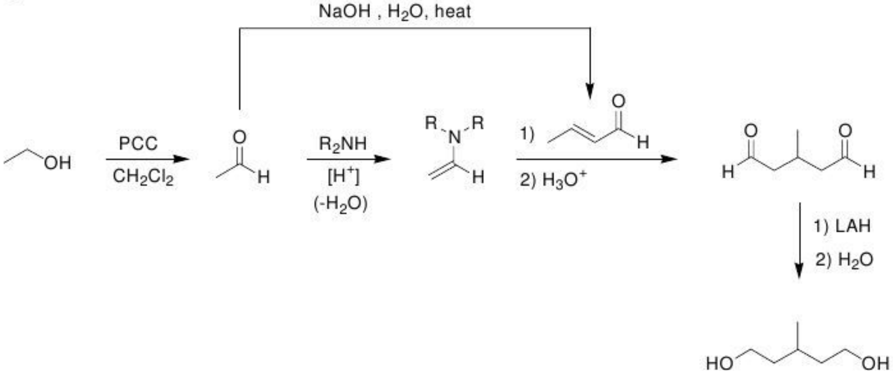

PCC
CH2Cl2
NaOH
PCC
CH2Cl2
[H+]
NH3
(-H2O)

22.53.

a)

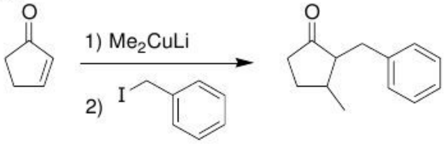


b)

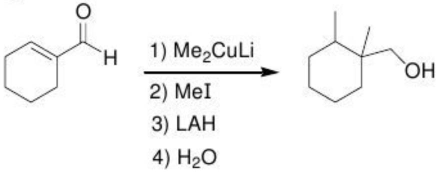


22.54.

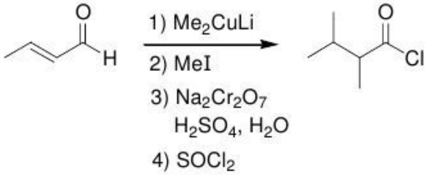
a)



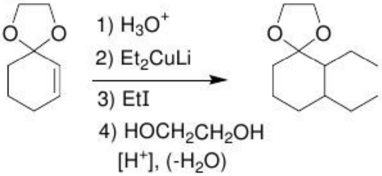
b)


O
H
1) Me_2CuLi
2) MeI
3) LAH
4) H_2O
OH

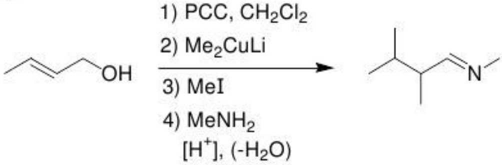
c)


O
H
1) Me_2CuLi
2) MeI
3) $Na_2Cr_2O_7$
H_2SO_4, H_2O
4) $SOCl_2$
O
Cl

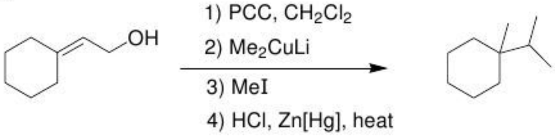
d)


O
O
1) H_3O^+
2) Et_2CuLi
3) EtI
4) $HOCH_2CH_2OH$
$[H^+]$, $(-H_2O)$
O
O

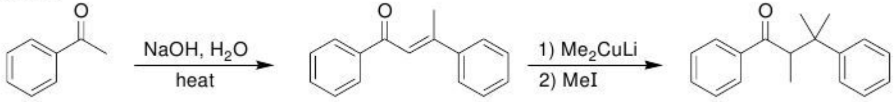
e)


OH
1) PCC, CH_2Cl_2
2) Me_2CuLi
3) MeI
4) $MeNH_2$
$[H^+]$, $(-H_2O)$
N

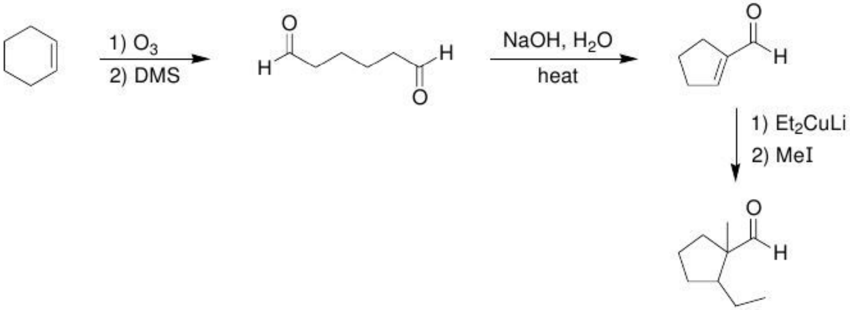
f)


OH
1) PCC, CH_2Cl_2
2) Me_2CuLi
3) MeI
4) HCl, Zn[Hg], heat

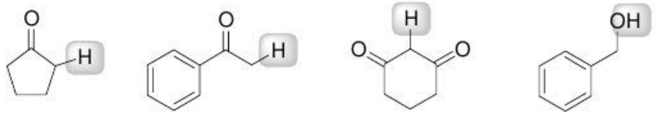
22.55.



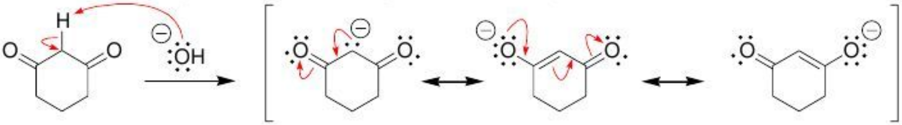
22.56.



22.57.

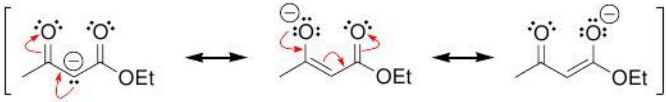


22.58. The conjugate base of this compound is a doubly stabilized enolate.

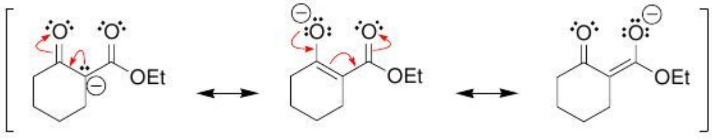


22.59.

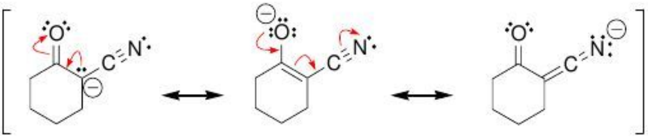
a)



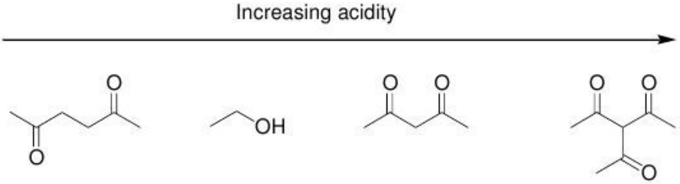
b)



c)

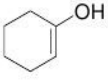


22.60.

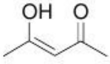


22.61.

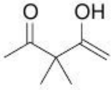
a) This enol does not exhibit a significant presence at equilibrium:



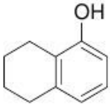
b) This enol does exhibit a significant presence at equilibrium:



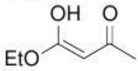
c) This enol does not exhibit a significant presence at equilibrium:

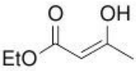


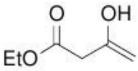
d) This enol does exhibit a significant presence at equilibrium:



22.62.

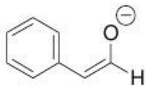




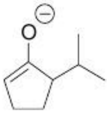


22.63.

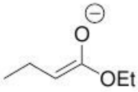
a)



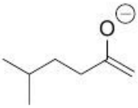
b)



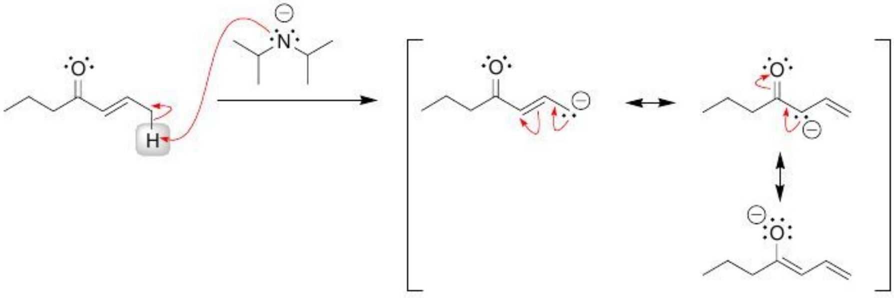
c)



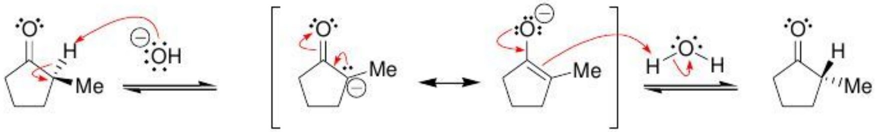
d)



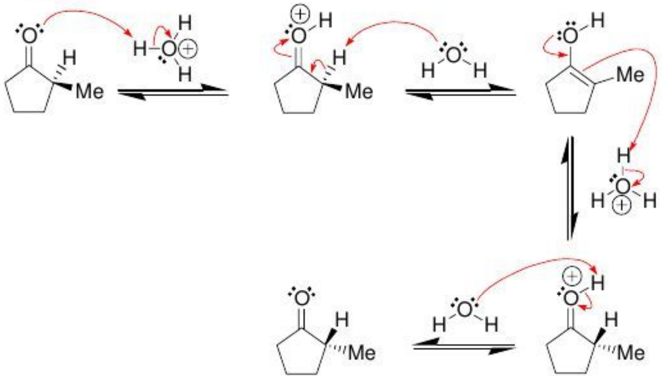
22.64. Deprotonation at the following γ-position results in an anion that has three resonance structures. The negative charge is spread over one oxygen atom and two carbon atoms:



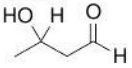
22.65. Deprotonation at the α carbon changes the hybridization state of the α carbon from sp^3 (tetrahedral) to sp^2 (planar). When the α position is protonated once again, the proton can be placed on either side of the planar α carbon, resulting in racemization:

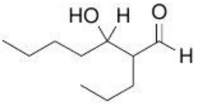


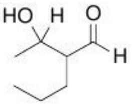
22.66.

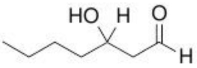


22.67.

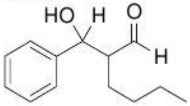


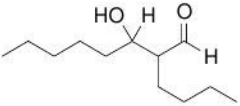




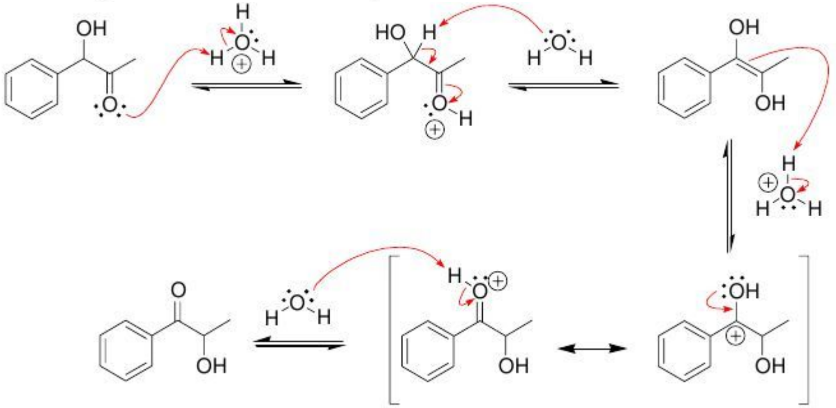


22.68.

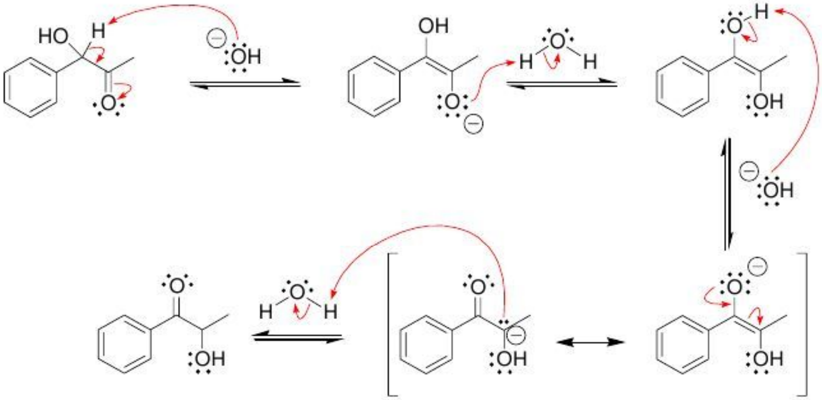




22.69. The carbonyl group and the aromatic ring are conjugated in the product, but are not conjugated in the starting material. Formation of conjugation serves as a driving force in formation of the product.

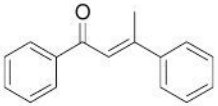


22.70.

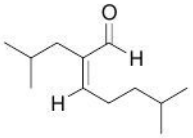


22.71.

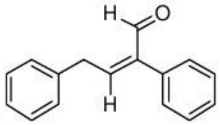
a)



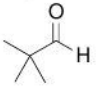
b)



c)

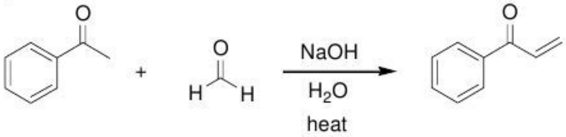


22.72. Trimethylacetaldehyde does not have any α protons.

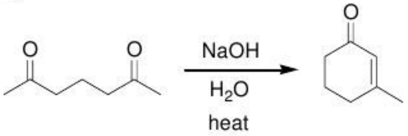


22.73.

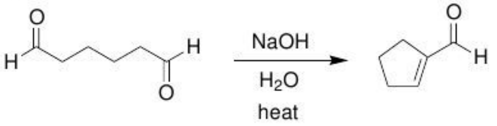
a)



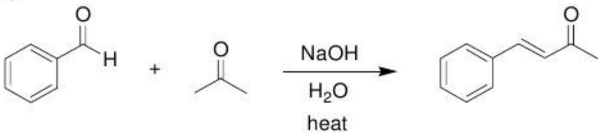
b)



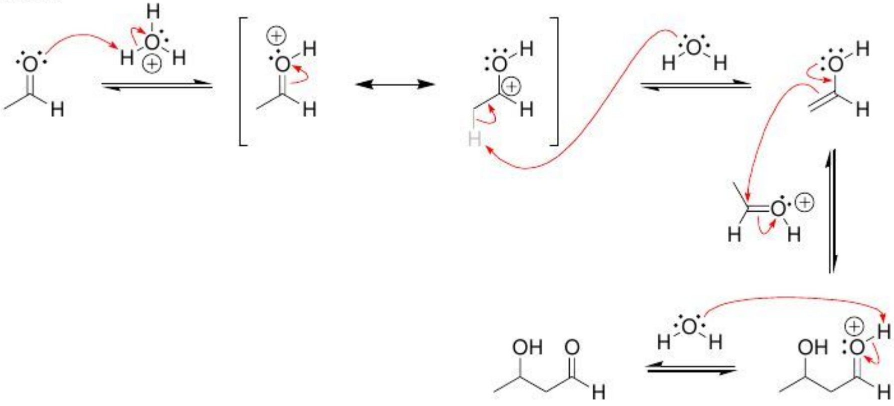
c)



d)

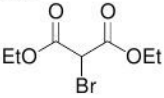


22.74.

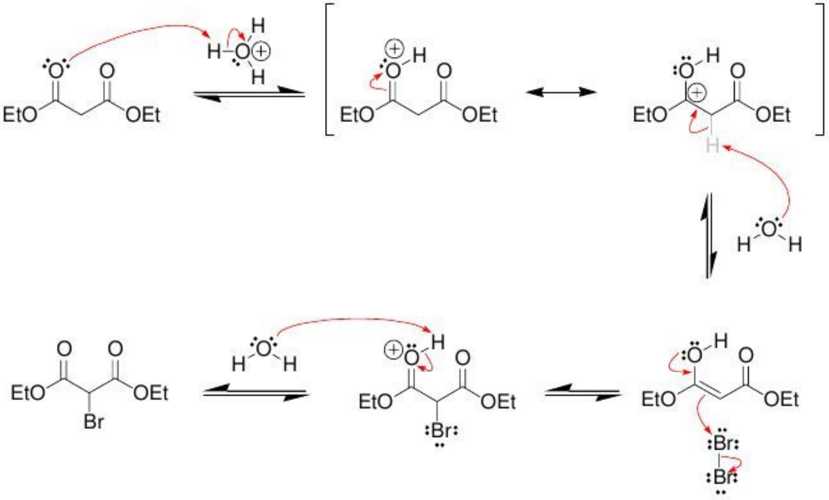


22.75.

a)

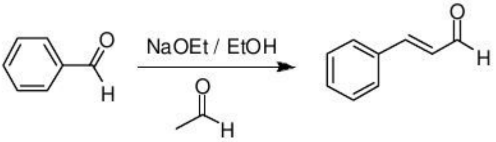


b)



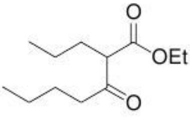
c) The product should be more acidic than diethyl malonate because of the inductive effect of the bromine atom.

22.76.

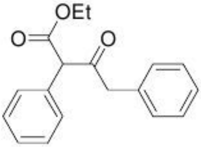


22.77.

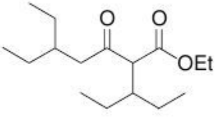
a)



b)

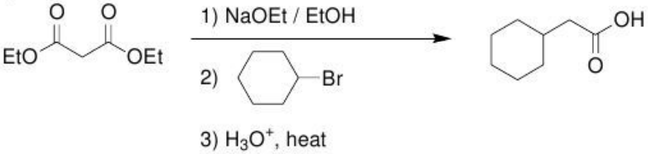


c)

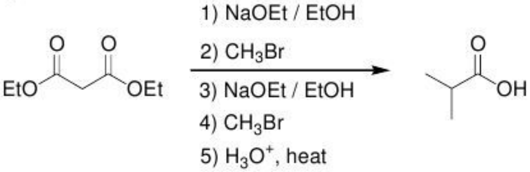


22.78.

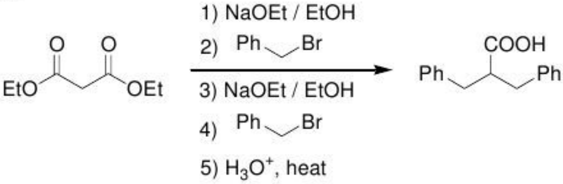
a)



b)

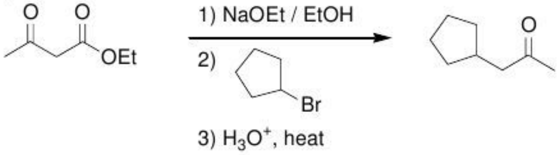


c)

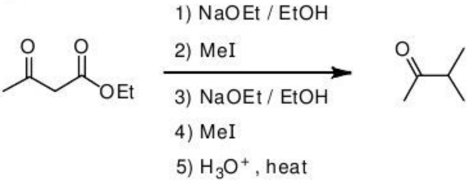


22.79.

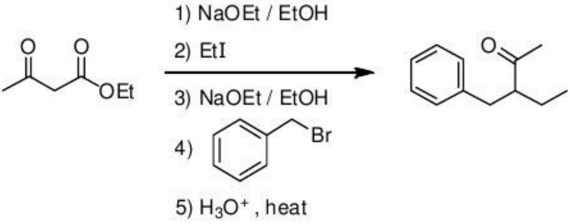
a)



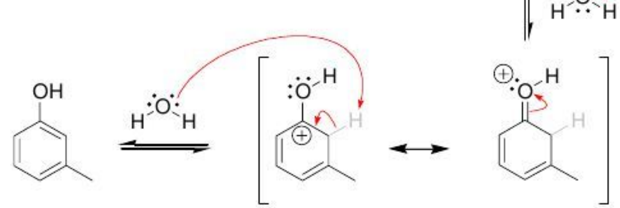
b)



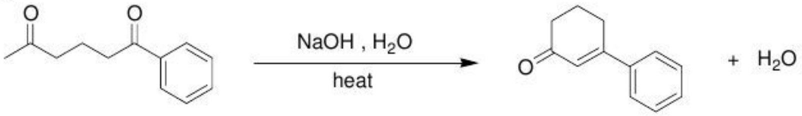
c)



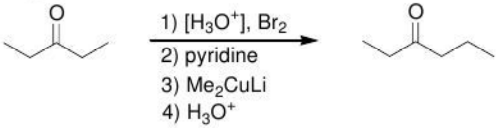
22.80.



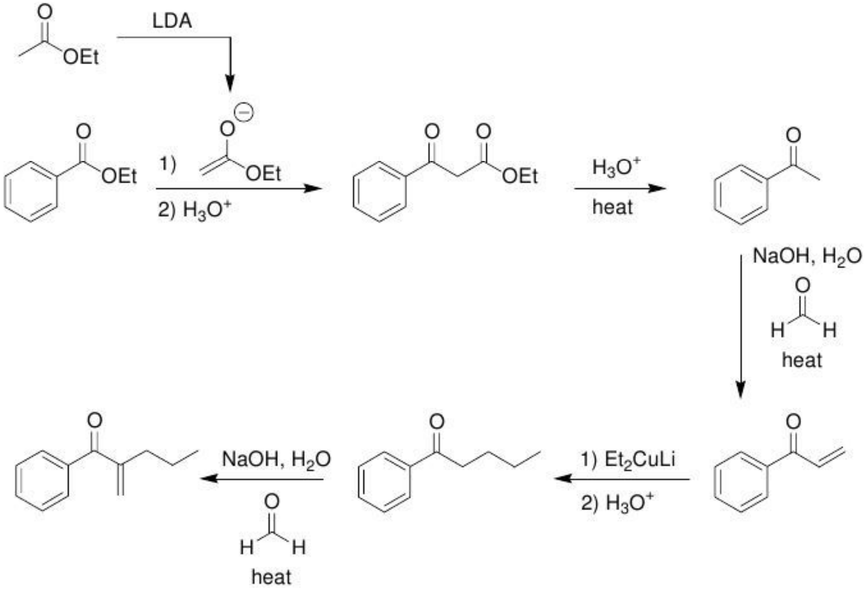
22.81.



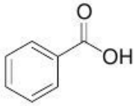
22.82.

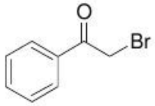


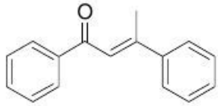
22.83.



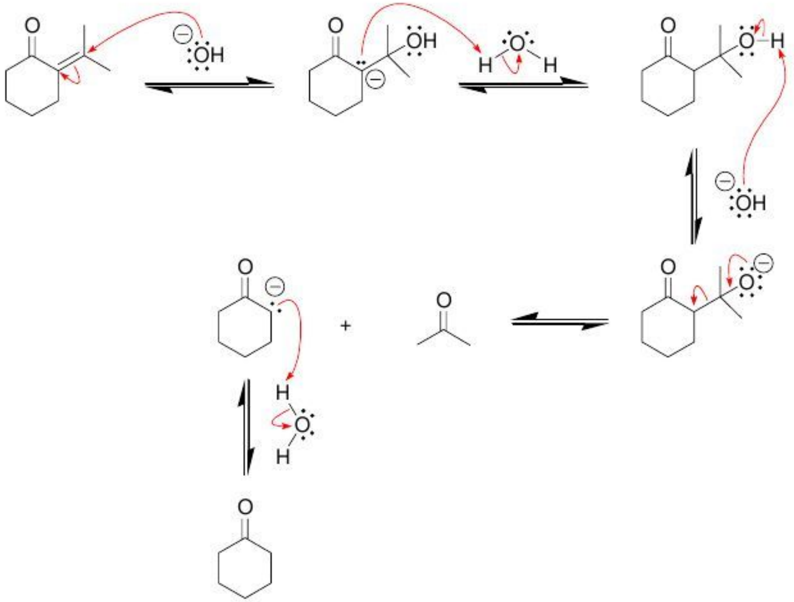
22.84.

a) 

b) 

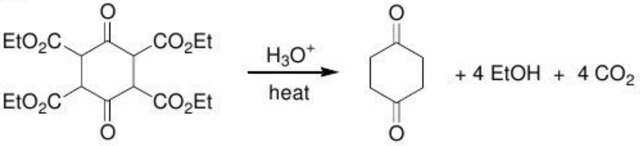
c) 

22.85.

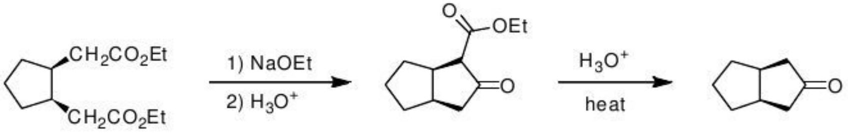

OH
H
O
H
O
H
OH
+

22.86.

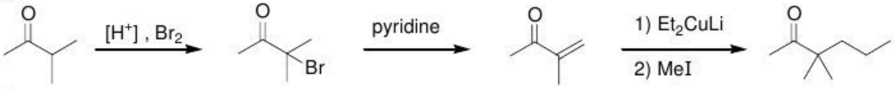
a)


EtO2C
CO2Et
EtO2C
CO2Et
O
O
H3O+
heat
O
O
+ 4 EtOH + 4 CO2

b)


CH2CO2Et
CH2CO2Et
1) NaOEt
2) H3O+
O
OEt
O
H3O+
heat
O

c)

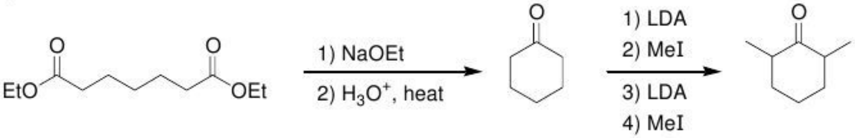

O
[H⁺] , Br₂
O
Br
pyridine
O
1) Et₂CuLi
2) MeI
O

d)

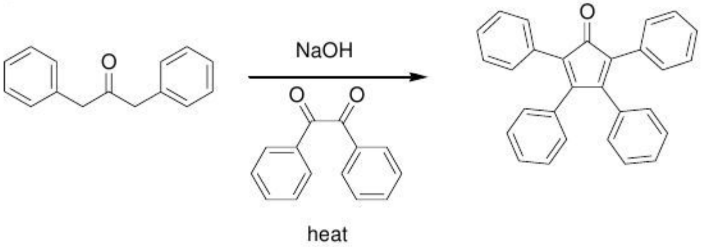

O
1) LDA
2) EtI
O

22.87.

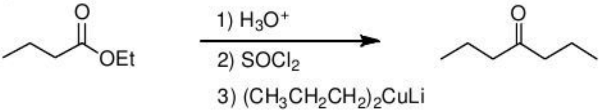
a)


O
O
EtO
OEt
1) NaOEt
2) H₃O⁺, heat
O
1) LDA
2) MeI
3) LDA
4) MeI
O

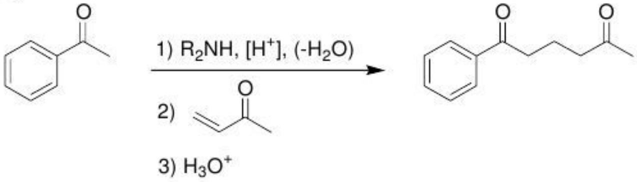
b)


O
NaOH
O
O
heat
O

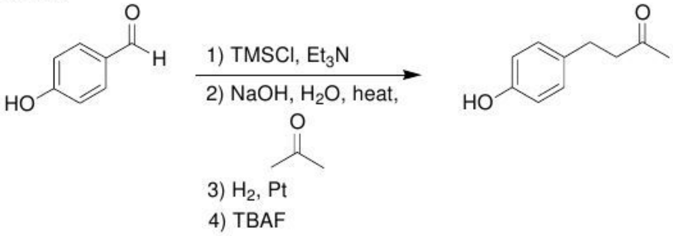
c)


O
OEt
1) H₃O⁺
2) SOCl₂
3) (CH₃CH₂CH₂)₂CuLi
O

d)

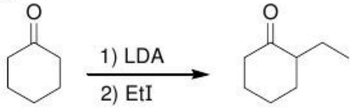

O
1) R₂NH, [H⁺], (-H₂O)
2)
O
3) H₃O⁺
O
O

22.88.

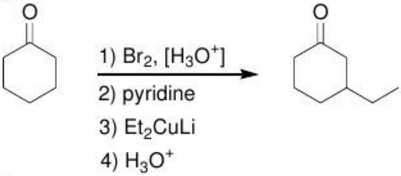


22.89.

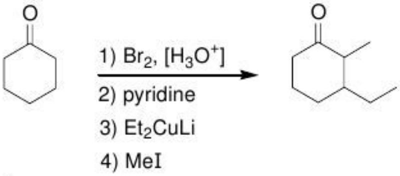
a)



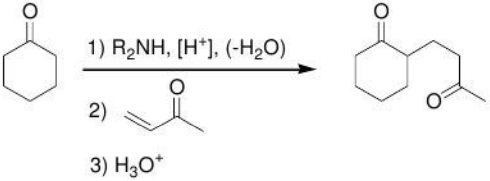
b)



c)



d)



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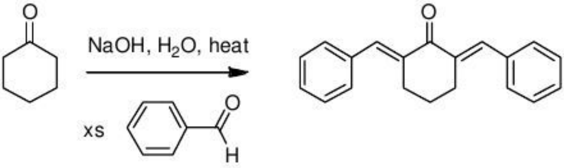

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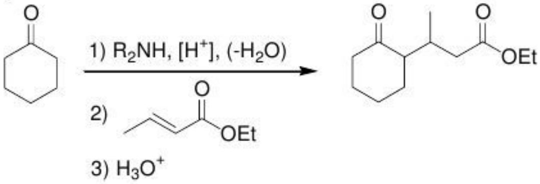

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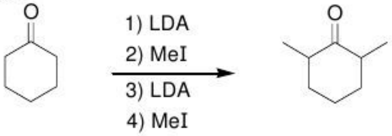
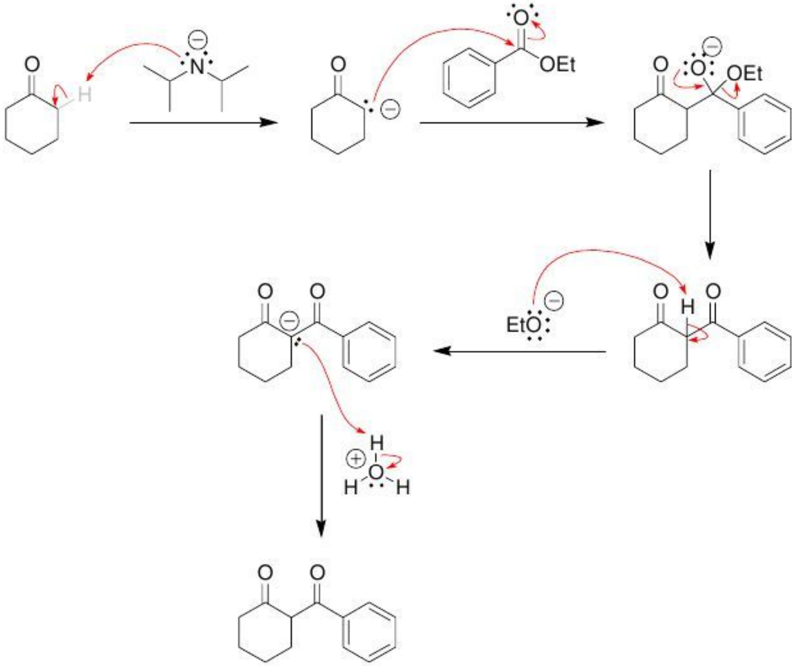
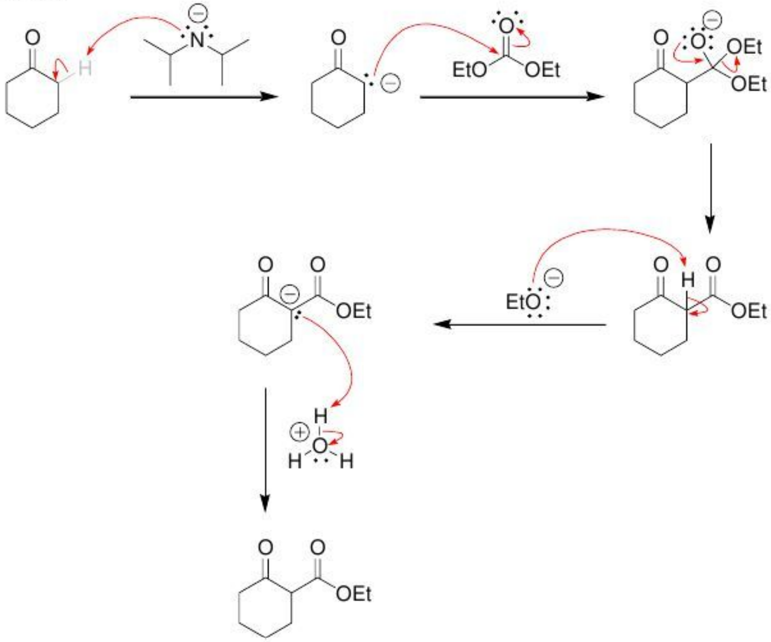


22.90. The driving force for this reaction is formation of a doubly stabilized enolate. After the reaction is complete, an acid is required to protonate this anion.



22.91.


O
N
H
O
O
EtO
OEt
O
O
OEt
OEt
EtO
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OEt
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OEt
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H
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H
O
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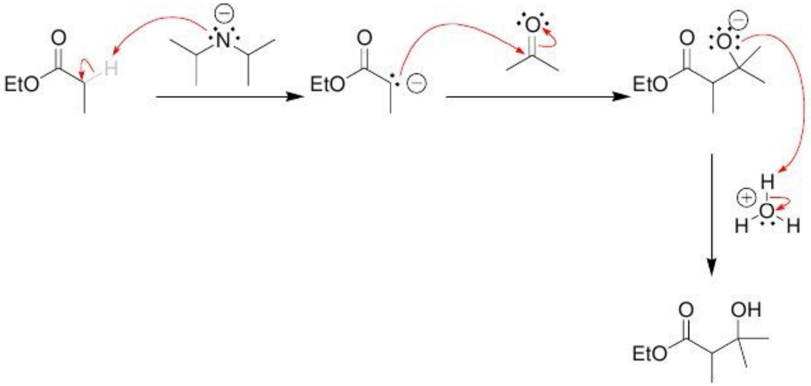
OEt

22.92.


O
EtO
H
N
O
EtO
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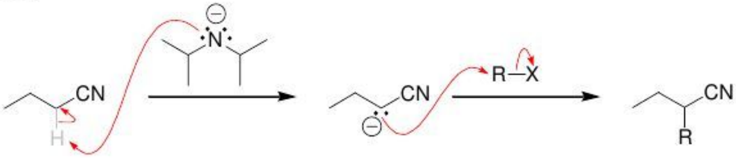
O
EtO
O
H
H
O
H
O
OH
EtO

22.93.

a)



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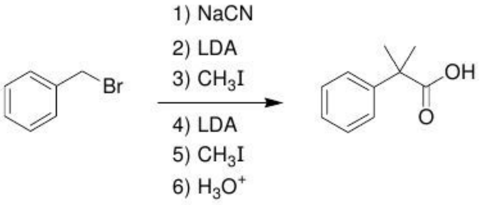
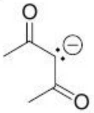
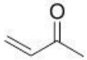


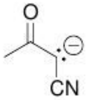
22.94.



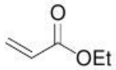
a) Michael Donor



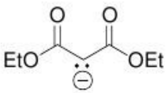
Michael Acceptor



b) Michael Donor



Michael Acceptor



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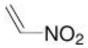
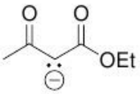
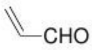


Michael Acceptor

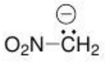


d) Michael Donor



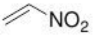
Michael Acceptor

e)



$O_2N-\overset{\ominus}{\ddot{C}}H_2$

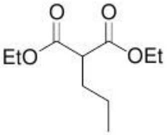
Michael Donor



Michael Acceptor

22.95.

a)



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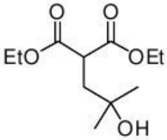

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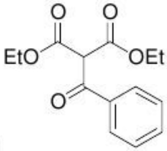

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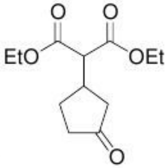

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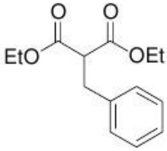

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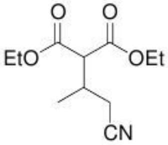

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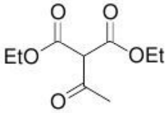
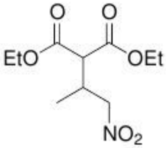
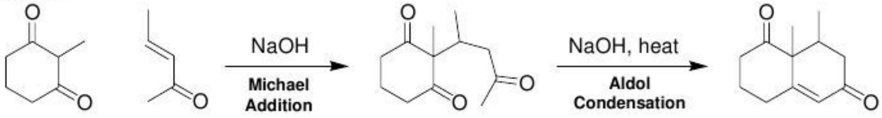


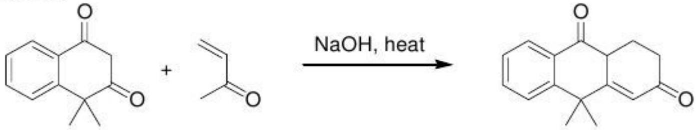
h)



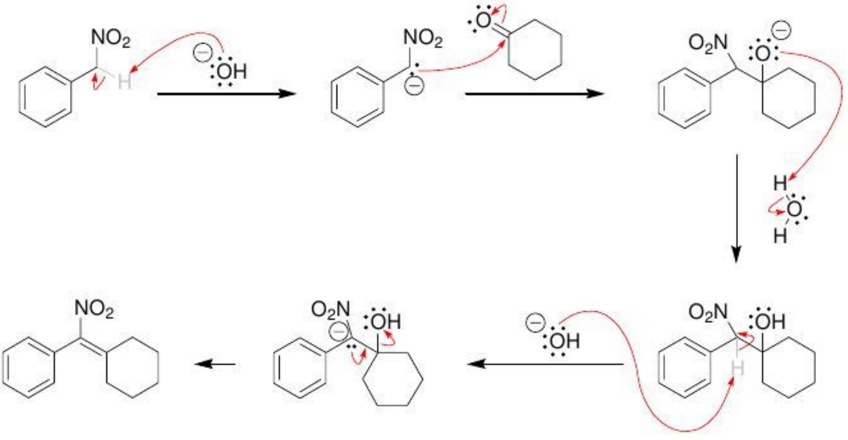
22.96.



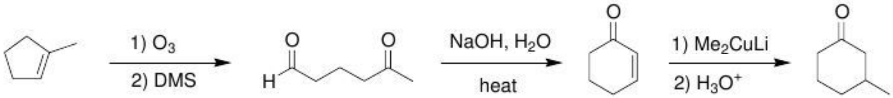
22.97.



22.98.

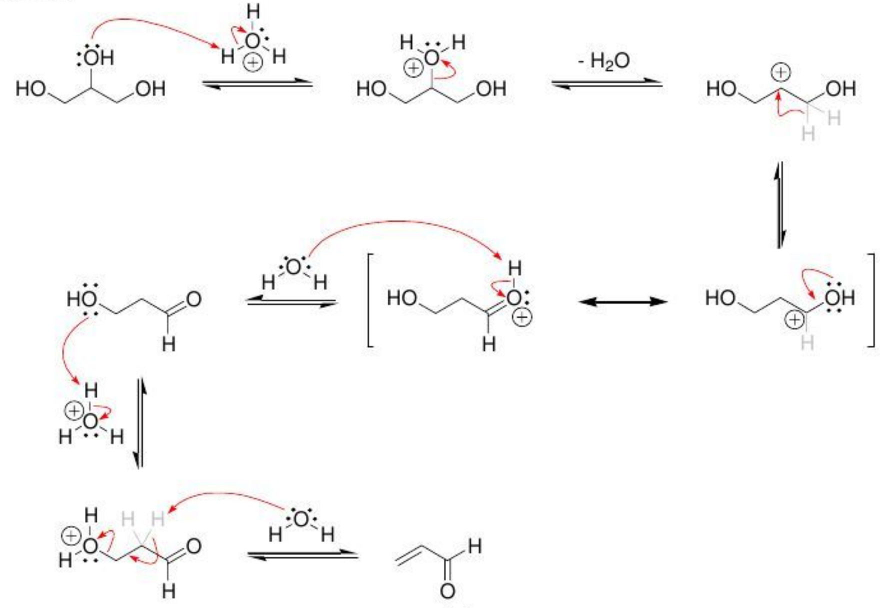


22.99.



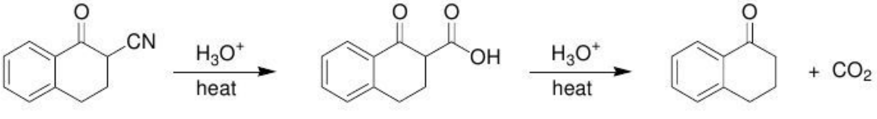
22.100. A ketone generally produces a strong signal at approximately 1720 cm^{-1} (C=O stretching), while an alcohol produces a broad signal between 3200 and 3600 cm^{-1} (O-H stretching). These regions of an IR spectrum can be inspected to determine whether the ketone or the enol predominates.

22.101.



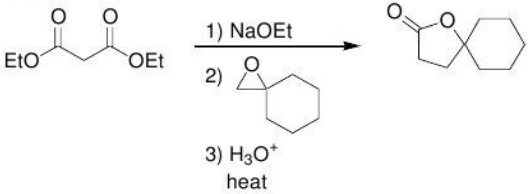
acrolein

22.102.

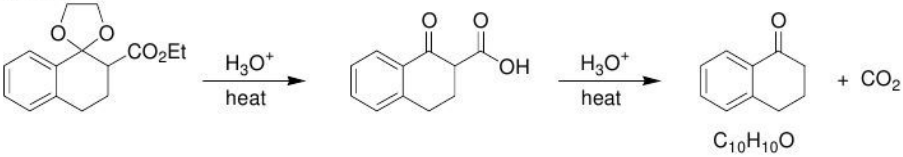


$C_{10}H_{10}O$

22.103.



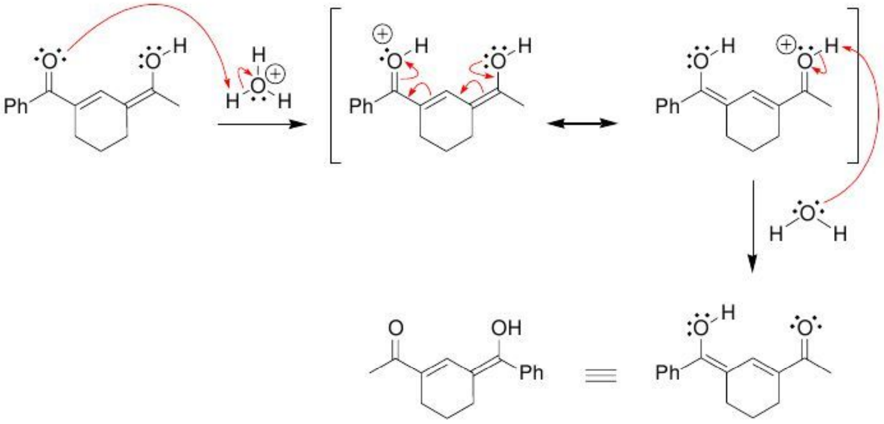
22.104.



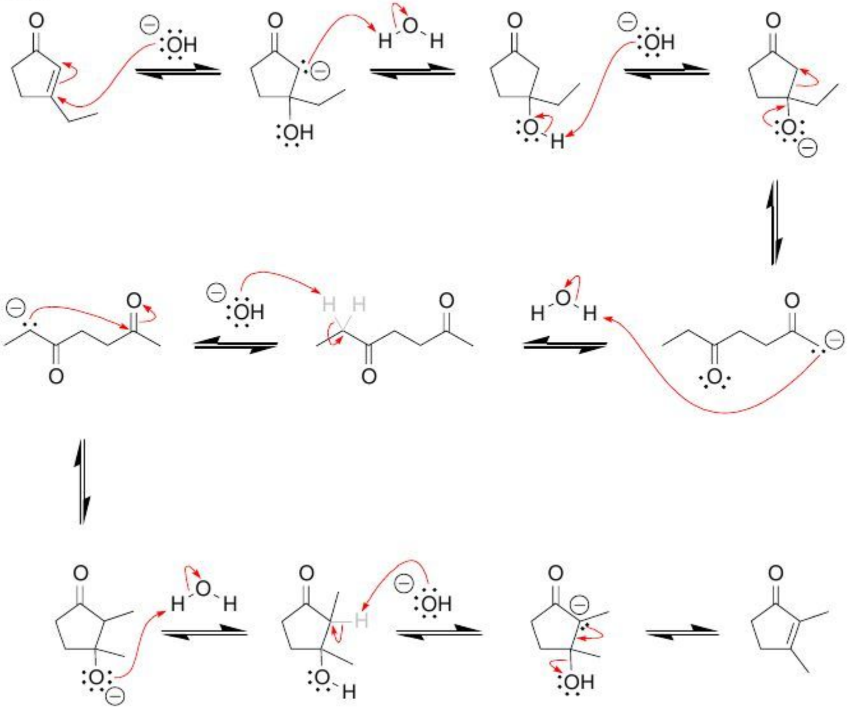
22.105.

When treated with aqueous acid, both compound A and compound B undergo racemization at the α position (via the enol as an intermediate, see problem 22.65). Each of these compounds establishes an equilibrium between *cis* and *trans* isomers. But the position of equilibrium is very different for compound A than it is for compound B. The equilibrium for compound A favors a *cis* configuration, because that is the configuration for which the compound can adopt a chair conformation in which both groups occupy equatorial positions. The equilibrium for compound B favors a *trans* configuration, because that is the configuration for which that compound can adopt a chair conformation in which both groups occupy equatorial positions.

22.106.

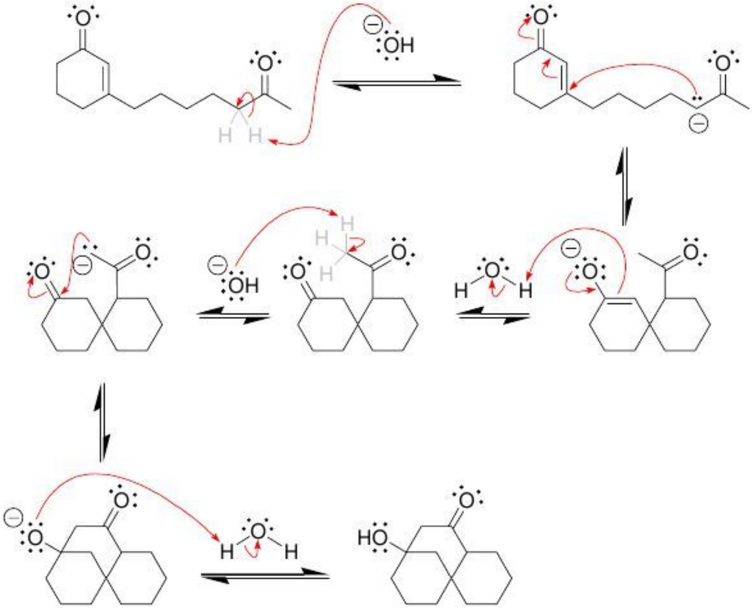


22.107.

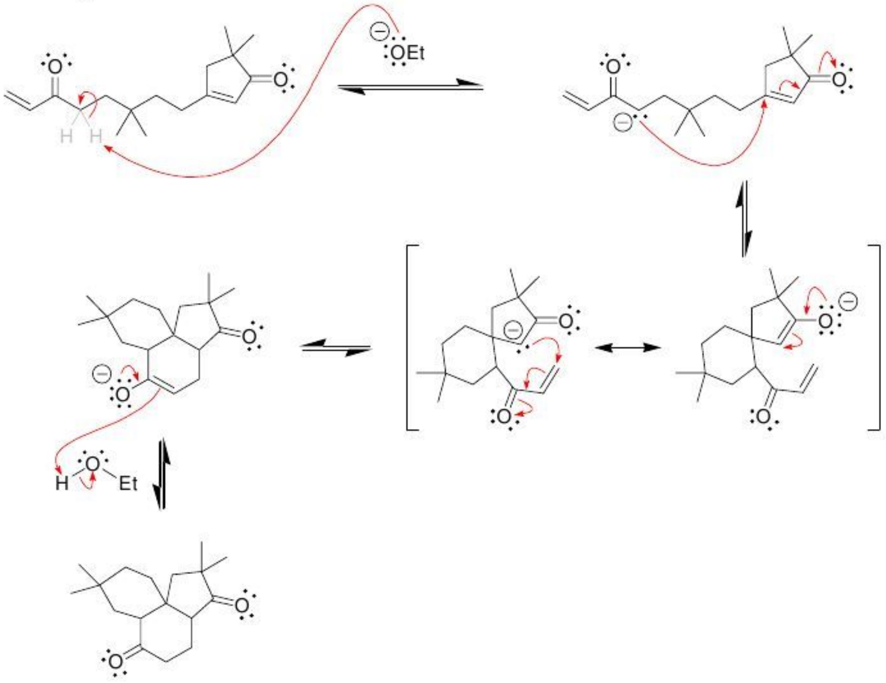


22.108.

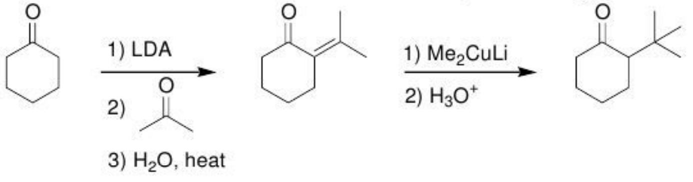
a)



b)



22.109. Direct alkylation would require performing an S_N2 reaction on a tertiary substrate, which will not occur. Instead the enolate would function as a base and E2 elimination would be observed instead of S_N2. The desired transformation can be achieved via a crossed aldol condensation, followed by a Michael addition:



Chapter 23
Amines

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 23. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

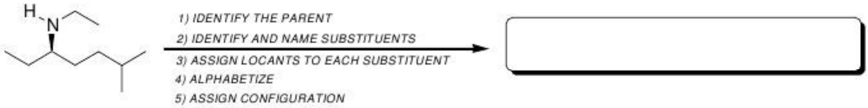
- Amines are ___________, ___________, or ___________, depending on the number of groups attached to the nitrogen atom.
- The lone pair on the nitrogen atom of an amine can function as a _______ or _________________.
- The basicity of an amine can be quantified by measuring the pK_a of the corresponding ___________________.
- Aryl amines are less basic than alkyl amines, because the lone pair is _________.
- Pyridine is a stronger base than pyrrole, because the lone pair in pyrrole participates in ____________.
- An amine moiety exists primarily as ______________________________ at physiological pH.
- The **azide synthesis** involves treating an ________________ with sodium azide, followed by _______________.
- The __________ **synthesis** generates primary amines upon treatment of potassium phthalimide with an alkyl halide, followed by hydrolysis or reaction with N_2H_4.
- Amines can be prepared via **reductive amination**, in which a ketone or aldehyde is converted into an imine in the presence of a _____________ agent, such as **sodium cyanoborohydride** ($NaBH_3CN$).
- Amines react with acyl halides to produce __________.
- In the **Hofmann elimination**, and amino group is converted into a better leaving group which is expelled in an ____ process to form an ___________.
- Primary amines react with a nitrosonium ion to yield a ______________ **salt** in a process called **diazotization**.
- **Sandmeyer reactions** utilize copper salts (CuX), enabling the installation of a halogen or a ________ group.
- In the **Schiemann reaction**, an aryl diazonium salt is converted into a fluorobenzene by treatment with _________________.
- Aryldiazonium salts react with activated aromatic rings in a process called _____ **coupling**, to produce colored compounds called _____ **dyes**.
- A _______**cycle** is a ring that contains atoms of more than one element.
- Pyrrole undergoes electrophilic aromatic substitution reactions, which occur primarily at C__.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 23. The answers appear in the section entitled *SkillBuilder Review*.

23.1 Naming an Amine

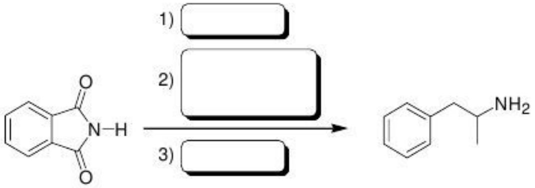
PROVIDE A SYSTEMATIC NAME FOR THE FOLLOWING COMPOUND



1) IDENTIFY THE PARENT
2) IDENTIFY AND NAME SUBSTITUENTS
3) ASSIGN LOCANTS TO EACH SUBSTITUENT
4) ALPHABETIZE
5) ASSIGN CONFIGURATION

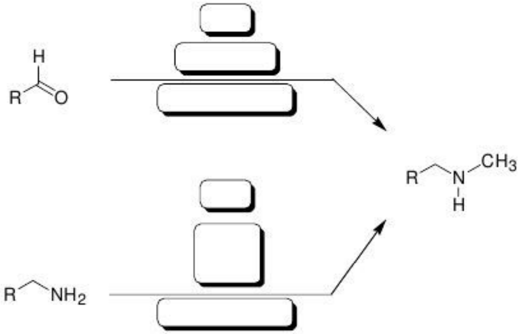
23.2 Preparing a Primary Amine via the Gabriel Reaction

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:

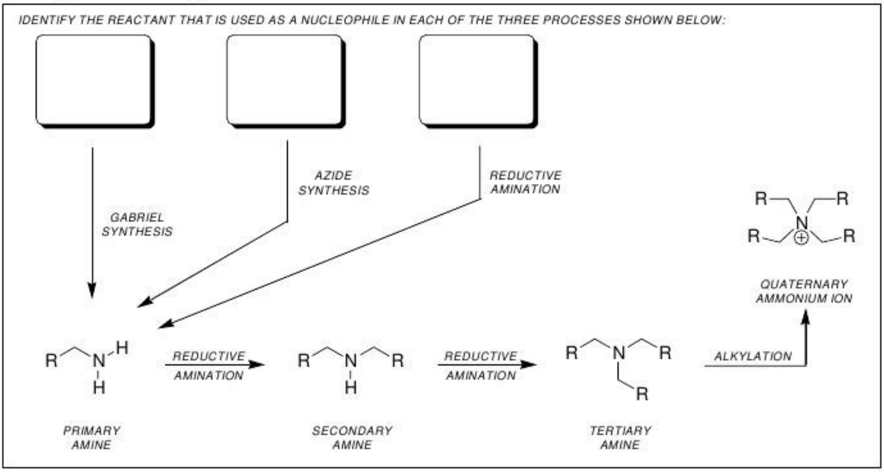


23.3 Preparing an Amine via a Reductive Amination

IDENTIFY REAGENTS THAT WILL ACHIEVE EACH OF THE FOLLOWING TRANSFORMATIONS:

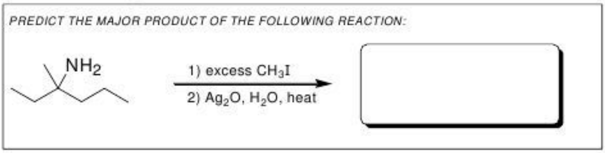


23.4 Synthesis Strategies



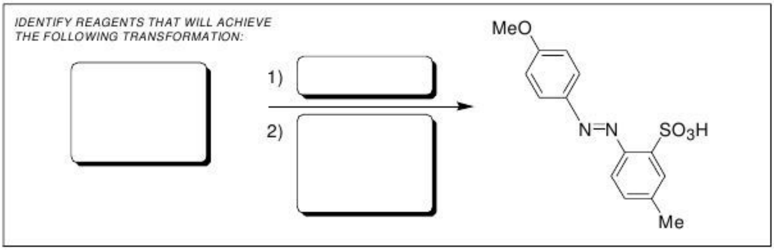
IDENTIFY THE REACTANT THAT IS USED AS A NUCLEOPHILE IN EACH OF THE THREE PROCESSES SHOWN BELOW:

23.5 Predicting the Product of a Hofmann Elimination



PREDICT THE MAJOR PRODUCT OF THE FOLLOWING REACTION:

23.6 Determining the Reactants for Preparing an Azo Dye

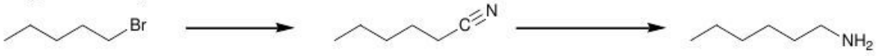


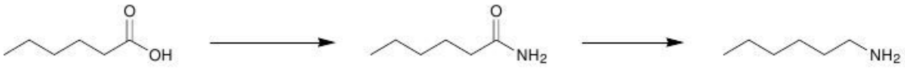
IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:

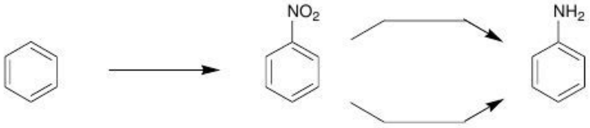
Review of Reactions

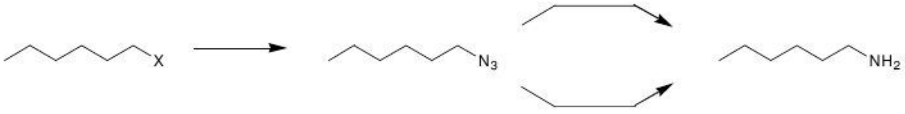
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 23. The answers appear in the section entitled *Review of Reactions*.

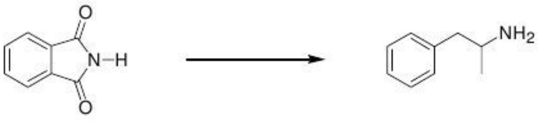
Preparation of Amines

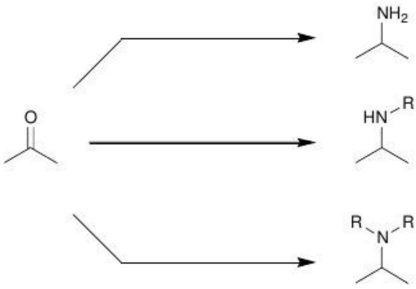




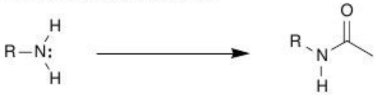




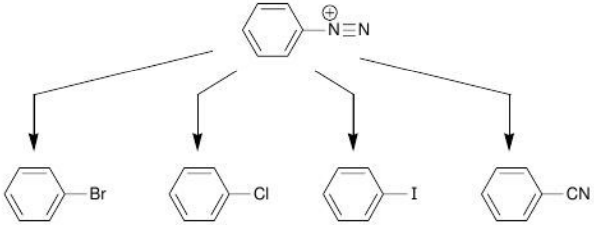


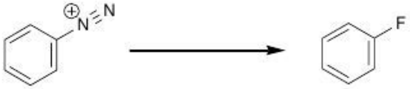


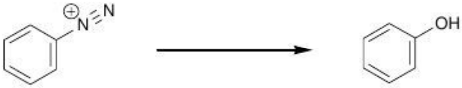
Reactions of Amines

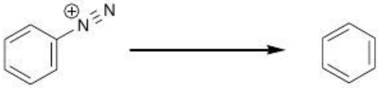


Reactions of Aryldiazonium Salts

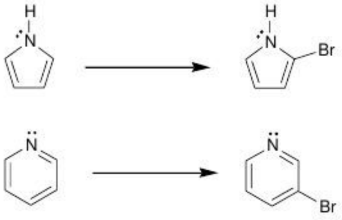








Reactions of Nitrogen Heterocycles



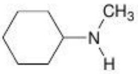
Solutions

23.1.

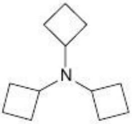
a) 3,3-dimethyl-1-butanamine
b) cyclopentylamine
c) *N,N*-dimethylcyclopentylamine
d) triethylamine
e) (*1S,3R*)-3-isopropylcyclohexanamine
f) (*1S, 3S*)-3-aminocyclohexanol

23.2.

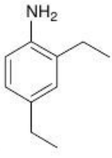
a)



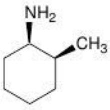
b)



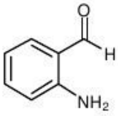
c)



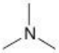
d)



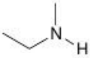
e)



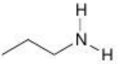
23.3.



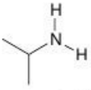
trimethylamine



ethyl methyl amine

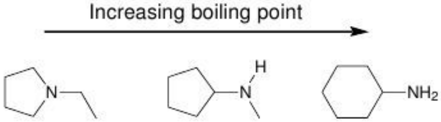


propylamine



isopropylamine

23.4.



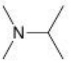
23.5.

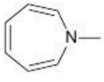
a) No. This compound has eight carbon atoms and only one functional group.

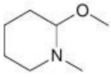
b) Yes.

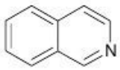
c) Yes.

23.6.

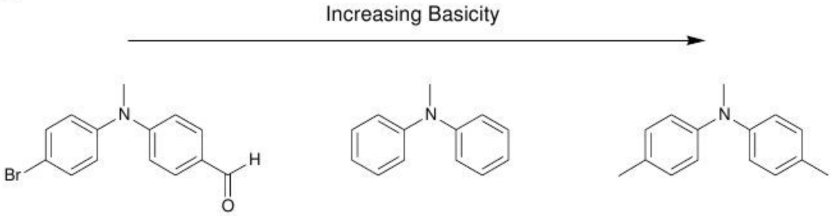
a) 

b) 

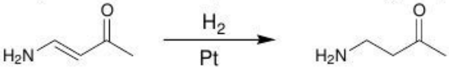
c) 

d) 

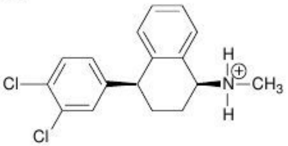
23.7.

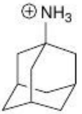


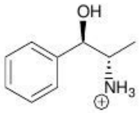
23.8. In the reactant, the lone pair of the amino group is delocalized via resonance. In the product, the lone pair of the amino group is localized.



23.9.

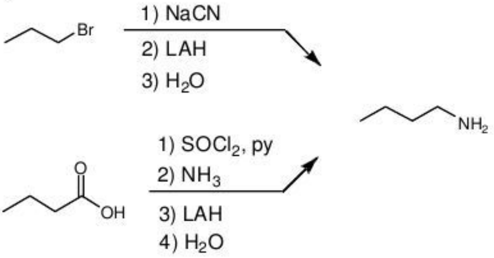
a) 

b) 

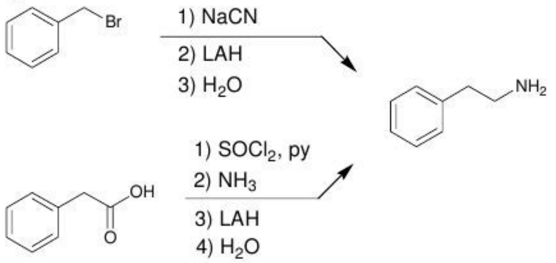
c) 

23.10.

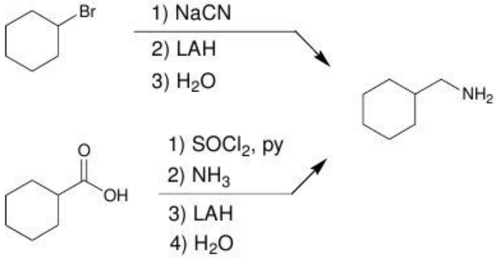
a)



b)

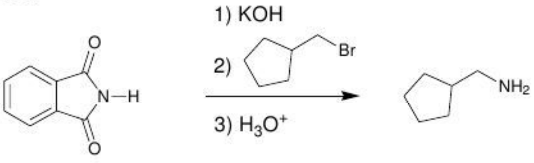


c)

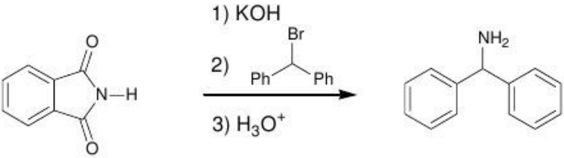


23.11. This compound cannot be prepared from an alkyl halide or a carboxylic acid, using the methods described in this section, because there are two methyl groups at the alpha position (the carbon atom connected to the amino group). These two methyl groups cannot be installed with either of the synthetic methods above, because both methods produce an amine with two alpha protons.

23.12.

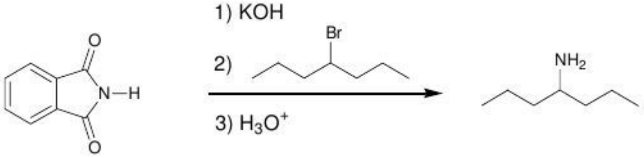


a)

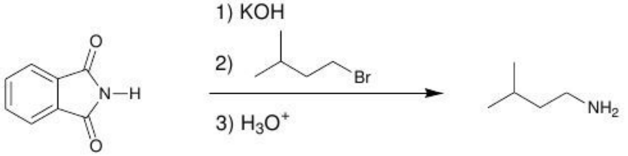


b)

c)

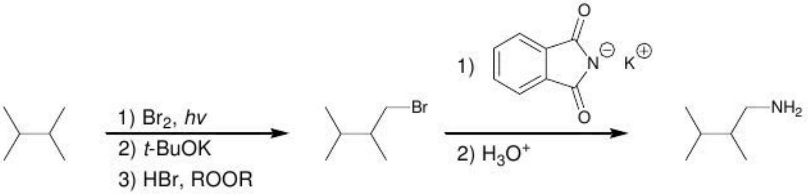


d)

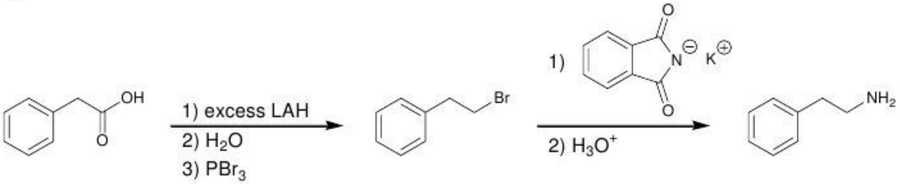


23.13.

a)

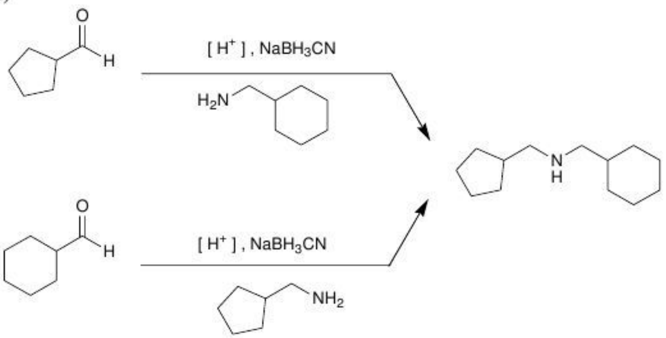


b)

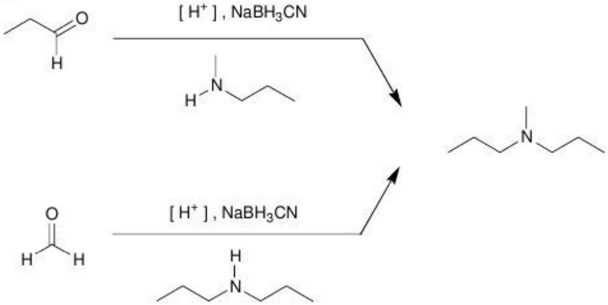


23.14.

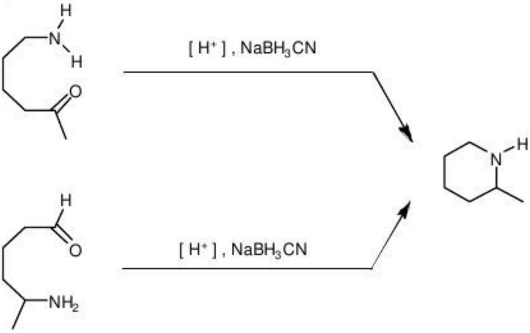
a)



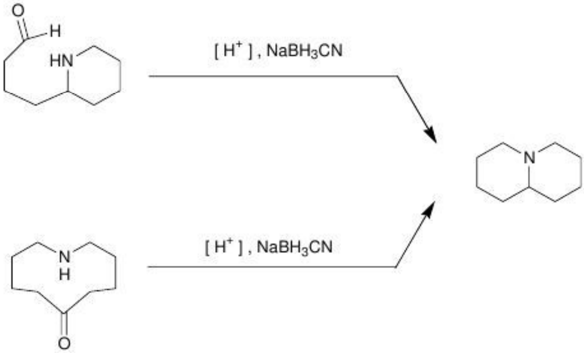
b)



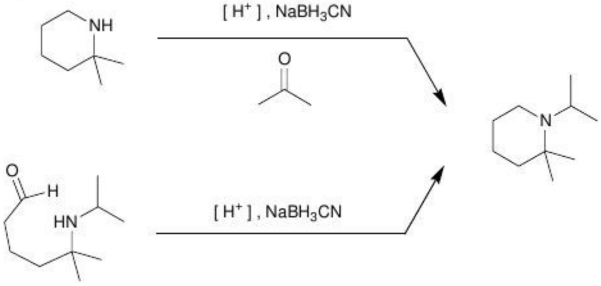
c)



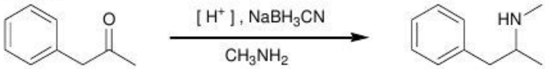
d)



e)

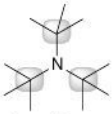


23.15.



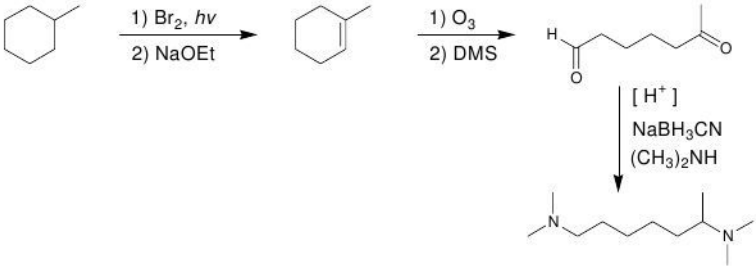
23.16. The last step of reductive amination is the reduction of a C=N bond. That step introduces a proton on the alpha position (the carbon atom that is connected to the nitrogen atom in the product):

As a result, the product of a reductive amination must have at least one proton at the alpha position. In the case of tri-*tert*-butyl amine, there are three alpha positions, and none of them bears a proton. Each of the alpha positions has three alkyl groups and no protons.



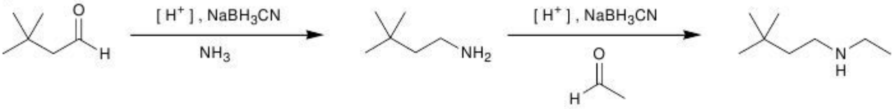
Therefore, this compound cannot be made with a reductive amination.

23.17.

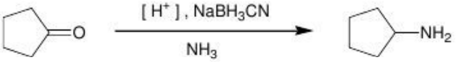


23.18.

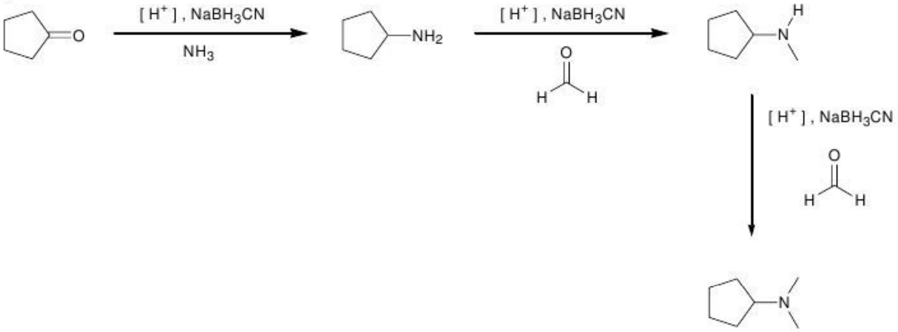
a)


O
H
[H⁺] , NaBH₃CN
NH₃
NH₂
[H⁺] , NaBH₃CN
O
H
N
H

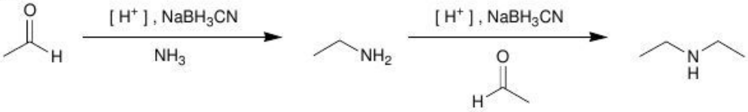
b)


O
[H⁺] , NaBH₃CN
NH₃
NH₂

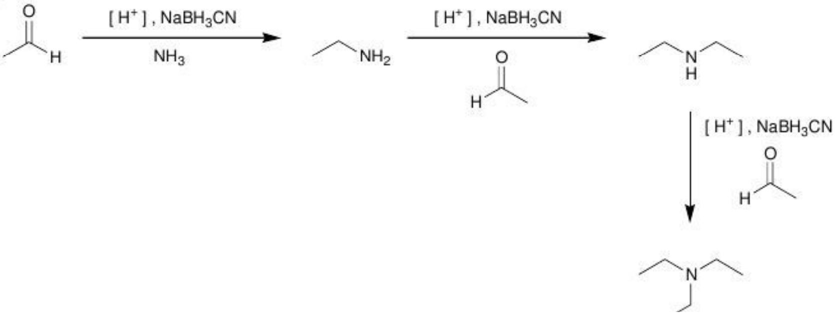
c)


O
[H⁺] , NaBH₃CN
NH₃
NH₂
[H⁺] , NaBH₃CN
O
H
H
H
N
[H⁺] , NaBH₃CN
O
H
H
N

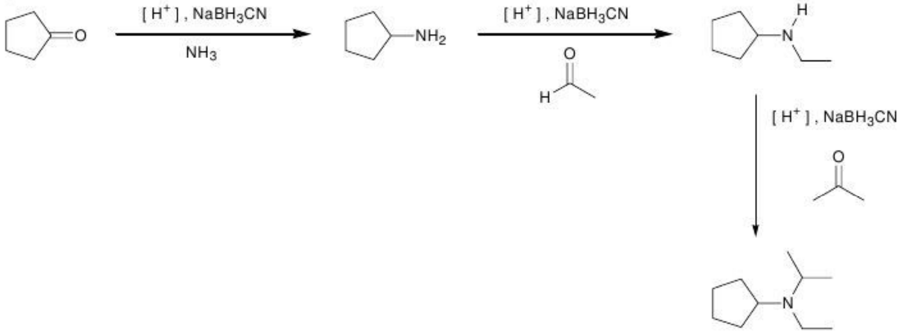
d)


O
H
[H⁺] , NaBH₃CN
NH₃
NH₂
[H⁺] , NaBH₃CN
O
H
N
H

e)

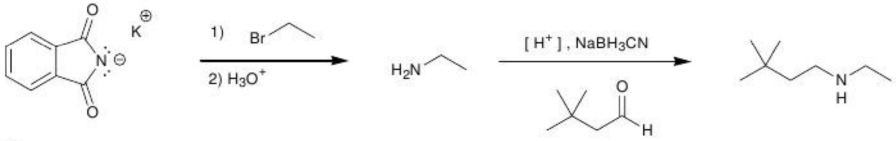

O
H
[H⁺] , NaBH₃CN
NH₃
NH₂
[H⁺] , NaBH₃CN
O
H
N
H
[H⁺] , NaBH₃CN
O
H
N

f)

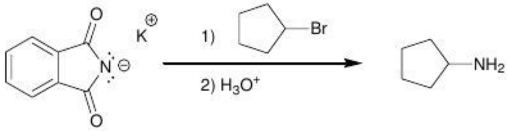


23.19. The first alkyl group is installed via a Gabriel synthesis, and the remaining alkyl groups are installed via reductive amination processes. For most of the following syntheses, there is a choice regarding which group to attach via the initial Gabriel synthesis. In such cases, the least sterically hindered group is chosen (the group whose installation involves the least hindered alkyl halide):

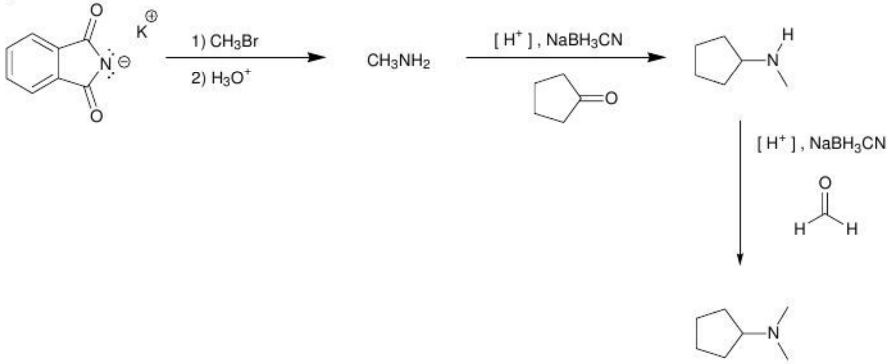
a)



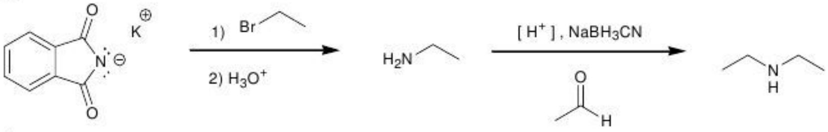
b)



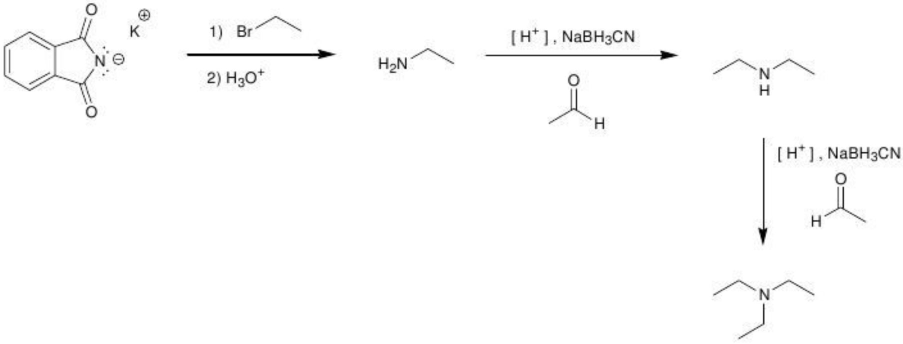
c)



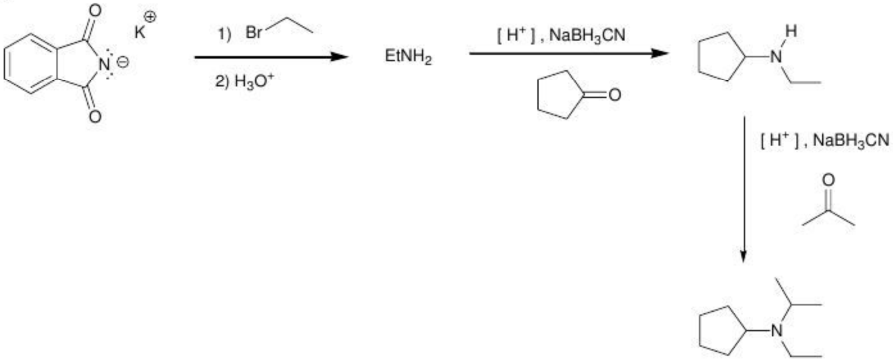
d)



e)

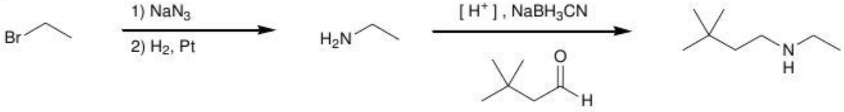


f)

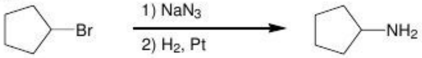


23.20. The first alkyl group is installed via an azide synthesis, and the remaining alkyl groups are installed via reductive amination processes. For most of the following syntheses, there is a choice regarding which group to attach via the initial azide synthesis. In such cases, the least sterically hindered group is chosen (the group whose installation involves the least hindered alkyl halide):

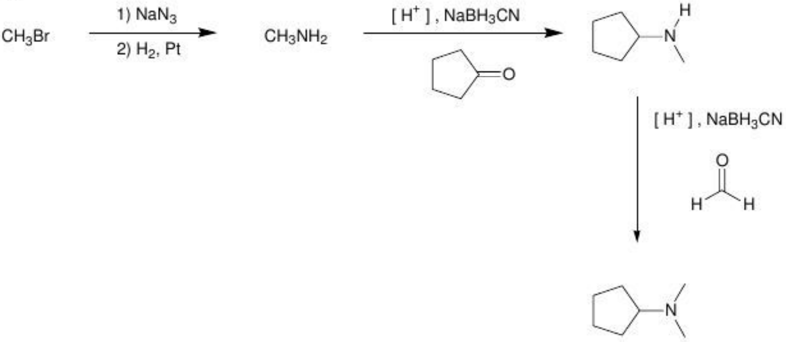
a)



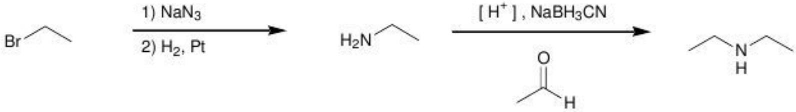
b)


Br
1) NaN$_3$
2) H$_2$, Pt
NH$_2$

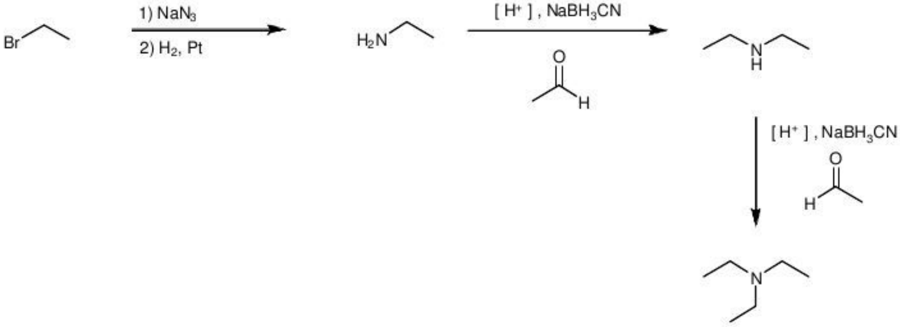
c)


CH$_3$Br
1) NaN$_3$
2) H$_2$, Pt
CH$_3$NH$_2$
[H$^+$] , NaBH$_3$CN
O
H
N
[H$^+$] , NaBH$_3$CN
O
H
H
N

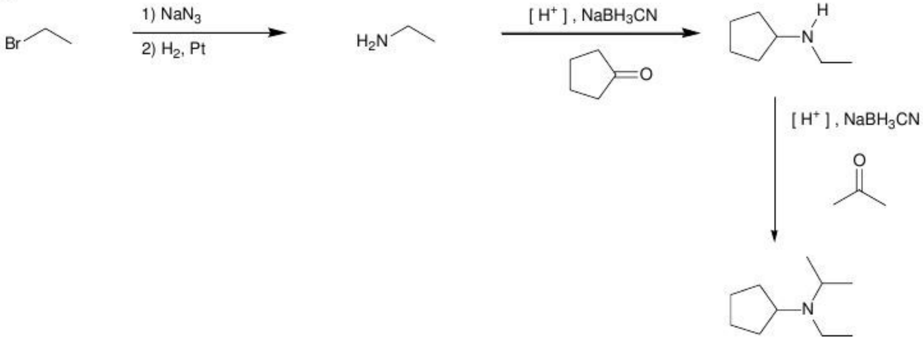
d)


Br
1) NaN$_3$
2) H$_2$, Pt
H$_2$N
[H$^+$] , NaBH$_3$CN
O
H
N
H

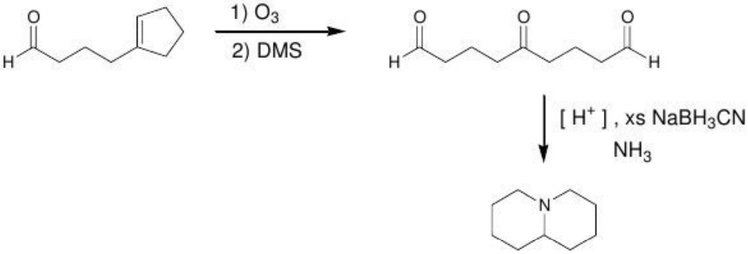
e)


Br
1) NaN$_3$
2) H$_2$, Pt
H$_2$N
[H$^+$] , NaBH$_3$CN
O
H
N
H
[H$^+$] , NaBH$_3$CN
O
H
N

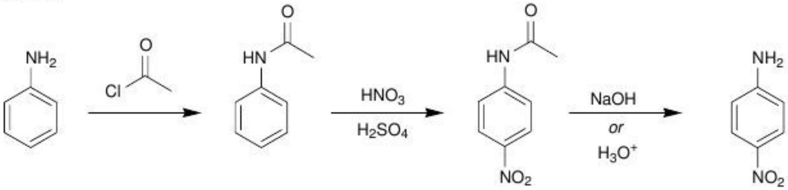
f)



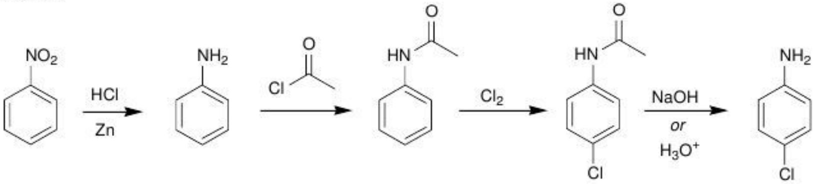
23.21.



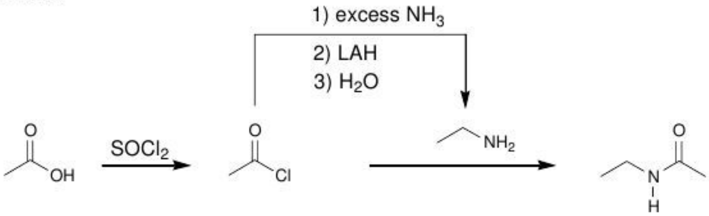
23.22.



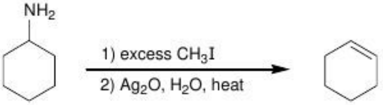
23.23.

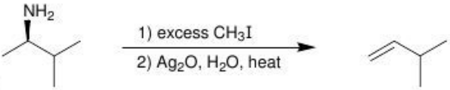


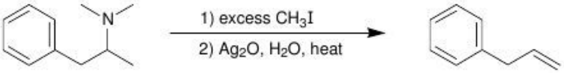
23.24.



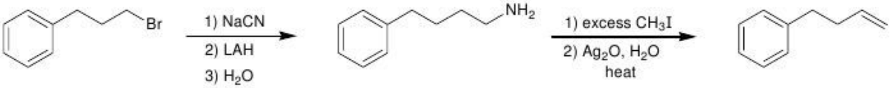
23.25.

a)


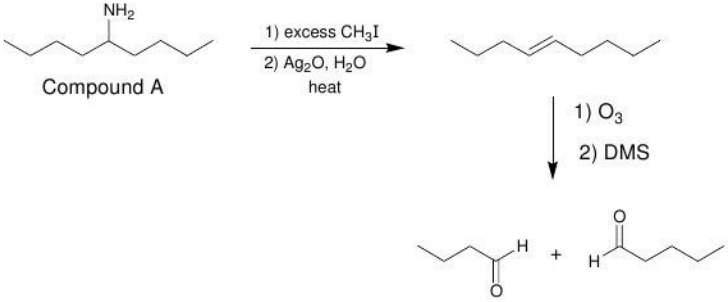
b)


c)


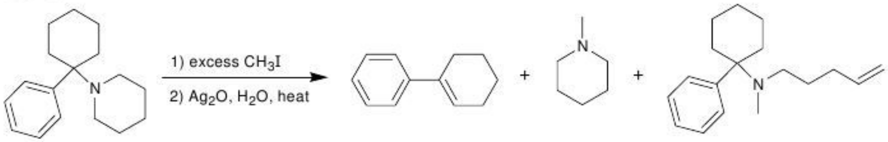
23.26.



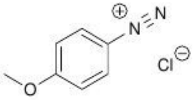
23.27.

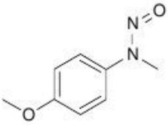


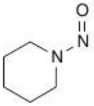
23.28.

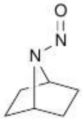


23.29.

a)


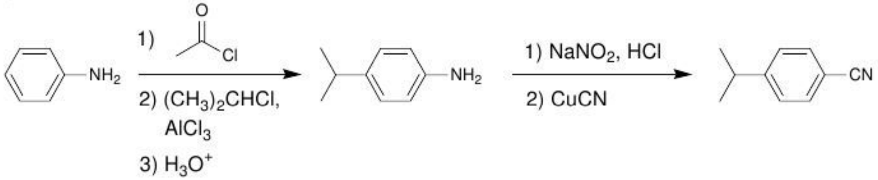
b)


c)


d)


23.30.

a)



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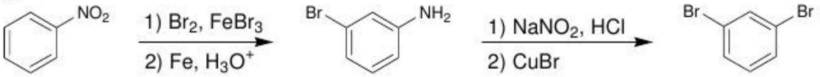
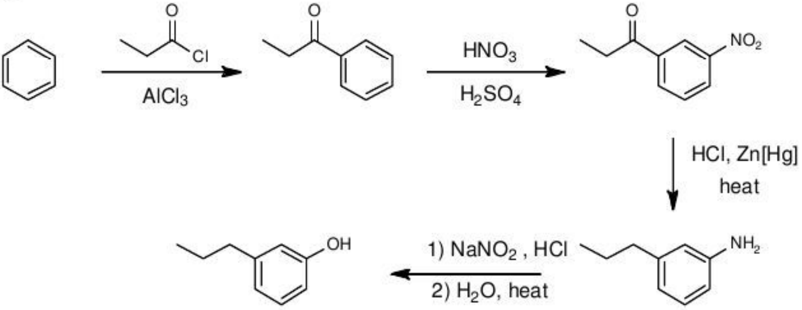
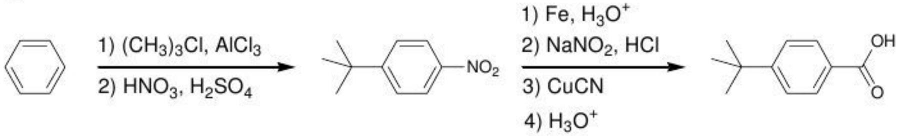


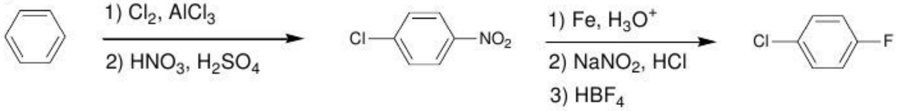
c)



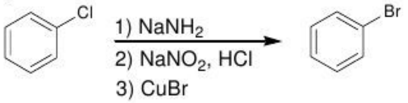
d)


1) $(CH_3)_3CCl$, $AlCl_3$
2) HNO_3, H_2SO_4
NO_2
1) Fe, H_3O^+
2) $NaNO_2$, HCl
3) CuCN
4) H_3O^+
OH
O

e)

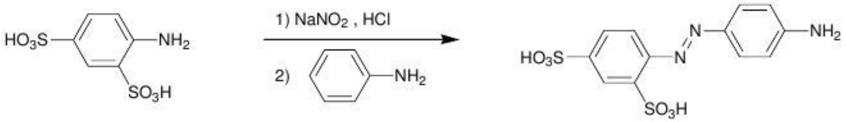

1) Cl_2, $AlCl_3$
2) HNO_3, H_2SO_4
Cl
NO_2
1) Fe, H_3O^+
2) $NaNO_2$, HCl
3) HBF_4
Cl
F

f)

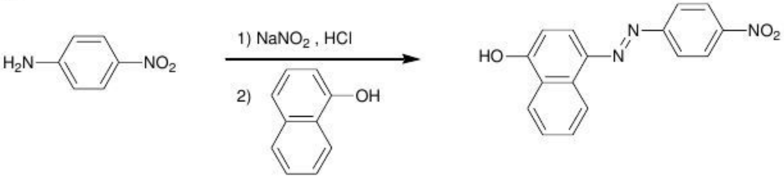

Cl
1) $NaNH_2$
2) $NaNO_2$, HCl
3) CuBr
Br

23.31.

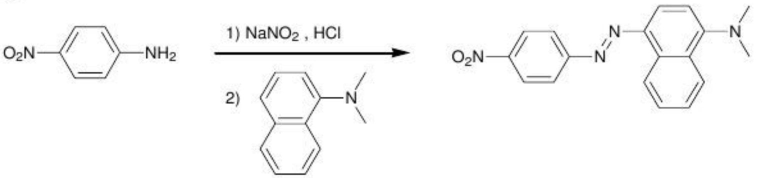
a)


HO_3S
NH_2
SO_3H
1) $NaNO_2$, HCl
2)
NH_2
HO_3S
N
N
NH_2
SO_3H

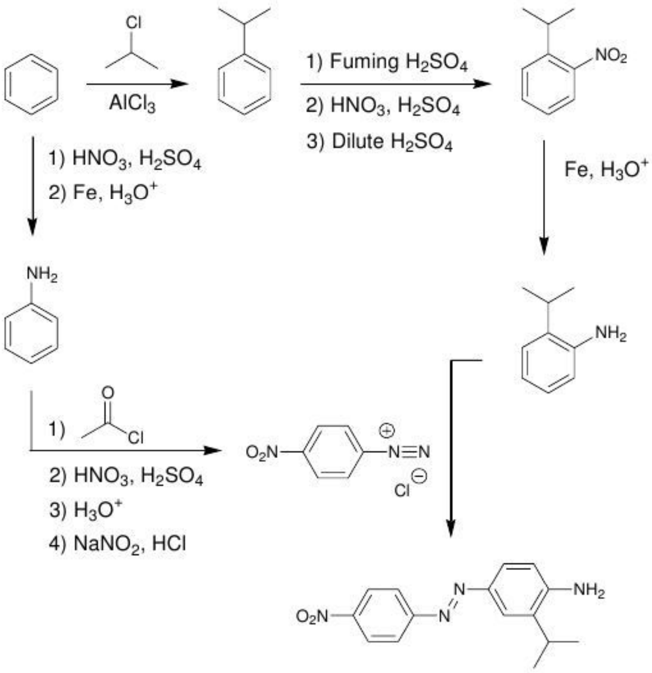
b)


H_2N
NO_2
1) $NaNO_2$, HCl
2)
OH
HO
N
N
NO_2

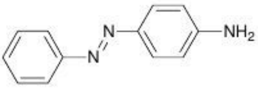
c)

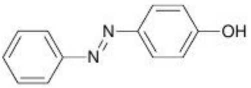

O_2N
NH_2
1) $NaNO_2$, HCl
2)
N
O_2N
N
N
N

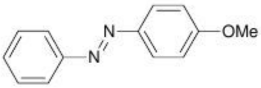
23.32.



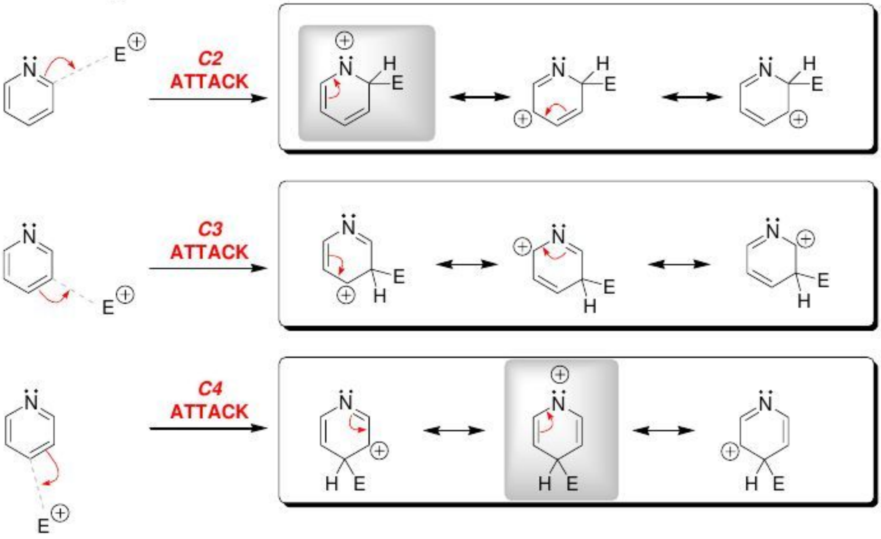
23.33.

a) 

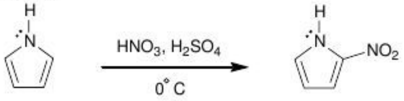
b) 

c) 

23.34. Attack at either C2 or C4 generates an intermediate that exhibits a resonance structure with a nitrogen atom that lacks an octet (highlighted below). Attack at C3 generates a more stable intermediate:



23.35.



23.36.

a) The second compound will have an N-H stretching signal between 3300 and 3500 cm^{-1}. The first compound will not have such a signal.

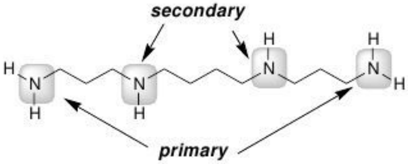
b) When treated with HCl, the first compound will be protonated to form an ammonium salt that will produce an IR signal between 2200 and 3000 cm^{-1}. The second compound is not an amine and will not exhibit the same behavior.

23.37.

a) The ^{1}H NMR spectrum of the first compound will have a singlet resulting from the N-methyl group. ^{1}H NMR spectrum of the second compound will not have any singlets.

b) The ^{1}H NMR spectrum of the first compound will have six signals, while the ^{1}H NMR spectrum of the second compound will have only three signals.

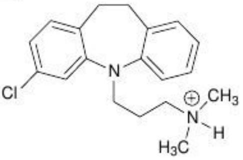
23.38.



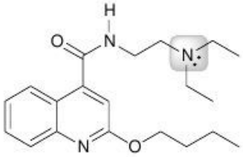
23.39.

a) The lone pair that is farthest away from the rings is the most basic, because its lone pair is localized. The lone pair of the other nitrogen atom is delocalized via resonance.

b)



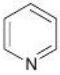
23.40.



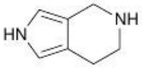
23.41.

a)

b)

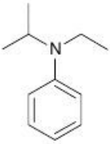


c)

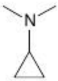


23.42.

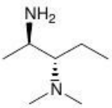
a)



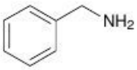
b)



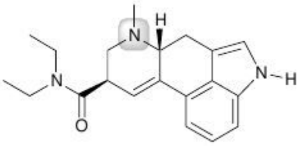
c)



d)



23.43. Only one of the nitrogen atoms has a localized lone pair (highlighted in the following structure). The other two nitrogen atoms have delocalized lone pairs.



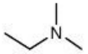
23.44.

a) two b) two c) one

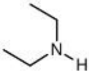
23.45.

a) 2,2,3,3-tetramethyl-1-hexanamine
b) (*S*)-4-amino-2,2-dimethylcyclohexanone
c) dicyclobutylmethylamine
d) 3-bromo-2,6-dimethylaniline
e) *N,N*-dimethyl-3-propylaniline
f) 2,5-diethyl-*N*-methyl pyrrole

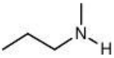
23.46.



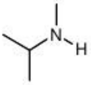
ethyldimethylamine



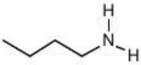
diethylamine



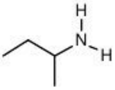
methylpropylamine



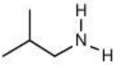
isopropylmethylamine



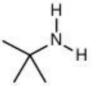
1-butanamine



2-butanamine

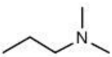


2-methyl-
1-propanamine

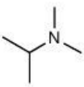


2-methyl-
2-propanamine

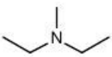
23.47. None of these compounds are chiral.



dimethylpropylamine



isopropyldimethylamine



diethylmethylamine

23.48.

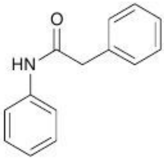
a)

b)

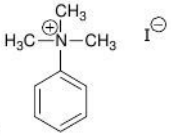
23.49.

a)

b)

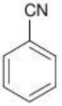


c)



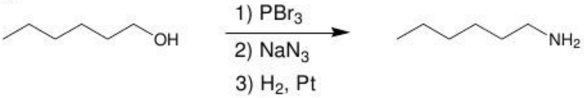
d)

e)



23.50.

a)



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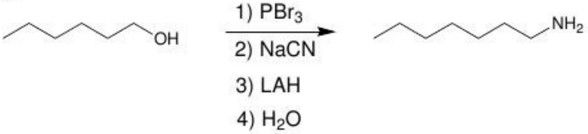

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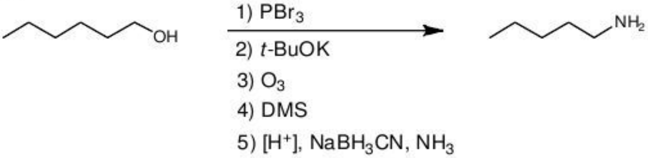
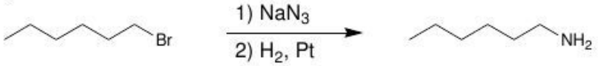
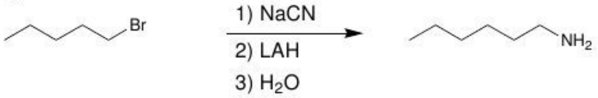


23.51.

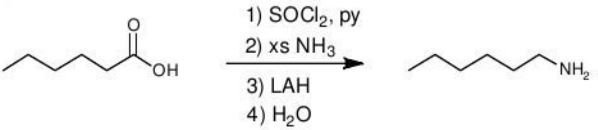
a)



b)



c)



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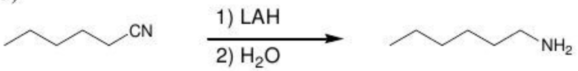
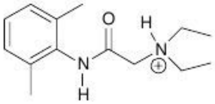
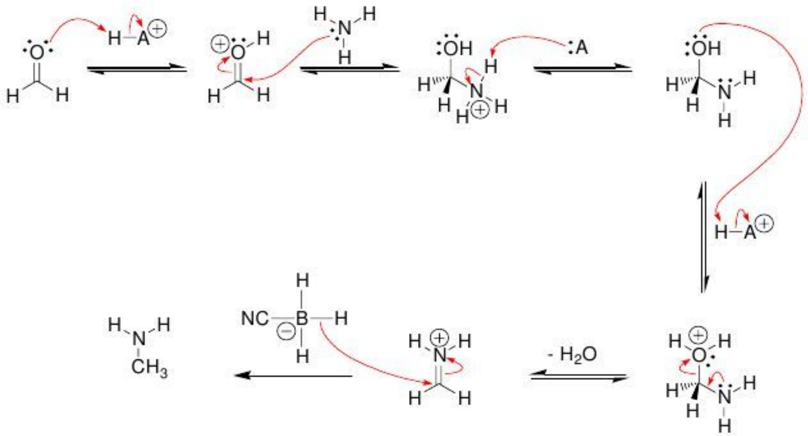


23.52. Aziridine has significant ring strain, which would increase significantly during pyramidal inversion. This provides a significant energy barrier that prevents pyramidal inversion at room temperature.

23.53.



23.54.



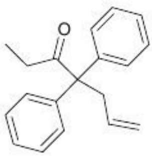
23.55. In acidic conditions, the amino group is protonated to give an ammonium ion. The ammonium group is a powerful deactivator and meta-director.

23.56.

a) The presence of the nitro group in the para position helps stabilize the conjugate base via resonance. As seen in chapter 19, this effect only occurs when the nitro group is in the ortho and para positions.

b) The basicity of *ortho*-nitroaniline should be closer in value to *para*-nitroaniline.

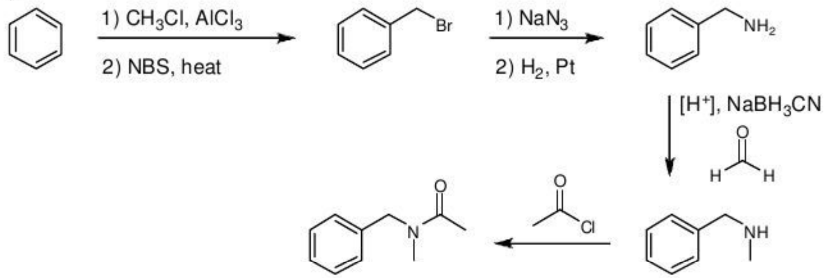
23.57.



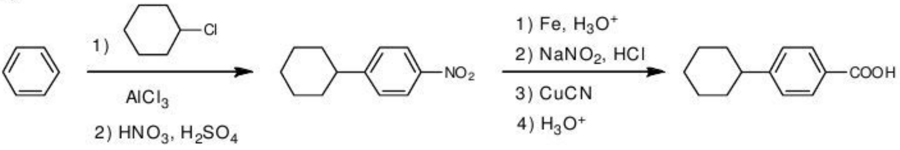
23.58. Protonation of the oxygen atom gives a resonance stabilized cation (as seen in chapter 20). In contrast, protonation of the nitrogen atom gives a cation that is not resonance stabilized.

23.59.

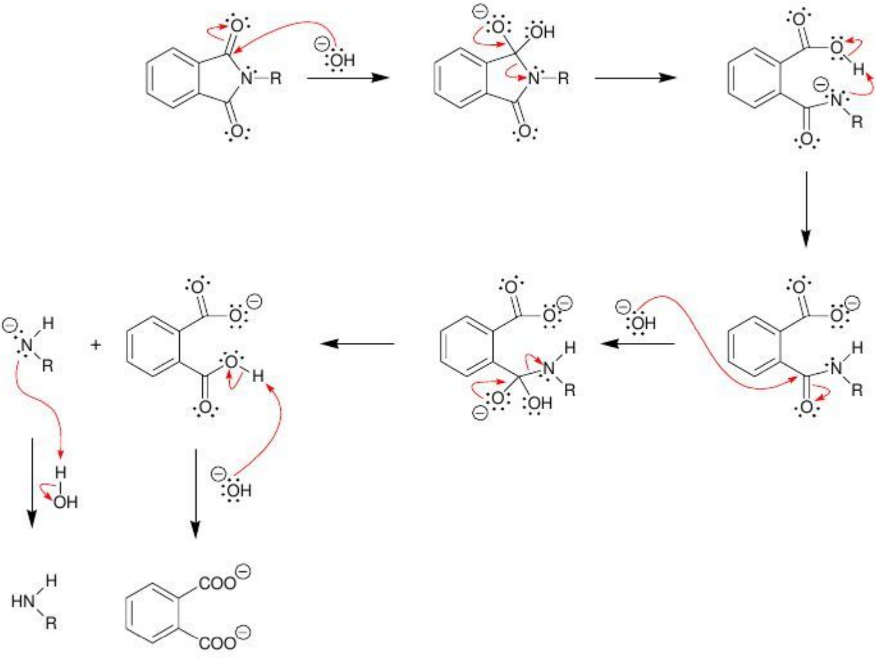
a)



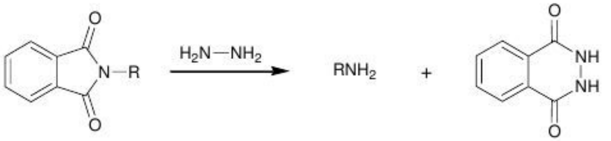
b)



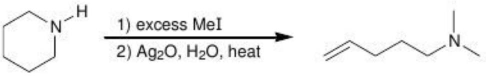
23.60.



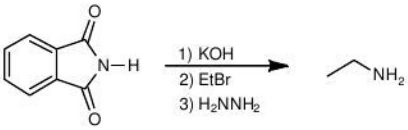
23.61.



23.62.

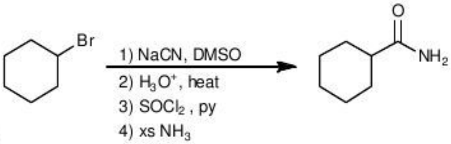


a)

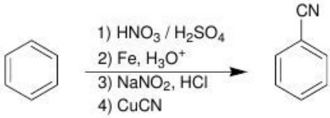


b)

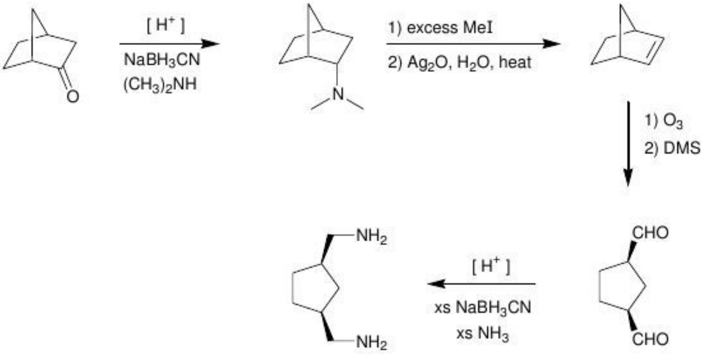
c)



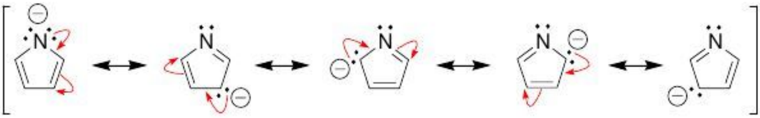
d)



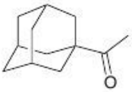
23.63.



23.64. The conjugate base of pyrrole is highly stabilized because it is an aromatic anion and it is resonance stabilized, spreading the negative charge over all five atoms of the ring:



23.65.



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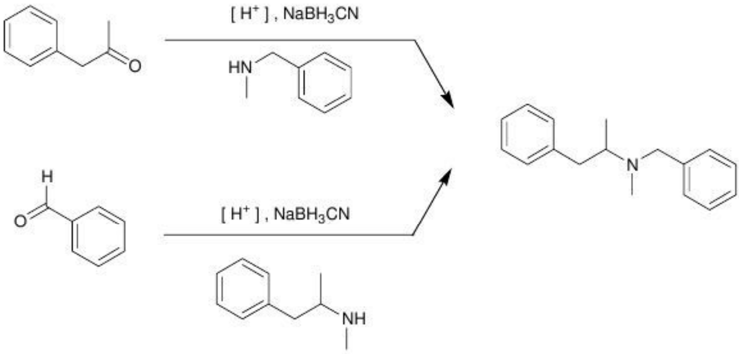

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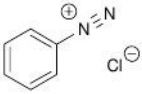
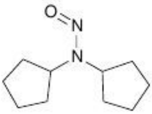
a) 

b) 

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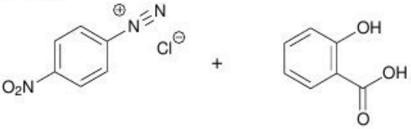

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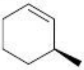
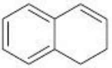
a) 

b) 

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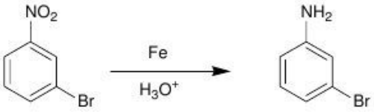
a) 

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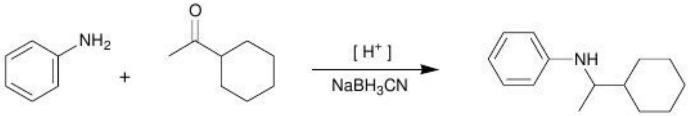

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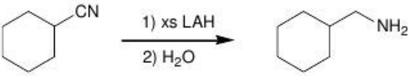

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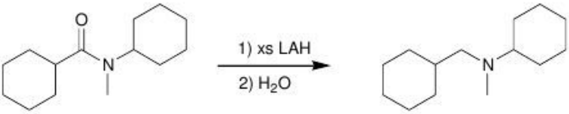

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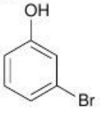
a)



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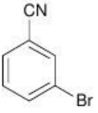

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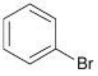

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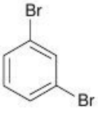

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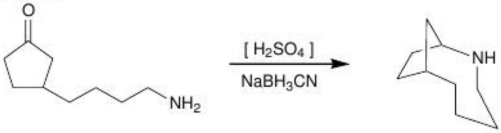
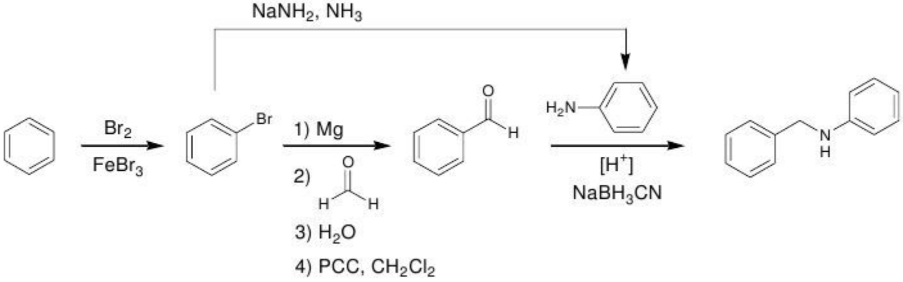


23.73.

a)



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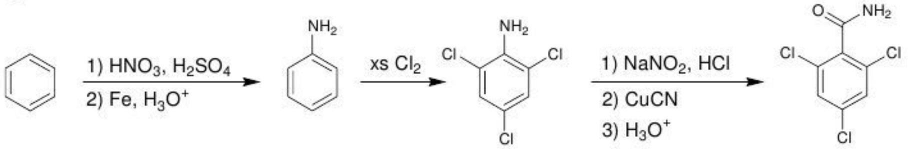
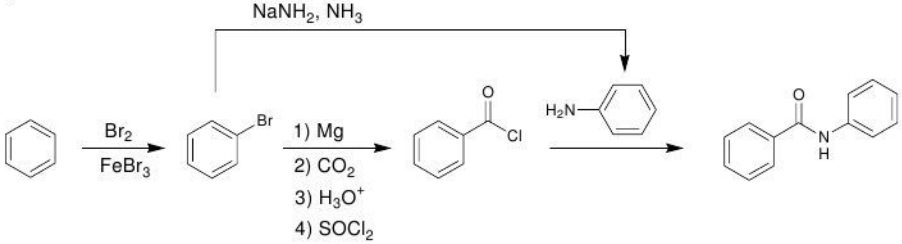
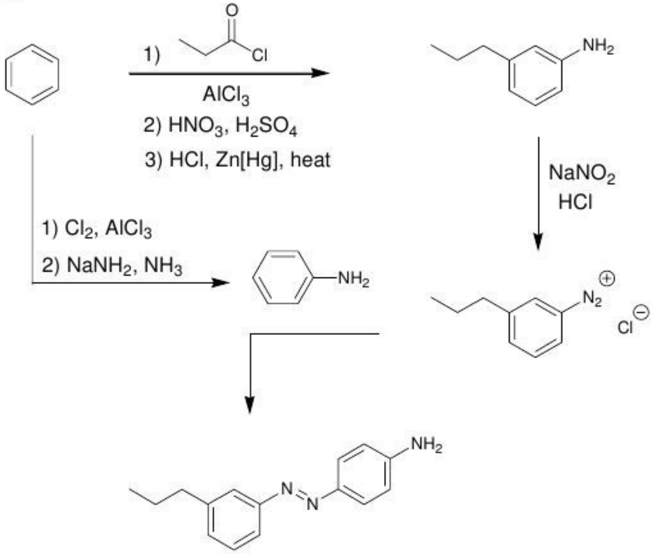

1) HNO3, H2SO4
2) Fe, H3O+
NH2
xs Cl2
Cl
Cl
NH2
Cl
1) NaNO2, HCl
2) CuCN
3) H3O+
O
NH2
Cl
Cl
Cl

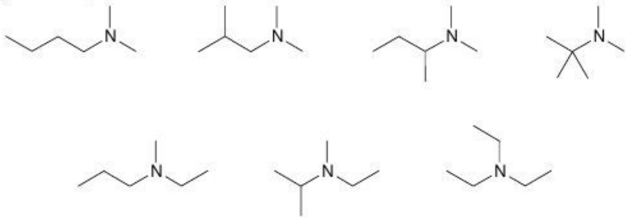
c)


NaNH2, NH3
Br2
FeBr3
Br
1) Mg
2) CO2
3) H3O+
4) SOCl2
O
Cl
H2N
O
N
H

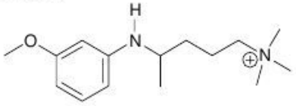
d)


1)
O
Cl
AlCl3
2) HNO3, H2SO4
3) HCl, Zn[Hg], heat
NH2
NaNO2
HCl
1) Cl2, AlCl3
2) NaNH2, NH3
NH2
N2 ⊕
Cl ⊖
N
N
NH2

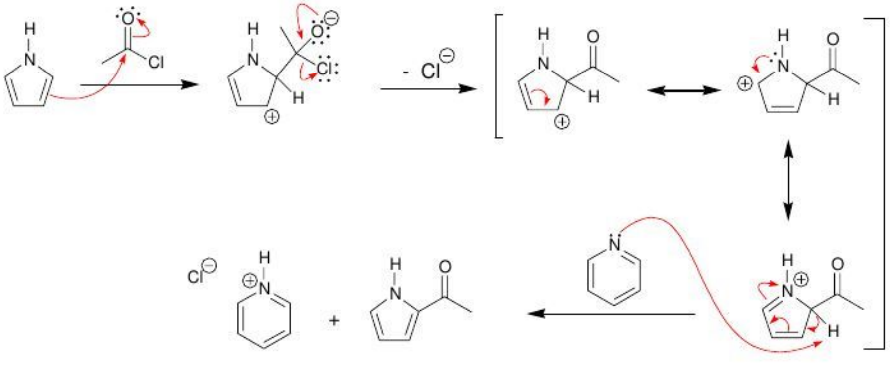
23.74. The IR data indicates that we are looking for structures that lack an N-H bond (i.e tertiary amines):



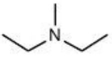
23.75.



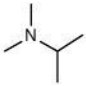
23.76.



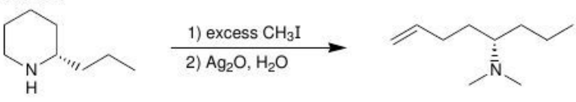
23.77. The compound is a tertiary amine with the appropriate symmetry that provides for only three signals:



or

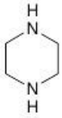


23.78.

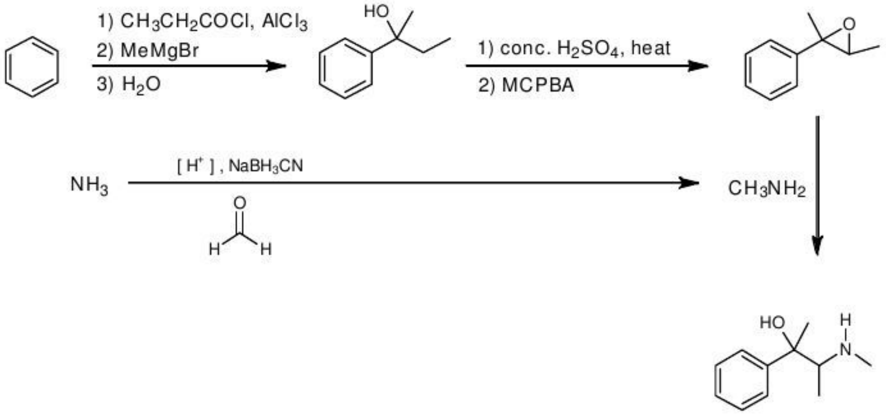


Coniine

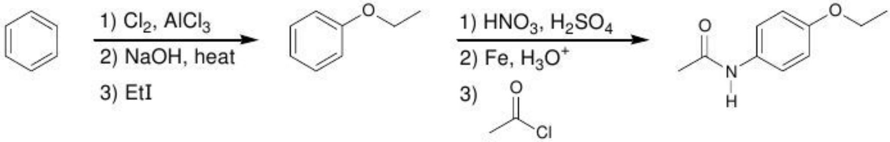
23.79.



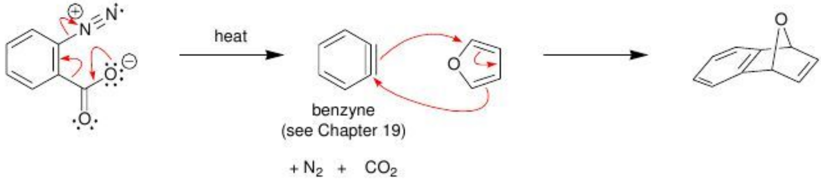
23.80.



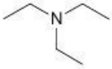
23.81.



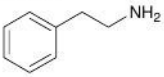
23.82.



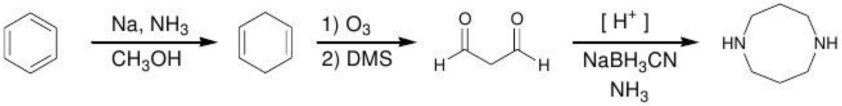
23.83.



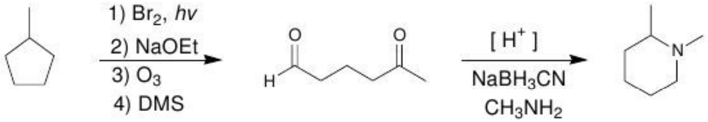
23.84.



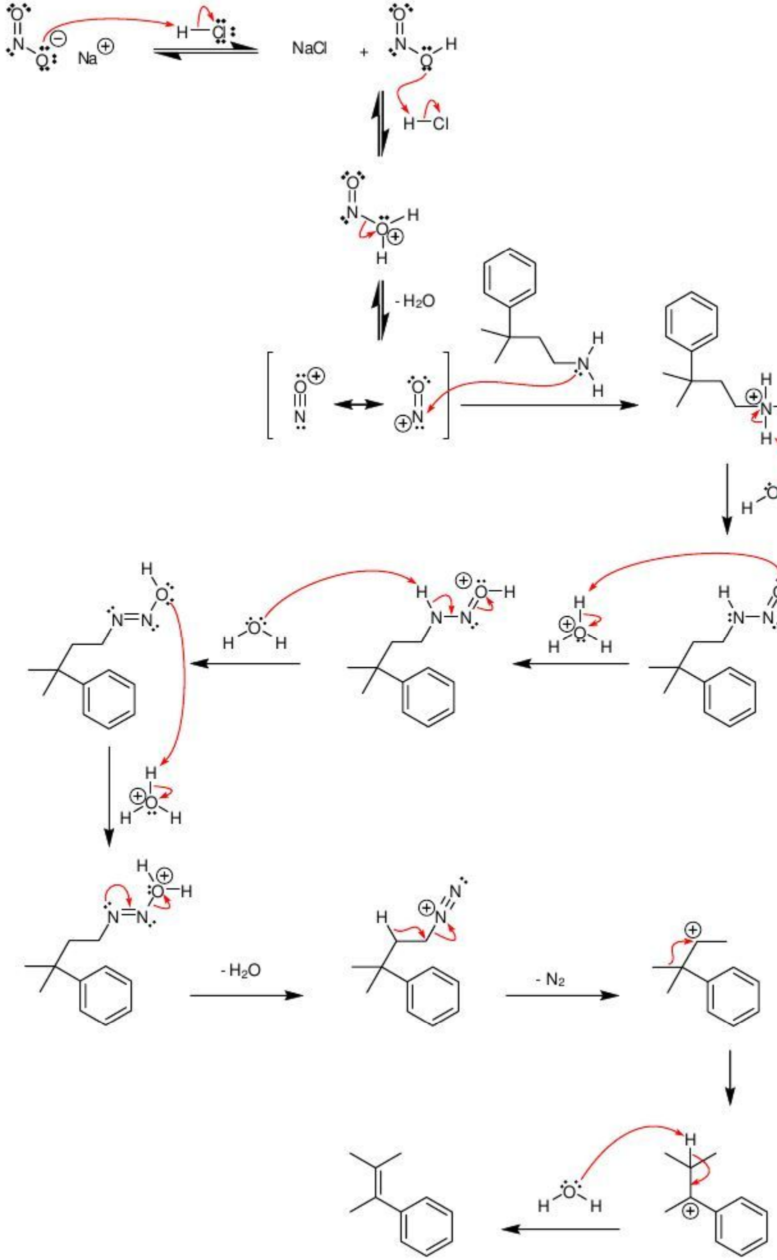
23.85.



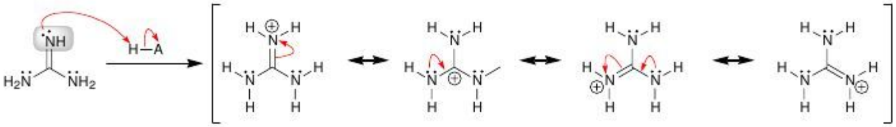
23.86.



23.87.



23.88. Protonation of the nitrogen highlighted below results in a cation that is highly resonance stabilized. Protonation of either of the other nitrogen atoms would not result in a resonance stabilized cation:



Chapter 24
Carbohydrates

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 24. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

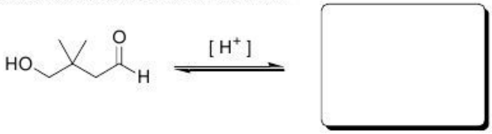
- **Carbohydrates** are polyhydroxy ___________ or ketones.
- Simple sugars are called _______________ and are generally classified as **aldoses** and _________**.**
- For all **D sugars**, the chirality center farthest from the carbonyl group has the ___ configuration.
- Aldohexoses can form cyclic hemi______ that exhibit a **pyranose** ring.
- Cyclization produces two stereoisomeric hemiacetals, called ___________. The newly created chirality center is called the ___________ **carbon.**
- In the **α anomer**, the hydroxyl group at the anomeric position is ______ to the CH_2OH group, while in the **β anomer**, the hydroxyl group is ______ to the CH_2OH group.
- Anomers equilibrate by a process called _____________, which is catalyzed by either ______ or _______.
- Some carbohydrates, such as D-fructose, can also form five-membered rings, called ___________ rings.
- Monosaccharides are converted into their ester derivatives when treated with excess ______________________________.
- Monosaccharides are converted into their ether derivatives when treated with excess ____________________ and silver oxide.
- When treated with an alcohol under acid-catalyzed conditions, monosaccharides are converted into acetals, called ___________. Both anomers are formed.
- Upon treatment with sodium borohydride an aldose or ketose can be reduced to yield an ___________.
- When treated with a suitable oxidizing agent, an aldose can be oxidized to yield an __________.
- When treated with HNO_3 , an aldose is oxidized to give a dicarboxylic acid called an ________________.
- D-Glucose and D-mannose are **epimers** and are interconverted under strongly __________ conditions.
- The **Kiliani-Fischer synthesis** can be used to lengthen the chain of an ________.
- The **Wohl degradation** can be used to shorten the chain of an _________.
- ________________ are comprised of two monosaccharide units, joined together via a glycosidic linkage.
- **Polysaccharides** are polymers consisting of repeating monosaccharide units linked by ____________ bonds.
- When treated with an ________ in the presence of an acid catalyst, monosaccharides are converted into their corresponding **N-glycosides**.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 24. The answers appear in the section entitled *SkillBuilder Review*.

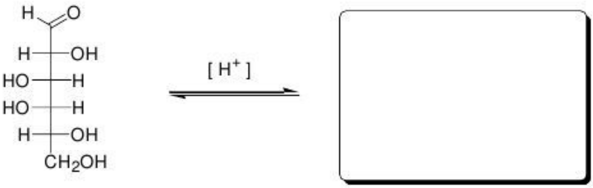
24.1 Drawing the Cyclic Hemiacetal of a Hydroxyaldehyde

DRAW THE CYCLIC HEMIACETAL THAT IS FORMED WHEN THE FOLLOWING HYDROXYALDEHYDE UNDERGOES CYCLIZATION UNDER ACIDIC CONDITIONS.



24.2: Drawing a Haworth Projection of an Aldohexose

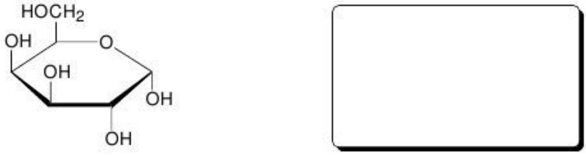
DRAW A HAWORTH PROJECTION OF α-D-GALACTOPYRANOSE.



D-GALACTOSE

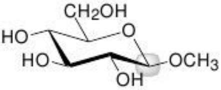
24.3: Drawing the More Stable Chair Conformation of a Pyranose Ring

DRAW THE MORE STABLE CHAIR CONFORMATION OF α-D-GALACTOPYRANOSE.



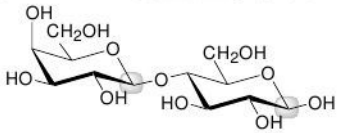
α-D-GALACTOPYRANOSE **MORE STABLE CHAIR CONFORMATION**

24.4 Identifying a Reducing Sugar

STEP 1 - *IDENTIFY THE ______________ POSITION.* 	**STEP 2 -** *DETERMINE IF THE GROUP ATTACHED TO THE ANOMERIC POSITION IS A ______________ GROUP OR ____________ GROUP.* *- IF ____________ GROUP, THEN THE COMPOUND IS A REDUCING SUGAR* *- IF ____________ GROUP, THEN THE COMPOUND IS NOT A REDUCING SUGAR.*

24.5 Determining Whether a Disaccharide Is a Reducing Sugar

***STEP 1** - IDENTIFY THE ______________ POSITIONS.*



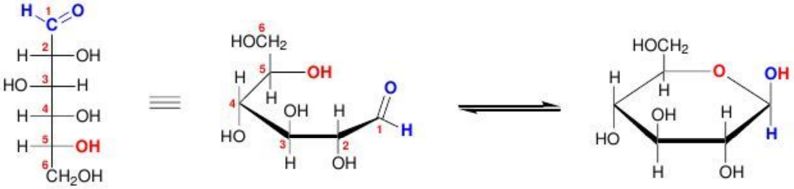
***STEP 2** - DETERMINE IF THE GROUPS ATTACHED TO THE ANOMERIC POSITIONS ARE HYDROXY GROUPS OR ALKOXY GROUPS.*

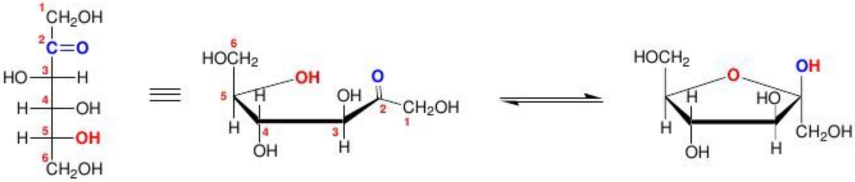
- IF ONE IS A ____________ GROUP, THEN THE COMPOUND IS A REDUCING SUGAR.
- IF NEITHER ARE _____________ GROUPS, THEN THE COMPOUND IS NOT A REDUCING SUGAR.

Review of Reactions

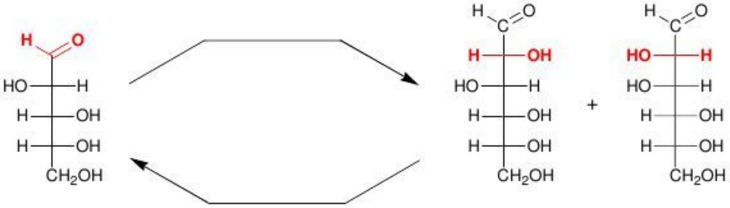
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 24. The answers appear in the section entitled *Review of Reactions*.

Hemiacetal Formation

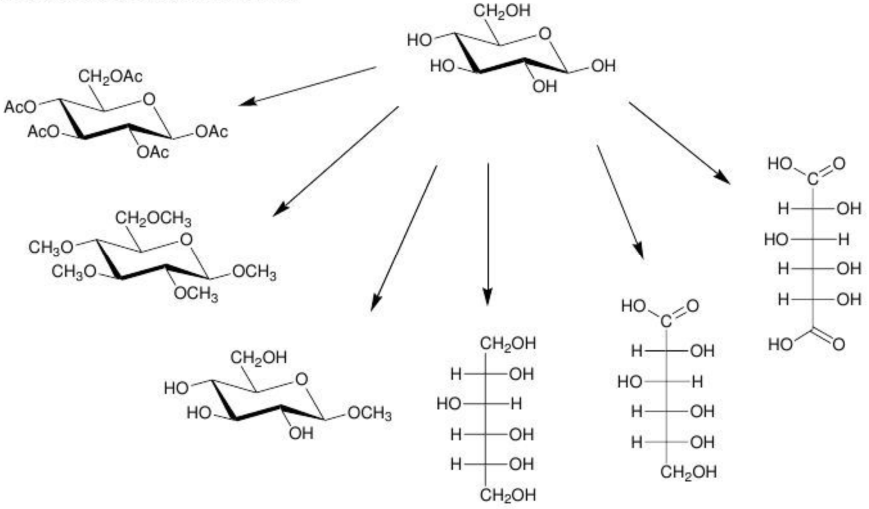




Chain Lengthening and Chain Shortening



Reactions of Monosaccharides



Solutions

24.1.

a) an aldohexose b) an aldopentose c) a ketopentose

d) an aldotetrose e) a ketohexose

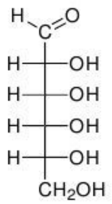
24.2. Both are hexoses so both have molecular formula ($C_6H_{12}O_6$). Although they have the same molecular formula, they have different constitution – one is an aldehyde and the other is a ketone. Therefore, they are constitutional isomers.

24.3. All are D sugars except for (b), which is an L sugar.

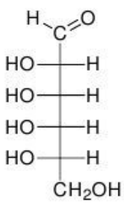
a) 2S, 3S, 4R, 5R b) 2R, 3S, 4S c) 3R, 4R d) 2S, 3R e) 3S, 4S, 5R

Pay special attention to the following trend: The configuration of each chirality center is *R* when the OH group is on the right side of the Fischer projection, and the configuration is *S* when the OH group is on the left side.

24.4.

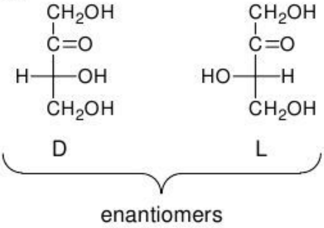


a)

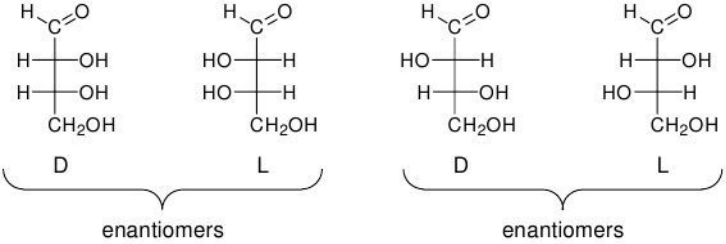


b)

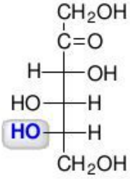
24.5.



24.6.

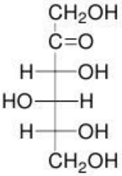


24.7.

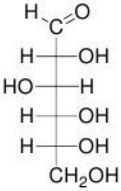


L-Fructose

24.8. D-fructose and D-glucose are constitutional isomers. Both have molecular formula ($C_6H_{12}O_6$). Although they have the same molecular formula, they have different constitution – one is a ketone, and the other is an aldehyde.

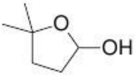


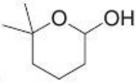
D-Fructose

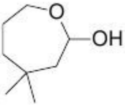


D-Glucose

24.9.

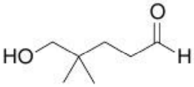
a) 

b) 

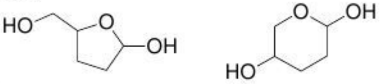
c) 

d) 

24.10.

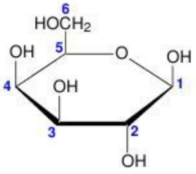


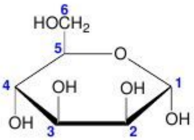
24.11.

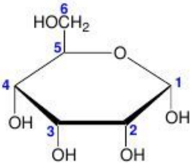
a) 

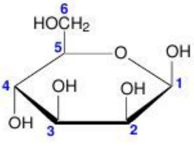
b) The six-membered ring is expected to predominate because it has less ring strain than a five-membered ring.

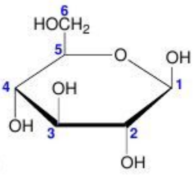
24.12.

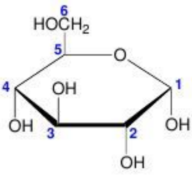
a) 

b) 

c) 

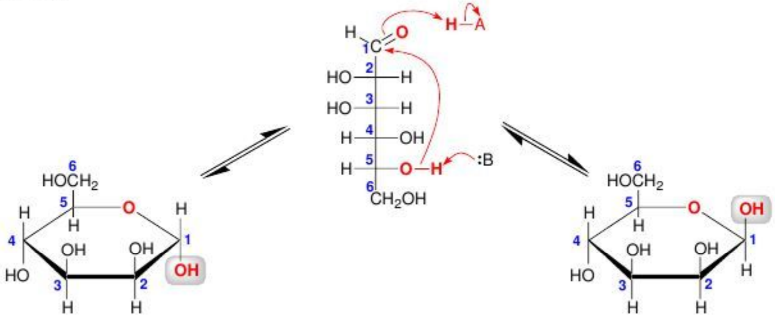
d) 

e) 

f) 

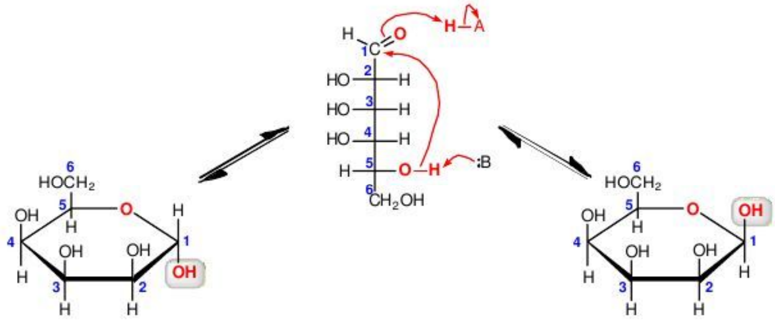
24.13. β-D-galactopyranose

24.14.



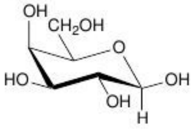
α-D-Mannopyranose *β-D-Mannopyranose*

24.15.

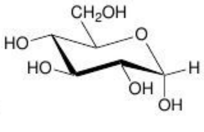


α-D-Talopyranose *β-D-Talopyranose*

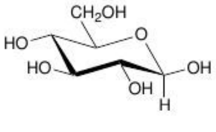
24.16.



a)

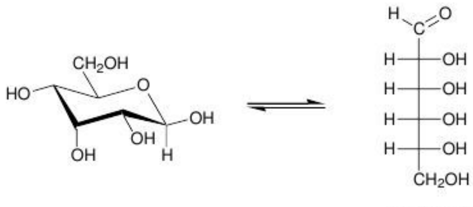


b)



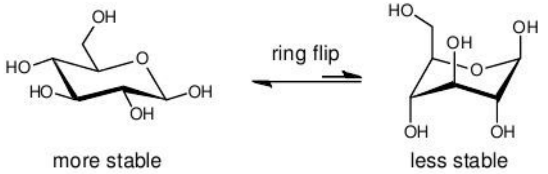
c)

24.17.

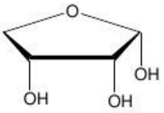


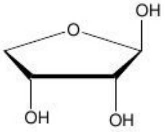
D-Allose

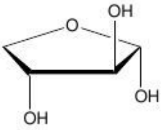
24.18.

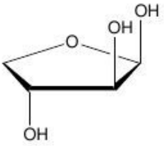


24.19.

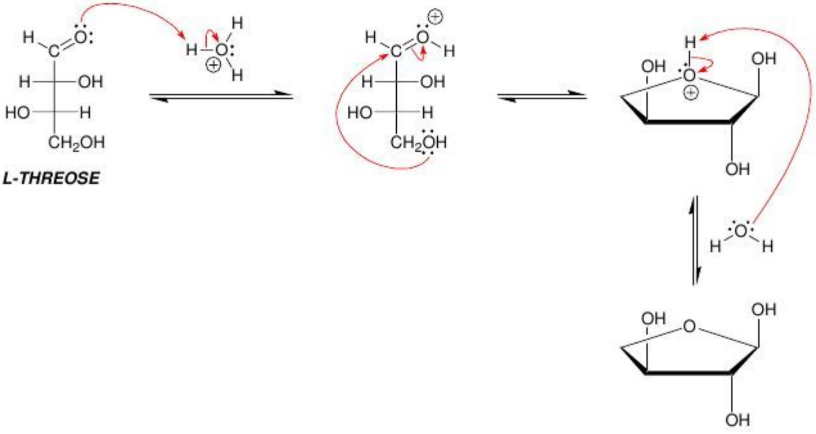
a) 

b) 

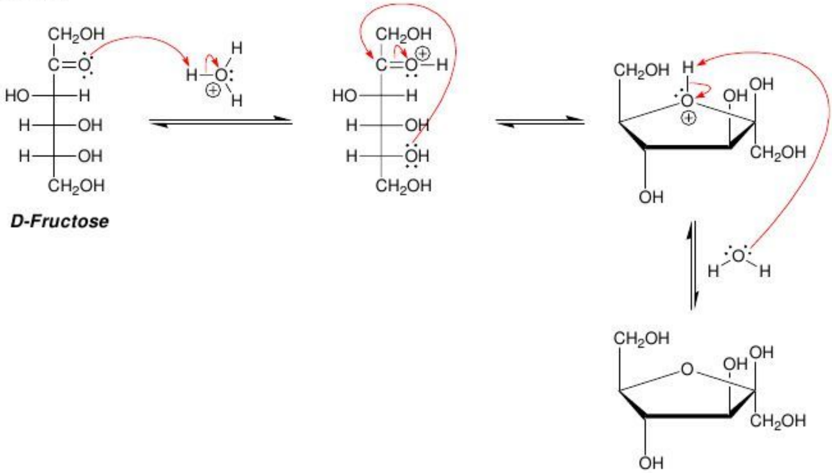
c) 

d) 

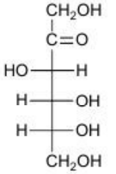
24.20.



24.21.



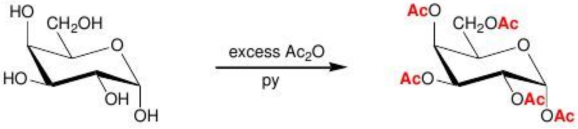
24.22.



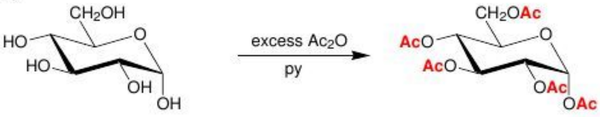
D-Fructose

24.23.

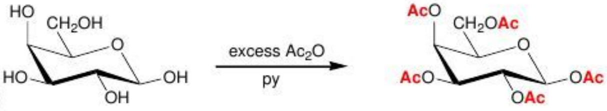
a)



b)

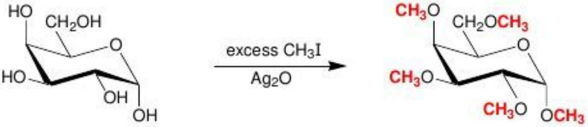


c)

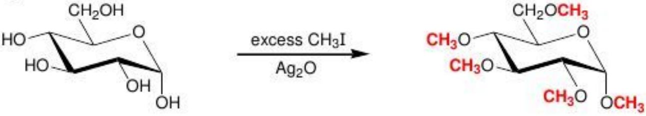


24.24.

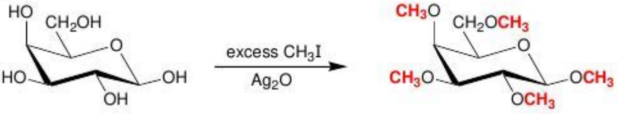
a)



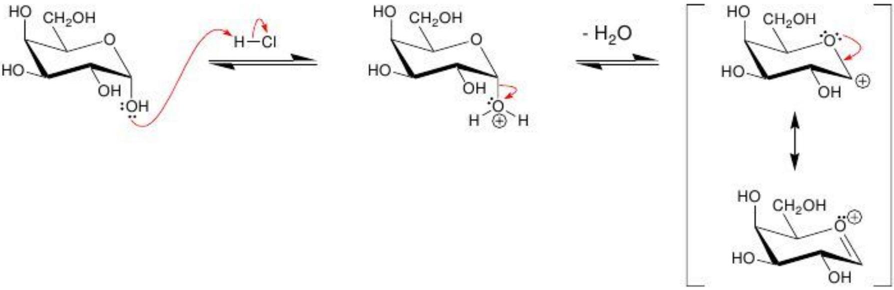
b)

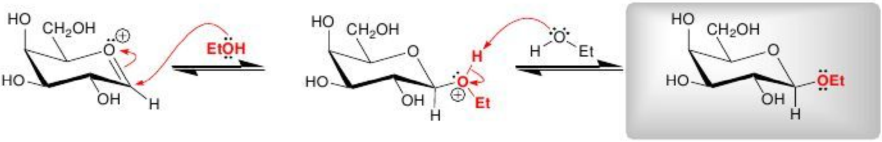


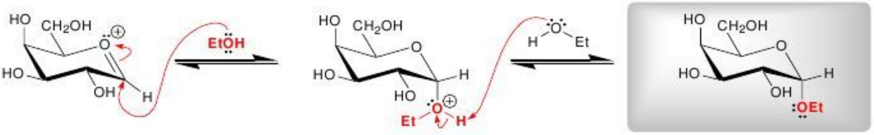
c)



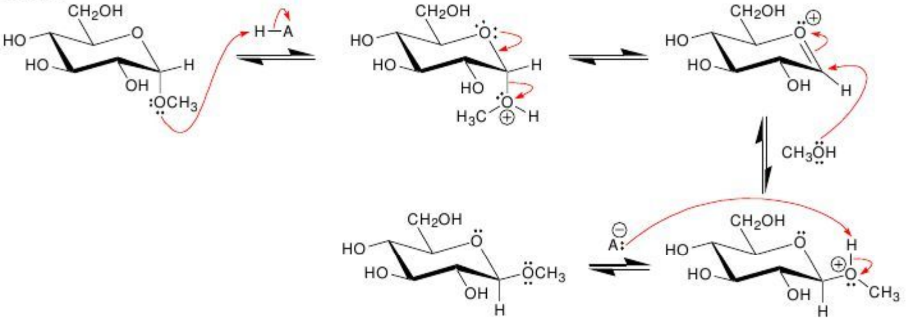
24.25.



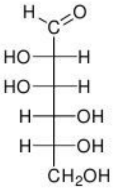




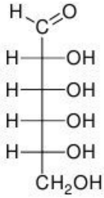
24.26.



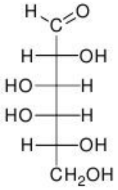
24.27.



a) ***D-Mannose***

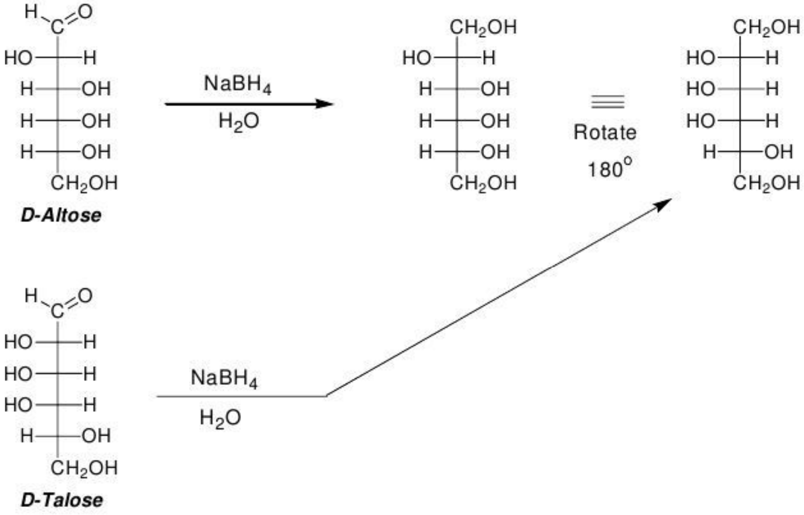


b) ***D-Allose***

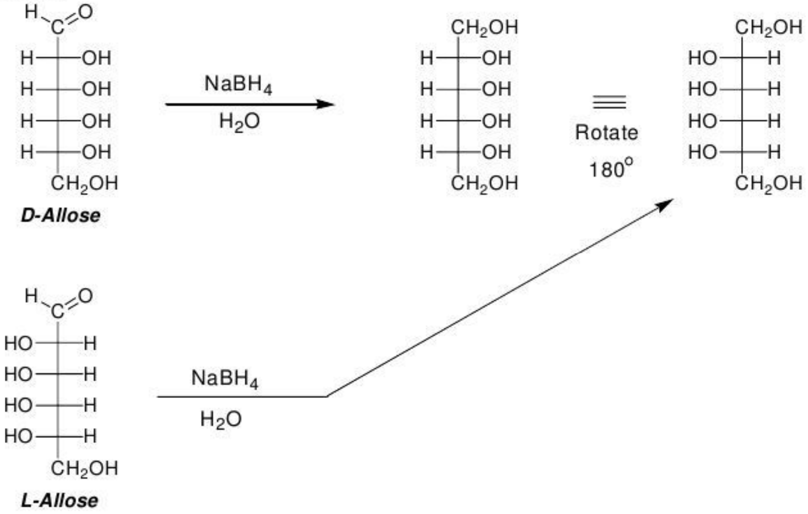


c) ***D-Galactose***

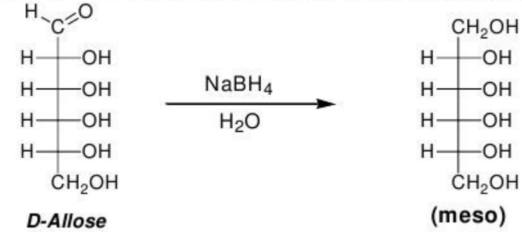
24.28.

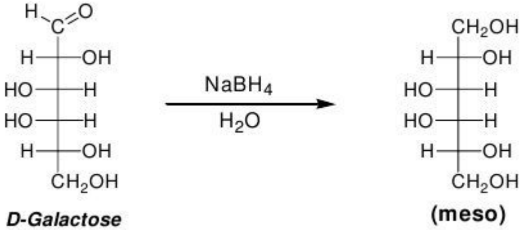


24.29.



24.30. The following alditols are meso compounds, and are therefore optically inactive:

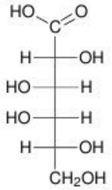




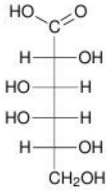
24.31.

a) No (an acetal) b) Yes c) Yes

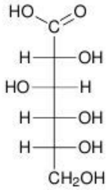
24.32.



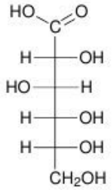
a) ***D-Galactonic acid***



b) ***D-Galactonic acid***

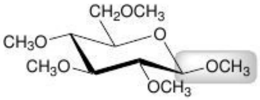


c) ***D-Gluconic acid***



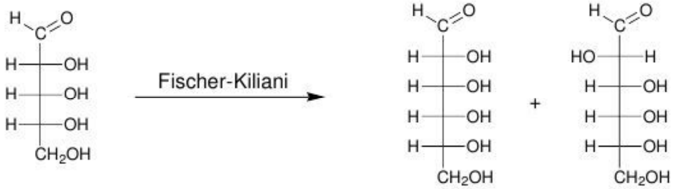
d) ***D-Gluconic acid***

24.33. This compound will not be a reducing sugar because the anomeric position is an acetal group.



β-D-Glucopyranose pentamethyl ether

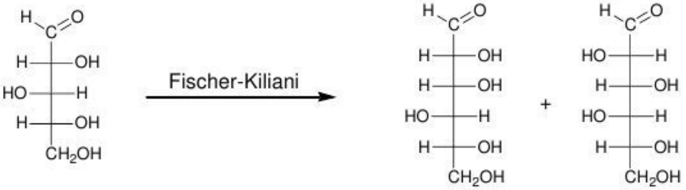
24.34.



D-Ribose

a)

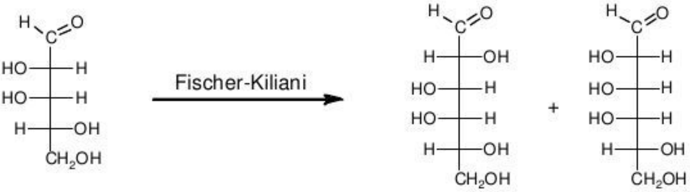
D-Allose ***D-Altose***



D-Xylose

b)

D-Gulose ***D-Idose***

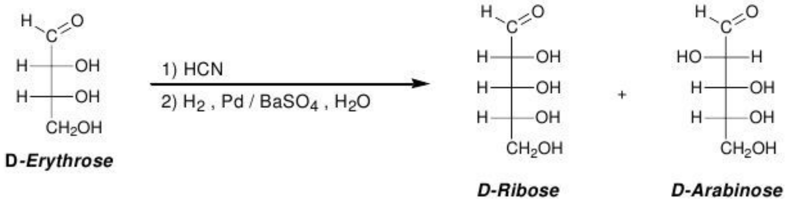


D-Lyxose

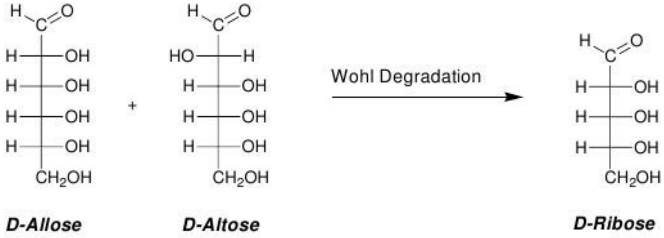
c)

D-Galactose ***D-Talose***

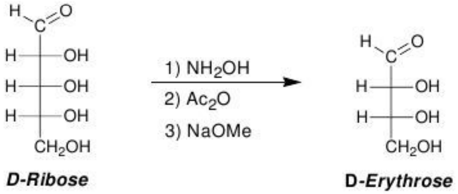
24.35.



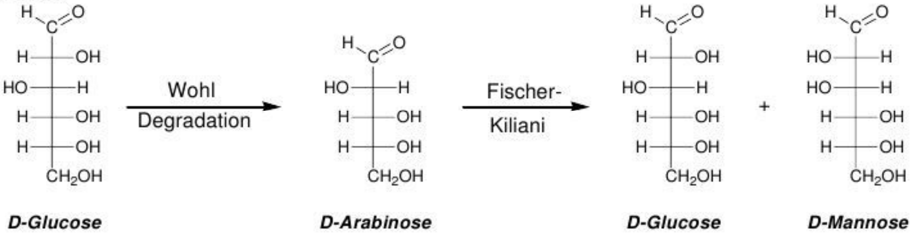
24.36.



24.37.



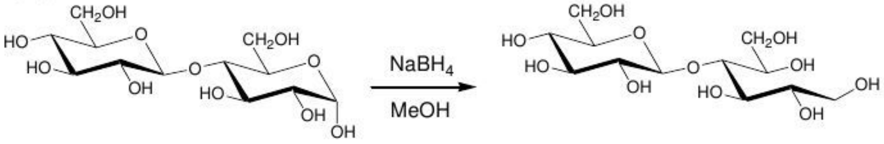
24.38.



24.39.

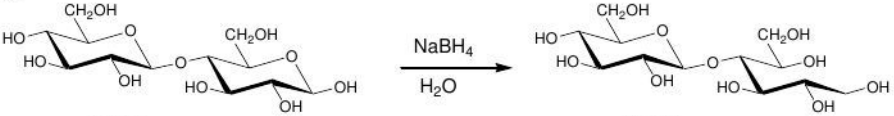
a) Yes, one of the anomeric positions bears an OH group.
b) No, both anomeric positions bear acetal groups.
c) No, both anomeric positions bear acetal groups.

24.40.

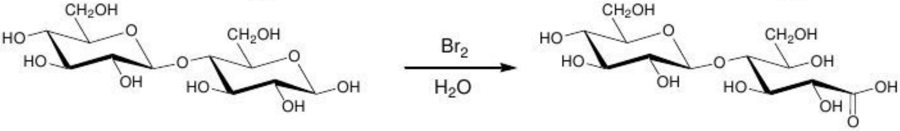


24.41.

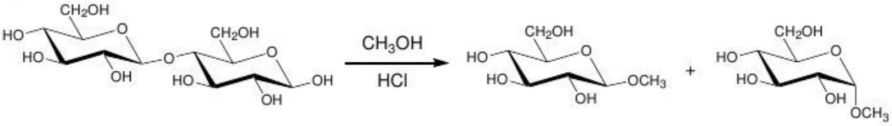
a)



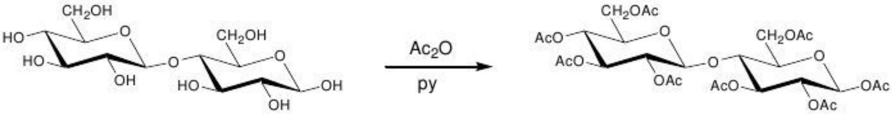
b)



c)



d)



24.42.

a) a D-aldotetrose b) an L-aldopentose c) a D-aldopentose
d) a D-aldohexose e) a D-ketopentose

24.43.

a) D-glyceraldehyde b) L-glyceraldehyde c) D-glyceraldehyde d) L-glyceraldehyde

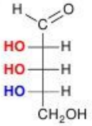
24.44.

a) D-Glucose b) D-Mannose c) D- Galactose d) L-Glucose

24.45.

a) D-Ribose

b) D-Arabinose



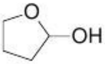
c) ***L-Ribose***

d) Same compound

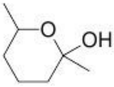
e) Diastereomers

24.46.

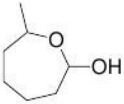
a)



b)

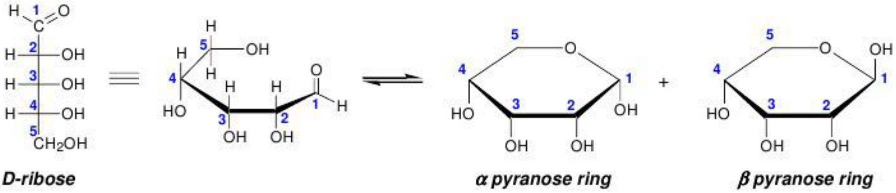


c)

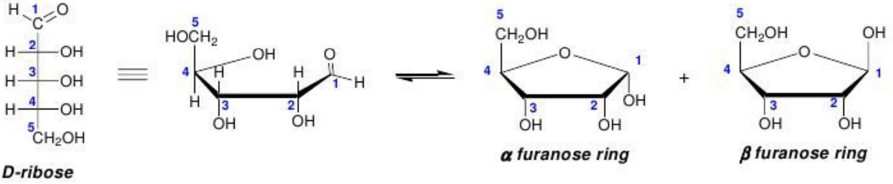


24.47.

24.48.



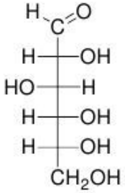
b)



24.49.

a) epimers b) diastereomers c) enantiomers d) identical compounds

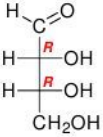
24.50.



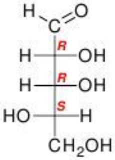
D-Glucose

24.51.

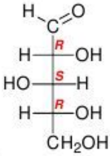
a)



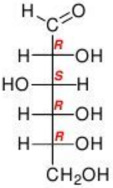
b)



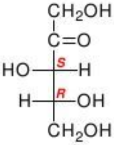
c)



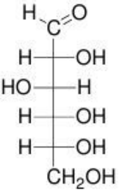
d)



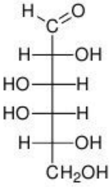
e)



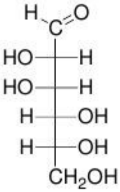
24.52.



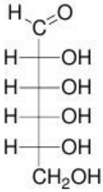
a) ***D-Glucose***



b) ***D-Galactose***



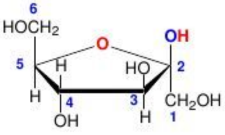
c) ***D-Mannose***



d) ***D-Allose***

24.53.

a)



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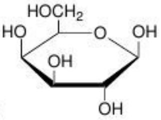
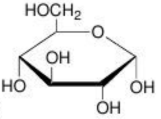
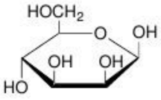


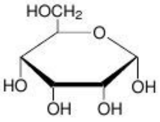
c)



d)



24.54.



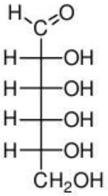
24.55.

a) α-D-allopyranose

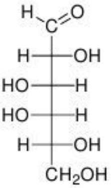
b) β-D-galactopyranose

c) methyl β-D-glucopyranoside

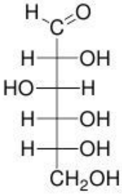
24.56.



a) ***D-Allose***

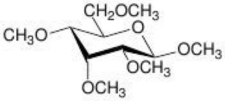


b) ***D-Galactose***

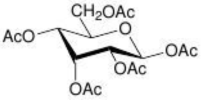


c) ***D-Glucose***

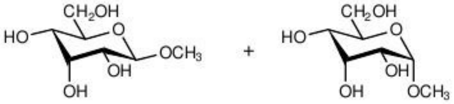
24.57.



a)

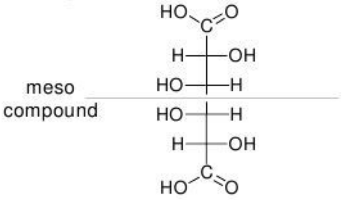


b)

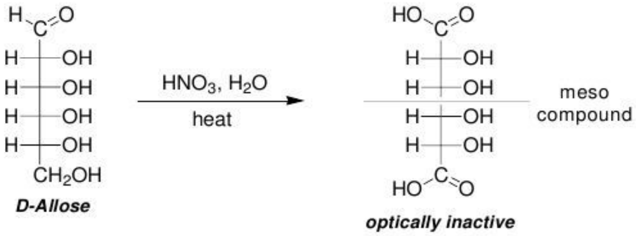


c)

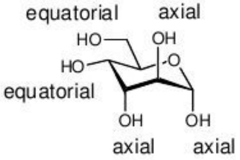
24.58. The product is a meso compound



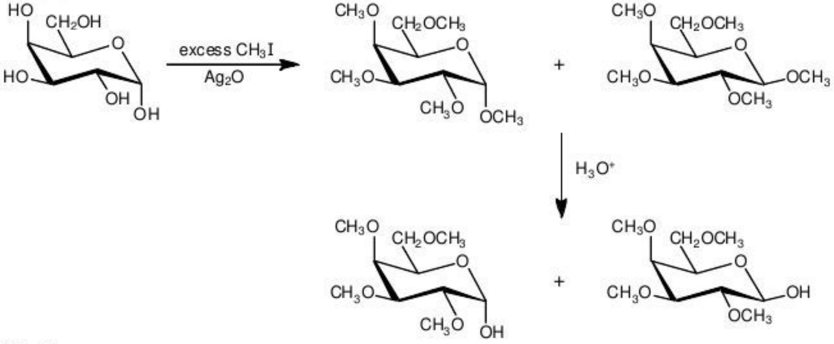
24.59.



24.60.



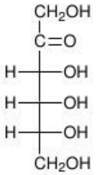
24.61.

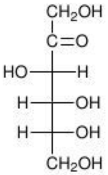


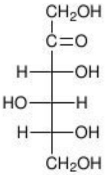
24.62.

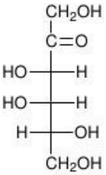
a) diastereomers
b) same compound

24.63.

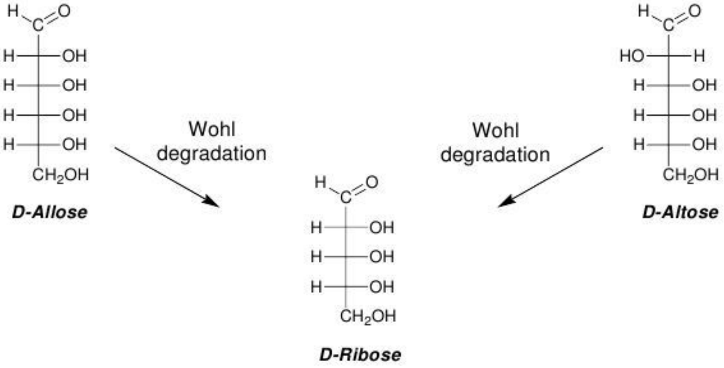




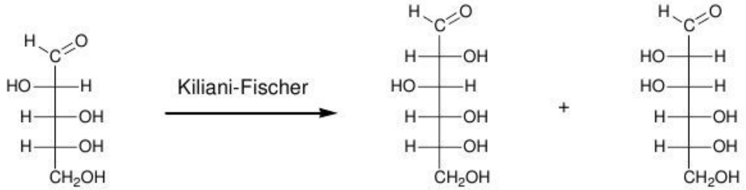




24.64.

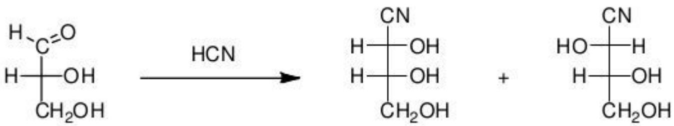


24.65.



D-Arabinose ***D-Glucose*** ***D-Mannose***

24.66.

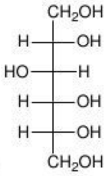


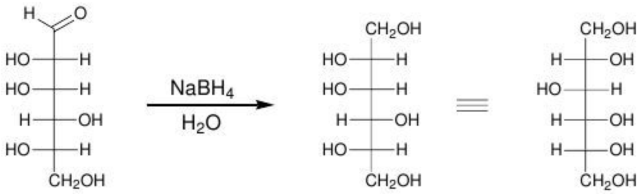
D-Glyceraldehyde

Diastereomers

24.67.

a)





b) ***L-Gulose***

24.68. D-Allose and D-Galactose

24.69.

a) This compound will not be a reducing sugar because the anomeric position is an acetal group.

b) This compound will be a reducing sugar because the anomeric position bears an OH group.

24.70.

a) CH_3OH, HCl

b) CH_3OH, HCl

c) HNO_3, H_2O, heat

d) excess CH_3I, Ag_2O followed by H_3O^+

24.71.

a) α-D-glucopyranose and β-D-glucopyranose

b) α-D-galactopyranose and β-D-galactopyranose

24.72.

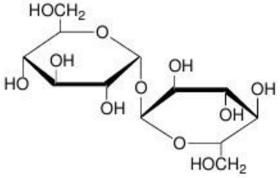
a) D-Arabinose

b) D-Ribose and D-xylose

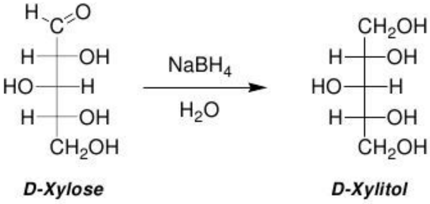
c) D-xylose

d) D-xylose

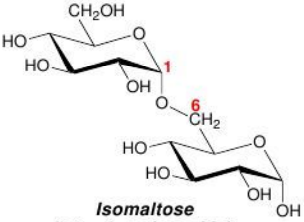
24.73.



24.74.



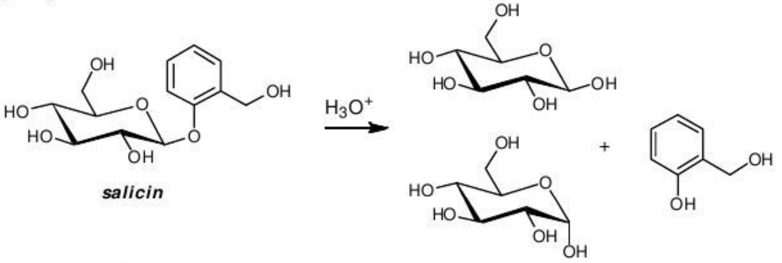
24.75.



Isomaltose
(a 1 → 6-α-glycoside)

24.76.

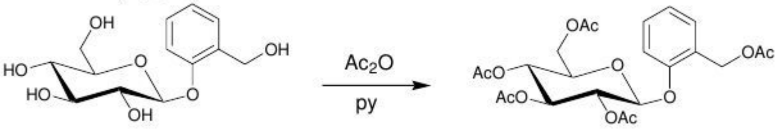
a) No, it is not a reducing sugar because the anomeric position has an acetal group.



salicin

b)

c) Salicin is a β-glycoside.

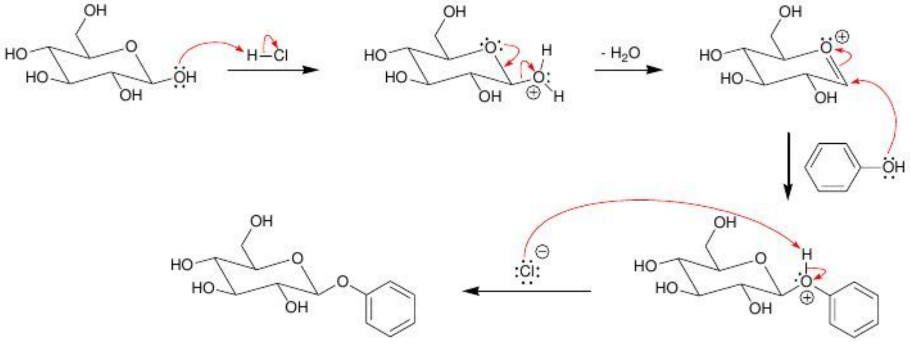


salicin

d)

e) No. In the absence of acid catalysis, the acetal group is not readily hydrolyzed.

24.77.



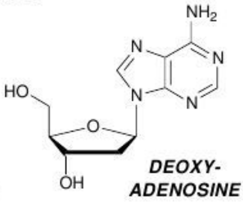
24.78.

an α-N-Glycoside

a β-N-Glycoside

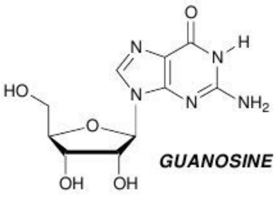
24.79.

a)



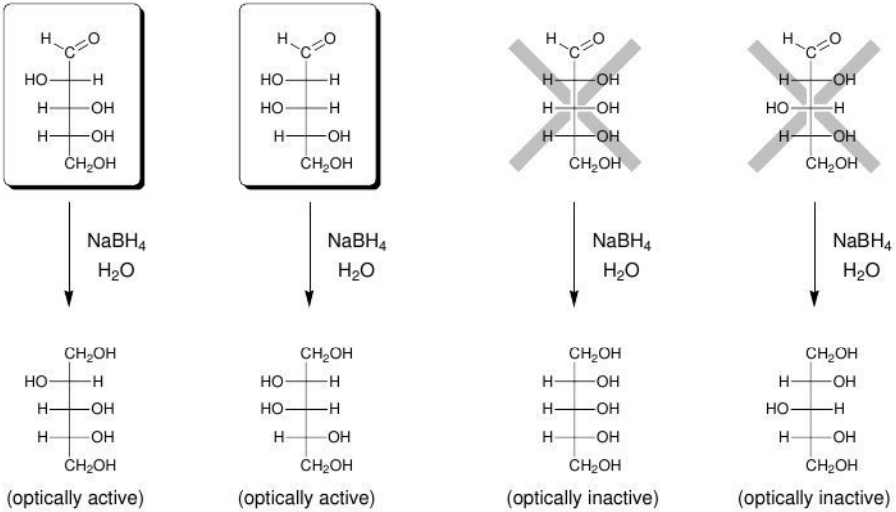
DEOXY-ADENOSINE

b)



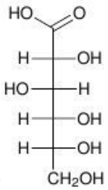
GUANOSINE

24.80.

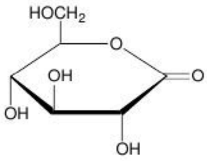


24.81.

a)



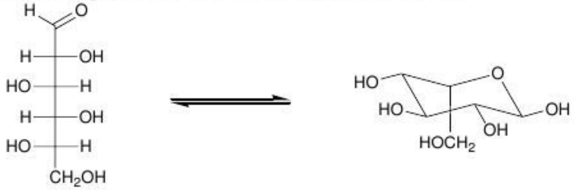
b)



c) Yes. The compound has chirality centers, and it is not a meso compound. Therefore, it will be optically active.

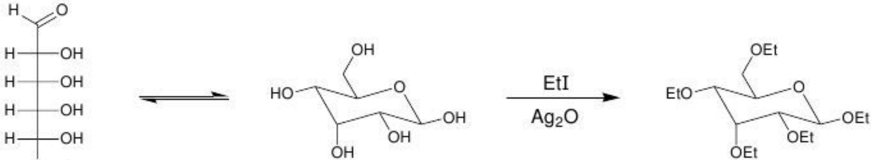
d) The gluconic acid is a carboxylic acid and its IR spectrum is expected to have a broad signal between 2500 and 3600 cm^{-1}. The IR spectrum of the lactone will not have this broad signal.

24.82. In order for the CH_2OH group to occupy an equatorial position, all of the OH groups on the ring must occupy axial positions. The combined steric hindrance of all the OH groups is more than the steric hindrance associated with one CH_2OH group. Therefore, the equilibrium will favor the form in which the CH_2OH group occupies an axial position. The structure of L-idose is:



L-Idose

24.83.

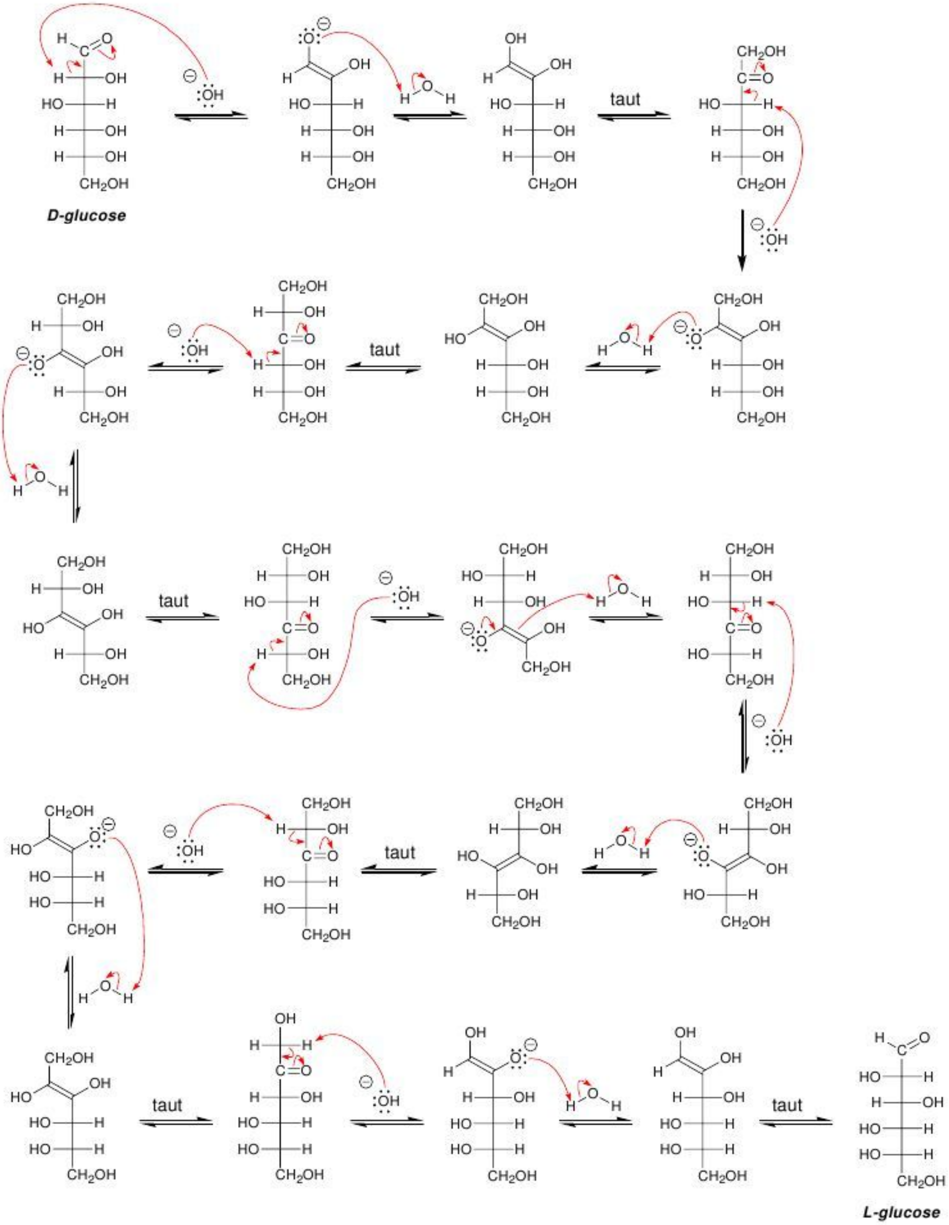


β-pyranose form

D-Allose
(Compound A)

24.84. Glucose can adopt a chair conformation in which all of the substituents on the ring occupy equatorial positions. Therefore, D-glucose can achieve a lower energy conformation than any of the other D-aldohexoses.

24.85.



24.86. Compound X is a D-aldohexose that can adopt a β-pyranose form with only one axial substituent. Recall that D-glucose has all substituents in equatorial positions, so compound X must be epimeric with D-glucose either at C2 (D-mannose), C3 (D-allose), or C4 (D-galactose).

Compound X undergoes a Wohl degradation to produce an aldopentose, which is converted into an optically active alditol when treated with sodium borohydride. Therefore, compound X cannot be D-allose, because a Wohl degradation of D-allose followed by reduction produces an optically *inactive* alditol.

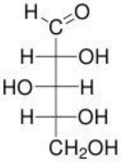
We conclude that compound X must be either D-mannose or D-galactose.

The identity of compound X can be determined by treating compound X with sodium borohohydride. Reduction of D-mannose should give an optically active alditol, while reduction of D-galactose gives an optically inactive alditol.

24.87. Compound A is a D-aldopentose. Therefore, there are four possible structures to consider (Figure 24.4).

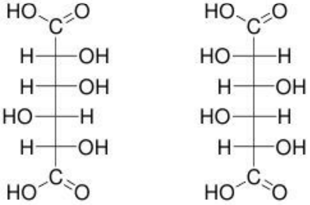
When treated with sodium borohydride, compound A is converted into an alditol that exhibits three signals in its ^{13}C NMR spectrum. Therefore, compound A must be D-ribose or D-xylose both of which are reduced to give symmetrical alditols (thus, three signals for five carbon atoms).

When compound A undergoes a Kiliani-Fischer synthesis, both products can be treated with nitric acid to give optically active aldaric acids. Therefore, compound A cannot be D-ribose, because when D-ribose undergoes a Kiliani-Fischer synthesis, one of the products is D-allose, which is oxidized to give an optically inactive aldaric acid. We conclude that the structure of compound A must be D-xylose.



a) ***D-Xylose***

b) Compound D is expected have six signals in its ^{13}C NMR spectrum, while compound E is expected to have only three signals in its ^{13}C NMR spectrum.



Compound D Compound E

Chapter 25
Amino Acids, Peptides, and Proteins

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 25. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

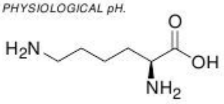
- Amino acids in which the two functional groups are separated by exactly one carbon atom are called _______ **amino acids.**
- Amino acids are coupled together by amide linkages called ____________ **bonds.**
- Relatively short chains of amino acids are called ___________.
- Only twenty amino acids are abundantly found in proteins, all of which are ___ **amino acids**, except for ____________ which lacks a chirality center.
- Amino acids exist primarily as _______________ at physiological pH
- The ___________________ of an amino acid is the pH at which the concentration of the zwitterionic form reaches its maximum value.
- Peptides are comprised of **amino acid** _________ joined by peptide bonds.
- Peptide bonds experience restricted rotation, giving rise to two possible conformations, called _______ and _______**.** The _______ conformation is more stable.
- Cysteine residues are uniquely capable of being joined to one another via ______________ **bridges.**
- ______ is commonly used to form peptide bonds.
- In the **Merrifield synthesis**, a peptide chain is assembled while tethered to ____________________________.
- The **primary structure** of a protein is the sequence of _____________________.
- The **secondary structure** of a protein refers to the _________________________ _____________________ of localized regions of the protein. Two particularly stable arrangements are the ___ **helix** and ____ **pleated sheet**.
- The **tertiary structure** of a protein refers to its ___________________________.
- Under conditions of mild heating, a protein can unfold, a process called _________________.
- **Quaternary structure** arises when a protein consists of two or more folded polypeptide chains, called _____________, that aggregate to form one protein complex.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 25. The answers appear in the section entitled *SkillBuilder Review*.

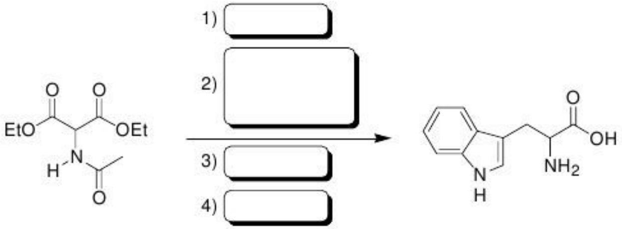
25.1 Determining the Predominant Form of an Amino Acid at a Specific pH

CONSIDER THE FOLLOWING AMINO ACID, AND DRAW THE FORM THAT PREDOMINATES AT PHYSIOLOGICAL pH.



25.2 Using the Amidomalonate Synthesis

IDENTIFY REAGENTS THAT WILL ACHIEVE THE FOLLOWING TRANSFORMATION:



25.3 Drawing a Peptide

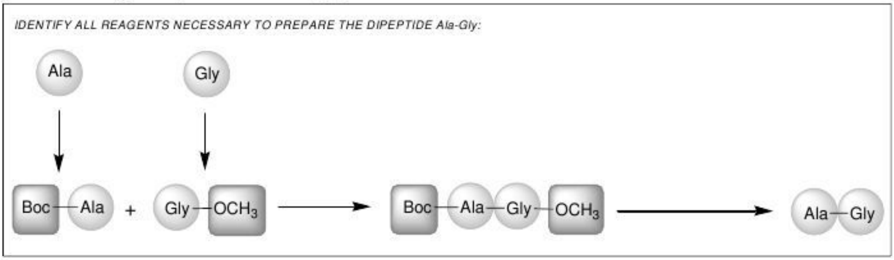
DRAW A BOND-LINE STRUCTURE FOR THE TRIPEPTIDE Phe-Val-Trp.

25.4 Sequencing a Peptide via Enzymatic Cleavage

IDENTIFY THE FRAGMENTS OBTAINED FROM ENZYMATIC CLEAVAGE OF THE FOLLOWING PEPTIDE:

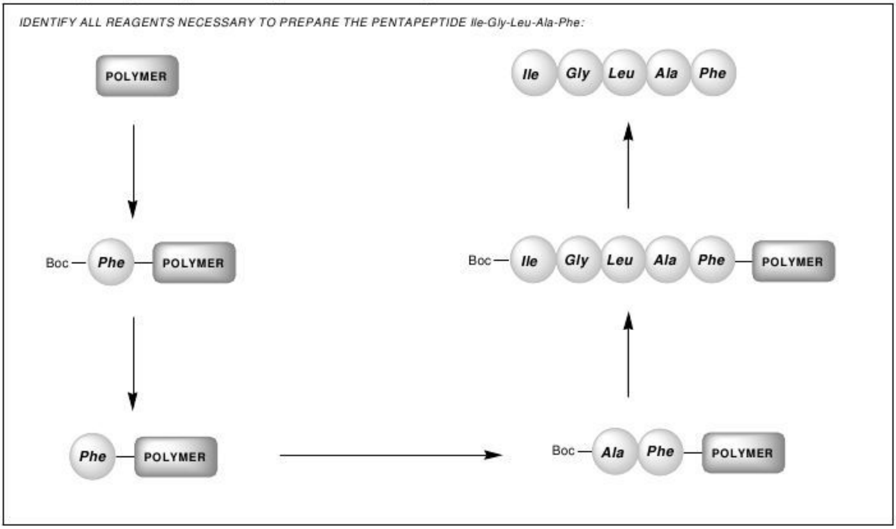
Ala-Phe-Lys-Pro-Met-Tyr-Gly-Arg-Ser-Trp-Leu-Hist

25.5 Planning the Synthesis of a Dipeptide



IDENTIFY ALL REAGENTS NECESSARY TO PREPARE THE DIPEPTIDE Ala-Gly:

25.6 Preparing a Peptide using the Merrifield Synthesis

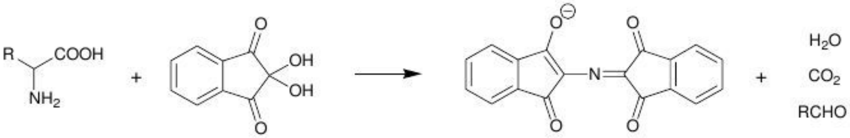


IDENTIFY ALL REAGENTS NECESSARY TO PREPARE THE PENTAPEPTIDE Ile-Gly-Leu-Ala-Phe:

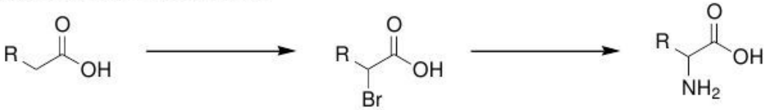
Review of Reactions

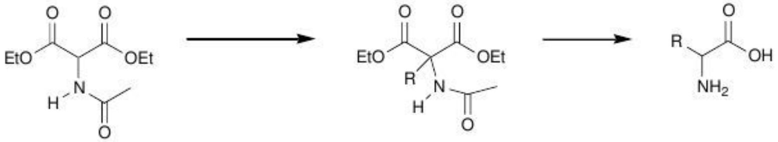
Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 25. The answers appear in the section entitled *Review of Reactions*.

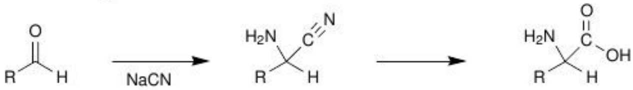
Analysis of Amino Acids

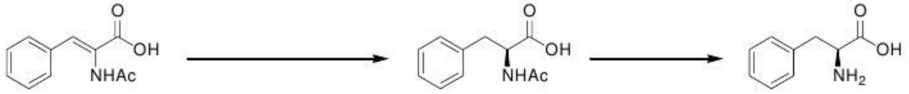


Synthesis of Amino Acids



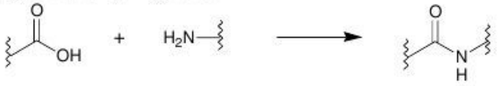


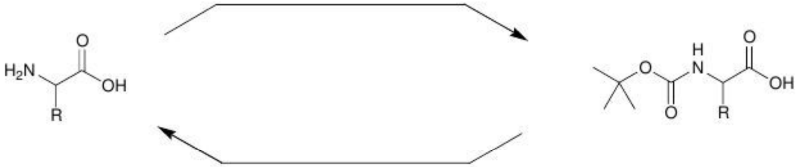


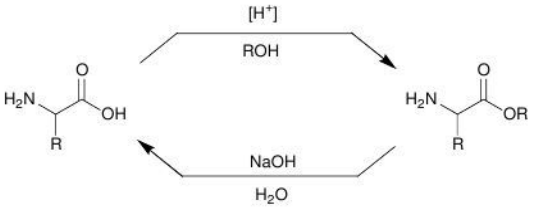


Analysis of Amino Acids

Synthesis of Peptides



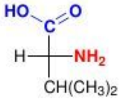




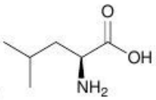
Solutions

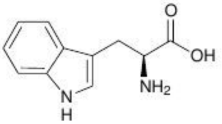
25.1. In each case, the chirality center has the *R* configuration.

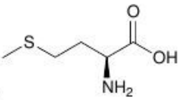

D-Alanine

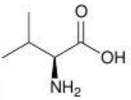

D-Valine

25.2.

a) 

b) 

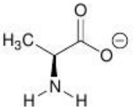
c) 

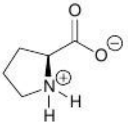
d) 

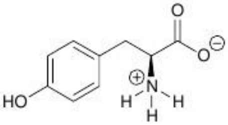
25.3.

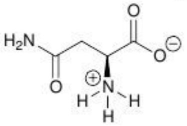
a) Pro, Phe, Trp, Tyr, and His
b) Phe, Trp, Tyr, and His
c) Arg, His, and Lys
d) Met and Cys
e) Asp and Glu
f) Pro, Trp, Asn, Gln, Ser, Thr, Tyr, Cys, Asp, Glu, Arg, His, and Lys

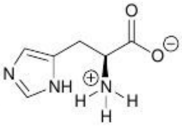
25.4.

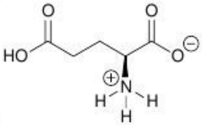
a) 

b) 

c) 

d) 

e) 

f) 

25.5. Arginine has a basic side chain, while asparagine does not. At a pH of 11, arginine exists predominantly in a form in which the side chain is protonated. Therefore, it can serve as a proton donor.

25.6. Tyrosine possesses a phenolic proton which is more readily deprotonated because deprotonation forms a resonance-stabilized phenolate ion. In contrast, deprotonation of the OH group of serine gives an alkoxide ion that is not resonance-stabilized. As a result, the OH group of tyrosine is more acidic than the OH group of serine.

25.7.

a) 2.77 b) 5.98 c) 9.74 d) 6.30

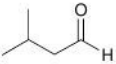
25.8.

a) aspartic acid
b) glutamic acid

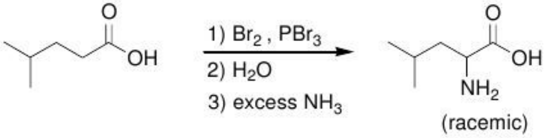
25.9. Leucine and isoleucine

25.10. The pI of Phe = 5.48, the pI of Trp = 6.11, and the pI of Leu = 6.00.
a) At pH = 6.0, Phe will travel the farthest distance.
b) At pH = 5.0, Trp will travel the farthest distance.

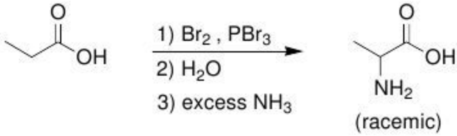
25.11.



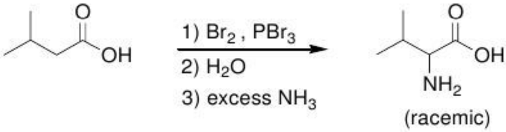
25.12.



a)

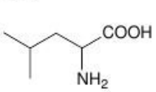


b)

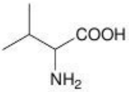


c)

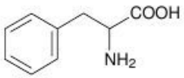
25.13.



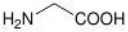
a) Leucine



b) Valine



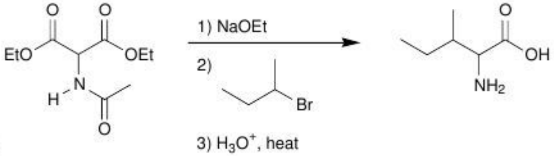
c) Phenylalanine



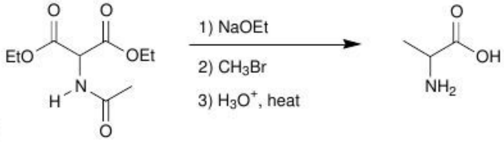
d) Glycine

25.14.

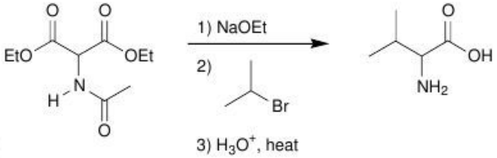
a)



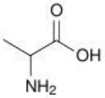
b)



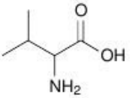
c)



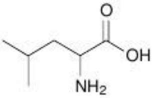
25.15.



a) **alanine**



b) **valine**

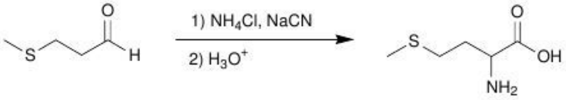


c) **leucine**

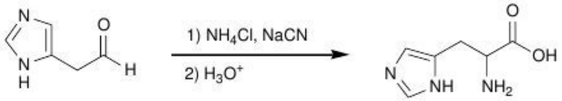
25.16. Leucine can be prepared via the amidomalonate synthesis with higher yields than isoleucine, because the former requires an S_N2 reaction with a primary alkyl halide, while the latter requires an S_N2 reaction with a secondary (more hindered) alkyl halide.

25.17.

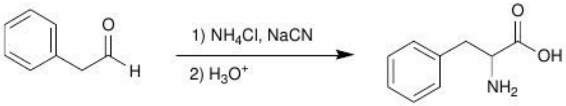
a)



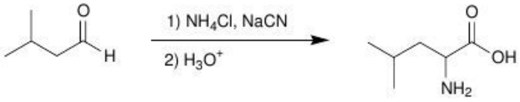
b)



c)

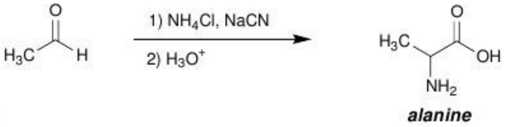


d)

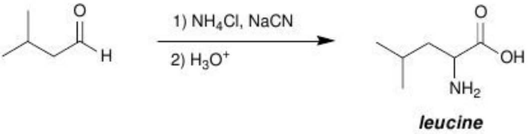


25.18.

a)



b)



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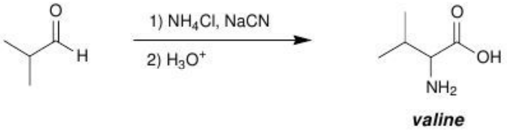
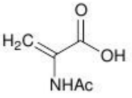


25.19.

a)



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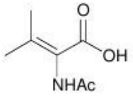

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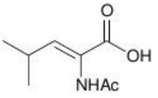
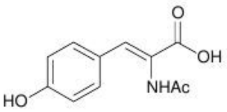


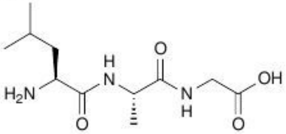
d)



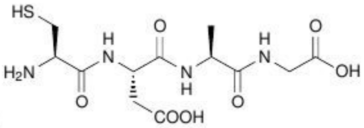
25.20. Glycine does not possess a chirality center, so the use of a chiral catalyst is unnecessary. Also, there is no alkene that would lead to glycine upon hydrogenation.

25.21.

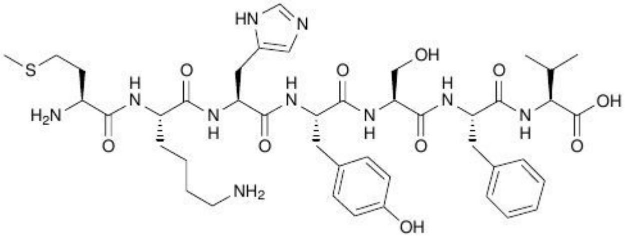
a)



b)



c)

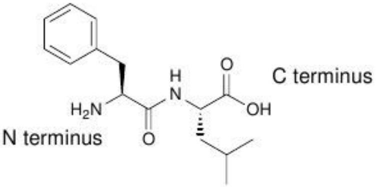


25.22. Leu-Ala-Phe-Cys-Asp or L-A-F-C-D.

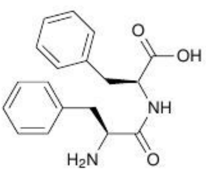
25.23. Cys-Tyr-Leu

25.24. Constitutional isomers

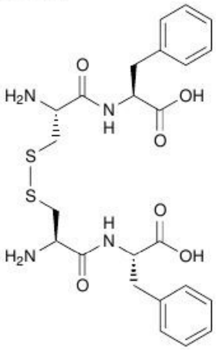
25.25.



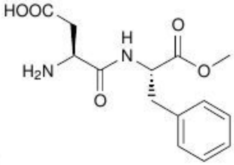
25.26. Steric hindrance results from the phenyl groups:



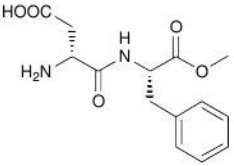
25.27.

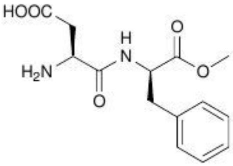


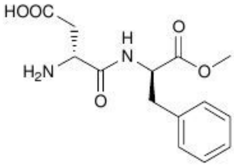
25.28.



a)

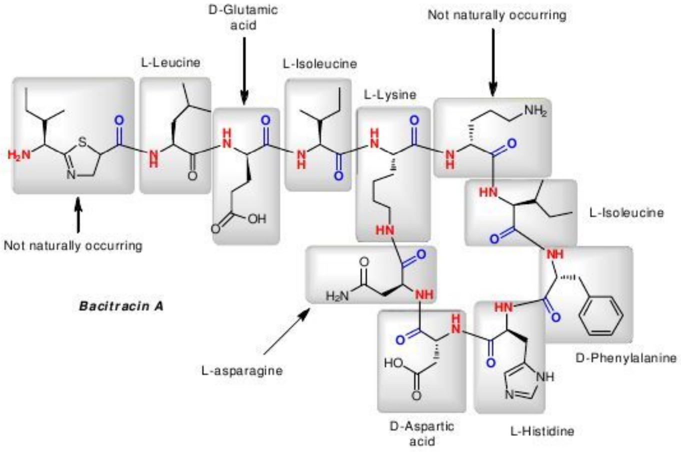




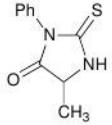


b)

25.29.



25.30. An Edman degradation will remove the amino acid residue at the N terminus, and Ala is the N terminus in Ala-Phe-Val. Therefore, alanine is removed, giving the following PTH derivative:

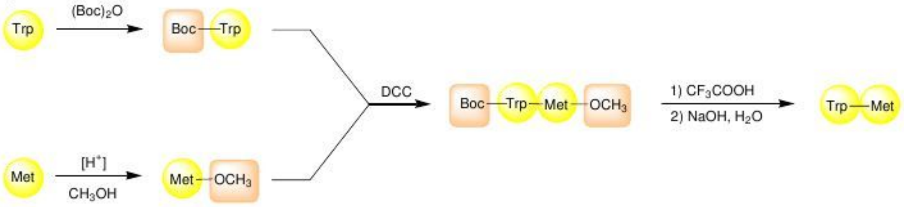


25.31.
Met-Phe-Val-Ala-Tyr-Lys-Pro-Val-Ile-Leu-Arg-Trp-His-Phe-Met-Cys-Arg-Gly-Pro-Phe-Ala-Val

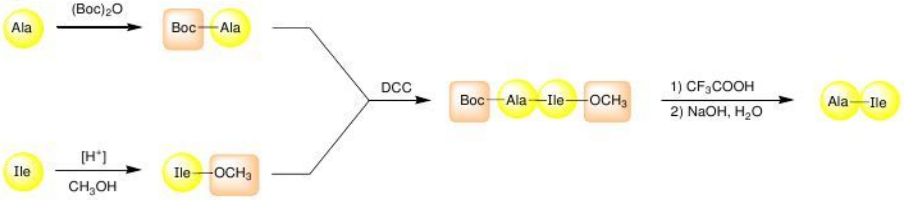
25.32. Ala-Phe-Val-Lys

25.33. Cleavage with trypsin will produce Phe-Arg, while cleavage with chymotrypsin will produce Arg-Phe. These dipeptides are not the same. They are constitutional isomers.

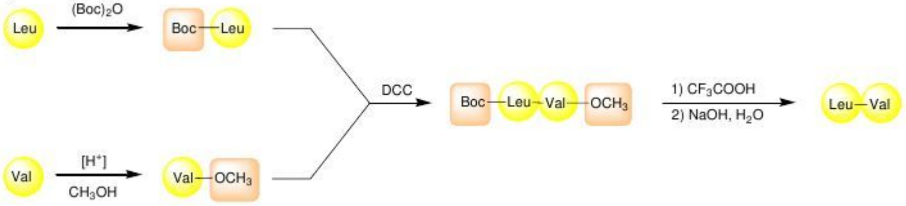
25.34.
a)



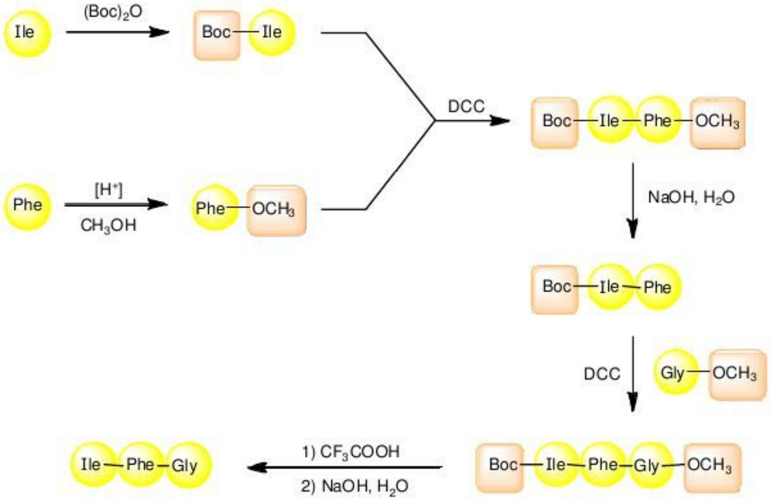
b)



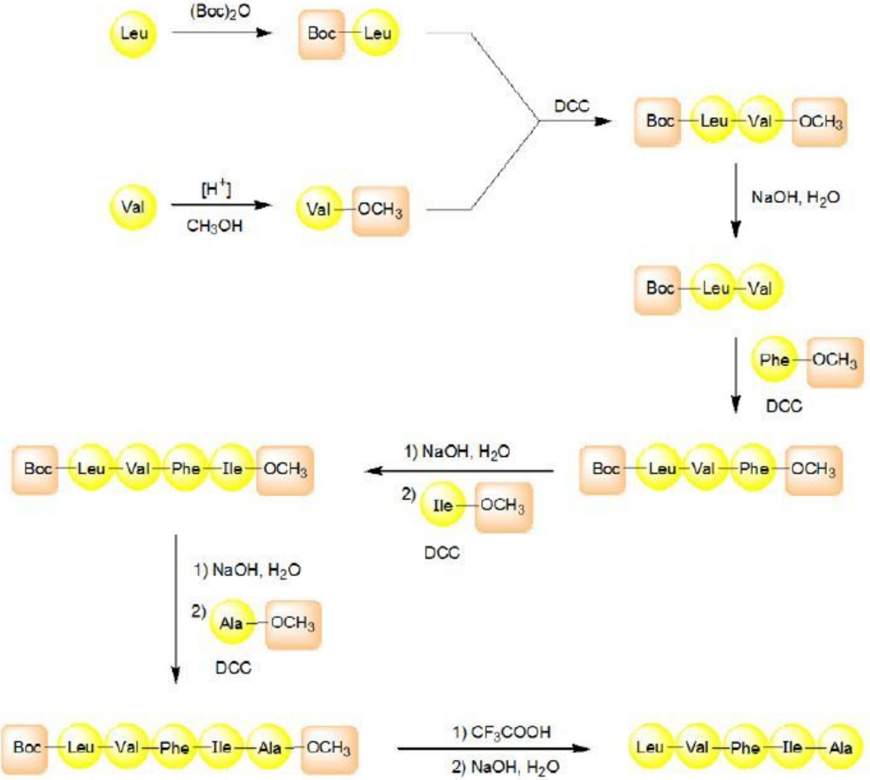
c)


Leu
$(Boc)_2O$
Boc—Leu
Val
$[H^+]$
CH_3OH
Val—OCH_3
DCC
Boc—Leu—Val—OCH_3
1) CF_3COOH
2) NaOH, H_2O
Leu—Val

25.35.

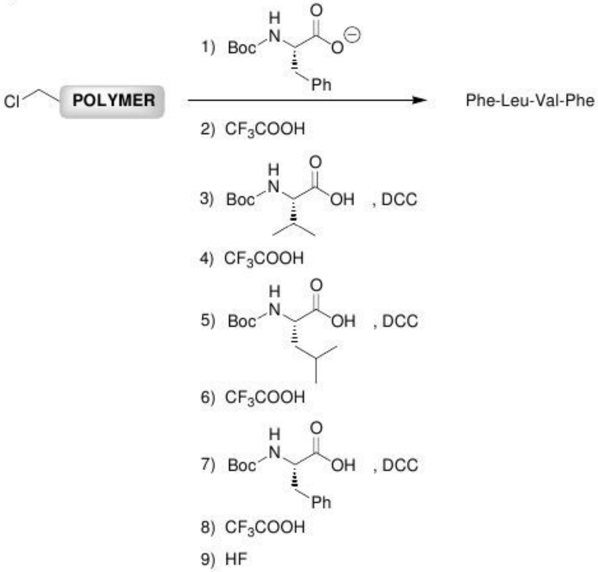

Ile
$(Boc)_2O$
Boc—Ile
Phe
$[H^+]$
CH_3OH
Phe—OCH_3
DCC
Boc—Ile—Phe—OCH_3
NaOH, H_2O
Boc—Ile—Phe
DCC
Gly—OCH_3
Boc—Ile—Phe—Gly—OCH_3
1) CF_3COOH
2) NaOH, H_2O
Ile—Phe—Gly

25.36.

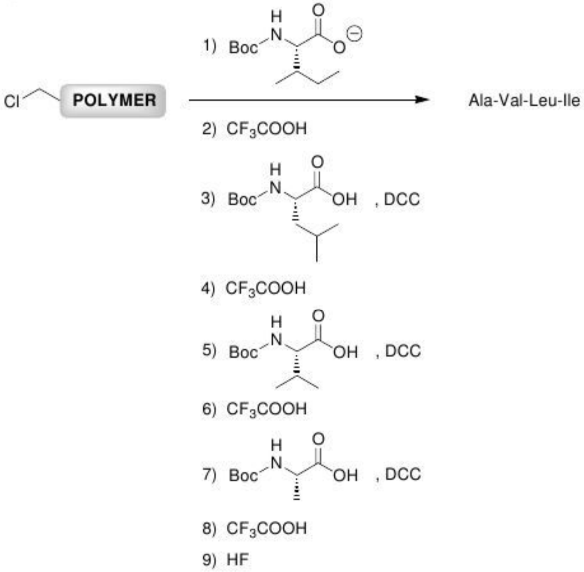

Leu
(Boc)$_2$O
Boc—Leu
Val
[H$^+$]
CH$_3$OH
Val—OCH$_3$
DCC
Boc—Leu—Val—OCH$_3$
NaOH, H$_2$O
Boc—Leu—Val
Phe—OCH$_3$
DCC
Boc—Leu—Val—Phe—OCH$_3$
1) NaOH, H$_2$O
2) Ile—OCH$_3$
DCC
Boc—Leu—Val—Phe—Ile—OCH$_3$
1) NaOH, H$_2$O
2) Ala—OCH$_3$
DCC
Boc—Leu—Val—Phe—Ile—Ala—OCH$_3$
1) CF$_3$COOH
2) NaOH, H$_2$O
Leu—Val—Phe—Ile—Ala

25.37.

a)


Cl
POLYMER
1) Boc
2) CF3COOH
3) Boc , DCC
4) CF3COOH
5) Boc , DCC
6) CF3COOH
7) Boc , DCC
8) CF3COOH
9) HF
Phe-Leu-Val-Phe

b)


Cl
POLYMER
1) Boc
2) CF3COOH
3) Boc , DCC
4) CF3COOH
5) Boc , DCC
6) CF3COOH
7) Boc , DCC
8) CF3COOH
9) HF
Ala-Val-Leu-Ile

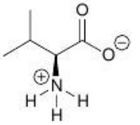
25.38. (N terminus) Val-Ala-Phe (C terminus)

25.39. The regions that contain repeating glycine and/or alanine units are the most likely regions to form β sheets:

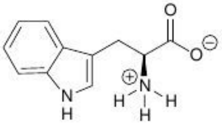
Trp-His-Pro-Ala-Gly-Gly-Ala-Val-His-Cyst-Asp-Ser-Arg-Arg-Ala-Gly-Ala-Phe

25.40.

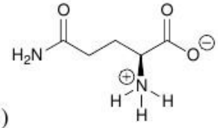
a)



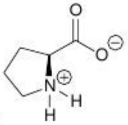
b)



c)



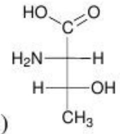
d)



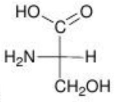
25.41. When applying the Cahn-Ingold-Prelog convention for assigning the configuration of a chirality center, the amino group generally receives the highest priority (1), followed by the carboxylic acid moiety (2), followed the side chain (3), and finally the H (4). Accordingly, the *S* configuration is assigned to L amino acids. Cysteine is the one exception because the side chain has a higher priority than the carboxylic acid moiety. As a result, the *R* configuration is assigned.

25.42.

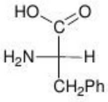
a)



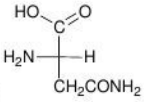
b)



c)



d)

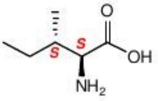


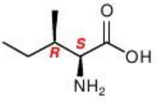
25.43.

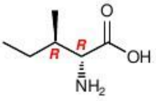
a) Isoleucine and threonine

b) Isoleucine = *2S,3S*. Threonine = *2S,3R*

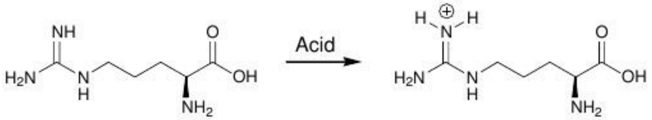
25.44.



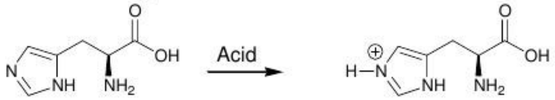




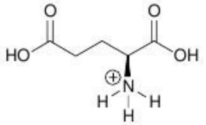
25.45. The protonated form below is highly stabilized by resonance, which spreads the positive charge over all three nitrogen atoms.

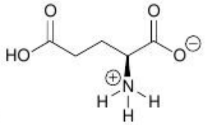


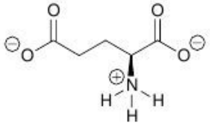
25.46. The protonated form below is aromatic. In contrast, protonation of the other nitrogen atom in the ring would result in loss of aromatic stabilization.

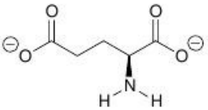


25.47.

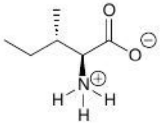

a)

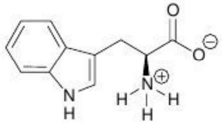

b)

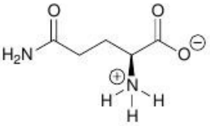

c)

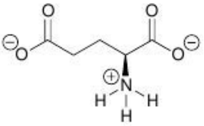

d)

25.48.


a)


b)


c)

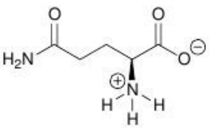

d)

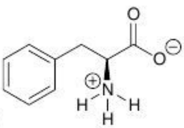
25.49.

a) 6.02 b) 5.41 c) 7.58 d) 3.22

25.50. Lysozyme is likely to be comprised primarily of amino acid residues that contain basic side chains (arginine, histindine, and lysine), while pepsin is comprised primarily of amino acid residues that contain acidic side chains (aspartic acid and glutamic acid).

25.51.


a)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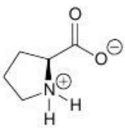
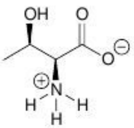
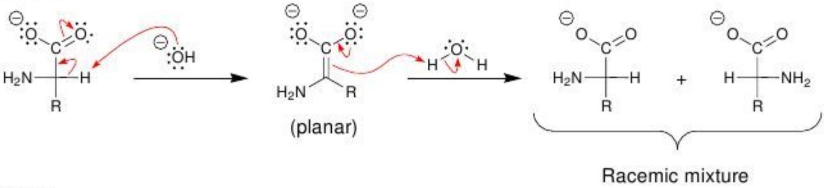

c)


d)

25.52.



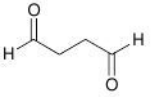
25.53.

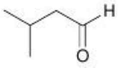
The pI of Gly = 5.97, the pI of Gln = 5.65, and the pI of Asn = 5.41.

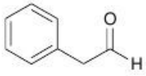
a) At pH = 6.0, Asn will travel the farthest distance.

b) At pH = 5.0, Gly will travel the farthest distance.

25.54.

a)


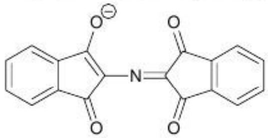
b)


c)


d) no reaction

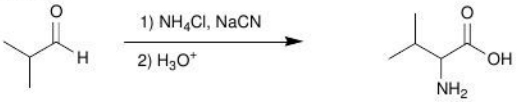
25.55.

a) Methionine, valine, and glycine.

b)


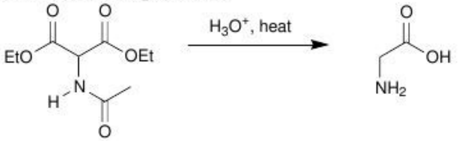
c) The compound is highly conjugated and has a λ_{max} that is greater than 400 nm (see Section 17.12)

25.56.



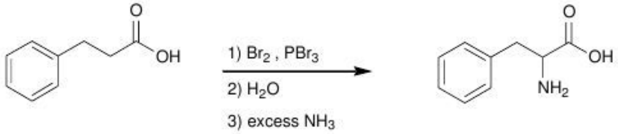
25.57. Alanine can be prepared via the amidomalonate synthesis with higher yields than valine, because the former requires an S_N2 reaction with a primary alkyl halide, while the latter requires an S_N2 reaction with a secondary (more hindered) alkyl halide.

25.58. The side chain (R) of glycine is a hydrogen atom (H). Therefore, no alkyl group needs to be installed at the α position.

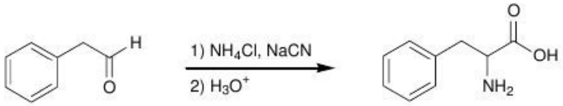


25.59.

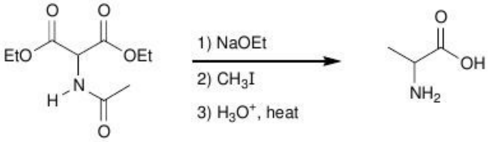
a)



b)

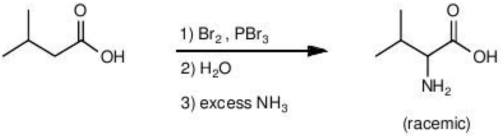


c)



25.60.

a)



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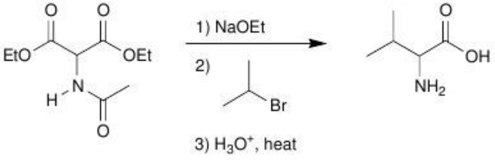
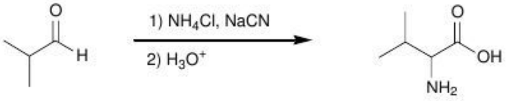
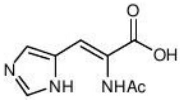


c)



25.61. $20^5 = 3{,}200{,}000$

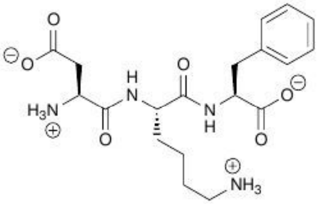
25.62.



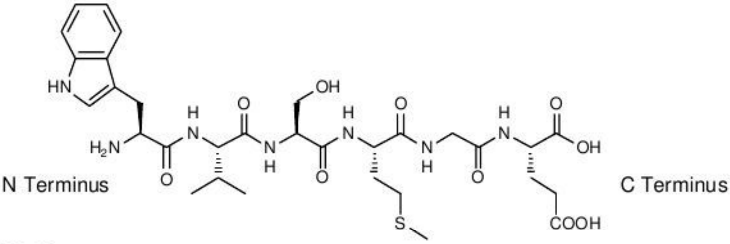
25.63.

1) Leu-Met-Val, 2) Leu-Val-Met, 3) Met-Val-Leu,
4) Met-Leu-Val, 5) Val-Met-Leu, 6) Val-Leu-Met

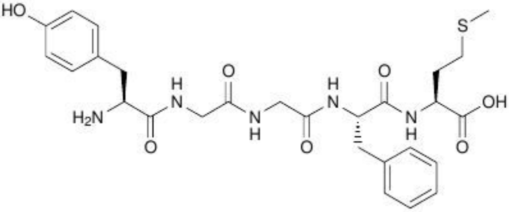
25.64.



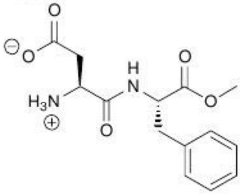
25.65.



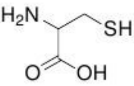
25.66.



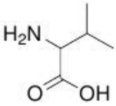
25.67.



25.68.

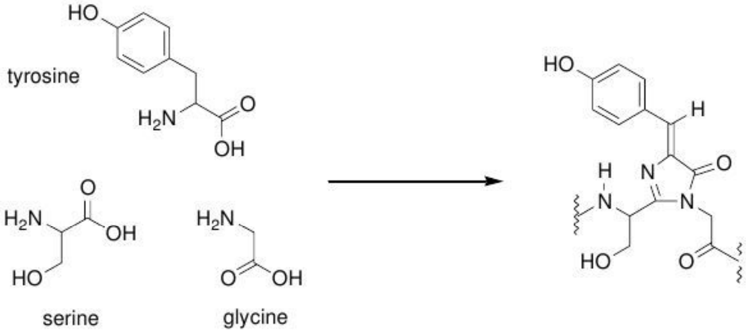


cysteine

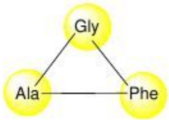


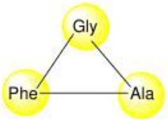
valine

25.69.



25.70. It does not react with phenyl isothiocyanate so it must not have a free N terminus. It must be a cyclic tripeptide:



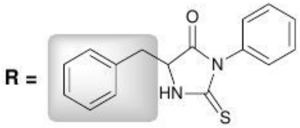


25.71.

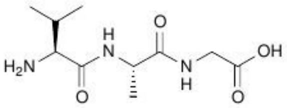
a) ***Arg*** + ***Pro-Pro-Gly-Phe-Ser-Pro-Phe-Arg***

b) ***Arg-Pro-Pro-Gly-Phe*** + ***Ser-Pro-Phe*** + ***Arg***

25.72. Phenylalanine



25.73. Val-Ala-Gly:

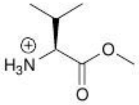


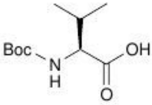
25.74. There cannot be any disulfide bridges in this peptide, because it has no cysteine residues, and only cysteine residues form disulfide bridges.

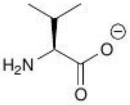
His-Ser-Gln-Gly-Thr-Phe-Thr-Ser-Asp-Tyr-Ser-Lys-Tyr-Leu-Asp-Ser-Arg-Arg-Ala-Gln-Asp-Phe-Val-Gln-Trp-Leu-Met-Asn-Thr

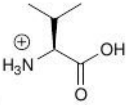
25.75. Prior to acylation, the nitrogen atom of the amino group is sufficiently nucleophilic to attack phenyl isothiocyanate. Acylation converts the amino group into an amide moiety, and the lone pair of the nitrogen atom is delocalized via resonance, rendering it much less nucleophilic.

25.76.

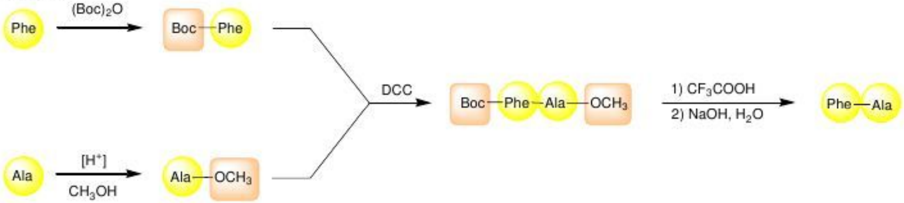
a) 

b) 

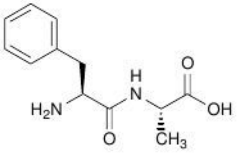
c) 

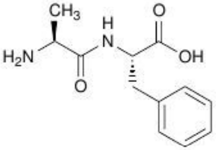
d) 

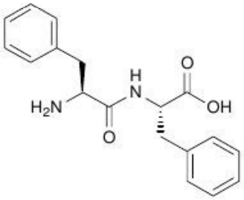
25.77.

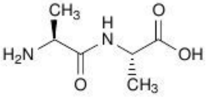


25.78.

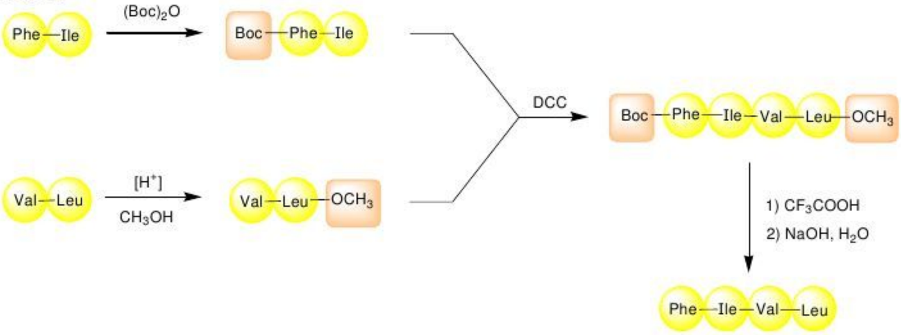




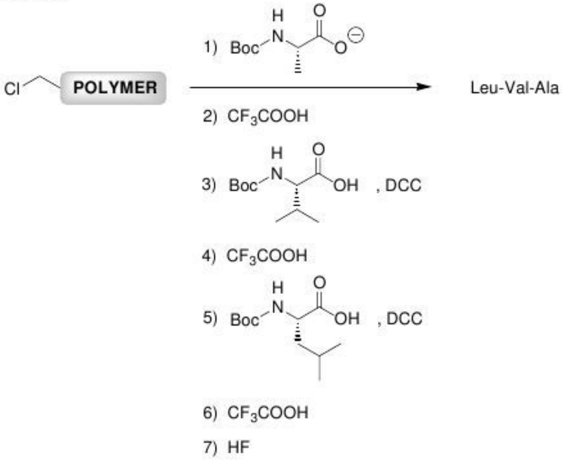




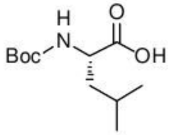
25.79.



25.80.

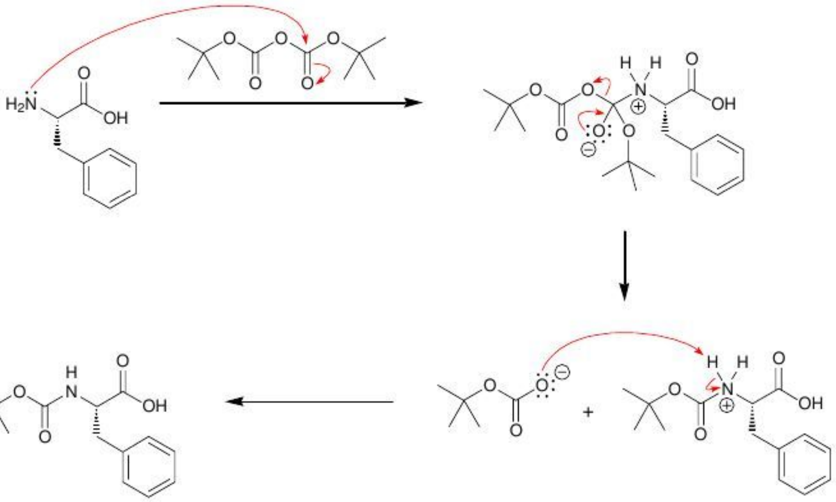


25.81.

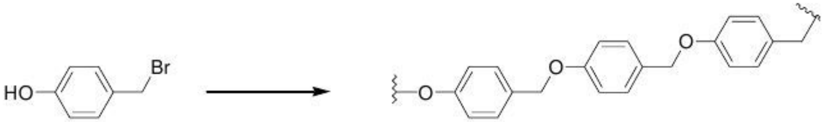


25.82. A proline residue cannot be part of an α helix, because it lacks an N-H proton and does not participate in hydrogen bonding. (The amino acid proline does indeed have an N-H group, but when incorporated into a peptide, the proline residue does not have an N-H group)

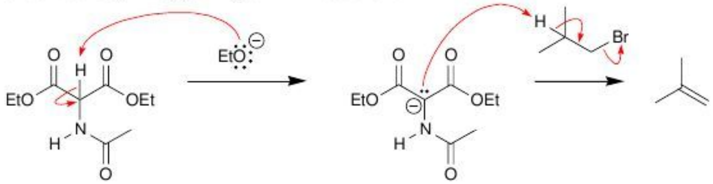
25.83.



25.84.

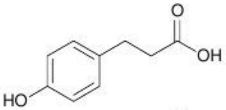


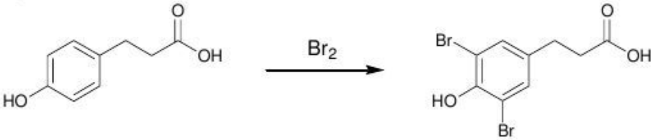
25.85. The stabilized enolate ion (formed in the first step) can function as a base, rather than a nucleophile, giving an E2 reaction:



25.86. The lone pair on that nitrogen atom is highly delocalized via resonance and is participating in aromaticity. Accordingly, the lone pair is not free to function as a base.

25.87.

a) 

b) 

25.88. At low temperature, the barrier to rotation keeps the two methyl groups in different electronic environments (one is *cis* to the C=O bond and the other is *trans* to the C=O bond), and they therefore give rise to separate signals. At high temperature, there is sufficient energy to overcome the energy barrier, and the protons change electronic environments on a timescale that is faster than the timescale of the NMR spectrometer. The result is an averaging effect which gives rise to only one signal.

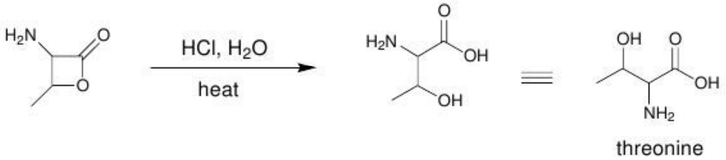
25.89.

a) The COOH group does not readily undergo nucleophilic acyl substitution because the OH group is not a good leaving group. By converting the COOH group into an activated ester, the compound can now undergo nucleophilic acyl substitution because it has a good leaving group.

b) The nitro group stabilizes the leaving group via resonance. As described in Chapter 19, the nitro group serves as a reservoir for electron density.

c) The nitro group must be in the ortho or para position in order to stabilize the negative charge via resonance. If the nitro group is in the meta position, the negative charge cannot be pushed onto the nitro group.

25.90.



Chapter 26
Lipids

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 26. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

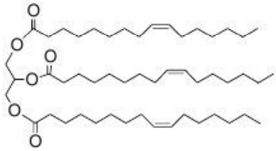
- **Lipids** are naturally occurring compounds that are extracted from cells using _______________ solvents.
- **Complex lipids** readily undergo ______________, while **simple lipids** do not.
- _________ are high molecular weight esters that are constructed from carboxylic acids and alcohols.
- ___________________ are the triesters formed from glycerol and three long-chain carboxylic acids, called **fatty acids**. The resulting triglyceride is said to contain three **fatty acid** _____________.
- For saturated fatty acids, the melting point increases with increasing __________ ____________. The presence of a _____ double bond causes a decrease in the melting point.
- Triglycerides that are solids at room temperature are called ______, while those that are liquids at room temperature are called _______.
- Triglycerides containing unsaturated fatty acid residues will undergo hydrogenation. During the hydrogenation process, some of the double bonds can isomerizes to give _______ π bonds
- In the presence of molecular oxygen, triglycerides are particularly susceptible to oxidation at the ____________ position to produce hydroperoxides.
- Transesterification of triglycerides can be achieved either via _____ catalysis or ______ catalysis to produce biodiesel.
- ________________ are similar in structure to triglycerides except that one of the three fatty acid residues is replaced by a phosphoester group.
- The structures of **steroids** are based on a tetracyclic ring system, involving three six-membered rings and one ______-membered ring.
- The ring fusions are all _______ in most steroids, giving steroids their rigid geometry.
- All steroids, including cholesterol, are biosynthesized from ____________.
- Prostaglandins contain twenty carbon atoms and are characterized by a ______-membered ring with two side chains.
- **Terpenes** are a class of naturally occurring compounds that can be thought of as being assembled from _________ units.
- A terpene with 10 carbon atoms is called a _______________, while a terpene with 20 carbon atoms is called a __________________.

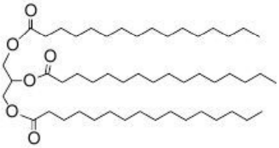
Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 26. The answers appear in the section entitled *SkillBuilder Review*.

26.1 Comparing Molecular Properties of Triglycerides

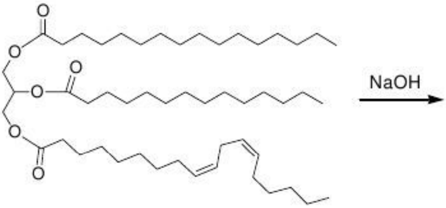
CIRCLE THE TRIGLYCERIDE BELOW THAT IS EXPECTECD TO HAVE A HIGHER MELTING POINT.





26.2 Identifying the Products of Triglyceride Hydrolysis

DRAW THE PRODUCTS OBTAINED WHEN THE FOLLOWING TRIGLYCERIDE IS TREATED WITH AQUEOUS SODIUM HYDROXIDE.



26.3 Drawing a Mechanism for Transesterification of a Triglyceride

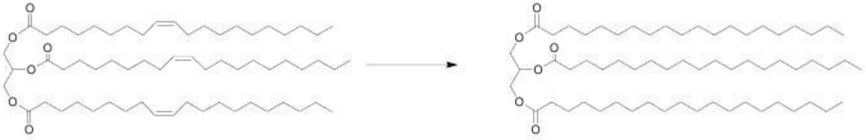
PROTON TRANSFER	**NUCLEOPHILIC ATTACK**	**PROTON TRANSFER**	**PROTON TRANSFER**	**LOSS OF A LEAVING GROUP**	**PROTON TRANSFER**
A ________ ________ IS PROTONATED	*THE ________ FUNCTIONS AS A NUCLEOPHILE AND ATTACKS THE PROTOANTED CARBONYL GROUP*	*THE RESULTING ________ INTERMEDIATE IS DEPROTOANTED, THEREBY REMOVING THE POSITIVE CHARGE*	*THE ________ ________ IS PROTONATED*	*THE ________ ________ IS REGENERATED VIA EXPULSION OF THE LEAVING GROUP*	*DEPROTONATION YIELDS THE PRODUCT*

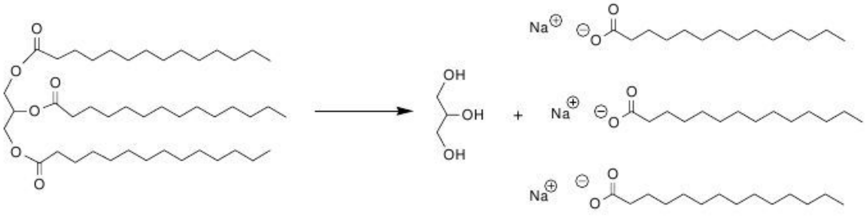
26.4 Identifying Isoprene Units in a Terpene

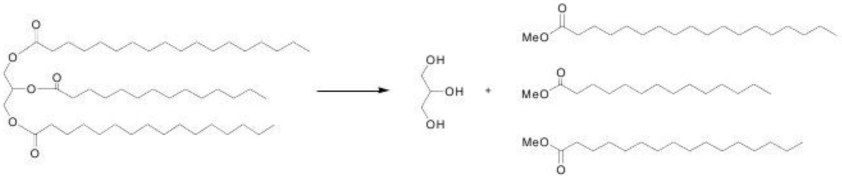
IDENTIFY THE ISOPRENE UNITS IN THE FOLLOWING TERPENE

Review of Reactions

Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 26. The answers appear in the section entitled *Review of Reactions*.



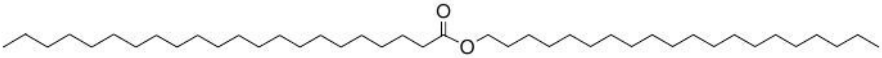




Solutions

26.1

26.2



26.3.

a) trimyristin° b) triarachadin c) triolein d) tristearin

26.4.

tripalmitolein, tripalmitin, and tristearin

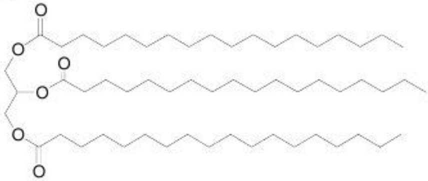
26.5. The fatty acid residues in triarachadin have more carbon atoms than the fatty acid residues in tristearin. Therefore, triarachadin is expected to have a higher melting point. It should be a solid at room temperature, and should therefore be classified as a fat, rather than an oil. Therefore, triglycerides made from lauric acid will also have a low melting point.

26.6.

a) All three fatty acid residues are saturated, with either 16 or 18 carbon atoms, so the triglyceride is expected to have a high melting point. It should be a solid at room temperature, so it is a fat.

b) All three fatty acid residues are unsaturated, so the triglyceride is expected to have a low melting point. It should be a liquid at room temperature, so it is an oil.

26.7.



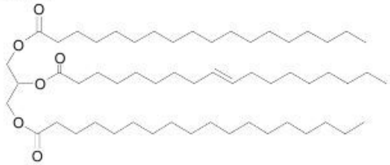
a)

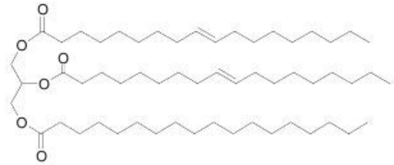
b) Tristearin

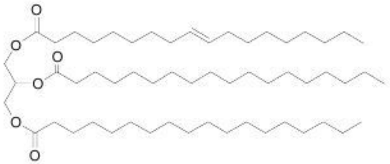
c) The melting point of tristearin is higher than triolein.

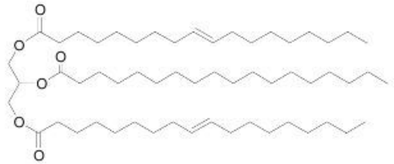
d) Stearic acid

26.8.

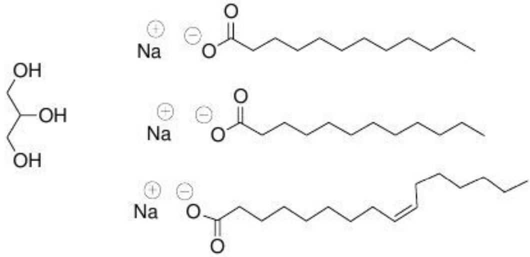




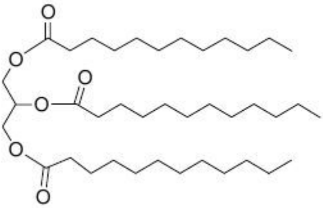




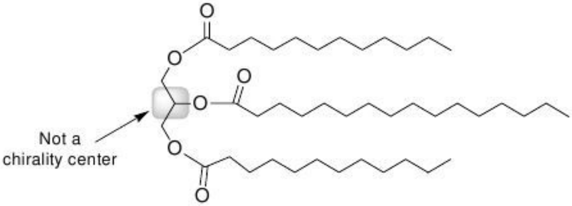
26.9.



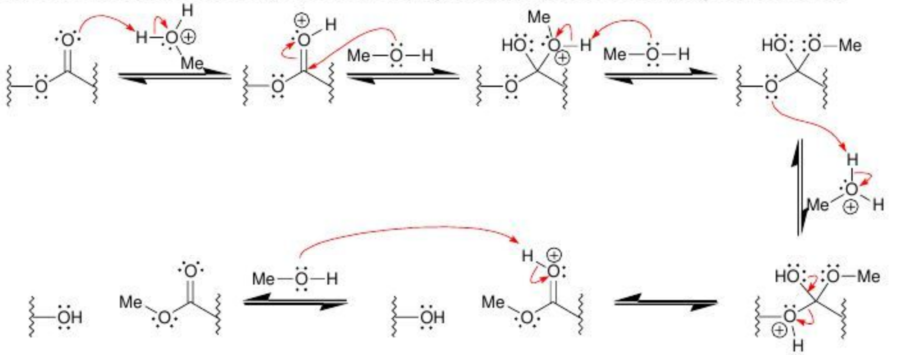
26.10.



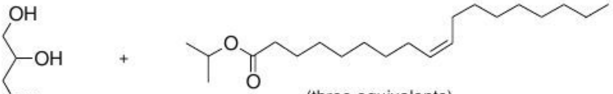
26.11



26.12. Each of the three ester moieties is hydrolyzed via the following mechanism:



26.13.



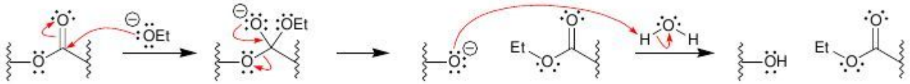
(three equivalents)

26.14.

a) Hydroxide functions as a catalyst by establishing an equilibrium in which some ethoxide ions are present.

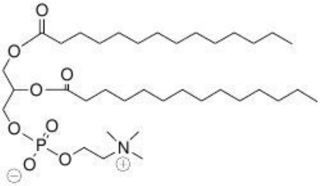
ethoxide

Then, each ester moiety undergoes transesterification via the following mechanism:

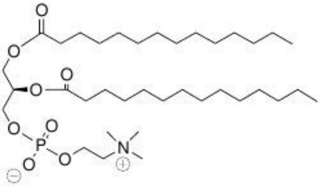


b) Hydroxide could function as a nucleophile and triglyceride would undergo hydrolysis rather than transesterification.

26.15.



a)

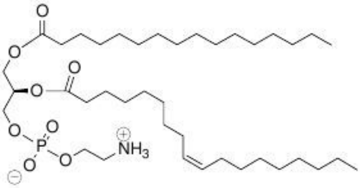


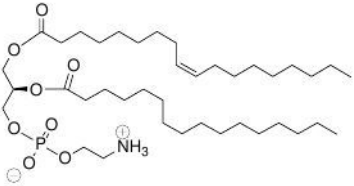
b)

c) No. The C2 position would no longer be a chirality center.

26.16.

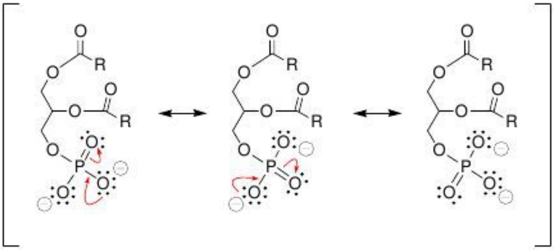
a)





b) Yes. The C2 position would still be a chirality center.

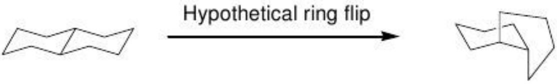
26.17.



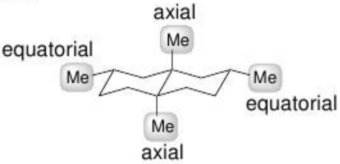
26.18. Octanol has a longer hydrophobic tail than hexanol and is therefore more efficient at crossing the nonpolar environment of the cell membrane.

26.19. No. Glycerol has three OH groups (hydrophilic) and no hydrophobic tail. It cannot cross the nonpolar environment of the cell membrane.

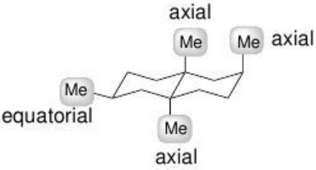
26.20. A ring-flip is not possible for *trans*-decalin because one of the rings would have to achieve a geometry that resembles a six-membered ring with a *trans*-alkene, which is not possible. The ring fusions of cholesterol all resemble the ring fusion in *trans*-decalin, so cholesterol cannot undergo ring-flipping.



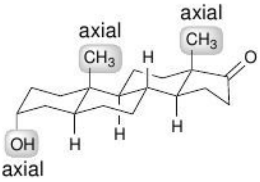
26.21.



a)

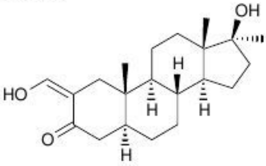


b)

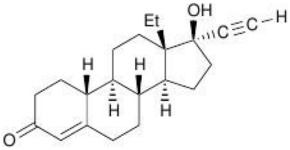


c)

26.22.

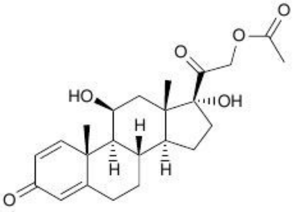


oxymetholone



norgestrel

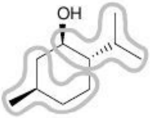
26.23.



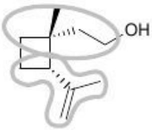
26.24.

a) PGE_1 b) $PGF_{1\alpha}$

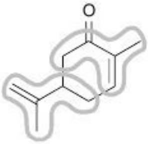
26.25.



a) ***menthol***



b) ***grandisol***

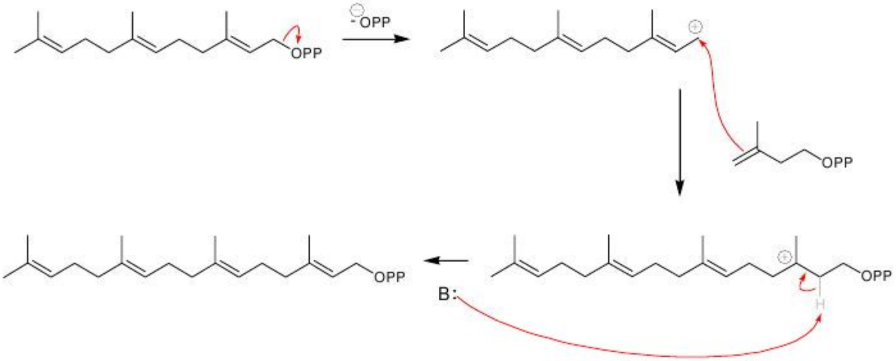


c) ***carvone***

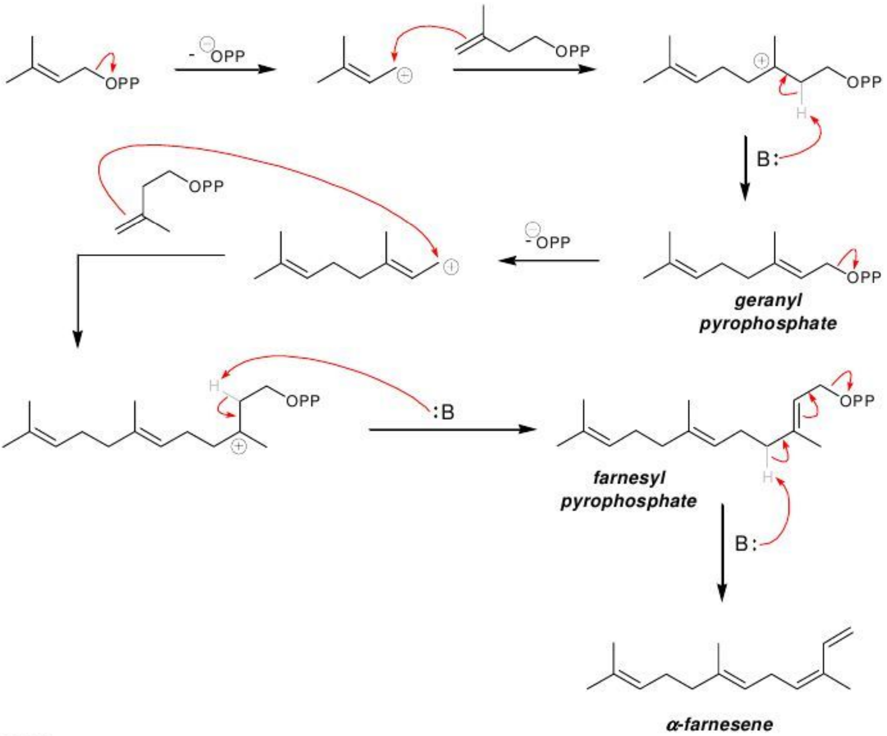
26.26.

a) Yes, it has 10 carbon atoms, which are comprised by the joining of two isoprene units.
b) No, it has 11 carbon atoms.
c) No, it has 11 carbon atoms.
d) No. It has 10 carbon atoms, but the branching pattern cannot be achieved by joining two isoprene units.

26.27.



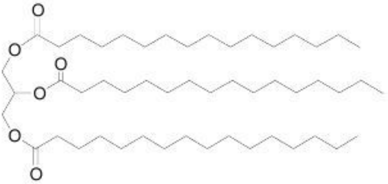
26.28.



26.29.

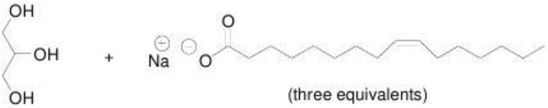
a) steroid
b) terpene
c) triglyceride
d) phospholipid
e) prostaglandin
f) wax

26.30.

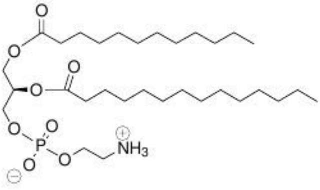


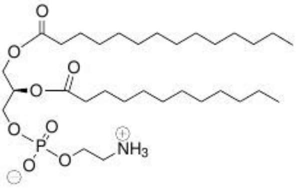
a)

b)

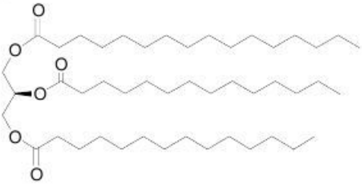


26.31. Both compounds are chiral:





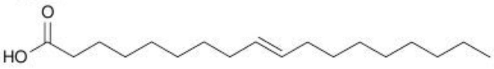
26.32. The fatty acid residues in this triglyceride are saturated, and will not react with molecular hydrogen.



26.33.

a) not a lipid
b) a lipid
c) a lipid
d) a lipid
e) a lipid
f) not a lipid
g) a lipid
h) not a lipid

26.34.



26.35. The fatty acid residues of tristearin are saturated and are therefore less susceptible to auto-oxidation than the unsaturated fatty acid residues in triolein.

26.36. a < b < c

26.37. Water would not be appropriate because it is a polar solvent, and terpenes are nonpolar compounds. Hexane is a nonpolar solvent and would be suitable.

26.38.

a) saturated
b) saturated
c) unsaturated
d) saturated
e) unsaturated
f) unsaturated

26.39. Arachidonic acid

26.40.

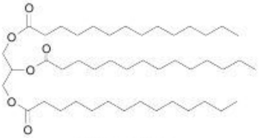
a) No. It is an oil.
b) No. It is reactive towards molecular hydrogen in the presence of Ni.
c) Yes. It undergoes hydrolysis to produce unsaturated fatty acids.
d) Yes. It is a complex lipid because it undergoes hydrolysis.
e) No. It is not a wax.
f) No. It does not have a phosphate group.

26.41.

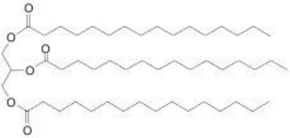
a) Yes. It is a fat.
b) Yes. It is unreactive towards molecular hydrogen in the presence of Ni.
c) No. It undergoes hydrolysis to produce fatty acids that are saturated.
d) Yes. It is a complex lipid because it undergoes hydrolysis.
e) No. It is not a wax.
f) No. It does not have a phosphate group.

26.42.

26.43. Trimyristin is expected to have a lower melting point than tripalmitin because the former is comprised of fatty acid residues with fewer carbon atoms (14 instead of 16).

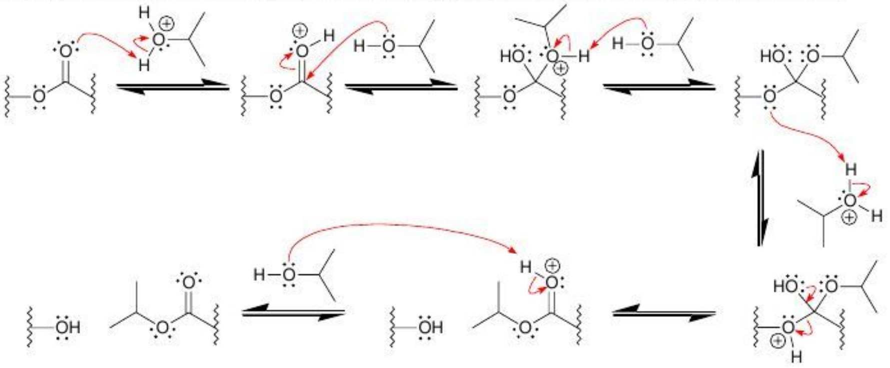


trimyristin



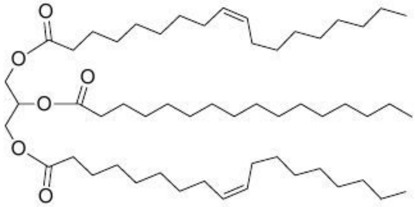
tripalmitin

26.44. Each of the three ester moieties is hydrolyzed via the following mechanism:

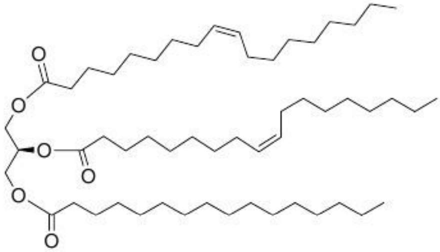


26.45. See the solution to Problem 26.14.

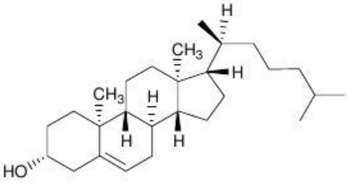
26.46.



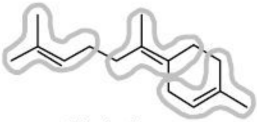
26.47.



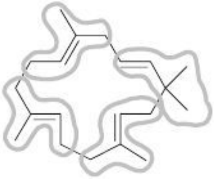
26.48.



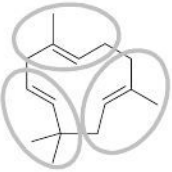
26.49.



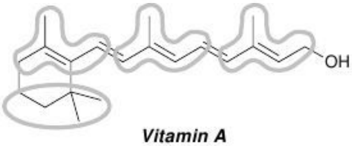
a) ***bisabolene***



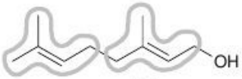
b) ***flexibilene***



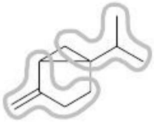
c) ***humulene***



d) ***Vitamin A***

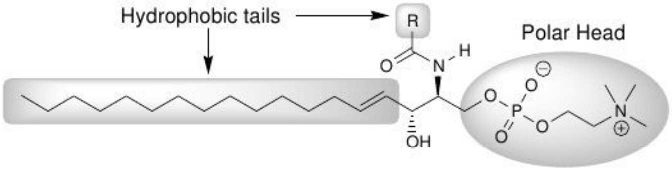


e) ***geraniol***



f) ***sabinene***

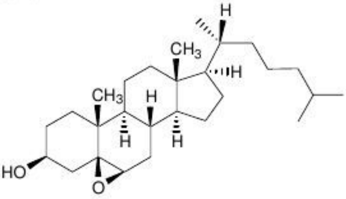
26.50.

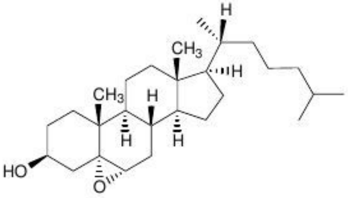


a)

b) Yes, they have one polar head and two hydrophobic tails.

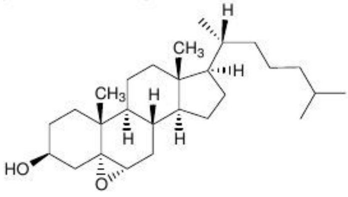
26.51.





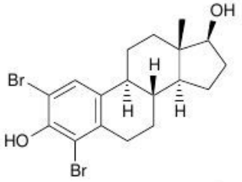
a)

b) The methyl group (C19) provides steric hindrance that blocks one side of the π bond, and only the following is obtained:

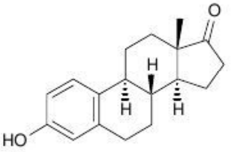


26.52.

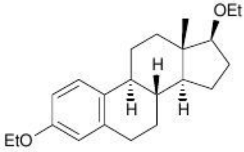
a)



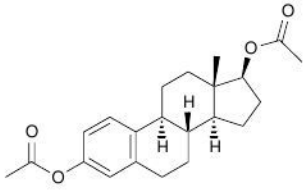
b)



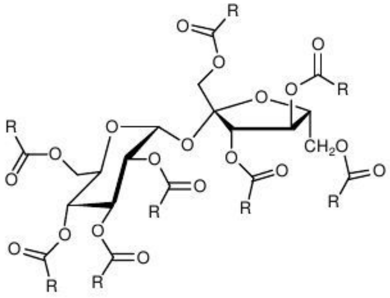
c)



d)



26.53. The compound is chiral.



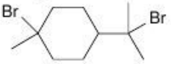
26.54.

a) H_2, Ni
b) H_2, Ni, followed by NaOH, followed by EtI.
c) H_2, Ni, followed by LAH, followed by H_2O
d) O_3, followed by DMS, followed by $Na_2Cr_2O_7$ and H_2SO_4
e) H_2, Ni, followed by PBr_3 and Br_2, followed by H_2O

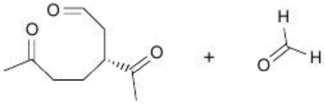
26.55.

a) Limonene is comprised of 10 carbon atoms and is, therefore, a monoterpene.

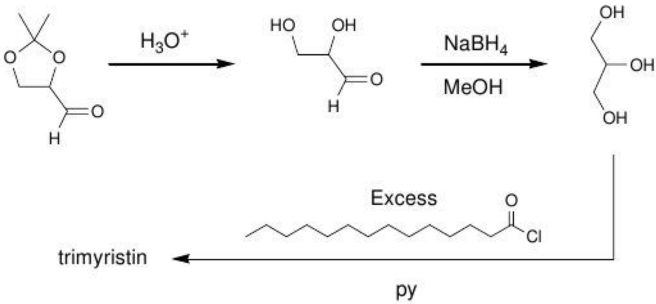
b) The compound does not have any chirality centers and is, therefore, achiral:



c)



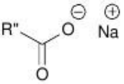
26.56.

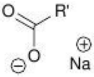


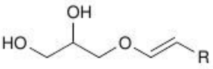
26.57.

a) Fats and oils have a glycerol backbone connected to three fatty acid residues. Plasmalogens also have a glycerol backbone, but it is only connected to two fatty acid residues. The third group is not a fatty acid residue.

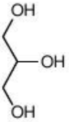
b)

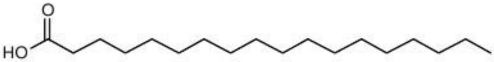


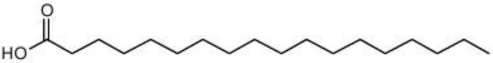


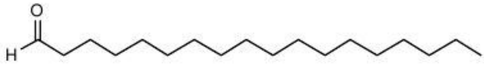


c)









Chapter 27
Synthetic Polymers

Review of Concepts

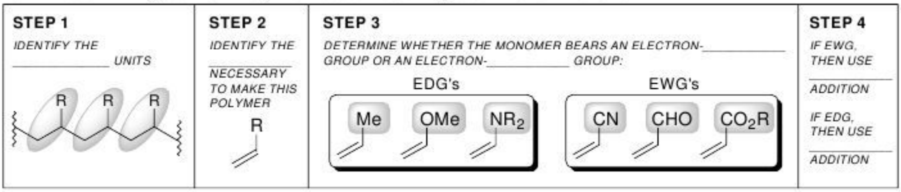
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 27. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- Polymers are comprised of repeating units that are constructed by joining _______________ together.
- A _______________ is a polymer made up of a single type of monomer. Polymers made from two or more different types of monomers are called __________________.
- In a ________ **copolymer**, different homopolymer subunits are connected together in one chain. In a ________ **copolymer**, sections of one homopolymer have been grafted onto a chain of another homopolymer.
- Monomers can join together to form **addition polymers** by cationic, anionic, or ______________ addition.
- Most derivatives of ethylene will undergo __________ polymerization under suitable conditions.
- Cationic addition is only efficient with derivatives of ethylene that contain an electron-____________ group.
- Anionic addition is only efficient with derivatives of ethylene that contain an electron-____________ group.
- Polymers generated via condensation reactions are called ________________ **polymers**.
- **_______-growth polymers** are formed under conditions in which each monomer is added to the growing chain one at a time. The monomers do not react directly with each other. ,
- **_______-growth polymers** are formed under conditions in which the individual monomers react with each other to form __________, which are then joined together to form polymers.
- **Crossed-linked polymers** contain ________ bridges or branches that connect neighboring chains.
- **Thermoplastics** are polymers that are _____ at room temperature but ______ when heated. They are often prepared in the presence ___________ to prevent the polymer from being brittle.
- ___________ are polymers that return to their original shape after being stretched.
- ________________ **polymers** can be broken down by enzymes produced by microorganisms in the soil.

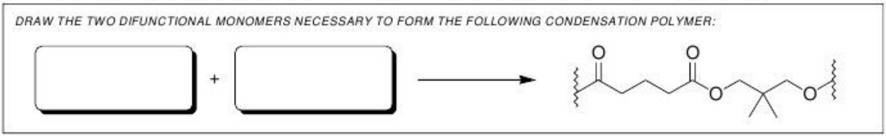
Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 27. The answers appear in the section entitled *SkillBuilder Review*.

27.1 Determining Which Polymerization Technique is More Efficient



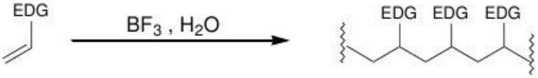
27.2 Identifying the Monomers Required to Produce a Desired Condensation Polymer



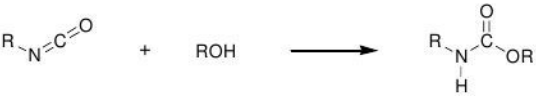
Review of Reactions

Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 27. The answers appear in the section entitled *Review of Reactions*.

Reactions for Formation of Chain-Growth Polymers

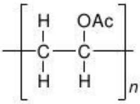


Reactions for Formation of Step-Growth Polymers

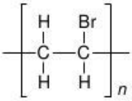


Solutions

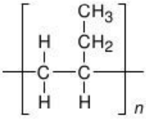
27.1.



a) ***poly(vinyl acetate)***

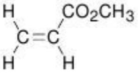


b) ***poly(vinyl bromide)***



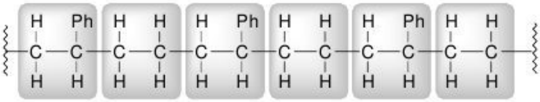
c) ***poly-α-butylene***

27.2.

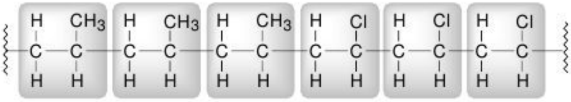


methyl acrylate

27.3.



27.4.

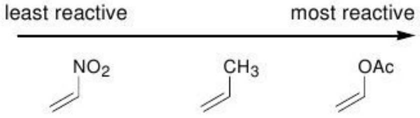


27.5. Isobutylene and styrene

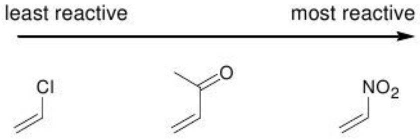
27.6.

a) anionic addition b) cationic addition c) cationic addition
d) cationic addition e) anionic addition f) anionic addition

27.7.



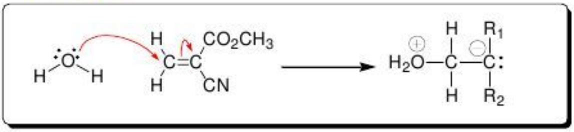
27.8.



27.9. An negative charge, positive charge, or unpaired electron (radical) in a benzylic position is stabilized via resonance.

27.10.

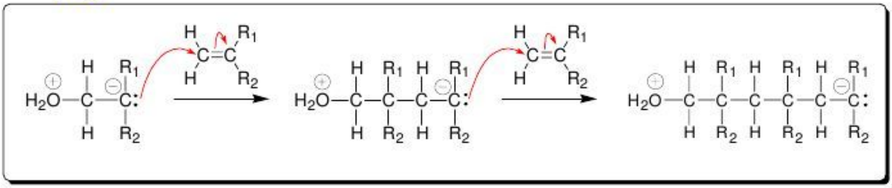
Initiation



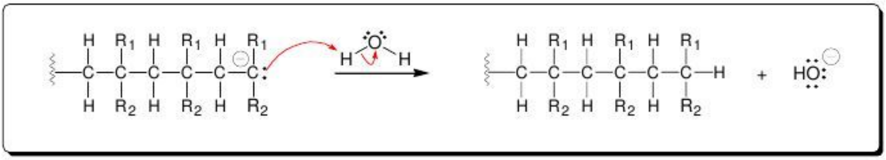
$R_1 = CO_2CH_3$

$R_2 = CN$

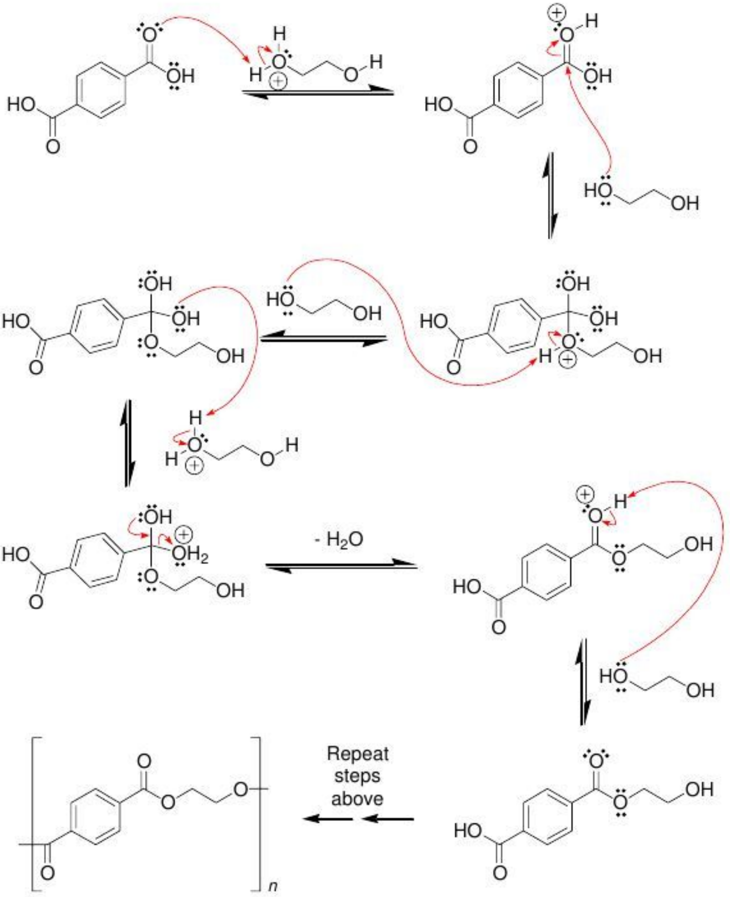
Propagation



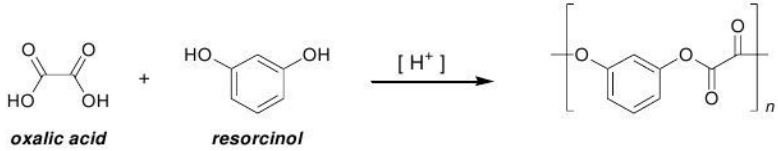
Termination



27.11.



27.12.

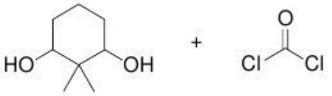


27.13.

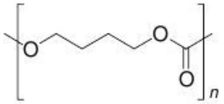
27.14.

a)

b)

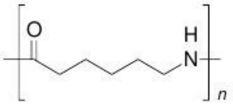


27.15.



27.16.

a)



b) Nylon 6 exhibits a smaller repeating unit.

27.17.

a) step growth

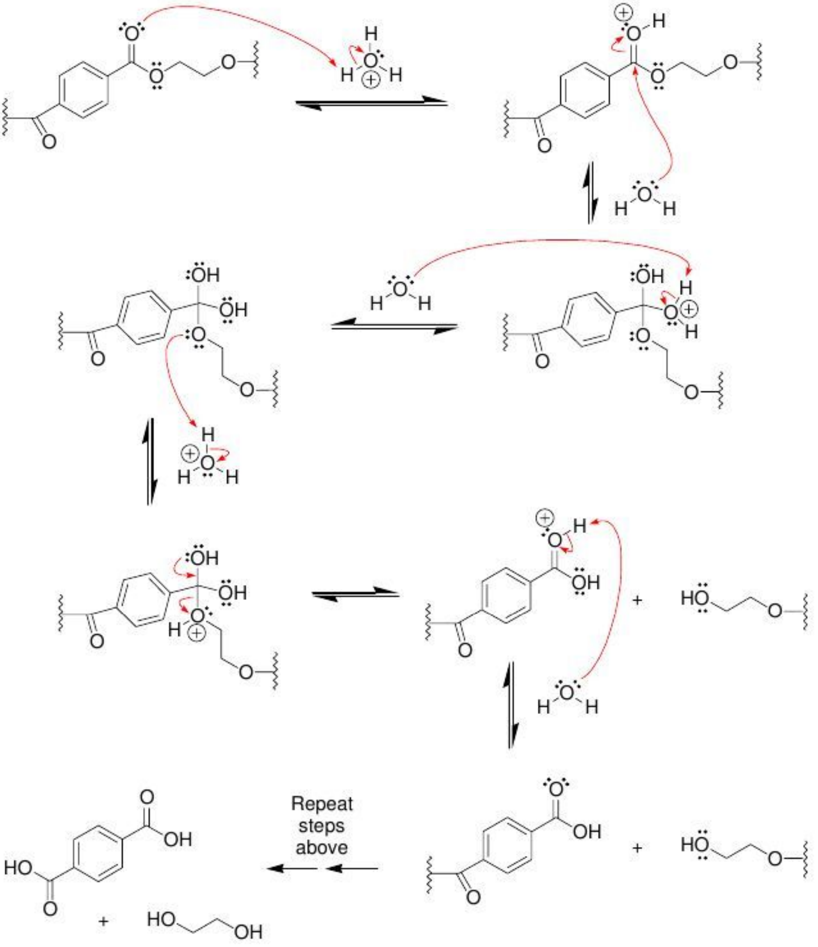
b) chain growth

27.18. Step growth

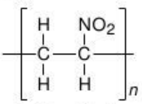
27.19. Polyisobutylene does not have any chirality centers.

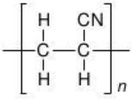
27.20. LDPE is used to make Ziploc bags and HDPE is used to make folding tables.

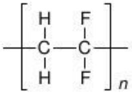
27.21.



27.22.

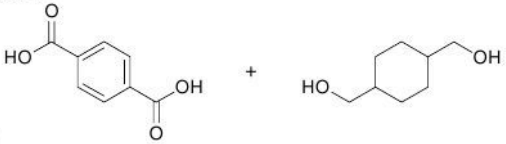

a) ***polynitroethylene***


b) ***polyacrylonitrile***


c) ***poly(vinylidene fluoride)***

27.23.

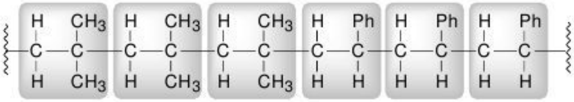
a)



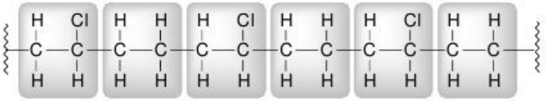
b) Acidic conditions.

27.24.

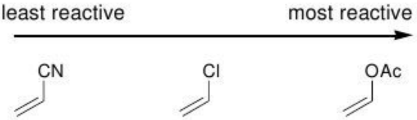
27.25.



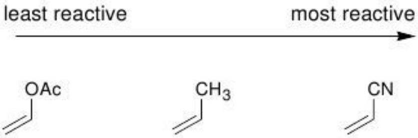
27.26.



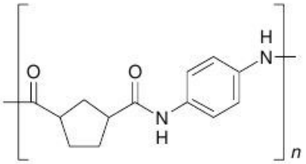
27.27.

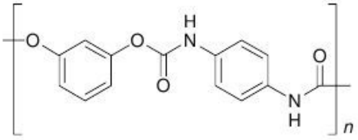


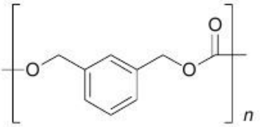
27.28.



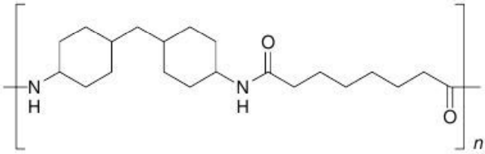
27.29. All three polymers are step-growth polymers.

a) 

b) 

c) 

27.30.

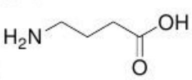
a) 

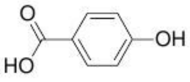
b) Quiana is a polyamide.

c) Quiana is a step-growth polymer.

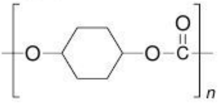
d) Quiana is a condensation polymer.

27.31.

a) 

b) 

27.32.



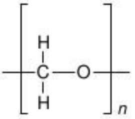
27.33.

a) Step growth b) Chain growth

27.34. Nitro groups are among the most powerful electron-withdrawing groups, and a nitro group stabilizes a negative charge on an adjacent carbon atom, thereby facilitating anionic polymerization.

27.35. Shower curtains are made from PVC, which is a thermoplastic polymer. To prevent the polymer from being brittle, the polymer is prepared in the presence of plasticizers which become trapped between the polymer chains where they function as lubricants. Over time, the plasticizers evaporate, and the polymer becomes brittle.

27.36. Polyformaldehyde, sold under the trade name Delrin, is a strong polymer used in the manufacture of many guitar picks. It is prepared via the acid-catalyzed polymerization of formaldehyde. [[LO 27.4]] [[LO 27.5]]



a) ***polyformaldehyde***

b) Polyformaldehyde is a polyether.

c) Polyformaldehyde is a chain-growth polymer.

d) Polyformaldehyde is an addition polymer.

27.37. It bears an electron-withdrawing group (CN) that can stabilize a negative charge via resonance, but it also bears an electron-donating group (OMe) that can stabilize a positive charge via resonance.

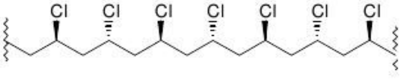
27.38. The nitro group serves as a reservoir of electron density that stabilizes an negative charge via resonance (see Chapter 19).

27.39. The methoxy group is an electron donating group that stabilizes a positive charge via resonance (see Chapter 19).

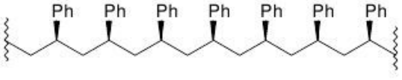
27.40. A methoxy group can only donate electron density via resonance if it is located in an ortho or para position. It cannot function as a electron donating group if it is located in a meta position (see Chapter 19).

27.41.

a)

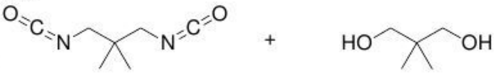


b)



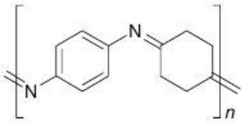
27.42.

a)



b) Step growth c) Addition polymer

27.43.

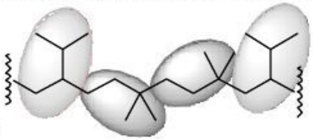


27.44. Vinyl alcohol is an enol, which is not stable. If it is prepared, it undergoes rapid tautomerization to give an aldehyde, which will not produce the desired product upon polymerization.

27.45. The ester moieties undergo hydrolysis in basic conditions, which breaks down the polymer into monomers.

27.46.

a) The carbocation that is initially formed is a secondary carbocation, and it can undergo a carbocation rearrangement to give a more stable, tertiary carbocation. In some cases, the secondary carbocation will be added to the growing polymer chain before it has a chance to rearrange. In other cases, the secondary carbocation will rearrange first and then be added to the growing polymer chain. The result is the incorporation of two different repeating units in the growing polymer chain.

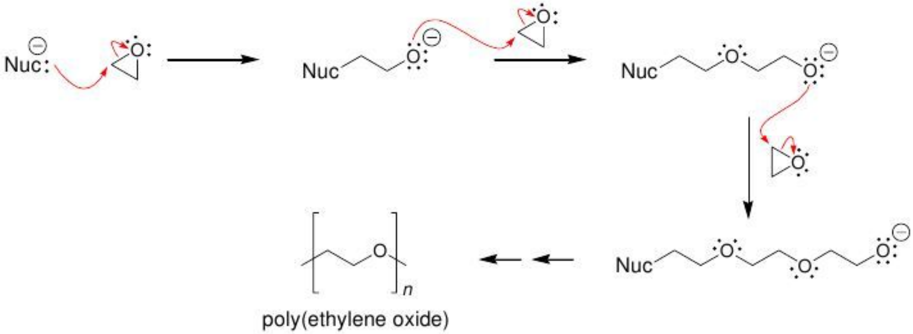


b)

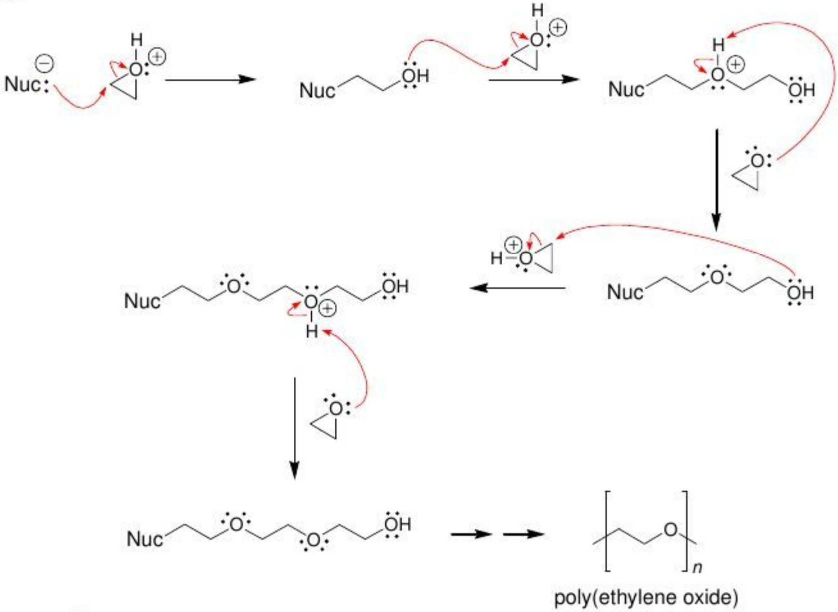
c) Yes, because a secondary carbocation is formed when 3,3-dimethyl-1-butene is protonated, and a methyl shift can occur that converts the secondary carbocation into a tertiary carbocation.

27.47.

a)



b)



c) 

d) Acidic conditions are required, because the epoxide is too sterically hindered to be attacked under basic conditions (see Section 14.10).

27.48.