# Chapter 19
The Chemistry of
Aldehydes and Ketones.
# Addition Reactions

Solutions to In-Text Problems
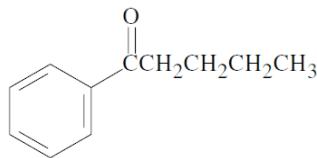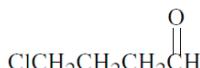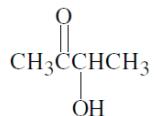
19.1   (b)   (d)   (e)   (g)
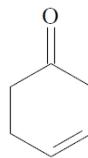
19.2   (a)   2-Propanone
        (d)   (*E*)-3-Ethoxy-2-propenal
        (f)   4,4-Dimethyl-2,5-cyclohexadienone

19.3   (b)   2-Cyclohexenone has a lower carbonyl stretching frequency because its two double bonds are conjugated.
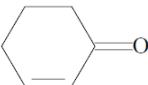
2-cyclohexenone
has conjugated double bonds
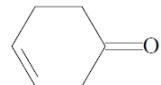
3-cyclohexenone

19.4   (b)   The compound is 2-butanone:

CH₃CCH₂CH₃   2-butanone
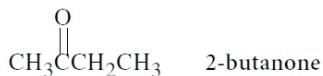
        (c)   The high frequency of the carbonyl absorption suggests a strained ring. (See Eq. 19.4, text p. 897.) In fact, cyclobutanone matches the IR stretching frequency perfectly and the NMR fits as well:

δ 3.09 (triplet)

δ 2.01 (quintuplet)

molecular mass = 70.1

δ 3.09 (triplet)
cyclobutanone
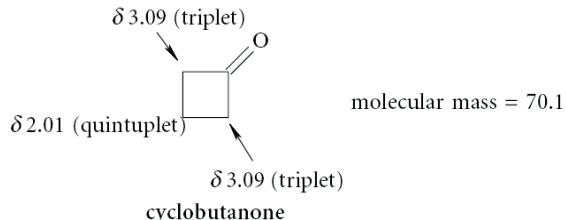
19.6   The structure and CMR assignments of 2-ethylbutanal are shown below. The two methyl groups are chemically equivalent, and the two methylene groups are chemically equivalent; all carbons with different CMR chemical shifts are chemically nonequivalent.

δ 21.7
CH$_3$CH$_2$
δ 204.7
δ 11.5 δ 55.2 CH—CH=O   2-ethylbutanal
CH$_3$CH$_2$
δ 21.7
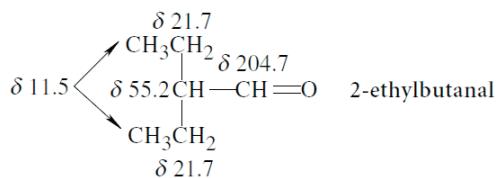
19.7   (a)   The double bonds in 2-cyclohexenone are conjugated, but the double bonds in 3-cyclohexenone are not. Consequently, 2-cyclohexenone has the UV spectrum with the greater λ_{max}.

2-cyclohexenone
(conjugated; has UV spectrum
with the greater λ_{max})

3-cyclohexenone
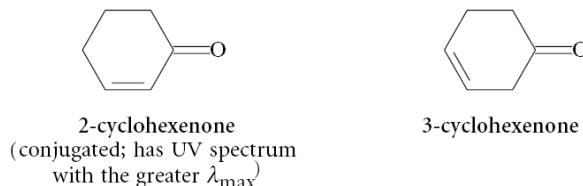
19.9   Compound *A*, vanillin, should have a $\pi \rightarrow \pi^*$ absorption at a greater λ_{max} when dissolved in NaOH solution because the resulting phenolate can delocalize into the carboxaldehyde group; the resulting phenolate from compound *B*, isovanillin, on the other hand, can only delocalize in the aromatic ring.
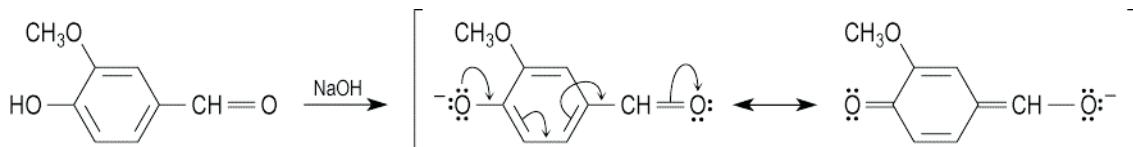
19.11   The mass spectrum of 2-heptanone should have major peaks at m/z = 43 (from α-cleavage), 71 (from inductive cleavage), and 58 (from McLafferty rearrangement). The mass spectrum of 3-heptanone should have a major peak resulting from both inductive cleavage and α-cleavage at m/z = 57 and a major peak resulting from McLafferty rearrangement at m/z = 72. Notice that the position of the even-mass, odd-electron ion is a major distinguishing feature. We leave it to you to draw out these fragmentations.

43 | 71

57 | 57

O
||
H$_3$C—C—CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$

2-heptanone
McLafferty rearrangement at m/z = 58

O
||
CH$_3$CH$_2$—C—CH$_2$CH$_2$CH$_2$CH$_3$

3-heptanone
McLafferty rearrangement at m/z = 72
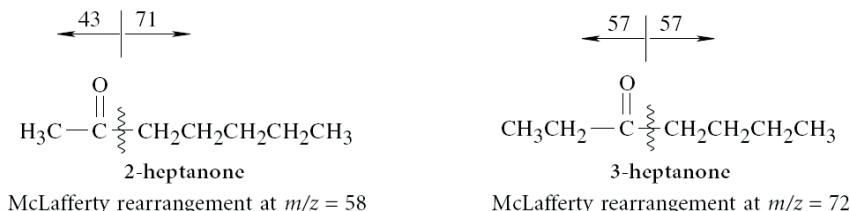
19.13   (b)   The reaction is exactly like the one shown in Study Problem 19.2 on text p. 905 with phenyl instead of methyl substituents. The product is the following ketone:

O
||
Ph$_3$C—C—Ph
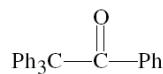
19.14   (b)   The conjugate acid of 3-buten-2-one has more important resonance structures than the conjugate acid of 2-butanone and is therefore more stable relative to unprotonated ketone than the conjugate acid of 2-butanone. Greater stability of the conjugate acid means that the ketone is more basic.

:ÖH
||
H$_2$C=CH—C—CH$_3$ ⟷   H$_2$C—CH—C—CH$_3$ ⟷   H$_2$C—CH=C—CH$_3$

conjugate acid of 3-buten-2-one
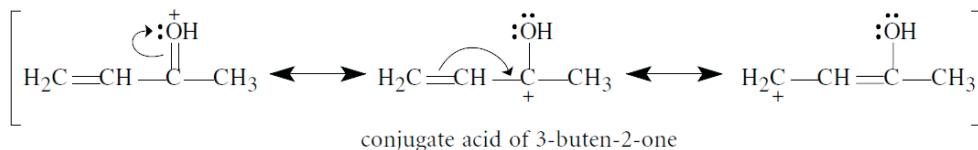
19.15   (a)   The mechanism of the hydroxide-catalyzed hydration of acetaldehyde:
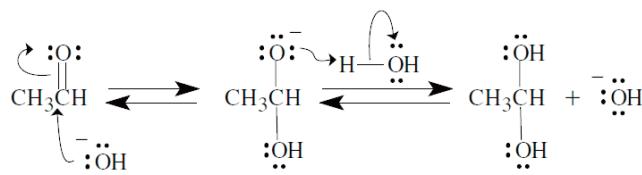
19.16   (b)   The methoxide-catalyzed addition of methanol to benzaldehyde is very similar to the hydroxide-catalyzed hydration mechanism (Problem 19.15a):
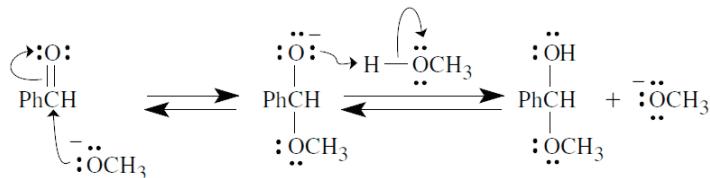

(See the discussion starting at the bottom of text p. 909.) We typically invoke as a base the conjugate base of whatever acid is involved in the mechanism. Thus, if H_3O^+ is involved in a mechanism, its conjugate base (H_2O) acts as the base. We would not invoke both H_3O^+ and ^-OH in the same mechanism because a strong acid and a strong base cannot coexist in solution.

19.17   The data in Table 19.2, text p. 911, of the text show that hydration of benzaldehyde is less than 0.01 times as favorable as hydration of an unconjugated aliphatic aldehyde such as acetaldehyde. The assumption that the same principles apply to cyanohydrin formation leads to the prediction that propanal should have the greater proportion of cyanohydrin at equilibrium. The structure of this cyanohydrin is as follows:
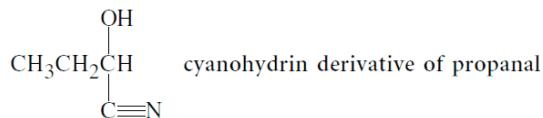

19.19   We use the same principles to predict reactivity that we use to predict relative equilibrium constants. The more prone a carbonyl compound is to form an addition product, the more reactive it is.

(b)   The first compound, 2,3-butanedione, is more reactive, because the partial positive charge on one carbonyl destabilizes the molecule by its repulsive interaction with the partial positive charge on the other. (See Problem 19.18, text p. 913, for a similar situation.)

19.20   (b)
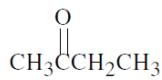
2-butanone

19.22   In each case, ethyl bromide, CH_3CH_2Br, reacts with Mg to give ethylmagnesium bromide, CH_3CH_2MgBr, which is then allowed to react as shown below.

(b)

(f)

cyclopentanone   1-ethyl-1-cyclopentanol
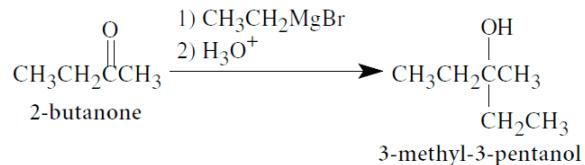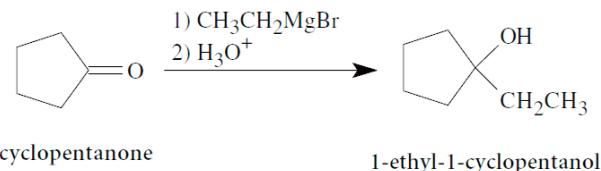
19.23   Either alkyl group bound to the α-carbon of the alcohol can in principle originate from the Grignard reagent.

Synthesis #1:

2-methylpropanal   3-methyl-2-butanol

Synthesis #2:

acetaldehyde   3-methyl-2-butanol
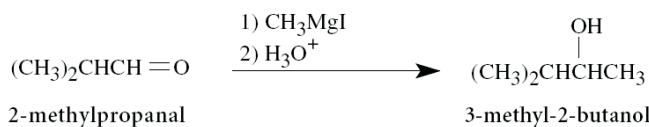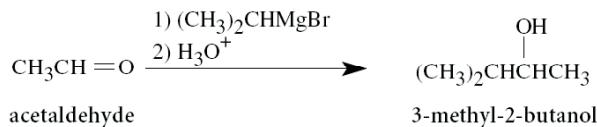
In synthesis #1, the Grignard reagent is prepared by the reaction of CH_3I (methyl iodide) and Mg in dry ether; in synthesis #2, the Grignard reagent is prepared from the similar reaction of $(CH_3)_2CH$—Br (isopropyl bromide) and Mg.

19.24   (b)

butyraldehyde diisopropyl acetal
(1,1-diisopropoxybutane)
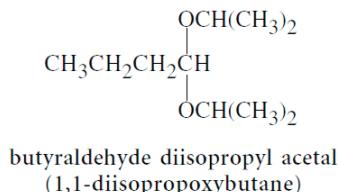
19.25   A diol reacts with a ketone to form a cyclic acetal.

(b)
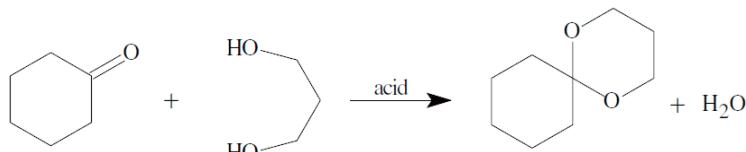
19.26   (b)   When five- and six-membered rings can be formed, diols generally react with aldehydes and ketones to give cyclic acetals, and this case is no exception:
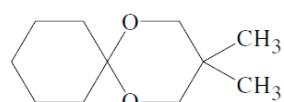

19.28   (b)
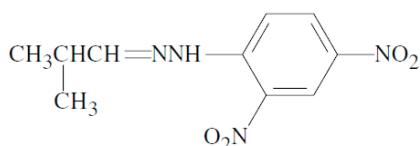
19.29   First, the carbinolamine intermediate is formed. This intermediate then undergoes acid-catalyzed dehydration to give the hydrazone. (Be sure to consult Study Guide Link 19.7 on p. 436 of the Study Guide and Solutions Manual.)
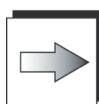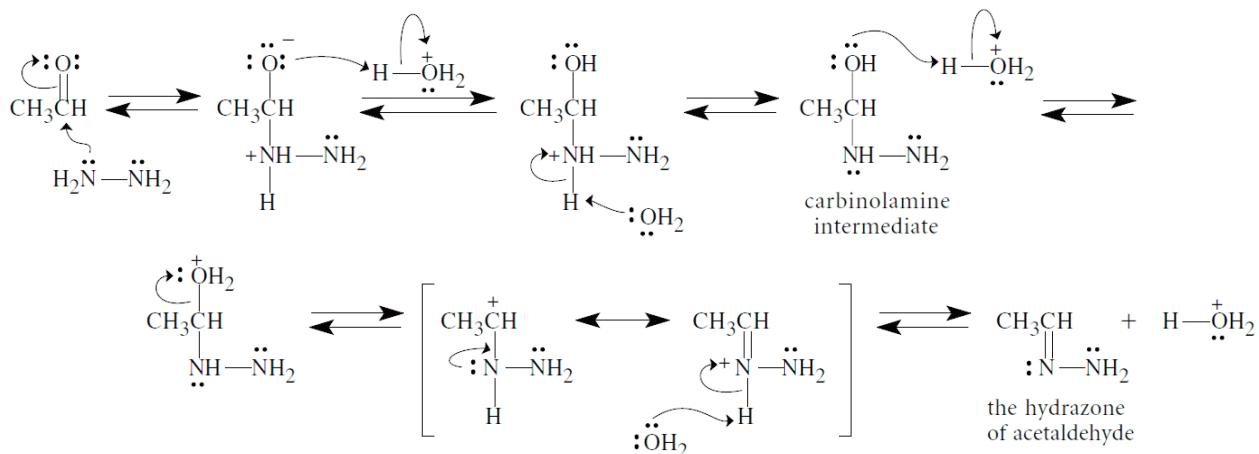
Note that it is equally appropriate to write the loss of water and formation of the carbon–nitrogen double bond as one step, thus avoiding the necessity of drawing resonance structures:
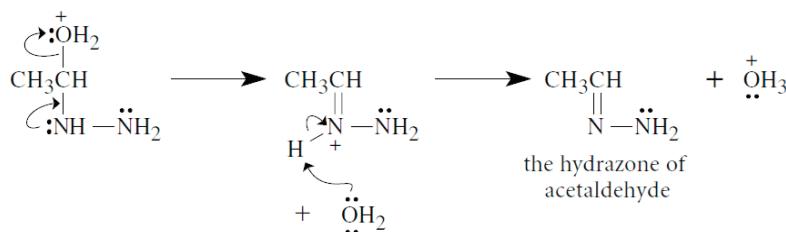
19.30   Imine hydrolysis is the reverse of imine formation. Therefore, retrace the steps of imine formation as illustrated in the solution to Problem 19.29, starting with the imine and working backwards to the aldehyde and the amine.
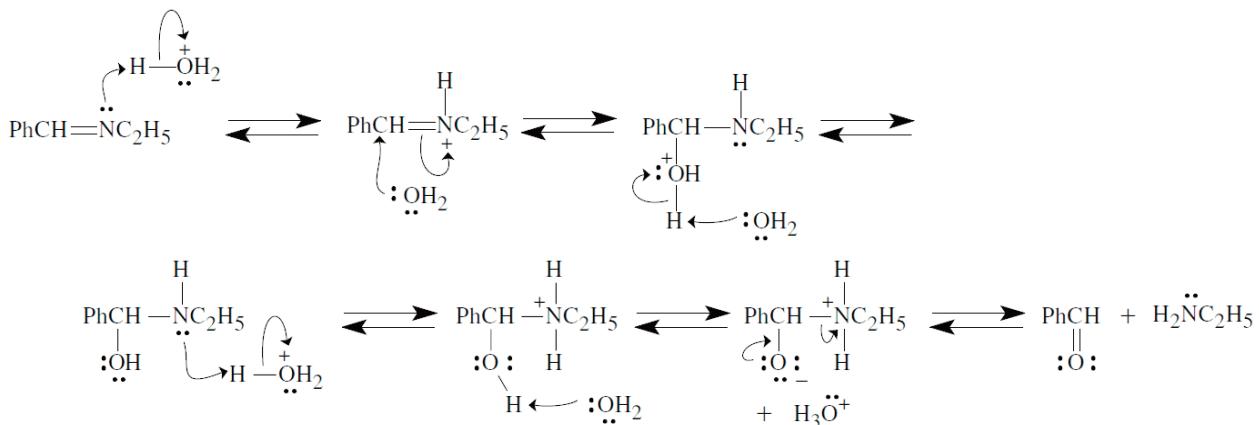
19.31   (b)
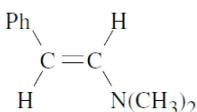
19.32   Any compound with a carbonyl group on any of the prospective alkyl carbons could in principle serve as a starting material. (The answer is restricted to compounds containing only one carbonyl group.)
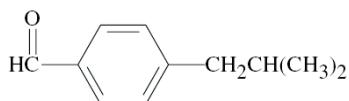
4-isobutylbenzaldehyde
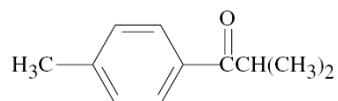
p-methylisobutyrophenone
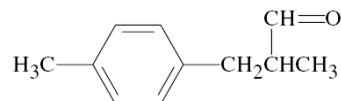
2-methyl-3-(4-methylphenyl)propanal

19.34   (b)

styrene

19.35   (b)

CH_3I $\xrightarrow{PPh_3}$ $CH_3\overset{+}{P}Ph_3$ I^- $\xrightarrow{CH_3CH_2CH_2CH_2Li}$ $H_2\overset{\cdot\cdot}{C}$ $\overset{+}{\longrightarrow}$ PPh_3 $\xrightarrow[\text{2-butanone}]{O=\overset{CH_3}{\underset{|}{C}}CH_2CH_3}$ $H_2C=\overset{CH_3}{\underset{|}{C}}CH_2CH_3$

methyl iodide

$+ CH_3CH_2CH_2CH_3$

2-methyl-1-butene
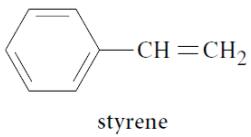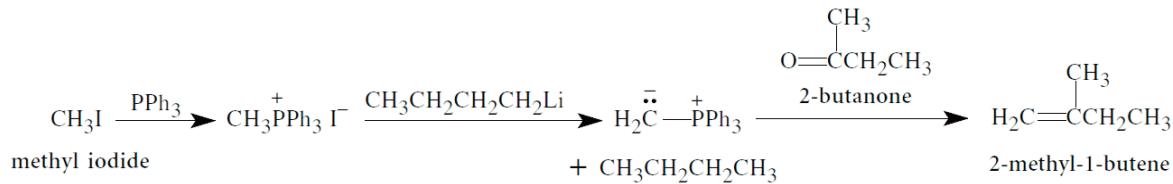
19.37   Silver(I) oxide oxidizes the aldehyde selectively to the following carboxylic acid:
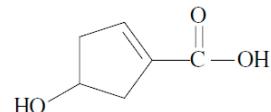
4-hydroxy-1-cyclopentenecarboxylic acid

Solutions to Additional Problems

19.39   Only organic products are shown.

(a)   (b)   (c)   (d)

OH	OH	O	O
$CH_3CH_2CH_2\overset{|}{C}HPh$	$CH_3CH_2CH_2\overset{|}{C}H_2$	$CH_3CH_2CH_2\overset{\|}{C}$—OH	$CH_3CH_2CH_2\overset{\|}{C}$—OH

(e)   (f)   (g)

NOH   O
$CH_3CH_2CH_2\overset{\|}{C}H$ $CH_3CH_2CH_2\overset{\|}{C}$—OH $CH_3CH_2CH_2CH_3$

(h)

$CH_3CH_2CH_2CH_2CH{=}CHCH_3$
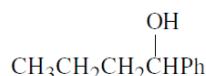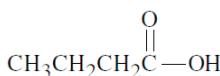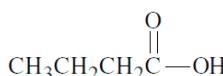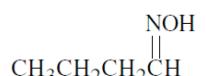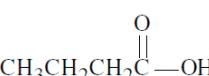
cis and trans

19.40   (c)   The bisulfite addition product of 2-methylpentanal:

OH   O
$CH_3CH_2CH_2CHCH{-}\overset{\|}{\underset{\|}{S}}{-}O^-\ Na^+$
CH₃   O
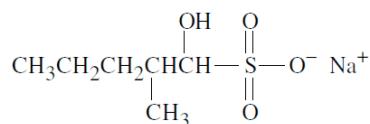
19.41   (b)   Both cis and trans isomers of the alkene PhCH=CHCH₃ [(1-propenyl)benzene, also known as β-methylstyrene] are formed.

19.43   (a)   Glycerol has three hydroxy groups. Two possible cyclic acetals can be formed; one (*A*) contains a six-membered ring, and the other (*B*) contains a five-membered ring.

O   OH
$H_3C{-}\overset{\|}{C}{-}CH_3$ + $HOCH_2{-}\overset{|}{C}H{-}CH_2OH$ $\xrightarrow{\text{acid}}$ *A*   and/or   *B*   + H₂O

acetone   glycerol
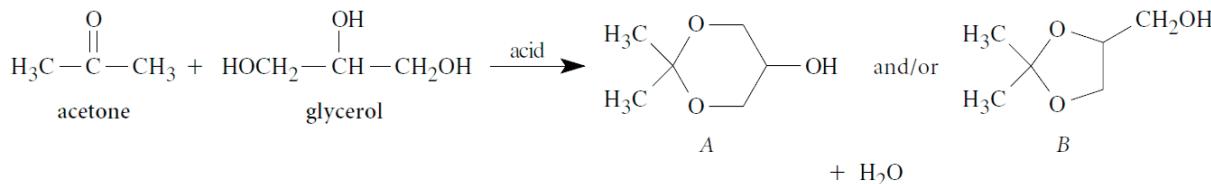
(b)   Only compound *B* is chiral, and for this reason only compound *B* can be resolved into enantiomers; hence, compound *B* is the observed compound.

19.45   (b)   The reaction is a straightforward dimethyl acetal formation.

1,1-dimethoxy-4-methylcyclohexane
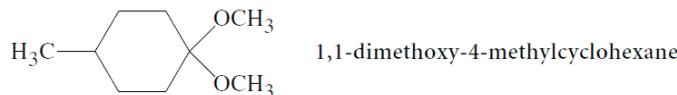
(e)   This is a Grignard addition to the ketone to give a tertiary alcohol that subsequently dehydrates under the acidic conditions to an alkene. Whether the dehydration occurs depends on the acid concentration and whether the conditions are designed to remove water.

$\xrightarrow{H_3O^+}$ + H₂O

1,1-diphenyl-1-propanol
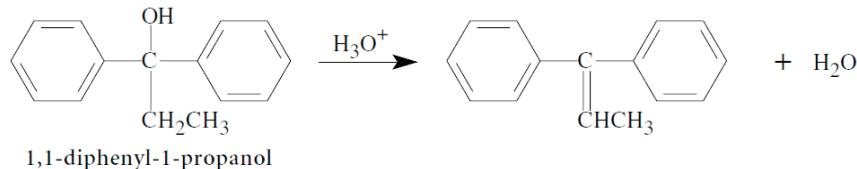
(f)   This is a Wittig reaction.
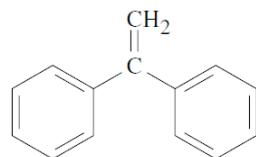
**19.46** **(b)** An initially formed imine reacts with sodium borohydride to form an amine. (Although this reaction is discussed in Sec. 23.7B, text p. 1133, the product follows directly from the hint.)

$$CH_3CH_2CH_2\overset{\overset{NPh}{\|}}{C}CH_3 \xrightarrow[CH_3OH]{NaBH_4} CH_3CH_2CH_2\overset{\overset{NHPh}{|}}{C}HCH_3$$
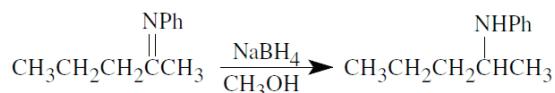
19.48 The data indicate that compound A is a benzene derivative with an additional degree of unsaturation. Its reactivity in the Clemmensen reduction and the formation of a xylene suggests that it has two substituents on a benzene ring, one of which is a methyl group and one of which is an aldehyde. Only p-methylbenzaldehyde would give, after Clemmensen reduction, a compound (p-xylene) that in turn gives, because of its symmetry, one and only one monobromination product, 2-bromo-1,4-dimethylbenzene.

4--methylbenzaldehyde   **p-xylene**   **2-bromo-1,4-dimethylbenzene**
(compound A)   (compound A)
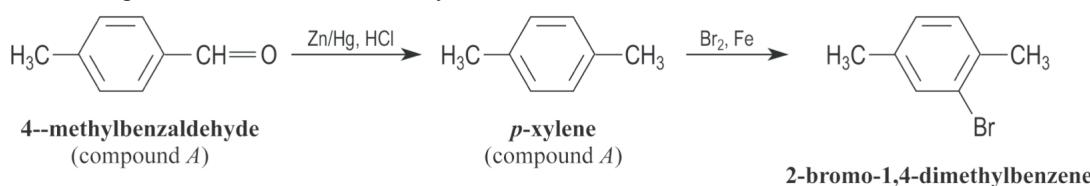
19.49 As always, bear in mind that there is often more than one acceptable synthesis that fits the parameters given.

(b)

cyclohexanone

2-cyclohexyl-2-propanol

(c)

cyclohexanone   cyclohexyl methyl ether
(methoxycyclohexane)

(e)

3-methyl-2-hexanone   2,3-dimethyl-2-hexene

(i)

cyclohexene   1,6-hexanediol
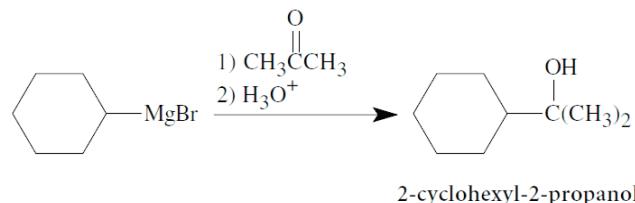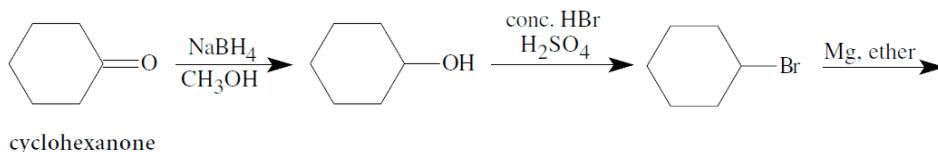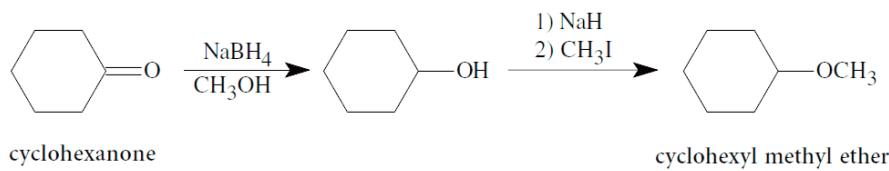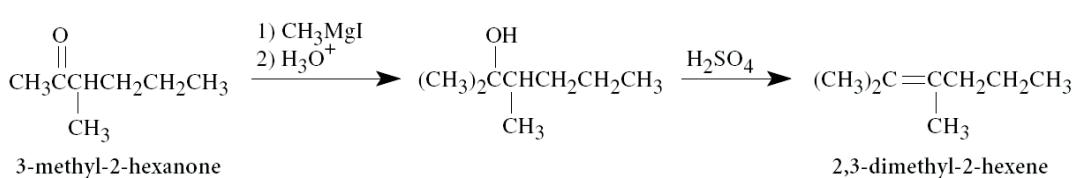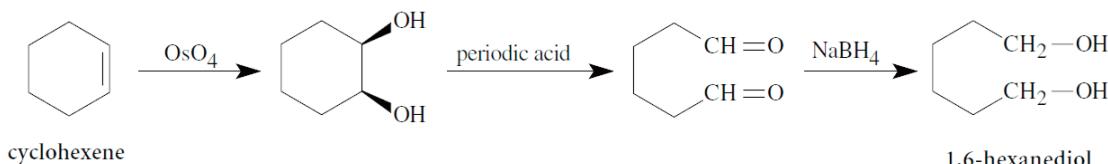
Ozonolysis could also be used to prepare the dialdehyde.

19.50   (a)   An Lewis acid–base dissociation of the bromide—essentially an S_N1 reaction—gives an α-hydroxy carbocation, which is, by resonance, also the conjugate acid of acetophenone. Deprotonation by bromide ion gives the ketone and HBr.
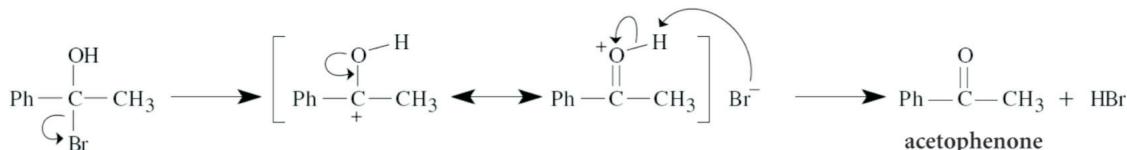

acetophenone

19.51   The molecular formula of compound A shows that two equivalents of methanol are added to the alkyne. The fact that the product hydrolyzes to acetophenone indicates that the two methoxy groups of compound A are on the same carbon, that is, that compound A is an acetal.


compound A
acetophenone
dimethyl acetal
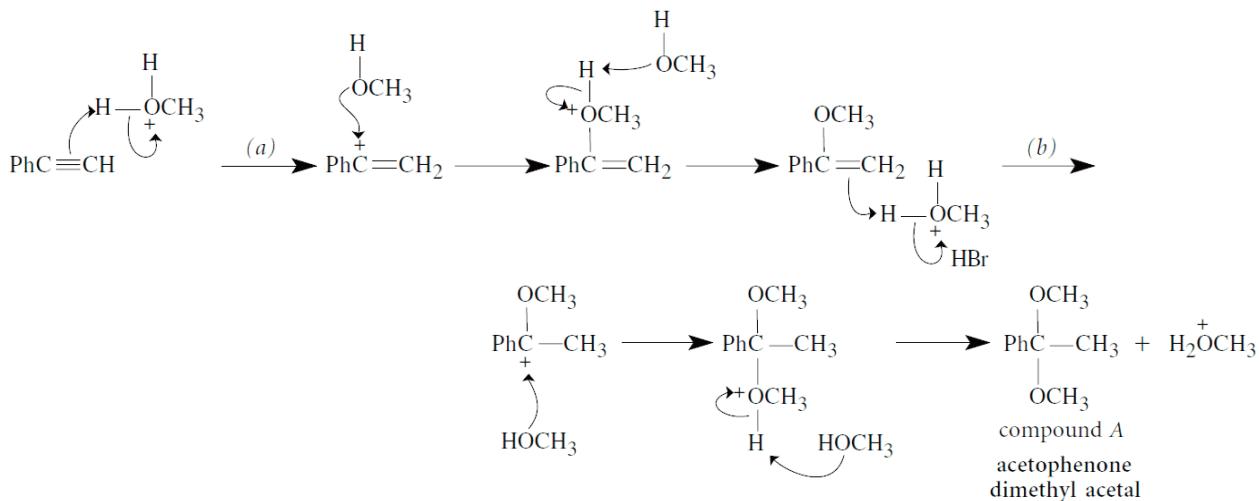
In the step labeled (a), the acid $CH_3\overset{+}{O}H_2$ is used to protonate the alkyne because it is the major acidic species present when H_2SO_4 is dissolved in methanol (just as H_3O^+ is the major acidic species present when H_2SO_4 is dissolved in water). Protonation occurs on the terminal carbon because it gives a carbocation that is benzylic and therefore resonance-stabilized. In the step labeled (b), protonation again occurs on the terminal carbon because the resulting carbocation is resonance-stabilized by electron donation from both the benzene ring and the neighboring oxygen.

19.53   (a)

$$CH_3CH_2CH_2CH_2CH=O \quad \text{and} \quad H_2NNH-\text{(ring)}-OCH_3$$

pentanal (valeraldehyde)

p-methoxyphenylhydrazine
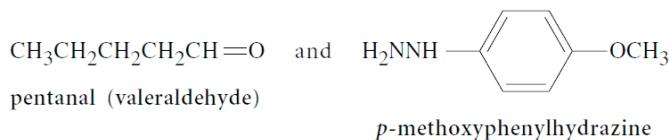
19.55   Compound A is an aldehyde because it is oxidized with Ag(I). Because there is no additional unsaturation, the remaining oxygen is accounted for by either an alcohol or an ether functional group. Because Clemmensen reduction of the CrO_3 oxidation product gives a compound without oxygens, the CrO_3 oxidation product of A must

be a keto aldehyde or a dialdehyde. Because compound A is oxidized to a dicarboxylic acid by H_2CrO_4, it must contain a primary alcohol; hence, its CrO_3 oxidation product must be a dialdehyde. Compound A, then, is a chiral hydroxy aldehyde that is oxidized by CrO_3 to an achiral dialdehyde. The Clemmensen reduction product shows that all compounds have the carbon skeleton of 3-methylpentane. The compounds with this carbon skeleton that fit all the data are the following.
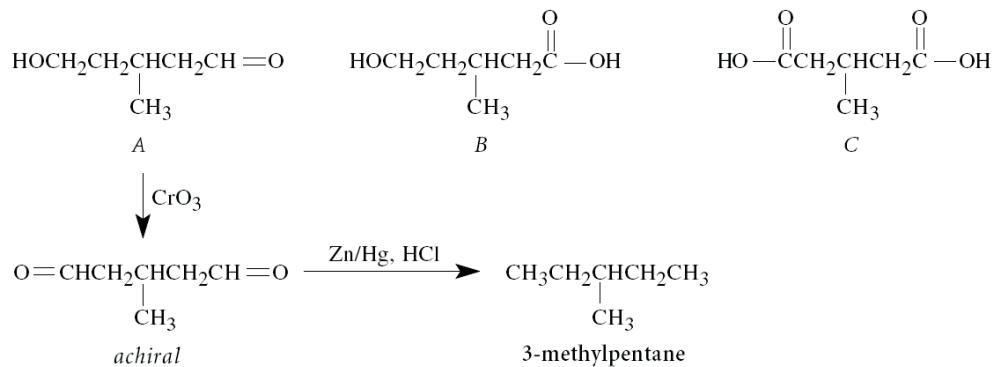
19.56   The mechanism below begins with the protonated aldehyde chloral, which serves as a carbocation electrophile in the ring alkylation of chlorobenzene. The resulting product, an alcohol, dehydrates under the acidic conditions to give another carbocation that alkylates a second chlorobenzene molecule and thus forms the product.
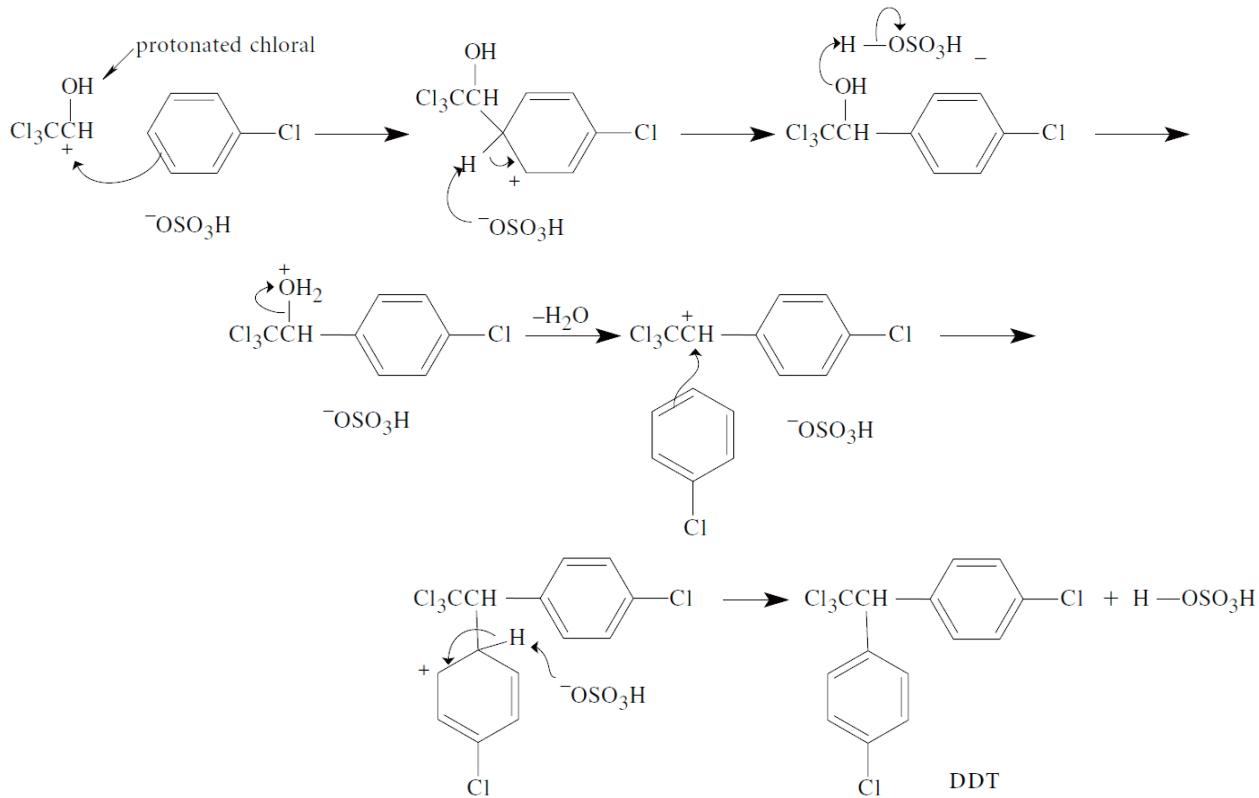

19.58   (a)   In this case, $LiAlD_4$ serves as a source of nucleophilic isotopic hydride (deuteride); deuteride opens the epoxide with inversion of configuration.


(racemate)
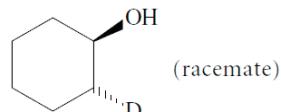
19.59   (a)   Thumbs wants a Grignard reagent to react selectively with a ketone in the presence of an aldehyde. Because aldehydes are more reactive than ketones, the aldehyde, not the ketone, will react most rapidly.

19.62   (b)   The NMR spectrum indicates the presence of a *tert*-butyl group and an aldehyde. The compound is

$$(CH_3)_3C-CH=O \qquad \text{2,2-dimethylpropanal (pivalaldehyde)}$$
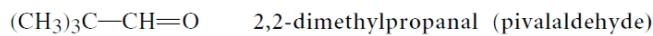
19.65   (b)   Allow benzyl phenyl ketone to react with $LiAlD_4$.

benzyl phenyl ketone
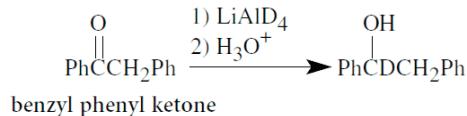
19.66   (b)   The $n \rightarrow \pi^*$ absorption is characteristic of the carbonyl group. This absorption disappears because a reaction occurs in which the carbonyl group is converted into another group that does not have this absorption. This reaction is addition of ethanethiol to give the sulfur analog of a hemiacetal:

has a carbonyl
group; has $n \rightarrow \pi^*$
absorption

has no carbonyl
group; has no $n \rightarrow \pi^*$
absorption