Chapter 21: Aldehydes and Ketones—Nucleophilic Addition

◆ General facts

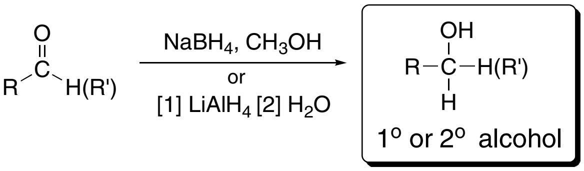
- Aldehydes and ketones contain a carbonyl group bonded to only H atoms or R groups. The carbonyl carbon is *sp*^{2} hybridized and trigonal planar (21.1).
- Aldehydes are identified by the suffix -*al*, while ketones are identified by the suffix -*one* (21.2).
- Aldehydes and ketones are polar compounds that exhibit dipole–dipole interactions (21.3).

◆ Summary of spectroscopic absorptions of RCHO and R_2CO (21.4)

IR absorptions	C=O	~1715 cm^{-1} for ketones • increasing frequency with decreasing ring size ~1730 cm^{-1} for aldehydes • For both RCHO and R_2CO, the frequency decreases with conjugation.
	C_{sp^2}–H of CHO	~2700–2830 cm^{-1} (one or two peaks)
^{1}H NMR absorptions	CHO	9–10 ppm (highly deshielded proton)
	C–H α to C=O	2–2.5 ppm (somewhat deshielded C_{sp^3}–H)
^{13}C NMR absorption	C=O	190–215 ppm

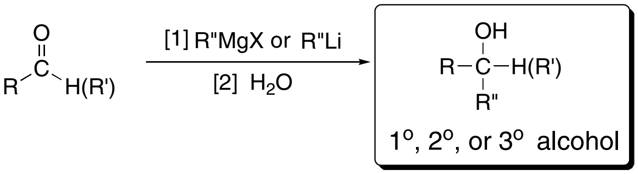
◆ Nucleophilic addition reactions

[1] Addition of hydride (H$^-$) (21.8)



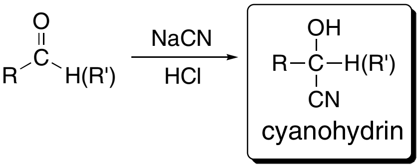
- The mechanism has two steps.
- H:$^-$ adds to the planar C=O from both sides.

[2] Addition of organometallic reagents (R$^-$) (21.8)



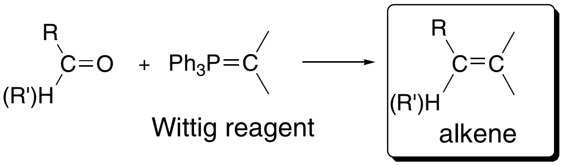
- The mechanism has two steps.
- R:$^-$ adds to the planar C=O from both sides.

[3] Addition of cyanide ($^-$CN) (21.9)



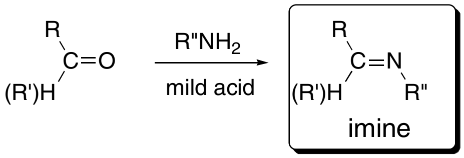
- The mechanism has two steps.
- $^-$CN adds to the planar C=O from both sides.

[4] Wittig reaction (21.10)



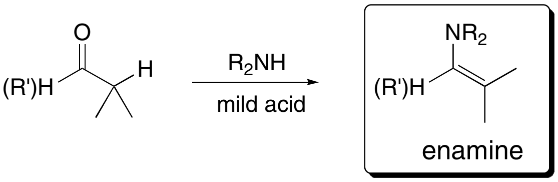
- The reaction forms a new C–C σ bond and a new C–C π bond.
- $Ph_3P{=}O$ is formed as by-product.

[5] Addition of 1° amines (21.11)



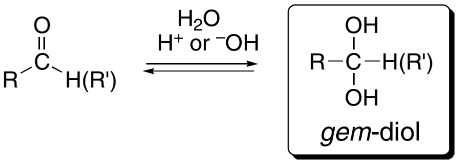
- The reaction is fastest at pH 4–5.
- The intermediate carbinolamine is unstable, and loses H_2O to form the C=N.

[6] Addition of 2° amines (21.12)



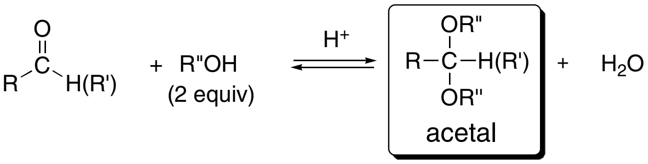
- The reaction is fastest at pH 4–5.
- The intermediate carbinolamine is unstable, and loses H_2O to form the C=C.

[7] Addition of H_2O—Hydration (21.13)



- The reaction is reversible. Equilibrium favors the product only with less stable carbonyl compounds (e.g., H_2CO and Cl_3CCHO).
- The reaction is catalyzed with either H^+ or ^-OH.

[8] Addition of alcohols (21.14)



- The reaction is reversible.
- The reaction is catalyzed with acid.
- Removal of H_2O drives the equilibrium to favor the products.

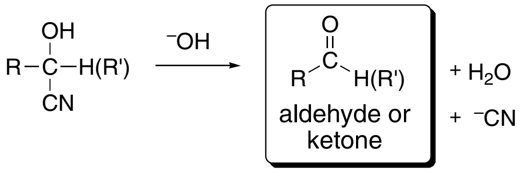
◆ Other reactions

[1] Synthesis of Wittig reagents (21.10A)

$$RCH_2X \xrightarrow[\text{[2] Bu–Li}]{\text{[1] }Ph_3P:} Ph_3P{=}CHR$$

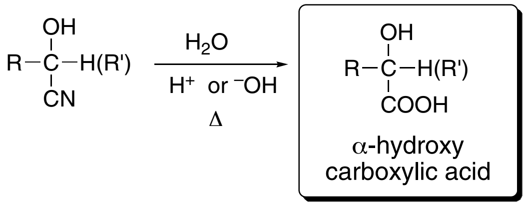
- Step [1] is best with CH_3X and RCH_2X since the reaction follows an S_N2 mechanism.
- A strong base is needed for proton removal in Step [2].

[2] Conversion of cyanohydrins to aldehydes and ketones (21.9)

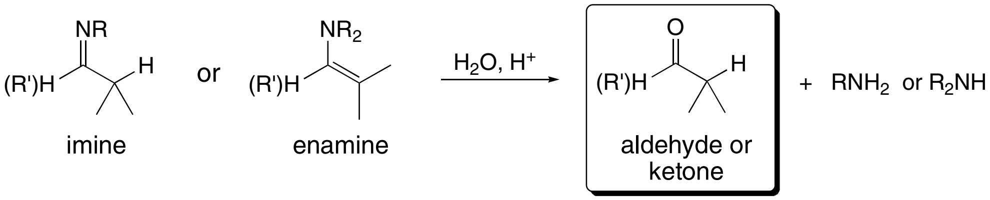


- This reaction is the reverse of cyanohydrin formation.

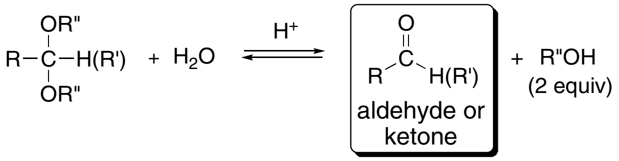
[3] Hydrolysis of nitriles (21.9)



[4] Hydrolysis of imines and enamines (21.12)



[5] Hydrolysis of acetals (21.14)



- The reaction is acid catalyzed and is the reverse of acetal synthesis.
- A large excess of H_2O drives the equilibrium to favor the products.

21.1 As the number of R groups bonded to the carbonyl C increases, reactivity towards nucleophilic attack decreases.

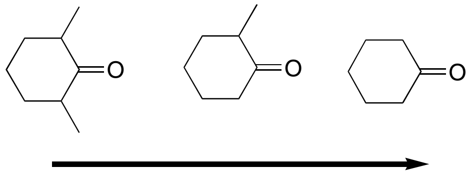
a.

$(CH_3)_2C{=}O$	$CH_3CH{=}O$	$CH_2{=}O$
2 R groups	1 R group	0 R groups

→

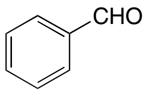
Increasing reactivity
decreasing alkyl substitution

b.

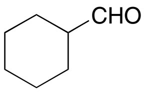


Increasing reactivity
decreasing steric hindrance

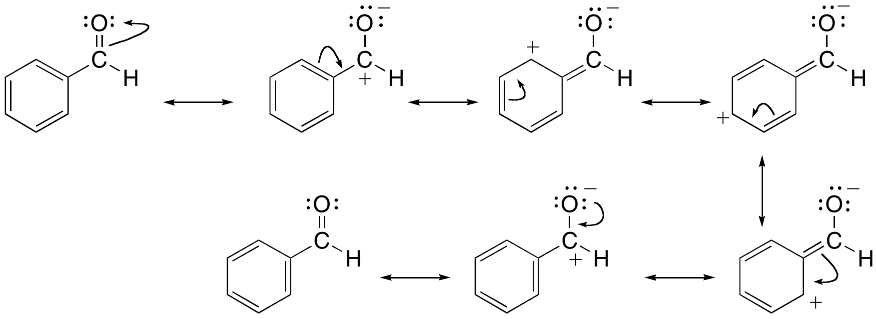
21.2 More stable aldehydes are less reactive towards nucleophilic attack.



benzaldehyde
Several resonance structures delocalize the partial positive charge on the carbonyl carbon, making it more stable and less reactive towards nucleophilic attack.



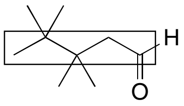
cyclohexanecarbaldehyde
This aldehyde has no added resonance stabilization.



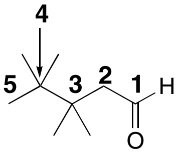
21.3 • To name an aldehyde with a chain of atoms: [1] Find the longest chain with the CHO group and change the *-e* ending to *-al*. [2] Number the carbon chain to put the CHO at C1, but omit this number from the name. Apply all other nomenclature rules.

• To name an aldehyde with the CHO bonded to a ring: [1] Name the ring and add the suffix *-carbaldehyde*. [2] Number the ring to put the CHO group at C1, but omit this number from the name. Apply all other nomenclature rules.

a. $(CH_3)_3CC(CH_3)_2CH_2CHO$

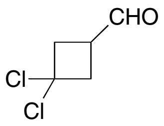


5 C chain = pentanal

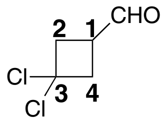


3,3,4,4-tetramethylpentanal

c.

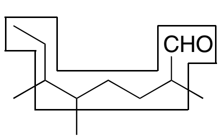


4 C ring = cyclobutanecarbaldehyde

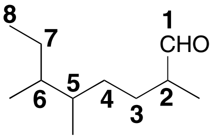


3,3-dichlorocyclobutane-carbaldehyde

b.



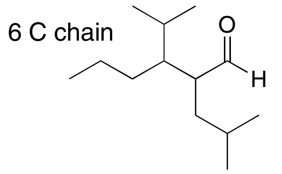
8 C chain = octanal



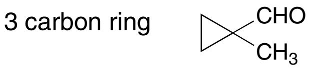
2,5,6-trimethyloctanal

21.4 Work backwards from the name to the structure, referring to the nomenclature rules in Answer 21.3.

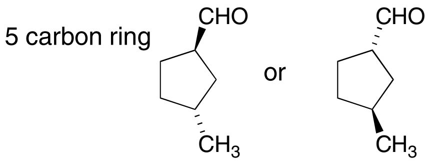
a. 2-isobutyl-3-isopropyl**hexanal**



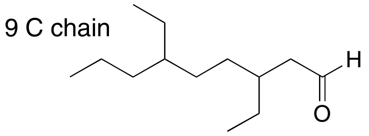
c. 1-methyl**cyclopropanecarbaldehyde**



b. *trans*-3-methyl**cyclopentanecarbaldehyde**



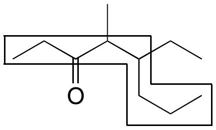
d. 3,6-diethyl**nonanal**



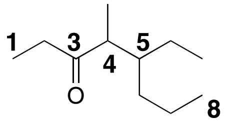
21.5 • To name an acyclic ketone: [1] Find the longest chain with the carbonyl group and change the *-e* ending to *-one*. [2] Number the carbon chain to give the carbonyl C the lower number. Apply all other nomenclature rules.

• To name a cyclic ketone: [1] Name the ring and change the *-e* ending to *-one*. [2] Number the C's to put the carbonyl C at C1 and give the next substituent the lower number. Apply all other nomenclature rules.

a.

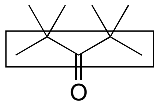


8 C chain = octanone

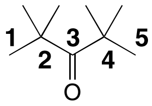


5-ethyl-4-methyl-3-octanone

c. $(CH_3)_3CCOC(CH_3)_3$

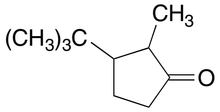


5 C chain = pentanone

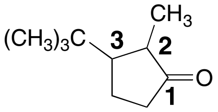


2,2,4,4-tetramethyl-3-pentanone

b.



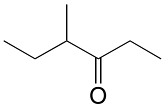
5 C ring = cyclopentanone



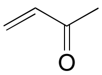
3-*tert*-butyl-2-methylcyclopentanone

21.6 Most common names are formed by naming both alkyl groups on the carbonyl C, arranging them alphabetically, and adding the word ketone.

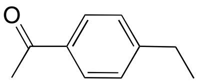
a. *sec*-butyl ethyl ketone



b. methyl vinyl ketone

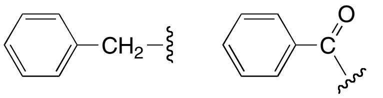


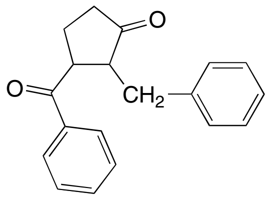
c. *p*-ethylacetophenone



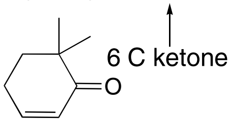
d. 3-benzoyl-2-benzylcyclopentanone

benzyl group: benzoyl group: 5 C ketone

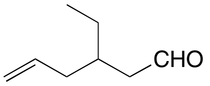




e. 6,6-dimethyl-2-cyclohexenone

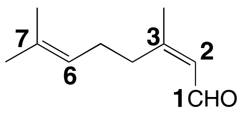


f. 3-ethyl-5-hexenal



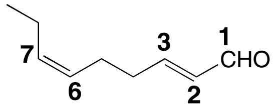
21.7 Compounds with both a C–C double bond and an aldehyde are named as enals.

a. (2*Z*)-3,7-dimethyl-2,6-octadienal



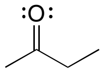
neral

b. (2*E*,6*Z*)-2,6-nonadienal

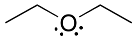


cucumber aldehyde

21.8 Even though both compounds have polar C–O bonds, the electron pairs around the sp^3 hybridized O atom of diethyl ether are more crowded and less able to interact with electron-deficient sites in other diethyl ether molecules. The O atom of the carbonyl group of 2-butanone extends out from the carbon chain making it less crowded. The lone pairs of electrons on the O atom can more readily interact with the electron-deficient sites in the other molecules, resulting in stronger forces.



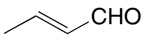
2-butanone



diethyl ether

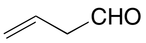
21.9 For cyclic ketones, the carbonyl absorption shifts to higher wavenumber as the size of the ring decreases and the ring strain increases. Conjugation of the carbonyl group with a C=C or a benzene ring shifts the absorption to lower wavenumber.

a.



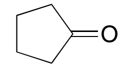
conjugated C=O
lower wavenumber

or

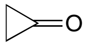


higher wavenumber

b.

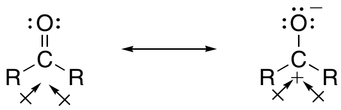


or

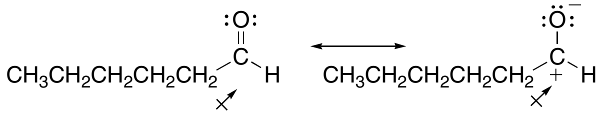


smaller ring
higher wavenumber

21.10 Since a charge-separated resonance structure can be drawn for a carbonyl group, more electron donor R groups stabilize the (+) charge on this resonance form. The two R groups on the ketone C=O thus help to stabilize it.

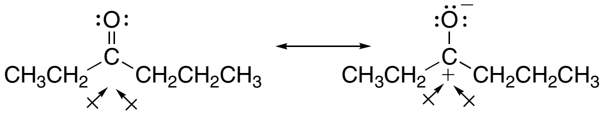


With an aldehyde, only one electron-donor R:



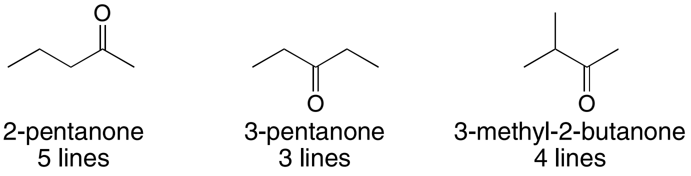
The H of RCHO does not stabilize the charge-separated resonance structure, so it contributes less to the hybrid.
The C=O has more double bond character.
higher wavenumber

With a ketone, two electron-donor R groups:



The 2 R groups stabilize the charge-separated resonance structure, so it contributes more to the hybrid.
The C=O has more single bond character.
weaker bond
lower wavenumber

21.11 The number of lines in their ^{13}C NMR spectra can distinguish the constitutional isomers.



21.12

a. $CH_3CH_2CH_2COOCH_3 \xrightarrow[\text{[2] } H_2O]{\text{[1] DIBAL-H}} CH_3CH_2CH_2CHO$

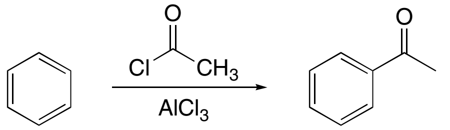
b. $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{PCC}} CH_3CH_2CH_2CHO$

c. $HC{\equiv}CCH_2CH_3 \xrightarrow[\text{[2] } H_2O_2\text{, } HO^-]{\text{[1] } BH_3} CH_3CH_2CH_2CHO$

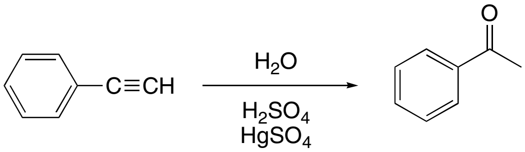
d. $CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3 \xrightarrow[\text{[2] Zn, } H_2O]{\text{[1] } O_3} CH_3CH_2CH_2CHO$

21.13

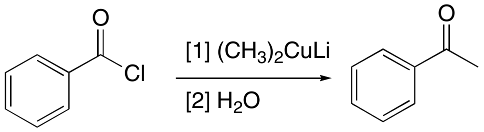
a.



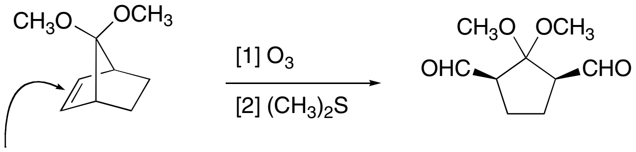
c.



b.

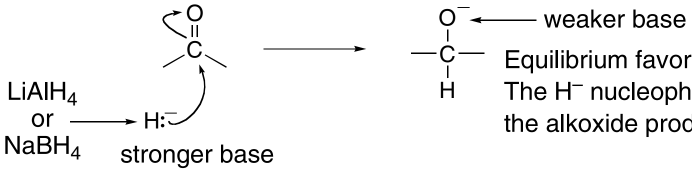


21.14



Cleave this C=C with O_3.

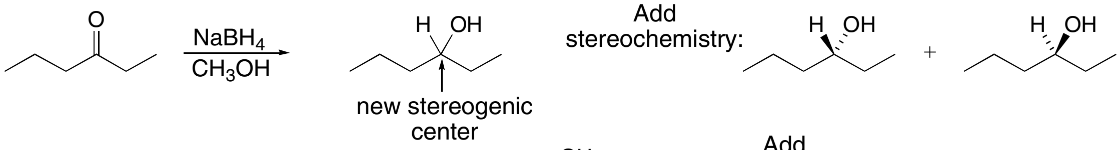
21.15



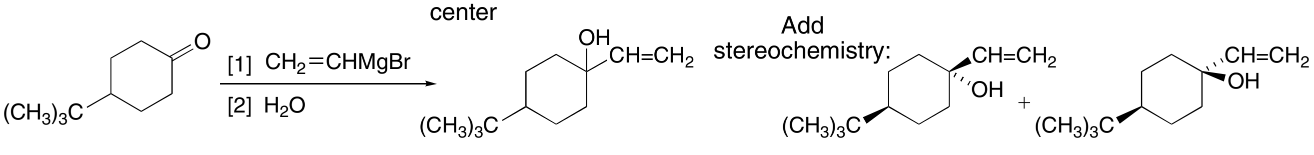
Equilibrium favors the weaker base.
The H^- nucleophile is a much stronger base than the alkoxide product.

21.16 Addition of hydride or R–M occurs at a planar carbonyl C, so two different configurations at a new stereogenic center are possible.

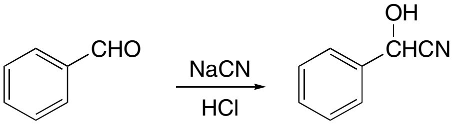
a.

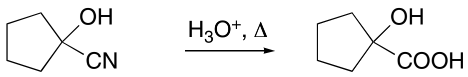


b.

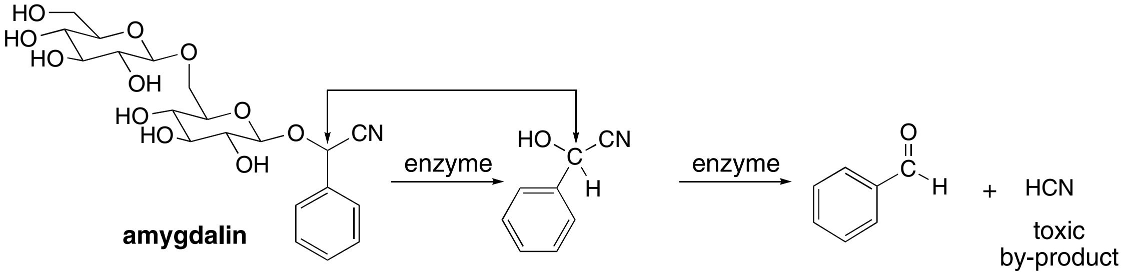


21.17 Treatment of an aldehyde or ketone with NaCN, HCl adds HCN across the double bond. Cyano groups are hydrolyzed by H_3O^+ to replace the 3 C–N bonds with 3 C–O bonds.

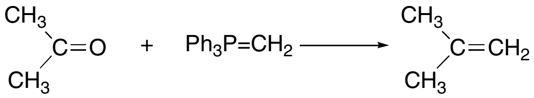
a.


b.


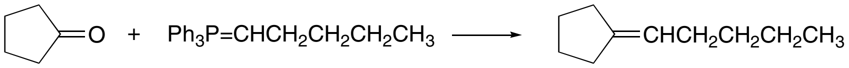
21.18



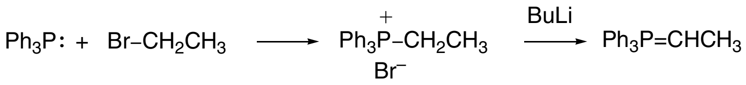
21.19

a.


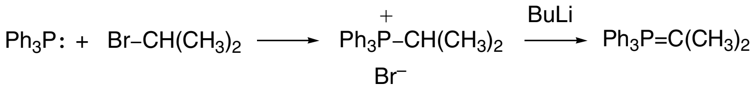
$$(CH_3)_2C=O + Ph_3P=CH_2 \longrightarrow (CH_3)_2C=CH_2$$

b.


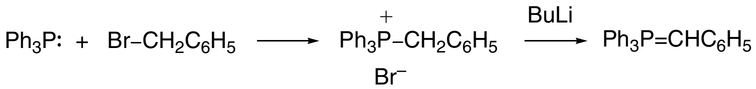
21.20

a.


$$Ph_3P: + Br{-}CH_2CH_3 \longrightarrow \overset{+}{Ph_3P}{-}CH_2CH_3 \; Br^- \xrightarrow{BuLi} Ph_3P=CHCH_3$$

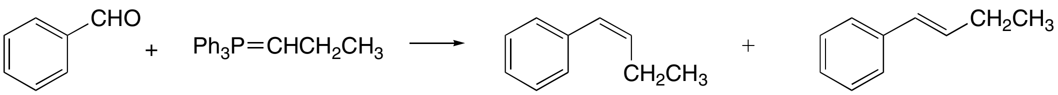
b.


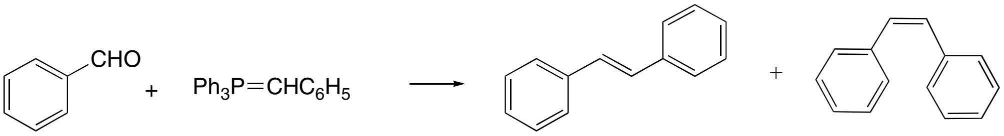
$$Ph_3P: + Br{-}CH(CH_3)_2 \longrightarrow \overset{+}{Ph_3P}{-}CH(CH_3)_2 \; Br^- \xrightarrow{BuLi} Ph_3P=C(CH_3)_2$$

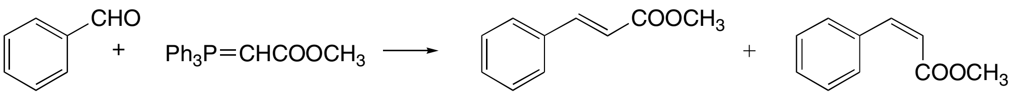
c.


$$Ph_3P: + Br{-}CH_2C_6H_5 \longrightarrow \overset{+}{Ph_3P}{-}CH_2C_6H_5 \; Br^- \xrightarrow{BuLi} Ph_3P=CHC_6H_5$$

21.21

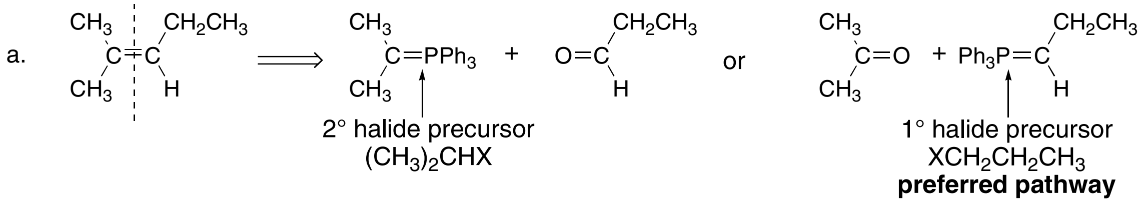
a.


b.


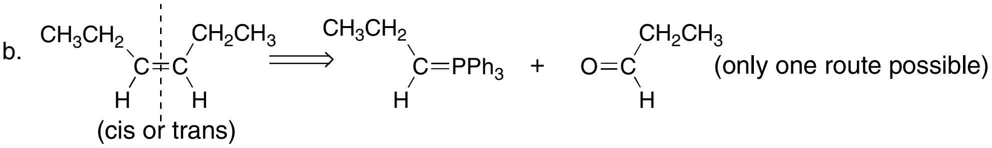
c.


21.22 To draw the starting materials of the Wittig reactions, find the C=C and cleave it. Replace it with a C=O in one half of the molecule and a C=PPh_3 in the other half. The preferred pathway uses a Wittig reagent derived from a less hindered alkyl halide.

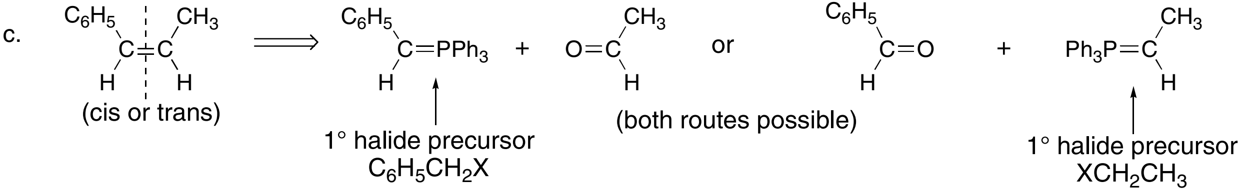
a.



b.



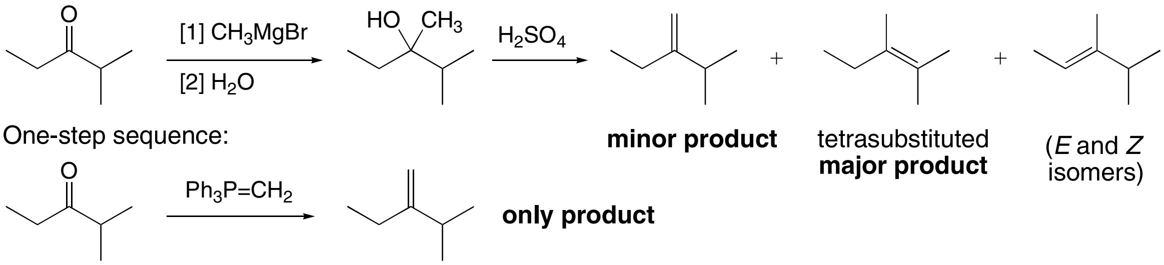
c.



21.23

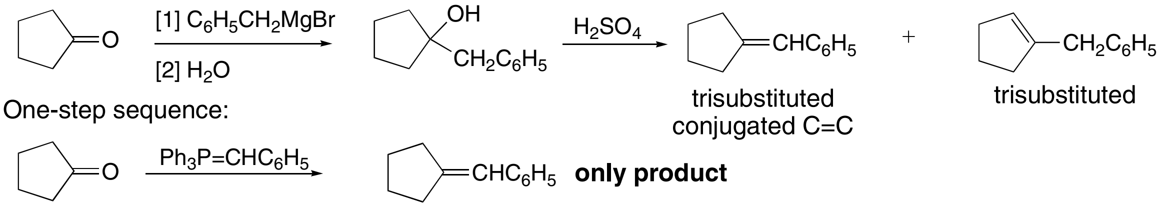
a. Two-step sequence:

One-step sequence:



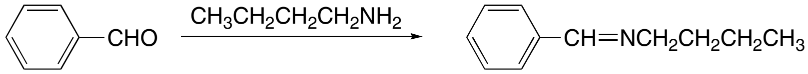
b. Two-step sequence:

One-step sequence:

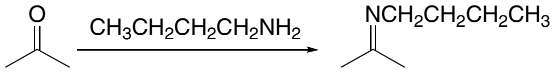


21.24 When a 1° amine reacts with an aldehyde or ketone, the C=O is replaced by C=NR.

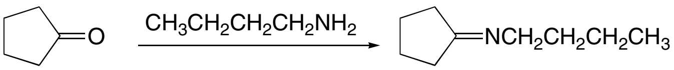
a.



b.

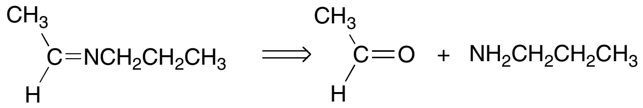


c.



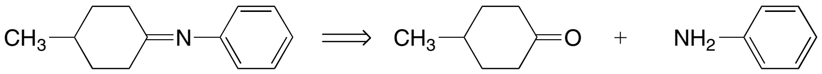
21.25 Remember that the C=NR is formed from a C=O and an NH_2 group of a 1° amine.

a.

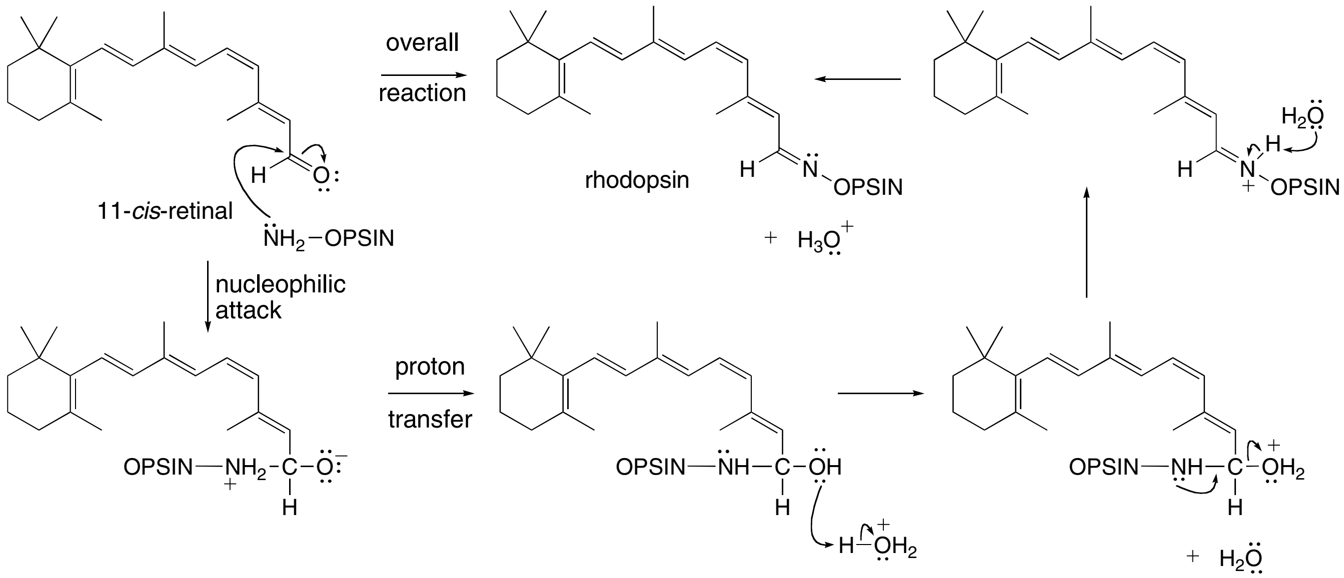


$$CH_3(H)C{=}NCH_2CH_2CH_3 \Longrightarrow CH_3(H)C{=}O + NH_2CH_2CH_2CH_3$$

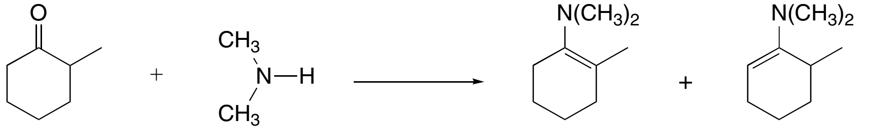
b.



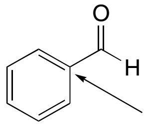
21.26



21.27



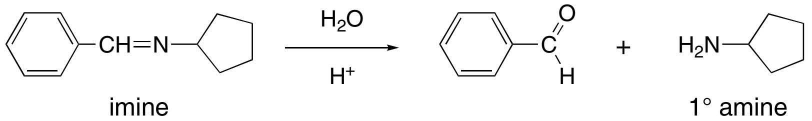
21.28



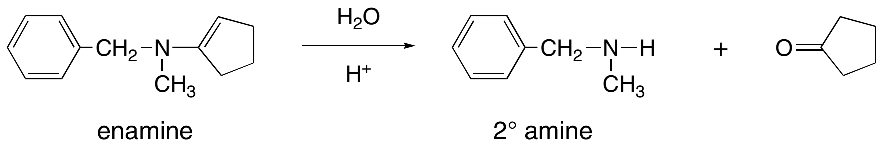
This carbon has four bonds to C's. To make an enamine, it needs a H atom, which is lost as H_2O when the enamine is formed.

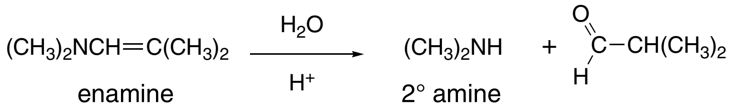
21.29 • Imines are hydrolyzed to 1° amines and a carbonyl compound.
• Enamines are hydrolyzed to 2° amines and a carbonyl compound.

a.



b.

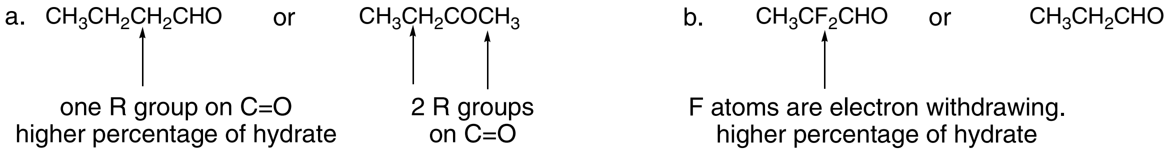


c. 

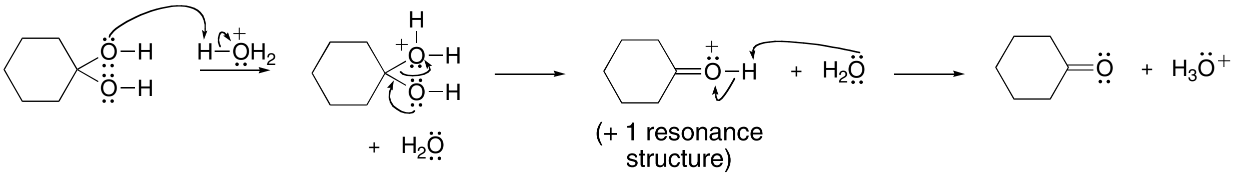
$$(CH_3)_2NCH{=}C(CH_3)_2 \xrightarrow[H^+]{H_2O} (CH_3)_2NH + \overset{O}{\overset{\|}{\underset{H}{C}}}{-}CH(CH_3)_2$$

21.30 • A substituent that **donates** electron density to the carbonyl C stabilizes it, **decreasing** the percentage of hydrate at equilibrium.

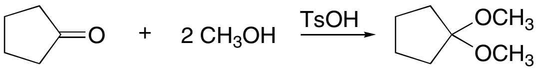
• A substituent that **withdraws** electron density from the carbonyl C destabilizes it, **increasing** the percentage of hydrate at equilibrium.

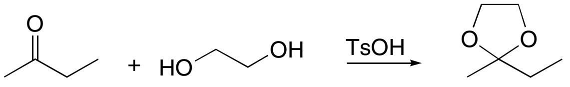


21.31

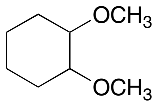


21.32 Treatment of an aldehyde or ketone with two equivalents of alcohol results in the formation of an acetal (a C bonded to 2 OR groups).

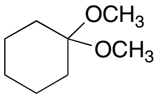
a. 

b. 

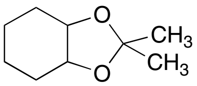
21.33

a. 

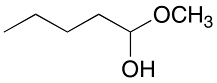
2 OR groups
on different C's
2 ethers

b. 

2 OR groups
on same C
acetal

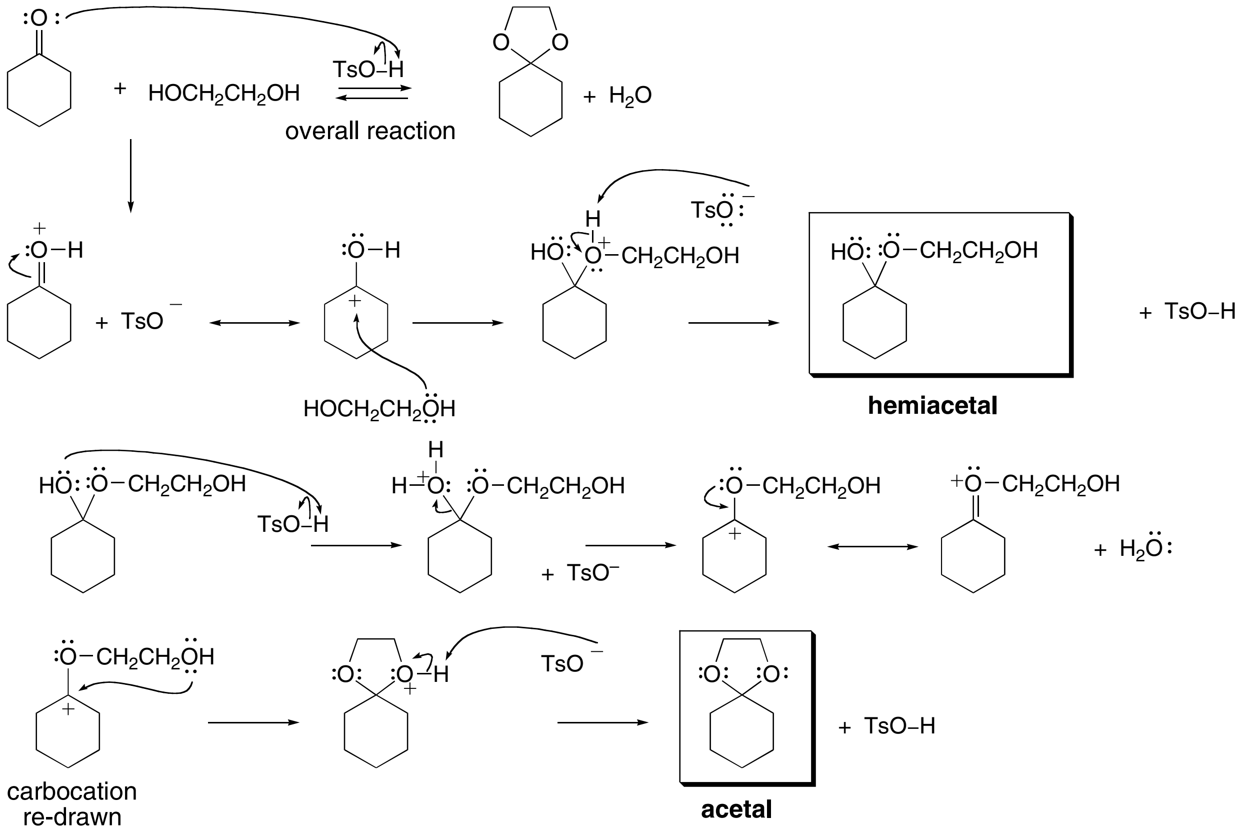
c. 

2 OR groups
on same C
acetal

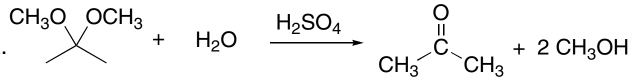
d. 

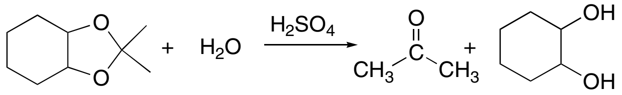
1 OR group and
1 OH group
on same C
hemiacetal

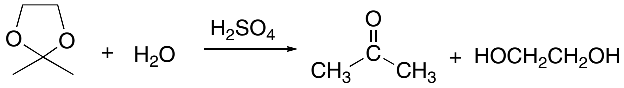
21.34 The mechanism has two parts: [1] nucleophilic addition of ROH to form a hemiacetal; [2] conversion of the hemiacetal to an acetal.



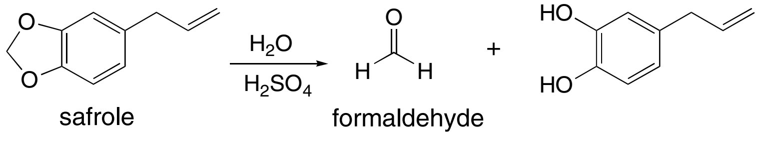
21.35

a.


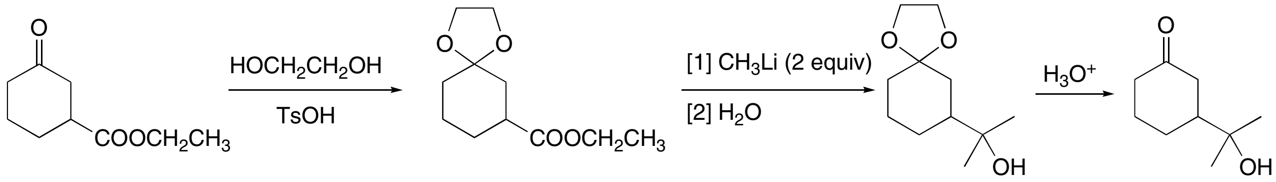
c.


b.


21.36

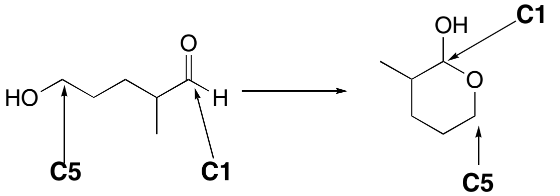


21.37 Use an acetal protecting group to carry out the reaction.

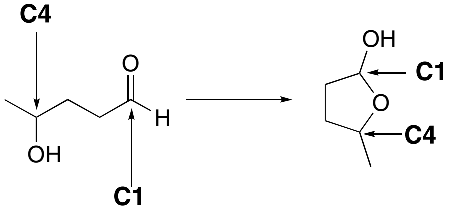


21.38

a.

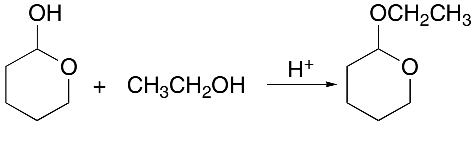


b.

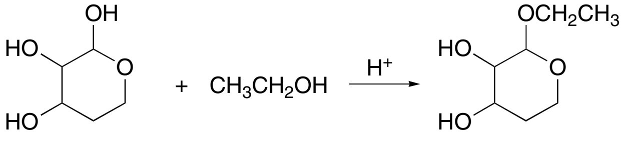


21.39 The hemiacetal OH is replaced by an OR group to form an acetal.

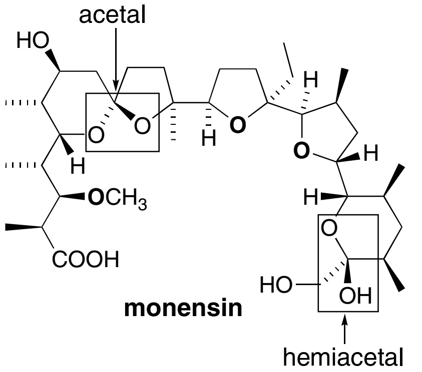
a.



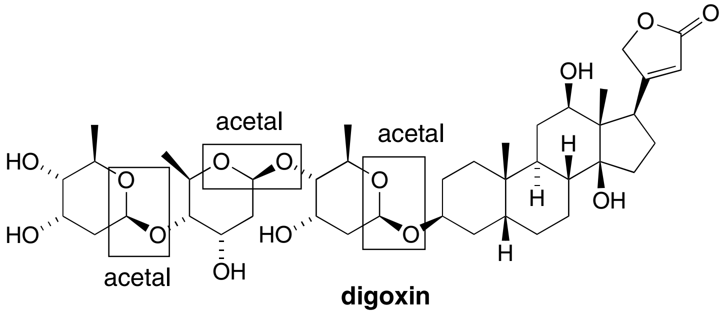
b.



21.40

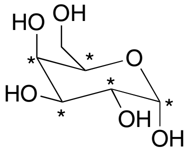


Ether **O** atoms are indicated in **bold.**



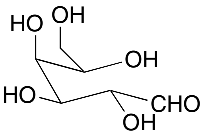
21.41

a.

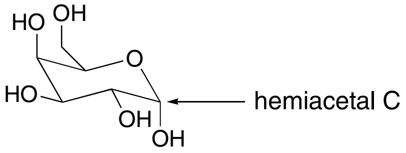


5 stereogenic centers (labeled with *)

d.

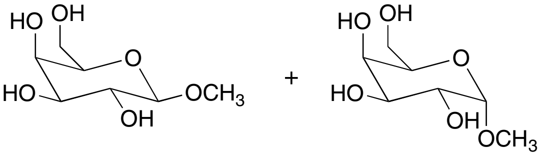


b.

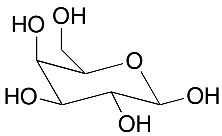


α-D-galactose

e.



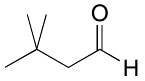
c.



β-D-galactose

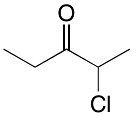
21.42 Use the rules from Answers 21.3 and 21.5 to name the aldehydes and ketones.

a. $(CH_3)_3CCH_2CHO \xrightarrow{\text{re-draw}}$



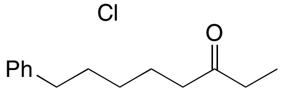
4 C = butanal
3,3-dimethylbutanal

b.



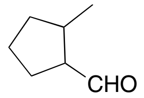
5 C = pentanone
2-chloro-3-pentanone

c.



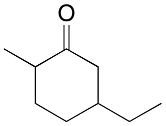
8 C = octanone
8-phenyl-3-octanone

d.



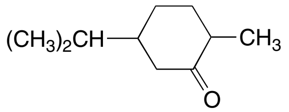
5 C ring
2-methyl-
cyclopentanecarbaldehyde

e.



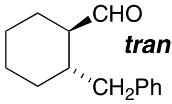
6 C ring = cyclohexanone
5-ethyl-2-methyl-
cyclohexanone

f.



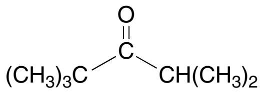
6 C ring = cyclohexanone
5-isopropyl-2-methyl-
cyclohexanone

g.

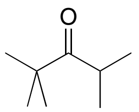


***trans*-2-benzylcyclohexanecarbaldehyde**

h.

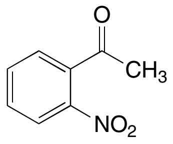


$(CH_3)_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH(CH_3)_2 \xrightarrow{\text{re-draw}}$



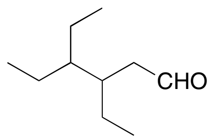
5 C = pentanone
2,2,4-trimethyl-
3-pentanone
(common name:
***tert*-butyl isopropyl ketone)**

i.



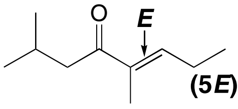
***o*-nitroacetophenone**

j.



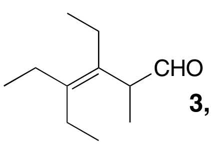
6 C = hexanal
3,4-diethylhexanal

k.



8 C = octenone
(5*E*)-2,5-dimethyl-5-octen-4-one

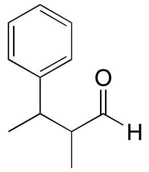
l.



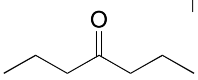
6 C = hexenal
3,4-diethyl-2-methyl-3-hexenal

21.43

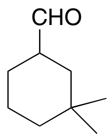
a. 2-methyl-3-phenylbutanal



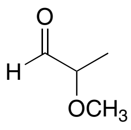
b. dipropyl ketone



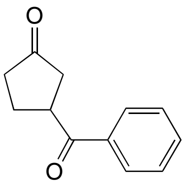
c. 3,3-dimethylcyclohexanecarbaldehyde



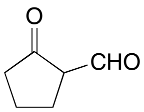
d. α-methoxypropionaldehyde



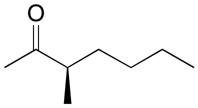
e. 3-benzoylcyclopentanone



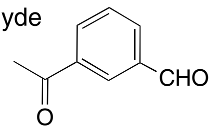
f. 2-formylcyclopentanone



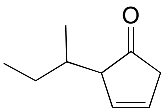
g. (3*R*)-3-methyl-2-heptanone



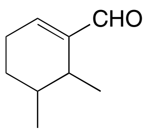
h. *m*-acetylbenzaldehyde



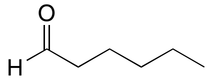
i. 2-*sec*-butyl-3-cyclopentenone



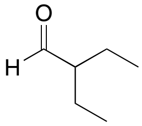
j. 5,6-dimethyl-1-cyclohexenecarbaldehyde



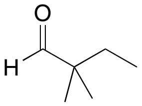
21.44



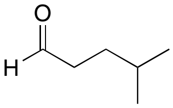
hexanal



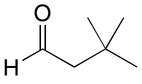
2-ethylbutanal



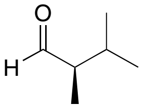
2,2-dimethylbutanal



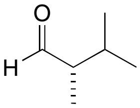
4-methylpentanal



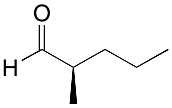
3,3-dimethylbutanal



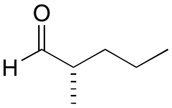
(2*R*)-2,3-dimethylbutanal



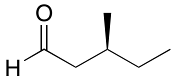
(2*S*)-2,3-dimethylbutanal



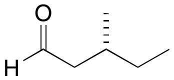
(2*R*)-2-methylpentanal



(2*S*)-2-methylpentanal

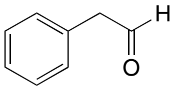


(3*S*)-3-methylpentanal



(3*R*)-3-methylpentanal

21.45



= $C_6H_5CH_2CHO$ phenylacetaldehyde

a. $\xrightarrow{NaBH_4,\ CH_3OH}$ $C_6H_5CH_2CH_2OH$

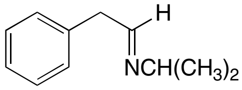
b. $\xrightarrow{[1]\ LiAlH_4;\ [2]\ H_2O}$ $C_6H_5CH_2CH_2OH$

c. $\xrightarrow{[1]\ CH_3MgBr;\ [2]\ H_2O}$ $C_6H_5CH_2CH(OH)CH_3$

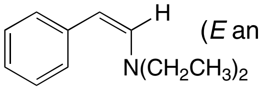
d. $\xrightarrow{NaCN,\ HCl}$ $C_6H_5CH_2CH(OH)CN$

e. $\xrightarrow{Ph_3P{=}CHCH_3}$ $C_6H_5CH_2CH{=}CHCH_3$
(*E* and *Z* isomers)

f. $\xrightarrow[\text{mild acid}]{(CH_3)_2CHNH_2}$

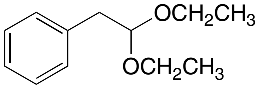


g. $\xrightarrow{(CH_3CH_2)_2NH,\ \text{mild acid}}$

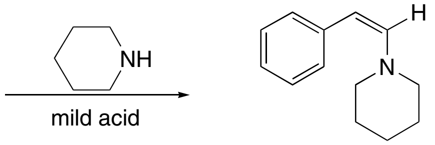


(*E* and *Z* isomers)

h. $\xrightarrow{CH_3CH_2OH\ (\text{excess}),\ H^+}$

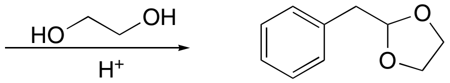


i.

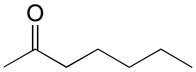


(*E* and *Z* isomers)

j.

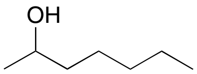


21.46

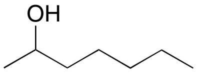


2-heptanone

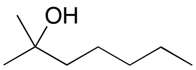
a. $\xrightarrow{NaBH_4,\ CH_3OH}$



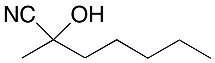
b. $\xrightarrow{[1]\ LiAlH_4;\ [2]\ H_2O}$



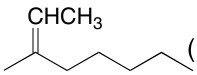
c. $\xrightarrow{[1]\ CH_3MgBr;\ [2]\ H_2O}$



d. $\xrightarrow{NaCN,\ HCl}$

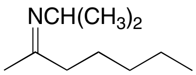


e. $\xrightarrow{Ph_3P{=}CHCH_3}$

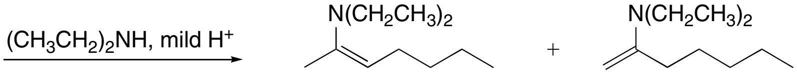


(*E* and *Z* isomers)

f. $\xrightarrow{(CH_3)_2CHNH_2,\ \text{mild}\ H^+}$

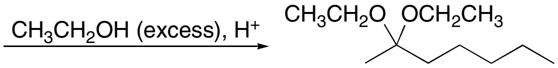


g.

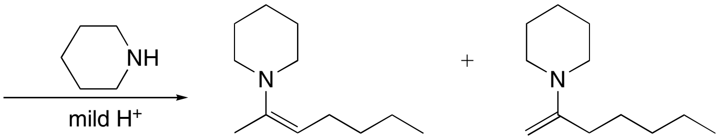


(*E* and *Z* isomers)

h.

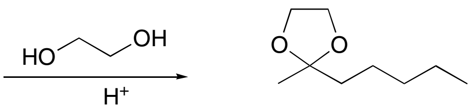


i.



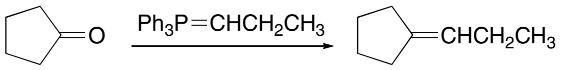
(*E* and *Z* isomers)

j.

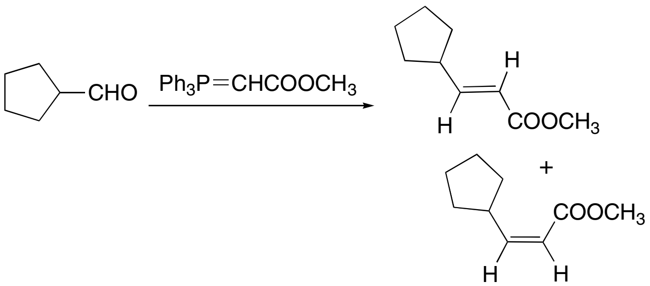


21.47

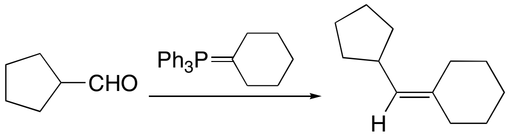
a.



c.



b.

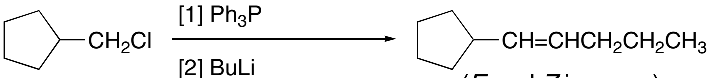


d.

21.48

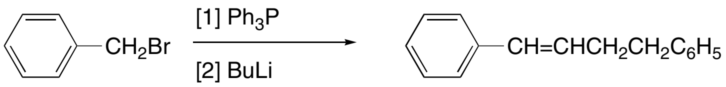
a. $CH_3CH_2Cl \xrightarrow[\substack{\text{[2] BuLi} \\ \text{[3] } (CH_3)_2C{=}O}]{\text{[1] } Ph_3P} CH_3CH{=}C(CH_3)_2$

c.



(*E* and *Z* isomers)

b.



(*E* and *Z* isomers)

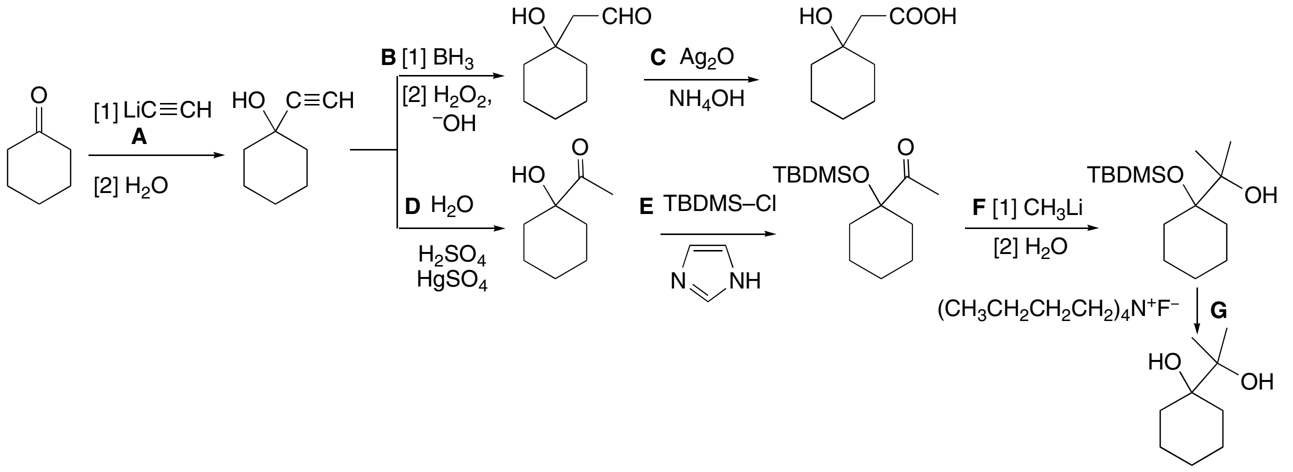
21.49

a. $Ph_3P{=}CHCH_2CH_2CH_3 \Longrightarrow BrCH_2CH_2CH_2CH_3$

c. $Ph_3P{=}CHCH{=}CH_2 \Longrightarrow BrCH_2CH{=}CH_2$

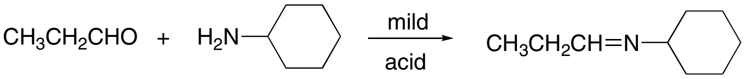
b. $Ph_3P{=}C(CH_2CH_2CH_3)_2 \Longrightarrow BrCH(CH_2CH_2CH_3)_2$

21.50

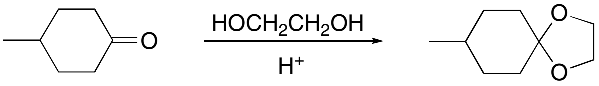


21.51

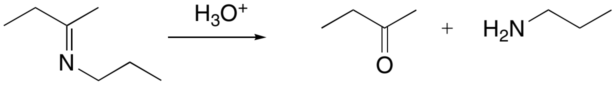
a.



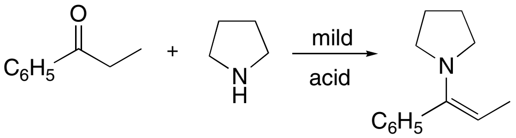
b.



c.

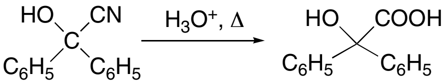


d.

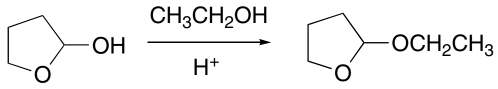


(*E* and *Z* isomers)

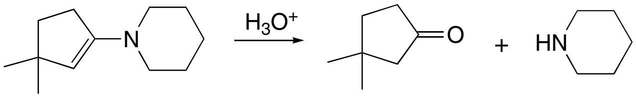
e.



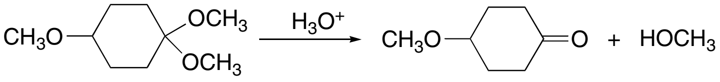
f.



g.

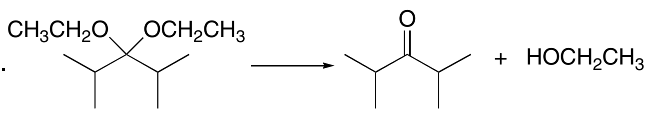


h.

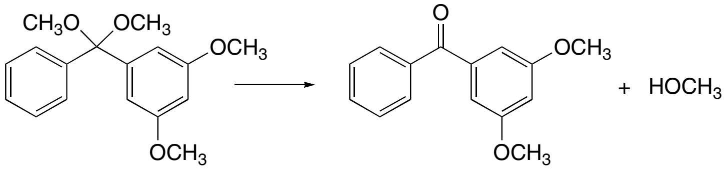


21.52

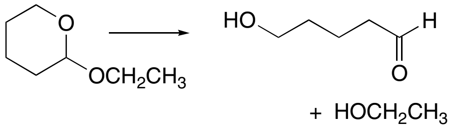
a.



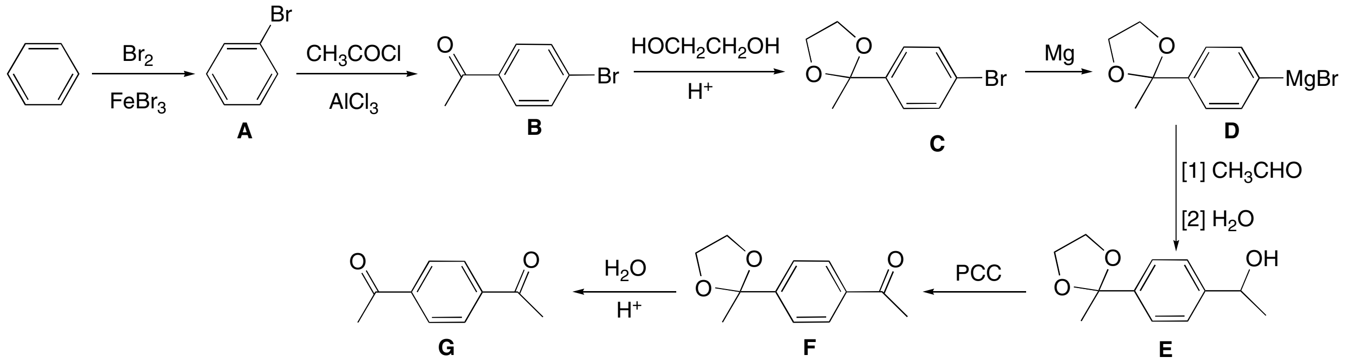
b.



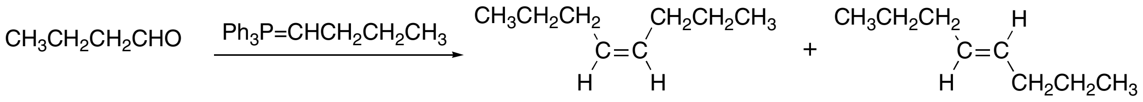
c.

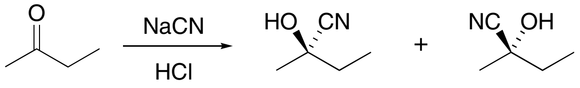


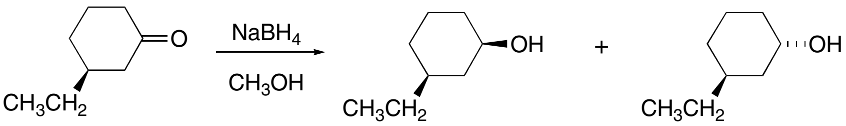
21.53 Consider para product only, when an ortho, para mixture can result.

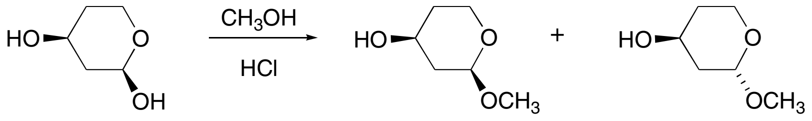


21.54

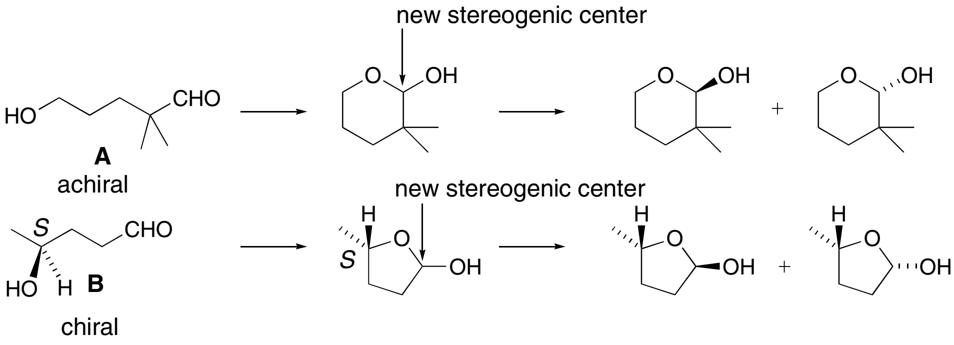
a.


b.


c.


d.


21.55

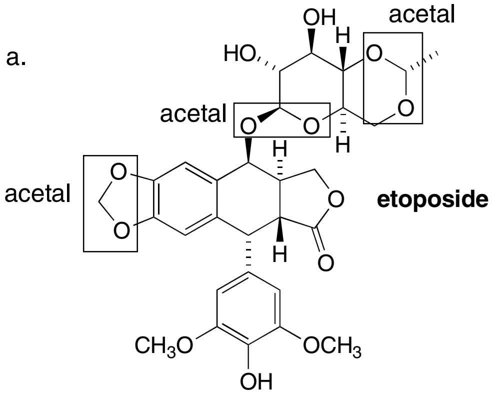


An equal mixture of enantiomers results, so the product is optically inactive.

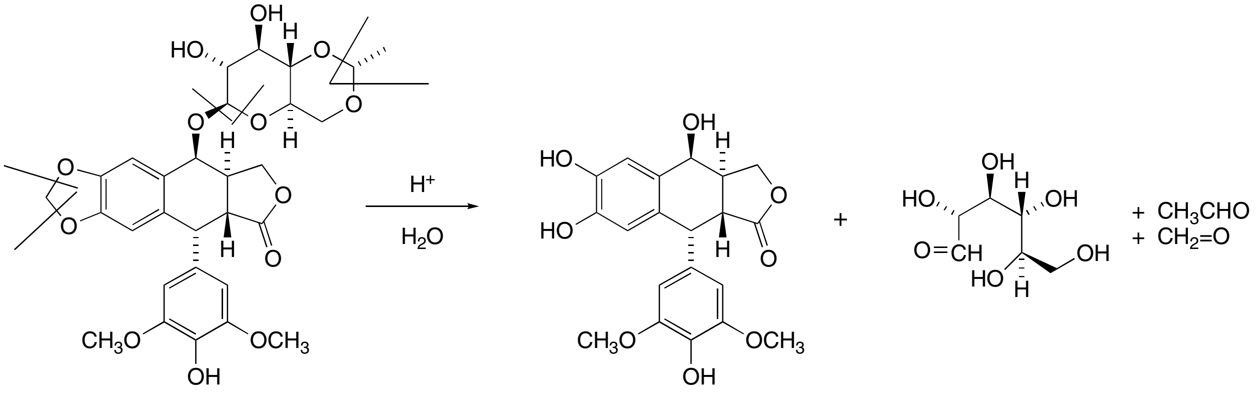
A mixture of diastereomers results. Both compounds are chiral and they are not enantiomers, so the mixture is optically active.

21.56

a.

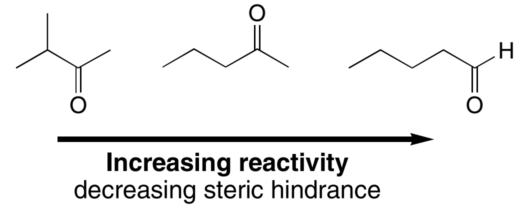


b. Lines of cleavage are drawn in.

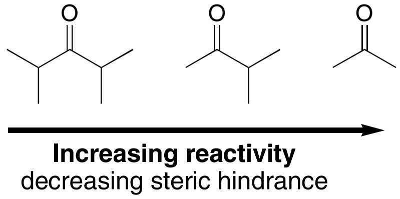


21.57 Use the rule from Answer 21.1.

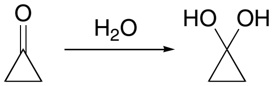
a.



b.

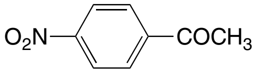


21.58

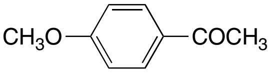


Less stable carbonyl compounds give a higher percentage of hydrate. Cyclopropanone is an unstable carbonyl compound because the bond angles around the carbonyl carbon deviate considerably from the desired angle. Since the carbonyl carbon is *sp*^{2} hybridized, the optimum bond angle is 120°, but the three-membered ring makes the C–C–C bond angles only 60°. This destabilizes the ketone, giving a high concentration of hydrate when dissolved in H_2O.

21.59 Electron-donating groups decrease the amount of hydrate at equilibrium by stabilizing the carbonyl starting material. Electron-withdrawing groups increase the amount of hydrate at equilibrium by destabilizing the carbonyl starting material. Electron-donating groups make the IR absorption of the C=O shift to lower wavenumber because they stabilize the charge-separated resonance form, giving the C=O more single bond character.



p-nitroacetophenone

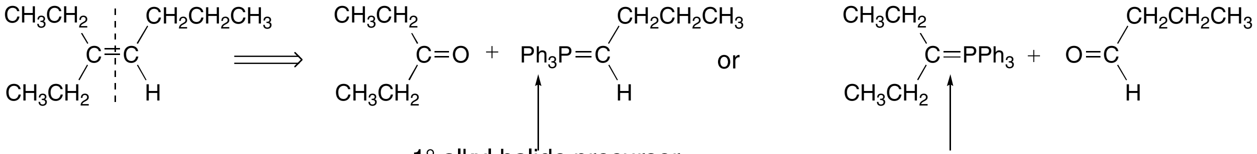


p-methoxyacetophenone

	p-nitroacetophenone	*p*-methoxyacetophenone
a.	NO_2 withdrawing group **less stable**	CH_3O donating group **more stable**
b.	**higher percentage of hydrate**	**lower percentage of hydrate**
c.	**higher wavenumber**	**lower wavenumber**

21.60 Use the principles from Answer 21.22.

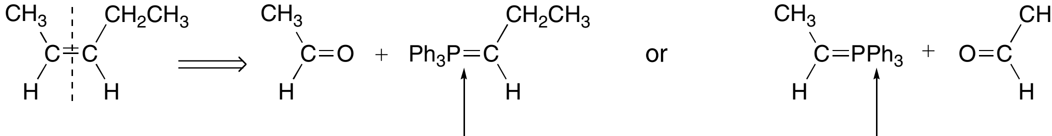
a.



1° alkyl halide precursor
($XCH_2CH_2CH_2CH_3$)
preferred pathway

2° alkyl halide precursor
[$(CH_3CH_2)_2CHX$]

b.

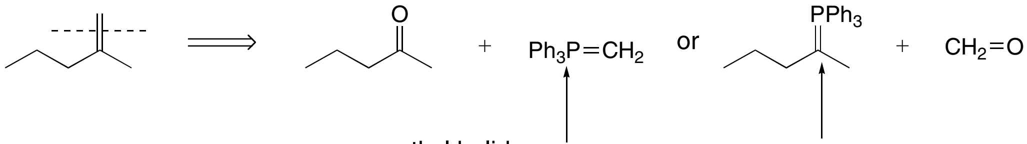


1° alkyl halide precursor
($XCH_2CH_2CH_3$)

1° alkyl halide precursor
(XCH_2CH_3)

(Both routes possible.)

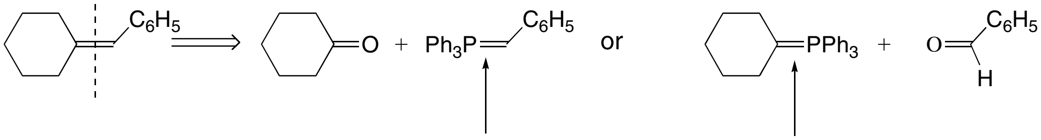
c.



methyl halide precursor
(CH_3X)
preferred pathway

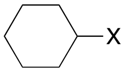
2° alkyl halide precursor
($CH_3CH_2CH_2CHXCH_3$)

d.



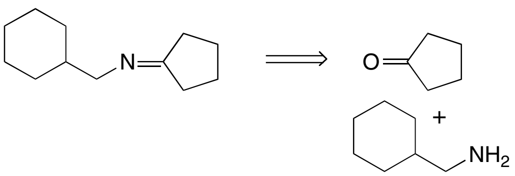
1° alkyl halide precursor
($C_6H_5CH_2X$)
preferred pathway

2° alkyl halide precursor

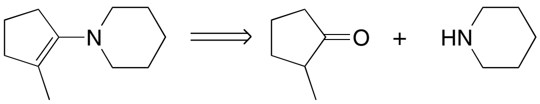


21.61

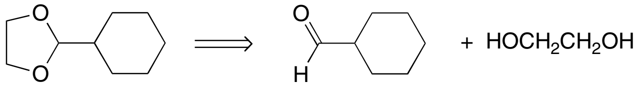
a.



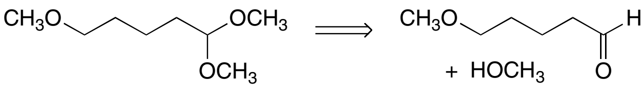
b.



c.



d.



21.62

a. $C_6H_5\text{–}CH_2OH \xrightarrow{\text{PCC}} C_6H_5\text{–}CHO$

b. $C_6H_5\text{–}COCl \xrightarrow[\text{[2] }H_2O]{\text{[1] }LiAlH[OC(CH_3)_3]_3} C_6H_5\text{–}CHO$

c. $C_6H_5\text{–}COOCH_3 \xrightarrow[\text{[2] }H_2O]{\text{[1] DIBAL-H}} C_6H_5\text{–}CHO$

d. $C_6H_5\text{–}COOH \xrightarrow[\text{[2] }H_2O]{\text{[1] }LiAlH_4} C_6H_5\text{–}CH_2OH \xrightarrow{\text{PCC}} C_6H_5\text{–}CHO$

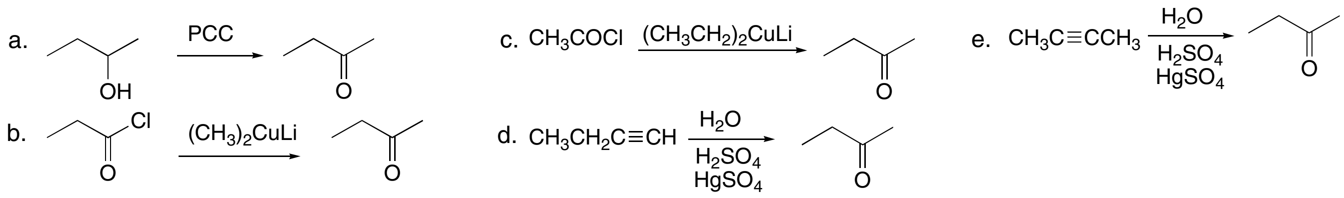
e. $C_6H_5\text{–}CH_3 \xrightarrow{KMnO_4} C_6H_5\text{–}COOH \xrightarrow[\text{[2] }H_2O]{\text{[1] }LiAlH_4} C_6H_5\text{–}CH_2OH \xrightarrow{\text{PCC}} C_6H_5\text{–}CHO$

f. $C_6H_5\text{–}CH{=}CH_2 \xrightarrow[\text{[2] Zn, }H_2O]{\text{[1] }O_3} C_6H_5\text{–}CHO$

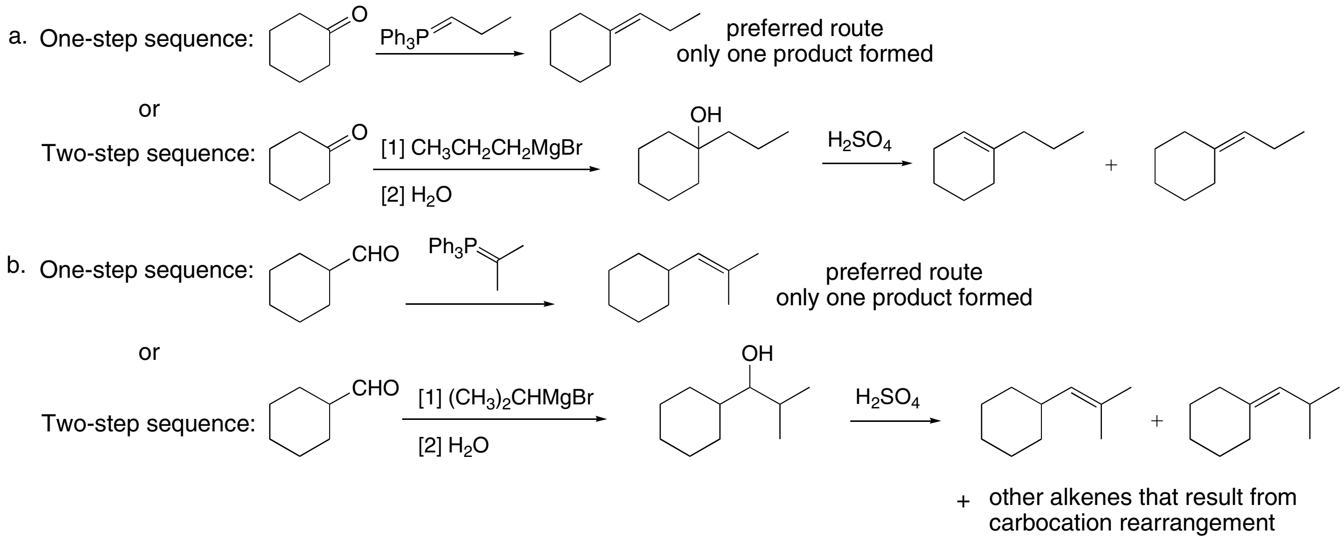
g. $C_6H_5\text{–}CH{=}NCH_2CH_2CH_3 \xrightarrow[H^+]{H_2O} C_6H_5\text{–}CHO$

h. $C_6H_5\text{–}CH(OCH_2CH_3)_2 \xrightarrow[H^+]{H_2O} C_6H_5\text{–}CHO$

21.63



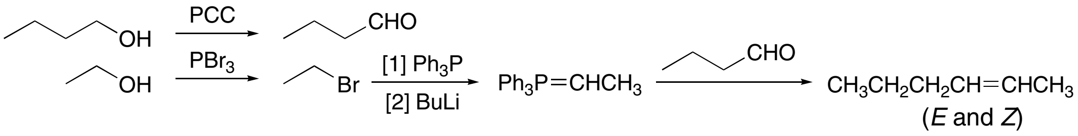
21.64



21.65

a. $CH_3CH_2CH_2CH{\vdots}{=}CHCH_3$

One possibility:



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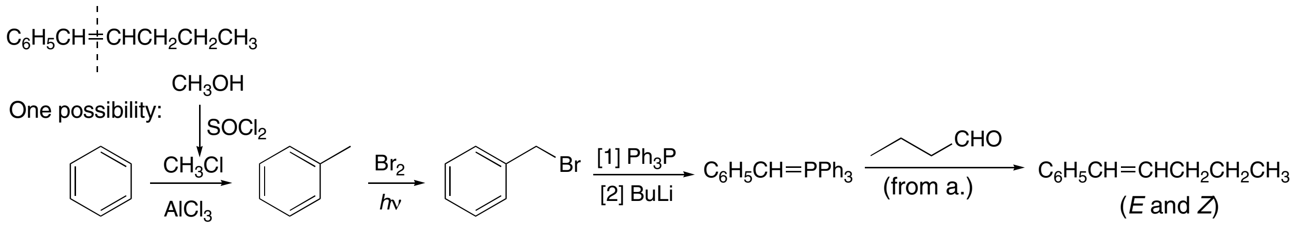

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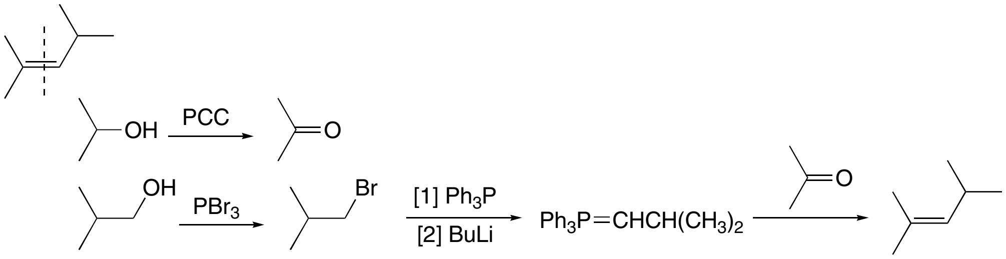
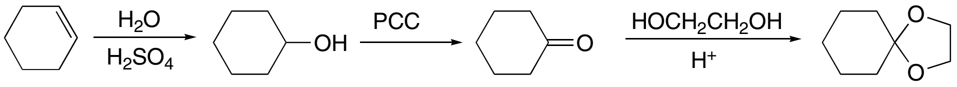
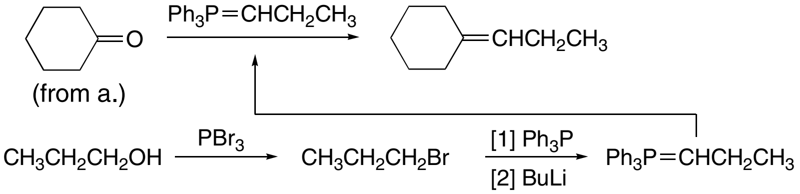


21.66

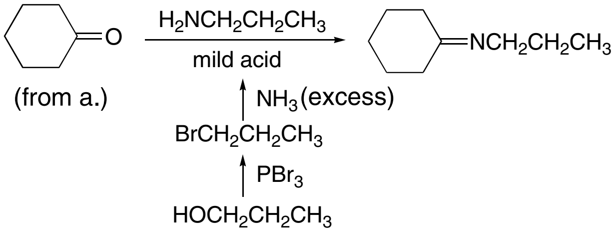
a.



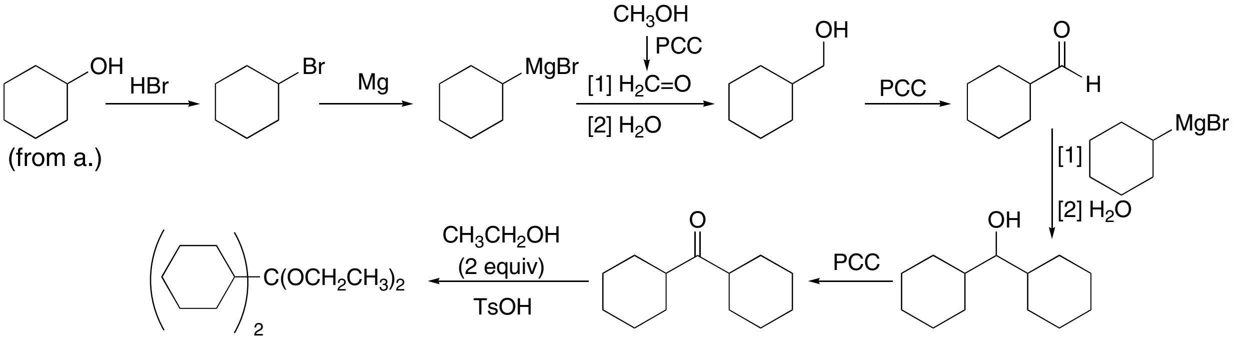
b.



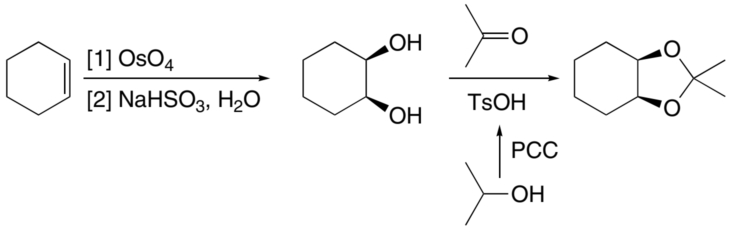
c.



d.

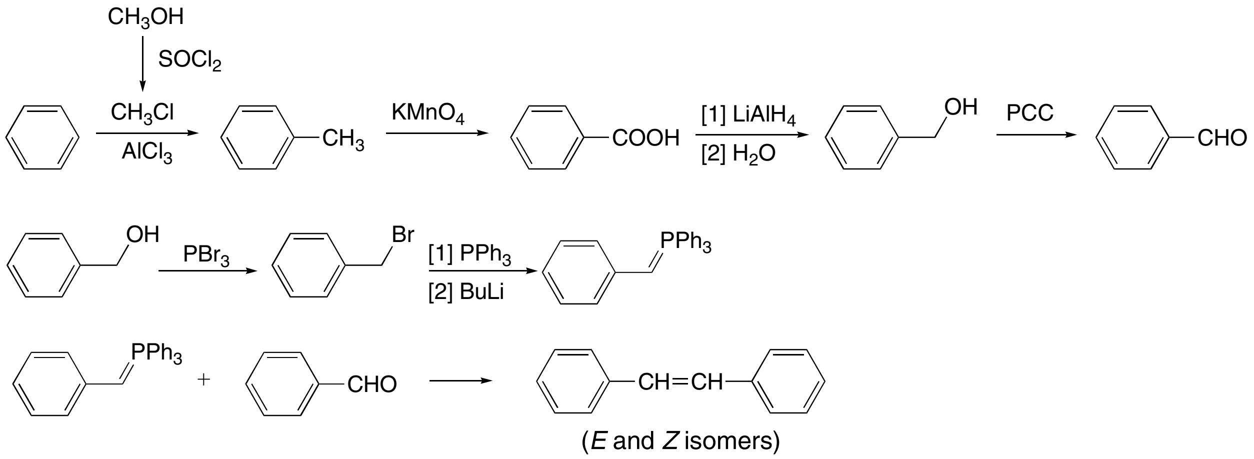


e.

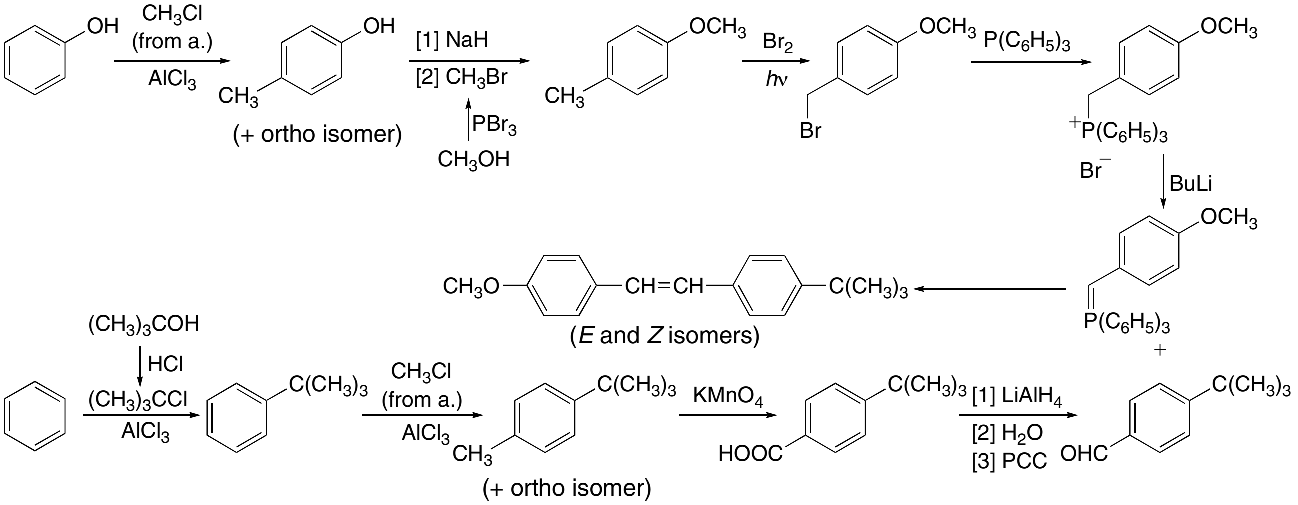


21.67

a.

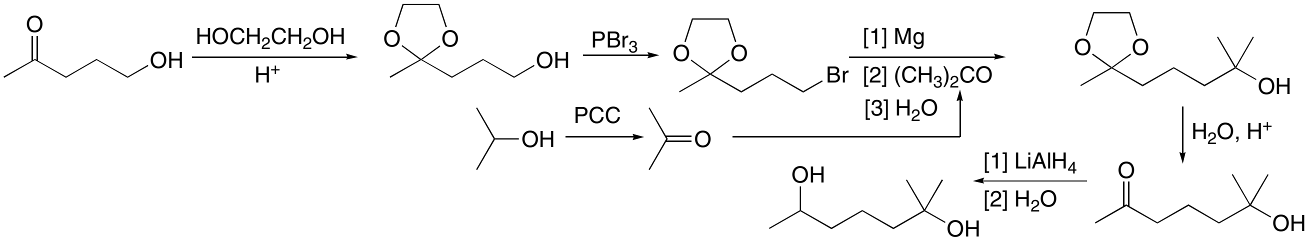


b.



21.68

a.



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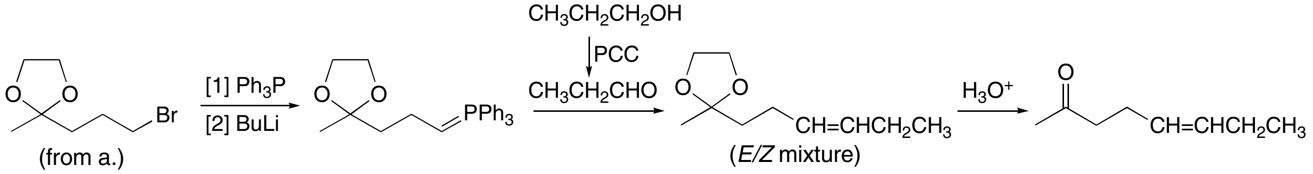
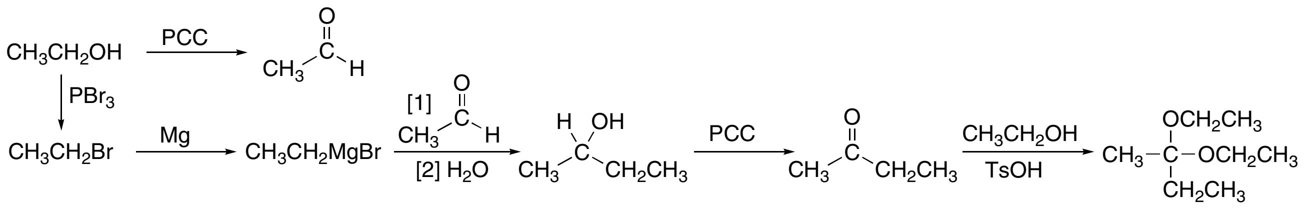


21.69

a.



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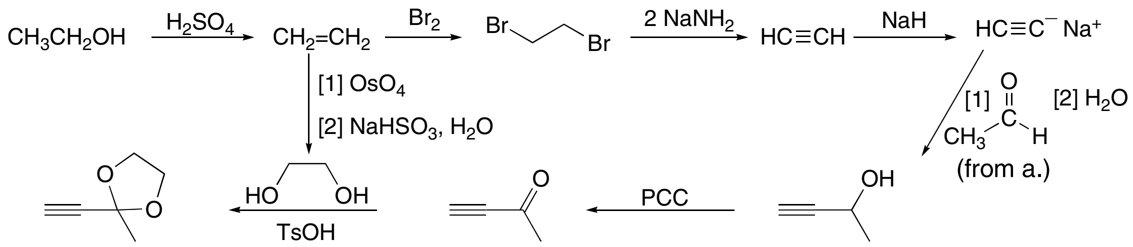
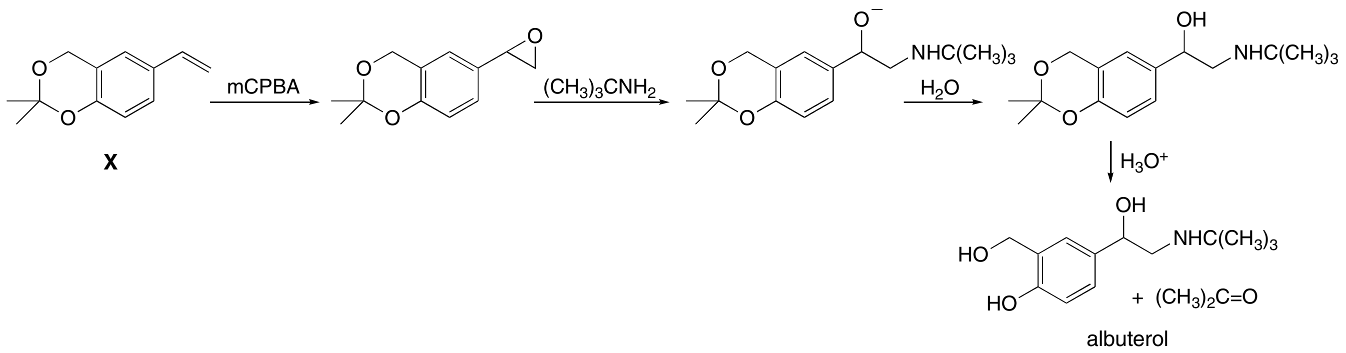
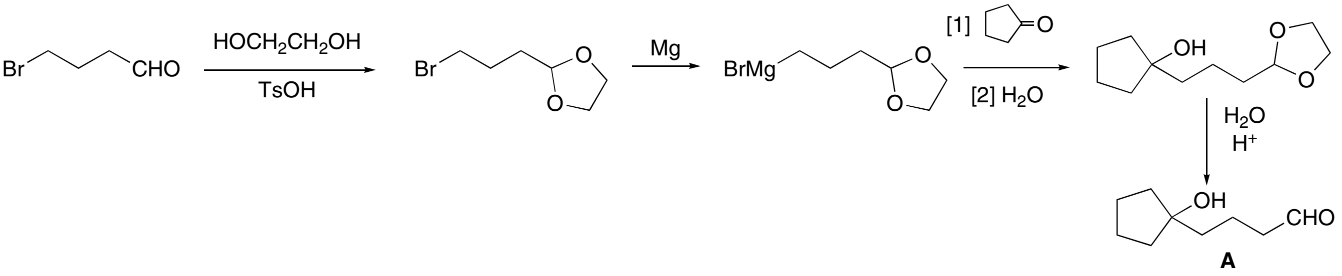


21.70

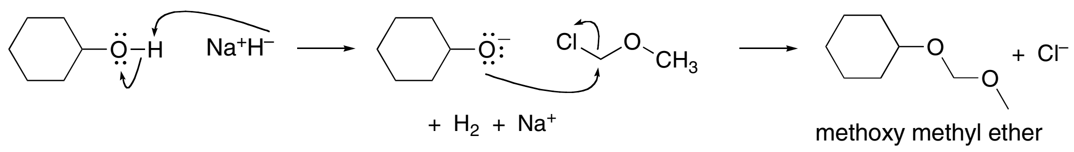


21.71

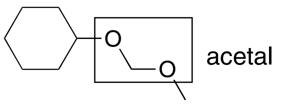


21.72

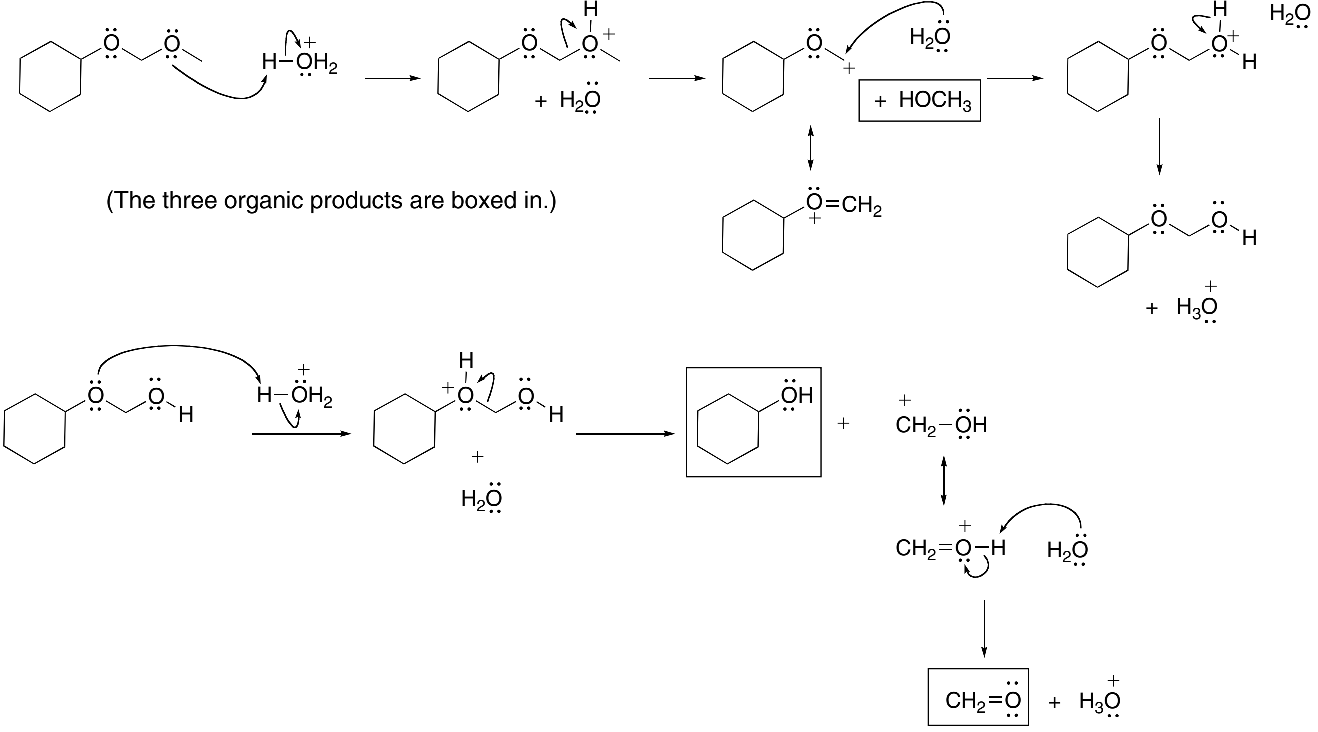
a.



b.



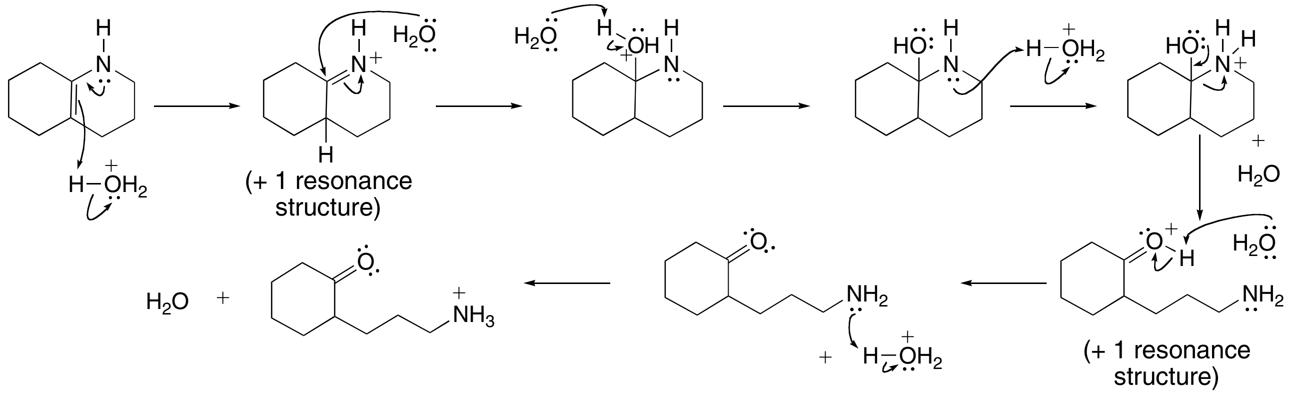
c.



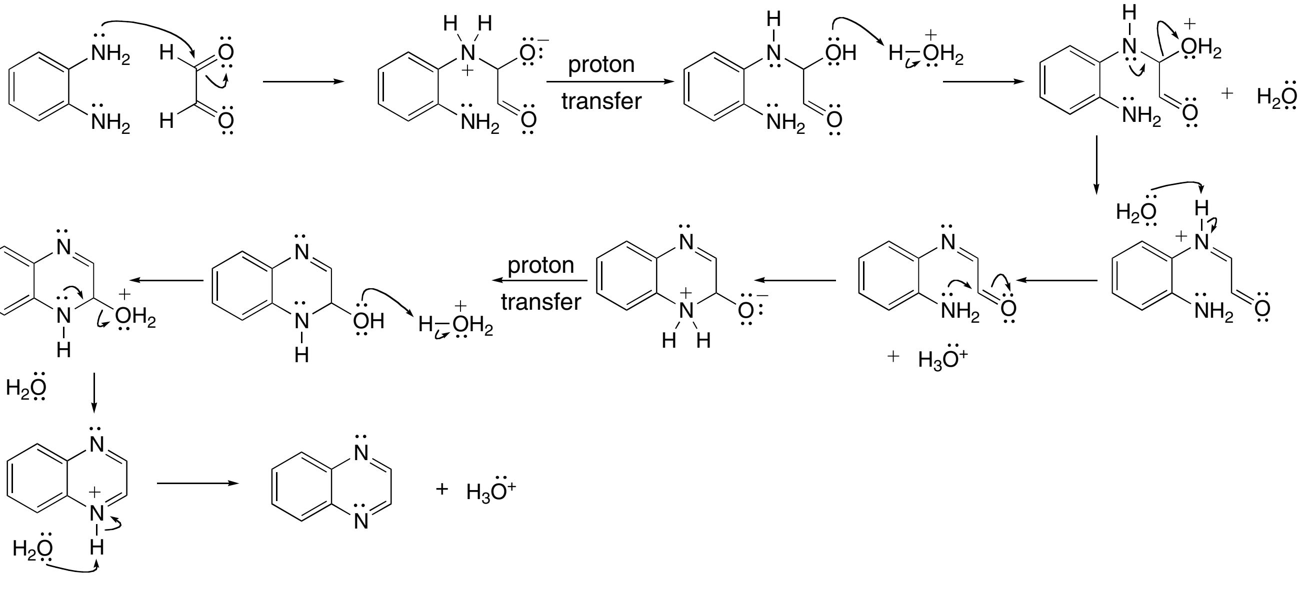
(The three organic products are boxed in.)

21.73

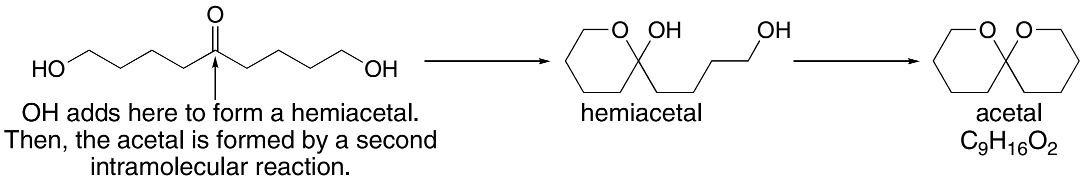
a.



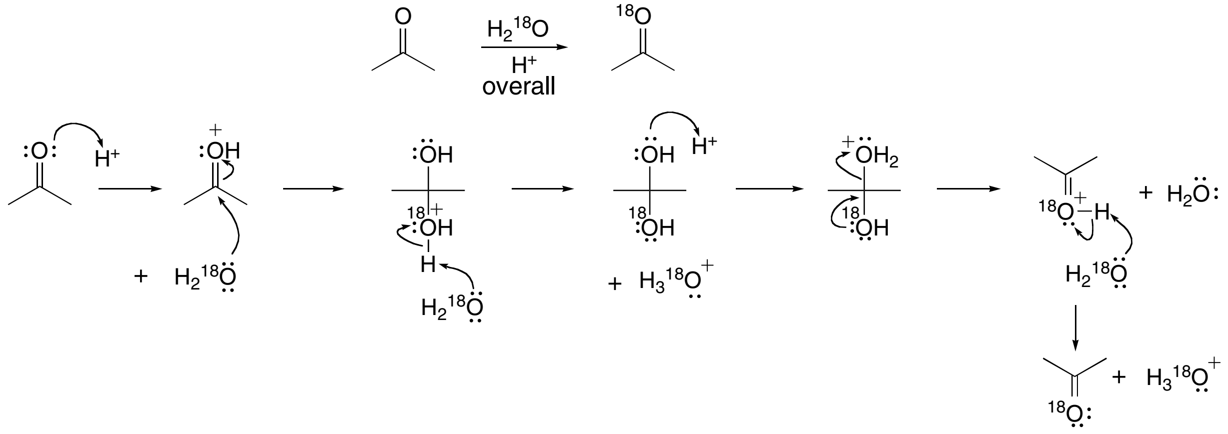
b.



21.74 The OH groups react with the C=O in an intramolecular reaction, first to form a hemiacetal, and then to form an acetal.

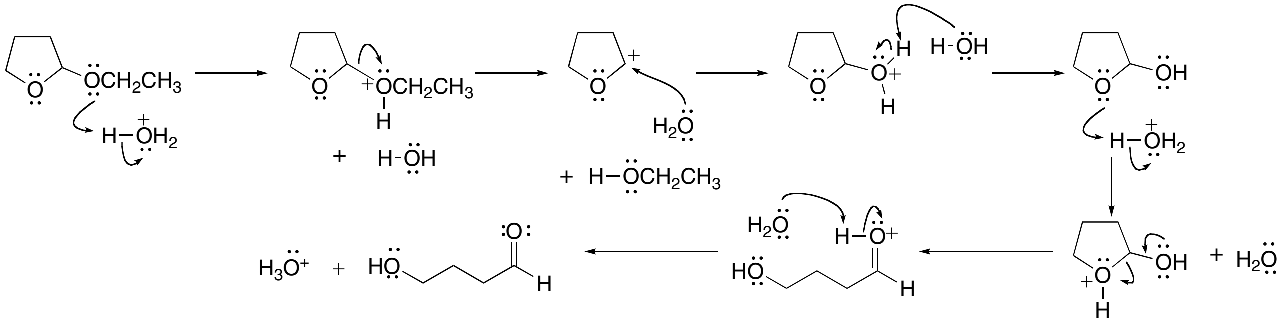


21.75

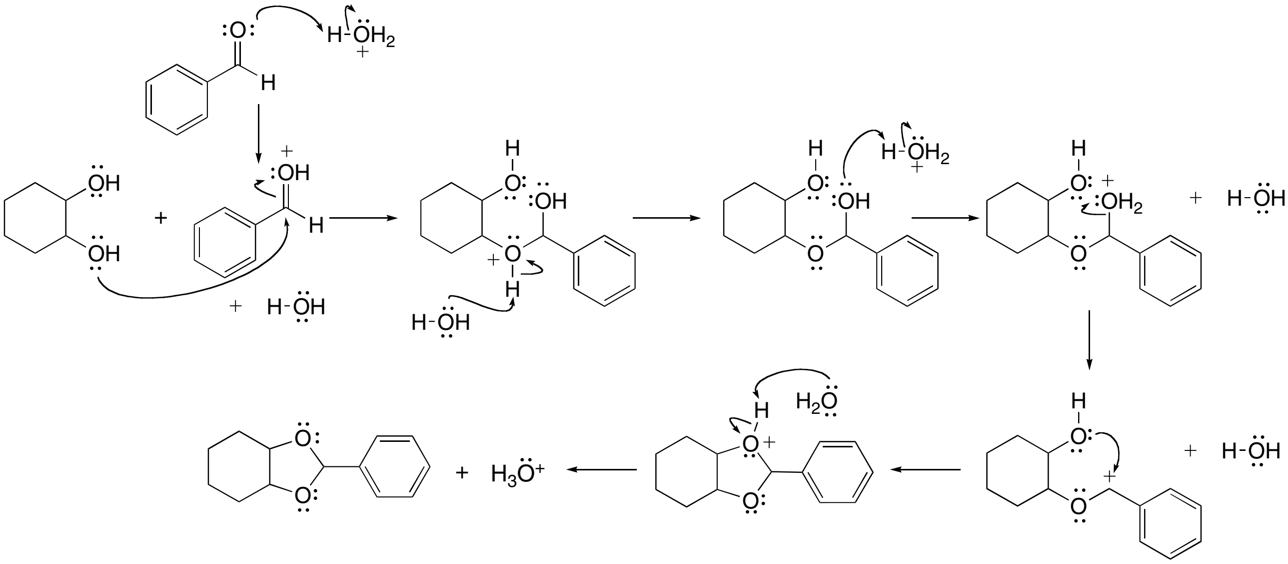


21.76

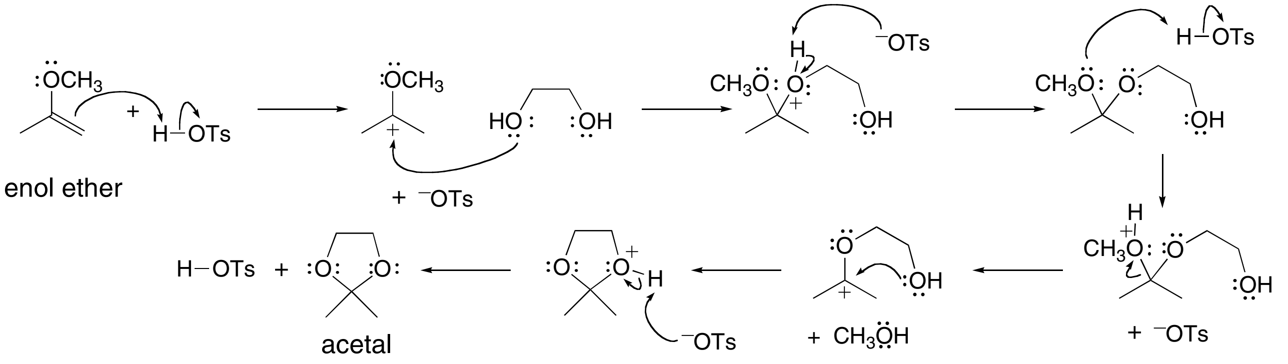
a.


OCH2CH3
H–OH2
+ H-OH
H2O
+ H–OCH2CH3
H-OH
OH
H–OH2
+ H2O
H2O
H3O+
HO
H

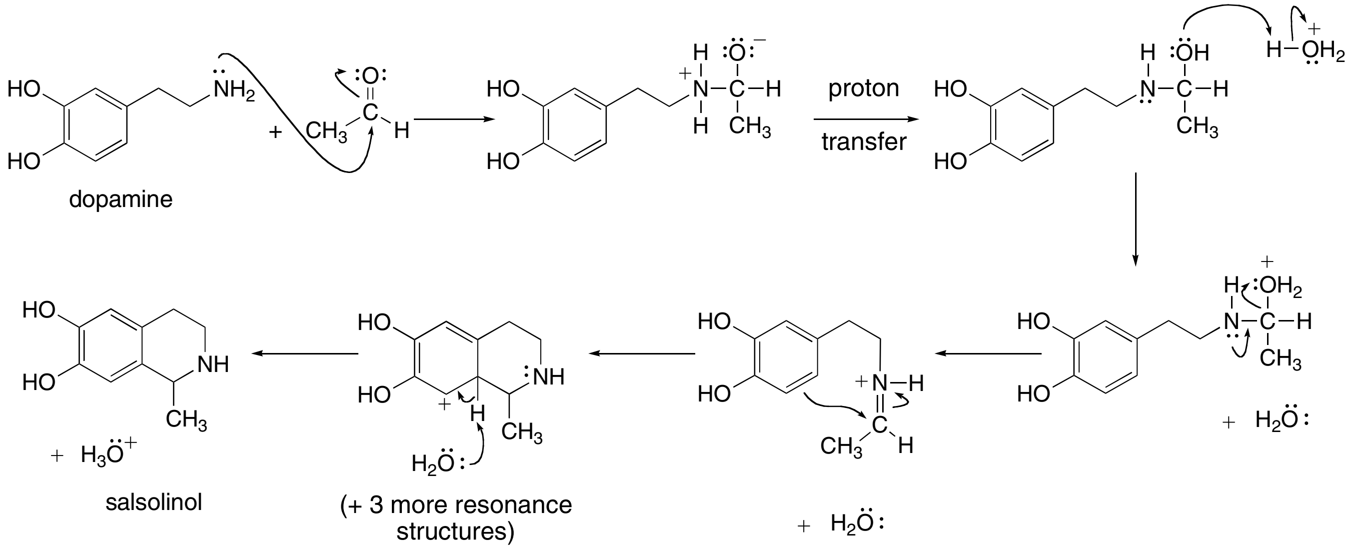
b.


H-OH2
OH
+
H
+ H-OH
H-OH
H-OH2
OH2
+ H-OH
H2O
+ H3O+
+ H-OH

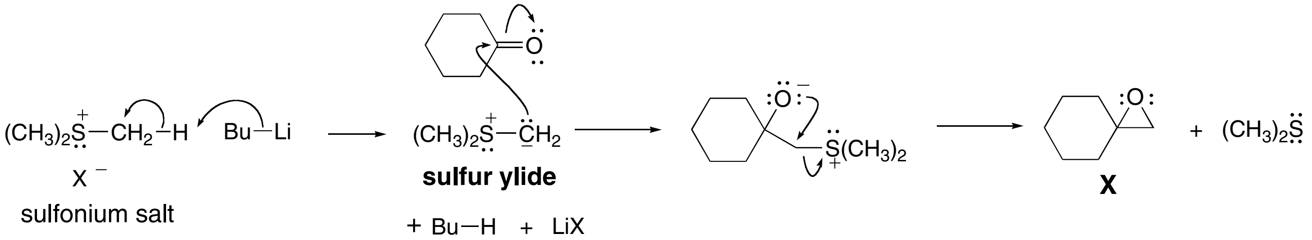
21.77


OCH3
H–OTs
enol ether
HO
OH
+ ⁻OTs
⁻OTs
CH3O
H–OTs
+ CH3OH
H–OTs
acetal

21.78

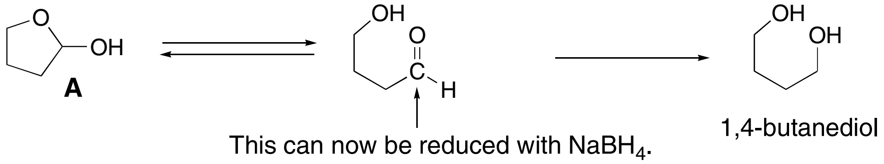


21.79

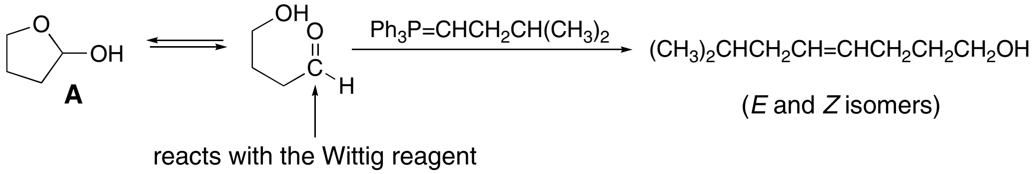


21.80 Hemiacetal **A** is in equilibrium with its acyclic hydroxy aldehyde. The aldehyde can undergo hydride reduction to form 1,4-butanediol and Wittig reaction to form an alkene.

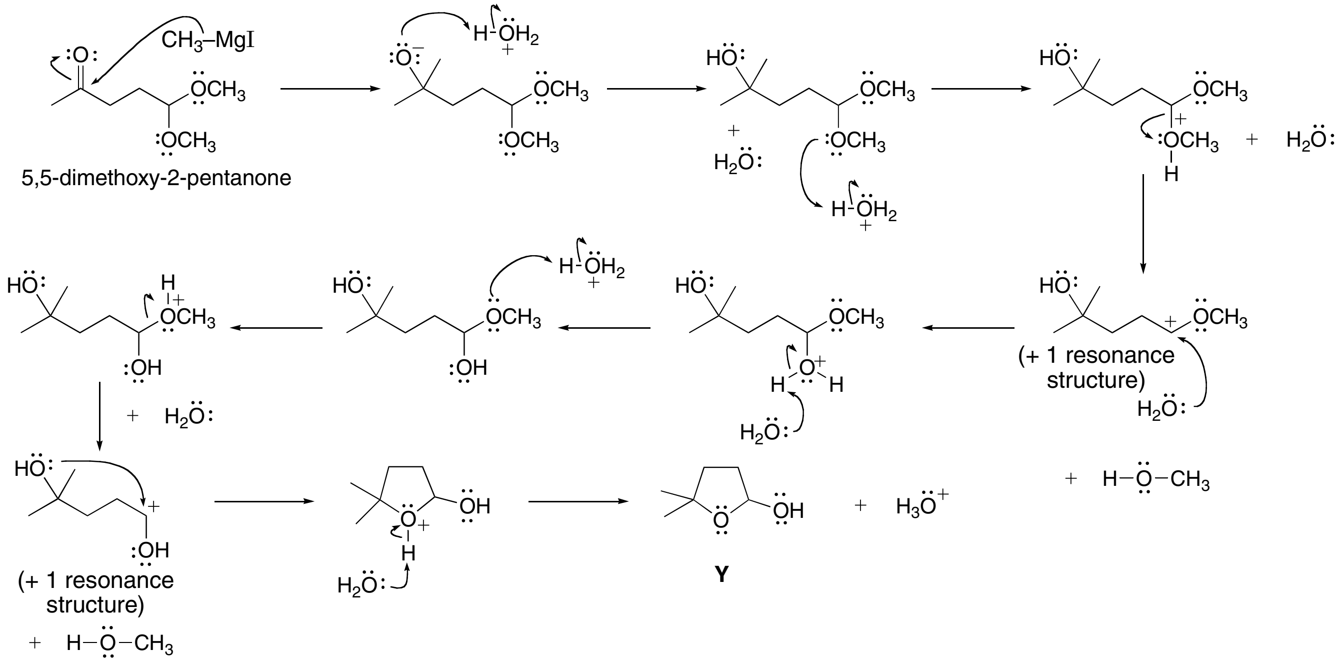
a.



b.

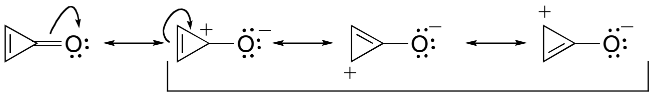


21.81

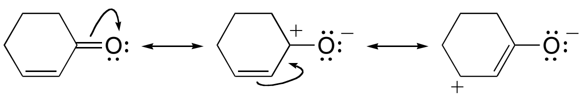


21.82

cyclopropenone
($1640\ cm^{-1}$)



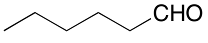
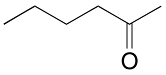
2-cyclohexenone
($1685\ cm^{-1}$)



These three resonance structures include an aromatic ring; $4n + 2 = 2\ \pi$ electrons. Although they are charge separated, the stabilized aromatic ring makes these three structures contribute to the hybrid more than usual. Since these three resonance contributors have a C–O single bond, the absorption is shifted to a lower wavenumber.

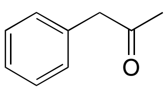
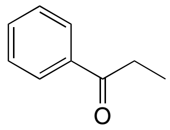
There are three resonance structures for 2-cyclohexenone, but the charge-separated resonance structures are not aromatic so they contribute less to the resonance hybrid. The C=O absorbs in the usual region for a conjugated carbonyl.

21.83

a.  and 

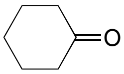
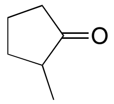
aldehyde ketone

The sp^2 hybridized C–H bond of the aldehyde absorbs at 2700–2830 cm^{-1}.

b.  and 

higher wavenumber for C=O

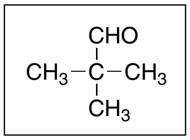
conjugated with a benzene ring lower wavenumber

c.  and 

smaller ring
higher wavenumber for C=O

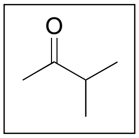
21.84

A. Molecular formula $C_5H_{10}O$ → 1 degree of unsaturation
IR absorptions at 1728, 2791, 2700 cm^{-1} → C=O, CHO
NMR data: singlet at 1.08 (9 H) → 3 CH_3 groups
singlet at 9.48 (1 H) ppm → CHO

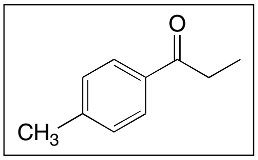


$$CH_3-\overset{\displaystyle CHO}{\underset{\displaystyle CH_3}{C}}-CH_3$$

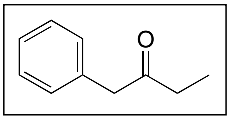
B. Molecular formula $C_5H_{10}O$ → 1 degree of unsaturation
IR absorption at 1718 cm^{-1} → C=O
NMR data: doublet at 1.10 (6 H) → 2 CH_3's adjacent to H
singlet at 2.14 (3 H) → CH_3
septet at 2.58 (1 H) ppm → CH adjacent to 2 CH_3's



C. Molecular formula $C_{10}H_{12}O$ → 5 degrees of unsaturation (4 due to a benzene ring)
IR absorption at 1686 cm^{-1} → C=O
NMR data: triplet at 1.21 (3 H) → CH_3 adjacent to 2 H's
singlet at 2.39 (3 H) → CH_3
quartet at 2.95 (2 H) → CH_2 adjacent to 3 H's
doublet at 7.24 (2 H) → 2 H's on benzene ring
doublet at 7.85 (2 H) ppm → 2 H's on benzene ring

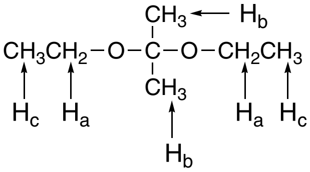


D. Molecular formula $C_{10}H_{12}O$ → 5 degrees of unsaturation (4 due to a benzene ring)
IR absorption at 1719 cm^{-1} → C=O
NMR data: triplet at 1.02 (3 H) → CH_3 adjacent 2 H's
quartet at 2.45 (2 H) → 2 H's adjacent to 3 H's
singlet at 3.67 (2 H) → CH_2
multiplet at 7.06–7.48 (5 H) ppm → a monosubstituted benzene ring



21.85

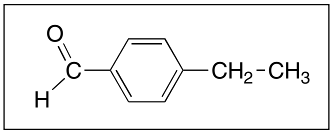
$C_7H_{16}O_2$: 0 degrees of unsaturation
IR: 3000 cm^{-1}: **C–H bonds**
NMR data (ppm):
H_a: quartet at 3.5 (**4 H**), split by 3 H's
H_b: singlet at 1.4 (**6 H**)
H_c: triplet at 1.2 (**6 H**), split by 2 H's



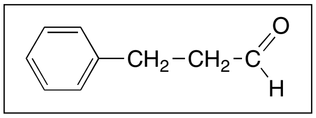
$$CH_3CH_2-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O-CH_2CH_3$$

21.86

A. Molecular formula $C_9H_{10}O$
5 degrees of unsaturation
IR absorption at 1700 cm^{-1} → C=O
IR absorption at ~2700 cm^{-1} → CH of RCHO
NMR data (ppm):
triplet at 1.2 (2 H's adjacent)
quartet at 2.7 (3 H's adjacent)
doublet at 7.3 (2 H's on benzene)
doublet at 7.7 (2 H's on benzene)
singlet at 9.9 (CHO)



B. Molecular formula $C_9H_{10}O$
5 degrees of unsaturation
IR absorption at 1720 cm^{-1} → C=O
IR absorption at ~2700 cm^{-1} → CH of RCHO
NMR data (ppm):
2 triplets at 2.85 and 2.95 (suggests $–CH_2CH_2–$)
multiplet at 7.2 (benzene H's)
signal at 9.8 (CHO)



21.87

C. Molecular formula $C_6H_{12}O_3$

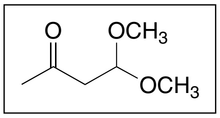
1 degree of unsaturation

IR absorption at 1718 cm^{-1} → C=O

To determine the number of H's that give rise to each signal, first find the number of integration units per H by dividing the total number of integration units (7 + 40 + 14 + 21 = 82) by the number of H's (12); 82/12 = 6.8. Then divide each integration unit by this number (6.8).

NMR data (ppm):

singlet at 2.2 (3 H's)
doublet at 2.7 (2 H's)
singlet at 3.2 (6 H's – 2 OCH_3 groups)
triplet at 4.8 (1 H)



21.88

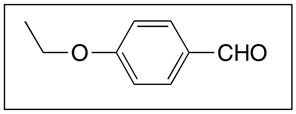
D. Molecular ion at *m*/*z* = 150: $C_9H_{10}O_2$ (possible molecular formula)

5 degrees of unsaturation

IR absorption at 1692 cm^{-1} → C=O

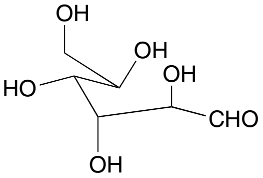
NMR data (ppm):

triplet at 1.5 (3 H's – CH_3CH_2)
quartet at 4.1 (2 H's – CH_3CH_2)
doublet at 7.0 (2 H's – on benzene ring)
doublet at 7.8 (2 H's – on benzene ring)
singlet at 9.9 (1 H – on aldehyde)

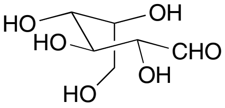


21.89

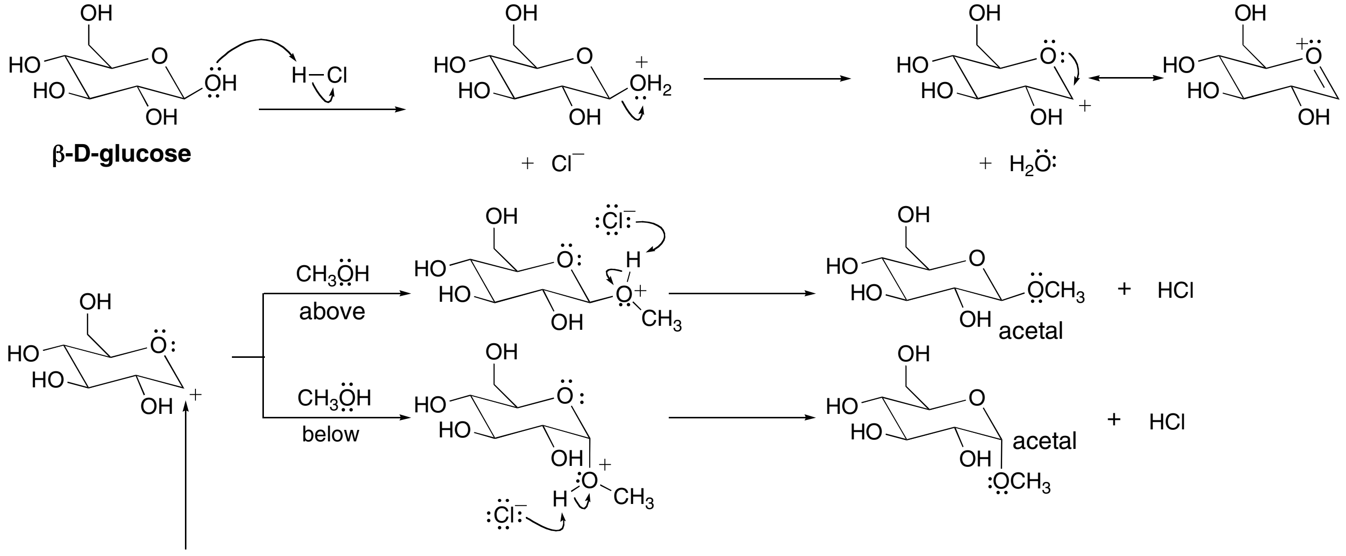
a.



b.

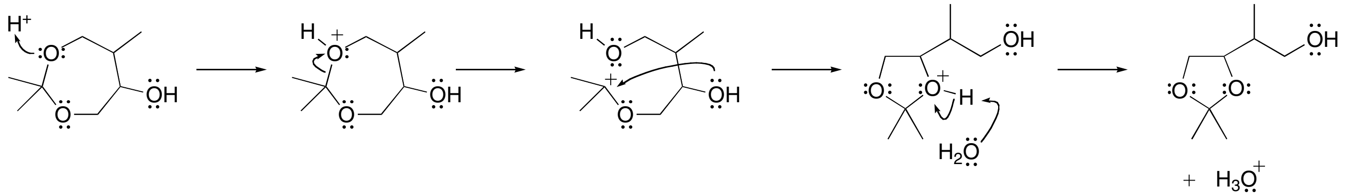


21.90



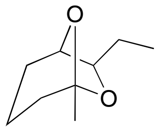
The carbocation is trigonal planar, so CH_3OH attacks from two different directions, and two different acetals are formed.

21.91



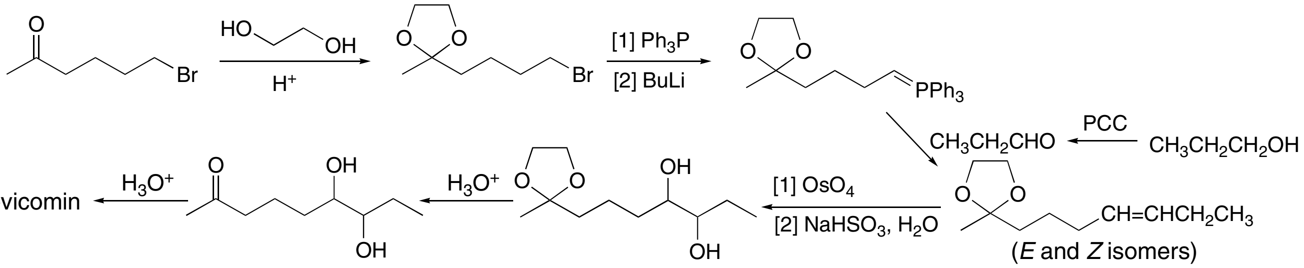
21.92

a.



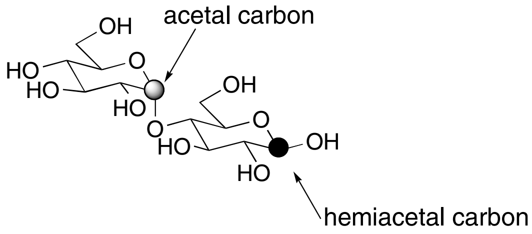
brevicomin

b.

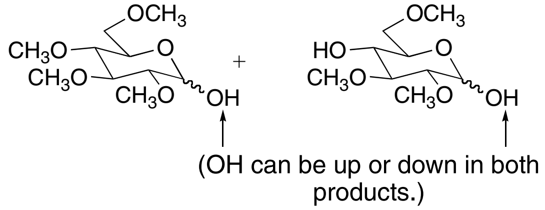


21.93

a.



c.



b.