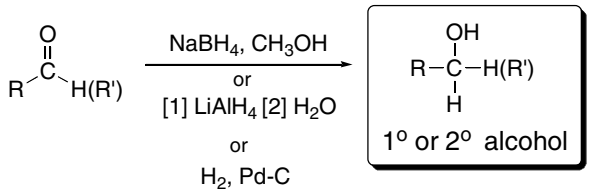
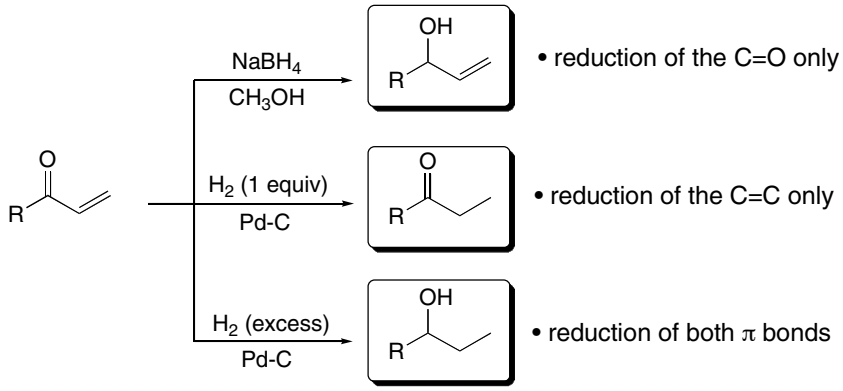
Chapter 20: Introduction to Carbonyl Chemistry

♦ Reduction reactions

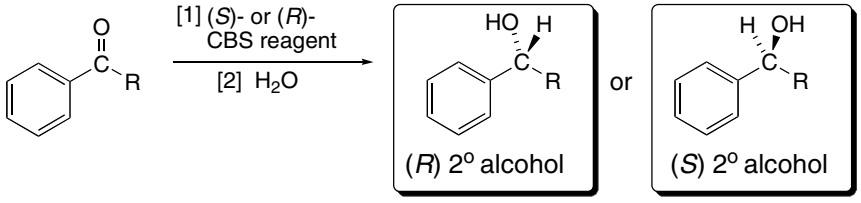
[1] Reduction of aldehydes and ketones to 1° and 2° alcohols (20.4)



[2] Reduction of α,β-unsaturated aldehydes and ketones (20.4C)

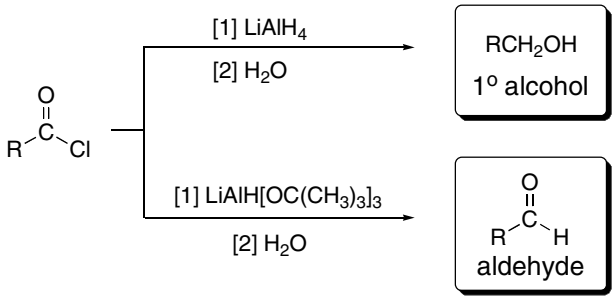


[3] Enantioselective ketone reduction (20.6)



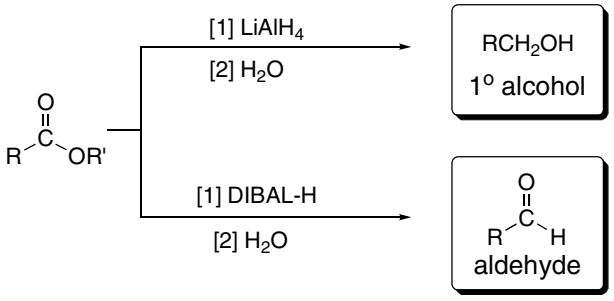
- A single enantiomer is formed.

[4] Reduction of acid chlorides (20.7A)



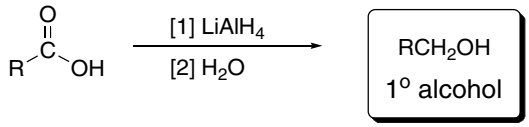
- $LiAlH_4$, a strong reducing agent, reduces an acid chloride to a 1° alcohol.
- With $LiAlH[OC(CH_3)_3]_3$, a milder reducing agent, reduction stops at the aldehyde stage.

[5] Reduction of esters (20.7A)

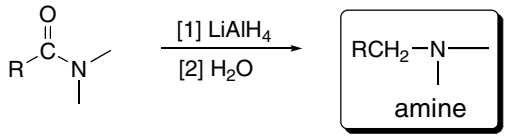


- $LiAlH_4$, a strong reducing agent, reduces an ester to a 1° alcohol.
- With DIBAL-H, a milder reducing agent, reduction stops at the aldehyde stage.

[6] Reduction of carboxylic acids to 1° alcohols (20.7B)

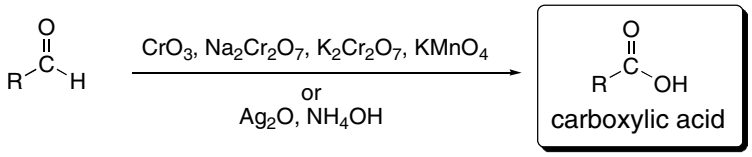


[7] Reduction of amides to amines (20.7B)



♦ Oxidation reactions

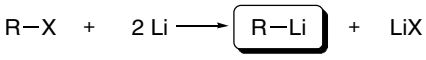
Oxidation of aldehydes to carboxylic acids (20.8)



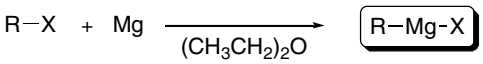
- All Cr^{6+} reagents except PCC oxidize RCHO to RCOOH.
- Tollens reagent ($Ag_2O + NH_4OH$) oxidizes RCHO only. Primary (1°) and secondary (2°) alcohols do not react with Tollens reagent.

♦ Preparation of organometallic reagents (20.9)

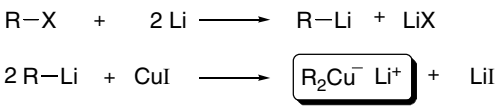
[1] Organolithium reagents:



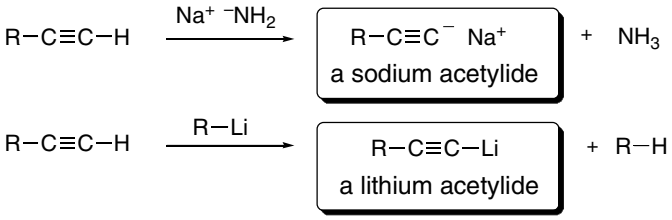
[2] Grignard reagents:



[3] Organocuprate reagents:

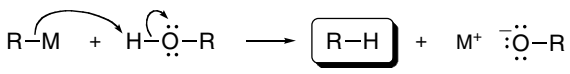


[4] Lithium and sodium acetylides:



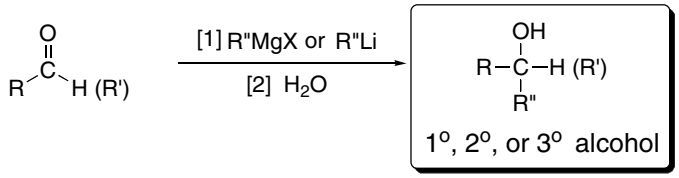
♦ Reactions with organometallic reagents

[1] Reaction as a base (20.9C)

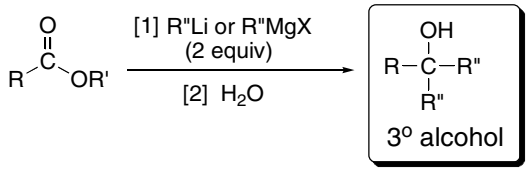


- RM = RLi, RMgX, R_2CuLi
- This acid–base reaction occurs with H_2O, ROH, RNH_2, R_2NH, RSH, RCOOH, $RCONH_2$, and RCONHR.

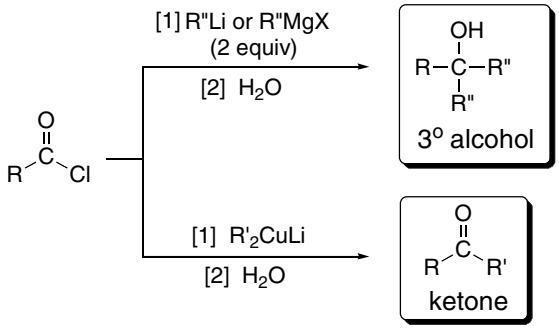
[2] Reaction with aldehydes and ketones to form 1°, 2°, and 3° alcohols (20.10)



[3] Reaction with esters to form 3° alcohols (20.13A)

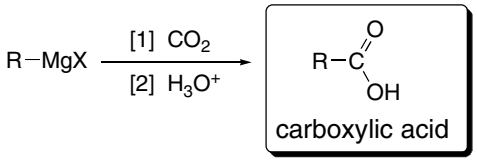


[4] Reaction with acid chlorides (20.13)

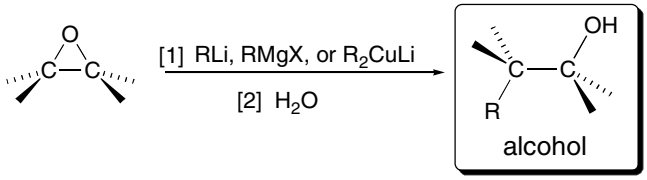


- More reactive organometallic reagents—R"Li and R"MgX—add two equivalents of R" to an acid chloride to form a 3° alcohol with two identical R" groups.
- Less reactive organometallic reagents—R'_2CuLi—add only one equivalent of R' to an acid chloride to form a ketone.

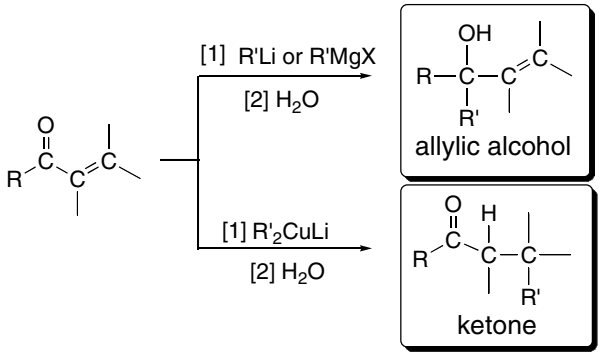
[5] Reaction with carbon dioxide—Carboxylation (20.14A)



[6] Reaction with epoxides (20.14B)



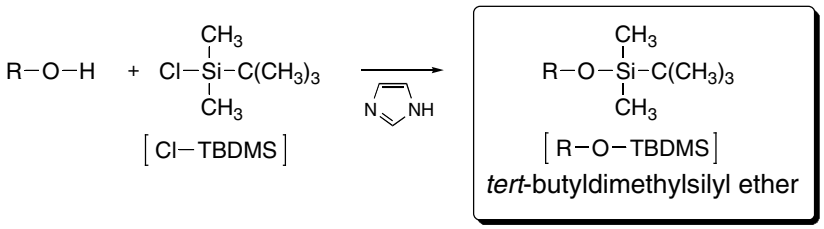
[7] Reaction with α,β-unsaturated aldehydes and ketones (20.15B)



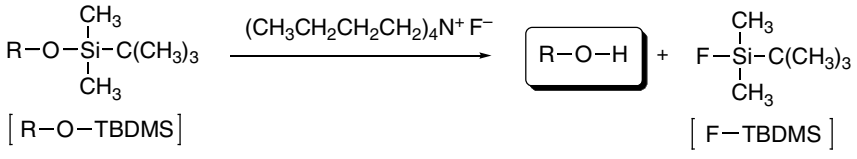
- More reactive organometallic reagents—R'Li and R'MgX—react with α,β-unsaturated carbonyls by 1,2-addition.
- Less reactive organometallic reagents—R'$_2$CuLi— react with α,β-unsaturated carbonyls by 1,4-addition.

♦ Protecting groups (20.12)

[1] Protecting an alcohol as a *tert*-butyldimethylsilyl ether

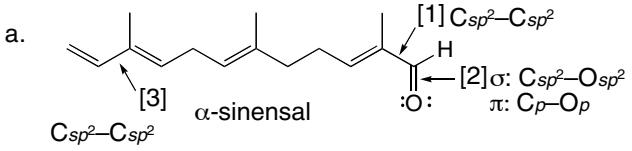


[2] Deprotecting a *tert*-butyldimethylsilyl ether to re-form an alcohol



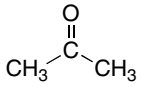
Chapter 20: Answers to Problems

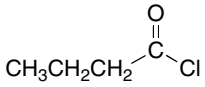
20.1

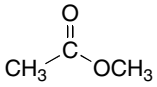
a. 

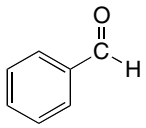
b. The O is sp^2 hybridized.
Both lone pairs occupy sp^2 hybrid orbitals.

20.2 A carbonyl compound with a reasonable leaving group undergoes substitution reactions. Those without good leaving groups undergo addition.

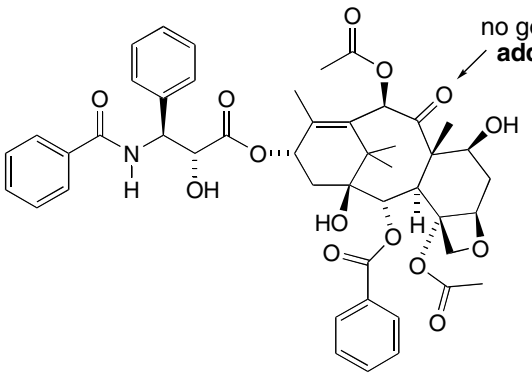
a. 
no good leaving group
addition reactions

b. 
Cl–good leaving group
substitution reactions

c. 
OCH_3–reasonable leaving group
substitution reactions

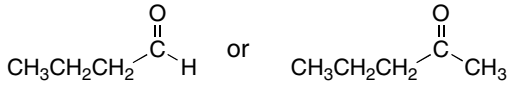
d. 
no good leaving group
addition reactions

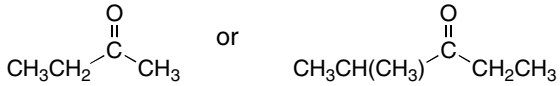
20.3 A carbonyl compound with a reasonable leaving group (NR_2 or OR bonded to the C=O) undergoes substitution reactions. Those without good leaving groups undergo addition.

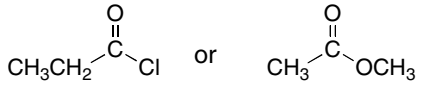


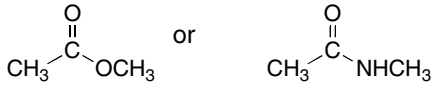
All other C=O's have leaving groups.
substitution reactions

20.4 Aldehydes are more reactive than ketones. In carbonyl compounds with leaving groups, the better the leaving group, the more reactive the carbonyl compound.

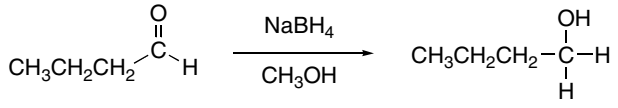
a. 
less hindered carbonyl
more reactive

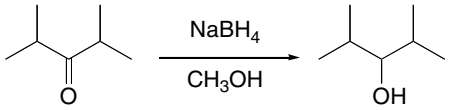
b. 
less hindered carbonyl
more reactive

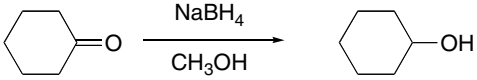
c. 
better leaving group
more reactive

d. 
better leaving group
more reactive

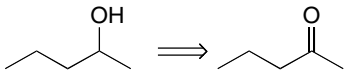
20.5 $NaBH_4$ reduces aldehydes to 1° alcohols, and ketones to 2° alcohols.

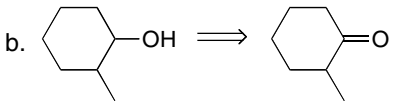
a. 

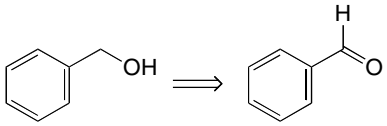
c. 

b. 

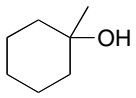
20.6 1° Alcohols are prepared from aldehydes and 2° alcohols are from ketones.

a. 

b. 

c. 

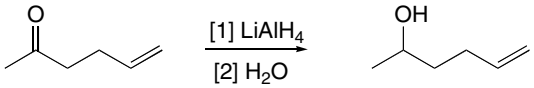
20.7

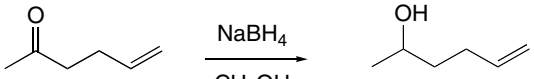


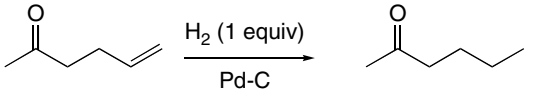
1-methylcyclohexanol

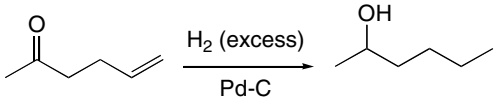
3° Alcohols cannot be made by reduction of a carbonyl group, because they do not contain a H on the C with the OH.

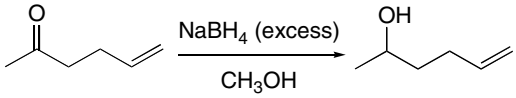
20.8

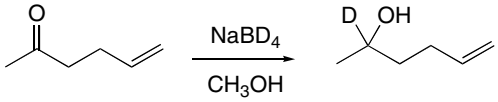
a. 

b. 

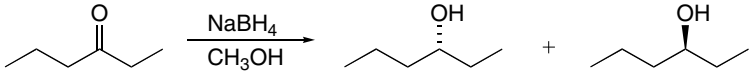
c. 

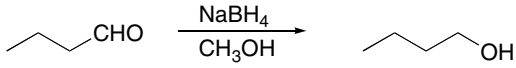
d. 

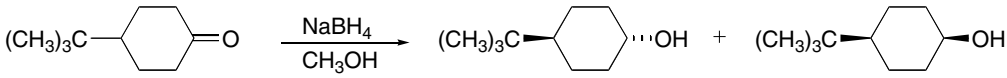
e. 

f. 

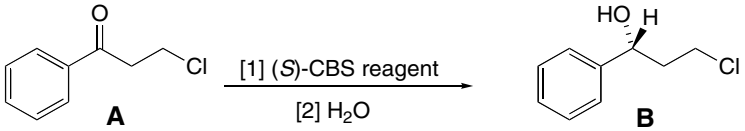
20.9

a. 

b. 

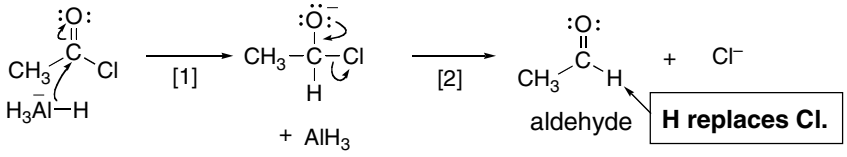
c. 

20.10

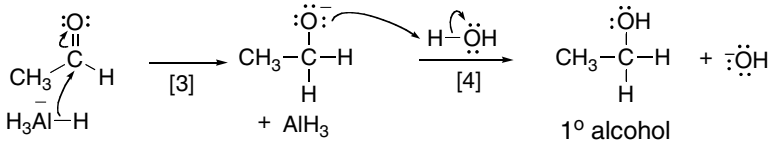


20.11

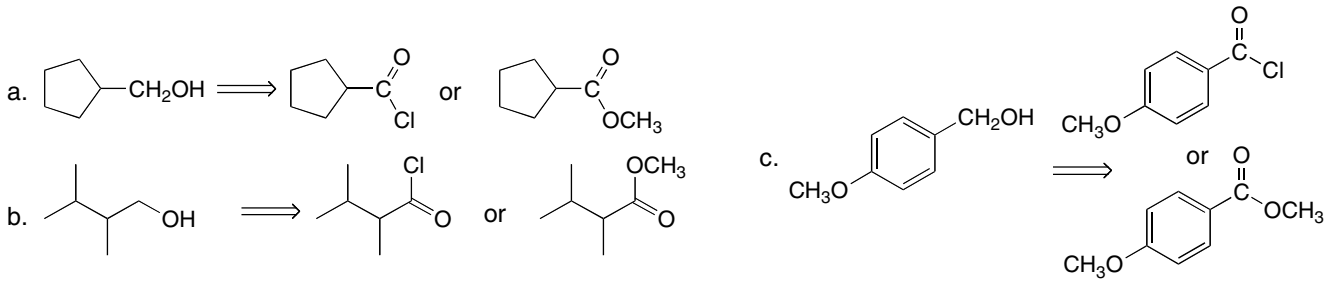
Part [1]: Nucleophilic substitution of H for Cl



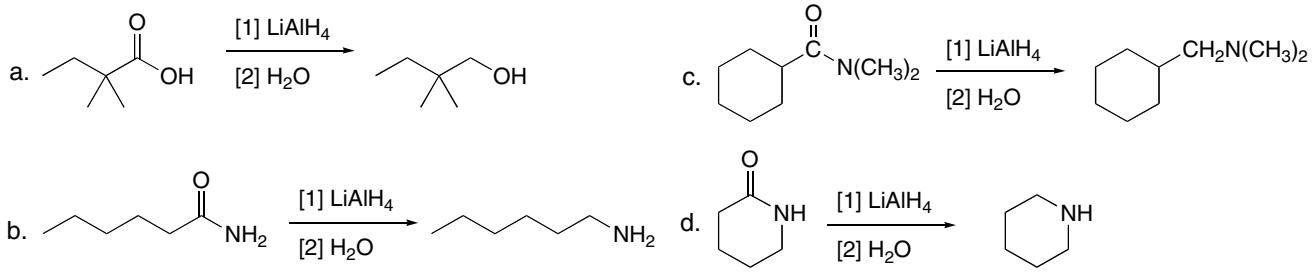
Part [2]: Nucleophilic addition of H^- to form an alcohol



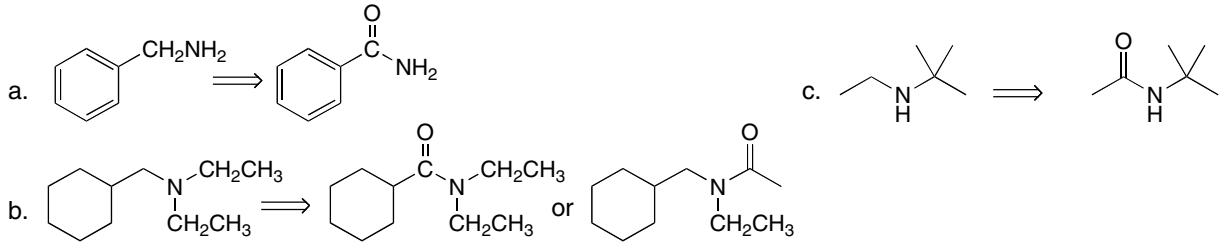
20.12 Acid chlorides and esters can be reduced to 1° alcohols. Keep the carbon skeleton the same in drawing an ester and acid chloride precursor.



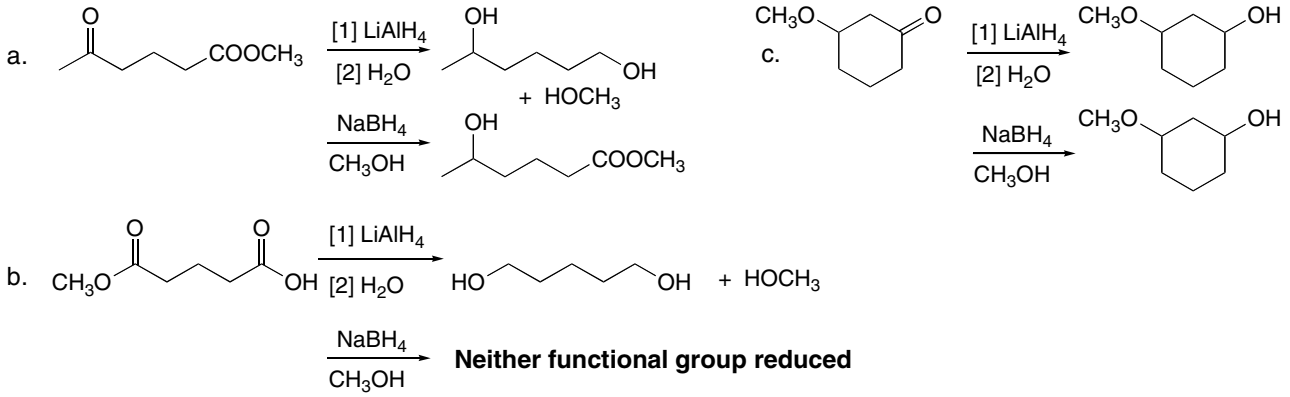
20.13



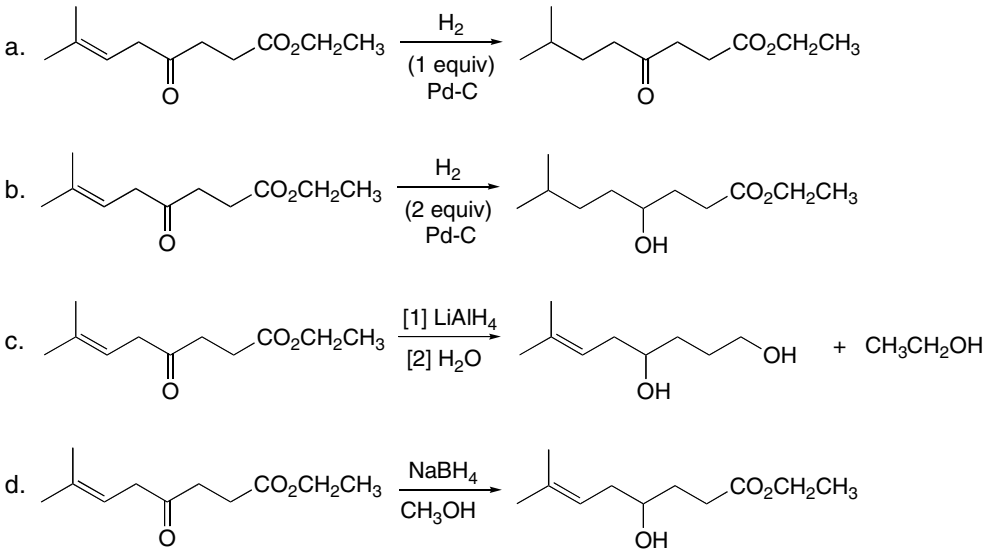
20.14



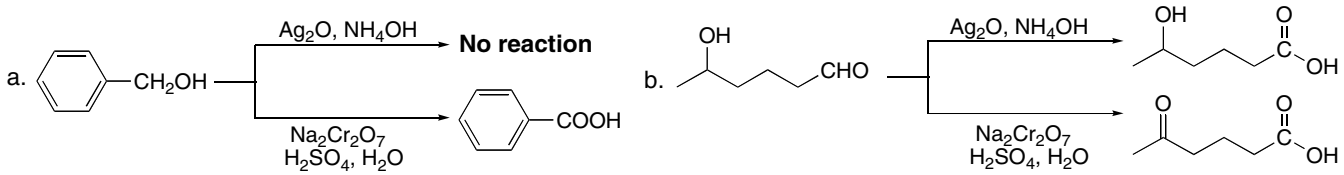
20.15



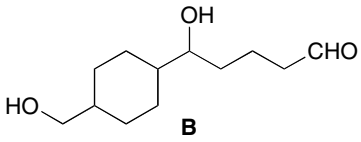
20.16

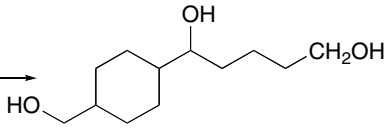


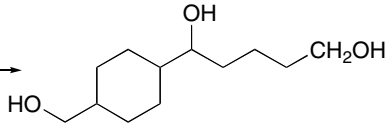
20.17 Tollens reagent reacts only with aldehydes.

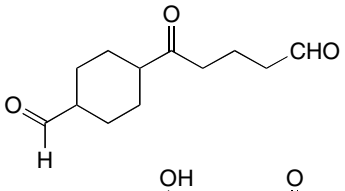


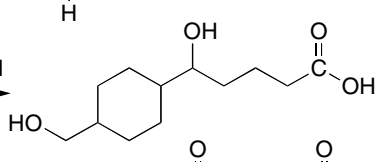
20.18

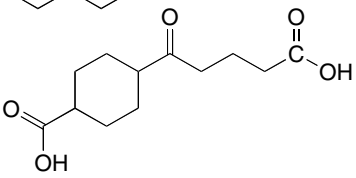


a. **B** $\xrightarrow[CH_3OH]{NaBH_4}$ 

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

c. **B** $\xrightarrow{PCC}$ 

d. **B** $\xrightarrow{Ag_2O,\ NH_4OH}$ 

e. **B** $\xrightarrow[H_2SO_4,\ H_2O]{CrO_3}$ 

20.19

a. $CH_3CH_2Br + 2\ Li \longrightarrow CH_3CH_2Li + LiBr$

b. $CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr$

c. $CH_3CH_2Br + 2\ Li \longrightarrow CH_3CH_2Li + LiBr$

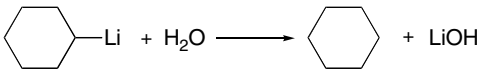
$2\ CH_3CH_2Li + CuI \longrightarrow LiCu(CH_2CH_3)_2 + LiI$

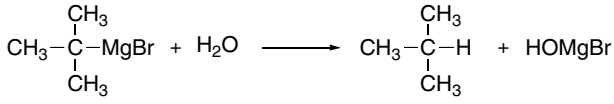
20.20

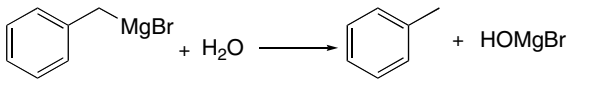
$HC{\equiv}CCH_2CH_2CH_2CH_2CH_2CH_3 + NaH \longrightarrow Na^{+-}C{\equiv}CCH_2CH_2CH_2CH_2CH_2CH_3 + H_2 \longleftarrow$ hydrogen gas

$HC{\equiv}CCH_2CH_2CH_2CH_2CH_2CH_3 + CH_3MgBr \longrightarrow BrMgC{\equiv}CCH_2CH_2CH_2CH_2CH_2CH_3 + CH_4 \longleftarrow$ methane gas

20.21

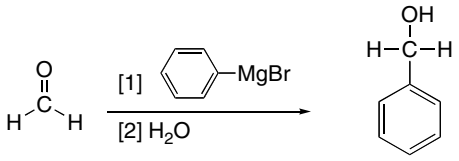
a. 

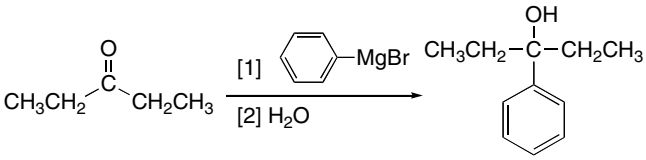
b. 

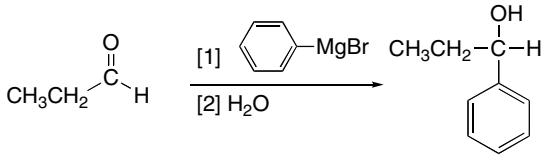
c. 

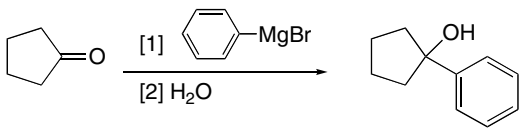
d. $CH_3CH_2C{\equiv}C{-}Li + H_2O \longrightarrow CH_3CH_2C{\equiv}CH + LiOH$

20.22 To draw the product, add the benzene ring to the carbonyl carbon and protonate the oxygen.

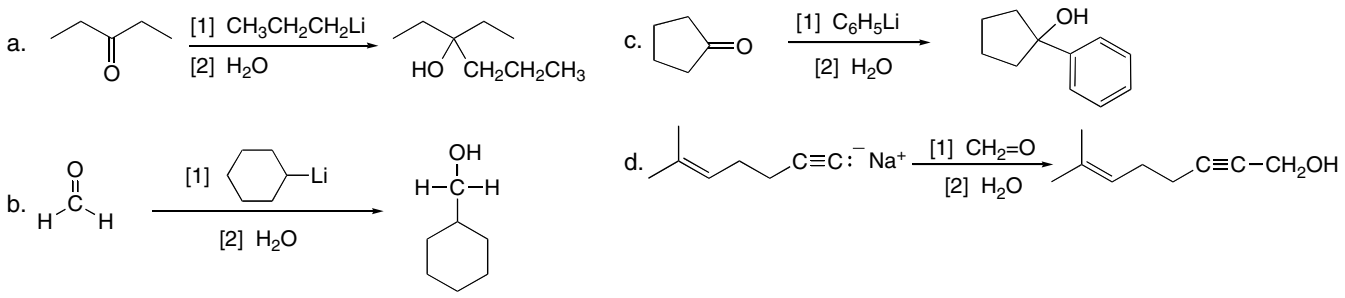
a. 

b. 

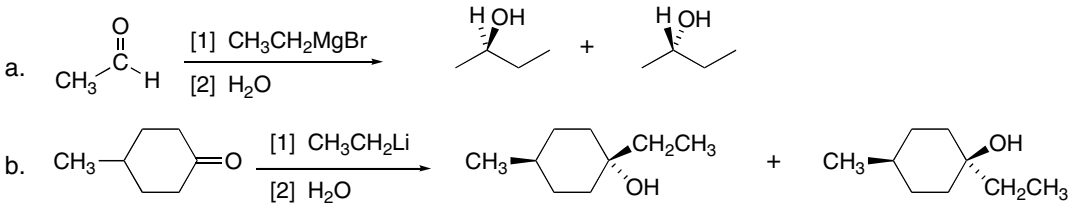
c. 

d. 

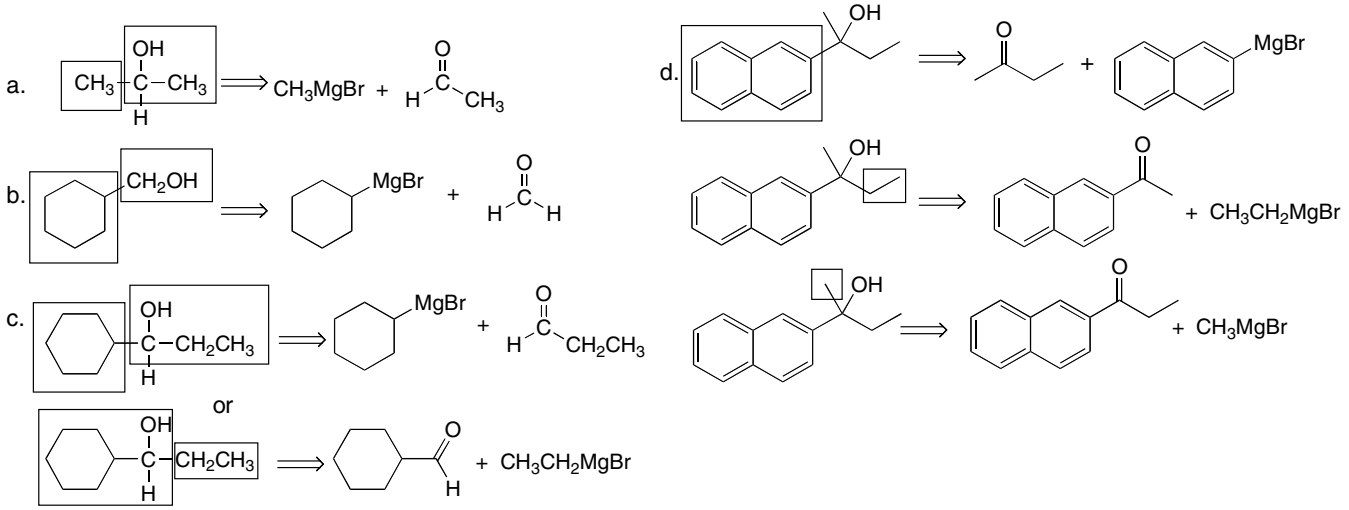
20.23 To draw the products, add the alkyl or phenyl group to the carbonyl carbon and protonate the oxygen.



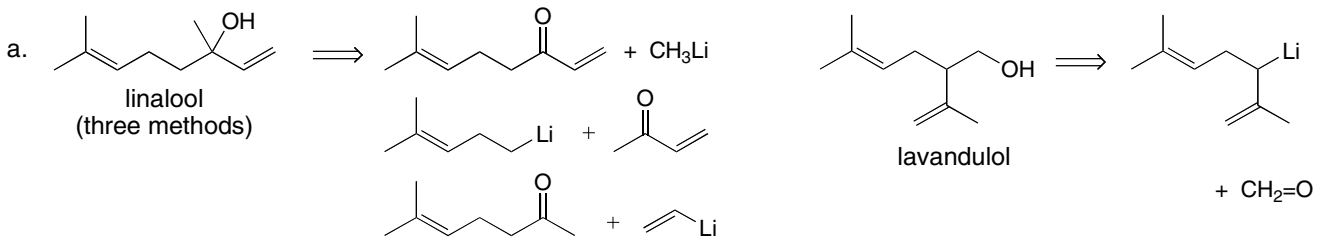
20.24 Addition of RM always occurs from above and below the plane of the molecule.

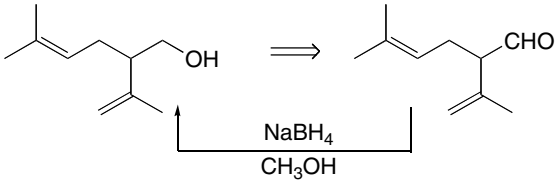


20.25



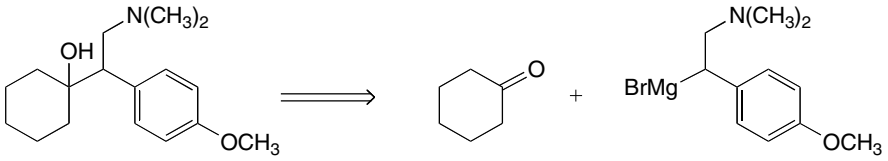
20.26



b. 

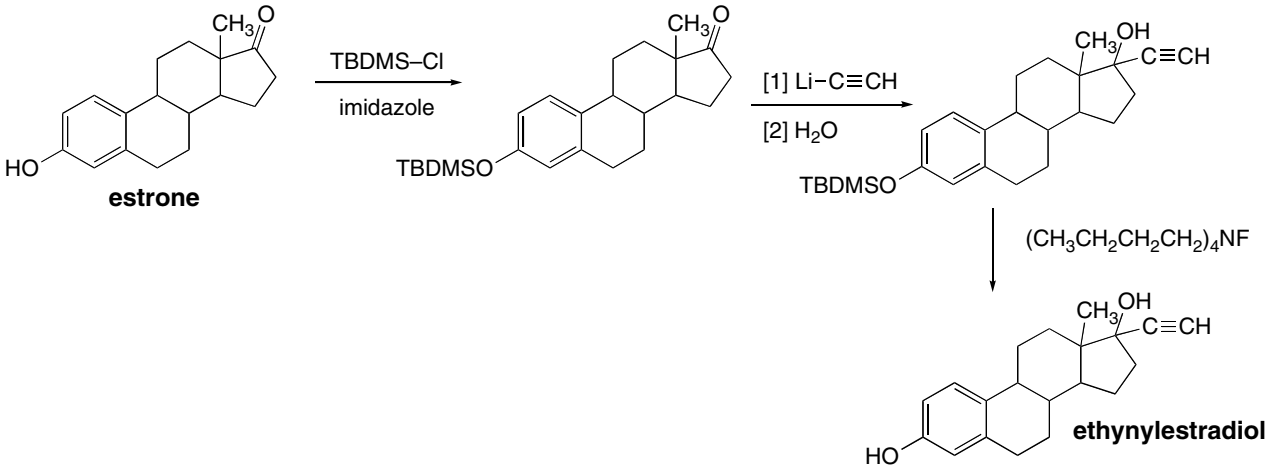
c. Linalool is a 3° ROH. Therefore, it has no H on the carbon with the OH group, and cannot be prepared by reduction of a carbonyl compound.

20.27



venlafaxine

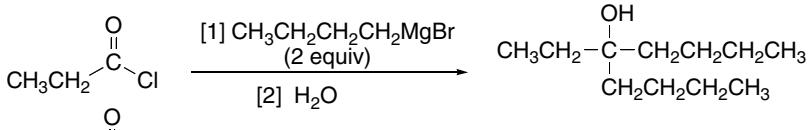
20.28

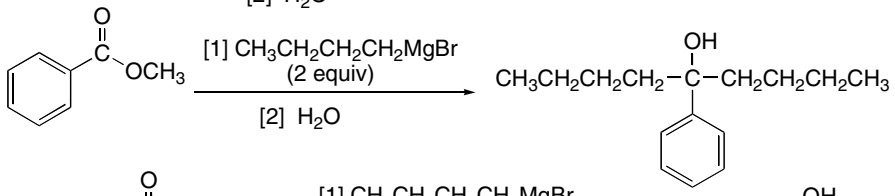


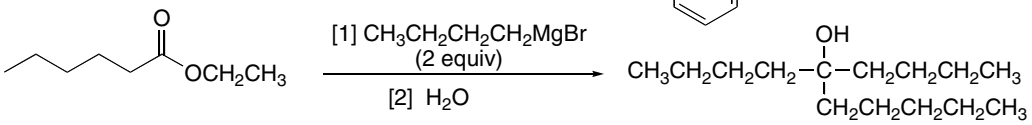
estrone

ethynylestradiol

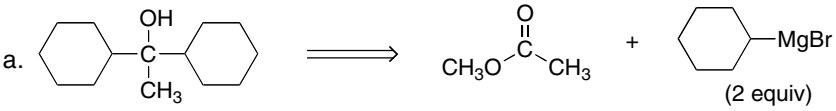
20.29

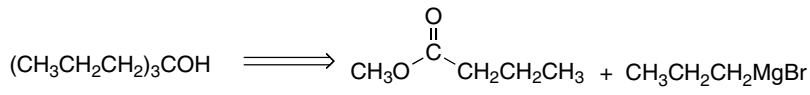
a. 

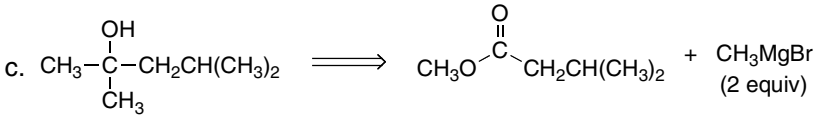
b. 

c. 

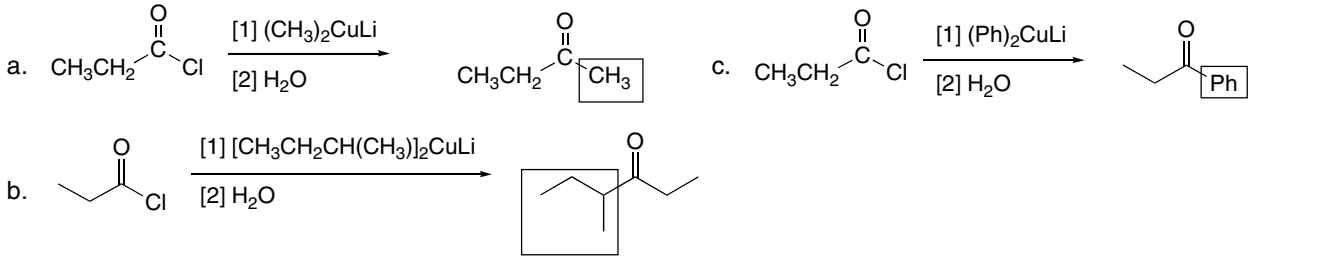
20.30

a. 

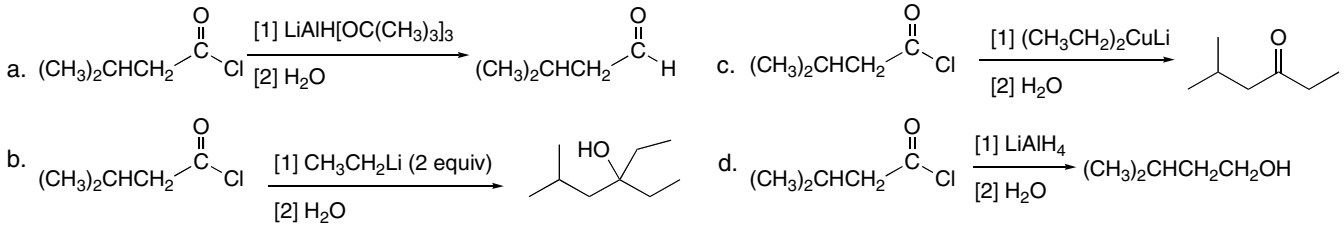
b. 



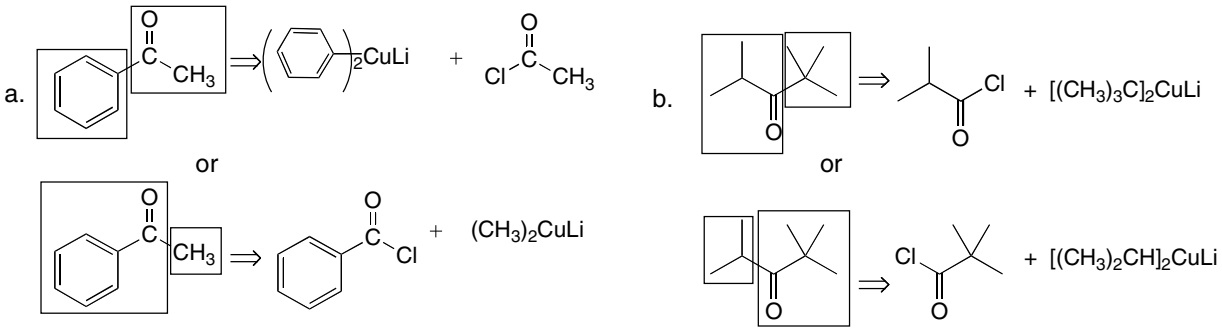
20.31 The R group of the organocuprate has replaced the Cl on the acid chloride.



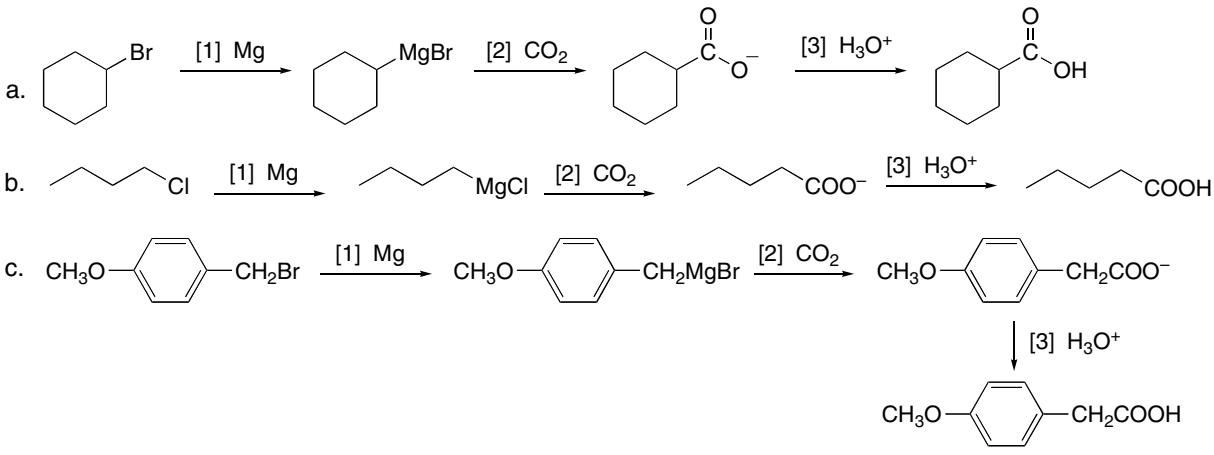
20.32



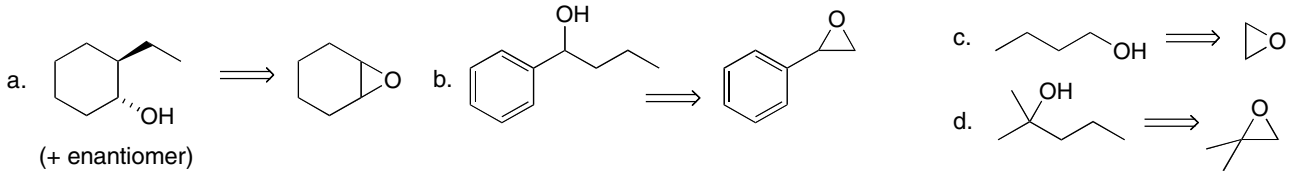
20.33



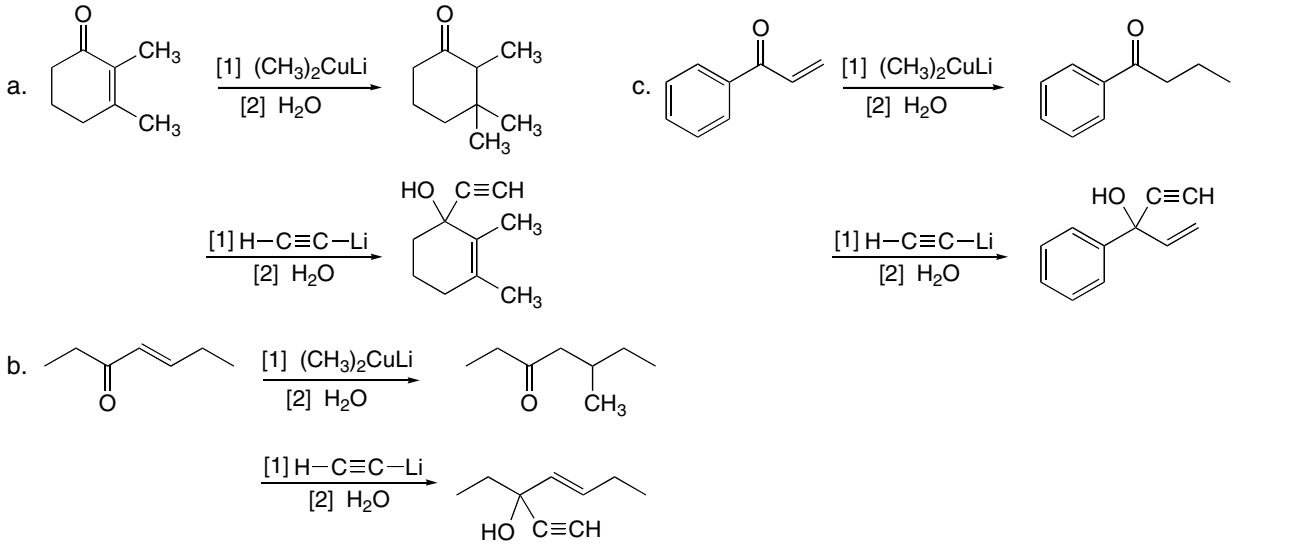
20.34



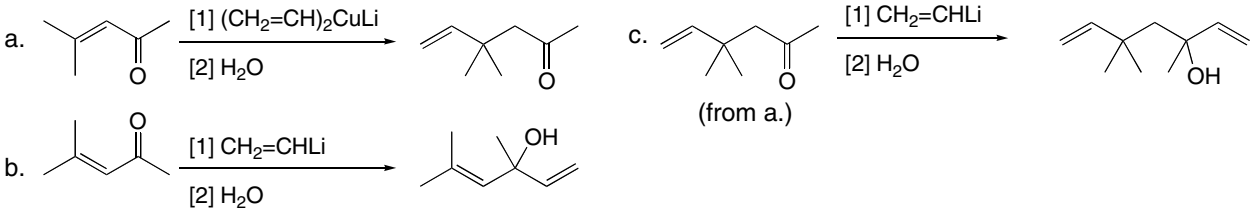
20.35



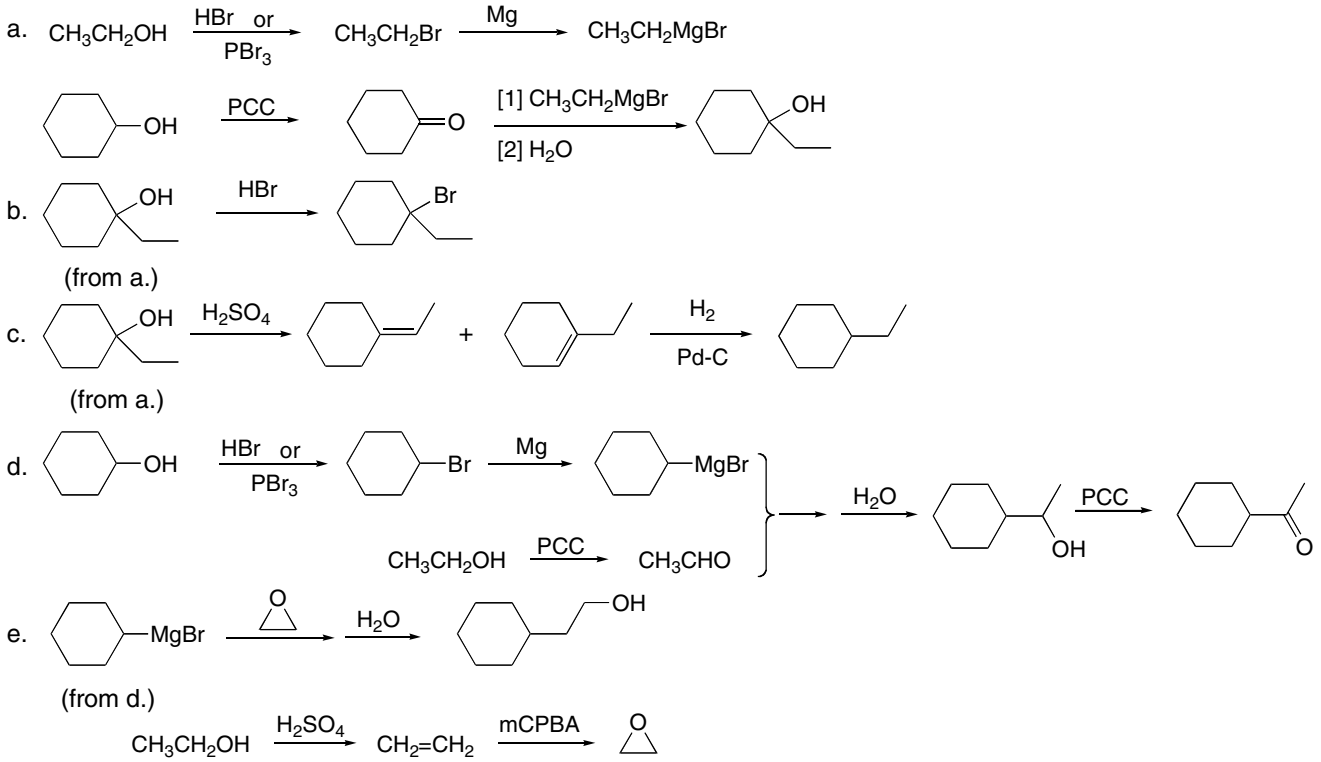
20.36 The characteristic reaction of α,β-unsaturated carbonyl compounds is nucleophilic addition. Grignard and organolithium reagents react by 1,2-addition and organocuprate reagents react by 1,4-addition.



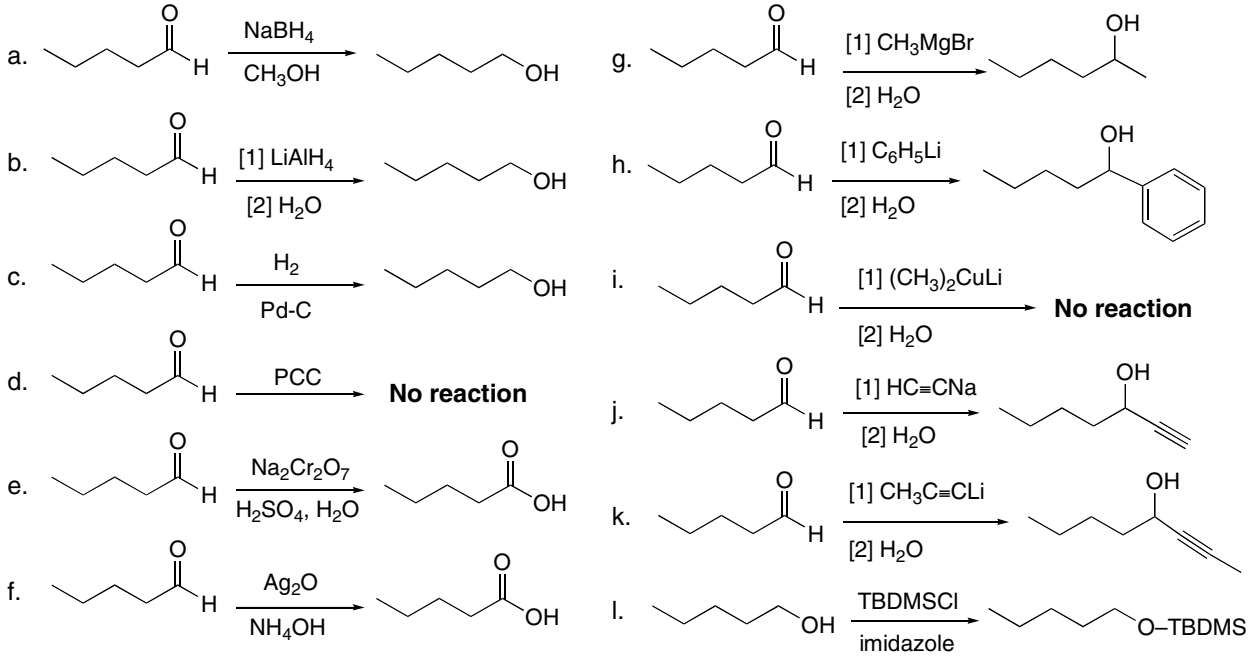
20.37



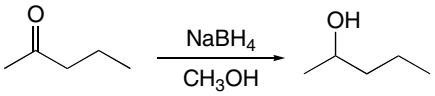
20.38

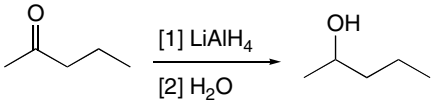

a.
CH3CH2OH
HBr or PBr3
CH3CH2Br
Mg
CH3CH2MgBr
OH
PCC
O
[1] CH3CH2MgBr
[2] H2O
OH
b.
OH
HBr
Br
(from a.)
c.
OH
H2SO4
+
H2
Pd-C
(from a.)
d.
OH
HBr or PBr3
Br
Mg
MgBr
CH3CH2OH
PCC
CH3CHO
H2O
OH
PCC
O
e.
MgBr
O
H2O
OH
(from d.)
CH3CH2OH
H2SO4
CH2=CH2
mCPBA
O

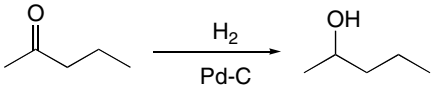
20.39

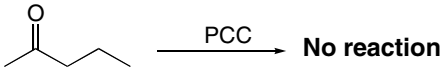

a.
O
H
NaBH4
CH3OH
OH
b.
[1] LiAlH4
[2] H2O
c.
H2
Pd-C
d.
PCC
No reaction
e.
Na2Cr2O7
H2SO4, H2O
f.
Ag2O
NH4OH
g.
[1] CH3MgBr
[2] H2O
h.
[1] C6H5Li
[2] H2O
i.
[1] (CH3)2CuLi
[2] H2O
No reaction
j.
[1] HC≡CNa
[2] H2O
k.
[1] CH3C≡CLi
[2] H2O
l.
TBDMSCl
imidazole
O–TBDMS

20.40

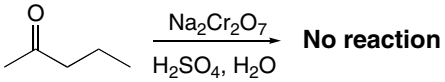
a. 

b. 

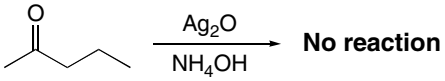
c. 

d. 

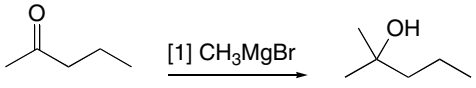
No reaction

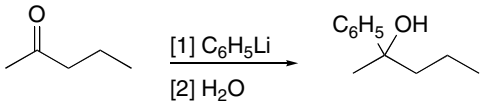
e. 

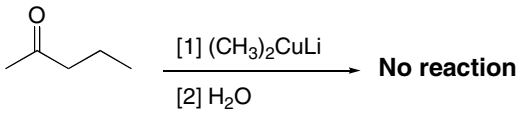
No reaction

f. 

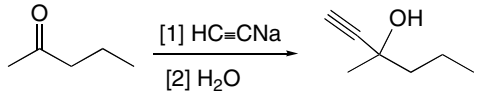
No reaction

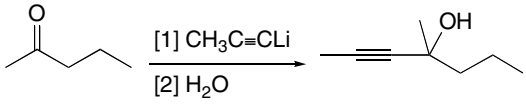
g. 

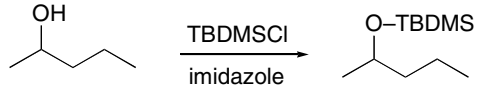
h. 

i. 

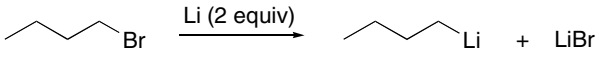
No reaction

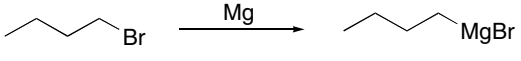
j. 

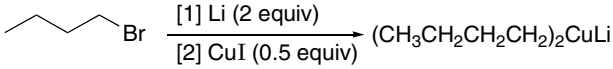
k. 

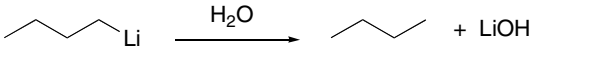
l. 

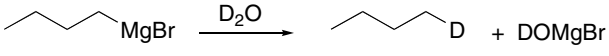
20.41

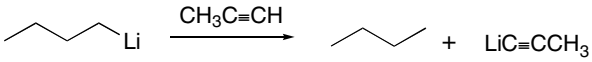
a. 

b. 

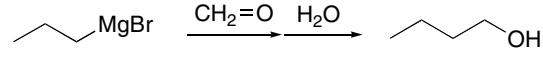
c. 

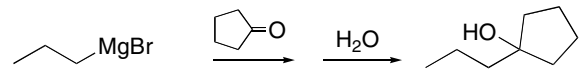
d. 

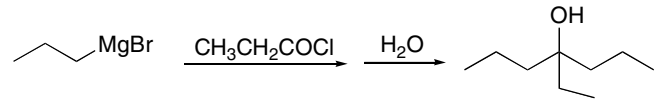
e. 

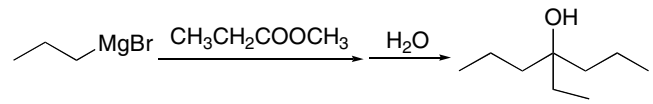
f. 

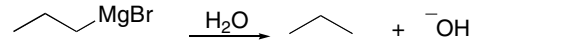
20.42

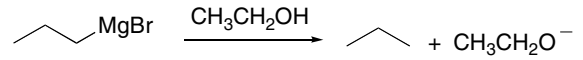
a. 

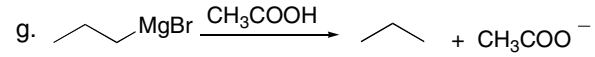
b. 

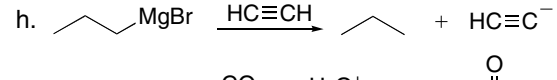
c. 

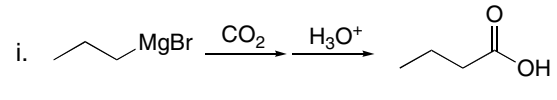
d. 

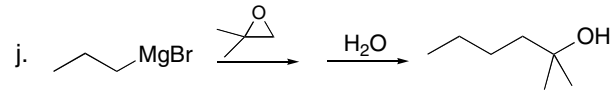
e. 

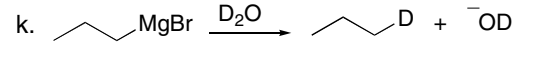
f. 

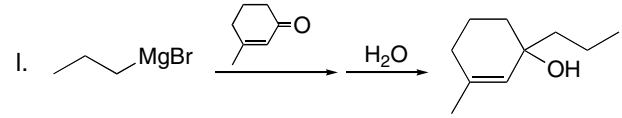
g. 

h. 

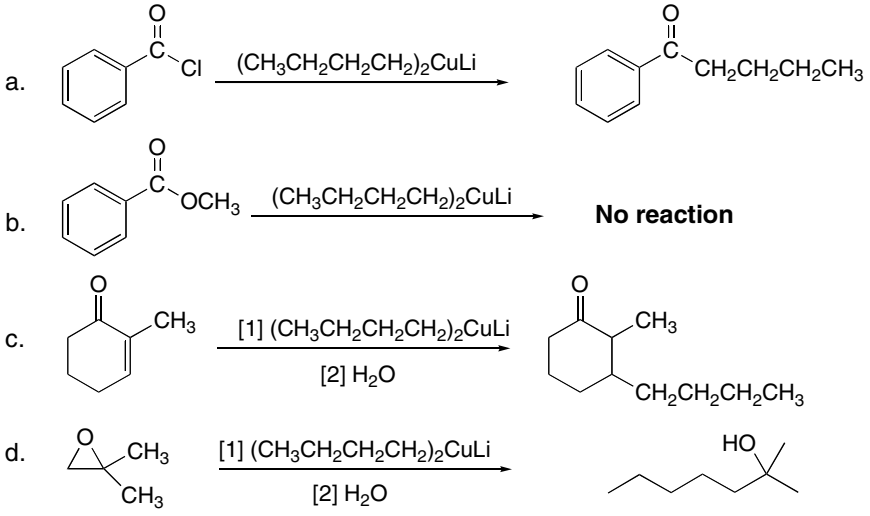
i. 

j. 

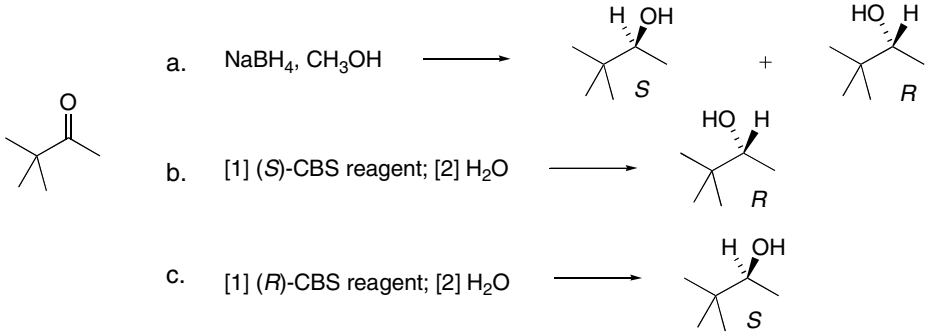
k. 

l. 

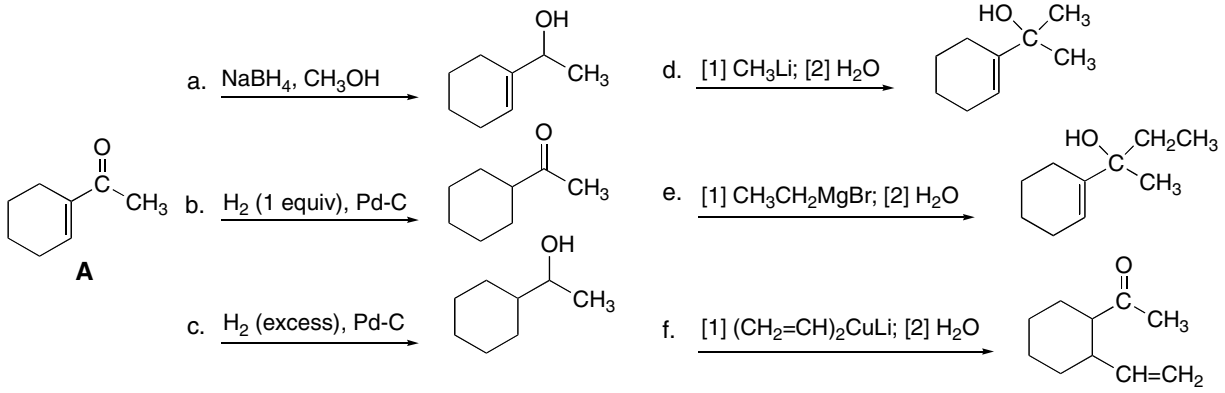
20.43



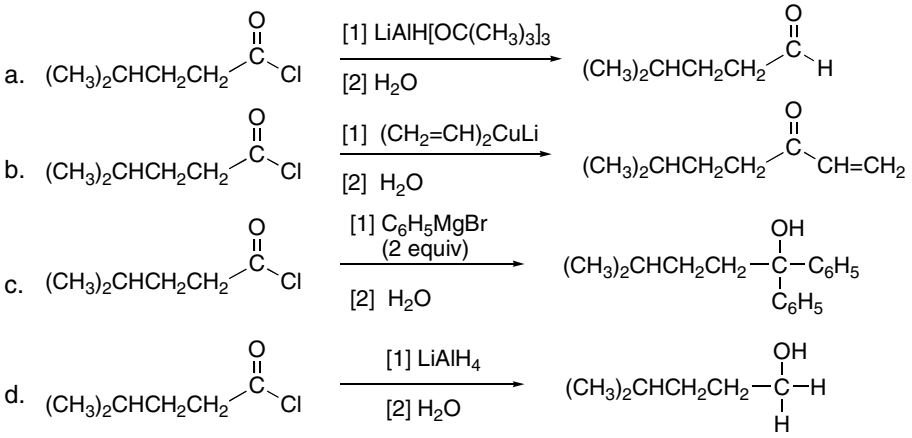
20.44 Arrange the larger group [$(CH_3)_3C$–] on the left side of the carbonyl.



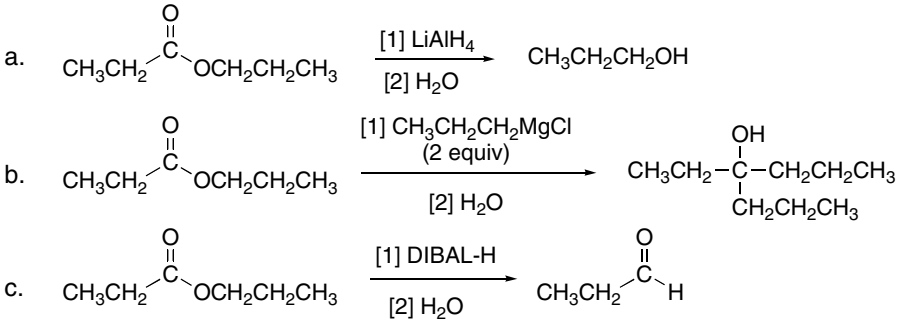
20.45



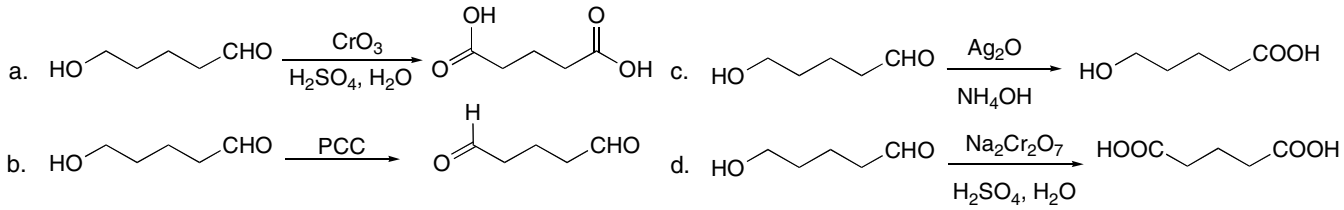
20.46



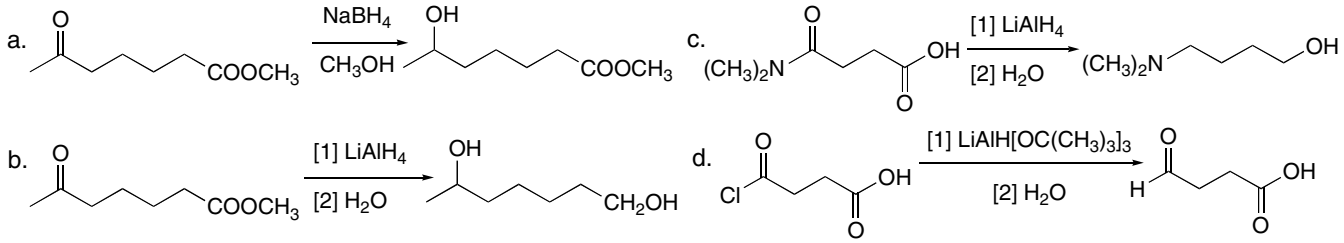
20.47



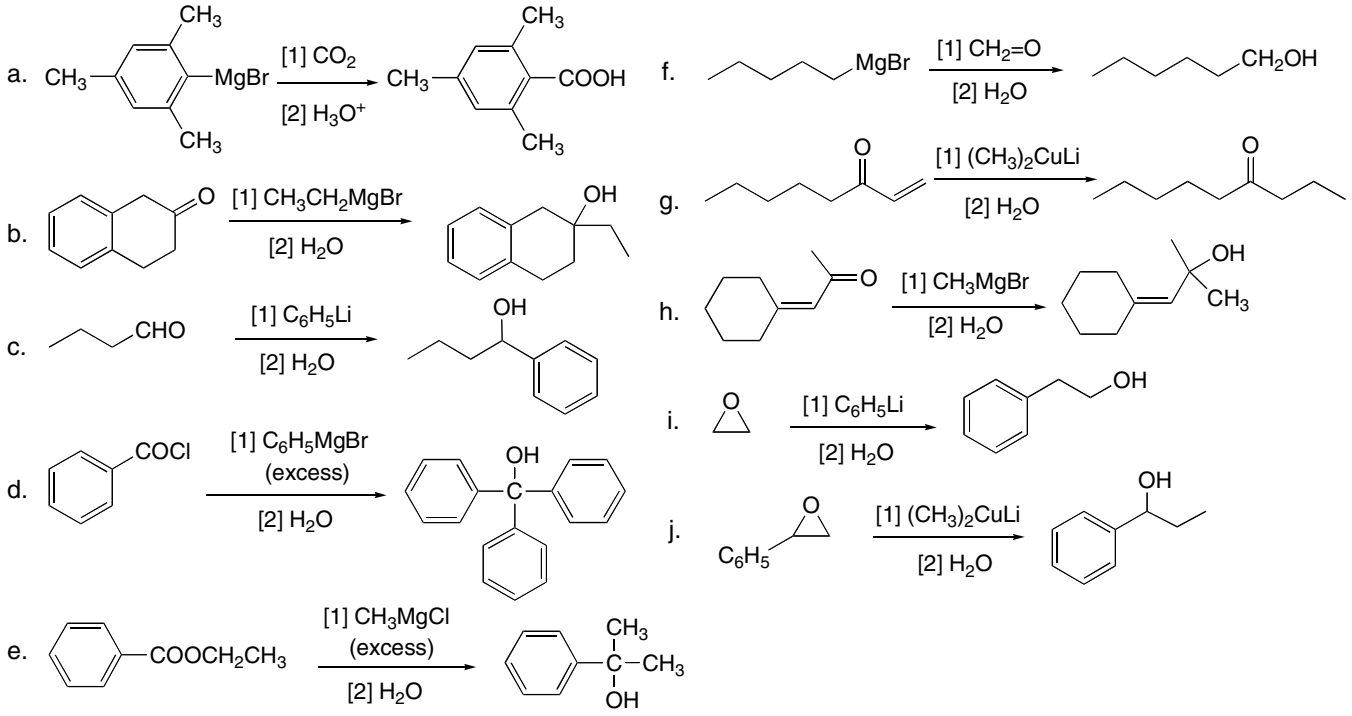
20.48



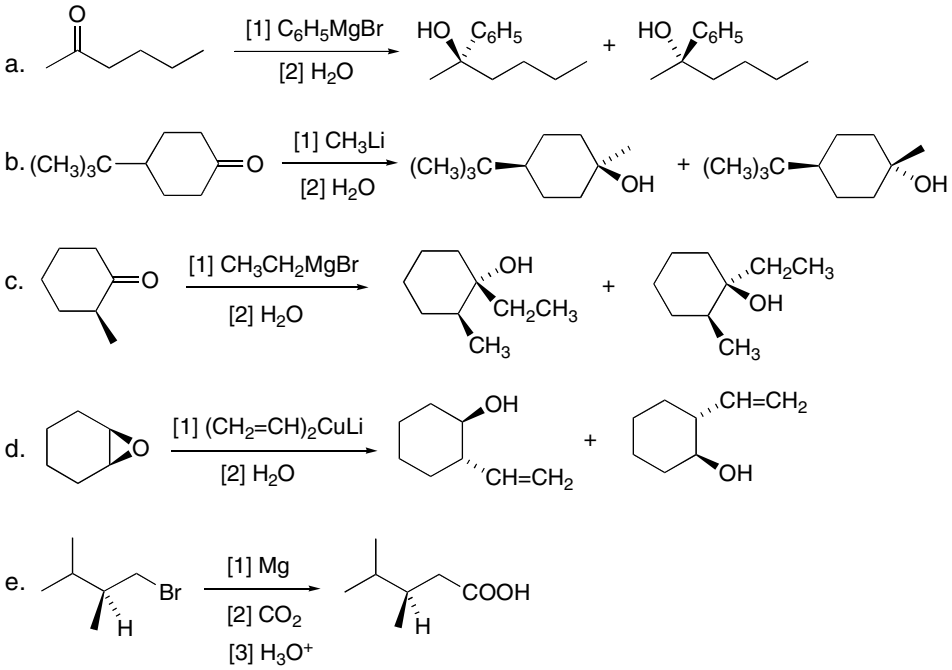
20.49

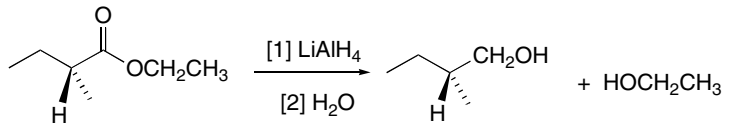


20.50

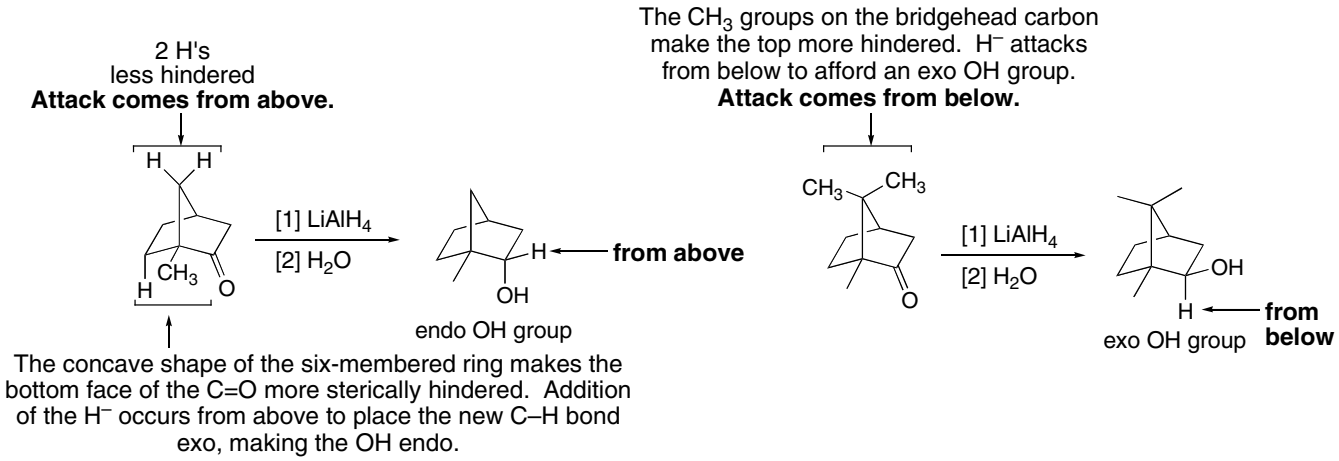

a.
[1] CO_2
[2] H_3O^+
b.
[1] CH_3CH_2MgBr
[2] H_2O
c.
[1] C_6H_5Li
[2] H_2O
d.
[1] C_6H_5MgBr (excess)
[2] H_2O
e.
[1] CH_3MgCl (excess)
[2] H_2O
f.
[1] $CH_2=O$
[2] H_2O
g.
[1] $(CH_3)_2CuLi$
[2] H_2O
h.
[1] CH_3MgBr
[2] H_2O
i.
[1] C_6H_5Li
[2] H_2O
j.
[1] $(CH_3)_2CuLi$
[2] H_2O

20.51

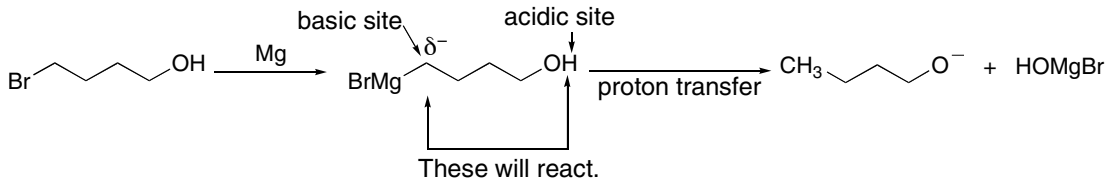

a.
[1] C_6H_5MgBr
[2] H_2O
b.
[1] CH_3Li
[2] H_2O
c.
[1] CH_3CH_2MgBr
[2] H_2O
d.
[1] $(CH_2=CH)_2CuLi$
[2] H_2O
e.
[1] Mg
[2] CO_2
[3] H_3O^+
f.
[1] (*S*)-CBS reagent
[2] H_2O
g.
[1] (*R*)-CBS reagent
[2] H_2O

h. 

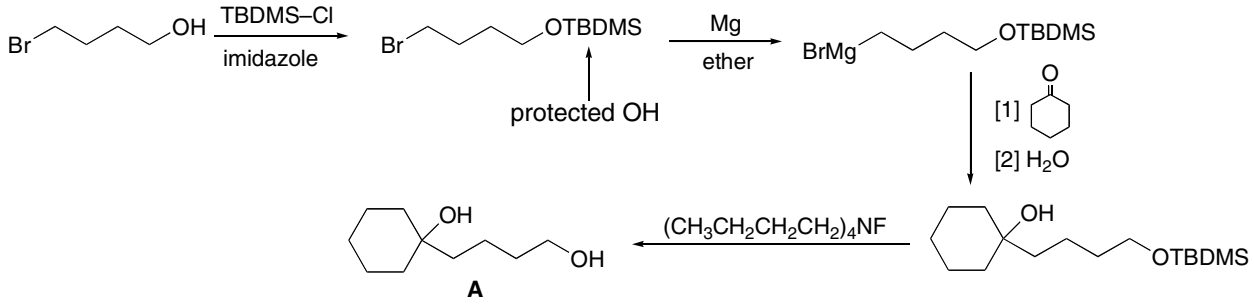
20.52 Both ketones are chiral molecules with carbonyl groups that have one side more sterically hindered than the other. In both reductions, hydride approaches from the less hindered side.



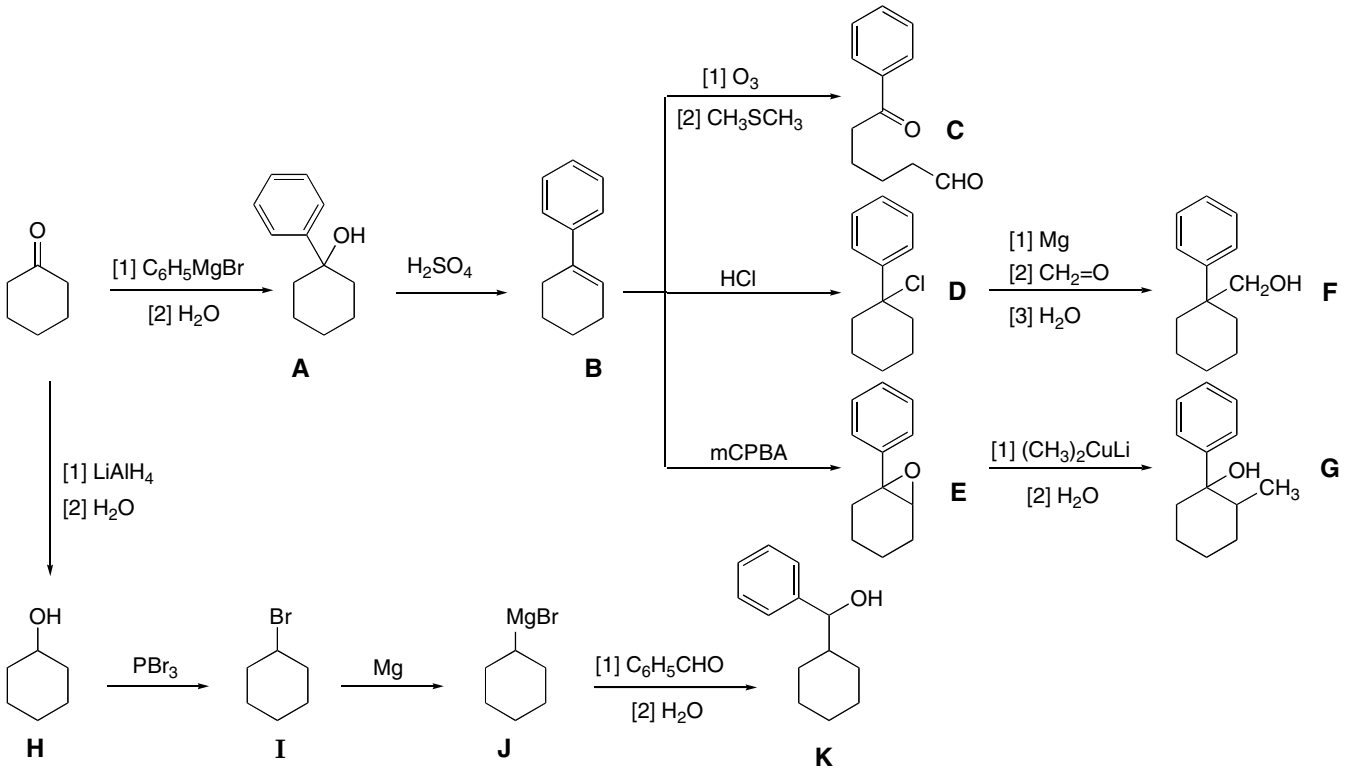
20.53 Since a Grignard reagent contains a carbon atom with a partial negative charge, it acts as a base and reacts with the OH of the starting halide, $BrCH_2CH_2CH_2CH_2OH$. This acid–base reaction destroys the Grignard reagent so that addition cannot occur. To get around this problem, the OH group can be protected as a *tert*-butyldimethylsilyl ether, from which a Grignard reagent can be made.



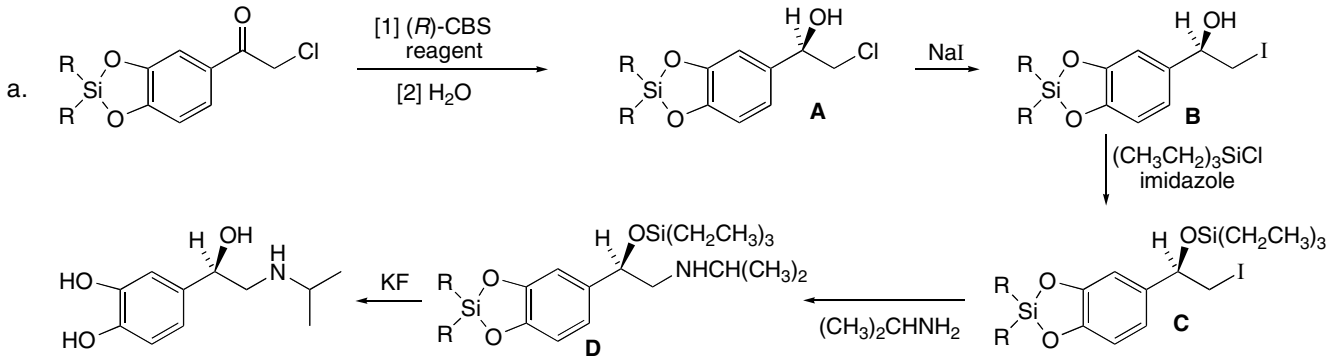
INSTEAD: Use a protecting group.

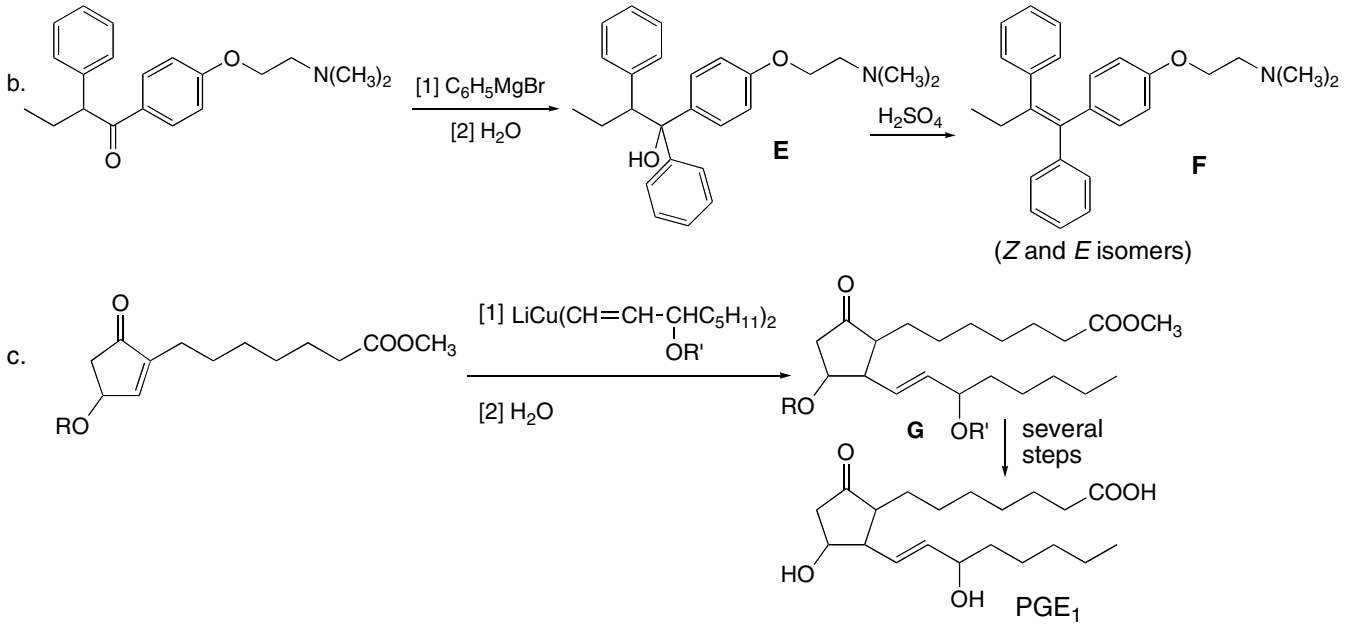


20.54 Compounds **F**, **G**, and **K** are all alcohols with aromatic rings so there will be many similarities in their proton NMR spectra. These compounds will, however, show differences in absorptions due to the CH protons on the carbon bearing the OH group**.** **F** has a CH_2OH group, which will give a singlet in the 3–4 ppm region of the spectrum. **G** is a 3° alcohol that has no protons on the C bonded to the OH group so it will have no peak in the 3–4 ppm region of the spectrum. **K** is a 2° alcohol that will give a doublet in the 3–4 ppm region of the spectrum for the CH proton on the carbon with the OH group.

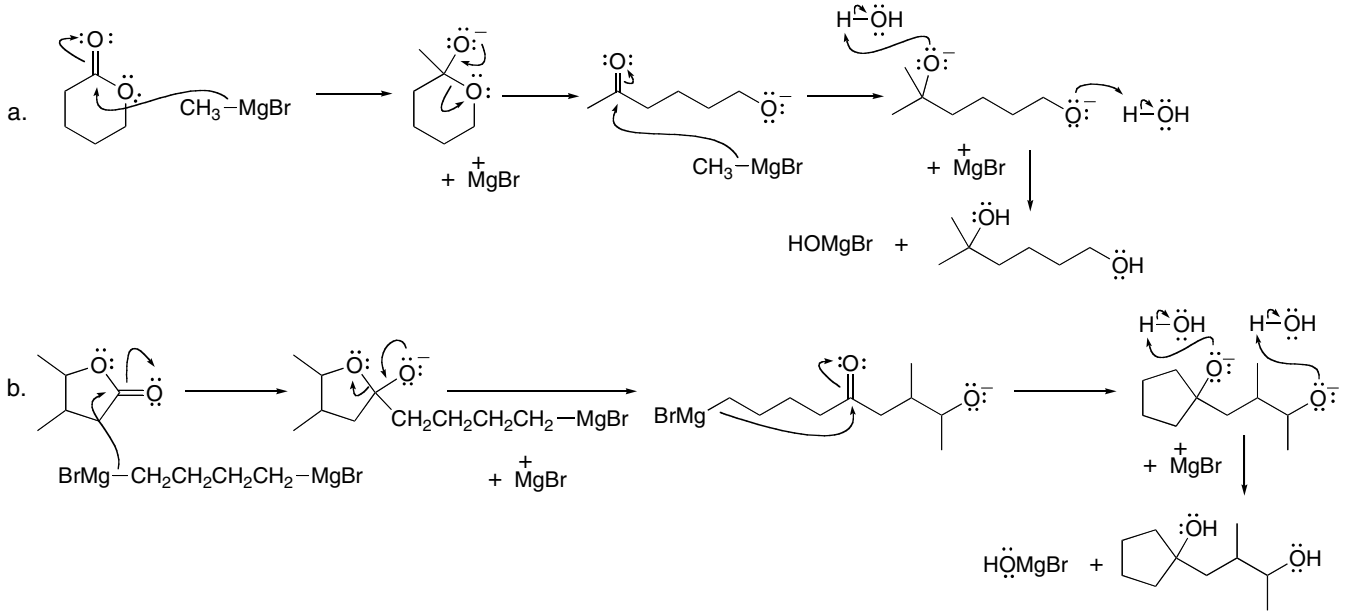


20.55

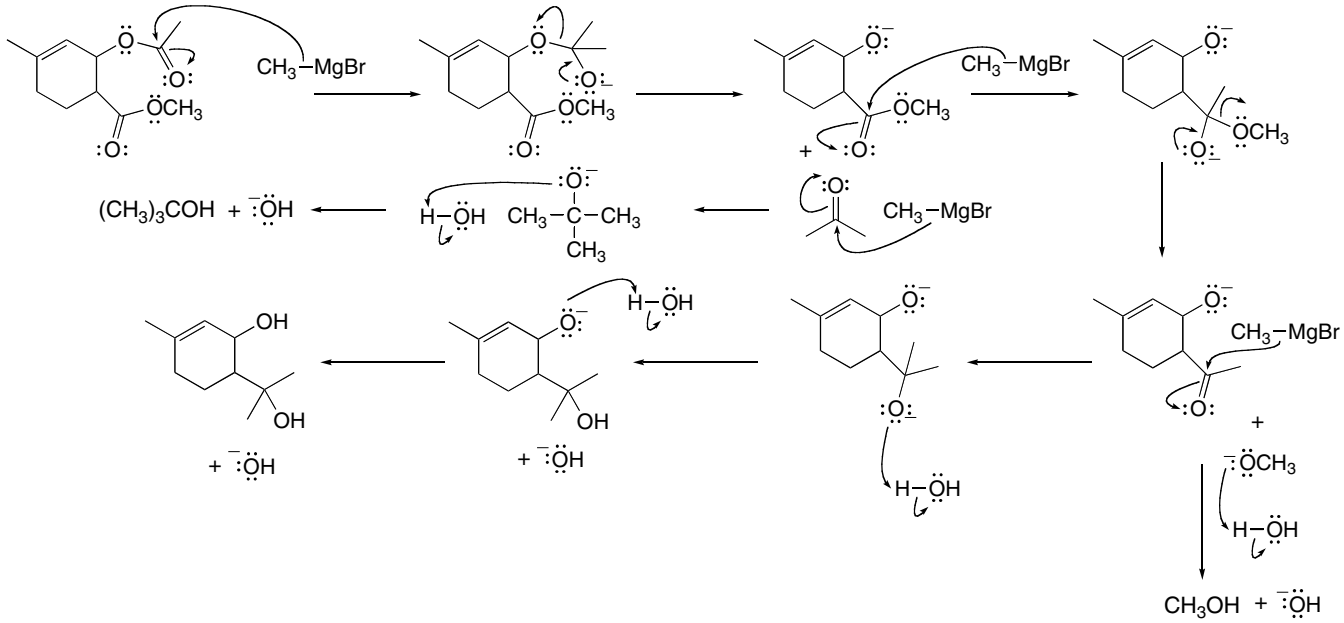



b.
[1] C_6H_5MgBr
[2] H_2O
E
H_2SO_4
F
(Z and E isomers)
c.
[1] $LiCu(CH{=}CH\text{-}CHC_5H_{11})_2$
OR'
[2] H_2O
G
several steps
PGE_1

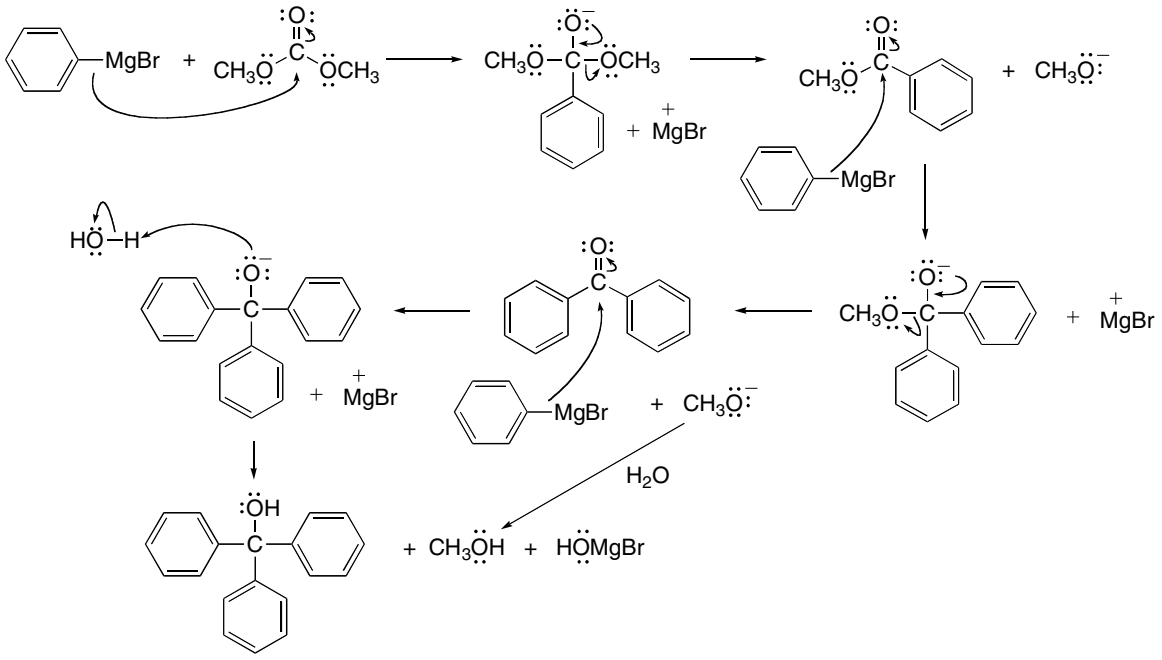
20.56


a.
$CH_3{-}MgBr$
$+ MgBr$
$CH_3{-}MgBr$
$+ MgBr$
$HOMgBr +$
b.
$BrMg{-}CH_2CH_2CH_2CH_2{-}MgBr$
$CH_2CH_2CH_2CH_2{-}MgBr$
$+ MgBr$
BrMg
$+ MgBr$
$HOMgBr +$

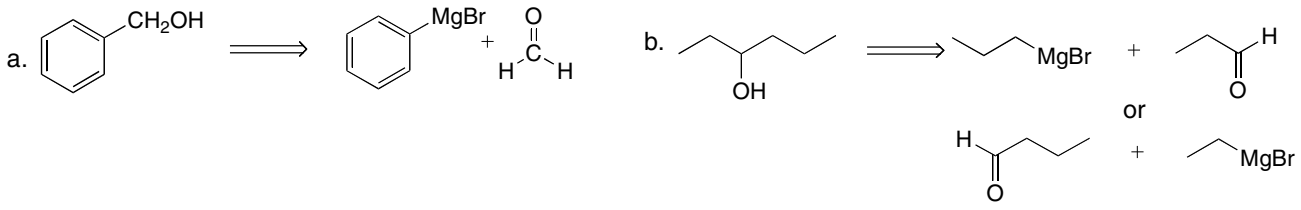
20.57



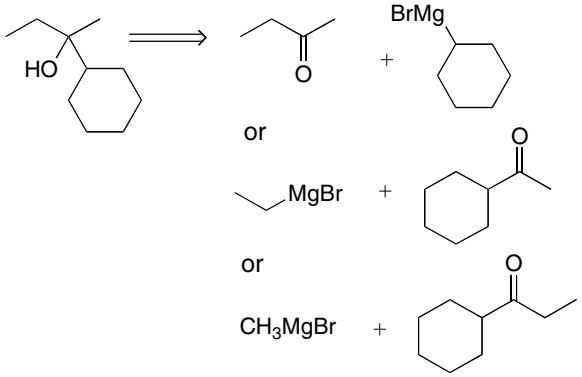
20.58

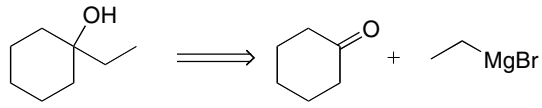


20.59

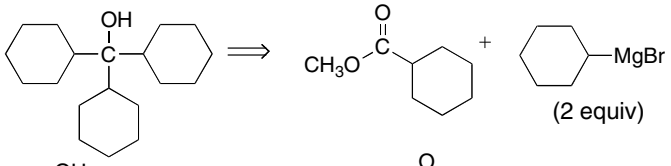


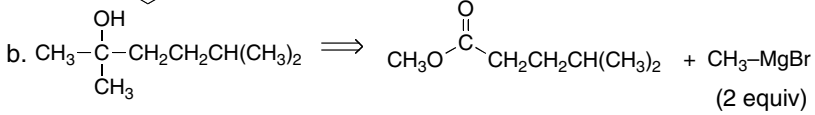
c. $(C_6H_5)_3COH \Longrightarrow (C_6H_5)_2C{=}O$ + BrMg–Ph

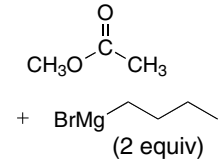
d. 

e. 

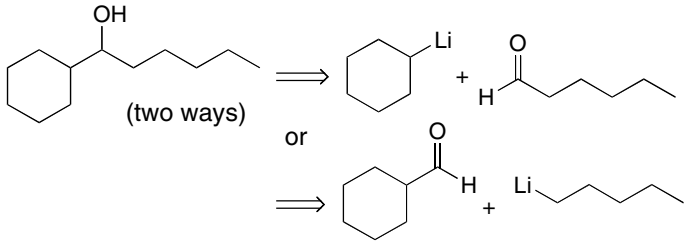
20.60

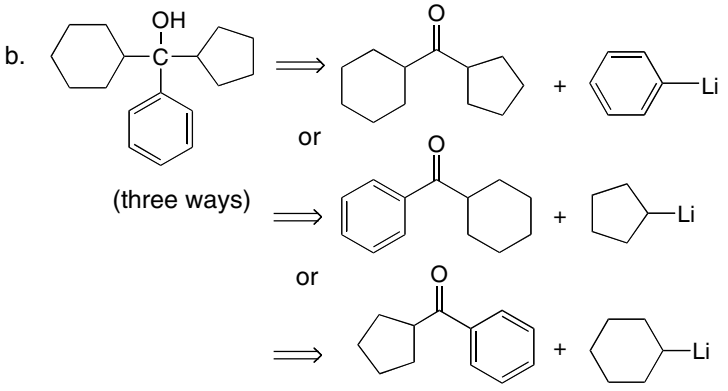
a. 

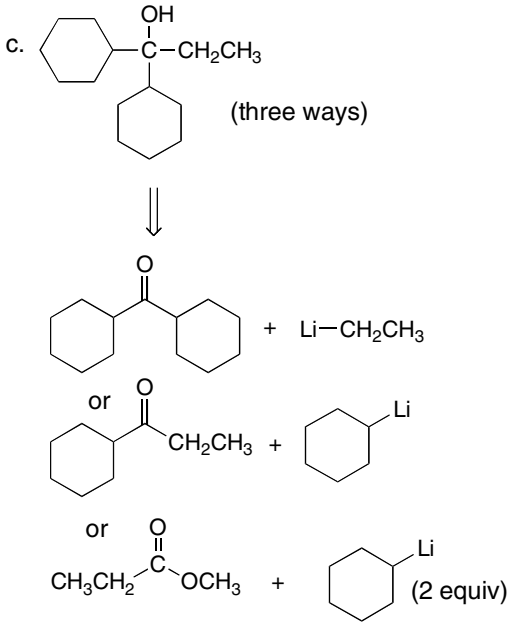
b. 

c. $(CH_3CH_2CH_2CH_2)_2C(OH)CH_3 \Longrightarrow$ 

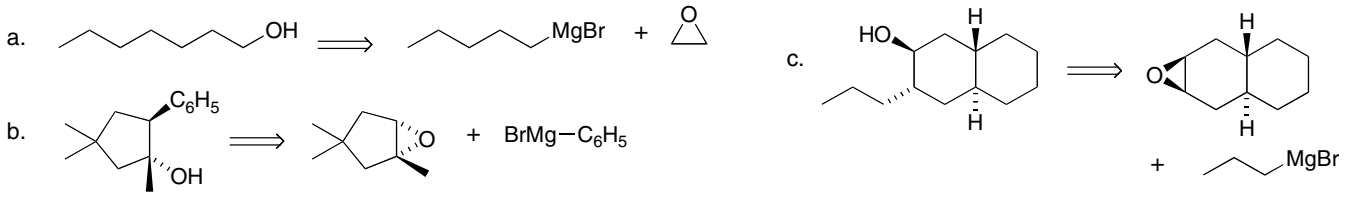
20.61

a. 

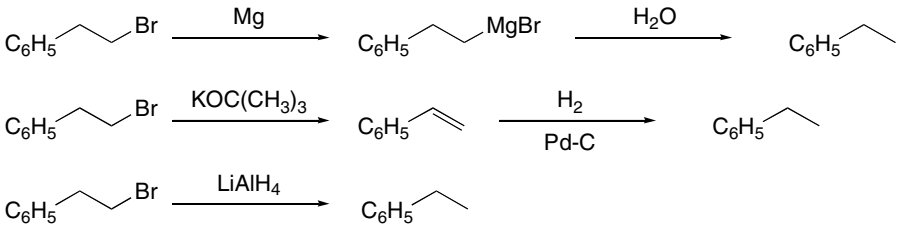
b. 

c. 

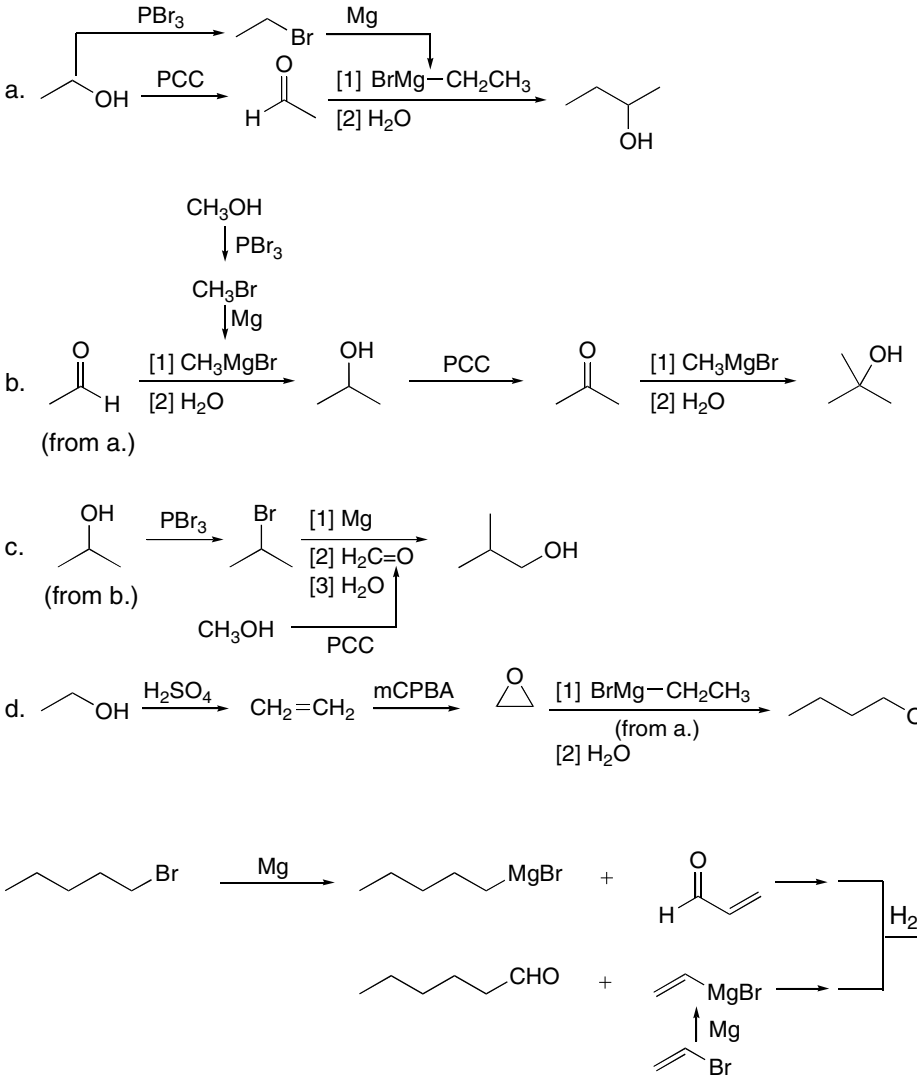
20.62



20.63

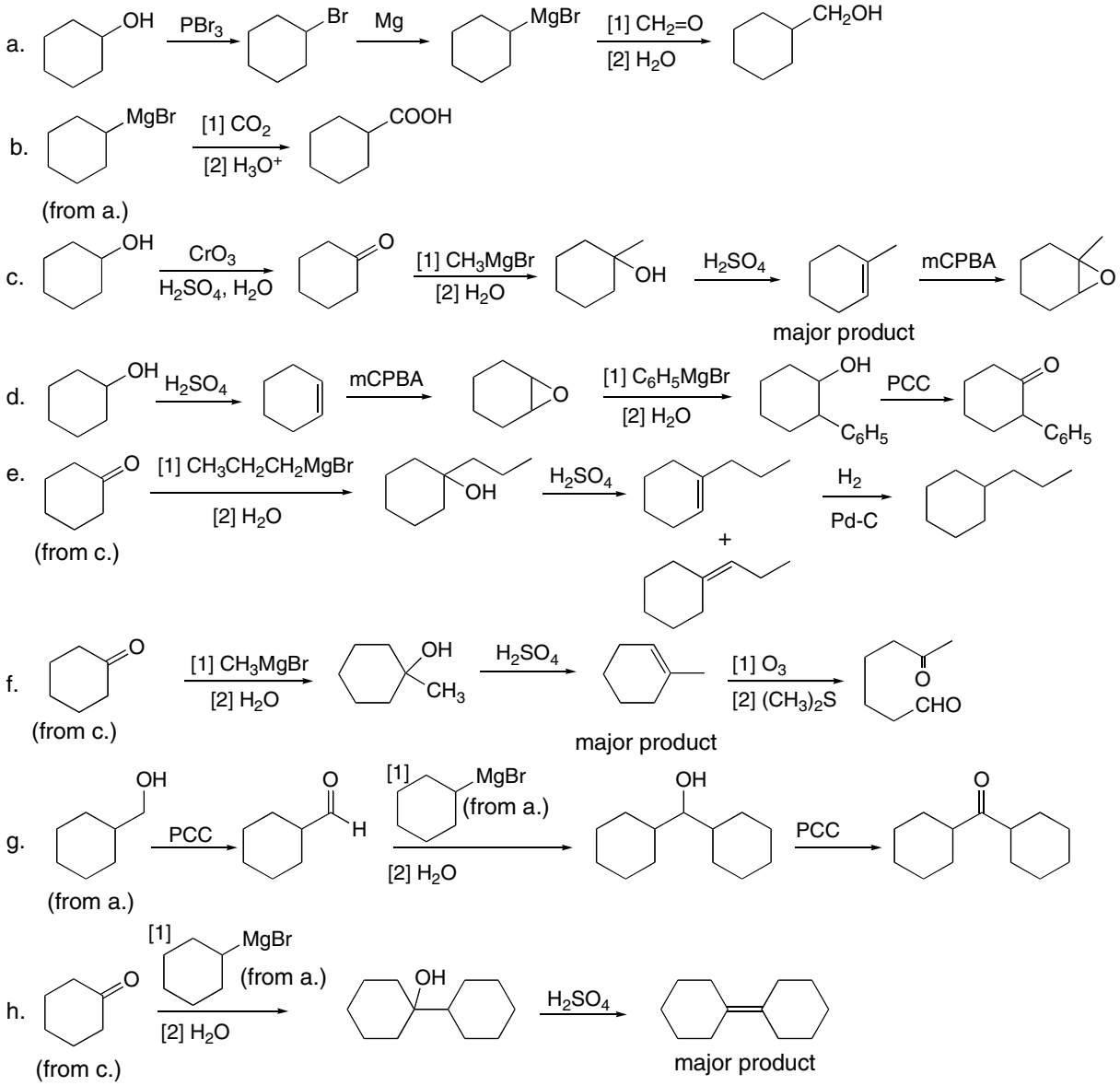


20.64

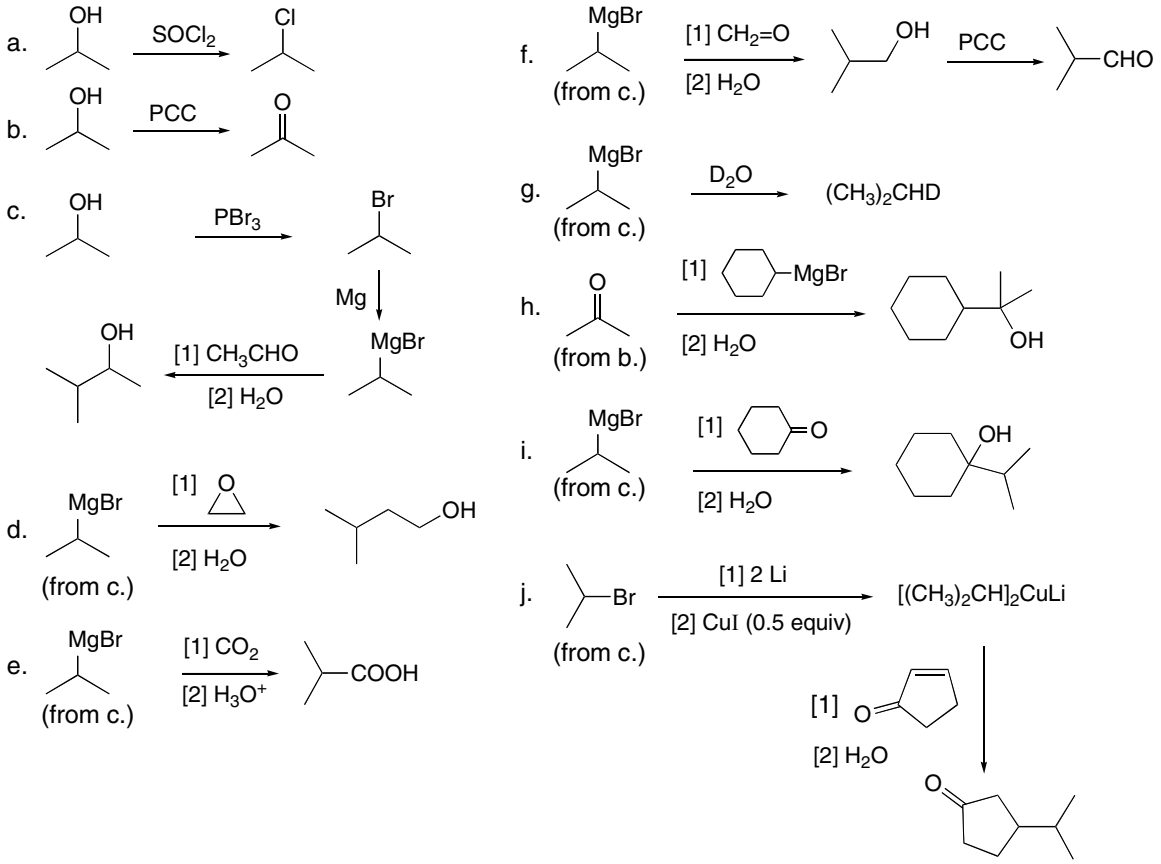


20.65

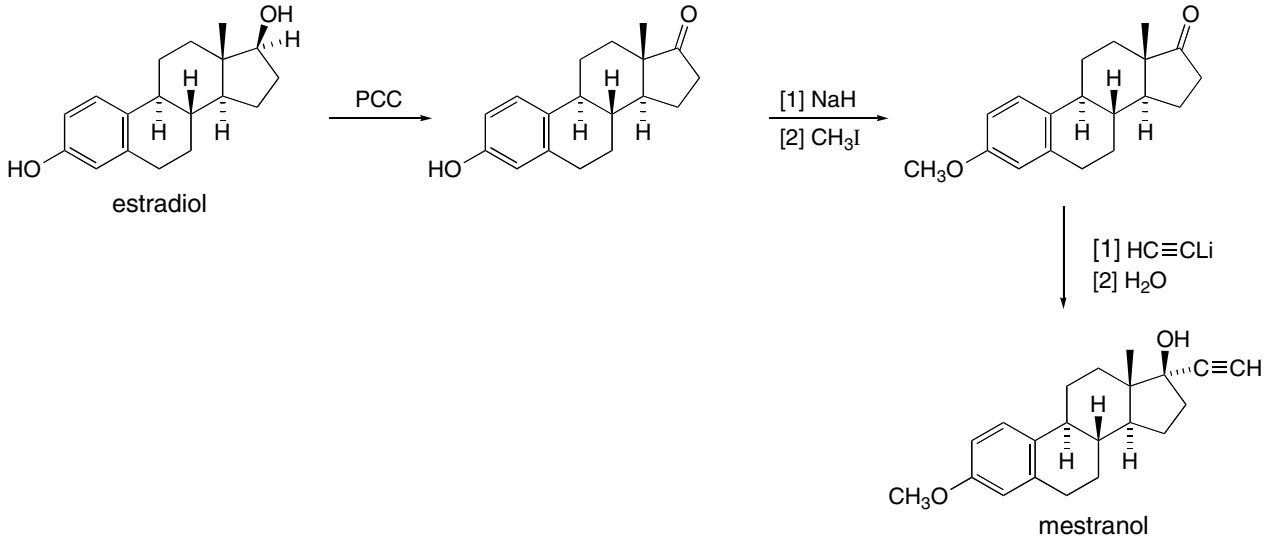
20.66


a.
OH
PBr3
Br
Mg
MgBr
[1] CH2=O
[2] H2O
CH2OH
b.
MgBr
[1] CO2
[2] H3O+
COOH
(from a.)
c.
OH
CrO3
H2SO4, H2O
O
[1] CH3MgBr
[2] H2O
OH
H2SO4
mCPBA
O
major product
d.
OH
H2SO4
mCPBA
O
[1] C6H5MgBr
[2] H2O
OH
C6H5
PCC
O
C6H5
e.
O
[1] CH3CH2CH2MgBr
[2] H2O
OH
H2SO4
+
H2
Pd-C
(from c.)
f.
O
[1] CH3MgBr
[2] H2O
OH
CH3
H2SO4
[1] O3
[2] (CH3)2S
O
CHO
(from c.)
major product
g.
OH
PCC
O
H
[1]
MgBr
(from a.)
[2] H2O
OH
PCC
O
(from a.)
h.
O
[1]
MgBr
(from a.)
[2] H2O
OH
H2SO4
major product
(from c.)

20.67

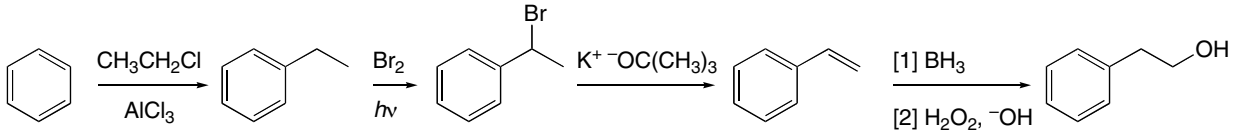

a.
OH
SOCl2
Cl
b.
OH
PCC
O
c.
OH
PBr3
Br
Mg
MgBr
[1] CH3CHO
[2] H2O
OH
d.
MgBr
(from c.)
[1]
O
[2] H2O
OH
e.
MgBr
(from c.)
[1] CO2
[2] H3O+
COOH
f.
MgBr
(from c.)
[1] CH2=O
[2] H2O
OH
PCC
CHO
g.
MgBr
(from c.)
D2O
(CH3)2CHD
h.
O
(from b.)
[1]
MgBr
[2] H2O
OH
i.
MgBr
(from c.)
[1]
O
[2] H2O
OH
j.
Br
(from c.)
[1] 2 Li
[2] CuI (0.5 equiv)
[(CH3)2CH]2CuLi
[1]
O
[2] H2O
O

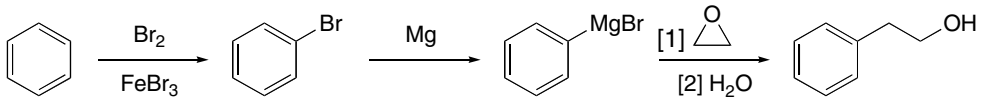
20.68

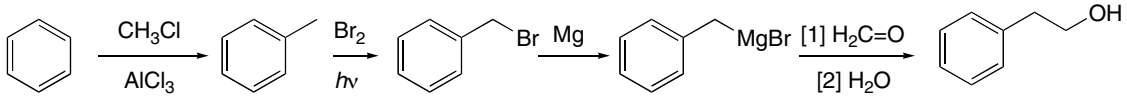

OH
H
H
H
HO
estradiol
PCC
O
[1] NaH
[2] CH3I
CH3O
[1] HC≡CLi
[2] H2O
OH
C≡CH
CH3O
mestranol

20.69

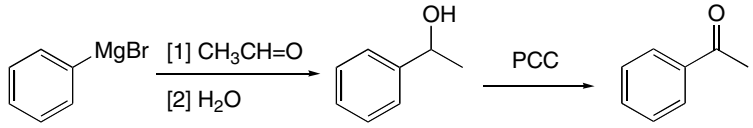
a.



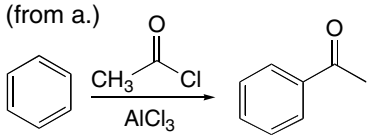




b.



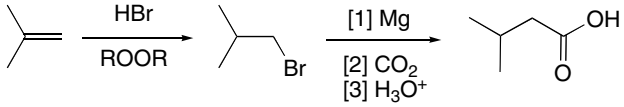
(from a.)



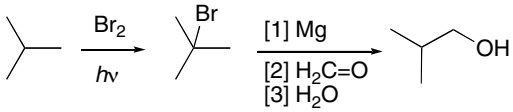
(from a.)

20.70

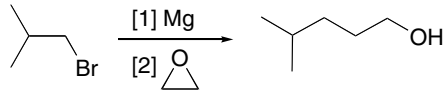
a.



c.



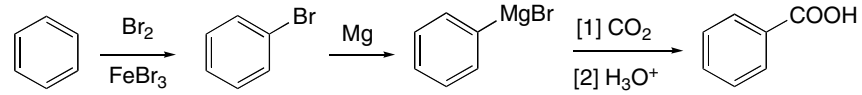
b.



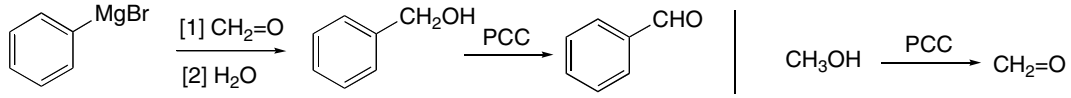
(from a.)

20.71

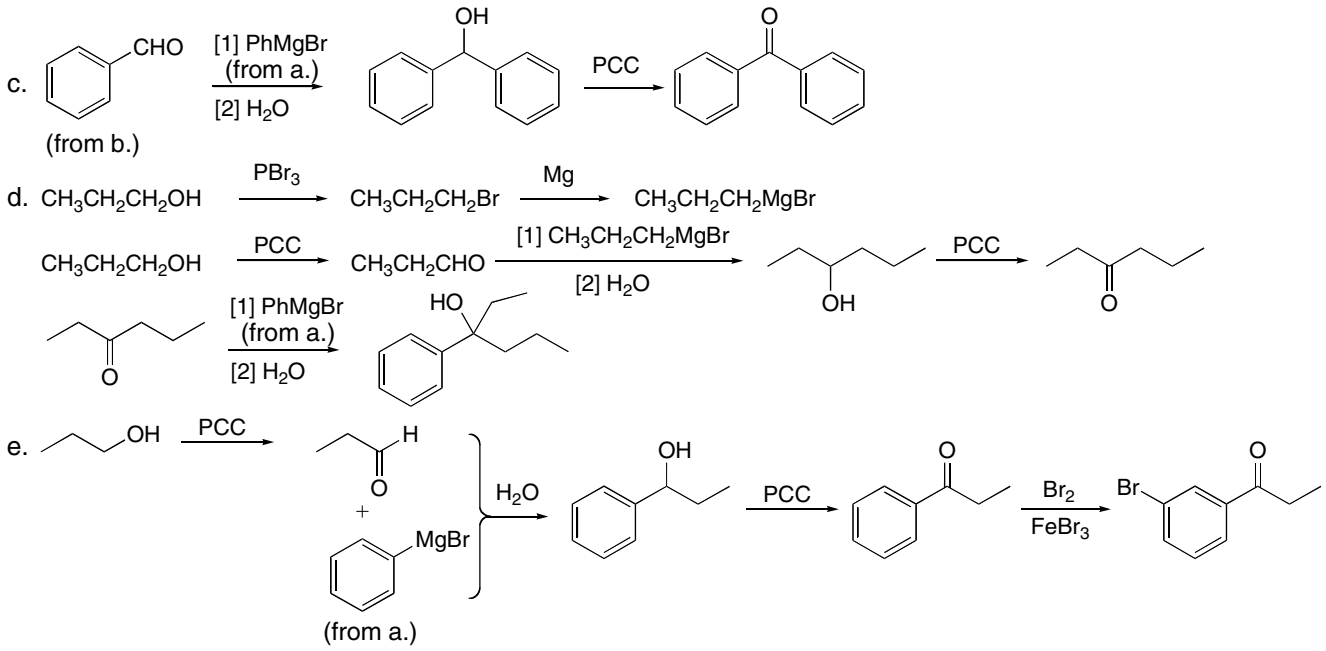
a.



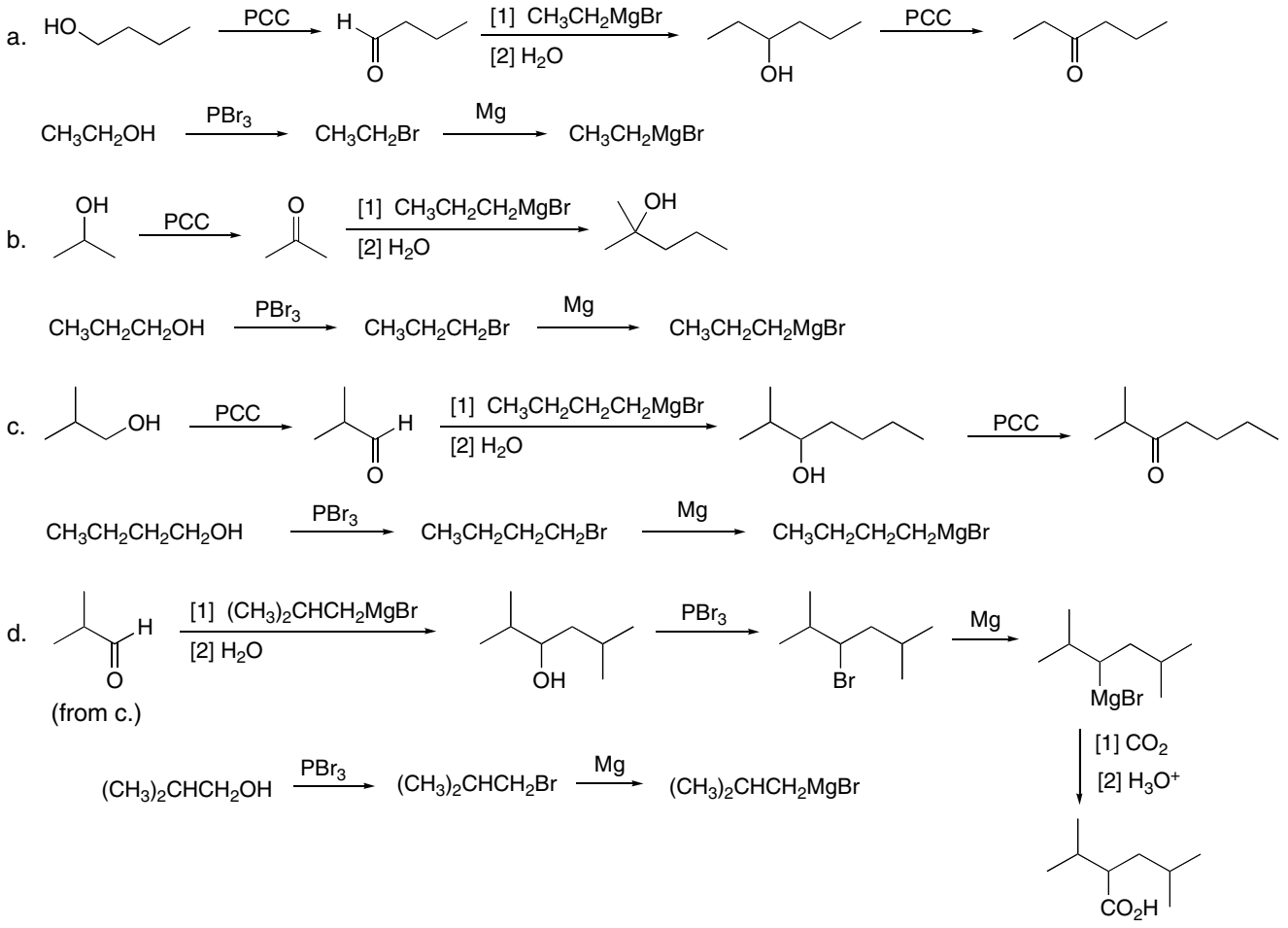
b.

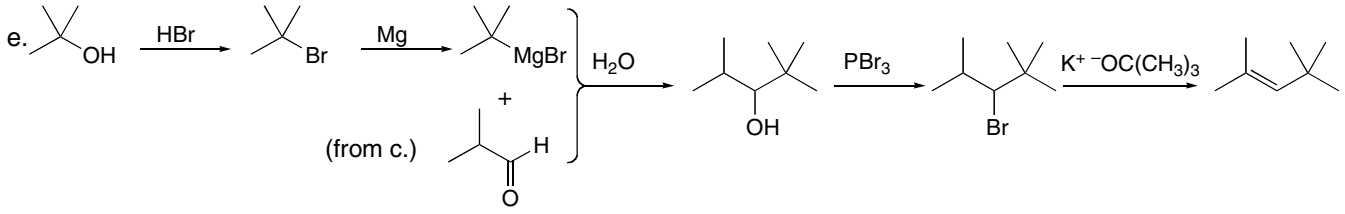


(from a.)

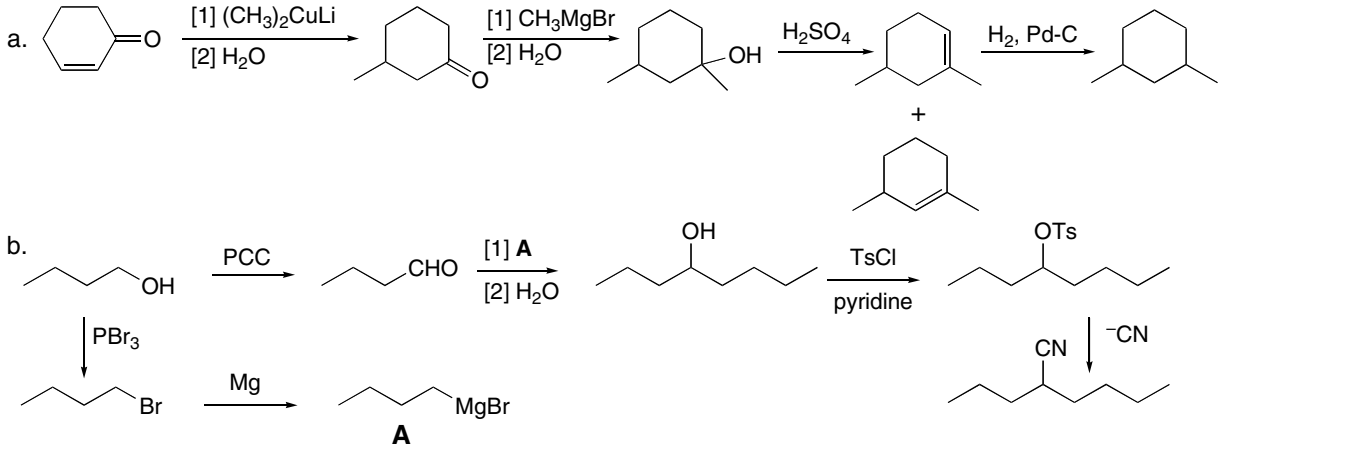

c.
CHO
[1] PhMgBr
(from a.)
[2] H2O
OH
PCC
O
(from b.)
d. CH3CH2CH2OH
PBr3
CH3CH2CH2Br
Mg
CH3CH2CH2MgBr
CH3CH2CH2OH
PCC
CH3CH2CHO
[1] CH3CH2CH2MgBr
[2] H2O
OH
PCC
O
O
[1] PhMgBr
(from a.)
[2] H2O
HO
e.
OH
PCC
H
O
+
MgBr
H2O
OH
PCC
O
Br2
FeBr3
Br
O
(from a.)

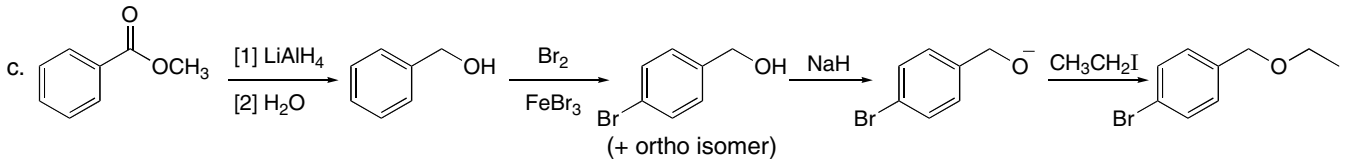
20.72

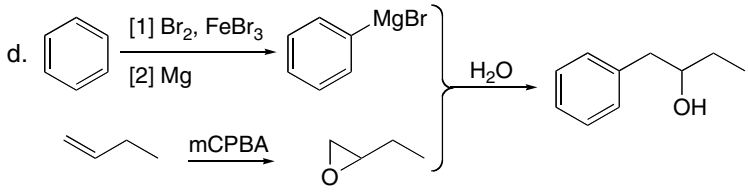

a.
HO
PCC
H
O
[1] CH3CH2MgBr
[2] H2O
OH
PCC
O
CH3CH2OH
PBr3
CH3CH2Br
Mg
CH3CH2MgBr
b.
OH
PCC
O
[1] CH3CH2CH2MgBr
[2] H2O
OH
CH3CH2CH2OH
PBr3
CH3CH2CH2Br
Mg
CH3CH2CH2MgBr
c.
OH
PCC
H
O
[1] CH3CH2CH2CH2MgBr
[2] H2O
OH
PCC
O
CH3CH2CH2CH2OH
PBr3
CH3CH2CH2CH2Br
Mg
CH3CH2CH2CH2MgBr
d.
H
O
(from c.)
[1] (CH3)2CHCH2MgBr
[2] H2O
OH
PBr3
Br
Mg
MgBr
[1] CO2
[2] H3O+
CO2H
(CH3)2CHCH2OH
PBr3
(CH3)2CHCH2Br
Mg
(CH3)2CHCH2MgBr

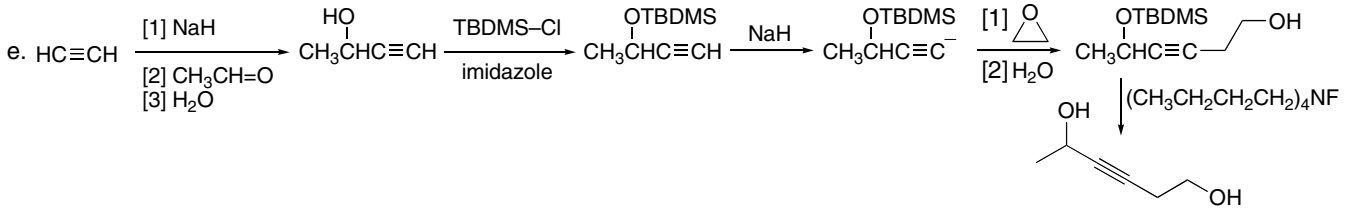

e.
OH
HBr
Br
Mg
MgBr
+
(from c.)
H
O
H2O
OH
PBr3
Br
K+ −OC(CH3)3

20.73

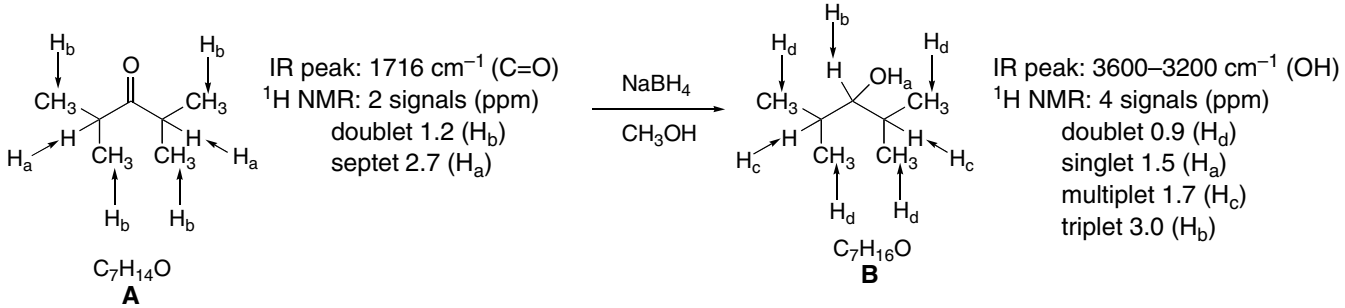

a.
O
[1] (CH3)2CuLi
[2] H2O
O
[1] CH3MgBr
[2] H2O
OH
H2SO4
H2, Pd-C
+
b.
OH
PCC
CHO
[1] A
[2] H2O
OH
TsCl
pyridine
OTs
PBr3
Br
Mg
MgBr
A
CN
−CN


c.
O
OCH3
[1] LiAlH4
[2] H2O
OH
Br2
FeBr3
OH
Br
(+ ortho isomer)
NaH
O−
Br
CH3CH2I
O
Br

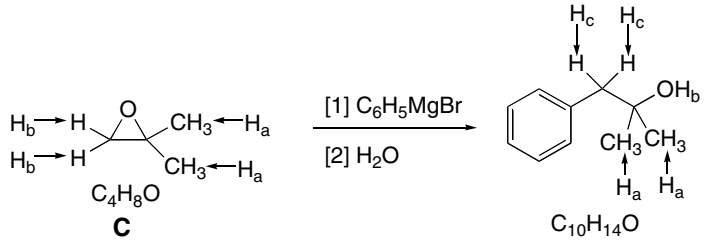

d.
[1] Br2, FeBr3
[2] Mg
MgBr
mCPBA
O
H2O
OH


e. HC≡CH
[1] NaH
[2] CH3CH=O
[3] H2O
HO
CH3CHC≡CH
TBDMS–Cl
imidazole
OTBDMS
CH3CHC≡CH
NaH
OTBDMS
CH3CHC≡C−
[1]
O
[2] H2O
OTBDMS
CH3CHC≡C
OH
(CH3CH2CH2CH2)4NF
OH
OH

20.74


Hb
O
Hb
CH3
CH3
H
H
Ha
Ha
CH3
CH3
Hb
Hb
C7H14O
A
IR peak: 1716 cm−1 (C=O)
1H NMR: 2 signals (ppm)
doublet 1.2 (Hb)
septet 2.7 (Ha)
NaBH4
CH3OH
Hb
Hd
Hd
H
OHa
CH3
CH3
H
H
Hc
Hc
CH3
CH3
Hd
Hd
C7H16O
B
IR peak: 3600–3200 cm−1 (OH)
1H NMR: 4 signals (ppm)
doublet 0.9 (Hd)
singlet 1.5 (Ha)
multiplet 1.7 (Hc)
triplet 3.0 (Hb)

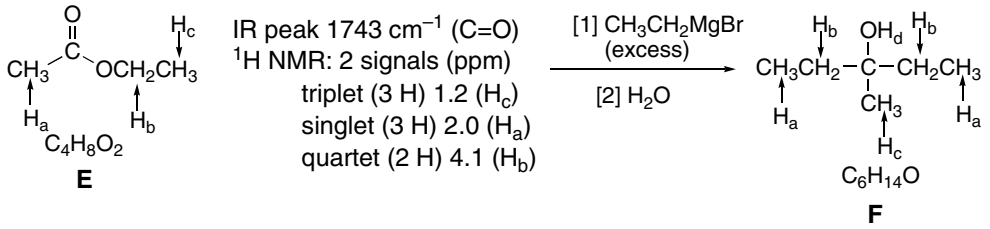
20.75



^{1}H NMR: 2 signals (ppm)
singlet (6 H) 1.3 (H_a)
singlet (2 H) 2.4 (H_b)

IR peak 3600–3200 cm^{-1} (OH)
^{1}H NMR: 4 signals (ppm)
singlet (6 H) 1.2 (H_a)
singlet (1 H) 1.6 (H_b)
singlet (2 H) 2.7 (H_c)
multiplet (5 H) 7.2 (benzene ring)

20.76

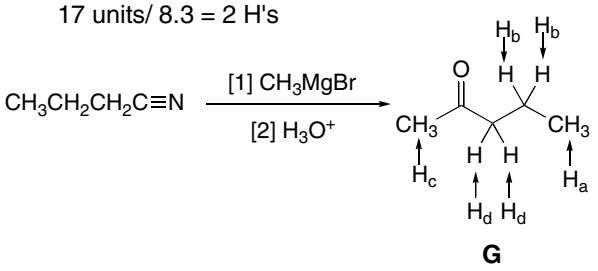


IR peak 1743 cm^{-1} (C=O)
^{1}H NMR: 2 signals (ppm)
triplet (3 H) 1.2 (H_c)
singlet (3 H) 2.0 (H_a)
quartet (2 H) 4.1 (H_b)

IR peak 3600–3200 cm^{-1} (OH)
^{1}H NMR: 4 signals (ppm)
triplet (6 H) 0.9 (H_a)
singlet (3 H) 1.1 (H_c)
quartet (4 H) 1.5 (H_b)
singlet (1 H) 1.55 (H_d)

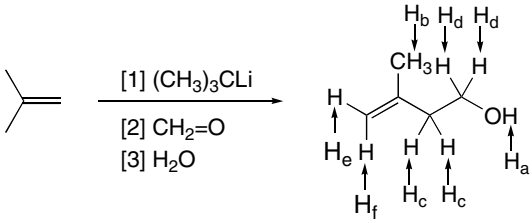
20.77 Molecular ion at m/z = 86: $C_5H_{10}O$ (possible molecular formula).

Determine the number of integration units per H:
Total number of integration units: 25 + 17 + 24 + 17 = 83
83 units/10 H's = 8.3 units per H
Divide each integration value by 8.3 to determine the number of H's per signal:
25 units/ 8.3 = 3 H's
24 units/ 8.3 = 3 H's
17 units/ 8.3 = 2 H's



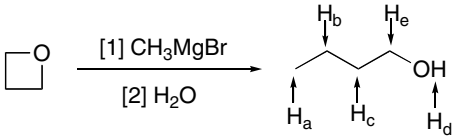
IR peak 1721 cm^{-1} (C=O)
^{1}H NMR: 4 signals (ppm)
triplet (3 H) 0.9 (H_a)
sextet (2 H) 1.6 (H_b)
singlet (3 H) 2.1 (H_c)
triplet (2 H) 2.4 (H_d)

20.78 Molecular ion at m/z = 86: $C_5H_{10}O$ (possible molecular formula).

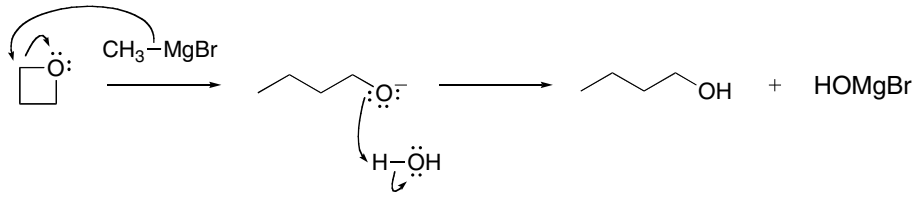


IR peaks: 3600–3200 cm^{-1} (OH)
1651cm^{-1} (C=C)
^{1}H NMR: 6 signals (ppm)
singlet (1 H) 1.7 (H_a)
singlet (3 H) 1.8 (H_b)
triplet (2 H) 2.2 (H_c)
triplet (2 H) 3.8 (H_d)
two signals at 4.8 and 4.9
due to 2 H's: H_e and H_f

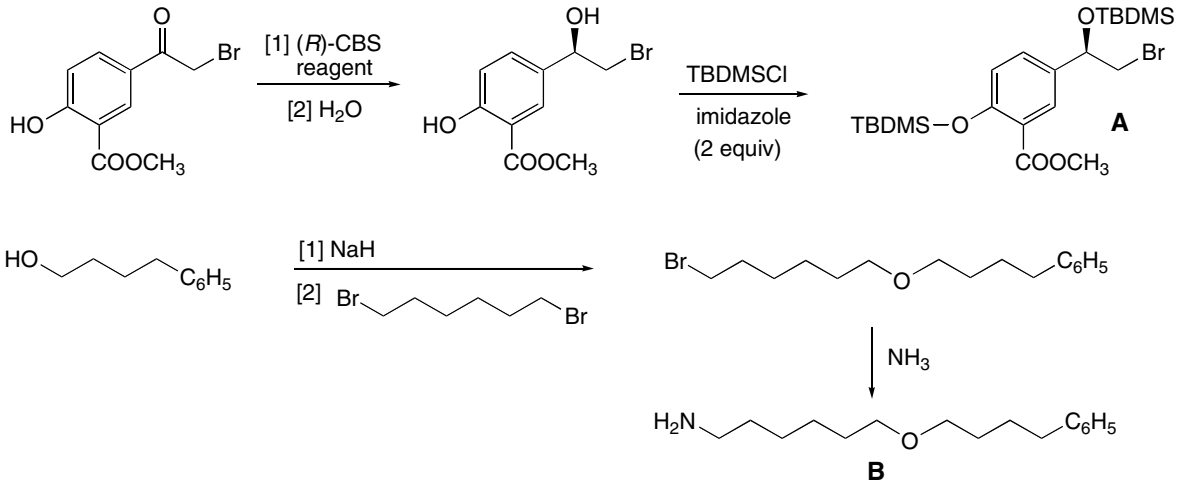
20.79

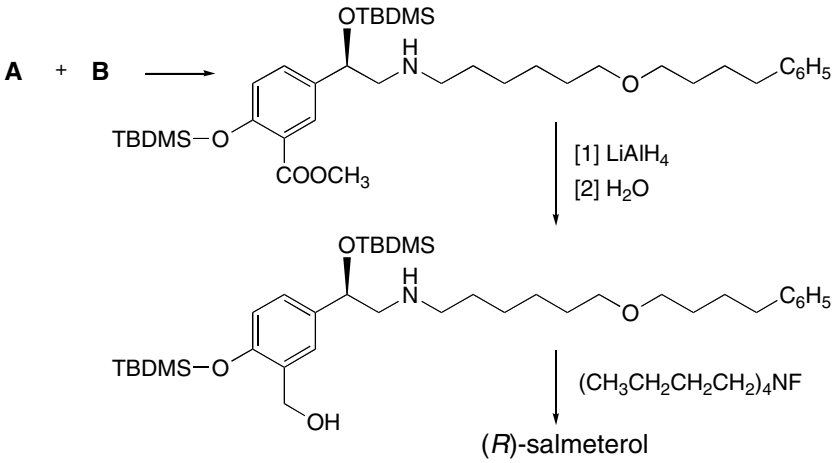


IR peak 3600–3200 cm^{-1} (OH)
^1H NMR: 5 signals (ppm)
triplet (3 H) 0.94 (H_a)
multiplet (2 H) 1.39 (H_b)
multiplet (2 H) 1.53 (H_c)
singlet (1 H) 2.24 (H_d)
triplet (2 H) 3.63 (H_e)

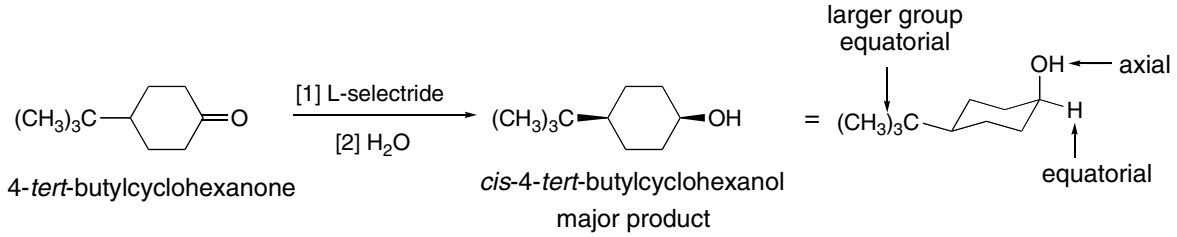


20.80

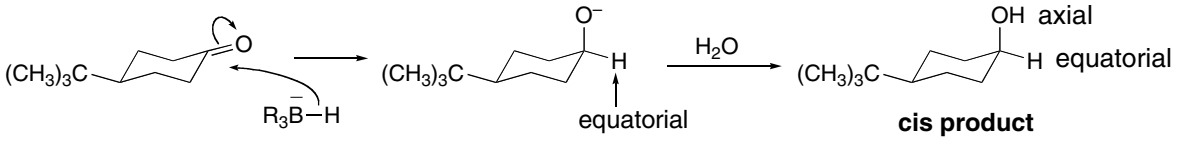




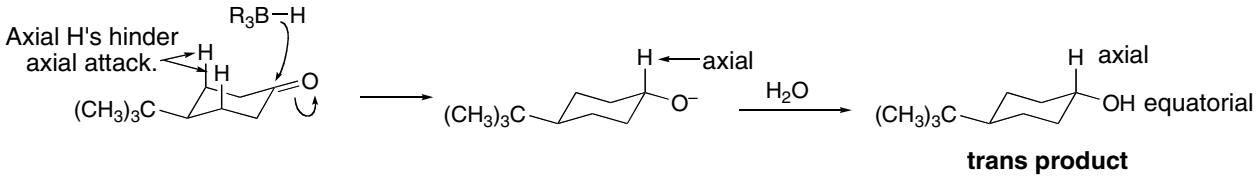
20.81



L-Selectride adds H^- to a C=O group. There are two possible reduction products—cis and trans isomers—but the cis isomer is favored. The key element is that the three *sec*-butyl groups make L-selectride a large, bulky reducing agent that attacks the carbonyl group from the less hindered direction.

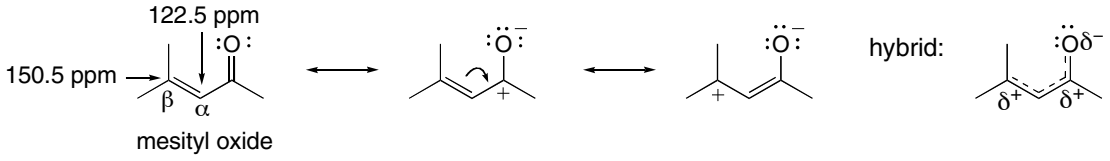


When H^- adds from the equatorial direction, the product has an axial OH and a new equatorial H. Since the equatorial direction is less hindered, this mode of attack is favored with large bulky reducing agents like L-selectride. In this case, the product is cis.

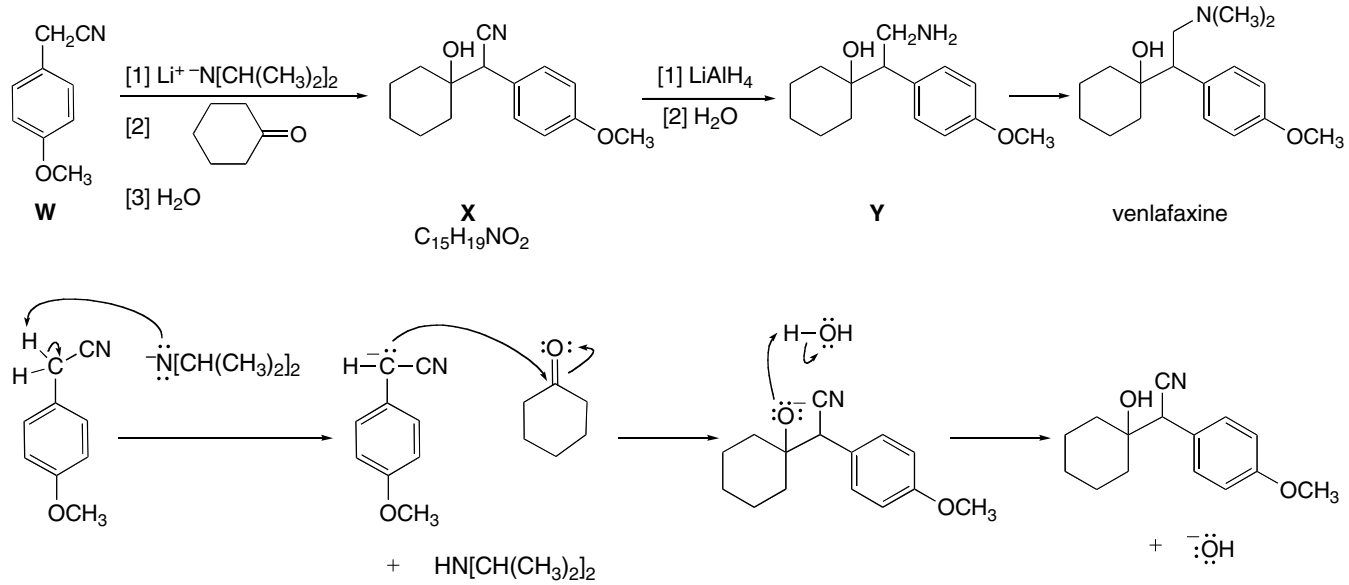


The axial H's hinder H^- attack from the axial direction. As a result, this mode of attack is more difficult with larger reducing agents. In this case the product is trans. This product is not formed to any appreciable extent.

20.82 The β carbon of an α,β-unsaturated carbonyl compound absorbs farther downfield in the ^{13}C NMR spectrum than the α carbon, because the β carbon is deshielded and bears a partial positive charge as a result of resonance. Since three resonance structures can be drawn for an α,β-unsaturated carbonyl compound, one of which places a positive charge on the β carbon, the decrease of electron density at this carbon deshields it, shifting the ^{13}C absorption downfield. This is not the case for the α carbon.



20.83


CH2CN
OCH3
W
[1] Li+ −N[CH(CH3)2]2
[2]
O
[3] H2O
OH
CN
OCH3
X
C15H19NO2
[1] LiAlH4
[2] H2O
OH
CH2NH2
OCH3
Y
OH
N(CH3)2
OCH3
venlafaxine
H
CN
H
−N[CH(CH3)2]2
OCH3
H−C−CN
O
OCH3
+ HN[CH(CH3)2]2
H−OH
O
CN
OCH3
OH
CN
OCH3
+ −OH