

## Chapter 17 – Alcohols and Phenols

### Chapter Outline

- I. Naming alcohols and phenols (Section 17.1).
  1. Alcohols are classified as primary, secondary or tertiary, depending on the number of organic groups bonded to the –OH carbon.
  2. Rules for naming simple alcohols.
    - a. The longest chain containing the –OH group is the parent chain, and the parent name replaces *-e* with *-ol*.
    - b. Numbering begins at the end of the chain nearer the –OH group.
    - c. The substituents are numbered according to their position on the chain and cited in alphabetical order.
  3. Phenols are named according to rules discussed in Section 15.1.
- II. Properties of alcohols and phenols (Section 17.2).
  - B. Hydrogen bonding of alcohols and phenols.
    1. Alcohols have  $sp^3$  hybridization and a nearly tetrahedral bond angle.
    2. Alcohols and phenols have elevated boiling points, relative to hydrocarbons, due to hydrogen bonding.
      - a. In hydrogen bonding, an –OH hydrogen is attracted to a lone pair of electrons on another molecule, resulting in a weak electrostatic force that holds the molecules together.
      - b. These weak forces must be overcome in boiling.
  - C. Acidity and basicity of alcohols and phenols.
    1. Alcohols and phenols are weakly acidic as well as weakly basic.
    2. Alcohols and phenols dissociate to a slight extent to form alkoxide ions and phenoxide ions.
    3. Acidity of alcohols.
      - a. Alcohols are similar in acidity to water.
      - b. Alkyl substituents decrease acidity by preventing solvation of the alkoxide ion.
      - c. Electron-withdrawing substituents increase acidity by delocalizing negative charge.
      - d. Alcohols don't react with weak bases, but they do react with alkali metals and strong bases.
    4. Acidity of phenols.
      - a. Phenols are a million times more acidic than alcohols and are soluble in dilute NaOH.
      - b. Phenol acidity is due to resonance stabilization of the phenoxide anion.
      - c. Electron-withdrawing substituents increase phenol acidity, and electron-donating substituents decrease phenol acidity.
- II. Alcohols (Sections 17.3 – 17.8).
  - A. Preparation of alcohols (Sections 17.3 – 17.5).
    1. Familiar methods (Section 17.3).
      - a. Hydration of alkenes.
        - i. Hydroboration/oxidation yields non-Markovnikov products.
        - ii. Oxymercuration/reduction yields Markovnikov products.
      - b. 1,2-diols can be prepared by  $OsO_4$  hydroxylation, followed by reduction.
        - i. This reaction occurs with syn stereochemistry.
        - ii. Ring-opening of epoxides produces 1,2-diols with anti stereochemistry.
    2. Reduction of carbonyl compounds (Section 17.4).
      - a. Aldehydes are reduced to primary alcohols.

- b. Ketones are reduced to secondary alcohols.  
Either  $\text{NaBH}_4$  (milder) or  $\text{LiAlH}_4$  (more reactive) can be used to reduce aldehydes and ketones.
  - c. Carboxylic acids and esters are reduced to primary alcohols with  $\text{LiAlH}_4$ .
    - i. These reactions occur by addition of hydride to the positively polarized carbon of a carbonyl group.
    - ii. Water adds to the alkoxide intermediate during workup to yield alcohol product.
3. Reaction of carbonyl compounds with Grignard reagents (Section 17.5).
- a.  $\text{RMgX}$  adds to carbonyl compounds to give alcohol products.
    - i. Reaction of  $\text{RMgX}$  with formaldehyde yields primary alcohols.
    - ii. Reaction of  $\text{RMgX}$  with aldehydes yields secondary alcohols.
    - iii. Reaction of  $\text{RMgX}$  with ketones yields tertiary alcohols.
    - iv. Reaction of  $\text{RMgX}$  with esters yields tertiary alcohols with at least two identical R groups bonded to the alcohol carbon.
    - v. No reaction occurs with carboxylic acids because the acidic hydrogen quenches the Grignard reagent.
  - b. Limitations of the Grignard reaction.
    - i. Grignard reagents can't be prepared from reagents containing other reactive functional groups.
    - ii. Grignard reagents can't be prepared from compounds having acidic hydrogens.
  - c. Grignard reagents behave as carbon anions and add to the carbonyl carbon.  
A proton from water is added to the alkoxide intermediate to produce the alcohol.
- B. Reactions of alcohols (Sections 17.6 – 17.8).
1. Conversion to alkyl halides (Section 17.6).
- a. Tertiary alcohols ( $\text{ROH}$ ) are converted to  $\text{RX}$  by treatment with  $\text{HX}$ .  
The reaction occurs by an  $\text{S}_{\text{N}}1$  mechanism.
  - b. Primary alcohols are converted by the reagents  $\text{PBr}_3$  and  $\text{SOCl}_2$ .  
The reaction occurs by an  $\text{S}_{\text{N}}2$  mechanism.
2. Conversion into tosylates.
- a. Reaction with *p*-toluenesulfonyl chloride converts alcohols to tosylates.
  - b. Only the O–H bond is broken.
  - c. Tosylates behave as halides in substitution reactions.
  - d.  $\text{S}_{\text{N}}2$  reactions involving tosylates proceed with inversion of configuration.
3. Dehydration to yield alkenes.
- a. Tertiary alcohols can undergo acid-catalyzed dehydration with warm aqueous  $\text{H}_2\text{SO}_4$ .
    - i. Zaitsev products are usually formed.
    - ii. The severe conditions needed for dehydration of secondary and primary alcohols restrict this method to tertiary alcohols.
    - iii. Tertiary alcohols react fastest because the intermediate carbocation formed in this  $\text{E}1$  reaction is most stable.
  - b. Secondary and primary alcohols are dehydrated with  $\text{POCl}_3$  in pyridine.
    - i. This reaction occurs by an  $\text{E}2$  mechanism.
    - ii. Pyridine serves as a base and as a solvent.
4. Conversion into esters.
5. Oxidation of alcohols (Section 17.7).
- a. Primary alcohols can be oxidized to aldehydes or carboxylic acids.
  - b. Secondary alcohols can be oxidized to ketones.
  - c. Tertiary alcohols aren't oxidized.
  - d. Oxidation to ketones and carboxylic acids can be carried out with  $\text{KMnO}_4$ ,  $\text{CrO}_3$ , or  $\text{Na}_2\text{Cr}_2\text{O}_7$ .

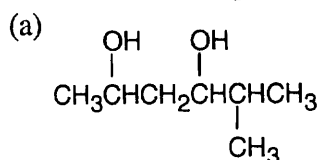
- e. Oxidation of a primary alcohol to an aldehyde is achieved with PCC.  
PCC is also used on sensitive alcohols.
  - f. Oxidation occurs by a mechanism closely related to an E2 mechanism.  
The reaction involves a chromate intermediate.
5. Protection of alcohols (Section 17.8).
- a. It is sometimes necessary to protect an alcohol when it interferes with a reaction involving a functional group in another part of a molecule.
  - b. The following reaction sequence may be applied:
    - i. Protect the alcohol.
    - ii. Carry out the reaction.
    - iii. Remove the protecting group.
  - c. A trimethylsilyl (TMS) ether can be used for protection.
    - i. TMS ether formation occurs by an  $S_N2$  route.
    - ii. TMS ethers are quite unreactive.
    - iii. TMS ethers can be cleaved by aqueous acid or by  $F^-$ .
- III. Phenols (Sections 17.9 – 17.10).
- A. Preparation and uses of phenols (Section 17.9).
1. Phenols can be prepared by treating chlorobenzene with NaOH.
  2. Phenols can also be prepared from isopropylbenzene (cumene).
    - a. Cumene reacts with  $O_2$  by a radical mechanism to form cumene hydroperoxide.
    - b. Treatment of the hydroperoxide with acid gives phenol and acetone.  
The mechanism involves protonation, rearrangement, loss of water, readdition of water to form a hemiacetal, and breakdown to acetone and phenol.
  3. Chlorinated phenols, such as 2,4-D, are formed by chlorinating phenol.
  4. BHT is prepared by Friedel–Crafts alkylation of *p*-cresol with 2-methylpropene.
- B. Reactions of phenols (Section 17.10).
1. Phenols undergo electrophilic aromatic substitution reactions (Chapter 16).  
The  $-OH$  group is a *o,p*-director.
  2. Strong oxidizing agents convert phenols to quinones.
    - a. Reaction with Fremy's salt to form a quinone occurs by a radical mechanism.
    - b. The redox reaction quinone  $\rightarrow$  hydroquinone occurs readily.
    - c. Ubiquinones are an important class of biochemical oxidizing agents that function as a quinone/hydroquinone redox system.
- IV. Spectroscopy of alcohols and phenols (Section 17.11).
- A. IR spectroscopy.
1. Both alcohols and phenols show  $-OH$  stretches in the region  $3300\text{--}3600\text{ cm}^{-1}$ .
    - a. Unassociated alcohols show a peak at  $3600\text{ cm}^{-1}$ .
    - b. Associated alcohols show a broader peak at  $3300\text{--}3400\text{ cm}^{-1}$ .
  2. Alcohols show a  $C-O$  stretch near  $1050\text{ cm}^{-1}$ .
  3. Phenols show aromatic bands at  $1500\text{--}1600\text{ cm}^{-1}$ .
  4. Phenol shows monosubstituted aromatic bands at  $690$  and  $760\text{ cm}^{-1}$ .
- B. NMR spectroscopy.
1. In  $^{13}C$  NMR spectroscopy, carbons bonded to  $-OH$  groups absorb in the range  $50\text{--}80\text{ }\delta$ .
  2.  $^1H$  NMR.
    - a. Hydrogens on carbons bearing  $-OH$  groups absorb in the range  $3.5\text{--}4.5\text{ }\delta$ .  
The hydroxyl hydrogen doesn't split these signals.
    - b.  $D_2O$  exchange can be used to locate the  $O-H$  signal.
    - c. Spin–spin splitting occurs between protons on the oxygen-bearing carbon and neighboring  $-H$ .
    - d. Phenols show aromatic ring absorptions, as well as an  $O-H$  absorption in the range  $3\text{--}8\text{ }\delta$ .

## C. Mass Spectrometry.

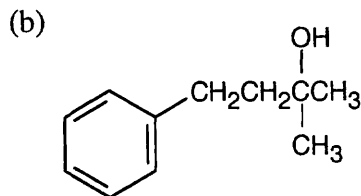
1. Alcohols undergo alpha cleavage to give a neutral radical and an oxygen-containing cation.
2. Alcohols also undergo dehydration to give an alkene radical cation.

## Solutions to Problems

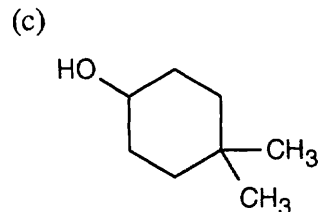
- 17.1** The parent chain must contain the hydroxyl group, and the hydroxyl group(s) should receive the lowest possible number.



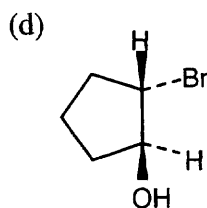
**5-Methyl-2,4-hexanediol**



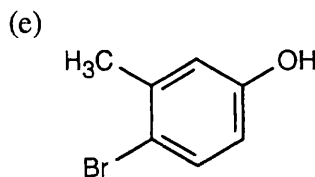
**2-Methyl-4-phenyl-2-butanol**



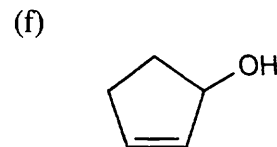
**4,4-Dimethylcyclohexanol**



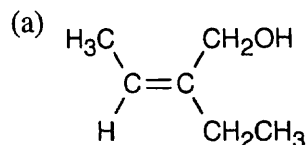
**trans-2-Bromocyclopentanol**



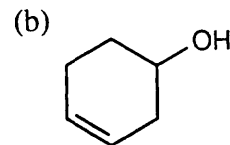
**4-Bromo-3-methylphenol**



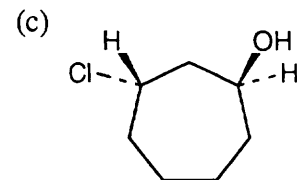
**3-Cyclopenten-1-ol**

**17.2**

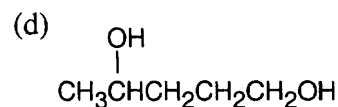
**(Z)-2-Ethyl-2-buten-1-ol**



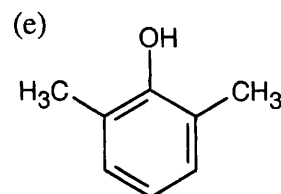
**3-Cyclohexen-1-ol**



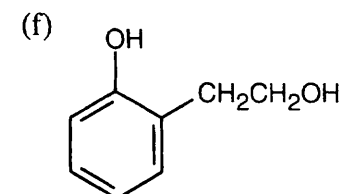
**trans-3-Chlorocycloheptanol**



**1,4-Pentanediol**



**2,6-Dimethylphenol**

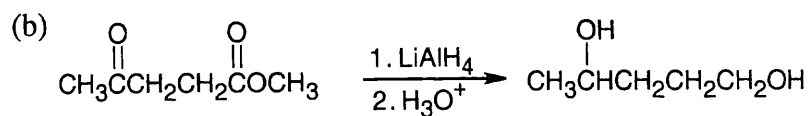


**o-(2-Hydroxyethyl)phenol**

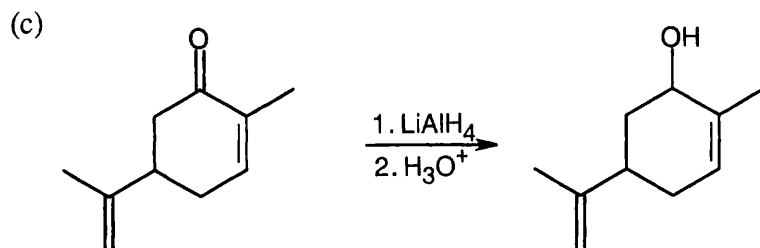
- 17.3** In general, the boiling points of a series of isomers decrease with branching. The more nearly spherical a compound becomes, the less surface area it has relative to a straight chain compound of the same molecular weight and functional group type. A smaller surface area allows fewer van der Waals interactions, the weak forces that cause covalent molecules to be attracted to each other.

In addition, branching in alcohols makes it more difficult for hydroxyl groups to approach each other to form hydrogen bonds. A given volume of 2-methyl-2-propanol therefore contains fewer hydrogen bonds than the same volume of 1-butanol, and less energy is needed to break them in boiling.



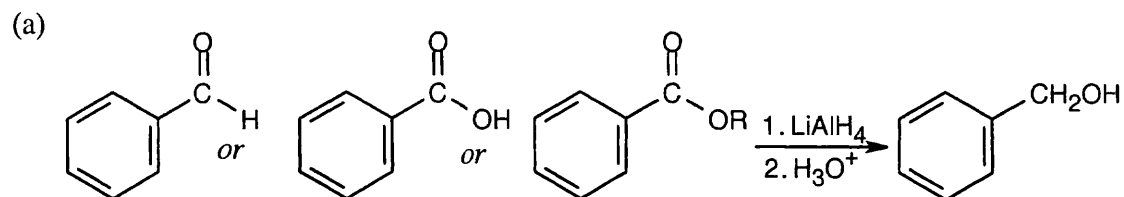


$\text{LiAlH}_4$  reduces both ketones and esters.

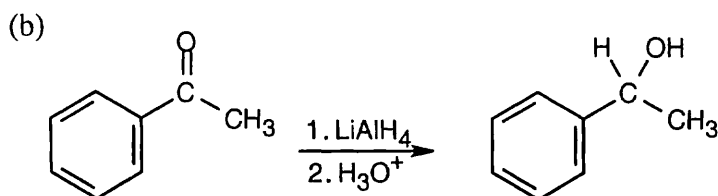


$\text{LiAlH}_4$  reduces carbonyl functional groups without reducing double bonds.

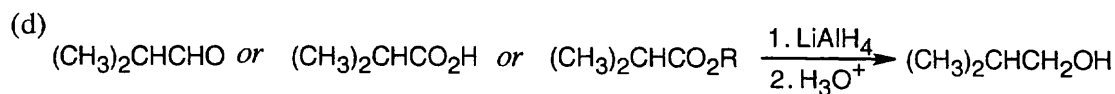
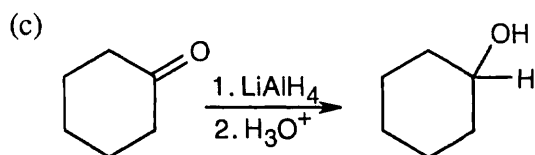
### 17.8



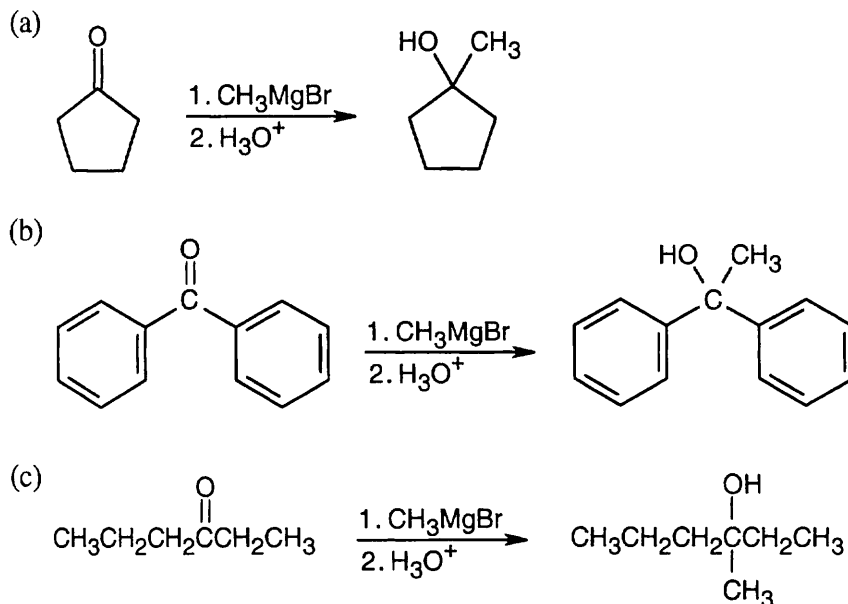
Benzyl alcohol may be the reduction product of an aldehyde, a carboxylic acid, or an ester.



Reduction of a ketone yields this secondary alcohol.



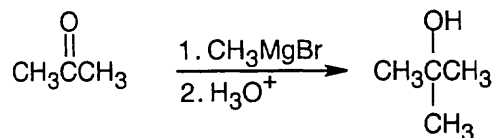
**17.9** All of the products have an  $\text{-OH}$  and a methyl group bonded to what was formerly a ketone carbon.



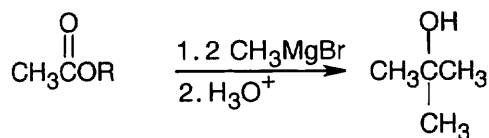
**17.10 Strategy:** First, identify the type of alcohol. If the alcohol is primary, it can only be synthesized from formaldehyde plus the appropriate Grignard reagent. If the alcohol is secondary, it is synthesized from an aldehyde and a Grignard reagent. (Usually, there are two combinations of aldehyde and Grignard reagent). A tertiary alcohol is synthesized from a ketone and a Grignard reagent. If all three groups on the tertiary alcohol are different, there are often three different combinations of ketone and Grignard reagent. If two of the groups on the alcohol carbon are the same, the alcohol may also be synthesized from an ester and two equivalents of Grignard reagent.

**Solution:**

(a) 2-Methyl-2-propanol is a tertiary alcohol. To synthesize a tertiary alcohol, start with a ketone.

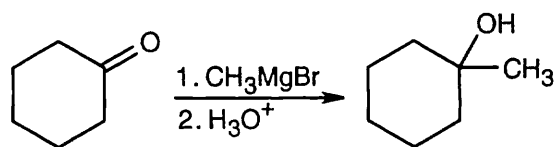


If two or more alkyl groups bonded to the carbon bearing the  $\text{-OH}$  group are the same, an alcohol can be synthesized from an ester and a Grignard reagent.



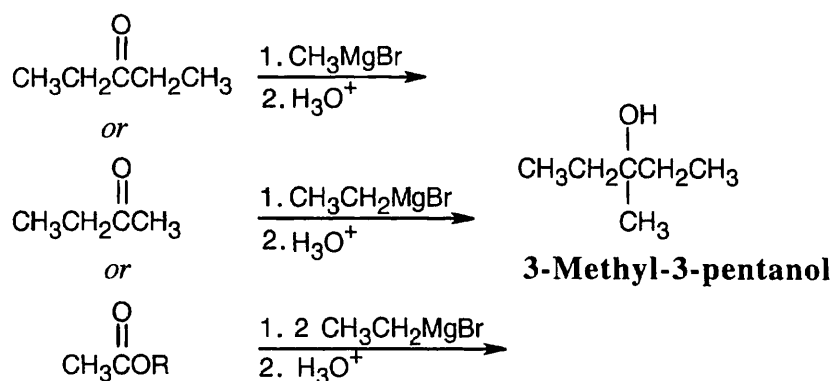
**2-Methyl-2-propanol**

(b) Since 1-methylcyclohexanol is a tertiary alcohol, start with a ketone.



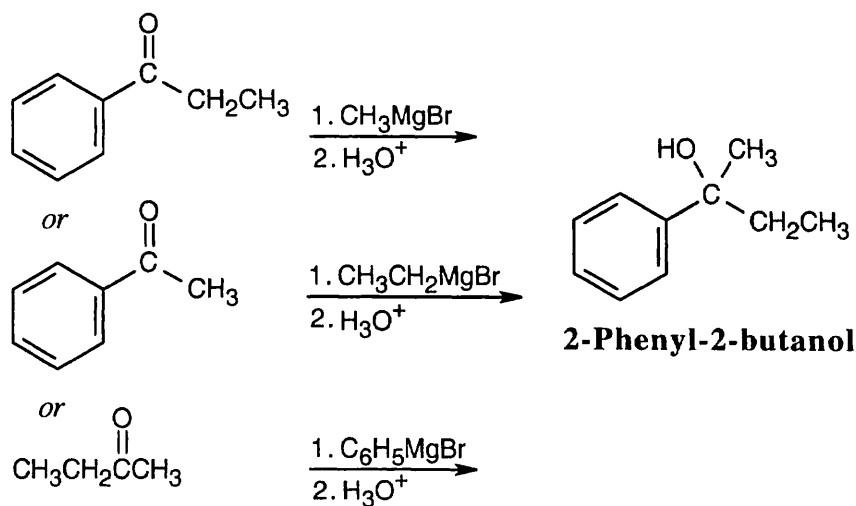
**1-Methylcyclohexanol**

(c) 3-Methyl-3-pentanol is a tertiary alcohol. When two of the three groups bonded to the alcohol carbon are the same, either a ketone or an ester can be used as a starting material.



**3-Methyl-3-pentanol**

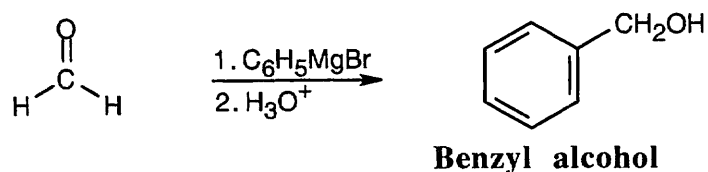
(d) Three possible combinations of ketone plus Grignard reagent can be used to synthesize this tertiary alcohol.



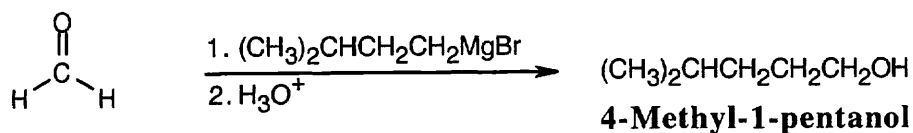
**2-Phenyl-2-butanol**



(e) Formaldehyde must be used to synthesize this primary alcohol.

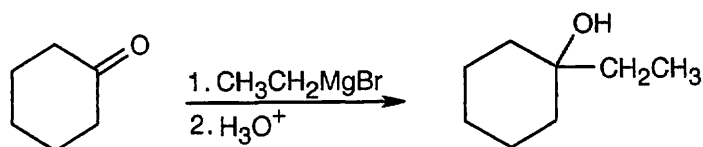


(f) As in (e), use formaldehyde to synthesize a primary alcohol.



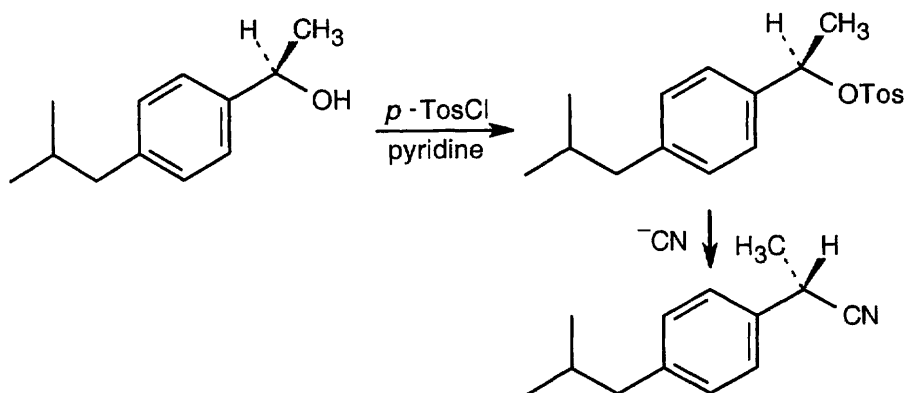
**17.11 Strategy:** First, interpret the structure of the alcohol. This alcohol, 1-ethylcyclohexanol, is a tertiary alcohol that can be synthesized from a ketone. Only one combination of ketone and Grignard reagent is possible.

**Solution:**

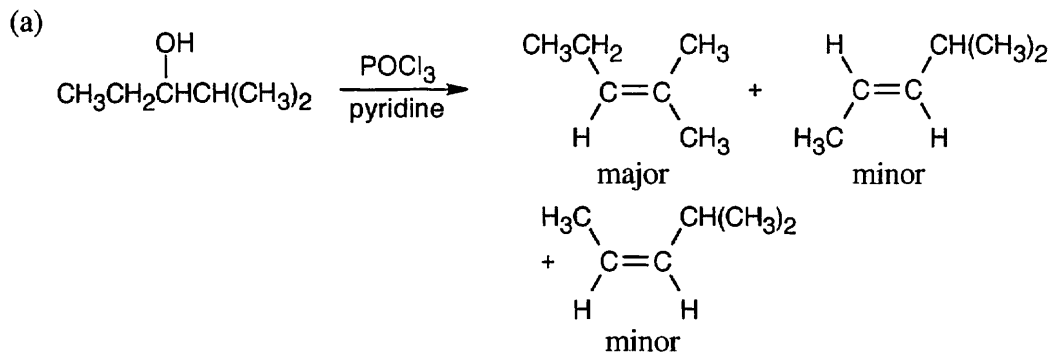


**17.12 Strategy:** Recall from Chapter 11 that  $-\text{OH}$  is a very poor leaving group in reactions run under  $\text{S}_{\text{N}}2$  conditions. A toluenesulfonate, however, is a very good leaving group, and reaction of the toluenesulfonate of the alcohol with  $^-\text{CN}$  proceeds readily under  $\text{S}_{\text{N}}2$  conditions to give a product with inversion of configuration at the chirality center.

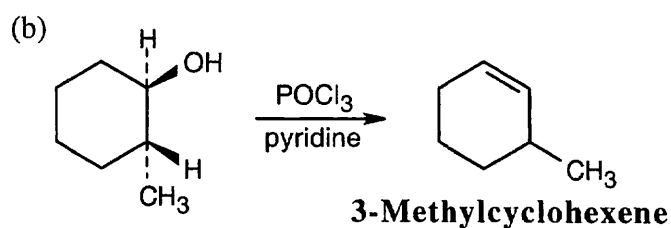
**Solution:**



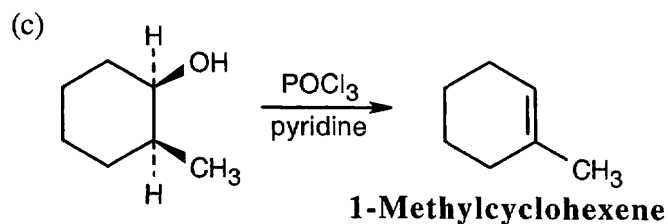
## 17.13



The major product has the more substituted double bond.

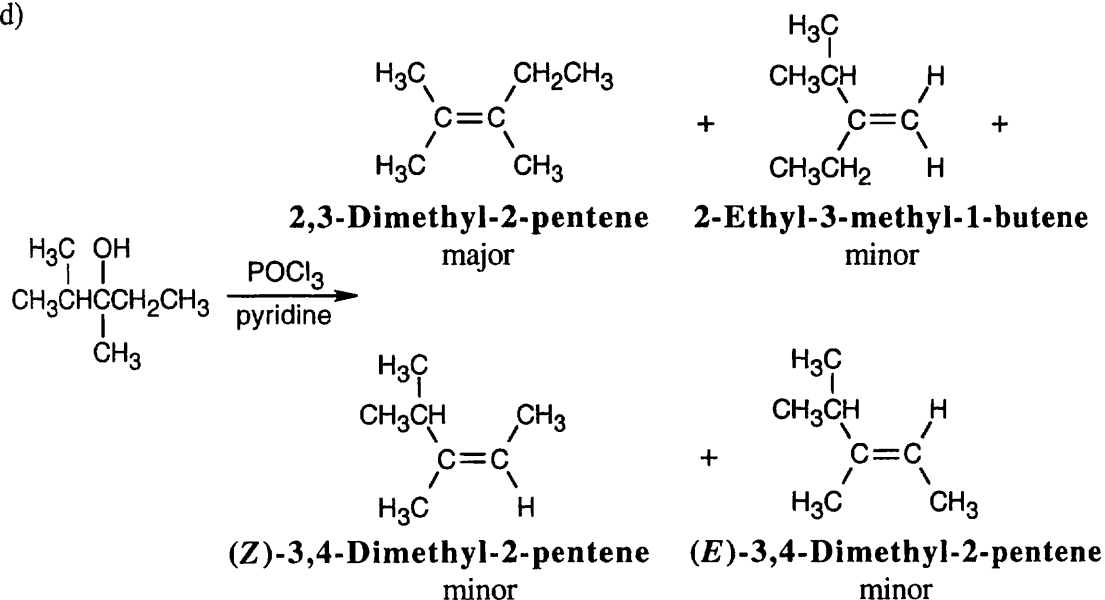


In E2 elimination, dehydration proceeds most readily when the two groups to be eliminated have an anti periplanar relationship. In this compound, the only hydrogen with the proper stereochemical relationship to the  $-\text{OH}$  group is at C6. Thus, the non-Zaitsev product 3-methylcyclohexene is formed.



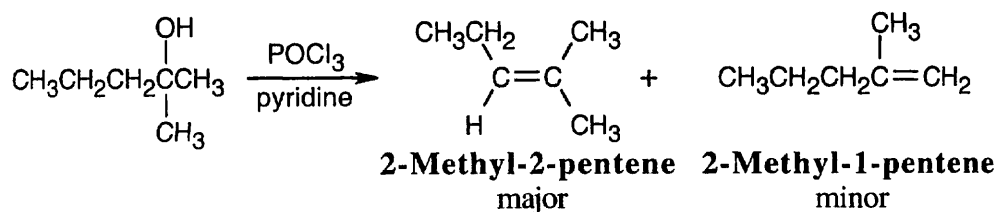
Here, the hydrogen at C2 is trans to the hydroxyl, and dehydration yields the Zaitsev product, 1-methylcyclohexene.

(d)



Four different products (including *E,Z* isomers) can result from dehydration of 2,3-dimethyl-2-pentanol. The major product has the most substituted double bond, according to Zaitsev's rule.

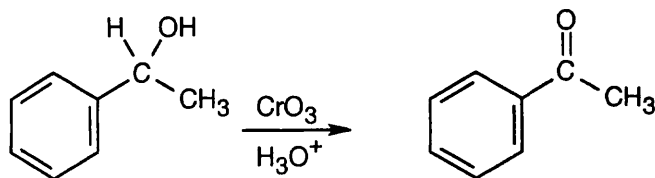
(e)



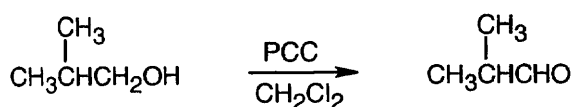
**17.14 Strategy:** Aldehydes are synthesized from oxidation of primary alcohols, and ketones are synthesized from oxidation of secondary alcohols.

**Solution:**

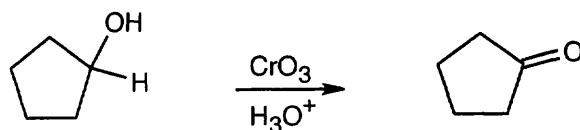
(a)



(b)



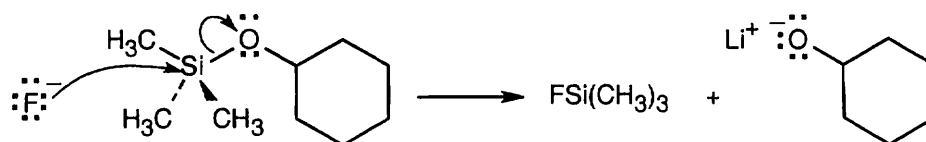
(c)



## 17.15

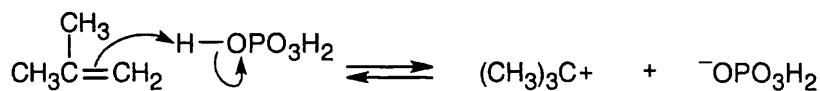
Starting material	$\text{CrO}_3, \text{H}_3\text{O}^+$ Product	PCC Product
(a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
(b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{CH}_3$
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	no reaction

## 17.16

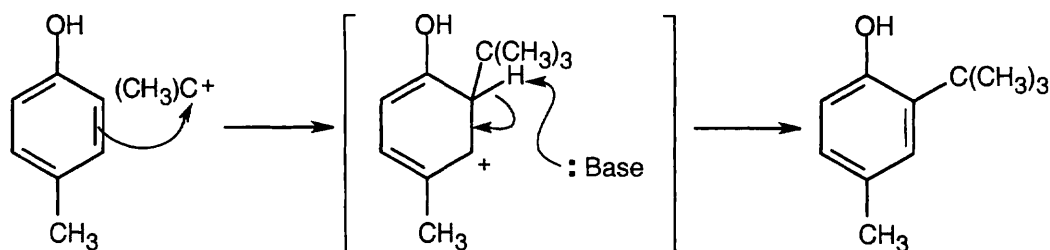


This is an  $\text{S}_{\text{N}}2$  reaction in which the nucleophile  $\text{F}^-$  attacks silicon and displaces an alkoxide ion as leaving group.

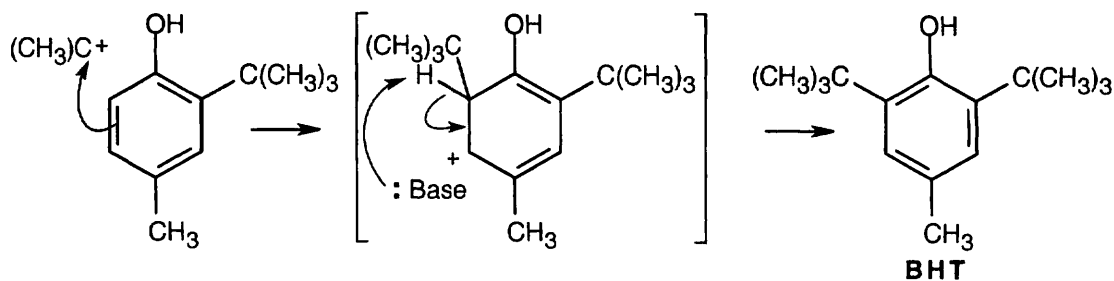
## 17.17



Phosphoric acid protonates 2-methylpropene, forming a *tert*-butyl carbocation.



The *tert*-butyl carbocation acts as an electrophile and alkylates *p*-cresol. Alkylation occurs ortho to the  $-\text{OH}$  group for both steric and electronic reasons.



A second *tert*-butyl carbocation alkylation forms BHT.

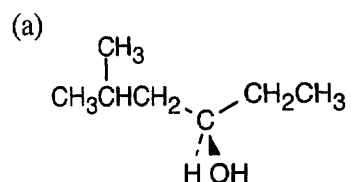
**17.18** The infrared spectra of cholesterol and 5-cholestene-3-one each exhibit a unique absorption that makes it easy to distinguish between them. Cholesterol shows an  $\text{-OH}$  stretch at  $3300\text{--}3600\text{ cm}^{-1}$ , and 5-cholestene-3-one shows a  $\text{C=O}$  stretch at  $1715\text{ cm}^{-1}$ . In the oxidation of cholesterol to 5-cholestene-3-one, the  $\text{-OH}$  band will disappear and will be replaced by a  $\text{C=O}$  band. When oxidation is complete, no  $\text{-OH}$  absorption should be visible.

**17.19** Under conditions of slow exchange, the  $\text{-OH}$  signal of a tertiary alcohol ( $\text{R}_3\text{COH}$ ) is unsplit, the signal of a secondary alcohol ( $\text{R}_2\text{CHOH}$ ) is split into a doublet, and the signal of a primary alcohol ( $\text{RCH}_2\text{OH}$ ) is split into a triplet.

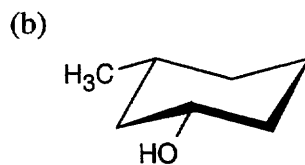
- (a) 2-Methyl-2-propanol is a tertiary alcohol; its  $\text{-OH}$  signal is unsplit.  
 (b) Cyclohexanol is a secondary alcohol; its  $\text{-OH}$  absorption is a doublet.  
 (c) Ethanol is a primary alcohol; its  $\text{-OH}$  signal appears as a triplet.  
 (d) 2-Propanol is a secondary alcohol; its  $\text{-OH}$  absorption is split into a doublet.  
 (e) Cholesterol is a secondary alcohol; its  $\text{-OH}$  absorption is split into a doublet.  
 (f) 1-Methylcyclohexanol is a tertiary alcohol; its  $\text{-OH}$  signal is unsplit.

## Visualizing Chemistry

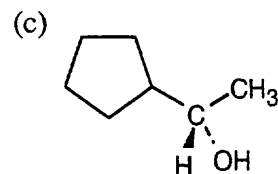
### 17.20



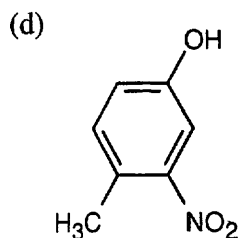
**(R)-5-Methyl-3-hexanol**



**cis-3-Methylcyclohexanol**

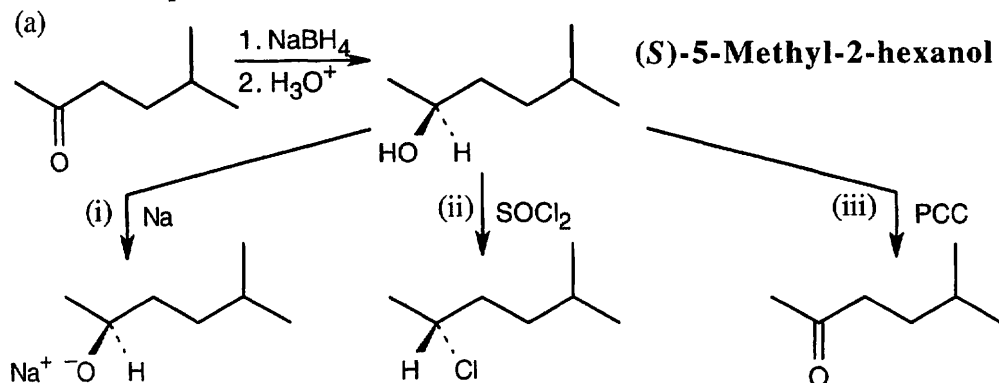


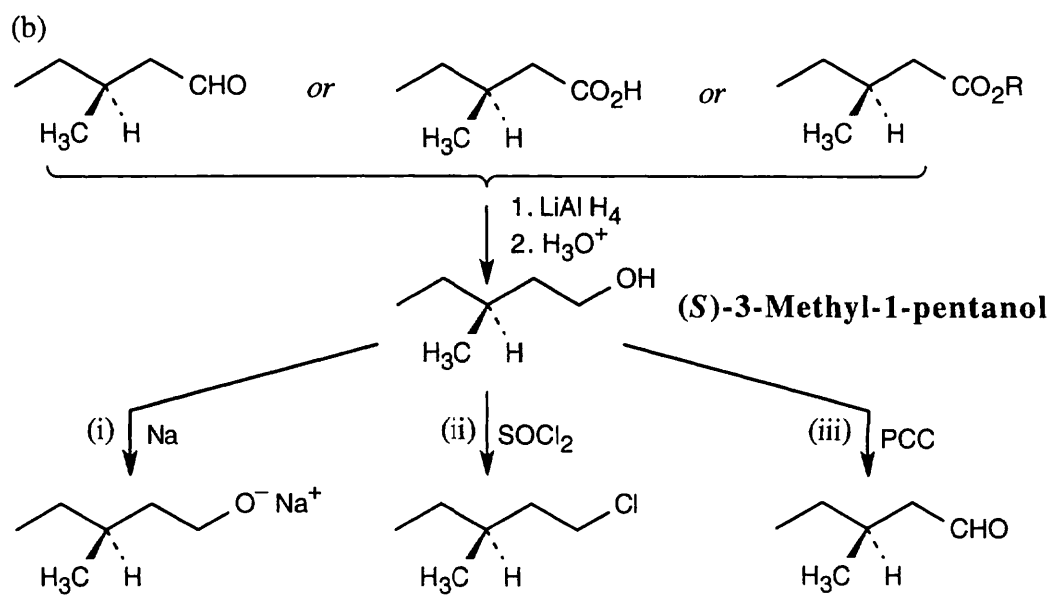
**(S)-1-Cyclopentylethanol**



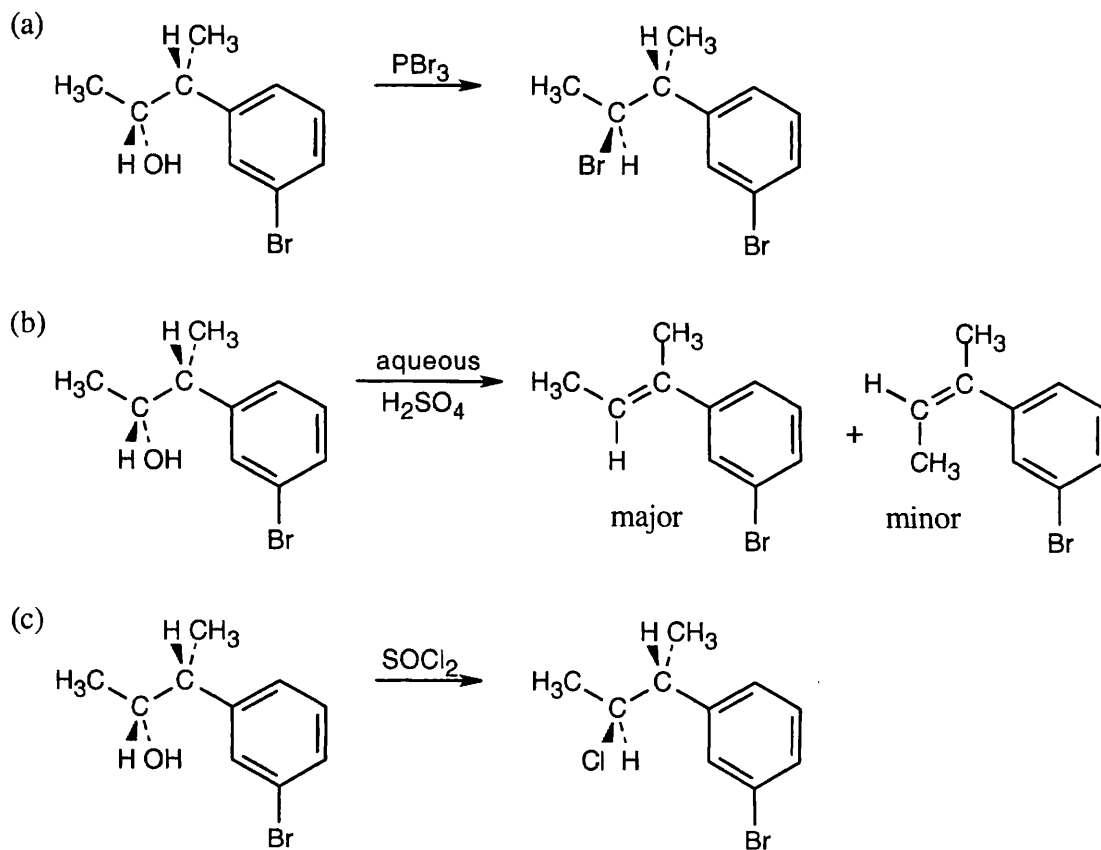
**4-Methyl-3-nitrophenol**

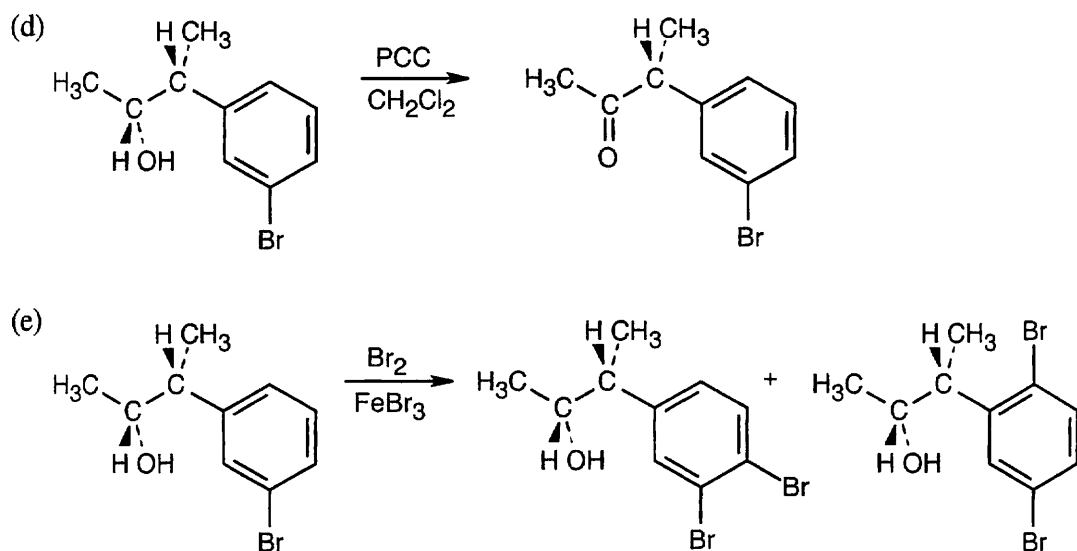
**17.21** The reduction product is a racemic mixture.



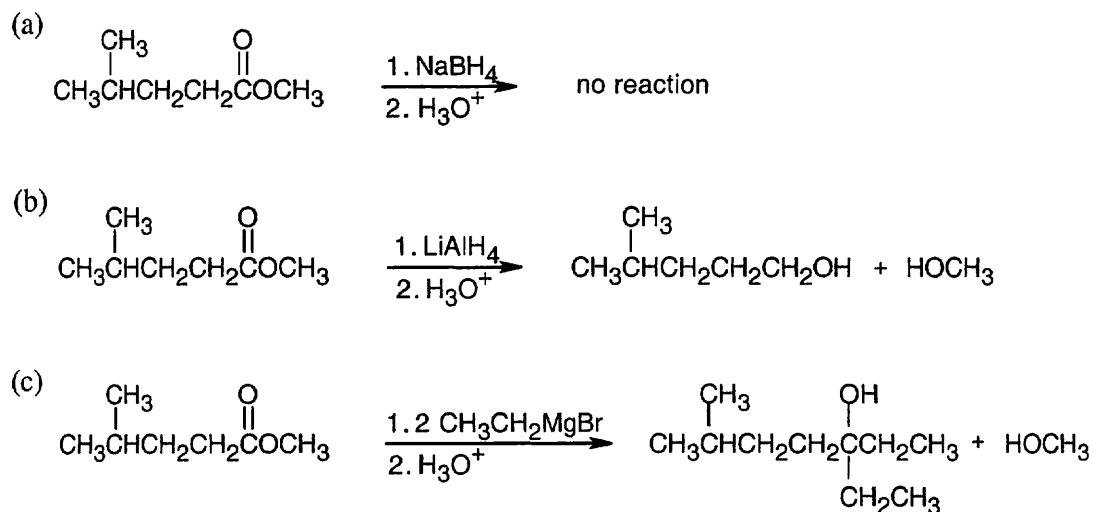


## 17.22

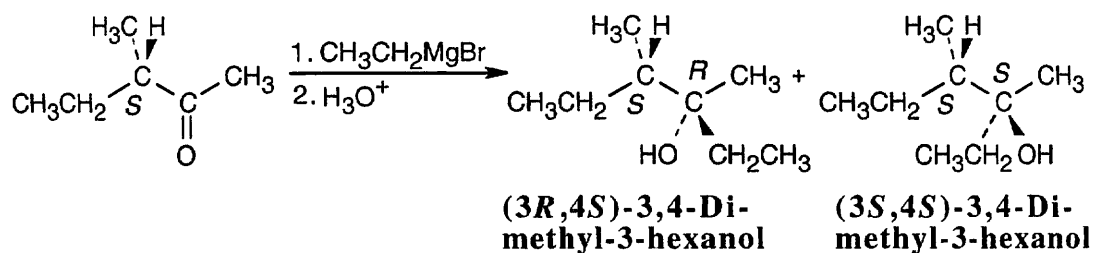




## 17.23



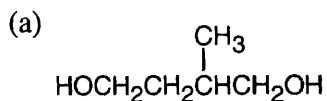
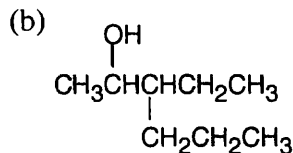
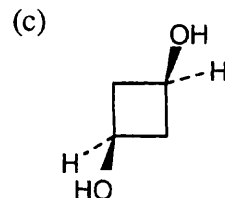
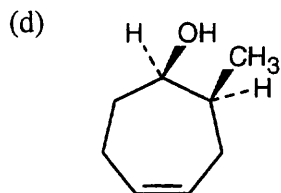
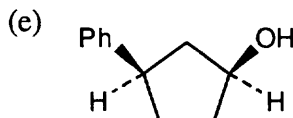
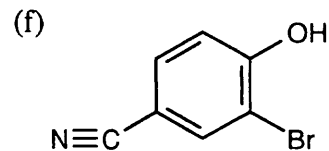
## 17.24



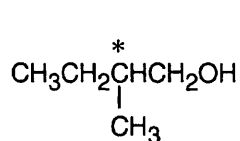
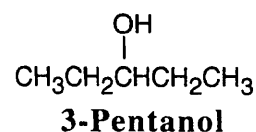
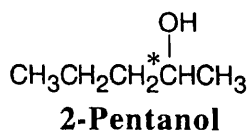
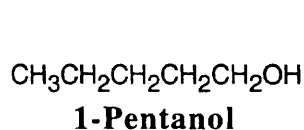
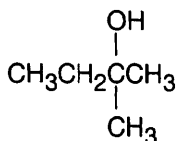
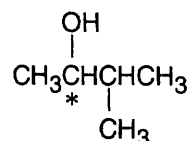
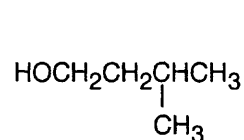
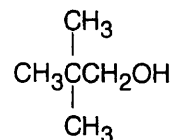
The product is a mixture of the (3*R*,4*S*) and (3*S*,4*S*) diastereomers. The diastereomers are formed in unequal amounts, and the product mixture is optically active. We can't predict which diastereomer will predominate.

## Additional Problems

17.25

**2-Methyl-1,4-butanediol****3-Ethyl-2-hexanol****cis-1,3-Cyclobutanediol****cis-2-Methyl-4-cyclohepten-1-ol****cis-3-Phenylcyclopentanol****2-Bromo-4-cyanophenol  
or  
3-Bromo-4-hydroxybenzonitrile**

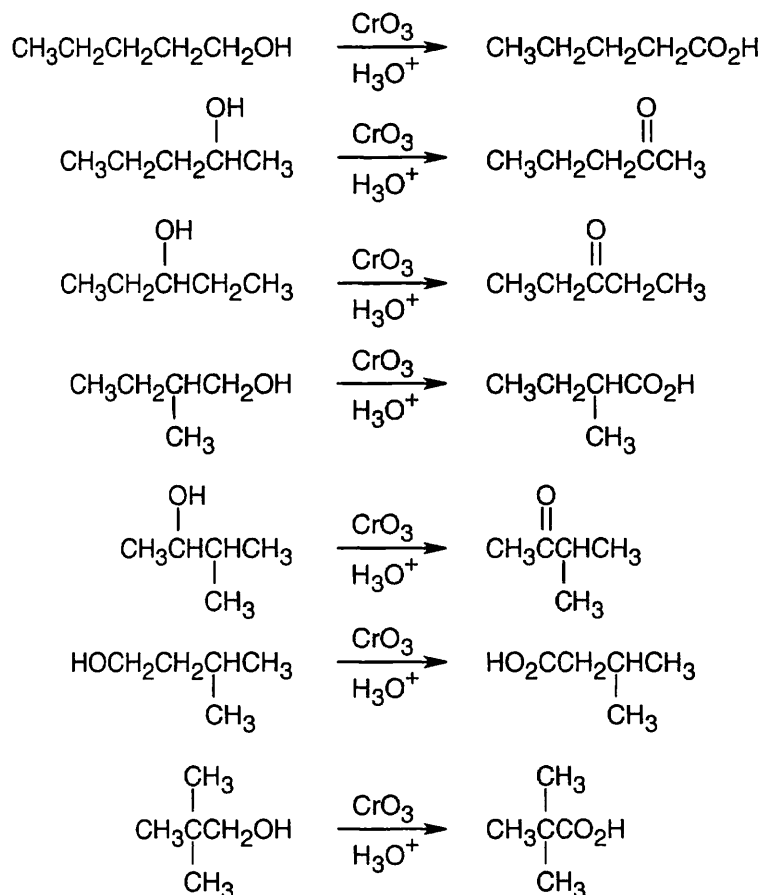
17.26 None of these alcohols has multiple bonds or rings.

**2-Methyl-1-butanol****2-Methyl-2-butanol****3-Methyl-2-butanol****3-Methyl-1-butanol****2,2-Dimethyl-1-propanol**

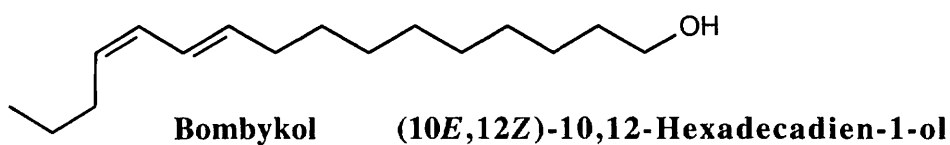
2-Pentanol, 2-methyl-1-butanol and 3-methyl-2-butanol have chiral carbons.



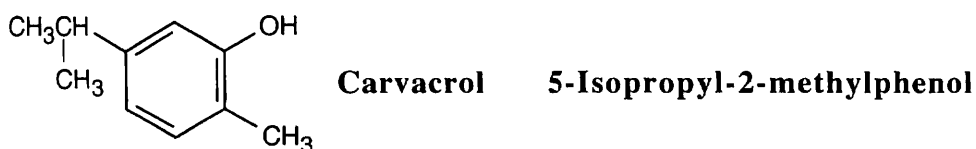
**17.27** Primary alcohols react with  $\text{CrO}_3$  in aqueous acid to form carboxylic acids, secondary alcohols yield ketones, and tertiary alcohols are unreactive to oxidation. Of the eight alcohols in the previous problem, only 2-methyl-2-butanol is unreactive to  $\text{CrO}_3$  oxidation.



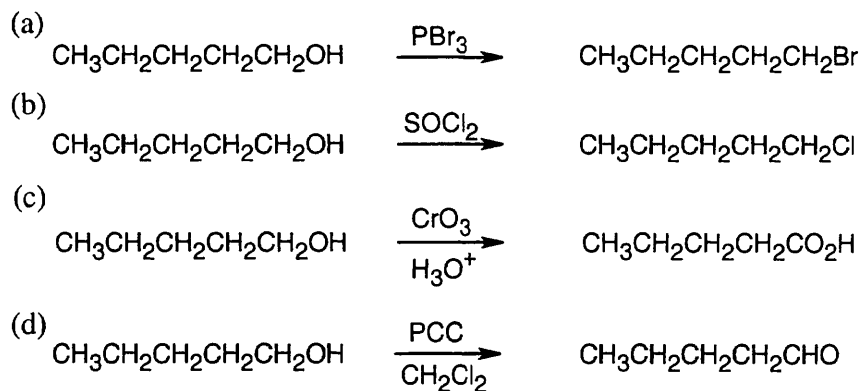
**17.28**



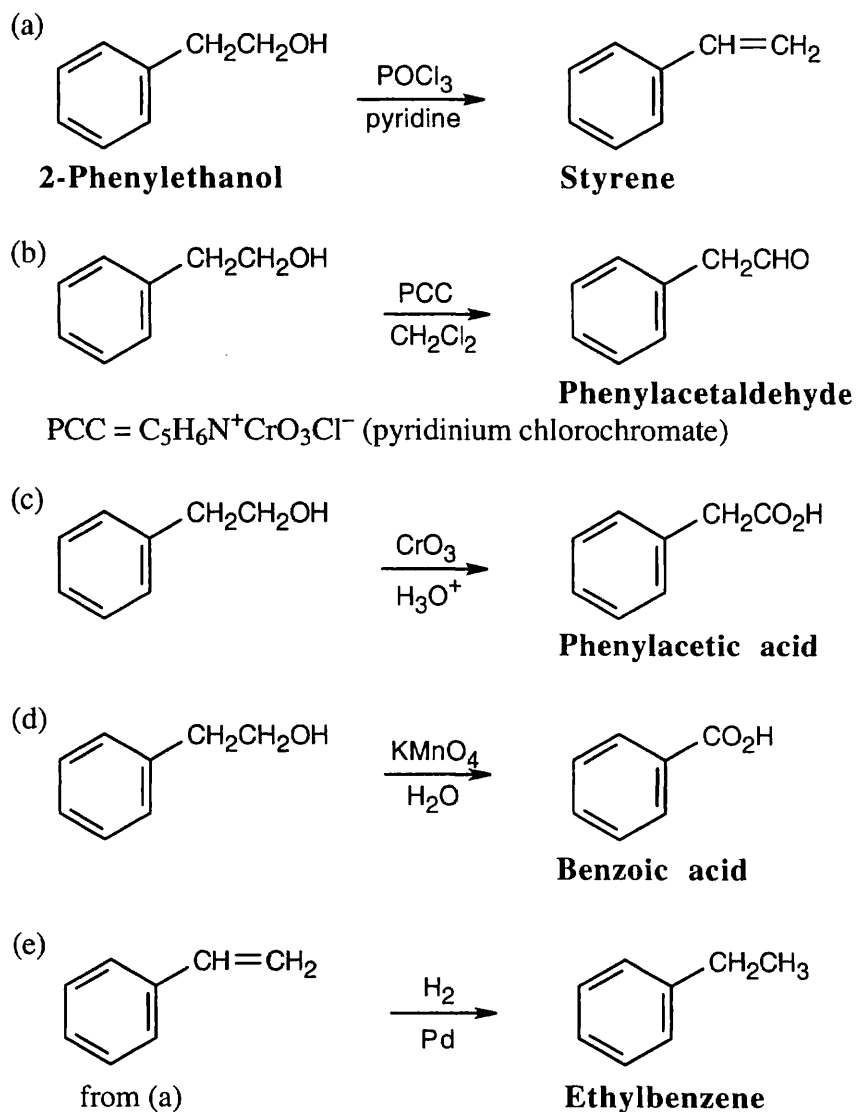
**17.29**

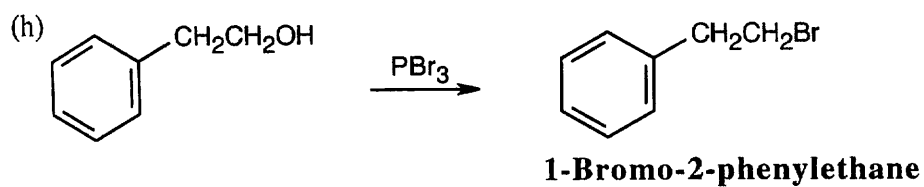
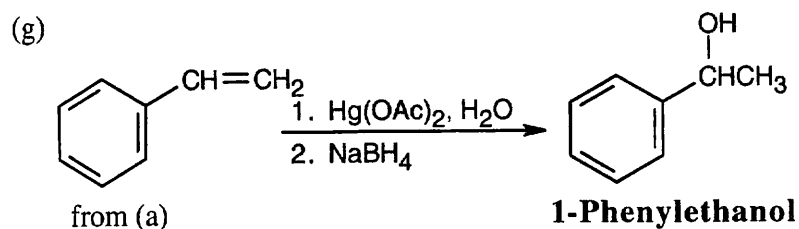
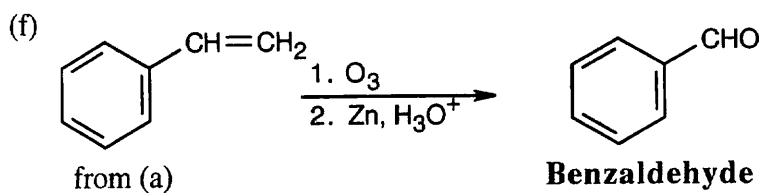


## 17.30

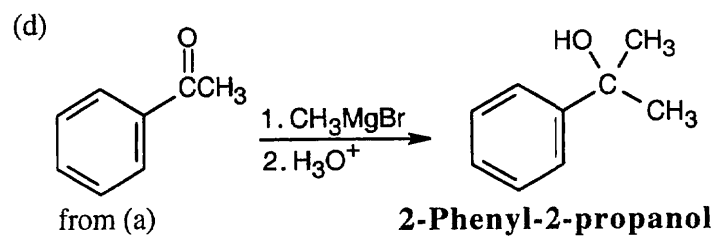
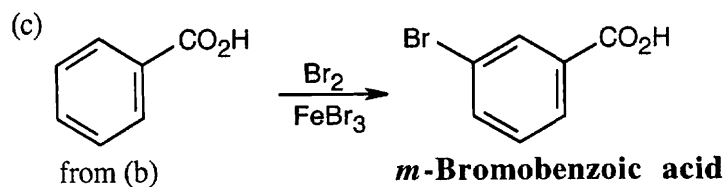
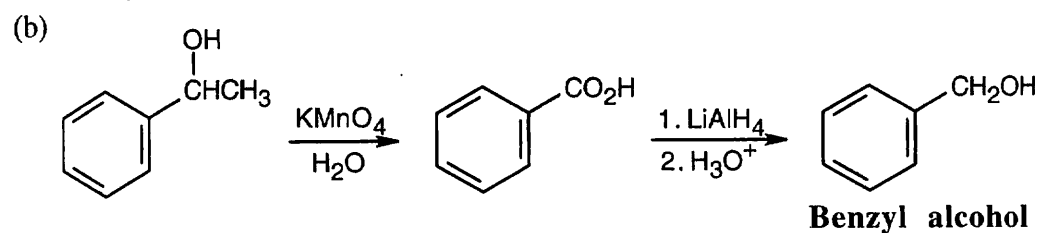
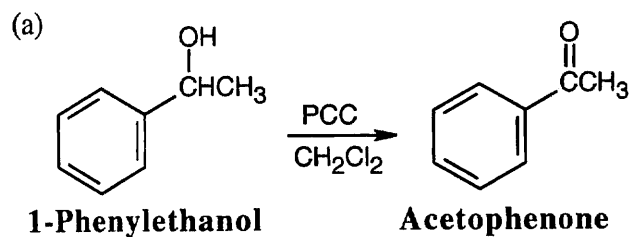


## 17.31

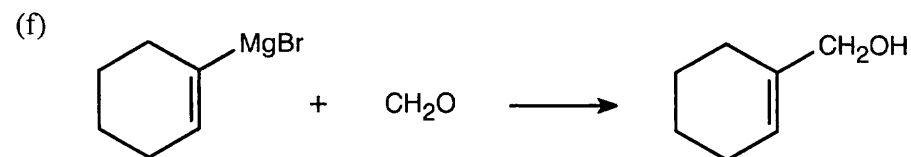
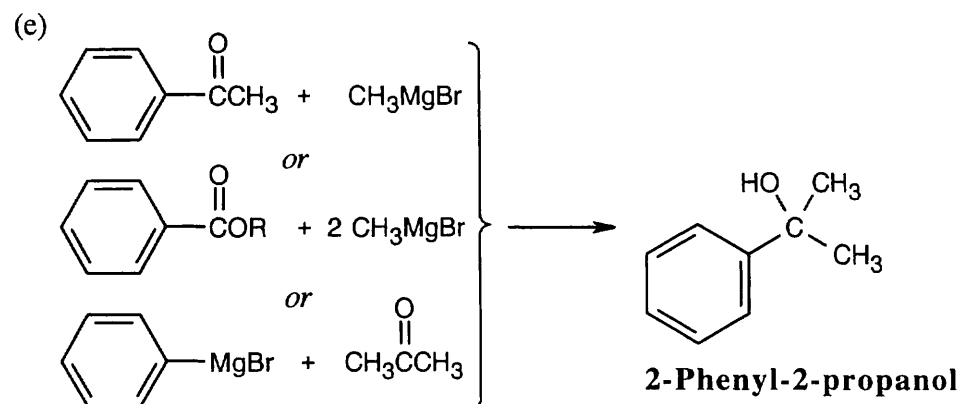
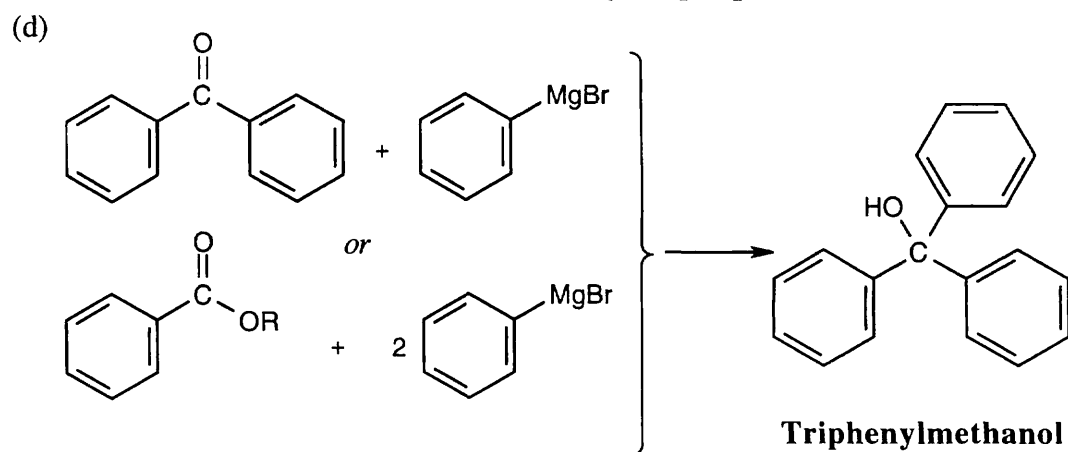
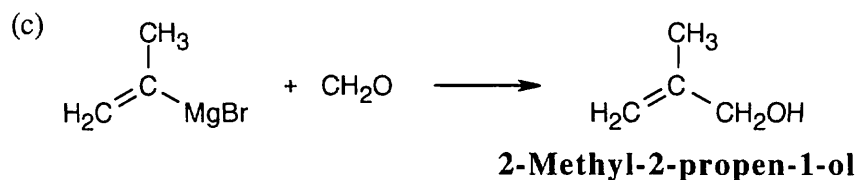
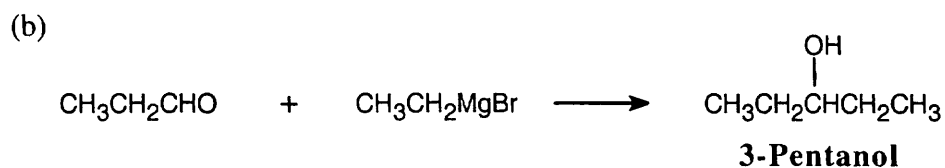
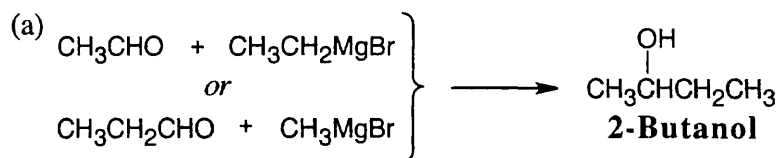




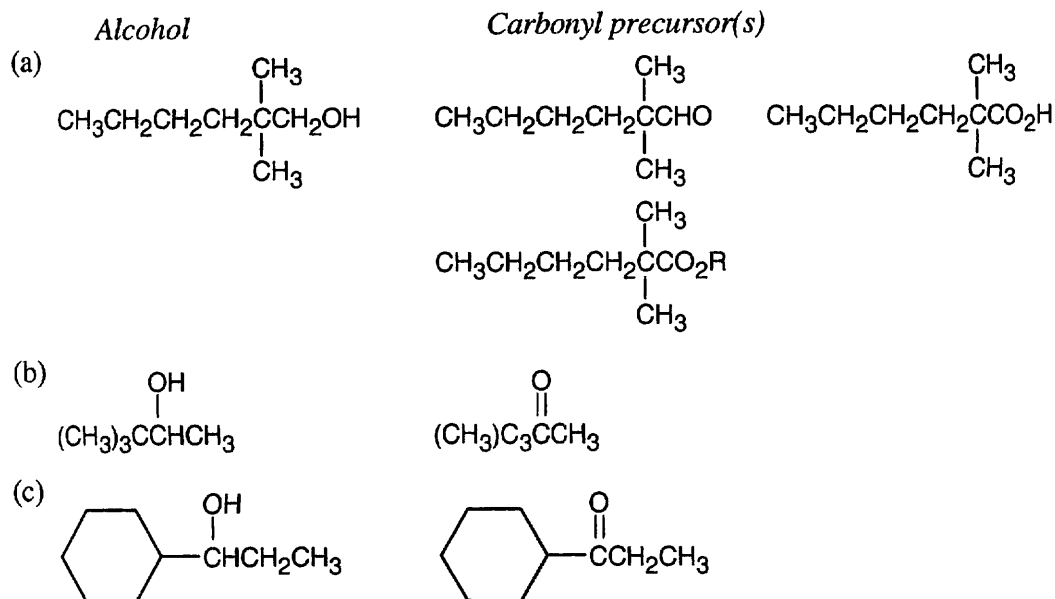
## 17.32



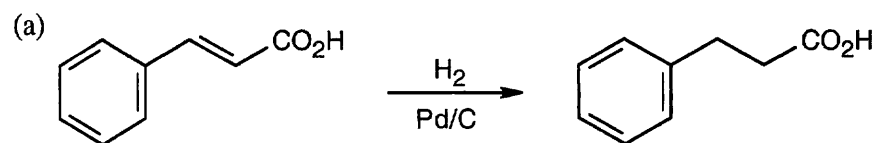
**17.33** In some of these problems, different combinations of Grignard reagent and carbonyl compound are possible. Remember that aqueous acid is added to the initial Grignard adduct to yield the alcohol.



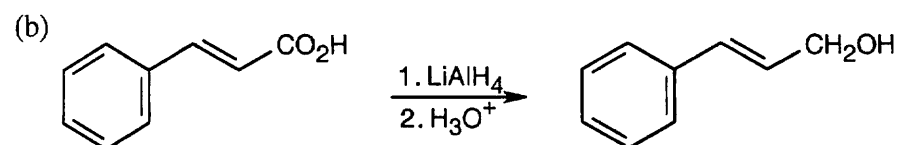
## 17.34



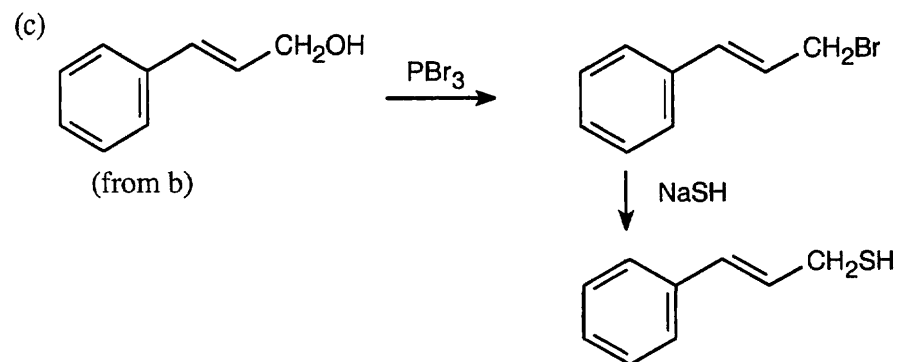
**17.35** In these compounds you want to reduce some, but not all, of the functional groups present. To do this, you must choose the correct reducing agent.



$\text{H}_2$  with a palladium catalyst hydrogenates carbon-carbon double bonds without affecting carbonyl double bonds.



$\text{LiAlH}_4$  reduces carbonyl groups without affecting carbon-carbon double bonds.

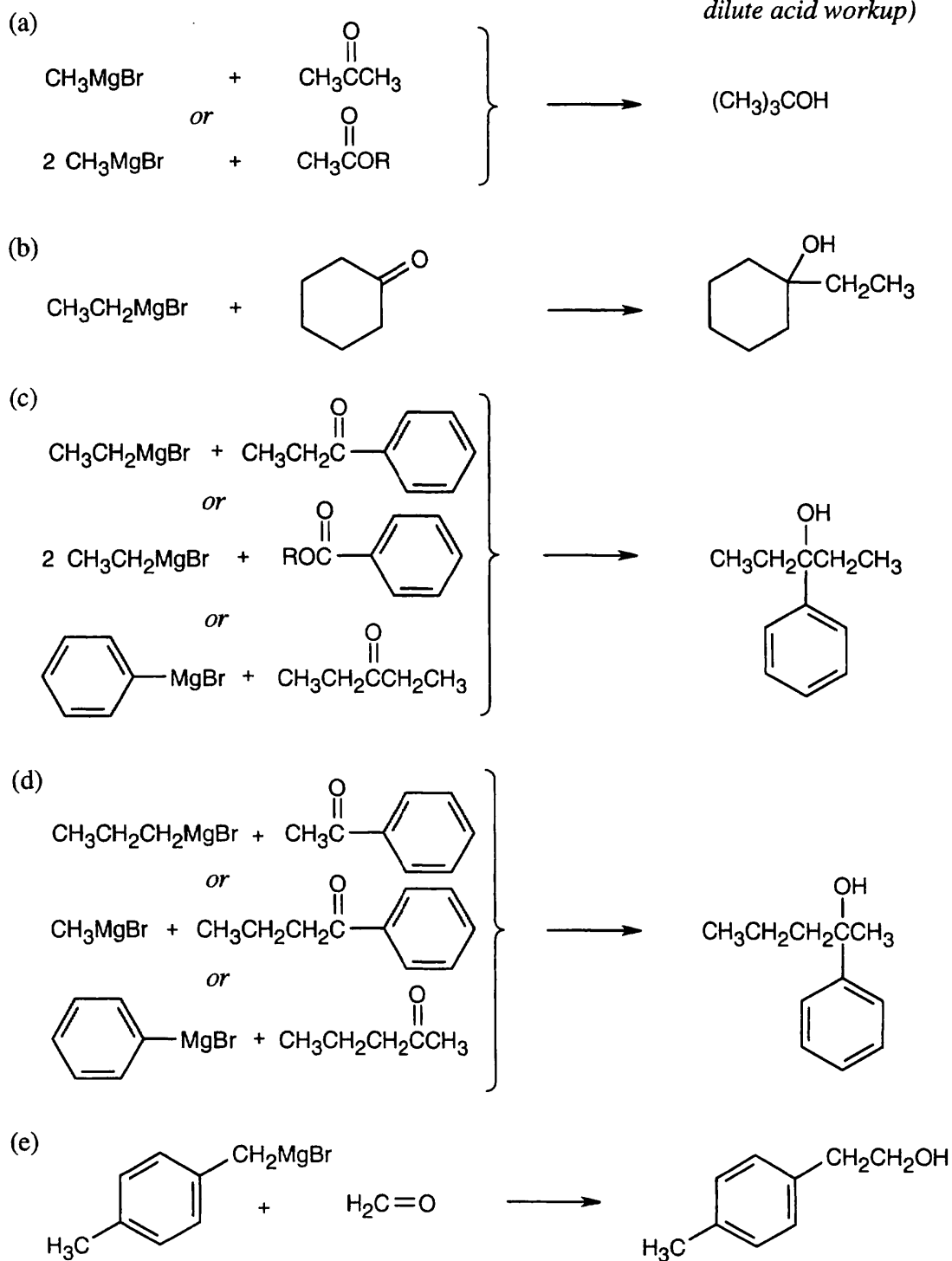


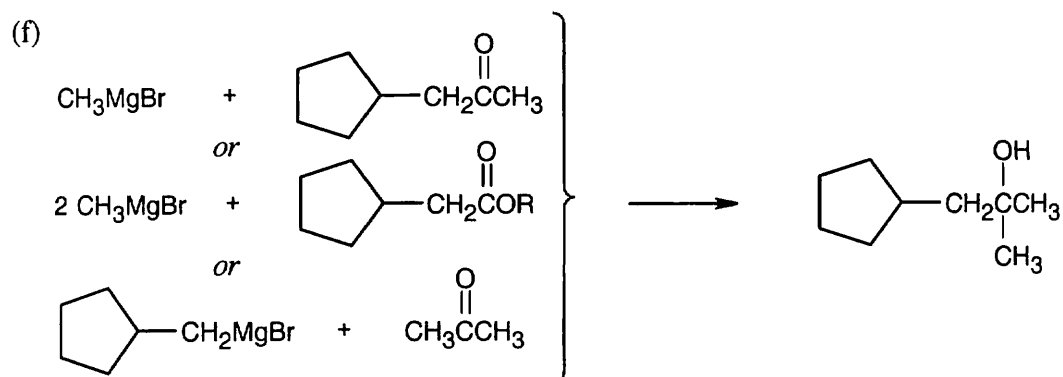
## 17.36

Grignard Reagent + Carbonyl Compound

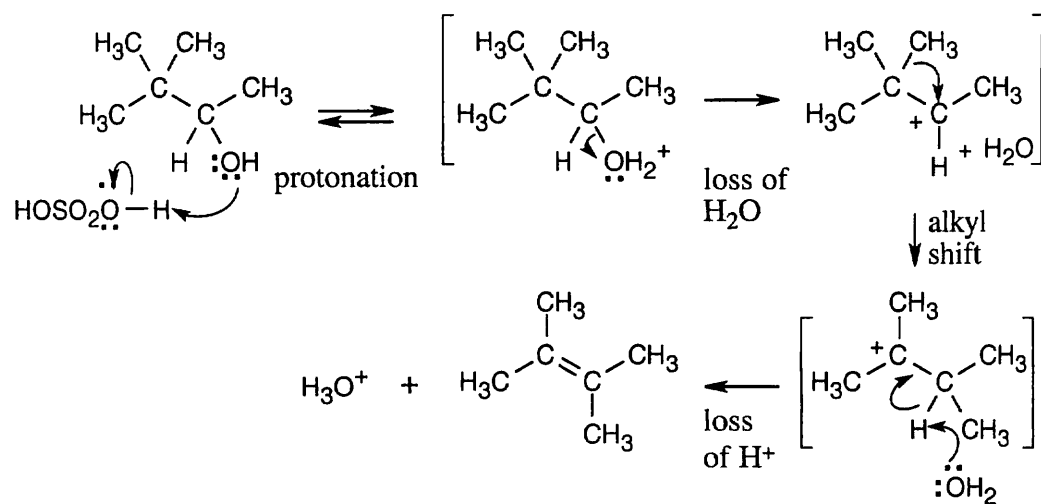


Product (after dilute acid workup)

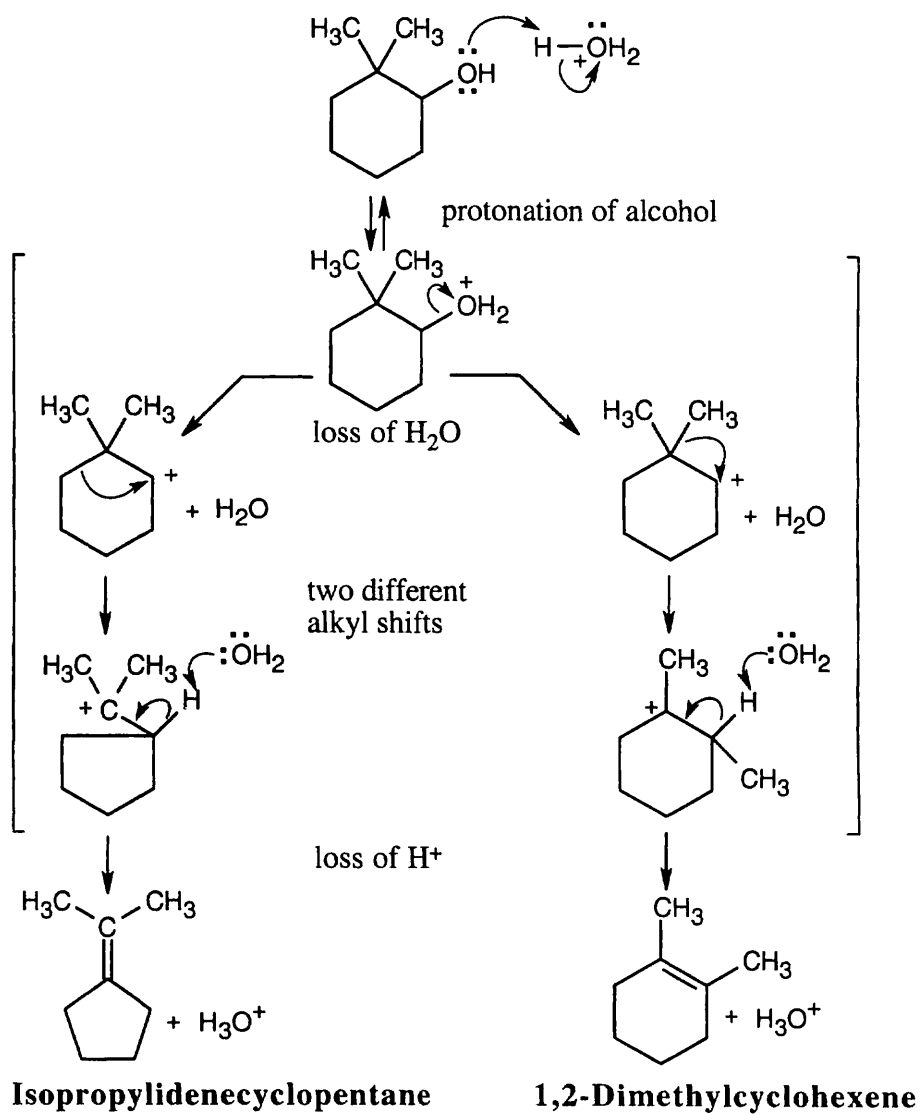




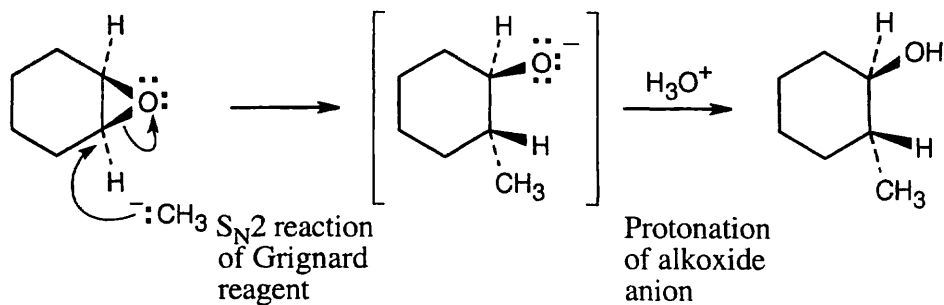
## 17.37



**17.38** This mechanism consists of the same steps as are seen in Problem 17.37. Two different alkyl shifts result in two different cycloalkenes.



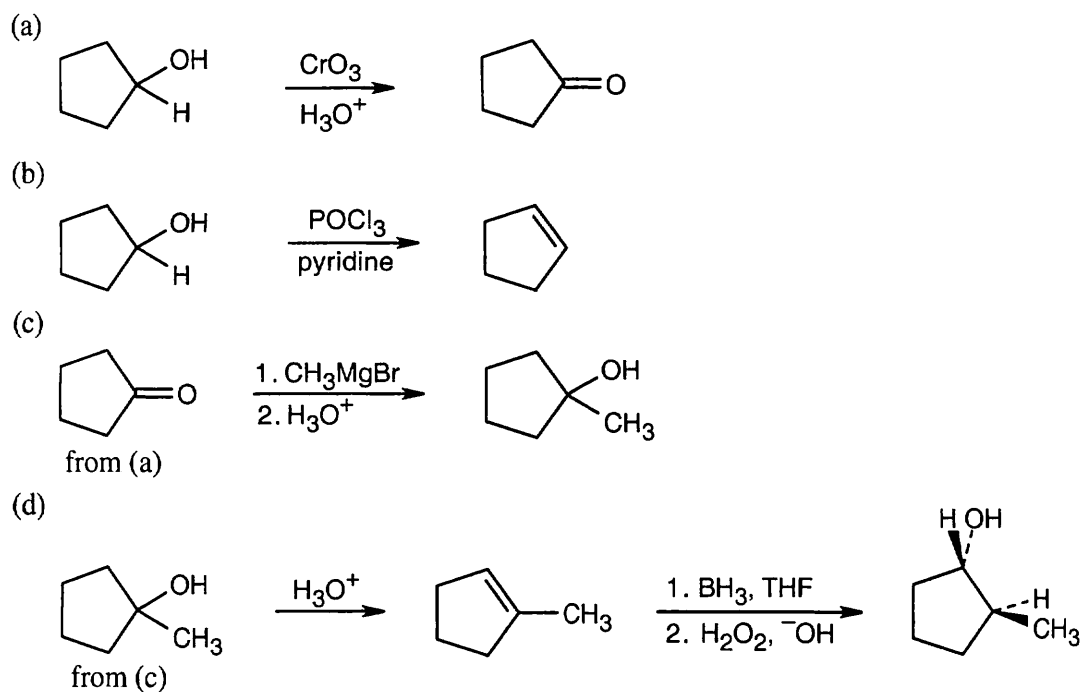
**17.39**



The methyl group and the hydroxyl group have a trans relationship.

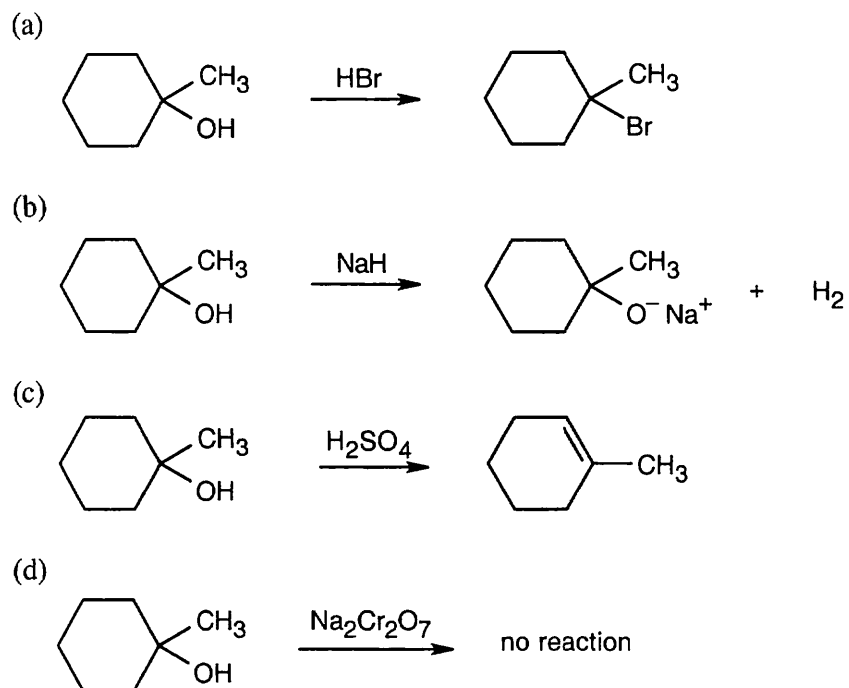


## 17.40



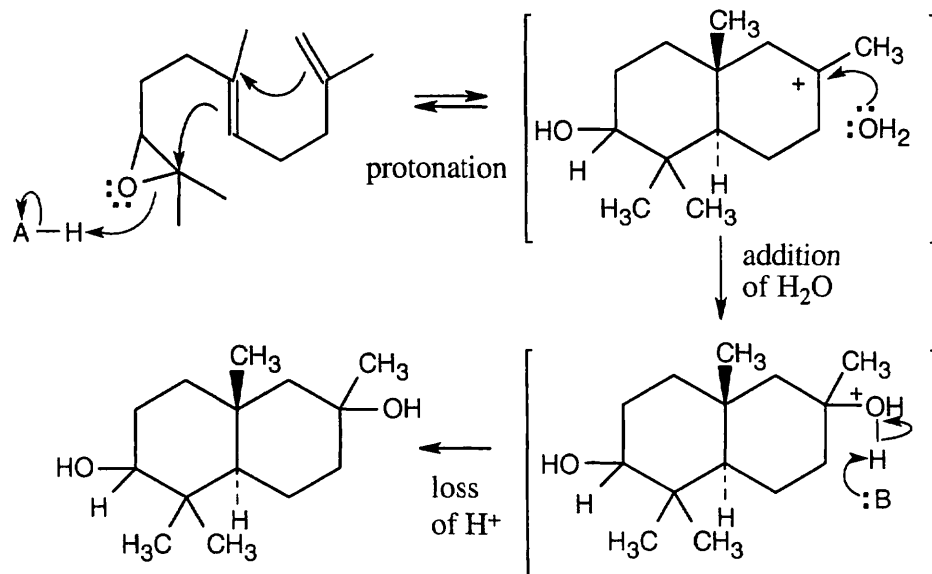
Remember that hydroboration proceeds with syn stereochemistry, and the  $\text{-H}$  and  $\text{-OH}$  added have a cis relationship.

## 17.41

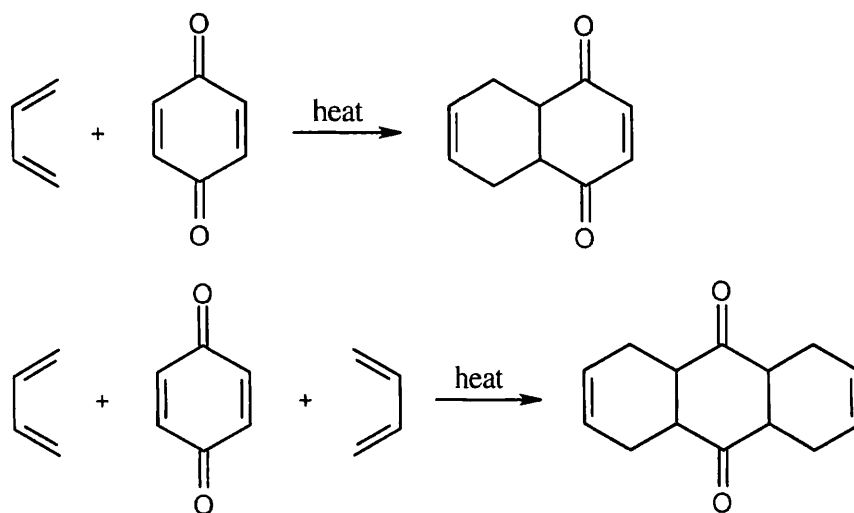


Tertiary alcohols aren't oxidized by sodium dichromate.

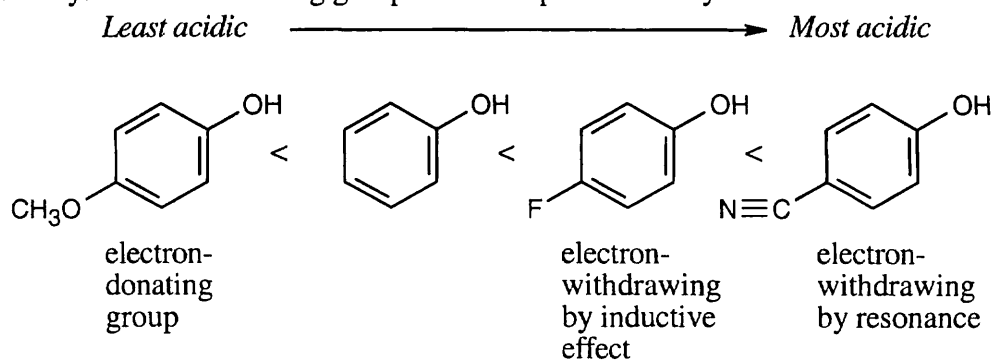
17.42



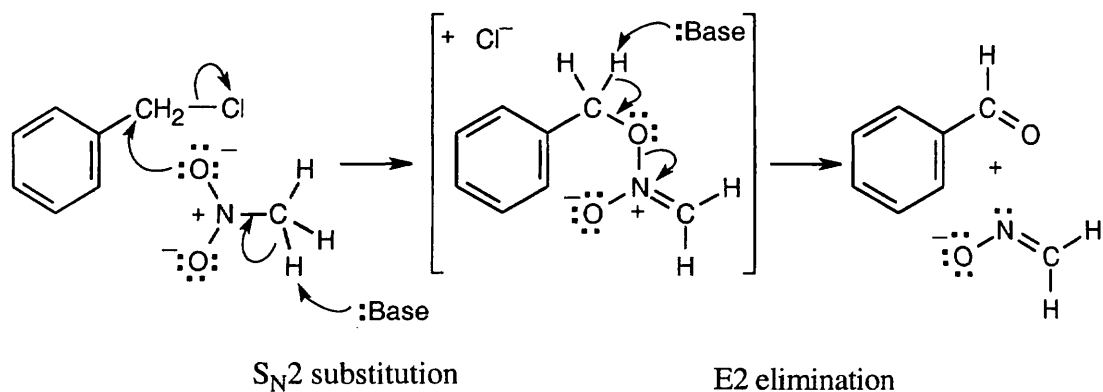
17.43



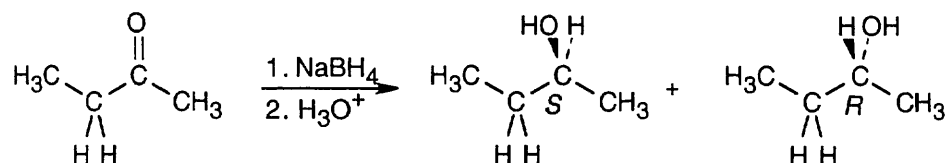
**17.44** Remember that electron-withdrawing groups stabilize phenoxide anions and increase acidity. Electron-donating groups decrease phenol acidity.



## 17.45

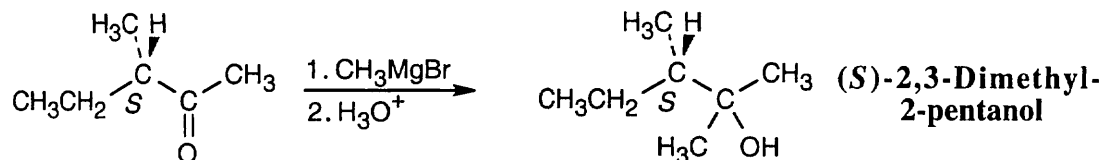


## 17.46



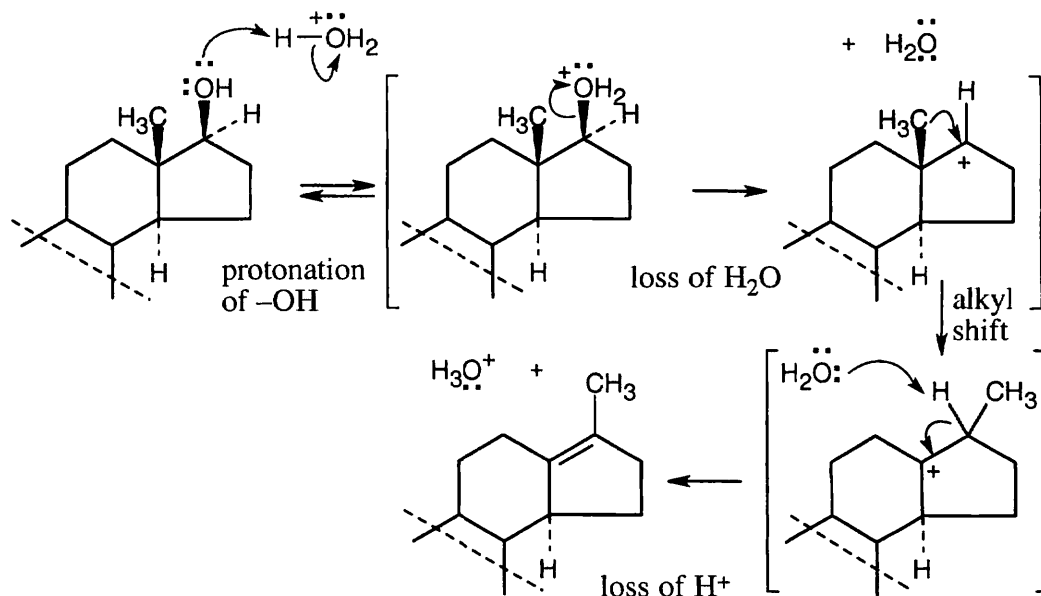
Reaction of 2-butanone with  $\text{NaBH}_4$  produces a racemic mixture of (*R*)-2-butanol and (*S*)-2-butanol.

## 17.47



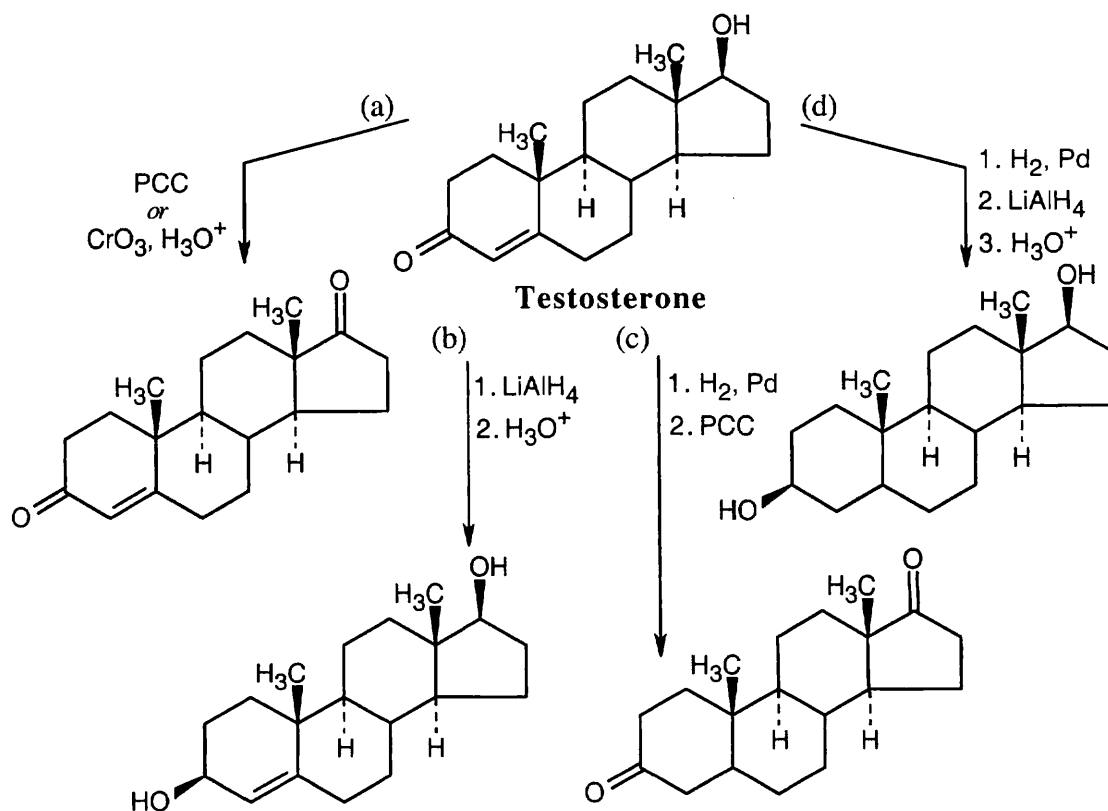
Despite this problem's resemblance to Problem 17.24, the stereochemical outcome is different. Addition of methylmagnesium bromide to the carbonyl group doesn't produce a new chirality center and doesn't affect the chirality center already present. The product is pure (*S*)-2,3-dimethyl-2-pentanol.

17.48



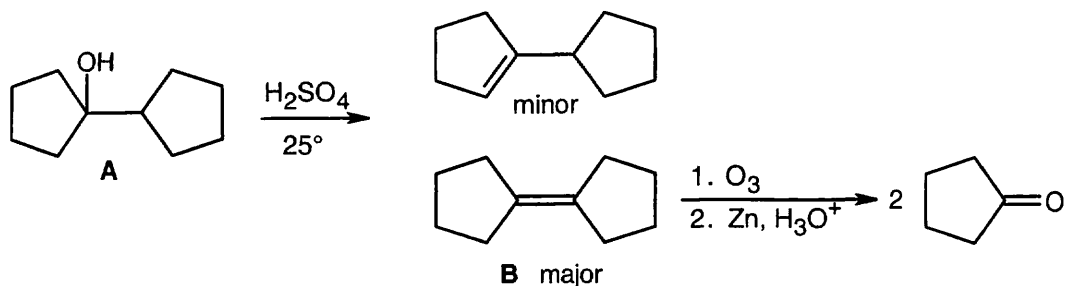
This is a carbocation rearrangement involving the shift of an alkyl group. The sequence of steps is the same as those seen in Problems 17.37 and 17.38.

17.49

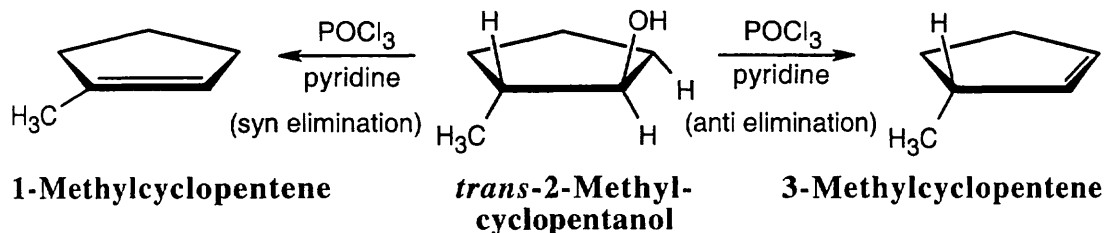


All of these transformations require the proper sequence of oxidations and reductions. In (d),  $\text{NaBH}_4$  can also be used for reduction.

## 17.50

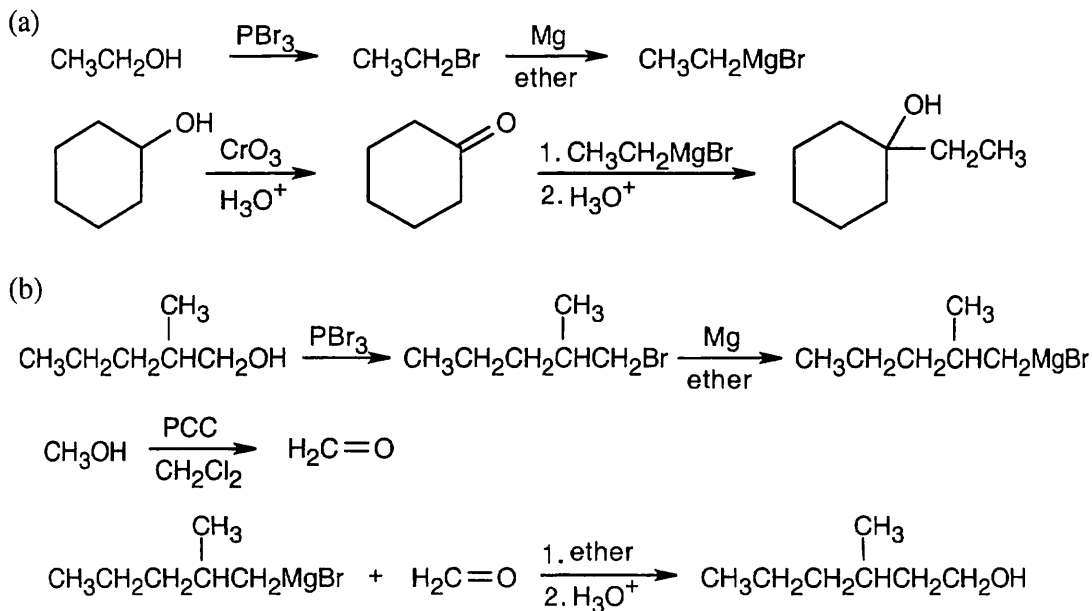


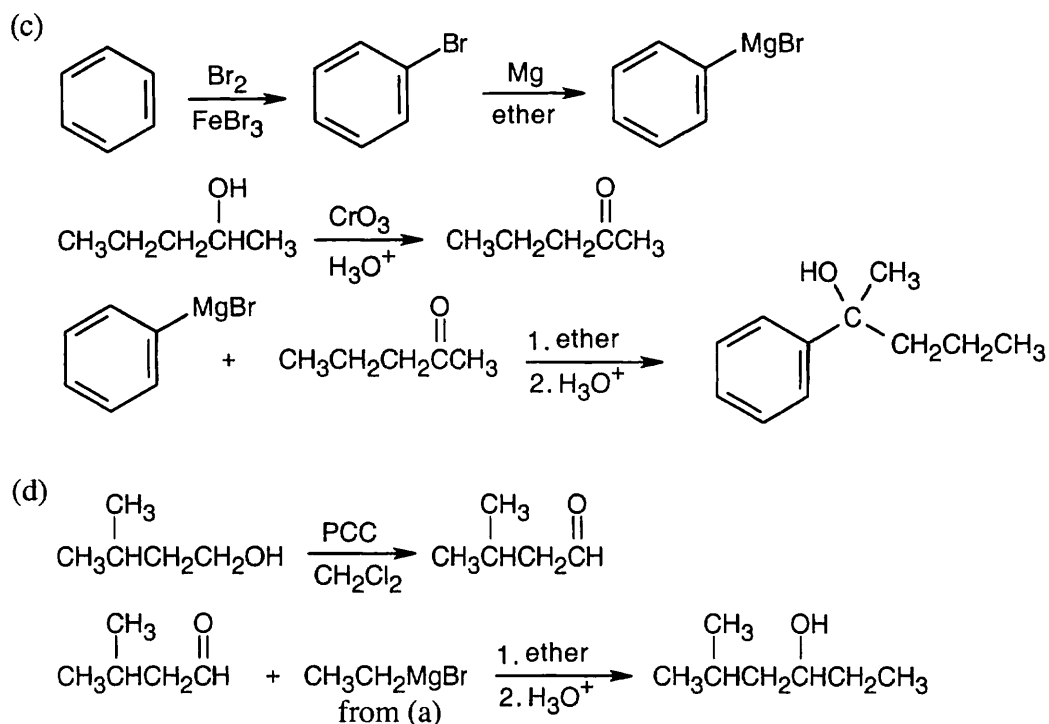
## 17.51



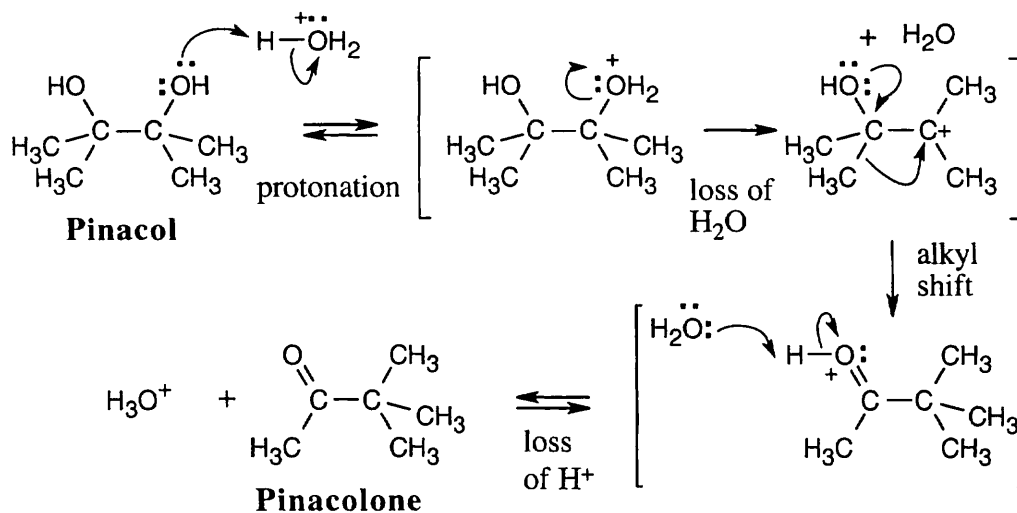
The more stable dehydration product is 1-methylcyclopentene, which can be formed only via syn elimination. The product of anti elimination is 3-methylcyclopentene. Since this product predominates, the requirement of anti periplanar geometry must be more important than formation of the more stable product.

**17.52** All of these syntheses involve a Grignard reaction at some step. Both the carbonyl compound and the Grignard reagent must be prepared from alcohols.

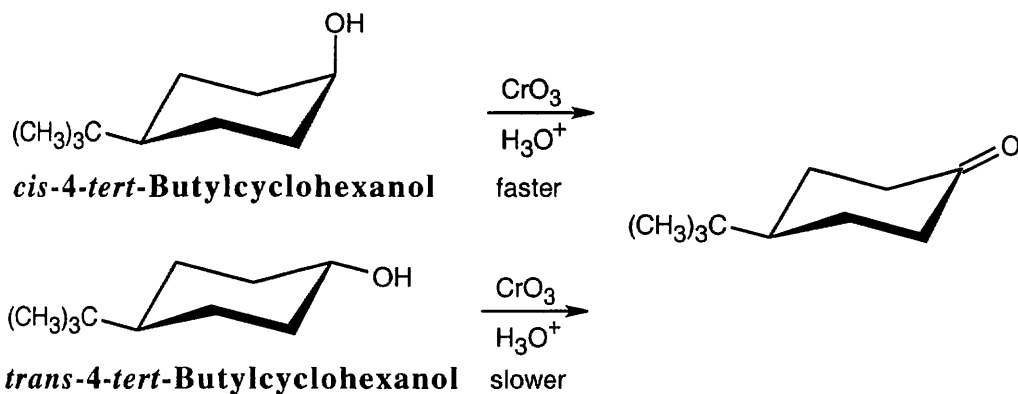




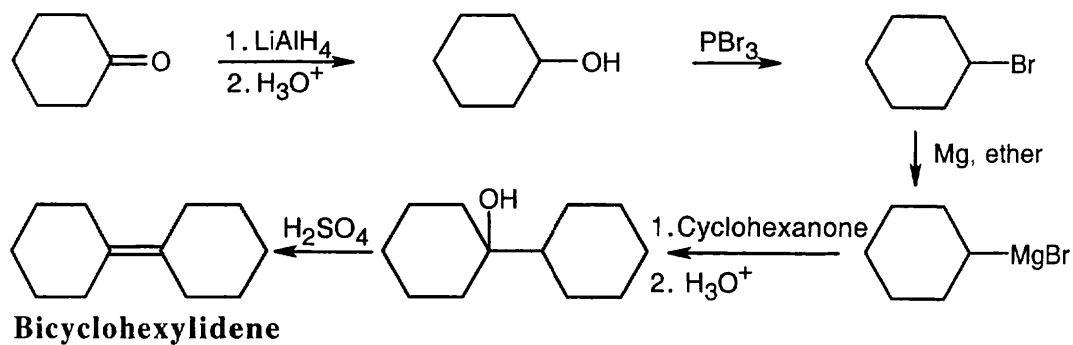
**17.53** The pinacol rearrangement follows a sequence of steps similar to other rearrangements we have studied in this chapter. The second hydroxyl group assists in the alkyl shift.



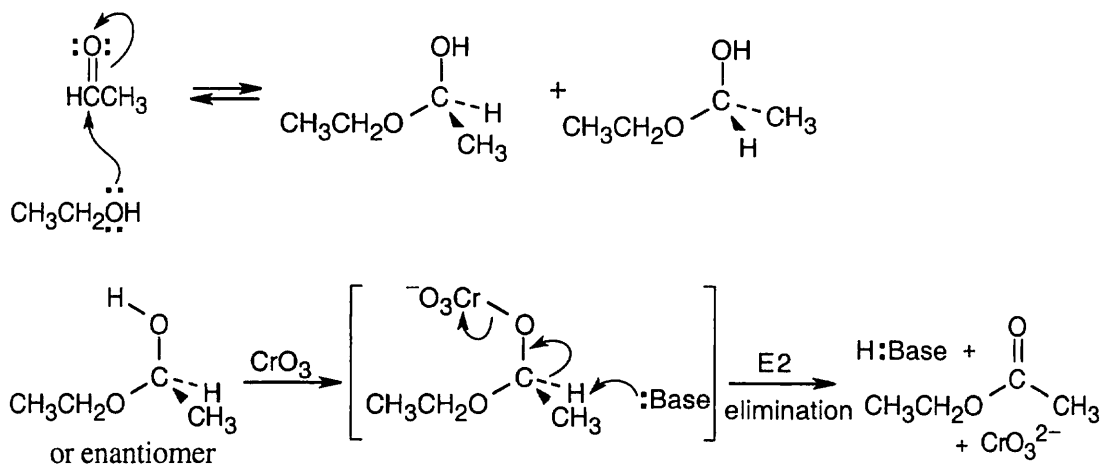
**17.54** The hydroxyl group is axial in the cis isomer, which is expected to oxidize faster than the trans isomer. (Remember that the bulky *tert*-butyl group is always equatorial in the more stable isomer.)



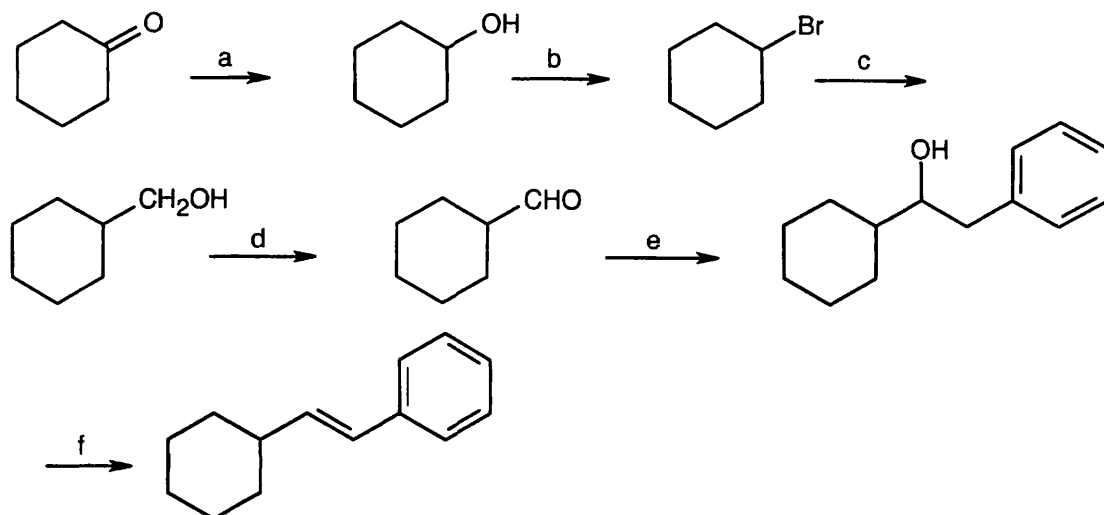
**17.55**



**17.56** An alcohol adds to an aldehyde by a mechanism that we will study in a later chapter. The hydroxyl group of the addition intermediate undergoes oxidation (as shown in Section 17.7), and an ester is formed.

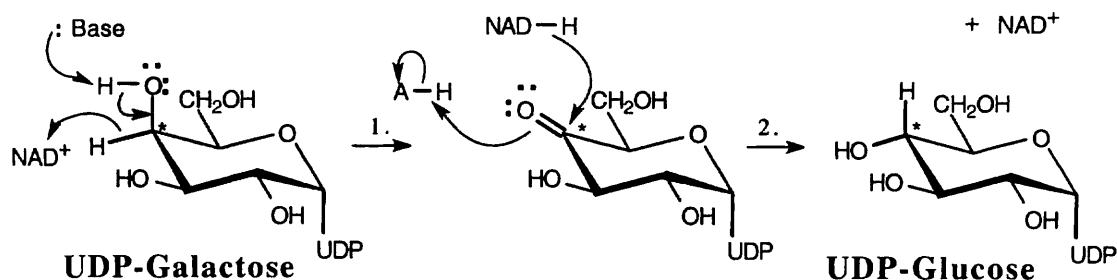


17.57



(a)  $\text{NaBH}_4$ , then  $\text{H}_3\text{O}^+$  (b)  $\text{PBr}_3$  (c)  $\text{Mg}$ , ether, then  $\text{CH}_2\text{O}$  (d)  $\text{PCC}$ ,  $\text{CH}_2\text{Cl}_2$  (e)  $\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$ , then  $\text{H}_3\text{O}^+$  (f)  $\text{POCl}_3$ , pyridine

17.58



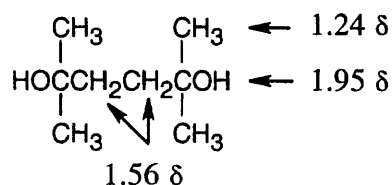
*Step 1:* Base deprotonates the C4 hydroxyl group while  $\text{NAD}^+$  oxidizes the alcohol to a ketone.

*Step 2:* When the ketone is reduced by the  $\text{NADH}$  formed in Step 1, the configuration at the starred carbon is inverted, and UDP-glucose is formed.

17.59 Strategy:

1.  $\text{C}_8\text{H}_{18}\text{O}_2$  has *no* double bonds or rings.
2. The IR band at  $3350\text{ cm}^{-1}$  shows the presence of a hydroxyl group.
3. The compound is symmetrical (simple NMR).
4. There is no splitting.

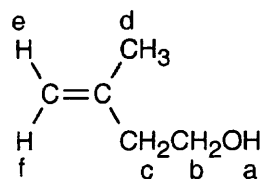
Solution:



**2,5-Dimethyl-2,5-hexanediol**



## 17.60

**3-Methyl-3-buten-3-ol**

The peak absorbing at 1.75  $\delta$  (3 H) is due to the d protons. This peak, which occurs in the allylic region of the spectrum, is unsplit.

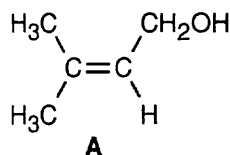
The peak absorbing at 2.13  $\delta$  (1 H) is due to the –OH proton a.

The peak absorbing at 2.30  $\delta$  (2 H) is due to protons c. The peak is a triplet because of splitting by the adjacent b protons.

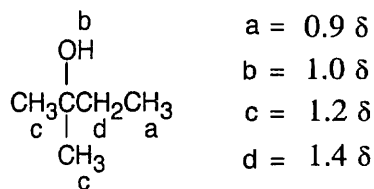
The peak absorbing at 3.70  $\delta$  (2 H) is due to the b protons. The adjacent oxygen causes the peak to be downfield, and the adjacent –CH<sub>2</sub>– group splits the peak into a triplet.

The peaks at 4.78  $\delta$  and 4.85  $\delta$  (2 H) are due to protons e and f.

- 17.61** (a) Compound **A** has one double bond or ring.  
 (b) The infrared absorption at 3400  $\text{cm}^{-1}$  indicates the presence of an alcohol. The weak absorption at 1640  $\text{cm}^{-1}$  is due to a C=C stretch.  
 (c) (1) The absorptions at 1.63  $\delta$  and 1.70  $\delta$  are due to unsplit methyl protons. Because the absorptions are shifted slightly downfield, the protons are adjacent to an unsaturated center.  
 (2) The broad singlet at 3.83  $\delta$  is due to an alcohol proton.  
 (3) The doublet at 4.15  $\delta$  is due to two protons bonded to a carbon bearing an electronegative atom (oxygen, in this case).  
 (4) The proton absorbing at 5.70  $\delta$  is a vinylic proton.  
 (d)

**3-Methyl-2-buten-1-ol**

- 17.62** (a) C<sub>5</sub>H<sub>12</sub>O, C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>  
 (b) The <sup>1</sup>H NMR data show that the compound has twelve protons.  
 (c) The IR absorption at 3600  $\text{cm}^{-1}$  shows that the compound is an alcohol.  
 (d) The compound contains five carbons, two of which are identical.  
 (e) C<sub>5</sub>H<sub>12</sub>O is the molecular formula of the compound.  
 (f), (g)

**2-Methyl-2-butanol**

$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{CH}_2-\text{OH}$

Chemical shift values ( $\delta$ ) are indicated:

- Methyl group ( $\text{H}_3\text{C}$ ):  $2.3 \delta$
- Aromatic protons ( $\text{C}_6\text{H}_4$ ):  $7.1 \delta$
- Benzyl methylene group ( $\text{CH}_2$ ):  $4.5 \delta$
- Hydroxyl group ( $\text{OH}$ ):  $2.5 \delta$

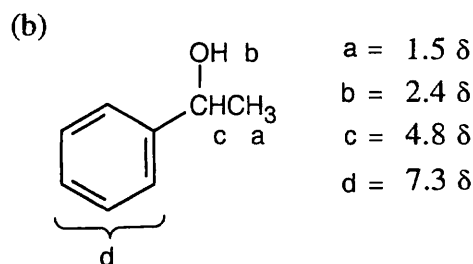
***p*-Methylbenzyl alcohol**

(a)

$$\begin{array}{c} \text{OH} \\ | \\ \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\ \text{a} \quad \text{b} \quad \text{d} \quad \text{b} \quad \text{a} \end{array}$$

**3-Pentanol**

$a = 0.9 \delta$   
 $b = 1.5 \delta$   
 $c = 1.9 \delta$   
 $d = 3.4 \delta$



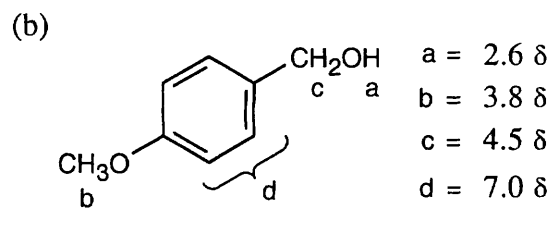
## 1-Phenylethanol

(a)

Chemical structure of 1-phenylbutan-1-ol with carbon labels:

- a = 0.9  $\delta$
- b = 1.8  $\delta$
- c = 2.3  $\delta$
- d = 4.5  $\delta$
- e = 7.3  $\delta$

### 1-Phenyl-1-propanol



***p*-Methoxybenzyl alcohol**

*Structural formula:*  $\text{C}_8\text{H}_{10}\text{O}$  contains 4 multiple bonds and/or rings.

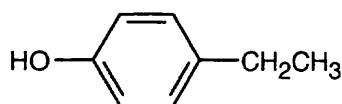
**Infrared:** The broad band at  $3500\text{ cm}^{-1}$  indicates a hydroxyl group. The absorptions at  $1500\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  are due to an aromatic ring. The absorption at  $830\text{ cm}^{-1}$  shows that the ring is *p*-disubstituted. Compound **A** is probably a phenol.

**<sup>1</sup>H NMR:** The triplet at 1.18 δ (3 H) is coupled with the quartet at 2.56 δ (2 H). These two absorptions are due to an ethyl group.

The peaks at 6.75  $\delta$ -7.05  $\delta$  (4 H) are due to aromatic ring protons. The symmetrical splitting pattern of these peaks indicate that the aromatic ring is *p*-disubstituted.

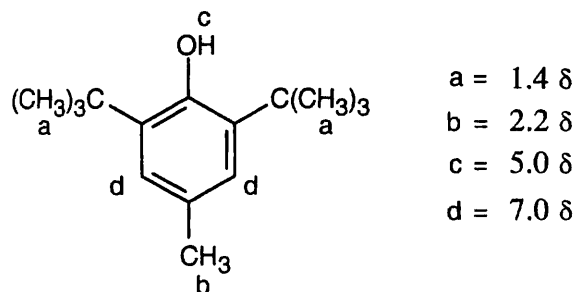
The absorption at 5.50  $\delta$  (1 H) is due to an -OH proton.

### Compound A

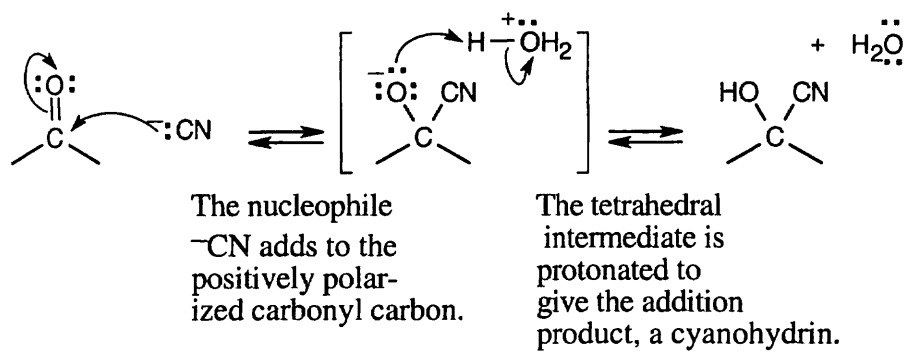


***p*-Ethylphenol**

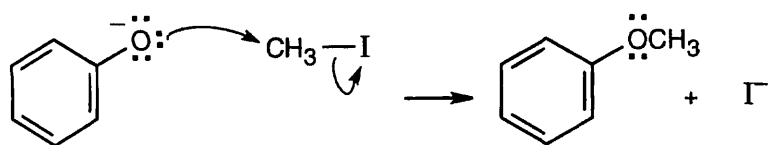
## 17.67



## 17.68



## 17.69



The reaction is an  $\text{S}_{\text{N}}2$  displacement of iodide by phenoxide ion.