



คณะวิทยาศาสตร์ มหาวิทยาลัยแม่โจ้

Organic Chemistry 1 (คม 251)

Atomic structure, hybridization, chemical bonding, stereochemistry, classification, nomenclature, synthesis, reaction mechanisms, physical and chemical properties of

- 1) Alcohols and Phenols (7 %)**
- 2) Ethers and Epoxides (7 %)**
- 3) Aldehydes and Ketones (7 %)**
- 4) Carboxylic acids and their derivatives (7 %)**

Referents

Organic Chemistry, 8th (2012) and 7th (2008) Edition

John McMurry.

http://www.4shared.com/office/VbLzueBV/McMurry_Organic_Chemistry_8th_.htm

Organic Chemistry, 4th (2000) Edition

Francis A. Carey.

http://www.4shared.com/office/ca4aCoED/ORGANIC_CHEMISTRY_4th_ed_-_Fra.htm

Organic Chemistry, 7th (2010) Pearson International Edition

Leroy G. Wade, JR.

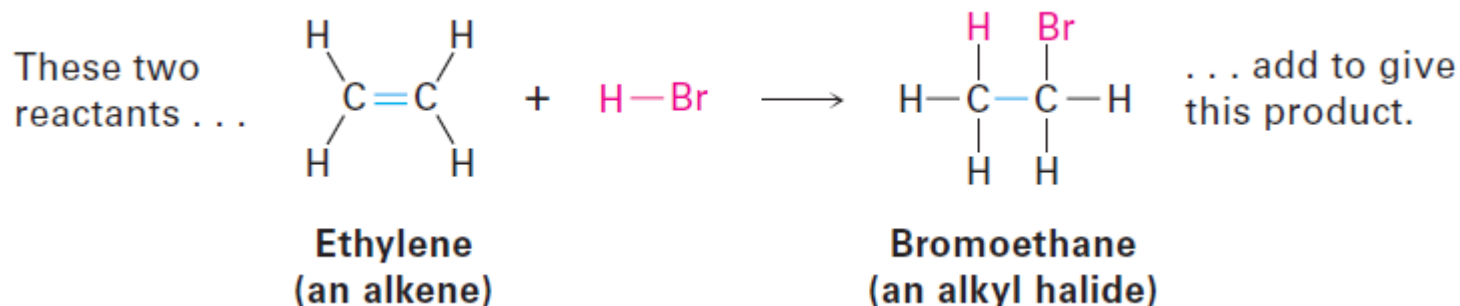
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อาจารย์ ดร. วชิระ ชุ่มมงคล

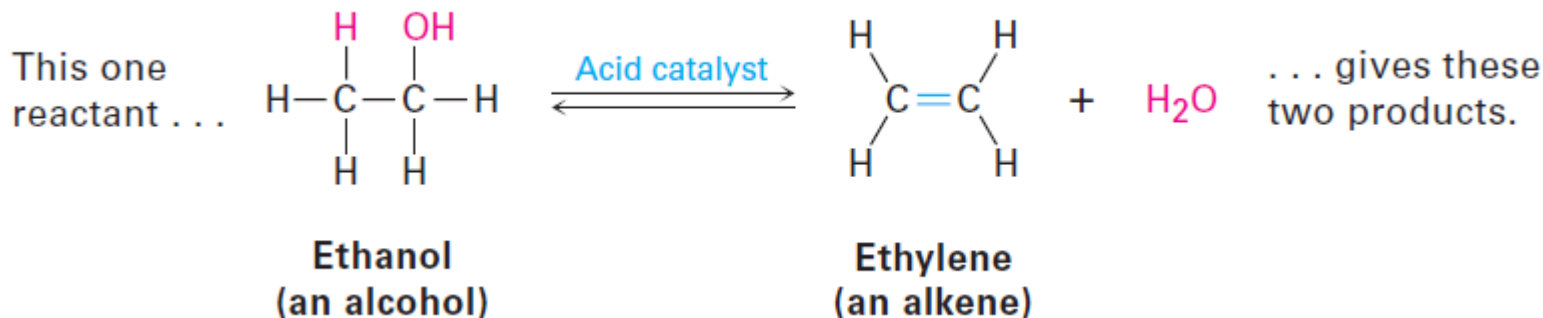
Overview of Organic Reaction

Kinds of Organic Reactions

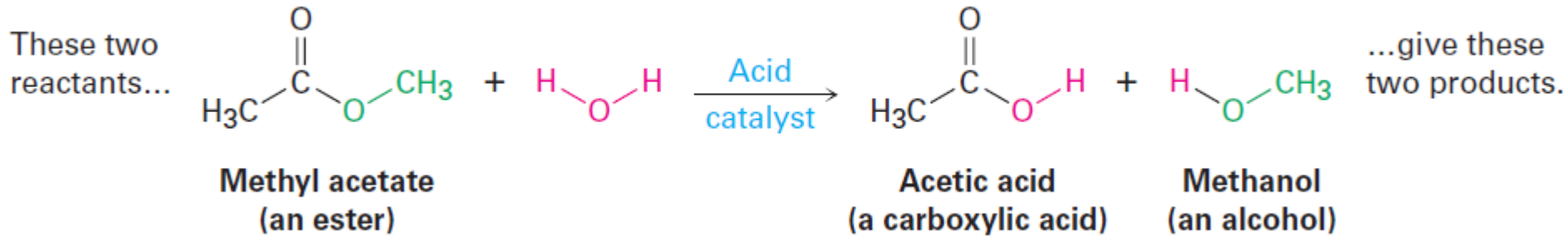
* Addition reactions



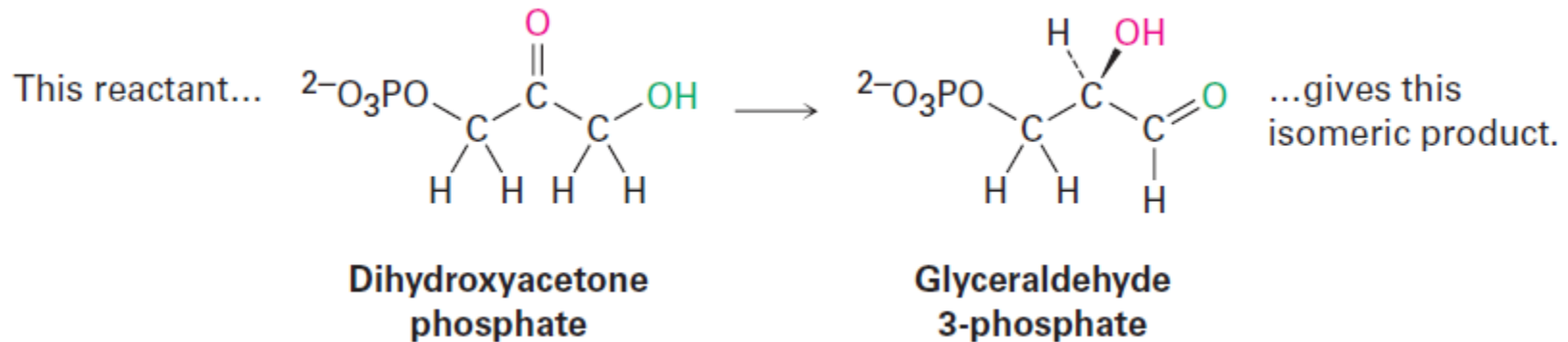
* Elimination reactions



* Substitution reactions

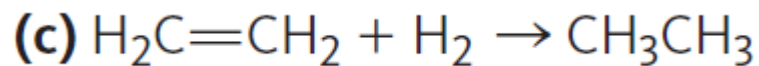
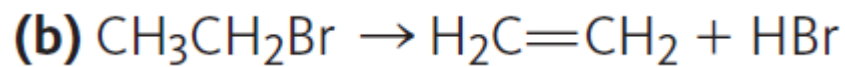
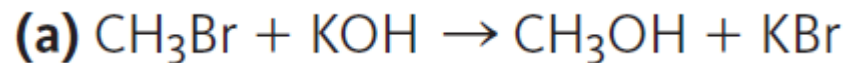


* Rearrangement reactions

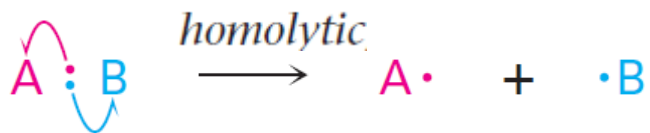


Problem 6.1

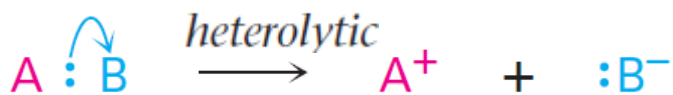
Classify each of the following reactions as an addition, elimination, substitution, or rearrangement:



6.2 How Organic Reactions Occur: Mechanisms



Symmetrical bond-breaking (radical):
one bonding electron stays with each product.



Unsymmetrical bond-breaking (polar):
two bonding electrons stay with one product.

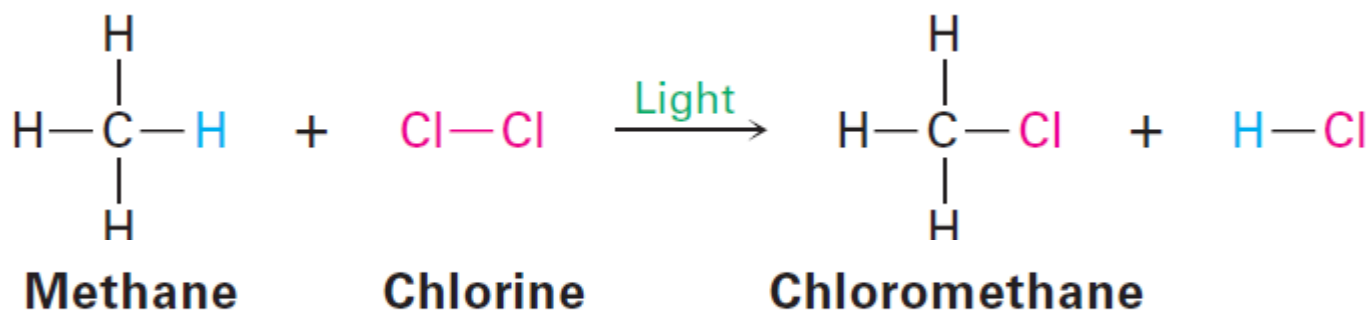
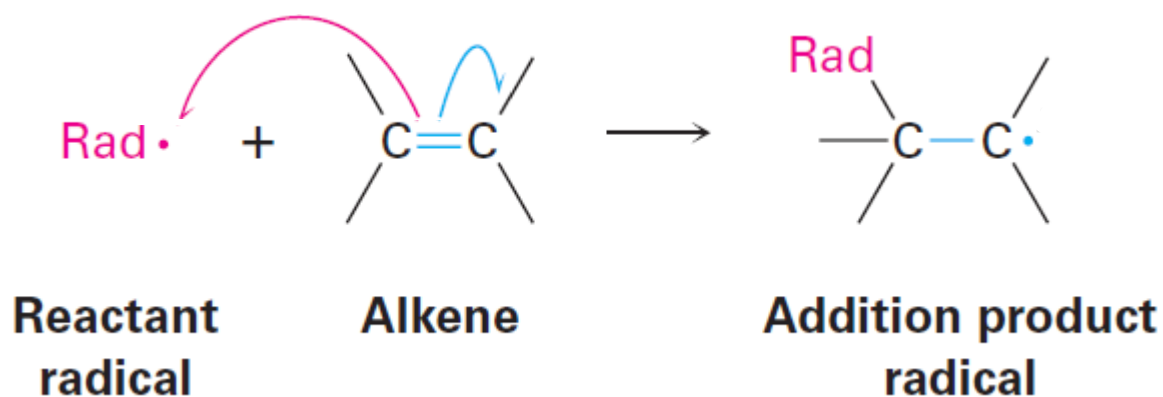
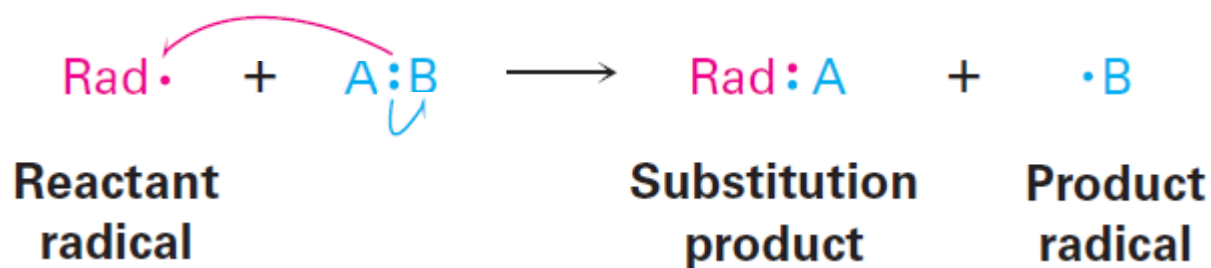


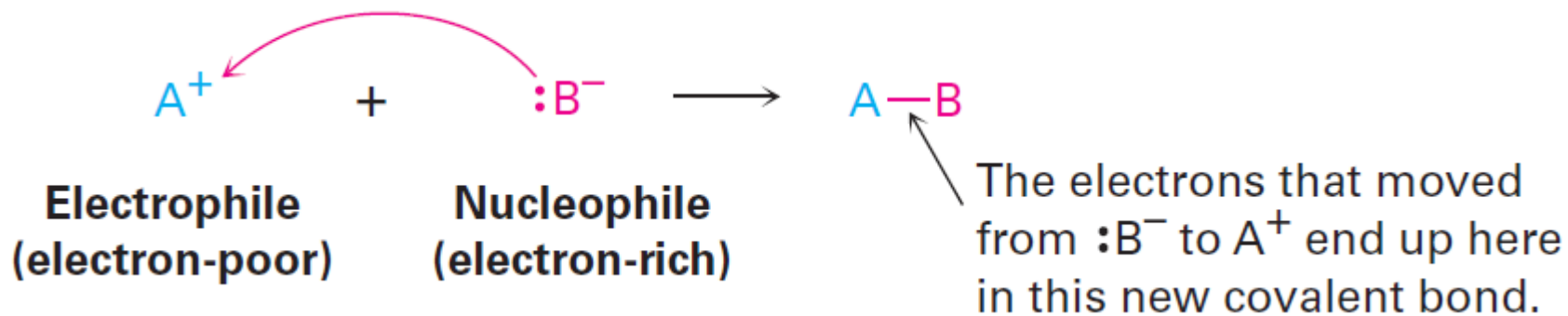
Symmetrical bond-making (radical):
one bonding electron is donated by each reactant.

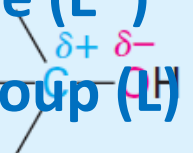
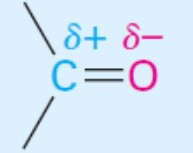
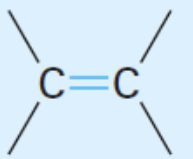
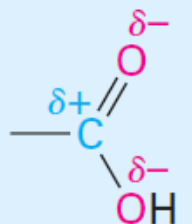
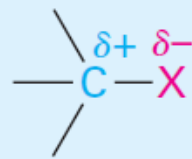
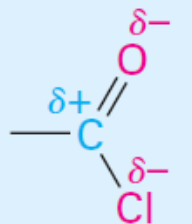


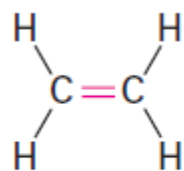
Unsymmetrical bond-making (polar):
two bonding electrons are donated by one reactant.

6.3 Radical Reactions





| Compound type Functional group structure Nucleophile (Nu ⁻) Electrophile (E ⁺) Leaving Group (L) | Compound type Functional group structure Bases (H ⁺ acceptors) Acids (H ⁺ donors) |
|--|--|
| Alcohol  | Carbonyl  |
| Alkene  <p style="text-align: center;">Symmetrical, nonpolar</p> | Carboxylic acid  |
| Alkyl halide  | Carboxylic acid chloride  |

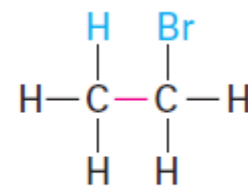


Ethylene

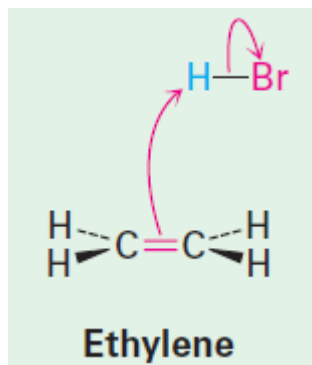
+



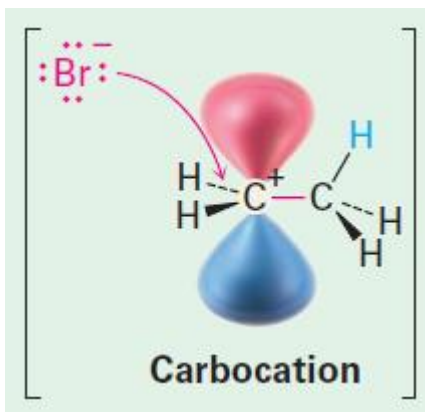
Hydrogen bromide



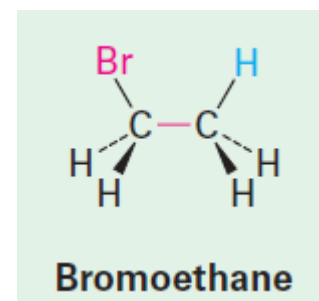
Bromoethane



Ethylene



Carbocation

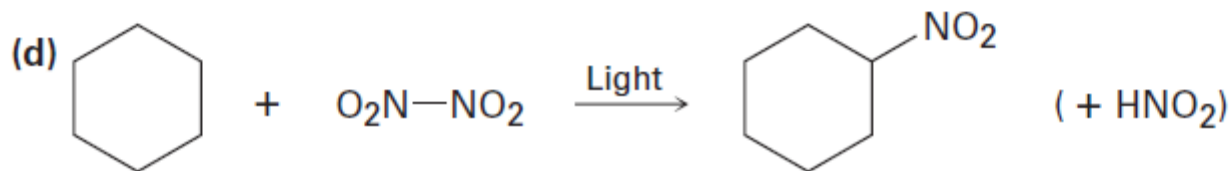
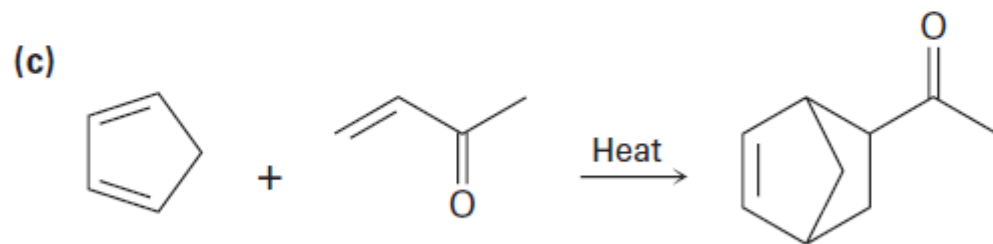
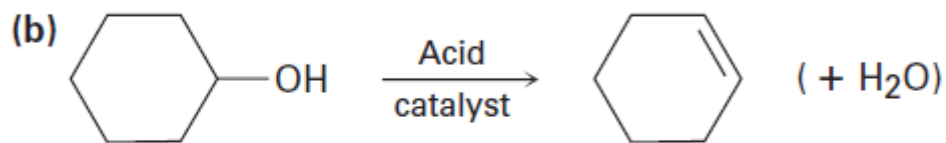
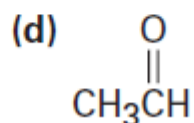
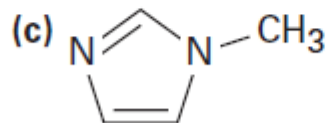
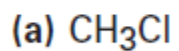


Bromoethane

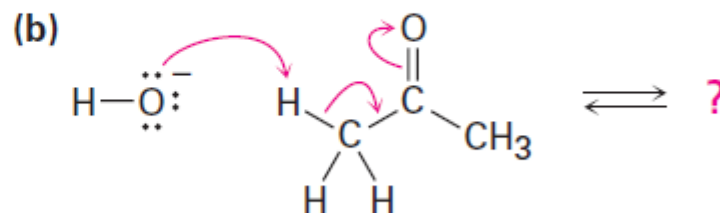
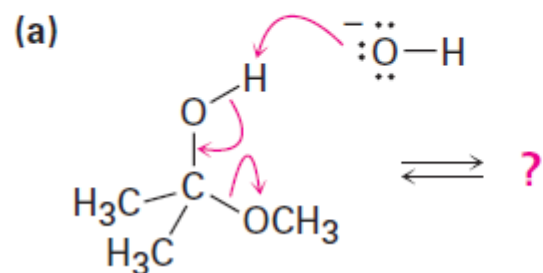
Problem 6.4

Which of the following species are likely to be nucleophiles and which electrophiles? Which might be both?

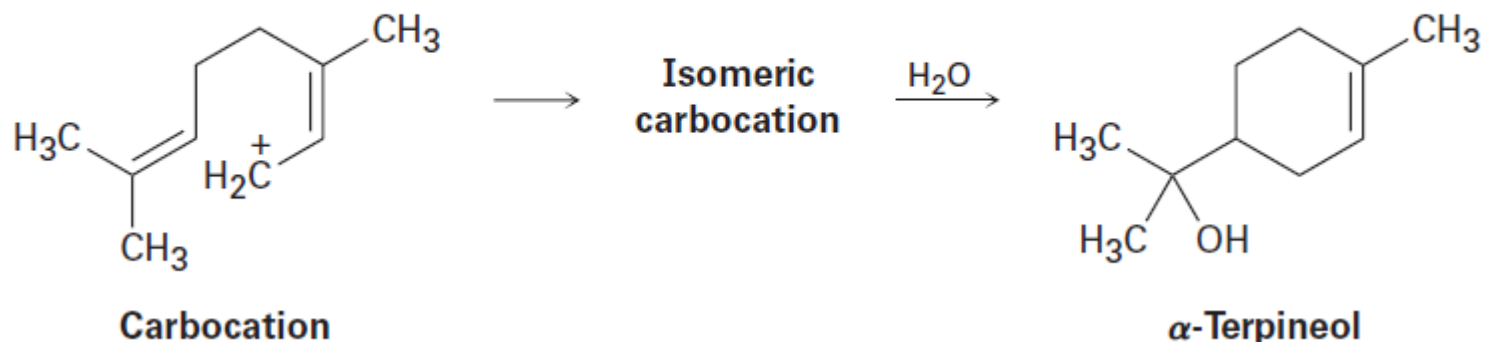
r



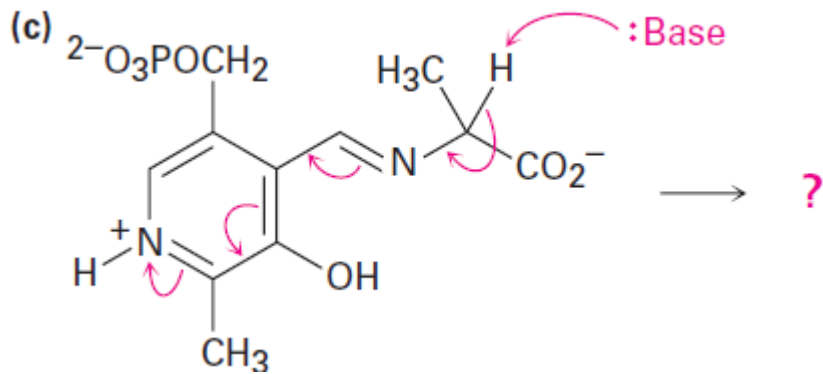
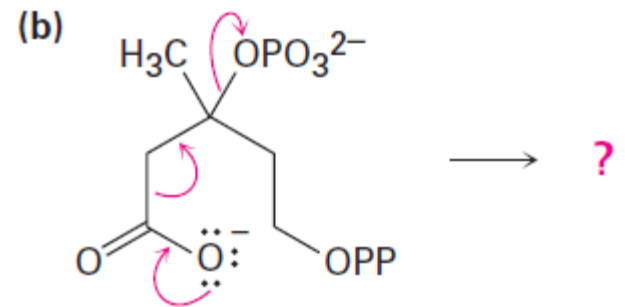
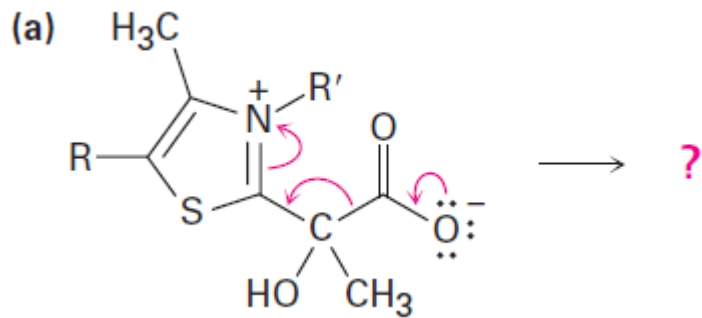
6.23 ▲ Follow the flow of electrons indicated by the curved arrows in each of the following polar reactions, and predict the products that result:



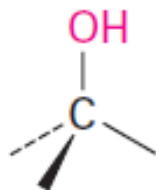
6.40 The naturally occurring molecule α -terpineol is biosynthesized by a route that includes the following step:



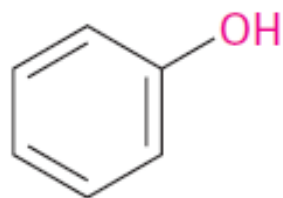
6.41 Predict the product(s) of each of the following biological reactions by interpreting the flow of electrons as indicated by the curved arrows:



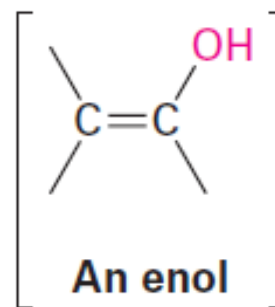
Alcohols and Phenols



An alcohol

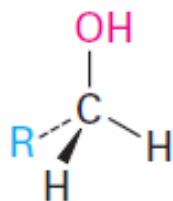


A phenol

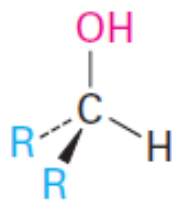


An enol

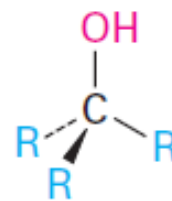
17.1 Naming Alcohols and Phenols



A primary (1°) alcohol



A secondary (2°) alcohol



A tertiary (3°) alcohol

RULE 1

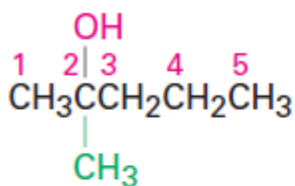
Select the longest carbon chain containing the hydroxyl group, and derive the parent name by replacing the *-e* ending of the corresponding alkane with *-ol*. The *-e* is deleted to prevent the occurrence of two adjacent vowels: propanol rather than propaneol, for example.

RULE 2

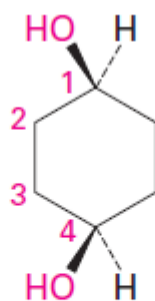
Number the alkane chain beginning at the end nearer the hydroxyl group.

RULE 3

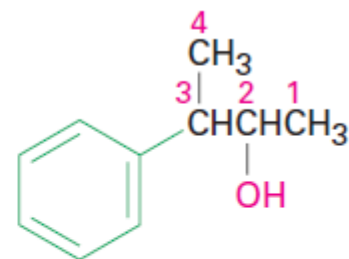
Number the substituents according to their position on the chain, and write the name, listing the substituents in alphabetical order and identifying the position to which the -OH is bonded. Note that in naming *cis*-1,4-cyclohexanediol, the final *-e* of cyclohexane is not deleted because the next letter, *d*, is not a vowel; that is, cyclohexanediol rather than cyclohexandiol. Also, as with alkenes (**Section 7.3**), newer IUPAC naming recommendations place the locant immediately before the suffix rather than before the parent.



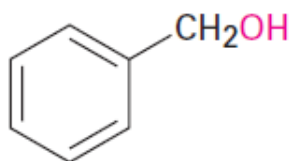
2-Methyl-2-pentanol
(New: **2-Methylpentan-2-ol**)



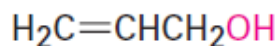
cis-1,4-Cyclohexanediol
(New: **cis-Cyclohexane-1,4-diol**)



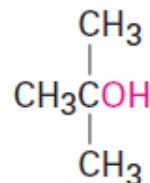
3-Phenyl-2-butanol
(New: **3-Phenylbutan-2-ol**)



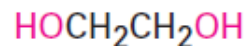
Benzyl alcohol
(phenylmethanol)



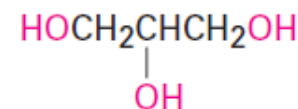
Allyl alcohol
(2-propen-1-ol)



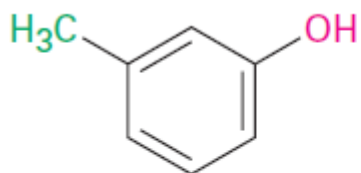
tert-Butyl alcohol
(2-methyl-2-propanol)



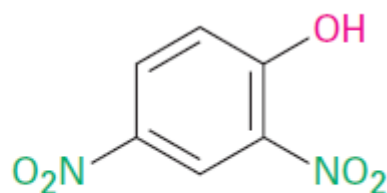
Ethylene glycol
(1,2-ethanediol)



Glycerol
(1,2,3-propanetriol)



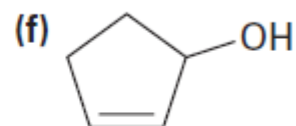
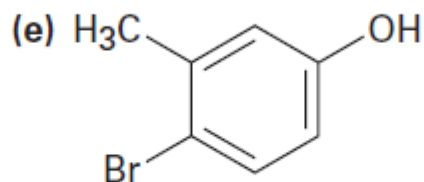
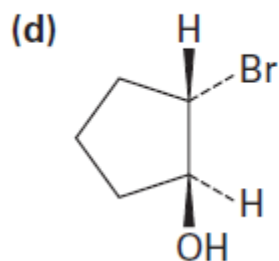
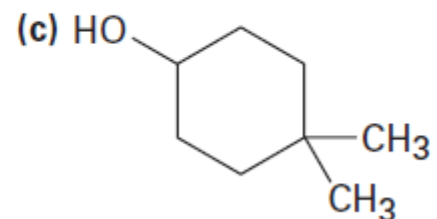
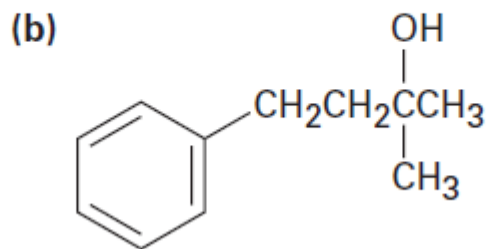
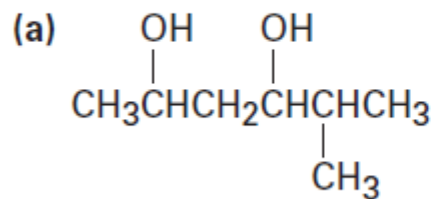
m-Methylphenol
(*m*-Cresol)



2,4-Dinitrophenol

Problem 17.1

Give IUPAC names for the following compounds:



17.2 Properties of Alcohols and Phenols

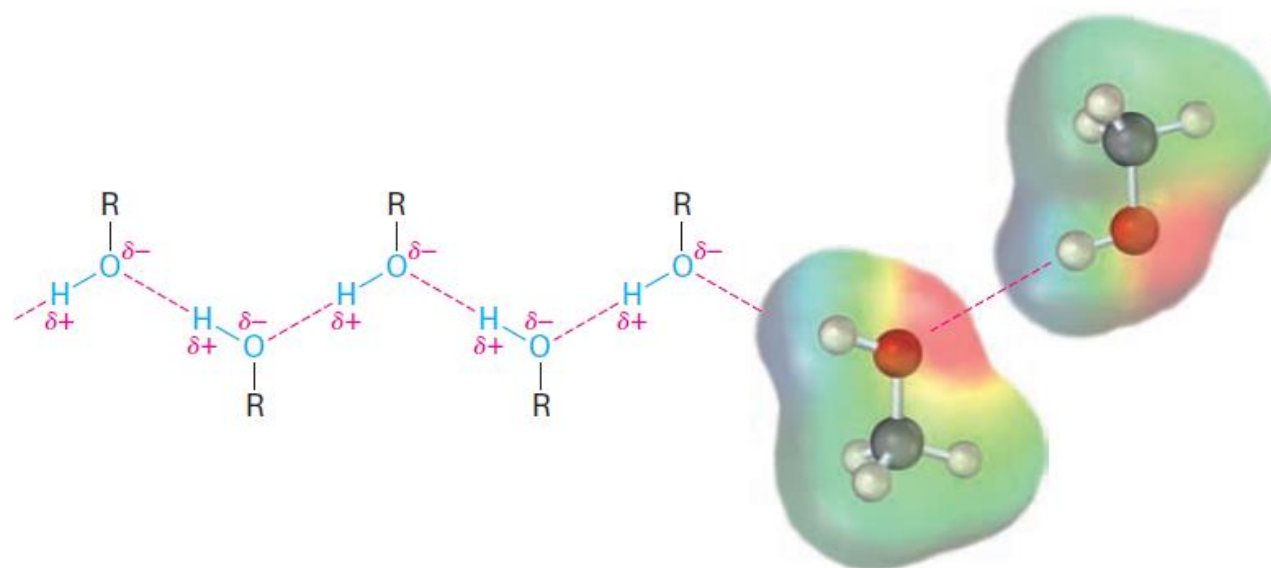
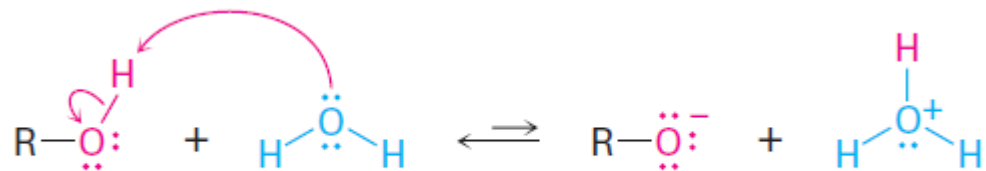


Figure 17.1 Hydrogen-bonding in alcohols and phenols. Attraction between a positively polarized OH hydrogen and a negatively polarized oxygen holds molecules together. The electrostatic potential map of methanol shows the **positively polarized** O—H hydrogen and the **negatively polarized** oxygen.



An alcohol

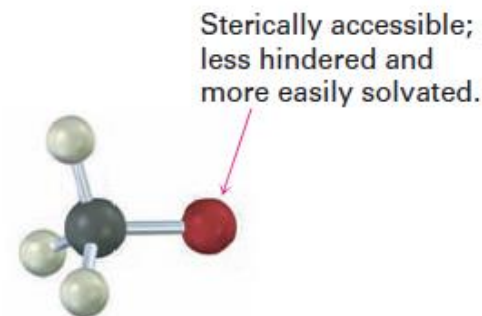
An alkoxide ion

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \quad \text{p}K_a = -\log K_a$$

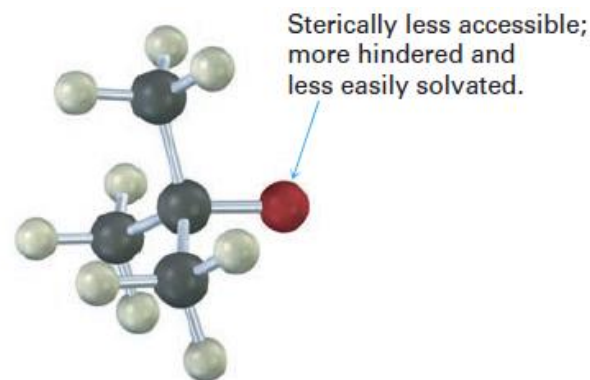
Table 17.1 Acidity Constants of Some Alcohols and Phenols

| Compound | pK _a | |
|-------------------------------------|-----------------|-------------|
| (CH ₃) ₃ COH | 18.00 | Weaker acid |
| CH ₃ CH ₂ OH | 16.00 | |
| H ₂ O | 15.74 | |
| CH ₃ OH | 15.54 | |
| CF ₃ CH ₂ OH | 12.43 | |
| <i>p</i> -Aminophenol | 10.46 | |
| CH ₃ SH | 10.3 | |
| <i>p</i> -Methylphenol | 10.17 | |
| Phenol | 9.89 | |
| <i>p</i> -Chlorophenol | 9.38 | |
| <i>p</i> -Nitrophenol | 7.15 | |

1 Steric effect



Methoxide ion, CH₃O⁻
(pK_a = 15.54)



tert-Butoxide ion, (CH₃)₃CO⁻
(pK_a = 18.00)



An alcohol

An alkoxide ion

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

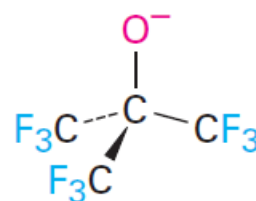
$$pK_a = -\log K_a$$

Table 17.1 Acidity Constants of Some Alcohols and Phenols

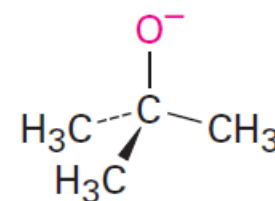
| Compound | pK _a | |
|-------------------------------------|-----------------|-------------|
| (CH ₃) ₃ COH | 18.00 | Weaker acid |
| CH ₃ CH ₂ OH | 16.00 | |
| H ₂ O | 15.74 | |
| CH ₃ OH | 15.54 | |
| CF ₃ CH ₂ OH | 12.43 | |
| <i>p</i> -Aminophenol | 10.46 | |
| CH ₃ SH | 10.3 | |
| <i>p</i> -Methylphenol | 10.17 | |
| Phenol | 9.89 | |
| <i>p</i> -Chlorophenol | 9.38 | |
| <i>p</i> -Nitrophenol | 7.15 | |

2 Electronic effect

- Inductive effect



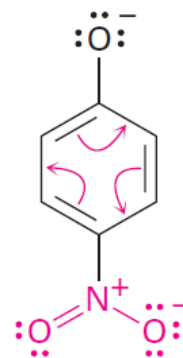
versus



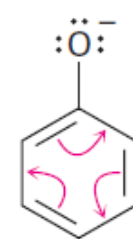
$$pK_a = 5.4$$

$$pK_a = 18.0$$

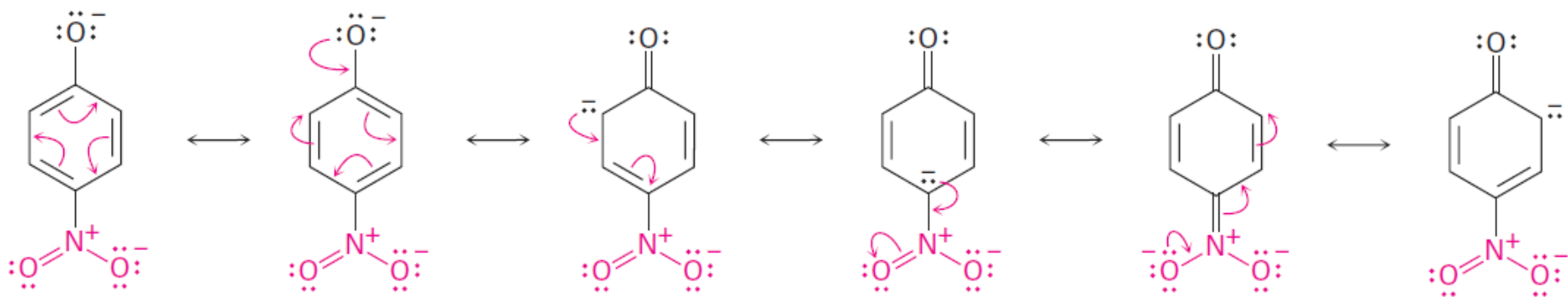
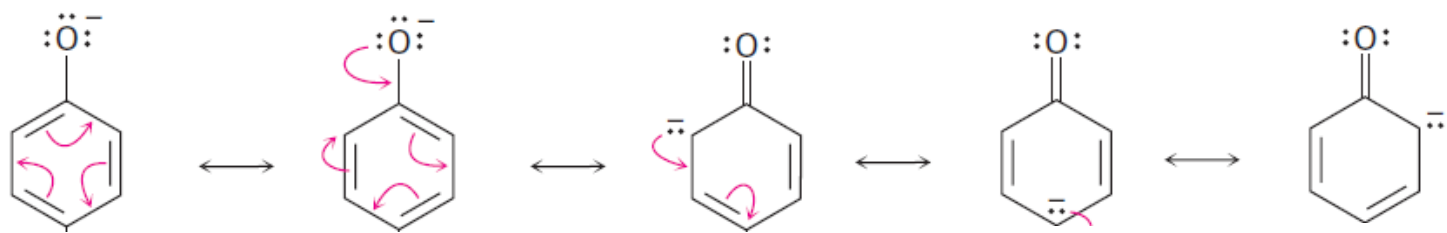
- Resonance effect



p-Nitrophenol

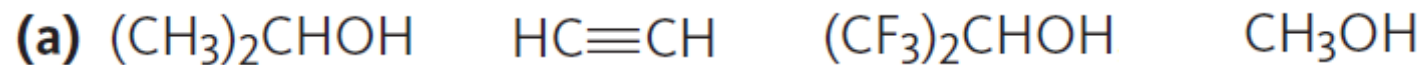


Phenol



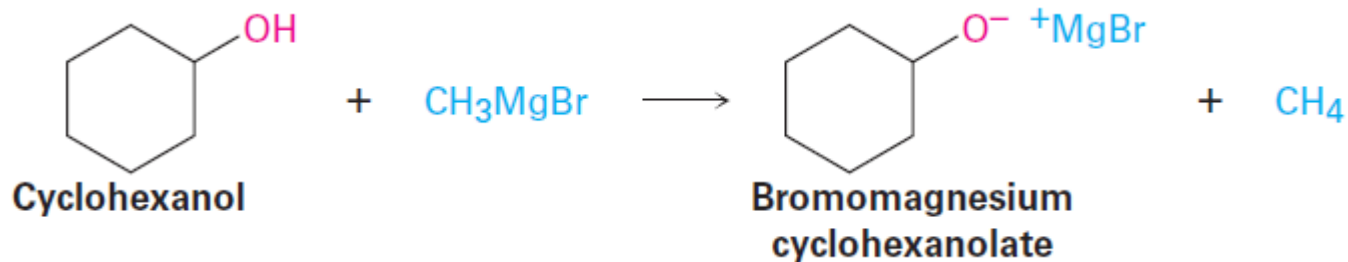
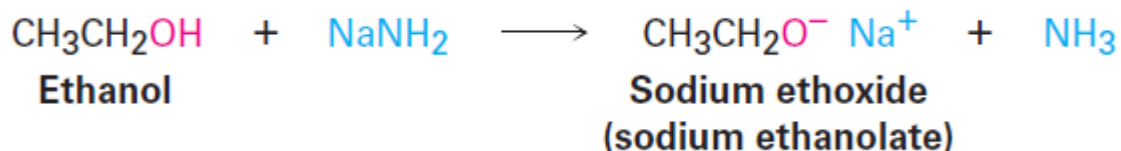
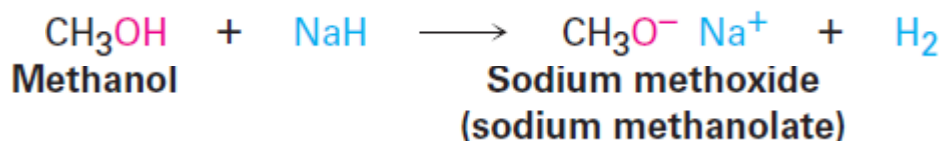
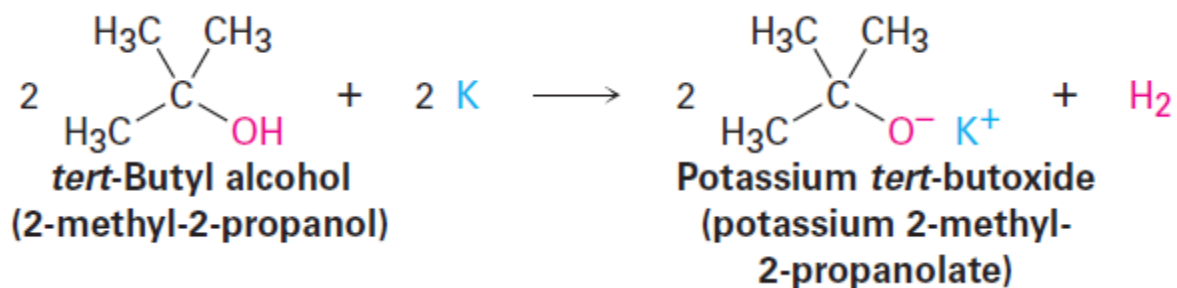
Problem 17.4

Rank the following substances in order of increasing acidity:

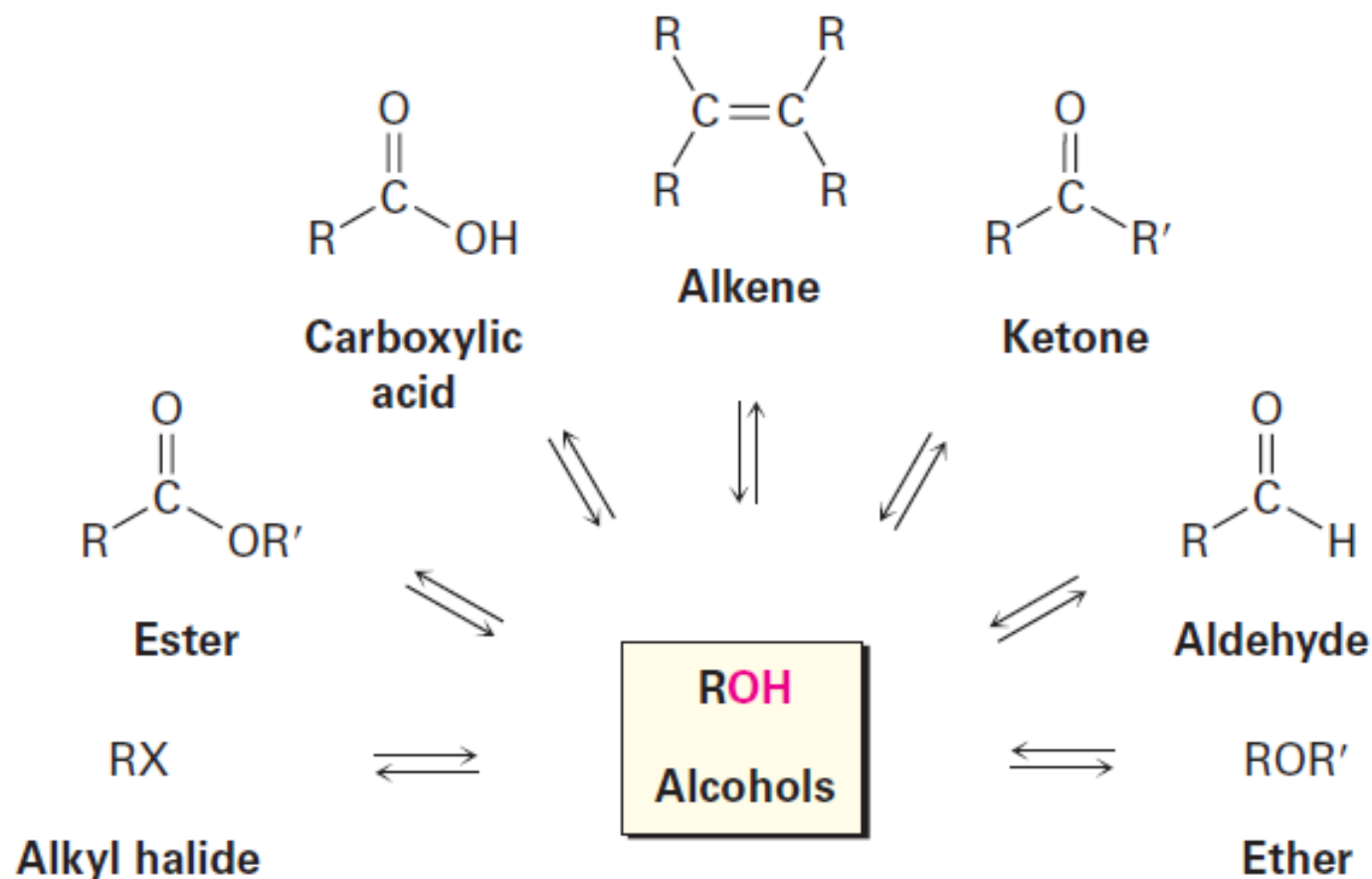


(b) Phenol, *p*-methylphenol, *p*-(trifluoromethyl)phenol

(c) Benzyl alcohol, phenol, *p*-hydroxybenzoic acid

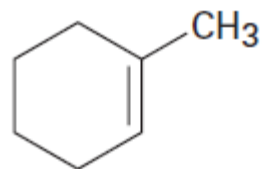
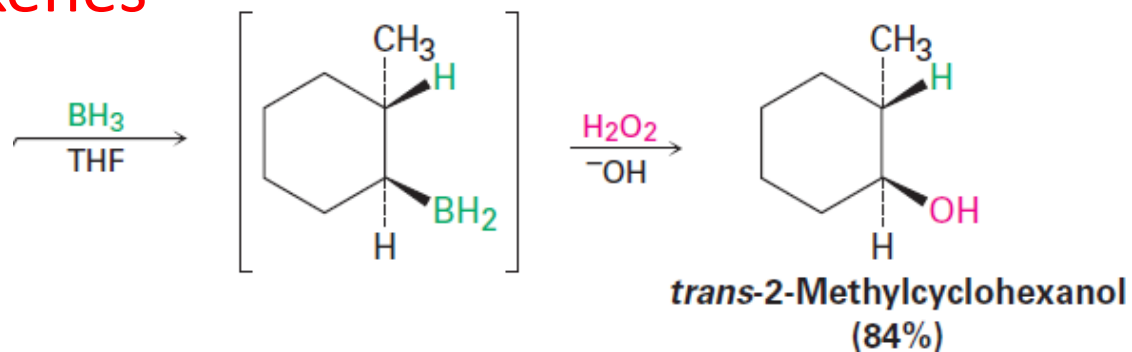


17.3 Preparation of Alcohols: A Review

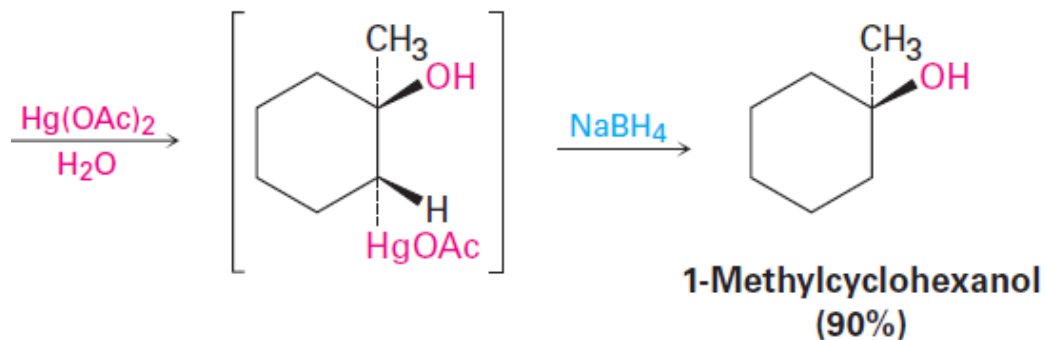


Hydration of alkenes

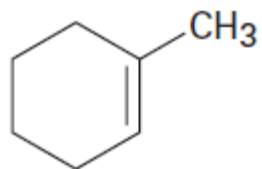
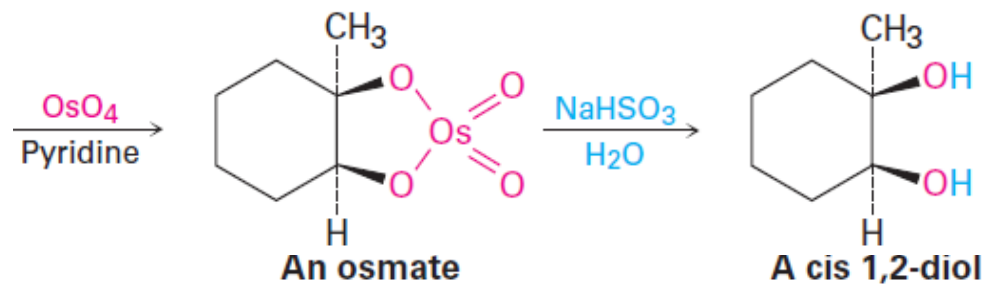
hydration of alkenes



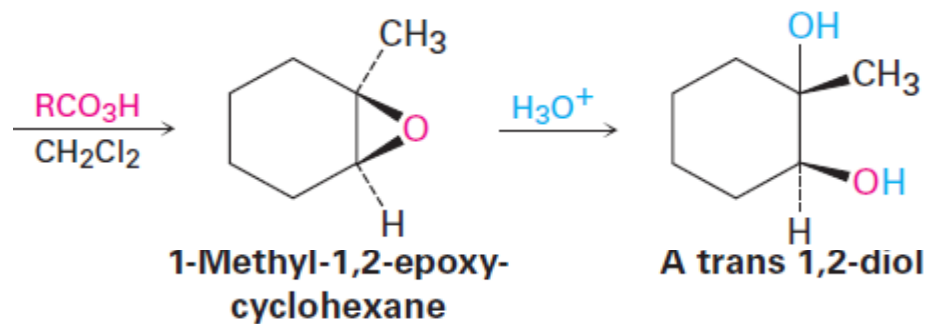
1-Methylcyclohexene

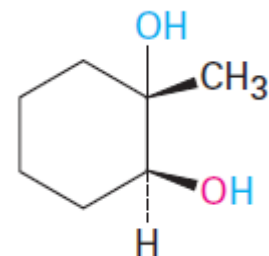
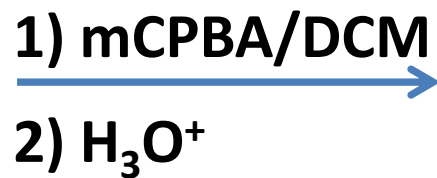
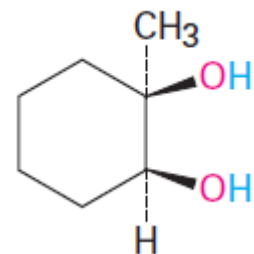
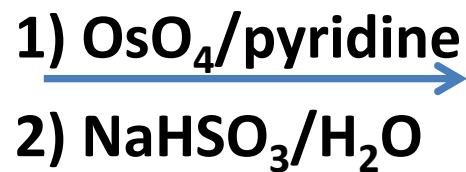
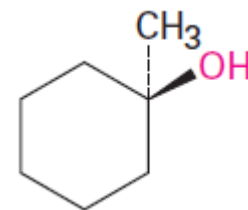
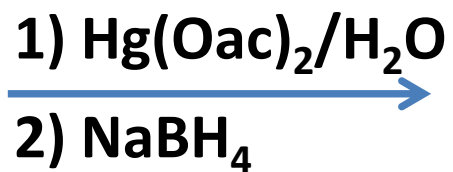
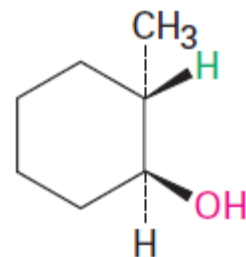
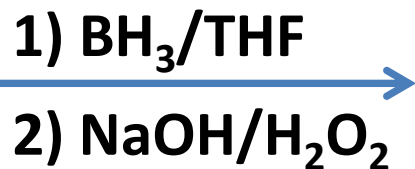
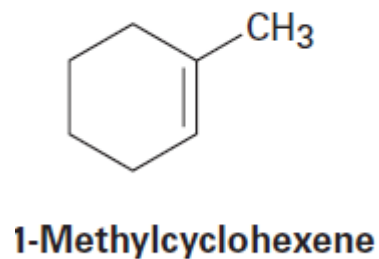


1-Methylcyclohexanol
(90%)



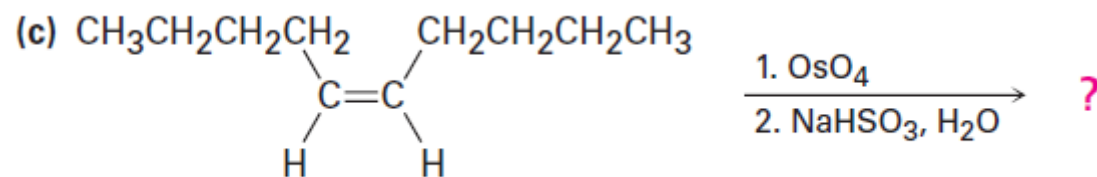
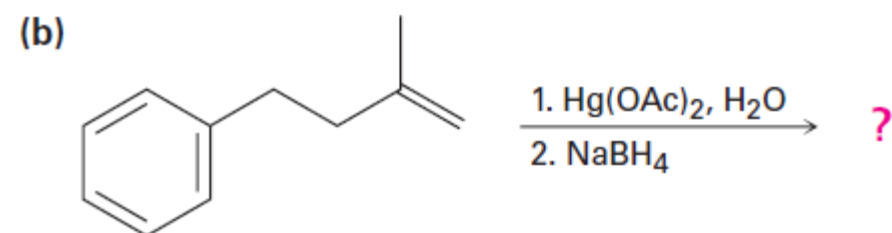
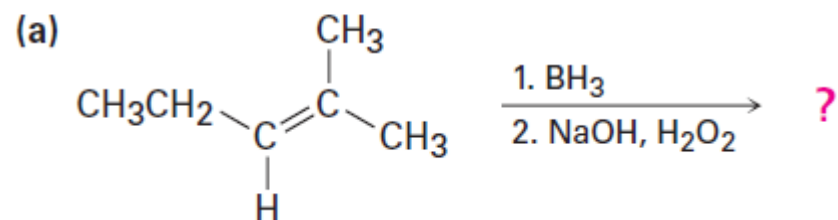
1-Methylcyclohexene



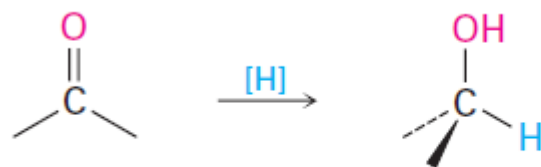


Problem 17.6

Predict the products of the following reactions:



17.4 Alcohols from Carbonyl Compounds: Reduction

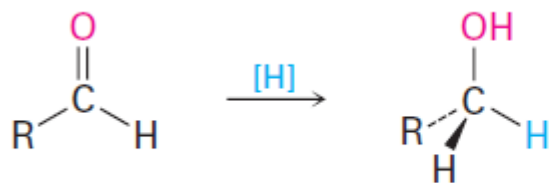


where [H] is a reducing agent

A carbonyl compound

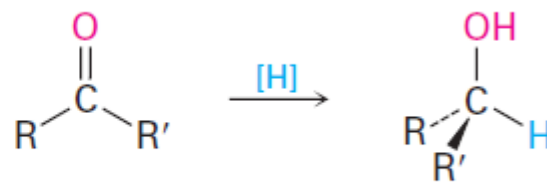
An alcohol

Reduction of Aldehydes and Ketones



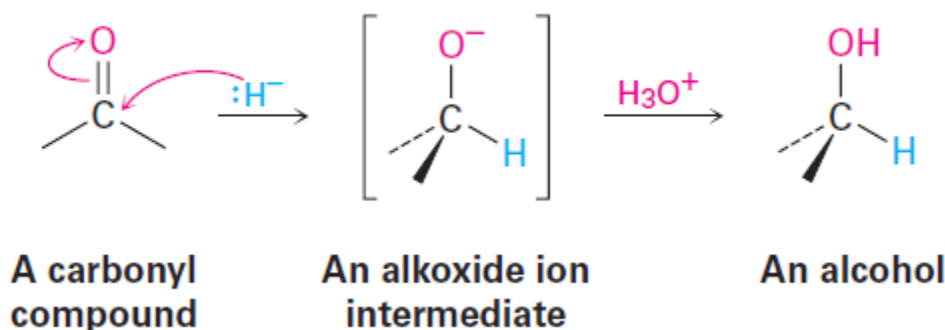
An aldehyde

A primary alcohol



A ketone

A secondary alcohol

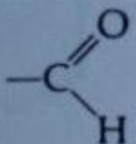
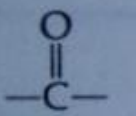
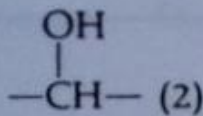
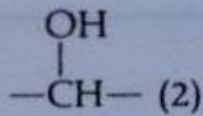
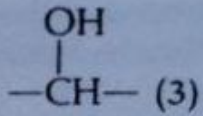
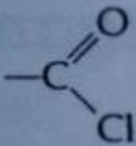
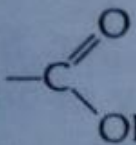
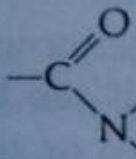
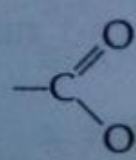


A carbonyl compound

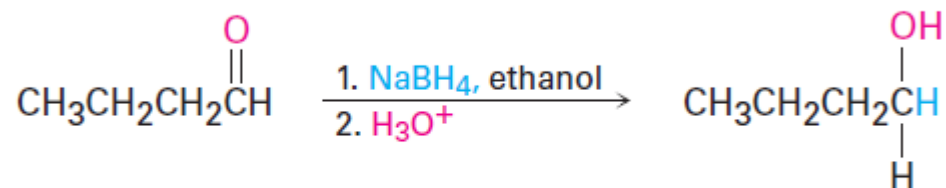
An alkoxide ion intermediate

An alcohol

Reduction of carbonyl Groups by Hydride Donors

| Functional Group | Product of Reduction Using | | |
|---|---|--|---|
| | LiAlH_4 | NaBH_4 | $(\text{BH}_3)_2$ |
|  | $-\text{CH}_2\text{OH}$ (1) | $-\text{CH}_2\text{OH}$ (1) | $-\text{CH}_2\text{OH}$ (2) |
|  |  $-\text{CH}-$ (2) |  $-\text{CH}-$ (2) |  $-\text{CH}-$ (3) |
|  | $-\text{CH}_2\text{OH}$ (3) | $-\text{CH}_2\text{OH}$ (3) | — |
|  | $-\text{CH}_2\text{OH} + \text{ROH}$ (4) | — | $-\text{CH}_2\text{OH} + \text{ROH}$ (5) |
|  | $-\text{CH}_2\text{N}$ (5) | — | $-\text{CH}_2\text{N}$ (4) |
|  | $-\text{CH}_2\text{OH}$ (6) | — | $-\text{CH}_2\text{OH}$ (1) |

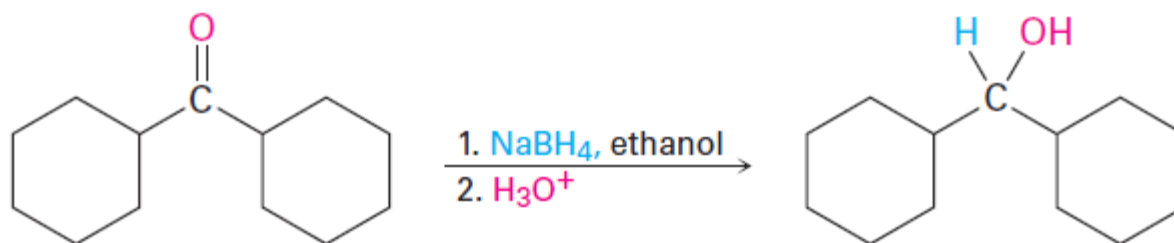
Aldehyde reduction



Butanal

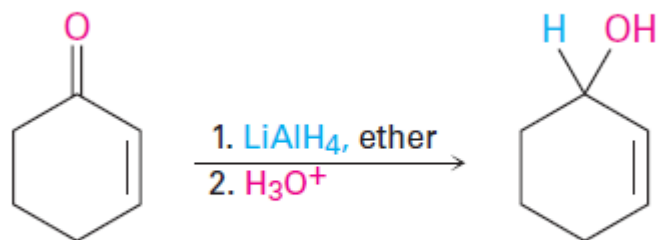
1-Butanol (85%)
(a 1° alcohol)

Ketone reduction



Dicyclohexyl ketone

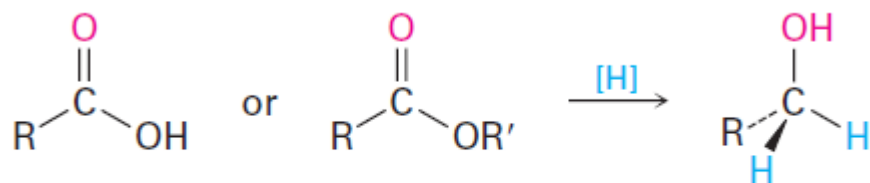
Dicyclohexylmethanol (88%)
(a 2° alcohol)



2-Cyclohexenone

2-Cyclohexenol (94%)

Reduction of Carboxylic Acids and Esters

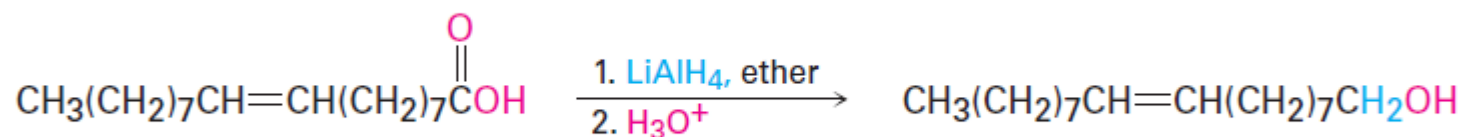


A carboxylic acid

An ester

A primary alcohol

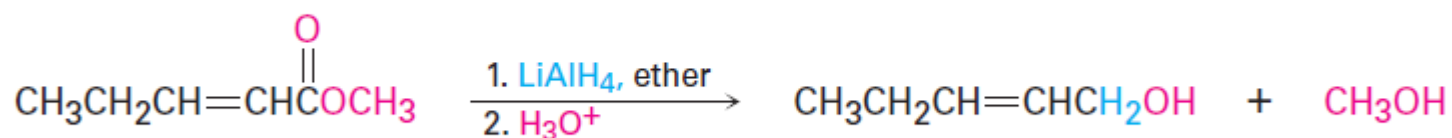
Carboxylic acid reduction



9-Octadecenoic acid
(oleic acid)

9-Octadecen-1-ol (87%)

Ester reduction

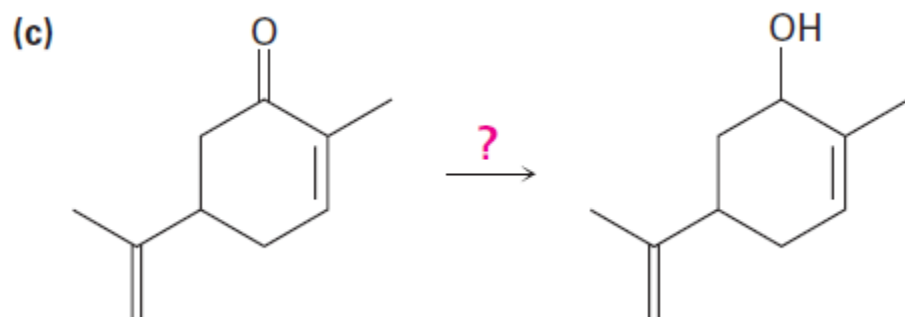
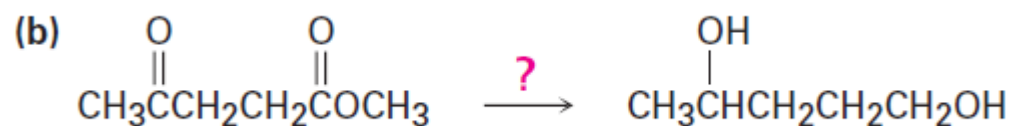
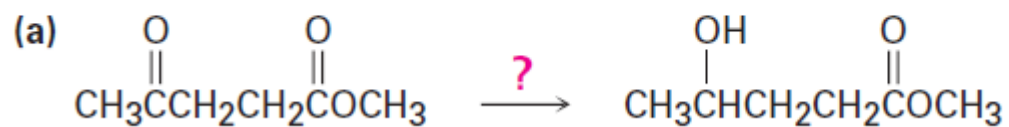


Methyl 2-pentenoate

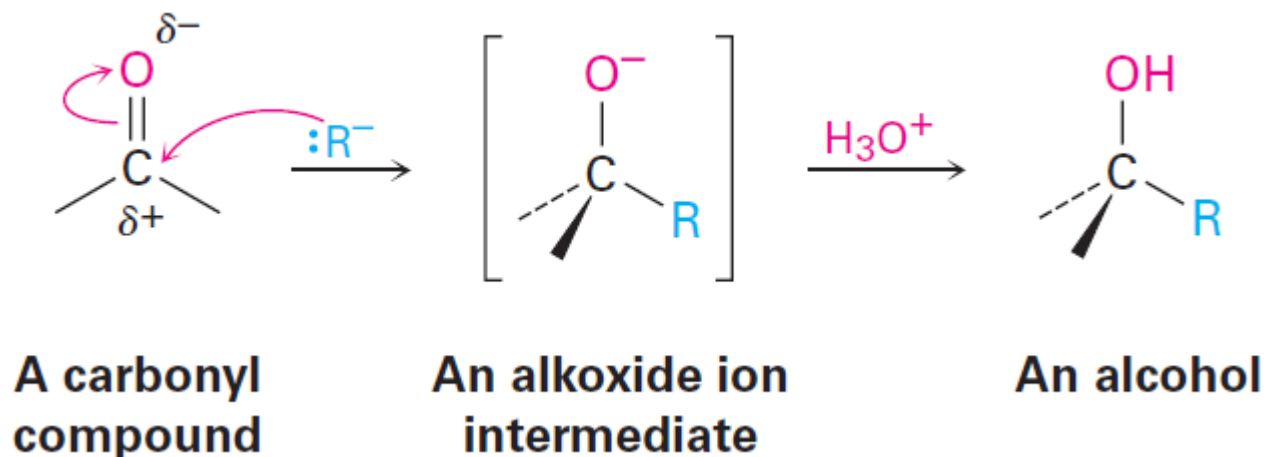
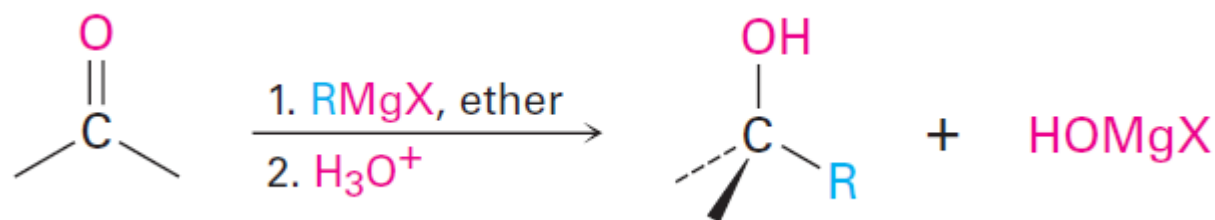
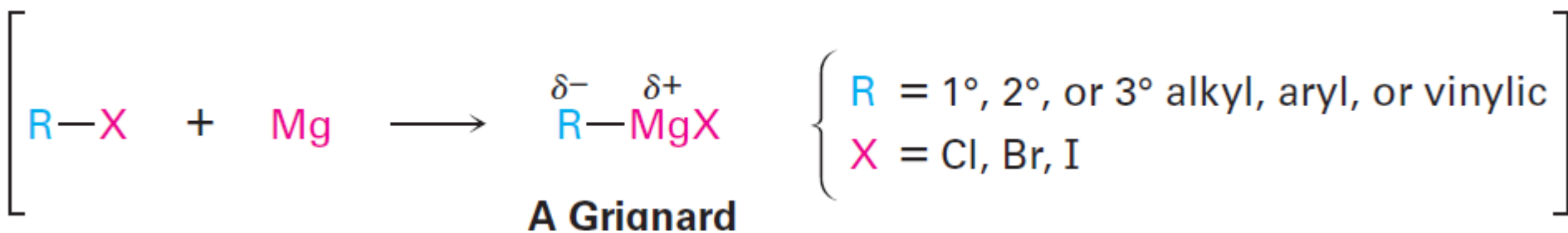
2-Penten-1-ol (91%)

Problem 17.7

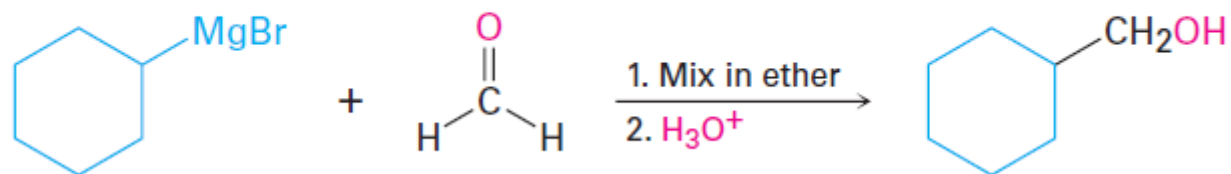
What reagent would you use to accomplish each of the following reactions?



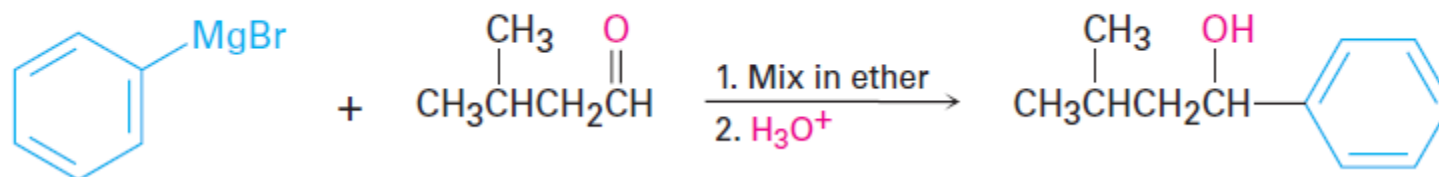
17.5 Alcohols from Carbonyl Compounds: Grignard Reaction



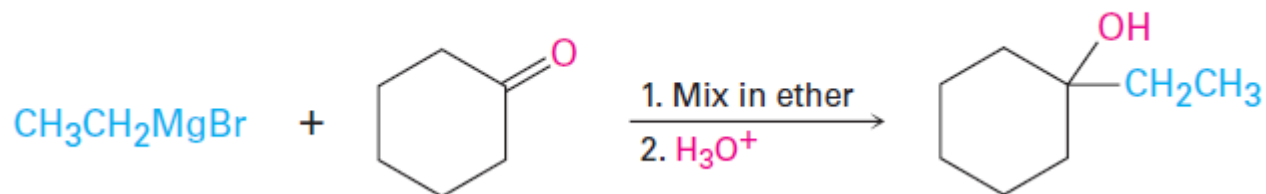
Formaldehyde reaction



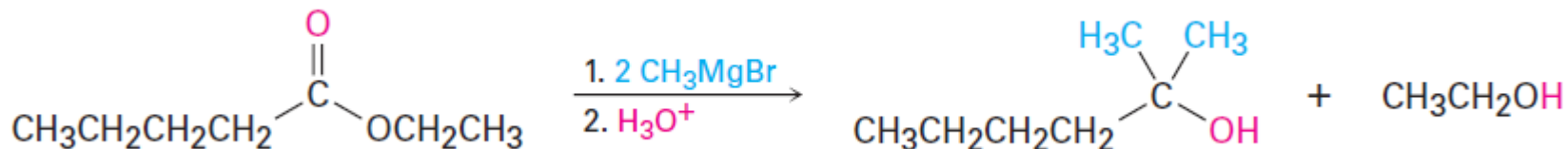
Aldehyde reaction

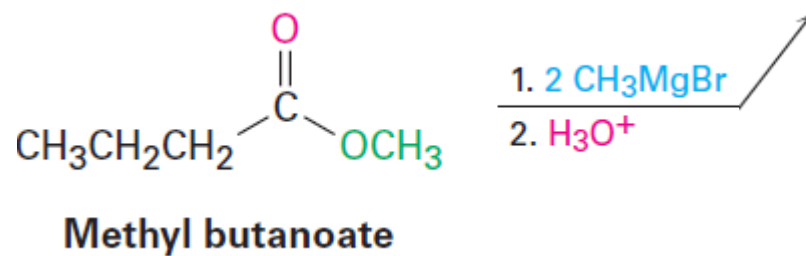
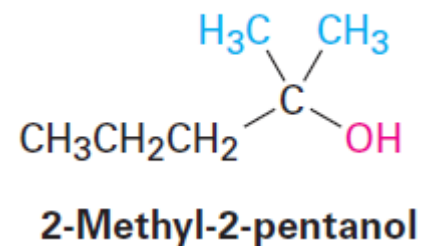
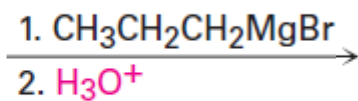
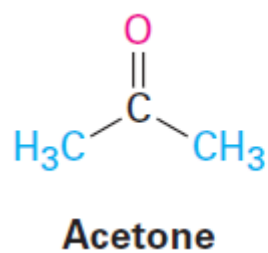
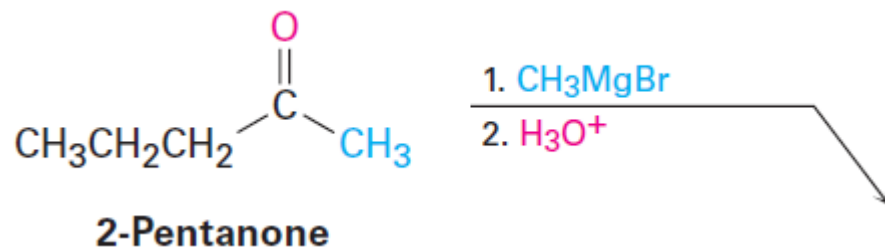


Ketone reaction

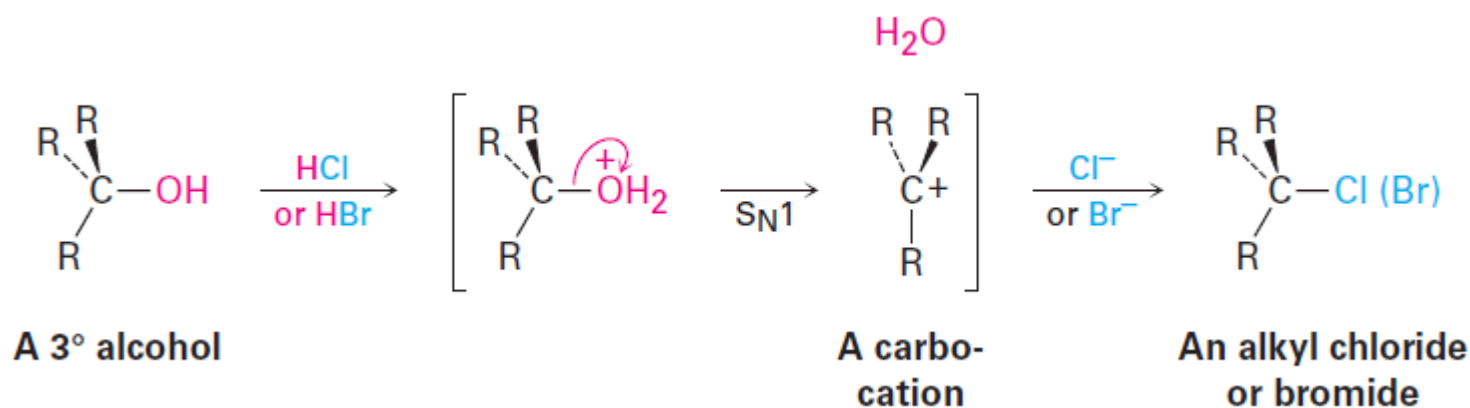


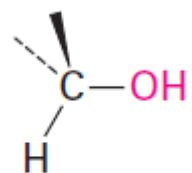
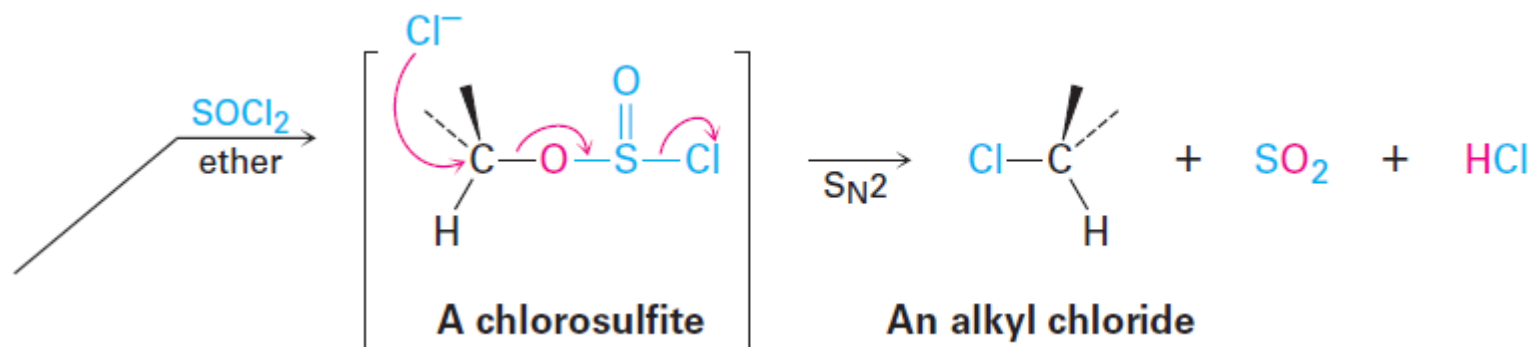
Ester reaction



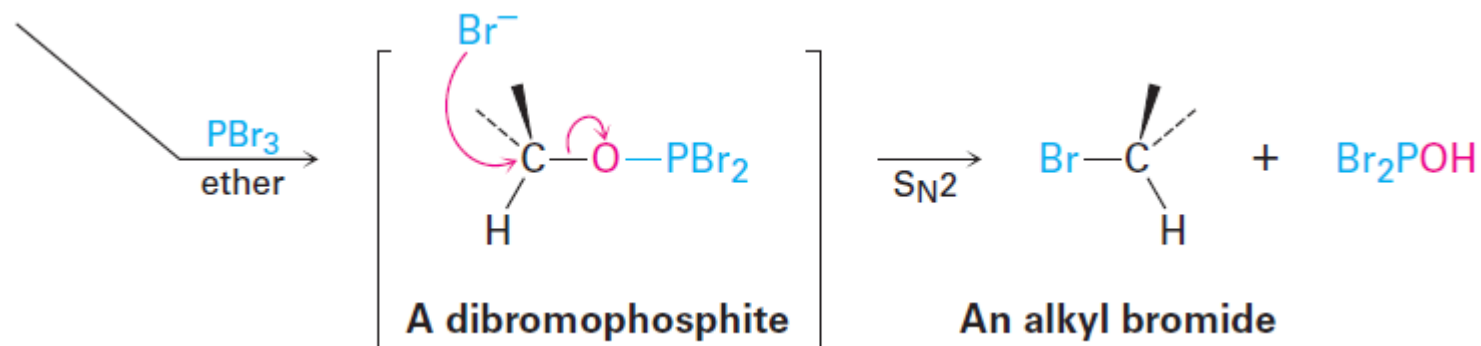


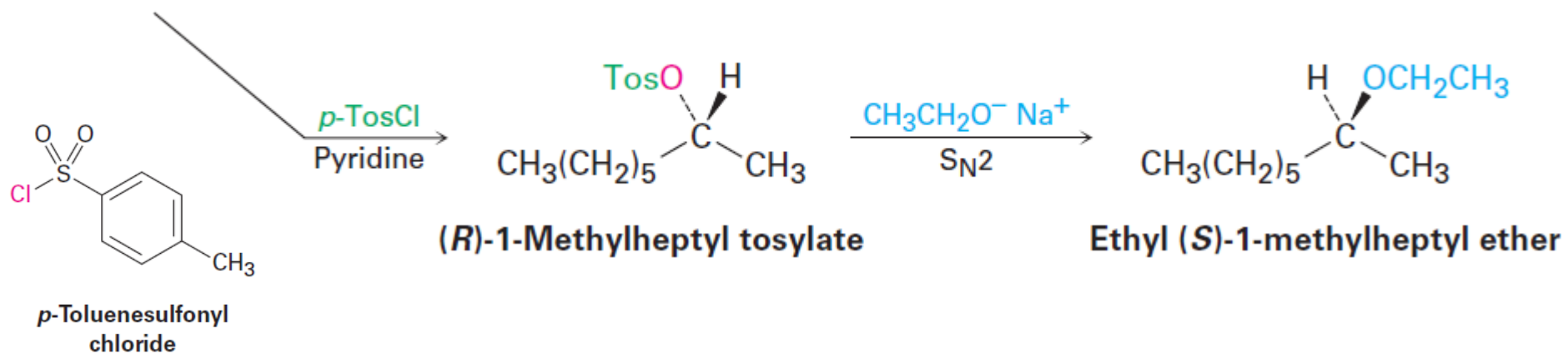
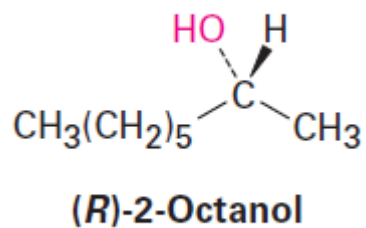
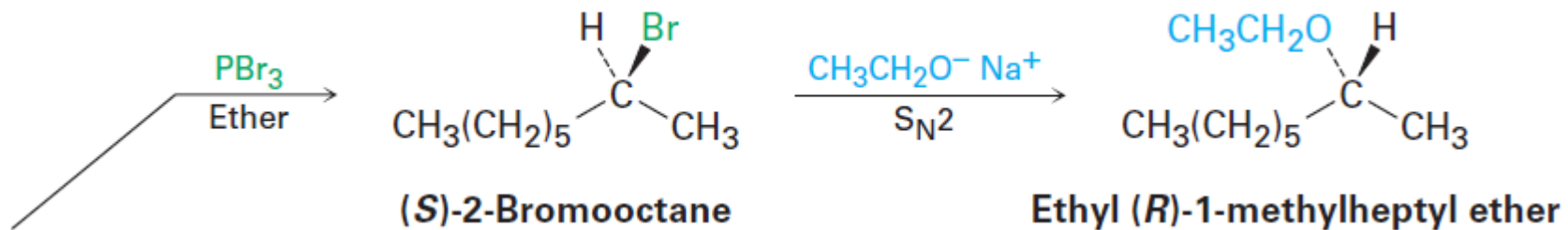
17.6 Reactions of Alcohols Conversion of Alcohols into Alkyl Halides





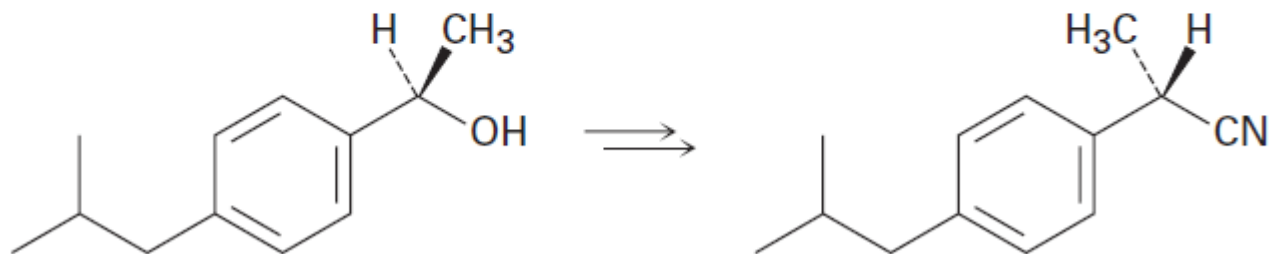
**A 1° or 2°
 alcohol**



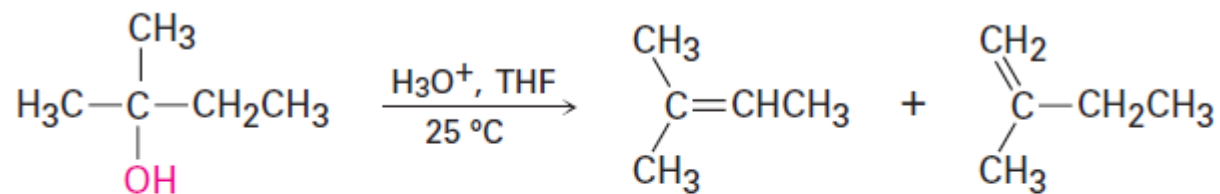


Problem 17.12

How would you carry out the following transformation, a step used in the commercial synthesis of (S)-ibuprofen?



Dehydration of Alcohols to Yield Alkenes



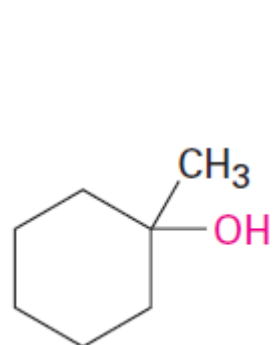
2-Methyl-2-butanol

2-Methyl-2-butene
(trisubstituted)

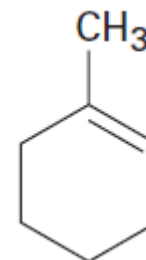
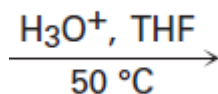
Major product

2-Methyl-1-butene
(disubstituted)

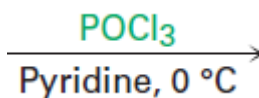
Minor product



1-Methylcyclohexanol

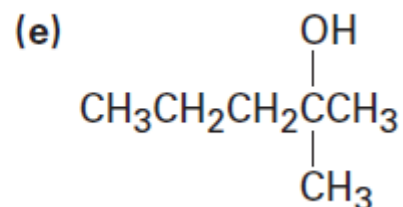
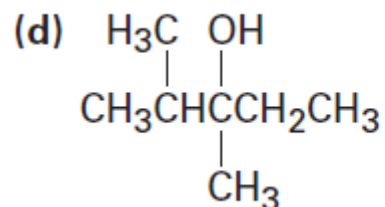
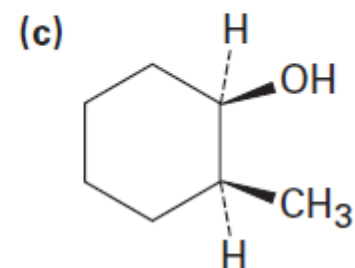
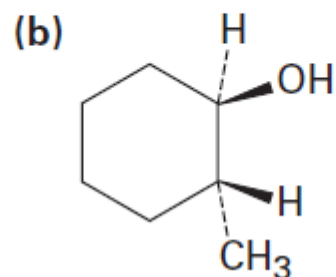
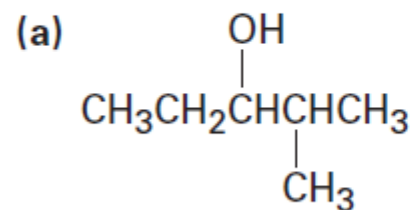


1-Methylcyclohexene (91%)



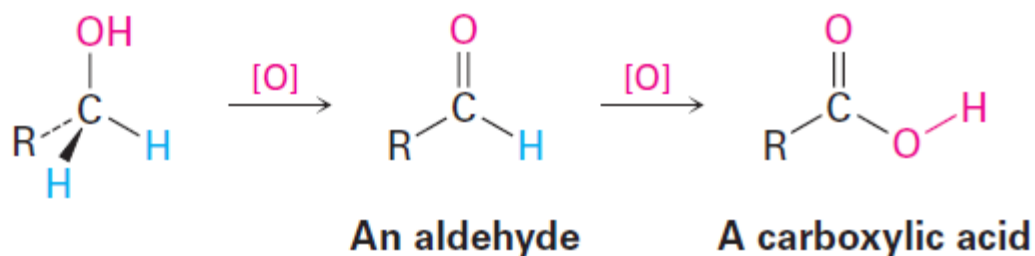
Problem 17.13

What product(s) would you expect from dehydration of the following alcohols with POCl_3 in pyridine? Indicate the major product in each case.

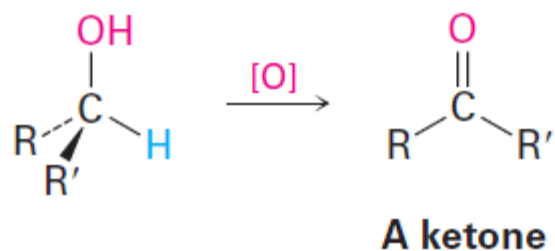


17.7 Oxidation of Alcohols

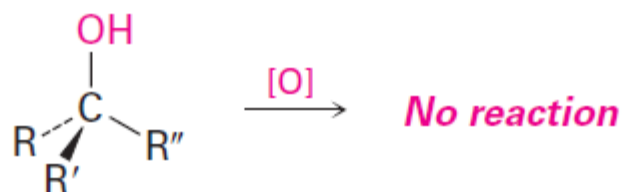
Primary alcohol

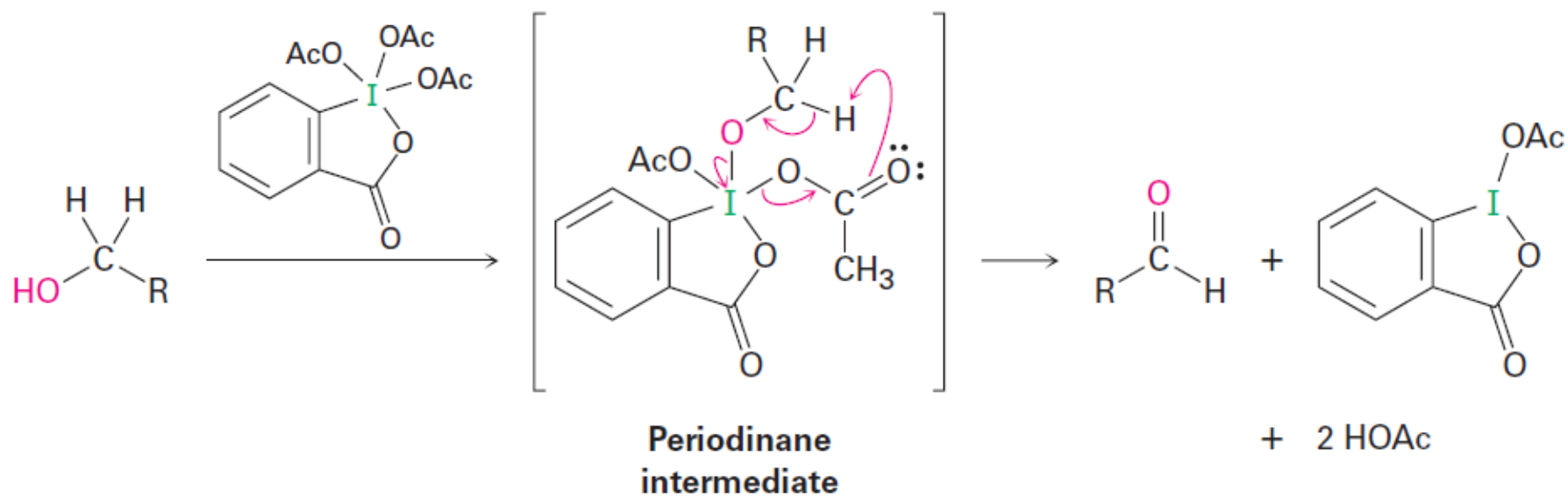
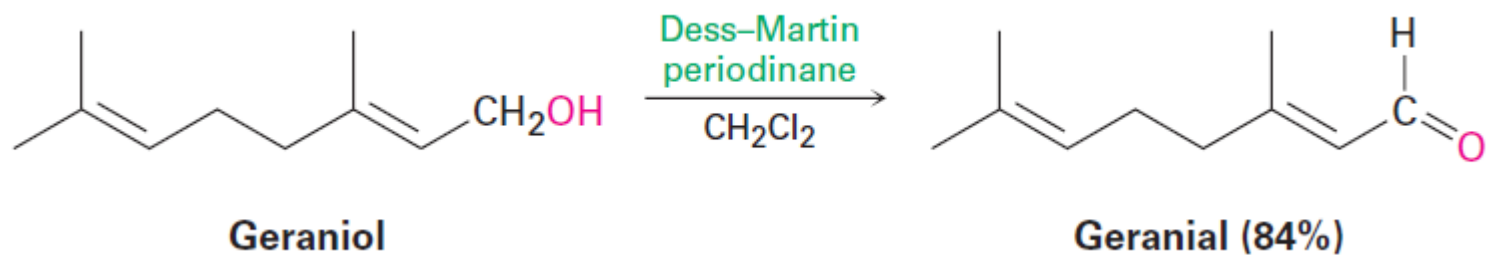


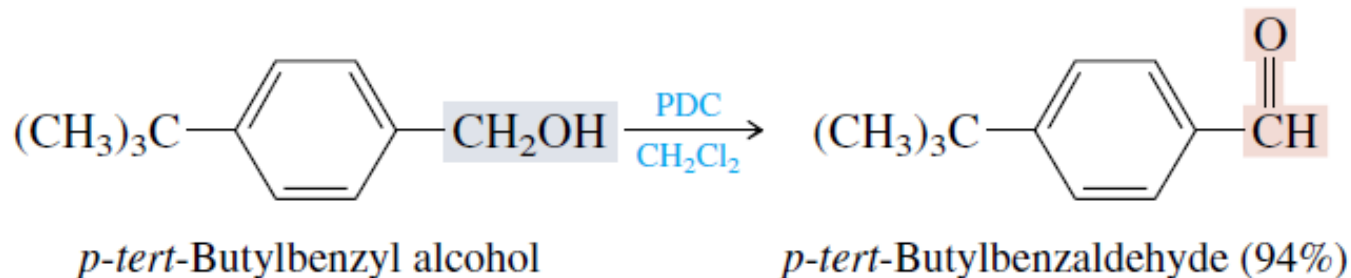
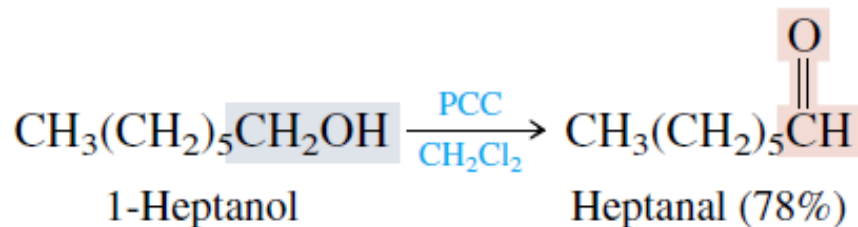
Secondary alcohol



Tertiary alcohol

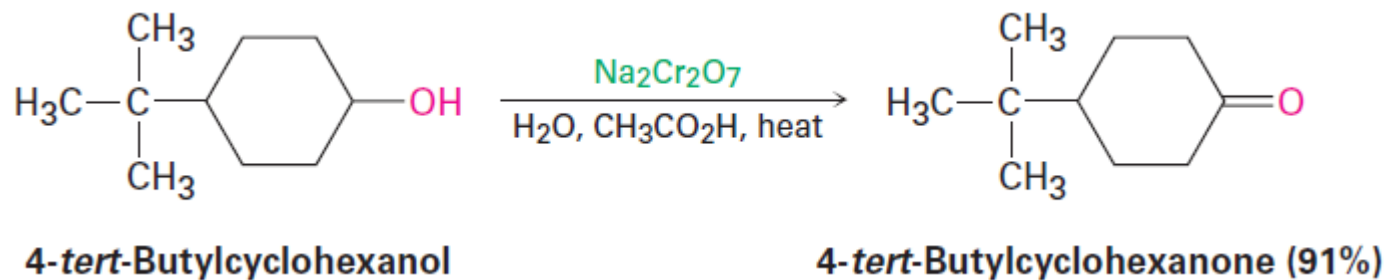
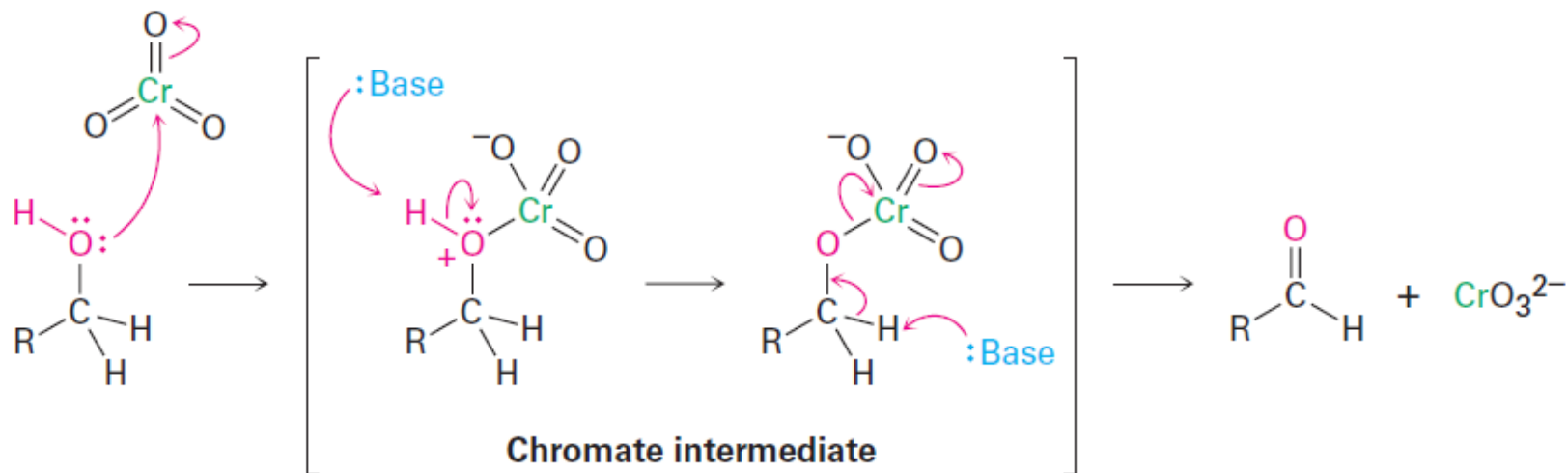
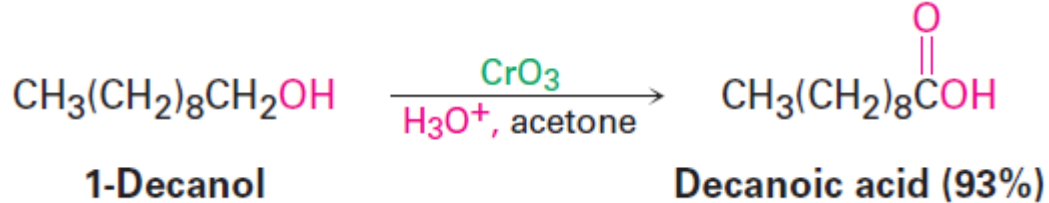






pyridinium chlorochromate (PCC), $\text{C}_5\text{H}_5\text{NH}^+ \text{ClCrO}_3^-$.

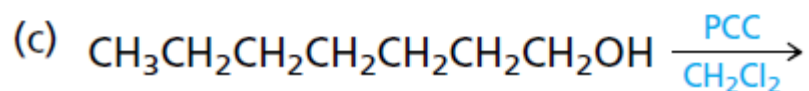
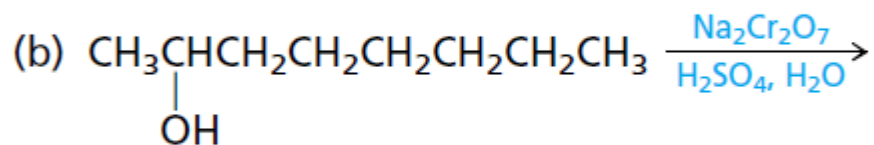
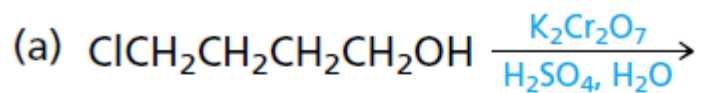
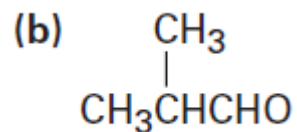
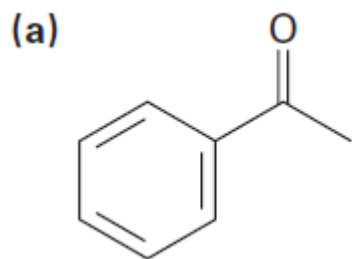
pyridinium dichromate (PDC), $(\text{C}_5\text{H}_5\text{NH})_2^{2+} \text{Cr}_2\text{O}_7^{2-}$.



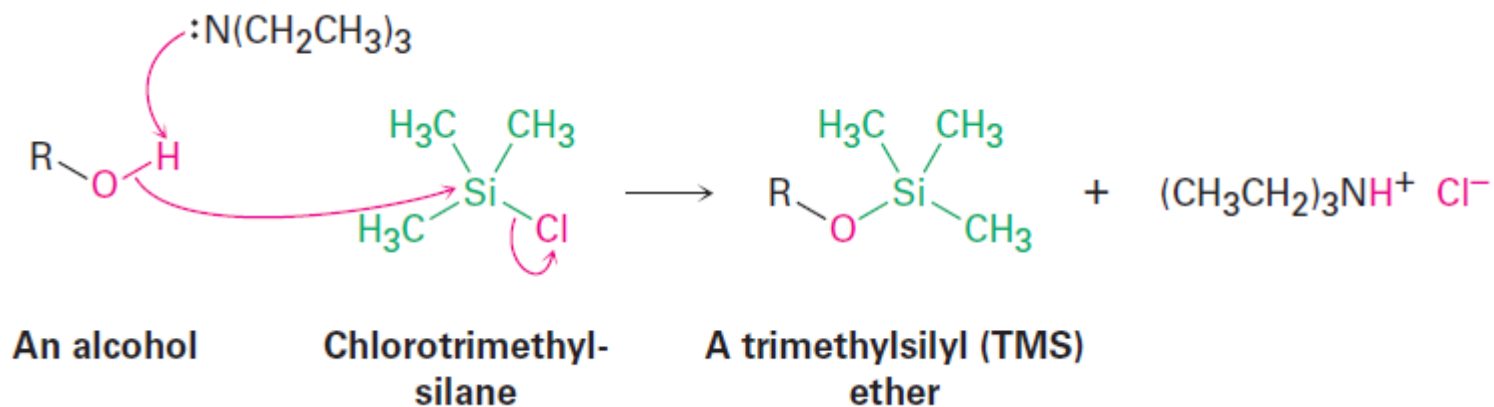
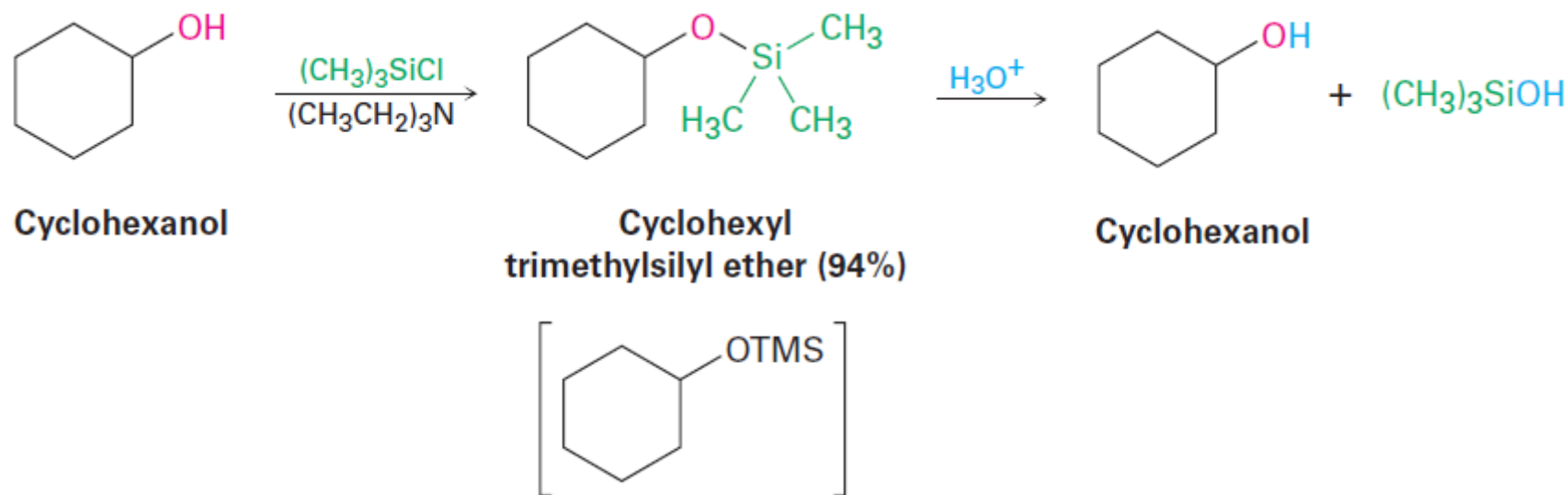
| | | | | |
|---|-----------------|---|---|------------------------------------|
| Primary, RCH_2OH | Aldehyde | $\text{R}\overset{\text{O}}{\parallel}\text{CH}$ | PCC* PDC | Dess-Martin periodinane |
| Primary, RCH_2OH | Carboxylic acid | $\text{R}\overset{\text{O}}{\parallel}\text{COH}$ | $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O H_2CrO_4 | |
| Secondary, RCHR' OH | Ketone | $\text{RCR}'\overset{\text{O}}{\parallel}$ | PCC PDC $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O H_2CrO_4 | |

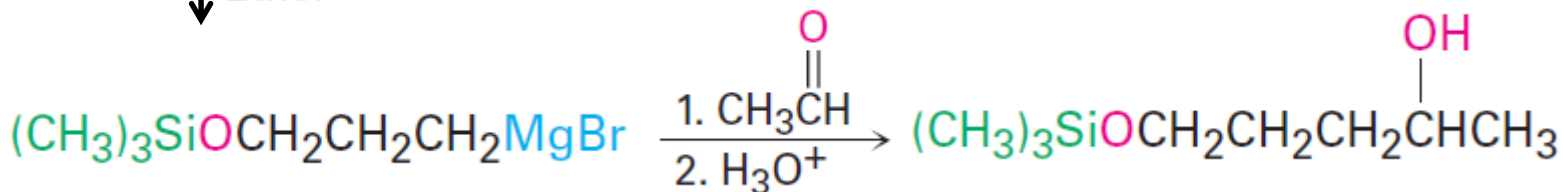
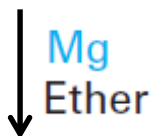
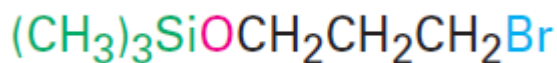
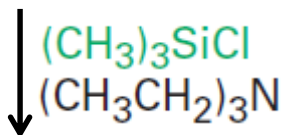
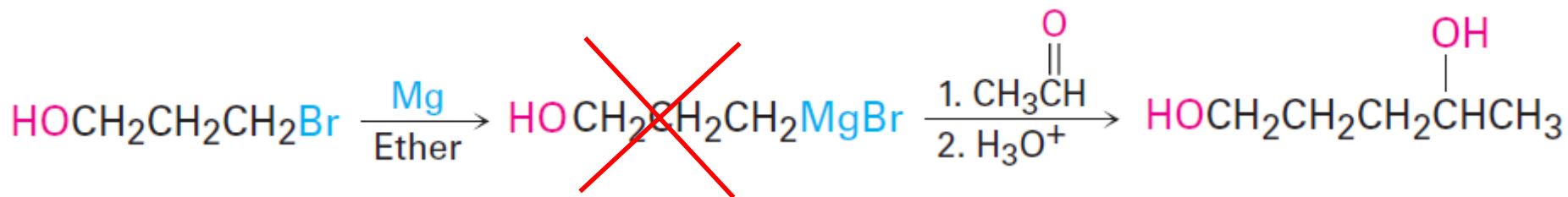
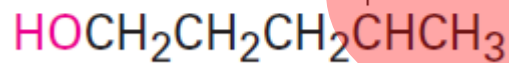
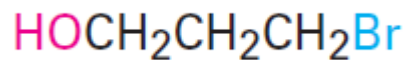
Problem 17.14

What alcohols would give the following products on oxidation?



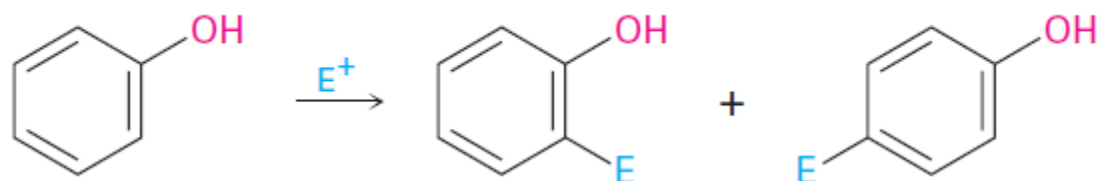
17.8 Protection of Alcohols



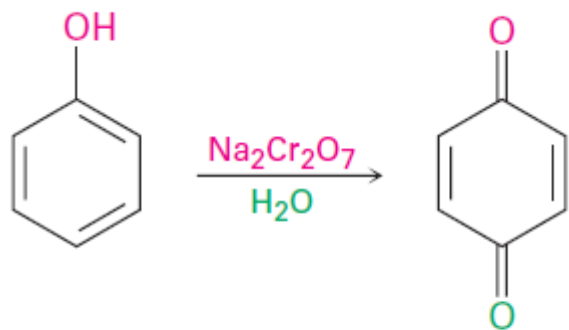


17.10 Reactions of Phenols

Electrophilic Aromatic Substitution Reactions

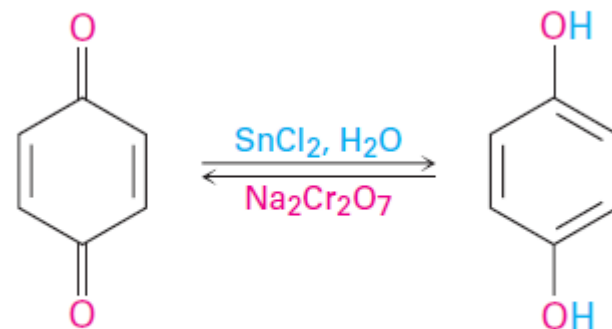


Oxidation of Phenols: Quinones



Phenol

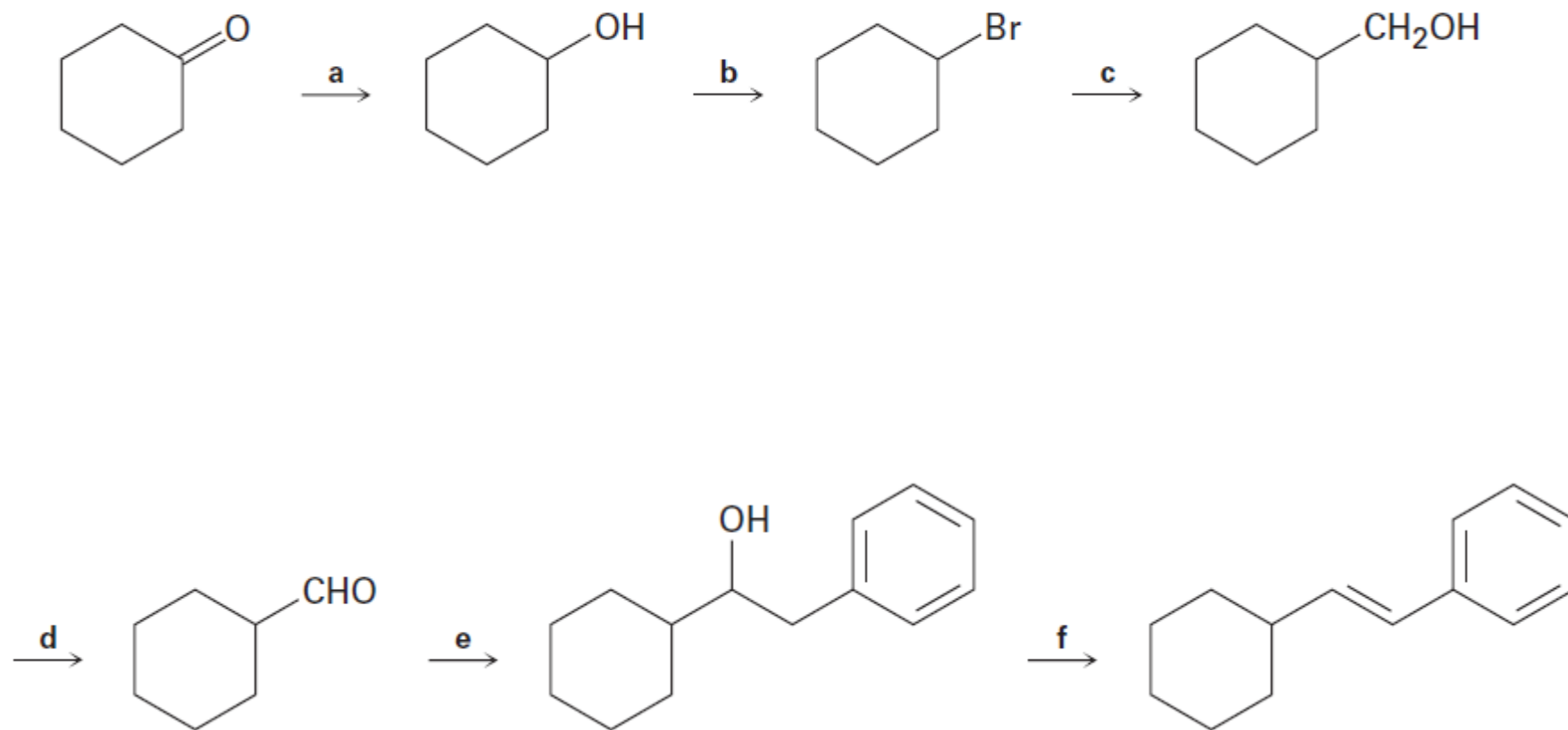
Benzoquinone (79%)



Benzoquinone

Hydroquinone

17.65 Identify the reagents a–f in the following scheme:



17.3 Preparation of Alcohols: A Review

