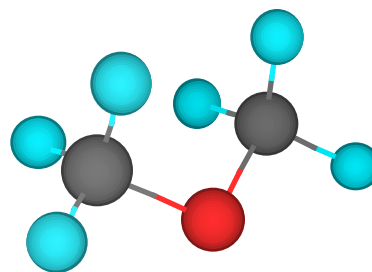
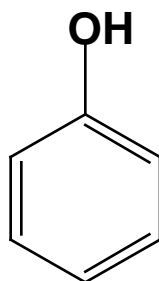
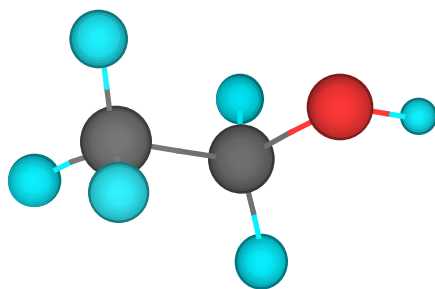


9



Alcohols, Phenols, and Ethers

CHAPTER SUMMARY

9.1 Structure and Nomenclature

Alcohols, phenols, and ethers can be thought of as derivatives of water. Replacement of one hydrogen on water results in an **alcohol**, and replacement of both gives an **ether**. In **phenols**, one hydrogen of water is replaced by an aromatic ring. A **primary alcohol** has only one alkyl group attached to the carbon bearing the OH; a **secondary alcohol** has two and a **tertiary alcohol** has three.

A. IUPAC Nomenclature of Alcohols

The base name of an alcohol is derived from the Greek for the longest continuous carbon chain followed by the suffix **-ol**. If the alcohol is unsaturated, the double or triple bonds are designated with the suffixes -

en and **-yn** respectively. The carbon chain is numbered to give the lowest number to the alcohol group.

B. IUPAC Nomenclature of Ethers

The name of an ether is based on the longest carbon chain connected to the ether oxygen. The other alkyl group is named as an **alkoxy group**.

C. IUPAC Nomenclature of Phenols

Phenols are named according to the rules for a substituted benzene ring, except that the family name is phenol rather than benzene. Numbering of the ring begins with the hydroxyl group.

D. Common Nomenclature of Alcohols and Ethers

In common nomenclature, alcohols are often named with the alkyl group followed by alcohol (such as ethyl alcohol) and ethers are named using the names of the two alkyl groups followed by ether (such as diethyl ether).

9.2 Physical Properties - Hydrogen Bonding

Hydrogen bonding causes the boiling points of alcohols to be higher than those of compounds of similar molecular weight in other functional groups. Hydrogen bonding is an electrostatic attraction between the partially positive OH hydrogen of one molecule and a non-bonding electron-pair on the oxygen of another molecule. Because of hydrogen bonding, low molecular weight alcohols are water soluble. Hydrogen bonding occurs in molecules where hydrogen is bonded to a strongly electronegative element such as nitrogen, oxygen, or fluorine.

CONNECTIONS 9.1 Methyl, Ethyl, and Isopropyl Alcohols

9.3 Uses of Alcohols, Ethers, and Phenols

A. Alcohols

Methyl alcohol is used in industrial synthesis, as a solvent, and as a clean burning fuel. **Ethyl alcohol** is beverage alcohol; it is also used as a solvent and antiseptic. **Isopropyl alcohol** is rubbing alcohol.

B. Polyhydric Alcohols

Ethylene glycol is antifreeze and **glycerol** is a humectant. Glycerol can be converted into the explosive nitroglycerin.

C. Diethyl Ether

Diethyl ether is an important solvent and was once widely used as a general anesthetic.

D. Phenols

Phenol and many of its derivatives are used in over-the-counter medications as disinfectants and local anesthetics. They are also used as antioxidants, preservatives and photographic developers.

CONNECTIONS 9.2 Neurotransmitters - The Heart of the Matter**9.4 Preparations of Alcohols and Ethers****A. Hydration of Alkenes****B. Nucleophilic Substitution****C. Reduction of Aldehydes and Ketones****9.5 Reaction Sites in Alcohols, Phenols, and Ethers**

The **reaction sites** in alcohols, phenols, and ethers are the **polar bonds** (carbon-oxygen and oxygen-hydrogen) and the **lone pairs of electrons** on the oxygen. The unshared electron-pairs on alcohols and ethers make these compounds **Lewis bases**. Oxonium ions, in which the oxygen has three bonds and is positive, result from the protonation of alcohols and ethers. Most reactions of alcohols involve the **O-H bond, C-O bond, or both**.

9.6 Reactions Involving the O-H Bond of Alcohols and Phenols**A. Relative Acidities of Alcohols and Phenols**

The polar O-H bond of alcohols makes them weak acids. By the **Bronsted-Lowry** definition, acids are hydrogen ion donors and bases are hydrogen ion acceptors in chemical reactions. **Strong acids** are 100% ionized in water and **weak acids** are only partially ionized. Weak acids establish an equilibrium in water between their ionized and un-ionized forms. This equilibrium and the strength of an acid is described by the **acidity constant, K_a** . K_a is defined as the concentrations of the ionized forms of the acids (H_3O^+ and A^-) divided by the un-ionized form (HA). The stronger the acid, the greater will be the value of the acidity constant. Acid strengths are also expressed by **p K_a** , which is defined as the negative logarithm of K_a . Numerically smaller p K_a 's signify stronger acids and larger p K_a 's, weaker acids. Approximate p K_a 's include 50 for alkanes, 25 for terminal alkynes, 16 for alcohols, 10 for phenols, 5 for carboxylic acids, and -2 or so for strong inorganic acids.

The ion or molecule formed by the loss of a proton from an acid is the **conjugate base**. Strong acids form weak conjugate bases and weak acids form strong conjugate bases.

Phenols are one million to one billion times more acidic than alcohols and this is the characteristic property that distinguishes them. Phenols will react with the base sodium hydroxide but alcohols will not. The acidity of phenols is explained by **resonance stabilization** of the **phenoxide ion**; the negative charge is dispersed throughout the benzene ring as opposed to being concentrated on the oxygen as it is in the **alkoxide ion**. **Electron-withdrawing groups** on the benzene ring increase the acidity of phenols.

B. Reactions of Alcohols with Sodium Metal:

Reaction of the O-H Bond

Although alcohols will not react with sodium hydroxide as do phenols, they will react with sodium metal to form alkoxide ions and hydrogen gas.

C. Formation of Esters: Reaction of the O-H Bond

Alcohols will also react with organic and inorganic acids to form **esters**.

CONNECTIONS 9.3 Insecticides and Nerve Gases

9.7 Reactions of Alcohols and Ethers with Hydrogen Halides: Reaction of the C-O Bond by Nucleophilic Substitution

A. Reactions of Alcohols with Hydrogen Halides:

S_N1 and S_N2 Mechanisms

Alcohols react with hydrogen halides by nucleophilic substitution. The OH group is replaced by a halogen; water is the by-product. In the reaction mechanism, the first step involves formation of an **oxonium ion** by the Lewis acid-base reaction of the hydrogen ion of the hydrogen halide and alcohol oxygen. The rest of the reaction occurs by one of the nucleophilic substitution mechanisms depending on structure of the alcohol. In the **S_N2** reaction, the next step involves displacement of the water molecule by halide ion to form the final products. In the **S_N1** reaction, the water molecule departs leaving a carbocation that is neutralized by halide ion. The S_N2 reaction with an optically active alcohol proceeds with **inversion of configuration** whereas the S_N1 reaction produces **racemization**. Tertiary and secondary alcohols react by the S_N1 mechanism because they can form relatively stable intermediate carbocations; primary alcohols react by the S_N2 mechanism that does not require a carbocation. The relative rates of reaction are **$3^\circ > 2^\circ > 1^\circ$** .

B. Methods for Converting Alcohols to Alkyl Halides:

Reaction of the C-O Bond

Alcohols can also be converted to alkyl halides using **thionyl chloride** or **phosphorus trihalides**.

C. Reactions of Ethers with Hydrogen Halides:

S_N1 and S_N2 Mechanisms

Ethers react with hydrogen halides to form an alkyl halide and an alcohol. The alcohol in turn can react to form a second molecule of alkyl halide and water. Thus in the presence of two mole-equivalents of hydrogen halide, an ether produces two moles of alkyl halide and one of water. The reaction mechanism is analogous to that of alcohols and hydrogen halides. The ether is protonated first to form an oxonium ion. In

the **S_N2** reaction, the next step involves displacement of the alcohol molecule by halide ion to form the final products. In the **S_N1** reaction, the alcohol molecule departs leaving a carbocation that is neutralized by halide ion. Tertiary and secondary ethers react by the **S_N1** mechanism and primary and methyl ether carbons react by **S_N2**.

9.8 Dehydration of Alcohols by E₁ Elimination: Reaction of the C-O Bond

Alcohols dehydrate in the presence of strong acids such as sulfuric acid. The reaction proceeds via an **E₁ mechanism**. The alcohol oxygen is first protonated to give an oxonium ion which loses water to form a carbocation; subsequent loss of hydrogen ion forms the double bond. When more than one alkene is possible from a dehydration reaction, the more substituted one predominates.

9.9 Oxidation of Alcohols:

Reaction of the C-O and O-H Bonds

Primary alcohols oxidize to carboxylic acids; secondary alcohols oxidize to ketones with chromium trioxide or sodium dichromate. Tertiary alcohols do not oxidize under mild conditions. With **pyridinium chlorochromate (PCC)** the oxidation of primary alcohols can be stopped at **aldehydes**.

CONNECTIONS 9.4 Measuring Blood Alcohol

CONNECTIONS 9.5 Methanol and Ethylene Glycol Poisoning

9.10 Epoxides

Epoxides are three-membered cyclic ethers. The simplest, ethylene oxide is prepared from ethylene and oxygen. Epoxides are prepared more generally from alkenes using a peroxycarboxylic acid.

A. Reactions of Ethylene Oxide

The characteristic chemical property of epoxides is ring-opening reactions initiated by acid or base. Ethylene oxide undergoes such reactions with

water, alcohols, and amines to form commercially important products. The reaction is nucleophilic substitution.

B. Epoxy Resins

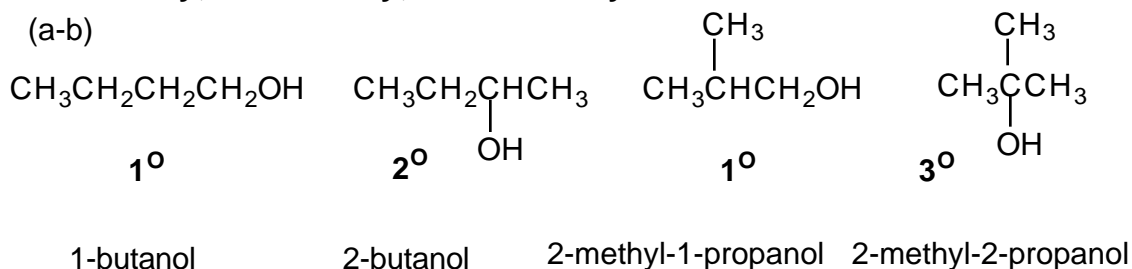
Epoxy resins are polymers with tremendous adhesive properties and are used to bind glass, porcelain, metal, and wood. The production involves a ring opening reaction on the epoxide epichlorohydrin as it reacts with bisphenol A.

9.11 Sulfur Analogues of Alcohols and Ethers

Thiols or alkyl hydrogen sulfides are sulfur analogues of alcohols and **sulfides** are sulfur analogues of ethers. Many of the lower molecular weight examples have strong odors and are naturally found in onions, garlic, and the spray of skunks.

SOLUTIONS TO PROBLEMS

9.1 Primary, Secondary, and Tertiary Alcohols



9.2 Nomenclature of Alcohols

(a) 4-methyl-2-cyclohexenol; (b) 5-bromo-3-hexynol

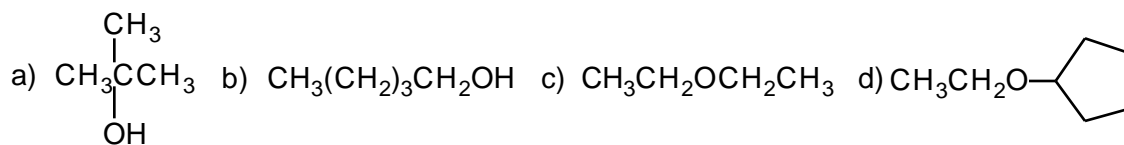
9.3 Nomenclature of Ethers

(a) 1-propoxyheptane; (b) dimethoxymethane; (c) 2-ethoxy-1-ethanol

9.4 Nomenclature of Phenols

(a) meta nitrophenol; (b) para butoxyphenol

9.5 Nomenclature of Alcohols, Phenols, and Ethers



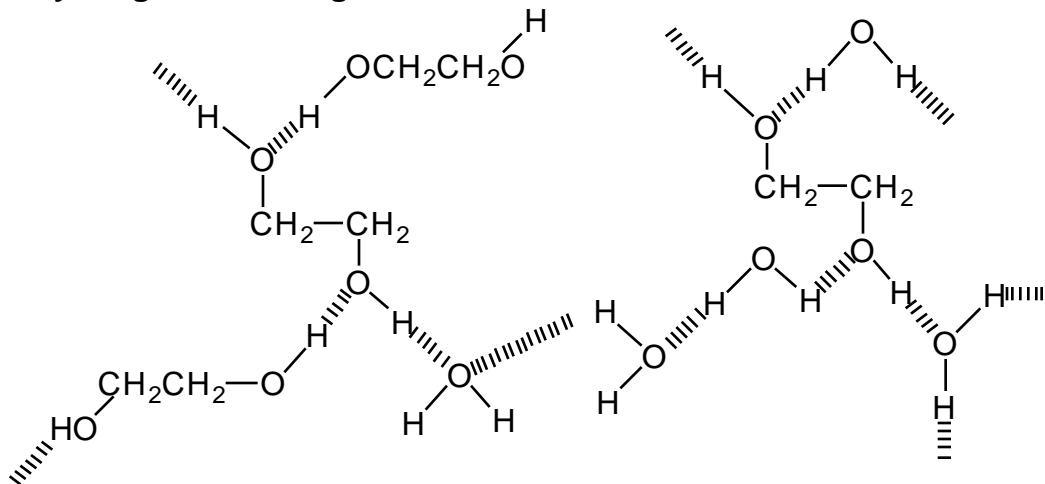
9.6 Physical Properties

Even though the molecular weights of these three compounds are similar, they have very different boiling points. Butane has the lowest boiling point because it is a non-polar compound (only carbon-carbon and carbon-hydrogen bonds) and thus has weak intermolecular attractions. Propanol has an O-H bond and is capable of hydrogen bonding, a phenomenon that causes strong intermolecular attractions and elevated boiling points. 1,2-Ethandiol has two O-H groups and thus greater opportunity for hydrogen bonding; as a result it has a drastically higher boiling point.

9.7 Physical Properties

Ethylbenzene, the third compound and gasoline component, has the lowest boiling point (136°C) because it has only carbon-carbon and carbon-hydrogen bonds and is non-polar. The first compound, rose oil, has the highest boiling point (221°C) because it has an O-H bond and is capable of hydrogen-bonding. The middle compound is an ether; though it is polar because of the C-O-C bonds, it is not capable of hydrogen-bonding and thus has an intermediate boiling point (171°C).

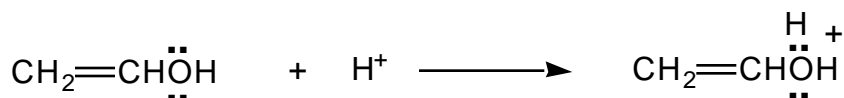
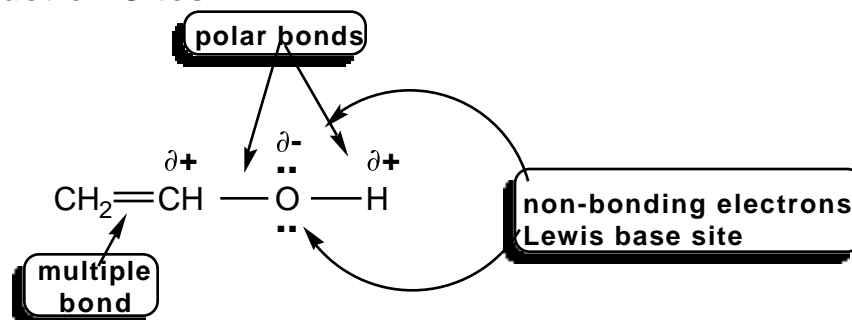
9.8 Hydrogen-Bonding



9.9 Physical Properties and Hydrogen-Bonding

The two compounds are isomers and have the same molecular weight. Butanoic acid has an OH group, is thus capable of hydrogen bonding and has the higher boiling point. Ethyl acetate cannot hydrogen bond..

9.10 Reaction Sites



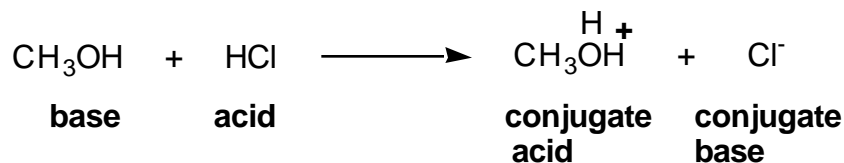
9.11 Relative Acidities

(a) pK_a 's: $11.8 < 6.2 < 3.4$

(b) K_a 's: $9.8 \times 10^{-12} < 6.7 \times 10^{-5} < 3.4 \times 10^{-3}$

(c) $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} < \text{CH}_3\text{CH}_2\text{CO}_2\text{H}$

9.12 Acids and Bases

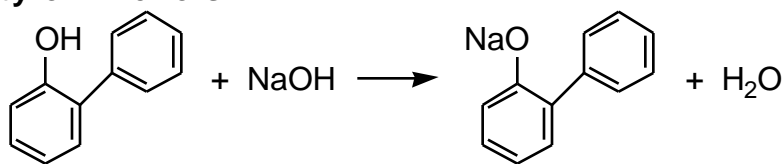


9.13 Relative Acidities

(a) No reaction: the conjugate acid that would be produced, $\text{CH}_3\text{CH}_2\text{OH}_2^+$, is stronger than the original acid, CH_4 . The conjugate base is likewise stronger than the original base. Thus the products of the theoretical neutralization would be more acidic and basic than the original compounds and immediately react to reform them.

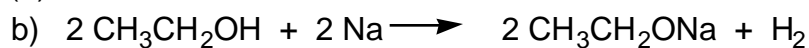
(b) Yes, neutralization would occur: HCl is a stronger acid than the conjugate acid, $\text{CH}_3\text{CO}_2\text{H}$. The conjugate base is weaker than the original base. Thus the two reactants shown are more reactive, i.e. more acidic and basic, than the theoretical products of the reaction.

9.14 Acidity of Phenols

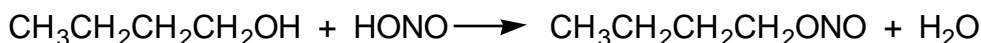


9.15 Reactions of the O-H Bond of Alcohols: Acidity

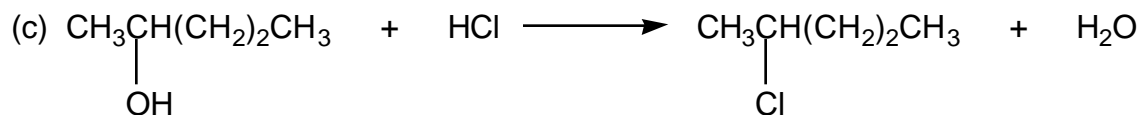
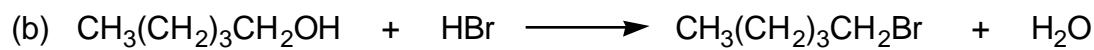
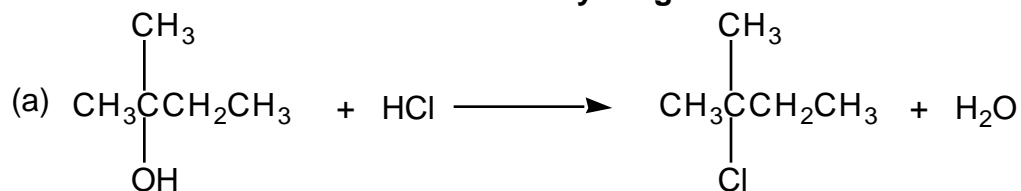
(a) No reaction with NaOH



9.16 Reactions of the O-H Bond of Alcohols: Ester Formation



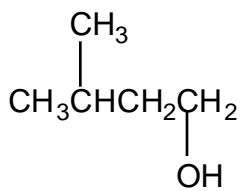
9.17 Reactions of Alcohols with Hydrogen Halides



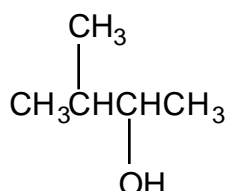
9.18 Reactions of Alcohols with Hydrogen Halides: Relative Rates

The compounds in Problem 9.17 show relative reactions rates in the following order: **a > c > b** since the relative rates of reaction of alcohols with hydrogen halides is **3° > 2° > 1°**. S_N2: (b); S_N1: (a) and (c).

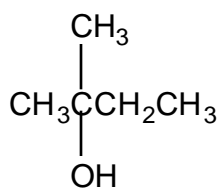
9.19 Lucas Reagent

Rate of Reaction with the Lucas Reagent

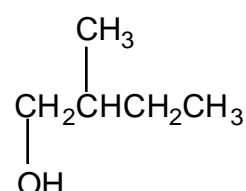
1° Alcohol one
hour with heat



2° Alcohol
5-15 minutes

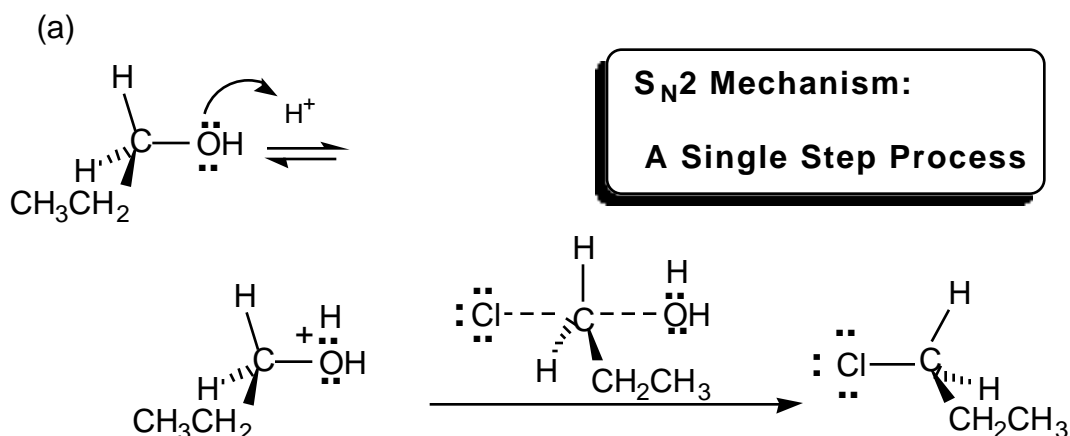


3° Alcohol
instantaneous



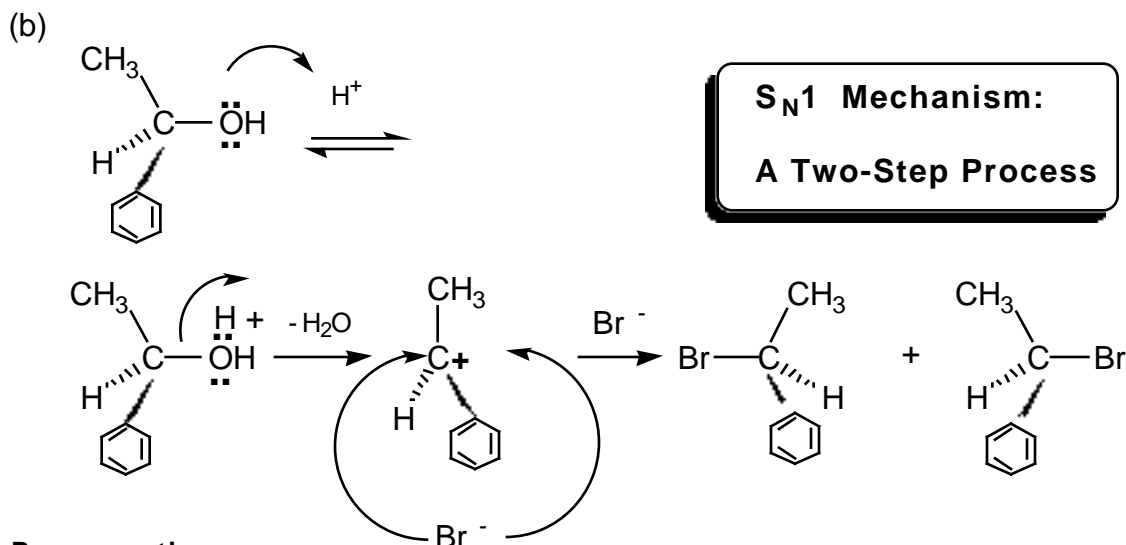
1° Alcohol one
hour with heat

9.20 Nucleophilic Substitution Mechanisms



Primary alcohol protonated to form primary oxonium ion. Oxonium ion is attacked by bromide.

Transition state showing bromide displacing water molecule from the opposite side to form final product.

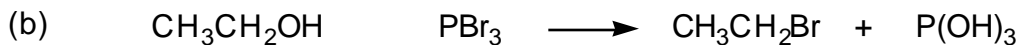
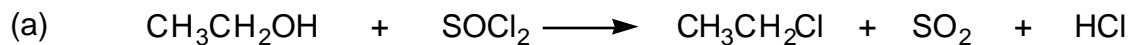


Pure enantiomer; optically active alcohol is protonated to optically active oxonium ion.

Nucleophile, Br⁻ attacks planar carbocation from either side.

Both inversion and retention of configuration occur equally. A pair of enantiomers results. This is an optically inactive racemic mixture.

9.21 Preparation of Alkyl Halides

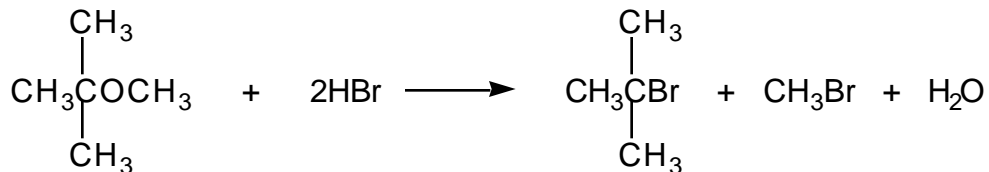
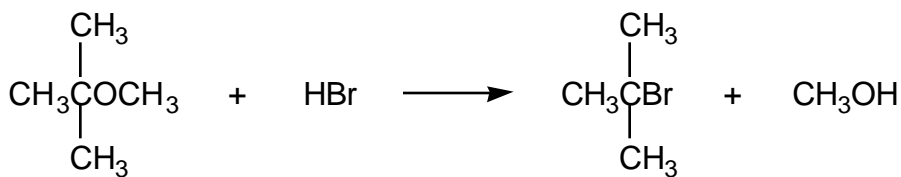
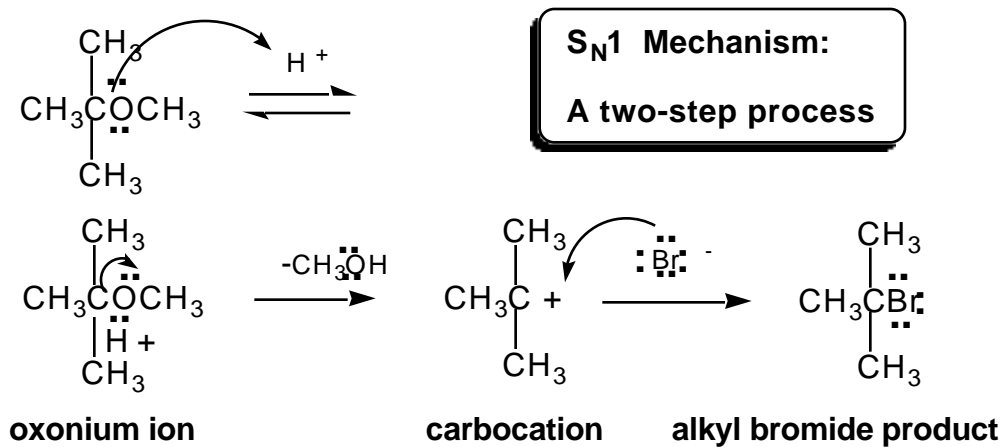


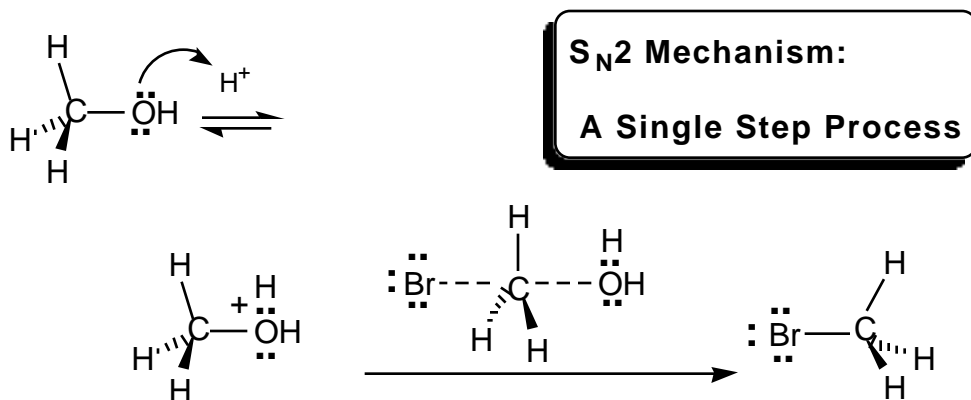
9.22 Preparation of Alkyl Halides

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ can be converted to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

using the following reagents: (1) HCl with ZnCl_2
 (2) SOCl_2
 (3) PCl_3

9.23 Reaction of Ethers with Hydrogen Halides

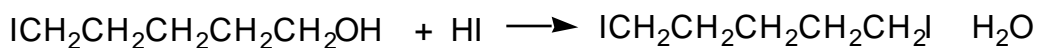
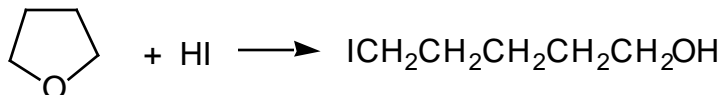
9.24 $\text{S}_{\text{N}}1$ Mechanism: Ethers and Hydrogen Halides



Primary alcohol protonated to form primary oxonium ion. Oxonium ion is attacked by bromide.

Transition state showing bromide displacing water molecule from the opposite side to form the final product.

9.25 Reactions of Ethers with Hydrogen Halides



9.26 E₁ and S_N1 Mechanisms

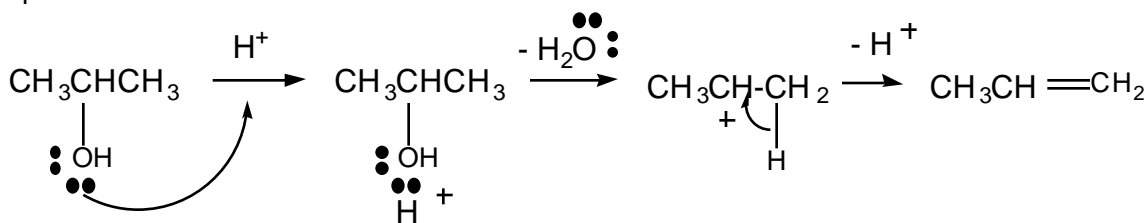
In all three mechanisms:

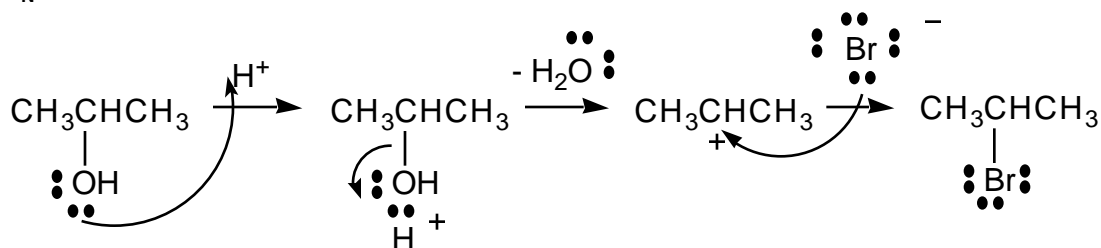
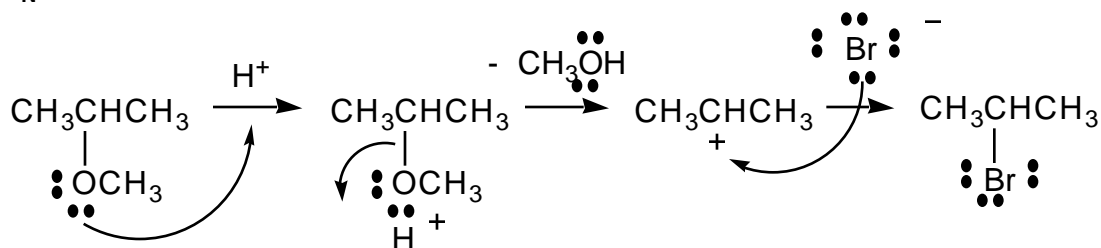
First step: alcohol or ether acts as Lewis base and reacts with hydrogen ion to form an oxonium ion.

Second step: water or methanol leaves and a carbocation is the result.

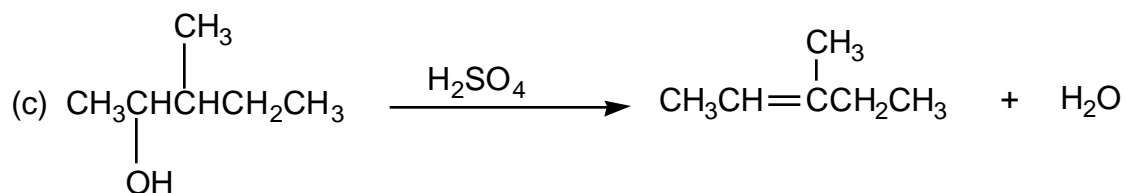
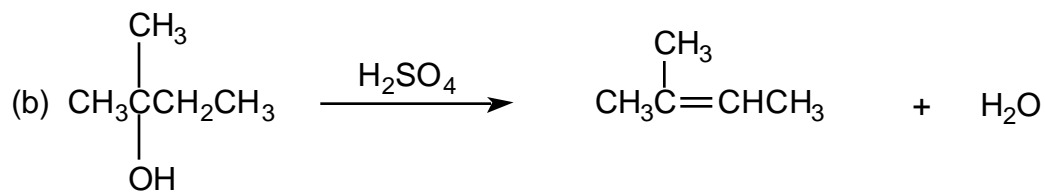
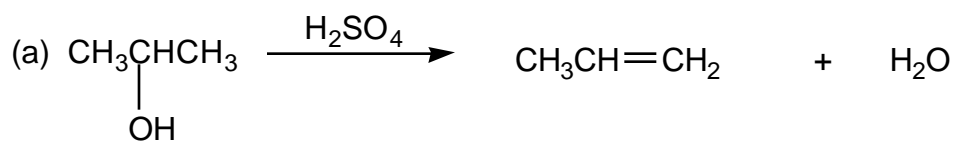
Third step: the carbocation can be neutralized by the loss of a hydrogen ion in the elimination reaction or by bromide in the substitution reactions.

E₁

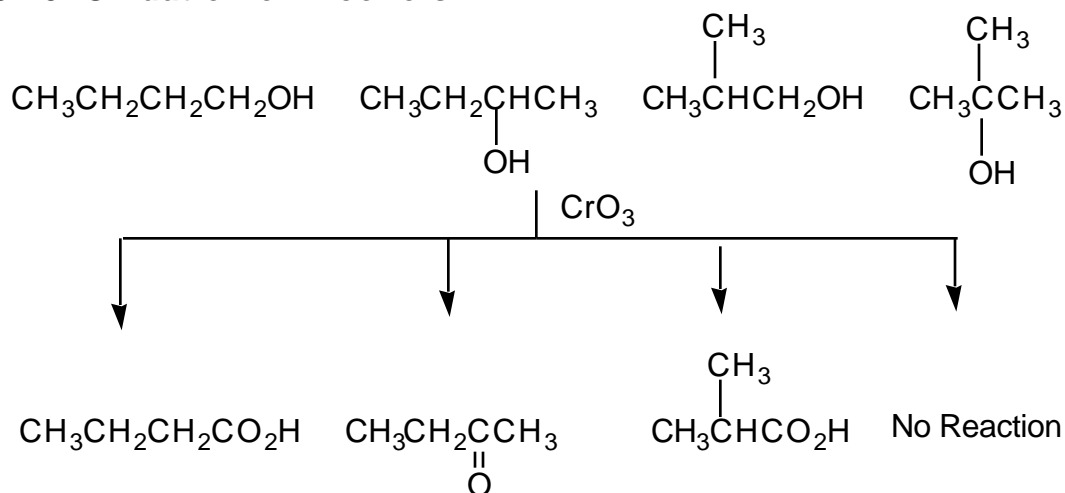


S_N1  S_N1 **9.27 Dehydration Reactions**

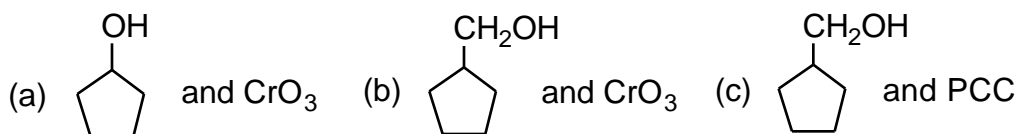
Focus your attention on the OH; remove it and a hydrogen from an adjacent carbon. The double bond forms between these two carbons. When more than one elimination product is possible, the most substituted alkene forms predominantly (Section 4.5B).



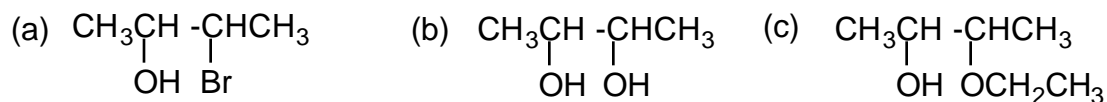
9.28 Oxidation of Alcohols



9.29 Oxidation of Alcohols

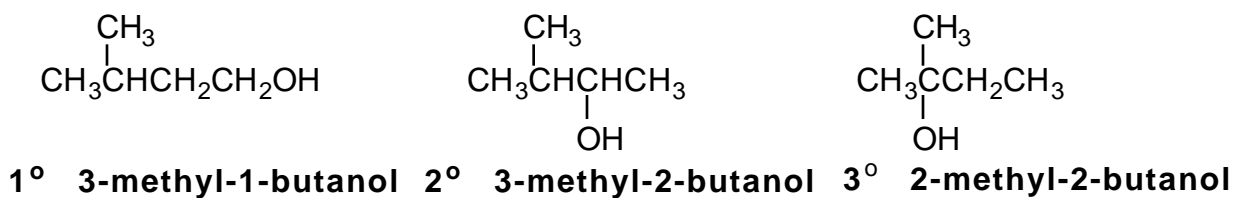
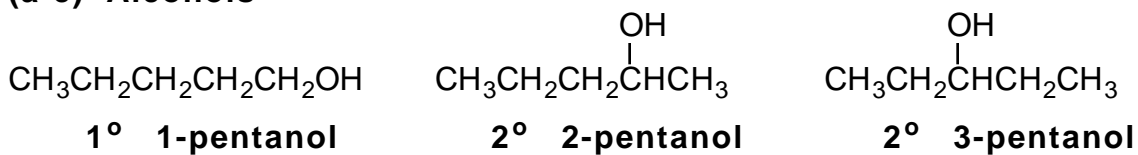


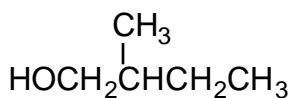
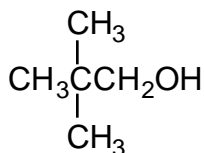
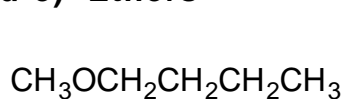
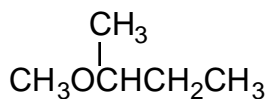
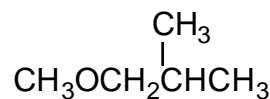
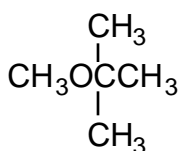
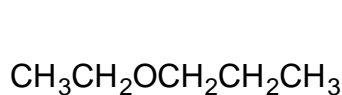
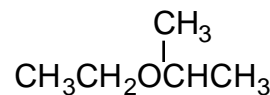
9.30 Reactions of Epoxides



9.31 Isomerism and Nomenclature: Section 9.1

(a-c) Alcohols



**1° 2-methyl-1-butanol****1° 2,2-dimethyl-1-propanol****(d-e) Ethers****1-methoxybutane****2-methoxybutane****1-methoxy-2-methylpropane****2-methoxy-2-methylpropane****1-ethoxypropane****2-ethoxypropane****9.32 IUPAC Nomenclature of Alcohols:** Section 9.1A

- (a) 1-nonanol; (b) 2-hexanol; (c) 2-methyl-2-butanol; (d) cyclopentanol;
 (e) 3,3-dimethyl-1-butanol; (f) 4-ethyl-4-methyl-1-cyclohexanol;
 (g) 2,2,3-trimethyl-3-pentanol; (h) 2,5-dimethyl-2-hexanol

9.33 IUPAC Nomenclature of Alcohols: Section 9.1A

- (a) 4,5-dibromo-3-hexanol; (b) 5-methyl-3-heptanol; (c) 1,5-pentandiol;
 (d) 1,3,5-cyclohexanetriol

9.34 IUPAC Nomenclature of Unsaturated Alcohols: Section 9.1A

- (a) 3-buten-2-ol; (b) 4-ethyl-2-hexyn-1-ol; (c) 2,4-hexadien-1,6-diol;
 (d) 3-cyclopenten-1-ol; (e) 2-phenyl-1-ethanol; (f) 1-hexyn-4-en-3-ol

9.35 IUPAC Nomenclature of Ethers: Section 9.1B

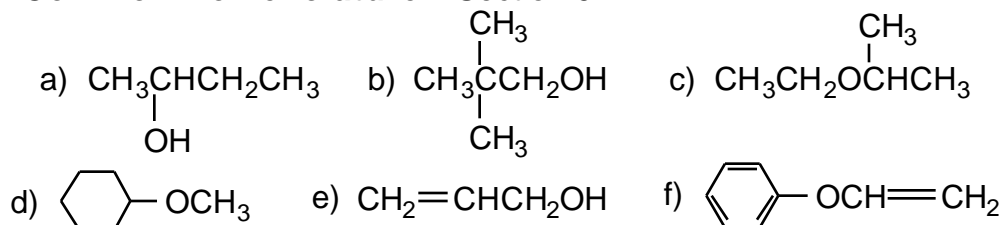
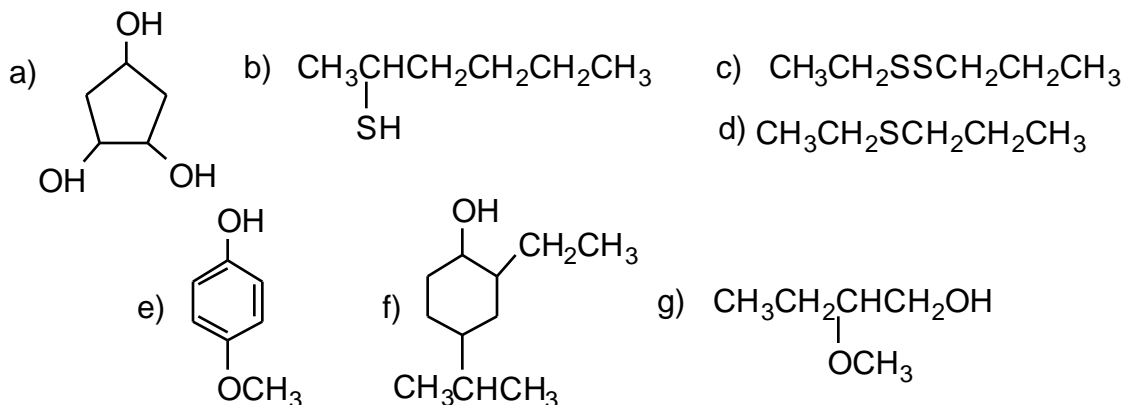
- (a) methoxyethane; (b) ethoxyethane; (c) 1-ethoxy-6-methoxyhexane;
 (d) propoxycyclopentane; (e) methoxycyclopropane

9.36 IUPAC Nomenclature of Ethers: Section 9.1B

- (a) tetramethoxymethane; (b) 3-methoxy-1-propanol; (c) 1-ethoxypropene;
 (d) 4-methoxy-2-buten-1-ol

9.37 IUPAC Nomenclature of Phenols: Section 9.1C

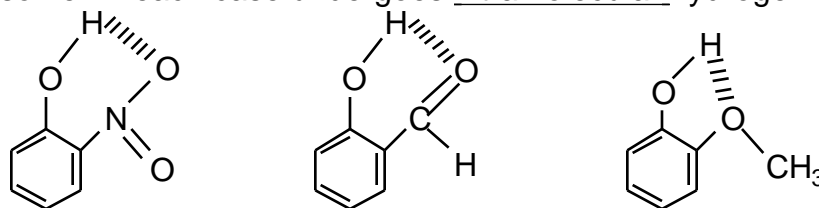
- (a) 2-methylphenol; (b) 3-bromophenol; (c) 4-ethylphenol;
 (ortho, meta, and para in a,b,c respectively is correct also)
 d) 4-methoxy-2-nitrophenol

9.38 Common Nomenclature: Section 9.1D**9.39 IUPAC Nomenclature:** Section 9.1**9.40 Physical Properties:** Sections 2.9 and 9.2

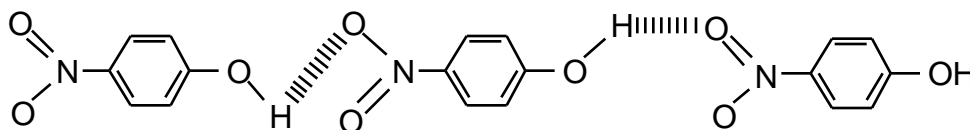
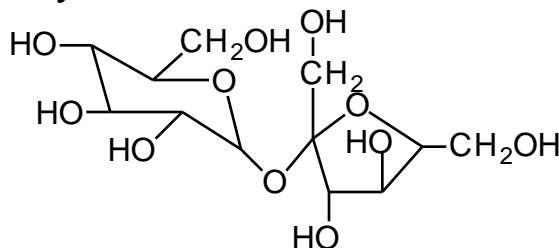
- (a) $\text{I} < \text{II} < \text{III}$ increasing molecular weight in homologous series
 (b) $\text{III} < \text{II} < \text{I}$ more OH groups and thus more hydrogen bonding
 (c) $\text{I} < \text{II} < \text{III}$ increasing number OH groups, increasing hydrogen bonding
 (d) $\text{III} < \text{II} < \text{I}$ increasing number OH groups, increasing hydrogen bonding
 (e) $\text{III} < \text{II} < \text{I}$ increasing number N-H bonds, increasing hydrogen bonding
 (f) $\text{II} < \text{I}$ no hydrogen bonding in II; I has OH and hydrogen bonding
 (g) $\text{III} < \text{II} < \text{I}$ OH bond more polar than NH; OH further polarized by C=O
 (h) $\text{II} < \text{I} < \text{III}$ II is non-polar; I is polar but no hydrogen bonding; III has OH and thus hydrogen bonding
 (i) $\text{III} < \text{I} < \text{II}$ II has strongest hydrogen bonding due to C=O next to OH; III has no hydrogen bonding.
 (j) $\text{I} < \text{II} < \text{III} < \text{IV} < \text{V} < \text{VI}$ increasing molecular weight

9.41 Physical Properties: Section 9.2

The ortho isomer in each case undergoes intramolecular hydrogen bonding.



Because of this, the attractions between molecules are diminished and boiling points are lower than might be expected. The relationship between the two substituents is not favorable for intramolecular hydrogen bonding in the para compounds, however. Thus, intermolecular hydrogen bonding occurs (as shown with p-nitrophenol) increasing attractions between molecules and thus the boiling points.

**9.42 Water Solubility:** Section 9.2

Sucrose has 12 carbons; there are OH groups on eight of them. This allows for tremendous hydrogen bonding with water and thus high water solubility.

9.43 Water Solubility: Section 9.2

(a) **hexanol < pentanol < ethanol:** increasing ratio of OH to hydrocarbon as boiling points increase.

(b) **pentane < heptanol < propanol:** pentane has no OH and cannot hydrogen bond to water; propanol has a higher ratio of OH to hydrocarbon than heptanol, is more like water and more water soluble.

(c) **hexane < hexanol < 1,2-ethanediol:** hexane has no OH and no hydrogen bonding; hexanol can hydrogen bond with water but has only one OH for all six carbons and has only slight water solubility; ethanediol has an OH on each carbon and is infinitely soluble in water.

(d) **pentane < ethoxyethane < butanol**: these compounds have similar molecular weights but the first two have no OH and thus no hydrogen bonding; the second is polar and has some slight water solubility and butanol has an OH and thus can hydrogen bond with water.

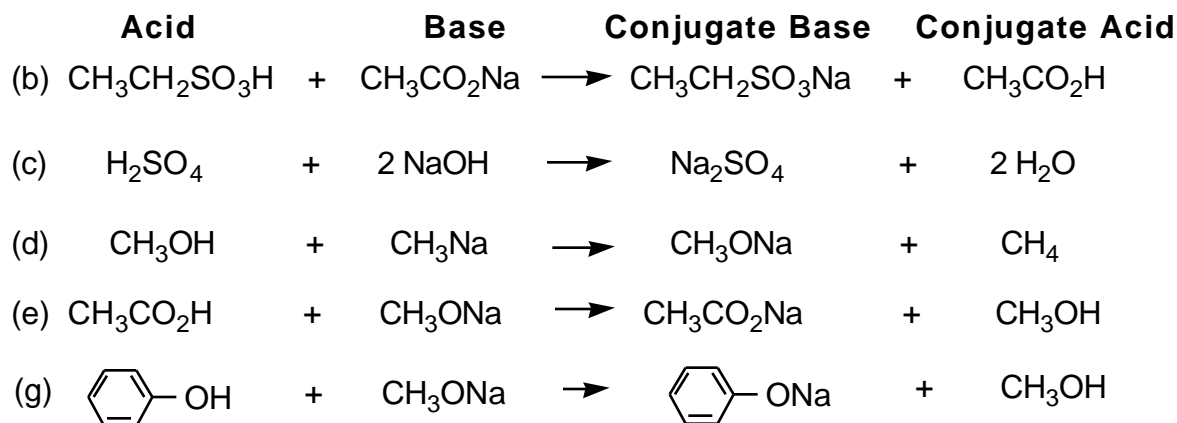
9.44 Acidity: Section 9.6A

(a) **No**: the conjugate acid and base are stronger than the original acid and base

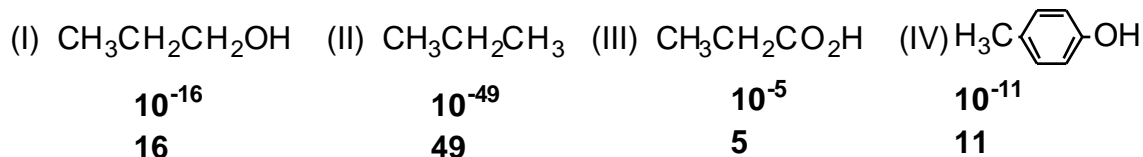
(b) **Yes**: the original acid and base are stronger than the conjugate forms

(c) **Yes**; (d) **Yes**; (e) **Yes**; (f) **No**; (g) **Yes**; (h) **No**

9.45 Acid Base Neutralization: Section 9.6A



9.46 Acidity Constants: Section 9.6A



Relative Acidities: II < I < IV < III

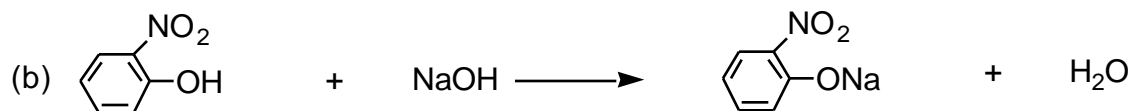
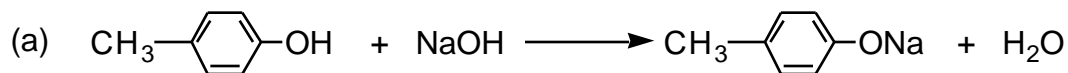
9.47 Acidity of Phenols: Section 9.6A.2

(a) **III < I < IV < II**: The methyl group is electron-releasing and decreases basicity; it is most effective ortho and para and probably a little more effective ortho due to proximity.

(b) **II < IV < I < III**: The acetyl group is electron-withdrawing and increases acidity; it is most effective ortho and para and probably a little more effective ortho due to proximity.

(c) $\text{II} < \text{IV} < \text{I} < \text{III}$: The methyl group decreases acidity and thus IV is more acidic than II. The nitro group increases acidity and III has more of them than does I.

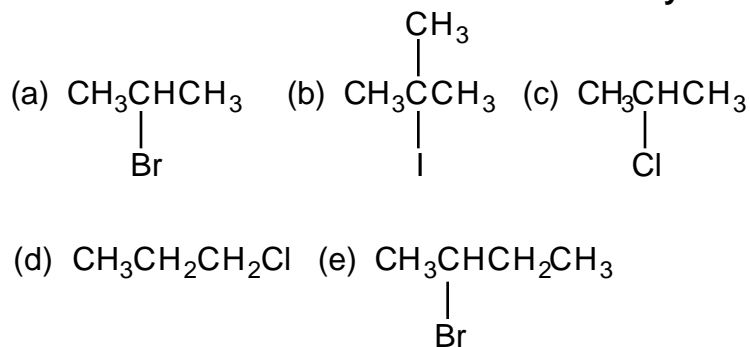
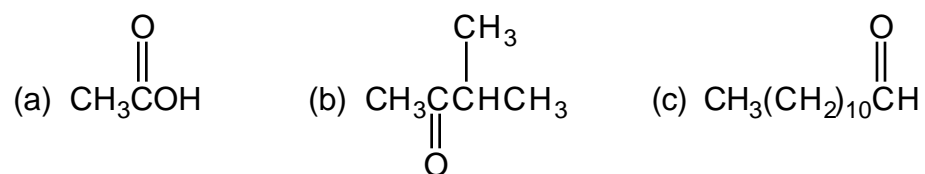
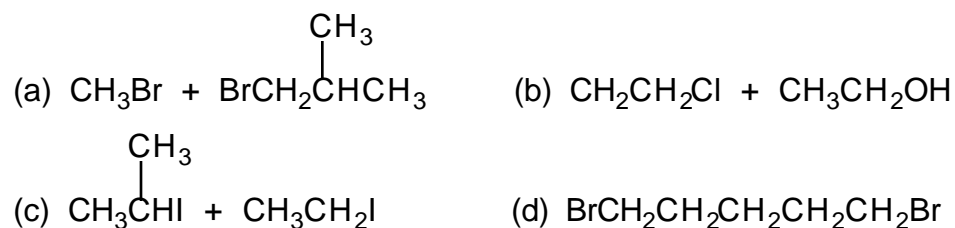
9.48 Acidity of Phenols: Section 9.6A.2



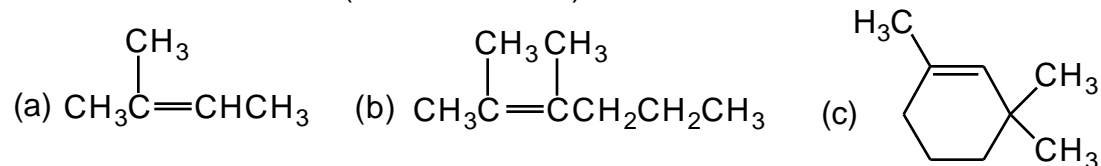
9.49 Reactions of Alcohols: Sections 9.5-9.9

Reagent

	I	II	III
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_3$	$\text{CH}_3\overset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}}\text{CH}_3$
a) Na	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{ONa}$	$\text{CH}_3\underset{\text{ONa}}{\text{CH}}\text{CH}_2\text{CH}_3$	$\text{CH}_3\overset{\text{CH}_3}{\underset{\text{ONa}}{\text{C}}}\text{CH}_3$
b) H_2SO_4	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	$\text{CH}_3\text{CH}=\text{CHCH}_3$	$\text{CH}_3\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$
c) HCl/ZnCl_2	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	$\text{CH}_3\underset{\text{Cl}}{\text{CH}}\text{CH}_2\text{CH}_3$	$\text{CH}_3\overset{\text{CH}_3}{\underset{\text{Cl}}{\text{C}}}\text{CH}_3$
d) CrO_3/H^+	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	$\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_2\text{CH}_3$	No Reaction
e) HNO_3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{ONO}_2$	$\text{CH}_3\underset{\text{ONO}_2}{\text{CH}}\text{CH}_2\text{CH}_3$	$\text{CH}_3\overset{\text{CH}_3}{\underset{\text{ONO}_2}{\text{C}}}\text{CH}_3$

9.50 Reactions of Alcohols to Form Alkyl Halides: Section 9.7A-B**9.51 Oxidation of Alcohols:** Section 9.9**9.52 Reactions of Ethers:** Section 9.7C**9.53 Dehydration of Alcohols:** Sections 4.5B and 9.8

The predominant product is shown for each dehydration. Direct your attention to the OH group. Remove it and a hydrogen from an adjacent carbon. Draw a double bond between the two carbons. In cases where there is more than one adjacent carbon with hydrogens, remove the hydrogen from the one with the greatest number of alkyl groups (fewest number of hydrogens) to produce the most substituted alkene (the most stable).



9.54 Reactions of Alcohols with Hydrogen Halides: Section 9.7A

Refer to the structures in Problem 9.53. **Replace the OH groups with Br.**

9.55 Reactions of Epoxides: Section 9.10A

(a) HOCH₂CH₂OH (b) HOCH₂CH₂OCH₂CH₃ (c) HOCH₂CH₂N(CH₃)₂

(d) HOCH₂CH₂Br (e) BrCH₂CH₂Br

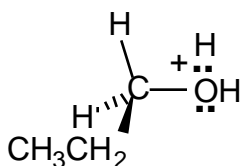
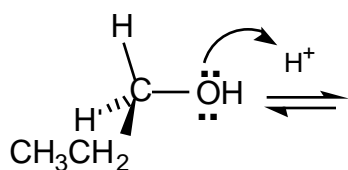
9.56 Reaction Mechanisms: Section 9.7A and C

Look at the carbon(s) directly bonded to the oxygens. If a carbon is primary, the mechanism of displacement is S_N2 because primary carbocations are unstable and the S_N2 reaction does not require a carbocation. If it is secondary or tertiary, the mechanism is S_N1. Secondary and tertiary carbocations are relatively stable and thus the S_N1 mechanism is possible.

(a) S_N2: primary alcohol; (b) S_N2 for both carbons: this is an ether where one carbon is methyl, one is primary; (c) S_N1: secondary alcohol; (d) S_N2 for the CH₃ carbon and S_N1 for the secondary carbon; (e) S_N2 for both carbons since both are primary.

9.57 Nucleophilic Substitution Mechanisms: Sections 9.7A and C

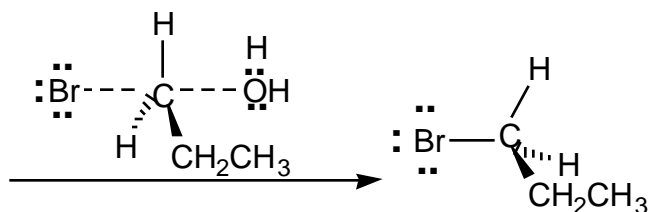
(a)



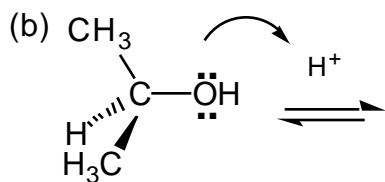
Primary alcohol protonated to form primary oxonium ion. Oxonium ion is attacked by bromide.

S_N2 Mechanism:

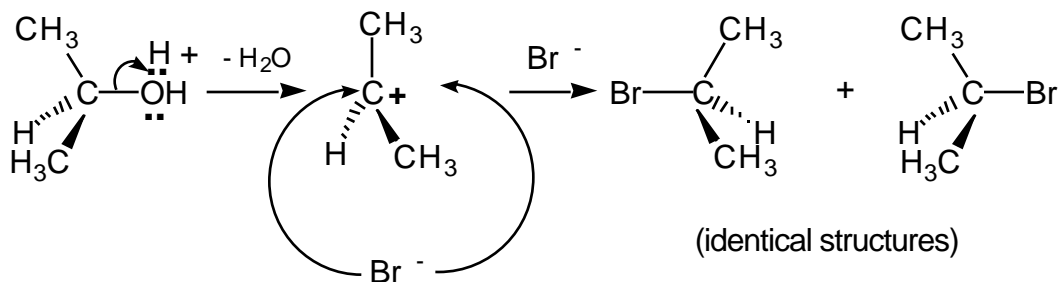
A Single Step Process



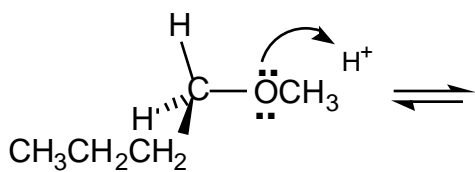
Transition state showing bromide displacing water molecule from the opposite side to form final product.



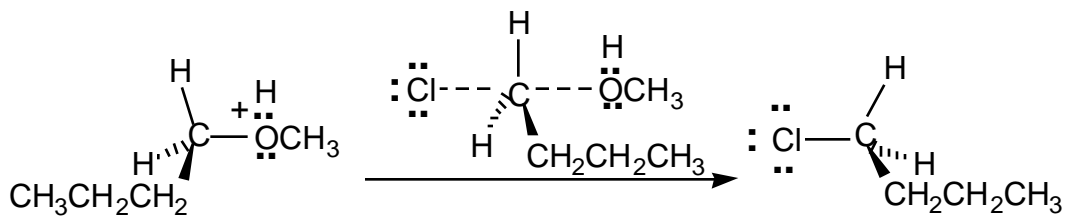
S_N1 Mechanism:
A Two-Step Process



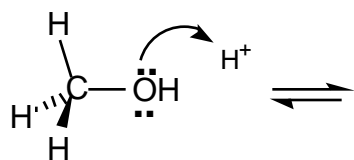
(c)



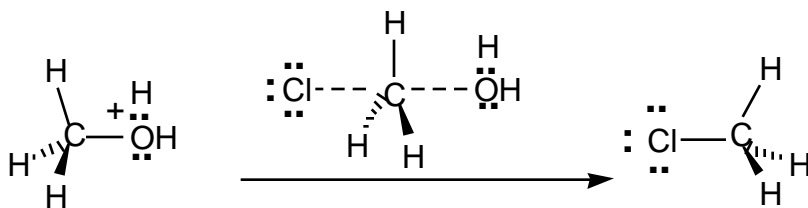
S_N2 Mechanism:
A Single Step Process

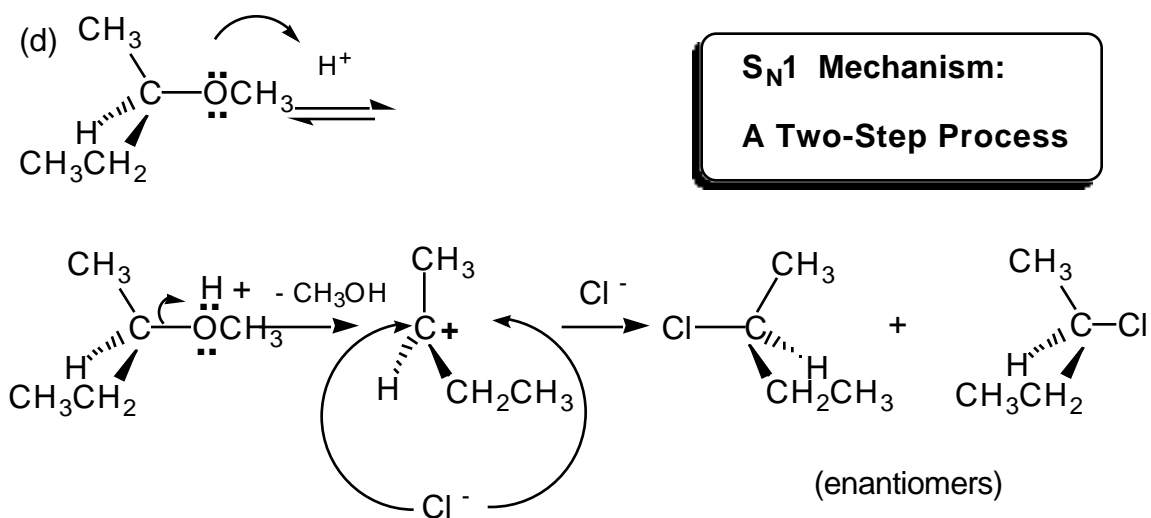


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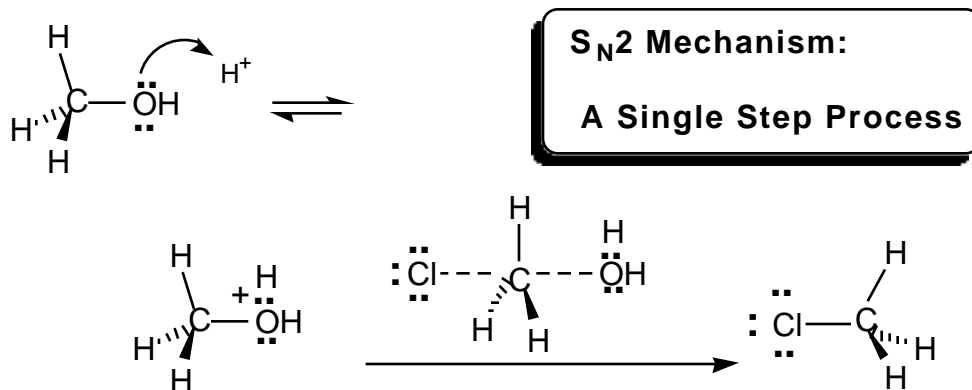


S_N2 Mechanism:
A Single Step Process

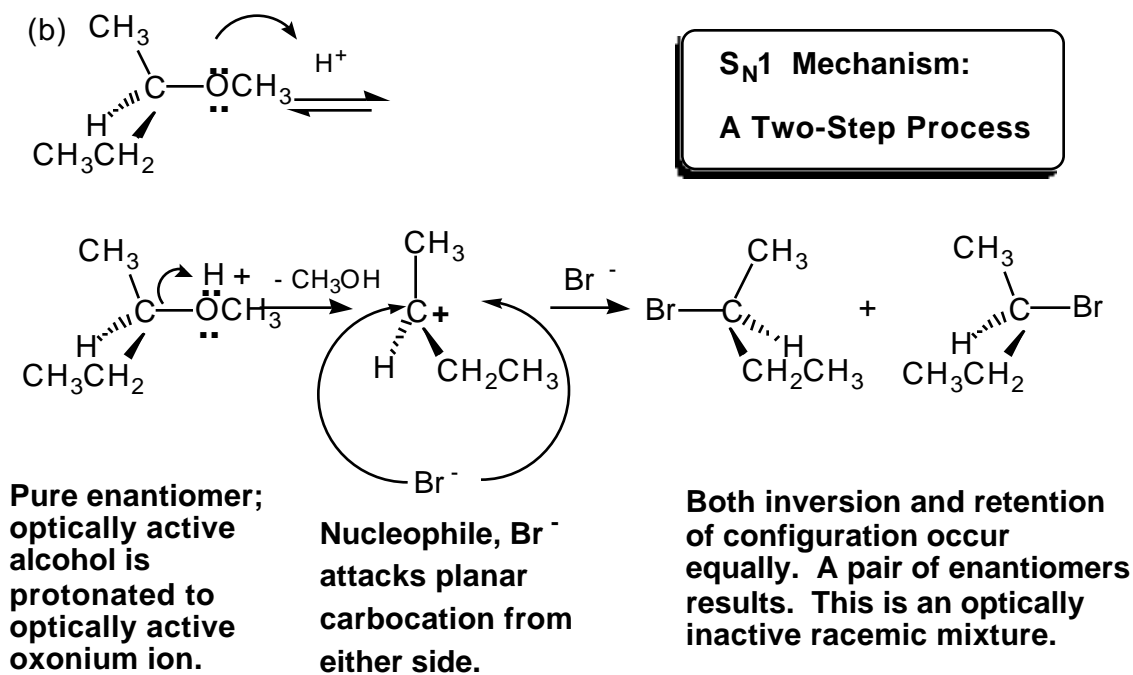
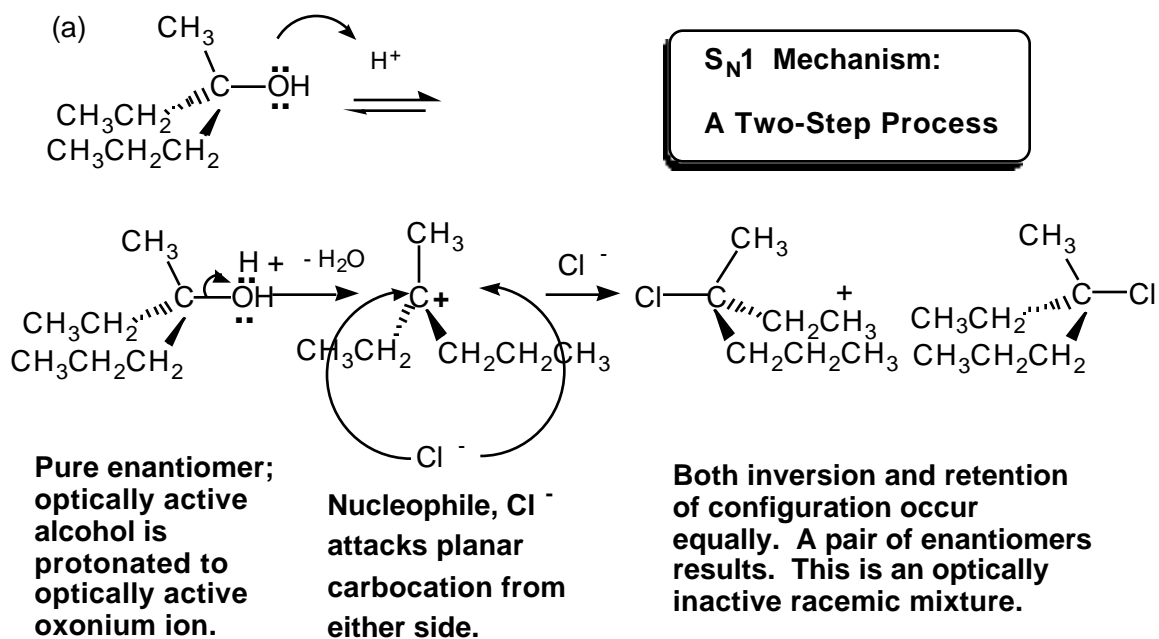




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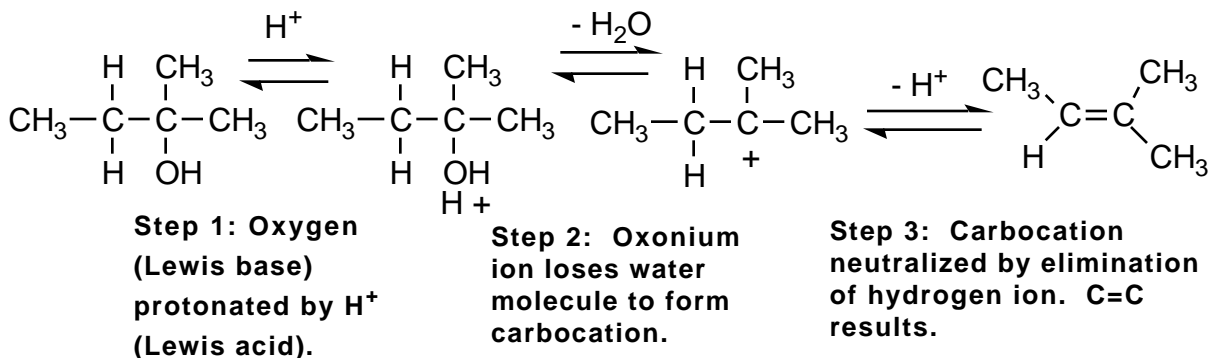
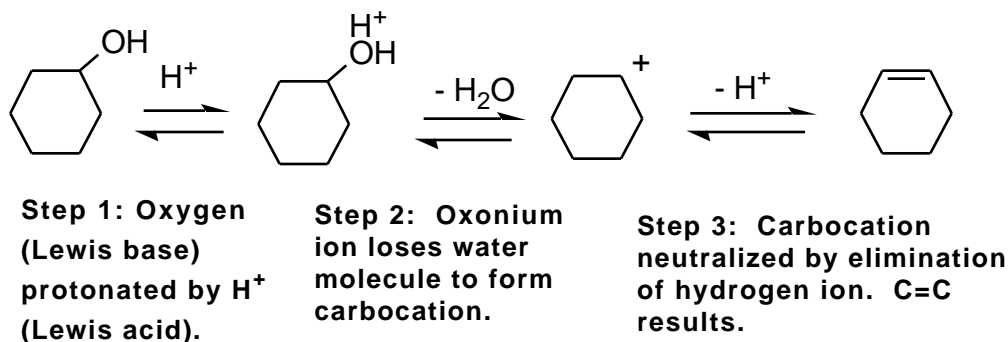


9.58 Nucleophilic Substitution Mechanisms: Section 9.7A and C



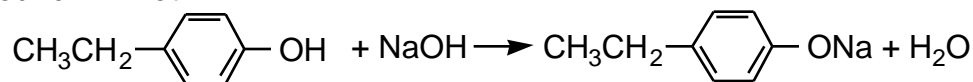
9.59 Dehydration Mechanism: Sections 4.5C and 9.8

(a)

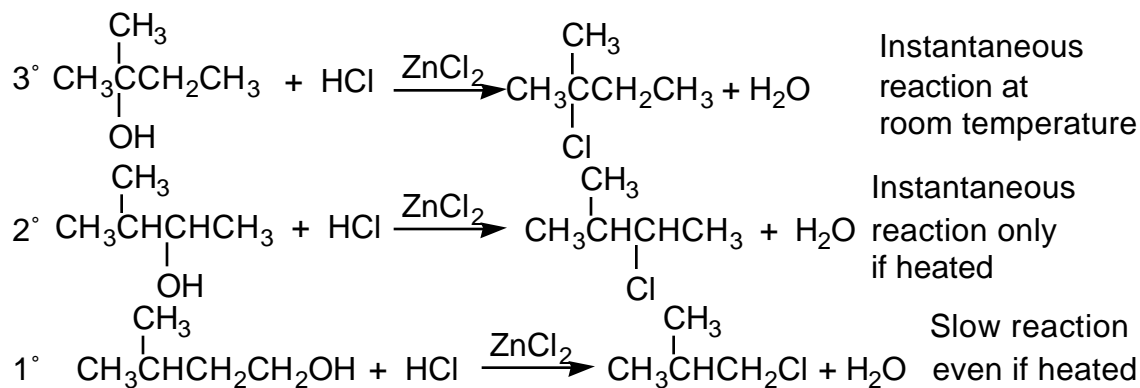
E₁ Mechanism for Dehydration of Alcohols**E₁ Mechanism for Dehydration of Alcohols**

9.60 Qualitative Analysis: Sections 9.6A.2 and 9.7A

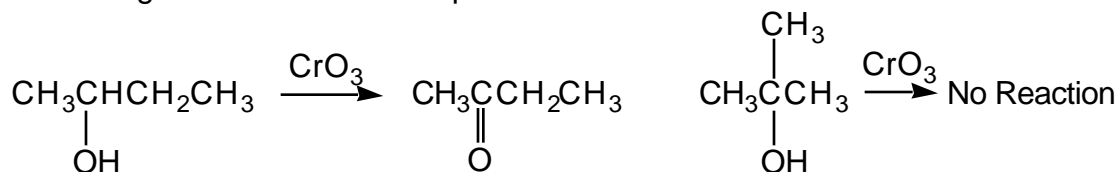
(a) p-Ethylphenol being a phenol is acidic and reacts with sodium hydroxide. Alcohols are not so acidic and do not react with sodium hydroxide. p-Ethylphenol will dissolve in a sodium hydroxide solution and the other compound will not.



(b) Treatment of each of these alcohols with the Lucas reagent will produce a turbid mixture as the alkyl halide is formed. However the reaction proceeds at different rates depending on the structure of the alcohol.

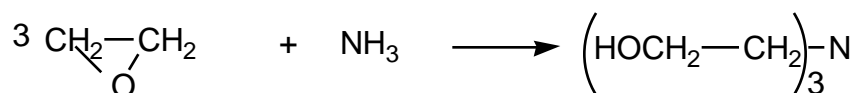


(c) The secondary alcohol is subject to oxidation but the tertiary alcohol is not. The positive reaction is observable as the yellow-orange oxidation reagent becomes green as the reaction proceeds.

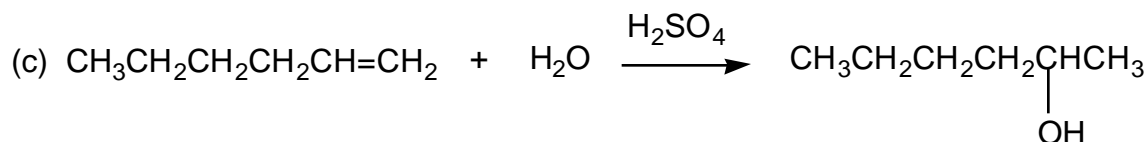
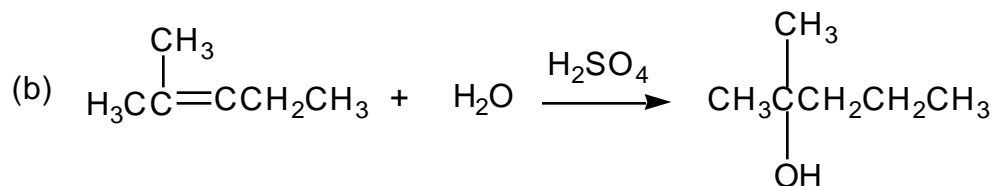
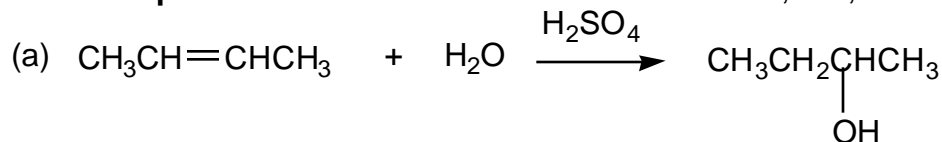


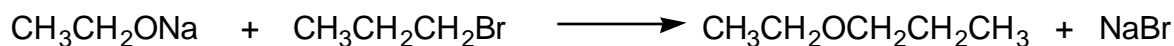
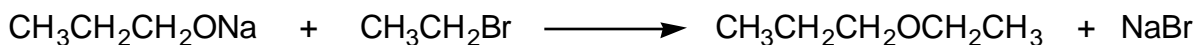
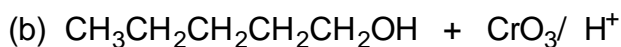
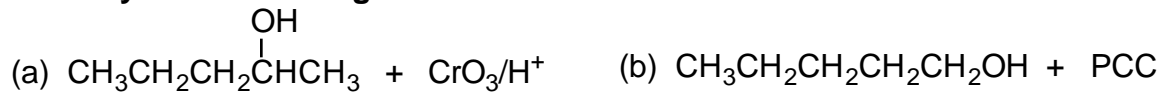
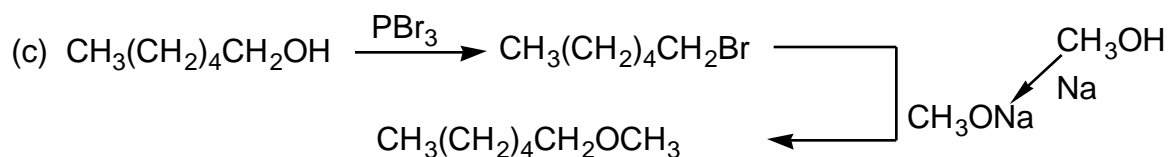
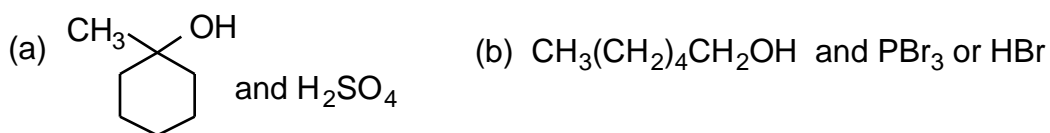
9.61 Epoxide Chemistry: Section 9.10

There are three N-H bonds to add across the epoxide ring.

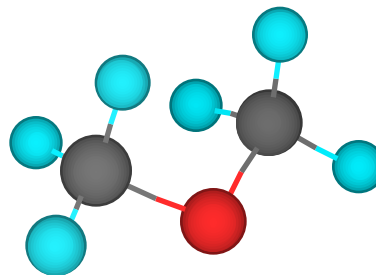
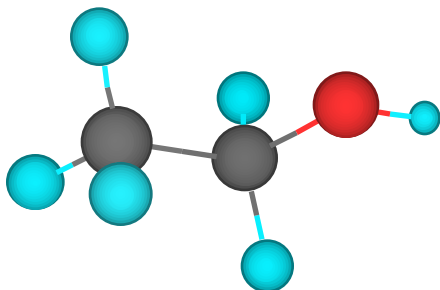


9.62 Preparations of Alcohols: Sections 5.1A.3, B.3, C and 9.4A



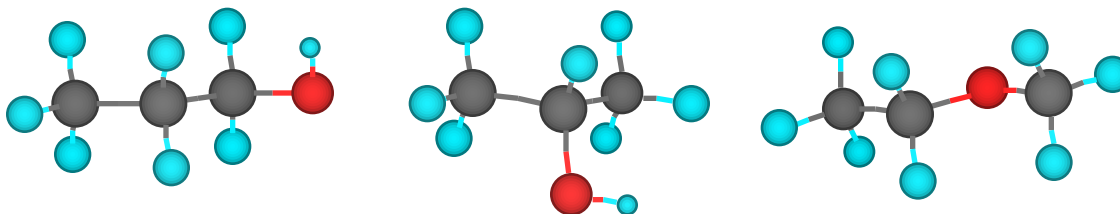
9.63 Williamson Synthesis of Ethers: Sections 8.4A, 8.6, and 9.4B**9.64 Synthesis Using Alcohols:** Section 9.9**9.65 Synthesis Using Alcohols:** Sections 9.7-9.8**ACTIVITIES WITH MOLECULAR MODELS**

1. Make molecular models of $\text{C}_2\text{H}_6\text{O}$, one alcohol and one ether.



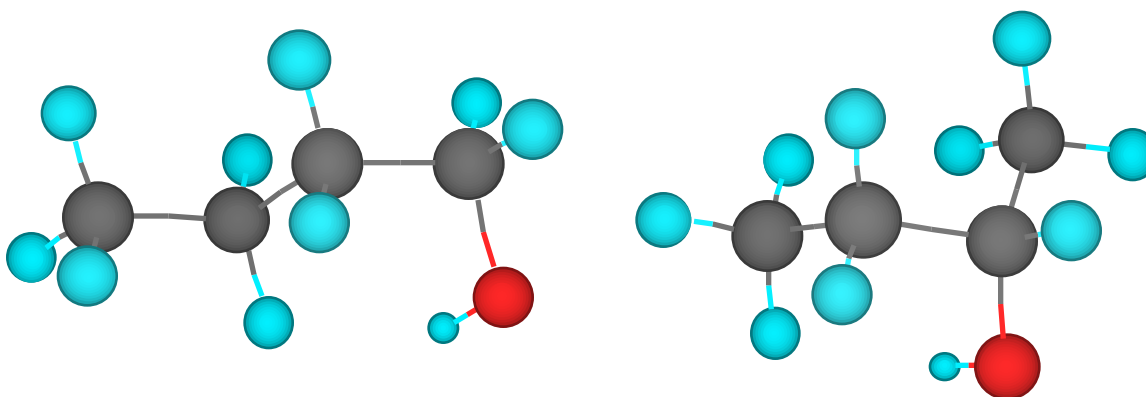
2. Make molecular models of the isomers of C_3H_6O , two alcohols and one ether. How many non-bonding electron pairs reside on the oxygen? What is the hybridization and geometric orientation of the carbons and the oxygen?

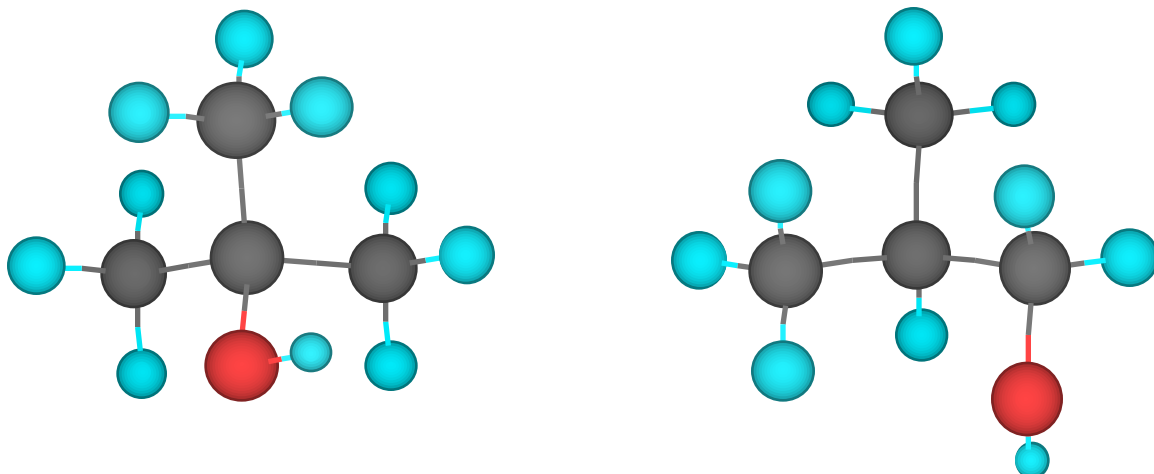
Each oxygen has two non-bonding electron pairs. The carbons and oxygens all have four bonding and non-bonding electron pairs total and are sp^3 hybridized with a tetrahedral geometry.



3. Make a model of one of the seven isomers of $C_4H_{10}O$ and then convert it into the other alcohols (four total) and ethers (three total). Draw each structure. Identify skeletal, positional, and functional isomers. Determine if the alcohols are primary, secondary, or tertiary.

The four structures below are alcohols. The first two are positional isomers of one another and the second two are also positional isomers of one another. The first two are skeletal isomers of the second two. The first and last alcohol are primary, the second is secondary, and the third is tertiary.





The following three compounds are all ethers and they are functional isomers of the previous four alcohols. The first two ethers are positional isomers of each other and the third is a skeletal isomer of the other two.

