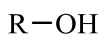


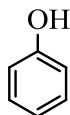
UNIT (8) OXYGEN CONTAINING ORGANIC COMPOUNDS

8.1 | Alcohols, Phenols, and Ethers

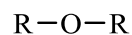
An **alcohol** is an organic compound that contains the *hydroxyl group* (-OH) attached to an alkyl group. They are essentially alkanes in which a single hydrogen has been replaced with an -OH group. A **phenol** has an -OH group bonded directly to a benzene ring. An **ether** has an oxygen atom bound to two alkyl groups. Recall that “R” represents a generic alkyl group.



An alcohol



A phenol



An ether

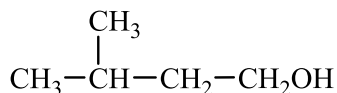
8.2 | Naming Alcohols

According to the IUPAC system, the names of alcohols end in “-ol,” indicating the presence of the hydroxyl group, i.e.: **methanol** (fuel), **ethanol** (drinking alcohol), **isopropanol** (rubbing alcohol), etc. When naming alcohols, the “-e” is dropped from the alkane containing the “-OH” group and replaced with the suffix “-ol”. The location of the hydroxyl group must be specified in alcohols containing three or more carbons. The chain is numbered in a manner which places the lowest number on the carbon containing the -OH group. The rules for naming alcohols are a slight variation on the rules for naming alkanes.

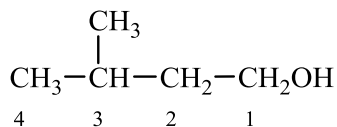
General Guideline

- The parent name is the longest chain that contains the -OH group.
- Number the carbon chain from the end nearest to the -OH group (location of OH group take precedence over alkyl groups).
- Name and number all substituted groups on the parent chain. In cases of multiple substitutions, list them in alphabetical order.
- Locate the -OH group using the carbon number it's attached to.

Example: Name the following alcohol:



The longest chain that containing -OH group has four carbon atoms. The carbon chain is numbered from right to left so that the -OH group has the smallest possible number.

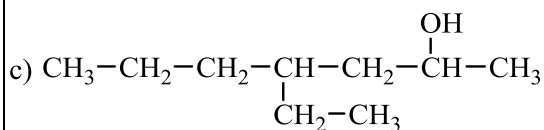
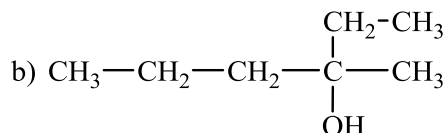
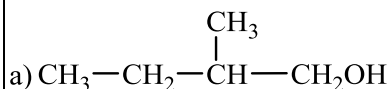


The methyl group is located on C-3.

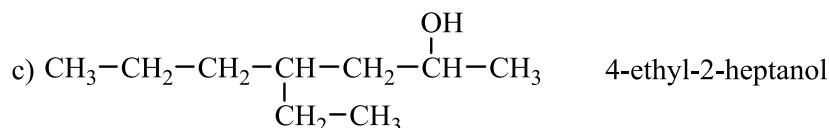
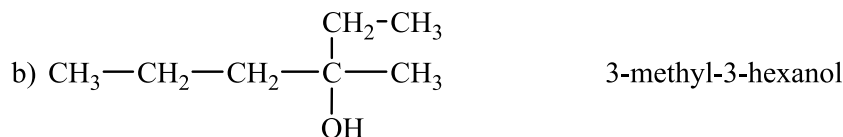
The name of the alcohol is: **3-methyl-1-butanol**.

Worked Example 8-1

Give the IUPAC name for each of the following compounds:



Solution



Common names of Alcohols

The common names for alcohols are based on the name of the alkyl group.

Methyl Alcohol (CH_3OH , methanol)

Methyl alcohol is the simplest (smallest) alcohol and is commonly known as wood alcohol because it was once prepared by heating wood in the absence of air.

Ethyl Alcohol ($\text{CH}_3\text{CH}_2\text{OH}$, ethanol)

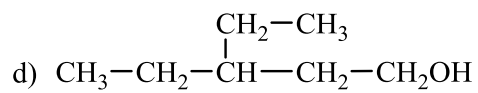
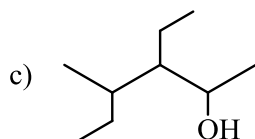
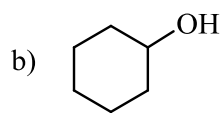
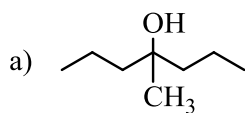
Ethyl alcohol is one of the oldest known pure organic compounds. Ethyl alcohol is used in toiletries, pharmaceuticals, and fuels. Ethyl alcohol is also called *grain alcohol* and it is the alcohol in **alcoholic beverages**.

Isopropyl Alcohol ($\text{CH}_3\text{CHOHCH}_3$, 2-propanol)

Isopropyl alcohol is often called *rubbing alcohol*. This alcohol is used as a disinfectant and astringent (skin-drying agent).

Practice 8-1

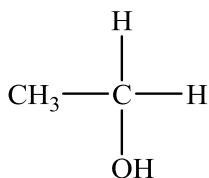
Give the IUPAC name of each of the following alcohols:



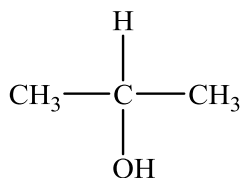
Answer

8.3 | Classification of Alcohols

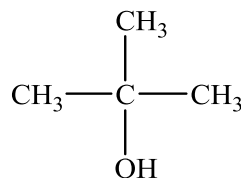
Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon atoms bound to the hydroxyl-bearing carbon. A **primary alcohol** has one alkyl group attached to the carbon bound to the -OH , a **secondary alcohol** has two alkyl groups, and a **tertiary alcohol** has three alkyl groups.



Primary (1°) alcohol



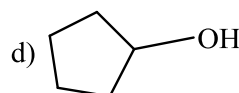
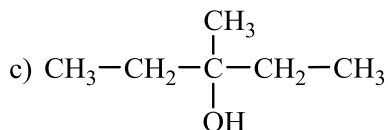
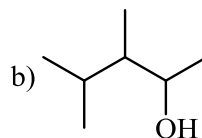
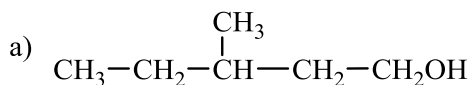
Secondary (2°) alcohol



Tertiary (3°) alcohol

Practice 8-2

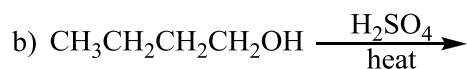
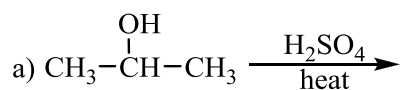
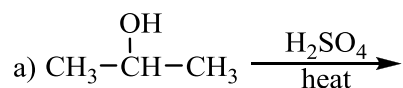
Classify the following alcohols as primary, secondary, or tertiary:



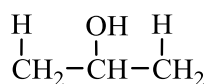
Answer

Worked Example 8-2

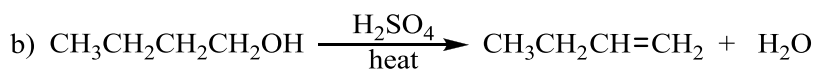
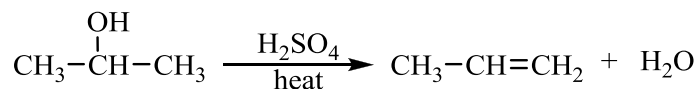
Give the product for each of the following dehydration reactions:

**Solution**

Find the hydrogens on carbons adjacent to the OH-bearing carbon, then remove the possible combinations of -H and -OH drawing a double bond between the carbons that contained the removed -H and -OH.

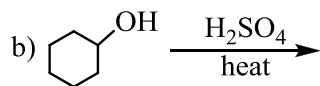
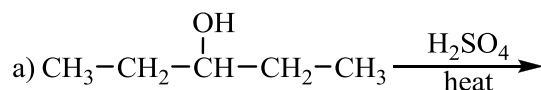


The -OH group is from carbon 2, the -H could come from carbon 1 or carbon 3, giving the same product, propene.



Practice 8-3

Give the products for each of the following dehydration reactions. Name each reactant and product.



Answer

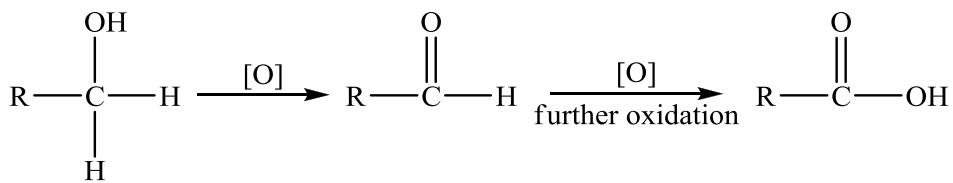
2. Oxidation of Alcohols

Oxidation is the gain of oxygens and /or the loss of hydrogens.

Primary alcohols oxidize to aldehydes and may further oxidize to carboxylic acids.

Secondary alcohols oxidize to ketones. Tertiary alcohols normally do not oxidize.

A number of oxidizing agents are commonly available to perform oxidation. It is often of little importance which specific reagent is chosen. When writing oxidation reactions, the symbol [O] is frequently used to represent common oxidizing agents.

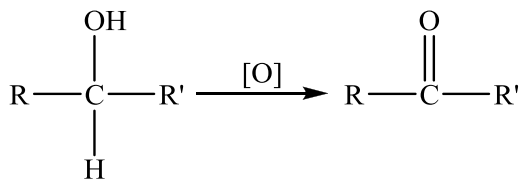


A primary alcohol

An aldehyde

A carboxylic acid

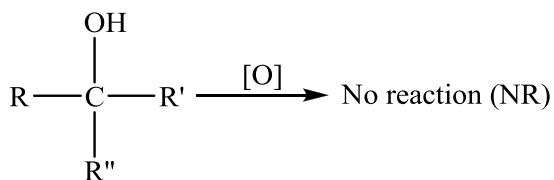
Secondary alcohols oxidize to ketones on treatment with oxidizing agents:



A secondary
alcohol

A ketone

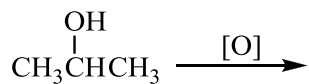
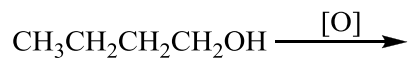
Tertiary alcohols do not oxidize readily.



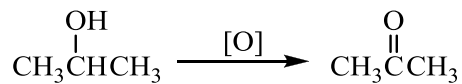
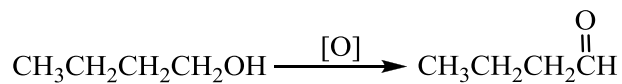
A tertiary
alcohol

Worked Example 8-3

Give the product for each of the following oxidation reactions:



Solution



Practice 8-4

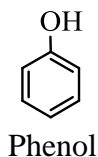
Write a chemical equation showing reactant and product for each of the following. If no reaction occurs, write "NR".

- oxidation of 2-methyl-1-propanol
- oxidation of 3-methyl-3-pentanol
- oxidation of cyclobutanol

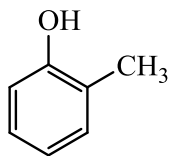
Answer

8.5 | Phenols

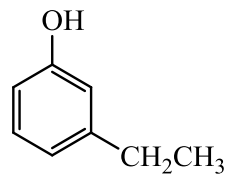
A phenol is an organic compound in which the hydroxyl group is directly attached to the benzene ring.



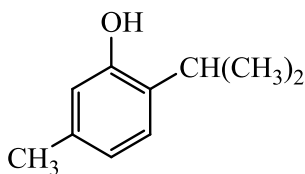
The word phenol is both the name of a specific compound and of a family of compounds. Substituted phenols are named as either a derivative of phenol or by common names. When naming compounds as phenol derivatives, the carbon containing the -OH is always carbon number 1. The following are examples of compounds classified as phenols.



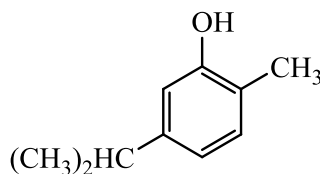
2-methylphenol



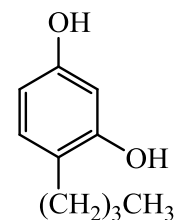
3-ethylphenol



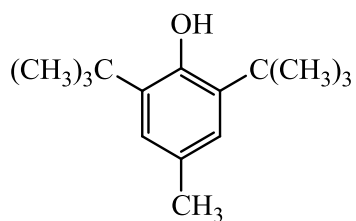
Thymol (mint)



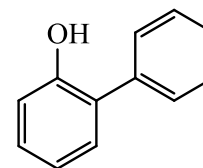
Carvacrol (savory)



Hexylresorcinol (antiseptic)



Butylated hydroxytoluene, BHT (food preservative)



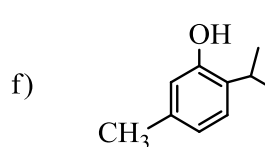
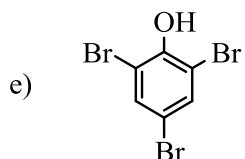
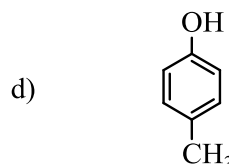
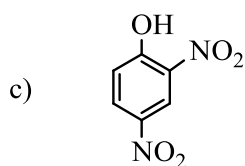
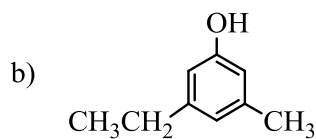
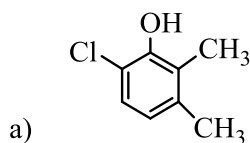
2-phenylphenol (antiseptic)

Worked Example 8-4

Draw the structure corresponding to the following names:

- | | |
|--------------------------------|-------------------------------|
| a) 6-chloro-2,3-dimethylphenol | b) 3,5-diethylphenol |
| c) 2,4-dinitrophenol | d) 4-methylphenol |
| e) 2,4,6-tribromophenol | f) 2-isopropyl-5-methylphenol |

Solution

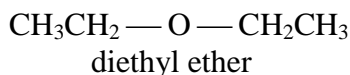


8.6 | Ethers

Ethers contain an oxygen atom bound to two alkyl groups, each of which may be aliphatic or aromatic. Ethers are distinguished from other organic compounds because they lack a continuous chain of carbons. This is the first time we have encountered an organic compound containing a heteroatom (non-carbon) in the carbon chain. The general formula for ethers with aliphatic carbons can be shown as:

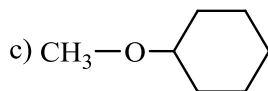
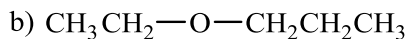
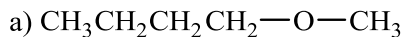


Common names for ethers are determined by naming the two alkyl groups attached to the oxygen atom and adding the word *ether*. The alkyl groups are listed in alphabetic order. There are spaces between the names of the alkyl groups and the word ether. The prefix *di-* is used in cases when the alkyl groups are the same. The best-known ether is diethyl ether, which is commonly called ether.



Worked Example 8-5

Write the name for each of the following:



Solution

a) butyl methyl ether

b) ethyl propyl ether

c) cyclohexyl methyl ether

d) dipropyl ether

Practice 8-5

Draw structures for each of the following

a) 4-chloro-3,5-dimethylphenol

c) pentachlorophenol

e) cyclopropyl propyl ether

b) 2,3,5-triethylphenol

d) cyclobutyl ethyl ether

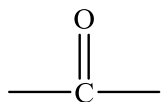
f) dicyclohexyl ether

Answer

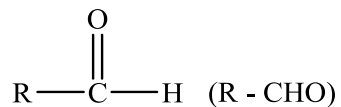


8.7 | Aldehydes and Ketones

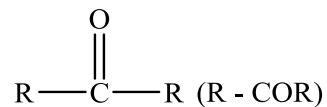
Aldehydes and ketones each contain a carbonyl group (C=O). In an aldehyde, at least one hydrogen atom is directly attached to the carbonyl carbon. In ketones, only carbon atoms are directly attached to the carbonyl carbon (no hydrogens). The groups attached to the carbonyl carbon can be either aliphatic or aromatic.



carbonyl group



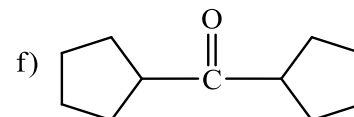
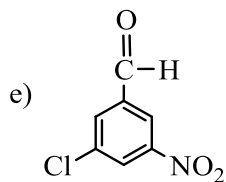
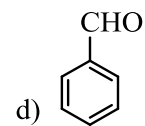
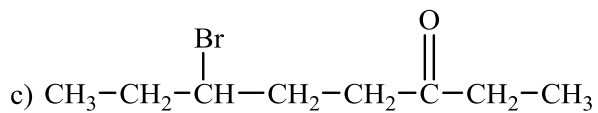
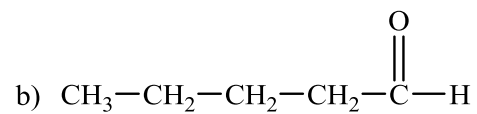
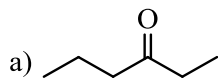
aldehyde



ketone

Worked Example 8-6

Identify each of the following as an aldehyde or a ketone:



Solution

a) ketone

b) aldehyde

c) ketone

d) aldehyde

e) aldehyde

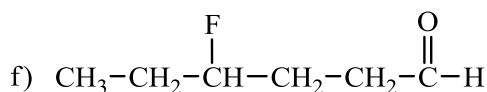
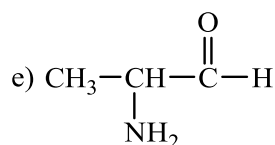
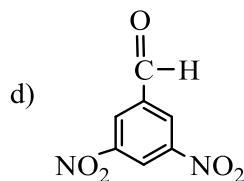
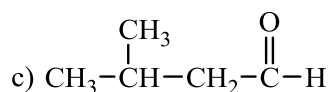
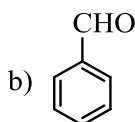
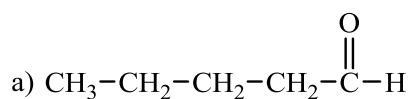
f) ketone

Naming Aldehydes

According to the IUPAC system, the names of **aldehydes** end in “-**al**,” indicating the presence of the aldehyde group, i.e.: **propanal**, **butanal**, **pentanal**, etc. When naming aldehydes, the “-e” is dropped from the alkane containing the aldehyde group and replaced with the suffix “-al”. The chain is numbered from the aldehyde group which is always located on the first carbon. Unlike other functional groups, the location of the aldehyde group is *not* included in the name.

Worked Example 8-7

Name each of the following:



Solution

- a) pentanal (not 1-pentanal)
c) 3-methylbutanal
e) 2-aminopropanal

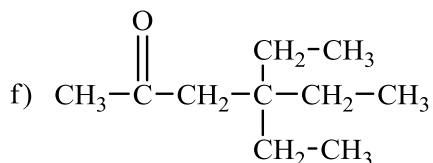
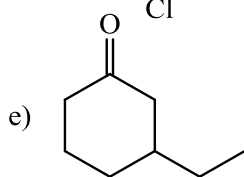
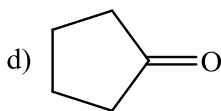
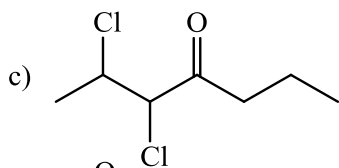
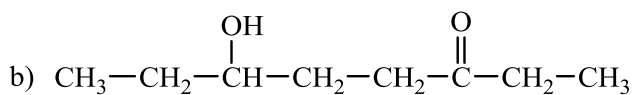
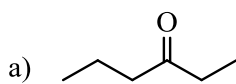
- b) benzaldehyde
d) 3,5-dinitrobenzaldehyde
f) 4-fluorohexanal

Naming Ketones

According to the IUPAC system, the names of **ketones** end in “-**one**,” indicating the presence of the carbonyl group, i.e.: **acetone**, **butanone**, **pentanone**, etc. When naming ketones, the “-e” is dropped from the alkane containing the carbonyl group and replaced with the suffix “-one”. The location of the carbonyl group must be specified in ketones containing five or more carbons. The chain is numbered in a manner which places the lowest number on the carbon containing the double bond to oxygen. It is worth noting that the carbonyl group can never appear on the end carbons (terminal carbons) in ketones. Carbonyl groups on terminal carbons would be aldehydes (see above) or carboxylic acids (see *unit 9*).

Worked Example 8-8

Name each of the following:



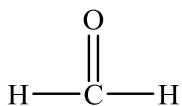
Solution

- a) 3-hexanone
c) 2,3-dichloro-4-heptanone
e) 3-ethylcyclohexanone

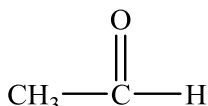
- b) 6-hydroxy-3-octanone
d) cyclopentanone
f) 4,4-diethyl-2-hexanone

Common names for Aldehydes and Ketones

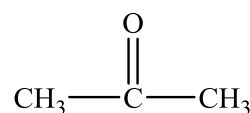
Simple (small chain) aldehydes and ketones are best known by their “common” names. You should learn the following common names:



Formaldehyde



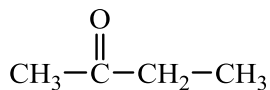
Acetaldehyde



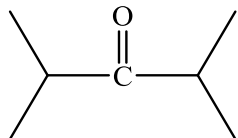
Acetone

Common names of ketones are obtained by naming the groups attached to the carbonyl carbon followed by the word ketone. The alkyl groups are generally listed alphabetically. (Note the similarity of this method to ether naming.)

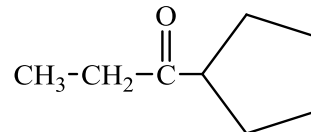
Examples



ethyl methyl ketone



diisopropyl ketone



cyclopentyl ethyl ketone

Practice 8-6

Draw structures corresponding to the following names:

a) 2,2-dimethylcyclopentanone

b) 2,4,6-trimethylheptanal

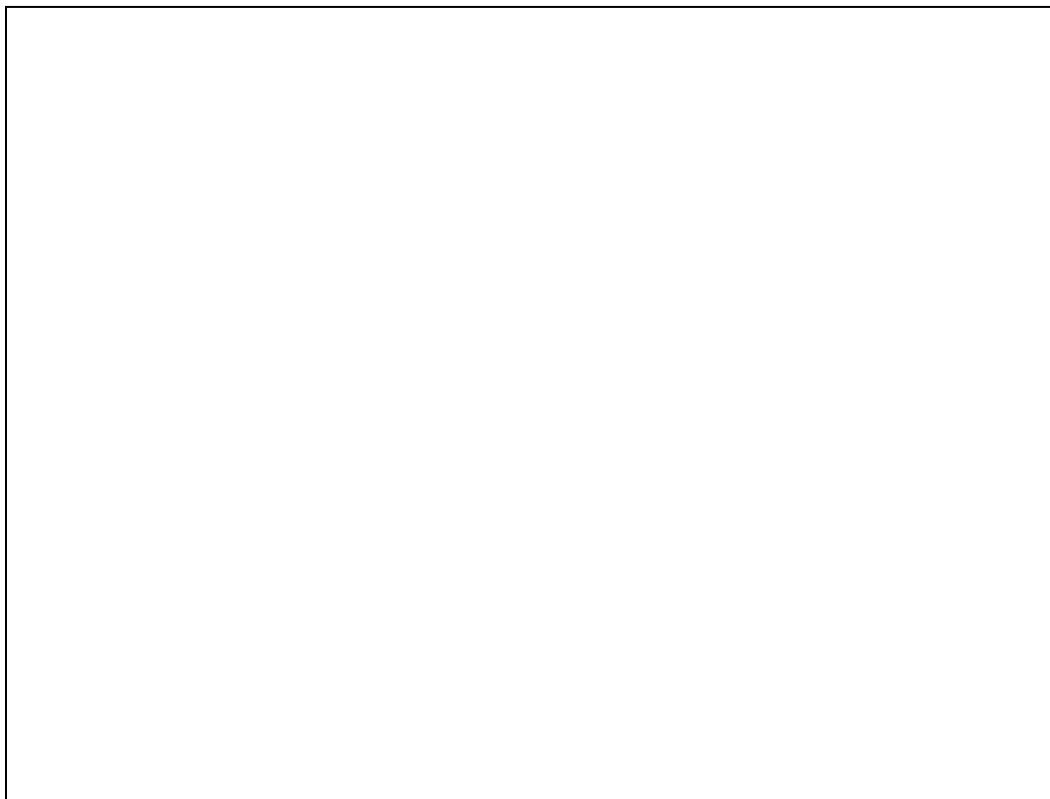
c) bromopropanone

d) dichloromethyl ethyl ketone

e) dichloroacetaldehyde

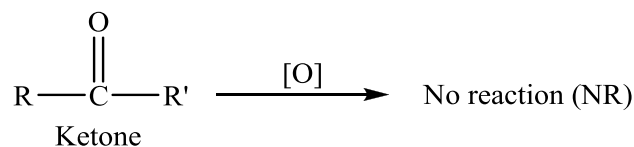
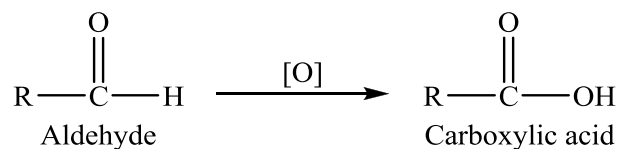
f) 2,4-dimethylbenzaldehyde

Answer

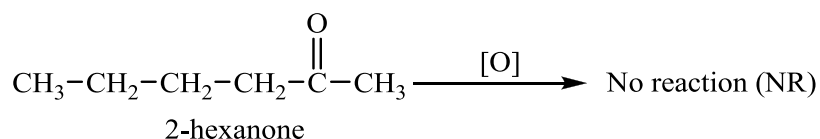
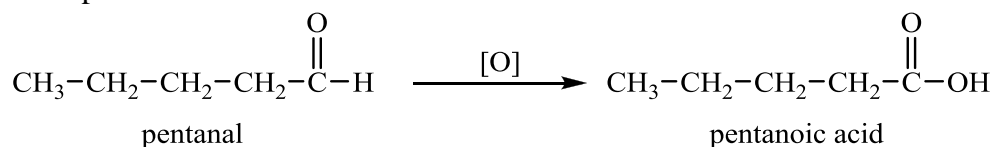


8.8 | Oxidation of Aldehydes and Ketones

Recall that primary alcohols can oxidize to aldehydes and aldehydes may further oxidize to carboxylic acids. Secondary alcohols can oxidize to ketones and ketones **cannot** be further oxidized. Note the additional bonds to oxygen, a requirement for oxidation.

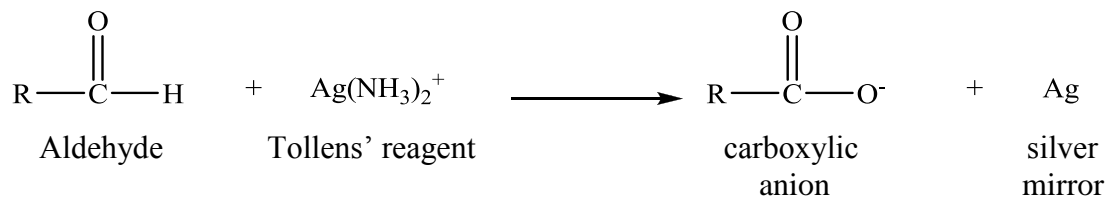


Examples:



Most reagents that oxidize alcohols can also oxidize aldehydes. In addition to oxidation by dichromate or permanganate, aldehydes can also be oxidized by very mild oxidizing reagents. **Tollens' reagent** and **Benedict's reagent** are mild oxidizing reagents used in simple chemical tests to distinguish aldehydes from ketones.

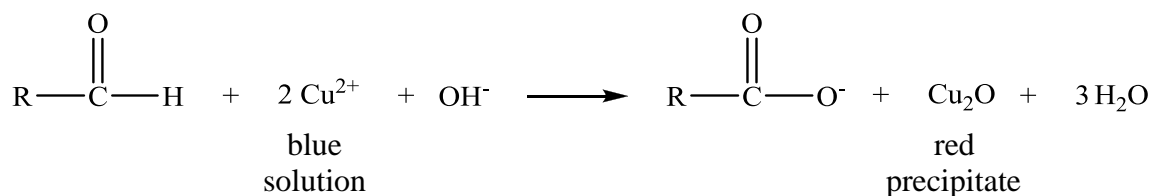
Tollens' reagent consists of a solution containing silver ion (Ag^+) in aqueous ammonia. Treatment of an aldehyde with this reagent yields silver metal. The silver deposits on the inside of the test tube and gives the appearance of a silver mirror. This test is called **Tollens' test** or **silver mirror test**.



Benedict's reagent is prepared by dissolving copper(II) sulfate, sodium citrate, and sodium carbonate in water. The color of this solution is blue due to the presence of Cu^{2+} ions.

As Benedict's reagent oxidizes an aldehyde, the initial blue color changes as Cu^{2+} is reduced to Cu^+ . The final color of the solution depends on the amount of aldehyde initially present.

In a positive Benedict's test, the blue color of the solution turns greenish, and a dark red, orange, brown, or yellow **precipitate** forms. Benedict's test requires heating the test solution in boiling water for several minutes. This test will detect the presence of any aldehydes except the aromatic aldehydes.



Practice 8-7

Write a chemical equation showing reactant and product for each of the following. If no reaction occurs, write "NR".

- oxidation of 5-methylhexanal
- oxidation of 3,3-dimethylpentanal
- oxidation of 3-ethylcyclohexanone

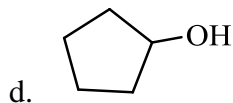
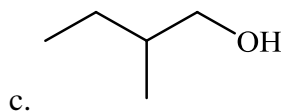
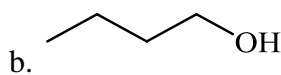
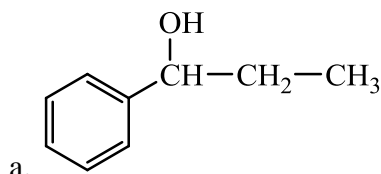
Answer

Homework Problems

8.1 Draw the structural formula for each of the following:

- 5-chloro-4-methyl-2-hexanol
- 2,3-dimethylcyclopentanol
- 5,5-diethyl-1-heptanol
- 2-ethyl-4-isopropylcyclohexanol
- 4-ethylphenol
- 2-nitrophenol
- cyclopropyl methyl ether
- isopropyl propyl ether

8.2 Give the product for the dehydration of each of the following alcohols.



8.3 What product would result from the oxidation of each of the following alcohols? Write the chemical equations.

- 2-butanol
- 2-methyl-2-pentanol
- cyclohexanol
- 3-ethylcyclopentanol

8.4 Name all alcohol and ether isomers with formula $C_4H_{10}O$, and write their structural formulas. There are seven isomers.

8.5 Draw the structure for each of the following compounds:

- a. 2-methylbutanal
- b. 3-iodohexanal
- c. 3-bromobenzaldehyde
- d. 2-hydroxy-3-methylpentanal
- e. ethyl butyl ketone
- f. 3-bromocyclopentanone
- g. 3-ethyl -2-heptanone
- h. 3-ethyl-2-pentanone

8.6 Draw the products, if any, of each of the following reactions:

