Chapter 11 Lecture Notes: Alcohols, Ethers, Aldehydes, and Ketones

Educational Goals

1. Given the structure of an **alcohol**, **ether**, **thiol**, **sulfide**, **aldehyde**, **or ketone** molecule, be able to give the systemic names and vice versa.
2. Know and understand the intermolecular forces that attract alcohol, ether, thiol, sulfide, disulfide, aldehyde, and ketone molecules to one another, and how these forces affect boiling points and melting points.
3. Identify **alcohols** as primary (1^o), secondary (2^o), or tertiary (3^o).
4. Predict the products of the reactions in chapter 11 that involve alcohols, thiols, aldehydes, and/or ketones:
   - oxidation of thiols to produce disulfides
   - nucleophilic substitution reaction of alkyl halides and hydroxide
   - hydration of alkenes
   - dehydration of alcohols
   - oxidation of alcohols
   - oxidation of aldehydes
   - reduction of aldehydes and ketones
   - hemiacetal and acetal formation
5. Predict the **major** and **minor products** for the **hydration of an alkene**.
6. Predict the **major** and **minor products** for the **dehydration of an alcohol**.

Alcohols, Ethers, and Related Compounds

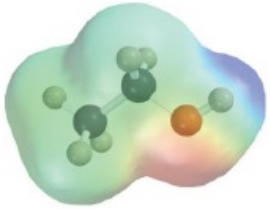
Alcohols

An _____ is a compound with an –OH bonded to a non-aromatic(alkyl) carbon (R-OH).

Some Common Alcohols

Example: CH_3CH_2OH

Ethyl alcohol



- Methyl alcohol, CH_3OH (methanol; wood alcohol)
- Ethyl alcohol, CH_3CH_2OH (ethanol; grain alcohol; "alcohol")
- Isopropyl alcohol, $(CH_3)_2CHOH$ (isopropanol; 2-propanol; rubbing alcohol)
- Ethylene glycol, $HOCH_2CH_2OH$ (1,2-ethanediol; antifreeze)
- Glycerol, $HOCH_2CH(OH)CH_2OH$ (1,2,3-propanetriol; glycerin)

Naming Alcohols

- When the IUPAC rules are used to name an alcohol, the parent (the longest continuous carbon chain carrying the -OH group) is numbered from the end nearer the -OH and named by dropping the "***e***" ending on the name of the corresponding hydrocarbon by adding "***ol***."
- When a parent chain contains more than two carbon atoms, the position of the -OH group must be specified with a number.
- Any alkyl groups attached to the parent chain are identified by name, position, and number of appearances.

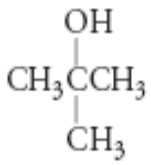
Examples:

CH_3CH_2OH
Ethanol
(ethyl alcohol)

$CH_3CH_2CH_2OH$
1-Propanol
(propyl alcohol)

$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$
2-Propanol
(isopropyl alcohol)

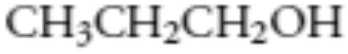
You try it: Name this molecule:



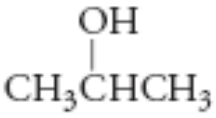
1°, 2°, and 3° Alcohols

- **Primary alcohol (1°)** - the carbon atom carrying the -OH group is attached to _____other carbon atom

Ethanol
(ethyl alcohol)



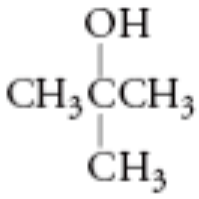
1-Propanol
(propyl alcohol)



2-Propanol
(isopropyl alcohol)

- **Secondary alcohol (2°)** - the carbon atom carrying the -OH group is attached to _____ other carbon atoms

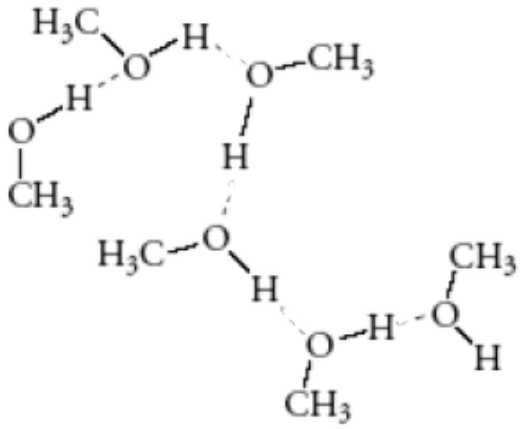
- **Tertiary alcohol (3°)** - the carbon atom carrying the -OH group is attached to _____other carbon atoms



2-Methyl-2-propanol
(*t*-butyl alcohol)

Properties of Alcohols

Compared to hydrocarbons with a similar molecular weight, alcohols have relatively _____ boiling points.



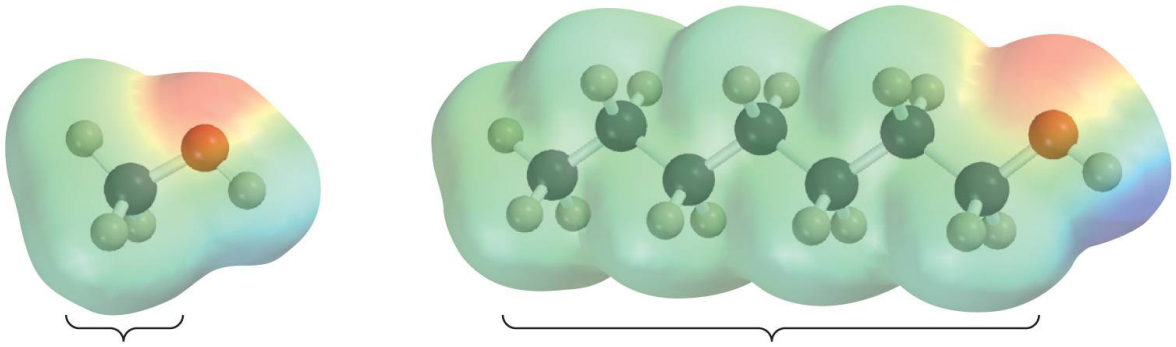
This is because of their ability to form _____ _____.

Formula	IUPAC Name	Common Name	Boiling Point (°C)	Water Solubility (g/100 mL)
Alcohols				
CH_3OH	Methanol	Methyl alcohol	65.0	Miscible[a]
CH_3CH_2OH	Ethanol	Ethyl alcohol	78.5	Miscible
$CH_3CH_2CH_2OH$	1-Propanol	Propyl alcohol	97.4	Miscible
$CH_3CH_2CH_2CH_2OH$	1-Butanol	Butyl alcohol	117.3	8.0
$CH_3CH_2CH_2CH_2CH_2OH$	1-Pentanol	Pentyl alcohol	138	2.2
Alkanes				
CH_3CH_3	Ethane		−89	~0
$CH_3CH_2CH_3$	Propane		−42	~0
$CH_3CH_2CH_2CH_3$	Butane		0	~0
$CH_3CH_2CH_2CH_2CH_3$	Pentane		36	~0

[a]Can be mixed in all proportions.

Alcohols with a small hydrocarbon part are H_2O soluble.
Alcohols with a large hydrocarbon part are insoluble in H_2O.

$CH_3—OH$ $CH_3CH_2CH_2CH_2CH_2CH_2CH_2—OH$



Methanol: has a small organic part and is therefore water-like.

1-Heptanol: has a large organic part and is therefore alkane-like.

London dispersion forces can increase the boiling point of alcohols as the _____

_____ of the molecule grows larger:

Formula	IUPAC Name	Common Name	Boiling Point (°C)	Water Solubility (g/100 mL)
Alcohols				
CH_3OH	Methanol	Methyl alcohol	65.0	Miscible[a]
CH_3CH_2OH	Ethanol	Ethyl alcohol	78.5	Miscible
$CH_3CH_2CH_2OH$	1-Propanol	Propyl alcohol	97.4	Miscible
$CH_3CH_2CH_2CH_2OH$	1-Butanol	Butyl alcohol	117.3	8.0
$CH_3CH_2CH_2CH_2CH_2OH$	1-Pentanol	Pentyl alcohol	138	2.2

Which of the following molecules can form hydrogen bonds to another molecule of the same type?

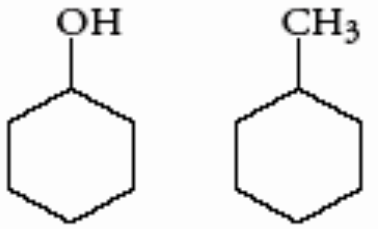
a. H_2O

b. $CH_3\overset{\overset{O}{\|}}{C}CH_3$

c. CH_3CH_2OH

d. $CH_3\overset{\overset{O}{\|}}{C}-OH$

Which molecule has the higher boiling point?

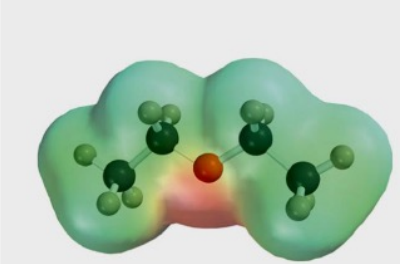


Ethers

- An _____ is a compound that has an oxygen bonded to two organic groups, R-O-R.

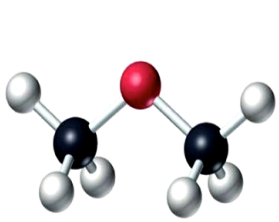
$CH_3CH_2OCH_2CH_3$

Diethyl ether



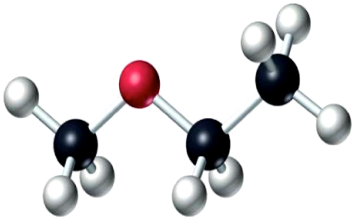
Naming Ethers

- Ethers are named by identifying the two organic groups and adding the word "ether".



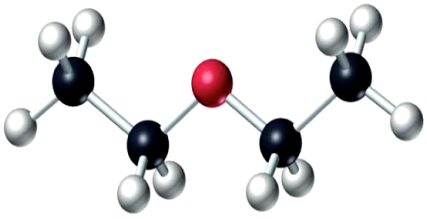
$CH_3—O—CH_3$

Dimethyl ether



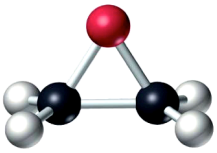
$CH_3—O—CH_2CH_3$

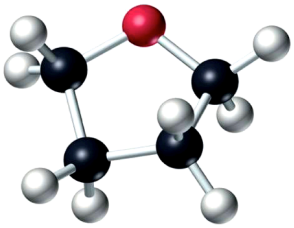
Ethyl methyl ether

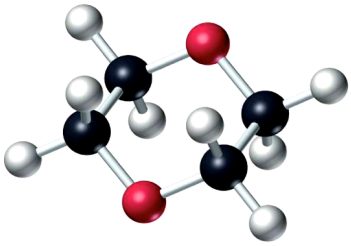


$CH_3CH_2—O—CH_2CH_3$

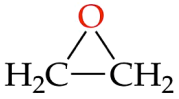
Diethyl ether







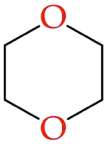
- Compounds containing oxygen in a ring are classified as cyclic ethers and are often given common names.



$H_2C—CH_2$ (O)

Ethylene oxide

Tetrahydrofuran
(a solvent)



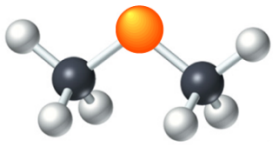
1,4-Dioxane
(a solvent)

Properties of Ethers

- Ethers do not hydrogen bond to one another. As a result they have lower boiling point than alcohols.
- The ether oxygen can form hydrogen bonds with water, causing low molecular weight ethers to be water soluble. Ethers with large organic groups are water insoluble.
- Simple ethers are highly flammable solvents.

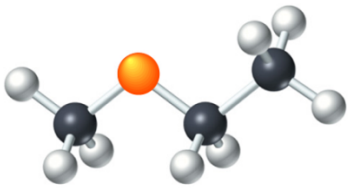
Sulfides

- Sulfides (R-S-R) are sulfur analog of ethers (R-O-R).
- We will use common names by placing the word sulfide after the alkyl groups as done with ethers**.**



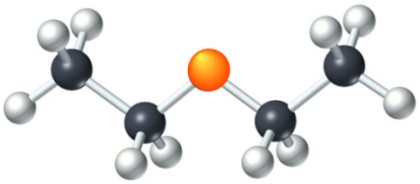
$CH_3— S —CH_3$

Dimethyl sulfide



$CH_3— S —CH_2CH_3$

Ethyl methyl sulfide



$CH_3CH_2— S —CH_2CH_3$

Diethyl sulfide

Thiols

- Thiols (R-SH) are sulfur analog of alcohols (R-OH).
- The systematic name of a thiol is formed by adding -thiol to the parent hydrocarbon name.
- Thiols have a characteristic foul smell.

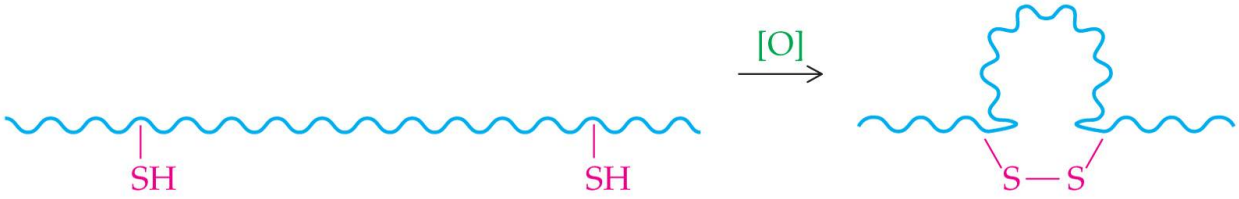
CH_3CH_2SH
Ethanethiol

$CH_3CHCH_2CH_2SH$ (with CH_3 branch)
3-Methyl-1-butanethiol

Disulfides

Thiols (R-SH) react with mild oxidizing agents to yield _____ (R-S-S-R).

- S-S bonds between two cysteines (amino acids) contribute to giving protein molecules their required shapes in order to function.
- Hair protein is rich in S-S and –SH groups. When hair is 'permed' some of the disulfide bonds are broken and new ones are formed giving hairs a different shape.



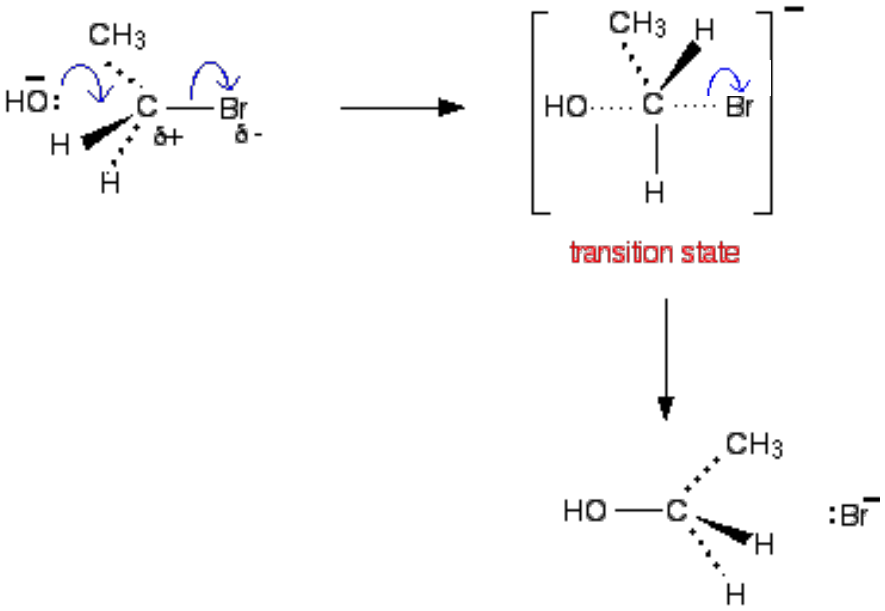
The boiling points of **thiols**, **sulfides**, and **disulfides** are much lower than those of alcohols with similar molecular weights, because none of these compounds are able to form hydrogen bonds to like molecules.

Preparation of Alcohols

Preparation of Alcohols: "Nucleophilic Substitution" Reactions

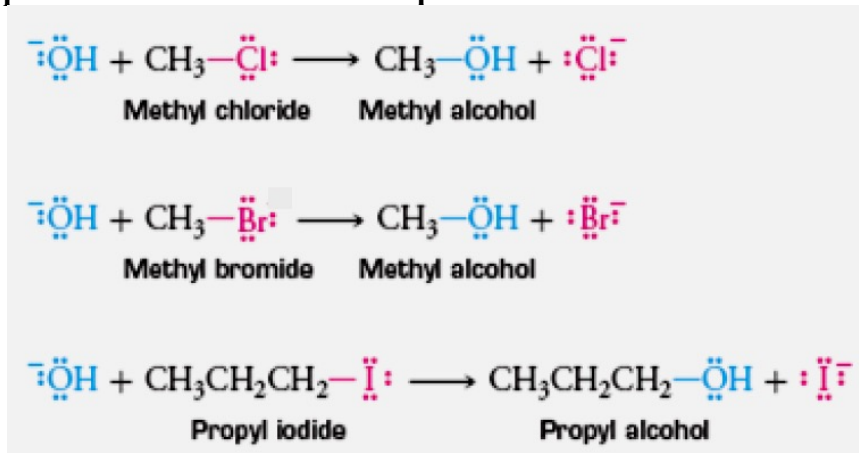
- Reaction of a hydroxide ion with and alkyl halide
  - an alkyl halide is a halogen (F, Cl, Br, or I) bonded to a hydrocarbon.

- Alcohols can be prepared using a _____ _____reaction, in which *an electron-rich atom or group of atoms*, called a ***nucleophile***, replaces a ***leaving group***, *an easily replaced atom or group of atoms*. Chlorine, bromine, and iodine are common leaving groups used in organic chemistry.



Arrows indicate the movement of electron pairs

Preparation of Alcohols: "Nucleophilic Substitution" Reactions

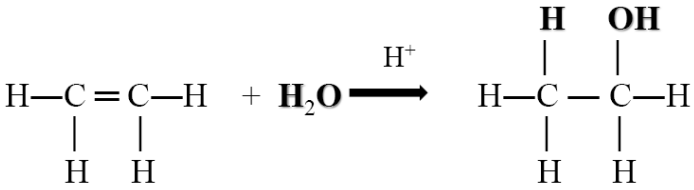


Draw the organic product for the nucleophilic substitution reaction.

$^{-}OH + CH_3CH_2Br \longrightarrow$

Preparation of Alcohols: Hydration of Alkenes (From Chapter 6)

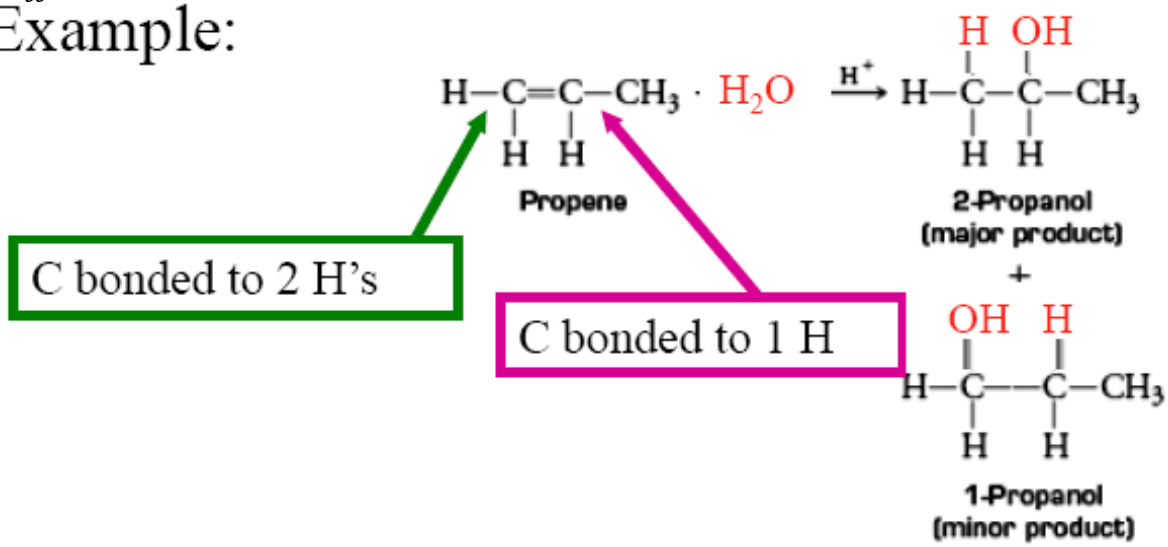
- In a _____ reaction, water is added to a double bond.



Hydration of Alkenes (Markovnikov's Rule)

In the preparation of alcohols from _____alkenes, it is possible to form ***two different alcohols***.

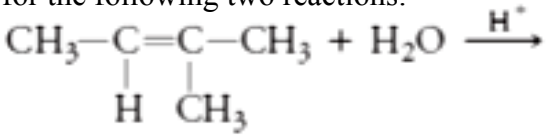
Example:



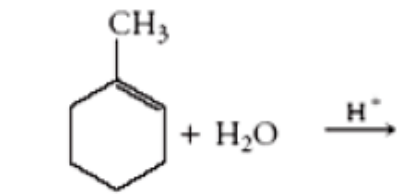
Markovnikov's rule says that, to **predict the major product**:

a hydrogen is added to the double-bonded carbon atom that originally carried the _____hydrogens.

Group Work: Predict the two possible products and indicate which is the major and minor product for the following two reactions:



2-Methyl-2-butene

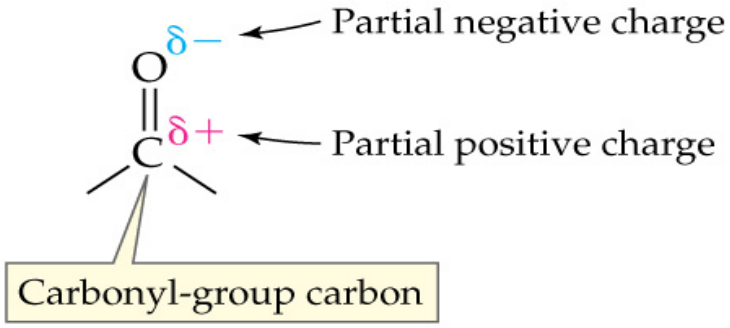


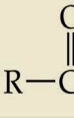
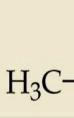
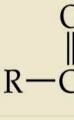
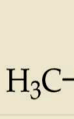
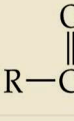
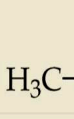
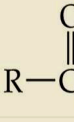
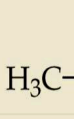
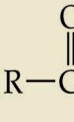
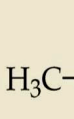
Methylcyclohexene

Aldehydes and Ketones

The Carbonyl Group

Carbonyl compound: Any compound that contains a carbonyl group (C=O). Carbonyl groups are strongly polarized, with a partial positive charge on carbon and partial negative charge on oxygen.



FAMILY NAME	STRUCTURE	EXAMPLE	
Aldehyde			Acetaldehyde
Ketone			Acetone
Carboxylic acid			Acetic acid
Ester			Methyl acetate
Amide			Acetamide

Carbonyl compounds include: aldehydes and ketones, carboxylic acids, esters, and amides.

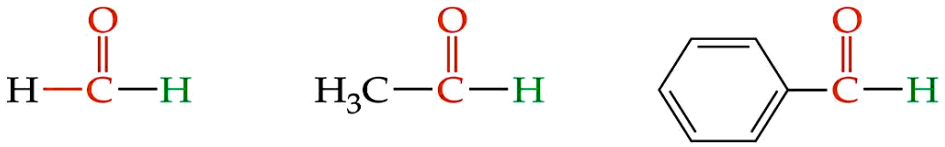
Aldehyde and Ketones

Aldehyde Ketone

Naming Aldehydes & Ketones

The simplest aldehydes are known by their common names, formaldehyde, acetaldehyde, benzaldehyde, and so on.

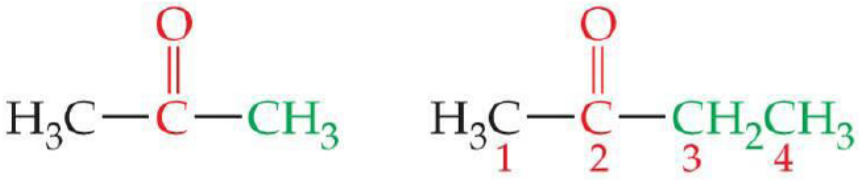
Aldehydes



Formaldehyde Acetaldehyde Benzaldehyde

Some ketones are best known by their common names that give the names of the two alkyl groups bonded to the ***carbonyl group*** followed by the word ketone.

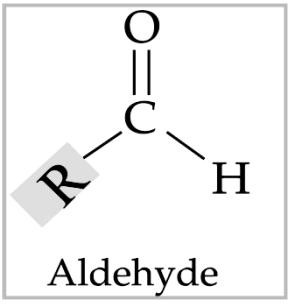
Ketones



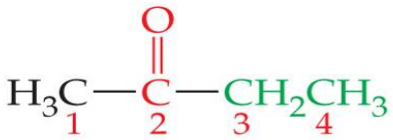
Acetone Ethyl methyl ketone

When naming aldehydes and ketones according to the **IUPAC rules**, the carbonyl (C=O) must be part of the parent chain, which is numbered from the end nearer this group.

Since the carbonyl carbon atom of an _____is always in position number 1, its position is not specified in the name.

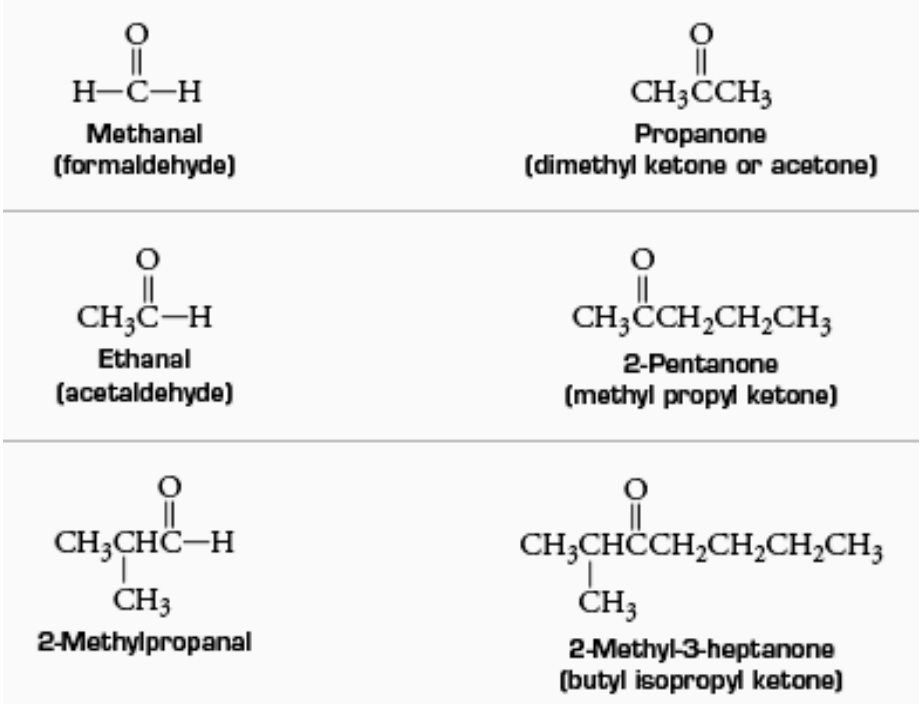


Aldehyde



For ketones, however, the position of the carbonyl carbon is given, *unless* the molecule is small enough that there is no question as to carbonyl placement.

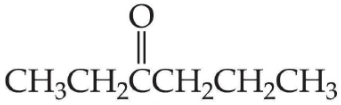
Parent chains are named by dropping the final "**e**" from the name of the corresponding hydrocarbon and adding "**al**" for **aldehydes** or "**one**" for **ketones**.

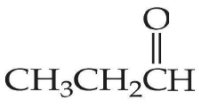


Common names in parenthesis

You try it!

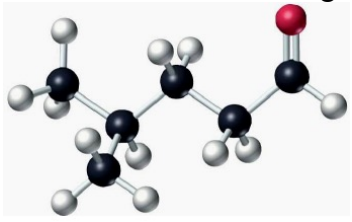
(1) Give the systematic names for these compounds:

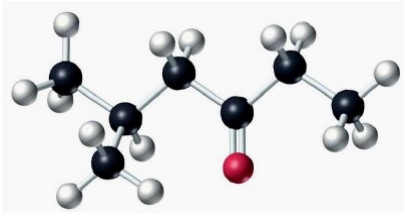




(2) Draw structures for 4-methylhexanal

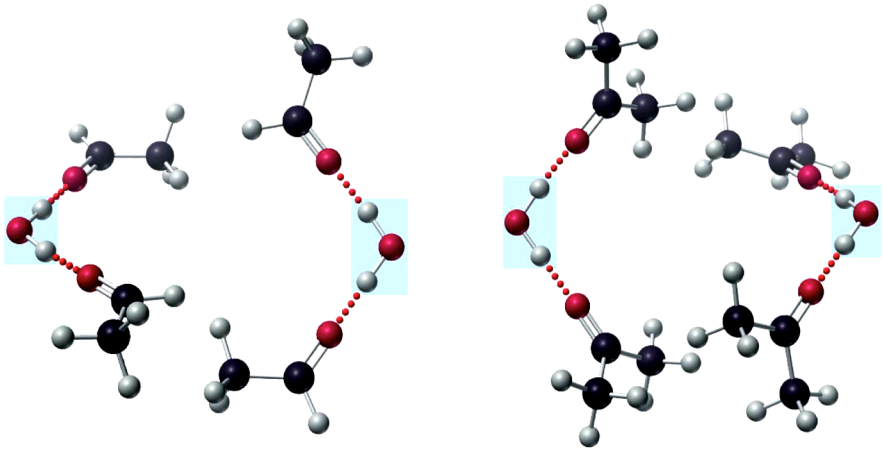
Draw line structures and give the systematic names for the following two compounds.





Properties of Aldehydes & Ketones

- The polarity of _____ group makes aldehydes and ketones moderately polar compounds.
- Aldehydes and ketones don't form hydrogen bonds to each other; however, they form hydrogen bond with water using the electron lone pairs on oxygen.



Aldehyde Ketone

- Aldehydes and ketones have lower boiling points compared to alcohols of similar size.

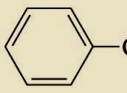
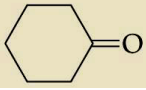
$CH_3CH_2CH_2CH_3$
Butane, bp 0°C

$CH_3CH_2\overset{\overset{O}{\|}}{C}H$
Propanal, bp 50°C

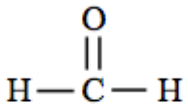
$CH_3\overset{\overset{O}{\|}}{C}CH_3$
Acetone, bp 56°C

$CH_3CH_2CH_2OH$
Propanol, bp 97°C

Aldehydes and ketones with fewer than five carbons are soluble in water.

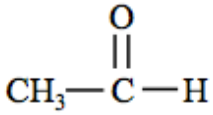
STRUCTURE	NAME	BOILING POINT (°C)	WATER SOLUBILITY (g/100 mL H_2O)
HCHO	Formaldehyde	−21	55
CH_3CHO	Acetaldehyde	21	Soluble
CH_3CH_2CHO	Propanal	49	16
$CH_3CH_2CH_2CHO$	Butanal	76	7
$CH_3CH_2CH_2CH_2CHO$	Pentanal	103	1
	Benzaldehyde	178	0.3
CH_3COCH_3	Acetone	56	Soluble
$CH_3CH_2COCH_3$	2-Butanone	80	26
$CH_3CH_2CH_2COCH_3$	2-Pentanone	102	6
	Cyclohexanone	156	2

Some Common Aldehydes & Ketones



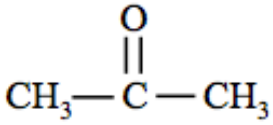
methanal (*or* formaldehyde)

Formaldehyde is quite toxic, however it is frequently used because of its ability to kill viruses, fungi, and bacteria. It is used to disinfect and sterilize equipment. Formaldehyde will react with other molecules, and chemically bond multiple molecules together into "polymers." Polymers are molecules *composed of multiple repeated subunits*. The polymers that are formed using formaldehyde as "linking agents" are used to make plastics and adhesives. Newly made formaldehyde-linked polymers may "out-gas" unreacted formaldehyde, therefore it is important to use safety precautions when handling these materials. In 2011, the US National Toxicology Program categorized formaldehyde as "known to be a human carcinogen".



ethanal (*or* acetaldehyde)

Acetaldehyde has a sweet aroma. In large quantities, it is narcotic. It occurs in smaller quantities naturally in coffee, bread, and ripe fruit, especially in apples. Its use is widespread in industry, notably in the formation of PVA polymer adhesives such as carpenter's glue (also known as white glue or Elmer's glue). I will discuss acetaldehyde's biological significance in later sections of this chapter.



propanone (*or* acetone)

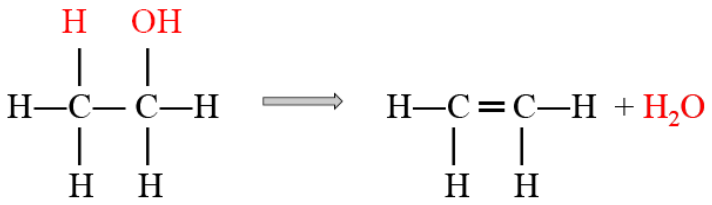
Acetone is often used as a solvent. It has the ability to dissolve many organic compounds and is also miscible with water. It is often used as nail-polish remover. Acetone has a high vapor pressure and is highly flammable. It is not significantly toxic and is not currently regarded as a carcinogen, a mutagenic chemical, or a concern for chronic neurotoxicity issues.

Reactions of Alcohols

1) Dehydration of Alcohols

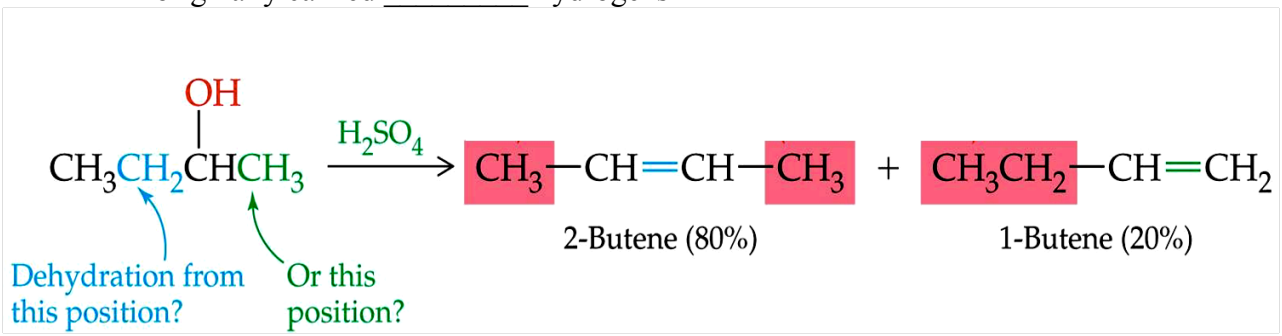
- Alcohols undergo _____ upon treatment with a strong acid catalyst to form *alkenes*. (Chapter 6)

- The –OH group is lost from one carbon and an H is lost from an _____ _____ to yield an alkene product:
-



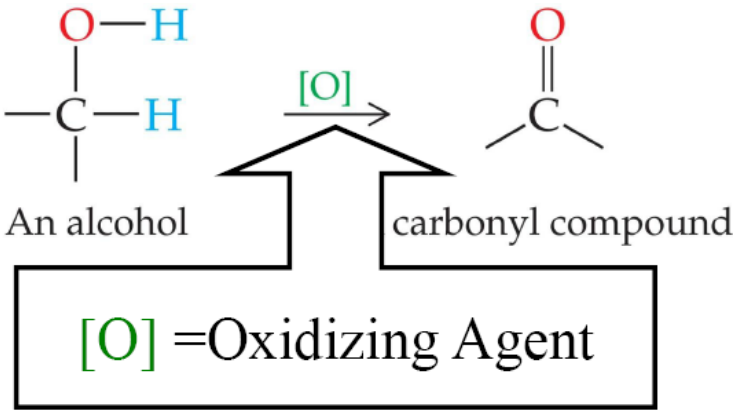
- When more than one alkene can result from dehydration of an alcohol, a mixture of products is usually formed.

    - The double bond forms better (forms the major product) with the ***adjacent carbon*** that originally carried _____ hydrogens



2) Oxidation of Alcohols

VERY IMPORTANT TO REMEMBER:
In organic chemistry:
Oxidation means adding O or removing H.
Reduction means adding H or removing O.

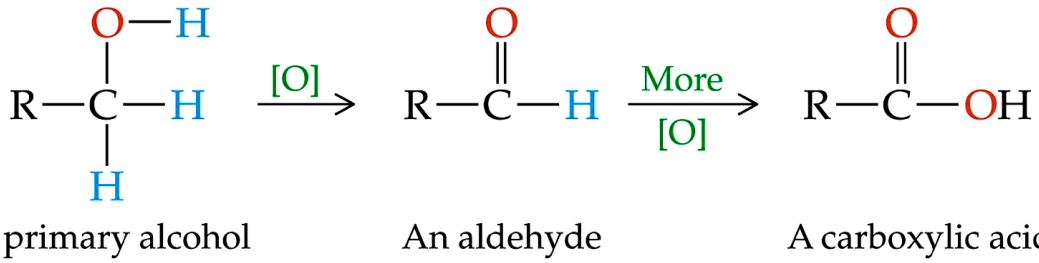


In the **oxidation of an alcohol**, two hydrogen atoms are removed from the alcohol: one hydrogen comes from the OH group and the other comes from the carbon bonded to the OH group.

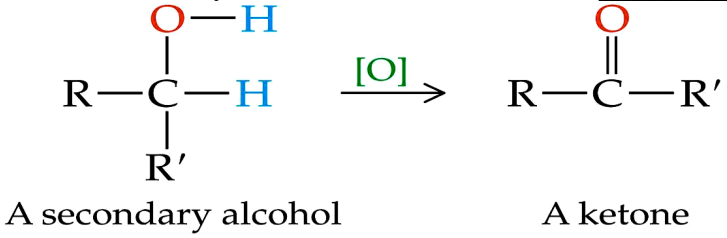
Many different oxidizing agents, such as potassium permanganate ($KMnO_4$), potassium dichromate ($K_2Cr_2O_7$) can be used.

Different kinds of carbonyl compounds are formed, depending on the _____ of the starting alcohol and the reaction conditions.

- ***Primary alcohols*** are converted either into an _____ if carefully controlled conditions are used, or into a _____ _____if an ***excess of oxidant*** is used.



- ***Secondary alcohols*** are converted into _____on treatment with oxidizing agent.

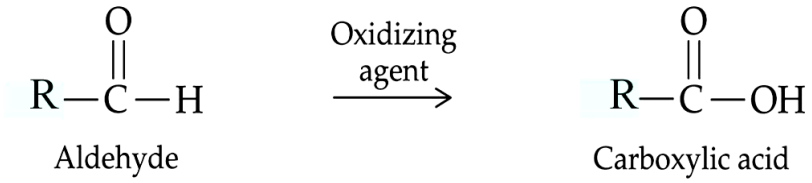


- ***Tertiary alcohols*** _____ _____with oxidizing agents because they do not have a hydrogen on the carbon atom to which the OH group is attached.

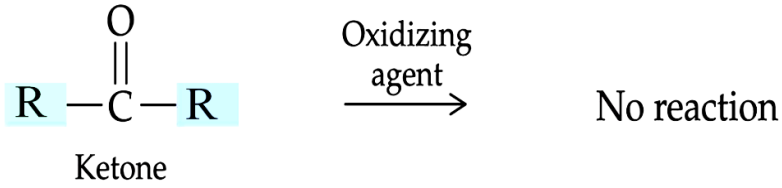
Reactions of Aldehydes and Ketones

1) Oxidation of Aldehydes and Ketones

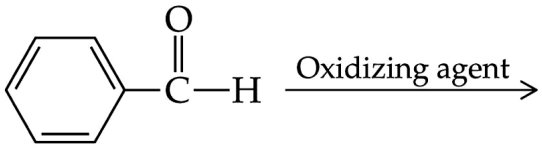
- **Aldehydes** can be further oxidized to **carboxylic acids**.



- **Ketones** *cannot* be oxidized.



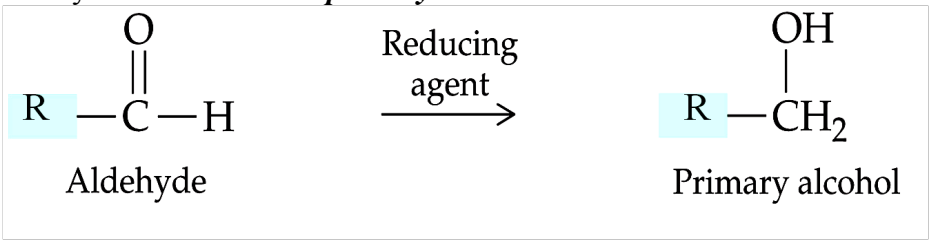
Draw the structure of the product of the following reaction.



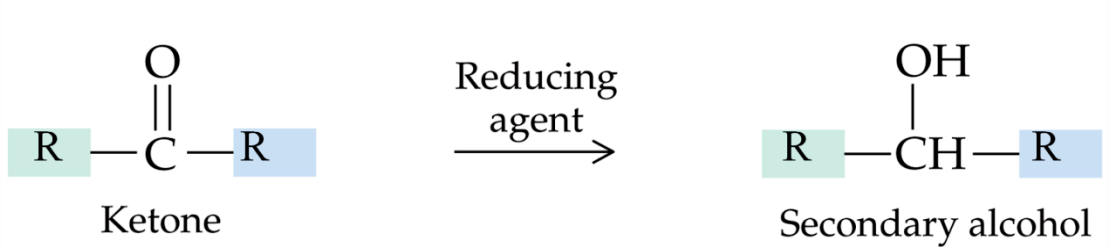
2) Reduction of Aldehydes and Ketones

- Reduction is the _____ of the oxidation reaction.
  - Reduction of a carbonyl group is the addition of 2 hydrogens "across" the double bond, one H to the C and one H to the O. *This produces an alcohol*.

- Aldehydes are reduced to ***primary*** alcohols

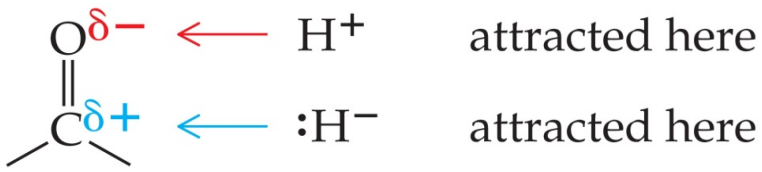


- Ketones are reduced to _____ alcohols.



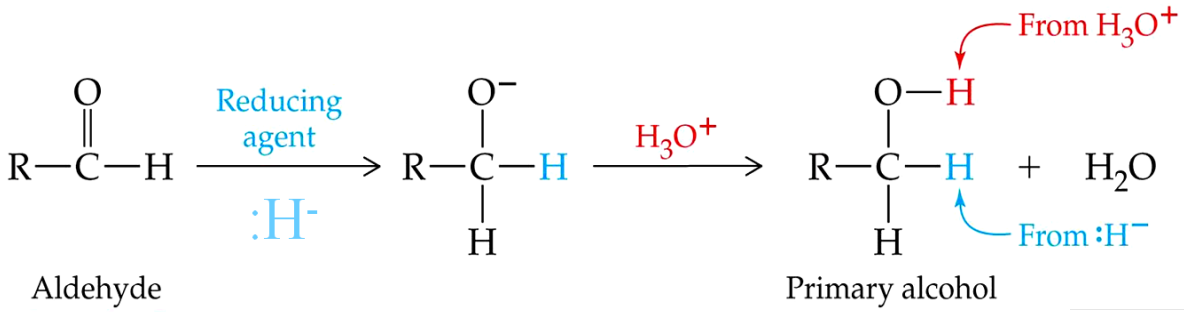
Reduction of Aldehydes & Ketones (continued)

- Reduction of the carbonyl group occurs by formation of a bond to the carbonyl carbon by a hydride, $H:^-$ ion accompanied by bonding of a H^+ ion to the carbonyl oxygen atom.
- H_2/Pt catalyst, $LiAlH_4$ or $NaBH_4$ can be used; in biochemical systems NADH can supply the hydride ion.

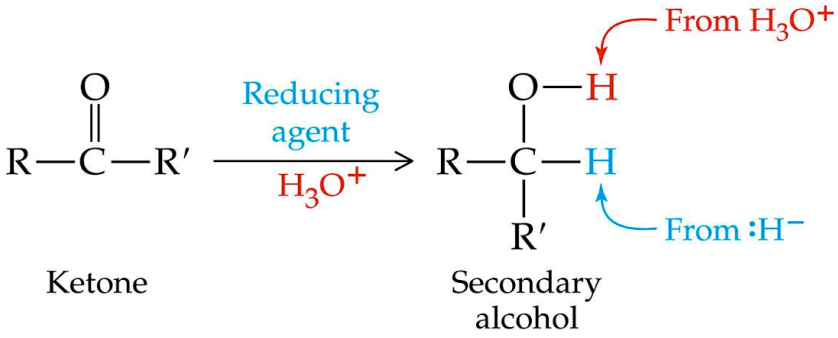


Examples:

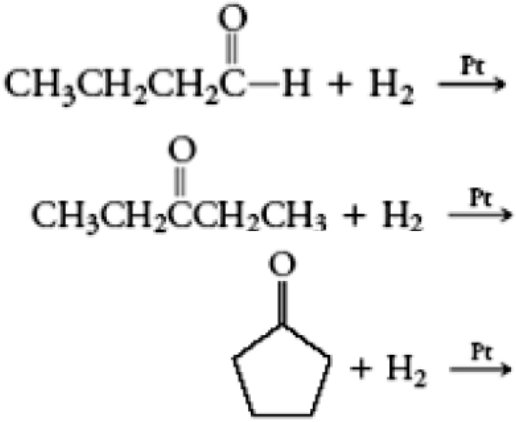
Reduction of an aldehyde



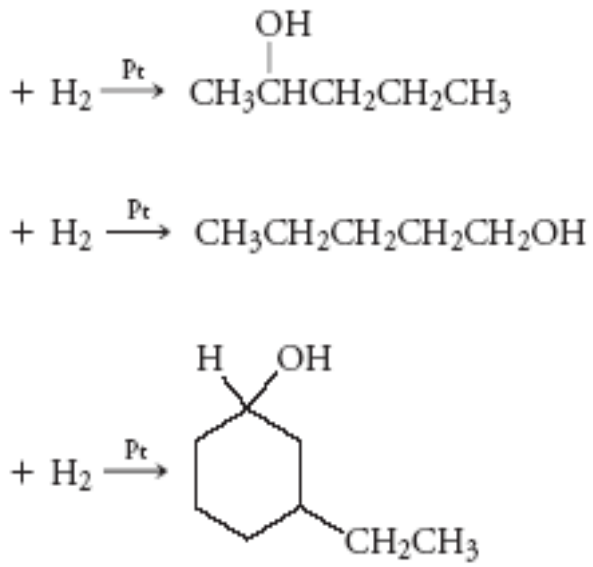
Reduction of a ketone



Draw the alcohol product expected from each reduction reaction.



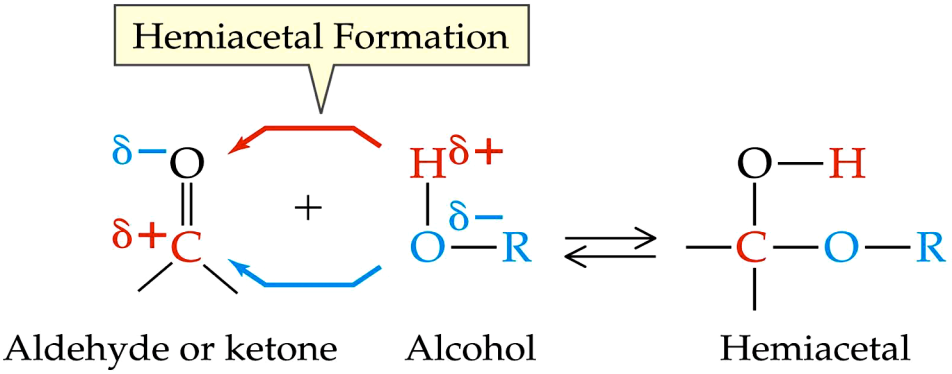
Provide the missing reactant for each reaction.



Reactions of Alcohols with Aldehydes and Ketones

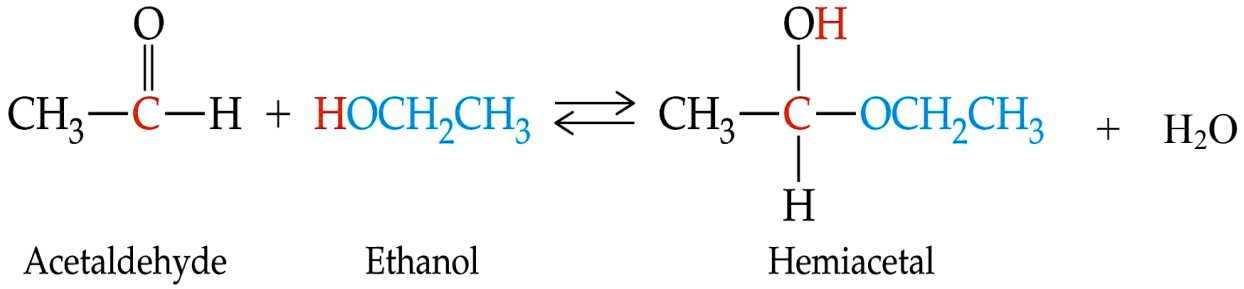
Addition of Alcohols: Hemiacetals & Acetals

Hemiacetal formation: Aldehydes and ketones undergo reactions in which and alcohol molecule is added "across" the carbonyl group (C=O) double bond.



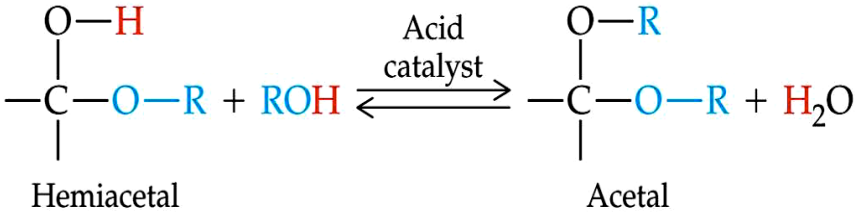
A ***hemiacetal*** is a molecule that has ***both*** an –OH ***and*** an –OR bonded to the _____ carbon.

The reaction is reversible. Hemiacetals rapidly revert back to aldehydes or ketones by loss of alcohol.

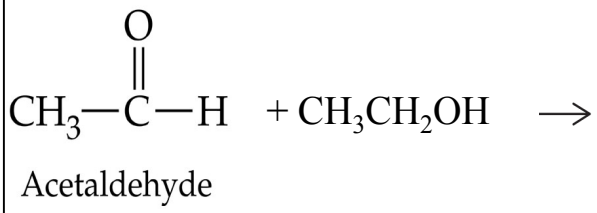


Acetal Formation: In the presence of a small amount of acid catalyst, **hemiacetals** are converted to **acetals**.

- Acetals have ***two*** –OR groups attached to the same carbon.



Draw the hemiacetal ***and*** acetal reaction products for the reaction of acetaldehyde and ethanol:

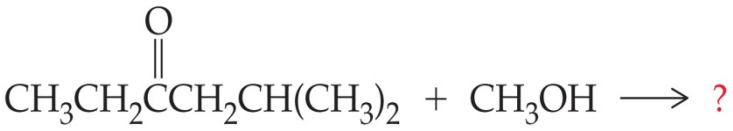


→ ?

hemiacetal

acetal

Draw the hemiacetal and acetal produced by this reaction:

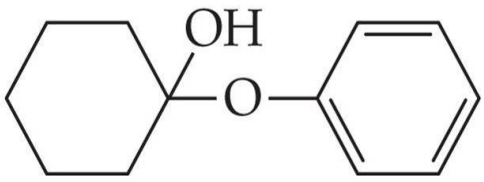


→ ?

hemiacetal

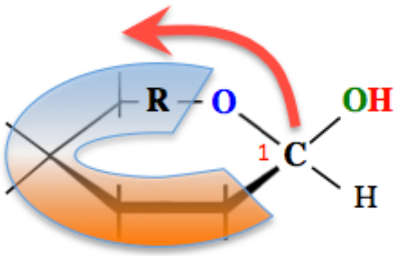
acetal

Identity the following as either hemiacetal or acetal:



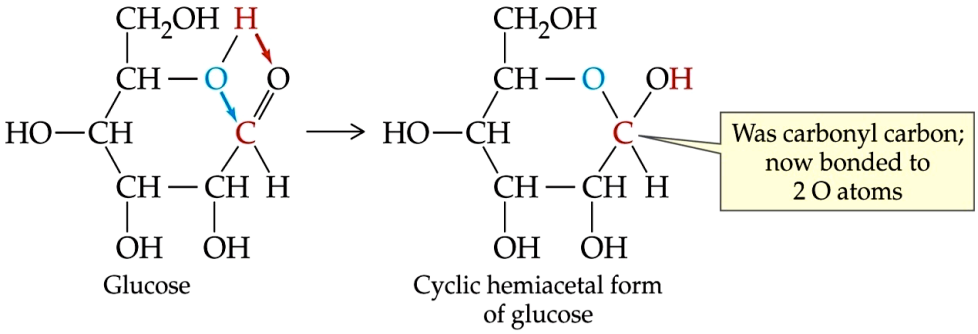
Cyclic Hemiacetals

Recall that a **hemiacetal** is a molecule that contains ***both*** an **-OR** group *and* an **-OH** group that are bonded to the ***same*** carbon. Carbons that are bonded to ***both*** an **-OR** group *and* an **-OH** group are called **hemiacetal carbons**. Carbon number **1** in the ring structure shown meets this criterion. The **OH** that is bonded to carbon number **1** is obvious, but the **OR** may not be immediately obvious to you. However, note that, beginning at carbon number **1** and moving *counter-clockwise* - as indicated by the **arrow** in the structure shown below - the **OR** bonding pattern can be seen. When the **OR** bonding pattern occurs in this way, ***forming a ring***, the molecule is referred to as a **cyclic hemiacetal.**



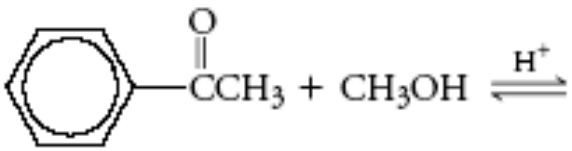
a cyclic hemiacetal

Why study about the acetal and hemiacetal formation reaction?
Answer: Cyclization of carbohydrates! (Coming soon!)



THE FOLLOWING PRACTICE PROBLEMS **ARE NOT** IN THE VIDEO LECTURE.
HEMICACETAL/ACETAL PRACTICE PROBLEMS (**SEE LAST PAGE FOR KEY**)

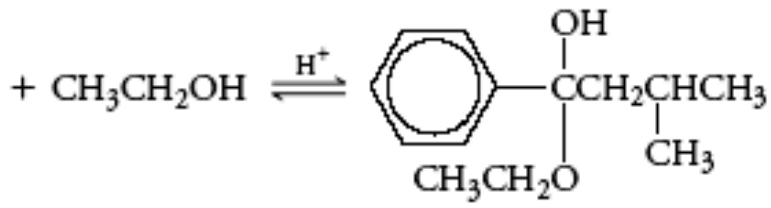
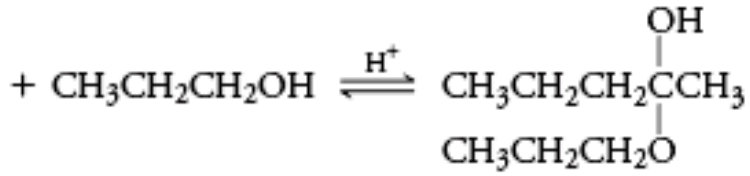
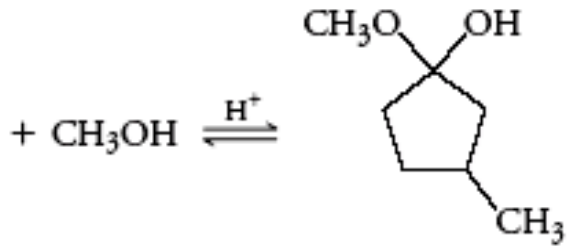
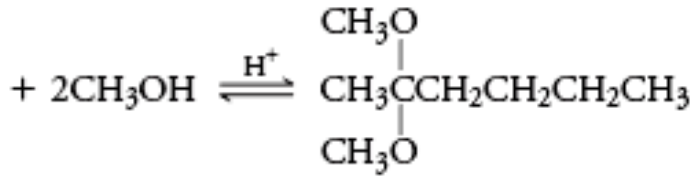
a. $CH_3CH_2\overset{O}{\overset{\|}{C}}-H + CH_3CH_2CH_2OH \overset{H^+}{\rightleftharpoons}$

b. 

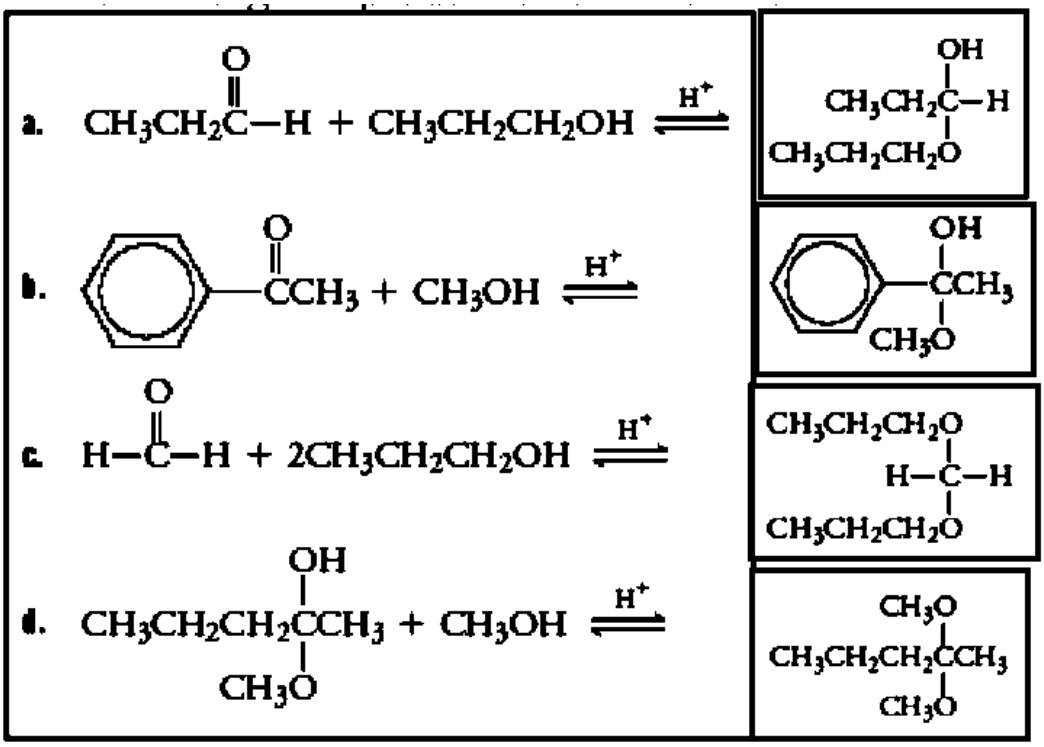
c. $H-\overset{O}{\overset{\|}{C}}-H + 2CH_3CH_2CH_2OH \overset{H^+}{\rightleftharpoons}$

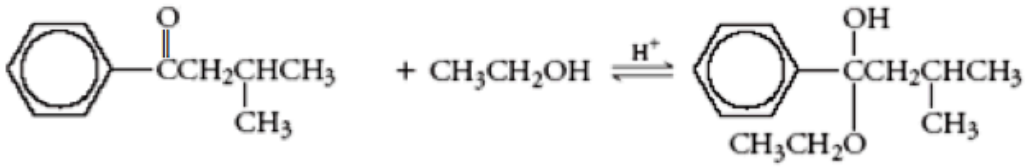
d. $CH_3CH_2CH_2\overset{OH}{\overset{|}{\underset{CH_3O}{\underset{|}{C}}}}CH_3 + CH_3OH \overset{H^+}{\rightleftharpoons}$

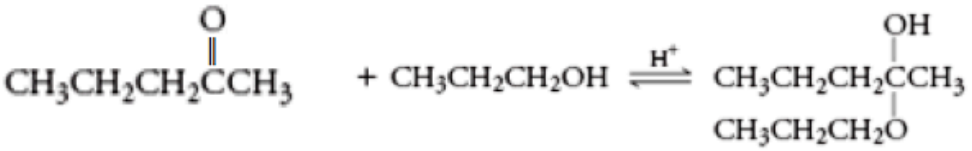
Draw the missing **reactant** for each reaction.

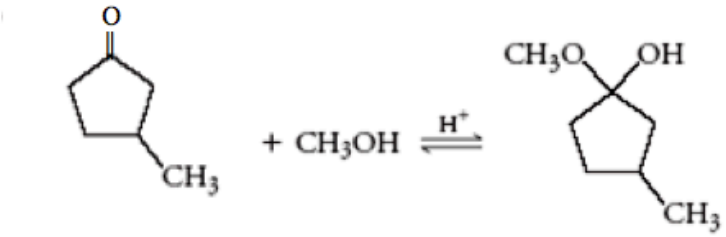
	
	
	
	

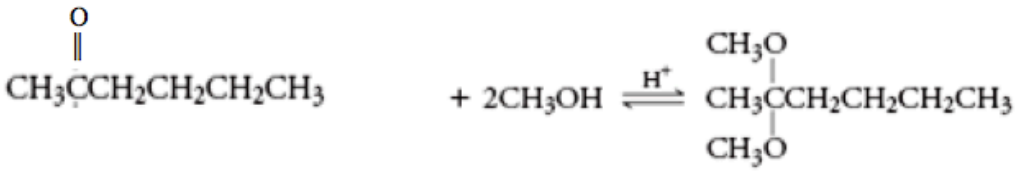
SEE NEXT PAGE FOR KEYS


a. CH3CH2C(=O)H + CH3CH2CH2OH ⇌ (H+) CH3CH2C(OH)(H)OCH2CH2CH3
b. C6H5C(=O)CH3 + CH3OH ⇌ (H+) C6H5C(OH)(CH3)OCH3
c. HC(=O)H + 2CH3CH2CH2OH ⇌ (H+) HC(OCH2CH2CH3)2H
d. CH3CH2CH2C(OH)(CH3)OCH3 + CH3OH ⇌ (H+) CH3CH2CH2C(OCH3)2CH3


C6H5C(=O)CH2CH(CH3)CH3 + CH3CH2OH ⇌ (H+) C6H5C(OH)(OCH2CH3)CH2CH(CH3)CH3


CH3CH2CH2C(=O)CH3 + CH3CH2CH2OH ⇌ (H+) CH3CH2CH2C(OH)(OCH2CH2CH3)CH3


C5H8O + CH3OH ⇌ (H+) C5H8(OH)(OCH3)


CH3C(=O)CH2CH2CH2CH3 + 2CH3OH ⇌ (H+) CH3C(OCH3)2CH2CH2CH2CH3