Chapter 4
Aldehydes and Ketones

Chapter Objectives:

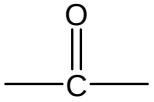
- Learn to recognize the aldehyde and ketone functional groups.
- Learn the IUPAC system for naming aldehydes and ketones.
- Learn the important physical properties of the aldehydes and ketones.
- Learn the major chemical reaction of aldehydes and ketones, and learn how to predict the products of hydrogenation, oxidation, and addition of alcohol reactions.
- Learn to recognize the acetal, hemiacetal, ketal, and hemiketal group, and how these are related to aldehydes and ketones.

Mr. Kevin A. Boudreaux
Angelo State University
CHEM 2353 Fundamentals of Organic Chemistry
Organic and Biochemistry for Today (Seager & Slabaugh)
www.angelo.edu/faculty/kboudrea

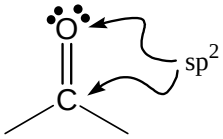
The Carbonyl Group

The Carbonyl Group

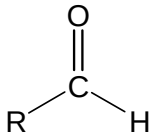
- The **carbonyl group** (C=O) is found in **aldehydes**, **ketones**, and many other organic functional groups.
- The carbon and oxygen in the carbonyl group are sp^2-hybridized, with bond angles of 120°.



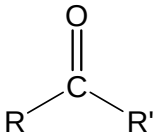
the **carbonyl** group



- In **ketones**, two carbon groups are attached to the carbonyl carbon, while in **aldehydes** at least one hydrogen is attached to the carbon.



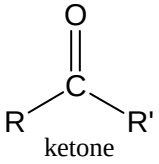
aldehyde



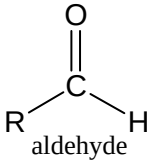
ketone

3

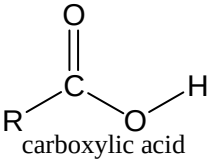
Functional Groups Containing Carbonyls



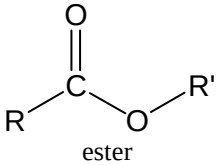
ketone



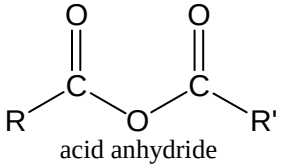
aldehyde



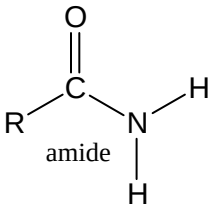
carboxylic acid



ester



acid anhydride



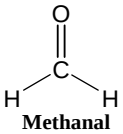
amide

4

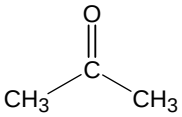
Nomenclature of Aldehydes and Ketones

5

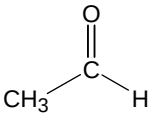
Some Common Aldehydes and Ketones



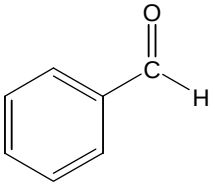
Methanal
(Formaldehyde)
Gas at room temperature; 35-40% solution in water, called **formalin**, used to preserve biological specimens, sterilize instruments, and embalm cadavers; present in wood smoke, and helps to preserve smoked meats by killing bacteria.



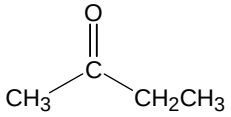
2-Propanone
(Acetone)
1 billion pounds used annually in U.S.; good solvent for most organic compounds, and is also soluble in water; solvent for coatings such as fingernail polish and enamel paints, etc.



Ethanal
(Acetaldehyde)
Product of oxidation of ethanol in the liver; consuming large quantities of ethanol causes acetaldehyde to build up in bloodstream faster than it can be consumed in the liver to make other products, leading to nausea, sweating, reduced blood pressure, etc.



Benzaldehyde
Causes the odor of almonds and cherries, and is also found in apricots and peaches.

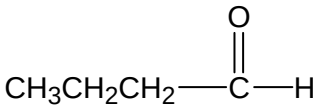


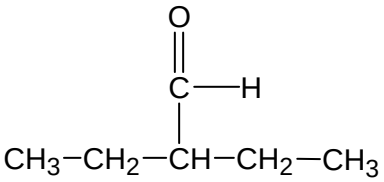
2-Butanone
(Methyl ethyl ketone, MEK)
Common industrial solvent

6

Nomenclature of Aldehydes

- Select the longest carbon chain *containing the carbonyl carbon*.
- The **-e** ending of the parent alkane name is replaced by the suffix **-al**.
- The carbonyl carbon is always numbered "1." (It is not necessary to include the number in the name.)
- Name the substituents attached to the chain in the usual way.

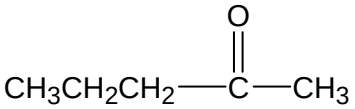


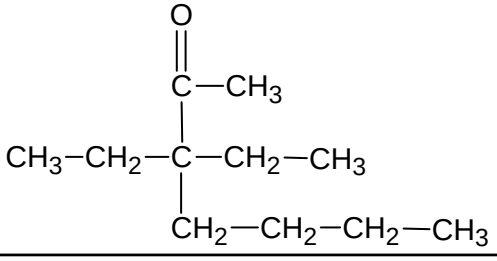


7

Nomenclature of Ketones

- Select the longest carbon chain *containing the carbonyl carbon*.
- The **-e** ending of the parent alkane name is replaced by the suffix **-one**.
- Number the chain starting with the end closest to the ketone group (the carbonyl carbon should have the lowest possible number). The location # for the ketone group precedes the name for the longest chain.
- Name the substituents attached to the chain in the usual way.

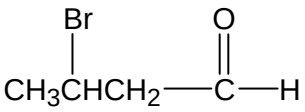


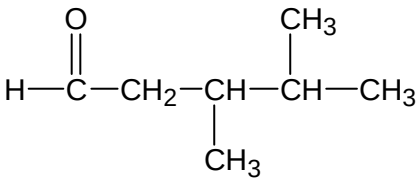


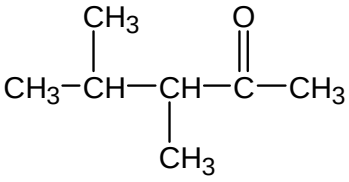
8

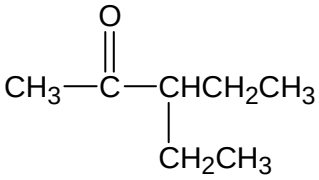
Examples: Naming Aldehydes and Ketones

- Name the following compounds:









9

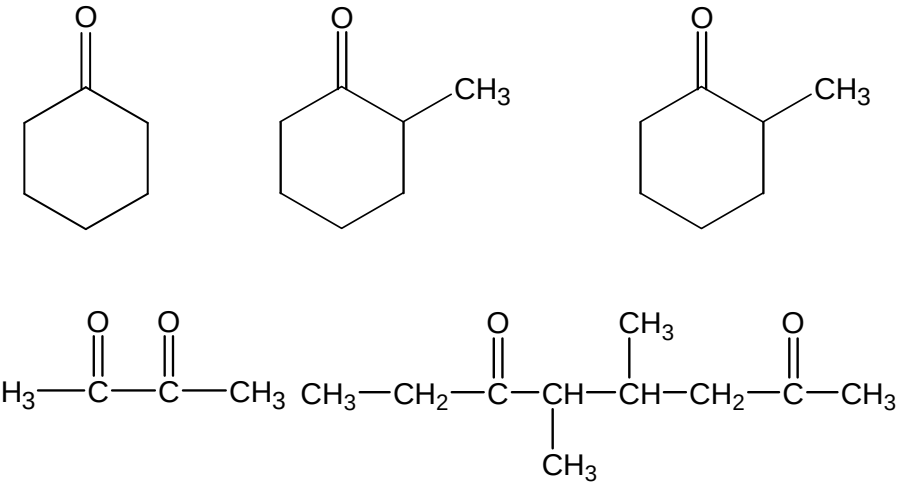
Other Nomenclature Rules

- In cyclic ketones, the carbonyl group is always numbered “1”; this does not need to be included in the name. The numbering continues clockwise or counterclockwise to give the lowest number for the next substituent.
- Molecules with more than one ketone group are named by preceding the suffix with a counting prefix (*di*one, *tri*one, etc.); position numbers must be used for each ketone group.
- Aromatic aldehydes (containing an aldehyde group directly attached to a benzene ring) are named after the parent compound **benzaldehyde**. (The carbon to which the aldehyde group is attached is carbon “1”).

10

Examples: Naming Aldehydes and Ketones

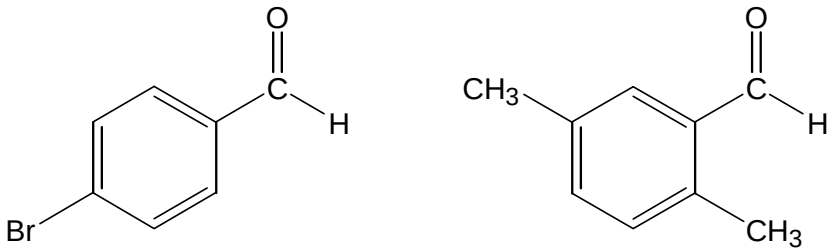
- Name the following compounds:

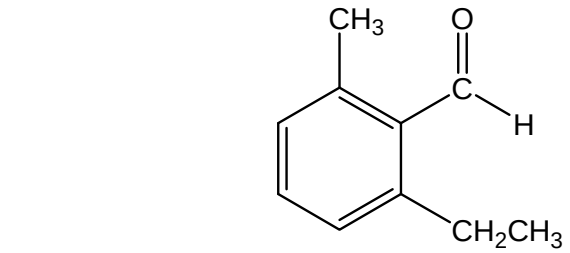


11

Examples: Naming Aldehydes and Ketones

- Name the following compounds:





12

Examples: Naming Aldehydes and Ketones

- Draw structural formulas for the following molecules:
  - 3-ethyl-2-pentanone
  - 2,4,6-trimethylheptanal
  - 3-ethylcyclopentanone

13

Examples: Naming Aldehydes and Ketones

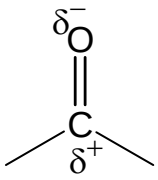
- Draw structural formulas for the following molecules:
  - 4-chloro-2-phenylpentanal
  - para-nitrobenzaldehyde
  - 3-ethyl-2-butanone (what's wrong with this name?)

14

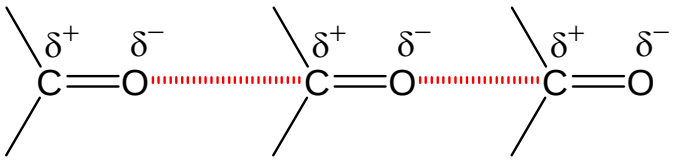
Physical Properties of Aldehydes and Ketones

The Polarity of the Carbonyl Group

- Carbonyl compounds are polar, containing a dipole along the carbon-oxygen double bond.



- This creates weak attractive forces between carbonyl compounds, but these attractions are not as strong as those that result from hydrogen-bonding.

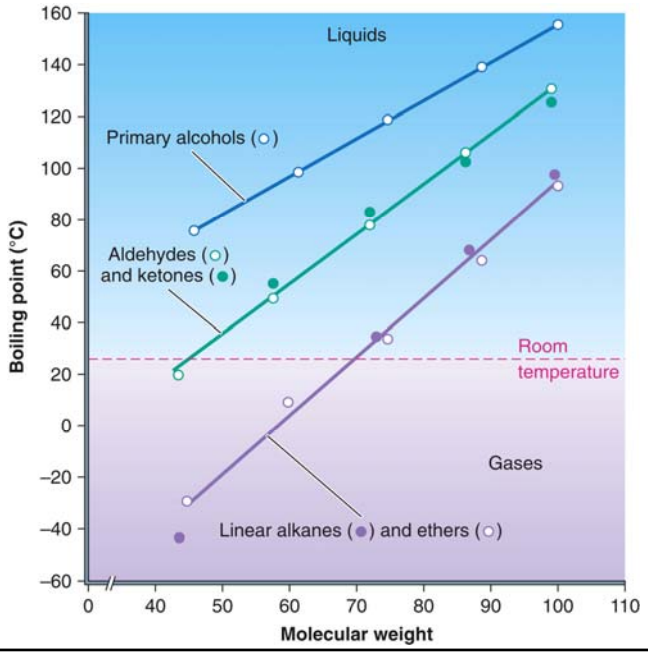


The Boiling Points of Aldehydes and Ketones

- Since there is no hydrogen on the carbonyl oxygen, aldehydes and ketones *do not form hydrogen bonds with themselves*.
- Aldehydes and ketones therefore have boiling points that are in between those of alcohols and hydrocarbons of the same molecular weight:
  - Alcohols form hydrogen bonds, and have high boiling points.
  - Hydrocarbons are nonpolar, and have low boiling points.
  - Aldehydes and ketones are polar, so they have higher boiling points than hydrocarbons, but they are not as polar as molecules which can hydrogen bond.

17

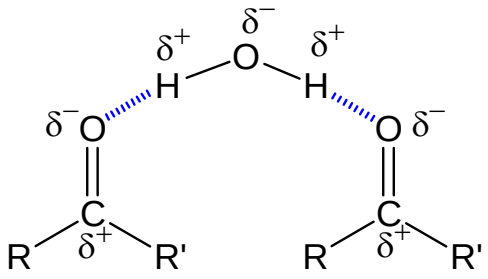
The Boiling Points of Aldehydes and Ketones



18

Physical Properties of Aldehydes and Ketones

- Carbonyl compounds cannot hydrogen-bond to each other, but they can hydrogen-bond to water through the carbonyl oxygen.
- Low-molecular weight aldehydes and ketones are water-soluble; water solubility decreases as the size of the molecule increases.



19

Physical Properties of Aldehydes and Ketones

Boiling Points:

↑ Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Water Solubility:

↑ Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Name	Molecular weight	Boiling point	Solubility in water
butane	58 g/mol	0°C	Insoluble
propanal	58 g/mol	49°C	Soluble
acetone	58 g/mol	56°C	Soluble
1-propanol	60 g/mol	97°C	Soluble

20

Examples: Predicting Boiling Points

- Arrange the following compounds in order of increasing boiling point:
  - 2-pentanone
  - 2-methylpentane
  - 2-pentanol

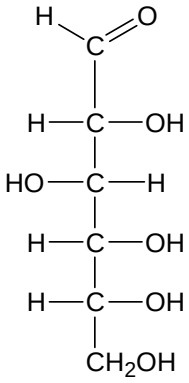
21

22

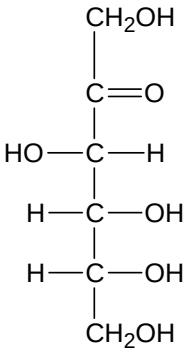
Some Important Aldehydes and Ketones

23

Important Aldehydes and Ketones



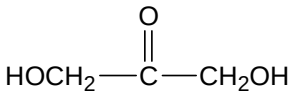
Glucose
One of the most important of the **carbohydrates**, which are *polyhydroxy aldehydes and ketones*; the metabolism of glucose is a major source of energy for living organisms



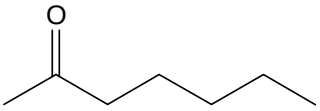
Fructose
Another important carbohydrate; a major component of corn syrup; found in honey, syrups, and preserves; in combination with glucose it forms the disaccharide **sucrose**.

24

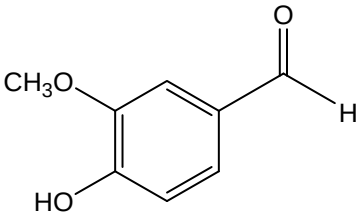
Important Aldehydes and Ketones



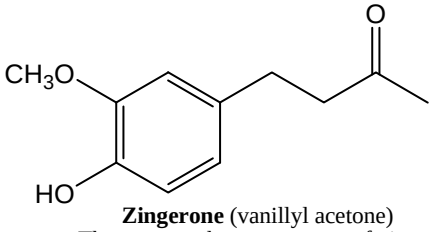
Dihydroxyacetone
Active ingredient in "bronzers" that provide fake suntan coloration; reacts with dead, outer skin cells to produce a darker color; fades as the dead skin cells slough off.



2-Heptanone
Found in oil of clove; also present in the odor of many fruits and dairy products, and is also responsible for the odor of blue cheese.

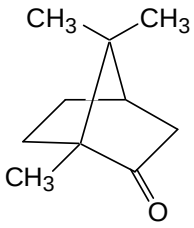


Vanillin
flavoring in Vanilla beans
(parent compound of the *vanniloids*)

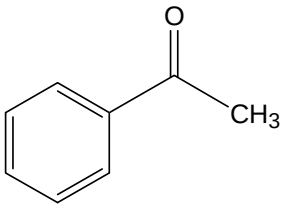


Zingerone (vanillyl acetone)
The pungent, hot component of ginger

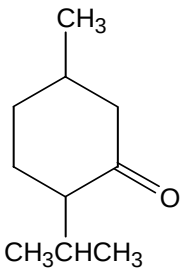
25



Camphor
Isolated by steam distillation from the camphor tree of China and Japan. Camphor is a counter-irritant (produces a superficial inflammation to reduce deeper inflammation) and antipruritic (anti-itching) medication; it appears to selectively stimulate cold sensors. It also stimulates the respiratory systems and inspires deep breathing, but can cause convulsions and respiratory collapse in larger doses.

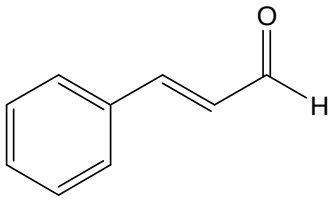


Acetophenone
Used in perfurmery, and as an organic solvent; also used in the synthesis of some pharmeceuticals

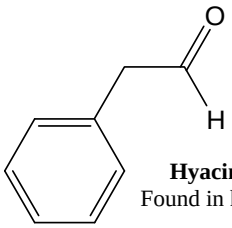


Menthone

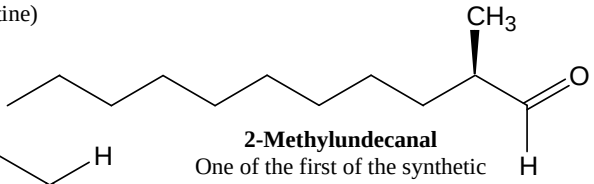
26



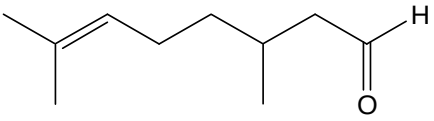
Cinnamaldehyde
The flavoring in oil of cinnamon; obtained by steam distillation from the bark of the cinnamon tree; has a *carminative* action (releases hydrogen sulfide, methane, and hydrogen from the intestine)



Hyacinthin
Found in hyacinth

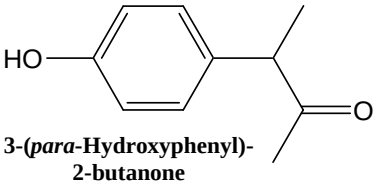


2-Methylundecanal
One of the first of the synthetic perfumes, introduced by Coco Chanel in 1921 as *Chanel No. 5*

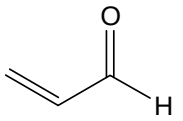


Citronellal
Found in citronella oil; used as an insect repellant

27

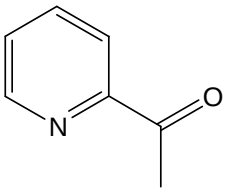


3-(*para*-Hydroxyphenyl)-2-butanone
Responsible for the odor of ripe raspberries.



Acrolein
Produced from the breakdown of triglycerides in meat during cooking; the acrid smell of this compound is obvious during barbeques. It also contributes to the taste of caramel, where it is produced by decomposing sucrose

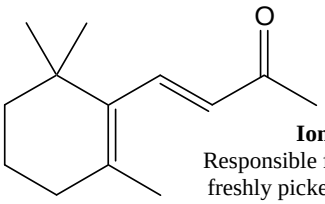
Methyl 2-pyridyl ketone
Found in the odor of popcorn



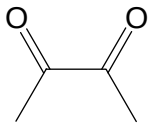
Vitamin K_1

A fat soluble vitamin btained from green leafy vegetables, cabbage, cauliflower, kale, spinach, pork liver; also made by intestinal bacteria. Essential for blood clotting.

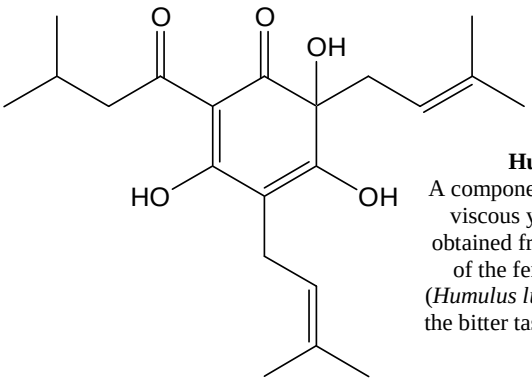
28



Ionone
Responsible for the odor of freshly picked raspberries, violets (and the extract, oil of violets), and sun-dried hay.



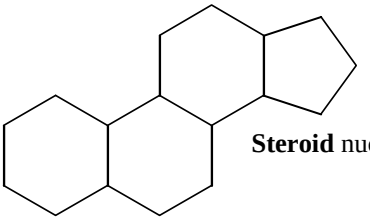
Butanedione
A volatile yellow liquid compound with the odor of cheese; gives butter its characteristic flavor. It also contributes to the odor of armpits and unwashed feet by the action of bacteria which ferment the compounds in perspiration.



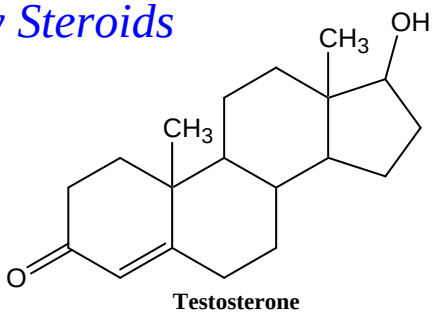
Humulone
A component of hop resin, a viscous yellow material obtained from the blossoms of the female hop plant (*Humulus lupulus*); it adds to the bitter taste of some beers.

29

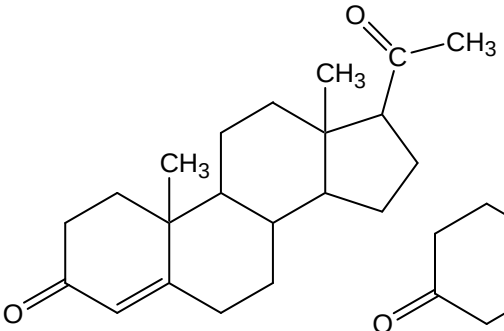
A Few Steroids



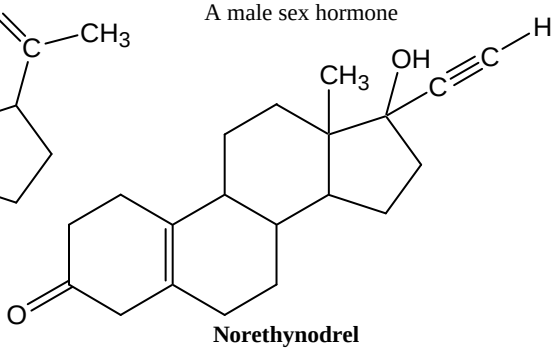
Steroid nucleus



Testosterone
A male sex hormone



Progesterone
A female sex hormone



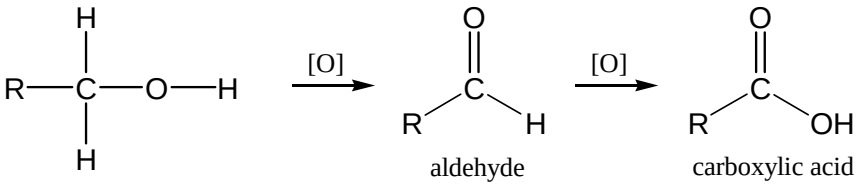
Norethynodrel
Active ingredient in birth-control pills

30

Reactions of Aldehydes and Ketones

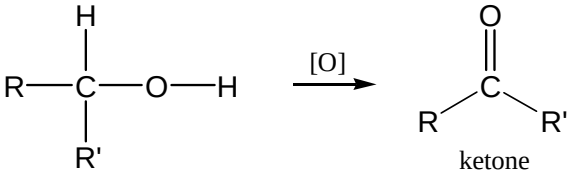
Oxidation of Alcohols to Produce Carbonyls

- Aldehydes, like primary alcohols, can be oxidized to produce carboxylic acids:



1° alcohol aldehyde carboxylic acid

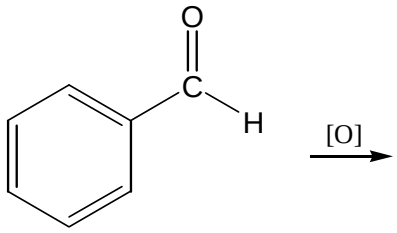
- Secondary alcohols can be oxidized to produce ketones, which are not further oxidized:

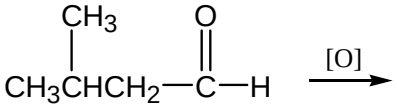


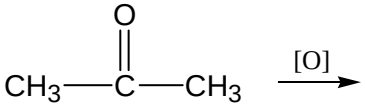
2° alcohol ketone

Examples: Oxidation Reactions

- Complete the following reactions:



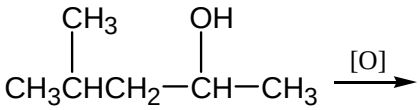


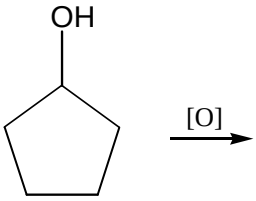


33

Examples: Oxidation Reactions

- Complete the following reactions:

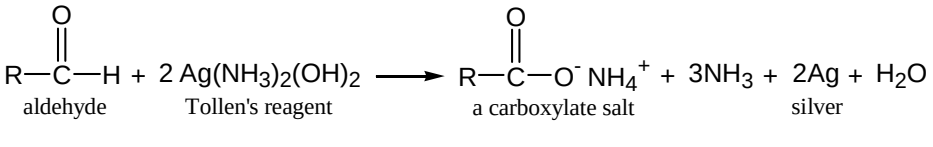


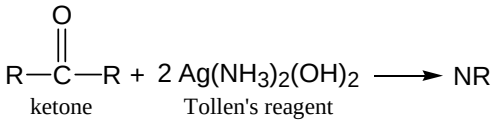


34

Oxidation of Aldehydes: The Tollens' Test

- **Tollens' reagent** is a mild oxidizing agent composed of silver ions in an aqueous basic solution of ammonia.
- Aldehydes are oxidized to carboxylate salts (since the solution is basic), and the silver ions are reduced to solid silver, which coats the bottom of the test tube with a "silver mirror."
- Ketones are not oxidized, so no silver mirror forms.

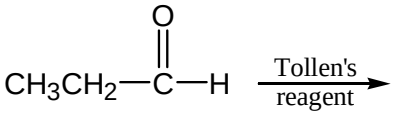


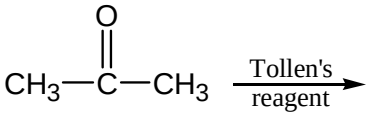


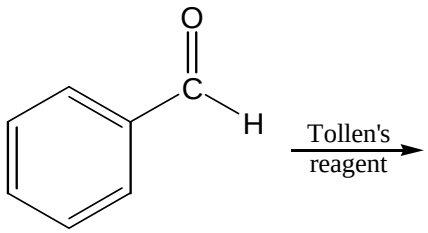
35

Examples: The Tollens' Test

- What observations would be made in the following reactions?





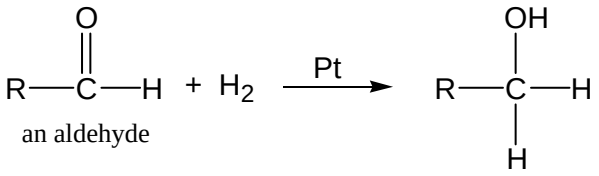


Unknown $\xrightarrow[\text{reagent}]{\text{Tollen's}}$ silver ppt

36

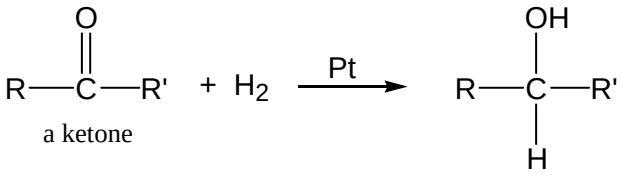
Hydrogenation of Aldehydes and Ketones

- **Hydrogenation** of aldehydes and ketones with hydrogen gas and a platinum catalyst produces alcohols:



an aldehyde

a primary alcohol



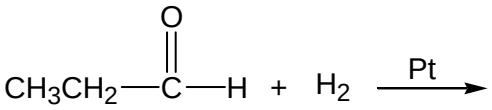
a ketone

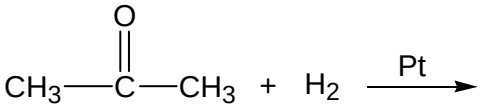
a secondary alcohol

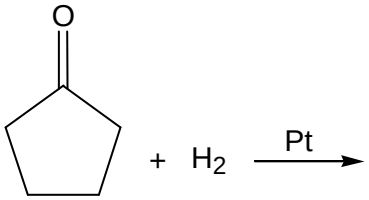
37

Examples: Hydrogenation Reactions

- Complete the following reactions:



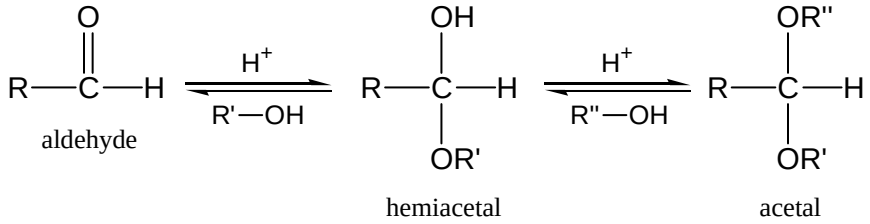




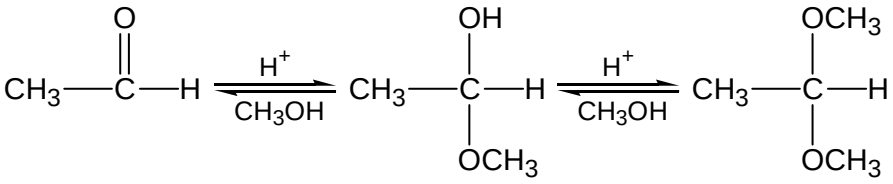
38

Addition of Alcohols to Aldehydes

- Aldehydes react with alcohols first to form **hemiacetals**, which then react with excess alcohol to produce **acetals**.

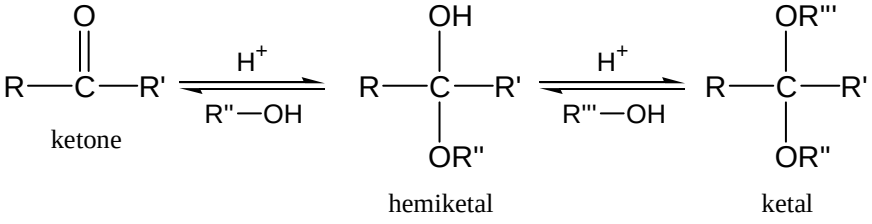


aldehyde hemiacetal acetal

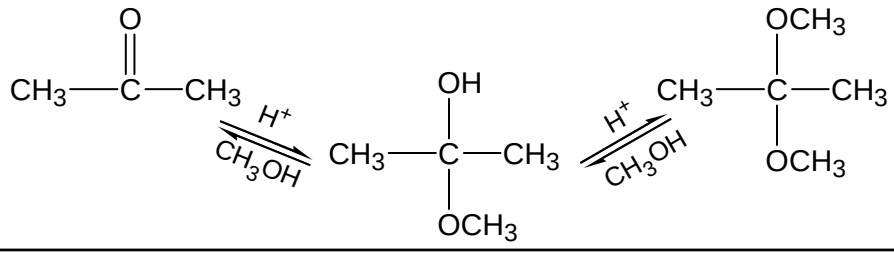


Addition of Alcohols to Ketones

- Ketones react with alcohols first to form **hemiketals**, which then react with excess alcohol to produce **ketals**.

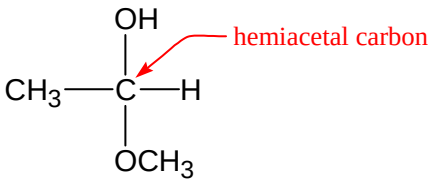


ketone hemiketal ketal

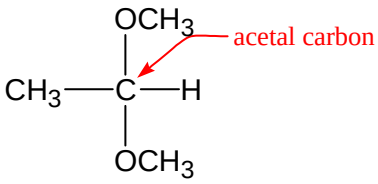


Hemiacetals, Acetals, Hemiketals, and Ketals

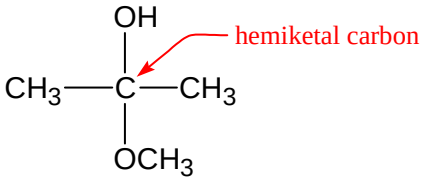
(oh my)



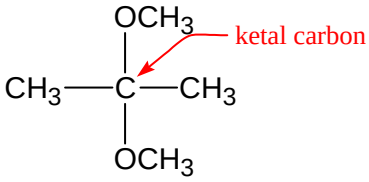
a **hemiacetal**



an **acetal**



a **hemiketal**

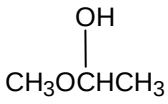


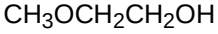
a **ketal**

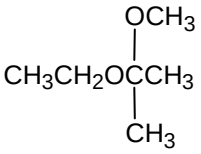
41

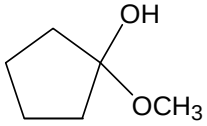
Examples: Identifying Acetals and Ketals

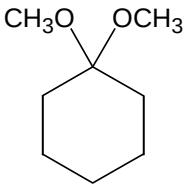
- Identify the following compounds as being acetals, ketals, hemiacetals, or hemiketals.

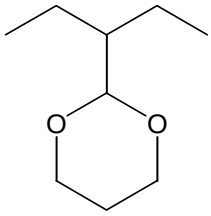








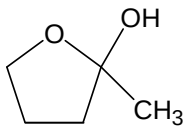


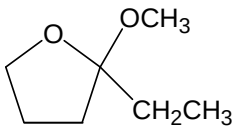


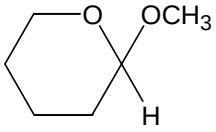
42

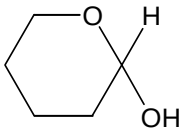
Examples: Identifying Acetals and Ketals

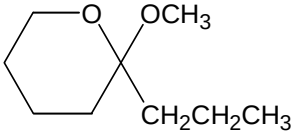
- Identify the following compounds as being acetals, ketals, hemiacetals, or hemiketals.

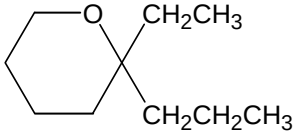








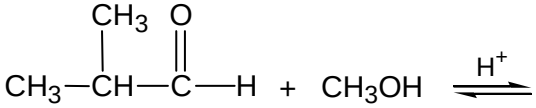


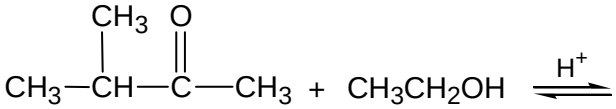


43

Examples: Formation of Acetals and Ketals

- Complete the following reactions.

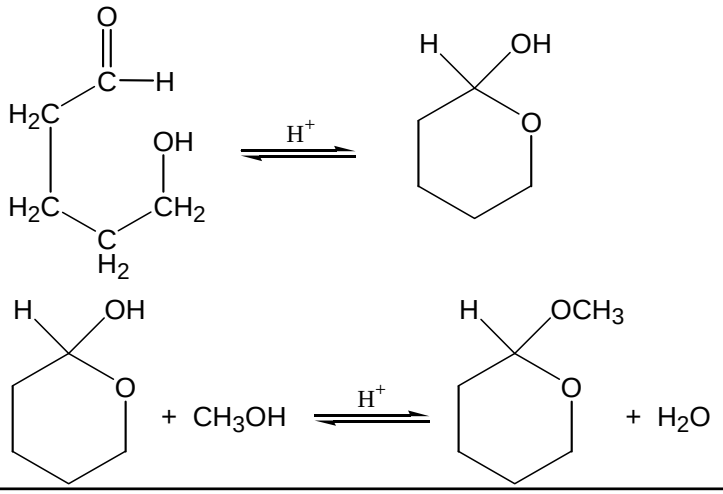




44

Intramolecular Addition Reactions

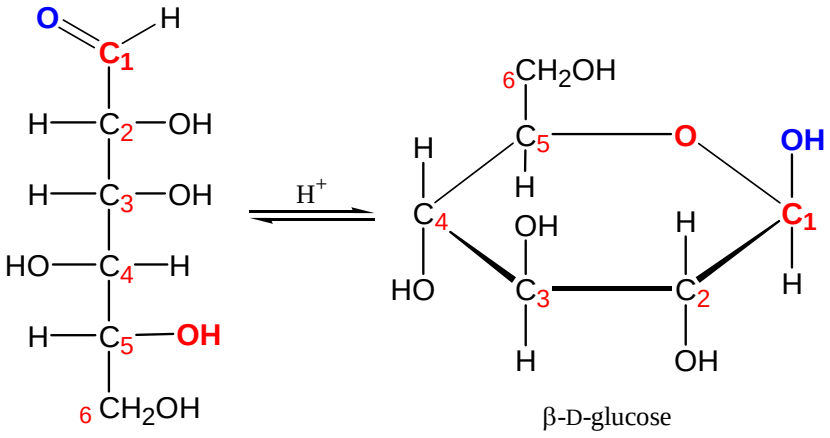
- In molecules which have both OH and C=O groups on different carbon atoms, an *intramolecular* addition reaction can occur, producing a cyclic hemiacetal or hemiketal:



45

Intramolecular Addition Reactions

- These kinds of reactions are very important in carbohydrate chemistry:



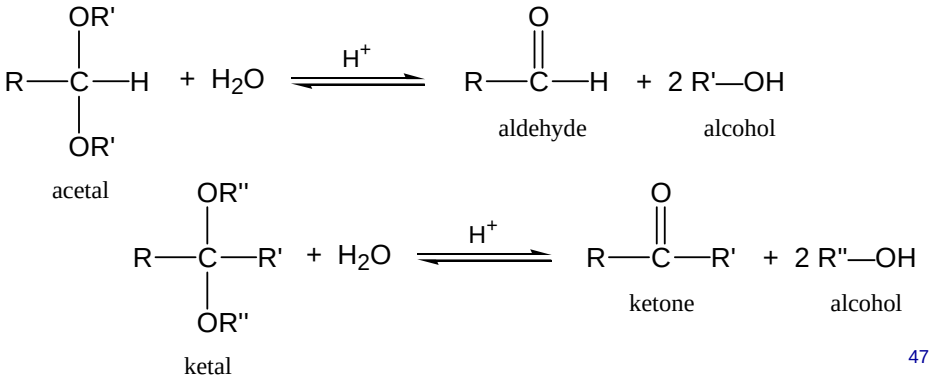
D-glucose

β-D-glucose

46

Hydrolysis of Acetals and Ketals

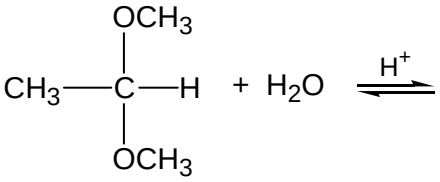
- Under acidic conditions, water can be used to reverse the previous reaction, and regenerate the original aldehyde or ketone from the acetal or ketal.
- This is an example of a **hydrolysis** reaction, in which water causes a compound to be split into its component substances.

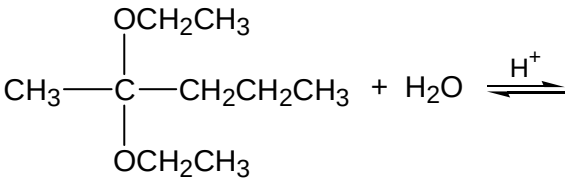


47

Examples: Hydrolysis of Acetals and Ketals

- Complete the following reactions.

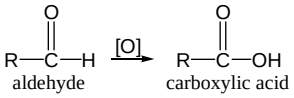




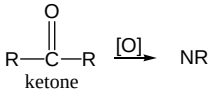
48

Reactions of Aldehydes and Ketones

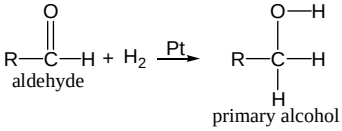
1. Oxidation of Aldehydes to give Carboxylic Acids



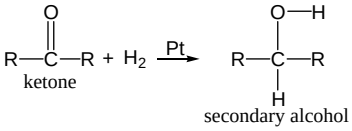
2. Oxidation of Ketones — No Reaction



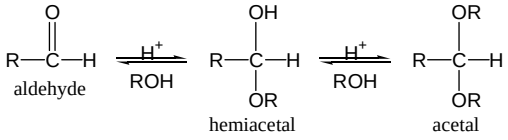
3. Hydrogenation of Aldehydes to give Primary Alcohols



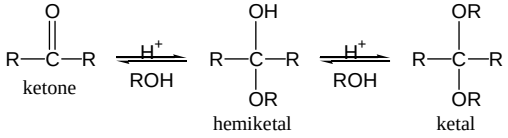
4. Hydrogenation of Ketones to give Secondary Alcohols



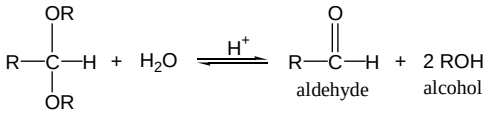
5. Addition of an Alcohol to an Aldehyde to form an Acetal



6. Addition of an Alcohol to a Ketone to form a Ketal



7. Hydrolysis of an Acetal to give an Aldehyde



8. Hydrolysis of a Ketal to give a Ketone