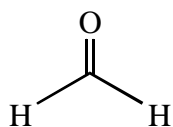


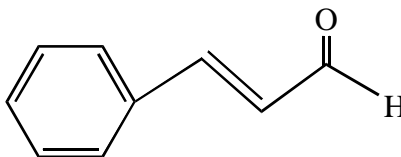
Chapter 14 – Aldehydes and Ketones

14.1 Structures and Physical Properties of Aldehydes and Ketones

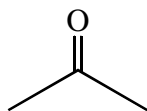
Ketones and aldehydes are related in that they each possess a C=O (carbonyl) group. They differ in that the carbonyl carbon in ketones is bound to two carbon atoms (RCOR'), while that in aldehydes is bound to at least one hydrogen (H₂CO and RCHO). Thus aldehydes always place the carbonyl group on a terminal (end) carbon, while the carbonyl group in ketones is always internal. Some common examples include (common name in parentheses):



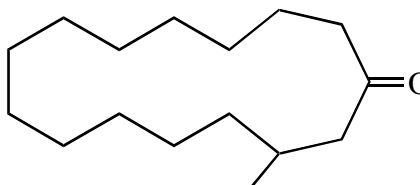
methanal (formaldehyde)
preservative



trans-3-phenyl-2-propenal (cinnamaldehyde)
oil of cinnamon



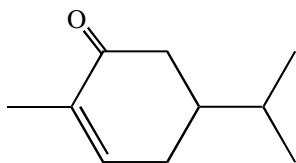
propanone (acetone)
nail polish remover



3-methylcyclopentadecanone (muscone)
a component of one type of musk oil

Simple aldehydes (e.g. formaldehyde) typically have an unpleasant, irritating odor. Aldehydes adjacent to a string of double bonds (e.g. 3-phenyl-2-propenal) frequently have pleasant odors. Other examples include the primary flavoring agents in oil of bitter almond (Ph-CHO) and vanilla (C₆H₃(OH)(OCH₃)(CHO)).

As your book says, simple ketones have distinctive odors (similar to acetone) that are typically not unpleasant in low doses. Like aldehydes, placing a collection of double bonds adjacent to a ketone carbonyl generally makes the substance more fragrant. The primary flavoring agent in oil of caraway is just a such a ketone.



oil of caraway

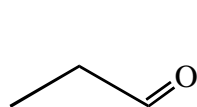
Because the C=O group is polar, small aldehydes and ketones enjoy significant water solubility. They are also quite soluble in typical organic solvents.

14.2 Naming Aldehydes and Ketones

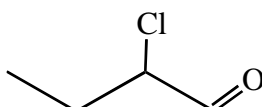
Aldehydes

The IUPAC names for aldehydes are obtained by using rules similar to those we've seen for other functional groups (e.g. -OH):

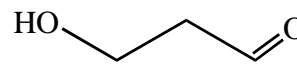
- 1) Locate the longest carbon chain in the molecule that includes the aldehyde group. Name it like an alkane, except use the ending *-al* in place of *-e*.
- 2) Number the carbonyl carbon "1" and name all other functional groups as you've seen previously. (Since aldehydes are always terminal, there is no need to number them.)



propanal



2-chlorobutanal



3-hydroxypropanal

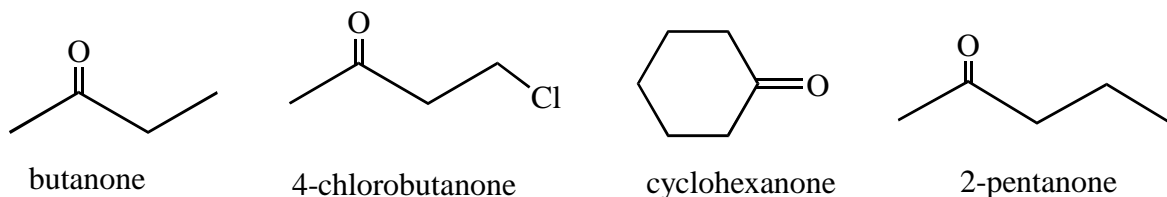
Common names occur frequently for aldehydes. These fall into two broad classes. The first type of name is derived from the name used for a common carboxylic acid. The name of the carboxylic acid typically comes from a Latin origin. For example, formaldehyde (CH₂O) is derived from formic acid (HCO₂H). You may know of formic acid as the major component of an ant bite. The bite stings because the ant has injected formic acid into some of your cells and the acid causes those cells to die or be damaged. For a creature the same size as an ant, the effect is devastating. The beginning *form-* in formaldehyde comes from the Latin word for ant *formica*.

Note this is the same word as is used for some synthetic countertops. Formica® tabletops are made of a polymer of formaldehyde (with a second substance).

The other type of common name occurs in compounds such as flavorants. On the first page of the notes the compound 3-phenyl-2-propenal was presented. In fact, it is never called this. Rather it goes by its common name cinnamaldehyde. Chemical names derived from terms such as this are common for substances that had been identified before their structures could be determined.

Ketones

- 1) As usual, find the longest carbon chain that includes the carbonyl group. Use the alkane name except drop the final “-e” and insert “-one”. Ketones (except propanone and butanone) must have a number to indicate the location of the carbonyl group.
- 2) Name other functional groups as usual.



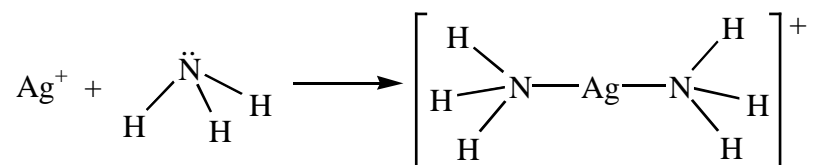
An older way of naming ketones was to name the groups attached to the carbonyl then add the word “ketone.” Thus, *butanone* was methyl ethyl ketone and *2-pentanone* was methyl propyl ketone. Finally, propanone is nearly always called *acetone*.

14.3 Oxidation of Aldehydes and Ketones

Your book begins this section discussing Tollens’ and Benedict’s tests. Both tests are commonly used in qualitative organic chemistry to detect the presence of aldehydes (by converting them to the corresponding carboxylate anions), however neither is a particularly

practical way of making aldehydes on the large scale. The major reason is cost and this can be seen in the use of silver and copper reagents respectively. On the industrial scale, when compounds are frequently made in thousand to million pound quantities, the use of this much precious or semi-precious metal would be prohibitively expensive. When all one is trying to do is find out if you have *some* aldehyde present these are quick and cost effective methods of accomplishing this. It is in this context that they are of value in a medical laboratory. As your book notes, this method is of great importance when checking urine for glucose (since glucose exists in an equilibrium in which one of its forms is an aldehyde, see p. 7 of notes). When the latter is found, it means that the body is not properly metabolizing sugar and there is a real possibility of diabetes.

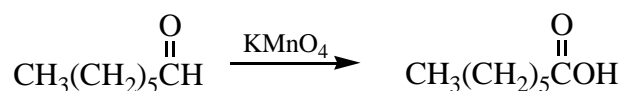
$\text{Ag}(\text{NH}_3)_2^+$ is a complex ion. These are species in which a *simple* metal ion (e.g. Ag^+) binds to a lone pair of electrons on a second species (called a ligand). The bond is reasonably strong so the species behave as a single unit. Formation of the diammine silver(I) complex is shown below. Your book points out that Benedict's reagent is a complex between Cu^{2+} and citrate ion,



however the formula $\text{Cu}(\text{citrate})^{2+}$ is undoubtedly wrong. The correct structure is complicated. These complexes are common in nature. For example, hemoglobin (containing Fe^{3+}) and chlorophyll (Mg^{2+}) are complex ions. Many of the metals your body needs are used as complex ions in your body (frequently by enzymes). Heavy metal poisoning frequently occurs when the heavy metal (e.g. lead (Pb^{2+}) or mercury (Hg^{2+})) replaces another metal ion (e.g. Mg^{2+} or Zn^{2+}) and thereby deactivates the enzyme. This also explains why mercury and lead salts are much

more dangerous than the metals. As metals, they don't form complex ions in the body. Thus they must first be oxidized and that generally doesn't happen in your body. (Nonetheless, the metals are still bad for your health for other reasons and shouldn't be ingested.)

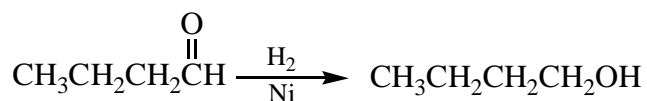
Large scale conversions of aldehydes to carboxylic acids frequently employ either potassium permanganate (KMnO_4) or chromic acid (H_2CrO_4) as the oxidant. The metal by-products of this reaction are more readily recycled than either the Tollens' or Benedict's reagents. For example:



14.4 Reduction of Aldehydes and Ketones

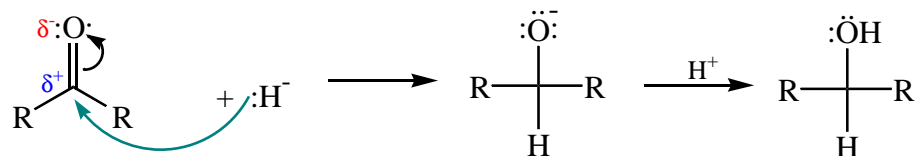
In reduction reactions of aldehydes and ketones we add hydrogen across the double bond. That is, a hydrogen atom will be added to each atom of the double bond, converting the aldehyde or ketone into an alcohol. We can add this hydrogen in one of two different ways. The first is to split apart a hydrogen molecule and add the two product hydrogen atoms or to use a hydride donor, followed by adding a proton (H^+).

For industrial scale reductions of small aldehydes and ketones the former reactions are frequently employed. Hydrogen is mixed with either an aldehyde or ketone in the presence of a metal catalyst, usually nickel, platinum, or palladium. Aldehydes reduce to 1° alcohols and ketones to 2° alcohols (and under extreme conditions (not shown) the hydroxy group can be removed altogether).



Chemical reductions employing hydride reagents such as NaBH_4 and LiAlH_4 are also

common. Each acts as a source of the H^- ion (although this ion never actually exists freely in solution). The reaction proceeds in two steps. In the first the electrons on the negatively charged hydride ion attack the positive end of the $\text{C}=\text{O}$ dipole. The source of H^+ ions may be either a

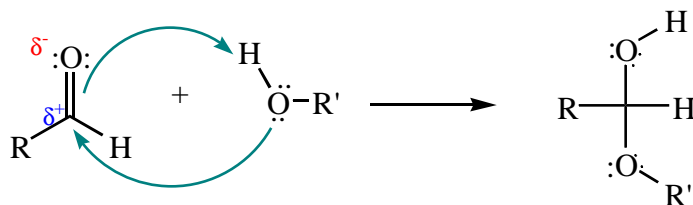


dilute acid or even water. Reagents like NaBH_4 and LiAlH_4 could never survive most biological conditions and your body uses enzymes to accomplish the same reactions. (For example, LiAlH_4 frequently ignites on exposure to water.) In the human body, the NADH unit serves as the hydride ion source (NAD^+ = nicotinamide adenine dinucleotide) and water as the H^+ source. But otherwise the mechanism of reaction is largely the same.

14.5 Reactions of Aldehydes and Ketones with Alcohols

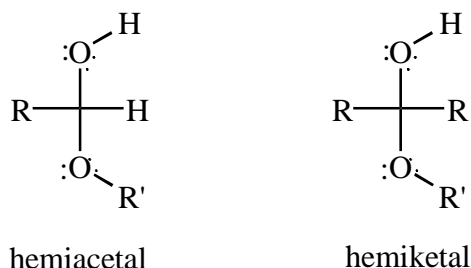
We will discuss a few other reactions of aldehydes and ketones now. The first is that with alcohols. This reaction is unusual in that the products of these reactions are normally unstable. We are interested in them because in one important biological case, the synthesis of carbohydrates, the products possess high stability.

In this reaction an alcohol molecule adds across the carbonyl double bond with the alcoholic hydrogen atom attaching to the carbonyl oxygen. If you look back in your notes, you will see

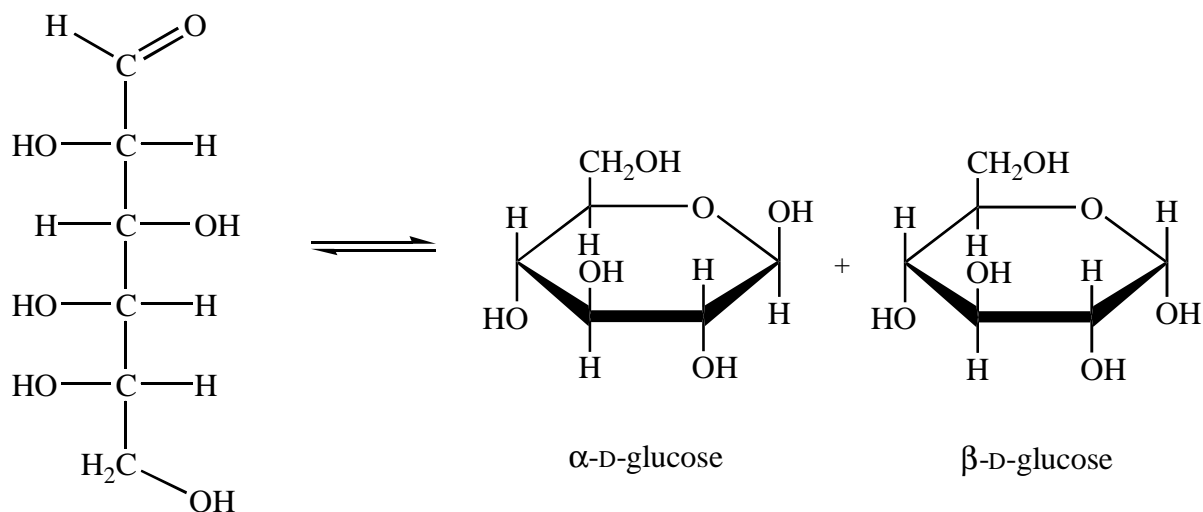


that this reaction resembles the addition of water to a $\text{C}=\text{C}$ double bond to form an alcohol (Chapter 12 notes, p. 7). This molecule, one in which the same carbon is bound to both an OH

and an OR group is called a hemiacetal. A nearly identical reaction takes place with ketones to yield a hemiketal. The difference is that the hemiacetal carbon is also bound to an H atom, while the hemiketal carbon is bound to an R group.

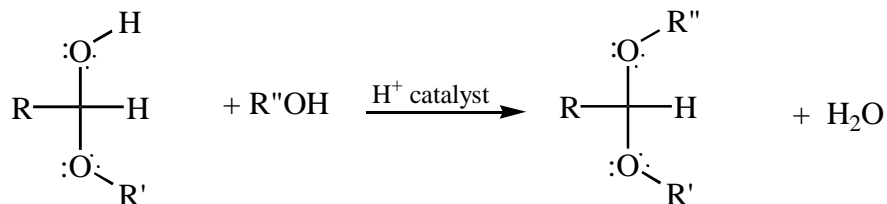


In sugars, the molecule has an aldehyde group at one end and an alcohol group on the other. The chain that connects them is 5 or 6 carbons long. If the molecule does an intramolecular (internal) reaction of this type, the resulting product is a 5- or 6-membered ring. Rings of this size are particularly stable and, in the case of sugars, can polymerize into carbohydrates in a way the straight chain molecules can't. Even so, individual sugar molecules exist in an equilibrium between the ring-open and ring-closed forms.



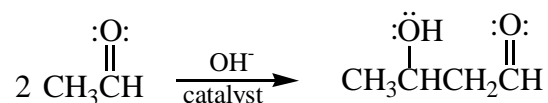
Hemiacetals and hemiketals can react with another equivalent of alcohol to yield acetals and ketals, respectively. The net effect is to replace the alcoholic hydrogen on the former with the R group of the alcohol. An acid catalyst and large excess of added alcohol are needed for this

reaction to proceed. A typical conversion of a hemiacetal to an acetal would proceed as follows:

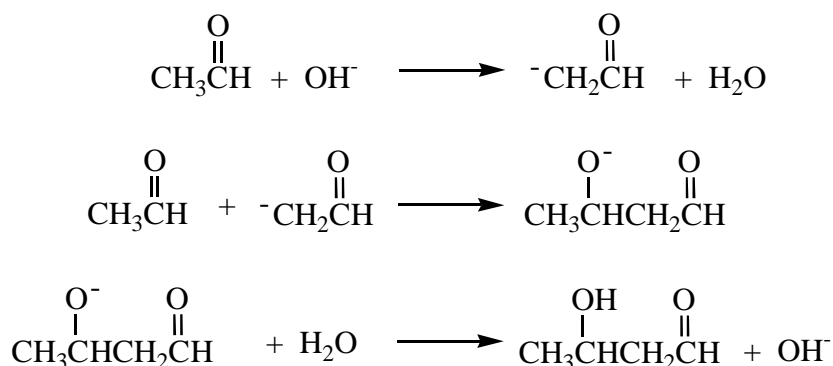


In the presence of a large excess of water, the reaction will run in reverse. (When comparable amounts of water and alcohol are present the reaction is an equilibrium.) This is how the cyclic (hemiacetal) form of D-glucose polymerizes to form a carbohydrate chain. Have you ever noticed that if you chew a piece of bread or a saltine cracker for a few seconds and then leave it in your mouth for a minute or so it begins to taste sweet? This is the acid and water in your saliva breaking down the carbohydrates (starch) in bread to their component sugars. In your stomach this reaction occurs more quickly because it is more acidic there (stomach acid is approximately 0.1 M HCl).

The final reaction of aldehydes and ketones we will consider is the aldol condensation. This is a reaction where an aldehyde or ketone reacts with itself with the help of a base (OH^-) catalyst.



The reaction takes several steps (shown below). As you can see, the hydroxide ion used up in the first step is regenerated in the third.



This reaction is important because it leads to the formation of a new carbon-carbon single bond, a process that is generally difficult to do in organic chemistry. We will see this type of reaction again later when a biochemical reaction uses an enzyme in place of OH^- to accomplish the same synthetic goal.

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