Reactions of Aldehydes and Ketones

A few examples

- **Formaldehyde**
  - Colorless gas
  - Formalin – aqueous solution – biological preservative; germicide
- **Acetaldehyde**
  - Oxidation of ethanol (metabolism)
- **Acetone**
  - Colorless liquid
  - Solvent – nail polish remover
  - Produced from metabolism of fats when glucose is low or insulin is low - ketosis
Oxidation

- Aldehydes are oxidized to **carboxylic acids**
  - Change the –H to an –OH
- Ketones are not oxidized further

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \overset{[O]}{\longrightarrow} \quad \text{CH}_3\text{O} \cdot \\
\text{H}_2\text{C} & \quad \text{H} & \quad \text{O} \\
\text{H}_2\text{C} & \quad \text{O} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} & \quad \text{H} & \quad \overset{[O]}{\longrightarrow} \quad \text{H}_3\text{C} & \quad \text{O} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{O} & \quad \text{CH}_3 & \quad \overset{[O]}{\longrightarrow} & \quad \text{NR}
\end{align*}
\]

Oxidation – Tests for aldehydes

- **Tollen’s Test**
  - Silver is the oxidizing agent of the aldehyde—
    - it is reduced in the reaction
  - The aldehyde acts as the reducing agent of the silver—
    - it is oxidized
  - Since ketones are not oxidized, the oxidation reaction can distinguish between aldehydes and ketones
  - Silver deposits on sides of test tube.

\[
\begin{align*}
\text{R-C-H} & \quad \text{+ 2Ag(NH}_3\text{)}_2^+ & \quad \text{+ 3OH} & \quad \text{→} & \quad \text{R-C-O}^- & \quad \text{+ 2Ag} & \quad \text{+ 4NH}_3 & \quad \text{+ 2H}_2\text{O} \\
\text{Aldehyde} & \quad \text{Tollens’ reagent} & \quad & \quad & \quad \text{Carboxylic anion} & \quad \text{Silver mirror}
\end{align*}
\]
Reduction

- Aldehydes and ketones are both reduced to alcohols.
  - Add two hydrogens to the carbonyl group
  - The hydrogen may be added as in hydrogenation of alkenes, with a metal catalyst.

![Chemical reactions]

- Note the aldehyde gave a terminal alcohol while the ketone put one in the chain.

Reduction

- Reduction of acetaldehyde by microorganisms to produce ethanol is called **fermentation**
  - The reducing agent is a biological source of hydrogen called NADH. It is an important reducing agent in all animals.
  - NADH is made from Vitamin B - niacin

![Chemical reaction]
oxidation-reduction

- remember, oxidation and reduction occur in tandem. when the carbonyl is reduced, the reducing agent is oxidized.
- also the reverse of the reduction reaction is oxidation
  - the aldehyde is ____________ to an alcohol
  - an alcohol may be ________________ to an aldehyde.

examples

- draw the products of the oxidation of n-propanol and isopropanol.
  - remove the hydrogen from the hydroxy group
  - remove one hydrogen from the carbon with the hydroxy group.
  - change the c-o bond to a c=o bond.
  - remember an aldehyde may be oxidized further.

\[
\text{H}_3\text{C}-\text{CH}_2\cdot\text{CH}_2-\text{OH} \\
\quad \text{OH} \\
\quad \text{H}_3\text{C}-\text{HC}--\text{CH}_3
\]
Examples

- Draw the products of the reduction of propionaldehyde and dimethyl ketone.
  - Erase one bond of the C=O
  - Add a hydrogen to the O.
  - Add a hydrogen to the carbonyl carbon.

\[
\begin{align*}
H&-C-\text{CH}_2-\text{CH}_3 \\
\text{O} & \quad \text{O} \\
\text{H}_3\text{C} & \quad \text{CH}_3
\end{align*}
\]

Addition of Alcohols

- Addition of alcohol to the carbonyl group of an aldehyde or ketone forms a **hemiacetal** (a half-acetal)
  - the functional group of a hemiacetal is a *carbon bonded to one -OH group and one -OR group*
  - H of the alcohol adds to the carbonyl oxygen and OR adds to the carbonyl carbon
  - Reversible – goes back and forth

\[
\begin{align*}
\text{Benzaldehyde} & + \text{Ethanol} \quad \rightarrow \quad \text{A hemiacetal} \\
\end{align*}
\]
**Addition of Alcohols**

- Hemiacetals are generally unstable
  - Minor components in mixture
  - One exception – cyclic hemiacetals
    - Aldehyde and alcohol in same molecule
    - Long enough to form 5 or 6 membered ring

Circle the ether and alcohol groups in the hemiacetal

Cyclic hemiacetals are important in sugar structures.

**Cyclization of Glucose**

D-Glucose

Circle the group of atoms that make this a hemiacetal.
Addition of Alcohols

- A hemiacetal can react further with an alcohol to form an acetal plus water
  - the functional group of an acetal is a carbon bonded to two -OR groups

A hemiacetal
(from benzaldehyde)  
\[ \text{H} + \text{C} = \text{O} - \text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \]

An acetal

Condensation of sugars

Polysaccharides are formed from condensation of monosaccharides (hemiacetals) to form an acetal.

Condensation – joining together of two compounds with release of water

Breaking apart of molecule using water

α-Maltose, a disaccharide

α-1,4-Glycosidic bond

α-Glucose

α-1,4-Glycosidic bond

β-Glucose

α-1,4-Glycosidic bond

α-Maltose, a disaccharide
Aldol Reaction

- Joining two aldehydes together
- Aldol-aldehyde with alcohol group

\[ \text{H}_3\text{C} = \text{C} - \text{H} + \text{H}_3\text{C} = \text{C} - \text{H} \rightarrow \text{H}_3\text{C} - \text{C} - \text{CH}_2 - \text{H} \]

Aldol Condensation

- Why is the reaction shown below called a condensation?
- You performed this reaction in the lab.
  - cinnamaldehyde

\[ \text{C} = \text{H} + \text{H}_3\text{C} - \text{C} - \text{H} \rightarrow \text{C} = \text{C} - \text{CH}_2 - \text{H} + \text{H}_2\text{O} \]
Examples

- Give the names of the types of molecules shown
  - (alcohol, ketone, aldehyde, acetal, hemiacetal)

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Reaction</th>
<th>Reactant</th>
<th>Product</th>
<th>Notes</th>
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<tbody>
<tr>
<td>Aldehyde</td>
<td>Oxidation</td>
<td>[O]</td>
<td>Carboxylic acid</td>
<td></td>
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<tr>
<td>Aldehyde</td>
<td>Reduction</td>
<td>Hydrogen source</td>
<td>Alcohol</td>
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<td>1 Alcohol per aldehyde</td>
<td>Hemiacetal</td>
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<tr>
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<td>NR no reaction</td>
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<tr>
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<td>Alcohol inside chain</td>
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<tr>
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<td>1 alcohol per ketone</td>
<td>Hemiacetal</td>
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<tr>
<td>Hemiacetal</td>
<td>Addition of alcohol</td>
<td>Alcohol</td>
<td>acetal</td>
<td></td>
</tr>
</tbody>
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