Chapter 16  Aldehydes and Ketones I: Nucleophilic Addition to the Carbonyl Group
16.1 Introduction
Aldehydes and ketones contain an acyl group bonded either to hydrogen or to another carbon.

Formaldehyde

General formulas for an aldehydes

General formulas for a ketones
16.2 Nomenclature of Aldehydes and Ketones
**Aldehydes** are named by replacing the terminal \(-e\) of the corresponding alkane name with \(-al\).

The longest chain selected as the base name must contain the \(-CHO\) group, and the \(-CHO\) carbon is always numbered as carbon 1.

<table>
<thead>
<tr>
<th>Aldehyde Name</th>
<th>Structural Formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanal (Formaldehyde)</td>
<td>HCHO</td>
<td>CH(_3)CHO</td>
</tr>
<tr>
<td>Ethanal (Acetaldehyde)</td>
<td>CH(_3)CHO</td>
<td>ClCH(_2)CH(_2)CH(_2)CH(_2)CHO</td>
</tr>
<tr>
<td>Propanal (Propionaldehyde)</td>
<td>CH(_3)(_3)CHO</td>
<td>C(_6)H(_5)CH(_2)CHO</td>
</tr>
<tr>
<td>5-Chloropentanal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylethanal (Phenylacetaldehyde)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
For more complex aldehyde in which the –CHO group is attached to a ring, the suffix -carbaldehyde is used.

Benzenecarbaldehyde (benzaldehyde)  
Cyclohexanecarbaldehyde  
2-naphthalene carbaldehyde
Ketones are named by replacing the terminal \(-e\) of the corresponding alkane name with \(-one\).

The chain selected for the base name is the longest one that contains the ketone group, and the numbering begins at the end nearer the carbonyl carbon.

- 3-Hexanone
- 4-Hexen-2-one
- 2,4-Hexanedione

(common name: Ethyl propyl ketone)
Some ketones have common names that are retained in the IUPAC system.

- CH$_3$C=CH$_3$ (Acetone)
- CH$_3$C=CH$_2$O (Propanone)
- C$_6$H$_5$C=CH$_3$ (Acetophenone)
- C$_6$H$_5$C=CH$_2$O (1-phenylethanone)
- C$_6$H$_5$C=CH$_2$O (Benzophenone)
- C$_6$H$_5$C=CH$_2$O (Diphenylketone)

When RCO- group are named as substituents, they are called alkanoyl or acyl groups.

- RCO- (Acyl)
- HC=O (Formyl)
- CH$_3$CO- (Acetyl)
- C$_6$H$_5$CO- (Benzoyl)
If another functional groups or a –CHO are present and the doubly bonded oxygen must be considered a substituent, the prefix *oxo-* is used.

- **3-Oxopentanal**
  \[ CH_3CH_2C=CH_2CHO \]
  3'-\text{Oxo}-

- **4-Oxohexanoic acid**
  \[ CH_3CH_2C=CH_2CH_2CO_2H \]
  4'-\text{Oxo}-

- **2'-Oxocyclohexanecarbaldehyde**
  \[
  \begin{array}{c}
  \text{CHO} \\
  \end{array}
  \]
  2'\text{-Oxo-}
16.3 Physical Properties
Molecules of aldehyde (or ketone) cannot hydrogen bond to each other.

They rely only on intermolecular dipole-dipole interactions and therefore have lower boiling points than the corresponding alcohols.
Aldehydes and ketones can form hydrogen bonds with water and therefore low molecular weight aldehydes and ketones have appreciable water solubility.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>mp (°C)</th>
<th>bp (°C)</th>
<th>Solubility in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCHO</td>
<td>Formaldehyde</td>
<td>−92</td>
<td>−21</td>
<td>Very soluble</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>Acetaldehyde</td>
<td>−125</td>
<td>21</td>
<td>≈</td>
</tr>
<tr>
<td>CH₃CH₂CHO</td>
<td>Propanal</td>
<td>−81</td>
<td>49</td>
<td>Very soluble</td>
</tr>
<tr>
<td>CH₃(CH₂)₂CHO</td>
<td>Butanal</td>
<td>−99</td>
<td>76</td>
<td>Soluble</td>
</tr>
<tr>
<td>CH₃(CH₂)₃CHO</td>
<td>Pentanal</td>
<td>−91.5</td>
<td>102</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>CH₃(CH₂)₄CHO</td>
<td>Hexanal</td>
<td>−51</td>
<td>131</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>C₆H₅CHO</td>
<td>Benzaldehyde</td>
<td>−26</td>
<td>178</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>C₆H₅CH₂CHO</td>
<td>Phenylacetaldehyde</td>
<td>33</td>
<td>193</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>CH₃COCH₃</td>
<td>Acetone</td>
<td>−95</td>
<td>56.1</td>
<td>≈</td>
</tr>
<tr>
<td>CH₃COCH₂CH₃</td>
<td>Butanone</td>
<td>−86</td>
<td>79.6</td>
<td>Very soluble</td>
</tr>
<tr>
<td>CH₃COCH₂CH₂CH₃</td>
<td>2-Pentanone</td>
<td>−78</td>
<td>102</td>
<td>Soluble</td>
</tr>
<tr>
<td>CH₃CH₂COCH₂CH₃</td>
<td>3-Pentanone</td>
<td>−39</td>
<td>102</td>
<td>Soluble</td>
</tr>
<tr>
<td>C₆H₅COCH₃</td>
<td>Acetophenone</td>
<td>21</td>
<td>202</td>
<td>Insoluble</td>
</tr>
<tr>
<td>C₆H₅COC₆H₅</td>
<td>Benzophenone</td>
<td>48</td>
<td>306</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>
16.4 Synthesis of Aldehydes
16.4A Aldehydes by Oxidation of 1° Alcohols

\[ \text{RCH}_2\text{OH} \xrightarrow{\text{PCC}} \text{RCHO} \]
16.4B Aldehydes by Reduction of Acyl Chlorides, Esters, and Nitriles

\[ \text{RCO}_2\text{H} \xrightarrow{\text{LiAlH}_4} [\text{RCHO}] \xrightarrow{\text{LiAlH}_4} \text{RCH}_2\text{OH} \]

- Lithium tri-\textit{tert}-butoxyaluminium hydride: \text{LiAlH(O-t-Bu)}_3
- Diisobutylaluminium hydride: \text{i-Bu}_2\text{AlH} or DIBAL-H
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- **(1) LiAlH(O-t-Bu)$_3$, \(78^\circ\text{C}\)**
  - Reaction: $\text{R-Cl} \xrightarrow{(1) \text{LiAlH(O-t-Bu)$_3$, } 78^\circ\text{C}} \text{R-H}$
  - Followed by:
    - (2) Water

- **(1) DIBAL-H, hexane, \(78^\circ\text{C}\)**
  - Reaction: $\text{R-C-OR'} \xrightarrow{(1) \text{DIBAL-H, hexane, } 78^\circ\text{C}} \text{R-H}$
  - Followed by:
    - (2) Water

- **(1) DIBAL-H, hexane, \(78^\circ\text{C}\)**
  - Reaction: $\text{R-CON} \xrightarrow{(1) \text{DIBAL-H, hexane, } 78^\circ\text{C}} \text{R-H}$
  - Followed by:
    - (2) Water

- **COCl**
  - Reaction: $\text{COCl} + \text{H}_2 \xrightarrow{\text{Pd-BaSO}_4, \text{S-quinoline}} \text{CHO}$

**Rosenmund reduction**
16.5 Synthesis of Ketones
16.5A Ketones from Alkenes, Arenes, and 2° Alcohols

- Ketones (and aldehydes) by ozonolysis of alkenes — (1) $\text{O}_3$, (2) $\text{H}_2\text{O}/\text{Zn}$
- Ketones from arenes by Friedel-Crafts acylations — RCOCl or (RCO)$_2$O/AlCl$_3$
- Ketones from 2° alcohols by oxidation — $\text{H}_2\text{CrO}_4$
16.5B  Ketones from Alkynes

\[
R - C\equiv CH + H_2O \xrightarrow{HgSO_4} \xrightarrow{H_2SO_4} R - C - CH_3
\]

A vinylic alcohol (unstable)

Enol form \( R - C\equiv CH_2 \text{CH}_2 \text{OH} \)

Keto form \( R - C - CH_3 \)

Keto-enol tautomerizations
16.5C Ketones from Lithium Dialkylcuprates

\[ R\text{C} \text{Cl} + R'_{2}\text{CuLi} \rightarrow R\text{C}R' + R'\text{Cu} + \text{LiCl} \]

\[ \text{Et}_2\text{O} \]

(81%)
16.5B  Ketones from Nitriles

\[ R\text{-}C\equiv\text{N} \quad R\text{-}C\equiv\text{N} \]

[Diagram showing the reaction pathways involving R'MgX, R'Li, and H3O+ to form ketones from nitriles.]