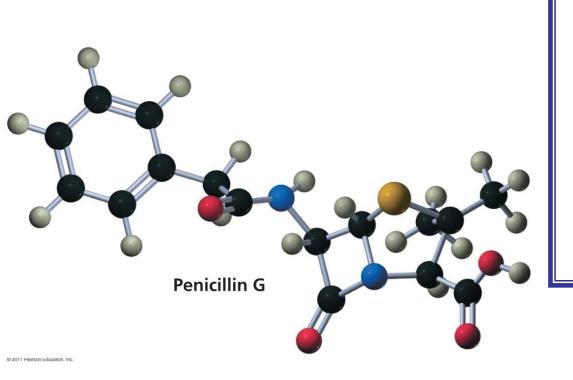
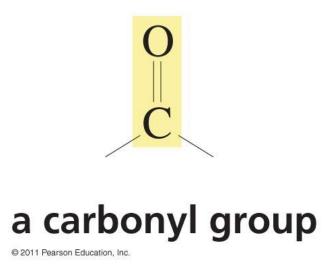
Organic Chemistry

2th Edition Paula Yurkanis Bruice



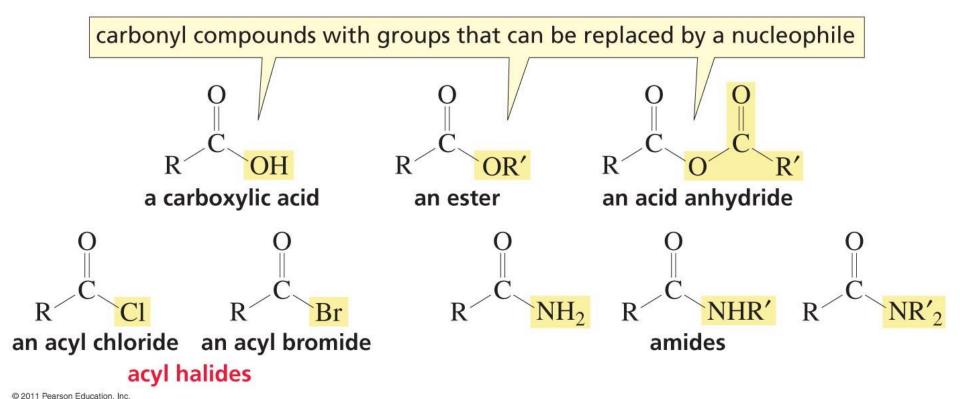
Chapter 11

Carbonyl Compounds I





Class I Carbonyl Compounds



3

Nomenclature of Carboxylic Acids

O H C OH methanoic acid formic acid

CH₃ OH ethanoic acid acetic acid

CH₃CH₂ OH

propanoic acid

propionic acid

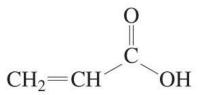
CH₃CH₂CH₂OH

butanoic acid

butyric acid

systematic name:

common name:



pentanoic acid valeric acid

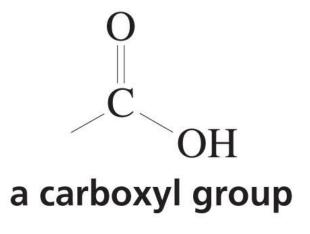
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hexanoic acid caproic acid

propenoic acid acrylic acid

benzenecarboxylic acid benzoic acid

The functional group of a carboxylic acid is called a carboxyl group



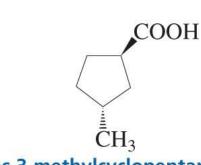
-COOH -CO₂H carboxyl groups are frequently shown in abbreviated forms

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Naming Cyclic Carboxylic Acid

cyclohexanecarboxylic acid

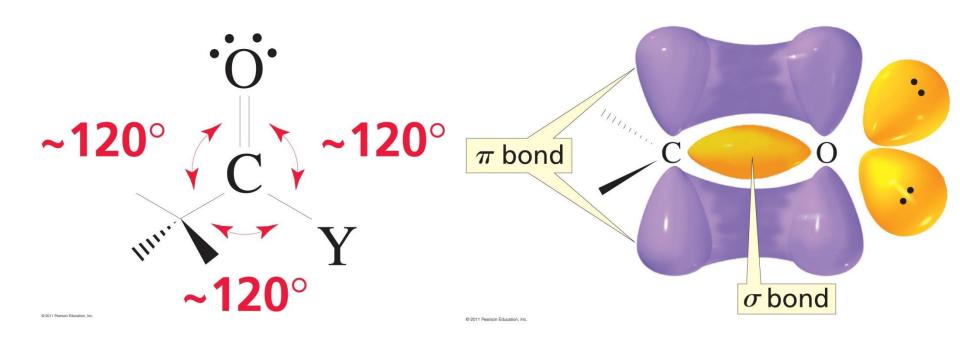
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trans-3-methylcyclopentanecarboxylic acid

1,2-benzenedicarboxylic acid

Structures of Carboxylic Acids and Carboxylic Acid Derivatives

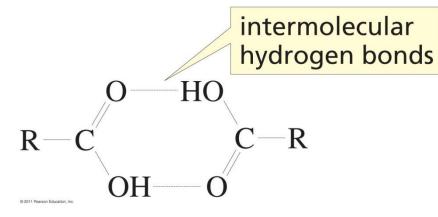


Physical Properties of Some Organic Compounds

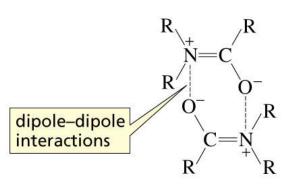
Formula	IUPAC Name	Molecular Weight	Boiling Point	Water Solubility
$\underline{CH_{\underline{3}}(CH_{\underline{2}})_{\underline{2}}}\underline{CONH_{\underline{2}}}$	<u>butanamide</u>	<u>87</u>	216 °C	<u>soluble</u>
CH ₃ (CH ₂) ₂ CO ₂ H	butanoic acid	<u>88</u>	<u>164 °C</u>	very soluble
CH ₃ (CH ₂) ₃ CN	<u>pentanenitrile</u>	<u>88</u>	<u>140 °C</u>	slightly <u>soluble</u>
CH ₃ (CH ₂) ₄ OH	1-pentanol	<u>88</u>	<u>138 °C</u>	slightly <u>soluble</u>
CH ₃ (CH ₂) ₃ CHO	<u>pentanal</u>	<u>86</u>	<u>103 °C</u>	slightly <u>soluble</u>
CH ₃ CO ₂ C ₂ H ₅	ethyl ethanoate	<u>88</u>	<u>77 °C</u>	moderately <u>soluble</u>
CH ₃ (CH ₂) ₄ CH ₃	<u>hexane</u>	<u>86</u>	<u>69 °C</u>	<u>insoluble</u>

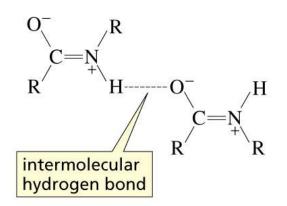
Carboxylic acids have relatively high boiling points

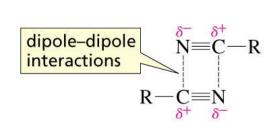
because...



Amides have the highest boiling points:

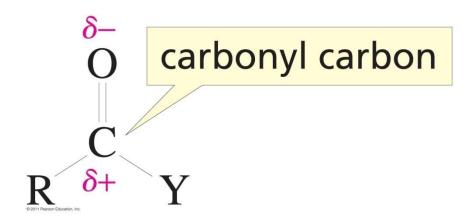




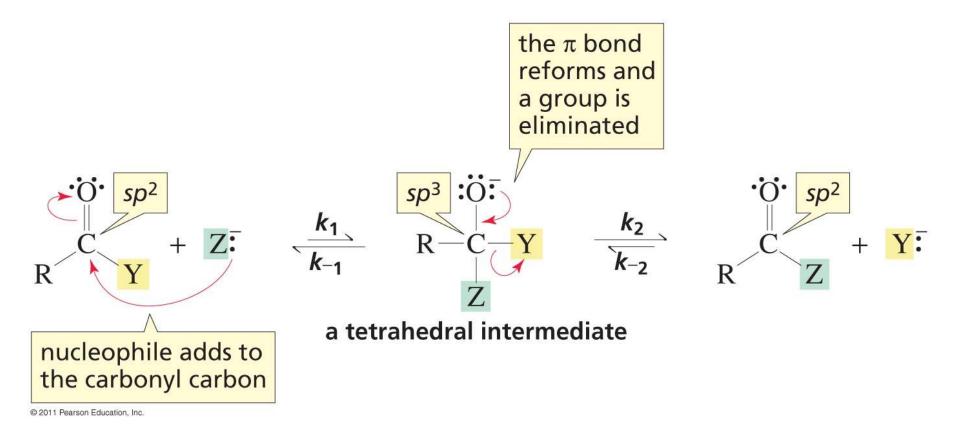


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The reactivity of carbonyl compounds resides in the polarity of the carbonyl group:



The tetrahedral intermediate is a transient species that eliminates the leaving group Y⁻ or the nucleophile Z⁻:



This is a nucleophilic acyl substitution reaction

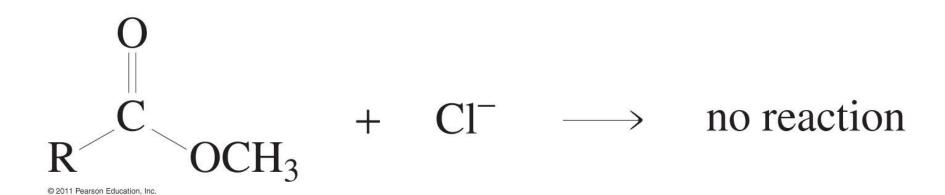
The reactivity of a carboxylic acid derivative depends on the basicity of the substituent attached to the acyl group:

relative basicities of the leaving groups

relative reactivities of carboxylic acid derivatives

12

A carboxylic acid derivative can be converted only into a less reactive carboxylic acid derivative:



Reactions of Acyl Halides

Suitable bases include triethylamine (TEA) and pyridine

trap the HCI product

$$\begin{array}{c} O \\ \\ C \\ CH_3CH_2 \end{array} + \begin{array}{c} O \\ \\ CH_3CH_2 \end{array} + \begin{array}{c} O \\ \\ CH_3CH_2 \end{array} \\ \begin{array}{c} C \\ CH_3CH_2 \end{array}$$

phenyl propionate

butyryl chloride

butyric acid

$$\begin{array}{c}
O \\
\parallel \\
C
\end{array}
+ 2 CH_3NH_2 \longrightarrow$$

cyclohexanecarbonyl chloride

N-methylcyclohexanecarboxamide

Formation of Amides from Acyl Halides

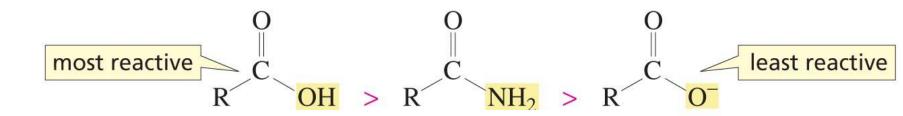
$$\begin{array}{c} O \\ C \\ R \\ \hline C \\ Cl \\ \end{array} + NH_{3} \longrightarrow \begin{array}{c} O \\ C \\ R \\ \hline NH_{2} \\ \end{array} + HCl \\ \hline \begin{array}{c} NH_{3} \\ NH_{4} \\ Cl \\ \end{array} + CH_{3}NH_{2} \\ \end{array} \begin{array}{c} O \\ C \\ Cl \\ \end{array} + CH_{3}NH_{3} \\ Cl \\ \end{array} \begin{array}{c} O \\ C \\ Cl \\ \end{array} + CH_{3}NH_{3} \\ Cl \\ \end{array} \begin{array}{c} O \\ Cl \\ \end{array} \begin{array}{c} C \\ Cl \\ \end{array} \begin{array}{c} O \\ Cl \\ \end{array} \begin{array}{c} C \\ Cl \\ \end{array} \begin{array}{c} Cl \\ Cl \\ Cl \\ \end{array} \begin{array}{c}$$

Tertiary amines cannot form amides

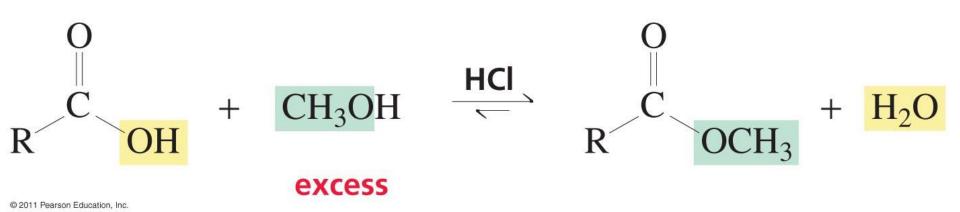
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Reactions of Carboxylic Acids

relative reactivities toward nucleophilic acyl substitution



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Reactions of Esters

a hydrolysis reaction

$$\begin{array}{c} O \\ \parallel \\ C \\ \hline \\ R \end{array} \begin{array}{c} + H_2O \end{array} \begin{array}{c} \begin{array}{c} \bullet \\ \bullet \\ \hline \\ R \end{array} \begin{array}{c} O \\ \parallel \\ OH \end{array} \begin{array}{c} + CH_3OH \end{array}$$

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a transesterification reaction

$$\begin{array}{c}
O \\
\parallel \\
C \\
OCH_3
\end{array}
+ CH_3CH_2OH$$

$$\begin{array}{c}
HCI \\
\longleftarrow \\
R
\end{array}$$

$$\begin{array}{c}
O \\
\parallel \\
C \\
OCH_2CH_3
\end{array}
+ CH_3OH$$

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Carboxylic acids do not undergo nucleophilic acyl substitution reactions with amines at room temperature

$$\begin{array}{c} O \\ C \\ \hline C \\ \hline OH \end{array} + \begin{array}{c} C \\ C \\ \hline O \end{array} + \begin{array}{c} C \\ \end{array} + \begin{array}{c} C \\ \hline O \end{array} + \begin{array}{c} C \\ \hline O \end{array} + \begin{array}{c} C \\ \hline O \end{array} + \begin{array}{c} C \\ \end{array}$$

$$\begin{array}{c}
O \\
C \\
R
\end{array}$$
 $\begin{array}{c}
O \\
H \\
O \\
\end{array}$
 $\begin{array}{c}
O \\
R
\end{array}$
 $\begin{array}{c}
O \\
O \\
\end{array}$
 $\begin{array}{c}
O \\
NH_4
\end{array}$
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Heating the ammonium carboxylate will afford the amide and water

Amides can react with water and alcohols if an acid catalyst is present:

$$\begin{array}{c} O \\ \downarrow \\ C \\ CH_{3} \end{array} + H_{2}O \xrightarrow{\text{HCI}} C \\ \downarrow \\ \text{N-ethylacetamide} \end{array} + CH_{3}CH_{2}OH \xrightarrow{\text{HCI}} C \\ \downarrow \\ CH_{3} \end{array} + CH_{3}CH_{2}OH \xrightarrow{\text{HCI}} C \\ \downarrow \\ CH_{3} \end{array} + CH_{3}CH_{2}OH \xrightarrow{\text{HCI}} C \\ \downarrow \\ CH_{3} CH_{2}OH \xrightarrow{\text{HCI}} C \\ \downarrow \\ CH_{3} CH_{2} CH_{3} CH_{2}OH \xrightarrow{\text{HCI}} C \\ \downarrow \\ CH_{3} CH_{2} CH_{3} CH_{2} CH_{2}$$

N-methylbenzamide

Synthesis of Carboxylic Acid Derivatives

 Acid chlorides are prepared from carboxylic acids by reaction with SOCI₂

The Hydrolysis of Nitriles. Synthesis of carboxylic acid

