

UNIT (9) CARBOXYLIC ACIDS, ESTERS, AMINES, AND AMIDES

9.1 | Carboxylic Acids

The functional group in carboxylic acids is called the carboxyl group. A **carboxyl group** is a carbonyl group (C = O) with a hydroxyl group (-OH) attached to the carbonyl carbon atom.

Representation of a carboxyl group $\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---OH} \end{array}$ or ---COOH or $\text{---CO}_2\text{H}$

Carboxylic acid: $\begin{array}{c} \text{O} \\ \parallel \\ \text{R---C---OH} \end{array}$
(R = H, or aliphatic or aromatic hydrocarbon)

9.2 | Naming Carboxylic Acids

The names of carboxylic acids end in “**-oic acid**,” indicating the presence of the carboxyl group, i.e.: propanoic acid, butanoic acid, pentanoic acid, etc. When naming carboxylic acids, the “-e” is dropped from the alkane containing the carboxyl group and replaced with “-oic acid”. The chain is numbered from the carboxylic acid group which is always located on the first carbon. The location of the functional group is *not* included in the name.

Examples:

$\text{CH}_3\text{-COOH}$
ethanoic acid

$\text{CH}_3\text{-CH}_2\text{-COOH}$
propanoic acid

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$
butanoic acid

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{-CH-CH}_2\text{-COOH} \\ 4 \quad 3 \quad 2 \quad 1 \end{array}$
3-methylbutanoic acid

$\begin{array}{c} \text{COOH} \\ | \\ \text{C}_6\text{H}_5 \end{array}$
benzoic acid

Some members of this class are widely known by their common names. Common names of acids you should know:

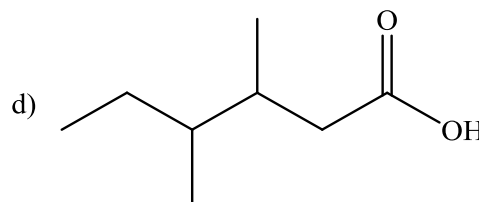
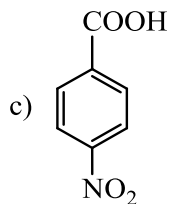
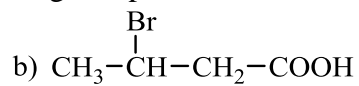
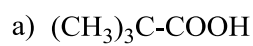
HCOOH
Formic acid

CH_3COOH
Acetic acid

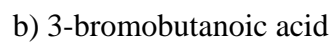
A solution of acetic acid and water is known as *vinegar*.

Worked Example 9-1

Give the IUPAC name for each of the following compounds:

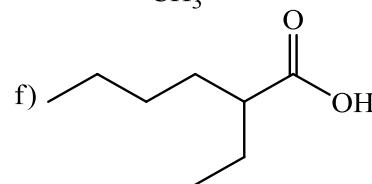
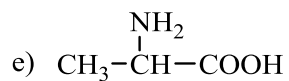
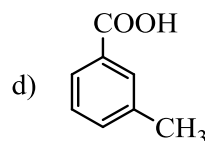
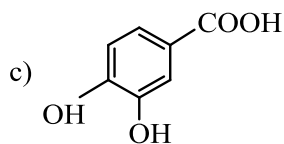
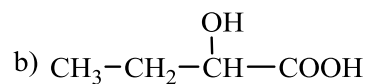


Solution



Practice 9-1

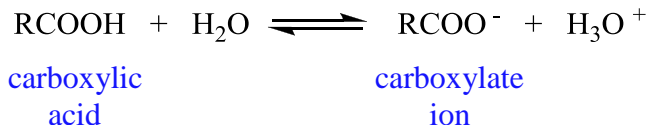
Name each of the following acids:



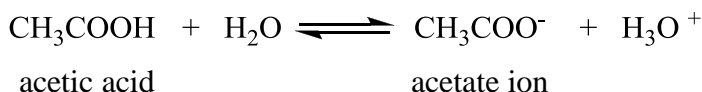
Answer

9.3 | Acidity of Carboxylic Acids

Carboxylic acids are weak acids. When a carboxylic acid is placed in water, the following equilibrium is established.

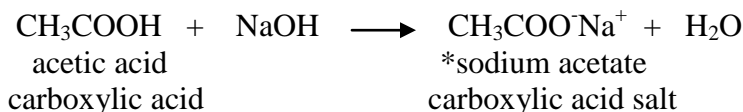


Carboxylate ions are named by dropping the *-ic* ending from the name of the parent acid and replacing it with *-ate*.



Neutralization of Carboxylic Acids (reaction of acids with bases)

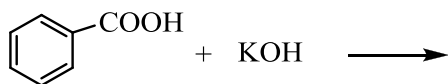
Carboxylic acids undergo neutralization reactions with strong bases as you have seen in *unit 6*, in a manner similar to that of inorganic acids. Neutralization of carboxylic acid produces a carboxylic acid salt and water.



*Note that carboxylic acid salts are named similarly to other ionic compounds (*unit 4*). The cation is named first, followed by the name of the anion.

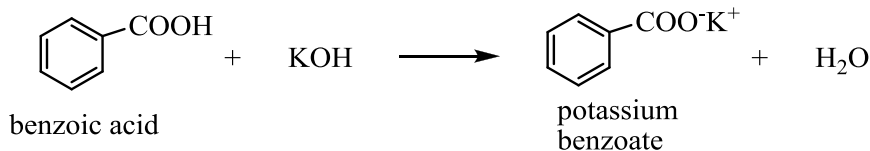
Worked Example 9-2

Complete the following reaction and name the carboxylic acid salt formed.



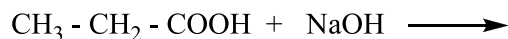
Solution

The “protons” of the acid are removed by the OH^- of the base to produce water. The cation of the base, in this case K^+ , forms the salt of the carboxylic acid.



Practice 9-2

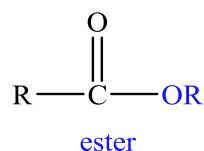
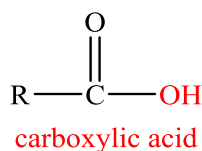
Complete the following reaction and name the carboxylic acid salt formed.



Answer

9.4 | Esters

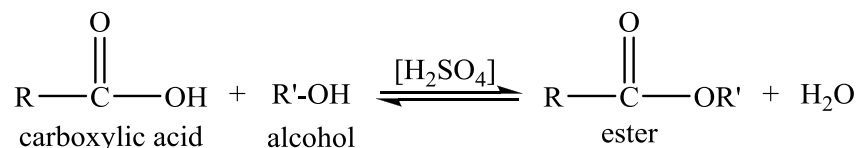
Esters are derivative of carboxylic acids in which the $-\text{OH}$ group on the carboxyl has been replaced with an $-\text{OR}$ group.



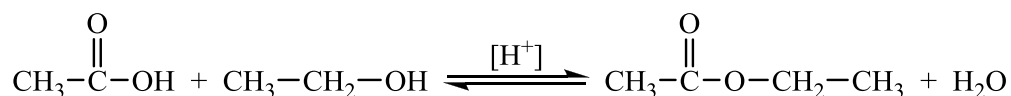
Esterification (Preparation of Esters)

The process of **esterification** involves the reaction of a carboxylic acid with an alcohol in the presence of an acid catalyst. Water is also a product in this reaction.

The generalized reaction can be shown as:

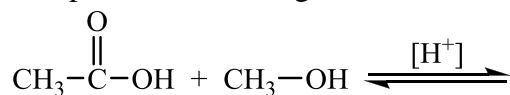


When ethanol is added to acetic acid and a drop of sulfuric acid (symbolized as H^+), the following equilibrium will result:



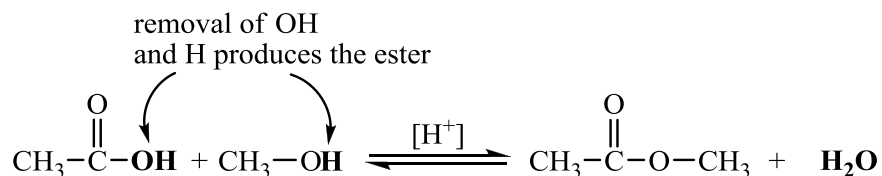
Worked Example 9-3

Complete the following esterification reaction:



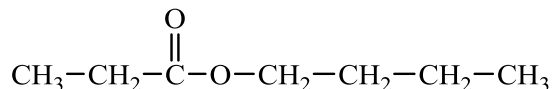
Solution

Each ester has an “acid part” and an “alcohol part”. The acid part is the carboxylic acid minus the $-\text{OH}$ group. The alcohol part is an alcohol molecule, minus the H atom of the $-\text{OH}$ group. The $-\text{OH}$ of the acid and the H of the alcohol form a H_2O molecule.



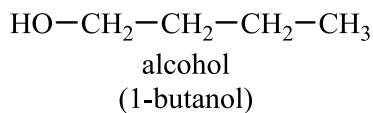
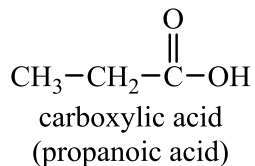
Worked Example 9-4

What carboxylic acid and alcohol are required to produce the following ester?



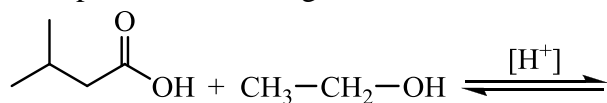
Solution

Separate the molecule by drawing a line down through the oxygen in the carbon chain. Add an $-\text{OH}$ on both sides of your line to create the carboxylic acid on the carbonyl side and the alcohol on the alkyl side.



Practice 9-3

Complete the following esterification reaction:



Answer

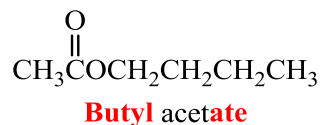
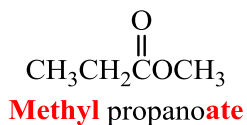
9.5 | Naming Esters

Ester names consist of two words.

Use the *alkyl* portion of the alcohol name first.

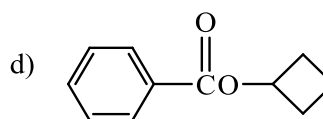
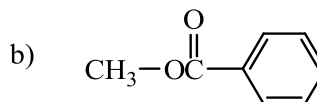
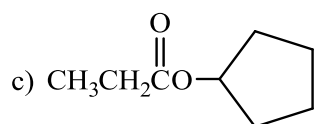
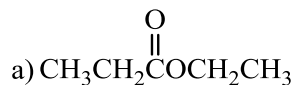
The *-ic acid* ending of the name of the carboxylic acid is replaced with *-ate* and follows the first name.

Examples:



Worked Example 9-5

Name each of the following esters:



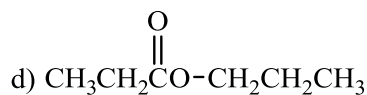
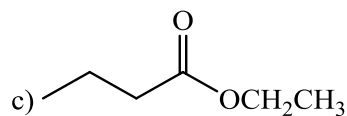
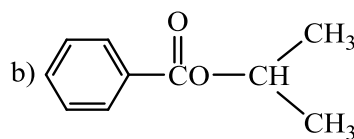
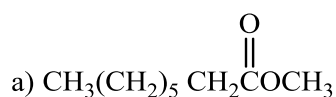
Solution

- a) ethyl propanoate
c) cyclopentyl propanoate

- b) methyl benzoate
d) cyclobutyl benzoate

Practice 9-4

Write the name for each of the following esters.



Answer

9.6 | The Hydrolysis of Esters

Hydrolysis is a reaction in which an organic molecule reacting with water splits into two parts, each of which has fewer carbons than the original organic molecule.

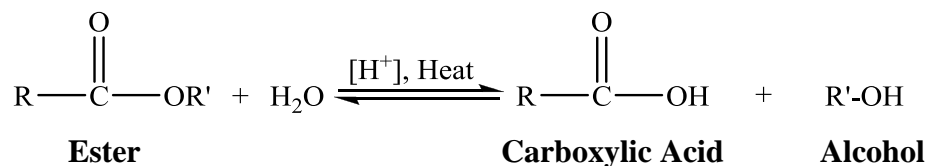
Esters hydrolysis is a very slow reaction. The reaction is considerably more rapid under either *acidic* or *basic* conditions.

Ester hydrolysis under acidic condition (acid hydrolysis) is the reverse of acid-catalyzed ester formation.

Ester hydrolysis under basic condition (base hydrolysis) produces the metal carboxylate salt instead of the carboxylic acid.

D) Acid Hydrolysis of Esters

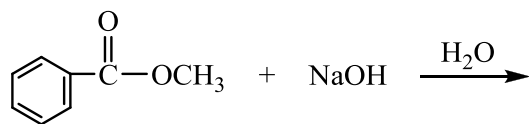
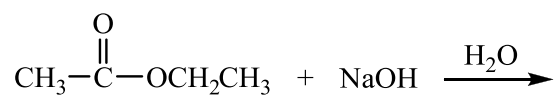
Acid hydrolysis of esters requires the presence of a strong acid catalyst such as sulfuric acid. This reaction requires heat. The generalized hydrolysis can be shown as:



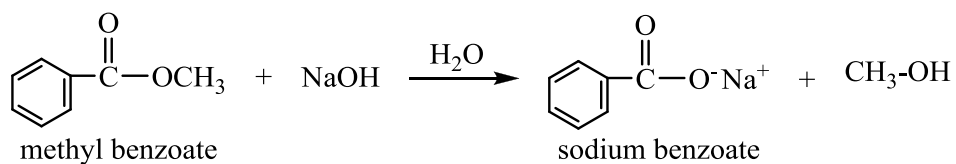
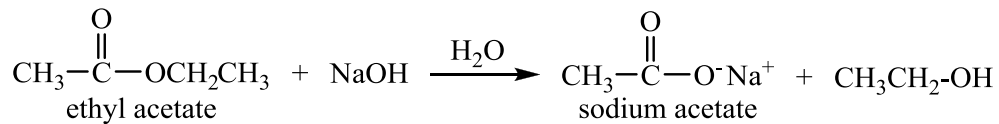
(This hydrolysis is the reverse of esterification.)

Worked Example 9-7

Complete the following saponification (base hydrolysis) reactions:

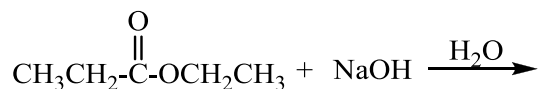
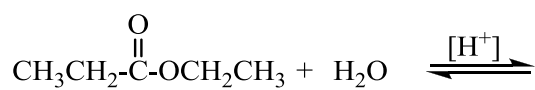
**Solution**

The hydrolysis of ester, under the basic condition, produces the carboxylic acid salt and an alcohol



Practice 9-5

Complete the following reactions:



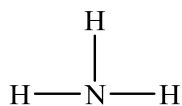
Answer

9.7 | Amines

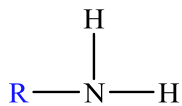
The three most common elements in organic compounds are carbon, hydrogen, and oxygen. Amines contain nitrogen and are commonly found in a wide variety of biomolecules and important pharmaceutical compounds. For this reason, nitrogen ranks fourth on the list of common elements found in organic compounds.

Amines are considered organic derivatives of ammonia (NH_3) in which one or more hydrogen atoms are replaced by an alkyl or aromatic group.

Amines are classified as primary, secondary, or tertiary, depending on the number of organic groups directly attached to the nitrogen atom.



Ammonia



primary
amine



secondary
amine



tertiary
amine

9.8 | Naming Amines

Common names are often used to name simple amines. If two or three alkyl groups are present, they are listed alphabetically along with the suffix –amine. The name is written as one word. Aromatic amines are usually named based on aniline.

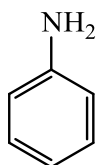
Examples:

$\text{CH}_3 - \text{NH}_2$
methylamine

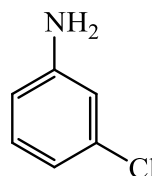
$\text{CH}_3\text{CH}_2 - \text{NH}_2$
ethylamine

$\text{CH}_3\text{CH}_2 - \text{NH} - \text{CH}_3$
ethylmethylamine

$\text{CH}_3 - \overset{\text{CH}_3}{\text{N}} - \text{CH}_3$
trimethylamine



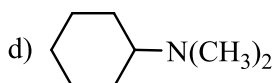
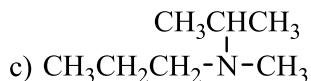
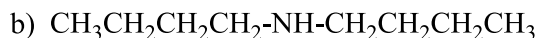
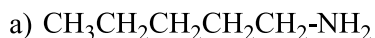
aniline



3-chloroaniline

Worked Example 9-8

Name each of the following:



Solution

a) pentylamine

(This amine has one alkyl group (pentyl) attached to the nitrogen atom.)

b) dibutylamine

(This amine has two identical alkyl groups (butyl) attached to the nitrogen atom.)

c) isopropylmethylpropylamine

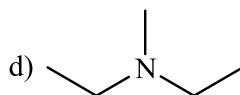
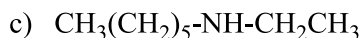
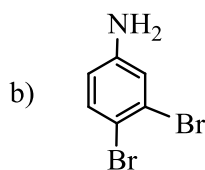
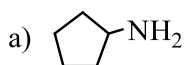
(This amine has three alkyl groups (isopropyl, methyl, and propyl) attached to the nitrogen atom.)

d) cyclohexyldimethylamine

(This amine has three alkyl groups (a cyclohexyl and two methyl group) attached to the nitrogen atom.)

Practice 9-6

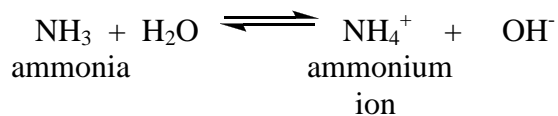
Name each of the following:



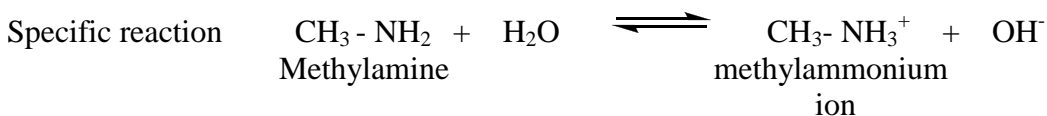
Answer

9.9 | Basicity of Amines

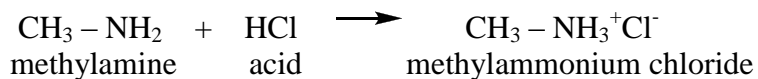
Recall (*unit 6*) that ammonia is also a weak base and accepts H^+ from water to produce ammonium ion (NH_4^+) and hydroxide ion (OH^-):



Because the amines are derivatives of ammonia, they react in a similar ways.

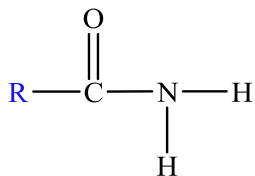


Just as amines accept H^+ from water, they can accept H^+ from acids and form salts. For example, when methylamine reacts with HCl, the acid-base reaction produces methylammonium chloride.

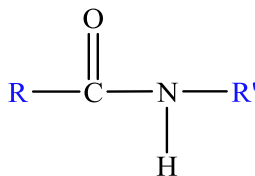


9.10 | Amides

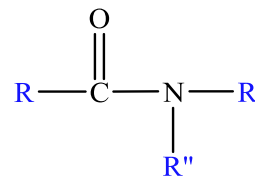
The functional group of an **amide** is a carbonyl group (C = O) linked to a nitrogen atom (N). Amides are classified as primary, secondary, and tertiary amides.



primary



secondary



tertiary

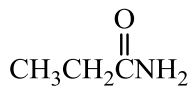
R, R', and R'' could be aliphatic or aromatic.

9.11 | Naming Amides

Naming Primary Amides

The ending of the name of the carboxylic acid is changed from -ic acid (common) or -oic acid (IUPAC) to -amide.

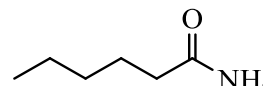
Examples



Propanamide



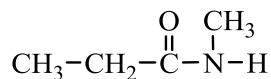
butanamide



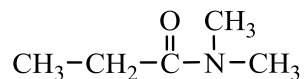
hexanamide

Naming Secondary and Tertiary Amides

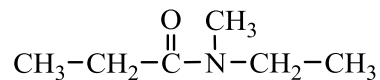
The names of groups attached to nitrogen are placed first, using an N-prefix for each group.



N-methylpropanamide



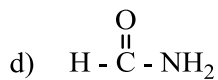
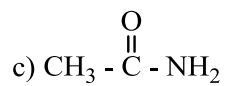
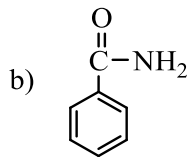
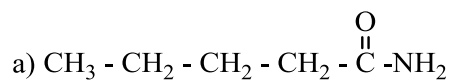
N,N-dimethylpropanamide



N-ethyl-N-methylpropanamide

Worked Example 9-9

Name each of the following amides:

**Solution**

a) pentanamide

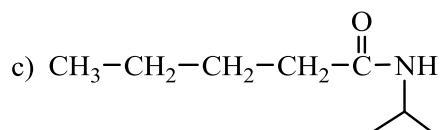
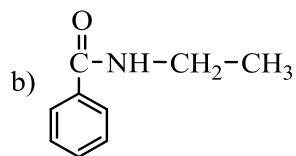
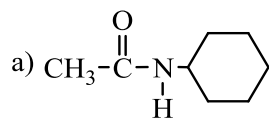
c) acetamide (ethanamide)

b) benzamide

d) formamide (methanamide)

Practice 9-7

Name each of the following amides:

**Answer**

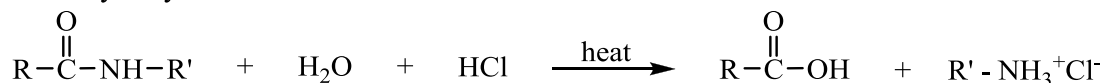
9.12 | Hydrolysis of Amides

Amides are very stable in water. Hydrolysis requires the heating of the amide in the presence of strong acid or base. Acidic hydrolysis gives a carboxylic acid and an amine salt.

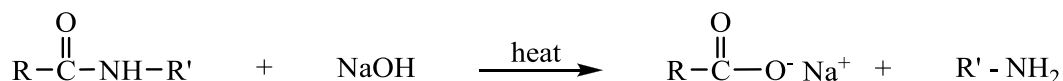
In aqueous base, the products of hydrolysis are a carboxylic acid salt and ammonia or an amine.

General Reactions:

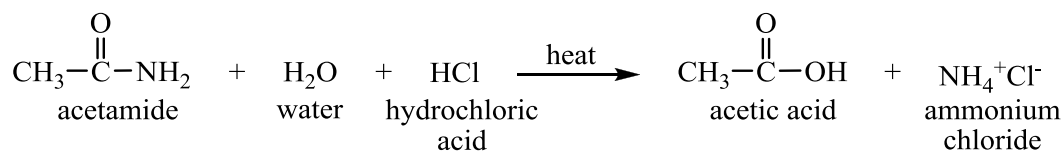
Acid Hydrolysis of Amides



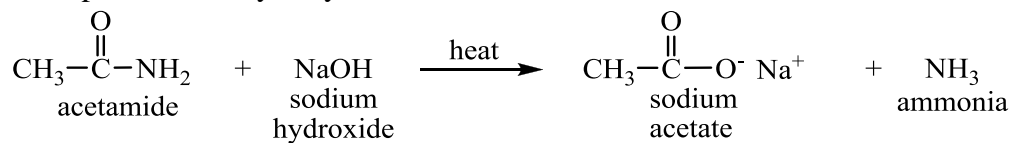
Base Hydrolysis of Amides



Example of Acid Hydrolysis of Amide:

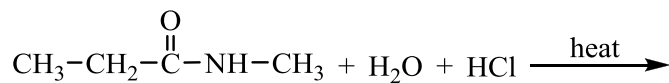
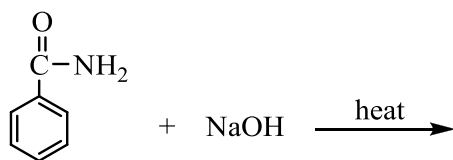


Example of Base Hydrolysis of Amide:

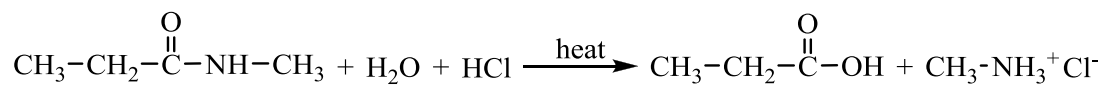
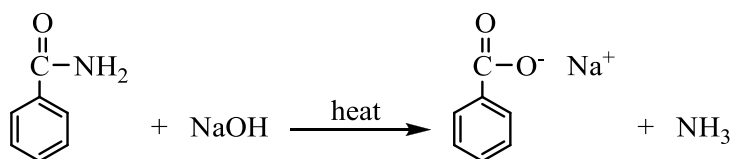


Worked Example 9-10

Draw the structures of the products in each of the following hydrolysis reactions.

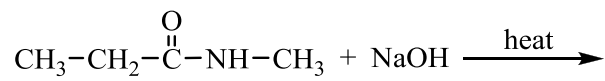
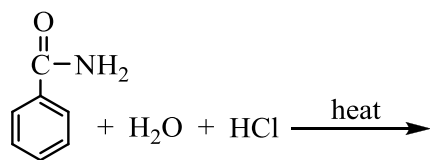


Answer



Practice 9-8

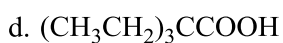
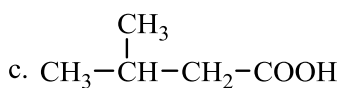
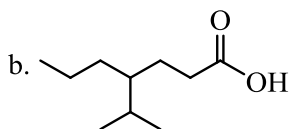
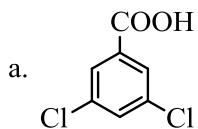
Draw the structures of the products in each of the following hydrolysis reactions.



Answer

Homework Problems

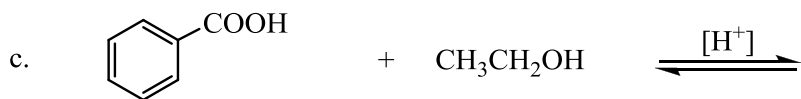
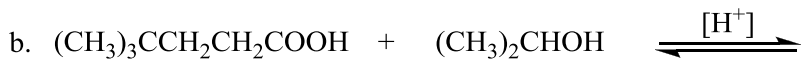
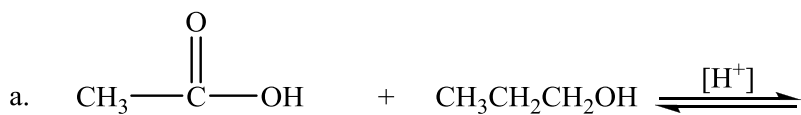
9.1 Give the name for each of the following:



9.2 Draw the structural formula for each of the following compounds:

- sodium hexanoate
- potassium acetate
- zinc benzoate
- calcium propanoate

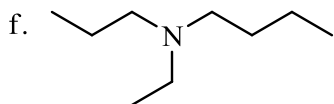
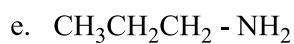
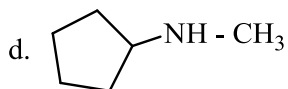
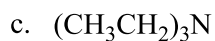
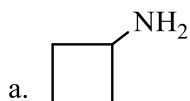
9.3 Complete the following reactions:



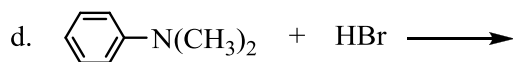
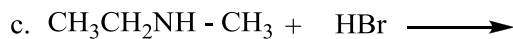
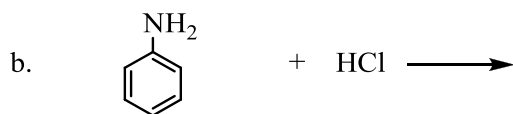
9.4 Draw a structural formula for each of the following esters:

- cyclohexyl propanoate
- methyl formate
- ethyl benzoate
- isopropyl acetate
- butyl butanoate
- propyl pentanoate

9.5 Assign names to each of the following amines:



9.6 Complete the following equations:



9.7 Draw the structures of 4 isomers of amides of formula $\text{C}_5\text{H}_{11}\text{NO}$.