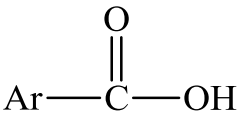
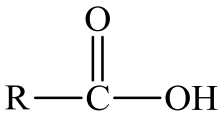
Carboxylic acids

Contains a *carboxyl group,* which is a carbonyl group (C=O) attached to a hydroxyl group (-OH). Has the carboxyl group on carbon 1. carbonyl group.



Aromatic Carboxylic acids

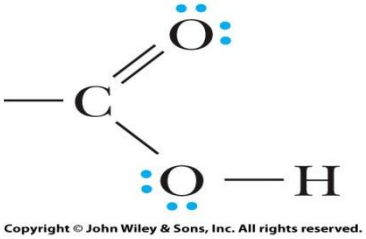


Aliphatic Carboxylic acids

or CH_3COOH

Structure of Carboxylic Acids

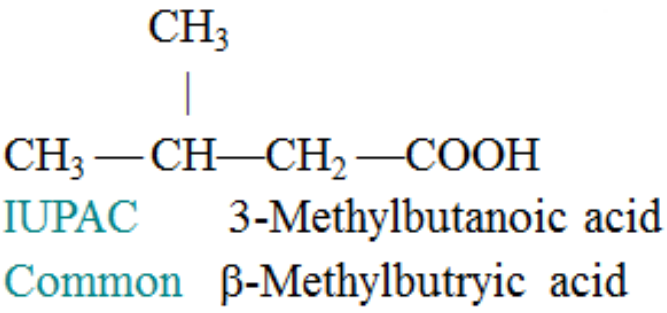
The functional group of a carboxylic acid is a carboxyl group.



- The general formula of an aliphatic carboxylic acid is RCOOH.
- For an aromatic carboxylic acid, the general formula is ArCOOH.
- Identify longest chain containing the carboxyl group

Nomenclature

- (IUPAC) Number carboxyl carbon as 1
- (Common) Assign α, β, g, δ to carbon atoms adjacent to carboxyl carbon



IUPAC 3-Methylbutanoic acid

Common β-Methylbutryic acid

The IUPAC system

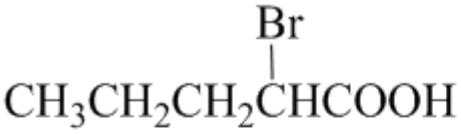
- In the IUPAC system, carboxylic acids are identified by a suffix added to the parent name of the longest chain with different end being used depending on whether the carboxyl group is bonded to a chain or a ring.
- If the COOH is bonded to a chain, find the longest chain containing the COOH, and change the "e" end of the parent alkane to the suffix "oic acid".
- If the COOH is bonded to a ring, name the ring and add the words "carboxylic acid".
- Number the carbon chain or ring to put the COOH group at C_1, but omit this number from the name.
- Apply all the other usually rules of nomenclature.

Naming Carboxylic Acids

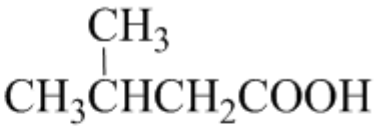
Formula	IUPAC alkan -oic acid	Common prefix – ic acid
HCOOH	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3CH_2CH_2COOH$	butanoic acid	butyric acid

Length of Carbon Chain	Structural Formula	Common Name[a]	IUPAC Name
C_1 monoacid	H—COOH	formic acid	methanoic acid
C_2 monoacid	CH_3—COOH	acetic acid	ethanoic acid
C_3 monoacid	CH_3—CH_2—COOH	propionic acid	propanoic acid
C_4 monoacid	CH_3—$(CH_2)_2$—COOH	butyric acid	butanoic acid
C_5 monoacid	CH_3—$(CH_2)_3$—COOH	valeric acid	pentanoic acid
C_6 monoacid	CH_3—$(CH_2)_4$—COOH	caproic acid	hexanoic acid

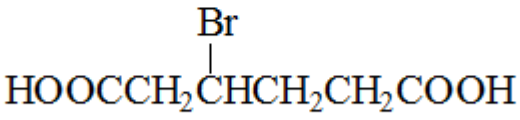
[a] The mnemonic "*F*rogs *a*re *p*olite, *b*eing *v*ery *c*ourteous" is helpful in remembering, in order, the first letters of the common names of these six simple saturated monocarboxylic acids.



α– Bromovaleric acid



β-Methylbutyric acid
Isovaleric acid

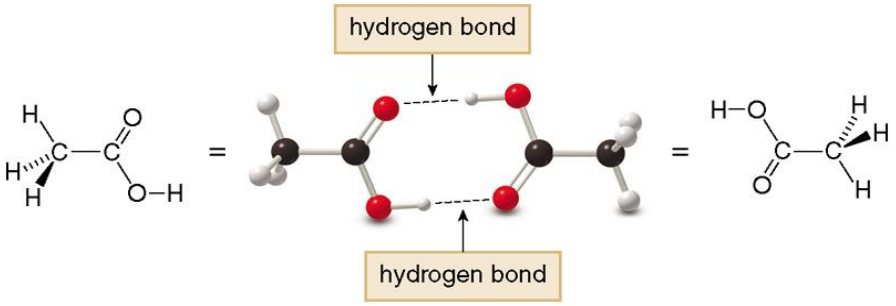


3-bromohexandioic acid
β-bromoadipic acid

HOOC-COOH	oxalic acid
HO_2C-CH_2-CO_2H	malonic acid
HO_2C-CH_2CH_2-CO_2H	succinic acid
HO_2C-$CH_2CH_2CH_2$-CO_2H	glutaric acid
HOOC-$(CH_2)_4$ -COOH	adipic acid
HOOC-$(CH_2)_6$ -COOH	pimelic acid

Carboxylic acids: Structure and physical properties

The carboxyl group consists of two very polar functional group, the carbonyl group and the hydroxyl group. Thus, carboxylic acids are very polar compounds. In addition, carboxylic acids can hydrogen bond to one another. As a result, they boil at higher temperatures than aldehydes, ketones, or even alcohols of comparable molecular weight. Carboxylic acids can form intermolecular hydrogen bonds with water molecules. Are high because they form dimers in which hydrogen bonds form between the polar groups in the two carboxyl groups.



Comparing Physical Properties

Boiling Point:
Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Water Solubility:
Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Name	Molecular weight	Boiling point	Solubility in water
Pentane	72 g/mol	35°C	Insoluble
Diethyl ether	74 g/mol	35°C	Insoluble
Butanal	72 g/mol	76°C	7.1 g / 100 mL H_2O
1-Butanol	74 g/mol	118°C	9.1 g / 100 mL H_2O
Propanoic acid	74 g/mol	141°C	Infinite

Example

Which member of each of the following sets of compounds has the highest boiling point?

1. Ethane or ethanol or ethanoic acid.
2. propanal or propanone or 1- propanol
3. methanal or methanol or methanoic acid

Answer

The boiling points of most alkanes, alcohols, aldehydes and carboxylic acids that have similar molecular weights obey the following relationship:

Alkane < aldehyde or ketone < alcohol < carboxylic acid

lowest highest

ethanoic acid 2. 1- propanol 3. methanoic acid

Examples: Predicting Physical Properties

- Arrange the following compounds in order of increasing boiling point. (All of the compounds have about the same molecular weight.)
  - 1-pentanol
  - hexane
  - butanoic acid
  - pentanal
- Which member of each of the following pairs of compounds would you expect to have a higher solubility in water?
  - 2-butanone *or* propanoic acid
  - hexanoic acid *or* ethanoic acid

Preparation of Carboxylic Acids

1. oxidation of primary alcohols

$$RCH_2OH + K_2Cr_2O_7 \rightarrow RCOOH$$

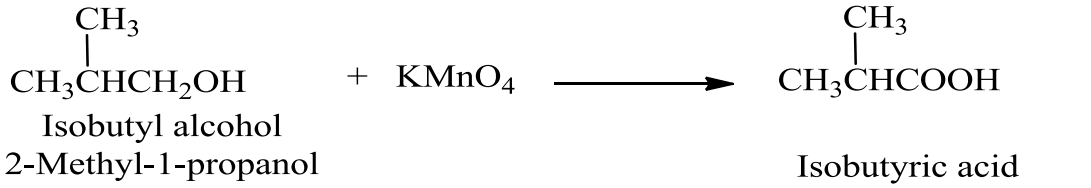
2. oxidation of arenes

$$ArR + KMnO_4, \text{heat} \rightarrow ArCOOH$$

$CH_3CH_2CH_2CH_2OH + K_2Cr_2O_7 \longrightarrow CH_3CH_2CH_2COOH$

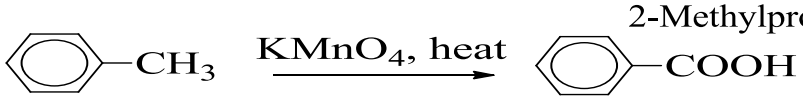
N-buty alcohol
1- Butanol

Butyric acid
Butanoic acid



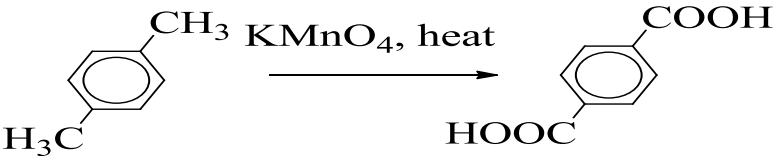
Isobutyl alcohol
2-Methyl-1-propanol

Isobutyric acid
2-Methylpropanoic acid



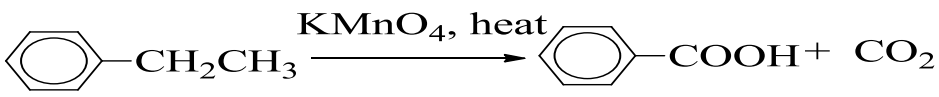
toluene

benzoic acid



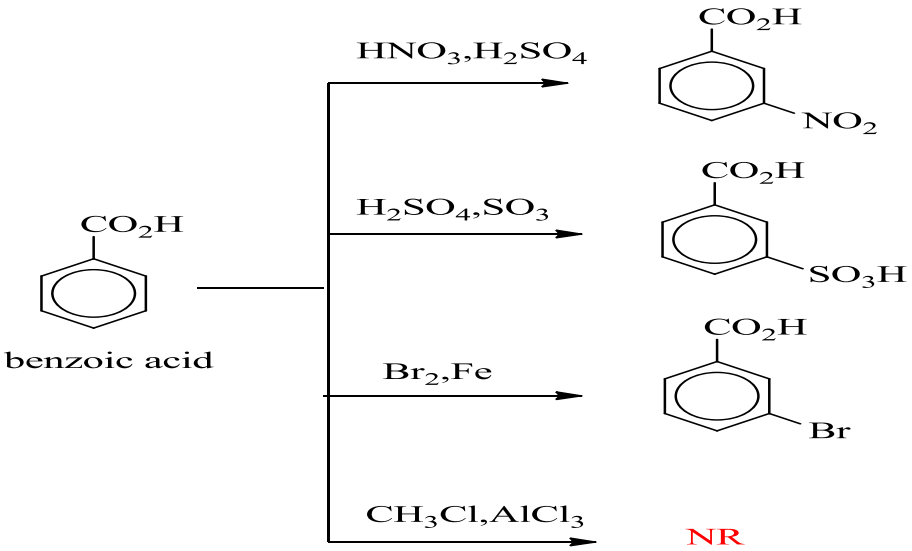
p-xylene

terephthalic acid



ethylbenzene

benzoic acid



Write the equation for the reaction of propanoic acid with

A. water

B. KOH

Write the equation for the reaction of propanoic acid with

A. water

$$CH_3\text{-}CH_2\text{-}COOH + H_2O \longleftrightarrow CH_3\text{-}CH_2\text{-}COO^- + H_3O^+$$

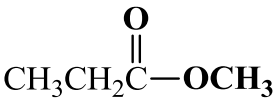
B. KOH

$$CH_3\text{-}CH_2\text{-}COOH + KOH \longleftrightarrow CH_3\text{-}CH_2\text{-}COO^- K^+ + H_2O$$

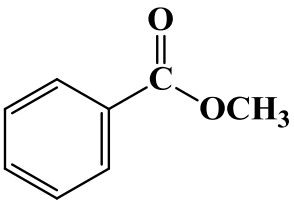
Derivatives of carboxylic acids:-

1- Esters

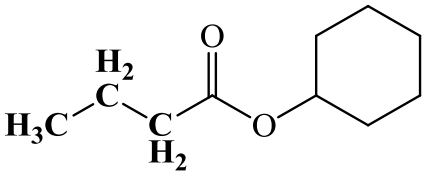
- The functional group of an ester is an acyl group bonded to **-OR** or **-OAr**.
- Name the alkyl or aryl group bonded to oxygen followed by the name of the acid.
- Change the suffix **-ic acid** to **-ate.**



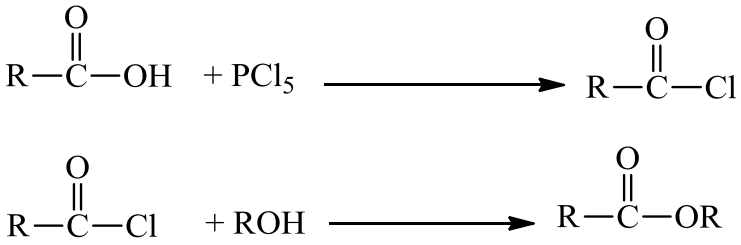
Methyl propionate



Methyl benzoate

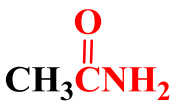


Cyclohexyl butaboate

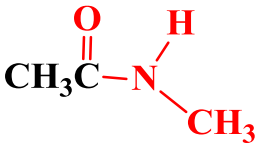


2- *Amides*

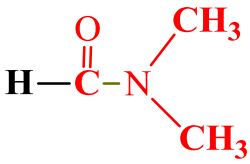
- The functional group of an amide is an acyl group bonded to a nitrogen atom.
- drop **-oic acid** from the name of the parent acid and add **-amide.** (For the common acid name, drop **-ic** of the acid name and add **-amide**.)
- an alkyl or aryl group bonded to the N: name the group and show its location on nitrogen by ***N*-.**



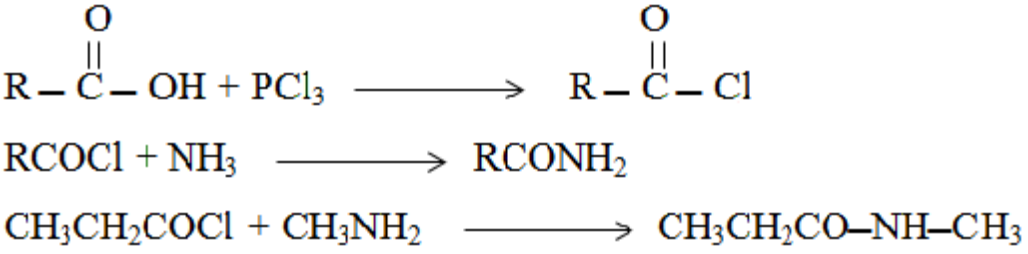
Acetamide (a1^0 amide)



***N*-methylacetamide (a2^0 amide)**

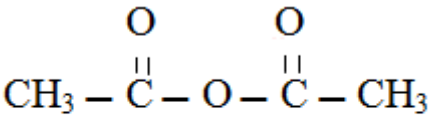


***N*,*N*-Dimethyl formamide(DMF) (a3^0 amide)**



3- *Anhydrides*

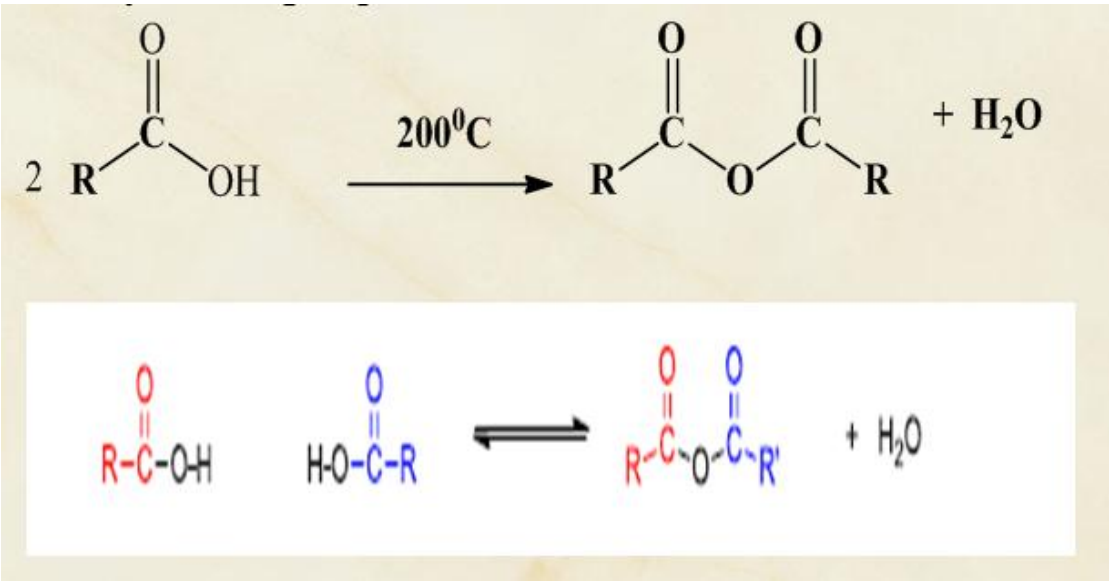
- Two acyl groups bonded to an oxygen atom.
- The anhydride may be symmetrical (two identical acyl groups) or mixed (two different acyl groups).
- To name, replace **acid** of the parent acid by **anhydride**.



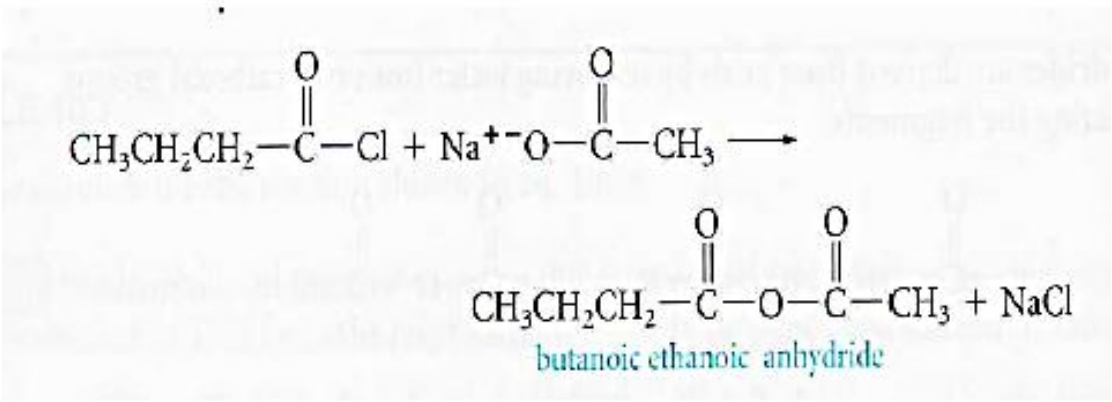
Acetic anhydride

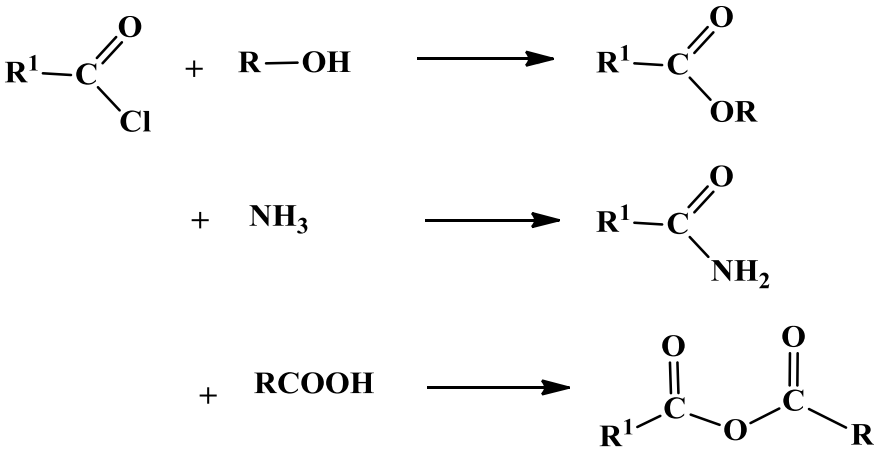
Preparation of anhydrides:

Heat promotes a **condensation reaction** between two carboxylic acid groups



Preparation of mixed anhydrides





Example

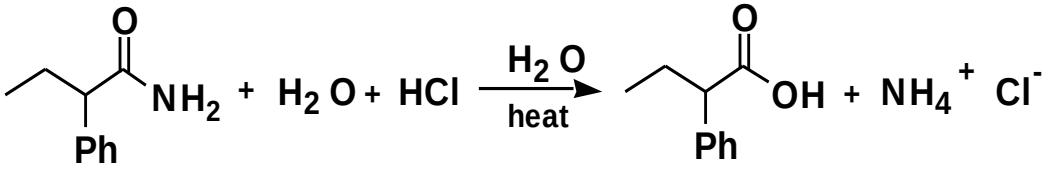
The following general formulas are used to represent different classes of organic compounds. Name each of the appropriate families.

1. ROH
2. RCHO
3. RCOR
4. ROR
5. RCOOH
6. RCOOR

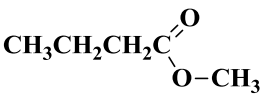
Answer

1. Alcohol
2. Aldehyde
3. Ketone
4. Ether
5. Carboxylic acid
6. Ester

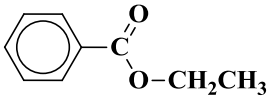
Acidic Reaction with H_2O - Amides



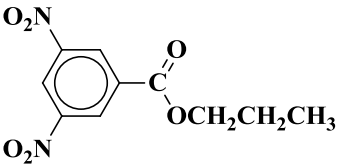
2-Phenylbutanamide **2-Phenylbutanoic acid**



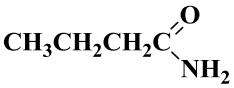
methyl butanoate
methyl butyrate



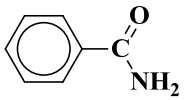
ethyl benzoate



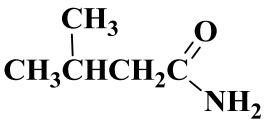
***n*-propyl-3,5-dinitrobenzoate**



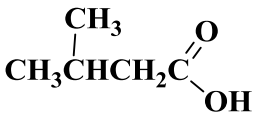
butanamide
butyramide



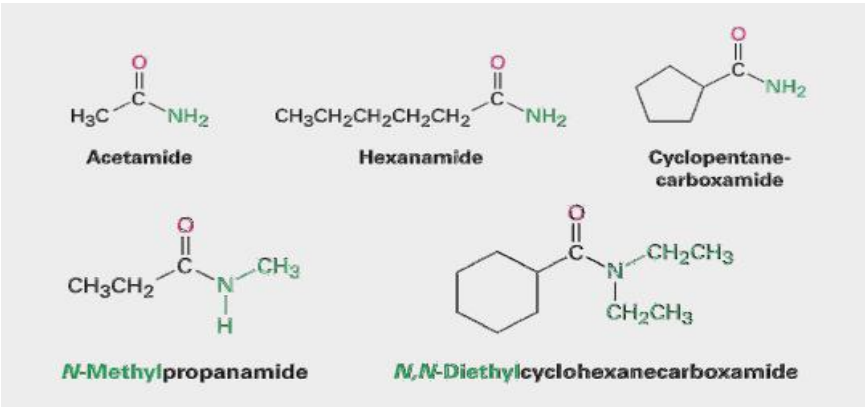
benzamide

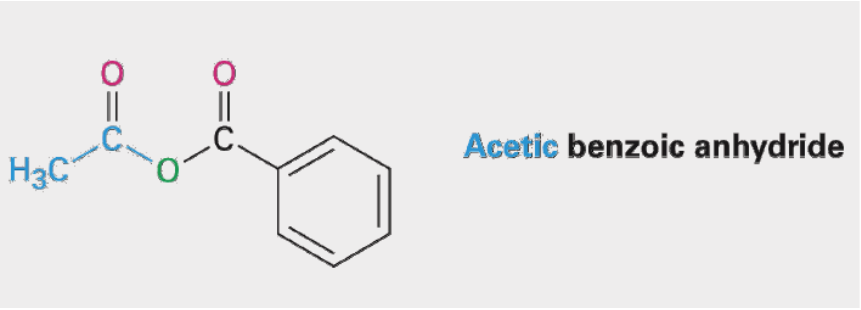


isovaleramide



isovaleric acid




O
O
C
C
H3C
O
Acetic benzoic anhydride