

Carboxylic Acid Derivatives

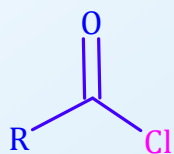
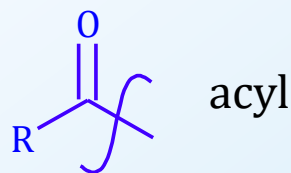
1 - Nomenclature, Properties and Applications

Dr. Sapna Gupta

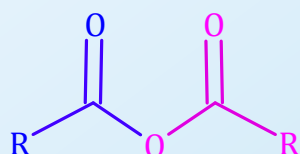
Derivatives

The carboxyl group ($-\text{CO}_2\text{H}$) is the parent group of a family of compounds called *acyl compounds* or *carboxylic acid derivatives*.

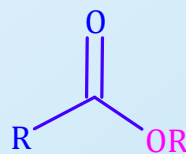
- The blue component below in the compounds are called “acyl”. The pink (right portion) is the various groups that differ in the derivatives. The names of all the derivatives are given below with the names.
- The only derivative that is different is nitrile which has a CN group. It does not have a carbonyl but is still part of the carboxylic derivatives.



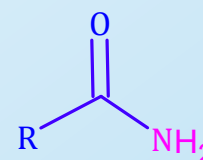
Acyl chloride



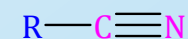
acid anhydride



carboxylic ester



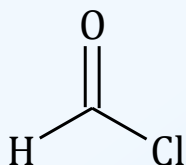
amide



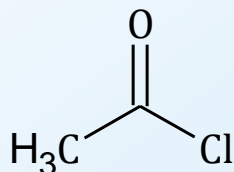
nitrile

Acyl Chlorides

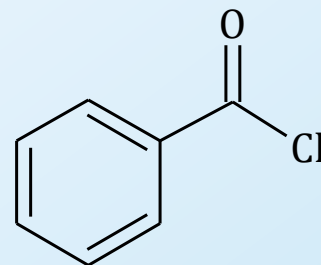
Acyl chlorides (RCOCl) have a Cl on the carbonyl carbon. Drop the *-ic acid* from the carboxylic acid and use *-yl chloride*.



Methanoyl chloride
Formoyl chloride



Ethanoyl chloride
Acetyl chloride



Benzoyl chloride

Properties: All acyl chlorides are soluble in water (they actually react with water). They are extremely reactive, toxic and foul smelling compounds.

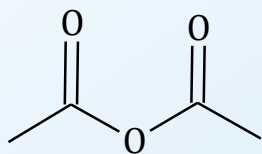
Carboxylic Anhydrides

Anhydrides $(\text{RCO})_2\text{O}$ means anything without water. These are made from dehydrating two carboxylic acids.

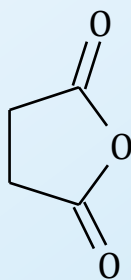
Anhydrides are named by dropping the *acid* of carboxylic acid and replacing it with *anhydride*.

Anhydrides are internal groups so can be found in cyclic compounds.

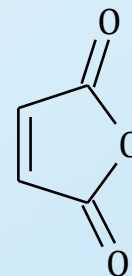
$(\text{HCO})_2\text{O}$ – methanoic anhydride



$(\text{CH}_3\text{CO})_2\text{O}$
Acetic anhydride



Succinic anhydride

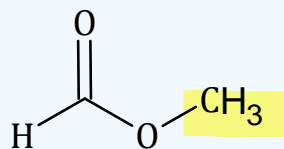


Maleic anhydride

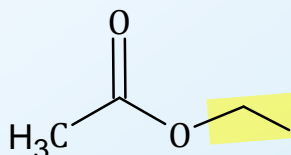
Properties: All anhydrides are soluble in water (they actually react with water). They are extremely reactive, toxic and foul smelling compounds.

Carboxylic Esters

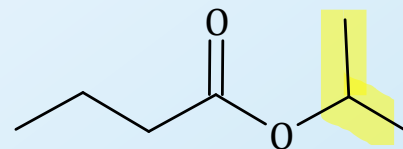
Carboxylic esters (RCOOR) are relatively stable compounds. Esters are named like salts ending in *ate*. The alkyl group on oxygen is named first and then the carbonyl carbon as the base name ending with *-ate*.



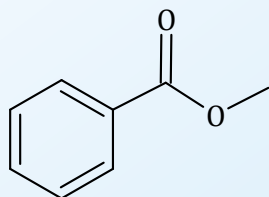
Methyl methanoate
Methyl formate



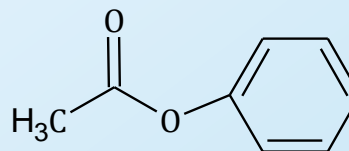
Ethyl ethanoate
Ethyl acetate



Isopropyl butanoate

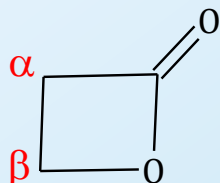


Methyl benzoate

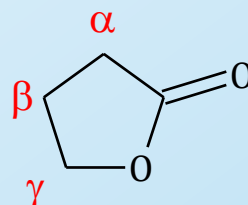


Phenyl ethanoate

Esters are internal groups, so can be found in cyclic compound. These esters are called lactones.



β -lactone



γ -lactone

Carboxylic Esters - Properties

Properties: Carboxylic esters (RCOOR) are relatively stable compounds.

- 1) Melting and Boiling point: They have low boiling points due to lack of hydrogen bonding, but they still have dipole moment.
- 2) Solubility in water: They are not soluble in water due to lack of hydrogen bonding.
- 3) Odor: The most unique aspect of esters is their smell. They have fruity smells.

Carboxylic Esters - Applications

1) Fruity flavors are mostly esters.

Orange – n-octyl acetate

Apple - Methylbutyrate

Pineapple - Ethyl butrate

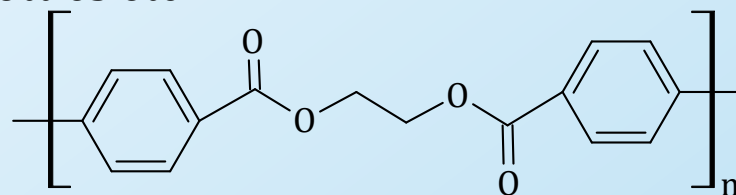
Banana - n-amyl acetate

Wintergreen - methyl salicylate

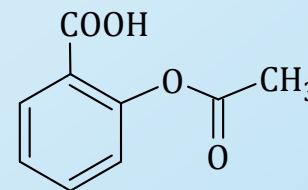
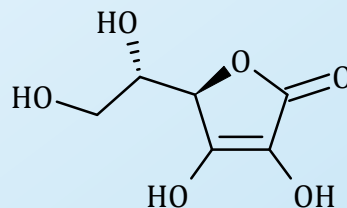
2) Solvents – Esters are generally unreactive and make for good solvents for paints. For e.g., nail polish remover is made in ethyl acetate.

3) Polyesters – used in clothing, tires, plastic bottles etc.

Polyethylene terephthalate (PET)



4) Aspirin – first painkiller to be synthesized by Bayer.

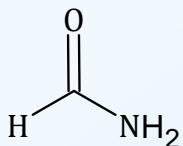


5) Vitamin C – is a lactone.

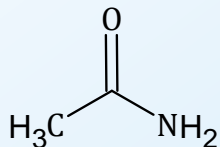
6) Enzymes – Human body has many esterases as enzymes.

Amides

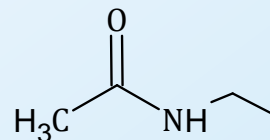
Amides (RCONR_2) have a N attached to carbonyl carbon. The nitrogen can have hydrogens or alkyl groups. To name the amide, drop the $-e$ from alkane and replace with *amide*. When there are alkyl groups, name the alkyl groups as *N-alkyl*.



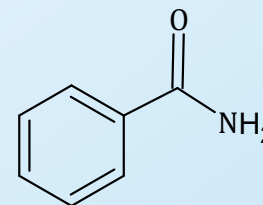
Methanamide
Formamide



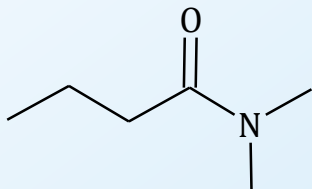
Ethanamide
Acetamide



N-ethyl ethanamide

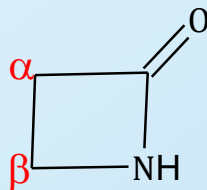


Benzanamide

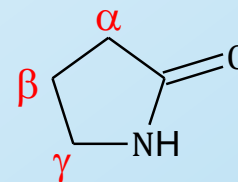


N,N-dimethyl butanamide

Amides are internal groups, so can be found in a cyclic structure – these are called lactams.



β -lactam



γ -lactam

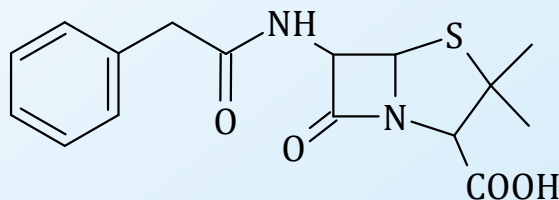
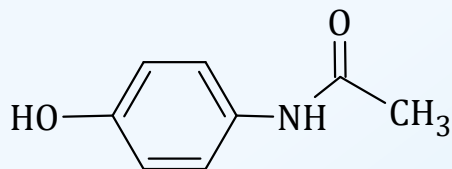
Amides - Properties

Properties: Amides are (RCONH_2) are relatively stable compounds.

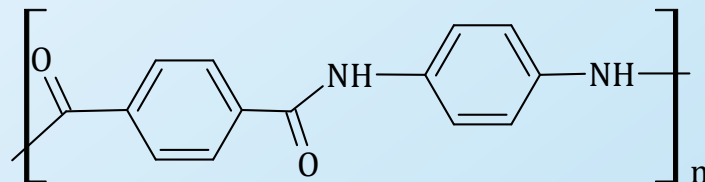
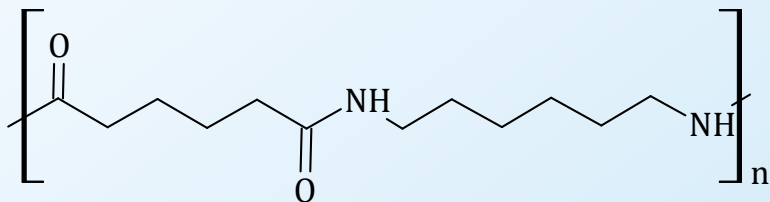
- 1) Melting and Boiling point: They have high boiling points due to hydrogen bonding of the nitrogen, however their boiling point can change if there are alkyl groups instead of H on the nitrogen.
- 2) Solubility in water: Smaller amides are soluble in water due to hydrogen bonding and polarity. Again, solubility can depend on how many Hs are on the nitrogen.
- 3) Odor: Amides don't have any odor.

Amides - Applications

- 1) Pharmaceuticals: Amide linkages are found in many drugs, e.g., acetaminophen, penicillin.



- 2) Plastics: Amides are used in the production of synthetic polymers like nylon, Kevlar, which are used in textiles and materials science.

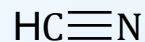


- 3) Solvents: Low-molecular weight amides, such as dimethylformamide and dimethylacetamide, are used as polar solvents.

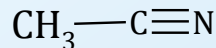
Nitriles

These are the most unusual of all carboxylic acid derivative – there is no carbonyl group! In inorganic chemistry CN^- is called cyanide; but in organic its called nitrile.

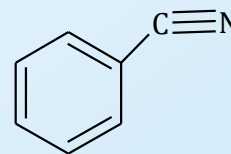
To name nitriles, remove the *-e* of the alkane and replace with *nitrile*.



Methanenitrile



Ethanenitrile



Benzonitrile

Properties: All nitriles are reactive and water sensitive.

Derivatives and Their Properties

| $\begin{array}{c} \text{O} \\ \\ \text{RCCI} \end{array}$ Acyl chloride | $\begin{array}{c} \text{O} \\ \\ \text{RCOR} \end{array}$ Esters | $\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{RCOCR} \end{array}$ Anhydrides | RCN Nitriles | $\begin{array}{c} \text{O} \\ \\ \text{RCNH}_2 \end{array}$ Amides |
|--|---|--|---------------------------------|---|
| No H bonding | No H bonding | No H bonding | No H bonding | H bonding |
| Low bpt and mpt | Low bpt and mpt | Low bpt and mpt | Low bpt and mpt | High bpt and mpt |
| | Salts of acid and alcohol | | | Salts of acid and amines |
| Soluble because of reaction | Slightly soluble in water | Soluble because of reaction | | Soluble in water |
| Pungent odor | Fruity smells | Pungent odor | | No odor |

Key Concepts

- Recognize the structure of all derivatives
- Name all types of derivatives
- Predict physical properties of all derivatives