## SLE155 Chemistry for the Professional Sciences

### Burwood and Geelong




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# Class 10 Carboxylic acids

## Structure and bonding

## Nomenclature

## Physical properties

## Preparation of carboxylic acids and derivatives

**References**

**Blackman A, Bottle S, Schmid G, Mocerino M and Wille U (2019a), *Chemistry*, 4th edn, John Wiley & Sons, Milton, Qld.**

**Blackman A, Southam D, Lawrie G, Williamson N, Thompson C and Bridgeman A (2019b), *Chemistry: core concepts*, 2nd edn, John Wiley & Sons, Milton, Qld.**

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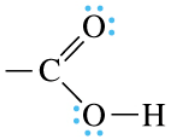
# Structure and Bonding

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



—COOH —$CO_2H$

Source: Blackman et al. (2019b:948).

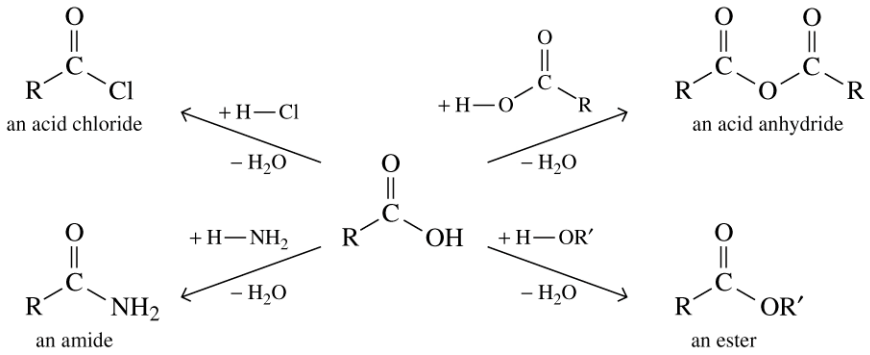
**The general formula of an aliphatic carboxylic acid is RCOOH.**

**The general formula of an aromatic carboxylic acid is ArCOOH.**



# Structure and Bonding

**The general formula for each of the four carboxylic acid derived functional groups is given below.** Source: Blackman et al. (2019b:949).



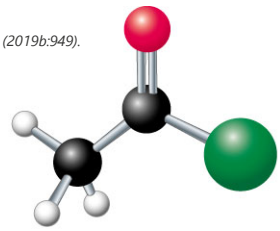
# Structure and Bonding

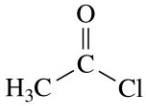
## Acid halides

**The functional group is the acyl group bonded to a halogen atom.**

**Abbreviated to RCOX or ArCOX (X = halide)**

*Source: Blackman et al. (2019b:949).*






acetyl chloride
(ethanoyl chloride)

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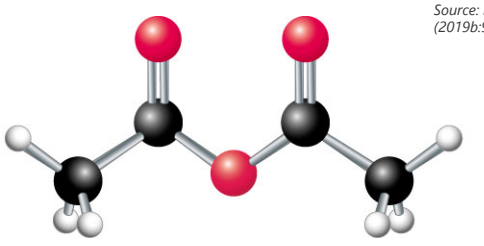
# Structure and Bonding

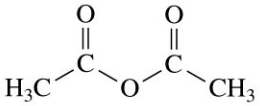
## Acid anhydrides

**The functional group is 2 acyl groups bonded to an oxygen atom.**

**It may be symmetrical or mixed.**

*Source: Blackman et al. (2019b:949).*






acetic anhydride
(ethanoic anhydride)

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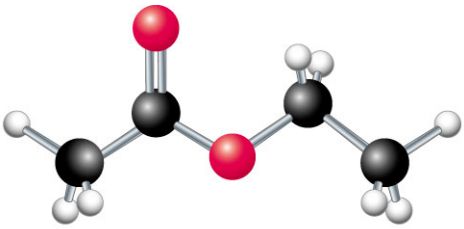
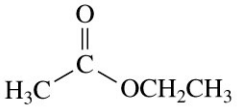
# Structure and Bonding

## Esters of carboxylic acids

**The functional group is an acyl group bonded to an –OR or an –OAr group.**

*Source: Blackman et al. (2019b:949).*






ethyl acetate
(ethyl ethanoate)



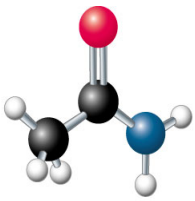
# Structure and Bonding

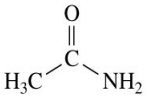
## Amides of carboxylic acids

**The functional group is an acyl group bonded to a trivalent nitrogen atom.**

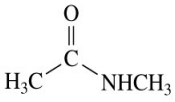
**Can be classified as primary, secondary or tertiary.**

*Source: Blackman et al. (2019b:950).*

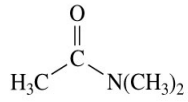





acetamide
(ethanamide)
(a 1° amide)




*N*-methylacetamide
(*N*-methylethanamide)
(a 2° amide)

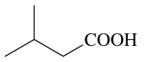



*N*,*N*-dimethylacetamide
(*N*,*N*-dimethylethanamide)
(a 3° amide)

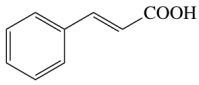
# Nomenclature

## Carboxylic Acids

**For the IUPAC name drop the final –e from the parent alkane and replace it with the suffix –oic acid**

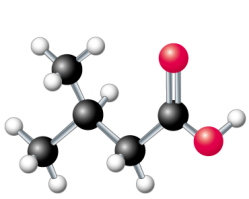


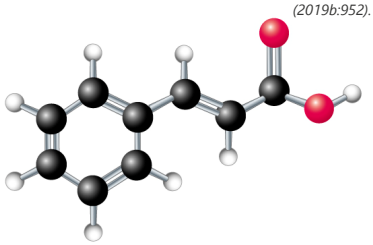

3-methylbutanoic acid
(isovaleric acid)




*trans*-3-phenylpropenoic acid
(*E*)-3-phenylpropenoic acid
(cinnamic acid)

*Source: Blackman et al. (2019b:952).*



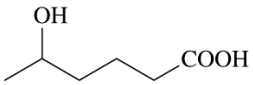




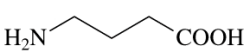
# Nomenclature

## Carboxylic acids

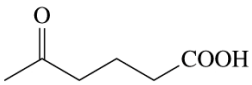
**A carboxyl group takes precedence over most other functional groups, including hydroxyl and amino groups, as well as the carbonyl groups of aldehydes and ketones.**




5-hydroxyhexanoic acid




4-aminobutanoic acid

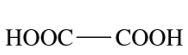



5-oxohexanoic acid

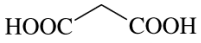
# Nomenclature

## Carboxylic acids

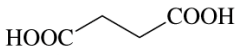
**Dicarboxylic acids are named by adding the suffix –dioic, followed by the word acid, to the name of the carbon chain that contains both carboxyl groups.**



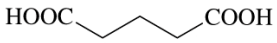
ethanedioic acid
(oxalic acid)



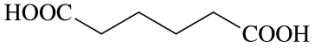
propanedioic acid
(malonic acid)



butanedioic acid
(succinic acid)



pentanedioic acid
(glutaric acid)

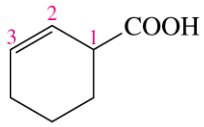


hexanedioic acid
(adipic acid)

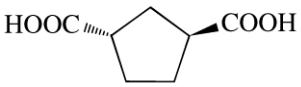
# Nomenclature

## Carboxylic acids

**A carboxylic acid containing a carboxyl group bonded to a cycloalkane ring is named by giving the name of the ring and adding the suffix – carboxylic acid**



cyclohex-2-enecarboxylic
acid



*trans*-cyclopentane-
1,3-dicarboxylic acid

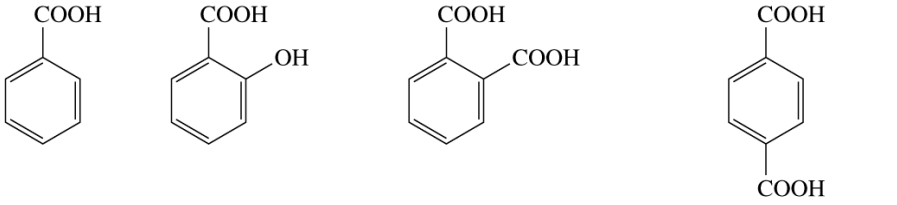
# Nomenclature

## Carboxylic acids

**The simplest aromatic carboxylic acid is benzoic acid.**

**Derivatives are named by using numbers and prefixes to show the presence and location of substituents.**

*Source: Blackman et al. (2019b:954).*




benzoic acid | 2-hydroxybenzoic acid (salicylic acid) | benzene-1,2-dicarboxylic acid (phthalic acid) | benzene-1,4-dicarboxylic acid (terephthalic acid)

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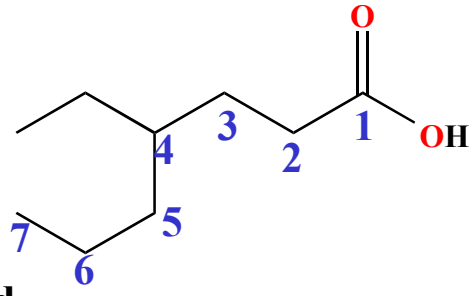
# Naming Carboxylic Acids

1. *Name the Parent Chain*
   **heptane**
2. *Add the Suffix*
   **heptanoic acid**
3. *Add the Prefix*
   **ethylheptanoic acid**
4. *Include the Locant*
   **4-ethylheptanoic acid**

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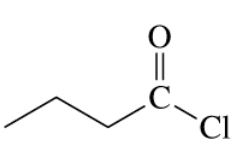
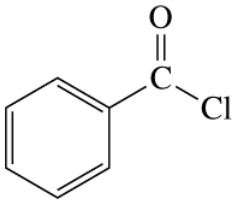
# Nomenclature

## Acid halides

**Change the suffix –ic acid in the name of the parent carboxylic acid to –yl halide**



butanoyl chloride



benzoyl chloride

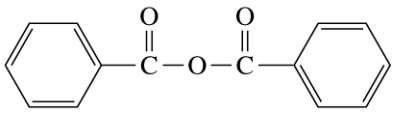
# Nomenclature

## Acid anhydrides

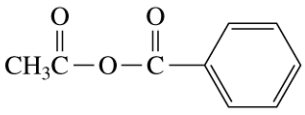
**Replace the word acid with anhydride**

**When the anhydride is not symmetrical, both acid groups are named.**

*Source: Blackman et al. (2019b:956).*



benzoic anhydride



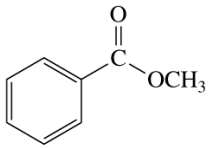
acetic benzoic anhydride
(a mixed anhydride)

# Nomenclature

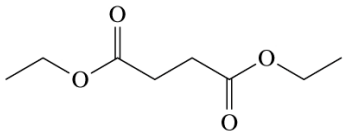
## Esters

**The alkyl or aryl group bonded to oxygen is named first.**

**This is followed, as a separate word, by the name of the acid, in which the suffix –ic acid is replaced by the suffix –ate**




methyl benzoate




diethyl butanedioate
(diethyl succinate)

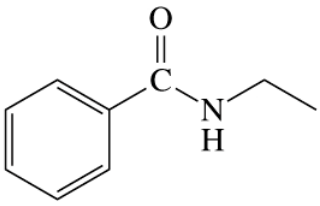


# Nomenclature

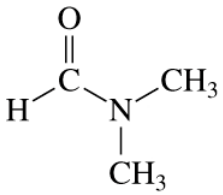
## Amides

**Drop the suffix –oic acid from the IUPAC name of the parent acid and add –amide**

*Source: Blackman et al. (2019b:956).*




*N*-ethylbenzamide

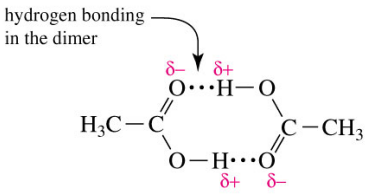


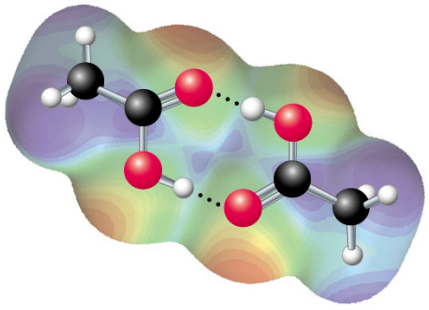

*N,N*-dimethylformamide

# Physical Properties

**In the liquid and solid states, carboxylic acids are associated by intermolecular hydrogen bonding into dimers.**

*Source: Blackman et al. (2019a:1394).*



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# Physical Properties

**Carboxylic acids have significantly high boiling points because they are polar compounds and form very strong intermolecular hydrogen bonds.**

**Their boiling points are higher than alcohols, ketones, and aldehydes of similar mass.**

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# Physical Properties

| Structure | Name | Molar mass | Number of electrons | Boiling point (°C) | Solubility (g/100 mL $H_2O$) |
|---|---|---|---|---|---|
| $CH_3COOH$ | acetic acid | 60.1 | 32 | 118 | infinite |
| $CH_3CH_2CH_2OH$ | propan-1-ol | 60.1 | 34 | 97 | infinite |
| $CH_3CH_2CHO$ | propanal | 58.1 | 32 | 48 | 16 |
| $CH_3(CH_2)_2COOH$ | butanoic acid | 88.1 | 48 | 163 | infinite |
| $CH_3(CH_2)_3CH_2OH$ | pentan-1-ol | 88.1 | 50 | 137 | 2.7 |
| $CH_3(CH_2)_3CHO$ | pentanal | 86.1 | 48 | 103 | slight |
| $CH_3(CH_2)_4COOH$ | hexanoic acid | 116.2 | 64 | 205 | 1.0 |
| $CH_3(CH_2)_5CH_2OH$ | heptan-1-ol | 116.2 | 66 | 176 | 0.2 |
| $CH_3(CH_2)_5CHO$ | heptanal | 114.1 | 64 | 153 | 0.1 |

*Source: Blackman et al. (2019a:1395).*

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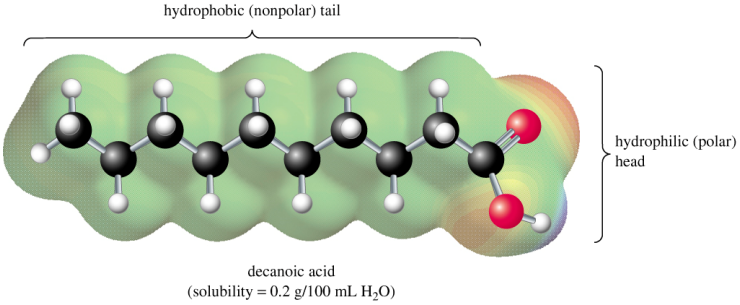
# Physical Properties

**Carboxylic acids are more soluble in water than alcohols, ethers, aldehydes, and ketones of similar molar mass because they form hydrogen bonds with water molecules through their C=O and OH groups.**

*Source: Blackman et al. (2019a:1395).*

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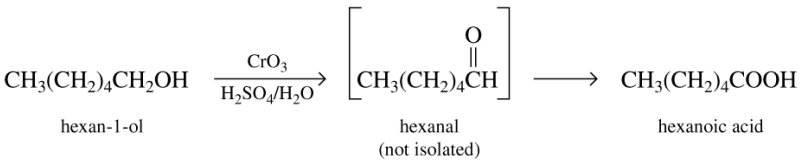
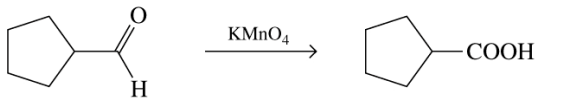
# Preparation of carboxylic acids

**Primary alcohols and aldehydes are readily oxidised to carboxylic acids.**




hexan-1-ol — hexanal (not isolated) — hexanoic acid

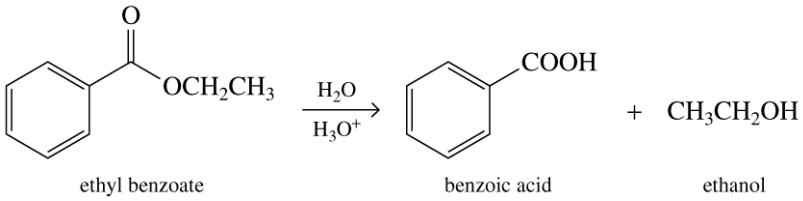



cyclopentanecarbaldehyde — cyclopentanecarboxylic acid



# Preparation of carboxylic acids

## Hydrolysis of carboxylic acid derivatives



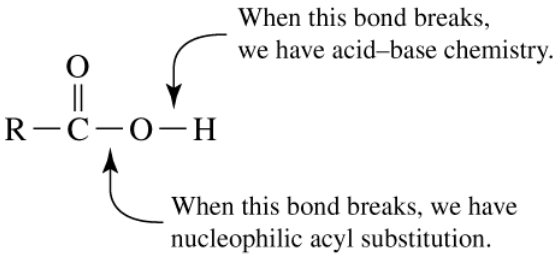

ethyl benzoate — benzoic acid — ethanol

*Source: Blackman et al. (2019a:1398).*

## Reactions of carboxylic acids and derivatives

**There are two general types:**

- **Acid-base**
- **Nucleophilic acyl substitution**




## Reactions of carboxylic acids and derivatives

### Acidity

**Carboxylic acids are weak acids**

**$K_a$ values range from $1\times10^{-4}$ to $1\times10^{-5}$**

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.8\times10^{-5}$$

$$pK_a = 4.74$$

*Source: Blackman et al. (2019a:1400).*

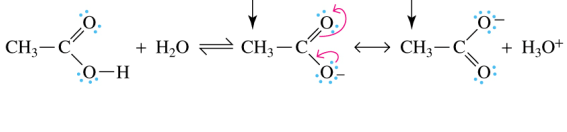
# Reactions of carboxylic acids and derivatives

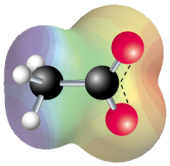
**Carboxylic acids are stronger acids than alcohols because resonance stabilises the carboxylate anion by delocalising its negative charge.**

**This resonance stabilisation does not exist in alkoxide forms.**

*Source: Blackman et al. (2019a:1400).*

These contributing structures are equivalent; the carboxylate anion is stabilised by delocalisation of the negative charge.





The electron density map shows the negative charge equally delocalised on the two carboxylate oxygen atoms.

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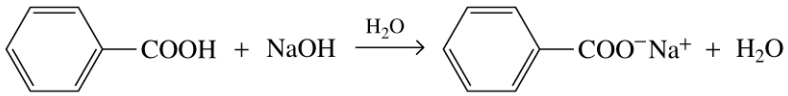
# Reactions of carboxylic acids and derivatives

## Reaction with bases

**All carboxylic acids react with strong bases to form water-soluble salts.**



benzoic acid
(slightly soluble in water)

sodium benzoate
(solubility = 60 g/100 mL $H_2O$)

**Carboxylic acids also form water-soluble salts with ammonia and amines.**

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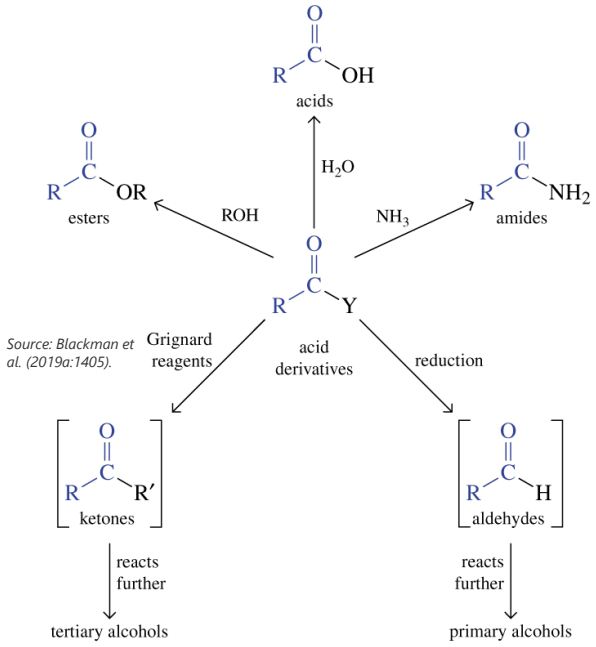
## Reactions of carboxylic acids and derivatives



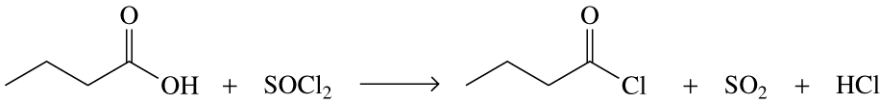

Source: Blackman et al. (2019a:1405).



## Reactions of carboxylic acids and derivatives

### Acid halide formation

**Prepared by treating a carboxylic acid with thionyl chloride, $SOCl_2$. (Cl replaces –OH)**




butanoic acid — thionyl chloride — butanoyl chloride

**Acid halides are the most reactive of the derivatives of carboxylic acids.**

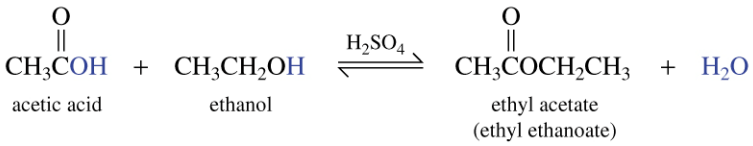
# Reactions with alcohols

## Esterification

**Treatment of a carboxylic acid with an alcohol in the presence of an acid catalyst gives an ester.**

**Acid-catalysed esterification is reversible.**

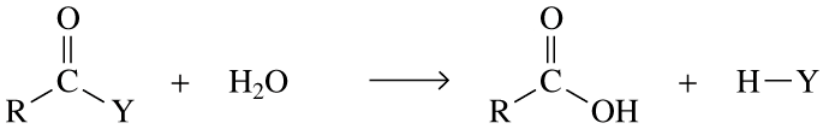
*Source: Blackman et al. (2019a:1406).*




# Reactions with water - hydrolysis

**Reaction with water is called hydrolysis**
**Hydroylsis is an example of a nucleophilic acyl substitution.**

**The carboxylic acid derivative reacts with water to give a carboxylic acid and H–Y.**

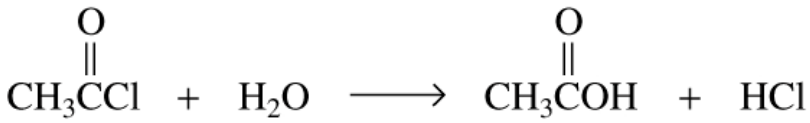


## Reactions with water - hydrolysis

### Acid chlorides

**Low-molar-mass acid chlorides react very rapidly with water to form carboxylic acids and HCl gas.**

**High-molar-mass acid chlorides are less water soluble so react less rapidly with water.**

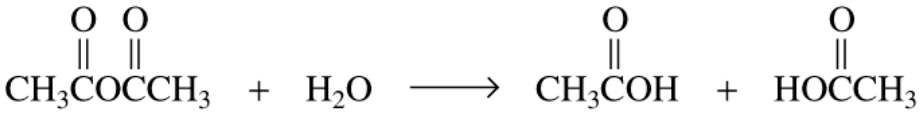



## Reactions with water - hydrolysis

### Acid anhydrides

**Generally less reactive than acid chlorides.**

**Low-molar-mass anhydrides react readily with water to form 2 molecules of carboxylic acid.**



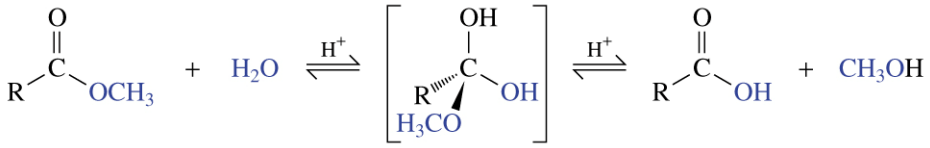
## Reactions with water - hydrolysis

**Esters are hydrolysed only very slowly**

**Heating esters in aqueous acid or base speeds up this reaction.**

**The role of the acid catalyst is to make the carbonyl carbon more susceptible towards attack by water.**

*Source: Blackman et al. (2019a:1412).*

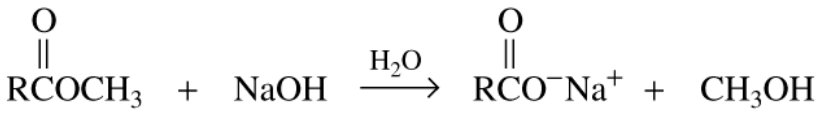



tetrahedral carbonyl addition intermediate



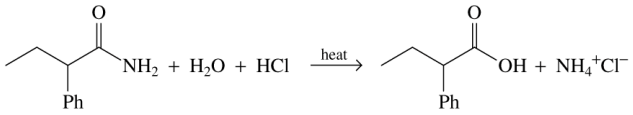
## Reactions with water - hydrolysis

**When carried out with hot aqueous base the reaction is often called saponification meaning "soap making".**



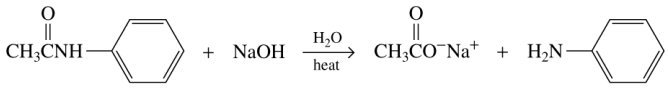
# Reactions with water - hydrolysis

**Amides undergo hydrolysis in hot aqueous acid to give a carboxylic acid and ammonia.**




2-phenylbutanamide — 2-phenylbutanoic acid

**In aqueous base, the products of amide hydrolysis are a carboxylic acid and ammonia.**




*N*-phenylethanamide (acetanilide) — sodium acetate — aniline

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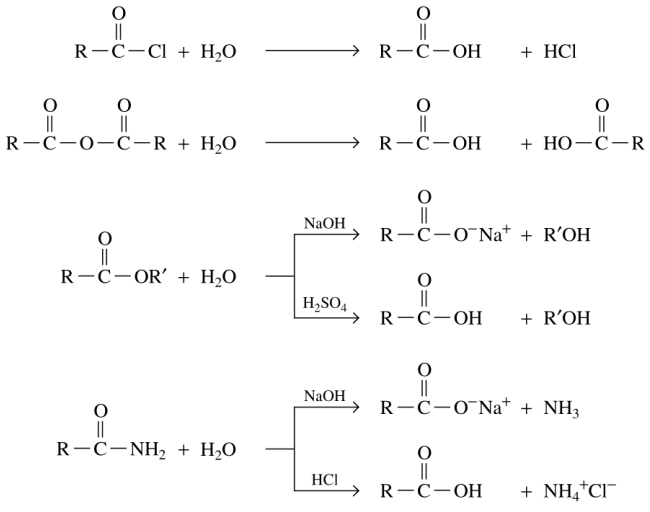
# Reactions with water - hydrolysis

**Summary:**

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# Reactions of carboxylic acids and derivatives

## Interconversion of functional derivatives