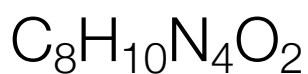
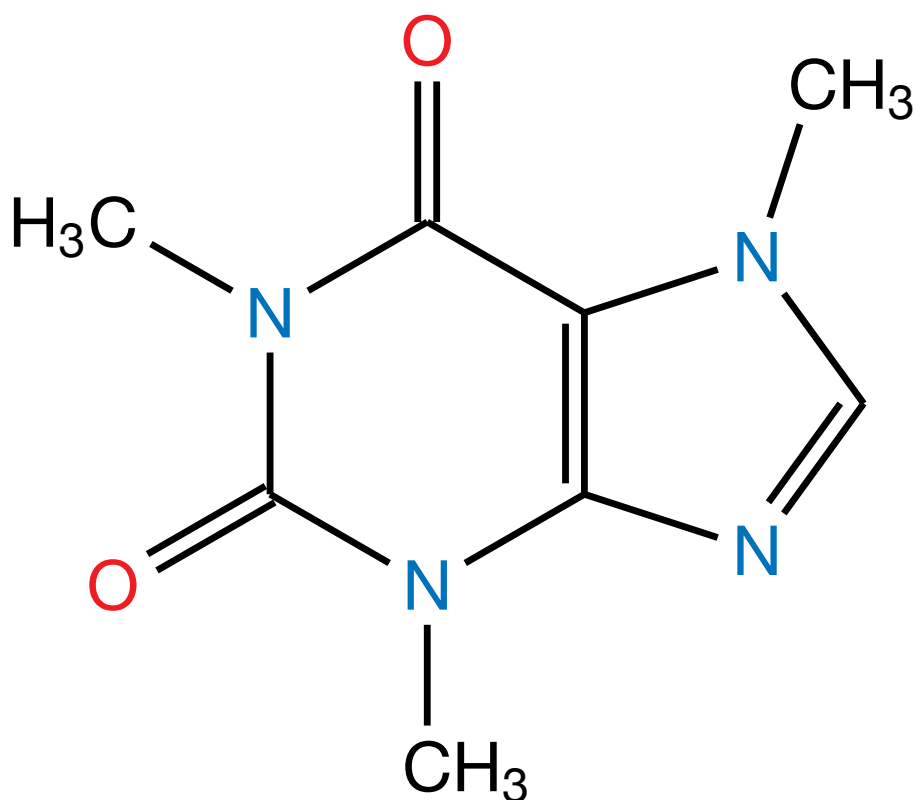


Organic Chemistry



1,3,7-trimethylpurine-2,6-dione

-

Caffeine

Chapters 8 to 12, 15 to 18

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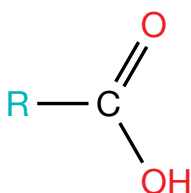
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I Carboxylic Acids

1 Structure

The structure of carboxylic acids is kind of an extension of a ketone or aldehyde — it features an oxygen atom double-bonded to a carbon atom, with an R group and an OH group attached as well.



The general structure of a carboxylic acid.

The central carbon is sp^2 hybridised, so the bond angle between all three groups is 120° .

2 Physical Properties

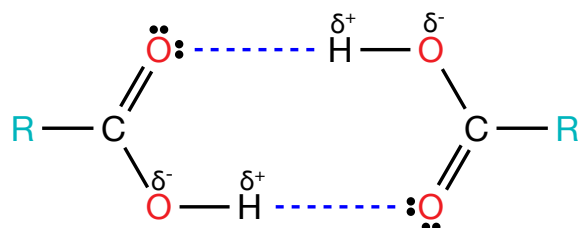
Melting and Boiling Points

Compared to both alkanes, carboxylic acids naturally have higher melting and boiling points. This is mostly due to the large permanent dipole moment, caused by the existence of two electron-withdrawing groups (the $C=O$ and $C-OH$), creating a large partial-positive charge (δ^+) on the carbon atom. Thus, hydrogen bonds can form; these bonds are stronger than that in alcohols, because the dipole moment is greater.

Their melting and boiling points are also higher than that of aldehydes and ketones, since carbonyls lack the $O-H$ partial charge disparity to form hydrogen bonds, and rely solely on permanent dipole interactions.

Note that hydrogen bonds between carboxylic acid molecules typically form between the H on the OH group, and the O atom double-bonded to the central carbon.

Furthermore, in both the liquid and gaseous state, two carboxylic acid molecules can *dimerise*, forming double-bonds between each other and effectively increasing molecular mass, which also increases id-id interaction strength.



An illustration of two carboxylic acids dimerising.

Solubility

Carboxylic acids are fairly soluble in non-polar solvents, as they exist as the dimerised form shown above. This means that carboxylic acids are not acidic in a non-polar solvent, as they do not dissociate.

In water, the molecules do not dimerise; instead, they form hydrogen bonds with the water, dissociating into $\text{R}-\text{CO}_2^-$ and H^+ ions. This tends to increase the solubility due to the formation of favourable solvent-solute interactions.

However, with carbon chains longer than 5 atoms, solubility decreases due to the bulky alkyl chain.

3 Creation of Carboxylic Acids

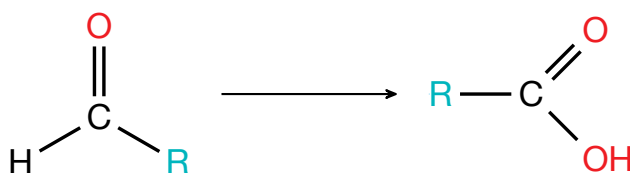
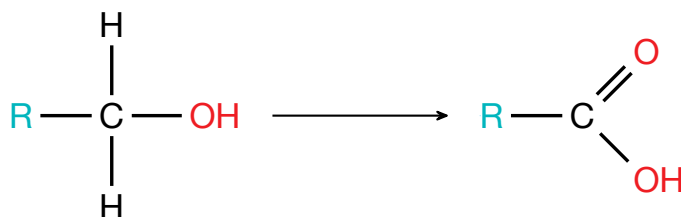
Carboxylic acids can be created in various ways, but one of the most common ways is through oxidation. Essentially, carboxylic acids are at the 'highest' oxidation state, followed by aldehydes and ketones, then alcohols.

3.1 Oxidation of Primary Alcohols

When the aldehydes can be oxidised to carboxylic acids. Alternatively, the strong oxidising agent KMnO_4 can be used to immediately create a carboxylic acid from a primary alcohol.

Conditions: $\text{K}_2\text{Cr}_2\text{O}_7$ with dilute H_2SO_4 , OR KMnO_4 with dilute H_2SO_4 , heat under reflux.

Observations: **Orange** $\text{Cr}_2\text{O}_7^{2-}$, turns **green** (Cr^{3+} formed), OR **Purple** MnO_4^- decolourises (Mn^{2+} formed)



It is also possible to start with aldehydes, and oxidise them to carboxylic acids.

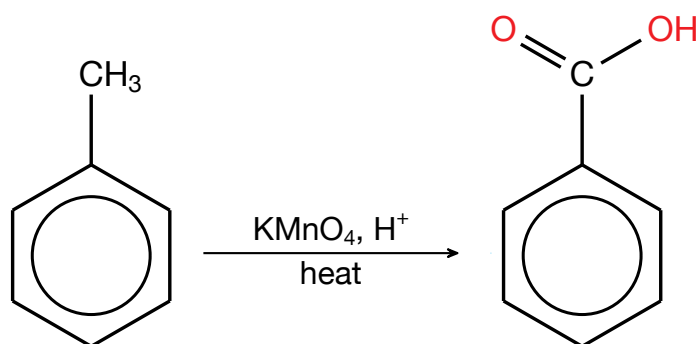
3.2 Side-chain Oxidation of Alkylbenzenes

As noted in the chapter on arenes, benzene rings with an alkyl chain can undergo side-chain oxidation to form benzoic acid.

Again, note that the carbon attached to the benzene ring *cannot* be tertiary, ie. it must have at least one hydrogen atom.

Conditions: Heat, KMnO_4 , dilute acid or alkali.

Observations: **Purple** KMnO_4 decolourises (*acid*), or forms **brown** precipitate of MnO_2 (*alkali*).



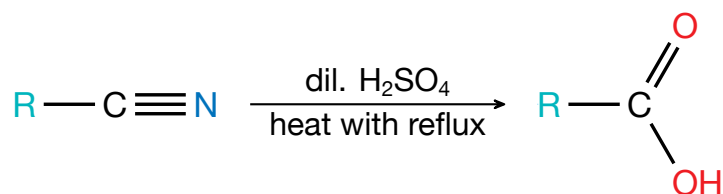
3.3 Hydrolysis of Nitriles

As covered in previous chapters, nitriles, $-\text{C}\equiv\text{N}$, can be hydrolysed to give carboxylic acids.

3.3.1 Acid Hydrolysis

The more straightforward method is acid hydrolysis — in this case, a carboxylic acid is immediately produced.

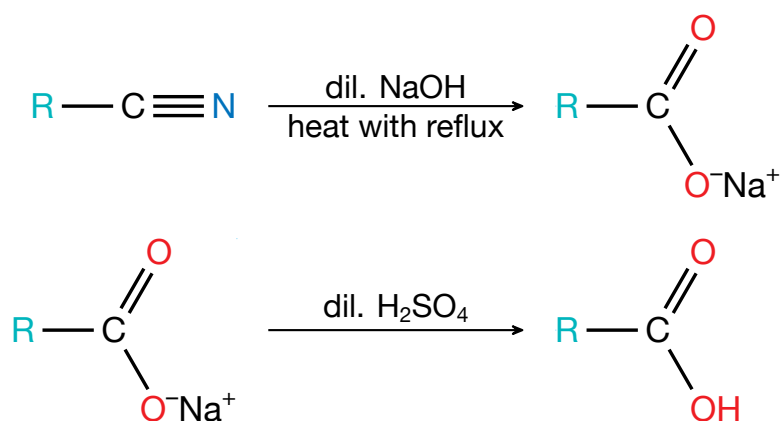
Conditions: Dilute H_2SO_4 or HCl , heat under reflux.



3.3.2 Alkaline Hydrolysis

The alternative is to conduct the hydrolysis in an alkaline medium using NaOH, which gives a carboxylate salt. This salt can be acidified using a dilute acid (I mean, why not start with an acid?) to yield the carboxylic acid.

Conditions: Dilute NaOH, heat under reflux.



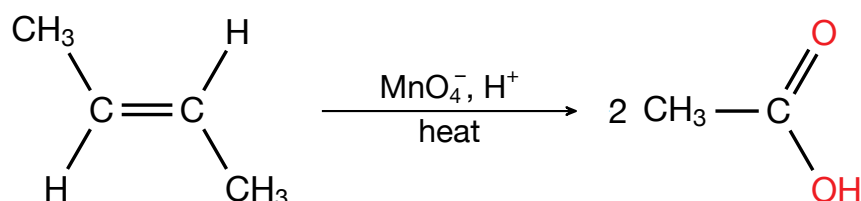
The carboxylate salt can be acidified.

3.4 Oxidative Cleavage of Alkenes

Alkenes can undergo strong oxidation, cleaving the double bond. The details are elaborated on [here](#), but only one kind of alkene can form a carboxylic, where the carbon atom has one alkyl group and one hydrogen atom.

Conditions: KMnO_4 , dilute H_2SO_4 , heat.

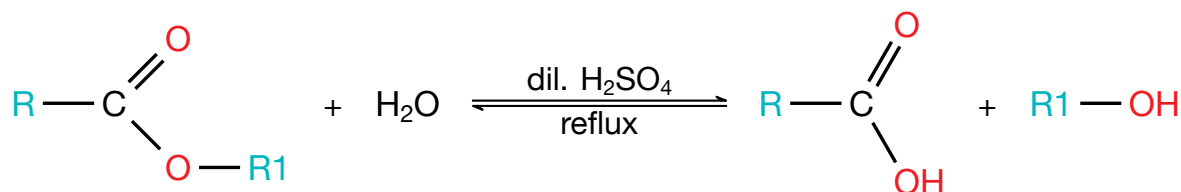
Observations: **Purple** KMnO_4 decolourises, forming colourless Mn^{2+} .



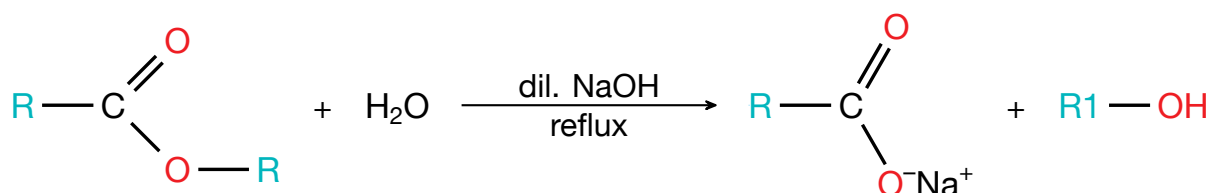
3.5 Hydrolysis of Esters

Finally, esters can be hydrolysed to form a carboxylic acid as one of its products. Note that this hydrolysis is preferably conducted in an alkaline medium, since the reaction is slow and reversible in an acidic medium, but fast and irreversible under alkaline conditions. All that is required is a dilute acid to protonate the carboxylate salt after.

Conditions: Dilute H_2SO_4 , heat under reflux, *OR*
Dilute NaOH , heat under reflux.



An alcohol is also formed, but for our purposes the carboxylic acid is the main product.

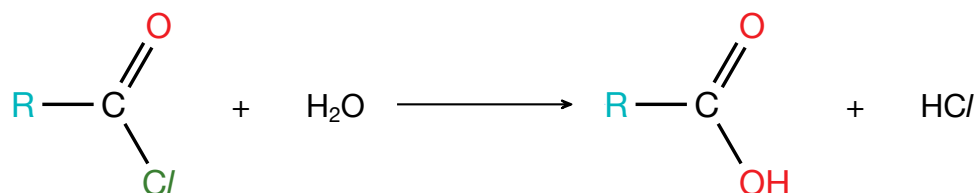


3.6 Hydrolysis of Acyl Chlorides

Acyl chlorides, which are a derivative of carboxylic acids where the OH group is replaced by a Cl atom, can be hydrolysed to form a carboxylic acid, and HCl.

Conditions: H_2O , room temperature.

Observations: Formation of white fumes of HCl gas.



3.7 Hydrolysis of Amides

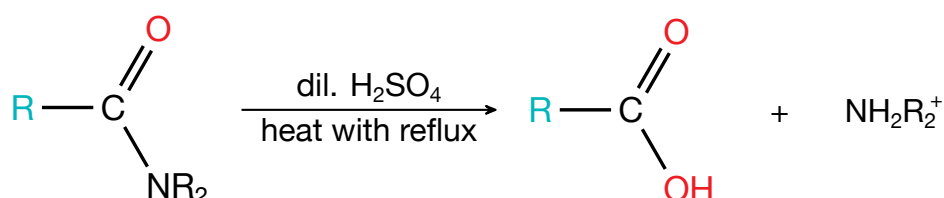
Amides can be hydrolysed with either acids or bases to give a carboxylic acid, and an amine. If the original amide is unsubstituted, then the result will be NH_3 , or, in an acidic medium, NH_4^+ . The products illustrated below can have R be an alkyl substituent or a hydrogen atom.

Note that the formation of NH_4^+ is due to the fact that NH_3 is a base, and will react with H^+ ions in the acidic medium.

3.7.1 Acid Hydrolysis

The hydrolysis of an amide in an acidic medium yields the carboxylic acid directly.

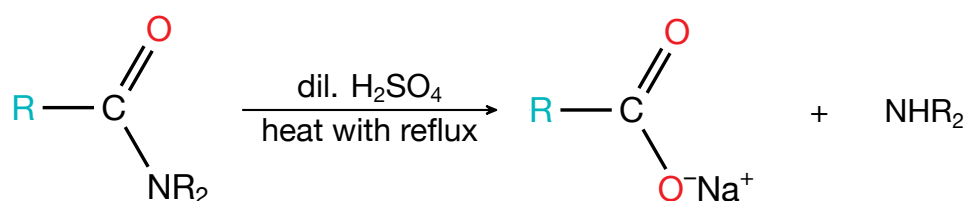
Conditions: Dilute H_2SO_4 or HCl , heat under reflux.



3.7.2 Alkaline Hydrolysis

The alternative is to conduct the hydrolysis in an alkaline medium using NaOH , which gives a carboxylate salt. This salt can be acidified using a dilute acid to yield the carboxylic acid.

Conditions: Dilute NaOH , heat under reflux.

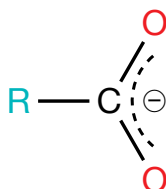


The carboxylate salt can be acidified later.

4 Carboxylic Acid Reactions

4.1 Acidity of Carboxylic Acids

Carboxylic acids are far more acidic than either alcohols or phenols, since the conjugate base (carboxylate anion) is greatly stabilised due to the delocalisation of the negative charge across the two electronegative oxygen atoms.



An illustration of this delocalisation.

This delocalisation immensely increases the stability of the anion, thus carboxylic acid is a much stronger acid, with a pK_a of 4.75, in contrast with that of ethanol and phenol, which are 15.9 and 9.95 respectively.

4.1.1 Effect of Substituents

In a similar vein to alcohols and phenols, substituents along the carbon chain can act to disperse or intensify the negative charge on the anion, modifying its stability and hence the acidity of the group. Naturally, groups closer to the central carbon have a greater effect than groups further away.

Electronegative groups and atoms, such as Cl or $-NO_2$, pull electron density away from the carboxyl carbon, dispersing the negative charge and stabilising the anion, hence increasing acidity.

Conversely, electron-donating groups, most notably alkyl chains, have the opposite effect, intensifying the negative charge and thus destabilising the anion and decreasing acidity. Note that the length of the alkyl chain does not have any significant impact on the acidity.

4.2 Reactions as an Acid

For all intents and purposes, carboxylic acid functions like a weak mineral acid, and can do all the things they can do; neutralise bases, react with metals, and liberate CO_2 gas from carbonates (CO_3^{2-}) and hydrogencarbonates (HCO_3^-).

The reactions will not be discussed in detail here, since they're basically normal acid-base reactions.

4.3 Nucleophilic Acyl Substitution

4.3.1 Formation of Acyl Chlorides

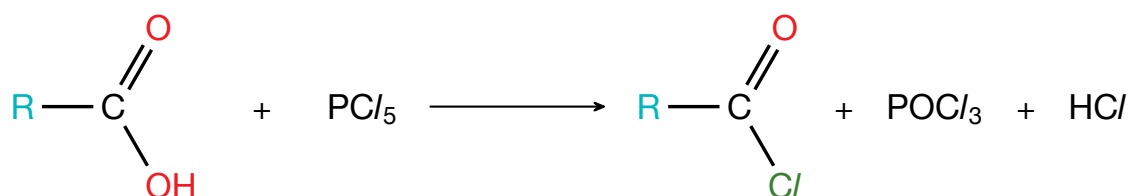
The carboxyl carbon undergoes a nucleophilic substitution, replacing the OH group with a Cl group, forming an acyl chloride.

Similar to alcohols, either PCl_5 , PCl_3 , or SOCl_2 can be used. However, HCl will not work to substitute the OH group on a carboxylic acid, unlike an alcohol.

Phosphorous Pentachloride (PCl_5)

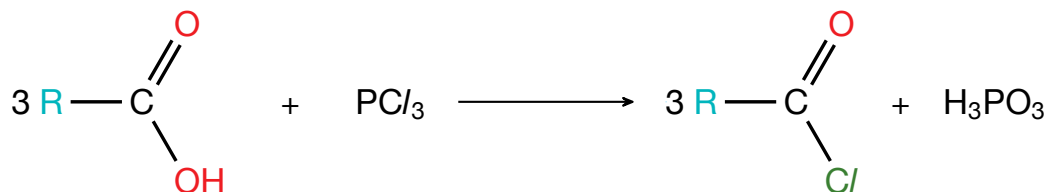
Conditions: Solid PCl_5 , room temperature.

Observations: Formation of white fumes of HCl gas.



Phosphorous Trichloride (PCl_3)

Conditions: Solid PCl_3 , room temperature.

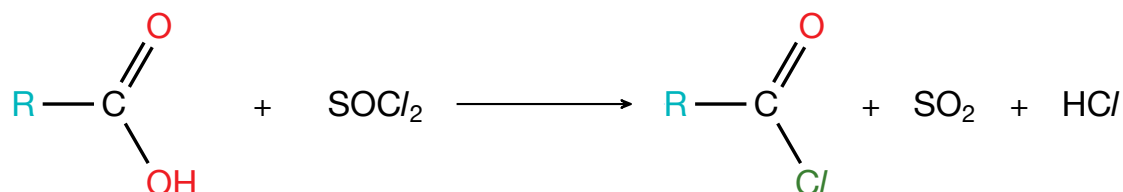


Thionyl Chloride (SOCl₂)

This reaction is slightly preferred over the others, since both by-products (SO₂ and HCl) are gaseous, and would bubble out of the solution, leaving mainly the halogenoalkane in the reaction mixture.

Conditions: Warm, liquid SOCl₂.

Observations: Formation of colourless, pungent SO₂ gas, white fumes of HCl gas.

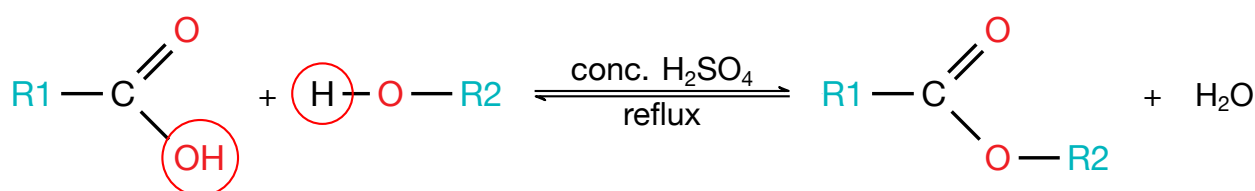


4.3.2 Esterification

As discussed *previously*, carboxylic acids can undergo esterification with alcohols, using concentrated H₂SO₄ as a catalyst and dehydrating agent.

Note that this is *not* the preferred method of creating esters, due to the need for heating and catalysis, and the fact that phenols cannot be used.

Conditions: Carboxylic acid and alcohol,
Several drops of concentrated H₂SO₄, heated under reflux.

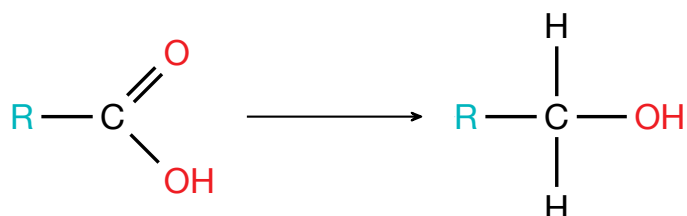


Note that it is the circled groups that form the water that is removed — this is important.

4.4 Reduction

Carboxylic acids can also be reduced to create alcohols. This reduction requires a strong reducing agent, so only LiAlH_4 can be used. See the *appendix* for a list of reducing agents and their applicable uses.

Conditions: LiAlH_4 in dry ether (diethyl ether).

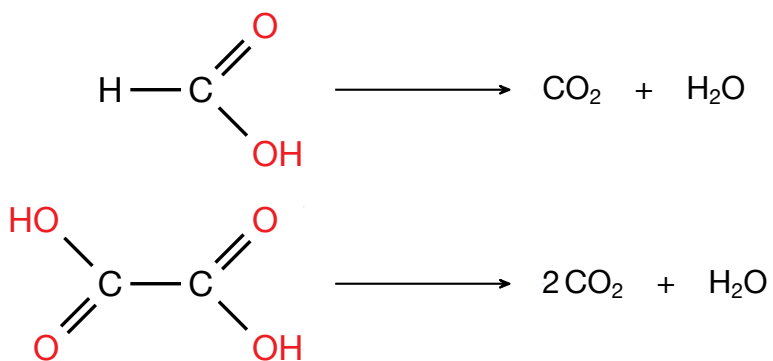


4.5 Oxidation

With the strong oxidising agent KMnO_4 , two special carboxylic acids can be *even further oxidised* to give CO_2 and H_2O ; they are ethanedioic acid and methanoic acid.

Conditions: KMnO_4 with dilute H_2SO_4 ,
heat under reflux.

Observations: *Purple* MnO_4^- decolourises (Mn^{2+} formed)



Appendices

Herein lie things that *must* be known, but for brevity are excluded from the main text.