

Carboxylic acids and derivatives A2

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What you need to know

At AS you met carboxylic acids and esters. At A Level this topic adds the **acyl chlorides**, RCOCl , the most reactive members of the family, and asks you to explain why some acids are stronger than others. You should be able to:

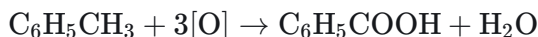
1. **Make benzoic acid from an alkylbenzene.** Heat the arene (methylbenzene is the standard example) with potassium manganate(VII) in alkali, then add dilute acid. The whole side chain becomes one COOH group on the ring.
2. **Turn a carboxylic acid into an acyl chloride** with any of three reagents: thionyl chloride (SOCl_2), phosphorus(V) chloride (PCl_5 , no heating needed) or phosphorus(III) chloride (PCl_3 , with heat). Know the other products of each.
3. **Know the two acids that can be oxidised further.** Methanoic acid, HCOOH , is oxidised to carbon dioxide and water by Tollens' reagent, Fehling's reagent, acidified KMnO_4 or acidified $\text{K}_2\text{Cr}_2\text{O}_7$. Ethanedioic acid, HOOC-COOH , is oxidised to carbon dioxide by warm acidified KMnO_4 .
4. **Put carboxylic acids, phenols and alcohols in order of acidity**, and explain the order.
5. **Explain how chlorine atoms change the strength of a carboxylic acid:** how many there are and where they are.
6. **Make esters from acyl chlorides:** with an alcohol (ethanoyl chloride and ethanol give ethyl ethanoate) or with phenol (benzoyl chloride and phenol give phenyl benzoate).
7. **Know five reactions of acyl chlorides, all at room temperature and all giving HCl :** with water (a carboxylic acid), an alcohol (an ester), phenol (an ester), ammonia (an amide), and a primary or secondary amine (a substituted amide).
8. **Draw the mechanism** of all five: nucleophilic addition–elimination.
9. **Explain why acyl chlorides are hydrolysed most easily**, alkyl chlorides less easily and aryl chlorides (chlorine on a benzene ring) hardly at all.

Exam questions often put these groups inside a larger molecule, or ask you to hydrolyse an ester or amide in it, so "How to do it" also recaps ester and amide hydrolysis (from AS "Carboxylic acids and derivatives" and A Level "Nitrogen compounds").

Understand it

Benzoic acid from an alkylbenzene

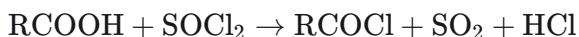
A benzene ring is very hard to oxidise, but a carbon chain attached to it is not. Heating an alkylbenzene under reflux with alkaline KMnO_4 oxidises the **carbon joined to the ring** to a carboxylate group, and any further carbons in the chain are lost (as carbon dioxide). The purple manganate(VII) turns to a brown precipitate of MnO_2 . Because the solution is alkaline, the product is the salt, the benzoate ion; adding dilute acid (for example HCl or H_2SO_4) afterwards turns it into benzoic acid, which is a white solid.



The rule to remember: **however long the side chain, one COOH stays on the ring**. An ethyl group gives benzoic acid plus CO_2 ; two side chains give two COOH groups in the same positions.

Making acyl chlorides

An acyl chloride has the OH of a carboxylic acid replaced by Cl: $\text{RCOOH} \rightarrow \text{RCOCl}$. Water must be kept out, because water destroys acyl chlorides (see below). The three reagents:



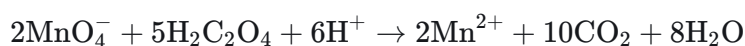
SOCl_2 is the most convenient: both of its other products are gases that leave the mixture, so the acyl chloride is left nearly pure. With PCl_5 the POCl_3 is a liquid that has to be separated by fractional distillation. With PCl_5 at room temperature you see steamy fumes of HCl , which is also a test for an OH group. Alcohol OH groups react with these reagents too, so an excess of SOCl_2 turns every OH in a molecule (acid or alcohol) into Cl.

Acyl chlorides are named from the acid: ethanoic acid $\rightarrow$ ethanoyl chloride, benzoic acid $\rightarrow$ benzoyl chloride, ethanedioic acid $\rightarrow$ ethanedioyl chloride (ClOCCOCl).

Two acids that oxidise

Most carboxylic acids resist oxidation. Two are exceptions:

- **Methanoic acid**, HCOOH , has an H on the carbonyl carbon, like an aldehyde: $\text{H}-\text{C}(=\text{O})-\text{OH}$. So it reduces the same reagents an aldehyde does: Tollens' reagent (a silver mirror), Fehling's reagent (blue solution to a red-brown precipitate), acidified KMnO_4 (purple to colourless) and acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (orange to green). The methanoic acid becomes carbon dioxide and water: $\text{HCOOH} + [\text{O}] \rightarrow \text{CO}_2 + \text{H}_2\text{O}$.
- **Ethanedioic acid**, HOOC-COOH , has a C-C bond between two COOH groups that breaks on oxidation. Warm acidified KMnO_4 is decolourised and bubbles of CO_2 are given off: $\text{HOOC-COOH} + [\text{O}] \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$. The full ionic equation is



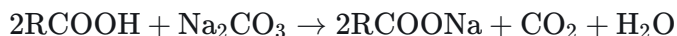
Other acids, such as ethanoic or benzoic acid, give no change with any of these reagents. That makes a two-test scheme to tell acids apart: only methanoic acid gives a silver mirror (or red-brown precipitate); methanoic **and** ethanedioic acid both decolourise acidified KMnO_4 ; an ordinary acid does neither.

Why carboxylic acids are stronger acids than phenols and alcohols

Any compound with an OH group can give away H^+ : $\text{X-OH} \rightleftharpoons \text{X-O}^- + \text{H}^+$. It is a **stronger acid** when the O–H bond is **weaker** (so H^+ is lost more easily) or when the anion left behind, the **conjugate base**, is **more stable**. What is attached to the O decides both.

- **Carboxylic acid.** The OH is joined to a C=O group. The electronegative O of C=O pulls electron density away from the O–H bond (a negative inductive effect), weakening it. In the carboxylate ion, RCOO^- , the negative charge is **delocalised over two oxygen atoms**, which makes the ion stable.
- **Phenol.** A lone pair (in a p orbital) on the O overlaps with the ring's π system. Electron density moves from the O into the ring, which weakens the O–H bond, and in the phenoxide ion the charge is spread over the ring. This helps, but less than a C=O group does, so phenols are weaker acids than carboxylic acids.
- **Alcohol.** The alkyl group **donates electrons** (a positive inductive effect). This strengthens the O–H bond and concentrates the charge on the one O of RO^- , so alcohols are weaker acids than water.

So: **carboxylic acid > phenol > water > alcohol**. You can see the order in reactions: carboxylic acids react with sodium, sodium hydroxide **and** sodium carbonate (fizzing, CO_2); phenols react with sodium and sodium hydroxide but not sodium carbonate; alcohols react only with sodium.



Chlorine-substituted acids

A chlorine atom on the carbon chain is electronegative, so it **withdraws electron density** along the chain towards itself. This makes the O–H bond weaker and spreads the charge of the carboxylate ion further, stabilising it. So a chloro acid is **stronger** than the acid without chlorine (larger K_a , smaller $\text{p}K_a$). Three rules follow:

- **More Cl atoms, stronger acid:** each one withdraws more electron density, so a dichloro acid is stronger than a monochloro acid, and a trichloro acid is stronger still.
- **Cl nearer the COOH, stronger acid:** the effect weakens with every C–C bond it passes through, so a Cl on carbon 2 (next to COOH) has a much bigger effect than one on carbon 4.
- **Cl beats Br:** chlorine is more electronegative than bromine, so a chloro acid is stronger than the matching bromo acid.

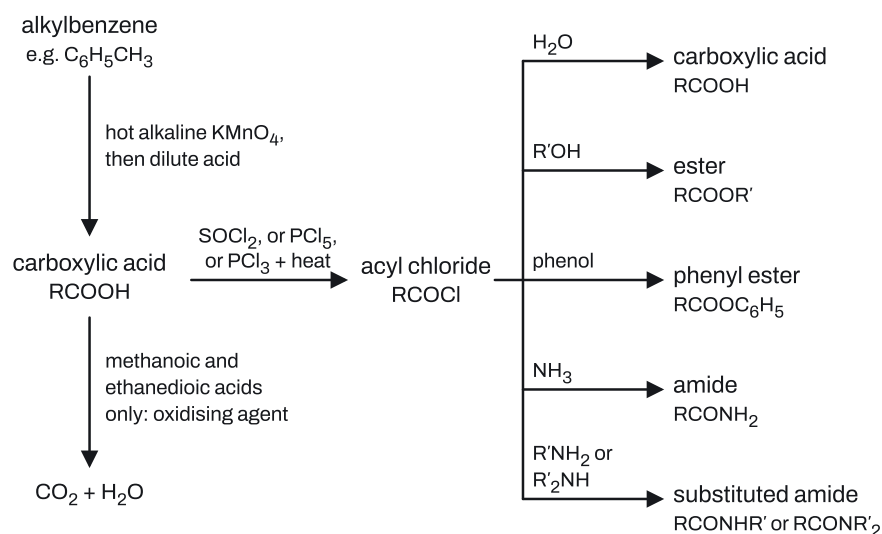
The same idea explains why ethanedioic acid is a much stronger acid than methanoic acid: its second C=O group also withdraws electrons from the O–H bond. An alkyl group does the opposite (it donates electrons), so a longer alkyl chain makes an acid very slightly weaker.

Reactions of acyl chlorides

The carbon of -COCl is bonded to **two** electronegative atoms, O and Cl, so it carries a large $\delta+$ charge. Anything with a lone pair, a **nucleophile**, attacks it, and Cl leaves. Each reaction is fast at room temperature, needs no catalyst, goes to completion, and gives off steamy fumes of HCl.

Nucleophile	Product	Example
Water	Carboxylic acid	$\text{CH}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HCl}$
Alcohol	Ester	$\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{HCl}$ (ethyl ethanoate)
Phenol	Ester	$\text{C}_6\text{H}_5\text{COCl} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{C}_6\text{H}_5\text{COOC}_6\text{H}_5 + \text{HCl}$ (phenyl benzoate)
Ammonia	Amide	$\text{RCOCl} + \text{NH}_3 \rightarrow \text{RCONH}_2 + \text{HCl}$
Primary amine	N-substituted amide	$\text{RCOCl} + \text{R}'\text{NH}_2 \rightarrow \text{RCONHR}' + \text{HCl}$
Secondary amine	N,N-disubstituted amide	$\text{RCOCl} + \text{R}'_2\text{NH} \rightarrow \text{RCONR}'_2 + \text{HCl}$

With ammonia or an amine, the HCl formed reacts with a second molecule of the base to make a salt, so two moles are used: $\text{RCOCl} + 2\text{NH}_3 \rightarrow \text{RCONH}_2 + \text{NH}_4\text{Cl}$. Phenols react very slowly with carboxylic acids, so an acyl chloride is how phenyl esters are made. Ammonia gives a plain amide (-CONH_2); a primary amine gives an amide with one group on N ($\text{-CONHR}'$); a secondary amine gives one with two ($\text{-CONR}'_2$). Tertiary amines have no H on N, so they cannot form an amide.

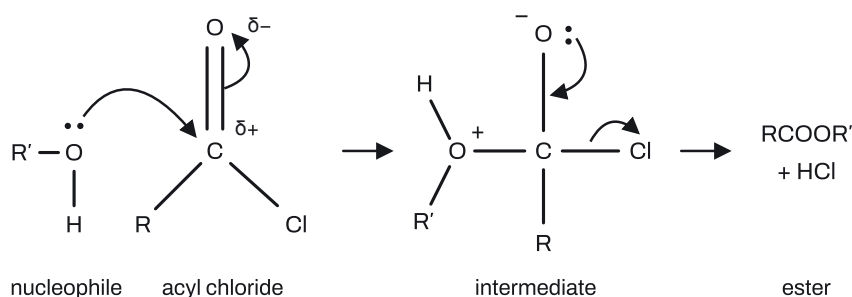


All five at room temperature; HCl is also formed each time.

The addition–elimination mechanism

All five reactions follow one mechanism, **nucleophilic addition–elimination**. Here it is with an alcohol, $\text{R}'\text{OH}$:

1. **Addition.** A lone pair on the nucleophile's O (or N) forms a bond to the $\delta+$ carbon of $\text{C}^{\delta+}=\text{O}^{\delta-}$. At the same moment the π electrons of $\text{C}=\text{O}$ move onto the oxygen. Two curly arrows: lone pair $\rightarrow$ C, and $\text{C}=\text{O}$ bond $\rightarrow$ O.
2. **The intermediate** has four groups around the carbon: O^- , Cl, R and the nucleophile, whose O (or N) now carries a + charge because it has shared its lone pair.
3. **Elimination.** A lone pair on O^- moves back to reform $\text{C}=\text{O}$, and the $\text{C}-\text{Cl}$ bond breaks with both electrons going to Cl, which leaves as Cl^- . Two curly arrows: $\text{O}^- \rightarrow \text{C}-\text{O}$ bond, and $\text{C}-\text{Cl}$ bond $\rightarrow$ Cl.
4. The positive O (or N) loses H^+ , which joins Cl^- as HCl .



For water the nucleophile is $\text{H}-\text{O}-\text{H}$; for ammonia or an amine the lone pair is on N and the intermediate carries N^+ . An acyl bromide, RCOBr , reacts the same way, even faster, because the $\text{C}-\text{Br}$ bond is weaker than $\text{C}-\text{Cl}$.

Ease of hydrolysis: acyl, alkyl and aryl chlorides

Compare CH_3COCl (acyl), $\text{CH}_3\text{CH}_2\text{Cl}$ (alkyl) and $\text{C}_6\text{H}_5\text{Cl}$ (aryl) with water or aqueous silver nitrate:

Compound	With water or $\text{AgNO}_3(\text{aq})$	Why
Acyl chloride	Reacts at once in cold water; white AgCl precipitate immediately; steamy fumes	The C is bonded to O and Cl, so it is very $\delta+$ and easily attacked
Alkyl chloride	Slow; needs warming; white precipitate forms slowly	The C is bonded to Cl only, so it is less $\delta+$
Aryl chloride	No reaction, even hot	A lone pair (p orbital) on Cl overlaps with the ring's π system, so the $\text{C}-\text{Cl}$ bond has partial double-bond character and is stronger; the electron-rich ring also repels nucleophiles

So the ease of hydrolysis is **acyl chloride > alkyl chloride > aryl chloride**.

Key facts and formulas

"Given" means it is printed on the Periodic Table or in the Data Booklet in the exam. "Learn it" means you must remember it; reagents, conditions, observations and explanations are never printed.

Formula	Status
Relative atomic masses: H 1.0, C 12.0, N 14.0, O 16.0, P 31.0, S 32.1, Cl 35.5	Given
Molar volume of gas at room conditions = $24.0 \text{ dm}^3 \text{ mol}^{-1}$	Given
Alkylbenzene $\xrightarrow{\text{hot alkaline KMnO}_4, \text{ then dilute acid}}$ benzoic acid (one COOH per side chain)	Learn it
$\text{RCOOH} + \text{SOCl}_2 \rightarrow \text{RCOCl} + \text{SO}_2 + \text{HCl}$	Learn it
$\text{RCOOH} + \text{PCl}_5 \rightarrow \text{RCOCl} + \text{POCl}_3 + \text{HCl}$	Learn it
$3\text{RCOOH} + \text{PCl}_3 \rightarrow 3\text{RCOCl} + \text{H}_3\text{PO}_3 \text{ (heat)}$	Learn it
$\text{HCOOH} + [\text{O}] \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ (Tollens', Fehling's, acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$)	Learn it
$\text{HOOC-COOH} + [\text{O}] \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$ (warm acidified KMnO_4)	Learn it
$\text{RCOCl} + \text{HX} \rightarrow \text{RCOX} + \text{HCl}$, where HX is H_2O , $\text{R}'\text{OH}$, $\text{C}_6\text{H}_5\text{OH}$, NH_3 , $\text{R}'\text{NH}_2$ or $\text{R}'_2\text{NH}$; room temperature	Learn it
Mechanism: nucleophilic addition–elimination	Learn it
Acidity: carboxylic acid > phenol > water > alcohol	Learn it
Chloro acids: more Cl, Cl nearer COOH, or Cl instead of Br $\rightarrow$ stronger acid	Learn it
Ease of hydrolysis: acyl chloride > alkyl chloride > aryl chloride	Learn it

How to do it

In the Paper 4 questions we have tagged for this topic (58 questions, 2021–2025; 41 different questions, 17 of them repeated in another variant), the types came up this often. 38 of the 58 mix more than one type, so the counts add up to 118. The topic is usually one or two parts of a longer organic question.

Question type	Questions
Order and explain acidities of acids, phenols and alcohols	20
Draw the product of an acid or acyl chloride reaction	20
Give reagents and conditions for a step	12

Question type	Questions
Draw the products of hydrolysing an ester or amide	11
Oxidation of alkylbenzenes, methanoic acid and ethanedioic acid	11
Draw or name the addition–elimination mechanism	11
Write the equation for making an acyl chloride	8
Name an ester or classify reaction types	7
Order and explain ease of hydrolysis of chlorides	6
Chemical tests to tell acids apart	6
Deduce structures from a reaction scheme and tests	6

1. Order and explain acidities of acids, phenols and alcohols (20 questions)

- Write the order**, most acidic first, in the boxes. Strong mineral acids such as H_2SO_4 (fully dissociated) come first; then chloro acids (most Cl, Cl nearest COOH , Cl before Br); then plain carboxylic acids; then phenols (a phenol with NO_2 or Cl above plain phenol); then water; then alcohols.
- Link acidity to losing H^+ once**: "the weaker the O–H bond, or the more stable the anion, the more easily H^+ is lost, so the stronger the acid".
- Give one structural reason for each compound**:
 - carboxylic acid: the $\text{C}=\text{O}$ is electron-withdrawing (negative inductive effect); the charge on RCOO^- is delocalised over two O atoms;
 - chloro acid: Cl is electronegative and withdraws electrons; more Cl atoms withdraw more; Cl is more electronegative than Br;
 - phenol: a lone pair (p orbital) on O overlaps with / is delocalised into the ring π system;
 - alcohol, including ArCH_2OH : the alkyl or CH_2 group donates electrons (positive inductive effect), strengthening the O–H bond.

Variations you will meet:

- "Explain why X is stronger than Y"** for just two compounds: give the reason that separates them. A carboxylic acid beats a phenol because of its $\text{C}=\text{O}$ group, not the phenol's lone pair.
- $\text{p}K_a$ values given** (smaller $\text{p}K_a$ = stronger acid): explain the difference with the Cl effect and link it to O–H strength or anion stability.
- Ethanedioic acid vs methanoic acid**: the second $\text{C}=\text{O}$ group withdraws electrons, so ethanedioic acid is stronger.

2. Draw the product of an acid or acyl chloride reaction (20 questions)

- Find every group that reacts** with the reagent:
 - SOCl_2 , PCl_5 : every $\text{COOH} \rightarrow \text{COCl}$, and every alcohol $\text{OH} \rightarrow \text{Cl}$ (not phenol OH);
 - acyl chloride + OH (alcohol or phenol) $\rightarrow$ ester; + NH_2 or NH $\rightarrow$ amide; + water $\rightarrow$ COOH ;

- LiAlH_4 (from AS and "Nitrogen compounds"): $\text{COOH} \rightarrow \text{CH}_2\text{OH}$, ester $\rightarrow$ two alcohols, amide $\text{CONH} \rightarrow$ amine CH_2NH ; $\text{C}=\text{C}$ and the ring are untouched.

2. **Use the molecular formula** if it is given: count the atoms to check how many groups reacted.
3. **Draw the new group clearly** (displayed if asked) and give the other product, usually HCl .

Variations you will meet:

- **A diacyl chloride with an excess of a molecule that has two groups:** each COCl reacts with one molecule, so you join three molecules. With a diol or diamine and no excess, a polyester or polyamide forms (see "Polymerisation").
- **A molecule with both OH and NH_2** can give an ester or an amide (two isomers), or both with an excess of acyl chloride.
- **One ester link between a diol and a diacid chloride** leaves a COCl and an OH at the ends; if they can reach, a cyclic ester forms, with no OH left (so no reaction with Na).

3. Give reagents and conditions for a step (12 questions)

Give the reagent **and** the condition every time:

Step	Reagents and conditions
Acid $\rightarrow$ acyl chloride	SOCl_2 (room temperature), or PCl_5 (room temperature), or PCl_3 and heat; keep dry
Alkylbenzene $\rightarrow$ benzoic acid	KMnO_4 and NaOH(aq) , heat under reflux; then dilute HCl or H_2SO_4
Halogenoalkane $\rightarrow$ nitrile	KCN in ethanol, heat under reflux
Nitrile $\rightarrow$ carboxylic acid	Dilute HCl(aq) (or H_2SO_4), heat under reflux
Acyl chloride $\rightarrow$ ester or amide	The alcohol, phenol, NH_3 or amine, room temperature
Arene $\rightarrow$ aryl ketone	Acyl chloride and AlCl_3 (see "Hydrocarbons")

Never use NaOH(aq) or any aqueous reagent with an acyl chloride: water hydrolyses it.

4. Draw the products of hydrolysing an ester or amide (11 questions)

1. **Find every ester, amide and nitrile** in the molecule, and mark the bond that breaks: C(=O)-O in an ester, C(=O)-N in an amide.
2. **Hot aqueous acid** (such as HCl(aq)): each ester $\rightarrow \text{COOH} + \text{alcohol}$; each amide $\rightarrow \text{COOH} + \text{an amine}$, which is protonated to $-\text{NH}_3^+$ (or NH_4^+ from $-\text{CONH}_2$); each nitrile $\rightarrow \text{COOH} (+ \text{NH}_4^+)$.
3. **Hot aqueous alkali** (such as NaOH(aq)): each ester $\rightarrow \text{COO}^- + \text{alcohol}$; each amide $\rightarrow \text{COO}^- + \text{a free amine } -\text{NH}_2$ (or NH_3); each nitrile $\rightarrow \text{COO}^- + \text{NH}_3$. Any COOH or phenol OH already in the molecule also becomes COO^- or O^- .

4. **Count the products:** one piece for every bond broken, plus one.

Variations you will meet:

- **"State the two types of reaction"** with hot NaOH(aq): hydrolysis and acid–base (neutralisation).
- **"Draw a line through the bond broken"** in acid: the C–O single bond of the ester or the C–N bond of the amide.
- **Why a weak base is used** in a step: a strong base such as NaOH(aq) would hydrolyse an ester elsewhere in the molecule.
- **Products "at pH 12" or "at pH 2"**: at pH 12 acids are COO^- and amines NH_2 ; at pH 2 acids are COOH and amines NH_3^+ .

5. Oxidation of alkylbenzenes, methanoic acid and ethanedioic acid (11 questions)

1. **Alkylbenzene:** each side chain, whatever its length, becomes one COOH on the ring. Reagent: hot alkaline KMnO_4 , then dilute acid.
2. **Equation with $[\text{O}]$:** balance C first (extra side-chain carbons $\rightarrow \text{CO}_2$), then H ($\rightarrow \text{H}_2\text{O}$), then count O to find the number of $[\text{O}]$. For example, propylbenzene: $\text{C}_9\text{H}_{12} + 9[\text{O}] \rightarrow \text{C}_7\text{H}_6\text{O}_2 + 2\text{CO}_2 + 3\text{H}_2\text{O}$.
3. **Methanoic acid** $\rightarrow \text{CO}_2 + \text{H}_2\text{O}$; **ethanedioic acid** $\rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$ with warm acidified KMnO_4 : the type of reaction is oxidation (or redox); you see the purple colour disappear and effervescence.

Variations you will meet:

- **Oxidising a molecule that makes ethanedioic acid:** with hot concentrated acidified KMnO_4 it is oxidised on to CO_2 , so write CO_2 , not HOOCCOOH , as the product. Examiners see this error often.
- **"Two reagents that oxidise ethanedioic acid to CO_2 and water"**: warm acidified KMnO_4 , and oxygen (it burns).
- **Hot alkaline KMnO_4 without acidifying** gives the carboxylate salt.

6. Draw or name the addition–elimination mechanism (11 questions)

1. **Name it:** nucleophilic addition–elimination.
2. **First diagram:** lone pair on the nucleophile's O or N; curly arrow from that lone pair to the C of $\text{C}=\text{O}$; dipole $\text{C}^{\delta+}=\text{O}^{\delta-}$; curly arrow from the $\text{C}=\text{O}$ bond to O.
3. **Intermediate:** C with four bonds, to O^- , Cl (or Br), R, and the nucleophile's atom, which now has a + charge and all its H atoms.
4. **Second step:** curly arrow from a lone pair on O^- to the C–O bond, and a curly arrow from the C–Cl bond to Cl. Products: the ester, acid or amide, plus HCl (or HBr).

Variations you will meet:

- **Different nucleophiles:** water, an alcohol, phenol, ammonia, an amine or an aryl amine (ArNH_2). The steps are the same; only the attacking atom changes.

- **"Why add sodium ethanoate (or another base)?"**: it reacts with the HCl formed, so the HCl does not protonate the amine (which would stop it acting as a nucleophile).

7. Write the equation for making an acyl chloride (8 questions)

1. **Swap each OH of a COOH for Cl.**
2. **Add the by-products** for each COOH: $\text{SO}_2 + \text{HCl}$ with SOCl_2 ; $\text{POCl}_3 + \text{HCl}$ with PCl_5 ; for PCl_3 , three acid molecules give one H_3PO_3 .
3. **Balance for more than one group**: a diacid with SOCl_2 needs 2SOCl_2 and gives $2\text{SO}_2 + 2\text{HCl}$. An alcohol OH in the same molecule also takes one SOCl_2 .

Variations you will meet:

- **Thionyl bromide**, SOBr_2 , makes an acyl bromide in the same way: $\text{RCOOH} + \text{SOBr}_2 \rightarrow \text{RCOBr} + \text{SO}_2 + \text{HBr}$.
- **Why SOCl_2 gives a purer product**: both by-products are gases and escape.

8. Name an ester or classify reaction types (7 questions)

1. **Ester name** = the alcohol's alkyl group + the acid part ending "-oate". Butanoyl chloride with methanol gives methyl butanoate; a phenol gives a "phenyl" ester.
2. **Reaction types**:
 - acid $\rightarrow$ acyl chloride, and acyl chloride + alcohol, phenol, water, ammonia or amine: (nucleophilic) substitution, or addition–elimination; ester and amide formation can also be called condensation;
 - ester or amide + water, acid or alkali: hydrolysis;
 - LiAlH_4 : reduction; KMnO_4 : oxidation.

When a table says "use each number once", check that your choices fit: acyl chloride + amine is then **substitution**.

9. Order and explain ease of hydrolysis of chlorides (6 questions)

1. **Order**: acyl chloride > alkyl chloride > aryl chloride.
2. **Acyl chloride**: its C is bonded to two electronegative atoms (O and Cl), so it is very δ^+ .
3. **Aryl chloride**: a lone pair (p orbital) on Cl overlaps with the ring π system, so the C–Cl bond has partial double-bond character and is stronger (harder to break).
4. **Observations with $\text{AgNO}_3(\text{aq})$** : acyl chloride, white precipitate at once; alkyl chloride, white precipitate slowly on warming; aryl chloride, no precipitate.

Variation: an acyl bromide hydrolyses faster than an acyl chloride because Br is a larger atom, so the C–Br bond is longer and weaker.

10. Chemical tests to tell acids apart (6 questions)

1. **Choose reagents that react differently:** Tollens' or Fehling's reagent (only methanoic acid reacts); warm acidified KMnO_4 (methanoic and ethanedioic acid decolourise it); $\text{Na}_2\text{CO}_3(\text{aq})$ (every carboxylic acid fizzes, phenols and alcohols do not); $\text{NaOH}(\text{aq})$ (acids and phenols react); Na (all OH compounds give H_2).
2. **Complete every box**, including "no change" for the ones that don't react.
3. **Give full observations:** "silver mirror", "red-brown precipitate", "purple to colourless", "effervescence".

An acid–base indicator is no use for telling weak acids apart: all of them are acidic.

11. Deduce structures from a reaction scheme and tests (6 questions)

1. **Read each test as a group:**
 - fizzes with $\text{Na}_2\text{CO}_3(\text{aq})$: COOH ;
 - reacts with Na but not NaOH : alcohol OH; with NaOH but not Na_2CO_3 : phenol;
 - orange precipitate with 2,4-DNPH: $\text{C}=\text{O}$ of an aldehyde or ketone;
 - silver mirror or red-brown precipitate: aldehyde (or methanoic acid);
 - yellow precipitate with alkaline $\text{I}_2(\text{aq})$: $\text{CH}_3\text{CO}-$ or $\text{CH}_3\text{CH}(\text{OH})-$;
 - decolourises $\text{Br}_2(\text{aq})$: $\text{C}=\text{C}$ (or phenol, with a white precipitate).
2. **Use the molecular formulae** of each product: compare atoms to see what was added or removed (Cl for OH, two H for reduction, and so on).
3. **Work forwards and backwards** until every structure fits every test.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

Four compounds are shown: 3,3,3-trichloropropanoic acid, $\text{CCl}_3\text{CH}_2\text{COOH}$; 3-chlorobutanoic acid, $\text{CH}_3\text{CHClCH}_2\text{COOH}$; 3-chlorophenol, $\text{ClC}_6\text{H}_4\text{OH}$; and cyclopentanol, $\text{C}_5\text{H}_9\text{OH}$.

(a) Put the four compounds in order of acidity, most acidic first. Explain your order. **[5]**

(b) State which of the four compounds react with $\text{Na}_2\text{CO}_3(\text{aq})$, and write an equation for one of these reactions. **[2]**

(a) 3,3,3-trichloropropanoic acid > 3-chlorobutanoic acid > 3-chlorophenol > cyclopentanol **B1**

The stronger acid loses H^+ more easily because its O–H bond is weaker or its anion is more stable. **B1**

- The acids: the C=O group withdraws electrons, and the charge of the carboxylate ion is delocalised over two O atoms. **B1**
- Chlorine is electronegative and withdraws electrons; both acids have Cl on carbon 3, but three Cl atoms withdraw more than one, so the trichloro acid is stronger. **B1**
- 3-chlorophenol: a lone pair on O is delocalised into the ring (and the Cl withdraws a little more), a smaller effect than a C=O group; cyclopentanol: the alkyl ring donates electrons (positive inductive effect), strengthening the O–H bond. **B1**

(b) Only the two carboxylic acids. **B1**



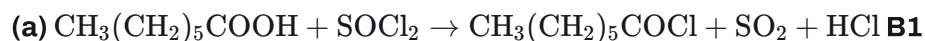
Example 2

A 5.20 g sample of heptanoic acid, $\text{CH}_3(\text{CH}_2)_5\text{COOH}$, a liquid, is converted into heptanoyl chloride with an excess of thionyl chloride.

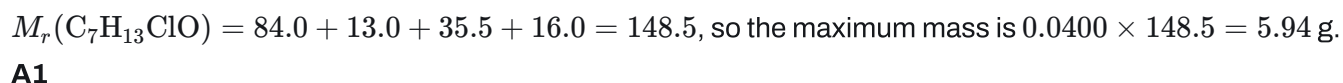
(a) Write an equation for the reaction, and explain why SOCl_2 is a better choice than PCl_5 for obtaining a pure product. **[2]**

(b) Calculate the maximum mass of heptanoyl chloride, and the total volume of gas at room conditions given off from 5.20 g of the acid. **[3]**

(c) Heptanoyl chloride is added separately to butan-1-ol, to 4-chlorophenol and to dimethylamine, $(\text{CH}_3)_2\text{NH}$, at room temperature. Give the structure and name of each organic product. **[3]**



SO_2 and HCl are both gases and escape, leaving the acyl chloride; PCl_5 gives liquid POCl_3 , which must be separated. **B1**



Each mole of acid gives one mole of SO_2 and one of HCl: $0.0800 \times 24.0 = 1.92 \text{ dm}^3$. **A1**

(c) Each is an addition–elimination; HCl is also formed.

- $\text{CH}_3(\text{CH}_2)_5\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, butyl heptanoate (an ester). **B1**

- $\text{CH}_3(\text{CH}_2)_5\text{COOC}_6\text{H}_4\text{Cl}$, with the Cl opposite the ester O on the ring: 4-chlorophenyl heptanoate (an ester). **B1**
- $\text{CH}_3(\text{CH}_2)_5\text{CON}(\text{CH}_3)_2$, N,N-dimethylheptanamide (an amide). **B1**

Example 3

A tertiary amide is made from 1-chloro-4-methylbenzene in three steps.



(a) Give the reagents and conditions for steps 1 to 3. Name the type of reaction in step 1 and in step 3, and name the reagent used in step 3. **[5]**

(b) Describe the mechanism of step 3. **[4]**

(c) 3.13 g of 4-chlorobenzoic acid gives 3.16 g of the amide. Calculate the percentage yield. **[2]**

(d) 4-chlorobenzoyl chloride, the product of step 2, has two C–Cl bonds. It is added to cold water. Give the organic product, and explain why only one of the C–Cl bonds reacts. **[3]**

(a) Step 1: KMnO_4 and $\text{NaOH}(\text{aq})$, heat under reflux, then dilute acid **B1**; oxidation. **B1** Step 2: PCl_5 (or SOCl_2) at room temperature, or PCl_3 and heat. **B1** Step 3: N-methylethanamine, $\text{CH}_3\text{NHCH}_2\text{CH}_3$ (a secondary amine), at room temperature **B1**; (nucleophilic) addition–elimination. **B1**

(b) The lone pair on the N of $\text{CH}_3\text{NHCH}_2\text{CH}_3$ attacks the $\delta+$ carbon of $\text{C}^{\delta+}=\text{O}^{\delta-}$, and the $\text{C}=\text{O}$ π electrons move onto O. **B1** This gives an intermediate with O^- , Cl, the ring and $-\text{N}^+\text{H}(\text{CH}_3)\text{CH}_2\text{CH}_3$ on the carbon. **B1** The O^- lone pair reforms $\text{C}=\text{O}$ and the $\text{C}-\text{Cl}$ bond breaks, releasing Cl^- . **B1** H^+ is lost from N^+ and forms HCl , which reacts with a second molecule of the amine to give a salt; the product has no H left on N. **B1**

(c) $M_r(\text{C}_7\text{H}_5\text{ClO}_2) = 156.5$, so $3.13 \div 156.5 = 0.0200$ mol. $M_r(\text{C}_{10}\text{H}_{12}\text{ClNO}) = 197.5$, so the maximum mass is $0.0200 \times 197.5 = 3.95$ g. **M1**

Yield = $3.16 \div 3.95 \times 100 = 80.0\%$. **A1**

(d) 4-chlorobenzoic acid, $\text{ClC}_6\text{H}_4\text{COOH}$ (and HCl): the Cl on the ring stays. **B1** The COCl carbon is bonded to both O and Cl, so it is very $\delta+$ and water attacks it at once. **B1** The ring Cl has a lone pair that overlaps with the ring's π system, giving that C–Cl bond partial double-bond character, so it is too strong to break. **B1**

Example 4

(a) 2.22 g of pentylbenzene, $\text{C}_6\text{H}_5(\text{CH}_2)_4\text{CH}_3$, is heated under reflux with alkaline KMnO_4 , and the mixture is then acidified. Name and draw the organic product, write an equation using [O], and calculate its maximum mass. **[4]**

(b) Methanoic acid is warmed with Fehling's reagent, and separately with acidified potassium dichromate(VI). State what is seen in each case, write an equation using [O], and explain why ethanoic acid gives neither result. **[3]**

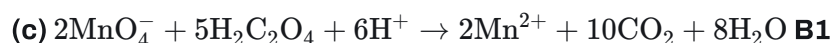
(c) Warm acidified KMnO_4 is added to 25.0 cm^3 of $0.0500 \text{ mol dm}^{-3}$ ethanedioic acid until the acid has all reacted. Write the ionic equation and calculate the volume of carbon dioxide formed at room conditions. **[3]**

(a) Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$: one COOH on the ring. **B1** The carbon joined to the ring becomes COOH ; the other four carbons of the chain are lost as CO_2 :



B1. $M_r(\text{C}_{11}\text{H}_{16}) = 148.0$, so $2.22 \div 148.0 = 0.0150 \text{ mol}$ **M1.** $M_r(\text{C}_7\text{H}_6\text{O}_2) = 122.0$, so the maximum mass is $0.0150 \times 122.0 = 1.83 \text{ g}$. **A1**

(b) Fehling's: the blue solution gives a red-brown precipitate. Dichromate: orange to green. **B1** $\text{HCOOH} + [\text{O}] \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ **B1.** Methanoic acid has an H on its carbonyl carbon (an aldehyde-like $\text{H}-\text{C}=\text{O}$), which can be oxidised; ethanoic acid has a CH_3 group there instead. **B1**



Ethanedioic acid = $0.0250 \times 0.0500 = 0.00125 \text{ mol}$, giving $2 \times 0.00125 = 0.00250 \text{ mol}$ of CO_2 **M1**, which is $0.00250 \times 24\,000 = 60.0 \text{ cm}^3$. **A1**

Common mistakes

- **Explaining acidity without linking it to losing H^+ .** Getting the order right earns one mark; the next needs "weakens the O–H bond" or "stabilises the anion". "Oxygen is electronegative" on its own earns nothing.
- **Leaving out the electron donors and withdrawers.** Say what the Cl, the C=O or the alkyl group does (withdraws or donates electrons) for each compound in the list.
- **Using NaOH(aq) in a step with an acyl chloride.** Any aqueous reagent hydrolyses it back to the acid.
- **Stopping the oxidation too early.** Hot acidified KMnO_4 oxidises ethanedioic acid on to CO_2 ; examiners often see ethanedioic acid given as the final product.
- **Unbalanced [O] equations**, without the H_2O , with O_2 as a product, or with $[\text{H}^+]$ written for $[\text{H}]$. Balance C, then H, then count [O].
- **Curly arrows that start from an atom** instead of from a lone pair or the middle of a bond, or that point at nothing. Each arrow needs a clear tail and a head on an atom or bond.
- **Forgetting the charges on the intermediate:** O^- and the $+$ on the nucleophile's O or N. Dipoles on C=O are a separate mark.
- **Saying acyl chlorides are the hardest to hydrolyse**, or giving the order without a bond-strength reason. For the aryl chloride, say the C–Cl bond is **stronger** because of the overlap with the ring.
- **Forgetting that an amine is protonated in acid.** Hydrolysing an amide in hot HCl gives $-\text{NH}_3^+$, not $-\text{NH}_2$.
- **Leaving an acyl chloride in a hydrolysis product.** Hydrolysis gives COOH (or COO^-), never COCl .
- **Writing "Tollens'" without the result.** A test needs the reagent **and** what you see: "silver mirror", not just "positive".

How to get the marks

- **Reagents and conditions** means both, with states where they matter: " KMnO_4 , NaOH(aq) , heat; then dilute acid", " SOCl_2 , room temperature", " HCl(aq) , heat under reflux". Name reagents as compounds, not ions.
- **Structures**: show the new group clearly (displayed if the question says so); keep the rest of the molecule the same. If a molecular formula is given, your structure must match it.
- **Equations**: balanced, with every product (HCl , SO_2 , POCl_3 , CO_2 , H_2O). Use $[\text{O}]$ for the oxidising agent.
- **"Explain" relative acidity**: order (1), link to H^+ loss once (1), then one structural reason per compound. Mark schemes accept "lone pair" or "p orbital", and "delocalised into" or "overlaps with" the ring.
- **Mechanisms**: lone pair, both first-step arrows and the dipole, the intermediate with its charges, then both second-step arrows. Name it in full: "nucleophilic addition–elimination".
- **"Suggest"** means apply the rules to an unfamiliar molecule (a drug, a diacid): the marks go to using the rules consistently.
- **"Describe" observations**: colours before and after, precipitates with their colour, effervescence. "No change" counts as an observation and must be written.
- **Calculations**: use the Data Booklet A_r values and $24.0 \text{ dm}^3 \text{ mol}^{-1}$, show the moles, and give 3 significant figures unless told otherwise.

Quick check

1. Put pentanoic acid, 2-chloropentanoic acid and 4-chloropentanoic acid in order of acidity, most acidic first, and explain the order.
2. A 4.08 g sample of 4-methylbenzoic acid, $\text{CH}_3\text{C}_6\text{H}_4\text{COOH}$, reacts completely with phosphorus(III) chloride. Write the equation and state the condition, and calculate the mass of PCl_3 needed.
3. 4-methylbenzoyl chloride is added to propan-1-amine at room temperature, and separately to water. Give the organic product of each and the other product.
4. Ethyl 3-acetamidopropanoate, $\text{CH}_3\text{CONHCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$, is heated with an excess of NaOH(aq) , and separately with an excess of HCl(aq) . Give the organic products of each.
5. An aqueous solution of compound K, $\text{C}_2\text{H}_2\text{O}_3$, fizzes with $\text{Na}_2\text{CO}_3(\text{aq})$, gives an orange precipitate with 2,4-DNPH and a silver mirror with Tollens' reagent. The Tollens' reaction turns K into L, $\text{C}_2\text{H}_2\text{O}_4$. L decolourises warm acidified KMnO_4 , giving a gas that turns limewater milky. Identify K and L, and write equations for $\text{K} \rightarrow \text{L}$ and for the oxidation of L, using $[\text{O}]$.

Answers

1. 2-chloropentanoic acid > 4-chloropentanoic acid > pentanoic acid. Chlorine is electronegative and withdraws electrons, which weakens the O–H bond and stabilises the carboxylate ion, so both chloro acids lose H^+ more easily than pentanoic acid. The effect gets weaker with distance along the chain, so the Cl on carbon 2, next to COOH , has the larger effect.
2. $3\text{CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{PCl}_3 \rightarrow 3\text{CH}_3\text{C}_6\text{H}_4\text{COCl} + \text{H}_3\text{PO}_3$, with heating. $M_r(\text{C}_8\text{H}_8\text{O}_2) = 136.0$, so $4.08 \div 136.0 = 0.0300$ mol of acid needs 0.0100 mol of PCl_3 ($M_r = 137.5$): 1.38 g.
3. With propan-1-amine: $\text{CH}_3\text{C}_6\text{H}_4\text{CONHCH}_2\text{CH}_2\text{CH}_3$, 4-methyl-N-propylbenzamide, and HCl (which reacts with more amine to give $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$). With water: $\text{CH}_3\text{C}_6\text{H}_4\text{COOH}$, 4-methylbenzoic acid, and HCl .
4. NaOH(aq) : $\text{CH}_3\text{COO}^-\text{Na}^+$, $\text{H}_2\text{NCH}_2\text{CH}_2\text{COO}^-\text{Na}^+$ and $\text{CH}_3\text{CH}_2\text{OH}$. HCl(aq) : CH_3COOH , $\text{HOOCCH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ and $\text{CH}_3\text{CH}_2\text{OH}$. Both the amide and the ester are hydrolysed, so there are three products each time.
5. K is OHC-COOH (oxoethanoic acid): COOH from the fizzing, an aldehyde CHO from 2,4-DNPH and Tollens'. L is ethanedioic acid, HOOC-COOH . $\text{C}_2\text{H}_2\text{O}_3 + [\text{O}] \rightarrow \text{C}_2\text{H}_2\text{O}_4$; $\text{C}_2\text{H}_2\text{O}_4 + [\text{O}] \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$.

Past questions to try

- **9701/43/M/J/22 Q5**: acidities of an acid, a phenol and an alcohol, a Na / NaOH / Na_2CO_3 table, making benzoyl chloride and its hydrolysis mechanism.
- **9701/42/M/J/21 Q8**: ease of hydrolysis of three kinds of chloride, then the products of hydrolysing a drug molecule.
- **9701/42/F/M/22 Q6**: making an acyl chloride with SOCl_2 and the addition–elimination mechanism with an aryl amine.
- **9701/43/O/N/23 Q9**: benzoyl chloride from ethylbenzene, then the mechanism that forms phenyl benzoate.