INTRODUCTION

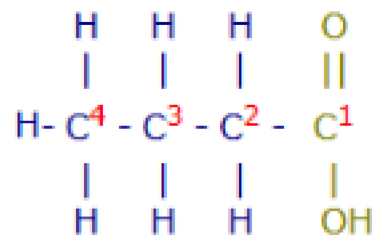
ALKANOIC OR CARBOXYLIC ACIDS

Alkanoic or carboxylic acids, are organic compounds characterized by the carboxyl functional group (COOH) attached to a hydrogen atom or an alkyl group (R). They have the general formula ($C_nH_{2n+1}COOH$). The general formula of a carboxylic acid is often written as **R−COOH** or **R−CO_2H**, sometimes as R−C(O)OH with R referring to an organyl group (e.g., alkyl, alkenyl, aryl), or hydrogen, or other groups. Carboxylic acids occur widely. Important examples include the amino acids and fatty acids. Deprotonation of a carboxylic acid gives a carboxylate anion. They are weak acids, soluble in water (lower members), and are used in making soaps, food flavoring, and vinegar (ethanoic acid).

A. NAMING /NOMENCLATURE OF ALKANOIC ACIDS

Carboxylic acids are commonly identified by their trivial names. They often have the suffix *-ic acid*. IUPAC-recommended names also exist; in this system, carboxylic acids have an *-oic acid* suffix. For example, butyric acid ($CH_3CH_2CH_2CO_2H$) is butanoic acid by IUPAC guidelines. For nomenclature of complex molecules containing a carboxylic acid, the carboxyl can be considered position one of the parent chain even if there are other substituents, such as 3-chloropropanoic acid. Alternately, it can be named as a "carboxy" or "carboxylic acid" substituent on another parent structure, such as 2-carboxyfuran. The carboxylate anion ($R-COO^-$ or $R-CO_2$) of a carboxylic acid is usually named with the suffix *-ate*, in keeping with the general pattern of *-ic acid* and *-ate* for a conjugate acid and its conjugate base, respectively. For example, the conjugate base of acetic acid is acetate.

Follow the steps below to name a straight-chain alkanoic acid Number the longest carbon chain starting with the carbon atom of the COOH functional group.



- Name the carbon chain as the alkane.
- Drop the "e" from the name of the alkane, butane becomes butan
- Add the suffix -oic acid, butan becomes butanoic acid

Examples of some straight chain saturated carboxylic acids (alkanoic acid)

Carbon atoms	Common name	IUPAC name	Chemical formula	Common location or use
1	**Formic acid**	Methanoic acid	$HCOOH$	**Insect stings**
2	**Acetic acid**	Ethanoic acid	CH_3COOH	**Vinegar**
3	**Propionic acid**	Propanoic acid	CH_3CH_2COOH	Preservative for stored grains, **body odour**, milk, butter, cheese
4	**Butyric acid**	Butanoic acid	$CH_3(CH_2)_2COOH$	**Butter**
5	**Valeric acid**	Pentanoic acid	$CH_3(CH_2)_3COOH$	**Valerian plant**
6	**Caproic acid**	Hexanoic acid	$CH_3(CH_2)_4COOH$	**Goat fat**
7	**Enanthic acid**	Heptanoic acid	$CH_3(CH_2)_5COOH$	Fragrance

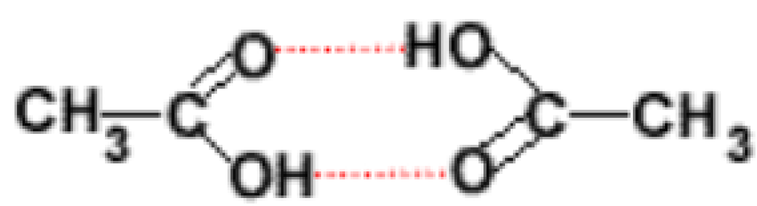
8	**Caprylic acid**	Octanoic acid	$CH_3(CH_2)_6COOH$	**Coconuts**
9	**Pelargonic acid**	Nonanoic acid	$CH_3(CH_2)_7COOH$	**Pelargonium plant**
10	**Capric acid**	Decanoic acid	$CH_3(CH_2)_8COOH$	**Coconut and Palm kernel oil**

B. PHYSICAL PROPERTIES

Alkanoic acids are weak acids, and as such are expected to have the **properties of acids:**

- taste sour
- conduct electricity in solution
- turn blue litmus red

Alkanoic acids are polar molecules. They exist as covalent molecular substances, so their melting points and boiling points are expected to be quite low but higher than alcohol because alkanoic acid can form two **hydrogen bonds** (shown in dotted red lines) between them. For this reason, alkanoic acids have higher melting and boiling points than other compounds with the same number of carbon atoms.

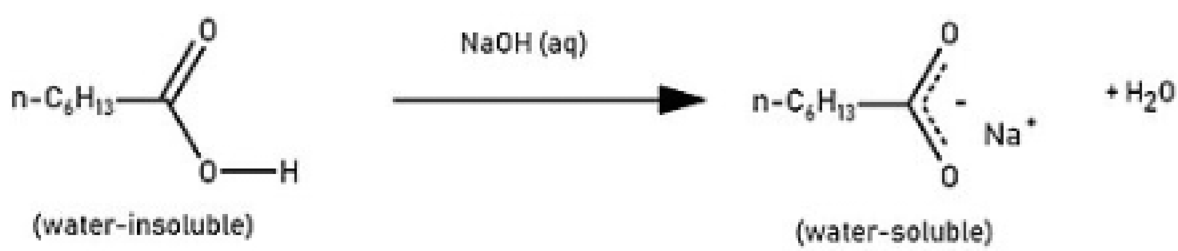


If two organic molecules have the same number of carbon atoms, then the molecule capable of forming the greatest number of hydrogen-bonds will have the highest melting point and boiling point.

The melting point and the boiling points of alkanoic acids increase with increa sing number of carbon atoms in the carbon chain. The boiling points of alkanoic acids increase by about 20°C for each carbon that is added to the chain

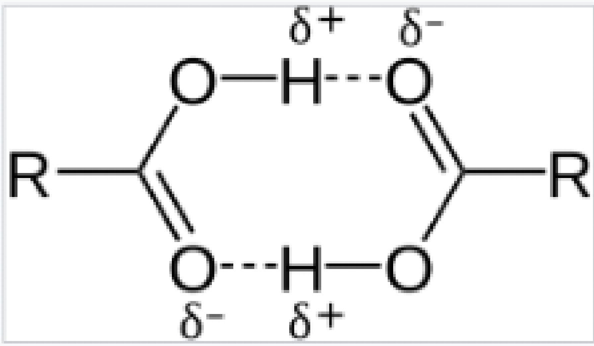
Solubility

Because alkanoic acids are capable of some dissociation in water, we expect them to display some solubility in water. (that is they are polar solvent). Because they are both hydrogen-bond acceptors (the carbonyl −C(=O)−) and hydrogen-bond donors (the hydroxyl −OH), they also participate in hydrogen bonding. Together, the hydroxyl and carbonyl group form the functional group carboxyl. Carboxylic acids usually exist as dimers in nonpolar media due to their tendency to "self-associate". Smaller carboxylic acids (1 to 5 carbons) are soluble in water, whereas bigger carboxylic acids have limited solubility due to the increasing hydrophobic nature of the alkyl chain. These longer chain acids tend to be soluble in less-polar solvents such as ethers and alcohols. Aqueous sodium hydroxide and carboxylic acids, even hydrophobic ones, react to yield water-soluble sodium salts. For example, enanthic acid has a low solubility in water (0.2 g/L), but its sodium salt is very soluble in water.



Boiling points

Carboxylic acids tend to have higher boiling points than water, because of their greater surface areas and their tendency to form stabilized dimers through hydrogen bonds. For boiling to occur, either the dimer bonds must be broken or the entire dimer arrangement must be vaporized, increasing the enthalpy of vaporization requirements significantly.



Carboxylic acid dimers

Acidity/ Resonance effects

Carboxylic acids are Brønsted–Lowry acids because they are proton (H^+) donors. They are the most common type of organic acid. Carboxylic acids are typically weak acids, meaning that they only partially dissociate into $[H_3O]^+$ cations and $R–CO_2$ anions in neutral aqueous solution. For example, at room temperature, in a 1-molar solution of acetic acid, only 0.001% of the acid are dissociated (i.e. 10^{-5} moles out of 1 mol). Deprotonation of carboxylic acids gives carboxylate anions; these are resonance stabilized, because the negative charge is delocalized over the two oxygen atoms, increasing the stability of the anion. Each of the carbon–oxygen bonds in the carboxylate anion have a partial double-bond character. The carbonyl carbon's partial positive charge is also weakened by the $-^1/_2$ negative charges on the 2 oxygen atoms.

Odour

Carboxylic acids often have strong sour odours. Esters of carboxylic acids tend to have fruity, pleasant odours, and many are used in perfume.

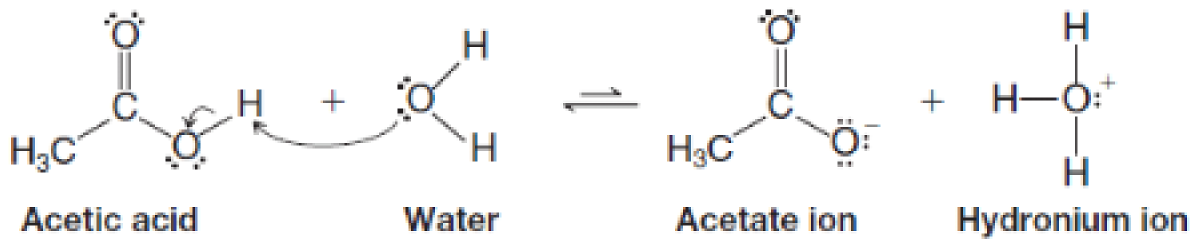
C. RESONANCE

Alkanoic acids are significantly more acidic than alkanols because resonance in the carboxylate conjugate base stabilizes the negative charge across two oxygen atoms. This resonance delocalization, combined with electronegative carbonyl oxygen induction, eases proton loss, whereas alkanols lack resonance stabilization and possess localized negative charges.

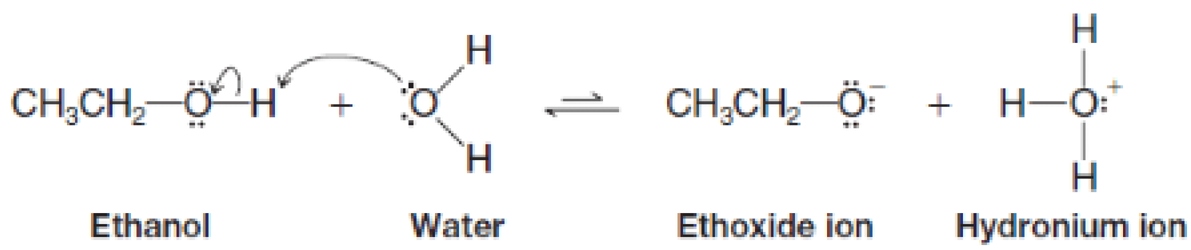
Acidity of Carboxylic Acids and Alcohols

The acidity of carboxylic acids is much greater than alcohols. Consider first th e structural changes that occur if both acetic acid and ethanol act as acids by donating a proton to water.

Acetic Acid Acting as an Acid



Ethanol Acting as an Acid



- Carboxylic acids are weak acids, typically having pK_a values in the ran ge of 3–5.
- Alcohols, by comparison, have pK_a values in the range of 15–18 and essentially do not give up a proton unless exposed to a very strong b ase.
- To understand the reasons for this difference, let’s consider acetic ac id and ethanol as representative examples of simple carboxylic acids and alcohols.

Acetic acid — **pK_a = 4.75** — **ΔG° = 27 kJ mol^{-1}**

Ethanol — **pK_a = 16** — **ΔG° = 90.8 kJ mol^{-1}**

(ΔG° values are for OH proton ionization.)

- Using the pK_a for acetic acid (4.75), one can calculate that the free energy change (ΔG^o) for ionization of the carboxyl proton of acetic acid is +27 kJ mol^{-1}, a moderately endergonic (unfavorable) process since the (ΔG^o) value is positive.
- Using the pK_a of ethanol (16), one can calculate that the corresponding free-energy change for ionization of the hydroxyl proton of ethanol is +90.8 kJ mol^{-1}, a much more endergonic (and hence even less favorable) process.
- These calculations reflect the fact that ethanol is much less acidic than acetic acid.

Explanation on much greater acidity of carboxylic acids than alcohols

What we need to focus on is the relative stability of the conjugate bases derived from a carboxylic acid and an alcohol.

This is because the smaller free-energy change for ionization of a carboxylic acid (e.g., acetic acid) as compared to an alcohol (e.g., ethanol) has been attributed to greater stabilization of the negative charge in the carboxylate ion as compared to an alkoxide ion.

Greater stabilization of the carboxylate ion appears to arise from two factors:

(a) Delocalization of charge (as depicted by resonance structures for the carboxylate ion).

(b) An inductive electron-withdrawing effect

D. PREPARATION OF ALKANOIC ACID

The methods to prepare carboxylic acids can be generally divided into three categories:

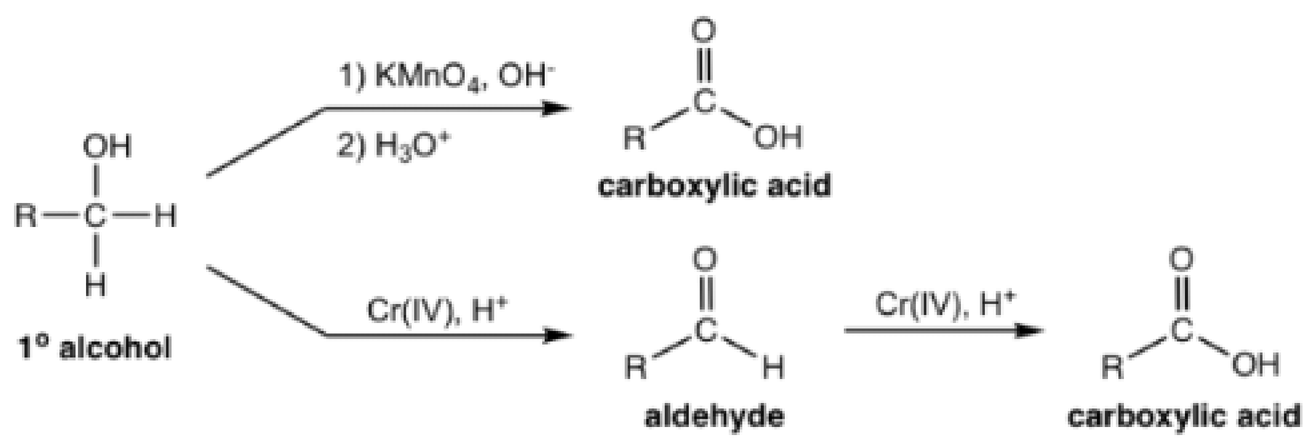
- Oxidation reaction,
- Grignard reaction and
- Hydrolysis of nitrile.

1. **Oxidation reaction:**

Since the carboxyl group COOH is in the high oxidation state, it can be pr epared by oxidation of other functional groups in the lower oxidation states, fo r example, alkene, alcohol, and aldehyde

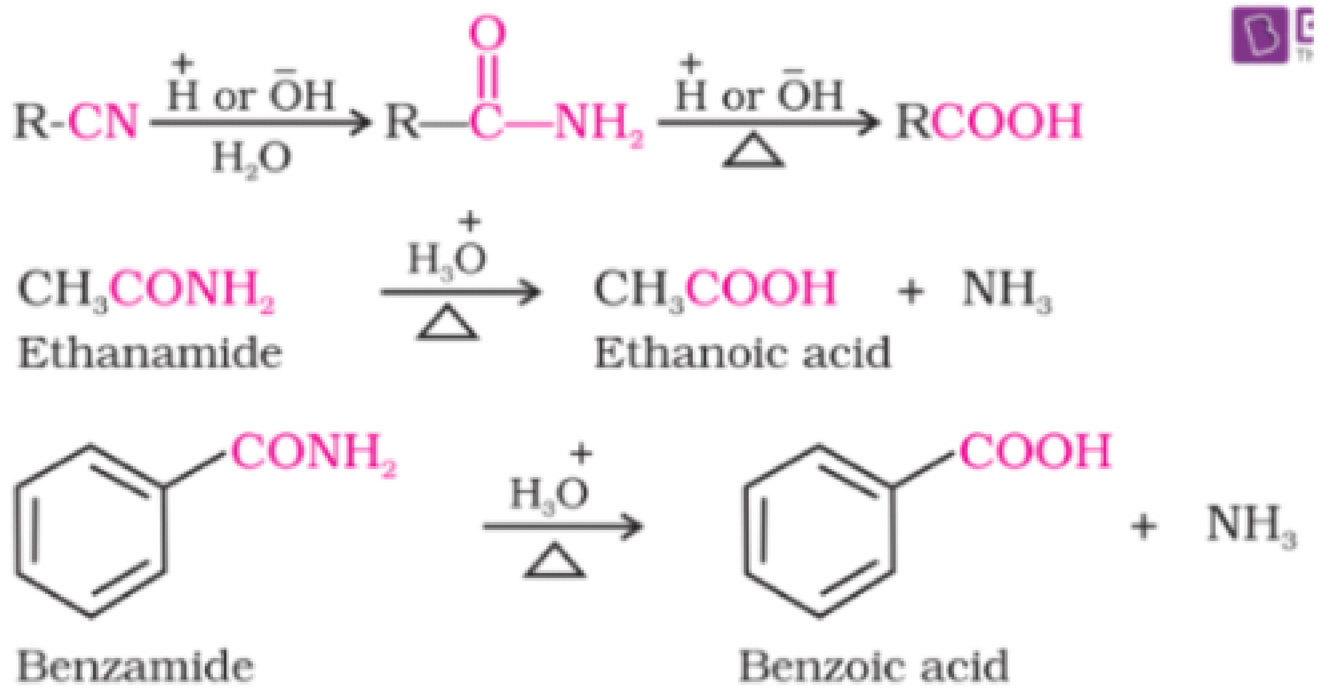
Oxidation of Primary Alkanols and Alkanals (Aldehydes)

When primary alcohols are oxidized by potassium permanganate $KMnO_4$ in basic condition, (salt of) carboxylic acid is produced. Under the acidic condi tion with Cr (VI) reagents (CrO_3, or H_2CrO_4), primary alcohols are oxidized to al dehydes first, then to carboxylic acids as final products.



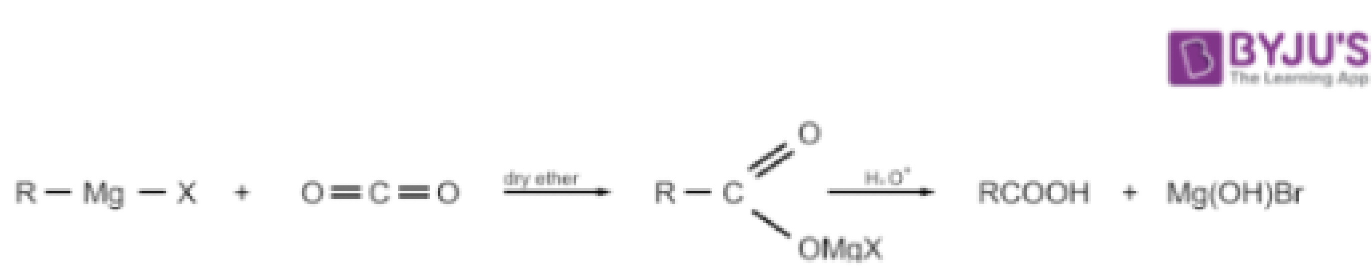
2. **Hydrolysis of Nitriles and Amides**

Amides are prepared by the hydrolysis of nitriles and then converted to acids in the presence of catalysts (H^+ or OH^{-1}). In order to stop the reaction at the amide stage, mild reaction conditions are used.



3. **By using Grignard Reagents and carbon (iv) oxide**

When Grignard reagent reacts with carbon dioxide, it forms salts of carboxy lic acids which after some time gives corresponding carboxylic acid after the a cidification with any mineral acid. We can prepare Grignard reagents as well a s nitriles from alkyl halides. These methods are very useful for the conversion of alkyl halides into corresponding carboxylic acids which has one carbon ato m more than what is present in alkyl halides.



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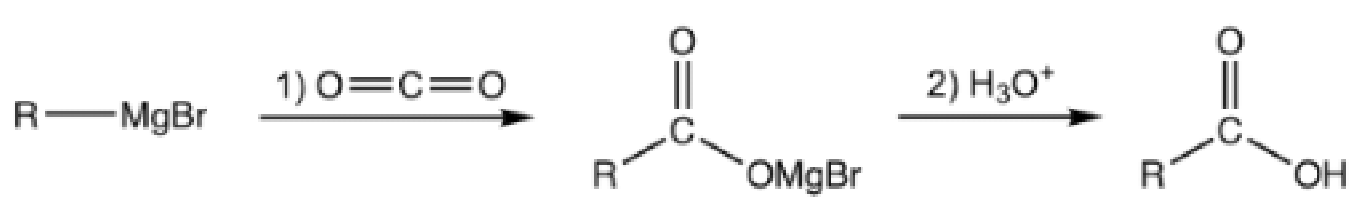
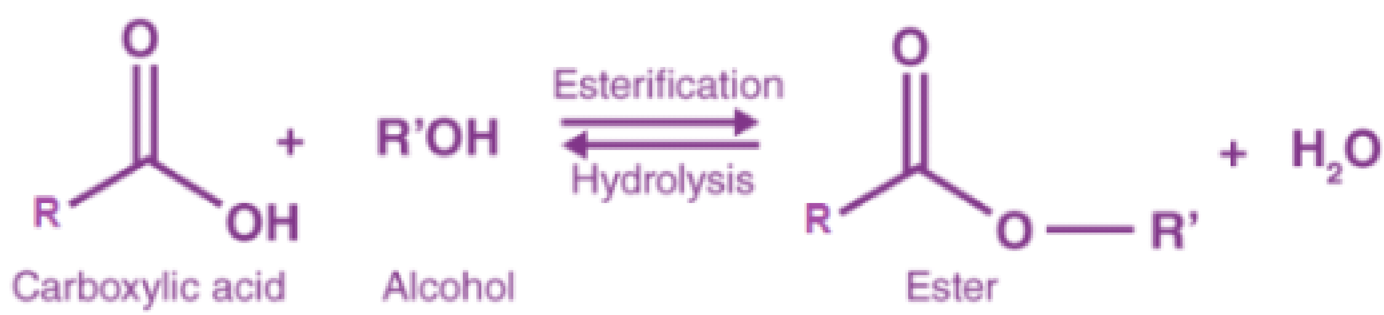


E. CHEMICAL PROPERTIES

1. **Esterification**

The chemical reaction that takes place during the formation of the ester is called esterification. Esterification is the process of ***combining an organic acid (RCOOH) with an alcohol (ROH) to form an ester (RCOOR)*** and water; or a chemical reaction resulting in the formation of at least one ester product. Ester is obtained by an esterification reaction of an alcohol and a carboxylic acid. The chemical reaction for esterification is given below.

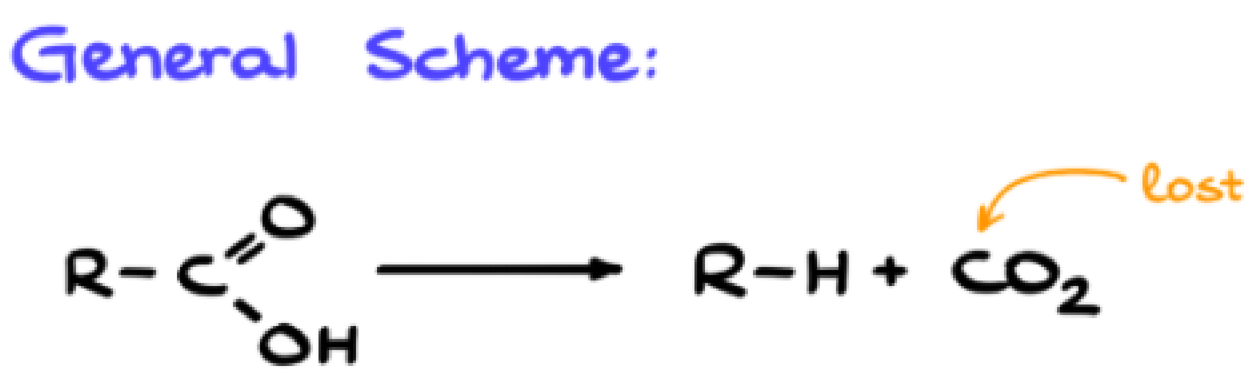


Example:

$CH_3OH + CH_3CH_2COOH \rightarrow CH_3COOCH_2CH_3$

2. **Decarboxylation Reaction**

Whenever we talk about decarboxylation, we're focusing on the removal of a carboxylic acid group, typically in the form of carbon dioxide gas, or CO_2.



There are a few types of decarboxylation reactions you might encounter. The most common, is **ionic decarboxylation**. However, we also have **radical decarboxylation**, which usually happens electrochemically or at very high temperatures, or **metal-assisted decarboxylation**, where heavy metals like copper or barium help out. These last two types are less useful for practical synthesis and tend to require extreme conditions.

Reaction Description

Decarboxylation is the removal of a carboxyl group ($-COOH$) from a carboxylic acid, releasing carbon dioxide (CO_2) and forming a hydrocarbon (alkane or aromatic compound).

General Reaction Equation

For a simple carboxylic acid:

$$\text{R-COOH} \xrightarrow{\Delta,\, NaOH,\, CaO} \text{R-H} + CO_2$$

Where:

- R-COOH = Carboxylic acid
- R-H = Corresponding hydrocarbon (alkane or aromatic compound)
- CO_2 = Carbon dioxide
- Δ = Heat
- $NaOH$ and CaO = Soda lime (mixture used to facilitate decarboxylation: catalyst)

Example:

Decarboxylation of Acetic Acid

$$\text{CH}_3\text{COOH} \xrightarrow{\Delta,\, NaOH,\, CaO} \text{CH}_4 + CO_2$$

Acetic acid (CH_3COOH) gives methane (CH_4) and carbon dioxide (CO_2)

Reduction:

Like esters, most carboxylic acids can be reduced to alcohols by hydrog enation, or using hydride transferring agents such as lithium aluminium hydride. Strong alkyl transferring agents, such as organolithium compounds but not Grignard reagents, will reduce carboxylic acids to ketones along with transfer of the alkyl group. The vilsmair reagent (*N,N*-Dimethyl(chloromethylene)ammonium chloride; $[ClHC=N^{+}(CH_3)_2]Cl^{-}$) is a highly chemoselective agent for carboxylic acid reduction. It selectively activates the carboxylic acid to give the carboxymethyleneammonium salt, which can be reduced by a mild reductant like lithium tris(*t*-butoxy)aluminum hydride to afford an aldehyde in a one pot procedure. This procedure is known to tolerate reactive carbonyl functionalities such as ketone as well as moderately reactive ester, olefin, nitrile, and halide moieties.

F. ALKANOIC ACID DERIVATIVES

The important classes of organic compounds known as alcohols, phenols, ethers, amines and halides consist of alkyl and/or aryl groups bonded to hydroxyl, alkoxyl, amino and halo substituents respectively. If these same functional groups are attached to an **acyl group** (RCO–) their properties are substantially changed, and they are designated as **carboxylic acid derivatives**. Carboxylic acids have a hydroxyl group bonded to an acyl group, and their functional derivatives are prepared by replacement of the hydroxyl group with substituents, such as halo, alkoxyl, amino and acyloxy.

Alkanoic acid derivatives are compounds containing the acyl group (RCO) where the hydroxyl (OH) group of a carboxylic acid is replaced by another group, such as halogen, nitrogen, or oxygen. Major types include acyl halides, anhydrides, esters, and amides, ranked by decreasing reactivity.

Types of Alkanoic Acid Derivatives

- **Acyl Halides (RCOX):** The most reactive derivative, often produced by reacting carboxylic acids with reagents like $SOCl_2$. Replacing the -OH group of a carboxylic acid by a chlorine atom. The functional group in acid chloride is -COCl. For example, acetyl chloride (CH_3COCl)
- **Acid Anhydrides (RCOOCOR):** Formed by the reaction of two carboxylic

acid molecules, often using heat or dehydrating agents so as to remove water. For example, acetic anhydride $(CH_3CO)_2O$

- **Esters (RCOOR"):** Formed by replacing the OH with an alkoxy group. Formed by a carboxylic acid and an alcohol in the presence of a small quantity of an acid. The functional group in esters is -COOR. For example, Ethyl acetate ($CH_3COOC_2H_5$). They are widely used in flavors and fragrances.
- **Amides ($RCONR_2$):** Formed by replacing the OH with an amino group, often the least reactive of the common derivatives. Formed by a carboxylic acid and ammonia or amine. The functional group in amides is $-CONH_2$. For example, Acetamide (CH_3CONH_2)
- **Nitriles (RCN):** While lacking a carbonyl group, they are considered derivatives because they can be hydrolyzed to carboxylic acids

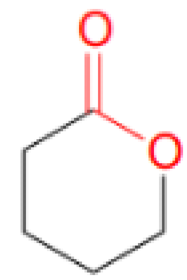
All of these carboxylic acid derivatives can undergo similar reactions due to the presence of the polar C-O group, but they differ in their reactivity.

Carboxylic acid derivatives can be distinguished from aldehydes and ketones by the presence of a group containing an electronegative heteroatom - usually oxygen, nitrogen, or sulfur – bonded directly to the carbonyl carbon. You can think of a carboxylic acid derivative as having two sides. One side is the acyl group, which is the carbonyl plus the attached alkyl (R) group. In the specific cases where R is a hydrogen or methyl, chemists use the terms formyl and acetyl group, respectively.

Nomenclature

Examples with their IUPAC and common names, common names are given in parentheses.

• **Esters:** The alkyl group is named first, followed by a derived name for the acyl group, the oic or ic suffix in the acid name is replaced by ate. e.g. $CH_3(CH_2)_2CO_2C_2H_5$ is ethyl butanoate (or ethyl butyrate). Cyclic esters are called lactones. A Greek letter identifies the location of the alkyl oxygen relative to the carboxyl carbonyl group.



a lactone

• **Acid Halides:** The acyl group is named first, followed by the halogen name as a separate word.

e.g. CH_3CH_2COCl is propanoyl chloride (or propionyl chloride).

• **Anhydrides:** The name of the related acid(s) is used first, followed by the separate word "anhydride".

e.g. $(CH_3(CH_2)_2CO)_2O$ is butanoic anhydride & $CH_3COOCOCH_2CH_3$ is ethanoic propanoic anhydride (or acetic propionic anhydride).

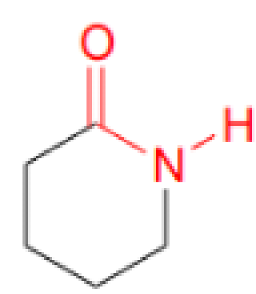
• **Amides:** The name of the related acid is used first and the oic acid or ic acid suffix is replaced by amide (only for 1º-amides).

e.g. CH_3CONH_2 is ethanamide (or acetamide).

2º & 3º-amides have alkyl substituents on the nitrogen atom. These are designated by "N-alkyl" term(s) at the beginning of the name.

e.g. $CH_3(CH_2)_2CONHC_2H_5$ is N-ethylbutanamide; & $HCON(CH_3)_2$ is N,N-dimethylmethanamide (or N,N-dimethylformamide).

Cyclic amides are called lactams. A Greek letter identifies the location of the nitrogen on the alkyl chain relative to the carboxyl carbonyl group.



a lactam

• **Nitriles:** Simple acyclic nitriles are named by adding nitrile as a suffix to the name of the corresponding alkane (same number of carbon atoms).

Chain numbering begins with the nitrile carbon. Commonly, the oic acid or ic acid ending of the corresponding carboxylic acid is replaced by onitrile. A nitrile substituent, e.g. on a ring, is named carbonitrile. e.g. $(CH_3)_2CHCH_2C{\equiv}N$ is 3-methylbutanenitrile (or isovaleronitrile).

1. **Acyl halide**

An **acyl halide** (also known as an **acid halide**) is a chemical compound derived from an oxoacid by replacing a hydroxyl group (−OH) with a halide group (−X, where X is a halogen). In organic chemistry, the term typically refers to acyl halides of carboxylic acids (−C(=O)OH), which contain a **−C(=O)X** functional group consisting of a carbonyl group (C=O) singly bonded to a halogen atom. The general formula for such an acyl halide can be written **RCOX**, where R may be, for example, an alkyl group, CO is the carbonyl group, and X represents the halide, such as chloride. Acyl chlorides are the most commonly encountered acyl halides, but acetyl iodide is the one produced (transiently) on the largest scale. Billions of kilograms are generated annually in the production of acetic acid.

Preparation

Aliphatic acyl halides

On an industrial scale, the reaction of acetic anhydride with hydrogen chloride produces a mixture of acetyl chloride and acetic acid:

$$(CH_3CO)_2O + HCl \rightarrow CH_3COCl + CH_3CO_2H$$

A common method for the synthesis of acyl halides in the laboratory is by reaction of carboxylic acids with reagents such as thionyl chloride or phosphorus pentachloride for acyl chlorides, phosphorus tribromide for acyl bromides and cyanuric fluoride for acyl fluorides.

Equation of the reactions

From thionyl chloride ($SOCl_2$)

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

From phosphoruos (V) chloride (PCl_5)

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

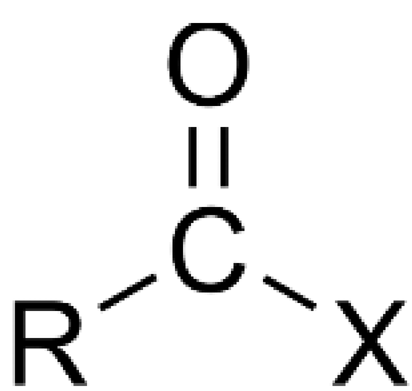
From phosphoruos (III) chloride (PCl_3)

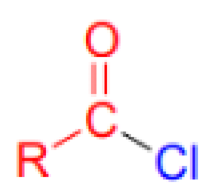
$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

Examples of Aliphatic Acyl Halides

Structure	Common name	IUPAC name
CH_3COCl	Acetyl chloride	Ethanoyl chloride
CH_3CH_2COCl	Propionyl chloride	Propanoyl chloride
$CH_3CH_2CH_2COBr$	Butyryl bromide	Butanoyl bromide
HCOCl	Formyl chloride	Methanoyl chloride
$(CH_3)_2CHCOCl$	Isobutyryl chloride	2-Methylpropanoyl chloride
CH_3COF	Acetyl fluoride	Ethanoyl fluoride

Structure





acid chloride

2. **Alkanoic anhydride**

Alkanoic (carboxylic) anhydrides are prepared by reacting an acyl chloride with a carboxylic acid salt (or in the presence of pyridine), or by heating carboxylic acids with a dehydrating agent like P2O5. They are formed via nucleophilic acyl substitution, commonly producing symmetric anhydrides (RCOOCOR) by removing a molecule of water between two acids.

Preparation

- **Acyl Chloride + Carboxylate Salt:** This is the most common laboratory method, involving the nucleophilic attack of a carboxylate anion (RCOO) on an acyl chloride (RCOCl).

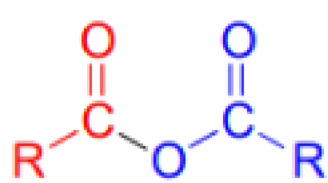
$$CH_3COCl + CH_3COONa \longrightarrow (CH_3CO)_2O + NaCl$$

- **Dehydration of Carboxylic Acids:** Heating carboxylic acids, typically with phosphorus pentoxide (P_2O_5) or at very high temperatures (approx. 800^{o} C), causes the loss of water and formation of the anhydride.

$$2RCOOH \xrightarrow[\text{Heat}]{\text{Dehydrating agent}} RCOOCOR + H_2O$$

- **Acyl Chloride + Carboxylic Acid (with Pyridine):** A carboxylic acid and a n acyl chloride can react directly in the presence of pyridine, which acts as a base to neutralize the HCl byproduct.
- **Cyclic Anhydrides:** Five- or six-membered cyclic anhydrides (e.g., succin ic anhydride, maleic anhydride) are easily prepared simply by heating th e corresponding dicarboxylic acids

Structure of alkanoic anhydride



acid anhydride

Examples of **Alkanoic Anhydrides**

- **Ethanoic Anhydride (Acetic Anhydride, $(CH_3CO)_2O$):** The most common anhydride, widely used in the production of cellulose acetate, aspirin (by reacting with salicylic acid), and as a laboratory reagent.

- **Propanoic Anhydride $(CH_3CH_2CO)_2O$:** Derived from propanoic acid, used in industrial synthesis.
- **Butanoic Anhydride $(CH_3CH_2CH_2CO)_2O$:** Derived from butanoic acid.
- **Pentanoic Anhydride $(C_4H_9CO)_2O$:** A higher homologue, often liquid.
- **Hexanoic Anhydride $(C_5H_{11}CO)_2O$:** Also used in organic synthesis

Ethanoic anhydride

Ethanoic anhydride (commonly known as acetic anhydride, $(CH_3CO)_2O$) is a key carboxylic acid derivative used primarily for acetylation. It is prepared through several methods, ranging from laboratory techniques involving acid chlorides to large-scale industrial processes using ketene.

Preparation

The most common and efficient method for preparing symmetrical anhydrides in the laboratory is the reaction between an acid chloride (acetyl chloride) and the sodium salt of the carboxylic acid (sodium acetate).

Equation of the reaction:

$$CH_3COCl + CH_3COONa \rightarrow (CH_3CO)_2O + NaCl$$

Acetyl chloride reacts with sodium acetate at room temperature to form acetic anhydride and sodium chloride.

3. **Alkanamides (Amides)**

Alkanamides, commonly known as primary amides, are organic compounds derived from carboxylic acids where the hydroxyl group (−OH) is replaced by an amino group ($-NH_2$). They possess the general formula **$RCONH_2$**, where R is an alkyl group. They are characterized by a carbonyl group (C=O) directly attached to a nitrogen atom.

Structure:

$R\text{-}CO\text{-}NH_2$ (where R is H or an alkyl group).

Functional Group:

The amide functional group consists of a carbonyl carbon atom (C=O) bonded to a nitrogen atom (N).

Nomenclature (Naming)

Alkanamides are named by taking the corresponding alkane name, removing the **"e"** and adding the suffix **"-amide"**.

- **Step 1:** Identify the parent carboxylic acid, counting the carbon atom in the carbonyl group as the first carbon.
- **Step 2:** Replace the "oic acid" suffix from the carboxylic acid name with "-amide".
- **Step 3:** For substituted nitrogen, use N- before the alkyl group name (e.g., N-methylpropanamide).

Examples:

CH_3CONH_2: Ethanamide (from ethanoic acid)

$CH_3CH_2CONH_2$: Propanamide (from propanoic acid)

$CH_3CH_2CH_2CONH_2$: Butanamide (from butanoic acid)

$CH_3CHCONHCH_3$ | CN 3-Cyano N-methyl propanamide

CH−C−N | CH_3 N-Ethyl. N-methyl benzanamide

$CH_3-CH=CH-C-NHC_2H_4$ || =C N-Ethyl but 2-enamide

Preparation

Alkanamides can be prepared through several methods, primarily involving the substitution of the -OH group of carboxylic acids or their derivatives.

1. **From Carboxylic Acids and Ammonia or amides:** Heating a carboxylic acid with ammonia (or amines) forms an ammonium salt, which decomposes upon heating to form the amide.

Equation of the reaction:

$$RCOOH + NH_3 \xrightarrow{Heat} RCONH_2 + H_2O$$

2. **From ammonium trioxocarbonate (IV), commonly known as ammon ium carbonate, and heat:**

This involves a two-step reaction process with a carboxylic acid. When heat ed, ammonium carbonate provides the ammonia necessary to form the amide bond, while the excess heat drives the dehydration of the intermediate ammo nium carboxylate salt to the final amide.

General Procedure

Formation of ammonium carboxylate:

Solid ammonium carbonate (NH_4CO_3) is added to a carboxylic acid (RCOOH) t o form an ammonium carboxylate salt intermediate.

Equation of the reaction:

$$RCOOH + (NH_4)_2CO_3 \rightarrow RCOONH_4 + H_2O + CO_2$$

Heating (Dehydration): The mixture is heated to approximately 170°C (often u nder reflux and later distillation) to eliminate water, which converts the salt int o an amide.

Equation of the reaction:

$$RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$

Example:

Preparation of Ethanamide (Acetamide)

To produce ethanamide, acetic acid (ethanoic acid) is used:

Formation of ammonium ethanoate:

$$CH_3COOH + (NH_4)_2CO_3 \rightarrow CH_3COONH_4 + H_2O + CO_2$$

Thermal dehydration:

$$CH_3COONH_4 \xrightarrow{170^\circ C} CH_3CONH_2 + H_2O$$

4. Nitriles

Nitriles are organic compounds containing a cyano functional group, characterized by a carbon atom triple-bonded to a nitrogen atom (R-C≡N). They are important intermediates in organic synthesis and industrial chemistry, commonly used to make polymers, pharmaceuticals, and solvents.

Structure and Formula

General Formula: R-C≡N

(where R is an alkyl or aryl group).

Functional Group: Cyano group (-C≡N).

Nomenclature/naming

Nitriles are named based on the longest carbon chain, including the carbon of the nitrile group. Using IUPAC system of naming, the suffix nitrile is added to the alkane name (eg CH_3CN is ethanenitrile)

Functional class names: Named as alkyl cyanides (eg CH_3CH_2CN is ethyl cyanides)

Cyclic Nitriles: If the C≡N group is attached to a ring, the suffix carbonitrile is used

(e.g cyclohexanecaronitrile)

Substituent: If a higher priority functional group is present, the prefix cyano is used.

Examples

CH_3CN: Ethanenitrile (acetonitrile)

CH_3CH_2CN: Propanenitrile (propionitrile)

CH_2=CHCN: Prop-2-enenitrile (acrylonitrile)

C_6H_5CN: Benzonitrile

Preparation of Nitriles

1. **Dehydration of Primary Amides:**

Primary amides ($RCONH_2$) are treated with dehydrating agents like phos phorus pentoxide (P_4O_{10}), thionyl chloride ($SOCl_2$), or $POCl_2$ to remove water a nd form nitriles.

$$RCONH_2 \xrightarrow{P_4O_{10}/heat} RCN + H_2O$$

2. **Heating haloalkanes with alcoholic potassium cyanide (Kolbe nitrile synthesis):**

The preparation of nitriles (alkyl cyanides) from haloalkanes involves a **n ucleophilic substitution reaction**, typically using an **alcoholic solution of potas sium cyanide (KCN).** This **is called Kolbe nitrile synthesis**. When a haloalkane (RX) is heated under reflux with alcoholic KCN, the cyanide ion (CN^-) acts as a nucleophile, replacing the halogen atom to form a nitrile (R-CN) and a potassiu m halide salt (KX). This reaction is highly valuable in organic chemistry becaus e it increases the length of the carbon chain by one carbon atom.

Equation of the reaction:

$$\mathrm{R{-}X + KCN \xrightarrow[\text{reflux}]{\text{ethanol}} R{-}CN + KX}$$

5. **Alkanoates (Esters)**

Alkanoates, commonly known as **esters**, are organic compounds with th e general formula **R−COOR'**, where R and R' are alkyl groups. They are formed by replacing the acidic hydrogen of a carboxylic acid with an alkyl group, often resulting in pleasant, fruity-smelling liquids.

Preparation

a. **Esterification reaction (reaction of alkanols with alkanoic acid):**

This is the reaction between alkanol and alkanoic acid in the presence of catalyst to form alkanoate. Alkanoates are primarily prepared through **esterification**, a reversible condensation reaction between an alkanoic acid (carboxylic acid) and an alkanol (alcohol) in the presence of a strong acid catalyst.

General reaction:

$$\text{Alkanoic Acid} + \text{Alkanol} \underset{\text{Heat}}{\overset{\text{Conc. } H_2SO_4}{\rightleftharpoons}} \text{Alkanoate} + \text{Water}$$

Example:

$$\text{Ethanoic acid} + \text{Ethanol} \rightleftharpoons \text{Ethyl ethanoate} + \text{Water}$$

Equation of the reaction:

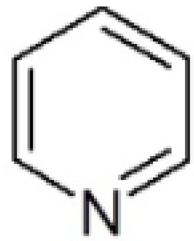
$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

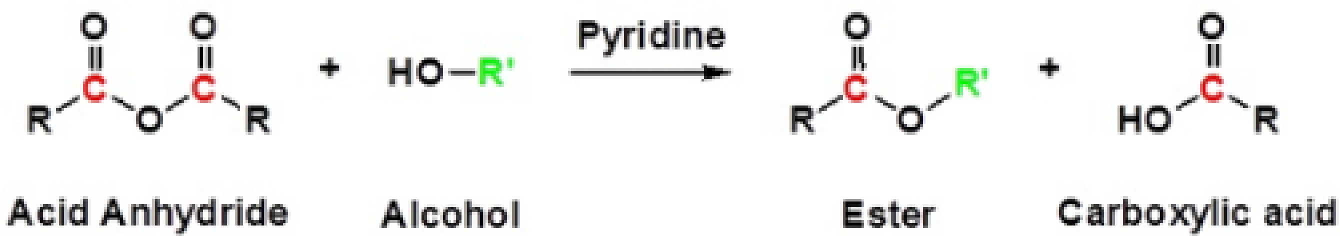
Conditions

The mixture is warmed with concentrated sulphuric acid (H_2SO_4) which acts as a catalyst and a dehydrating agent to remove water and drive the reaction forward.

b. **Reaction of alkanols with acyl chloride or acid anhydride:**

Acid anhydride reacts with alkanols to form esters. The reaction of alcohols with acid anhydrides is a type of nucleophilic acyl substitution, known as **alcoholysis**, which produces an ester and a carboxylic acid. This reaction is generally faster than Fischer esterification and safer/milder to use than acid chlorides.





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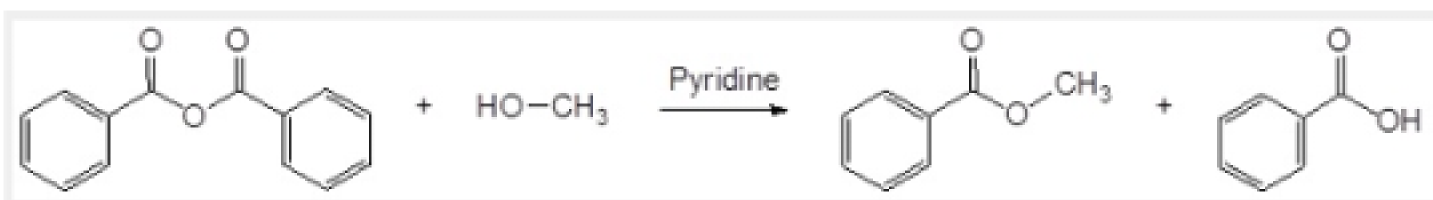

or

Acetic Anhydride + Ethanol:

$$(CH_3CO)_2O + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + CH_3COOH$$

Chemical Reactions of Alkanoates

Alkanoates are generally unreactive compared to acids but undergo cru cial reactions, primarily focusing on breaking the ester link.

i. **Hydrolysis (Breaking with Water)**
Hydrolysis is the reverse of esterification, breaking the ester back int o its constituent acid and alcohol.

Acid-Catalyzed Hydrolysis: Reversible reaction using a dilute acid catalyst (H Cl or H_2SO_4).

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{\text{dil. } H^+} CH_3COOH + C_2H_5OH$$

Alkaline hydrolysis (saponification): irreversible reaction with a strong base (e. g NaOH or KOH) producing a soap (salt of the carboxylic acid) and an alcohol.

Equation of the reaction:

(Ethyl ethanoate + Sodium hydroxide → Sodium ethanoate + Ethanol

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

ii Reduction

a. **W i t h L i A l H 4**
   Alkanoates can be reduced to primary alcohols using a strong reduci ng agent like lithium aluminum hydride (LiAlH4).

Equation of the reaction:

$$RCOOR' + 4[H] \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

b. **With sodium in ethanol**

The reduction of alkanoates (carboxylic acid esters) with sodium in ethanol is known as the **Bouveault-Blanc reduction**. This chemical reaction, first reporte d in 1903, is used to convert esters into their corresponding primary alcohols.

Reaction Mechanism and Summary

Sodium acts as a single-electron reducing agent, providing four electrons (four atoms of Na) to fully reduce one ester molecule, while ethanol serves as a pro ton source.

Overall Reaction:

$$RCOOR' + 4Na + 2CH_3CH_2OH \rightarrow RCH_2ONa + R'ONa + 2CH_3CH_2ONa$$

The reaction yields two alcohol products: the primary alcohol (RCH2OH) from t he acyl part of the ester, and another alcohol (R'OH) from the alkyl part.

Example

Ethyl Ethanoate Reduction:

$$CH_3COOC_2H_5 + Na/EtOH \rightarrow Ethanol + Ethanol$$