ANDERSON SERANGOON JUNIOR COLLEGE
JC2 H2 CHEMISTRY
CARBOXYLIC ACIDS AND DERIVATIVES

Content

1. Carboxylic acids (exemplified by ethanoic acid and benzoic acid)
   (i) Formation from primary alcohols and nitriles
   (ii) Reactions to form salt, ester and acyl chloride

2. Acyl chlorides (exemplified by ethanoyl chloride)
   (i) Ease of hydrolysis compared with alkyl and aryl chlorides
   (ii) Reaction with alcohols, phenols and primary amines

3. Esters (exemplified by ethyl ethanoate and phenyl benzoate)
   (i) Formation from carboxylic acids and from acyl chlorides
   (ii) Hydrolysis (under acidic and under basic conditions)

Learning Outcomes

Candidates should be able to:
(a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles
(b) describe the reactions of carboxylic acids in the formation of
   (i) salts
   (ii) esters on condensation with alcohols, using ethyl ethanoate as an example
   (iii) acyl chlorides, using ethanoyl chloride as an example
   (iv) primary alcohols, via reduction with lithium aluminium hydride, using ethanol as example
(c) explain the acidity of carboxylic acids and of chlorine–substituted ethanoic acids in terms of their structures
(d) describe the hydrolysis of acyl chlorides
(e) describe the condensation reactions of acyl chlorides with alcohols, phenols and primary amines
(f) explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides
(g) describe the formation of esters from acyl chlorides, using phenyl benzoate as an example
(h) describe the acid and base hydrolysis of esters

References

1. Chemistry for Advanced Level, Cann and Hughes, Murray
2. Organic Chemistry (5th Edition), McMurry, Brooks/Cole

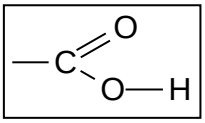
Outline

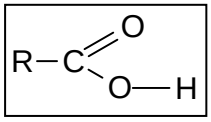
Part I: Carboxylic Acids
1. Introduction
2. Synthesis of carboxylic acids
3. Reaction of carboxylic acids
4. Acidity of carboxylic acids

Part II: Carboxylic Acid Derivatives
1. Introduction
2. Esters and its reactions
3. Acid Chlorides and its reactions
4. Amides – (to be discussed in greater details in Nitrogen Compounds)

PART 1: CARBOXYLIC ACID

1 INTRODUCTION

Contain the **carboxylic acid** functional group 

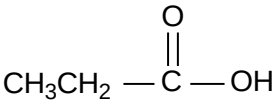
General structure:  *where R may be H, alkyl or aryl group*

1.1 Nomenclature

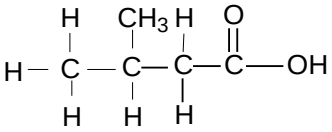
The longest carbon chain containing the carboxylic acid functional group is selected as the parent chain and named by replacing the 'e' of the corresponding alkane or alkene with '**oic acid**'.

The carbon atom in 'COOH' is assigned number **1**.

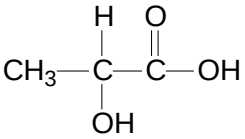
Examples of monocarboxylic acids



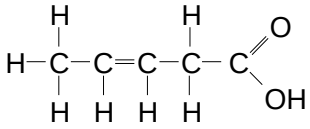
propanoic acid



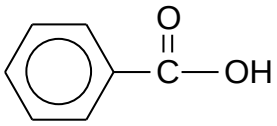
3–methylbutanoic acid



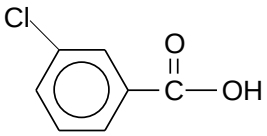
2–hydroxypropanoic acid



pent–3–enoic acid

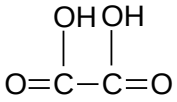


benzoic acid

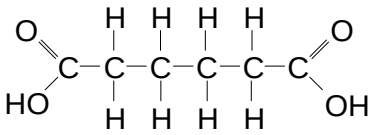


3–chlorobenzoic acid

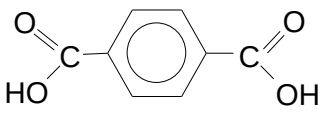
Examples of dicarboxylic acids



ethanedioic acid



hexane–1,6–dioic acid



benzene–1,4–dicarboxylic acid

2 PREPARATION OF CARBOXYLIC ACIDS

How are carboxylic acids synthesised?

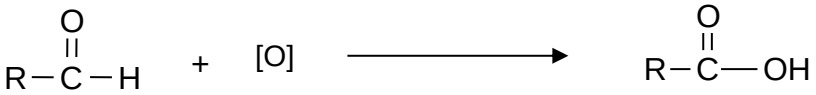
2.1 Oxidation from PRIMARY alcohols

(Refer to Hydroxy Compounds Lecture Notes for more details)

Type of reaction	Oxidation
Reagents & conditions	$K_2Cr_2O_7$ / $KMnO_4$, dilute H_2SO_4, heat under reflux
General equation	**primary alcohol** → **carboxylic acid** 

2.2 Oxidation from aldehyde

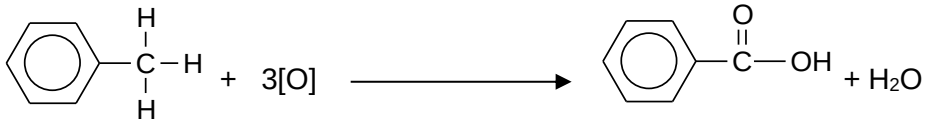
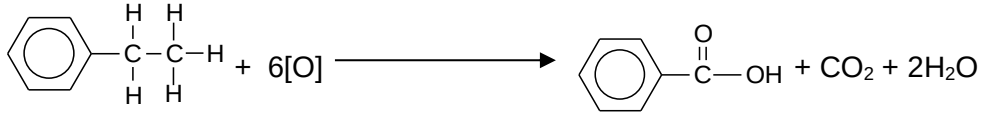
(Refer to Carbonyl Compounds Lecture Notes for more details)

Type of reaction	Oxidation
Reagents & conditions	$K_2Cr_2O_7$ / $KMnO_4$, dilute H_2SO_4, heat under reflux
General equation	**aldehyde** → **carboxylic acid** 

2.3 Oxidation from alkylbenzenes

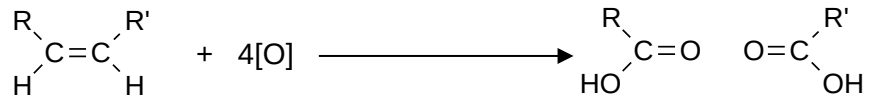
(Refer to Arenes Lecture Notes for more details)

Alkyl groups, regardless of the length of the carbon chain, directly bonded to the benzene ring are oxidised by $KMnO_4$ to a $-CO_2H$ group (except when the alkyl group is of the $-CR_3$ type).

Type of reaction	(Side chain) Oxidation
Reagents & conditions	$KMnO_4$, dilute H_2SO_4, heat under reflux
General equation	 methylbenzene → benzoic acid  ethylbenzene → benzoic acid

2.4 Oxidative cleavage from alkenes

(Refer to Alkenes Lecture Notes for more details)

Type of reaction	Oxidation (or Oxidative cleavage)
Reagents & conditions	$KMnO_4$, dilute H_2SO_4, heat under reflux
General equation	

2.5 Hydrolysis from nitriles

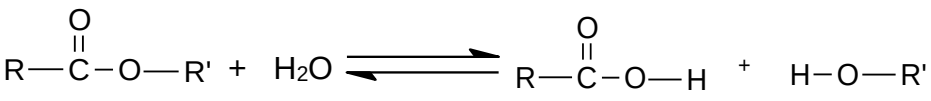
(Refer to Halogenoalkanes Lecture Notes for more details)

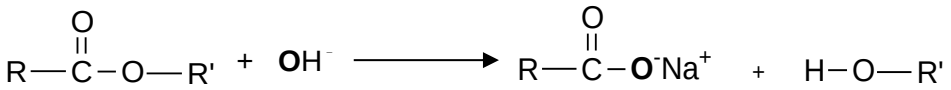
Type of reaction	(Acid) hydrolysis
Reagents & conditions	Dilute HC*l* / H_2SO_4, heat under reflux
General equation	**nitrile** **carboxylic acid** $R–CN + H^+ + 2H_2O \longrightarrow R–CO_2H + NH_4^+$

Type of reaction	(Base) hydrolysis
Reagents & conditions	NaOH(aq) / KOH(aq), heat under reflux followed by acidification by HC*l*, room temperature
General equation	$R—\mathbf{CN} + H_2O + OH^- \longrightarrow R\mathbf{COO}^- + NH_3$ Further acidification $R\mathbf{COO}^- + H^+ \longrightarrow R\mathbf{COOH}$

2.6 Hydrolysis from esters

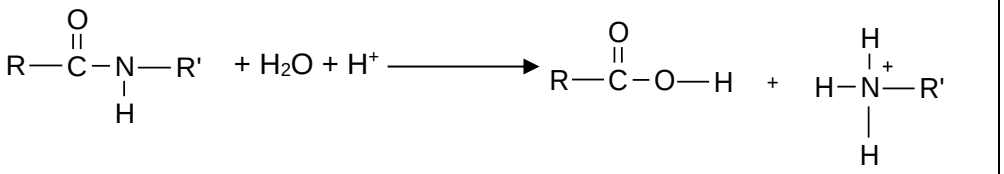
(Also covered in the section on Esters)

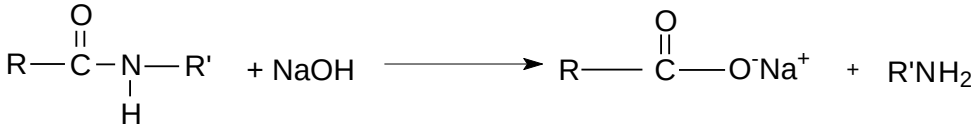
Type of reaction	(Acid) hydrolysis
Reagents & conditions	Dilute HC*l* / H_2SO_4, heat under reflux
General equation	**ester** **carboxylic acid** **alcohol** 

Type of reaction	(Base) hydrolysis
Reagents & conditions	NaOH(aq) / KOH(aq), heat under reflux followed by acidification by HC*l*, room temperature
General equation	**ester** **salt of carboxylic acid** **alcohol**  Further acidification 

2.7 Hydrolysis from amides

(To be covered in Nitrogen Compounds Lecture)

Type of reaction	(Acid) Hydrolysis
Reagents & conditions	Dilute HC*l* / H_2SO_4, heat under reflux
General equation	**amide** **carboxylic acid** **amine salt** 

Type of reaction	(Base) Hydrolysis
Reagents & conditions	NaOH(aq) / KOH(aq), heat under reflux followed by acidification by HC*l*, room temperature
General equation	 Further acidification 

2.8 Hydrolysis from acid chlorides

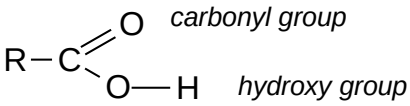
(Also covered in the section on Acid Chlorides)

Type of reaction	Nucleophilic (acyl) substitution / hydrolysis
Reagents & conditions	H_2O, room temperature
General equation	**acid chloride** + **carboxylic acid** + **hydrogen chloride** 

3 Reactions of carboxylic acids

What type of reactions do carboxylic acids undergo and why?

The characteristic chemical behaviour of carboxylic acid is determined by the functional group $–CO_2H$.



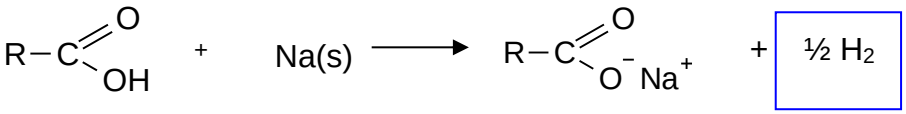
The C=O and O–H groups of the carboxylic acid group are in such close proximity that they modify each other's properties. Hence, carboxylic acids do not behave exactly like carbonyl compounds or alcohols.

The reactions of carboxylic acids almost invariably involve the hydroxy group, which either undergoes reactions involving the breaking of the O–H bond or C–O bond.

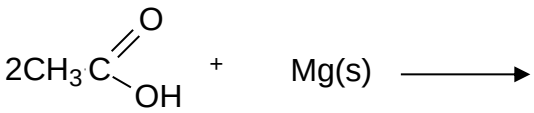
3.1 Formation of salts

Carboxylic acids form ionic carboxylate salts with reactive metals, alkalis, carbonates and hydrogencarbonates.

3.1.1 Reaction with metals

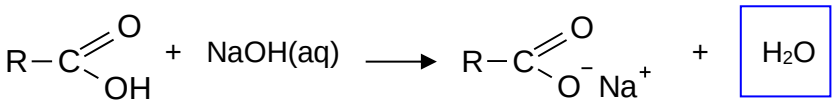
Type of reaction	Redox
Reagents & conditions	Na(s) / Mg(s), room temperature
General equation	 **carboxylic acid** **sodium carboxylate** **hydrogen gas**
Observations	(Strong) effervescence, gas evolved gives a "pop" sound with lighted splint

Exercise 1
Complete the equation for the following reaction

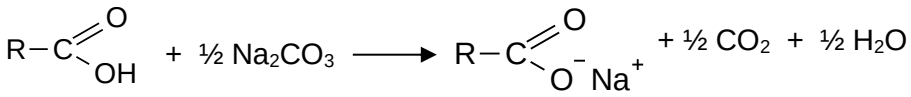
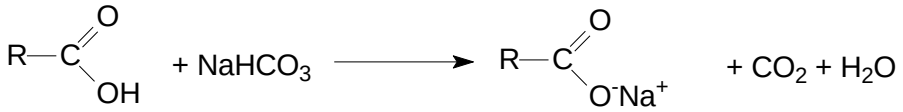


ethanoic acid

3.1.2 Reaction with NaOH

Type of reaction	Acid base
Reagent	NaOH(aq)
General equation	 **carboxylic acid** **sodium carboxylate** **water**

3.1.3 Reaction with Na_2CO_3 / $NaHCO_3$

Type of reaction	Acid base
Reagent	Na_2CO_3 / $NaHCO_3$
General equation	 **carboxylic acid** **sodium carboxylate** **carbon dioxide** 
Observations	(Strong) effervescence, gas evolved gives a white ppt with limewater (aqueous $Ca(OH)_2$)

Note:
Salts of alkali metals (Na, K) and NH_4^+ are soluble in water. The crystalline salts can be obtained by evaporating the aqueous solution.

The evolution of CO_2 from CO_3^{2-} or HCO_3^- is used as a test to distinguish carboxylic acids from weaker acids, such as phenols and alcohols. (refer to Hydroxy Compounds lecture notes)

Which compounds can react with Na(s), NaOH(aq), and Na_2CO_3(s)?

Compound	Na(s)	NaOH(aq)	Na_2CO_3(s)
alcohol			
phenol			
carboxylic acid			

Exercise 2

Which compounds react with an excess of sodium to give one mole of H_2 per mole of the compound?

1 $CH_3CH_2CH_2CH(OH)CO_2H$

2 $HOCH_2CH_2CH_2CH_2CH_2OH$

3 $CH_3COCH_2CH_2CO_2H$

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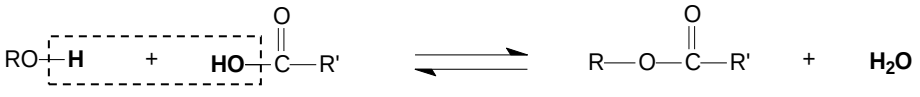
3.2 Formation of ester

Carboxylic acids can react with alcohols to form esters.

Type of reaction	Nucleophilic substitution
Reagents & conditions	alcohol with concentrated H_2SO_4, heat under reflux
General equation	 alcohol carboxylic acid ester
Observations	Sweet smell of ester. Immiscible layer with water.

Example

Reaction of propanol with ethanoic acid to form propyl ethanoate:

$CH_3CH_2CH_2O\mathbf{H}$ + $CH_3CO\mathbf{OH}$ $\rightleftharpoons$ $CH_3CO_2CH_2CH_2CH_3$ + $\mathbf{H_2O}$

Note:

1. Reaction is slow and reversible. This is usually a less preferred method of preparing the ester. A better method is to react the acyl chloride with alcohol.

2. Concentrated H_2SO_4 acts as both a catalyst and a drying agent.
   i) as a drying agent
   It removes water and shifts the position of equilibrium to the right, increasing the yield of the ester.

   ii) as a catalyst
   It speeds up the forward and backward reaction such that the equilibrium can be achieved faster.

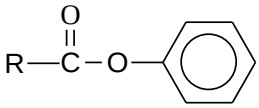
3. Carboxylic acid can only react with alcohol and NOT phenol to form ester.

carboxylic acid + **alcohol** ⇒ ester

carboxylic acid + **phenol** ⇏ ester

Phenol is a _____ nucleophile than alcohol as the lone pair of electrons on the oxygen is _____ into the benzene ring. Hence, it is not nucleophilic enough to react with a carboxylic acid to form ester.

But **phenylcarboxylate** esters do exist. How are these esters synthesised?



Refer to section on 'Acyl Chloride'

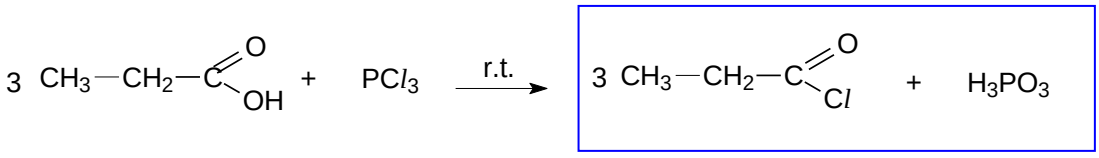
3.3 Formation of acyl chlorides

Carboxylic acids can react with various chlorine–containing compounds to form acyl chlorides.

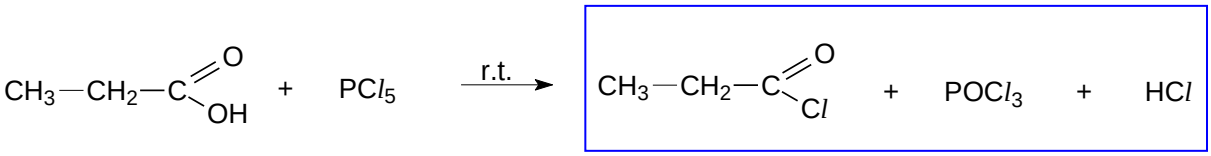
Type of reaction	Nucleophilic substitution
Reagents & conditions	$PCl_3(l)$, anhydrous, room temperature (r.t.)
	$PCl_5(s)$, anhydrous, r.t.
	$SOCl_2(l)$, anhydrous, r.t.
General equation	$RCOOH \xrightarrow{PCl_3} RCOCl + H_3PO_3$ $RCOOH \xrightarrow{PCl_5} RCOCl + POCl_3 + HCl(g)$ $RCOOH \xrightarrow{SOCl_2} RCOCl + SO_2 + HCl(g)$
Observations	white fumes (of HCl) evolved when PCl_5 or $SOCl_2$ is used

Examples

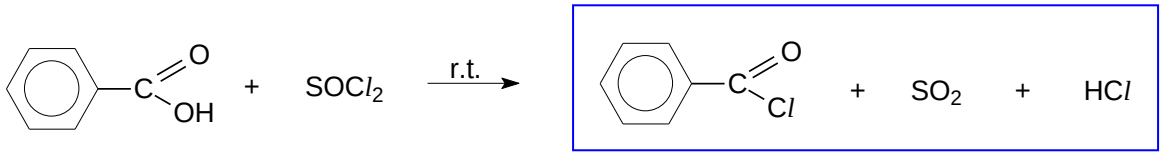
1. Reaction of propanoic acid with liquid phosphorous trichloride



2. Reaction of propanoic acid with solid phosphorous pentachloride



3. Reaction of benzoic acid with liquid thionyl chloride



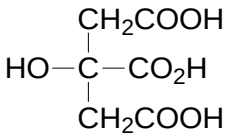
Note: (refer to 'Hydroxy Compounds' lecture notes)

1. Reactions resemble those in alcohols. The C*l* in PC*l*$_3$, PC*l*$_5$, and SOC*l*$_2$ will substitute the –OH group in alcohols.

2. Alcohols will also react with PC*l*$_5$ and SOC*l*$_2$ to form white fumes of HC*l*.

Exercise 3

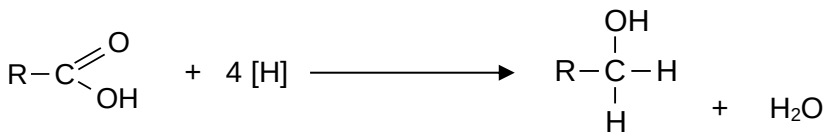
Citric acid, which causes the sharp taste of lemon juice, has the following formula.



What reacts completely with 1 mol of citric acid?

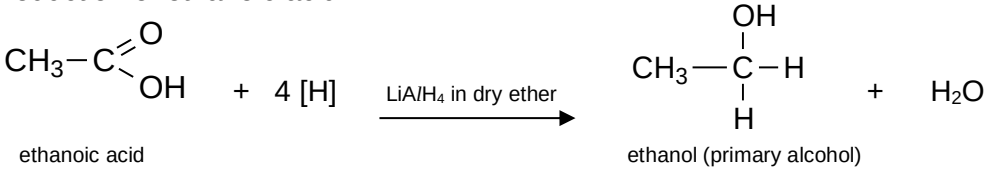
A 3 mol of PC*l*$_5$(s)
B 4 mol of HC*l*(g)
C 4 mol of Na(s)
D 4 mol of NaOH(aq)

3.4 Formation of primary alcohol

Type of reaction	Reduction
Reagents and conditions	Lithium aluminium hydride, LiA*l*H$_4$ in dry ether
General equation	 **carboxylic acid** **primary alcohol**

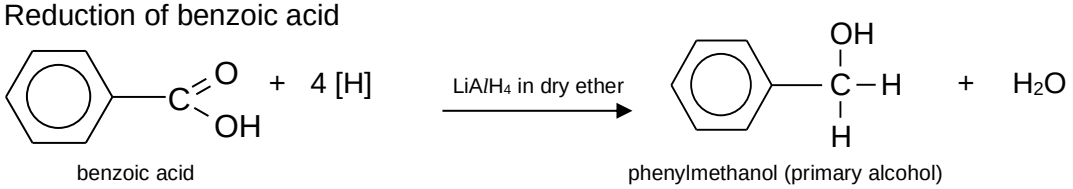
Example

1. Reduction of ethanoic acid



ethanoic acid — ethanol (primary alcohol)

2. Reduction of benzoic acid



benzoic acid — phenylmethanol (primary alcohol)

Note:
Reduction of carboxylic acid is more difficult compared to aldehydes and ketones. Hence, catalytic hydrogenation (i.e. using H_2 with Pt/Pd) and $NaBH_4$ do not work on carboxylic acids.

3.5 Oxidation of Methanoic Acid and Ethanedioic acid

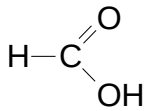
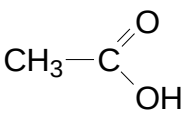
ONLY TWO exceptions are considered in our study on carboxylic acids that can undergo oxidation – **methanoic acid and ethanedioic acid**. Both acids will be oxidized to CO_2 and H_2O.

Type of reaction	Oxidation
Reagents and conditions	$KMnO_4$, dilute H_2SO_4, heat under reflux
Equations	Methanoic acid $HCOOH + [O] \longrightarrow CO_2 + H_2O$ Ethanedioic acid $(COOH)_2 + [O] \longrightarrow 2CO_2 + H_2O$

Note:
$K_2Cr_2O_7$ cannot oxidise both methanoic acid and ethanedioic acid.

Exercise 4

How do we distinguish between the following acids: methanoic acid and ethanoic acid?

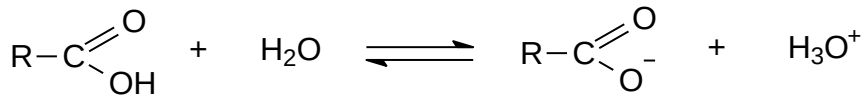
		
Procedure		
Observations		

4 Acidity of carboxylic acids

How do we compare the acidity of organic compounds in aqueous medium?

Carboxylic acids are classified as **<u>weak acids</u>**.

The dissociation equilibrium for carboxylic acid is written as:



carboxylic acid carboxylate ion

<u>THE BIG IDEA</u>

The strength of acid depends on the **<u>stability of the anion (conjugate base)</u>**.

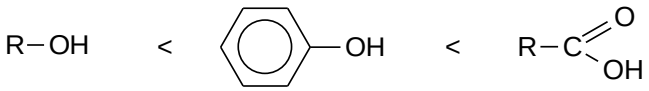
The anion is stabilised if its negative charge is **<u>dispersed</u>**.

The more stable the anion, the greater the extent of acid dissociation, the stronger the acid.

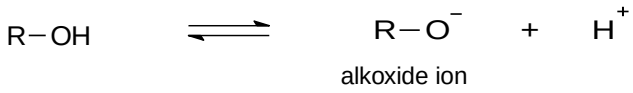
4.1 Comparing acidity of carboxylic acid to alcohol and phenol

Carboxylic acid is a **<u>stronger</u>** acid than alcohol and phenol.

<u>Weakest acid</u> <u>Strongest acid</u>

Relative acid strength: 

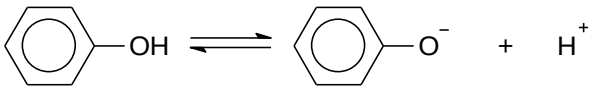
<u>Reason</u>

In **<u>alcohol</u>**, 

alkoxide ion

- The alkyl group, R, is _____.
- This _____ the negative charge on the O atom and makes the alkoxide ion _____.
  Hence, alcohols are less likely to dissociate to release H^+.

In **<u>phenol</u>**,

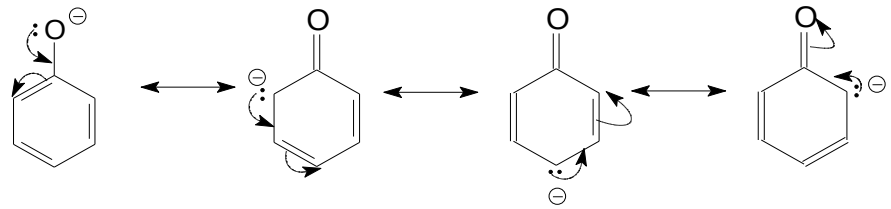


phenoxide ion

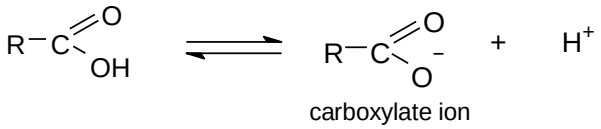
- *The lone pair of electrons on the O atom can _____ into the π electron cloud of the benzene ring**,** thus _____ the negative charge of the phenoxide ion.
- The phenoxide ion is _____**.**
- This favours the dissociation of phenol to release H^+.

Thus, phenol is a stronger acid than alcohol.

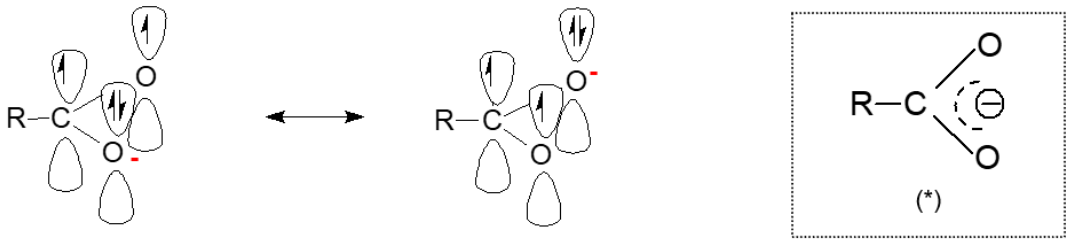
*FYI: The following shows how the lone pair on the O atom of phenoxide ion can delocalize into the benzene ring.



In **carboxylic acid**,



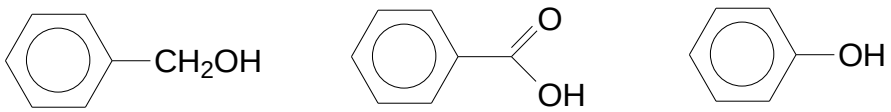
carboxylate ion



- The **p-orbital containing the lone pair** on the oxygen atom **overlaps with the adjacent carbonyl (C=O) group**, allowing the **lone pair to be delocalized into the carbonyl group**.
- As a result, the **negative charge is evenly shared between the two highly electronegative oxygen atoms**
- In the phenoxide ion ($C_6H_5O^-$), **part of the negative charge is delocalized into the carbon-containing benzene ring,** which is **less electronegative and less effective at stabilizing the negative charge** compared to an oxygen atom.
- The **carboxylate ion is more stable than the phenoxide ion**, which makes **carboxylic acids (RCOOH) more likely to release H^+** and, therefore, **stronger acids** compared to **phenol.**

Exercise 5

Predict the relative pK_a values for the following compounds.



Relative K_a values

_____ < _____ < _____

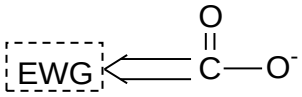
Relative pK_a values

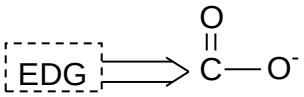
_____ < _____ < _____

4.2 Factors influencing the acid strength of carboxylic acids

4.2.1 Type of substituents

Electron–withdrawing groups increase the acid strength of carboxylic acids, whereas electron–donating groups decrease their acid strength.





Electron–**W**ithdrawing **G**roup
- disperses the negative charge
- stabilizes the carboxylate ion
- increases acid strength

Electron–**D**onating **G**roup
- _____ the negative charge
- _____ carboxylate ion
- _____ acid strength

Example

Acid	**chloroethanoic acid**	**methanoic acid**	**ethanoic acid**
Formula	**C*l*CH$_2$**CO$_2$H	**H**CO$_2$H	**CH$_3$**CO$_2$H
R =	CH$_2$C*l*	H	CH$_3$
***K*$_a$ values**	1.45 x 10^{-3}	1.77 x 10^{-4}	1.75 x 10^{-5}

Comparing **H**CO$_2$H and **CH$_3$**CO$_2$H:

–CH$_3$, an alkyl group, being **electron–donating**, **intensifies** the negative charge on the carboxylate anion, CH$_3$CO$_2^-$, **destabilising** it.

The **dissociation** of the acid, CH$_3$CO$_2$H, to release H$^+$ ions **becomes less favourable**. Hence, **CH$_3$CO$_2$H is a weaker acid than HCO$_2$H**.

Comparing **C*l*CH$_2$**CO$_2$H and **H**CO$_2$H:

Chlorine is **highly electronegative** and will exert an _____effect on the carboxylate anion, C*l*CH$_2$CO$_2^-$.

The **negative charge** on the anion becomes _____ and the anion **becomes more stable**.

The **dissociation** of the acid, C*l*CH$_2$CO$_2$H, to release H$^+$ ions is **more favoured**. Hence, **C*l*CH$_2$CO$_2$H is a stronger acid than HCO$_2$H**.

4.2.2 Strength of electron-withdrawing effect

More electronegative atom

- exerts _____electron-withdrawing effect on the on the carboxylate group ($–COO^–$)
- disperses the negative charge on anion to a greater extent
- stabilises anion to a greater extent
- increases acid strength

Example

Carboxylic acid	pK_a
C*l*CH_2COOH	2.86
BrCH_2COOH	2.90

Recall from 'Acid–base Equilibria': $K_a = \dfrac{[H^+][A^-]}{[HA]}$

$$pK_a = -\log_{10} K_a$$

The higher the pK_a, the smaller the K_a. Hence, the acid dissociates to a smaller extent and therefore is weaker.

4.2.3 Number of electron-withdrawing groups

Greater number of electron–withdrawing groups

- exerts _____ electron-withdrawing effect on the on the carboxylate group ($–COO^–$)
- disperses the negative charge on anion to a greater extent
- stabilises anion to a greater extent
- increases acid strength

Example

Carboxylic acid	pK_a
C*l*CH_2COOH	2.86
C**C*l*$_3$**COOH	0.65

4.2.4 Position of electron-withdrawing groups

Closer distance between the electron–withdrawing group and the carboxylate group ($–COO^–$)

- disperses the negative charge on anion to a greater extent
- stabilises anion to a greater extent
- increases acid strength

Example

Carboxylic acid	pK_a
$CH_3CH_2CHCl COOH$	2.84
$CH_3CHClCH_2COOH$	4.06

Exercise 6

Consider the following four compounds.

1. bromoethanoic acid
2. chloroethanoic acid
3. phenol
4. propanoic acid

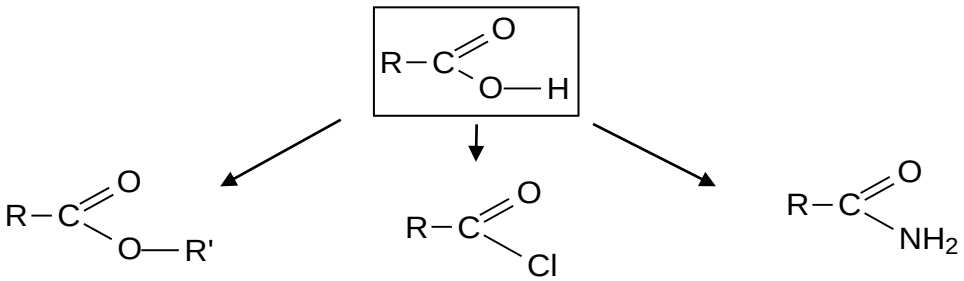
What is the relative order of **decreasing** acidity of these compounds?

A	1	2	4	3
B	2	1	3	4
C	2	1	4	3
D	3	2	1	4

N2009/I/27

PART 2: CARBOXYLIC ACID DERIVATIVES

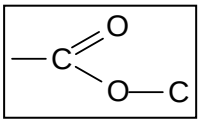
Carboxylic acids will react with suitable reagents to yield these derivatives:

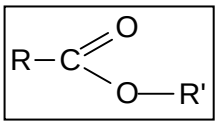


esters **acid chlorides** **amides**

1 INTRODUCTION

1.1 Esters

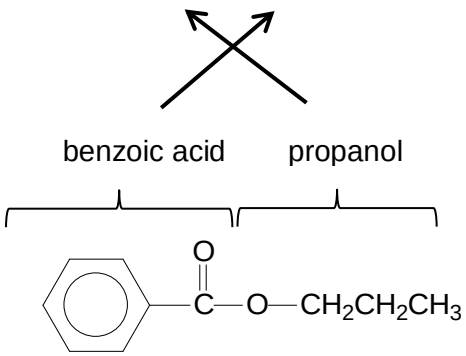
Esters have the ester functional group: 

Its general structure is  , *where R' may be an alkyl or aryl group*

Nomenclature

The name of an ester consists of two parts- one from the alcohol and the other part from the carboxylic acid.

e.g. propyl benzoate



Exercise 7

1. State the names of the carboxylic acid and alcohol that give these esters.

   (a) propylethanoate

   propanol and ethanoic acid

   (b) ethylbenzoate

   _____ and _____

2. State the name of the ester that is made from the following carboxylic acids and alcohols.

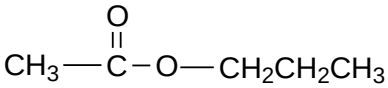
   (a) ethanol and propanoic acid

   ethylpropanoate

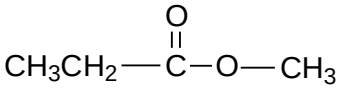
   (b) methanol and ethanoic acid

   _____

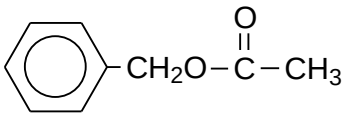
Examples



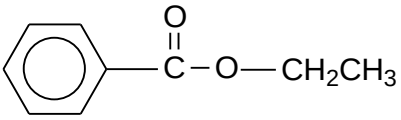
propylethanoate



methylpropanoate

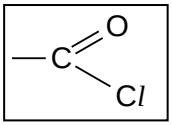


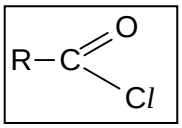
benzylethanoate



ethylbenzoate

1.2 Acid chlorides (or acyl chlorides)

Acid chlorides have the acid chloride functional group: 

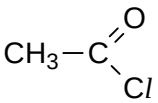
Its general structure is  , where R–C=O is known as an acyl group.

They are **highly reactive** organic compounds due to the two highly electronegative atoms (C*l* and O) bonded to the carbon of the C=O group.

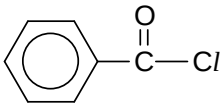
Nomenclature

The name is derived from the carboxylic acid name by replacing the '–oic acid' ending with '**–oyl chloride**'.

Examples

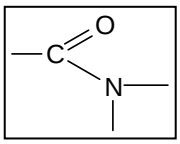


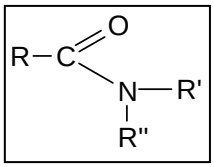
ethanoyl chloride



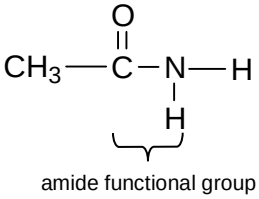
benzoyl chloride

1.3 Amides

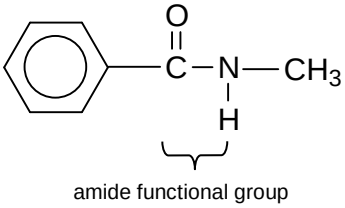
Amides have the **amide** functional group: 

Its general structure is  , *where R' & R'' may be H, alkyl or aryl groups*

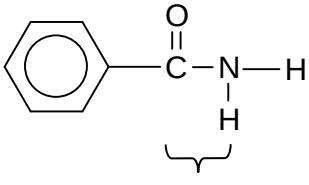
Examples



amide functional group



amide functional group



amide functional group

2 Reaction of carboxylic acid derivatives

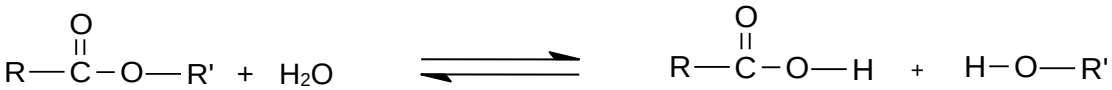
What type of reactions do acid chlorides and ester undergo and why?

2.1 Esters

2.1.1 Hydrolysis

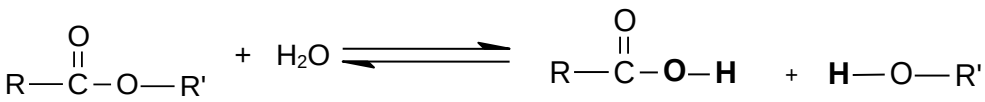
The reaction is the REVERSE of esterification. In the presence of water only, it is a VERY slow reaction.

ester **carboxylic acid & alcohol**



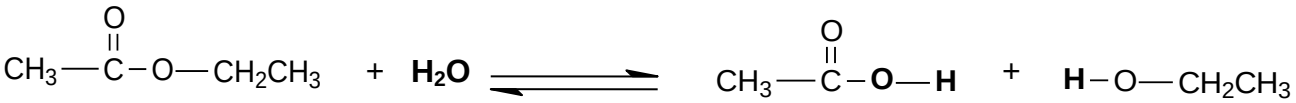
Therefore, reaction is performed in the **presence of an acid or base** to speed it up

(a) Acid hydrolysis

Type of reaction	Acid hydrolysis
Reagents & Conditions	DILUTE H_2SO_4, heat under reflux
General Equation	**ester** **carboxylic acid & alcohol** 

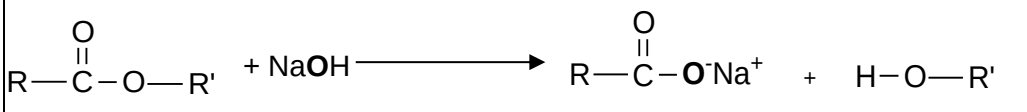
Note:
Acid hydrolysis is reversible

Example



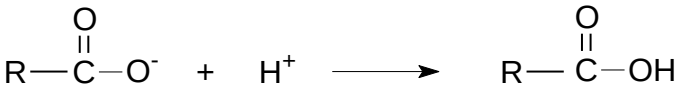
ethylethanoate ethanoic acid ethanol

(b) Base hydrolysis

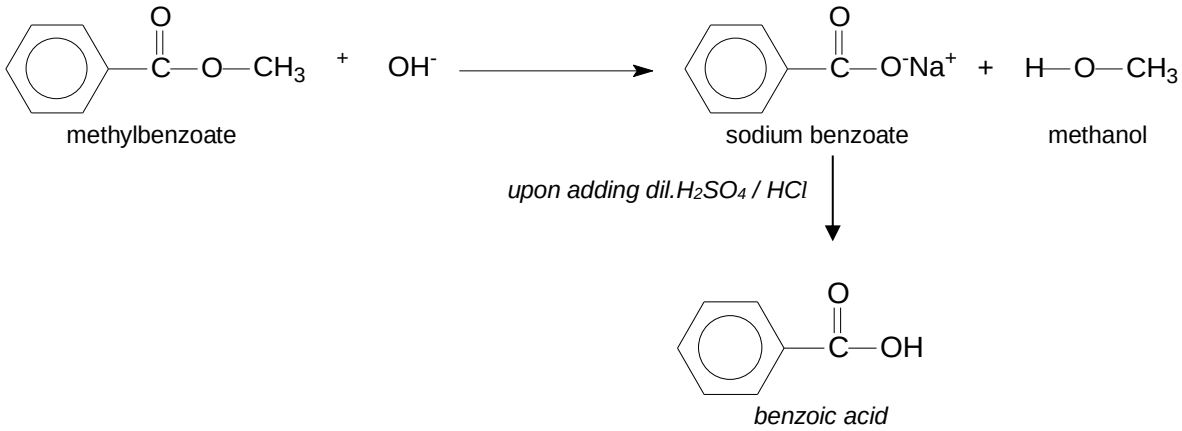
Type of reaction	Base hydrolysis (in the presence of base, RCOOH will deprotonate once formed, hence generating the carboxylate ion)
Reagents & Conditions	NaOH (aq), heat under reflux
General Equation	**ester** → **salt of carboxylic acid** & **alcohol** 

Note:
Base hydrolysis is **<u>an irreversible</u>** process.

To obtain the carboxylic acid from the salt, dilute H_2SO_4 or HC*l* can be added.



Example

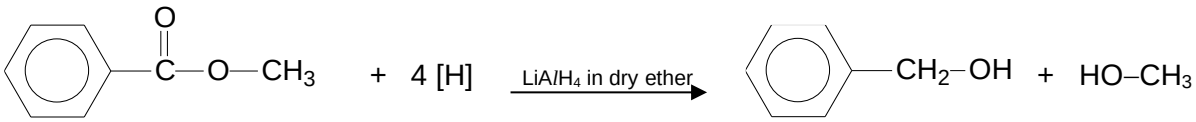


Exercise 8
Which compound is the product of the hydrolysis of $CH_3CO_2CH_2CH_2CH_3$ by boiling with aqueous sodium hydroxide?

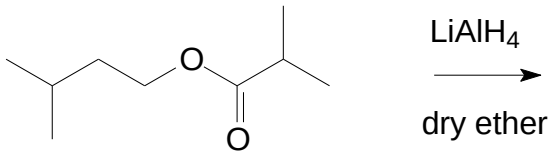
A CH_3OH **B** CH_3CO_2H **C** $CH_3CH_2CH_2OH$ **D** $CH_3CH_2CH_2CO_2^-Na^+$

2.1.2 Reduction of ester

Type of reaction	Reduction
Reagents & Conditions	**<u>LiA*l*H$_4$ in dry ether</u>**
Products	**<u>Two alcohols (one primary alcohol + one other alcohol)</u>**



Exercise 9



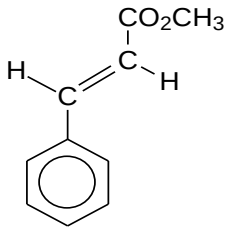
For your interest
Some major uses of esters

a. Food industry: as flavouring
Flavour refers to a combination of smell and taste.

Blending a mixture of appropriate esters reproduces odours of fruits.

These are then mixed with food products like bread, ice–cream, sweets and drinks to impart an attractive smell and introduce novelty to the product.

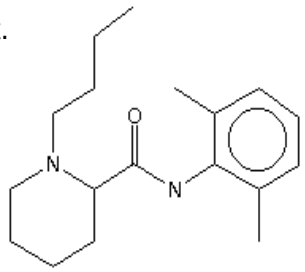
Methyl cinnamate – an ester that gives matsutake mushrooms their spicy aroma.



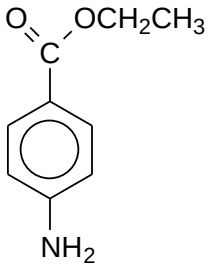
Methyl cinnamate

b. Medical field: in anesthetics
Benzocaine (ester) and marcaine (amide) are **local anesthetics** that play the role of numbing small areas of the body (making them insensitive to touch and pain) so as to make an operation more bearable for the patient.

Marcaine



Benzocaine



c. Solvents
Ethyl ethanoate is used as an industrial solvent.

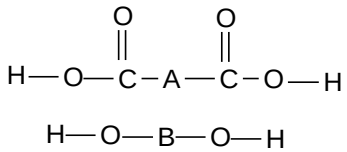
d. Polyesters
Synthetic fibres used in textile.

Polyesters

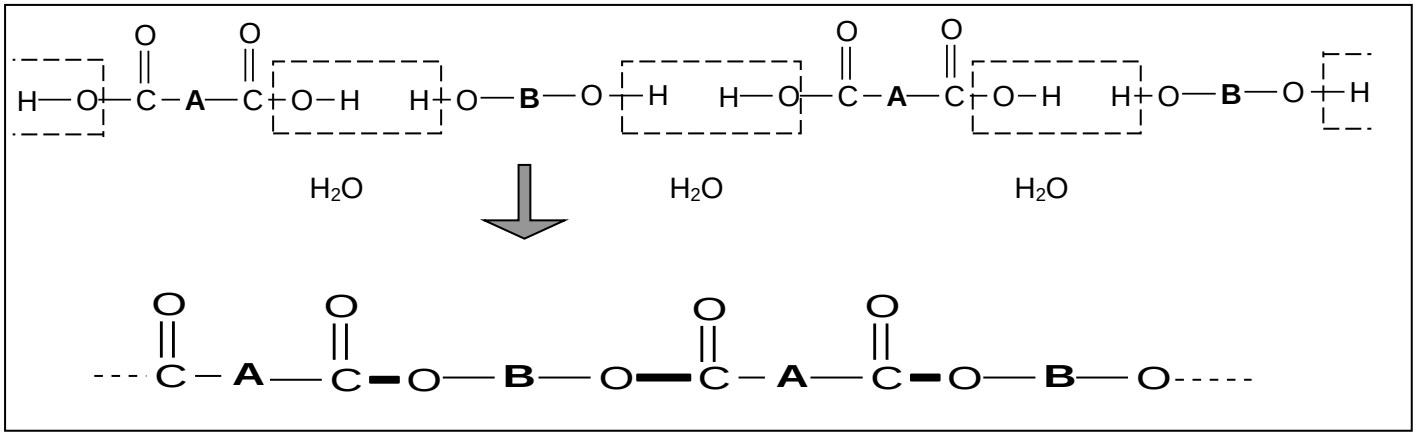
Condensation polymerisation

- Occurs when smaller molecules known as monomers join together to form a condensation polymer, with the elimination of small molecules such as HC*l*, H_2O or NH_3.
- Polyesters fall in this category of polymers.
- Each monomer must have TWO reactive ends

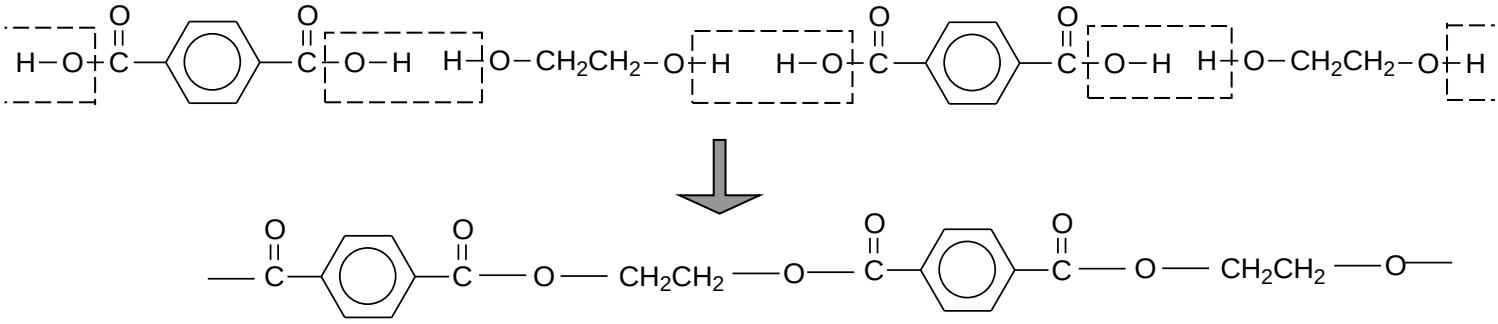
e.g. Monomer 1 – 2 carboxylic acid groups (diacid)
Monomer 2 – 2 alcohol groups (diol)



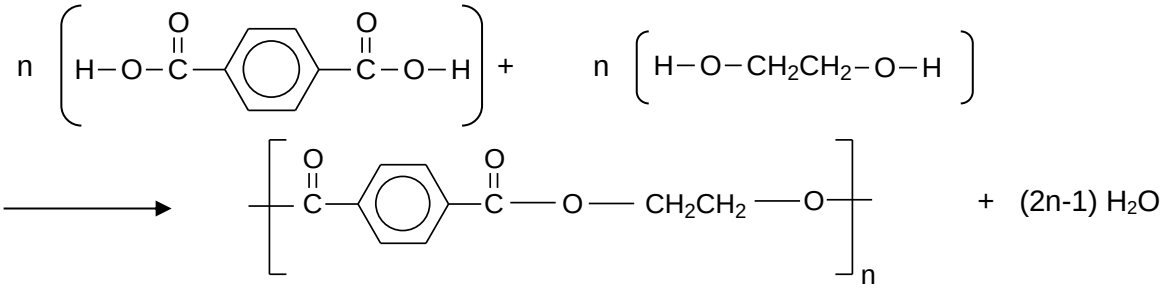
Formation of a polyester



TERYLENE (a polyester)



The reaction can be simplified as follows:



Uses of polyesters

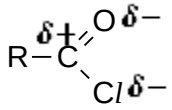
- leading synthetic fibre, its principal use is in clothing (crease resistant)
- as a good thermal insulator
- can be made into a thin but tough film
- used as containers/ packaging material

2.2 Acid chlorides (acyl chlorides)

2.2.1 Chemical Properties

Acid chlorides are highly reactivity.

There are two highly electron–withdrawing atoms (C*l* and O) bonded to the acyl carbon atom.

This makes the carbon atom of the acyl chloride  extremely **<u>electron–deficient</u>**.

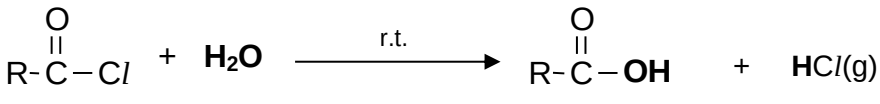
Therefore, the carbon is **<u>very susceptible</u>** to reaction with nucleophiles and acid chlorides undergo nucleophilic substitution readily.

This high reactivity will be more obvious when the hydrolysis reactions with water for acid chlorides (RCOC*l*), alkyl chlorides (R–C*l*) and aryl chlorides (Ar–C*l*) are compared on pg 25.

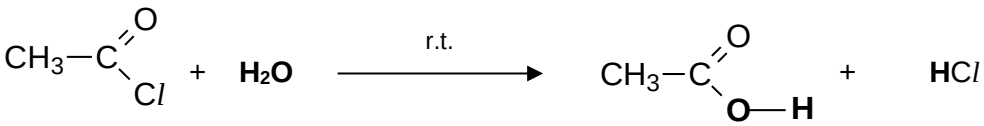
2.2.2 Nucleophilic (acyl) substitution reaction

(a) Reaction with water

(i)

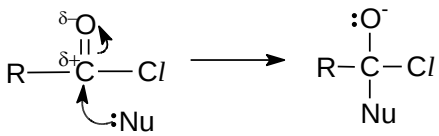
Type of reaction	Nucleophilic substitution
Reagents & Conditions	**H_2O, room temperature**
General equation	**acid chloride** + **H_2O** $\xrightarrow{\text{r.t.}}$ **acid** + **hydrogen chloride** 
Observation	white fumes (of HC*l*) evolved

<u>Example</u>

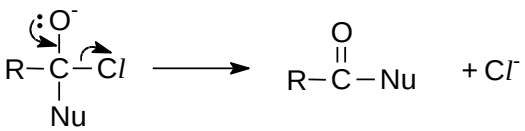


ethanoyl chloride | ethanoic acid | (white fumes evolved)

<u>Useful information on the mechanism of the reactions of acyl chlorides:</u>
The carbonyl group in acyl chlorides can undergo nucleophilic addition in a manner similar to carbonyl compounds:



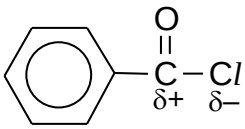
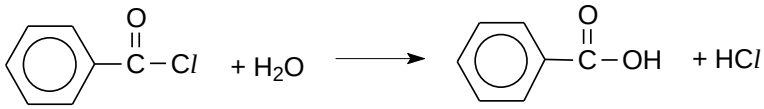
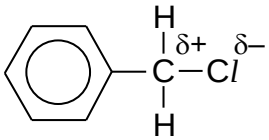
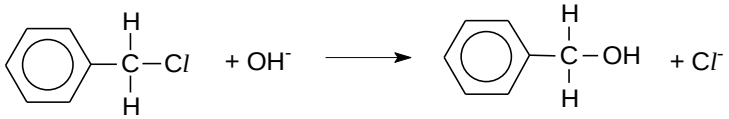
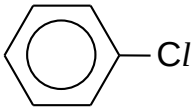
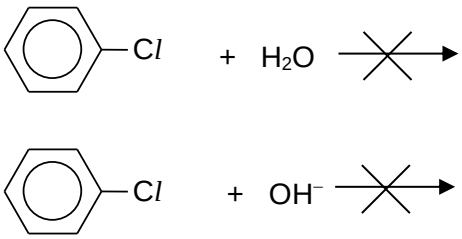
Unlike carbonyl compounds, the C*l* atom in acyl chlorides is a good leaving group:



Nucleophilic acyl substitution has taken place, via a mechanism involving nucleophilic addition, followed by elimination.

(ii) Relative ease of hydrolysis reactions between acid chlorides, alkyl chlorides and aryl chlorides

How does the ease of hydrolysis of acyl chlorides compare with that of alkyl and aryl chlorides?

	Hydrolysis reaction
ACID CHLORIDE  Benzoyl chloride **MOST REACTIVE**	 Nucleophile: **H_2O** Condition: **room temperature** ❑ The carbon of the acyl group is **highly electron–deficient** because it is bonded to **TWO highly electronegative** atoms, oxygen and chlorine. ❑ This makes the carbon **very susceptible** to reaction with nucleophiles. ❑ Therefore, even H_2O, a weak nucleophile, can hydrolyse it.
ALKYL CHLORIDE  (chloromethyl)benzene	 Nucleophile: **OH^-** Condition: **heat under reflux** ❑ The carbon atom is bonded to **only one electronegative** atom, chlorine. ❑ That carbon is less **electron–deficient**. ❑ With H_2O, reaction is very slow, if at all, even with heating. ❑ A stronger nucleophile like OH^-, with heat under reflux condition, is required for hydrolysis.
ARYL CHLORIDE  chlorobenzene **NO REACTION**	 ❑ **No hydrolysis** occurs under similar conditions mentioned above. ❑ The **lone pair on Cl** can **delocalise into** the **π electron cloud of the benzene ring** ❑ The C–Cl bond, having **partial double bond character**, is stronger and the carbon atom is also less electron–deficient.

(iii) Distinguishing test for acid chlorides, alkyl chlorides and aryl chlorides

By making use of the relative rate of hydrolysis and reaction of Cl^- with aqueous $AgNO_3$ to form a **white precipitate** ($AgCl$), the 3 types of chlorides can be distinguished.

Test	Observation
Aqueous $AgNO_3$, warm.	Acid chloride: white precipitate appears **immediately** Alkyl chloride: **slower** appearance of white precipitate Aryl chloride: **no** white precipitate.

Exercise 10

A comparison is made of the rate of the hydrolysis of four halogenocompounds by warm NaOH(aq).

CH_3CH_2COCl	C_6H_5Cl	$(CH_3)_3CBr$	$(CH_3)_3CI$
W	**X**	**Y**	**Z**

How will these rates compare?

fastest ⟶ slowest

A	**W**	**Y**	**Z**	**X**
B	**W**	**Z**	**Y**	**X**
C	**X**	**Z**	**Y**	**W**
D	**Z**	**Y**	**X**	**W**

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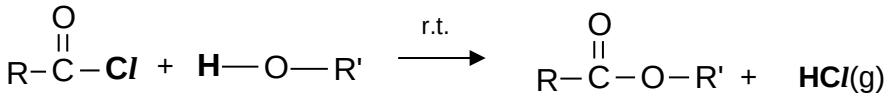
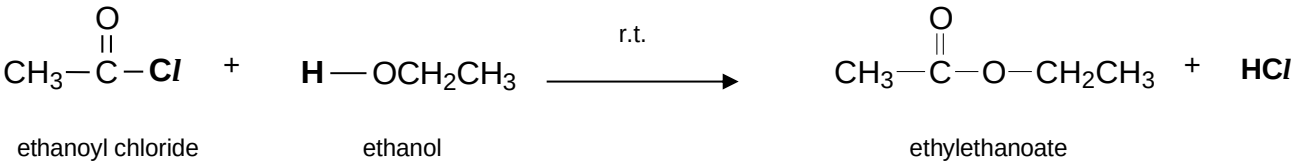
(b) Formation of esters

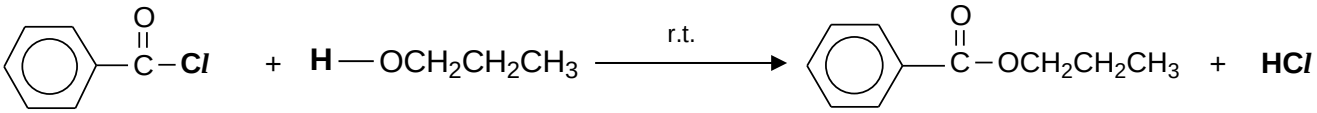
(i) Acid chloride with alcohols

Type of reaction	nucleophilic (acyl) substitution
Reagents & Conditions	alcohols, room temperature
General equation	**acid chloride** + **alcohol** → **ester** + **hydrogen chloride** 
Observation	white fumes (of HC*l*) evolved

Example



ethanoyl chloride + ethanol → ethylethanoate + **HC*l***

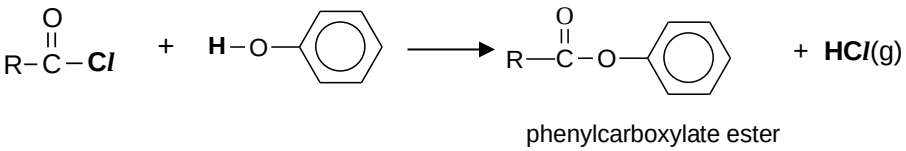


benzoyl chloride + propanol → propylbenzoate + **HC*l***

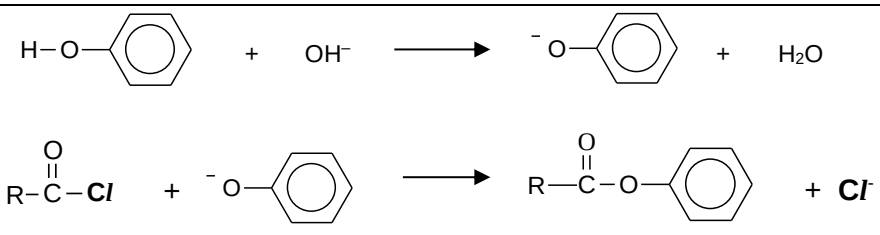
(ii) Acid chloride with phenol

Type of reaction	nucleophilic (acyl) substitution

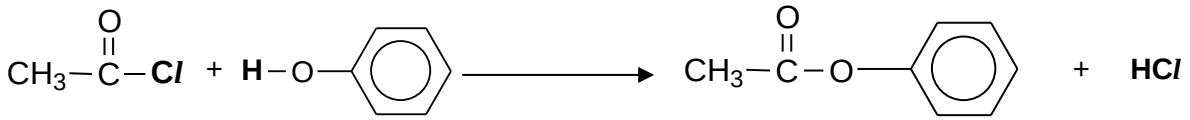
Method 1

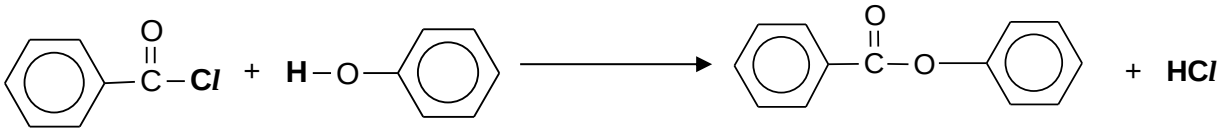
Reagents & Conditions	phenol, room temperature
General Eqn	**acid chloride** + **phenol** → **ester** + **hydrogen chloride**  phenylcarboxylate ester
Observation	white fumes (of HC*l*) evolved

Method 2

Reagents & Conditions	Stage 1: phenol and NaOH Stage 2: sodium phenoxide formed in stage 1 and acid chloride
General Eqn	 phenylcarboxylate ester
NaOH(aq) is added to phenol to form the phenoxide ion, which is a stronger nucleophile than phenol, before adding the acid chloride to the mixture. This will result in higher yield of the ester	

Example





SUMMARY for FORMATION OF ESTER

carboxylic acid + alcohol $\xrightarrow{\text{Conc. } H_2SO_4, \text{ heat under reflux}}$ ester + H_2O

carboxylic acid + phenol $\longrightarrow$ no reaction!!!

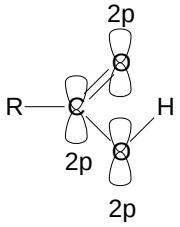
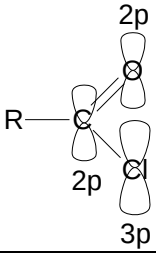
acid chloride + alcohol $\xrightarrow{\text{r.t.}}$ ester + HCl

acid chloride + phenol $\xrightarrow{\text{NaOH, r.t.}}$ ester + Cl^-

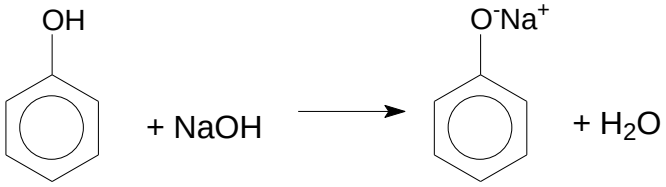
1. Why phenol cannot react with carboxylic acid to form ester?

   - Phenol is a weaker nucleophile than alcohol as the lone pair of electrons on the oxygen is delocalised into the benzene ring.
   - Hence, it is not nucleophilic enough to react with a carboxylic acid to form ester.

2. Why can alcohol react with acid chloride to form ester under a milder condition as compared to the reaction with carboxylic acid?

	
In **carboxylic acid** • **Overlap of 2p orbital of the C atom with the 2p orbitals of the two neighbouring O atoms** is **more effective.** • **Delocalisation of lone pair of electron from O atom is more effective** and **diminishes the electron deficiency in C.** • C is **less electron deficient and less susceptible to a reaction with a nucleophile** • Hence, **more vigorous condition** is required for reaction to take place. for reaction to take place.	In **acid chloride** • **Overlap of 2p orbital of the C atom with the 3p orbital of the Cl atom** is **less effective.** • **Delocalisation of lone pair of electron from Cl atom is less effective.** • C is **more electron deficient and more susceptible to a reaction with a nucleophile** • Hence, **a milder condition** (room temperature) is used.

3. Why is NaOH preferred in the formation of ester between acid chloride and phenol?



- NaOH reacts with phenol to form phenoxide ion.
- The resulting phenoxide ion is a **stronger nucleophile** than the phenol.
- Hence, nucleophilic acyl substitution can take place more readily.

4. Can carboxylic acid react with phenoxide ion, which is a stronger nucleophile, to form ester?

   No! Instead of nucleophilic substitution, an acid base reaction will take place.

$$RCOOH + C_6H_5O^- \longrightarrow RCOO^- + C_6H_5OH$$

Exercise 11

An ester with an odour of banana has the following formula, $CH_3COOCH_2CH(CH_3)CH_2CH_3$

In which of the following will the substances react together to produce this ester?

A $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CO_2H + CH_3OH$

B $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2COCl + CH_3OH$

C $CH_3COCl + CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$

D $CH_3CO_2H + CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl$

E $CH_3CO_2Na + CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl$

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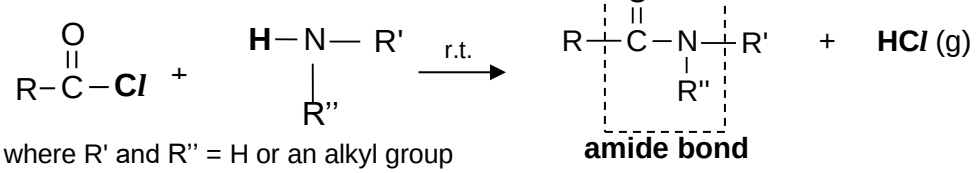
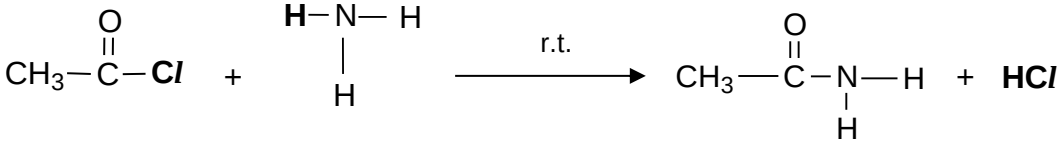
(c) Formation of amide

(This will also be covered in Nitrogen Compounds lecture)

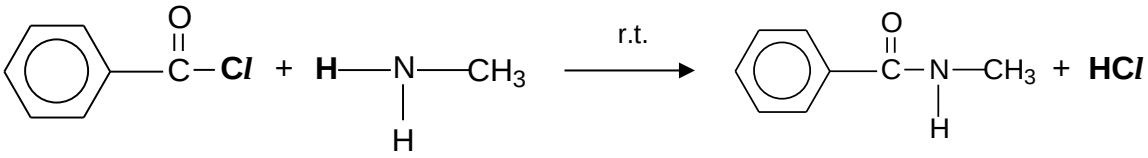
Type of reaction	nucleophilic (acyl) substitution / condensation
Reagents & Conditions	NH_3 / 1° amines / 2° amines, room temperature
General Eqn	**acid chloride** + **ammonia / 1° amine / 2° amine** → **amide** + **hydrogen chloride**  where R' and R'' = H or an alkyl group
Observation	white fumes (of HCl) evolved

Note:
Tertiary amines **do <u>not</u>** react with acid chlorides due to the absence of a hydrogen atom bonded to the N atom of tertiary amine.

Example



ethanoyl chloride ammonia ethanamide



benzoyl chloride methylamine N–methylbenzamide

Summary
FORMATION OF AMIDE

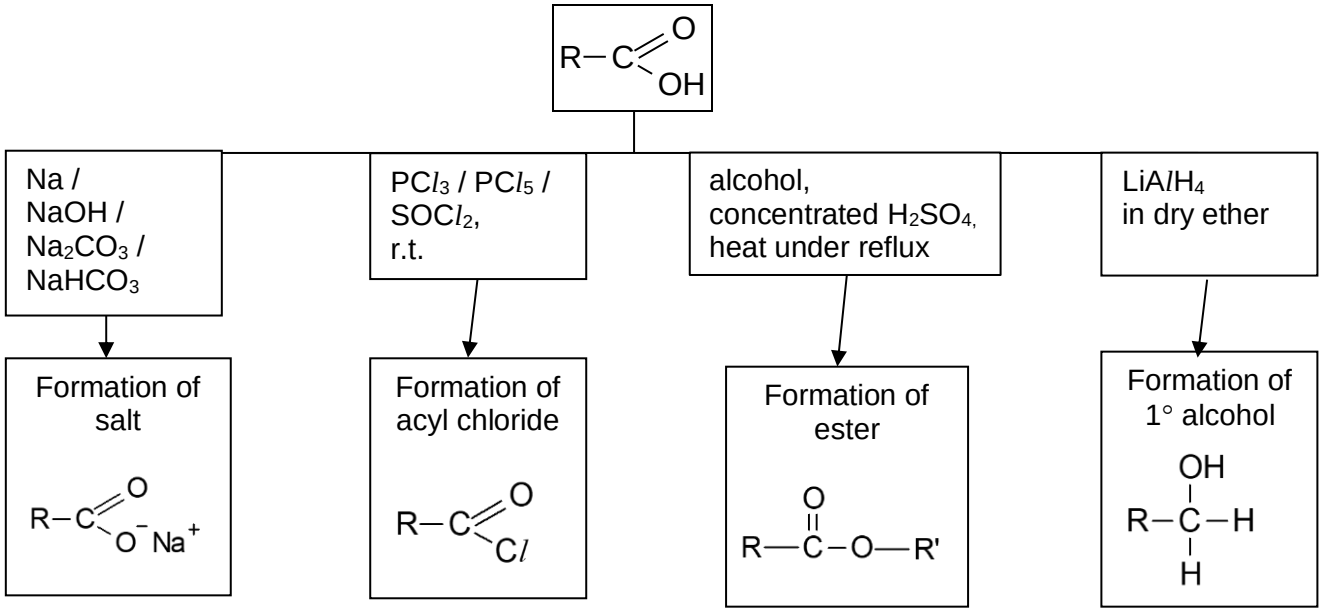
acid chloride + amine ⟶ amide + HC*l*

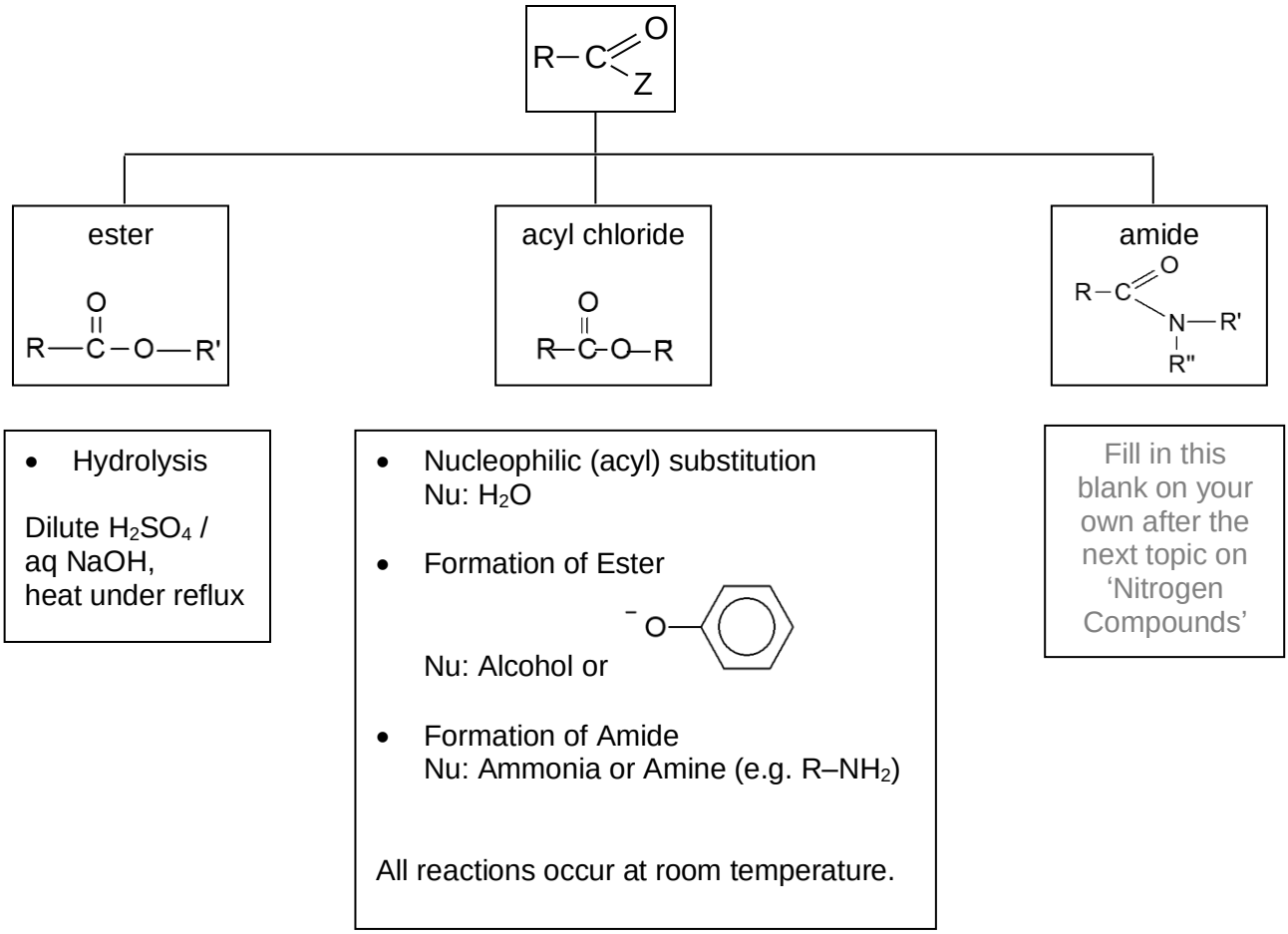
carboxylic acid + amine ⟶ DOES NOT GIVE AMIDE

This is because reaction between RCOOH + R'NH_2 is an acid–base reaction. A salt will be formed instead.

$$RCOOH + R'NH_2 \longrightarrow RCOO^-R'NH_3^+$$

Summary


Na / NaOH / Na_2CO_3 / $NaHCO_3$
PCl_3 / PCl_5 / $SOCl_2$, r.t.
alcohol, concentrated H_2SO_4, heat under reflux
$LiAlH_4$ in dry ether
Formation of salt
Formation of acyl chloride
Formation of ester
Formation of 1° alcohol


ester
acyl chloride
amide
• Hydrolysis
Dilute H_2SO_4 / aq NaOH, heat under reflux
• Nucleophilic (acyl) substitution
Nu: H_2O
• Formation of Ester
Nu: Alcohol or
• Formation of Amide
Nu: Ammonia or Amine (e.g. R–NH_2)
All reactions occur at room temperature.
Fill in this blank on your own after the next topic on 'Nitrogen Compounds'