



CIE A Level Chemistry



Your notes

33.3 Acyl Chlorides

Contents

- * Acyl Chlorides
- * Addition-Elimination Reactions of Acyl Chlorides
- * Relative Ease of Hydrolysis



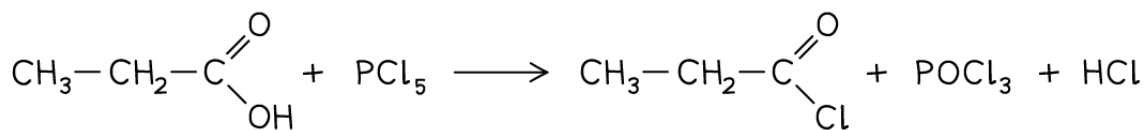
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Acyl Chlorides

Production of Acyl Chlorides

- Due to the increased reactivity of acyl chlorides compared to carboxylic acids, they are often used as **starting compounds** in organic reactions
- Acyl chlorides are compounds that contain an -COCl functional group and can be prepared from the reaction of carboxylic acids with:
 - Solid** phosphorus(V) chloride (PCl_5)
 - Liquid** phosphorus(III) chloride (PCl_3) and heat
 - Liquid** sulfur dichloride oxide (SOCl_2)
- Propanoyl chloride can this way be prepared from propanoic acid using the reactions above

Using propanoic acid to form propanoyl chloride



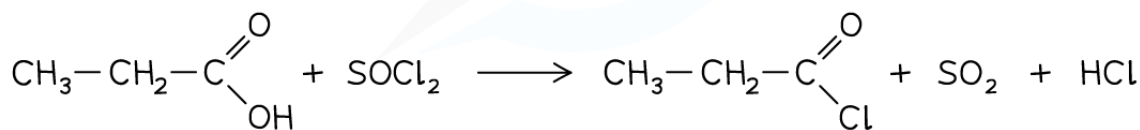
PROPANOIC ACID

PROPANOYL CHLORIDE



PROPANOIC ACID

PROPANOYL CHLORIDE



PROPANOIC ACID

PROPANOYL CHLORIDE

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Propanoic acid can be used to produce propanoyl chloride with different by-products depending on the reagent used



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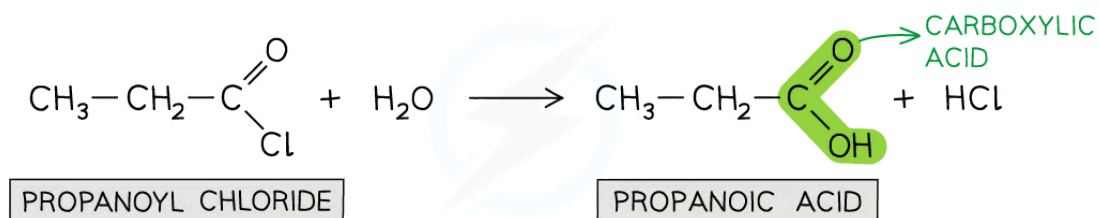
Reactions of Acyl Chlorides

- Acyl chlorides are **reactive** organic compounds that undergo many reactions such as **addition-elimination reactions**
- In addition-elimination reactions, the **addition** of a small molecule across the C=O bond takes place followed by **elimination** of a small molecule
- Examples of these addition-elimination reactions include:
 - Hydrolysis**
 - Reaction with alcohols and phenols to form **esters**
 - Reaction with ammonia and amines to form **amides**

Hydrolysis

- The **hydrolysis** of acyl chlorides results in the formation of a **carboxylic acid** and **HCl** molecule
- This is an **addition-elimination** reaction
 - A **water molecule** adds across the C=O bond
 - A hydrochloric acid (HCl) molecule is **eliminated**
- An example is the hydrolysis of propanoyl chloride to form propanoic acid and HCl

Hydrolysis of acyl chlorides



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Acyl chlorides are hydrolysed to carboxylic acids

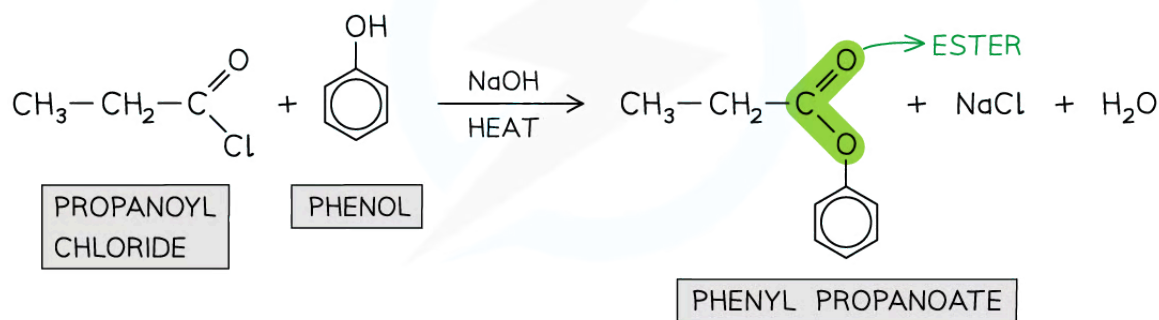
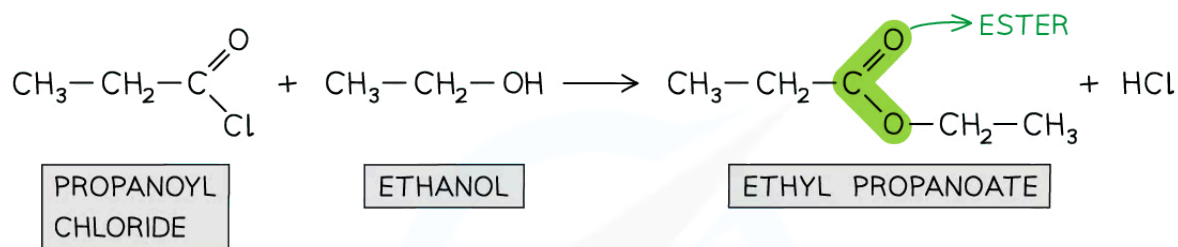
Formation of esters

- Acyl chlorides can react with **alcohols** and **phenols** to form esters
 - The reaction with phenols requires **heat** and a **base**
- Esters can also be formed from the reaction of **carboxylic acids** with phenol and alcohols however, this is a **slower** reaction as carboxylic acids are less reactive and the reaction does **not go to completion** (so less product is formed)
- Acyl chlorides are therefore more useful in the synthesis of esters
- The esterification of acyl chlorides is also an **addition-elimination** reaction
 - The alcohol or phenol adds across the C=O bond
 - A HCl molecule is eliminated

Esterification reactions using acyl chlorides



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Acyl chlorides undergo esterification with alcohols and phenols to form esters

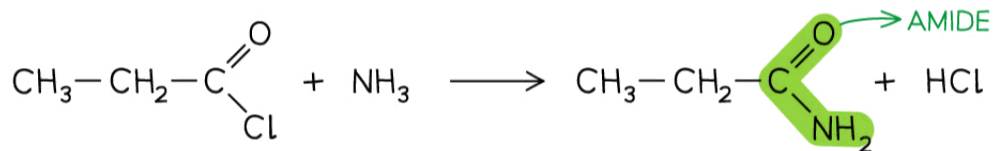
Formation of amides

- Acyl chlorides can form **amides** from their **condensation reaction** with **amines** and **ammonia**
- The nitrogen atom in ammonia and amines has a lone pair of electrons which can be used to attack the carbonyl carbon atom in the acyl chlorides
- The product is a **non-substituted** amide (when reacted with ammonia) or **substituted** amide (when reacted with primary and secondary amines)
- This is also an example of an **addition-elimination** reaction as
 - The amine or ammonia molecule adds across the C=O bond
 - A HCl molecule is eliminated

Amide formation reactions using acyl chlorides



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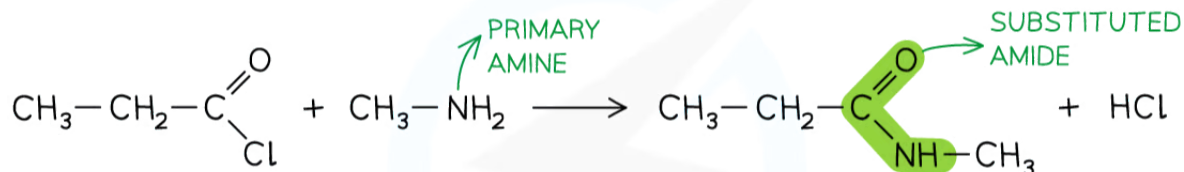


PROPANOYL
CHLORIDE

AMMONIA

PROPANAMIDE

AMIDE



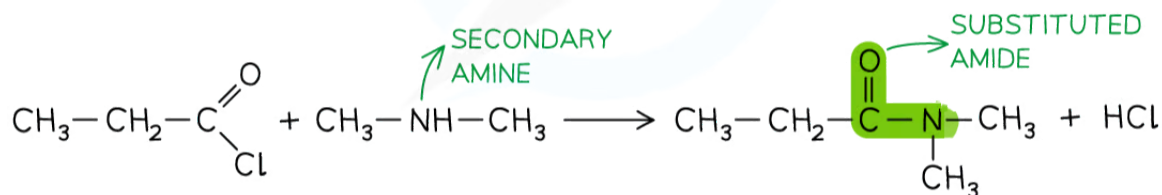
PROPANOYL
CHLORIDE

METHYLAMINE

N-METHYLPROPANAMIDE

SUBSTITUTED
AMIDE

PRIMARY
AMINE



PROPANOYL
CHLORIDE

DIMETHYL
AMINE

N,N-DIMETHYLPROPANAMIDE

SUBSTITUTED
AMIDE

SECONDARY
AMINE

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Acyl chlorides undergo condensation reactions with ammonia and amines to form amides



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Addition-Elimination Reactions of Acyl Chlorides

Mechanism of Addition – Elimination in Acyl Chloride Reactions

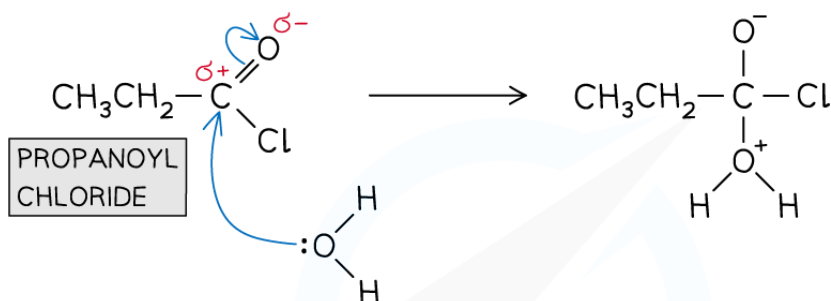
- Acyl chlorides undergo **addition-elimination** reactions such as **hydrolysis**, **esterification** reactions to form esters, and **condensation** reactions to form **amides**
- The general mechanism of these addition-elimination reactions involves two steps:
 - Step 1** – Addition of a **nucleophile** across the C=O bond
 - Step 2** – Elimination of a **small molecule** such as HCl or H₂O

Mechanism of hydrolysis of acyl chlorides

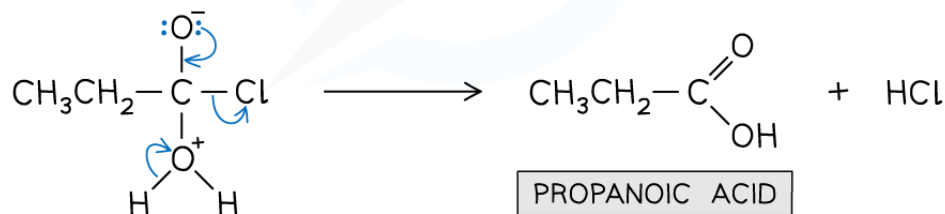
- In the **hydrolysis** of acyl chlorides, the water molecule acts as a **nucleophile**
 - The lone pair of the oxygen atom from water carries out an **initial attack** on the carbonyl carbon
 - This is followed by the elimination of a hydrochloric acid (HCl) molecule

Reaction mechanism of the hydrolysis of acyl chlorides

STEP 1: NUCLEOPHILIC ADDITION



STEP 2: ELIMINATION



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The two-step addition-elimination reaction mechanism of propanoyl chloride to form propanoic acid

Formation of esters: reaction mechanism

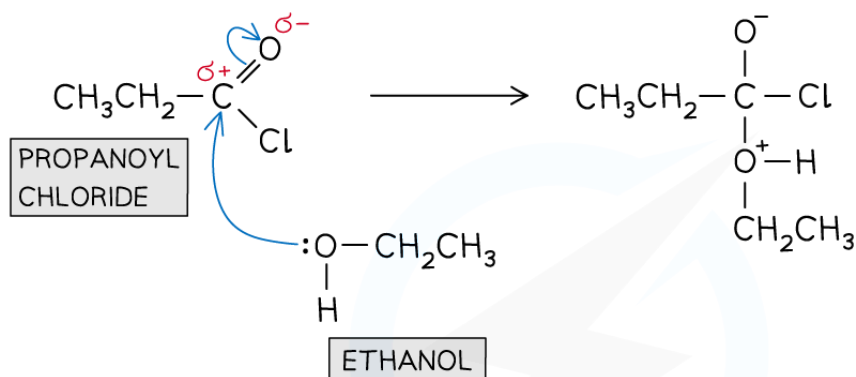


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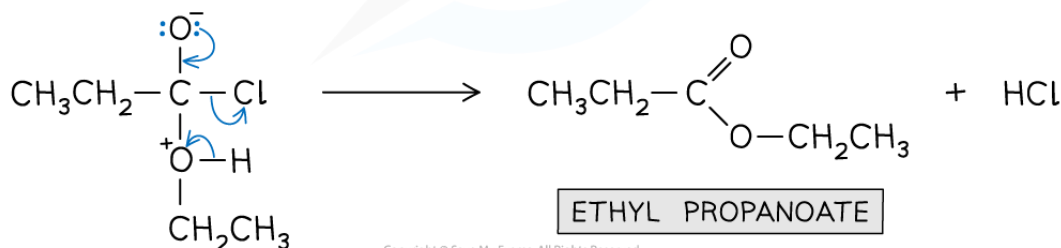
- In the **esterification** reaction of acyl chlorides, the alcohols or phenols act as a **nucleophile**
 - The lone pair of the alcohol / phenol oxygen atom carries out an **initial** attack on the carbonyl carbon
 - This is again followed by the elimination of an HCl molecule
- With phenols, the reaction requires **heat** to proceed and needs to be carried out in the presence of a **base**
- The base **deprotonates** the phenol to form a **phenoxide** ion which is a **better nucleophile** than the phenol molecule
 - The **phenoxide ion** carries out an **initial attack** on the carbonyl carbon
 - A small molecule of NaCl is eliminated

Reaction mechanism of the esterification of acyl chlorides with alcohols

STEP 1: NUCLEOPHILIC ADDITION



STEP 2: ELIMINATION

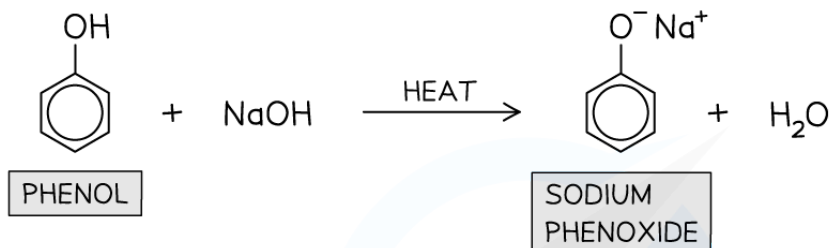


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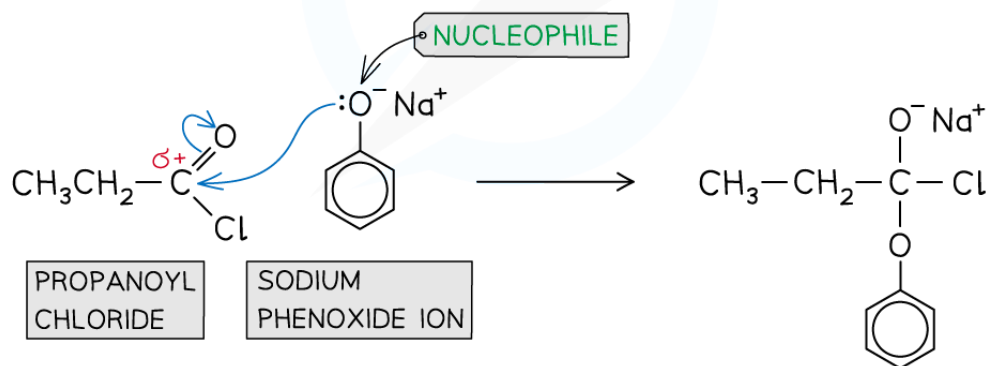
The two-step addition-elimination reaction mechanism of propanoyl chloride and ethanol to form ethyl propanoate and water

Reaction mechanism of the esterification of acyl chlorides with phenols

STEP 1: GENERATING THE NUCLEOPHILE

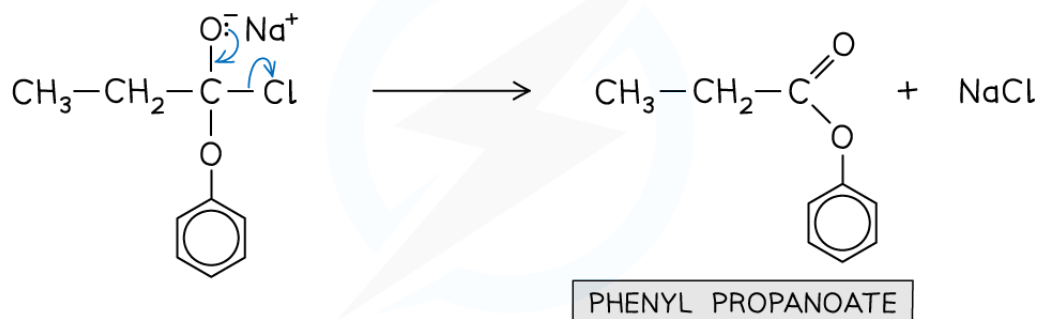


STEP 2: NUCLEOPHILIC ADDITION



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STEP 3: ELIMINATION



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The three-step addition-elimination reaction mechanism of propanoyl chloride with phenol to form phenyl propanoate

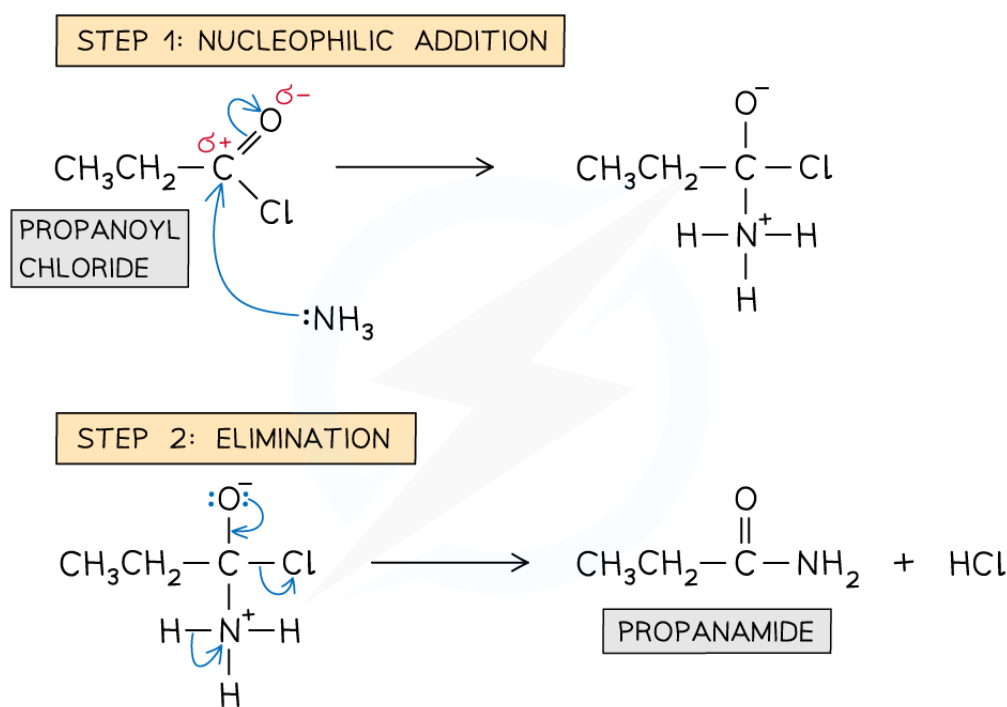
Formation of amides: reaction mechanism



Your notes

- The nitrogen atom in **ammonia** and **primary/secondary amines** act as a **nucleophile**
 - The lone pair of the nitrogen atom carries out an **initial** attack on the carbonyl carbon
 - This is followed by the elimination of an HCl molecule
- Both reactions of acyl chlorides with ammonia and amines are **vigorous** however there are also differences
 - With **ammonia** – The product is a **non-substituted amide** and **white fumes** of HCl are formed
 - With **amines** – The product is a **substituted amide** and the HCl formed reacts with the **unreacted amine** to form a **white organic ammonium salt**

Reaction mechanism of the formation of amides from acyl chlorides with ammonia



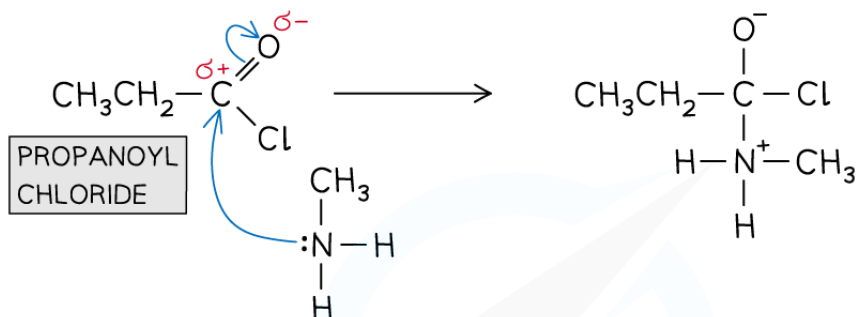
The two-step addition-elimination reaction mechanism of propanoyl chloride and ammonia to form propanamide

Reaction mechanism of the formation of amides from acyl chlorides with primary amines

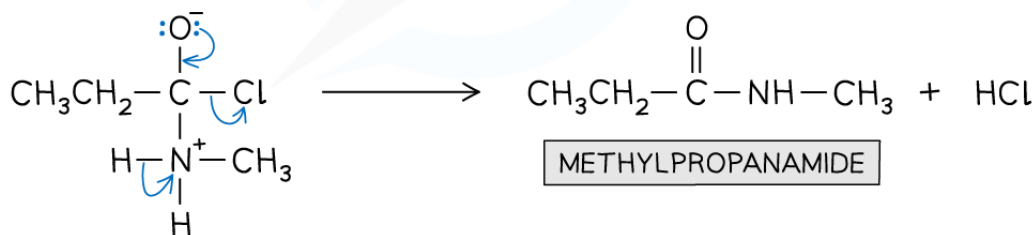


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STEP 1: NUCLEOPHILIC ADDITION

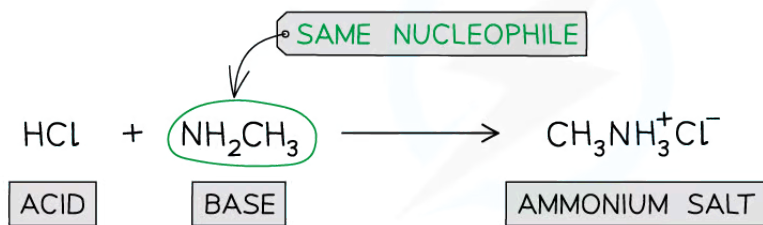


STEP 2: ELIMINATION



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STEP 3: ACID-BASE REACTION



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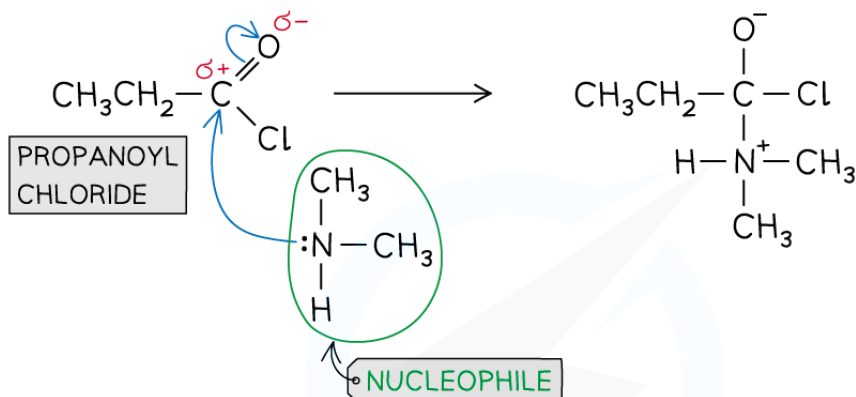
The addition-elimination reaction mechanism of propanoyl chloride and methylamine to form methylpropanamide

Reaction mechanism of the formation of amides from acyl chlorides with secondary amines

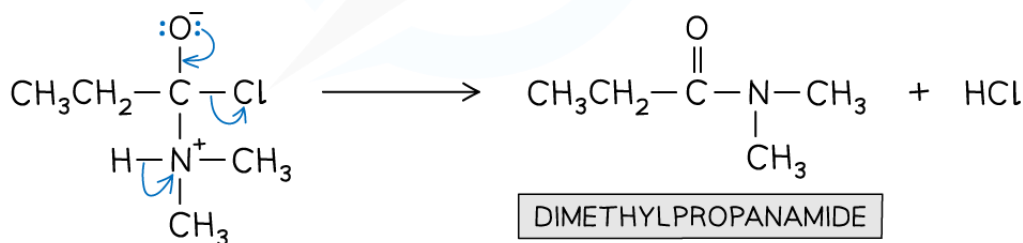


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STEP 1: NUCLEOPHILIC ADDITION

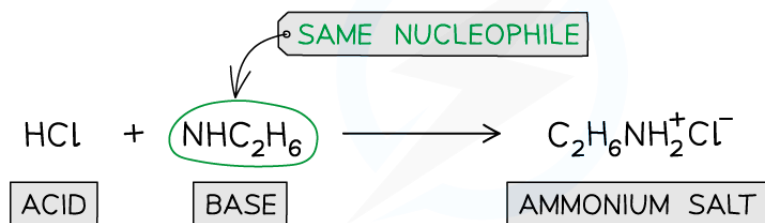


STEP 2: ELIMINATION



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STEP 3: ACID-BASE REACTION



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The addition-elimination reaction mechanism of propanoyl chloride and dimethylamine to form dimethylpropanamide



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Relative Ease of Hydrolysis

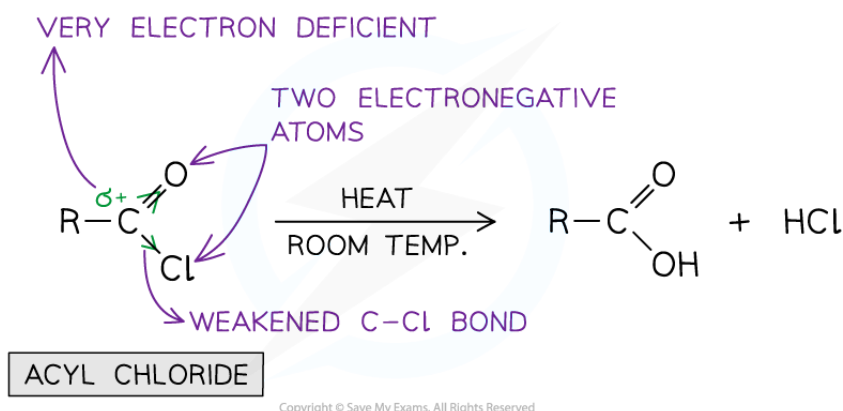
Hydrolysis of Acyl Chlorides, Alkyl Chlorides & Halogenoarenes

- Hydrolysis is the breakdown of a compound using **water**
- The ease of hydrolysis for different organic compounds may differ
- For example, the ease of hydrolysis, starting with the compounds most readily broken down, is: acyl chloride > alkyl chloride > aryl chloride
- This trend can be explained by looking at the **strength** of the C-Cl

Strength of C-Cl bond in acyl chlorides

- Acyl chlorides are hydrolysed most readily at **room temperature**
- This is because the carbon bonded to the chlorine atom is also attached to an oxygen atom
- There are two **strong electronegative** atoms pulling electrons away from the carbonyl carbon, leaving it very δ^+
- The C-Cl bond is therefore **weakened** and **nucleophilic attack** of the carbonyl carbon is much more **rapid**

Hydrolysis of acyl chlorides



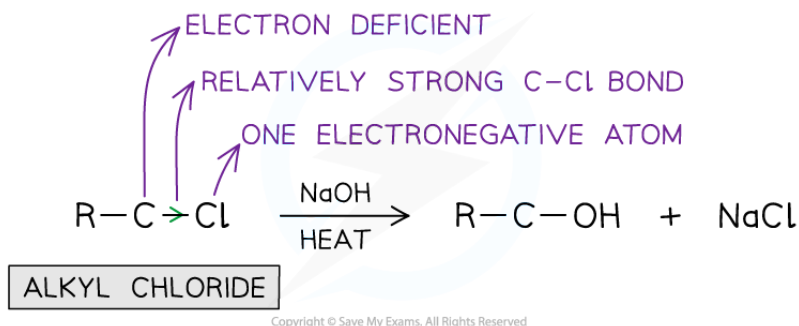
The hydrolysis of acyl chlorides occurs most readily

Strength of C-Cl bond in alkyl chlorides

- The carbonyl carbon in alkyl chlorides is only attached to **one electronegative** atom which pulls electrons away from it
- This carbon atom is therefore not very δ^+ and the C-Cl bond is stronger than the C-Cl bond in acyl chlorides
- The hydrolysis of alkyl chlorides, therefore, requires a **strong alkali** (such as OH^-) to be **refluxed** with it

- An OH^- ion will hydrolyse the alkyl chloride as it is a **stronger nucleophile** than H_2O

Hydrolysis of alkyl chlorides

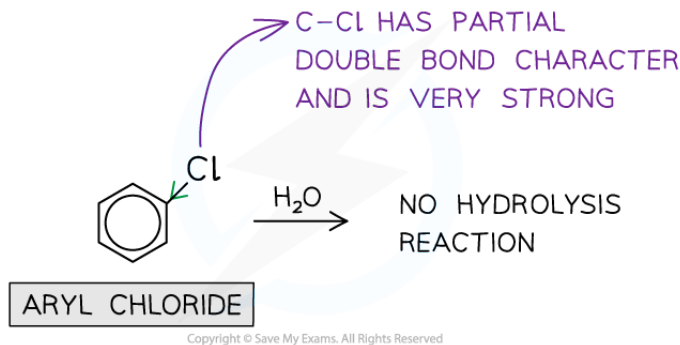


The hydrolysis of alkyl chlorides requires a strong nucleophile

Strength of C-Cl bond in aryl chlorides

- In aryl chlorides, the carbon atom bonded to the chlorine atom is part of the **delocalised π bonding system** of the benzene ring
- One of the lone pairs of electrons of the Cl atom **overlaps** with this **delocalised** system
- The C-Cl bond, therefore, has some **double-bond character** causing it to become **stronger**
- As a result, the C-Cl bond is difficult to break and **hydrolysis will not occur**

Hydrolysis of aryl chlorides



Due to the strong C-Cl bond in aryl chlorides, these compounds will not undergo hydrolysis



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