



# CIE A Level Chemistry



## 33.3 Acyl Chlorides

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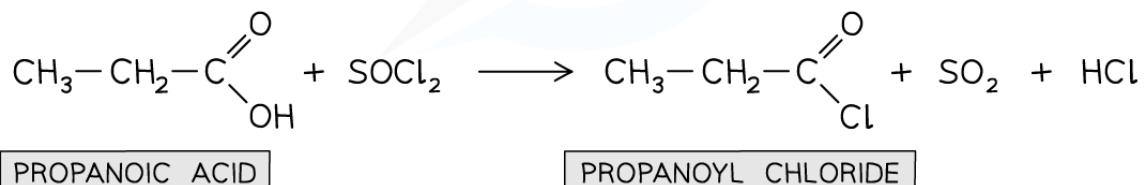
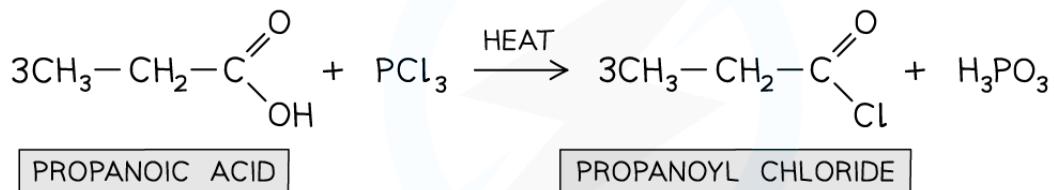
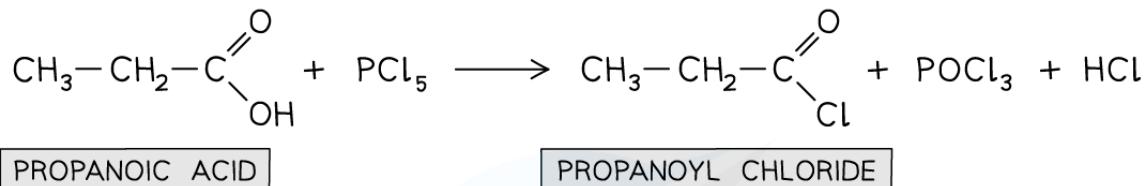
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## Acyl Chlorides

### 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  $\text{-COCl}$  functional group and can be prepared from the reaction of carboxylic acids with:
  - Solid** phosphorus(V) chloride ( $\text{PCl}_5$ )
  - Liquid** phosphorus(III) chloride ( $\text{PCl}_3$ ) and heat
  - Liquid** sulfur dichloride oxide ( $\text{SOCl}_2$ )
- Propanoyl chloride can this way be prepared from propanoic acid using the reactions above

#### Using propanoic acid to form 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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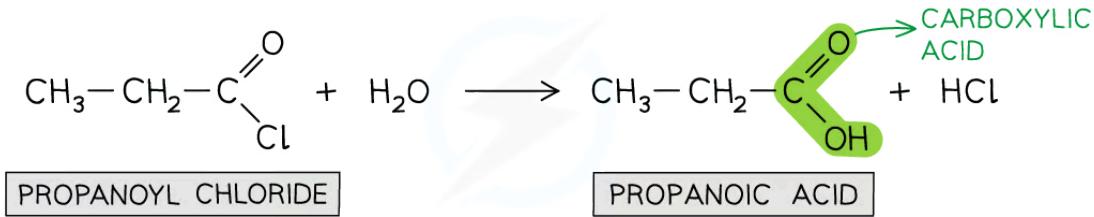
## Reactions of Acyl Chlorides

- **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

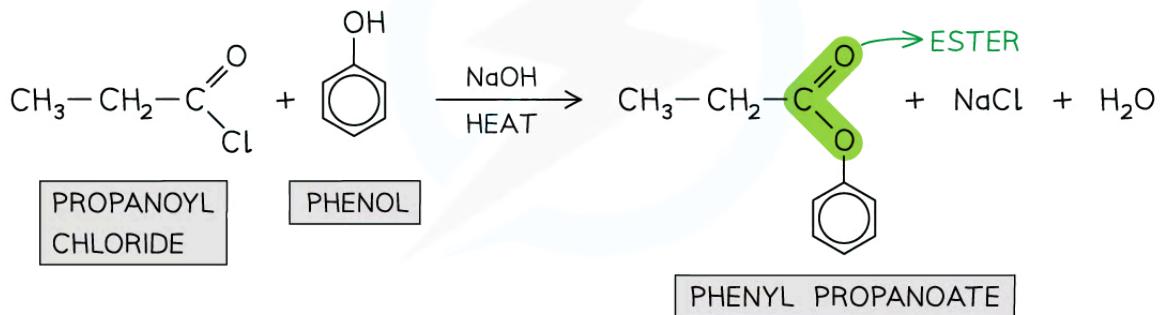
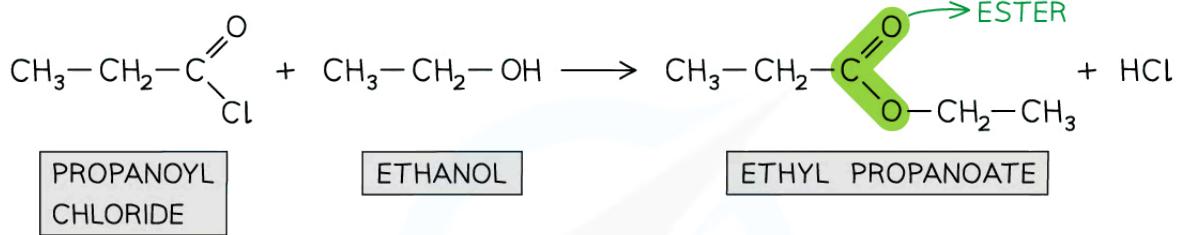


**Acyl chlorides are hydrolysed to carboxylic acids**

### 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**

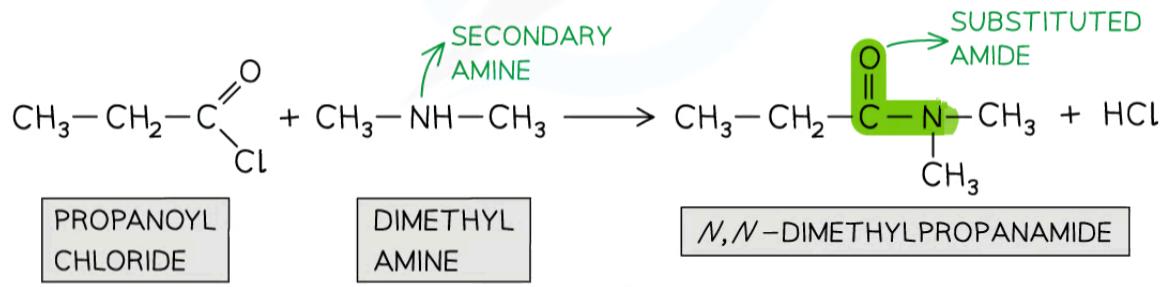
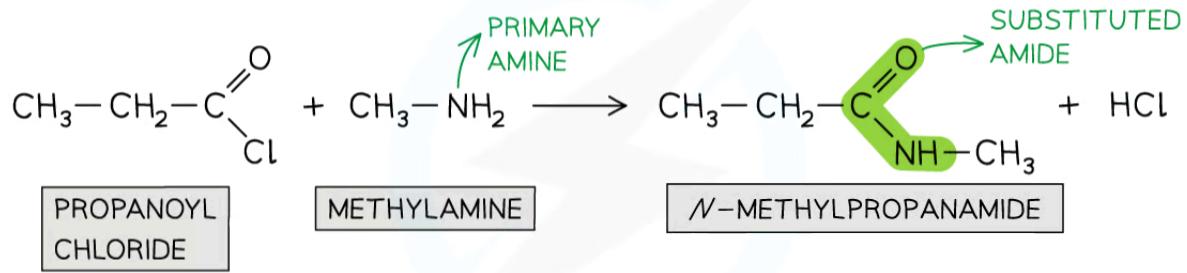
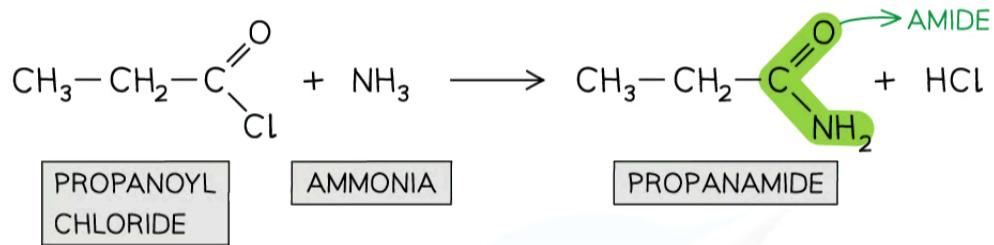
## Formation of amides

- 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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**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

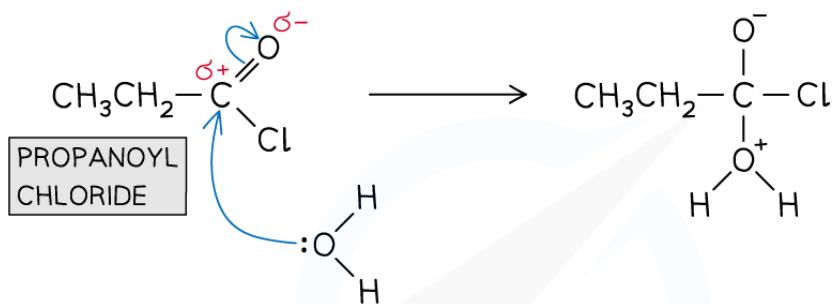
- Acyl chlorides undergo **addition-elimination** reactions such as **hydrolysis**, **esterification** reactions to form esters, and **condensation** reactions to form **amides**
- The general mechanism of these addition-elimination reactions involves two steps:
  - Step 1** – Addition of a **nucleophile**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

### Mechanism of hydrolysis of acyl chlorides

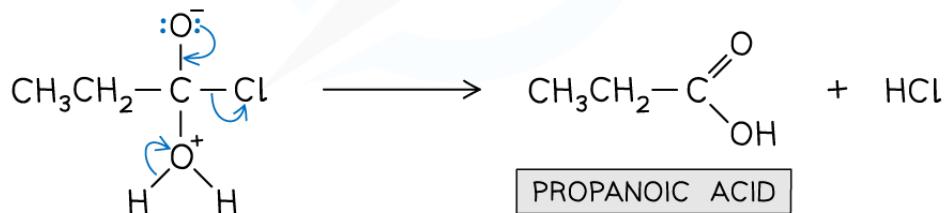
- In the **hydrolysis** of acyl chlorides, the water molecule acts as a **nucleophile**
  - The lone pair of the oxygen atom from water carries out an **initial attack** on the carbonyl carbon
  - This is followed by the elimination of a hydrochloric acid (HCl) molecule

#### 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

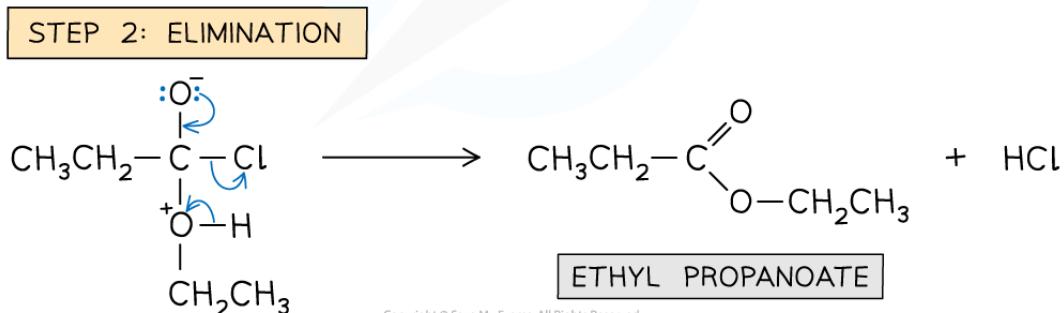
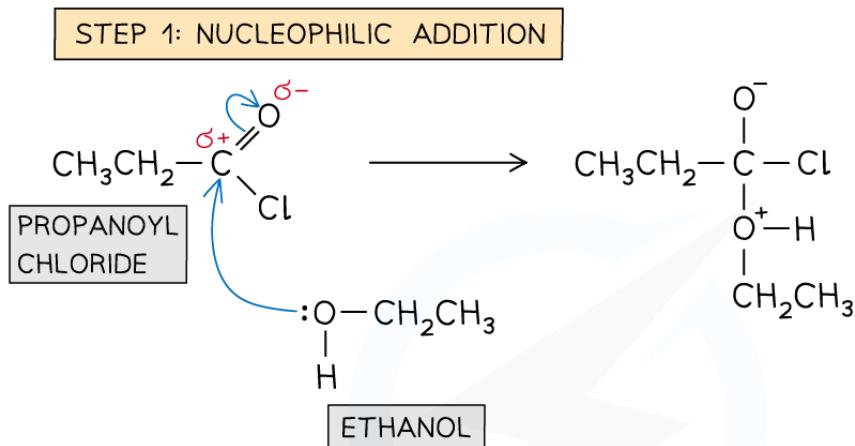
### Formation of esters: reaction mechanism



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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



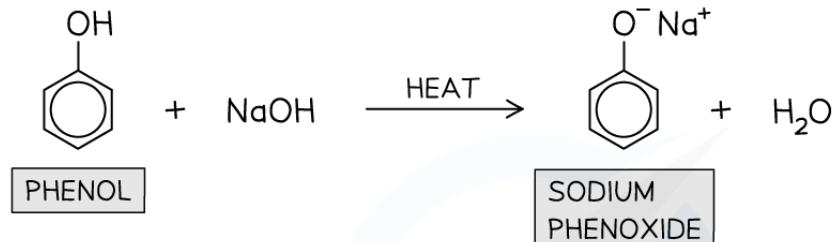
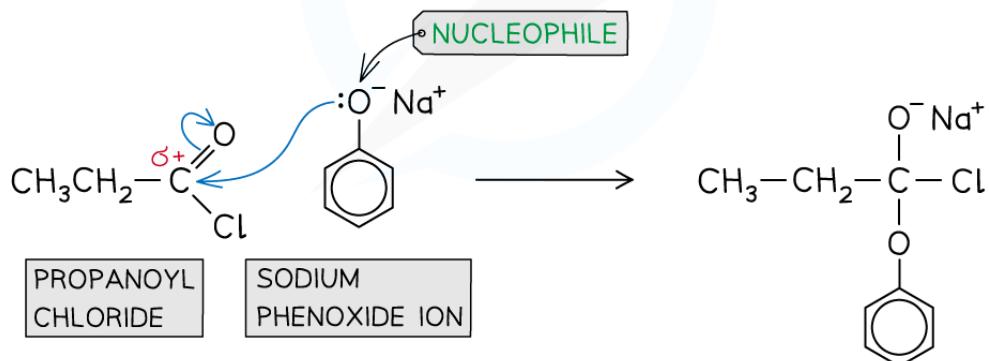
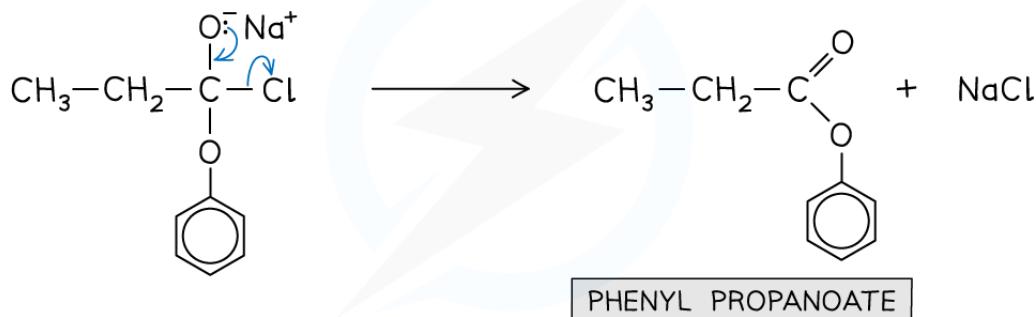
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The two-step addition-elimination reaction mechanism of propanoyl chloride and ethanol to form ethyl propanoate and water

### Reaction mechanism of the esterification of acyl chlorides with phenols



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**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**

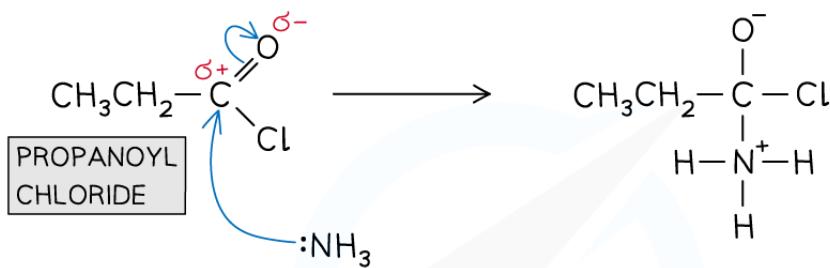


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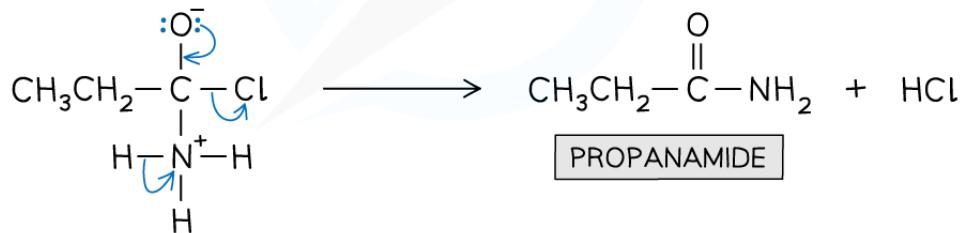
- The nitrogen atom in **ammonia** and **primary/secondary amines** act as a **nucleophile**
  - The lone pair of the nitrogen atom carries out an **initial** attack on the carbonyl carbon
  - This is followed by the elimination of an HCl molecule
- Both reactions of acyl chlorides with ammonia and amines 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

#### STEP 1: NUCLEOPHILIC ADDITION



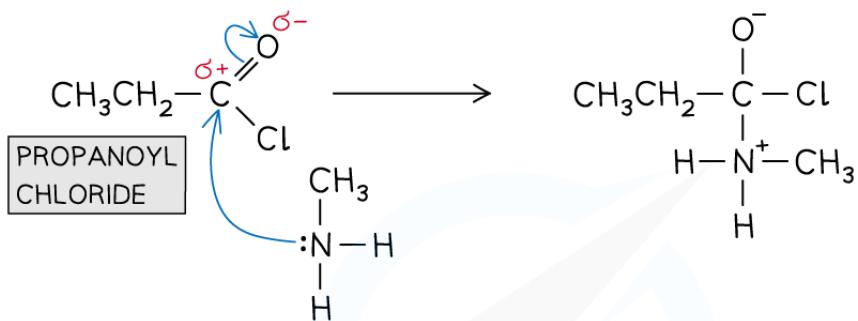
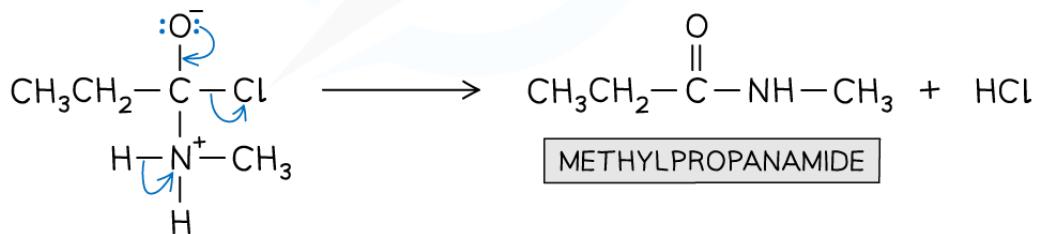
#### STEP 2: ELIMINATION



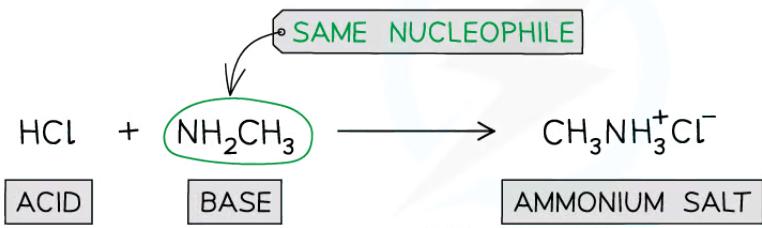
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**The two-step addition-elimination reaction mechanism of propanoyl chloride and ammonia to form propanamide**

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


**STEP 1: NUCLEOPHILIC ADDITION**

**STEP 2: ELIMINATION**


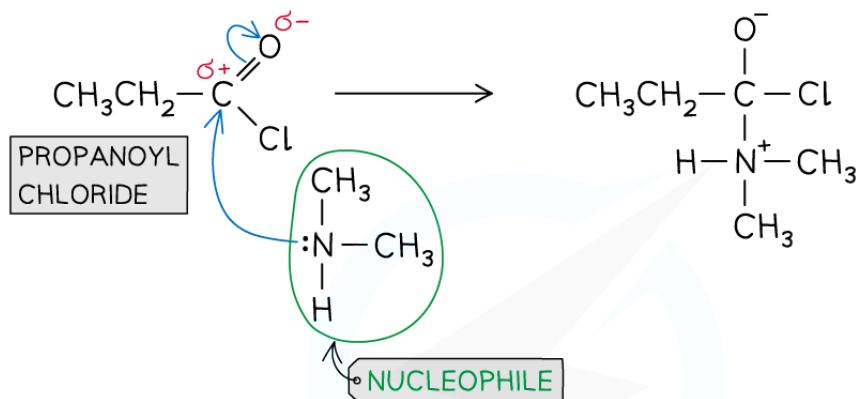
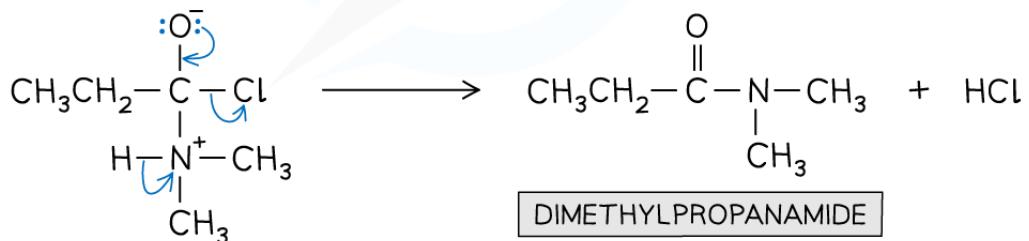
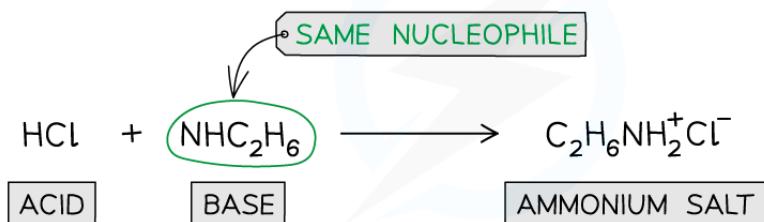
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**STEP 3: ACID-BASE REACTION**


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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**


**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

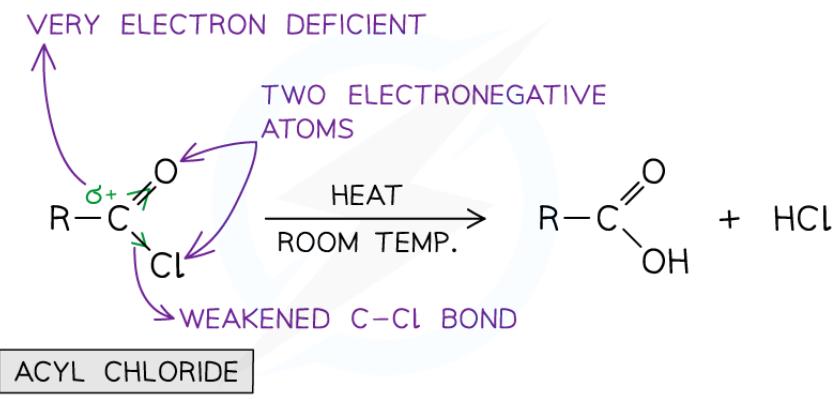
### Hydrolysis of Acyl Chlorides, Alkyl Chlorides & Halogenoarenes

- 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  $\delta^+$
- The C-Cl bond is therefore **weakened** and **nucleophilic attack** of the carbonyl carbon is much more **rapid**

#### Hydrolysis of acyl chlorides


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*The hydrolysis of acyl chlorides occurs most readily*

#### Strength of C-Cl bond in alkyl chlorides

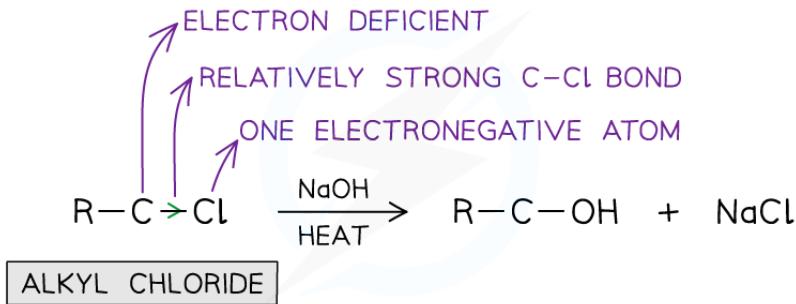
- The carbonyl carbon in alkyl chlorides is only attached to **one electronegative** atom which pulls electrons away from it
- This carbon atom is therefore not very  $\delta^+$  and the C-Cl bond is stronger than the C-Cl bond in acyl chlorides
- The hydrolysis of alkyl chlorides, therefore, requires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

- An  $\text{OH}^-$  ion will hydrolyse the alkyl chloride as it is a **stronger nucleophile** than  $\text{H}_2\text{O}$



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### Hydrolysis of alkyl chlorides

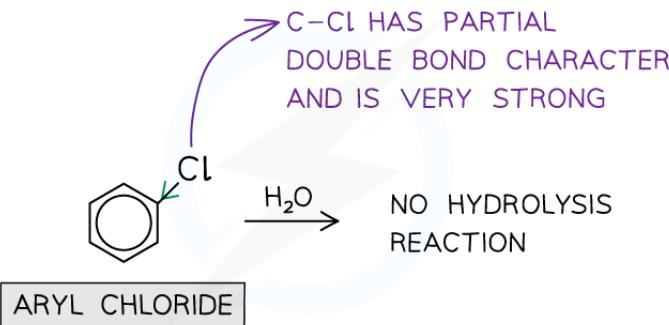
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*The hydrolysis of alkyl chlorides requires a strong nucleophile*

### Strength of C-Cl bond in aryl chlorides

- In aryl chlorides, the carbon atom bonded to the chlorine atom is part of the **delocalised  $\pi$  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

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