

# Cambridge (CIE) A Level Chemistry



Your notes

## Primary & Secondary Amines

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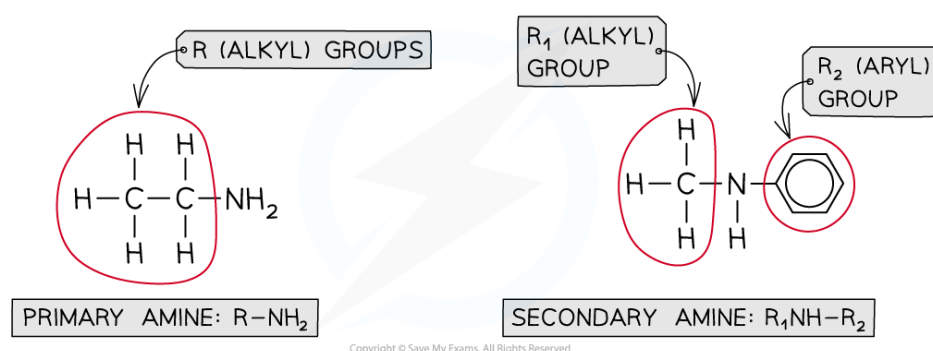
- \* Producing Amines
- \* Producing Amides
- \* Basicity of Amines



# Production of Primary & Secondary Amines

- **Primary amines** are organic compounds that have an  $\text{-NH}_2$  functional group attached to an alkyl or aryl group
- **Secondary amines** have two alkyl or aryl groups attached to an  $\text{-NH}$  group

## Structures of primary and secondary amines



*A primary amine has one R-group attached to the nitrogen atom, while a secondary amine has two R-groups attached to the nitrogen atom*

- Primary and secondary amines can be prepared from different reactions including:
  - The reaction of halogenoalkanes with ammonia
  - The reaction of halogenoalkanes with primary amines
  - The **reduction** of amides
  - The reduction of nitriles

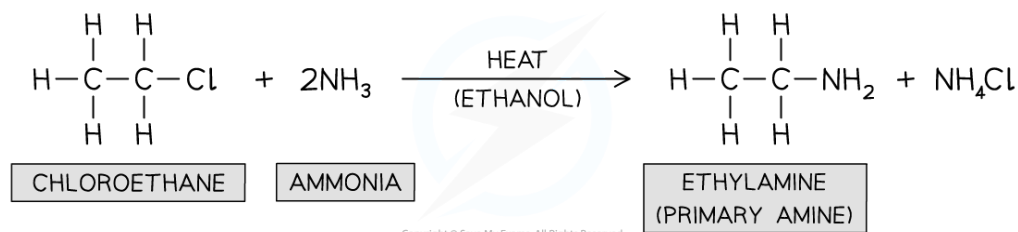
## Reaction of halogenoalkanes with ammonia

- This is a **nucleophilic substitution** reaction in which the nitrogen lone pair in ammonia acts as a **nucleophile** and **replaces** the halogen in the halogenoalkane
- When a halogenoalkane is reacted with **excess, hot ethanolic ammonia under pressure** a **primary amine** is formed

## Formation of primary amine



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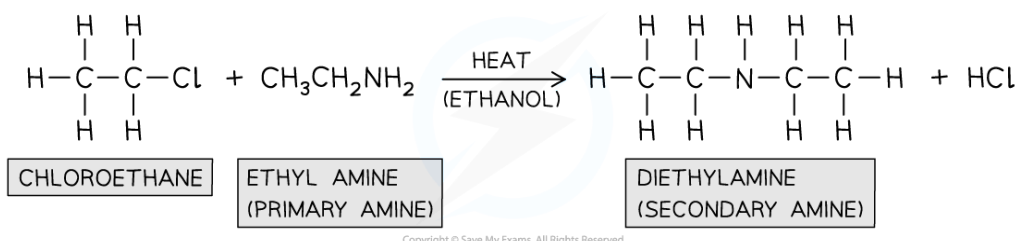


*Primary amines can be produced by a nucleophilic substitution of a halogenoalkane with an excess of ammonia*

## Reaction of halogenoalkanes with primary amine

- This is also a **nucleophilic substitution** reaction in which the nitrogen in the primary amine acts as a **nucleophile** and **replaces** the halogen in the halogenoalkane
- When a halogenoalkane is reacted with a **primary amine** in **ethanol** and **heated in a sealed tube, under pressure** a **secondary amine** is formed

### Formation of secondary amine



*Secondary amines can be produced by a nucleophilic substitution of a halogenoalkane with a primary amine*

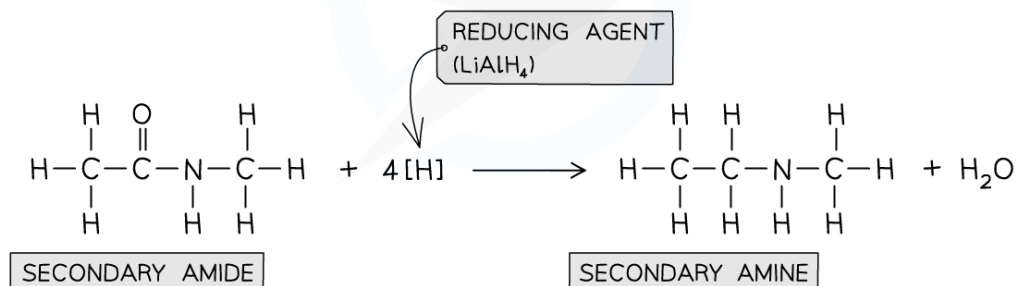
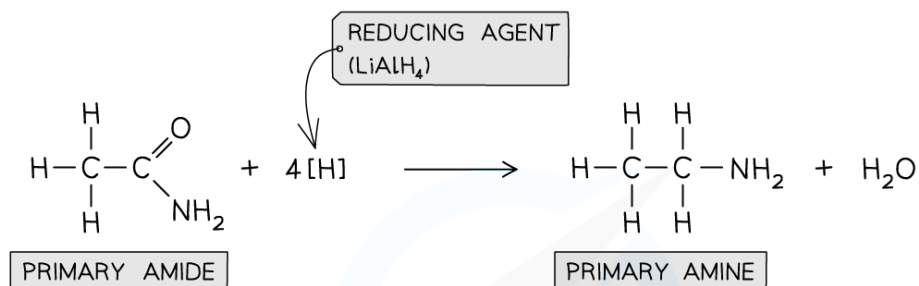
## Reduction of amides

- Amines can also be formed from the **reduction** of **amides** by  $\text{LiAlH}_4$  in **dry ether**
- Whether a primary or secondary amine is formed depends on the nature of the amide

### Formation of amines from amides



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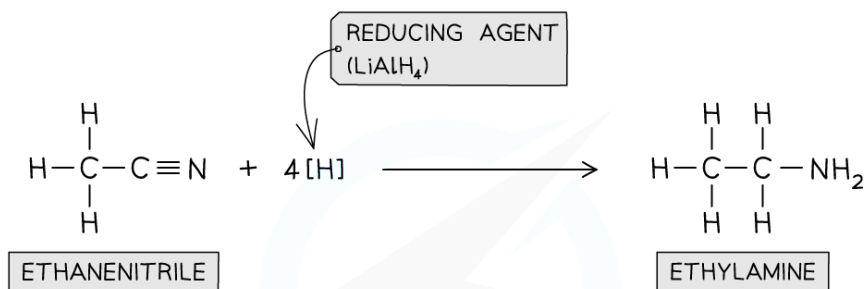
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*Amides can be reduced by  $\text{LiAlH}_4$  to form amines*

## Reduction of nitriles

- Nitriles contain a  $-\text{CN}$  functional group which can be **reduced** to an  $-\text{NH}_2$  group
- The nitrile vapour and **hydrogen gas** are passed over a **nickel catalyst** or  $\text{LiAlH}_4$  in **dry ether** to form a **primary amine**

## Formation of amines from nitriles



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*Nitriles can be reduced with  $\text{LiAlH}_4$  or  $\text{H}_2$  and Ni catalyst*



# Production of Amides

- **Amides** are organic compounds with an  $\text{-CONR}_2$  functional group
- They can be prepared from the **condensation reaction** between an **acyl chloride** and **ammonia** or **amine**
- In a **condensation** reaction, two organic molecules **join together** and in the process **eliminate** a small molecule
- In this case, the acyl chlorides and ammonia or amine **join together** to form an **amide** and **eliminate** an HCl molecule

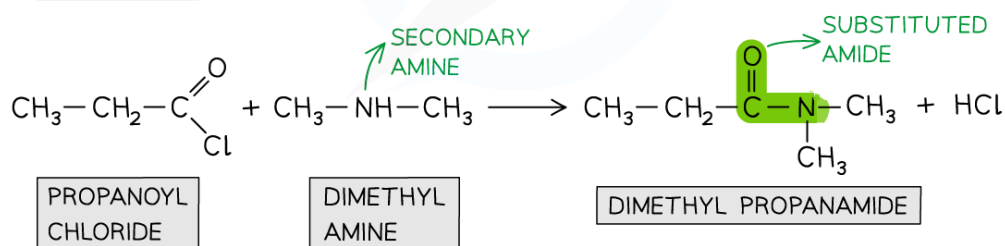
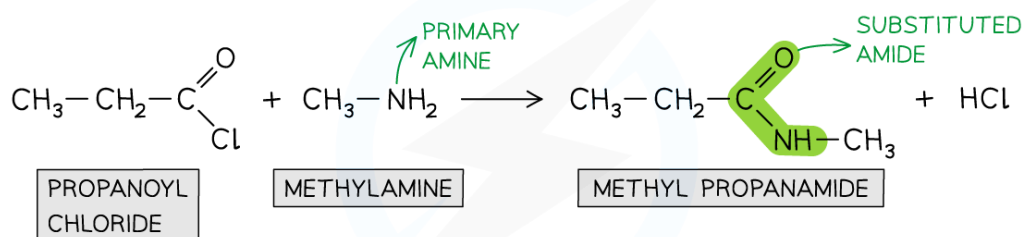
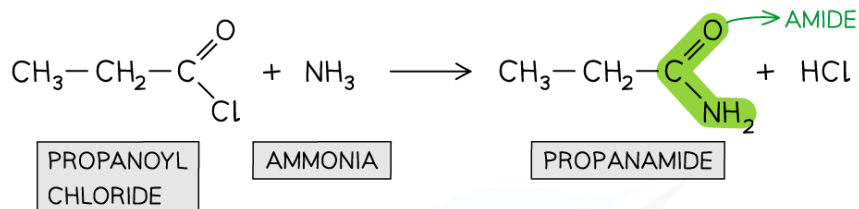
## Condensation reaction

- The chlorine atom in acyl chlorides is **electronegative** and draws electron density from the carbonyl carbon
- The carbonyl carbon is therefore **electron-deficient** and can be attacked by **nucleophiles**
- The nitrogen atom in ammonia and amines has a lone pair of electrons which can act as a **nucleophile** and attack the carbonyl carbon
- As a result, the C-Cl bond is **broken** and an **amide** is formed
- Whether the product is a **substituted** amide or not, depends on the nature of the **nucleophile**
  - Primary and secondary amines will give a **substituted amide**
  - The reaction of acyl chlorides with ammonia will produce a **non-substituted amide**
- **Note** that amides can also be formed from the condensation reaction between **carboxylic acids** and ammonia or amines
- However, this reaction is **slower** as carboxylic acids are **less reactive** than **acyl chlorides** and the reaction doesn't go to completion

## Condensation reactions of propanoyl chloride to form different substituted amides



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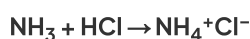
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**Acyl chlorides undergo condensation reactions with ammonia to form amides and with amines to form substituted amides**

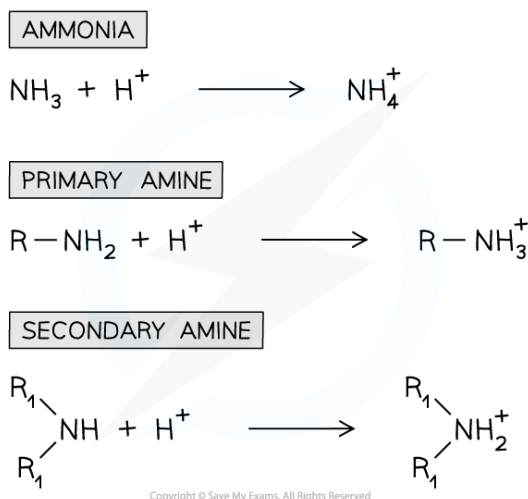


# Basicity of Aqueous Solutions of Amines

- The nitrogen atom in ammonia and amine molecules can **accept** a **proton** ( $\text{H}^+$  ion)
- They can therefore act as **bases** in aqueous solutions by **donating** their lone pair of electrons to a proton and forming a **dative bond**
  - For example, ammonia undergoes an **acid-base** reaction with dilute hydrochloric acid (HCl) to form a salt



## Ammonia and amines acting as a base



*The nitrogen atom in ammonia and amines can donate its lone pair of electrons to form a bond with a proton and therefore act as a base*

## Strength of ammonia and amines as bases

- The **strength** of amines depends on the **availability** of the lone pair of electrons on the nitrogen atom to form a dative covalent bond with a proton
- The **more readily** this lone pair of electrons is available, the **stronger the base** is
- Factors that may affect the **basicity** of amines include:
  - Positive inductive effect** - Some groups such as **alkyl groups** donate electron density to the nitrogen atom causing the lone pair of electrons to become more available and therefore **increasing** the amine's **basicity**
  - Delocalisation** - The presence of aromatic rings such as the **benzene ring** causes the lone pair of electrons on the nitrogen atom to be **delocalised** into the benzene

ring

- The lone pair becomes **less available** to form a dative covalent bond with ammonia and hence **decreases** the amine's **basicity**
- For example, ethylamine (which has an electron-donating ethyl group) is **more basic** than **phenylamine** (which has an electron-withdrawing benzene ring)



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