

34.1 Primary and secondary amines

Name: _____ Class: _____ Date: _____

Total: 10 marks

KEY WORDS amine 胺 • amide 酰胺 • basicity 碱性 • ammonia 氨 • nitrile 腈

Objective

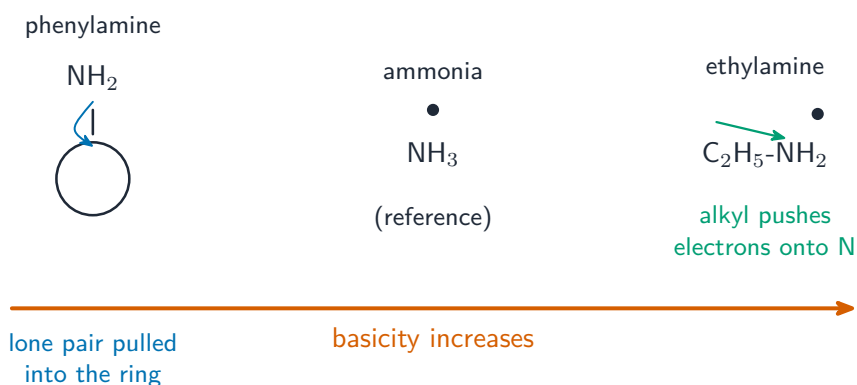
Build the skills to answer exam questions on **primary and secondary amines** 胺 — how they are made, and the trends in **basicity** 碱性.

You must be able to:

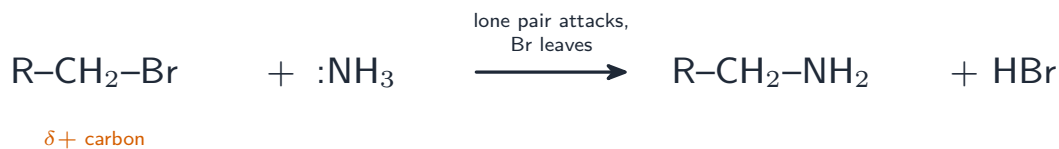
- give the reagents to make amines (from halogenoalkanes, amides, nitriles)
- explain why amines are basic
- explain and compare the basicity of ammonia, an aliphatic amine and phenylamine

1 Worked examples

■ Basicity



Basicity depends on the N lone pair: an alkyl group makes it more available (ethylamine strongest); a ring pulls it away (phenylamine weakest)



Routes to primary and secondary amines

- amines are basic because the **N lone pair** can accept an H^+ .
- basicity:** phenylamine < ammonia < ethylamine.
 - ethylamine: alkyl group pushes electrons onto N $\rightarrow$ lone pair more available $\rightarrow$ strongest.
 - phenylamine: lone pair delocalised into the ring $\rightarrow$ less available $\rightarrow$ weakest.
- make a primary amine:** halogenoalkane + excess NH_3 in ethanol, heat under pressure; or reduce a nitrile/amide with LiAlH_4 .

2 Practice

2.1 State why an amine is able to act as a base. [1]

2.2 Give the reagents to convert bromoethane into ethylamine. [2]

3 Exam-style questions

3.1 Which is the **strongest** base? [1]

- A** phenylamine
- B** ammonia
- C** ethylamine
- D** they are equal

3.2 Reduction of a nitrile, CH_3CN , with LiAlH_4 gives: [1]

- A** ethylamine
- B** ethanamide
- C** ethanoic acid

- D ethanenitrile

3.3 Explain why ethylamine is a stronger base than ammonia. [2]

3.4 Explain why phenylamine is a much weaker base than ethylamine. [3]

Solutions

2.1 the nitrogen lone pair can accept (donate to) an H^+ .

2.2 excess ammonia, NH_3 , in ethanol; heat under pressure.

3.1 C. Ethylamine — the alkyl group makes the lone pair most available.

3.2 A. LiAlH_4 reduces the nitrile to a primary amine, ethylamine.

3.3 the ethyl group pushes electron density onto the nitrogen (positive inductive effect); this makes the lone pair more available to accept an H^+ , so ethylamine is a stronger base than ammonia.

3.4 in phenylamine the nitrogen lone pair overlaps with / is delocalised into the benzene ring; so it is less available to accept an H^+ ; whereas in ethylamine the lone pair is fully available (and the alkyl group pushes electrons onto N), so phenylamine is much weaker.