

Exercise walk-through

Primary and secondary amines ■ 34.1

eXercise

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

Method — Basicity

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

- 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 .

Method — Basicity

phenylamine



ammonia



(reference)

ethylamine

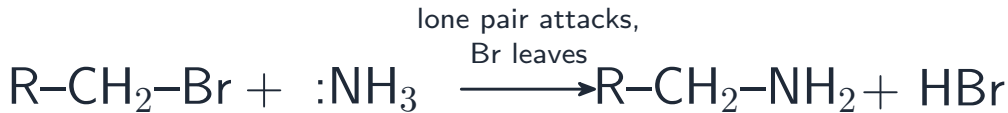


alkyl pushes
electrons onto N

lone pair pulled
into the ring

basicity increases

Method — Basicity



$\delta+$ carbon

Routes to primary and secondary amines

Practice 2.1 ■ 1 mark

State why an amine is able to act as a base.

Solution 2.1

Worked steps

the nitrogen lone pair can accept (donate to) an H^+ **B1**.

Practice 2.2 ■ 2 marks

Give the reagents to convert bromoethane into ethylamine.

Solution 2.2

Worked steps

excess ammonia, NH_3 , in ethanol **M1**; heat under pressure **A1**.

Exam-style 3.1 ■ 1 mark

Which is the **strongest** base?

A phenylamine

B ammonia

C ethylamine

D they are equal

Solution 3.1

A phenylamine

B ammonia

C ethylamine



D they are equal

Worked steps

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

Exam-style 3.2 ■ 1 mark

Reduction of a nitrile, CH_3CN , with LiAlH_4 gives:

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

Solution 3.2

Method: Basicity

A ethylamine



B ethanamide

C ethanoic acid

D ethanenitrile

Worked steps

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

Exam-style 3.3 ■ 2 marks

Explain why ethylamine is a stronger base than ammonia.

Solution 3.3

Method: Basicity

Worked steps

the ethyl group pushes electron density onto the nitrogen (positive inductive effect) **M1**; this makes the lone pair more available to accept an H^+ , so ethylamine is a stronger base than ammonia **A1**.

Exam-style 3.4 ■ 3 marks

Explain why phenylamine is a much weaker base than ethylamine.

Solution 3.4

Method: Basicity

Worked steps

in phenylamine the nitrogen lone pair overlaps with / is delocalised into the benzene ring (M1); so it is less available to accept an H^+ (M1); whereas in ethylamine the lone pair is fully available (and the alkyl group pushes electrons onto N), so phenylamine is much weaker (A1).