

Exercise walk-through

Phenylamine and azo compounds ■ 34.2

eXercise

You must be able to

- give the two-step route from benzene to phenylamine
- describe the formation of a diazonium salt and its conditions
- describe azo coupling and why azo compounds are coloured dyes

Method — Diazonium salts and azo dyes

- **make phenylamine:** benzene $\rightarrow$ (nitrate) $\rightarrow$ nitrobenzene $\rightarrow$ (Sn / conc. HCl, then NaOH) $\rightarrow$ phenylamine.
- **diazonium salt:** phenylamine + NaNO_2 + dilute acid, **below 10 °C** $\rightarrow$ benzenediazonium chloride.
- **azo coupling:** diazonium salt + phenol in NaOH(aq) $\rightarrow$ a coloured **azo compound** (a dye); the $-\text{N}=\text{N}-$ group links two rings.

Method — Diazonium salts and azo dyes



A pile of bright orange methyl orange azo dye powder

Method — Diazonium salts and azo dyes

phenylamine



ammonia



(reference)

ethylamine



alkyl pushes
electrons onto N

lone pair pulled
into the ring

basicity increases

Phenylamine is a weaker base than aliphatic amines

Practice 2.1 ■ 2 marks

Give the reagents to reduce nitrobenzene to phenylamine.

Solution 2.1

Method: Diazonium salts and azo dyes

Worked steps

tin (Sn) and concentrated hydrochloric acid **M1**; then NaOH(aq) **A1**.

Practice 2.2 ■ 1 mark

State the temperature needed to make a stable diazonium salt.

Solution 2.2

Method: Diazonium salts and azo dyes

Worked steps

below 10 °C (kept cold in an ice bath) **B1**.

Exam-style 3.1 ■ 1 mark

A diazonium salt is made from phenylamine using:

A NaNO_2 + dilute acid, below 10°C

B conc. HNO_3 + conc. H_2SO_4

C Br_2 water

D LiAlH_4

Solution 3.1

Method: Diazonium salts and azo dyes

A NaNO_2 + dilute acid, below 10°C



B conc. HNO_3 + conc. H_2SO_4

C Br_2 water

D LiAlH_4

Worked steps

A. NaNO_2 + dilute acid below 10°C makes the diazonium salt.

Exam-style 3.2 ■ 1 mark

The colour of an azo dye is due to the:

- A** -OH group
- B** -NH_2 group
- C** -N=N- group
- D** benzene ring alone

Solution 3.2

A -OH group

B -NH₂ group

C -N=N- group



D benzene ring alone

Worked steps

C. The -N=N- azo group is responsible for the colour.

Exam-style 3.3 ■ 3 marks

Outline the two-step synthesis of phenylamine from benzene, giving the reagents for each step.

Solution 3.3

Method: Diazonium salts and azo dyes

Worked steps

nitrate benzene with conc. HNO_3 + conc. H_2SO_4 to give nitrobenzene **M1**; reduce with Sn and conc. HCl **M1**; then add NaOH(aq) to free the phenylamine **A1**.

Exam-style 3.4 ■ 1 mark

A benzenediazonium salt is coupled with phenol in alkaline solution.

- (a) State the type of compound formed.
- (b) State **one** common use of such compounds.

Solution 3.4

Method: Diazonium salts and azo dyes

Worked steps

- (a) an azo compound / azo dye **B1**.
- (b) used as a dye (colouring) **B1**.