

Exercise walk-through

34.2

Phenylamine and azo compounds

A-Level Chemistry

What we will cover

- 1 Amines & basicity
- 2 Phenylamine & azo dyes
- 3 Amides
- 4 Zwitterions
- 5 Peptide bonds
- 6 Electrophoresis



azo compounds are dyes

Making phenylamine, and the azo route

step 1

nitrate benzene: concentrated HNO_3 and H_2SO_4 , giving nitrobenzene

step 2

reduce it with hot tin and concentrated HCl , then add alkali – giving **phenylamine**

diazotisation

phenylamine with HNO_2 (from NaNO_2 and HCl) below 10°C gives a diazonium salt

why cold

the diazonium salt decomposes above about 10°C

coupling

the diazonium salt with phenol in NaOH(aq) gives an **azo dye**

the colour

comes from the extended delocalisation across the $-\text{N}=\text{N}-$ bridge joining two rings

Two steps to phenylamine, then two more to the dye. Naming the **temperature** of the diazotisation is a marked condition, not a detail.

Exam tips

- **Phenylamine** is a **weaker base** than aliphatic amines because the N lone pair delocalises into the ring.
- **Diazotisation** (NaNO_2/HCl , below 10°C) then coupling gives **azo dyes** – learn the conditions and the coloured product.
- **Amino acids** are **zwitterions** (both $-\text{NH}_2$ and $-\text{COOH}$), so they are amphoteric; describe behaviour either side of the isoelectric point.

Exercises 2.1-2.3

2.1 Give the reagents to reduce nitrobenzene to phenylamine. [2]

2.2 State the temperature needed to make a stable diazonium salt. [1]

2.3 Give the reagents and conditions for converting nitrobenzene into phenylamine. [3]

Exercises 2.1-2.3

2.1 Give the reagents to reduce nitrobenzene to phenylamine. [2]

2.1

- tin (Sn) and concentrated hydrochloric acid; then NaOH(aq)
-

2.2 State the temperature needed to make a stable diazonium salt. [1]

2.2

- below 10 °C (kept cold in an ice bath)
-

2.3 Give the reagents and conditions for converting nitrobenzene into phenylamine. [3]

2.3

- Tin and concentrated hydrochloric acid; then an excess of sodium hydroxide; heat under reflux

Exercises 2.4·2.5

2.4 State why the diazotisation must be carried out below 10 °C. [2]

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

Exercises 2.4-2.5

2.4 State why the diazotisation must be carried out below 10 °C. [2]

2.4

- Above about 10 °C the diazonium ion is unstable and decomposes to phenol and nitrogen gas, so the yield is lost

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

2.5

- In phenylamine the nitrogen's lone pair is delocalised into the benzene ring, so it is less available to accept a proton; in ethylamine the alkyl group releases electron density towards the nitrogen, making the lone pair more available

Exercises 3.1·3.2

3.1 A diazonium salt is made from phenylamine using:

[1]

☐

A NaNO_2 + dilute acid, below 10°C

B conc. HNO_3 + conc. H_2SO_4

C Br_2 water

D LiAlH_4

3.2 The colour of an azo dye is due to the:

[1]

☐

A $-\text{OH}$ group

B $-\text{NH}_2$ group

C $-\text{N}=\text{N}-$ group

D benzene ring alone

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3.1 A

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

3.2 The colour of an azo dye is due to the:

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B $-\text{NH}_2$ group

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D benzene ring alone

3.2 C

- The $-\text{N}=\text{N}-$ azo group is responsible for the colour

Exercise 3.3

3.3 Outline the two-step synthesis of phenylamine from benzene, giving the reagents for each step. [3]

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3.3

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

Exercise 3.4 (a)

3.4 A benzenediazonium salt is coupled with phenol in alkaline solution.

(a) State the type of compound formed.

[1]

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(a)

- an azo compound / azo dye

Exercise 3.4 (b)

3.4 A benzenediazonium salt is coupled with phenol in alkaline solution.

(b) State **one** common use of such compounds.

[1]

Exercise 3.4 (b)

3.4 A benzenediazonium salt is coupled with phenol in alkaline solution.

(b) State **one** common use of such compounds.

[1]

(b)

- used as a dye (colouring)

Exercise 3.5 (a)

3.5 An azo dye is made from benzene in four steps.

(a) Give the reagents and conditions for step 1, the conversion of benzene into nitrobenzene, and name the mechanism. [3]

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- Concentrated nitric acid and concentrated sulfuric acid at about 55 °C; electrophilic substitution

Exercise 3.5 (b)

3.5 An azo dye is made from benzene in four steps.

(b) Give the reagents for step 2 and explain why a second reagent is needed after the reduction. [3]

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(b)

- Tin and concentrated hydrochloric acid; the product of the reduction is the phenylammonium salt, not the free amine, so excess sodium hydroxide is added to liberate phenylamine from it

Exercise 3.5 (c)

3.5 An azo dye is made from benzene in four steps.

(c) Give the reagents and conditions for the formation of the diazonium salt, and write its formula. [3]

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(c)

- Sodium nitrite with dilute hydrochloric acid, below 10 °C; $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$

Exercise 3.5 (d)

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(d) The diazonium salt is coupled with phenol in alkaline solution. Draw the structure of the azo compound formed. [2]

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(d)

- Two benzene rings joined by $-\text{N}=\text{N}-$, with the $-\text{OH}$ group para to the azo link on the phenol ring

Exercise 3.5 (e)

3.5 An azo dye is made from benzene in four steps.

(e) Explain, in terms of electrons, why azo compounds are coloured.

[3]

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(e)

- The azo group $\text{--N}=\text{N--}$ joins the two rings into one extended delocalised system; a larger delocalised system has a smaller gap between the energy levels; the gap now corresponds to visible light, which is absorbed, and the complementary colour is seen