

Exercise walk-through

Organic synthesis ■ 36.1

eXercise

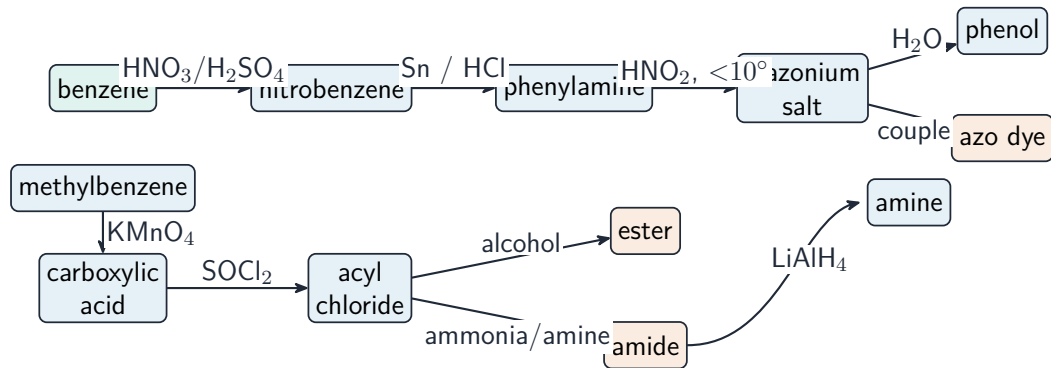
You must be able to

- choose reagents and conditions for each step of a synthesis
- devise a multi-step route by working backwards from the target
- state the reaction type at each step and identify likely by-products

Method — Planning a route

- **work backwards:** which single reaction makes the target, and from what?
Repeat until you reach the start.
- **key steps:** benzene $\rightarrow$ (HNO₃ / H₂SO₄) $\rightarrow$ nitrobenzene $\rightarrow$ (Sn/HCl, NaOH) $\rightarrow$ phenylamine $\rightarrow$ (HNO₂, <10 °C) $\rightarrow$ diazonium salt.
- carboxylic acid $\rightarrow$ (SOCl₂) $\rightarrow$ acyl chloride $\rightarrow$ (alcohol) $\rightarrow$ ester / $\rightarrow$ (amine) $\rightarrow$ amide.
- nitrile/amide $\rightarrow$ (LiAlH₄) $\rightarrow$ amine; halogenoalkane $\rightarrow$ (KCN) $\rightarrow$ nitrile (**adds one carbon**).

Method — Planning a route



Method — Planning a route

plan backwards from the target



Plan a synthesis by retrosynthesis

Practice 2.1 ■ 2 marks

Give the reagents to convert benzene into nitrobenzene.

Solution 2.1

Method: Planning a route

Worked steps

concentrated HNO_3 and concentrated H_2SO_4 **M1**; warm, 25–60 °C **A1**.

Practice 2.2 ■ 1 mark

State the reagent that reduces a nitrile to an amine.

Solution 2.2

Method: Planning a route

Worked steps

LiAlH_4 (or H_2/Ni) **B1**.

Exam-style 3.1 ■ 1 mark

To lengthen a carbon chain by one carbon, a halogenoalkane is reacted with:

A NH_3

B KCN

C LiAlH_4

D H_2O

Solution 3.1

Method: Planning a route

A NH_3

B KCN



C LiAlH_4

D H_2O

Worked steps

B. KCN adds a $-\text{CN}$ group, lengthening the chain by one carbon.

Exam-style 3.2 ■ 1 mark

In planning a synthesis, the best strategy is to:

- A** work forwards from any reagent
- B** work backwards from the target molecule
- C** guess reagents at random
- D** use only one reaction

Solution 3.2

Method: Planning a route

- A work forwards from any reagent
- B work backwards from the target molecule** 
- C guess reagents at random
- D use only one reaction

Worked steps

- B. Work backwards from the target molecule.**

Exam-style 3.3 ■ 3 marks

Devise a synthesis of **phenylamine** from benzene, giving the reagents and conditions for each step.

Solution 3.3

Method: Planning a route

Worked steps

nitrate benzene with conc. HNO_3 + conc. $\text{H}_2\text{SO}_4 \rightarrow$ nitrobenzene **M1**; reduce with Sn and conc. HCl **M1**; add NaOH(aq) to free phenylamine **A1**.

Exam-style 3.4 ■ 2 marks

A two-step synthesis converts bromoethane into propylamine via a nitrile.

- (a) Give the reagents for each step.
- (b) State **one** by-product/limitation of making an amine directly from a halogenoalkane and ammonia.

Solution 3.4

Method: Planning a route

Worked steps

- (a) KCN (in ethanol) to give propanenitrile **M1**; then LiAlH_4 (or H_2/Ni) to reduce it to propylamine **A1**.
- (b) the direct halogenoalkane + ammonia route also makes secondary/tertiary amines (over-substitution), lowering the yield of the primary amine **B1**.