

36.1 Organic synthesis

Name: _____ Class: _____ Date: _____

Total: 11 marks

KEY WORDS reagent 试剂 • amine 胺 • carboxylic acid 羧酸 • amide 酰胺 • nitrile 腈

Objective

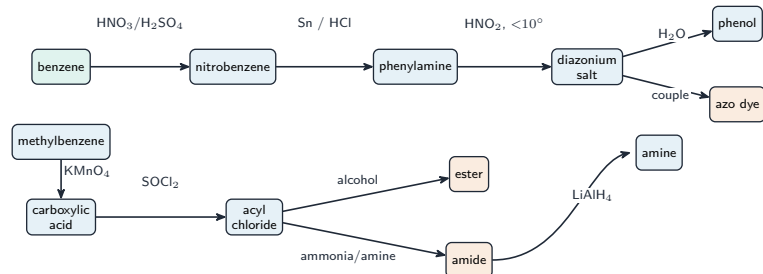
Build the skills to answer exam questions on **organic synthesis** 有机合成 — joining known reactions to build a target, working **backwards** from the product, and analysing a route.

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

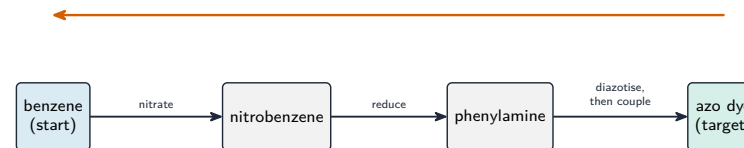
1 Worked examples

■ Planning a route



Two main chains: the aromatic chain (top) and the acyl-chloride chain (bottom).
Work backwards from your target

plan backwards from the target



Plan a synthesis by retrosynthesis

- 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**).

2 Practice

2.1 Give the reagents to convert benzene into nitrobenzene. [2]

2.2 State the reagent that reduces a nitrile to an amine. [1]

3 Exam-style questions

3.1 To lengthen a carbon chain by one carbon, a halogenoalkane is reacted with: [1]

- A NH₃
- B KCN
- C LiAlH₄
- D H₂O

3.2 In planning a synthesis, the best strategy is to:

[1]

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

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

[3]

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

(a) Give the reagents for each step.

[2]

(b) State **one** by-product/limitation of making an amine directly from a halogenoalkane and ammonia.

[1]

Solutions

2.1 concentrated HNO_3 and concentrated H_2SO_4 ; warm, 25–60 °C.

2.2 LiAlH_4 (or H_2/Ni).

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

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

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

3.4 (a) KCN (in ethanol) to give propanenitrile; then LiAlH_4 (or H_2/Ni) to reduce it to propylamine.

(b) the direct halogenoalkane + ammonia route also makes secondary/tertiary amines (over-substitution), lowering the yield of the primary amine.