

# 36.1 Organic synthesis

Name: \_\_\_\_\_ Class: \_\_\_\_\_ Date: \_\_\_\_\_

Total: 11 marks

KEY WORDS amine 胺 • reagent 试剂 • nitrile 腈 • amide 酰胺 • by-product 副产物

## Objective

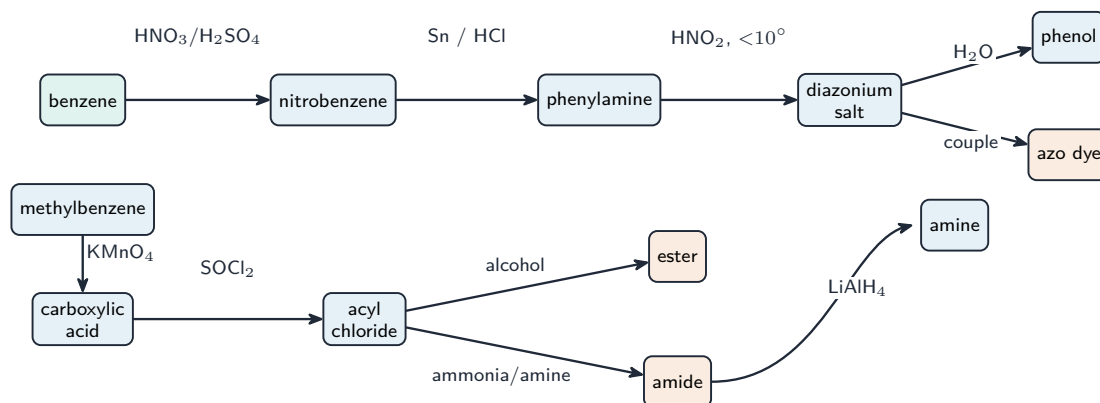
Build the skills to answer exam questions on **organic synthesis** 有机合成 — joining known reactions to build a target, working **backwards** from the product, and analysing a route.

**You must be able to:**

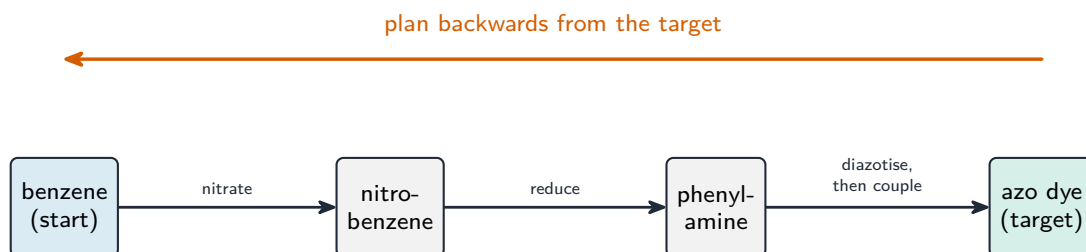
- choose reagents and conditions for each step of a synthesis
- devise a multi-step route by working backwards from the target
- state the reaction type at each step and identify likely by-products

## 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 a synthesis by retrosynthesis*

- **work backwards:** which single reaction makes the target, and from what? Repeat until you reach the start.
- **key steps:** benzene  $\rightarrow$  (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>)  $\rightarrow$  nitrobenzene  $\rightarrow$  (Sn/HCl, NaOH)  $\rightarrow$  phenylamine  $\rightarrow$  (HNO<sub>2</sub>, <10 °C)  $\rightarrow$  diazonium salt.
- carboxylic acid  $\rightarrow$  (SOCl<sub>2</sub>)  $\rightarrow$  acyl chloride  $\rightarrow$  (alcohol)  $\rightarrow$  ester /  $\rightarrow$  (amine)  $\rightarrow$  amide.
- nitrile/amide  $\rightarrow$  (LiAlH<sub>4</sub>)  $\rightarrow$  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 NH<sub>3</sub>
- B KCN
- C LiAlH<sub>4</sub>
- D H<sub>2</sub>O

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
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**3.3** Devise a synthesis of **phenylamine** from benzene, giving the reagents and conditions for each step. [3]

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

(a) Give the reagents for each step. [2]

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(b) State **one** by-product/limitation of making an amine directly from a halogenoalkane and ammonia. [1]

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## Solutions

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**2.1** concentrated  $\text{HNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$ ; warm, 25–60 °C.

**2.2**  $\text{LiAlH}_4$  (or  $\text{H}_2/\text{Ni}$ ).

**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.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4 \rightarrow$  nitrobenzene; reduce with Sn and conc. HCl; add  $\text{NaOH(aq)}$  to free phenylamine.

**3.4 (a)** KCN (in ethanol) to give propanenitrile; then  $\text{LiAlH}_4$  (or  $\text{H}_2/\text{Ni}$ ) 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.