

5.4.1 Select amine preparation and distinguish nitrogen reactions

Name: _____ Class: _____ Date: _____ Total: 17 marks

KEY WORDS evidence • conditions

Objective

Select amine preparation and distinguish nitrogen reactions. All questions and marking guidance are original.

1 Key knowledge and worked examples

Amines accept H^+ through the nitrogen lone pair. Alkyl groups generally increase basicity relative to ammonia; interaction of the lone pair with the ring makes phenylamine less basic. Amides contain $-\text{CONH}-$ and are much less basic than amines.

■ Worked method

$\text{CH}_3\text{CH}_2\text{Br}$ with excess ethanolic ammonia gives ethylamine; excess ammonia reduces further substitution. $\text{CH}_3\text{CH}_2\text{CN}$ reduced with LiAlH_4 in dry ether then worked up gives propan-1-amine: keep the nitrile carbon. Nitrobenzene with Sn /concentrated HCl gives an acidic phenylammonium mixture; alkali liberates phenylamine. Cold nitrous acid forms a diazonium salt from phenylamine, which then couples with phenol in alkaline solution.

2 Practice

2.1 Write butan-1-amine in condensed form and its equation with HCl . [2]

2.2 Explain why phenylamine is a weaker base than a typical primary alkylamine. [2]

2.3 Identify the product when propanenitrile is reduced. State reagents and count the product carbons. [3]

3 Exam-style questions

3.1 Plan preparation of phenylamine from nitrobenzene, including the work-up. Explain why the work-up is needed. [3]

3.2 Write the equation for ethanoyl chloride with excess ethylamine, including the salt by-product. [3]

3.3 State the two separate stages for making an azo product from phenylamine and phenol. Explain the cold condition and the colour. [4]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$; $\text{C}_4\text{H}_9\text{NH}_2 + \text{HCl} \rightarrow \text{C}_4\text{H}_9\text{NH}_3^+\text{Cl}^-$.

2.2 Phenylamine lone pair interacts with the ring, reducing availability for H^+ . Alkyl groups increase nitrogen electron density.

2.3 Propan-1-amine, LiAlH_4 /dry ether then aqueous work-up, three carbons because nitrile carbon is retained.

3.1 Sn and concentrated HCl under reflux; add alkali to convert the initially protonated phenylammonium species to free amine.

3.2 $\text{CH}_3\text{COCl} + 2\text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{CH}_3\text{CONHC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{NH}_3^+\text{Cl}^-$. Correct amide, second amine/coefficient, salt/complete balance.

3.3 Cold nitrous acid, from nitrite/acid, makes diazonium salt; alkaline phenol couples. Cold conditions reduce diazonium decomposition; extended delocalisation gives visible-light absorption.