



EXAM PAPERS PRACTICE

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Level: CIE A & AS Level Chemistry (9701)

Subject: Chemistry

Topic: A & AS Chemistry

Type: Mark Scheme

2002



1583

Chemistry CIE A & AS Level
To be used for all exam preparation for 2025+

CHEMISTRY

A & AS

Key skills



Mark Scheme

Answer 1

a)

i) The three molecules in order of increasing base strength is:

- Phenylamine < ammonia < *N*-methylethylamine

OR

Phenylamine is the weakest AND *N*-methylethylamine is the strongest base; [1 mark]

ii) Explaining the reason why:

- Base strength depends on the availability of the lone pair on the N atom; [1 mark]
- *N*-methylethylamine is strongest due to the positive inductive effect from alkyl groups
OR
Alkyl groups on *N*-methylethylamine push electrons / negative charge towards the N; [1 mark]
- The lone pair is more / most available to accept a proton in *N*-methylethylamine; [1 mark]
- In phenylamine, the N atom is bonded directly to the benzene ring; [1 mark]
- The lone pair on the N becomes delocalised within / into the benzene ring
OR
Overlap of the lone pair on N and the benzene ring electrons; [1 mark]
- The lone pair on N is no longer / not fully available to accept a proton; [1 mark]

[Total: 7 marks]

- The greater the electron density on the nitrogen atom in an amine the more likely the lone pair is to be available for bonding
 - Alkyl groups have a tendency to push electrons away from themselves and onto the nitrogen atom
 - There are two alkyl groups in *N*-methylethylamine, a secondary amine, and none in ammonia
- This is known as the positive inductive effect
 - The more alkyl groups there are the more available the lone pair of electrons is on the nitrogen atom
- In phenylamine, the lone pair on the nitrogen atom is drawn towards the delocalisation in the ring and this interaction makes the lone pair less available to bond with an incoming proton (H⁺ ion)

Answer 2

b)

i) The name of the type of reaction and suitable reagents and conditions for the conversion of nitrobenzene to phenylamine are:

- Reduction; [1 mark]

Method 1

- Sn / tin AND concentrated HCl; [1 mark]
- Heat AND NaOH solution; [1 mark]

Method 2

- H₂; [1 mark]
- Ni / Pt / Pd catalyst; [1 mark]

Method 3

- LiAlH₄; [1 mark]
- Dry ether; [1 mark]

[Total: 3 marks]

- Once the benzene ring has undergone nitration, the NO₂ group can then be reacted with appropriate reducing agents
- Nitration of a benzene ring followed by the reduction of the NH₂ group is a common pathway so it is worth making sure you have learned this thoroughly
- Method 1 is the method that you need to know, but the other methods are all suitable methods so are creditworthy
- LiAlH₄ in dry ether is an almost universal reducing agent and works in most examples of organic reduction. It can be used to convert nitrile groups (-CN) to amino groups (-NH₂) so is very important in the production of amines

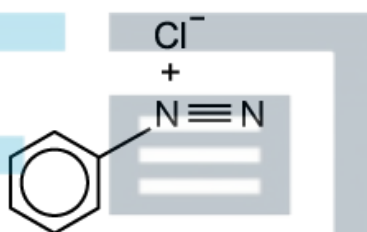
Answer 3

c)

i) A condition that could be added to ensure that the salt would not break down during the reaction is:

- Completed at a low temperature
OR
Done in ice / ice cold conditions; [1 mark]

ii) The structure of the organic compound formed in the ice-cold acidic mixture is:



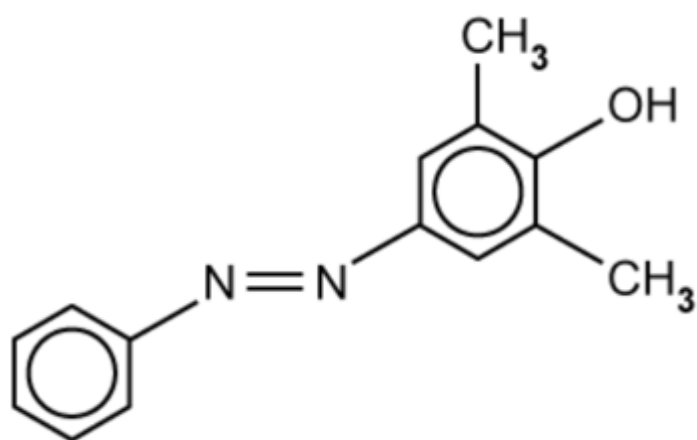
- Structure showing nitrogen containing group with triple bond AND positive charge on correct N atom AND negative charge on the Cl; [1 mark]

[Total: 2 marks]

- In order for the nitrous acid to be used in this process it must be made in situ as it is an unstable compound
 - The reaction must also be kept at a low temperature to prevent this from decomposing
- The equation for the reaction is:
 - $\text{NaNO}_2 (\text{aq}) + \text{HCl} (\text{aq}) \rightarrow \text{HNO}_2 (\text{aq}) + \text{NaCl} (\text{aq})$
- The acid can then react with the amine to produce a diazonium salt
- A nitrogen atom that has four bonds will have a positive charge as it is electron deficient

Answer 4

d) A structure for the azo dye if the coupling agent used is 2,6-dimethylphenol is:



- Correct bond link between N atom and the coupling agent; [1 mark]
- Correct overall structure; [1 mark]

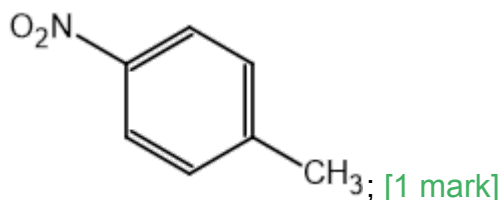
[Total: 2 marks]

- The -OH group should be the opposite side of the nitrogen containing group
 - A coupling agent is an arene compound that will bond to the diazonium salt
 - The diazonium salt acts as an electrophile
 - Coupling of diazonium salts with different aromatic compounds forms dyes of different colours

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Answer 5

a) The structure of the intermediate is:



[Total: 1 mark]

- In order to prepare the aromatic amine, we must first nitrate the benzene ring



Answer 6

b) The reagents and conditions required are:

- Concentrated nitric acid / conc HNO_3
AND
Concentrated sulfuric acid / conc H_2SO_4 ; [1 mark]
- Reflux (25 - 60 °C); [1 mark]

[Total: 2 marks]

- The electrophile must be generated by making a nitrating mixture of concentrated nitric acid and concentrated sulfuric acid.
- Once the electrophile has been generated, it will carry out an electrophilic attack on the benzene ring
- The nitrating mixture of HNO_3 and H_2SO_4 is refluxed at 25 - 60 °C
- This links to your study of benzene and electrophilic substitution

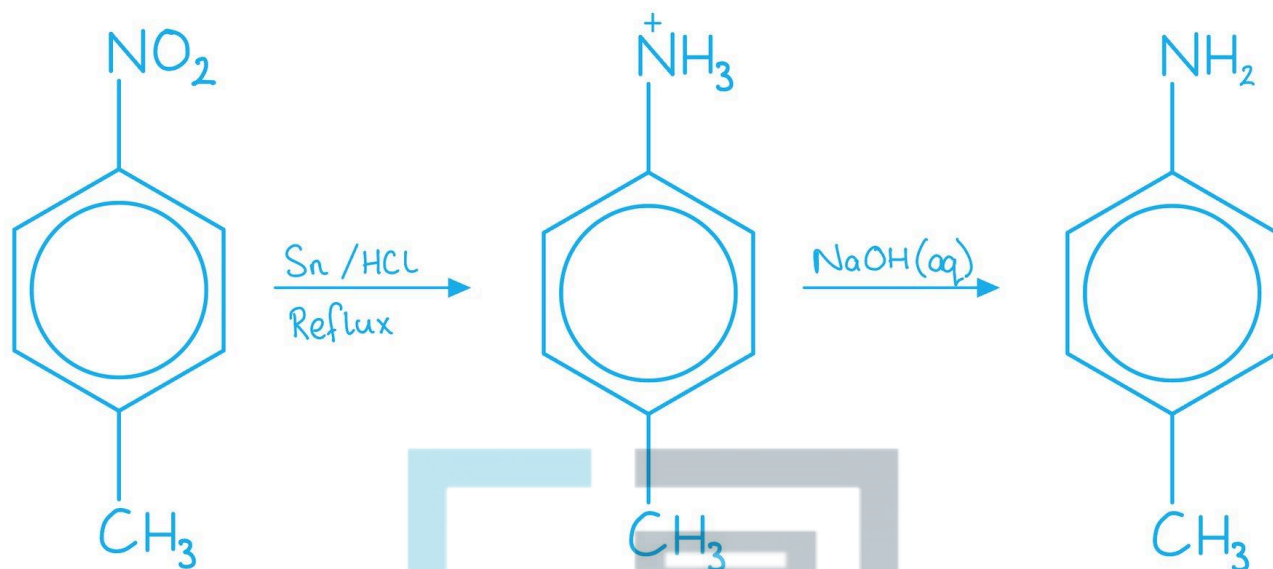
Answer 7

c) Sodium hydroxide is required for this step as well because:

- 4-methylphenylammonium ion is produced due to the acidic conditions; [1 mark]
- Sodium hydroxide can deprotonate the ion to form the amine group / NH_2 ; [1 mark]

[Total: 2 marks]

- 4-methylnitrobenzene must be reduced in order to produce the amine 4-methylphenylamine
- When using a combination of Sn / HCl to reduce the $-\text{NO}_2$ group a positive nitrogen atom is created due to the acidic environment
- The lone pair on the nitrogen in the phenylamine picks up a hydrogen ion from the acid
- Therefore to remove the extra proton dilute sodium hydroxide can act as a Brønsted-Lowry base and accept it
- The final step in the production of 4-methylphenylamine is shown below:



Answer 8

a)

i) The reagents and conditions for the formation of nitric(III) acid are:

Reagents:

- NaNO_2
AND
 HCl ; [1 mark]

Conditions:

- Ice; [1 mark]

ii) The equation for the reaction that takes place in step 1 is:

- $\text{C}_6\text{H}_5\text{NH}_2 + \text{HNO}_2 + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{N}_2\text{Cl} + 2\text{H}_2\text{O}$; [1 mark]

[Total: 3 marks]

- Nitric(III) acid is more commonly known as nitrous acid, which is HNO_2 as shown in Fig. 3.1
 - It is required for the formation of benzenediazonium chloride as part of the process of forming azo dyes
- Step 1 also requires the use of HCl and is conducted at temperatures below $10\text{ }^\circ\text{C}$

Answer 9

b) The other reagent involved in this coupling reaction is:

- Phenol / $\text{C}_6\text{H}_5\text{OH}$; [1 mark]

[Total: 1 mark]

- Careful: Many students suggest benzene compounds with an OH group and some form of nitrogen based group because they forget that the nitrogens are part of the benzenediazonium chloride

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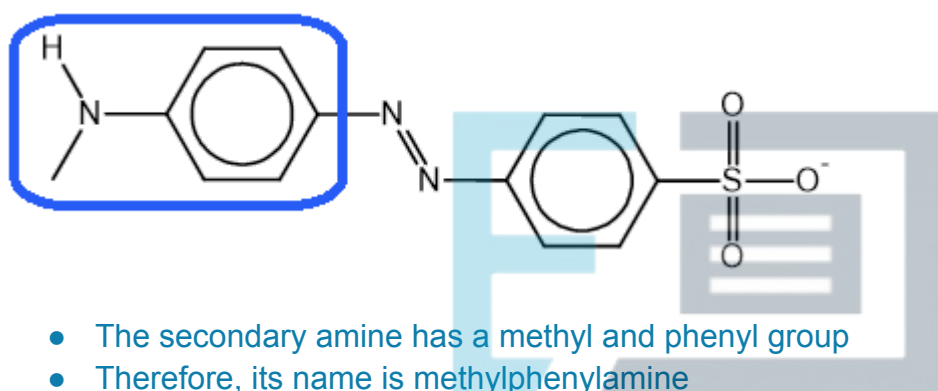
Answer 10

c) The name of the secondary amine used to form the structure in Fig. 3.2 is:

- Methylphenylamine
OR
Methylaniline; [1 mark]

[Total: 1 mark]

- The structure of the analogue can be used to identify the secondary amine



- The secondary amine has a methyl and phenyl group
- Therefore, its name is methylphenylamine
 - It is also called methyl aniline because a benzene ring with an amine group attached is known as aniline

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