WJEC A-LEVEL CHEMISTRY · UNIT 4

CHEMISTRY

EXAM QUESTION PACK

4.6 AMINES

SCORE	PERCENTAGE
/79	%

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1. *(a)* Primary aliphatic amines react with nitric(III) (nitrous) acid to give a quantitative yield of nitrogen gas, and an alcohol as the major organic product.

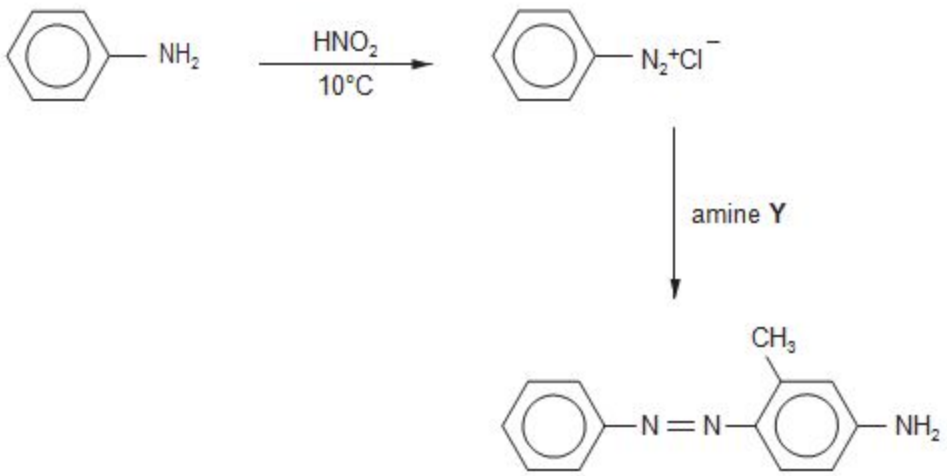
$$R{-}NH_2 + HNO_2 \longrightarrow R{-}OH + N_2 + H_2O$$

In an experiment 2.54 g of an amine gave 1.00 dm^3 of nitrogen, measured at 10 °C.

Calculate the relative molecular mass of the amine and hence its structural formula.

[At 10 °C, 1 mol of nitrogen gas has a volume of 23.2 dm^3] [3]

(b) At 10 °C and below a primary aromatic amine reacts with nitric(III) acid, HNO_2, to give a diazonium compound, which can then be coupled with a phenol or an amine.
An example of this reaction is shown below.

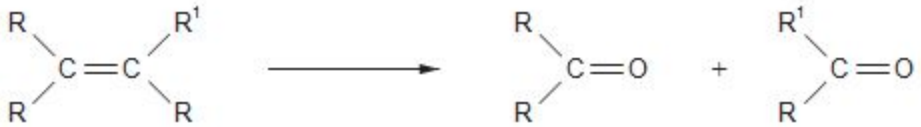


(i) The benzenediazonium ion acts as an electrophile in this reaction.
State the meaning of the term electrophile. [1]

(ii) State the **name** of amine **Y**. [1]

(iii) The product of this reaction contains an —N=N— group bonded to aromatic systems. State the general name for this type of grouping, which can give coloured compounds, and state why this type of reaction has industrial importance. [2]

(c) Alkenes react with ozone to give an intermediate product that can then be reduced to give aldehydes or ketones.



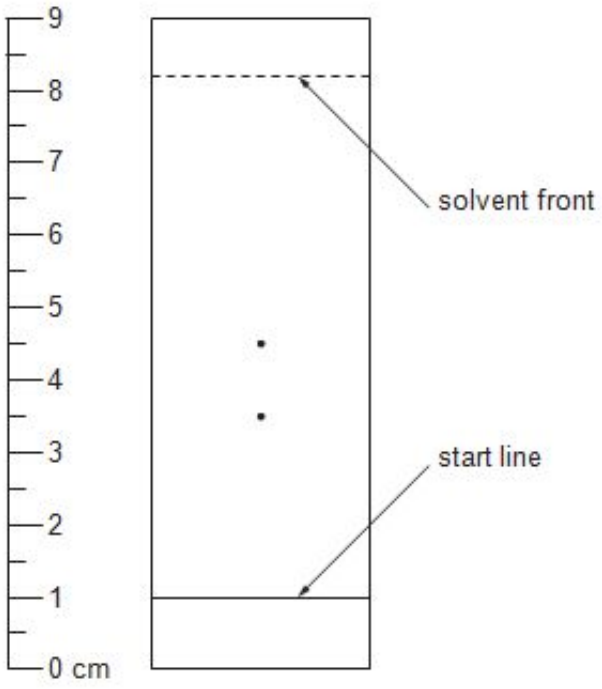
alkene **W**

An alkene **W** was reacted in this way to give two different ketones. R and R^1 represent **two different** alkyl groups.

These ketones were then separated by thin layer chromatography to give two spots. The ketone spots were colourless and their presence was found by spraying the chromatogram with a solution of 2,4-dinitrophenylhydrazine.

(i) State the type of reaction that occurs when a ketone reacts with 2,4-dinitrophenylhydrazine and how this reaction is able to show the presence of these ketones in the chromatogram. [2]

(ii) The chromatogram that was obtained is shown below.
Use the table of R_f values to identify the two ketones present and hence the displayed formula and the name of alkene **W**. [4]
QWC [1]



Ketone	R_f value
propanone	0.35
butanone	0.40
pentan-2-one	0.49
pentan-3-one	0.60
hexan-2-one	0.68

(iii) State how the **equation** for the reaction of alkene **W** with ozone shows that **W cannot be** 2-methyl-3-ethylpent-2-ene, $(CH_3)_2C{=}C(CH_2CH_3)_2$. [1]

(d) This is a brief method written by a student to enable others to prepare ethyl ethanoate by esterification.

- Heat under reflux together 0.45 mol of ethanoic acid with an equimolar quantity of ethanol
- Add 5 cm^3 of sulfuric acid
- Distil off everything boiling up to 82 °C
- Add the distillate to aqueous sodium hydrogencarbonate in a separating funnel
- Run off the ethyl ethanoate layer and dry it over anhydrous calcium chloride
- Distil off the dried ethyl ethanoate and collect the fraction boiling at 75-78 °C

(i) Give the equation for this reaction.

[1]

(ii) Calculate the mass of ethanoic acid needed for this experiment.

[1]

(iii) State an important detail that is missing from the first bullet point.

[1]

(iv) State why the sulfuric acid should have been added at the refluxing stage.

[1]

(v) State why sodium hydrogencarbonate needed to be added to the distillate.

[1]

(Total 20)

2. *(a)* The formulae of some compounds are shown below.

$CH_3CH_2NH_2$	$CH_3CH_2CONH_2$	$CH_3CHCHCHO$
A	**B**	**C**
$CH_3CH(OH)CH_2CH_3$	CH_2CHCH_3	$CH_3CH_2COCH_2CH_3$
D	**E**	**F**

Each letter may be used once, more than once or not at all, to answer the questions below.

Give the letter of the compound which

(i) is most basic,

[1]

(ii) forms yellow crystals when warmed with iodine in alkaline solution,

[1]

(iii) forms a silver mirror when warmed with Tollens' reagent,

[1]

(iv) exhibits E-Z isomerism.

[1]

(b)(i) Butylamine is one of the compounds responsible for the smell of rotting fish. It can be prepared in the laboratory from 1-chlorobutane.

Classify the reaction mechanism when butylamine is prepared in this way

[1]

(ii) Explain why phenylamine, an aromatic amine, cannot be prepared from chlorobenzene using a similar reaction to that in part (i).

[2]

(iii) Write a **balanced** equation for the reaction of butylamine with ethanoyl chloride,

[1]

(iv) Phenylamine is normally prepared from nitrobenzene.

I. Give the reagents used in this preparation and a technique to separate the product from the reaction mixture.

[3]

II. When phenylamine reacts with cold nitric(III) acid (nitrous acid) a colourless solution of benzenediazonium chloride is formed. Write the formula for benzenediazonium chloride.

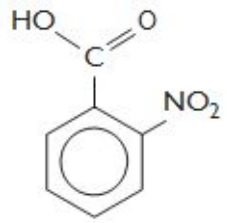
[1]

III. State the type of organic substance formed when aqueous benzenediazonium chloride reacts with an alkaline aqueous solution of naphthalene-2-ol.

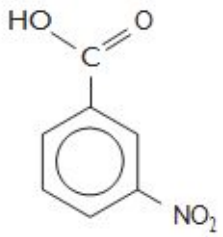
[1]

(Total 13)

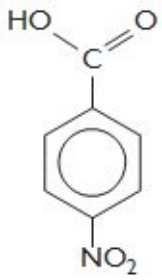
3. *(a)* Nitrobenzenecarboxylic acids *(nitrobenzoic acids)* are useful starting materials in the preparation of many dyes and can be prepared by nitration of benzenecarboxylic acid *(benzoic acid)*, C_6H_5COOH.
Many nitrobenzoic acids exist including those shown below:



2-nitrobenzoic acid



3-nitrobenzoic acid



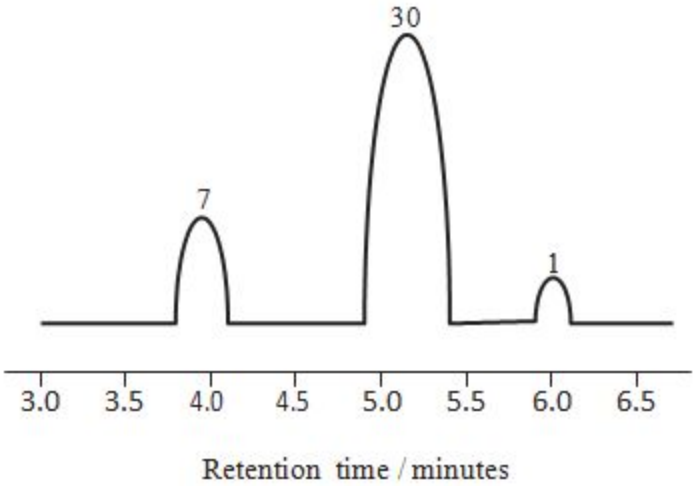
4-nitrobenzoic acid

(i) Benzenecarboxylic acid can be nitrated under similar conditions to the nitration of benzene.

Give the reagent(s) and condition(s) required and classify the mechanism of this reaction.

[3]

(ii) Nitration of benzenecarboxylic acid gives a mixture of products. These can be identified by gas chromatography followed by mass spectrometry *(GC-MS)*. The gas chromatograph for the products of this reaction is shown below, with the relative areas of each peak indicated.



I. The main isomer produced is 3-nitrobenzenecarboxylic acid. Calculate the percentage of this isomer produced.

[2]

II. The mass spectrum of 3-nitrobenzenecarboxylic acid has main peaks at m/z 45, 46, 122 and 167. Suggest which species are responsible for **each** of these peaks.

[2]

(iii) An impure sample of 3-nitrobenzenecarboxylic acid was obtained.

I. State how the melting temperature of the impure sample of 3-nitrobenzenecarboxylic acid would differ from that of pure 3-nitrobenzenecarboxylic acid, if at all.

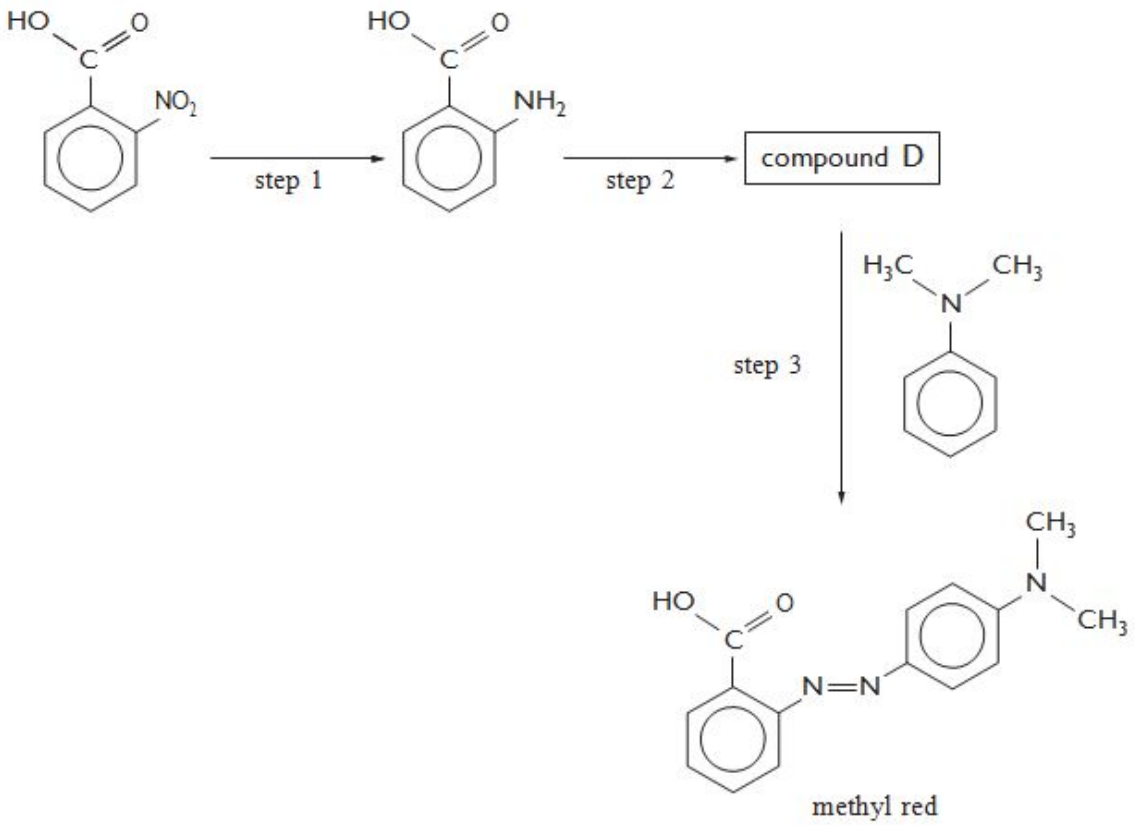
[1]

II. 3-nitrobenzenecarboxylic acid was found to be soluble in boiling water but not in cold water. It has a melting temperature of 142 °C.

Describe how impure 3-nitrobenzenecarboxylic acid could be purified by recrystallisation. Include full experimental details.

[4] QWC [1]

(b) 2-nitrobenzenecarboxylic acid may be used as a starting material for the production of the indicator methyl red. A reaction scheme for this process is given below.



(i) Give the reagent(s) necessary for step 1. [1]

(ii) Step 2 uses a mixture of sodium nitrate(III), $NaNO_2$, with dilute hydrochloric acid. Give the conditions required for this reaction and the structure of the product, compound **D**. [2]

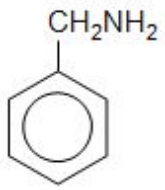
(iii) Methyl red is red below pH 4. Explain the origin of this colour. [2]

(c) Methyl red is used to differentiate between acids and bases. Explain why amines such as ethylamine are bases.

[2]

(Total 20)

4. *(a)* The formulae of the isomers phenylmethylamine and 4-methylphenylamine are shown below.



phenylmethylamine

4-methylphenylamine

These compounds are colourless liquids with different boiling temperatures.

(i) Give the name of a technique that can be used to separate these two liquids.

[1]

(ii) State and explain how the mass spectra of these two compounds would differ.

[1]

(iii) Phenylmethylamine reacts with ethanoyl chloride to give a white solid, compound **G**

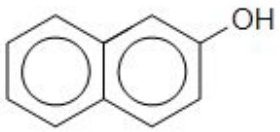
I. Give the equation for this reaction.

[1]

II. Compound **G** was purified by recrystallisation from ethanol. It has a melting temperature of 60 °C. Describe how you would recrystallise compound **G** from ethanol to obtain a pure dry product. You should assume that you are starting with cold ethanol and impure solid compound **G**. Washing of the purified solid product is unnecessary

[5] QWC [1]

(iv) 4-Methylphenylamine can be used to make an azo dye by reaction of its diazonium compound with an alkaline solution of naphthalene-2-ol.



naphthalene-2-ol

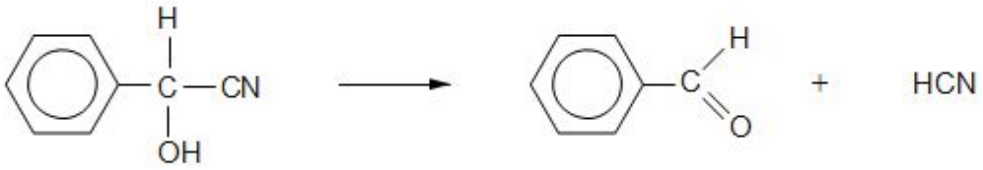
I. State how the diazonium compound can be made from 4-methylphenylamine, giving the reagents used and any essential conditions.

[2]

II. Give the structural formula of the azo dye produced.

[1]

(b) A species of millipede can protect itself by producing hydrogen cyanide. This poisonous gas is produced from mandelonitrile by enzyme action.



2-phenyl-2-hydroxyethanenitrile (mandelonitrile) benzaldehyde

The reaction can be carried out in the reverse direction in the laboratory.

(i) Draw the mechanism for the reaction between benzaldehyde and the cyanide ion. State the type of mechanism occurring.

[4]

(ii) Mandelonitrile is a yellow material. State the general name for groups that cause colour in organic compounds and give the appearance of mandelonitrile when viewed under blue light, giving a reason for your answer.

[3]

(iii) Give the structural formula of the organic compound obtained when mandelonitrile is warmed with dilute hydrochloric or sulfuric acid.

[1]

(Total 20)

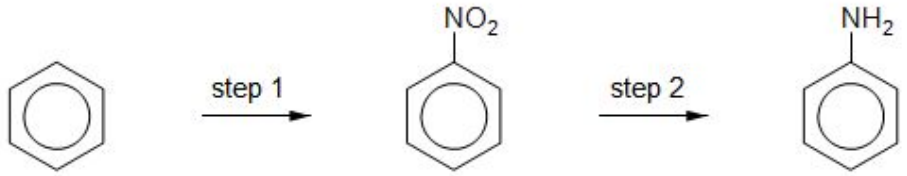
5. This question focuses on molecules that contain the $—NH_2$ group.

(a) Phenylamine and propylamine are both bases, with phenylamine being a weaker base than propylamine.

(i) Explain why both propylamine and phenylamine can act as bases. [2]

(ii) Give a reason why phenylamine is a weaker base than propylamine. [2]

(iii) Phenylamine can be prepared from benzene in a two-step process.



I. Step 1 uses a mixture of concentrated nitric and sulfuric acids to produce NO_2^+ during the reaction. Draw the mechanism of the reaction between NO_2^+ and benzene. [3]

II. During step 1, some dinitrobenzene is produced. Suggest a method of separating the different compounds in the product mixture. [1]

III. Give the reagent(s) required to produce phenylamine from nitrobenzene in step 2. [2]

(Total 10)

6. (a) Complete the gaps in the following sentences choosing from the words:

blue yellow higher lower

Each word can be used once, more than once or not at all.

[3]

Benzene is a colourless compound that absorbs energy in the ultraviolet region of the electromagnetic spectrum.
Nitrobenzene is a yellow compound that absorbs energy in the . . . . . region of the visible spectrum.

The absorption of energy for benzene occurs at a . . . . . energy and at a . . . . . frequency than for nitrobenzene.

(b) Methylbenzene can be produced from benzene using a Friedel-Crafts reaction.

(i) Give an equation for this reaction.

[1]

(ii) State the role of the catalyst used in this reaction, apart from increasing the rate.

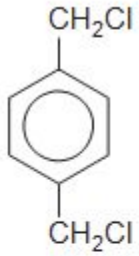
[1]

(c) The Friedel-Crafts reaction can also be used to introduce more than one methyl group to the benzene ring giving, for example, 1,4-dimethylbenzene.

The low resolution proton NMR spectrum of this compound shows two peaks with a peak area ratio of 3:2.

Explain how 1,4-dimethylbenzene produces this spectrum. [2]

(d) 1,4-Dimethylbenzene reacts with chlorine in a free radical reaction to give the liquid 1,4-di(chloromethyl)benzene.



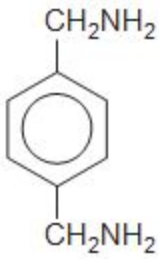
(i) State the names of **two** methods that could be used to show that a sample of this compound is pure. [2]

Method 1 .....

Method 2 .....

(ii) Give the displayed formula of the compound produced when 1,4-di(chloromethyl)benzene reacts with an excess of aqueous sodium hydroxide. [1]

(e) (i) 1,4-Di(chloromethyl)benzene reacts with ammonia to give the diamine below.



Draw the repeating section of the polymer obtained when this diamine reacts with benzene-1,4-dicarboxylic acid. [1]

(ii) The polymer obtained in *(e)*(i) above contains a peptide linkage.

State the name of a naturally occurring material that also contains a peptide linkage. [1]

Total [12]

2.

(a)	(i)	A	[1]
	(ii)	D	[1]
	(iii)	C	[1]
	(iv)	C	[1]
(b)	(i)	Nucleophilic substitution	[1]
	(ii)	The C–Cl bond in chlorobenzene is stronger than in 1-chlorobutane (1) due to delocalization of electron density from the ring with the bond (1) OR Delocalised electrons in chlorobenzene (1) repel lone pair of electrons on nucleophile / ammonia (1)	[2]
	(iii)	$C_4H_9NH_2 + CH_3COCl \longrightarrow C_4H_9NHCOCH_3 + HCl$	[1]
	(iv)	I Tin and **concentrated** hydrochloric acid (1) Add sodium hydroxide (after cooling) (1) Steam distillation to separate the product (1)	[3]
		II $C_6H_5NN^+Cl^-$	[1]
		III Azo dye / azo compound	[1]

Total [13]

3.

(a) (i) (Concentrated) nitric acid / (concentrated) sulfuric acid / Temperature of 40-80°C
(*Any 2 = 1 mark; All 3 = 2 marks*)
Electrophilic substitution (1) [3]

(ii) I. Peak area is proportional to amount of substance (1)
Percentage = (30 / 38) x 100 = 79% (1)
(Can obtain both marks from correct percentage) [2]

II. 45 = $COOH^+$, 46= NO_2^+, 122 = $C_6H_4NO_2^+$ and 167 = $C_7H_5NO_4^+$.
(*Any 2 = 1 mark; All 4 = 2 marks*) [2]

(iii) I. Lower melting point / melts over a range [1]
II. 1 mark for each point.

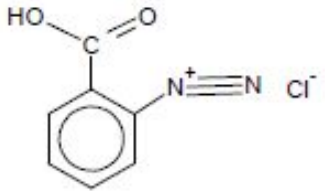
- Dissolve in the minimum volume
- Of hot water
- Filter hot
- Allow to cool
- Filter
- Dry residue under suction / in oven below 142°C

Max 4 marks [4]

QWC: legibility of text, accuracy of spelling, punctuation and grammar, clarity of meaning.[1]

(b) (i) Tin and concentrated hydrochloric acid [1]

(ii) Below 10°C (1)



(1) [2]

(iii) N=N double bond is chromophore (1)
Compound absorbs blue /green / complementary colours to red / all colours but red (1)
Remaining frequencies are transmitted, giving the red colour seen. (1)
Any 2 out of 3 [2]

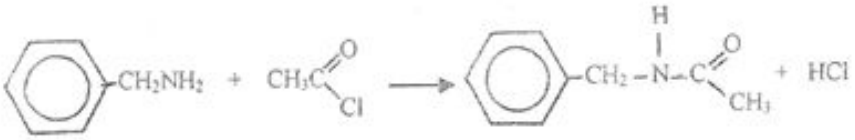
(c) Nitrogen has a lone pair (1) which can accept a proton (1) [2]

[20 marks]

4. (a) (i) (Fractional) distillation / (preparative) gas chromatography / HPLC / TLC column chromatography / solvent extraction [1]

(ii) the fragmentation pattern would be different / valid examples given [1]

(iii) I



[1]

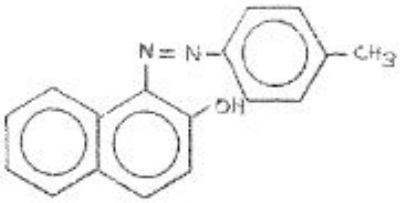
II Heated electrically / by a naked flame with a water bath (1)
Add compound **G** to the ethanol until the hot ethanol will (just) not dissolve any more solute (1)
Filter hot (1)
Allow to cool (1)
Filter (1)
Dry in air / window sill / < 60 °C in an oven (1) [5]

Maximum 4 out of 5 total if second marking point not given
Note 5 marks maximum here

QWC Information organised clearly and coherently, using specialist vocabulary where appropriate [1]

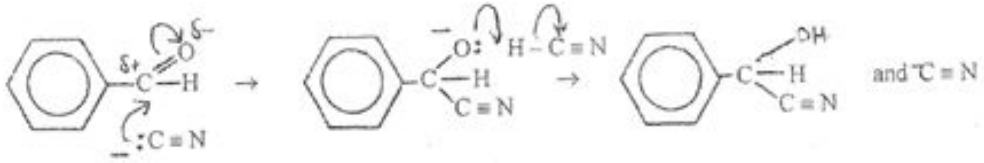
(iv) I The amine is reacted with sodium nitrite / HCl(aq) or nitrous acid (1) at a temperature of < 10 °C (1) [2]

II



[1]

(b) (i) Nucleophilic addition (1)

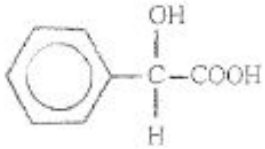


Accept a mechanism that shows HCN polarisation and nucleophilic addition as a concerted process

polarisation / charges shown (1) curly arrows on first structure (1)
regeneration of $^{-}C{\equiv}N$ or capture of H^{+} and curly arrow (1) [4]

(ii) Chromophores (1)
The colour will be black (1) as the compound absorbs blue / other colours (1)
[3]

(iii)



[1]

Total [20]

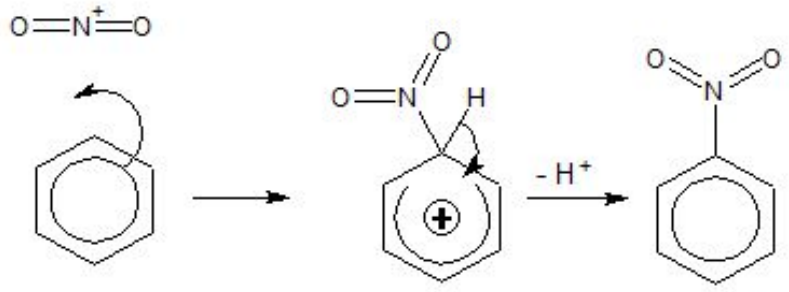
5.

(a) (i) Both molecules have lone pairs on nitrogen (1)

The lone pairs can form (coordinate) bonds with H^+ ions (1) [2]

(ii) Lone pair on N in phenylamine is delocalised over benzene ring (1) therefore less able to accept H^+ (1) [2]

(iii) I Arrow in first step (1)
Cation structure in second step (1)
Arrow in second step (1)

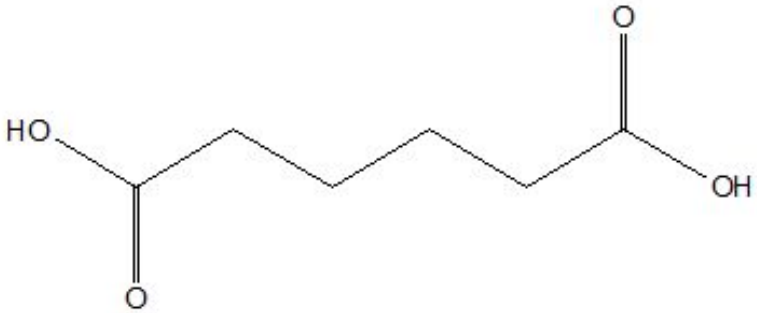


[3]

II (fractional) distillation / steam distillation [1]

III Sn and conc. HCl (1) followed by NaOH (1) [2]

(b) (i)



[1]

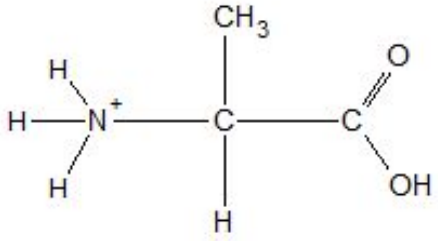
(ii) Addition polymerisation makes one product only /
Condensation produces one product plus a small molecule like water (1)

Addition polymerisation uses one starting material /
Condensation polymerisation has two different starting materials (1)

Addition polymerisation involves monomer with one functional group /
Condensation polymerisation involves monomer with two functional groups (1)

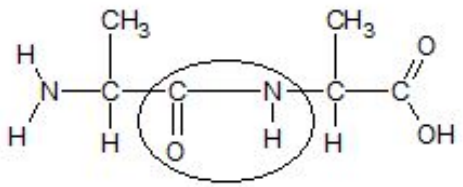
(max 2) [2]

(c) (i)



[1]

(ii)



[2]

(iii) Alanine has strong (electrostatic) forces between the zwitterions (1)

Butanoic acid has hydrogen bonding between molecules / electrostatic forces in alanine are stronger than forces in butanoic acid (1)

[2]

(iv) Soda lime (1) $CH_3CH_2NH_2$ (1) [2]

Total [20]

6.

(a) ……blue …….. (1) ……higher (1) ……higher (1) [3]

(b) (i)

[1]

accept C_6H_5 in place of the ring accept equations that show the catalyst

(ii) It acts as a halogen carrier / it helps produce the electrophile/CH_3^+ / increases polarity of the halogenoalkane [1]

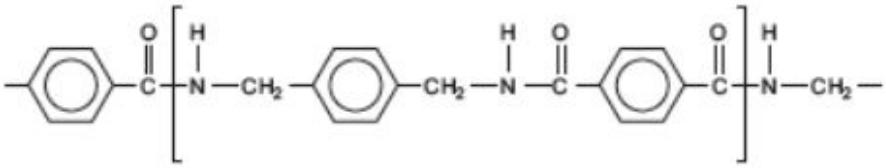
(c) There are 6 methyl protons and 4 aromatic protons, hence a ratio of 3:2 (1)
All the methyl protons are equivalent as are all the aromatic protons (1) [2]

(d) (i) Any 2 from NMR / HPLC / GC / refractive index / mass spectra / boiling temperature [2]

(ii)

[1]

(e) (i)



[1]

(ii) protein / dipeptide / polypeptide [1]

Total [12]