Mark Scheme - 4.8 Organic Synthesis and Analysis

1. (a) Chromophore [1]

(b) (i) Melting temperature **lower** than literature value / melting occurs over a temperature range [1]

(ii) Identify percentage or amount of impurities (1)
Identify the number of compounds present or number of impurities (1) [2]

(c) (i) Acidified potassium dichromate (1)
Heat and distil (1) do not accept 'reflux' [2]

(ii) M_r of phenylmethanol = 108.08 M_r of benzenecarbaldehyde = 106.06 (1)
100% conversion would be 10.0 ÷ 108.08 × 106.06 = 9.815g (1)
86% yield = 9.815 × 86 ÷ 100 = 8.44g (1) [3]

(iii) Two resonances in the range 5.8-7.0 ppm (1)
These are doublets (1)
One **singlet** at around 11.0 ppm (1)
All resonances have the same area (1) [4]

Total [13]

2.

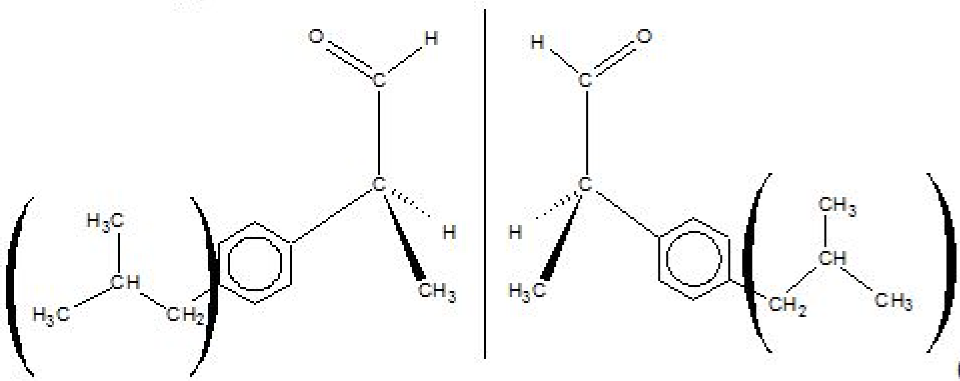
(a) $CH_3CH(CH_3)CH_2Cl$ (1) $AlCl_3$ / $FeCl_3$ (1) Room temperature / in the dark (1) [3]

(b) (i) 2,4-DNP (1) Orange precipitate (1) [2]

(ii) Tollen's reagent (1) Silver mirror with **C**, no reaction with **B** (1) [2]

(c) Optical isomerism is where a molecule and its mirror image are different / non-superimposable (1)

Compound **C** has a chiral centre / 4 different groups attached to one carbon atom (1)



(1)

The two isomers rotate the plane of polarised light in opposite directions (1) [4]

QWC: organisation of information clearly and coherently; use of specialist vocabulary where appropriate (1) [1]

(d) Dilute acid (1) heat (1) hydrolysis (1) [3]

(e) Acidified potassium dichromate (VI) (1) / heat (1)

One step reactions are generally better as they have a better yield / there is waste in each stage (1)

Two step process may be cheaper / use more sustainable reagents/ may give a better yield in this case / produce less harmful waste materials / potassium dichromate may react with other parts of the molecule as well / may be easier to separate product (1)

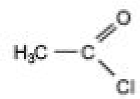
Do not credit same idea twice e.g. if 'better yield' gains first mark, a different point is required to gain second mark [4]

QWC: selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

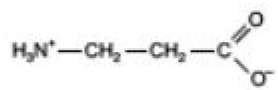
Total [20]

3.

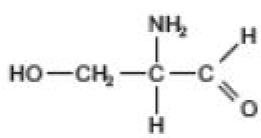
(a) (i) Sodium / potassium cyanide [1]

(ii)  [1]

(iii) Sulfuric / hydrochloric acid [1]

(iv)  [1]

(v) eg

 [1]

(vi) $LiAlH_4$ / H_2 / sodium, ethanol [1]

(vii) The nitrogen atoms act as electron pair donors / proton acceptors [1]

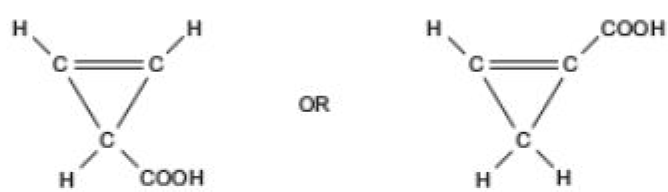
(b) (i) Molecular formula is $C_4H_4O_2$ [1]

(ii) 3 [1]

(iii) C = C / alkene [1]

(iv) Two of the (remaining) protons are in equivalent environments (and one is not) / there are CH and CH_2 present [1]

(v) Possibilities

 [1]

Total [12]

4.

(a) (i) 48.5 / 49 % **[1]**

(ii) Find a use for the calcium sulfate **[1]**

(b) Total volume of aqueous sodium hydroxide needed = $\frac{26.40 \times 250}{25.00}$ = 264.0 cm^3 (1)

from the graph this is equivalent to 0.011 mole of the acid (1)

$\therefore M_r$ of the acid = $\frac{\text{mass}}{\text{no. of moles}} = \frac{2.31}{0.011}$ = 210 (1)

$C_6H_8O_7 . n H_2O$ = 210

↑

192 $\therefore$ n = 18 (1)

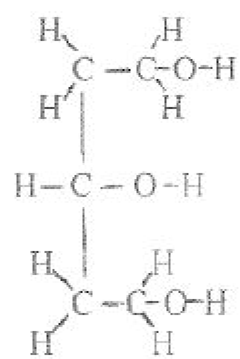
since M_r of water is 18 n = 1 (1) **[5]**

(c) The two 'ends' of the double bond have different groups bonded to the carbon atoms (of the double bond) / they have different structural formulae, so cannot be stereo / geometric isomers **[1]**

(d) eg sodium ethanoate / ethanoic acid (1) methane (1) **[2]**

(e) $C_5H_6O_5 \rightarrow CH_3COCH_3 + 2CO_2$ **[1]**

(f)



[1]

(g) (Fractional) distillation / (preparative) gas chromatography / HPLC **[1]**

(h) (i) eg An optically active isomer that will rotate the plane of polarised light / an isomer with a chiral centre **[1]**

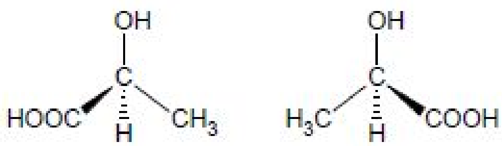
(ii) An equimolar mixture of both enantiomers (that has no apparent effect on the plane of polarised light) **[1]**

Total [15]

5.

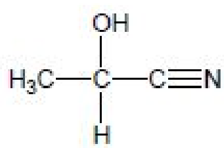
(a) (i) A compound that can rotate the plane of polarised light. [1]

(ii)



[1]

(iii)



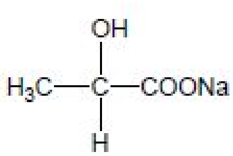
[1]

(iv) Reflux / heat with H_2O/H^+ [1]

(v) It contains an equal amount of the two enantiomers / it is a racemic mixture (1)

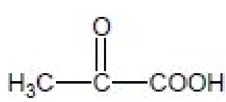
The rotating effect of one form exactly cancels out the effect of the other (1) [2]

(b) (i)



[1]

(ii)



[1]

(c) (i) 2-aminopropanoic acid [1]

(ii) Nitrous acid / nitric(III) acid / HNO_2 [1]

(iii) It exists as a zwitterion (1)

strong electrostatic attractions / ionic bonds between different zwitterions (1) [2]

Total [12]

6.

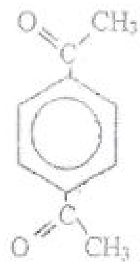
(a) (i) $CH_3CH_2CH_2CH_2CH_3$ + Cl_2 → $CH_3CH_2CH_2CH_2CH_2Cl$ + HCl [1]

(ii) $CH_3CH_2CH_2\dot{C}HCH_3$ [1]

(b) (Anhydrous) aluminium chloride / iron(III) chloride allow $AlCl_3$ / $FeCl_3$ [1]

(c) (i) orange / red precipitate [1]

(ii)



(1) —$COCH_3$ groups in any positions

It must contain a C=O group but it is not an aldehyde as it does not react with Tollens' reagent (1) [2]

(d) (i) (Alkaline) potassium manganate(VII) (solution) allow $KMnO_4$ / MnO_4^- [1]

(ii) Dilute acid allow HCl / H^+ [1]

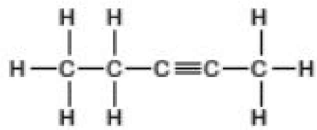
(iii) Lithium tetrahydridoaluminate(III) / lithium aluminium hydride allow $LiAlH_4$ [1]

(iv)

(e) Only the infrared spectrum of benzoic acid would have a peak at 1650–1750 cm^{-1} (1)
This is due to the carbonyl group present in the benzoic acid (1) [2]

Total [12]

7. (a)



[1]

(b) Moles of calcium carbide = 500/64.1 = 7.80 (1)

Moles of ethyne = 7.80

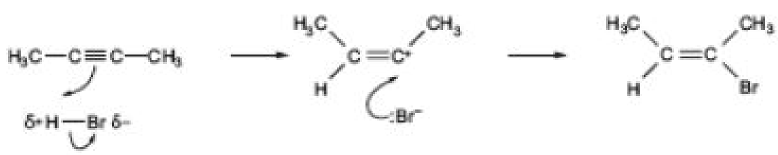
Volume of ethyne = 7.80 × 24.0 = 187 (dm^3) (1) [2]

(c) If the process is endothermic left to right then it needs to absorb energy – hence the high temperature / endothermic reactions need a high temperature [1]

(d)

[1]

(e)



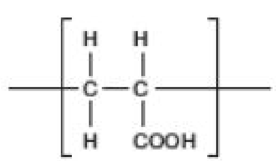
Curly arrows (1), full (1) and partial charges (1) [3]

(f) Any two for (1) each

energy costs / cost of **catalyst** / problems of separation of products / time taken / availability of starting materials / percentage yield / atom economy / relative health and safety [2]

(g) $C_6H_5 – C \equiv C – CH_2 – CH_3$ (1) C_1H_1 (1) [2]

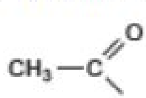
(h) (i)



[1]

(ii) I sulfuric acid / H_2SO_4 / phosphoric acid / H_3PO_4 / Al_2O_3 [1]

II 3-hydroxypropanoic acid does not show a C = C absorption at **1620–1670** cm^{-1} but this is present in propenoic acid [1]

III The  / $CH_3CH(OH)$ group is absent [1]

Total [16]

8.

(a) (i) 2 mol of ethanol gives 1 mol of ethoxyethane (1)

Moles of ethanol = $\frac{69}{46}$ = 1.5

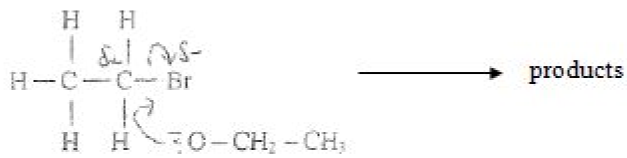
∴ Moles of ethoxyethane if theoretical yield = 0.75
∴ Moles of ethoxyethane if 45% yield = 0.75×0.45 = 0.34 (1)

Mass of ethoxyethane = 0.34×74 = 25g (1) allow error carried forward

[3]

(ii) Ethene / C_2H_4 [1]

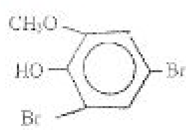
(iii)



(1) for correct curly arrows (1) for correct δ^+ and δ^- [2]

(iv) They need to have an N–H / O–H / F–H bond / a highly electronegative atom bonded to hydrogen [1]

(b) (i) For example



[1]

Accept any polybrominated species
Do not accept a monobrominated species

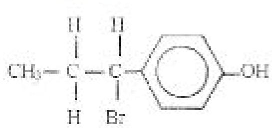
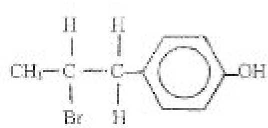
(ii) Bromine decolorised / orange to colourless / white solid [1]

(c) Reagent Iron(III) chloride solution / $FeCl_3$ (1)

Observation Purple coloration / solution (1) [2]

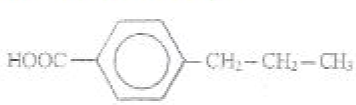
(d) (i) $C_{10}H_{12}O_1$ [1]

(ii)

[1]

(e) Displayed formula, for example



(1)

Functional group carboxylic acid (1) [2]

Total [15]

9.

(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]

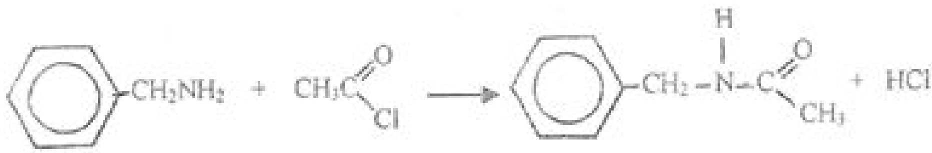
Total [13]

10.

(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]

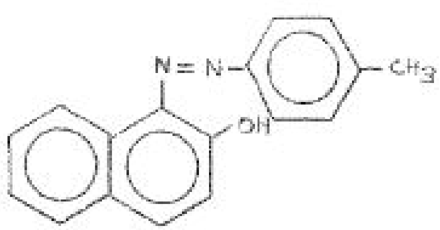
II Heated electrically / by a naked flame with a water bath (1)
Add compound **G** to the ethanol until the hot ethanol will (just) not dissolve any more solute (1)
Filter hot (1)
Allow to cool (1)
Filter (1)
Dry in air / window sill / < 60 °C in an oven (1) [5]

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]

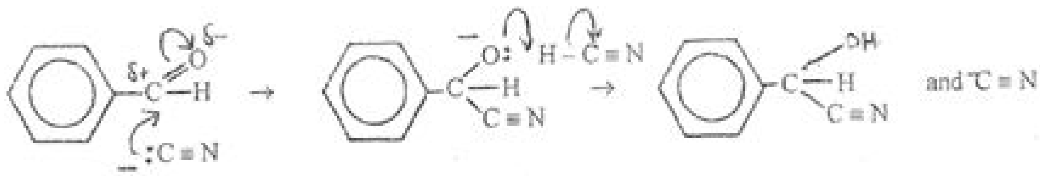
(iv) I The amine is reacted with sodium nitrite / HCl(aq) or nitrous acid (1)
at a temperature of < 10 °C (1) [2]

II



[1]

(b) (i) Nucleophilic addition (1)

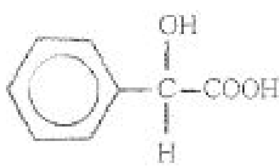


Accept a mechanism that shows HCN polarisation and nucleophilic addition as a concerted process

polarisation / charges shown (1) curly arrows on first structure (1)
regeneration of $^{-}$C≡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]

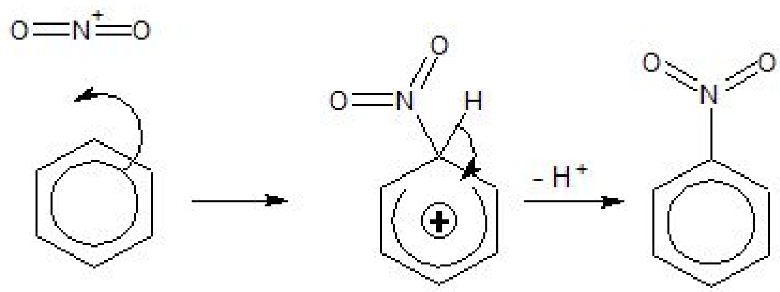
11.

(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)

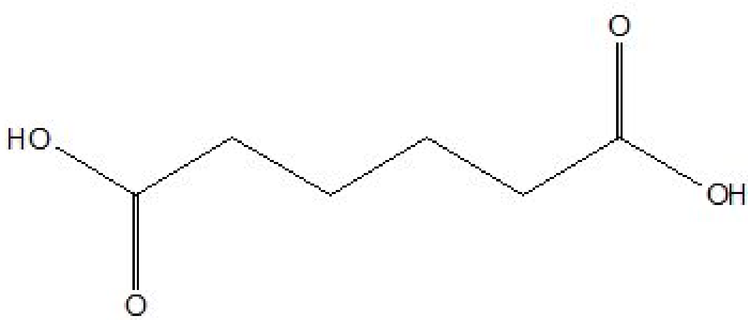


[3]

II (fractional) distillation / steam distillation [1]

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

(b) (i)



[1]

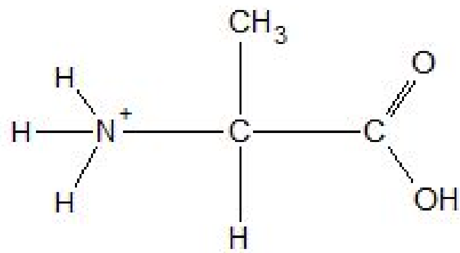
(ii) Addition polymerisation makes one product only /
Condensation produces one product plus a small molecule like water (1)

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)

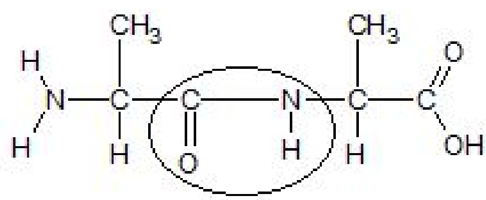
(max 2) [2]

(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]