Mark Scheme - 4.4 Aldehydes and Ketones

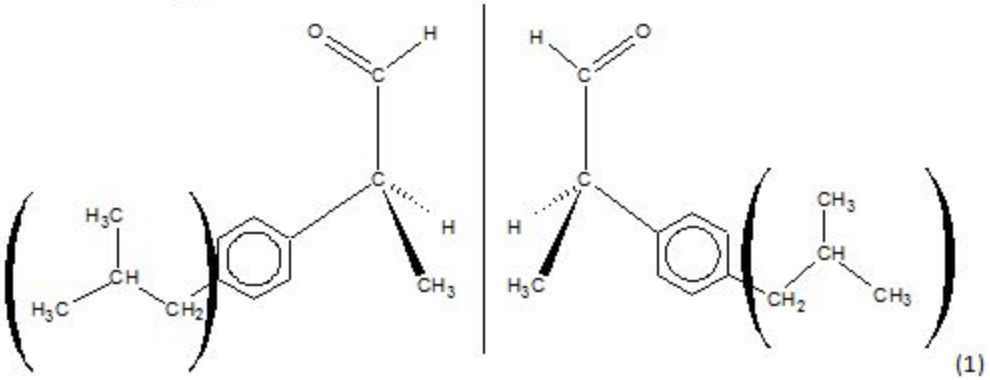
1.

(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]

2.

(a) Chromophore [1]

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

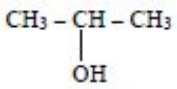
(ii) Identify percentage or amount of impurities (1)
Identify the number of compounds present or number of impurities (1) [2]

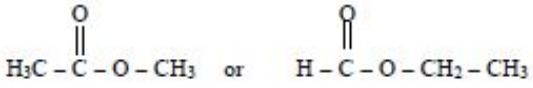
(c) (i) Acidified potassium dichromate (1)
Heat and distil (1) do not accept 'reflux' [2]

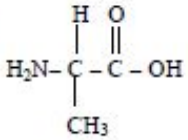
(ii) M_r of phenylmethanol = 108.08 M_r of benzenecarbaldehyde = 106.06 (1)
100% conversion would be 10.0 ÷ 108.08 × 106.06 = 9.815g (1)
86% yield = 9.815 × 86 ÷ 100 = 8.44g (1) [3]

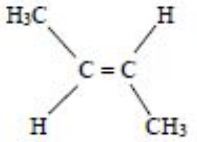
(iii) Two resonances in the range 5.8-7.0 ppm (1)
These are doublets (1)
One **singlet** at around 11.0 ppm (1)
All resonances have the same area (1) [4]

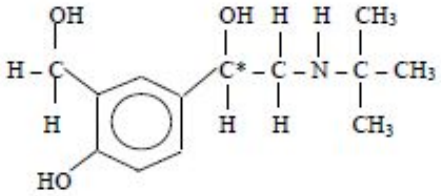
Total [13]

3. (a)(i)  [1]

(ii)  [1]

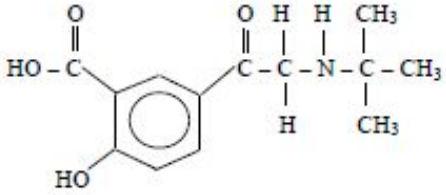
(iii)  [1]

(iv)  (or Z form) [1]

(b)(i)  [1]

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

(iii) Side effects from other optical isomer / lower dose needed / improved pharmacological activity / only one isomer has correct orientation to bind with biological molecule [1]

(iv)  [2]

(1 mark for acid (accept aldehyde), 1 mark for ketone)

(c)(i) Ethylamine, ethanol, phenol, ethanoic acid [1]

(ii) Ethylamine is basic because it accepts a proton readily (1) due to the lone pair of electrons on the nitrogen. (1)
Phenol is acidic because it loses a proton / the anion formed is stabilised (1) by delocalisation of the negative charge over the benzene ring. (1)
(Accept description e.g. in phenoxide ion lone pairs of electrons on oxygen become delocalised with electrons in benzene ring.) [4]

Total [14]

4.

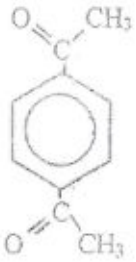
(a) (i) $CH_3CH_2CH_2CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2CH_2CH_2Cl + HCl$ [1]

(ii) $CH_3CH_2CH_2\overset{\bullet}{C}HCH_3$ [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]

5.

(a) (i) Moles NaOH = 5.675×10^{-3} (1)

M_r O = $\frac{0.50}{0.005675}$ = 88.1 (1) [2]

(ii) **K** contains C=O due to 2, 4-dinitrophenylhydrazine reaction (1)

Contains CH_3CO due to positive iodoform test (1)

From M_r **K** must be CH_3COCH_3 (1)

O contains COOH due to neutralisation / decarboxylation reaction (1)

From M_r O must be $CH_3CH_2CH_2COOH$ / $(CH_3)_2CHCOOH$ (1) [5]

(iii) L is $CH_3CH(OH)CH_3$ (1)

M is C_3H_6 (1)

N is C_3H_8 (1) [3]

(iv) Concentrated H_2SO_4 / Al_2O_3 / concentrated H_3PO_4 [1]

(b) (i) To form the acid from the salt / to precipitate the acid / the salt is water soluble [1]

(ii) The acid is soluble in hot water but insoluble in cold water [1]

(iii) Moles = 3.2/40 = 0.08 (1)

Concentration = 0.08/0.04 = 2 mol dm^{-3} (1) [2]

(iv) Mass = 2.90 x 1.06 = 3.074 g (1)

Moles = 3.074/150.1 = 0.0205 (1) [2]

(v) Maximum mass = 0.0205 x 122 = 2.50 g (1)

% yield = 1.45/2.50 = 58.0% (1) [2]

(vi) Hydrolysis not complete / equilibrium forms / C_6H_5COOH slightly soluble in water / two stages so some loss at both / mass lost during recrystallisation [1]

Total [20]

6.

(a)

	Butan-2-ol	Ethanal	Ethanol	Propanone
2,4-DNP	No reaction	Yellow-orange precipitate	No reaction	Yellow-orange precipitate
Tollens' reagent	No reaction	Silver mirror	No reaction	No reaction
I_2/NaOH	Yellow precipitate	Yellow precipitate	Yellow precipitate	Yellow precipitate

(1 mark for each column) [4]

(b)(i) Electrophilic addition [1]

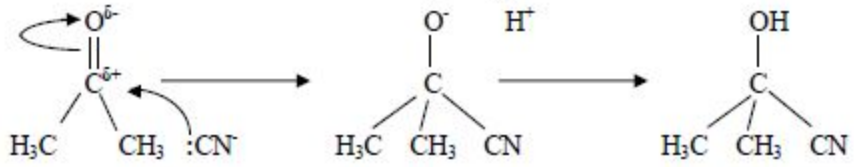
(ii) Carbonium ion / carbocation / electrophile [1]

(iii) Bromination / HBr addition / hydrogenation[1]

(iv) Secondary carbocation more stable than primary carbocation [1]

(c)(i) Nucleophilic addition [1]

(ii)



[3]

1 mark electron movement
1 mark charges

1 mark intermediate and electron movement

(Accept $CN^{\delta-} - H^{\delta+}$ for CN^-)

Total [12]