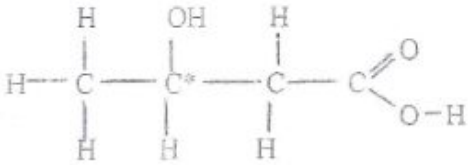
Mark Scheme - 4.5 Carboxylic Acids and Derivatives

1. Reagent: acidified potassium dichromate / $Cr_2O_7^{2-}$ and H^+
or acidified manganate(VII) / MnO_4^- and H^+ (1)

Colour change: from orange to green
or from purple to colourless (1) [2]

2. (a)



[1]

(b) (i) Acidified potassium dichromate allow H^+, $Cr_2O_7^{2-}$ [1]

(ii) I An equimolar mixture of two enantiomers / optical isomers
do not accept 'equal mixture' [1]

II It has no (apparent) effect on the plane of polarised light [1]

(c) (i) But-2-enoic acid; this is because each of the carbon atoms of the double bond has two different groups / atoms
allow reason based on the other isomer [1]

(ii) Any TWO from the following for (1) each
reagent used / temperature / quantities / time of reaction / catalyst / solvent [2]

(d) Reagent(s) KOH / I_2 or NaOCl / KI (1) allow names
Observation Yellow precipitate (1) [2]

(e) The NMR spectrum will consist of two peaks, as there are two discrete 'areas' of protons; these will be seen at between 2.0 to 2.5 (CH_3) and between 2.5 to 3.0 (CH_2) (1)
The peak area ratio will be 3:2 for the CH_3 and CH_2 protons respectively (1)
There will be no splitting of either signal as the protons causing these signals are not bonded directly to other carbon atoms that also have protons (1)

1 max if only one peak described correctly [3]

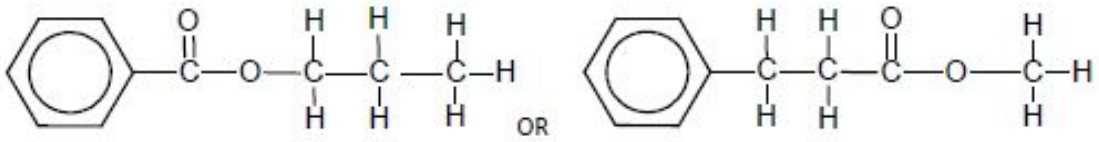
QWC *Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning.* [1]

Total [13]

3.

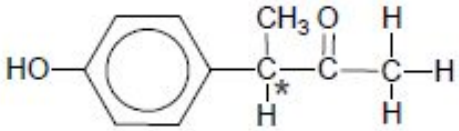
(a) Any valid ester structure with formula $C_{10}H_{12}O_2$ [1]

Examples:



(b) (i) Compound X [1]

(ii) [1]



(iii) Rotate the plane of polarised light in opposite directions [1]

(c)

Reagent(s)	*Observation if the test is positive*	*Compound(s) that would give a positive result*
I_2 / NaOH (aq)	Yellow solid	X
Na_2CO_3 (aq)	Bubbles of colourless gas / effervescence	W
$FeCl_3$ (aq)	Dark purple/blue/green - do not accept 'precipitate'	X, Z

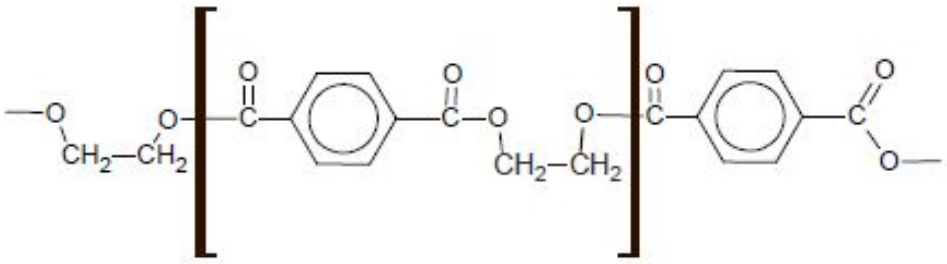
(1 mark for each box) [6]

(d) (i) Heat / Alkaline / Potassium manganate(VII) / then acidify
(1 mark for Potassium manganate + 1 other point; 2 marks for all) [2]

(ii) I. Addition polymer – One large molecule formed only / Condensation polymer – one large molecule with small molecules (e.g. water) lost. (1)

Addition polymer – one starting material / Condensation – two starting materials
OR Addition polymer – one functional group in each molecule/ Condensation polymer – two functional groups in each molecule (1) [2]

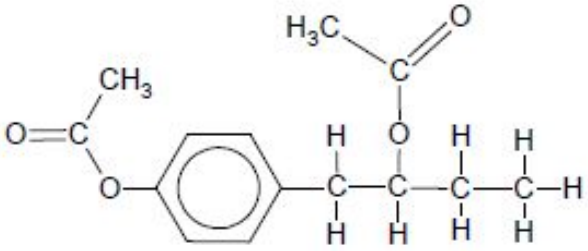
II.



[1]

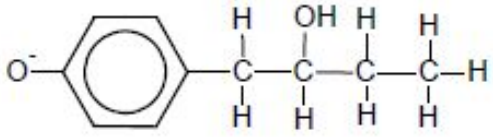
(e) (i) $NaBH_4$ / $LiAlH_4$ or name(1) Reduction (1) [2]
- ignore conditions unless $LiACH_4$ in water
- do not accept 'redox'

(ii)



Accept structures with only one –OH group reacted. [1]

(iii) [1]



[19 marks]

4.

(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]

5.

(a) Benzene is a compound whose molecules contain six carbon atoms bonded in a (hexagonal) ring (1)
All the carbon to carbon bond lengths are equal / intermediate (1)
Each carbon atom is bonded to two other carbon atoms and a hydrogen atom (1)
by σ-bonds (1)
All the C – $\hat{C}$ – C angles are the same / 120° (1)
The remaining p electron of each carbon atom / overlap of p orbitals forms a delocalised cloud of electrons / π-system (1) above and below the plane (1)
Credit can be gained from labelled diagram
[*Candidates can gain a maximum of (4) for this part*]

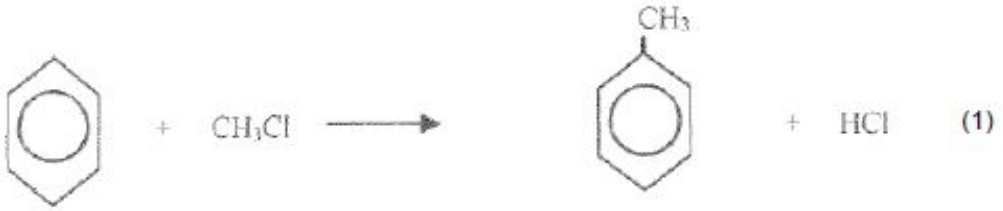
This delocalisation increases the **stability** (1) of the molecule and this stability is maintained by benzene undergoing substitution reactions in preference to addition reactions (that would destroy the delocalised system)
The π-cloud is **electron rich** and will be attracted to electron deficient electrophiles (1)
[*Candidates can gain (2) for this part*]

[6]

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter (1)

Legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning. (1) *QWC* **[2]**

(b)



(1)

catalyst eg $AlCl_3$ (anhydrous) (1) **[2]**

(c) (i) (There are two environments for the protons), the 3 aromatic protons at ~6.8 δ and the 9 methyl / aliphatic protons at ~ 2.3 δ (1)
These give a peak area of 3:9, ie.1:3 (1)
These environments are separate / discrete (1) therefore no splitting pattern

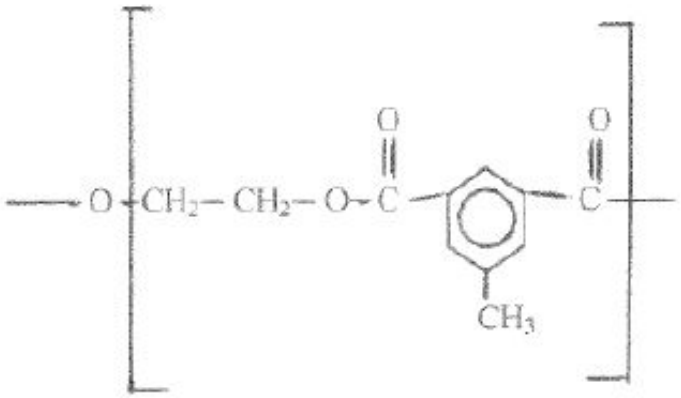
[3]

(ii) Dissolve in the minimum volume (1)
Of hot water (1)
(Filter hot) (1)
Cool (1)
Filter (1)
Dry (1)

(*up to 4 max but candidates must give the first two points in order to gain full credit*)

[4]

(iii)



[1]

(iv) Reagent **S** is alkaline potassium manganate(VII) (1)

Reagent **T** is eg hydrochloric acid (1)

[2]

Total [20]

6.

(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]

7.

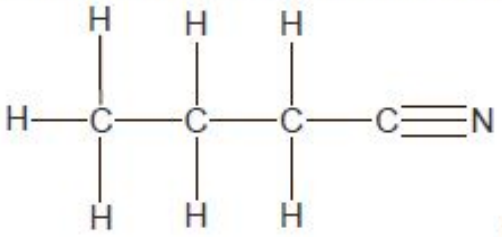
(a) (i) Nucleophilic substitution / Hydrolysis [1]

(ii) Dissolved in alcohol (1) Propene or unambiguous structure (1) [2]

(iii) Potassium manganate(VII) / Potassium dichromate(VI) - must be name (1)
Oxidation (1) [2]

(iv) (Add Potassium dichromate(VI)) and distil off the propanal from the reaction mixture [1]

(b) (i) Step 1: Potassium cyanide in ethanol / Heat (1)
Step 2: Heat with aqueous hydrochloric acid (or other acid) (1)



(1) [3]

(ii) Two points from different bullet points – 1 mark each.

- Atom economy / Amount of waste / Whether waste material was recyclable / Whether waste was toxic.
- Amount of energy required / temperature required / pressure required / conditions used
- Rate of production / time
- Availability of catalyst
- Cost of reactants / Availability of reactants / toxicity of reactants.
- Two step processes usually have lower yields than one step processes / percentage yield [2]
- Purification method / separation

(c) (i) Butanoic acid is $C_4H_8O_2$ so $M_r = 88$ (1)
Percentage carbon = 48/88 x 100 = 54.5%; percentage hydrogen = 8/88 = 9.1%;
Percentage oxygen = 32/88 = 36.4% (At least two of these for 1)
OR empirical formula for butanoic acid = C_2H_4O (1) and
calculate empirical formula from percentage masses = C_2H_4O (1) [2]

(ii) Structure 1 mark + 4 marks for explanations.

- Product is ethyl ethanoate. (1)
- Two points from the following required for each mark– MAX 4 marks
  - Sweet-smelling = ester
  - Peak at 1.0ppm implies – CH_3
  - Peak area 3 = CH_3
  - Peak area 2 = CH_2
  - Triplet shows CH_3 is next to a CH_2 group.
  - Singlet shows CH_3 no hydrogen atoms bonded to adjacent carbon.
  - Peak at 2.1 ppm suggests this is next to C=O.
  - Quartet shows CH_2 is adjacent to a CH_3 group.
  - Peak at 4.0 ppm shows it is –O-CH_2-
  - IR Peak at 1752 cm^{-1} = C=O
  - IR Peak at 2981 cm^{-1} = C-H or O-H
  - Cannot be –OH as we know there is no –OH in NMR spectrum

[5]

QWC: selection of a form and style of writing appropriate to purpose and to complexity of subject matter. (1)

QWC: organisation of information clearly and coherently; use of specialist vocabulary where appropriate. (1) [2]

[20 marks]