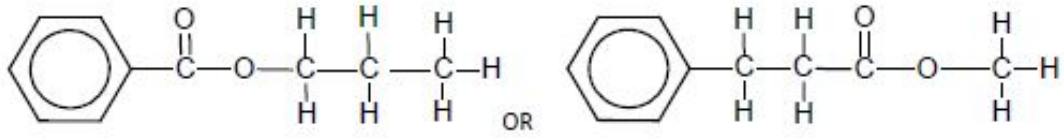
Mark Scheme - OA1.2 Aromaticity

1

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

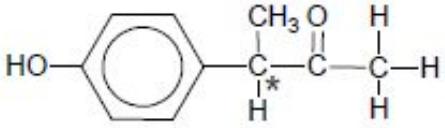
Examples:



OR

(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

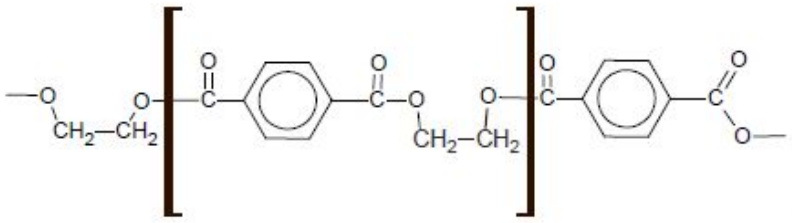
(1 mark for each box) [6]

(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]

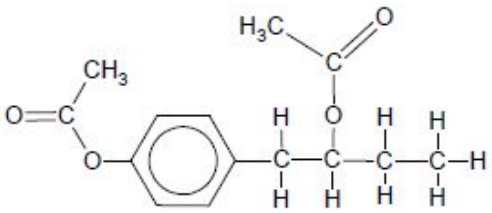
II.



[1]

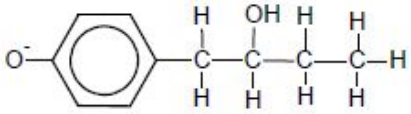
(e) (i) $NaBH_4$ / $LiAlH_4$ or name(1) Reduction (1) [2]
- ignore conditions unless $LiACH_4$ in water
- do not accept 'redox'

(ii)



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

(iii) [1]



[19 marks]

2 (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*]

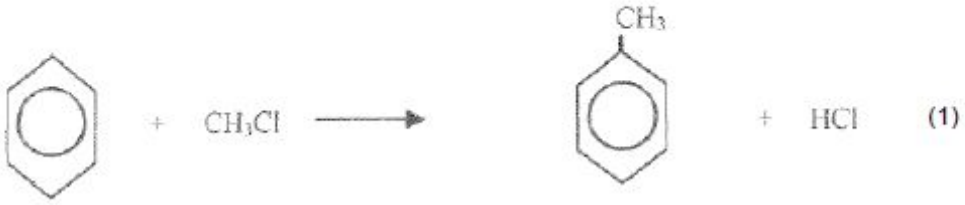
This delocalisation increases the **stability** (1) of the molecule and this stability is maintained by benzene undergoing substitution reactions in preference to addition reactions (that would destroy the delocalised system)
The π-cloud is **electron rich** and will be attracted to electron deficient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

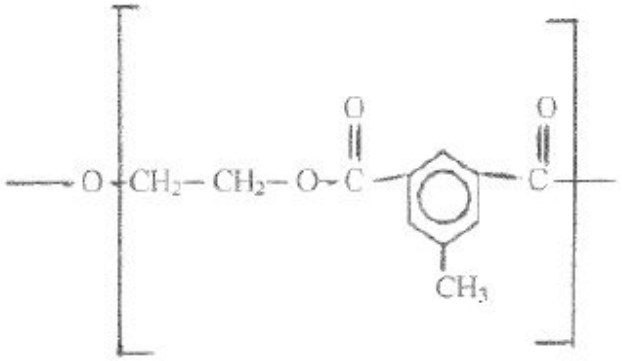
[3]

(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)

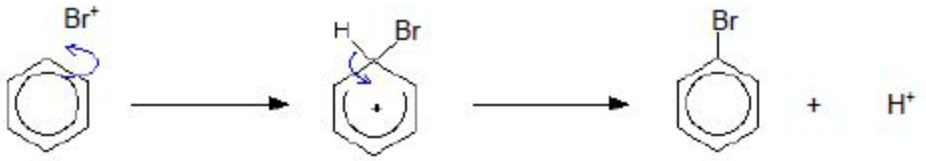
Reagent **T** is eg hydrochloric acid (1)

[2]

Total [20]

3 (a) (i) Electrophilic substitution [1]

(ii) $Br_2 + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$



Formation of Br^+ (1), curly arrows (1), intermediate (1) [3]

(b) (i) The extra stability in the benzene molecule due to electron delocalisation / the difference in energy between the experimental $\Delta H^\ominus$ reaction for benzene and the $\Delta H^\ominus$ reaction according to the Kekulé structure [1]

(ii) If benzene had 3 double bonds enthalpy change would be $3 \times -120 = -360$ kJ mol^{-1} (1)

Delocalisation energy is difference between -360 and $-208 = 152$ kJ mol^{-1} (1) [2]

(c) Benzene is carcinogenic / toxic [1]

4 (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]

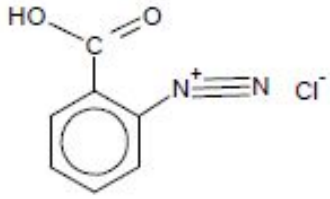
(iii) I. Lower melting point / melts over a range [1]
II. 1 mark for each point.
- Dissolve in the minimum volume
- Of hot water
- Filter hot
- Allow to cool
- Filter
- Dry residue under suction / in oven below 142°C

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]

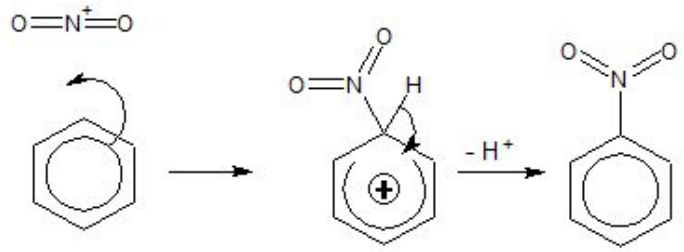
[20 marks]

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]

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

(b) (i)

[1]

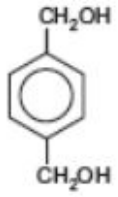
accept C_6H_5 in place of the ring accept equations that show the catalyst

(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]

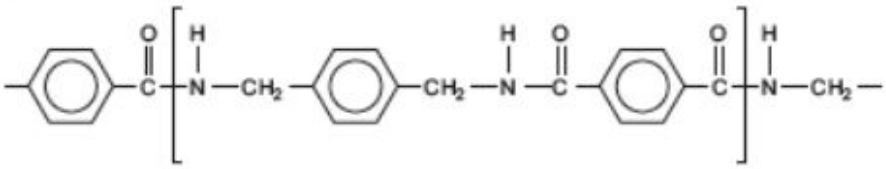
(d) (i) Any 2 from NMR / HPLC / GC / refractive index / mass spectra / boiling temperature [2]

(ii)



[1]

(e) (i)



[1]

(ii) protein / dipeptide / polypeptide [1]

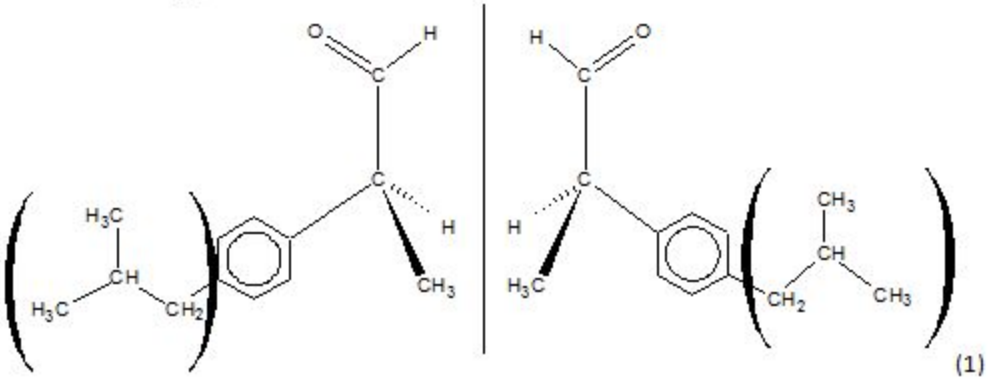
Total [12]

7 (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]