

- (c) (i) For each signal. (1) for identification and (1) for reason. [6]
- δ 11.7. H of -OH or -COOH; one H: ✓
 because it exchanges with D₂O/labile proton }
 or singlet because it has no ✓
 H atoms on an adjacent atom }
 or data table 11.0 - 11.7 }
- δ 2.4. 2H of -CH₂- ✓
 quartet because it has 3 H atoms on the adjacent carbon }
 (n+1) = 4 lines } ✓
 or data table 2.0 - 2.9 CHC=O }
- δ 1.1. 3H of CH₃- ✓
 triplet because it has 2 H atoms on the adjacent carbon }
 (n+1) = 3 lines ✓ } ✓
 or data table 0.7 - 1.6 CH₃-R }
- (ii) It is due to OH and the proton can exchange/swap/substitute [1]
 (1) with the D in D₂O. ✓
or D replaces H
 NOT just reacts with water

Total = 17

- 6 (a) (i) propanone ✓ [1]
accept acetone or propan-2-one
- (ii) propanal ✓ [1]
accept propanaldehyde but not ethanal
- (b) (i) reagent(s): e.g. 2,4-dinitrophenylhydrazine ✓ [2]
in words or formula
observation: e.g. orange / red / yellow precipitate / crystals ✓
no mark for observation if no reagent given
- (ii) reagent(s): e.g. ammoniacal AgNO₃ ✓ or Ag₂O or Ag⁺ or Tollens [3]
observation for D: No change ✓
observation for E: silver (mirror) ✓ grey ppte
or similarly for another chemical test that works e.g. acid dichromate, Fehlings or CHI₃ test
- (c) (i) Marked cross at $\nu \sim 1700$ ✓ [2]
D has carbonyl group or ketone or C=O ✓
- (ii) e.g. Reduction CH₃COCH₃ → CH₃CHOHCH₃ (1) [2]
(or product is an alcohol)
new (broad) peak at $\sim 3230 - 3550 \text{ cm}^{-1}$ (1)
loss of peak at $\sim 1700 \text{ cm}^{-1}$ (1)
any two good points ✓ ✓

| | | | | |
|-----------------------------------|--------------------------|------------------------|---------------------|----------------------|
| Mark Scheme Page 6 of 8 | Unit Code 2814 | Session June | Year 2002 | Final Version |
|-----------------------------------|--------------------------|------------------------|---------------------|----------------------|

| Qu. | Expected answers: | Marks |
|-----------|---|--|
| 6 (a) (i) | C_7H_8O ✓ | [1] |
| | (ii) $M_r = 108$ so m/e of molecular ion = 108 / ecf from (i) ✓ | [1] |
| | (iii) %C = $(84.0)/(108) \times 100\% = 77.8\%$ ✓ %H = $(8.0)/(108) \times 100\% = 7.4\%$ ✓ / ecf from (i) or (ii) | [2] |
| (b) | K has OH group ✓ K has peak at $3230 - 3550 \text{ cm}^{-1}$ ✓ L does not have OH group / peak at $3230 - 3550 \text{ cm}^{-1}$ ✓ | (ignore reference to any other bonds) [3] |
| (c) (i) | peak at $\delta = 7.3\text{ppm}$ / with area 5, is due to the benzene ring (protons) ✓ peak at $\delta = 4.5\text{ppm}$ / with area 2, is due to the $-CH_2-$ (protons) ✓ peak at $\delta = 3.2\text{ppm}$ / with area 1, is due to the OH (proton) ✓ | [3] |
| | (ii) peak at $\delta = 3.2\text{ppm}$ / with area 1 disappears / ecf from (i) ✓ | [1] |
| | (iii) expect peak at $\delta = 7.1-7.7 \text{ ppm}$ ✓ 5 protons responsible / area = 5 ✓ expect peak at $\delta = 3.3-4.3\text{ppm}$ ✓ 3 protons responsible / area = 3 ✓ | [4] |
| | | [Total: 15] |

3 (a) ester ✓
(primary) amine ✓ [2]

(b) (i) $C_8H_9NO_2$ ✓ [1]

(ii) M_r of A = 151 (or ecf from (i)) ✓
 moles A = $0.100g/151 = 0.000662$
 conc A = $0.000662/0.330dm^3$
 = 0.002 / 0.0020 (ecf from a wrong M_r) ✓ [2]

(c) (i) peaks identified
 peak X – benzene ring protons ✓
 peak Y – CH_2 protons ✓
 peak Z – CH_3 protons ✓

3 identification marks

reasoning from δ value . . for each, either.

- quotes the relevant functional group in the Data Sheet (eg $-O-CH_2-R$) /or
- quotes the relevant Data Sheet range (eg 3.3–4.3) / or
- from first principles using the expected deshielding to assign the peaks
 ✓✓✓

reasoning from the splitting pattern .

- Y peak is a quadruplet / 1:3:3:1 etc
 this is due to 3 neighbours / adjacent to a CH_3 ✓
 Z peak is a triplet / 1:2:1 etc
 this is due to 2 neighbours / adjacent to a CH_2 ✓

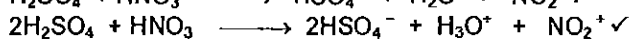
ANY 3 out of 5 reasoning marks [6]

(ii) peak at $1700cm^{-1}$ and/or at $1280cm^{-1}$ marked ✓ [1]

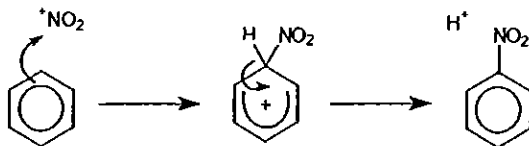
[Total: 12]

4 (a) (i) reagents conc $\text{H}_2\text{SO}_4 + \text{HNO}_3$ ✓

electrophile NO_2^+ ✓



mechanism

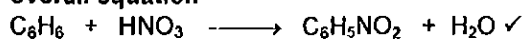


curly arrow from benzene π -bond to electrophile ✓

correct intermediate (ecf on electrophile formula) ✓

curly arrow from C-H bond to π -bond and H^+ formed ✓

overall equation



ANY 6 out of 7 [6]

(ii) NO_2^+ accepts an electron pair ✓
H is replaced / substituted by NO_2 ✓

[2]

(b) two peaks ✓
peak at/between 2.3-2.7 ✓
peak at/between 7.1-7.7 ✓

[3]

[Total: 11]

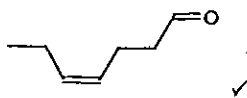
(b) 1 doublet and 1 quadruplet / 1 3 3 1 and 1.1 ✓
correct reason for at least one peak ✓
(eg 1,3 3,1 due to 3 neighbours / next to CH₃ / use of n+1 rule)

[2]

(c) (i) C₇H₁₂O ✓

[1]

(ii)



[1]

(iii)

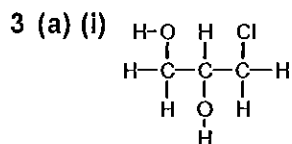


[2]

[Total: 13]

- 2 (a) (i) $\text{CH}_3\text{CHClCH}_3$ ✓ allow any formula that is unambiguously 2-chloropropane [1]
- (ii) $\text{CH}_3\text{CHClCH}_3 + \text{C}_6\text{H}_6 \longrightarrow \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2 + \text{HCl}$ ✓ [1]
- (iii) halogen carrier ✓ [1]
- (b) (i) **peaks identified**
- peak X – CH_3 (protons) ✓
 - peak Y – CH (proton) ✓
 - peak Z – benzene ring (protons) ✓
- 3 identification marks
- reasoning from δ value ... for each, either:**
- quotes a δ value for the peak and refers explicitly to the Data Sheet /or
 - quotes the relevant functional group in the Data Sheet (eg R- CH_3 for X) /or
 - quotes exactly the relevant Data Sheet range, ie (0.7–1.6 for X)
(2.3 – 2.7 for Y)
(7.1 – 7.7 for Z) ✓✓✓
- 3 reasoning marks
- ignore any attempts to reason from the splitting here, but look out for credit to parts (ii) and (iii) if not given below
- [6]
- (ii) 1 proton / CH/ 'n' = 1 (using the n+1 rule) ✓
- on the neighbouring/adjacent carbon ✓ [2]
- (iii) the CH_3 protons are all equivalent/in the same (chemical) environment / there are six protons adjacent to the CH ✓ [1]

[Total: 12]



the correct compound ✓

shown as a correctly displayed formula ✓

[2]

(ii) yes, because there are four different groups
around the central carbon ✓
(or ecf on the structure given in (i)) AW

allow asymmetric / non-super-
imposable on its mirror image

[1]

(b) infra-red/i.r. (spectroscopy) ✓
peak/absorption at 3230 - 3550 (cm^{-1}) ✓

n.m.r. (spectroscopy) ✓
peak at 3.5–5.5 (ppm) ... ✓
... which disappears in D_2O ✓

Quality of Written Communication

mark for good organisation / a logical response and
technical terms, using at least two of the following
words:

infra-red, nuclear magnetic resonance, spectroscopy,
wavenumber, cm^{-1} , chemical shift, ppm) ✓

[6]