

- (c) (i) For each signal. (1) for identification and (1) for reason. [6]
- $\delta$  11.7. H of -OH or -COOH; one H: ✓  
 because it exchanges with D<sub>2</sub>O/labile proton }  
 or singlet because it has no ✓  
 H atoms on an adjacent atom  
 or data table 11.0 – 11.7 }
- $\delta$  2.4. 2H of -CH<sub>2</sub>- ✓  
 quartet because it has 3 H atoms on the adjacent carbon }  
 (n+1) = 4 lines } ✓  
 or data table 2.0 – 2.9 CHC=O }
- $\delta$  1.1. 3H of CH<sub>3</sub>- ✓  
 triplet because it has 2 H atoms on the adjacent carbon }  
 (n+1) = 3 lines ✓ } ✓  
 or data table 0.7 – 1.6 CH<sub>3</sub>-R }
- (ii) It is due to OH and the proton can exchange/swap/substitute [1]  
 (1) with the D in D<sub>2</sub>O. ✓  
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 ✓
- (ii) no mark for observation if no reagent given  
*reagent(s)*: e.g. ammoniacal  $\text{AgNO}_3$  ✓ or  $\text{Ag}_2\text{O}$  or  $\text{Ag}^+$  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  $\text{CHI}_3$  test
- (c) (i) Marked cross at  $\nu \sim 1700$  ✓ [2]  
D has carbonyl group or ketone or  $\text{C}=\text{O}$  ✓
- (ii) e.g. Reduction  $\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{CHOHCH}_3$  (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 ✓ ✓

<b>Mark Scheme</b> Page 6 of 8	<b>Unit Code</b> 2814	<b>Session</b> June	<b>Year</b> 2002	<b>Final Version</b>
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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 $3230 - 3550\text{ cm}^{-1}$ ✓ (ignore reference to any other bonds) L does not have OH group / peak at $3230 - 3550\text{ cm}^{-1}$ ✓	[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  $\delta$  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  $CH_2$  ✓

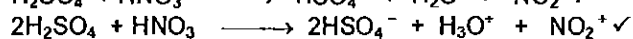
ANY 3 out of 5 reasoning marks [6]

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

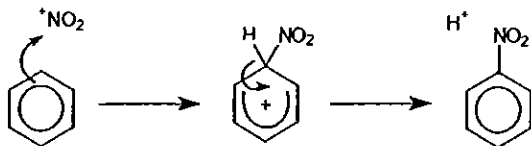
[Total: 12]

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

electrophile  $\text{NO}_2^+$  ✓



mechanism

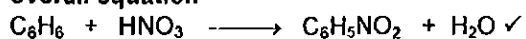


curly arrow from benzene  $\pi$ -bond to electrophile ✓

correct intermediate (ecf on electrophile formula) ✓

curly arrow from C-H bond to  $\pi$ -bond and  $\text{H}^+$  formed ✓

overall equation



ANY 6 out of 7 [6]

(ii)  $\text{NO}_2^+$  accepts an electron pair ✓  
H is replaced / substituted by  $\text{NO}_2$  ✓

[2]

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

[3]

[Total: 11]

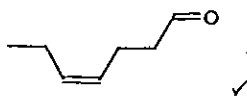
- (b) 1 doublet and 1 quadruplet / 1 3 3 1 and 1.1 ✓  
 correct reason for at least one peak ✓  
 (eg 1,3 3,1 due to 3 neighbours / next to CH<sub>3</sub> / use of n+1 rule)

[2]

- (c) (i) C<sub>7</sub>H<sub>12</sub>O ✓

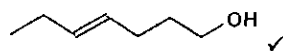
[1]

(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 –  $\text{CH}_3$  (protons) ✓

peak Y – CH (proton) ✓

peak Z – benzene ring (protons) ✓

3 identification marks

reasoning from  $\delta$  value ... for each, either:

- quotes a  $\delta$  value for the peak and refers explicitly to the Data Sheet /or
- quotes the relevant functional group in the Data Sheet (eg  $\text{R-CH}_3$  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) ✓✓✓

ignore any attempts to reason from  
the splitting here, but look out for  
credit to parts (ii) and (iii) if not  
given below

3 reasoning marks

[6]

(ii) 1 proton / CH/ 'n' = 1 (using the n+1 rule) ✓

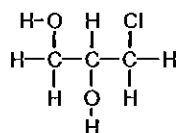
on the neighbouring/adjacent carbon ✓ [2]

(iii) the  $\text{CH}_3$  protons are all equivalent/in the same  
(chemical) environment / there are six protons  
adjacent to the CH ✓

[1]

[Total: 12]

3 (a) (i)



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 ( $\text{cm}^{-1}$ ) ✓

n.m.r. (spectroscopy) ✓  
peak at 3.5–5.5 (ppm) ... ✓  
... which disappears in  $\text{D}_2\text{O}$  ✓

**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,  $\text{cm}^{-1}$ , chemical shift, ppm) ✓

[6]