19 Modern analytical techniques II

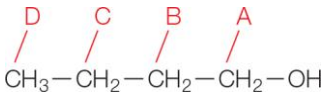
Answers to Exam practice questions

Pages 310–314

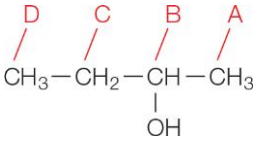
1 a) $C_4H_{10}O$ M_r = 74.1212 [1]

$C_3H_6O_2$ M_r = 74.0783 and $C_2H_6N_2O$ M_r = 74.0816 [1]

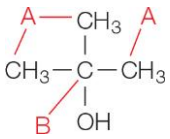
b) Isomer 1 – 4 peaks



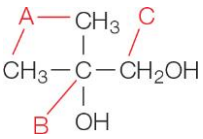
Isomer 2 – 4 peaks



Isomer 3 – 2 peaks



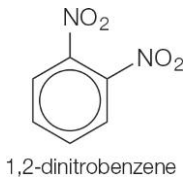
Isomer 4 – 3 peaks



c) If the compound in part **(a)** is an alcohol that is unaffected by acidified potassium dichromate(VI), it must be a tertiary alcohol. [1] Isomer 3 shown in the answer to part **(b)** is the tertiary alcohol, 2-methylpropan-2-ol. [1]

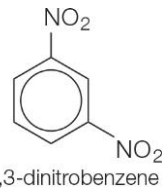
2 a) $C_6H_6 + 2HNO_3 \rightarrow C_6H_4(NO_2)_2 + 2H_2O$ [1]

b)



1,2-dinitrobenzene

[1]



1,3-dinitrobenzene

[1]

1,4-dinitrobenzene

[1]

c) ^{13}C NMR would confirm that the major product, 1,3-dinitrobenzene, has four peaks in its spectrum. [1]

The minor products are 1,2-dinitrobenzene with three peaks [1] and 1,4-dinitrobenzene with two peaks. [1]

3 a) Top spectrum: peak at *m/z* = 105: $C_6H_5CO^+$ [1]; peak at 77: $C_6H_5^+$ [1]

Bottom spectrum: peak at 93: $HO–C_6H_4^+$ [1]

b) Top spectrum: benzoic acid [1] can produce peaks at *m/z* = 105 and 77

but disubstituted 3-hydroxybenzaldehyde cannot. [1]

c) Tollens' reagent [1]: gives silver mirror with 3-hydroxybenzaldehyde [1]; no reaction with benzoic acid. [1]

Sodium hydrogen carbonate (aqueous) [1]: gives effervescence with benzoic acid [1]; no reaction with 3-hydroxybenzaldehyde. [1]

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4 a) i) Three environments. [1]

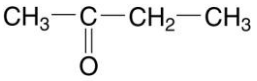
ii) From the integration trace data: 3 : 3 : 2 [1]

b) Peak at δ = 1.0: R–CH_3 [1]; peaks at δ = 2.1 and 2.5: consistent with H_3C–CO– and RCH_2CO–. [1]

c) Peak at δ = 1.0: triplet – two protons on an adjacent carbon atom. [1]

Peak at δ = 2.5: quadruplet – three protons on an adjacent carbon atom. [1]

d) The compound is a carbonyl compound. [1] It is a ketone and not an aldehyde. [1] There is no –OH group in the molecule so it is not an alcohol or acid. [1]

e) Butan-2-one  [1]

5 a) The larger the molecules, the more strongly they are adsorbed by the stationary phase. [1] Larger molecules are less volatile because they are more polarisable and London forces can act over a larger area. [1]

b) A more compact, branched molecule [1] is more volatile and less strongly adsorbed than an unbranched molecule. [1]

c) i) The chemicals in the beer sample: ethanol, propan-2-ol (or 2-methylpropan-1-ol), propanone, ethanoic acid, propanal (or butan-2-ol), butanal and butanoic acid.
6–7 correct [3]; 4–5 correct [2]; 2–3 correct [1]

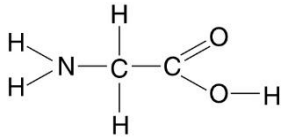
ii) The peaks where there are chemicals with very similar retention times are hard to identify [1] – see the answer to part **(i)**. [1]

d) The peak is propanal (CH_3CH_2CHO) and not butan-2-ol ($CH_3CH_2CH(OH)CH_3$). [1]

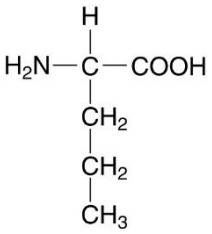
Reasons:

- the molecular ion has a mass-to-charge ratio of 58 (not 74) [1]
- the peak at 57 corresponds to $CH_3CH_2CO^+$ [1] and the large peak at 29 to CHO^+ or $CH_3CH_2^+$. [1]

6 a) Original spot of hydrolysed dipeptide [1]; solvent front [1]; correct length for distance B moved (0.60 × distance solvent moved) [1]; correct length for distance C moved (0.26 × distance solvent moved). [1]

b) i)  [1]

ii) $C_5H_{11}O_2N$ [1]

iii)  or branched chain [2]

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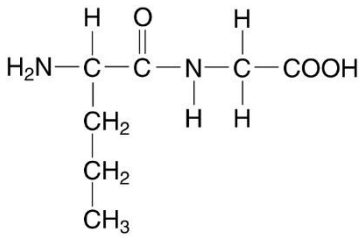
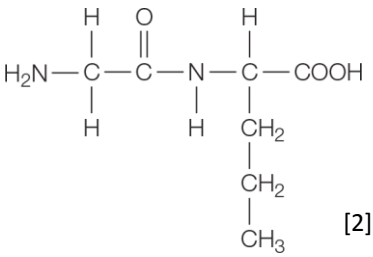
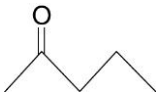
c)  OR  [2]

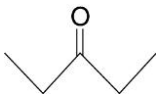
In either case, the C_3H_7– chain could also be branched.

d) Spray the chromatogram with a solution of ninhydrin [1] in propanone.

Heat the paper in an oven at about 100 °C. [1]

e) Make a solution of B in water. Use this in a polarimeter [1] and show that it rotates the plane of plane-polarised light. [1]

7 a) Pentan-2-one  [1]

pentan-3-one  [1]

b) The two isomers have the same molar mass. [1] Their molecular ion peaks have the same value for *m/z*. [1]

c) i) *m/z* = 29: $CH_3CH_2^+$ [1]

m/z = 43: CH_3CO^+ [1]

m/z = 57: $CH_3CH_2CO^+$ [1]

m/z = 71: $CH_3CH_2CH_2CO^+$ [1]

ii) Ketone X is pentan-2-one [1]; ketone Y is pentan-3-one. [1]

d) i) 5 peaks [1]

C=O (ketone) 200–220 ppm (actually 209 ppm). [1]

The other peaks in the region 0–60 [1] (actually 46 for C3 and 30 for C1 either side of the carbonyl group, 17 for C4 and, 14 for C5).

ii) Two environments for hydrogen [1], one with 6 atoms and the other 4. [1]

One peak at a chemical shift in the range 1.8 to 3.0 (actually 2.4) [1], split into four by the neighbouring methyl groups. [1]

A second peak in the range 0.2 to 1.8 (actually 1.1) [1], split into three by the adjacent CH_2 groups. [1]

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8 Mass spectrum shows M_r = 72. [1]

^{13}C NMR spectrum shows three carbon environments. [1]

172 ppm means C=O. [1]

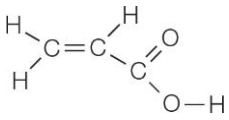
Two peaks [1] in range 120–140 ppm means C=C. [1]

Infrared broad peak in range 3300–2500 cm^{-1} means O–H carboxylic acid. [1]

COOH has mass 45, so this leaves 27 for the rest of the molecule [1], which is $H_2C{=}CH$. [1]

Compound is propenoic acid. [1]

Displayed formula:



[1]

9 **a)** The presence of pairs of lines of roughly equal height separated by 2 *m*/*z* units strongly suggests that there is a single bromine atom in the molecule of Z. [1] The bromine-79 and bromine-81 isotopes are equally abundant. [1]

b) There are four carbon atoms in the molecule plus Br, giving a mass of 48 + 79 = 127. This leaves 166 – 127 =39 [1], which is H_7O. So a possible molecular formula consistent with the relative molecular mass is $C_4H_7O_2Br$. [1]

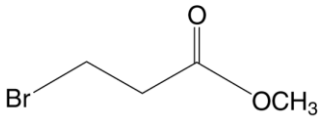
c) The ratios of the step heights are about 30 mm : 20 mm : 20 mm, or 3 : 2 : 2. [1] This shows that there are three hydrogens associated with the singlet peak and two hydrogens with each of the triplet peaks. [1]

d) The chemical shift at 3.7 ppm is consistent with H–C–O. The singlet peak is not split and so not next to a carbon atom with hydrogen atoms attached, so CH_3–O–. [1]

The chemical shift at 3.5 ppm fits with the range for CHBr. This peak is a triplet so the two hydrogens must be next to another carbon atom with two hydrogens. [1]

The chemical shift at 2.9 ppm is consistent with H–C–C=O. This, too, is a triplet, so must also be next to another carbon atom with two hydrogens [1]. So $–CH_2–CH_2–$ is present. [1]

e) The structure for Z that fits this information is:



[1]

f) Fragmentation to produce $[BrCH_2CH_2]^+$ gives fragments of masses 107 and 109, depending on which bromine isotope is present. [1]

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10 a) i) Four chemical environments. [1]

ii) Ratios: 3 : 2 : 6 : 1 [1] (which gives 12 hydrogens in total, which is consistent with the molecular formula).

b) The structure includes a carbonyl group and is a ketone and there are no –OH groups. [1] The formula shows that there can only be one double bond in each molecule and so only one carbonyl group. [1]

c) Chemical shift = 2.2 ppm (three H atoms): $H_3C–CO–$ [1]

Chemical shift = 2.7 ppm (two H atoms): $RCH_2CO–$ [1]

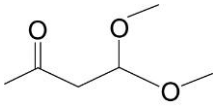
Chemical shift = 3.4 ppm (six H atoms): $–O–CH_3$ (twice) [1]

d) i) The hydrogen atoms corresponding to chemical shift 2.7 ppm have one proton on a neighbouring atom. [1]

The hydrogen atom corresponding to chemical shift 4.8 ppm has two protons on a neighbouring atom. [1]

ii) The hydrogen atoms corresponding to chemical shifts 2.2 ppm and 3.4 ppm have no protons on neighbouring atoms. [1]

e) The skeletal formula of a compound consistent with all this information is:



[1]

4,4-dimethoxybutan-2-one

11 a) This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully sustained line of reasoning. Assess the quality of the answer taking into account both the key points made (*up to 4 marks*) and the logic and coherence of the discussion (*up to 2 marks*).

Points to make in the answer:

- IR shows absorption at 1750 cm^{-1} so C=O (but no O–H) possibly ester [1]
- ^1H NMR spectrum shows three types of proton [1]
- quartet at δ = 4.12 ppm for H–C–O– (possibly ester) next to CH_3 [1]
- singlet at δ = 2.04 ppm for H–C–C=O– so $CH_3–C=O$ [1]
- triplet at δ = 1.26 ppm for H–C–C–next to CH_2 [1]
- compound A is $CH_3COOCH_2CH_3$ (ethyl ethanoate). [1]

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b) This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully sustained line of reasoning. Assess the quality of the answer taking into account both the key points made (*up to 6 marks*) and the logic and coherence of the discussion (*up to 3 marks*).

Points to make in the answer:

- IR shows absorption at 1710 cm^{-1} so C=O (possibly ester) [1]
- absorption at 3400 cm^{-1} so –O–H alcohol [1]
- ^{1}H NMR spectrum shows four types of proton [1]
- with integration ratio 2 : 1 : 2 : 3 [1]
- singlet (integration 1) at δ = 3.4 ppm is H–O of alcohol [1]
- triplet (integration 2) at δ = 3.84 ppm for H–C–O– [1] so –O $–CH_2$ (next to CH_2 [1])
- triplet (integration 2) at δ = 2.70 ppm for H–C–C=O so $–CH_2–C=O$ (next to CH_2 [1])
- singlet (integration 3) at δ = 2.20 ppm for H–C–C=O [1] so $CH_3–C=O$
- compound B is $CH_3COCH_2CH_2OH$ (4-hydroxybutan-2-one). [1]

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