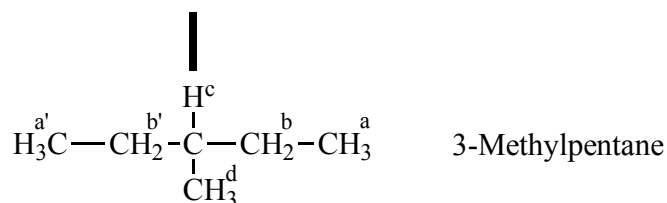


## CHAPTER 20

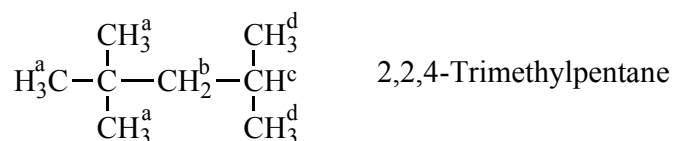
### Practice Exercises

- 20.1 The index of hydrogen deficiency is two. The structural possibilities include two double bonds, a double bond and a ring, or two rings.
- 20.3 (a) As this is an alkane, it contains only C and H and has the general formula  $C_nH_{2n+2}$ . Substituting the known values into  $C_nH_{2n+2}$  gives  $12 \times n + 1 \times (2n + 2) = 198$ . Solving gives  $n = 14$ . Therefore, the molecular formula of the compound is  $C_{14}H_{30}$ .
- (b) As this is a cycloalkane, it contains only C and H and has the general formula  $C_nH_{2n}$ . Substituting the known values into  $C_nH_{2n}$  gives  $12 \times n + 1 \times 2n = 140$ . Solving gives  $n = 10$ . Therefore, the molecular formula of the compound is  $C_{10}H_{20}$ .
- 20.5 Carboxylic acids have two strong absorptions. The first absorption, a broad peak between 2400 and 3400  $cm^{-1}$ , is due to the hydroxyl attached to the carbonyl carbon. The second absorption is a strong peak around 1715  $cm^{-1}$  due to the C=O stretching vibration.
- 20.7 As the wavenumber increases, so does the bond strength.
- 20.9 Letter superscripts are used to distinguish nonequivalent hydrogen atoms. (Use the 'test atom' approach if you have difficulty understanding the answers given.)
- (a) 3-methylpentane has four sets of equivalent hydrogen atoms ( $H^a$  through  $H^d$ ). Two sets of equivalent hydrogen atoms are related by a mirror plane of symmetry (the methyl hydrogen atoms  $H^a = H^a'$  for a total of 6H's and the methylene hydrogen atoms  $H^b = H^b'$  for a total of four hydrogen atoms). There are three  $H^d$  hydrogen atoms and only one  $H^c$  hydrogen atom.

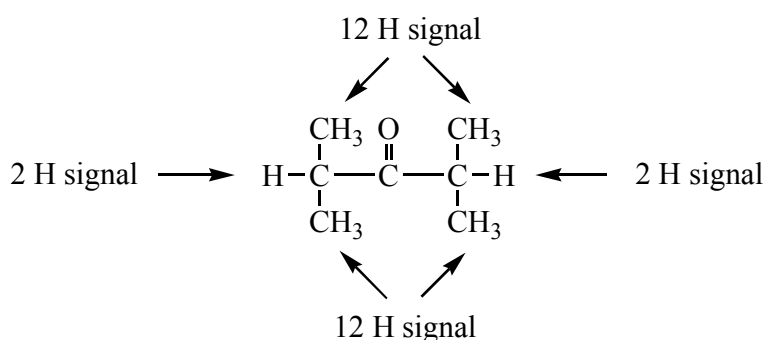


| mirror plane

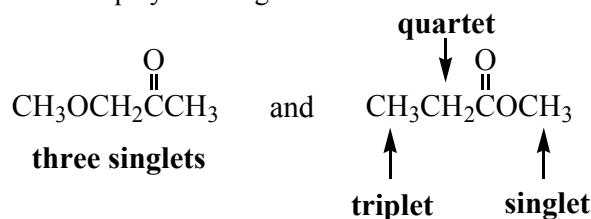
- (b) 2,2,4-trimethylpentane has four sets of equivalent hydrogens. Three equivalent methyl groups give nine  $H^a$  atoms, two methylene  $H^b$  hydrogen atoms, one methine  $H^c$  hydrogen, and two equivalent methyl groups give six  $H^d$  atoms.



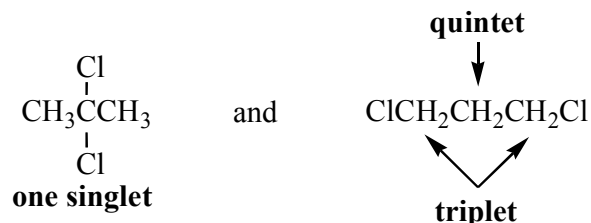
- 20.11 The number of hydrogens associated with each signal is proportional to the number of chart divisions. The ratio of signals is approximately 6:1, which corresponds to a 12:2 ratio for a total of 14 hydrogen atoms. With all the hydrogen atoms accounted for, the larger signal represents 12 hydrogen atoms and the smaller signal represents two hydrogen atoms. The structure consistent with the data is 2,4-dimethyl-3-pentanone.



- 20.13 (a) (i) Both compounds display three signals:



- (ii) The compound on the left has only one signal. The compound on the right has two signals, a triplet and a quintet.



- (b) Methyl acetate:  $H_a$  singlet (3H),  $H_b$  singlet (3H).  
 Ethyl formate:  $H_a$  singlet (1H),  $H_b$  quartet (2H),  $H_c$  triplet (3H).  
 Methoxyacetaldehyde:  $H_a$  triplet (1H),  $H_b$  doublet (2H),  $H_c$  singlet (3H). Note the splitting between  $H_a$  and  $H_b$  in methoxyacetaldehyde is very small and these signals may appear as singlets.

- 20.15 By Beer-Lambert law:

$$c = \frac{A}{\epsilon b}$$

$$A = 0.845 \text{ L mol}^{-1} \text{ cm}^{-1} : \epsilon = 29200 \text{ L mol}^{-1} \text{ cm}^{-1} \quad b = 5.00 \text{ cm}$$

So:

$$c = \frac{0.845}{29200} \times 5 = 1.45 \times 10^{-4} \text{M}$$

## Review Questions

20.1

Class of Compound	Molecular Formula	Index of Hydrogen Deficiency	Reason for Hydrogen Deficiency
alkane	$C_nH_{2n+2}$	0	(reference hydrocarbon)
alkene	$C_nH_{2n}$	1	one pi bond
alkyne	$C_nH_{2n-2}$	2	<u>two pi bonds</u>
alkadiene	$C_nH_{2n-2}$	2	<u>two pi bonds</u>
cycloalkane	$C_nH_{2n}$	1	<u>one ring</u>
cycloalkene	$C_nH_{2n-2}$	2	<u>one pi bond + one ring</u>

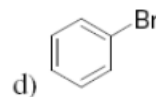
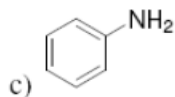
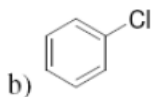
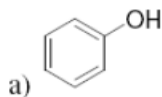
20.3 Mass spectrometry gives information about the mass of molecules and fragments of molecules. The fragmentation patterns can also give information about structural features in molecules (this process was not discussed in this chapter). High resolution mass spectrometry can be used to determine the molecular formula of a compound.

20.5  $m/z$  stands for mass per unit charge.

20.7 The peak at  $m/z = 112$  ( $M^+$ ) is due to the  $[C_6H_5^{35}Cl]^+$  ion and the peak at  $m/z = 114$  ( $M+2$ )<sup>+</sup> is due to the  $[C_6H_5^{37}Cl]^+$  ion.

20.9 High resolution mass spectrometry gives information about the molecular formula of a compound.

20.11

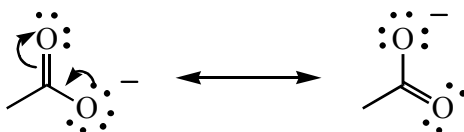


20.13 Photons in the UV have higher energy than those in the IR.

20.15 microwaves > infrared radiation > visible light > ultraviolet light > X-rays

20.17 The a C—O bond (1050–1250 cm<sup>-1</sup>) has a lower stretching frequency than the C=O bond (1630–1800 cm<sup>-1</sup>). The stronger the bond, the higher the stretching frequency and a double bond is stronger than a single bond.

20.19 The C=O stretches for the acetate anion occur at lower wave numbers (lower frequencies) relative to acetic acid due to greater resonance stabilisation of the acetate anion. The resonance hybrid of the acetate anion has greater C—O single bond character in the carbonyl bond, thus decreasing the frequency of stretching vibrations and lowering the wave number of absorption. The same effect is observed in the lowering of the C=O IR absorption stretching bands when a carbonyl C=O bond is conjugated to an adjacent pi bond.



20.21 (a) Reference alkane for C<sub>13</sub>H<sub>24</sub>O is C<sub>13</sub>H<sub>28</sub> so

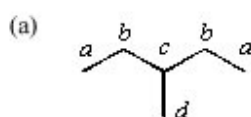
$$\text{HD} = \frac{28-24}{2} \quad \text{so 2 C=C bonds are present.}$$

(b) IR signal over range 3200-3600cm<sup>-1</sup> is due to -OH functional group 2 signals in range 1600-1700cm<sup>-1</sup> is due to C=C bonds.

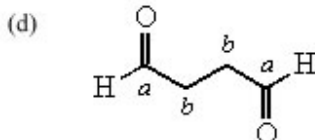
20.23 Electromagnetic radiation in the form of radiowaves is used in NMR spectroscopy.

20.25 Although there are seven carbon atoms in 5-methylhexan-3-ol, two are equivalent. Therefore, six signals are expected in the <sup>13</sup>C NMR spectrum of 5-methylhexan-3-ol.

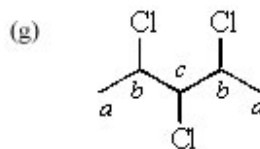
20.27



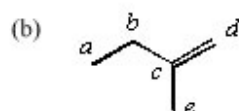
**4 signals**



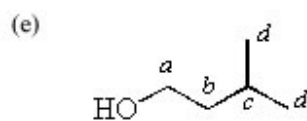
**2 signals**



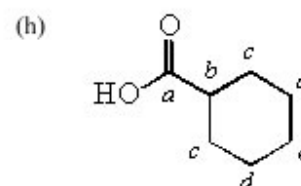
**3 signals**



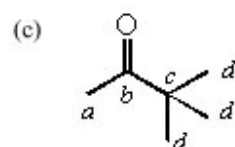
**5 signals**



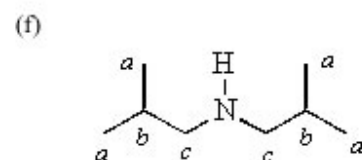
**4 signals**



**5 signals**



**4 signals**



**3 signals**

20.29 X-ray crystallography is the most important analytical technique for determining the three-dimensional structure of proteins.

20.31 By Beer-Lambert Law:

$$\epsilon = \frac{A}{bc}$$

$A = 0.845 \text{ L mol}^{-1} \text{ cm}^{-1}$  :  $b = 2 \text{ cm}$  :  $c = 5.6 \times 10^{-5} \text{ M}$

So

$$\epsilon = \frac{0.845}{2 \times 5.6 \times 10^{-5}} = 7.54 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$$

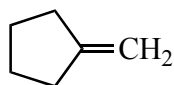
20.33 The molecular ion peak is at  $m/z = 114$

The base peak is at  $m/z = 43$

The compound is n-octane  $\text{C}_8\text{H}_{18}$

### Review Problems

- 20.35 (a) The index of hydrogen deficiency for compound A is two.
- (b) Compound A only added one molecule of hydrogen with  $\text{H}_2/\text{Ni}$ , therefore it is concluded that compound A has one pi bond, leaving the other site of hydrogen deficiency as a ring.
- (c) From the hydrogenation data, it is concluded that compound A contains only one C=C bond because it only added one molecule of  $\text{H}_2$ . Because rings do not hydrogenate under these conditions, the other hydrogen deficiency must be due to a ring. In addition, the C=C bond must be highly unsymmetrical, having a permanent dipole to explain the strong C=C stretching band around  $1650 \text{ cm}^{-1}$ . Additional chemical and spectroscopic data are required to unambiguously assign a structure to compound A. For example,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra would be extremely helpful. Such combined data indicate that compound A is methylenecyclopentane.

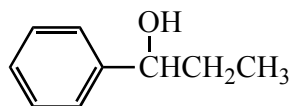


### Methylenecyclopentane

- 20.37 (a) The index of hydrogen deficiency for compound E is one.
- (b) Compound E may have one pi bond or one ring.
- (c) The infrared spectra of compound E indicates that the hydrogen deficiency is due to a C=C bond. The spectral evidence includes  $\text{C}(sp^2)\text{-H}$  stretching around  $3020 \text{ cm}^{-1}$ . The chemical data supports this conclusion because compound E added a hydrogen molecule upon hydrogenation with nickel catalyst. However, the absence of any C=C stretching bands near  $1650 \text{ cm}^{-1}$  in the IR spectrum indicates that this must be an entirely symmetrical carbon-carbon double bond. More information such as  $^1\text{H}$  and  $^{13}\text{C}$  NMR

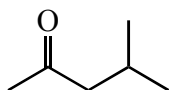
spectra are required to unambiguously deduce the detailed structure of compound E. Such combined data show that compound E is 2,3-dimethylbut-2-ene.

- 20.39 (a) The index of hydrogen deficiency for compound I is four.
- (b) Compound I has a total of four pi bonds and/or rings.
- (c) A single benzene ring can (and often does) account for a hydrogen deficiency index of four.
- (d) The strong, broad absorption near  $3400\text{ cm}^{-1}$  indicates the presence of an  $\text{-OH}$  group, so this must be the oxygen containing functional group. Again, other spectral methods are required to assign a structure to compound I, but  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data would confirm that compound I is 1-phenyl-1-propanol:



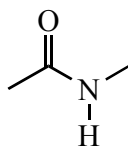
**1-Phenylpropan-1-ol**

- 20.41 (a) The index of hydrogen deficiency for compound K is one.
- (b) Based on the index of hydrogen deficiency, compound K can have only one ring or pi bond.
- (c) The very strong absorption band at about  $1710\text{ cm}^{-1}$  is characteristic of a  $\text{C=O}$  stretch, therefore the source of the hydrogen deficiency. Additional data from other spectroscopic methods would confirm that compound K is 4-methylpentan-2-one:



**4-Methylpentan-2-one**

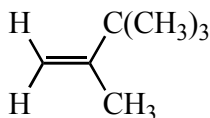
- 20.43 (a) The index of hydrogen deficiency for compound M is one.
- (b) Based on the index of hydrogen deficiency, compound M must have a ring or a pi bond.
- (c) The oxygen and nitrogen-containing functional group is an amide. The absorption at about  $1680\text{ cm}^{-1}$  indicates an amide carbonyl. The single absorption between  $3200$  and  $3400\text{ cm}^{-1}$  indicates the  $\text{N-H}$  stretching of a secondary amide. Other spectroscopic and chemical techniques reveal that compound M is N-methylacetamide:



**N-Methylacetamide**

- 20.45 (a) The O—H stretch is centred at  $3200\text{ cm}^{-1}$ .
- (b) The aromatic C—H stretching is a hard to see weak signal at  $3075\text{ cm}^{-1}$  that is partially obscured by the broad —OH stretch at  $3200\text{ cm}^{-1}$ . The sharp peak at  $2980\text{ cm}^{-1}$  is due to the C—H stretching of the —OCH<sub>3</sub> group.
- (c) The carbonyl group C=O stretching band is centred at  $1680\text{ cm}^{-1}$ . The carbonyl stretching bands for esters normally appear between  $1735$  and  $1750\text{ cm}^{-1}$ . In the case of methyl salicylate, the fact that the carbonyl group is (1) conjugated with the pi bonds in the aromatic ring and (2) involved in internal hydrogen bonding combine to lower the stretching frequency to  $1680\text{ cm}^{-1}$ .
- (d) IR absorbance bands for the aromatic C=C stretches are at  $1441\text{ cm}^{-1}$  and  $1615\text{ cm}^{-1}$ .
- 20.47
- Index of hydrogen deficiency is 1.
  - Chemical test suggests a double bond (decolourises bromine solution).
  - <sup>1</sup>H-NMR shows four different signals (four different types of hydrogen atoms).
  - The 3H and 9H singlet signals are most likely due to hydrogen atoms on methyl and tert-butyl groups respectively, and not split by other hydrogen atoms two or three bonds away.
  - The two downfield signals are terminal vinylic hydrogen atoms, evident by the upfield chemical shift ( $\delta$  4.6–4.7 relative to  $\delta$  5.0–5.7 for hydrogens attached to substituted vinylic carbons).

Based on these data, compound A is 2,3,3-trimethylbut-1-ene:



**Compound A**

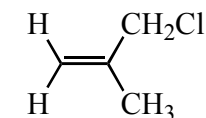
- 20.49
- The index of hydrogen deficiency for both compounds C and D is one. Both compounds C and D decolourise bromine solution, indicating that they have a pi bond and with an index of hydrogen deficiency of one, so both C and D must have only one pi bond each.
  - The <sup>1</sup>H-NMR spectrum for compound C shows a 3H singlet at  $\delta$  1.85 (most likely a —CH<sub>3</sub> group with no adjacent protons), a 2H singlet at  $\delta$  4.0 (most likely a —CH<sub>2</sub> with no adjacent hydrogen atoms) and two <sup>1</sup>H signals at  $\delta$  4.93 and  $\delta$  5.09 (most likely due to nonequivalent terminal vinylic R<sub>2</sub>C=CH<sub>2</sub> hydrogen atoms). The 2H singlet has a downfield shift and therefore must have an electronegative chlorine atom bonded to it. Put the fragments together as outlined above by building the structure around the H<sub>2</sub>C=C— fragment.

Compound C is 3-chloro-2-methyl-1-propene.

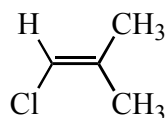
- The <sup>1</sup>H-NMR spectrum for compound D shows two 3H singlets at  $\delta$  1.75 and  $\delta$  1.79 (most likely two nonequivalent —CH<sub>3</sub> groups with no adjacent protons) and one <sup>1</sup>H signal

at  $\delta$  5.76 (most likely due to a  $R_2C=CRH$  proton). There is only one vinylic hydrogen atom, therefore place the methyl groups and chlorine atom on the  $R_2C=C-$  fragment.

Compound D is 1-chloro-2-methyl-1-propene.



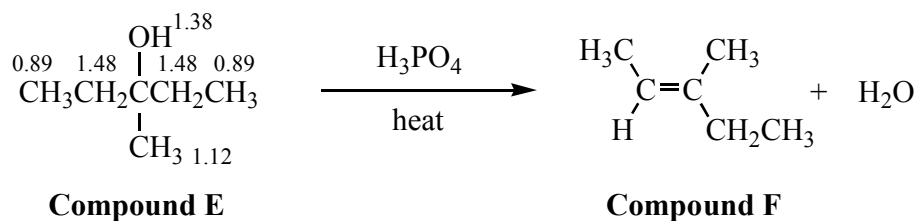
**Compound C**



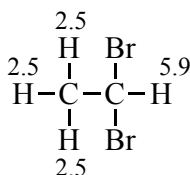
**Compound D**

- 20.51
- From the molecular formula, the calculated index of hydrogen deficiency is zero, so there are no rings or pi bonds.
  - From the  $^1\text{H-NMR}$ , there are four different sets of nonequivalent hydrogen atoms and that the OH is not on a carbon with a C—H bond (there are no signals between  $\delta$  3.3 and  $\delta$  4.0). The easiest way to construct a molecule with a 6H triplet (two methyl groups) is to have two equal ethyl groups in the molecule.
  - The  $^{13}\text{C-NMR}$  data reveals that there are four different sets of nonequivalent carbons in the molecule.

A proposed structure for compound E is 3-methylpentan-3-ol and the chemical shifts associated with each set of hydrogen atoms are indicated on the structure given below.

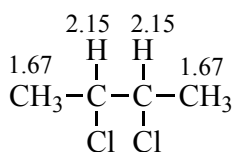


- 20.53 (a)  $\text{C}_2\text{H}_4\text{Br}_2$   $\delta$  2.5 (d, 3H) and 5.9 (q, 1H)

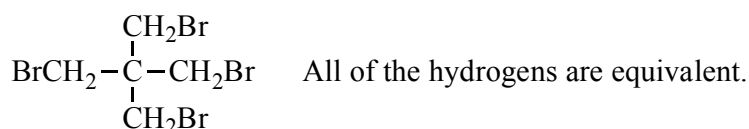


- (b)  $\text{C}_4\text{H}_8\text{Cl}_2$   $\delta$  1.67 (d, 6H), 2.15 (q, 2H)

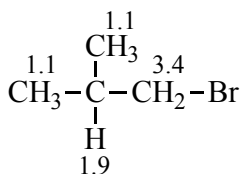




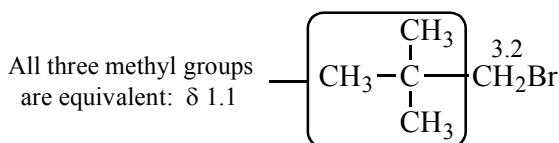
(c)  $\text{C}_5\text{H}_8\text{Br}_4$   $\delta$  3.6 (s, 8H)



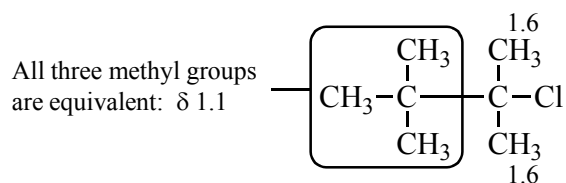
(d)  $\text{C}_4\text{H}_9\text{Br}$   $\delta$  1.1 (d, 6H), 1.9 (m, 1H), and 3.4 (d, 2H)



(e)  $\text{C}_5\text{H}_{11}\text{Br}$   $\delta$  1.1 (s, 9H) and 3.2 (s, 2H)

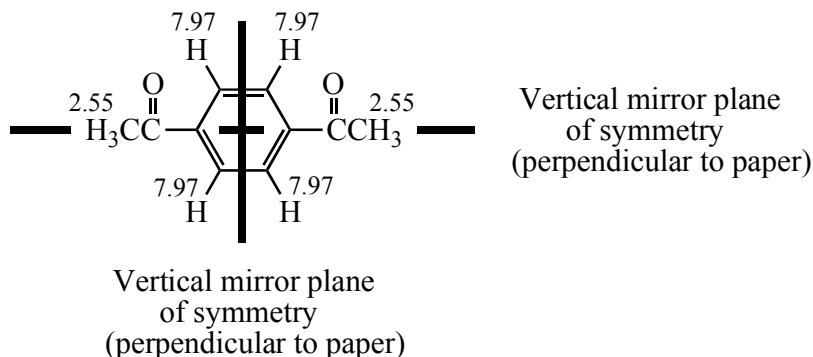


(f)  $\text{C}_7\text{H}_{15}\text{Cl}$   $\delta$  1.1 (s, 9H) and 1.6 (s, 6H)

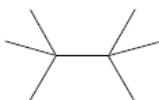


20.55 The chemical reactivity data rule out carboxylic acid and phenolic compounds. Compound K has an index of hydrogen deficiency of six, suggesting a benzene ring. A disubstituted benzene ring is supported by the 4H singlet  $^1\text{H}$ -NMR signal at  $\delta$  7.97. A compound with this many atoms and simple  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectrum indicates a high degree of symmetry. After the benzene ring is considered, there are four carbon atoms, six hydrogen atoms, and two oxygen atoms with two sites of hydrogen deficiencies to account for. The structure of compound K is shown below. Although the figure shows two mirror planes, the structure of compound K has other elements of

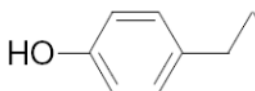
symmetry such as a rotation axis. Use model kits and try to observe these elements of symmetry and how they relate to hydrogen equivalency.



20.57 This compound will exhibit two signals in its  $^{13}\text{C}$  NMR spectrum:

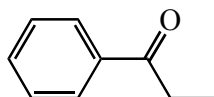


20.59



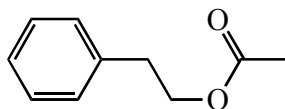
- 20.61 (a)  $\text{C}_9\text{H}_{10}\text{O}$ ;  $\delta$  1.2 (t, 3H), 3.0 (q, 2H) and 7.4–8.0 (m, 5H)
- Index of hydrogen deficiency is 5.
  - This suggests a double bond and an aromatic ring.
  - The integration value for the aromatic region ( $\delta$  7.4–8.0) indicates the aromatic ring is monosubstituted.
  - The triplet and quartet are diagnostic of an ethyl group.

The compound below best fits the data:



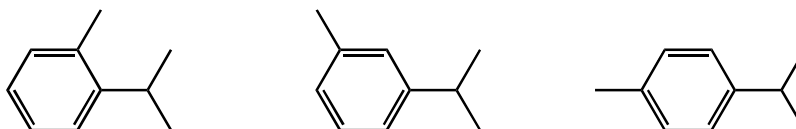
- (b)  $\text{C}_{10}\text{H}_{12}\text{O}_2$ ;  $\delta$  2.2 (s, 3H), 2.9 (t, 2H), 4.3 (t, 2H) and 7.3 (s, 5H)
- Index of hydrogen deficiency is 5.
  - This suggests a double bond and an aromatic ring.
  - The integration value for the aromatic region ( $\delta$  7.3) indicates the aromatic ring is monosubstituted.
  - The singlet at  $\delta$  2.2 (integrating for 3 H) is typical of a methyl group bonded to a carbonyl group.
  - The two triplets (each integrating for 2 H) are next to each other. The signal at  $\delta$  2.9 is typical of a methylene group bonded to an aromatic ring. The signal at  $\delta$  4.3 is typical of a methylene group bonded to an oxygen atom of an ester.

The compound below best fits the data:



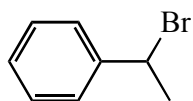
- (c)  $C_{10}H_{14}$ ;  $\delta$  1.2 (d, 6H), 2.3 (s, 3H), 2.9 (septet, 1H) and 7.0 (s, 4H)
- Index of hydrogen deficiency is 4.
  - This suggests an aromatic ring only.
  - The integration value for the aromatic region ( $\delta$  7.0) indicates the aromatic ring is disubstituted.
  - The singlet at  $\delta$  2.3 (integrating for 3 H) is typical of a methyl group bonded to an aromatic ring.
  - The doublet (6 H) and septet (1 H) are diagnostic of an isopropyl group.

The compounds below fit the data given. Distinguishing between the three isomers is not possible with the given information.



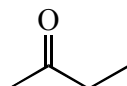
- (d)  $C_8H_9Br$ ;  $\delta$  1.8 (d, 3H), 5.0 (q, 1H) and 7.3 (s, 5H)
- Index of hydrogen deficiency is 4.
  - This suggests an aromatic ring only.
  - The integration value for the aromatic region ( $\delta$  7.3) indicates the aromatic ring is monosubstituted.
  - The doublet at  $\delta$  1.8 (integrating for 3 H) is typical of a methyl group bonded to a carbon atom with only 1 hydrogen atom.
  - The quartet at  $\delta$  5.0 (integrating for 1 H) is due to a methine H bonded to a methyl carbon.

The compound below best fits the data:



- 20.63 (a)  $C_4H_8O$ ;  $\delta$  1.0 (t, 3H), 2.1 (s 3H) and 2.4 (q, 2H)
- Index of hydrogen deficiency is 1, indicating a carbonyl group.
  - The triplet (3 H) & quartet (2 H) are diagnostic of an ethyl group.
  - The singlet at  $\delta$  2.1 (3 H) is typical of a methyl group bonded to a carbonyl group.

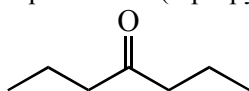
These data correspond to butanone:



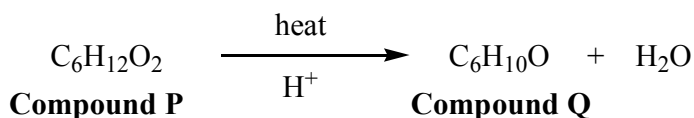
- (b)  $C_7H_{14}O$ ;  $\delta$  0.9 (t, 6H), 1.6 (sextet, 4H) and 2.4 (t, 4H).

- Index of hydrogen deficiency is 1, indicating a carbonyl group.
- The integration of 6, 4 and 4 suggest symmetry in the molecule, possibly  $2 \times (3 \text{ H}, 2 \text{ H and } 2 \text{ H})$ .
- The 6 H triplet suggests  $2 \times (\text{CH}_3 \text{ next to a } \text{CH}_2)$ . Similarly the 4 H triplet suggests  $2 \times (\text{CH}_2 \text{ next to a } \text{CH}_2)$ . The sextet suggests  $2 \times (\text{CH}_2 \text{ next to five hydrogen atoms, most likely between a } \text{CH}_3 \text{ and a } \text{CH}_2)$ .

These data correspond to heptan-4-one (dipropyl ketone):



20.65



**Index of hydrogen deficiency:**

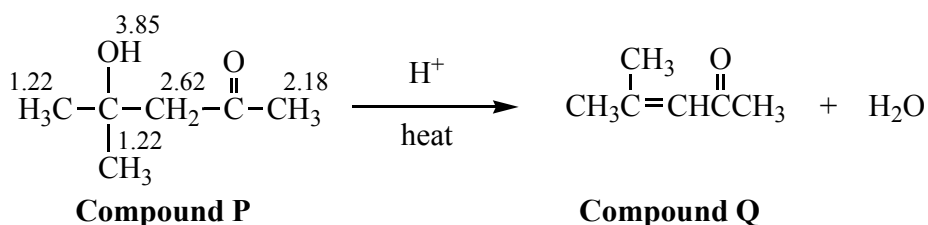
**1**

**2**

Compound P:

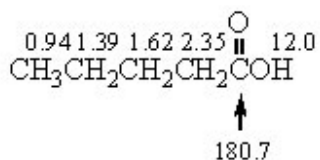
- Dehydrates under acidic conditions, which is consistent with an alcohol.
- Signal at  $\delta$  1.22 suggests two methyl groups with no adjacent hydrogen atoms.
- Signal at  $\delta$  2.18 indicates a methyl group with no adjacent hydrogen atoms.
- Signal at  $\delta$  2.62 is most likely due to a methylene group with no adjacent hydrogen atoms.

These data are consistent with:



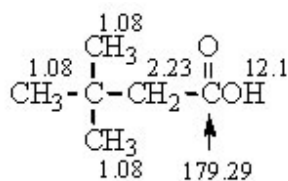
20.67 (a)  $\text{C}_5\text{H}_{10}\text{O}_2$

$^1\text{H-NMR}$	$^{13}\text{C-NMR}$
0.94 (t, 3H)	
1.39 (m, 2H)	33.89
1.62 (m, 2H)	26.76
2.35 (t, 2H)	22.21
12.0 (s, 1H)	13.69



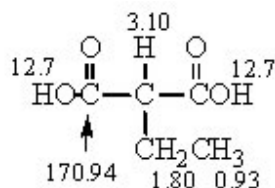
(b)  $\text{C}_6\text{H}_{12}\text{O}_2$

$^1\text{H-NMR}$	$^{13}\text{C-NMR}$
1.08 (s, 9H)	179.29
2.23 (s, 2H)	46.82
12.1 (s, 1H)	30.62
	29.57



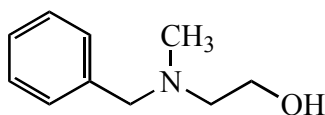
(c)  $\text{C}_3\text{H}_8\text{O}_4$

$^1\text{H-NMR}$	$^{13}\text{C-NMR}$
0.93 (t, 3H)	170.94
1.80 (m, 2H)	53.28
3.10 (t, 1H)	21.90
12.7 (s, 2H)	11.81



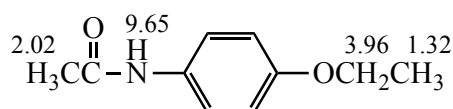
- 20.69
- Compound T has an index of hydrogen deficiency of four, which with the signal at  $\delta$  7.3 indicates a monosubstituted benzene ring.
  - The singlet at  $\delta$  2.2 (3H) in the  $^1\text{H}$  NMR spectrum represents a  $-\text{CH}_3$  with no neighbouring protons.
  - The two triplets (each 2H) are consistent with  $-\text{CH}_2\text{CH}_2-$  in which the downfield signal is bonded to oxygen and the upfield signal is bonded to nitrogen.
  - The broad signal at  $\delta$  3.2 is indicative of a  $-\text{OH}$  group.
  - The other singlet at  $\delta$  3.5 represents a  $-\text{CH}_2-$  group with no neighbouring protons.
  - The  $sp^3$ -C region of the  $^{13}\text{C}$  NMR, at first glance, appears to only have 3 signals. But very careful inspection reveals that the signal at  $\delta$  58 is actually two closely spaced signals, illustrating that the interpretation of NMR spectroscopy is not always straightforward.

The structure that fits the  $^1\text{H}$  and  $^{13}\text{C}$  data is the amino alcohol:



**Compound T**

- 20.71
- The  $^1\text{H-NMR}$  of phenacetin is as expected from its known structure.
  - The two signals  $\delta$  6.75 (d, 2H) and  $\delta$  7.50 (d, 2H) are characteristic of a 1,4-disubstituted phenyl ring.
  - The signal at  $\delta$  9.65 (s, 1H) indicates a secondary amide and the signal at  $\delta$  2.02 (s, 3H) comes from the acetyl methyl group on an acetamide (an amide of acetic acid).
  - The typical ethyl splitting pattern for the signals at  $\delta$  1.32 and  $\delta$  3.96 suggests the presence of an ethyl group bonded to an oxygen atom, evident by the downfield shift of the ethyl  $-\text{CH}_2-$  quartet at  $\delta$  3.96.

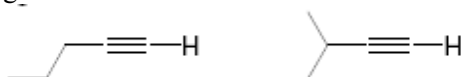


**Phenacetin**

### Additional Exercises

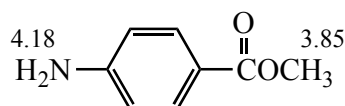
20.73 Limonene has three degrees of unsaturation and is comprised of only carbon and hydrogen atoms. The molecular weight is 136, so the molecular formula of limonene must be  $C_{10}H_{16}$ .

20.75 The IR spectrum indicates the presence of a triple bond as well as a C-H bond indicating that the triple bond is terminal. The mass spectrum indicates a molecular weight of 68. The following two structures are consistent with these data:



- 20.77
- Compound V has an index of hydrogen deficiency of five (a phenyl ring is likely).
  - The chemical data suggest an amine.
  - The two signals at  $\delta$  7.60 (d, 2H) and  $\delta$  8.7 (d, 2H) are characteristic of a 1,4-disubstituted phenyl ring.
  - The signal at  $\delta$  3.84 (s, 3H) is a methyl group bonded to an oxygen atom,  $-OCH_3$ .
  - The signal at  $\delta$  4.18 (s, 2H) is the primary amine hydrogen atoms.
  - This leaves only C and O to be accounted for and with the  $-OCH_3$  mentioned previously and a carbonyl group, it is concluded that the 1,4-disubstitution pattern involves an  $-NH_2$  group and a methyl ester.

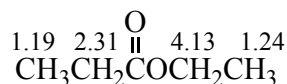
The only structure consistent with the above data and analysis is methyl 4-aminobenzoate:



**Compound V**

- 20.79
- Compound X has an index of hydrogen deficiency of one.
  - A notable feature of the IR spectrum is the strong peak at  $1750\text{ cm}^{-1}$ , which indicates the presence of a carboxyl group and accounts for the only site of hydrogen deficiency.
  - The absence of an  $-OH$  stretch between  $2400$  and  $3400\text{ cm}^{-1}$  rules out the possibility that the carboxyl group is a carboxylic acid.
  - Two characteristic triplet–quartet pairs suggest two ethyl groups.
  - The signals  $\delta$  4.13 (q, 2H) and  $\delta$  1.24 (t, 3H) come from the  $CH_3CH_2O-$  group and  $\delta$  2.31 (q, 2H) and  $\delta$  1.19 (t, 3H) come from the  $CH_3CH_2-$  group.

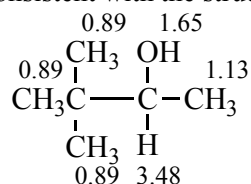
The structure of ethyl propanoate is consistent with the above IR and  $^1\text{H-NMR}$  spectral data:



**Compound X**

- 20.81
- Compound Z has an index of hydrogen deficiency of zero.
  - A notable feature of the IR spectrum is a very broad peak at  $3400\text{ cm}^{-1}$  (O—H stretch) indicating the presence of an alcohol hydroxyl group.
  - The  $^1\text{H-NMR}$  spectrum reveals a  $(\text{CH}_3)_3\text{C-}$  group with a signal at  $\delta$  0.89 (s, 9H), which accounts for four of the six carbon atoms in Compound Z.
  - The signal at  $\delta$  1.13 (d, 3H) indicates a methyl group coupled to an adjacent  $-\text{CH}-$  with a signal at  $\delta$  3.48 (q, 1H). The  $-\text{CH}-$  is also attached to the alcohol hydroxyl, evident by the downfield chemical shift.
  - The signal at  $\delta$  1.65 (broad singlet, 1H) is due to the alcohol hydroxyl's proton.

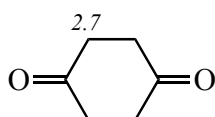
These data for compound Z are consistent with the structure of 3,3-dimethylbutan-2-ol:



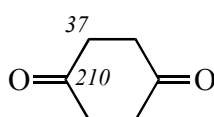
**Compound Z**

- 20.83
- From the mass spectrum, the molar mass is 112 and so the molecular formula is  $\text{C}_6\text{H}_8\text{O}_2$ .
  - This gives an index of hydrogen deficiency of 3.
  - The IR spectrum suggests a carbonyl group ( $1725\text{ cm}^{-1}$ ) and no OH group (no signal at  $3500\text{ cm}^{-1}$ ).
  - The  $^1\text{H-NMR}$  spectrum shows only one signal ( $\delta$  2.7) indicating all eight hydrogen atoms are equivalent ( $4 \times \text{CH}_2$ ). The chemical shift is typical for a methylene next to a carbonyl group.
  - The  $^{13}\text{C-NMR}$  spectrum shows only 2 signals,  $\delta \sim 210$  (ketone carbonyl carbon) and  $\delta \sim 37$  ( $\text{CH}_2$ ).
  - Given the IHD = 3 and the high symmetry of the compound, there are two ketone groups and a ring.

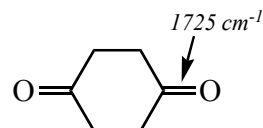
These data are consistent with cyclohexan-1,4-dione:



$^1\text{H-NMR}$



$^{13}\text{C-NMR}$



IR

