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## Molecular characterization

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### Answers to worked examples

#### WE 13.1 Identifying a bromoalkane (on p. 612 in *Chemistry*<sup>3</sup>)

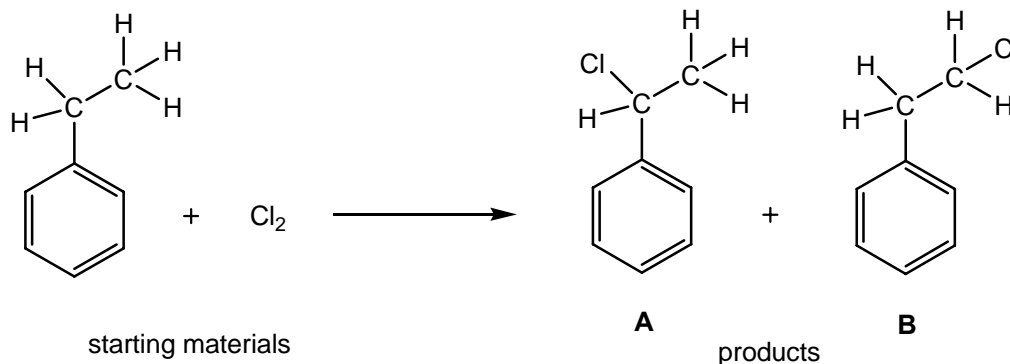
When a mixture of ethylbenzene ( $\text{PhCH}_2\text{CH}_3$ ) and chlorine is illuminated with UV radiation,  $\text{PhCHClCH}_3$  and  $\text{PhCH}_2\text{CH}_2\text{Cl}$  are formed in unequal amounts. After separation, the EI mass spectra of both products were recorded. The mass spectrum of the major product showed peaks at  $m/z$  values of 125 and 127, in the ratio 3:1. These peaks were not observed in the mass spectrum of the minor product. Use this information to identify which is the major and which is the minor product.

#### Strategy

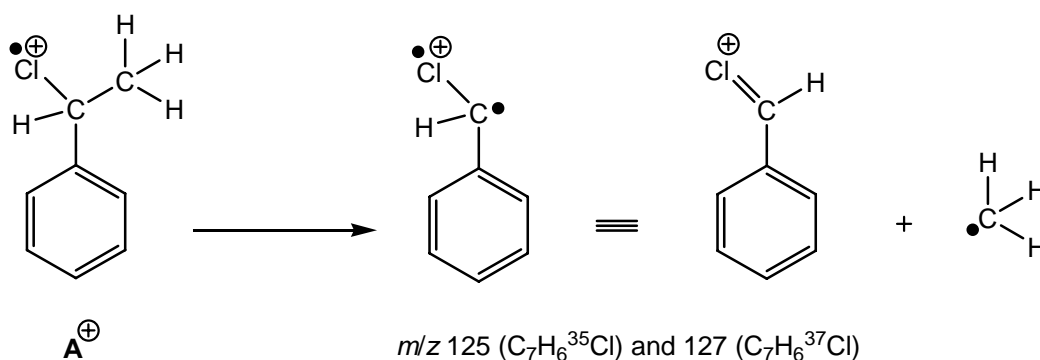
1. Draw out the proposed reaction and identify the starting materials and products.
2. Determine the molecular masses for the starting materials and products.
3. Are there any characteristic isotopic patterns?
4. For each product, try and fragment the molecular ion to form “stabilised” cations.

#### Solution

1. The reaction scheme is shown below:



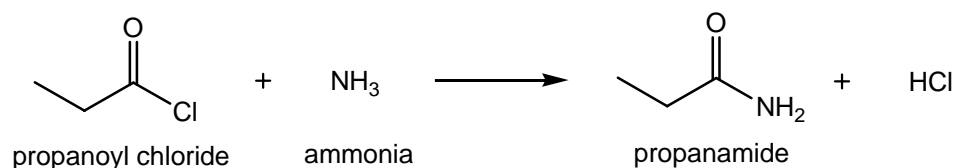
- The molecular mass of the starting material, ethylbenzene ( $\text{PhCH}_2\text{CH}_3$ ) is 106. The products, **A** and **B** ( $\text{C}_8\text{H}_9\text{Cl}$ ), are structural isomers of each other and have molecular masses of 140 ( $\text{C}_8\text{H}_9^{35}\text{Cl}$ ) and 142 ( $\text{C}_8\text{H}_9^{37}\text{Cl}$ ); the relative proportion of these molecular masses is 3:1.
- From the information given in this question, there is a characteristic isomeric pattern for the major product at  $m/z$  values of 125 and 127, in a ratio of 3:1. This fragment pattern is characteristic of an ion containing a chlorine atom.
- The molecular ions at  $m/z$  values of 125 and 127 must have a molecular formula of  $\text{C}_7\text{H}_6^{35}\text{Cl}^+$  and  $\text{C}_7\text{H}_6^{37}\text{Cl}^+$ , respectively in a ratio of 3:1 due to the isotopic abundance of chlorine. These molecular ions are formed by loss of a methyl ( $\text{CH}_3$ ) group (15 mass units). Only product, **A**, contains the necessary methyl group which will can be lost through fragmentation to give a resonance-stabilised carbocation. Product **A** is the major product from the chlorination of ethylbenzene.

Answer

The major product is  $\text{PhCHClCH}_3$ . For  $\text{PhCHClCH}_3$ , homolytic cleavage of the C–C bond in the molecular ion gives fragment cations with  $m/z$  values of 125 and 127. For  $\text{PhCH}_2\text{CH}_2\text{Cl}$ , homolytic cleavage of the C–C bond in the molecular ion gives fragment cations,  $\text{CH}_2\text{Cl}^{35}$  and  $\text{CH}_2\text{Cl}^{37}$ , with  $m/z$  values of 49 and 51.



amide carbonyl group has a stretching frequency  $\sim 1700\text{-}1600\text{ cm}^{-1}$ . The product of this reaction must be propanamide. The overall reaction is shown below.



### Answer

3400-3190  $\text{cm}^{-1}$  N-H stretch

3000-2800  $\text{cm}^{-1}$  C-H stretch (from **A** and/or Nujol)

1650  $\text{cm}^{-1}$  C=O stretch of the CONH<sub>2</sub> group

Compound **A** is CH<sub>3</sub>CH<sub>2</sub>CONH<sub>2</sub>

### **WE 13.5** Assigning a structure from a <sup>1</sup>H NMR spectrum (on p. 641 in *Chemistry*<sup>3</sup>)

The <sup>1</sup>H NMR spectrum of the major product from the enzyme-catalysed oxidation of 1-butylbenzene (PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) is shown on p. 641 in *Chemistry*<sup>3</sup>. Use this spectrum to predict a structure for this product and explain your reasoning.

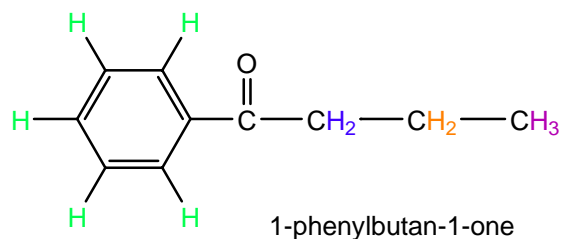
### Strategy

1. From this <sup>1</sup>H NMR spectrum, determine the reactive integration for each resonance signal.
2. Attempt to assign this <sup>1</sup>H NMR spectrum by examining the chemical shift of each resonance signal.
3. Attempt to assign this <sup>1</sup>H NMR spectrum by examining the splitting pattern of each resonance signal.
4. Draw out a possible structure of this product and include a potential reaction scheme.

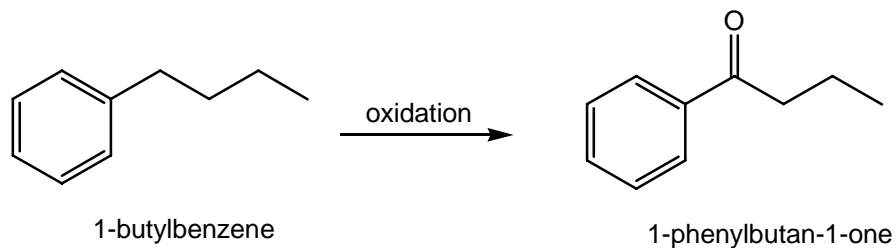
### Solution/Answer

1. There are five resonance signals,  $\delta$  8.00, 7.50, 3.00, 1.80 and 1.00 ppm with a relative integration of 2, 3, 2, 2 and 3, respectively.
2. From Figure 13.13 and Table 13.3 the following types of CH, CH<sub>2</sub> and CH<sub>3</sub> groups are assigned to the five signals.

- |         |    |   |
|---------|----|---|
| 8.0 ppm | 2H | 2 × aromatic CH (from Figure 13.13)                           |
| 7.6 ppm | 3H | 3 × aromatic CH (from Figure 13.13)                           |
| 2.9 ppm | 2H | possibly Ar-C(=O)-CH <sub>2</sub> -C or Ar-CH <sub>2</sub> -C |
| 1.8 ppm | 2H | possibly R-O-C-CH <sub>2</sub> -C                             |
| 1.0 ppm | 3H | C-CH <sub>3</sub>   |
3. The splitting pattern of each signal suggests the following partial structures.
- |         |         |  |
|---------|---------|--|
| 8.0 ppm | doublet | 2 × aromatic CH-CH                                 |
| 7.6 ppm | complex | 3 × aromatic CH                                    |
| 2.9 ppm | triplet | -CH <sub>2</sub> -CH <sub>2</sub> -C               |
| 1.8 ppm | sextet  | -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> |
| 1.0 ppm | triplet | -CH <sub>2</sub> -CH <sub>3</sub>                  |
4. Combining the partial structures gives 1-phenylbutan-1-one.



5. The overall reaction is shown below.



### WE 13.7 Assigning a structure from a combination of spectra (on p. 650 in *Chemistry*<sup>3</sup>)

A second compound, with the molecular formula C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>, was isolated from the same synthetic perfume. Using the IR, <sup>1</sup>H, and <sup>13</sup>C NMR (proton decoupled) spectra on p. 650 in *Chemistry*<sup>3</sup>; propose a structure for this unknown compound.

#### Strategy

1. Examine the IR spectrum and look for characteristic peaks, such as XH, C=O and Ph.

- Survey the <sup>1</sup>H and <sup>13</sup>C NMR spectra to confirm if these functional groups are present. Draw out as many structural isomers of C<sub>10</sub>H<sub>12</sub>O<sub>2</sub> and deduce which isomer matches the given spectra.
- Draw out the structure of the unknown compound.

### Solution

- The IR spectrum shows three absorption bands in the functional group region (see Table 13.2 on p. 622 and Figure 13.7 on p. 623 in *Chemistry*<sup>3</sup>). There is no absorption band due to an O–H bond.

3100–2800 cm<sup>-1</sup> C–H (stretch).

~1740 cm<sup>-1</sup> broad C=O (stretch), probably an ester.

~1500 cm<sup>-1</sup> 3 bands for aromatic ring.

- From the <sup>1</sup>H NMR spectrum, the following CH, CH<sub>2</sub> and CH<sub>3</sub> groups can be assigned to the four signals (Figure 13.13 and Table 13.3). Measuring the height (in cm) of each integration curve gives a ratio of hydrogen atoms of 1.5: 0.6: 0.6: 0.9. As the number of hydrogen atoms must be a whole number; multiplying by 3.3 gives a ratio of 5: 2: 2: 3.

7.4–7.1 ppm      5H              5 × aromatic CH (from Figure 13.13)

4.3 ppm            2H              possibly C(=O)O–CH<sub>2</sub>

2.9 ppm            2H              possibly Ar–C(=O)–CH<sub>2</sub>–C

2.0 ppm            3H              O–C(=O)–CH<sub>3</sub>

From the splitting pattern of each signal the following partial structures can be identified.

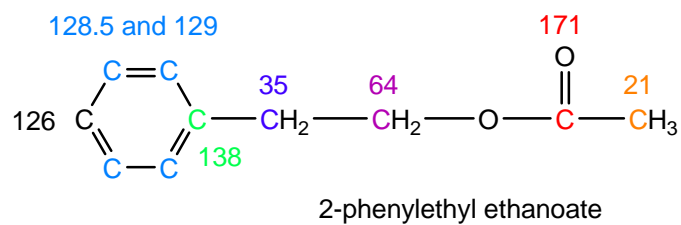
7.4–7.1 ppm      complex              substituted benzene

4.3 ppm            triplet              –CH<sub>2</sub>–CH<sub>2</sub>–

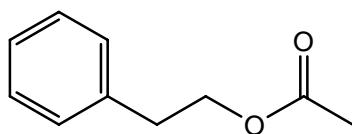
3.8 ppm            triplet              –CH<sub>2</sub>–CH<sub>2</sub>–

2.0 ppm            singlet              –CO–CH<sub>3</sub>

The position of all eight signals in the <sup>13</sup>C NMR spectrum is consistent with 2-phenylethyl ethanoate. Chemical shifts (in ppm) are indicated below. (Notice that the three signals from the benzene ring carbon atoms which are attached to H atoms are more intense than the signal for the benzene ring carbon atom attached to the functional group).



3. The unknown compound is 2-phenylethyl ethanoate.



2-phenylethyl ethanoate

## Answers to boxes

### Box 13.2 Using tandem mass spectrometry in newborn screening (on p. 617 in *Chemistry*<sup>3</sup>)

In the EI mass spectrum of (*S*)-phenylalanine, an intense fragment cation with a  $m/z$  value of 74 is observed. Suggest a structure for this fragment ion and propose a mechanism for its formation.

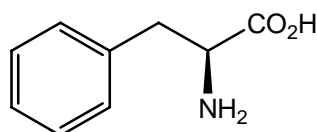
#### Strategy

Electron ionisation (EI) is the most common ionisation technique used for mass spectrometry. This type of ionisation produces positive ions by “knocking off” an electron from the parent molecule using high-energy electrons.

1. Draw out the structure of (*S*)-phenylalanine.
2. Determine the site of ionisation; this is usually at a heteroatom (O, N and S) that has a non-bonded pair of electrons.
3. Fragment this molecular ion; remember the more preferred fragmentation pathway will involve more stable intermediates.
4. Draw a mechanism to account for your fragmentation.

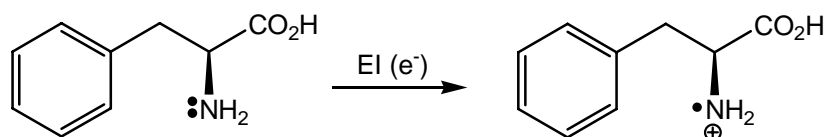
#### Solution

1. The structure of (*S*)-phenylalanine is shown below.



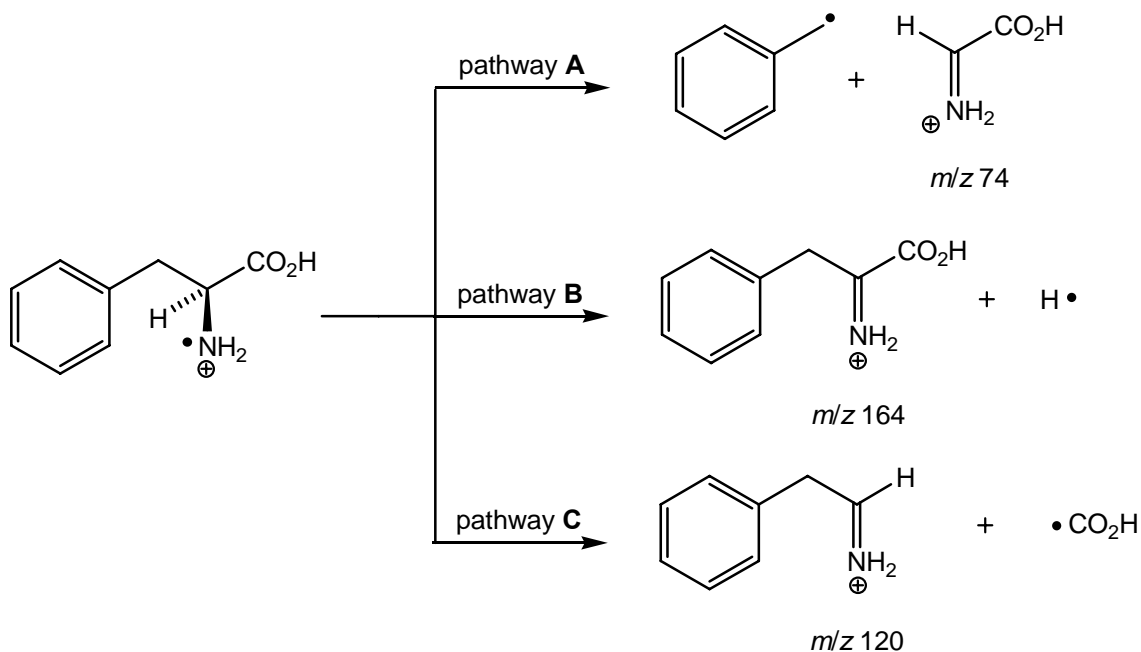
(*S*)-phenylalanine

2. The site of electron ionisation (EI) is at less electronegative nitrogen atom as it contains the highest energy non-bonded pair of electrons within this molecule; this ionisation is shown below.

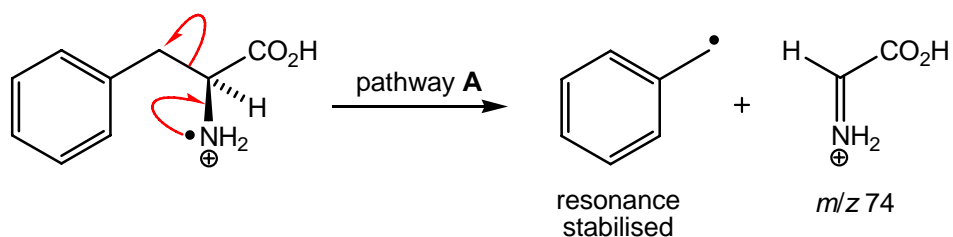


(*S*)-phenylalanine

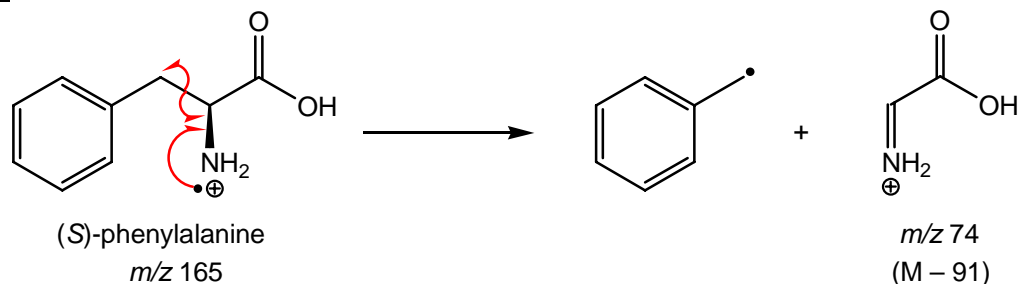
3. Fragmentation can occur by three pathways. Pathways **A**, **B** and **C** give the corresponding iminium ions with  $m/z$  values of 74, 164 and 120, respectively. From the experimental data given, pathway **A** is preferred as this leads to an iminium ion with a  $m/z$  value of 74.



4. The mechanism for the fragmentation pathway **A** is shown below. This pathway is evidently faster than pathways **B** and **C**; this is because the intermediate benzylic (PhCH<sub>2</sub>•) radical is resonance stabilised.



Answer



it is easier to lose an electron  
from nitrogen rather than from one of the  
(more electronegative) oxygen atoms

**Box 13.5 Drawing a <sup>1</sup>H NMR spectrum (on p. 642 in *Chemistry*<sup>3</sup>)**

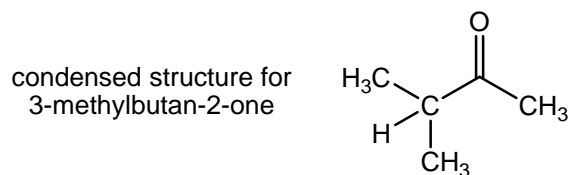
Draw the <sup>1</sup>H NMR spectrum for 3-methylbutan-2-one.

Strategy

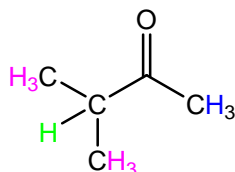
1. Draw out a condensed structure of 3-methylbutan-2-one.
2. From this structure, you will need to decide on the number and types of hydrogen atoms that are in different electronic environments.
3. Give the number of hydrogen atoms in each electronic environment.
4. Use Table 13.3 (p. 623 in *Chemistry*<sup>3</sup>) and Figure 13.3 (p. 634 in *Chemistry*<sup>3</sup>) to estimate the chemical shifts for each CH<sub>3</sub> and CH groups.
5. From the number of hydrogen atoms on the adjacent carbon, use the  $N + 1$  rule (see p. 639 and Box 11.8 on p.548 in *Chemistry*<sup>3</sup>) to calculate the splitting pattern for each resonance signal.

Solution

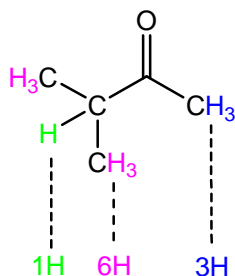
1. The condensed structure of 3-methylbutan-2-one is shown below.



2. There are three different types of hydrogen environments. Methyl groups (labelled purple) are magnetically equivalent.

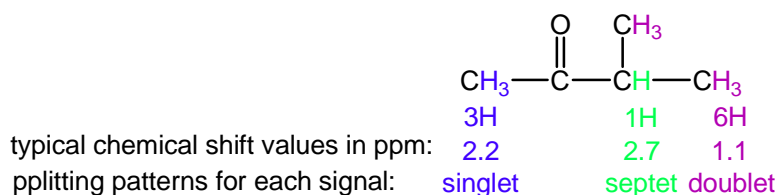
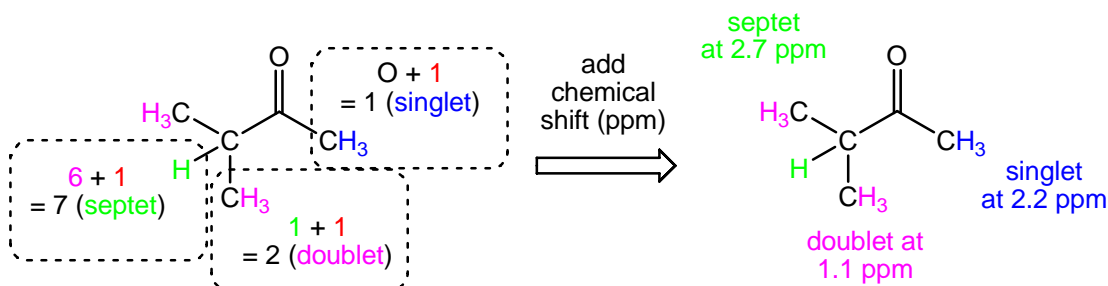


3. The number of hydrogen atoms in each environment is shown below.

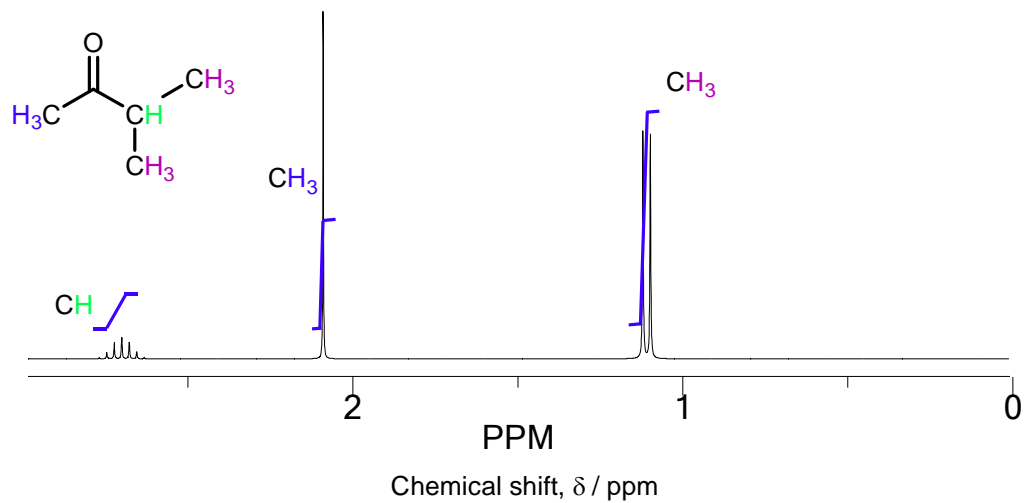


4. The number of hydrogen atoms in each environment, the estimated chemical shifts (using Table 13.3 and Figure 13.13) and the associated splitting pattern for each signal is shown below.

Splitting ( $N + 1$ ) pattern for 3-methylbutan-2-one

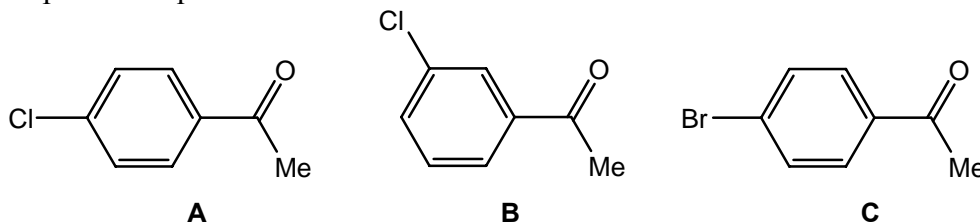


5. The  $^1\text{H}$  NMR spectrum of 3-methylbutan-2-one is shown below.



**Answers to end of chapter questions (on p. 655 in *Chemistry*<sup>3</sup>)**

1. The following queries relate to the analysis of the methyl ketones **A–C** using different spectroscopic techniques.



- (a) In the mass spectra of both **A** and **B**, explain the appearance of two molecular ion peaks at  $m/z$  154 and 156 in the ratio 3:1, respectively.

Strategy

1. Are molecules **A** and **B** isomers?
2. Look out for elements which exist as a mixture of isotopes.
3. Answer the question.

Solution

1. Molecules **A** and **B** are structural isomers and they have the same molecular formula of  $C_8H_7ClO$ .
2. Chlorine has a natural isotopic abundance of  $^{35}Cl$  and  $^{37}Cl$  in a 3:1 ratio.
3. The molecular ions at  $m/z$  values of 154 and 156 have a molecular formula of  $C_8H_7^{35}ClO^+$  and  $C_8H_7^{37}ClO^+$ , respectively, in a ratio of 3:1 due to the natural isotopic abundance of chlorine.

Answer

Both **A** and **B** contain a chlorine atom. Chlorine exists as a mixture of two isotopes,  $^{35}Cl$  and  $^{37}Cl$ , in a ratio of 3:1. So, both **A** and **B** give a 3:1 ratio for the relative abundances of two molecular ion peaks separated by two mass units.

- (b) Would you expect compound **C** to give two molecular ion peaks and, if so, would they also be in a 3:1 ratio? Briefly explain your reasoning.

Strategy

Each halogen has its own isotopic signature; bromine has a natural isotopic abundance of  $^{79}\text{Br}$  and  $^{81}\text{Br}$  in an approximate 1:1 ratio.

### Solution

Compound **C** contains a single bromine atom. Two molecular ions in a ratio of 1:1 at  $m/z$  values of 198 ( $\text{C}_8\text{H}_7^{79}\text{BrO}^+$ ) and 200 ( $\text{C}_8\text{H}_7^{81}\text{BrO}^+$ ) would be expected due to the natural isotopic abundance of bromine.

### Answer

Compound **C** contains a single bromine atom and it is expected to give two molecular ion peaks, in a 1:1 ratio, separated by two mass units. This is because the natural abundances of  $^{79}\text{Br}$  (50.7%) and  $^{81}\text{Br}$  (49.3%) are about the same.

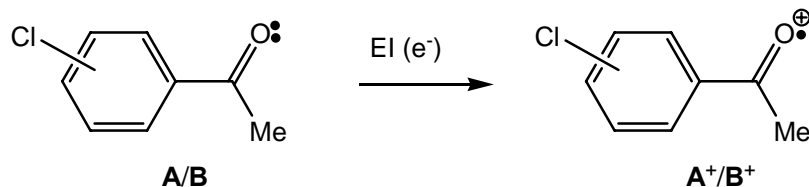
- (c) In the mass spectra of both **A** and **B**, explain the appearance of fragment cations at  $m/z$  141 and 139 in the ratio 3:1.

### Strategy

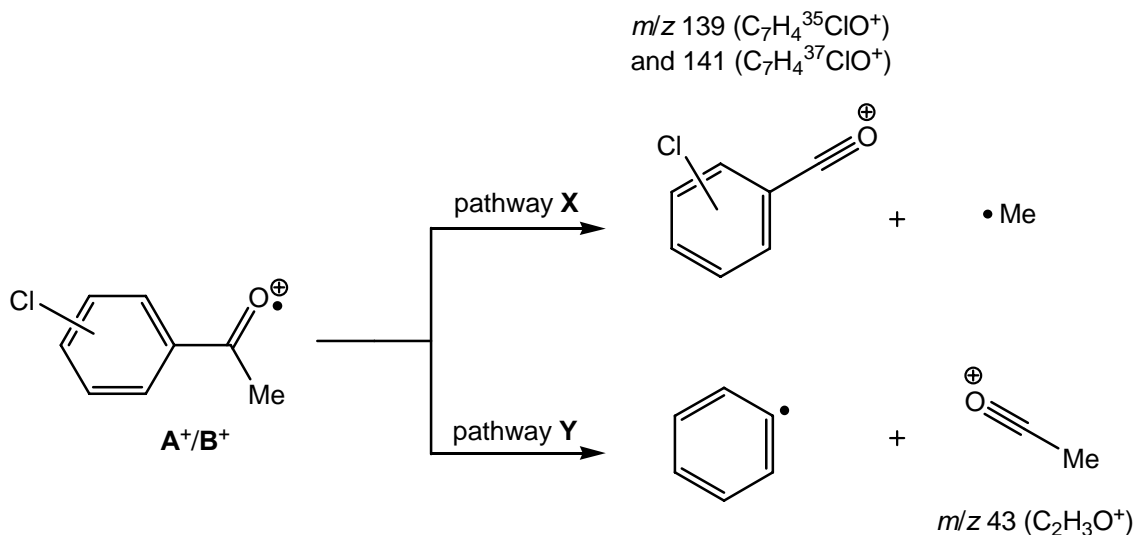
1. Determine the site of electron ionisation (EI).
2. Try and fragment the molecular ion. The fragment cations must contain a chlorine atom as they have the same abundance as the characteristic isotopic signature of chlorine ( $^{35}\text{Cl}$ : $^{37}\text{Cl}$  in a ratio of 3:1).

### Solution

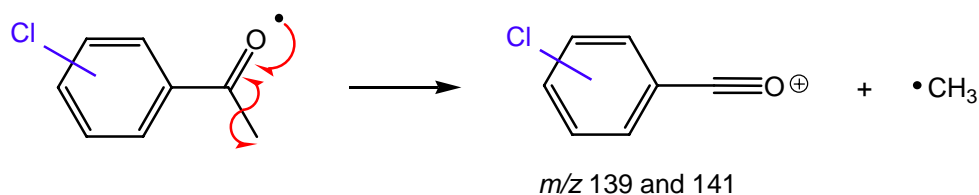
1. Electron ionisation will occur at the carbonyl oxygen atom as it contains the highest energy non-bonded pair of electrons within this molecule; this ionisation is shown below.



2. There are two fragmentation pathways **X** and **Y**. Pathway **X** is preferred as this leads to a resonance stabilised chlorine-containing carbocation ( $\text{Ar-C}\equiv\text{O}^+$ ). This isotopic fragment will have  $m/z$  values of 139 and 141 in a ratio of 3:1, respectively.

Answer

Fragment cations at  $m/z$  139 and 141, in the ratio 3:1, are due to chlorine-containing fragment ions produced by cleavage of the  $CH_3-CO$  bond in the ketone groups of **A** and **B**.



the Cl atom is at  
the 2- or 4-position  
of the ring

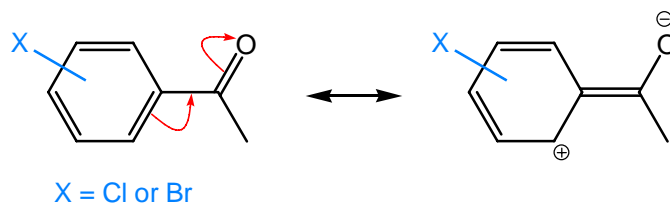
- (d) The IR spectra of **A–C** all show strong absorption peaks around  $1690\text{ cm}^{-1}$  due to the  $C=O$  stretching vibration. Suggest why these peaks are at a lower wavenumber than the  $C=O$  stretching vibration for propanone ( $CH_3COCH_3$ ).

Strategy

The stretching frequency of a bond is proportional to its bond strength; weak bonds vibrate slower than strong bonds, and therefore their frequency will be lower. Bonds with lower frequencies will have lower wavenumbers; *i.e.*, the number (or frequency) of waves per centimetre.

Solution/Answer

The C=O stretching vibration for **A-C** is lower than that for propanone because of the electron-donating (+M) effects of the benzene rings. Donating a pair of  $\pi$ -electrons from the benzene to the C=O bond produces a resonance structure with a single C–O bond. This resonance weakens the C=O bond, making it longer and easier to vibrate.



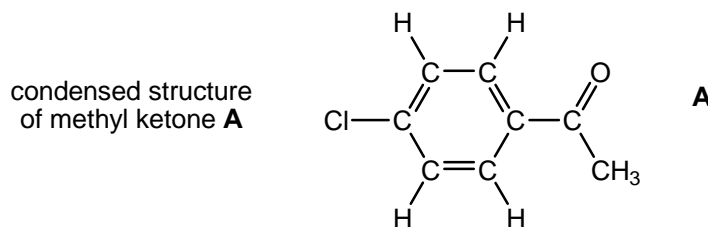
- (e) The  $^1\text{H}$  NMR spectrum of **A** shows three signals: a doublet at 7.88 ppm; a doublet at 7.43 ppm; and a singlet at 2.58 ppm. Explain the number of resonance signals and the splitting pattern for each signal.

### Strategy

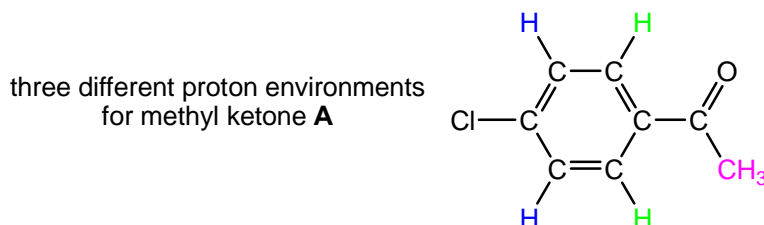
1. Draw out a condensed structure of methyl ketone **A**.
2. From this structure, you will need to decide on the number and types of hydrogen atoms that are in different electronic environments.
3. Give the number of hydrogen atoms in each electronic environment.
4. Use Table 13.3 (p. 633 in *Chemistry*<sup>3</sup>) and Figure 13.3 (p. 634 in *Chemistry*<sup>3</sup>) to estimate the chemical shifts for each  $\text{CH}_3$  and CH groups.
5. From the number of hydrogen atoms on the adjacent carbon, use the  $N + 1$  rule (see p. 639 and Box 11.8, p.548 in *Chemistry*<sup>3</sup>) to calculate the splitting pattern for each resonance signal.

### Solution

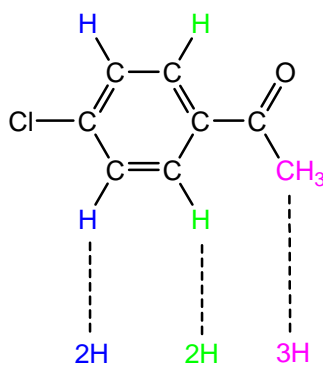
1. The condensed structure for methyl ketone **A** is shown below.



2. There are three different types of hydrogen environments. Hydrogen atoms (labelled blue and green) are magnetically equivalent.

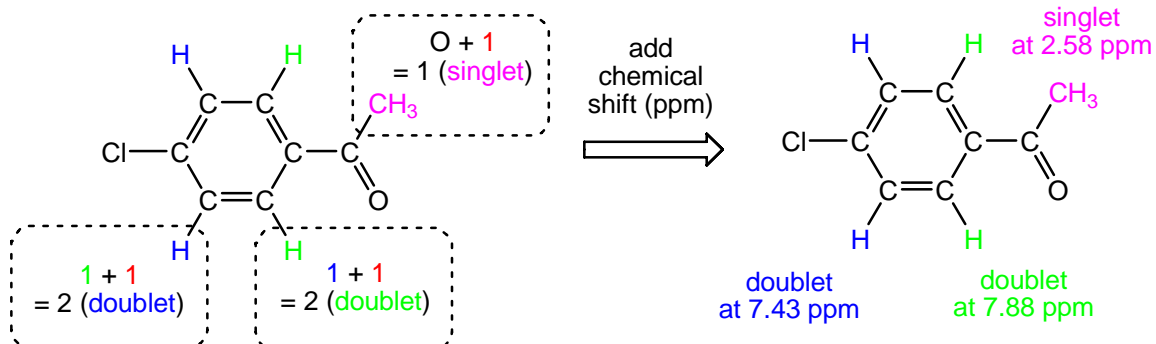


3. The number of hydrogen atoms in each environment is shown below.



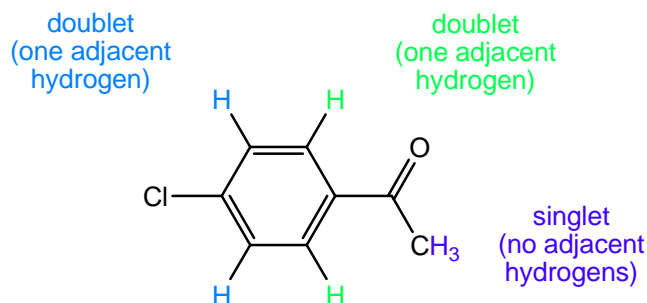
4. The number of hydrogen atoms in each environment, the estimated chemical shifts (using Table 13.3 and Figure 13.3 on p. 633 and p. 634, respectively in *Chemistry*<sup>3</sup>), and the splitting pattern for each signal is shown below.

Splitting ( $N + 1$ ) pattern for methyl ketone **A**



Answer

There are three types of hydrogen atoms in different electronic environments.



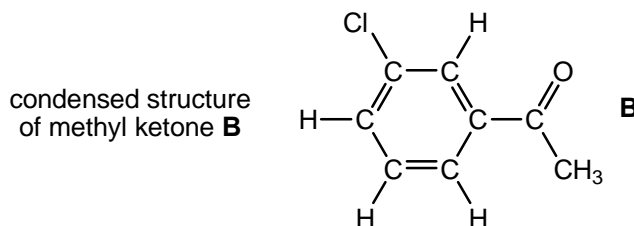
- (f) For the  $^1\text{H}$  NMR spectrum of **B**, how many resonance signals would you expect? Briefly explain your reasoning.

Strategy

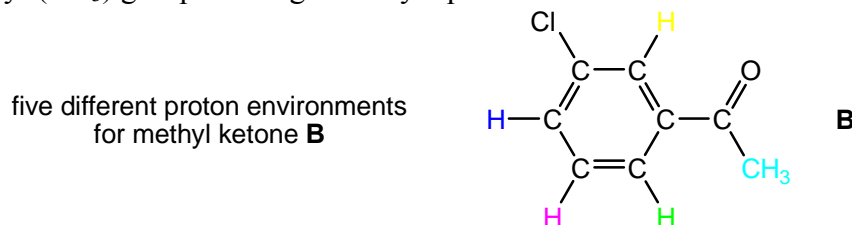
1. Draw out a condensed structure of methyl ketone **B**.
2. From your structure, you will need to decide on the number and types of hydrogen atoms that are in different electronic environments.

Solution

1. The condensed structure for methyl ketone **B** is shown below.



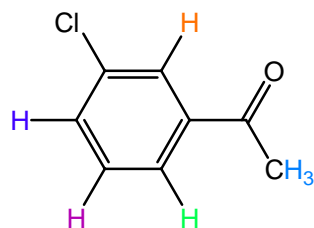
2. There are five different types of hydrogen environments. Only the hydrogen atoms on the methyl ( $\text{CH}_3$ ) group are magnetically equivalent.



Answer

The  $^1\text{H}$  NMR spectrum of **B** is expected to show FIVE resonance signals as there are FIVE types of hydrogen atoms in different electronic environments.

all four H atoms  
on the ring are in  
slightly different  
environments



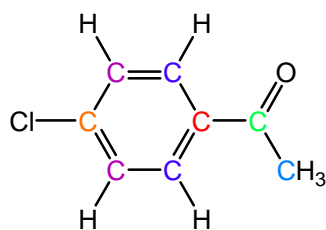
- (g) What major differences would you expect to see in the  $^{13}\text{C}$  NMR spectra (proton decoupled) of **A** and **B**?

Strategy

Work out the number of magnetically non-equivalent carbon atoms for both methyl ketones, **A** and **B**.

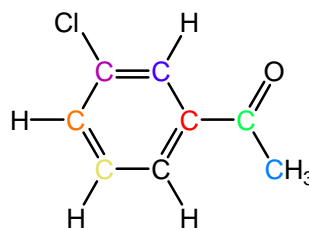
Solution/Answer

The  $^{13}\text{C}$  NMR spectrum of **A** is expected to show six signals, whereas the  $^{13}\text{C}$  NMR spectrum of **B** is expected to show eight signals.



**A**

six carbon atoms in  
different environments



**B**

all eight carbon atoms are in  
different electronic environments

3. A sample of ethyl propanoate,  $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ , is investigated by  $^1\text{H}$  NMR spectroscopy and  $^{13}\text{C}$  NMR (proton decoupled) spectroscopy and mass spectrometry.

- (a) Draw the expected  $^1\text{H}$  NMR spectrum showing spin-spin splittings and approximate chemical shifts.

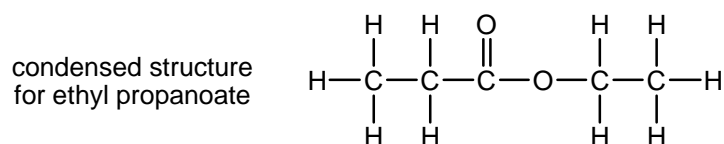
Strategy

1. Draw out a condensed structure of ethyl propanoate.

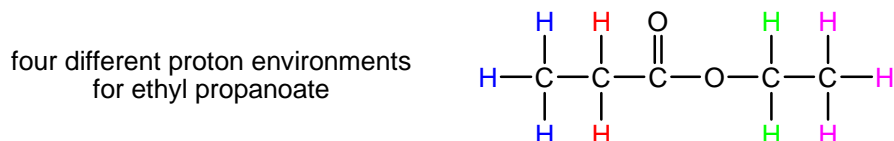
- From your structure, you will need to decide on the number and types of hydrogen atoms that are in different electronic environments.
- Give the number of hydrogen atoms in each electronic environment.
- Use Table 13.3 (p. 633 in *Chemistry*<sup>3</sup>) and Figure 13.3 (p. 634 in *Chemistry*<sup>3</sup>) to estimate the chemical shifts for each CH<sub>3</sub> and CH groups. From the number of hydrogen atoms on the adjacent carbon, use the  $N + 1$  rule (see p. 639 and Box 11.8, p. 548 in *Chemistry*<sup>3</sup>) to calculate the splitting pattern for each resonance signal.
- Draw out the <sup>1</sup>H NMR spectrum.

### Solution

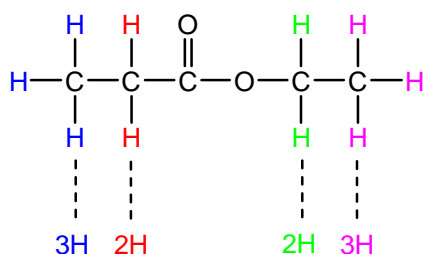
- The condensed structure of ethyl propanoate is shown below.



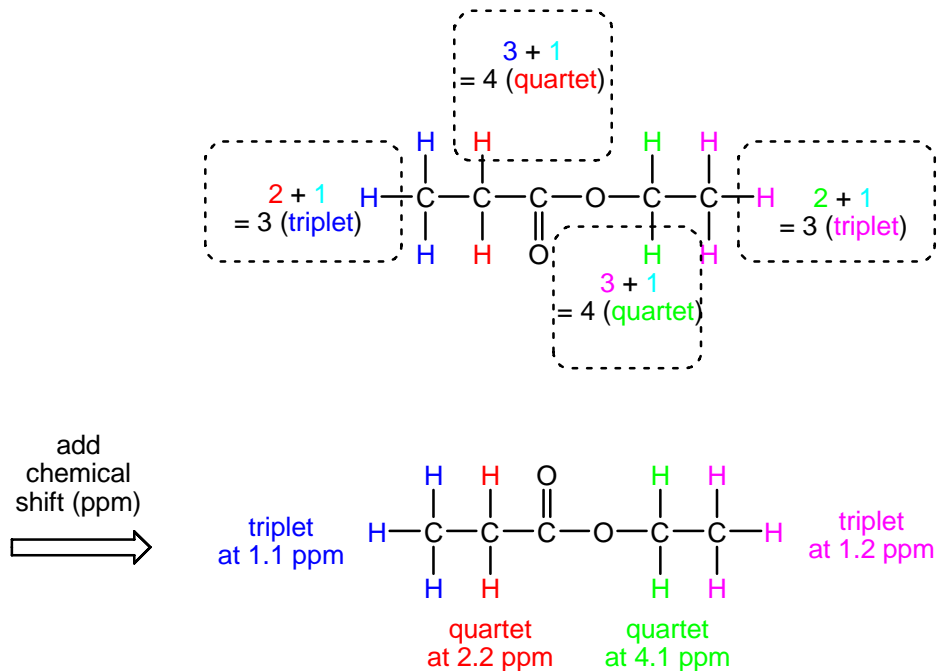
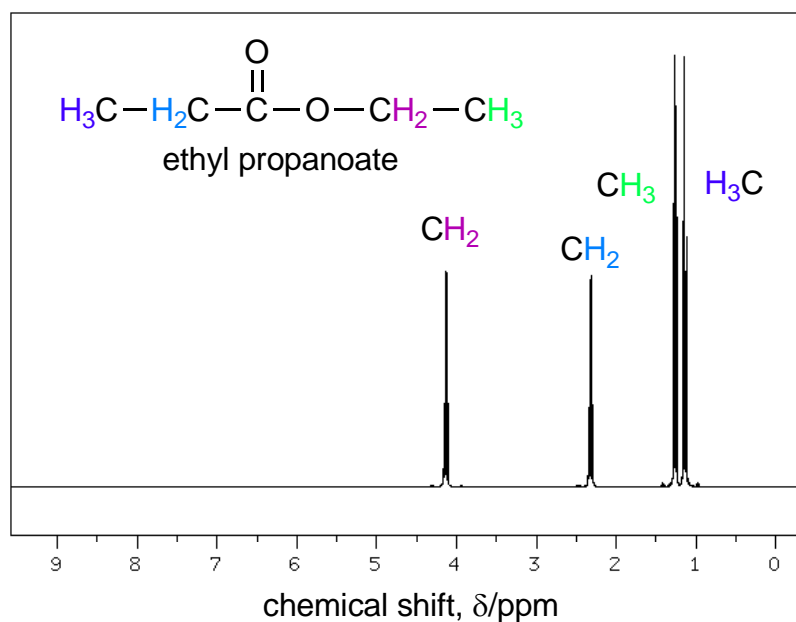
- There are four different types of hydrogen environments. The hydrogen atoms on each methyl (CH<sub>3</sub>) group and methylene (CH<sub>2</sub>) group are magnetically equivalent.



- The number of hydrogen atoms in each environment is shown below.



- The number of hydrogen atoms in each environment, the estimated chemical shifts (using Table 13.3 and Figure 13.13 on p. 633 and p. 634, respectively in *Chemistry*<sup>3</sup>) and the splitting pattern for each signal is shown below.

Splitting ( $N + 1$ ) pattern for ethyl propanoate5. The  $^1\text{H}$  NMR spectrum of ethyl propanoate is shown below.

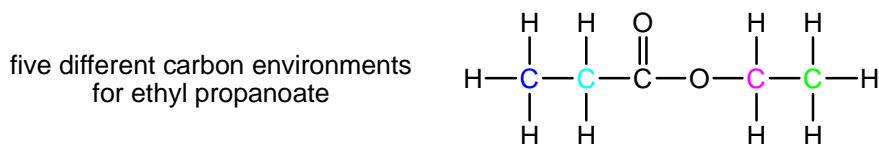
- (b) Draw the expected  $^{13}\text{C}$  NMR spectrum (proton decoupled) with approximate chemical shifts.

Strategy

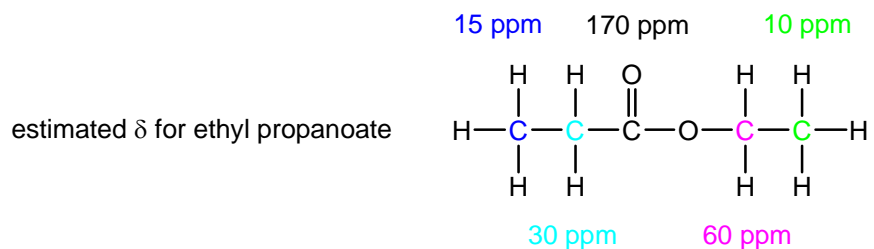
1. From its condensed structure, determine the number and types of non-magnetically equivalent carbon atoms.
2. Estimate the chemical shift for each  $\text{CH}_3$  and  $\text{CH}_2$  groups.
3. Draw out the  $^{13}\text{C}$  NMR (proton decoupled) spectrum.

Solution

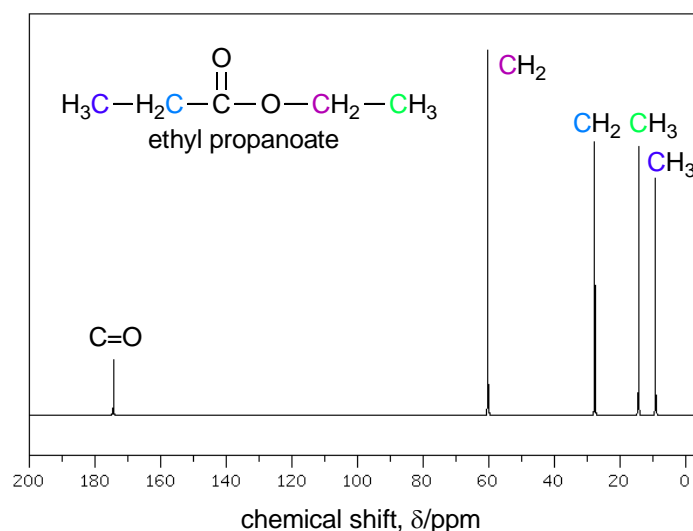
1. There are five different types of carbon environments. All these carbon atoms are non-equivalent.



2. The chemical shifts for each carbon atom is shown below.



3. The  $^{13}\text{C}$  NMR (proton decoupled) spectrum of ethyl propanoate is shown below.



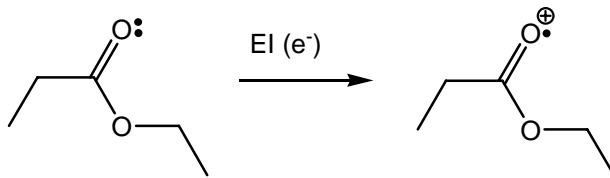
- (c) In the mass spectrum, an intense peak was observed at  $m/z$  57. Draw the structure of the cation that corresponds to this peak and give a mechanism for its formation.

### Strategy

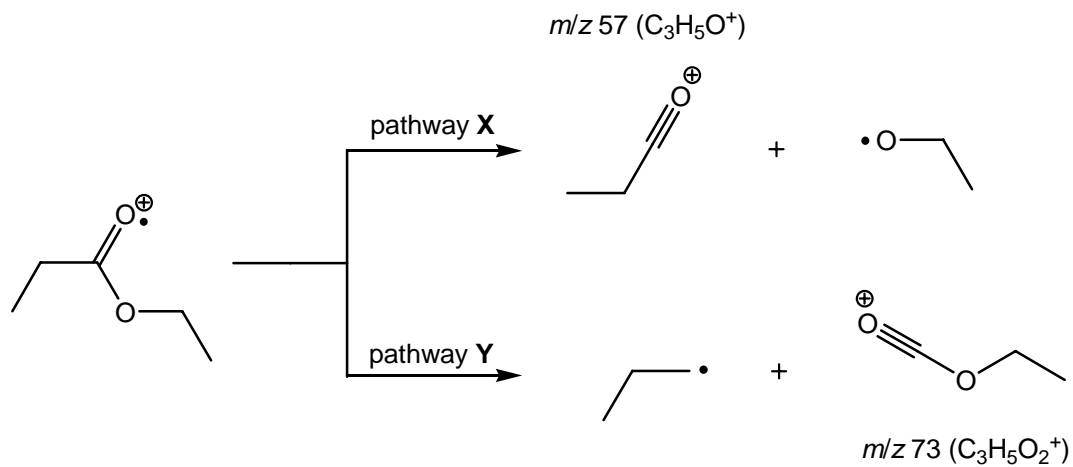
1. Determine the site of electron ionisation (EI).
2. Try and fragment the molecular ion to give a carbocation with a  $m/z$  value of 57.
3. Draw out a mechanism for this fragmentation.

### Solution

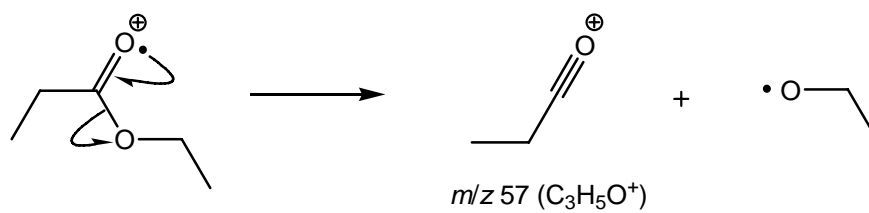
1. Electron ionisation will occur at the carbonyl oxygen atom as it contains the highest energy non-bonded pair of electrons within this molecule; this ionisation is shown below.



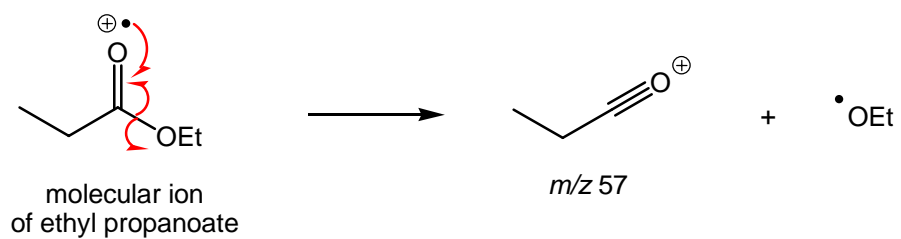
2. There are two fragmentation pathways **X** and **Y**. Pathway **X** leads to the carbocation,  $\text{Et}-\text{C}\equiv\text{O}^+$ , with the required  $m/z$  value of 57. In comparison, pathway **Y** leads to the related carbocation,  $\text{EtO}-\text{C}\equiv\text{O}^+$ , with a  $m/z$  value of 73.



3. The mechanism for this fragmentation is shown below.



Answer



5. A strong smelling compound was isolated from the anise plant. Using the mass, IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra given on p. 657 in *Chemistry*<sup>3</sup>, propose a structure for this compound.

### Strategy

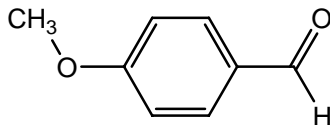
1. Examine the mass spectrum and pick out the molecular ion.
2. Examine the IR spectrum and look for characteristic peaks, such as XH, C=O and Ph groups.
3. Survey the <sup>1</sup>H and <sup>13</sup>C NMR spectra to confirm if any of these functional groups are present. Draw out some structural isomers and deduce which matches the given spectra.
4. Draw out the structure of this unknown compound.

### Solution

1. The molecular ion has a  $m/z$  value of 132. As this mass number is even, it contains either zero or an even number of nitrogen atoms. There are no signature isotope patterns for alogens. As the molecular ion has a  $m/z$  value greater than 77, it may contain a benzene ring.
2. From this IR spectrum, there are a number of characteristic peaks.
  - (a) There is no broad peak due to intermolecular XH bonding between 3500-3000  $\text{cm}^{-1}$ ; there are no OH and NH bonds.
  - (b) There are numerous C-H stretches (3000-2900  $\text{cm}^{-1}$ ).
  - (c) There is a carbonyl (C=O) stretch at 1700  $\text{cm}^{-1}$ ; possibly due to an aldehyde or ketone.
3. From this <sup>1</sup>H NMR spectrum, there is a characteristic 1 H singlet at 10 ppm (due to an aldehyde RCHO group), two aromatic 2 H singlets at 7.8 and 7.0 ppm, and a 3 H singlet at 3.9 ppm. This unknown molecule is clearly a disubstituted benzene; the remaining functionality must be attached to this benzene ring. The 3 H singlet at 3.9 ppm is due to a CH<sub>3</sub>O- group. From the symmetry of these aromatic signals at 7.8 and 7.0 ppm; this molecule must be a 1,4-disubstituted benzene; namely 4-methoxybenzaldehyde. This structure would account for the molecular ion at a  $m/z$  value of 136 (C<sub>8</sub>H<sub>8</sub>O<sub>2</sub><sup>+</sup>).  
Just to confirm this assignment, from its <sup>13</sup>C NMR spectrum, there are six non-equivalent carbon signals at 191 ppm (C=O), 165 ppm [*ipso*-C(4)-O; aromatic ring],

135 ppm [ $2 \times \text{C}(2)\text{H}$ ; aromatic], 130 ppm [*ipso*-C(1)-C; aromatic ring], 115 ppm [ $2 \times \text{C}(3)\text{H}$ ; aromatic] and 55 ppm [ $\text{CH}_3\text{O}$ -].

4. This structure of this unknown compound is shown below.



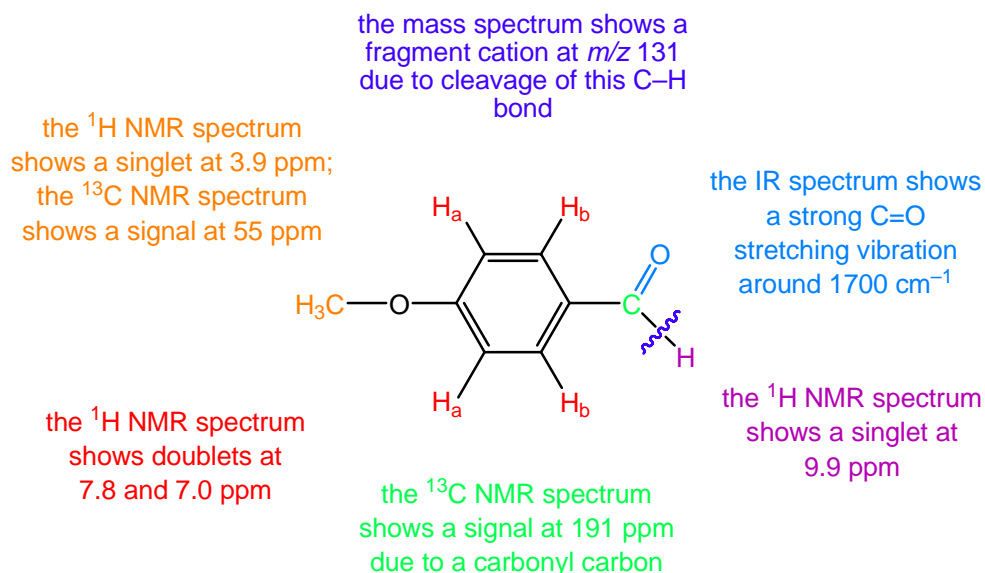
4-methoxybenzaldehyde

### Answer

The mass spectrum shows a molecular ion peak at  $m/z$  132.

The intense peak at  $m/z$  131 ( $M-1$ ) is characteristic of an aldehyde group.

The signal at 9.9 ppm in the  $^1\text{H}$  NMR spectrum is characteristic of a hydrogen atom in a formyl ( $-\text{CHO}$ ) group. Signals at 7.8 ppm and 7.0 ppm suggest the presence of a 1,4-disubstituted benzene ring. Detailed analysis of the spectra is shown below.



The unknown compound is 4-methoxybenzaldehyde (anisaldehyde).

Solutions provided by J. Eames (j.eames@hull.ac.uk)