
Molecular characterization

Answers to worked examples

WE 12.1 Identifying a bromoalkane (on p. 564 in *Chemistry*³)

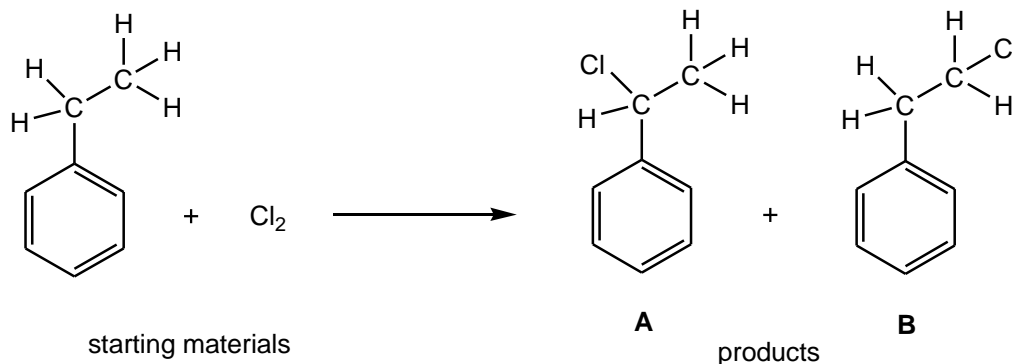
When a mixture of ethylbenzene (PhCH_2CH_3) and chlorine is illuminated with UV radiation, PhCHClCH_3 and $\text{PhCH}_2\text{CH}_2\text{Cl}$ are formed in unequal amounts. After separation, the EI mass spectra of both products were recorded. The mass spectrum of the major product showed peaks at m/z 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

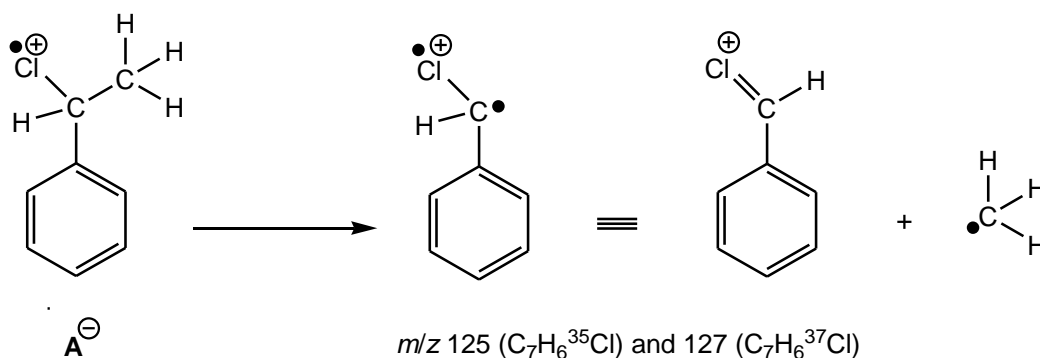
1. Draw out the proposed reaction and identify the starting materials and products.
2. Determine the molecular masses for the starting materials and products.
3. Are there any characteristic isotopic patterns?
4. For each product, try and fragment the molecular ion to form “stabilised” cations.

Solution

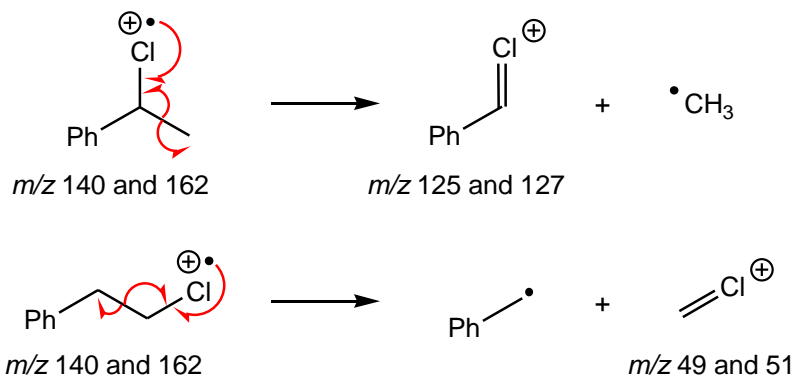
1. The reaction scheme is shown below:



- The molecular mass of the starting material, ethylbenzene (PhCH_2CH_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 (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 PhCHClCH_3 . For 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.

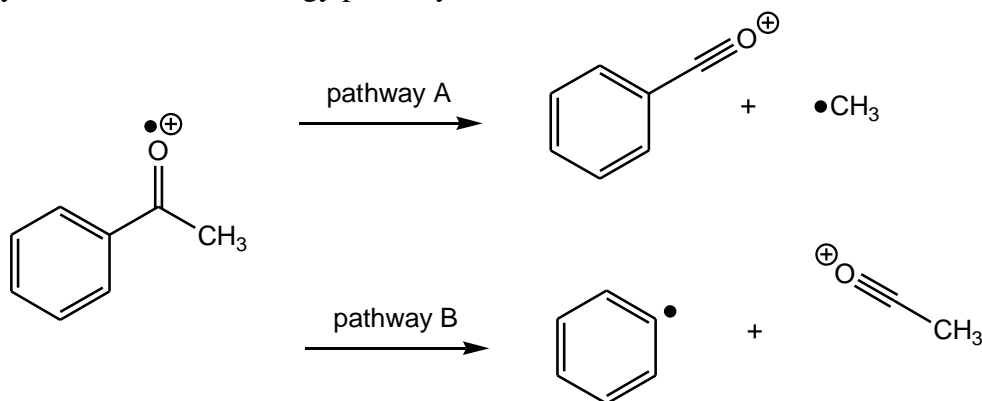
**WE 12.2 Using a fragmentation pattern to assign a structure (on p. 566 in *Chemistry*³)**

The following queries relate to the EI mass spectrum of acetophenone shown at the beginning of this worked example on p. 564 in *Chemistry*³.

- (a) Suggest why the $\text{PhC}\equiv\text{O}^+$ fragment cation, but not the $\text{CH}_3\text{C}\equiv\text{O}^+$ fragment cation, is the major fragment cation observed in the mass spectrum.

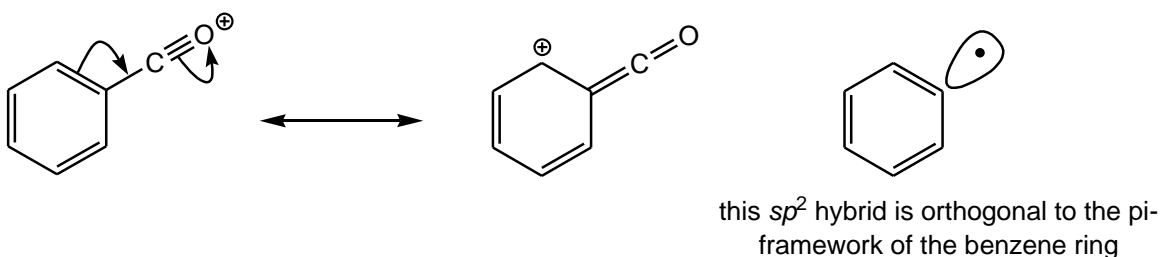
Strategy

The overall stability of the fragment carbocation and the corresponding radical will govern which fragmentation pathway is preferred. Consider the stability of the fragment cation, $\text{PhC}\equiv\text{O}^+$, and the methyl ($\text{CH}_3\cdot$) radical (for pathway A), versus the competitive formation of the fragment cation, $\text{CH}_3\text{C}\equiv\text{O}^+$, and phenyl ($\text{Ph}\cdot$) radical (for pathway B). The preferred pathway will be the lower energy pathway.

Solution

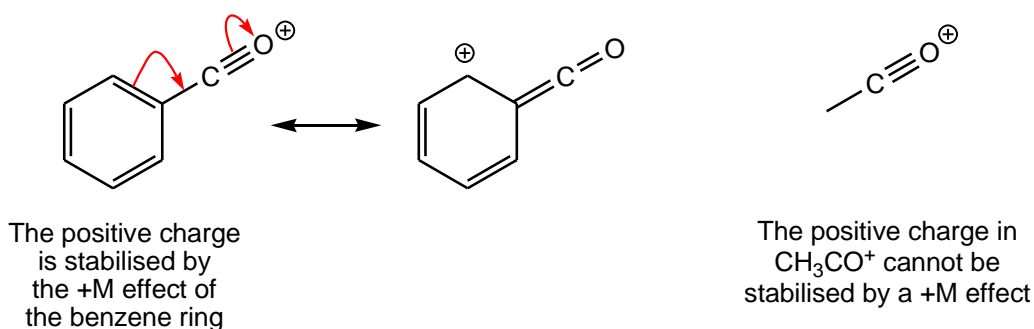
Pathway A is preferred, as the resulting carbocation ($\text{Ph}-\text{C}\equiv\text{O}^+$) is **substantially** more stable than that derived from pathway B ($\text{Me}-\text{C}\equiv\text{O}^+$). However, this is not compensated for by its complementary phenyl ($\text{Ph}\cdot$) radical (in pathway B) as this is only **marginally** more

stable than the corresponding methyl (CH_3^\bullet) radical (in pathway A). The carbocation ($\text{Ph-C}\equiv\text{O}^+$) is resonance stabilised, whereas the phenyl (Ph^\bullet) radical is not resonance stabilised.



Answer

Fragmentation of the C-CH_3 bond of acetophenone leads to the more stable cation. $\text{Ph-C}\equiv\text{O}^+$ is more stable than $\text{Me-C}\equiv\text{O}^+$ because it is stabilised by the +M effect of the benzene ring (see Section 19.1 on p. 857 in *Chemistry*³).



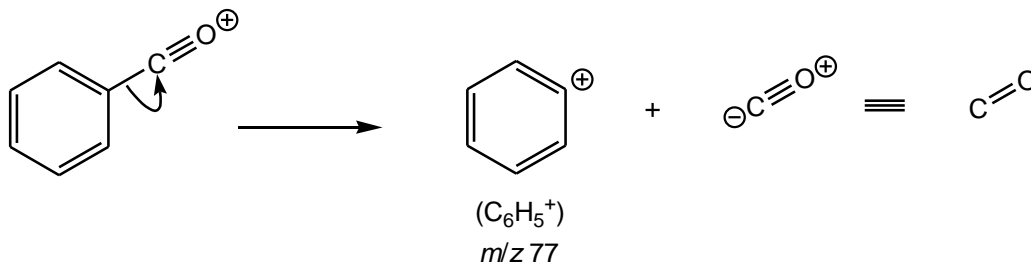
(b) Suggest a structure for the fragment ion that has an m/z value of 77.

Strategy

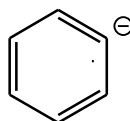
This fragment, with a m/z value of 77, must be derived from the major molecular ($\text{Ph-C}\equiv\text{O}^+$) ion with a m/z value of 105. Try and fragment this ion, $\text{Ph-C}\equiv\text{O}^+$, to give a carbocation with a m/z value of 77 and a byproduct with a molecular mass of 28 ($105 - 77$).

Solution

Fragmentation of $\text{Ph-C}\equiv\text{O}^+$ leads to the more stable Ph^+ carbocation with a m/z value of 77 and carbon monoxide (C=O) with a molecular mass of 28. Complementary, fragmentation of $\text{Ph-C}\equiv\text{O}^+$, to give the less stable C=O^+ (m/z 28) and the less stable phenyl (Ph^\bullet) radical is slower.



Answer



WE 12.3 Using IR spectroscopy to identify the products of the reactions of propanoyl chloride (on p. 576 in *Chemistry*³)

Propanoyl chloride ($\text{CH}_3\text{CH}_2\text{COCl}$) reacts with ammonia to give organic product **A** and HCl. Assign the characteristic absorption bands in the IR spectrum of **A** (shown on p. 574 in *Chemistry*³) and use this information to help you propose a structure for **A**.

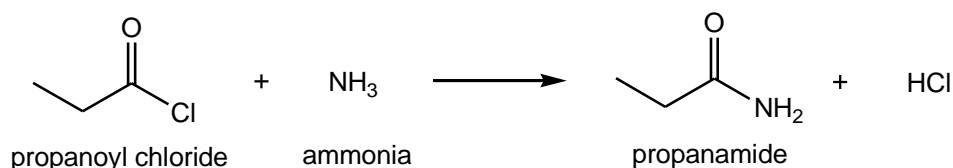
Strategy

1. Survey the IR spectrum looking for characteristic bands.
2. Are these characteristic bands present in the IR spectrum of propanoyl chloride?
3. Propose a structure for **A**, and draw out a reaction scheme.

Solution

1. The are characteristic peaks in spectrum **A** are:
 - (a) Two peaks between $3400\text{-}3200\ \text{cm}^{-1}$; these are more than like due to inter- and intramolecular hydrogen bonding.
 - (b) Broads peaks between $3000\text{-}2800\ \text{cm}^{-1}$; alkyl C-H bonds.
 - (c) Intense and broad peak between $1700\text{-}1600\ \text{cm}^{-1}$; this is the C=O region.
 - (d) The fingerprint region ($1400\text{-}600\ \text{cm}^{-1}$) is little help.
2. The two peaks between $3400\text{-}3200\ \text{cm}^{-1}$ (in the IR spectrum of **A**) are not present in the IR spectrum of propanoyl chloride. The carbonyl group of propanoyl chloride has a higher stretching frequency ($1800\ \text{cm}^{-1}$) than that of compound **A** ($1700\text{-}1600\ \text{cm}^{-1}$).
3. The two peaks, between $3400\text{-}3200\ \text{cm}^{-1}$, are due to N-H bonds; their broad absorption is due to intermolecular hydrogen bonding between different amide molecules. Less electrophilic carbonyl groups tend to have lower stretching frequency/wavenumbers; an

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 cm^{-1} N-H stretch

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

1650 cm^{-1} C=O stretch of the CONH₂ group

Compound **A** is CH₃CH₂CONH₂

WE 12.4 Using chemical shifts to assign structures (on p. 586 in *Chemistry*³)

An aldehyde or ketone, with the molecular formula C₄H₈O, gave a ¹H NMR spectrum with resonance signals at δ 9.57, 2.50, and 1.06 ppm. Propose a structure for this compound and explain your reasoning.

Strategy

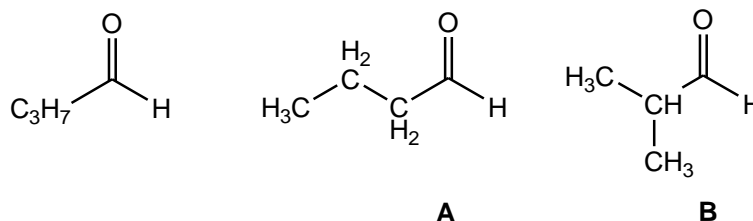
1. Deduce whether this unknown is an aldehyde or ketone from the given ¹H NMR data.
2. Draw out some structural isomers of C₄H₈O to see if they would match the given resonance signals.

Solution

1. Aldehydes and ketones are distinguishable by ¹H NMR spectroscopy; aldehydes have a characteristic **formyl** signal (RCHO) at δ 9-10 ppm. This unknown molecule is an aldehyde as it gives a characteristic resonance signal at δ 9.57 ppm.
2. As this molecule is an aldehyde, it must have a condensed structure of C₃H₇-CHO. There are only two structural isomers, **A** and **B**, which match this molecular formula. For the given ¹H NMR data, there are two resonance signals at δ 2.50 ppm and 1.06 ppm which have to be accounted for. Isomer **A** would give three additional resonance signals for its CH₃CH₂CH₂ group, whereas, isomer **B** would give the required two resonance signals for its (CH₃)₂CH group because these two methyl groups are

magnetically equivalent. The unknown compound is isomer **B**; its ¹H NMR spectrum has three resonance signals at δ 9.57 [(CH₃)₂CHCHO], 2.50 [(CH₃)₂CHCHO] and 1.06 ppm [(CH₃)₂CHCHO].

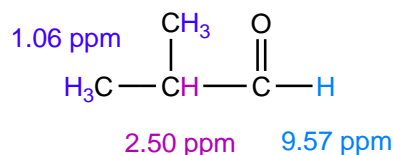
condensed structure



Answer

The compound is Me₂CHCHO.

The signal at δ 9.57 ppm is distinctive for an aldehyde. There are two possible structures: Me₂CHCHO or CH₃CH₂CH₂CHO. The compound cannot be CH₃CH₂CH₂CHO because this would give 4 resonance signals.



WE 12.5 Assigning a structure from a ¹H NMR spectrum (on p. 592 in *Chemistry*³)

The ¹H NMR spectrum of the major product from the enzyme-catalysed oxidation of 1-butylbenzene (PhCH₂CH₂CH₂CH₃) is shown on p. 590 in *Chemistry*³. Use this spectrum to predict a structure for this product and explain your reasoning.

Strategy

1. From this ¹H NMR spectrum, determine the reactive integration for each resonance signal.
2. Attempt to assign this ¹H NMR spectrum by examining the chemical shift of each resonance signal.
3. Attempt to assign this ¹H 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, δ 8.00, 7.50, 3.00, 1.80 and 1.00 ppm with a relative integration of 2, 3, 2, 2 and 3, respectively.

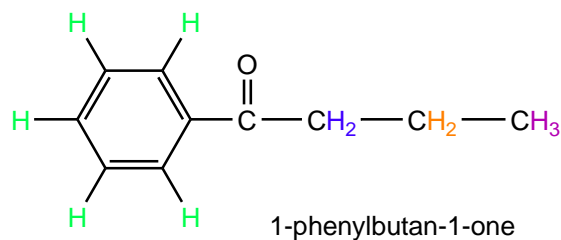
2. From Figure 12.13 and Table 12.3 the following types of CH, CH₂ and CH₃ groups are assigned to the five signals.

8.0 ppm	2H	2 × aromatic CH (from Figure 12.13)
7.6 ppm	3H	3 × aromatic CH (from Figure 12.13)
2.9 ppm	2H	possibly Ar-C(=O)-CH ₂ -C or Ar-CH ₂ -C
1.8 ppm	2H	possibly R-O-C-CH ₂ -C
1.0 ppm	3H	C-CH ₃

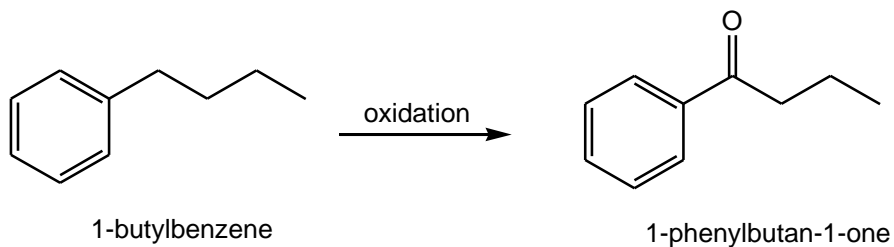
3. The splitting pattern of each signal suggests the following partial structures.

8.0 ppm	doublet	2 × aromatic CH-CH
7.6 ppm	complex	3 × aromatic CH
2.9 ppm	triplet	-CH ₂ -CH ₂ -C
1.8 ppm	sextet	-CH ₂ -CH ₂ -CH ₃
1.0 ppm	triplet	-CH ₂ -CH ₃

4. Combining the partial structures gives 1-phenylbutan-1-one.



5. The overall reaction is shown below.



WE 12.6 Assigning a structure from a ¹³C NMR spectrum (on p. 597 in *Chemistry*³)

Reaction of bromobenzene (C₆H₅Br) with a mixture of Br₂ and FeBr₃ gave a mixture of structural isomers with the molecular formula C₆H₄Br₂. Following separation of the mixture, the ¹³C NMR (proton decoupled) spectrum of one of the products was recorded and is shown on p. 595 in *Chemistry*³. Use this spectrum to predict a structure for the

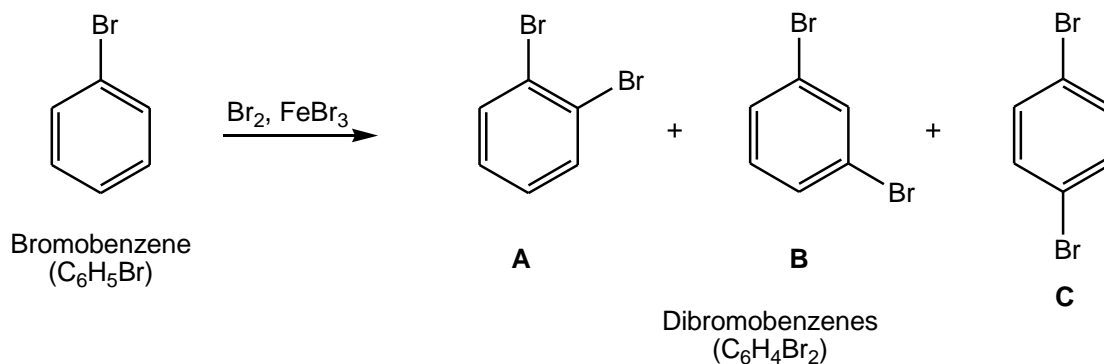
product and explain your reasoning. (The mechanism of this reaction is discussed in Section 22.2 on p.1007 in *Chemistry*³).

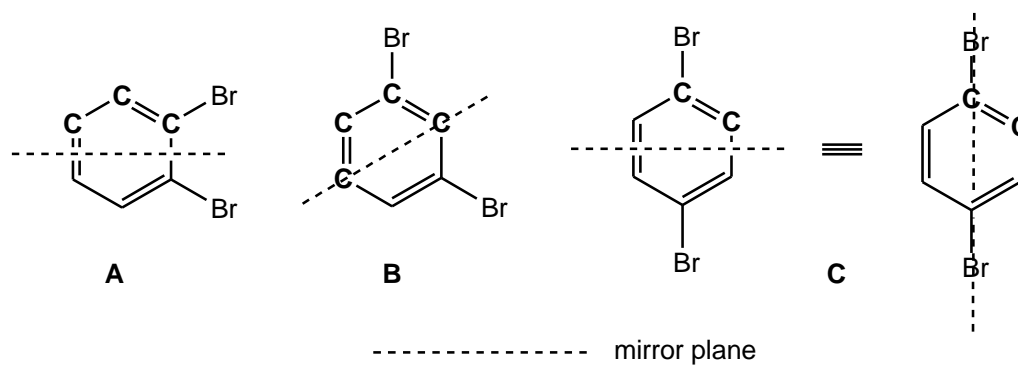
Strategy

1. From this ^{13}C NMR (proton decoupled) spectrum, determine the qualitative intensity for each resonance signal. Resonance signals, which have low intensity, have longer relaxation times due to the absence of C-H bonds.
2. Attempt to assign this ^{13}C NMR (proton decoupled) spectrum by examining the chemical shift of these resonance signals. As this ^{13}C NMR spectrum is proton decoupled, there will be no splitting patterns associated with these resonance signals.
3. Draw out a possible structure of this product, and consider if there is any symmetry present which may reduce the overall number of resonance signals.

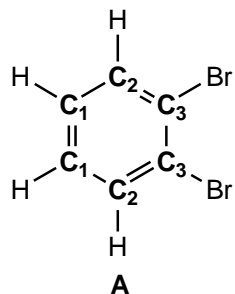
Solution

1. There are three resonance signals in this ^{13}C NMR (proton decoupled) spectrum; δ 133.6, 128.4 and 124.7 ppm. Two of these signals (δ 133.6 and 128.4 ppm) have similarly high intensity, and will more than likely be C-H bonds. The remaining resonance signal (δ 124.7 ppm) has lower intensity and must be an *ipso*-carbon atom.
2. These resonance signals are characteristic for an aromatic ring.
3. There are three potential products, **A-C**, from this reaction. Product **A** gives three carbon signals due to a horizontal mirror plane; product **B** gives four carbon signals due to a diagonal mirror plane; and product **C** gives two carbon signals due to horizontal and vertical mirror planes.



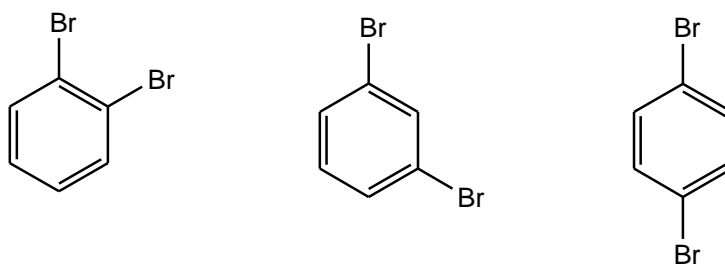


The unknown product is isomer **A**; its ^{13}C NMR spectrum has three resonance signals at δ 133.6 [C₁-H], 128.4 [C₂-H] and 124.7 ppm [C₃-Br].

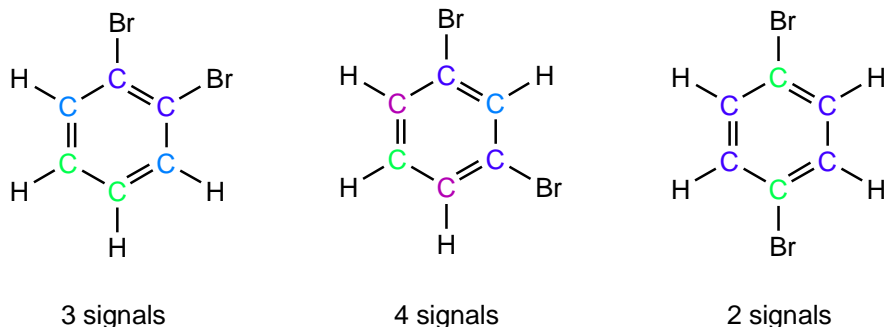


Answer

Possible products are shown below.



The product is 1,2-dibromobenzene as this is the only structural isomer which will give 3 signals in its ^{13}C NMR (proton decoupled) spectrum.

**WE 12.7 Assigning a structure from a combination of spectra (on p. 600 in *Chemistry*³)**

A second compound, with the molecular formula $C_{10}H_{12}O_2$, was isolated from the same synthetic perfume. Using the IR, 1H , and ^{13}C NMR (proton decoupled) spectra on p. 598 in *Chemistry*³; 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.
2. Survey the 1H and ^{13}C NMR spectra to confirm if these functional groups are present.
Draw out as many structural isomers of $C_{10}H_{12}O_2$ and deduce which isomer matches the given spectra.
3. Draw out the structure of the unknown compound.

Solution

1. The IR spectrum shows three absorption bands in the functional group region (see Table 12.2 on p. 571 and Figure 12.7 on p. 572 in *Chemistry*³). There is no absorption band due to an O–H bond.

3100-2800 cm^{-1} C–H (stretch).

~1740 cm^{-1} broad C=O (stretch), probably an ester.

~1500 cm^{-1} 3 bands for aromatic ring.

2. From the 1H NMR spectrum, the following CH, CH_2 and CH_3 groups can be assigned to the four signals (Figure 12.13 and Table 12.3). 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 12.13)

4.3 ppm 2H possibly C(=O)O– CH_2

2.9 ppm 2H possibly Ar–C(=O)– CH_2 –C

2.0 ppm 3H O–C(=O)–CH₃

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

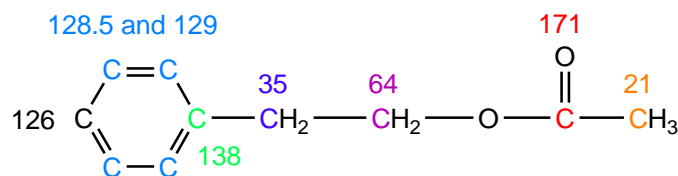
7.4-7.1 ppm complex substituted benzene

4.3 ppm triplet –CH₂–CH₂–

3.8 ppm triplet –CH₂–CH₂–

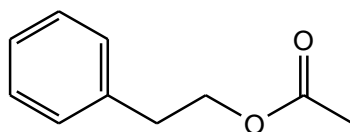
2.0 ppm singlet –CO–CH₃

The position of all eight signals in the ¹³C 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).



2-phenylethyl ethanoate

3. The unknown compound is 2-phenylethyl ethanoate.



2-phenylethyl ethanoate

Answers to boxes

Box 12.2 Using tandem mass spectrometry in newborn screening (on p. 568 in *Chemistry*³)

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.

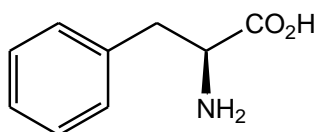
Strategy

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.

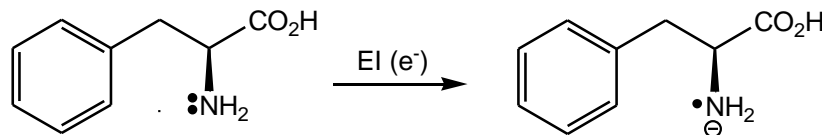
Solution

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



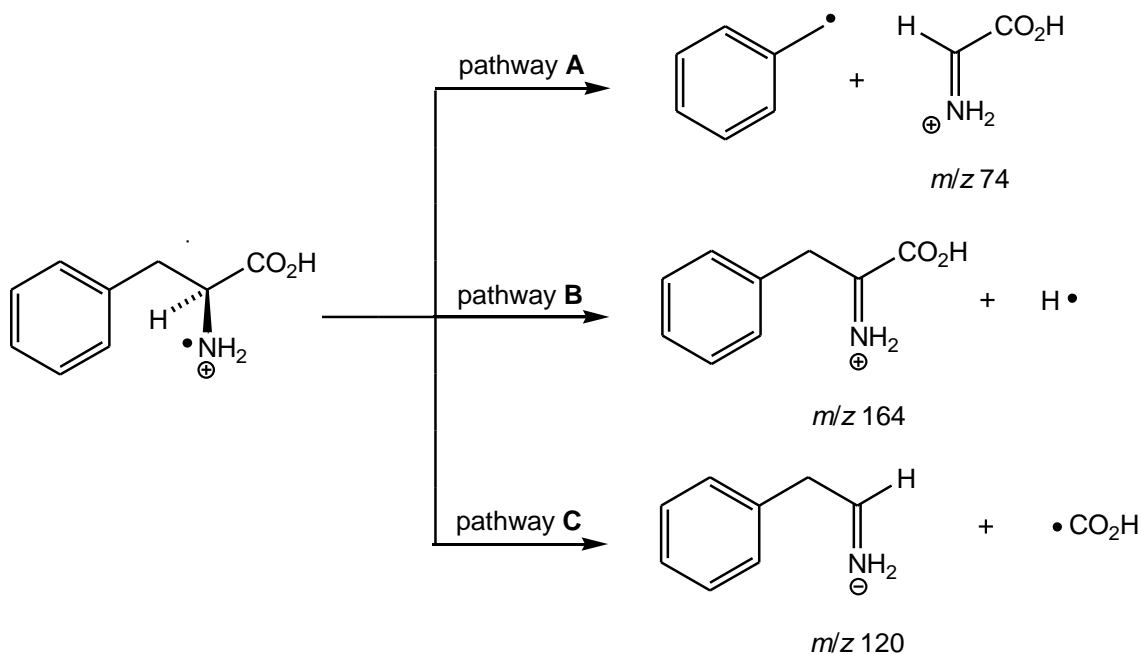
(*S*)-phenylalanine

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.

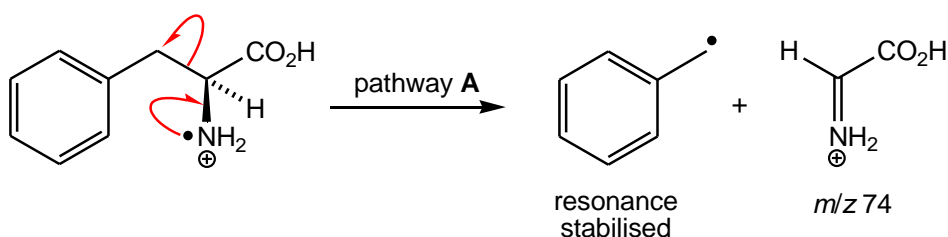


(*S*)-phenylalanine

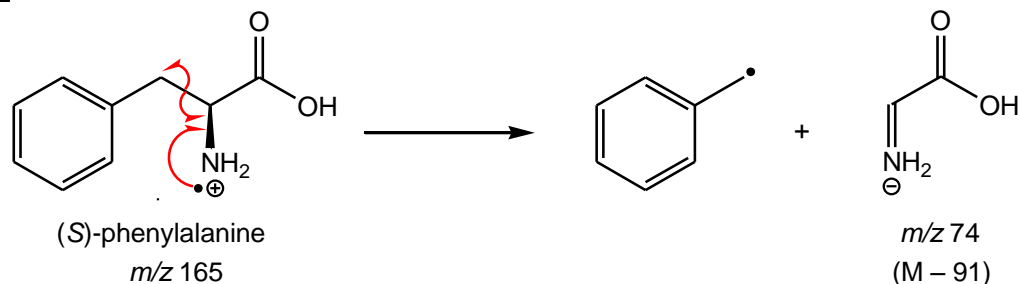
3. Fragmentation can occur by three pathways. Pathways **A**, **B** and **C** give the corresponding iminium ions with m/z values of 74, 164 and 120, respectively. From the experimental data given, pathway **A** is preferred as this leads to an iminium ion with a m/z value of 74.



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 (PhCH₂•) 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 12.4 Magnetic field strength and resolution (on p. 580 in *Chemistry*³)

For a 900 MHz NMR spectrometer, what is the radiofrequency separation between signals at chemical shifts, δ 3 ppm and δ 4 ppm?

Strategy

This can be easily calculated by looking at the chemical shift units; these are in ppm (**part per million**). The spectrometer has a radiofrequency of 900 MHz (900,000,000 Hz).

Solution

These two signals are separated by 1 ppm (4 ppm – 3 ppm). The separation of these signals will be 1 ppm \times 900 MHz [or = (1/1,000,000) \times 900,000,000] = 900 Hz. (Please note, how the millionth and million cancel each other out.)

Answer

1 ppm = 900 Hz

Box 12.5 Drawing a ¹H NMR spectrum (on p. 594 in *Chemistry*³)

Draw the ¹H NMR spectrum for 3-methylbutan-2-one.

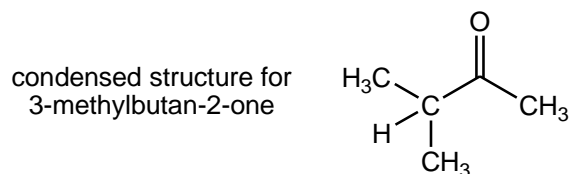
Strategy

1. Draw out a condensed structure of 3-methylbutan-2-one.

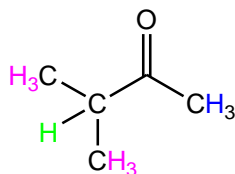
- From this structure, you will need to decide on the number and types of hydrogen atoms that are in different electronic environments.
- Give the number of hydrogen atoms in each electronic environment.
- Use Table 12.3 (p. 582 in *Chemistry*³) and Figure 12.3 (p. 560 in *Chemistry*³) to estimate the chemical shifts for each CH₃ and CH groups.
- From the number of hydrogen atoms on the adjacent carbon, use the $N + 1$ rule (see p. 588 and Box 10.8 on p.499 in *Chemistry*³) to calculate the splitting pattern for each resonance signal.

Solution

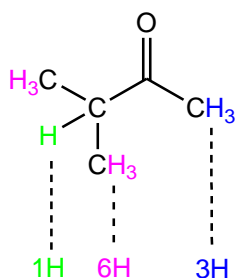
- The condensed structure of 3-methylbutan-2-one is shown below.



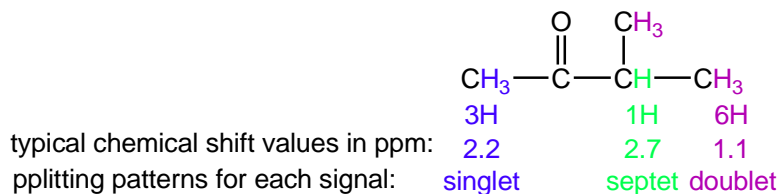
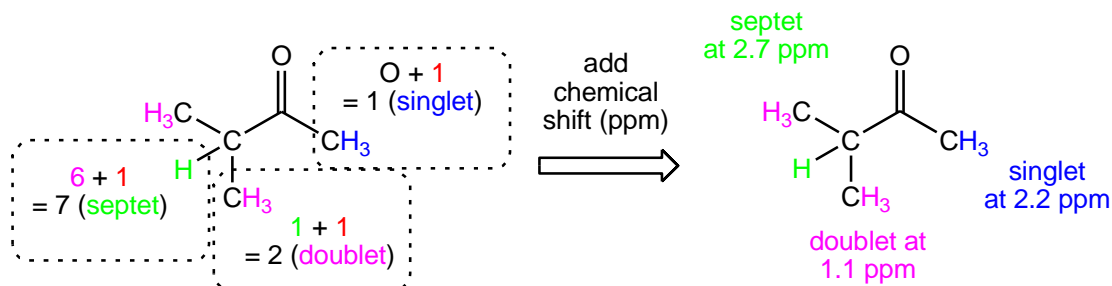
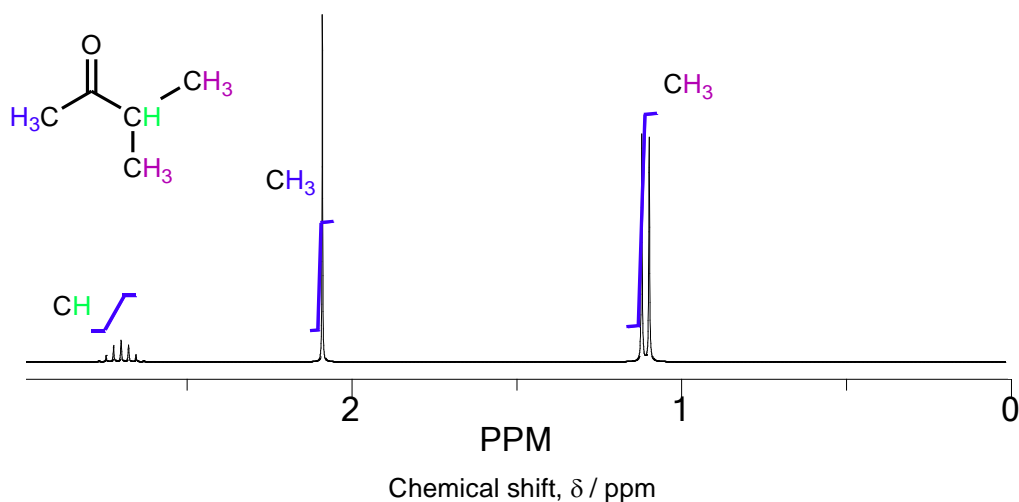
- There are three different types of hydrogen environments. **Methyl** groups (labelled **purple**) are magnetically equivalent.



- 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 12.3 and Figure 12.13) and the associated splitting pattern for each signal is shown below.

Splitting ($N + 1$) pattern for 3-methylbutan-2-one5. The ^1H NMR spectrum of 3-methylbutan-2-one is shown below.**Box 12.6 Determining degrees of unsaturation (on p. 600 in *Chemistry*³)**

Calculate the number of degrees of unsaturation for molecules with the following molecular formulae: (a) $\text{C}_8\text{H}_9\text{NO}_2$; (b) $\text{C}_3\text{H}_3\text{ClO}$.

Strategy

The degree of unsaturation gives valuable information about its structural arrangement. It gives a *molar equivalence* of unsaturation above its fully saturated acyclic form.

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Each degree of unsaturation confirms the presence of either a pi-bond or a ring structure.

For example:

1 degree of unsaturation confirms either a double bond or a ring structure.

2 degrees of unsaturation confirms a triple bond, two double bonds, two rings, or a double bond and ring.

4 degrees of unsaturation generally confirms a phenyl ring (three double bonds and a ring).

The degree of unsaturation for a molecule, containing C, H, N, O and X atoms can be calculated from the following formula:

Number of degrees of unsaturation = $C - (\text{number of hydrogens}/2) - (\text{number of alogens}/2) + (\text{number of nitrogen atoms}/2) + 1$.

Solution

(a) $C_8H_9NO_2$

$$\text{Degrees of unsaturation} = 8 - \frac{9}{2} - \frac{0}{2} + \frac{1}{2} + 1$$

$$\text{Degrees of unsaturation} = 5$$

(b) C_3H_3ClO .

$$\text{Degrees of unsaturation} = 3 - \frac{3}{2} - \frac{1}{2} + \frac{0}{2} + 1$$

$$\text{Degrees of unsaturation} = 2$$

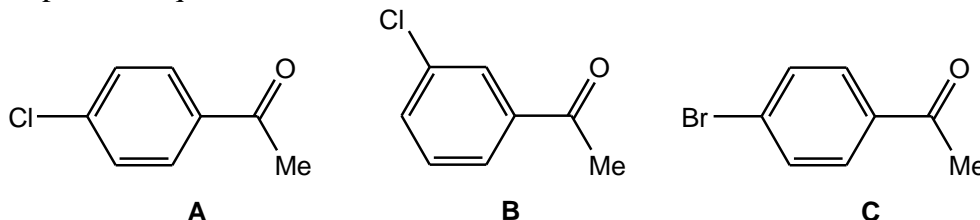
Answers

(a) 5 degrees of unsaturation.

(b) 2 degrees of unsaturation.

Answers to end of chapter questions (on p. 606 in *Chemistry*³)

1. The following questions 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}Br and ^{81}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}Br (50.7%) and ^{81}Br (49.3%) are about the same.

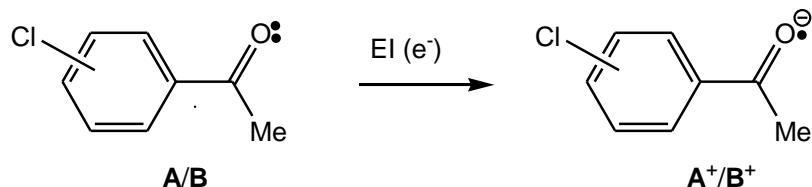
- (c) In the mass spectra of both **A** and **B**, explain the appearance of fragment cations at m/z 141 and 139 in the ratio 3:1.

Strategy

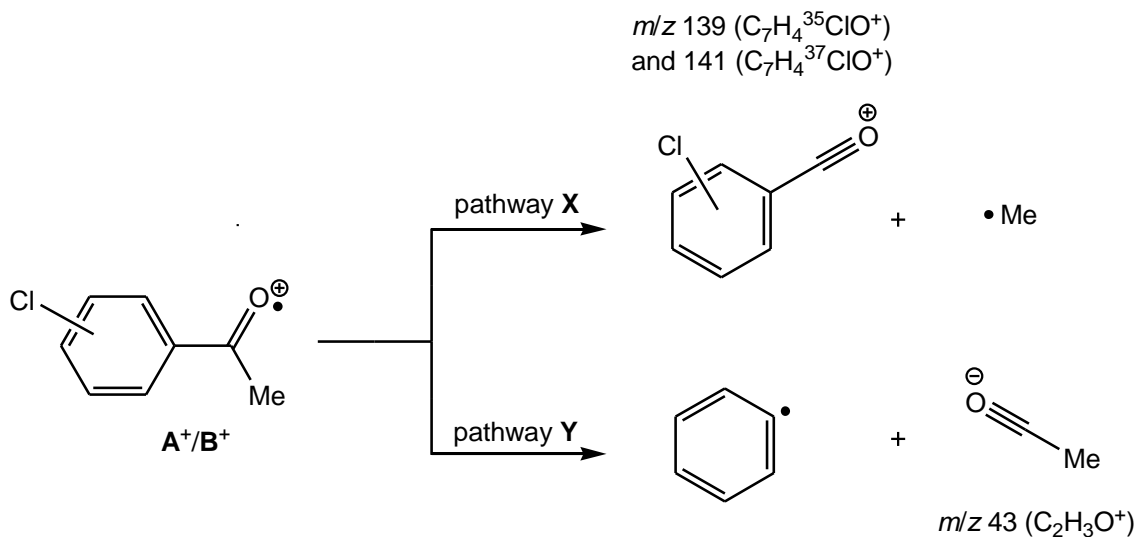
1. Determine the site of electron ionisation (EI).
2. Try and fragment the molecular ion. The fragment cations must contain a chlorine atom as they have the same abundance as the characteristic isotopic signature of chlorine (^{35}Cl : ^{37}Cl in a ratio of 3:1).

Solution

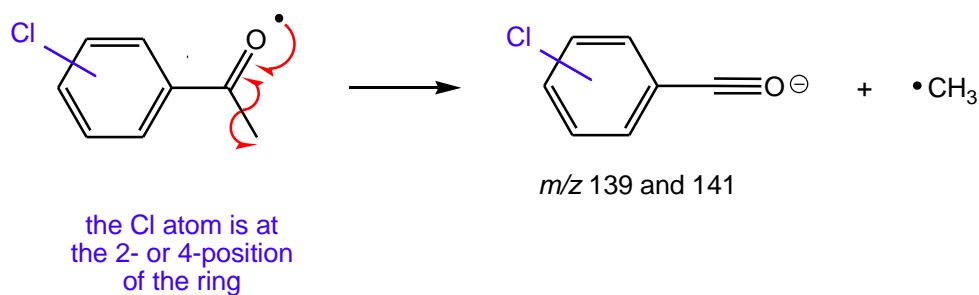
1. Electron ionisation will occur at the carbonyl oxygen atom as it contains the highest energy non-bonded pair of electrons within this molecule; this ionisation is shown below.



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**.



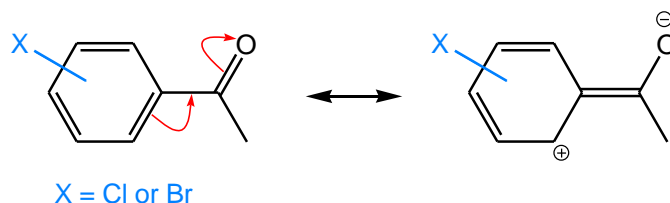
- (d) The IR spectra of **A–C** all show strong absorption peaks around 1690 cm^{-1} due to the $C=O$ stretching vibration. Suggest why these peaks are at a lower wavenumber than the $C=O$ stretching vibration for propanone (CH_3COCH_3).

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 π -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.



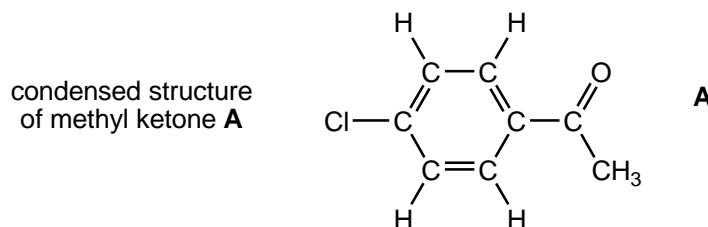
- (e) The ^1H NMR spectrum of **A** shows three signals: a doublet at 7.88 ppm; a doublet at 7.43 ppm; and a singlet at 2.58 ppm. Explain the number of resonance signals and the splitting pattern for each signal.

Strategy

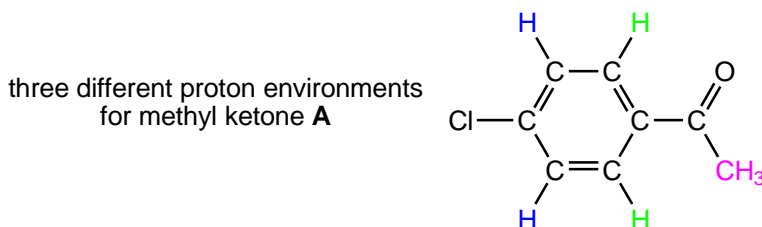
1. Draw out a condensed structure of methyl ketone **A**.
2. From this structure, you will need to decide on the number and types of hydrogen atoms that are in different electronic environments.
3. Give the number of hydrogen atoms in each electronic environment.
4. Use Table 12.3 (p. 582 in *Chemistry*³) and Figure 12.3 (p. 559 in *Chemistry*³) to estimate the chemical shifts for each CH_3 and CH groups.
5. From the number of hydrogen atoms on the adjacent carbon, use the $N + 1$ rule (see p. 588 and Box 10.8, p.499 in *Chemistry*³) to calculate the splitting pattern for each resonance signal.

Solution

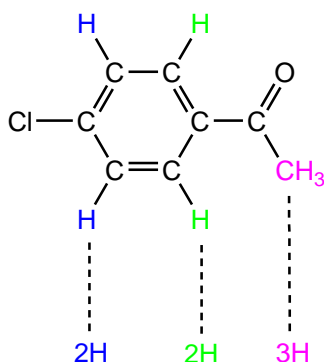
1. The condensed structure for methyl ketone **A** is shown below.



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

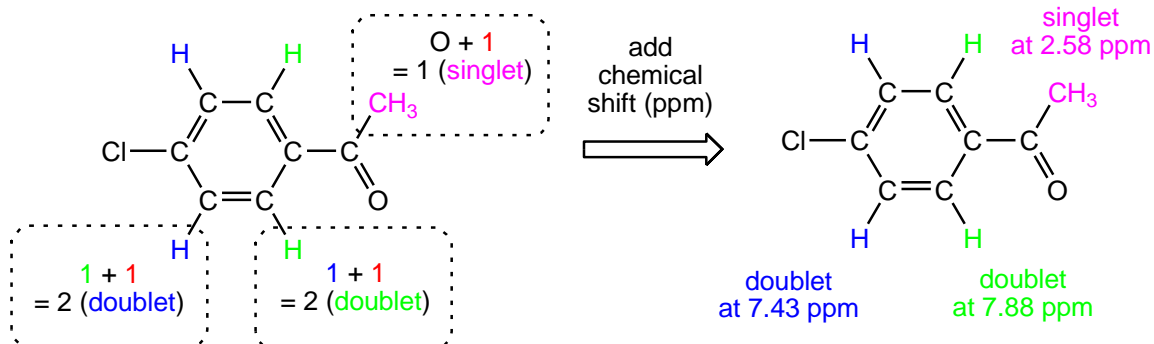


3. The number of hydrogen atoms in each environment is shown below.



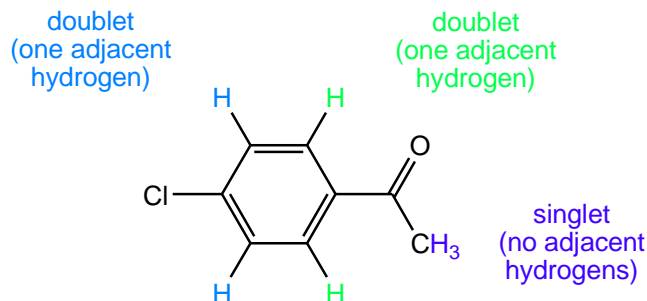
4. The number of hydrogen atoms in each environment, the estimated chemical shifts (using Table 12.3 and Figure 12.3 on p. 582 and p. 560, respectively in *Chemistry*³), and the splitting pattern for each signal is shown below.

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



Answer

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



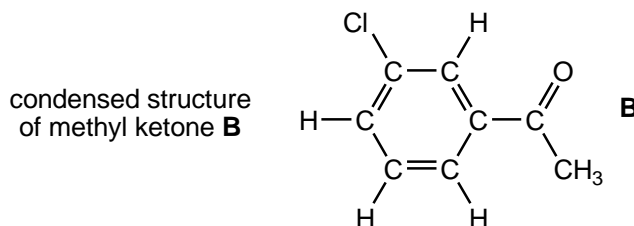
- (f) For the ^1H NMR spectrum of **B**, how many resonance signals would you expect? Briefly explain your reasoning.

Strategy

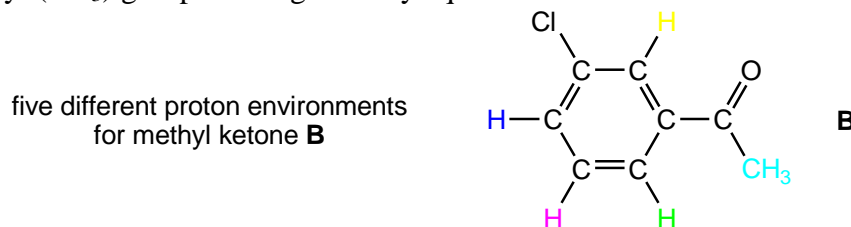
1. Draw out a condensed structure of methyl ketone **B**.
2. From your structure, you will need to decide on the number and types of hydrogen atoms that are in different electronic environments.

Solution

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



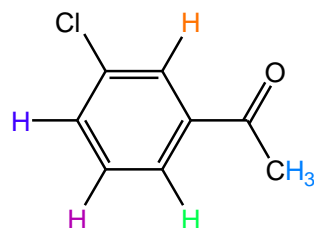
2. There are five different types of hydrogen environments. Only the hydrogen atoms on the methyl (CH_3) group are magnetically equivalent.



Answer

The ^1H 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



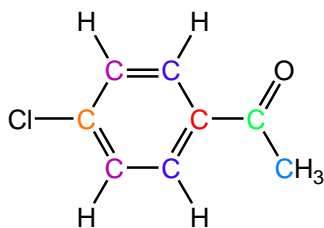
- (g) What major differences would you expect to see in the ^{13}C NMR spectra (proton decoupled) of **A** and **B**?

Strategy

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

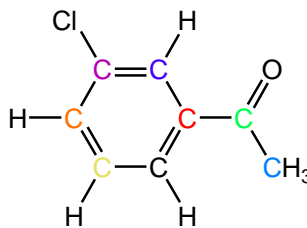
Solution/Answer

The ^{13}C NMR spectrum of **A** is expected to show six signals, whereas the ^{13}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

2. The ^1H NMR spectra [labelled (a), (b), (c)] of three isomers with the molecular formula $\text{C}_4\text{H}_9\text{Cl}$ are shown on p. 603 in *Chemistry*³. Identify the isomer that produces each spectrum, briefly giving your reasons.

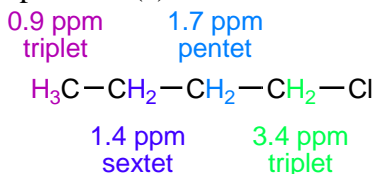
Strategy

From this molecular formula ($\text{C}_4\text{H}_9\text{Cl}$), draw out all possible structural isomers. For each structural isomer, work out its structural features, such as the number of non-equivalent hydrogen atoms and chemical shift, which are likely to be present in its ^1H NMR spectrum.

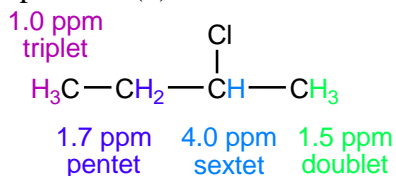
Solution

Possible compounds with the molecular formula, C₄H₉Cl, are shown below.

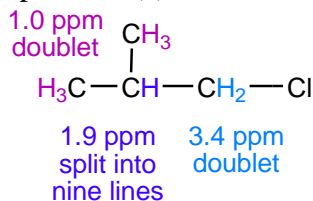
Spectrum (a) is 1-chlorobutane.



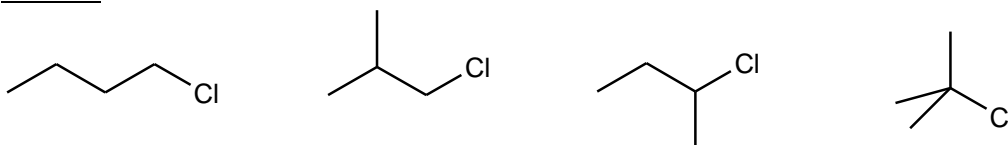
Spectrum (b) is 2-chlorobutane.



Spectrum (c) is 1-chloro-2-methylpropane.



Answer



2-chloro-2-methylpropane can be discounted because all nine hydrogens are chemically equivalent

3. A sample of ethyl propanoate, CH₃CH₂CO₂CH₂CH₃, is investigated by ¹H NMR spectroscopy and ¹³C NMR (proton decoupled) spectroscopy and mass spectrometry.

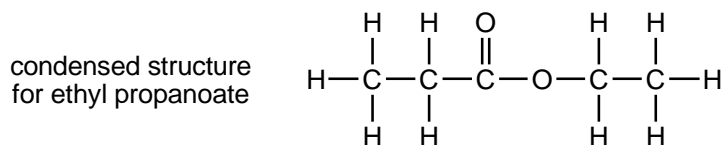
- (a) Draw the expected ¹H NMR spectrum showing spin-spin splittings and approximate chemical shifts.

Strategy

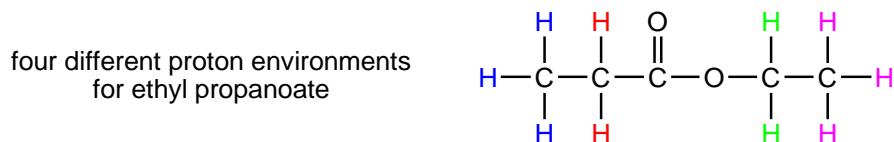
1. Draw out a condensed structure of ethyl propanoate.
2. From your structure, you will need to decide on the number and types of hydrogen atoms that are in different electronic environments.
3. Give the number of hydrogen atoms in each electronic environment.
4. Use Table 12.3 (p. 582 in *Chemistry*³) and Figure 12.3 (p. 560 in *Chemistry*³) to estimate the chemical shifts for each CH₃ and CH groups. From the number of hydrogen atoms on the adjacent carbon, use the $N + 1$ rule (see p. 588 and Box 10.8, p. 499 in *Chemistry*³) to calculate the splitting pattern for each resonance signal.
5. Draw out the ¹H NMR spectrum.

Solution

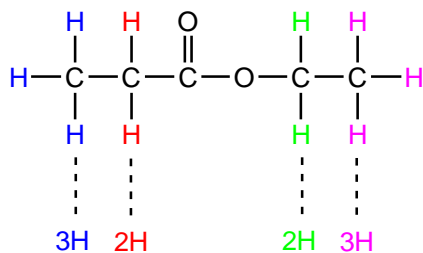
1. The condensed structure of ethyl propanoate is shown below.



2. There are four different types of hydrogen environments. The hydrogen atoms on each methyl (CH₃) group and methylene (CH₂) group are magnetically equivalent.

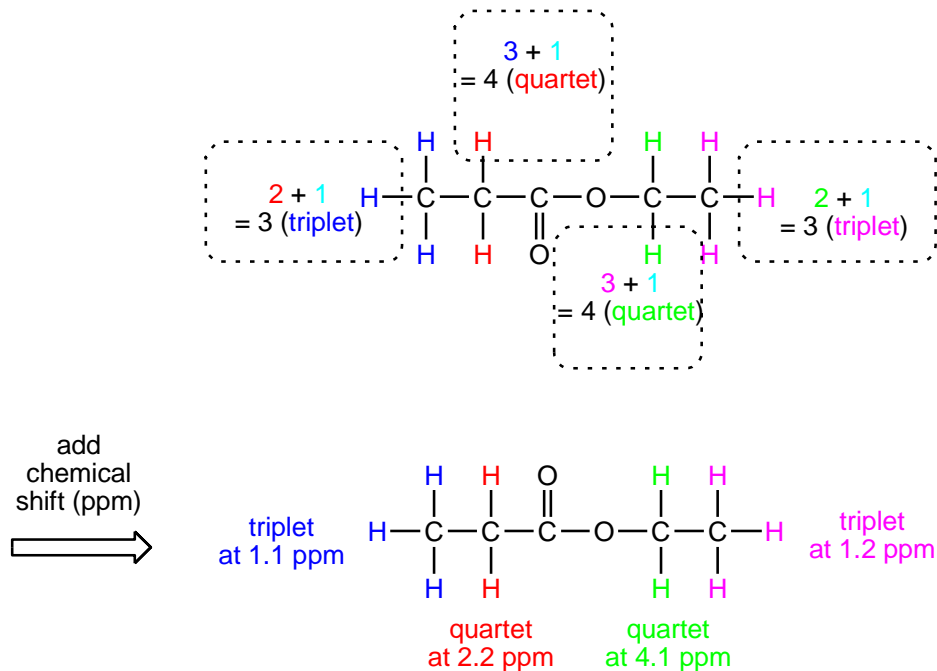


3. The number of hydrogen atoms in each environment is shown below.

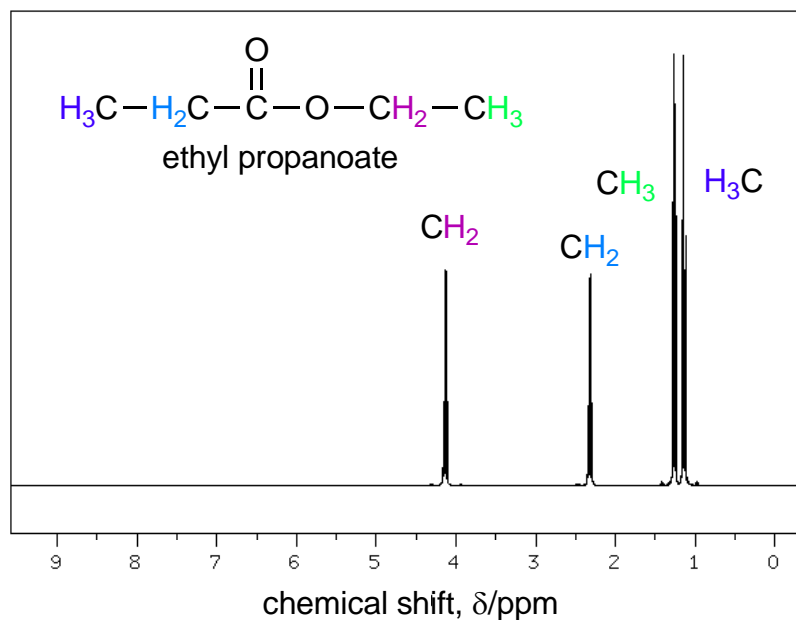


4. The number of hydrogen atoms in each environment, the estimated chemical shifts (using Table 12.3 and Figure 12.13 on p. 582 in *Chemistry*³) and the splitting pattern for each signal is shown below.

Splitting ($N + 1$) pattern for ethyl propanoate



5. The ^1H NMR spectrum of ethyl propanoate is shown below.



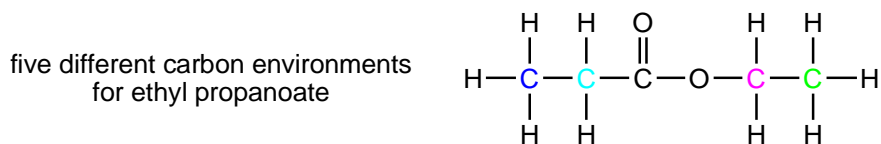
- (b) Draw the expected ^{13}C NMR spectrum (proton decoupled) with approximate chemical shifts.

Strategy

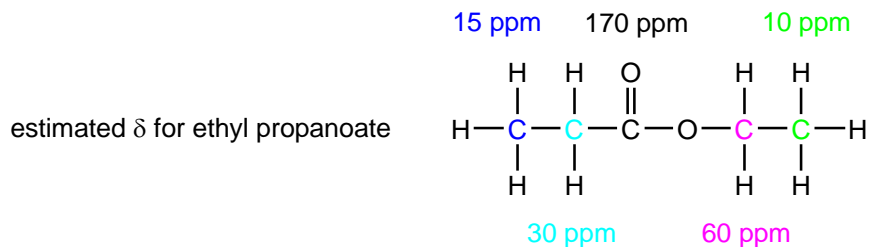
1. From its condensed structure, determine the number and types of non-magnetically equivalent carbon atoms.
2. Estimate the chemical shift for each CH_3 and CH_2 groups.
3. Draw out the ^{13}C NMR (proton decoupled) spectrum.

Solution

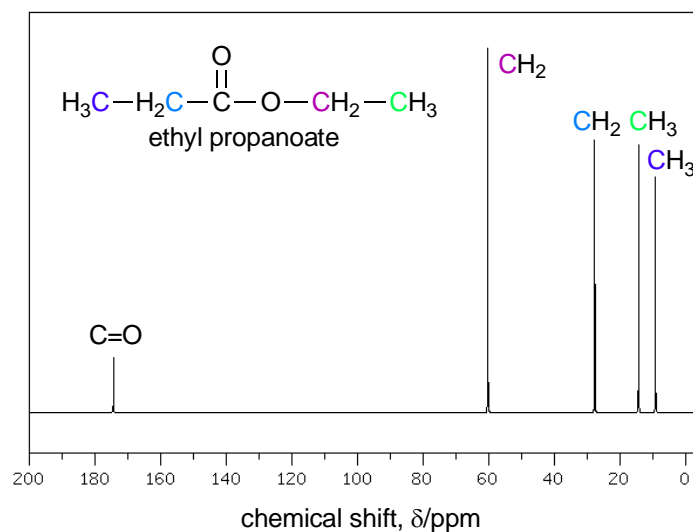
1. There are five different types of carbon environments. All these carbon atoms are non-equivalent.



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



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



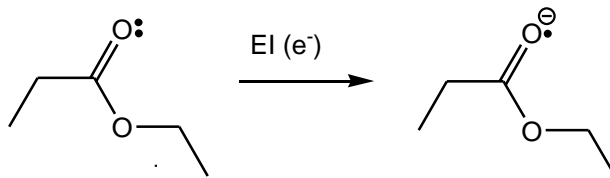
- (c) In the mass spectrum, an intense peak was observed at m/z 57. Draw the structure of the cation that corresponds to this peak and give a mechanism for its formation.

Strategy

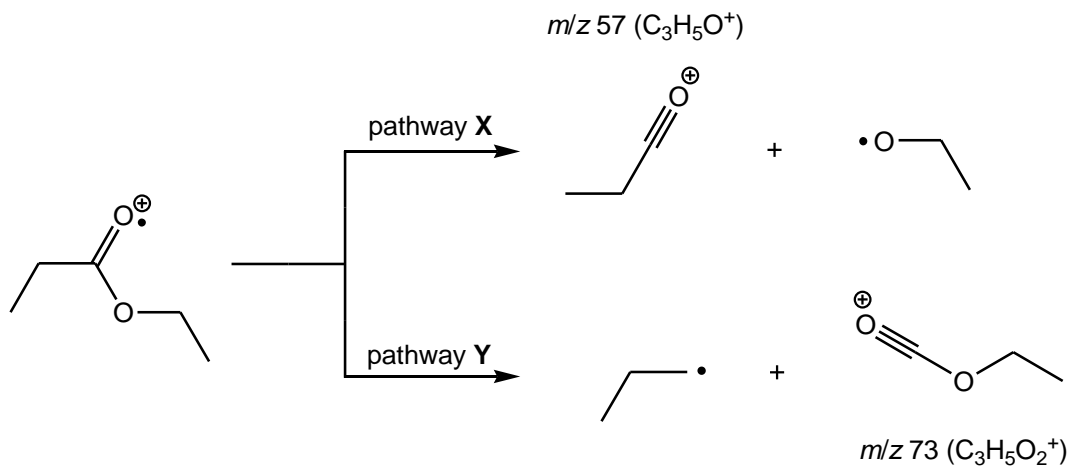
1. Determine the site of electron ionisation (EI).
2. Try and fragment the molecular ion to give a carbocation with a m/z value of 57.
3. Draw out a mechanism for this fragmentation.

Solution

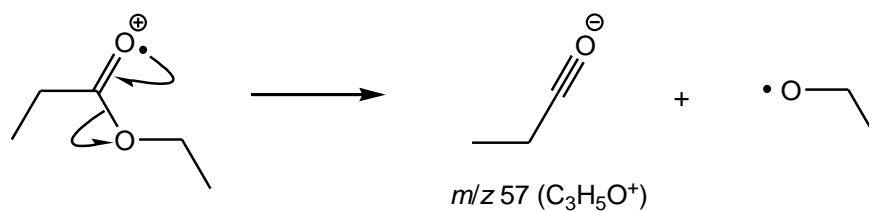
1. Electron ionisation will occur at the carbonyl oxygen atom as it contains the highest energy non-bonded pair of electrons within this molecule; this ionisation is shown below.



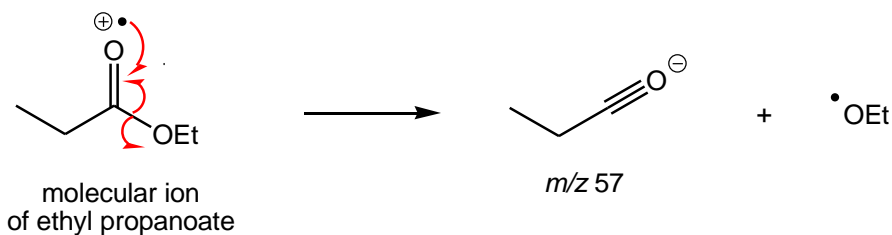
2. There are two fragmentation pathways **X** and **Y**. Pathway **X** leads to the carbocation, $\text{Et}-\text{C}\equiv\text{O}^+$, with the required m/z value of 57. In comparison, pathway **Y** leads to the related carbocation, $\text{EtO}-\text{C}\equiv\text{O}^+$, with a m/z value of 73.



3. The mechanism for this fragmentation is shown below.



Answer



4. A compound was isolated from a synthetic attractant for beetles. Using the mass, IR, and ¹H NMR spectra given on p. 604 in *Chemistry*³, propose a structure for this compound.

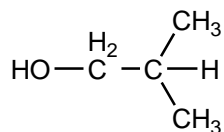
Strategy

1. Examine the mass spectrum and pick out the molecular ion.

- Examine the IR spectrum and look for characteristic peaks, such as XH, C=O and Ph groups.
- Survey the ¹H and ¹³C NMR spectra to confirm if any of these functional groups are present. Draw out some structural isomers and deduce which matches the given spectra.
- Draw out the structure of this unknown compound.

Solution

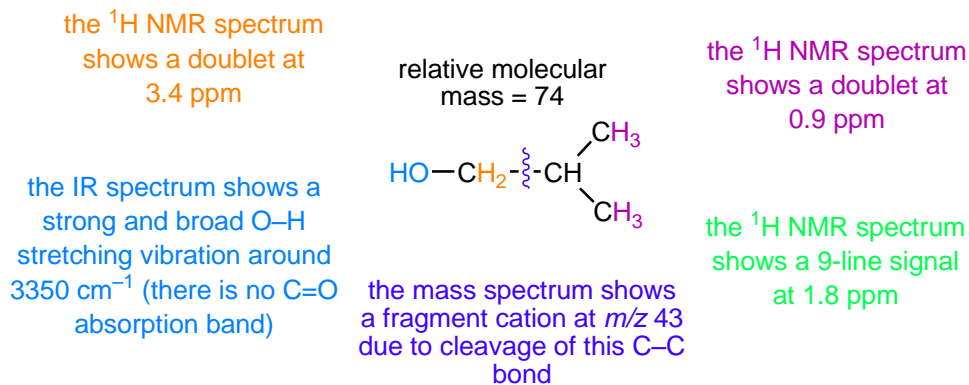
- The molecular ion has a m/z value of 74. As this mass number is even, it contains either zero or an even number of nitrogen atoms. There are no signature isotope patterns for alogens. This molecule has to be a hydrocarbon molecule, containing C and H atoms, and an O atom. There is also a more abundant cation at m/z of 43 ($C_3H_7^+$); this is probably due to an isopropyl cation $[(CH_3)_2CH^+]$.
- From this IR spectrum, there are a number of characteristic peaks.
 - There is a broad peak between $3500-3000\text{ cm}^{-1}$ possibly due to intermolecular OH bonding.
 - There are numerous C-H stretches ($3000-2900\text{ cm}^{-1}$).
 - There is no carbonyl (C=O) stretch ($1800-1600\text{ cm}^{-1}$).
- From this ¹H NMR spectrum, there is a 2 H doublet at 3.4 ppm, 1 H singlet at 2.0 ppm, 1 H nonet at 1.8 ppm and a 6 H doublet at 0.9 ppm. The characteristic nonet must come from a $-CH_2-CH-(CH_3)_2$ grouping, in order to have the required nine lines ($9 = 8 + 1$; $N + 1$ rule). This fragment also accounts for the 6 H doublet at 0.9 ppm ($-CH_2-CH-(CH_3)_2$) and the 2 H doublet 3.4 ppm ($-CH_2-CH-(CH_3)_2$). The remaining 1 H singlet at 2.0 ppm must be for an OH group. From this information, the structure appears to be 2-methyl-1-propanol ($C_4H_{10}O$); this would also account for the molecular ion at a m/z value of 74 ($C_4H_{10}O^+$).
- This structure of this unknown compound is shown below.



2-methyl-1-propanol

Answer

The unknown compound is 2-methyl-1-propanol.



5. A strong smelling compound was isolated from the anise plant. Using the mass, IR, ¹H NMR, and ¹³C NMR spectra given on p. 605 in *Chemistry*³, propose a structure for this compound.

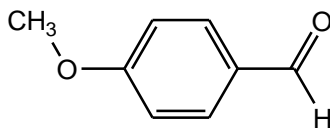
Strategy

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 ¹H and ¹³C 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 cm^{-1} ; there are no OH and NH bonds.
 - (b) There are numerous C-H stretches (3000-2900 cm^{-1}).
 - (c) There is a carbonyl (C=O) stretch at 1700 cm^{-1} ; possibly due to an aldehyde or ketone.
3. From this ^1H 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_3O - 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 ($\text{C}_8\text{H}_8\text{O}_2^+$).
- Just to confirm this assignment, from its ^{13}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 [CH_3O -].
4. This structure of this unknown compound is shown below.



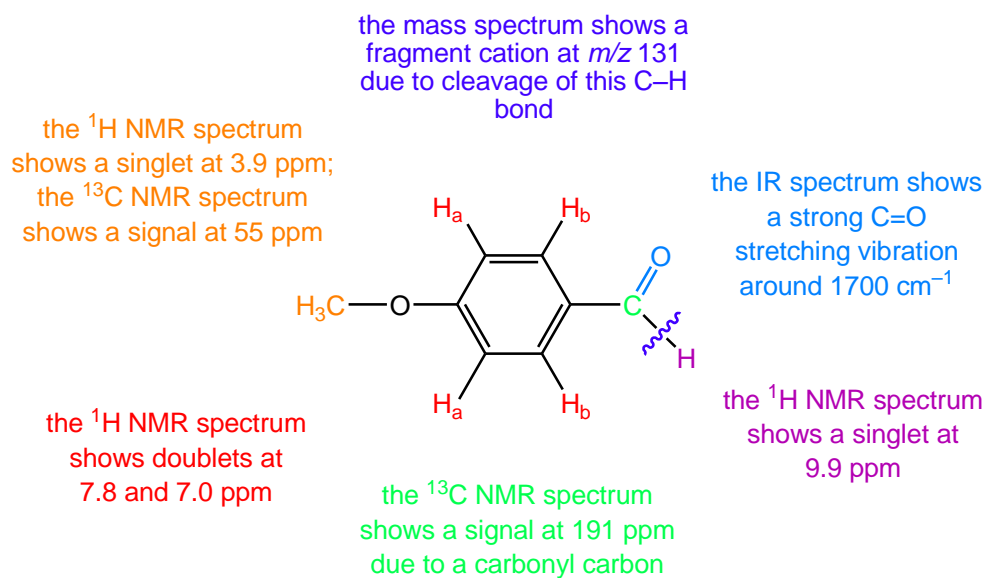
4-methoxybenzaldehyde

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 ^1H 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).