# Analytical techniques - 2023 A2 Chemistry 9701

**1.** Nov/2023/Paper_9701/41/No.7(d)

Sunset Yellow is an additive used for colouring foods.

A synthetic route for making Sunset Yellow is shown.

Molecules **E** and **G** each contain one $–SO_3^-$ group. These groups are unchanged in the formation of Sunset Yellow.

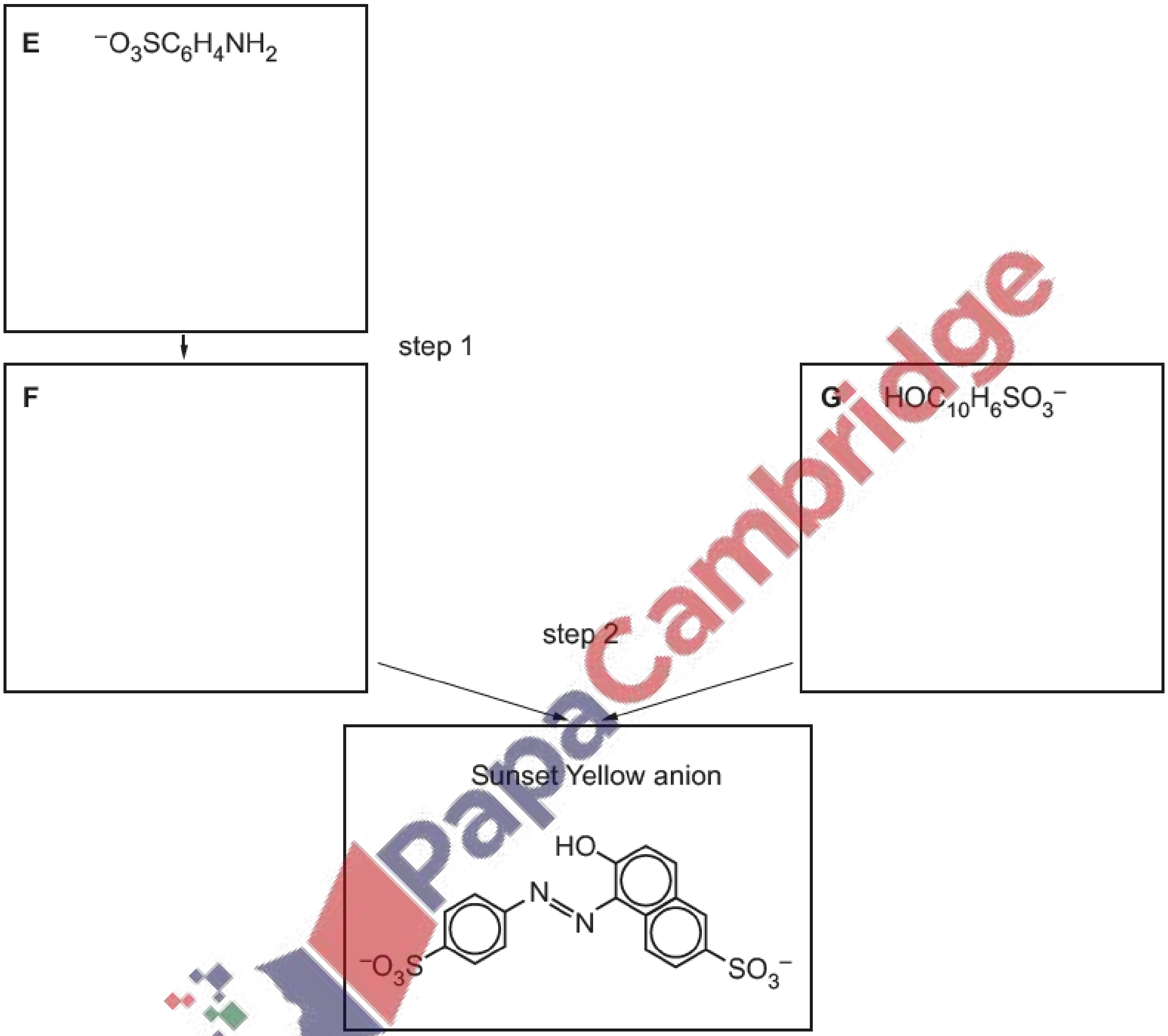


**Fig. 7.1**

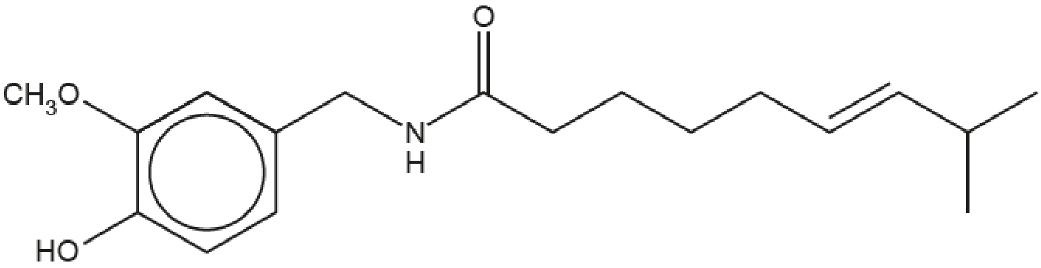
**(d)** Predict the number of peaks in the carbon-13 NMR spectrum of the Sunset Yellow anion.

.................................................................................................................................... [1]

**2.** Nov/2023/Paper_9701/41/No.8(d)

Capsaicin is found in chilli peppers.

capsaicin



You should assume the $CH_3O$ group is unreactive in the reactions involved in this question.

**(d)** When capsaicin is treated with reagent **J** under suitable conditions one of the products is methylpropanoic acid, $CH_3CH(CH_3)COOH$.

**(i)** Identify reagent **J** and any necessary conditions.

.................................................................................................................................. [1]

**(ii)** There are three different peaks in the proton ($^1H$) NMR spectrum of $CH_3CH(CH_3)COOH$ in $CDCl_3$.

**Table 8.1**

| environment of proton | example | chemical shift range δ / ppm |
|---|---|---|
| alkane | $-C\mathbf{H}_3$, $-C\mathbf{H}_2-$, $>C\mathbf{H}-$ | 0.9–1.7 |
| alkyl next to C=O | $C\mathbf{H}_3-C=O$, $-C\mathbf{H}_2-C=O$, $>C\mathbf{H}-C=O$ | 2.2–3.0 |
| alkyl next to aromatic ring | $C\mathbf{H}_3-Ar$, $-C\mathbf{H}_2-Ar$, $>C\mathbf{H}-Ar$ | 2.3–3.0 |
| alkyl next to electronegative atom | $C\mathbf{H}_3-O$, $-C\mathbf{H}_2-O$, $-C\mathbf{H}_2-Cl$ | 3.2–4.0 |
| attached to alkene | $=C\mathbf{H}R$ | 4.5–6.0 |
| attached to aromatic ring | $\mathbf{H}-Ar$ | 6.0–9.0 |
| aldehyde | $\mathbf{H}COR$ | 9.3–10.5 |
| alcohol | $RO\mathbf{H}$ | 0.5–6.0 |
| phenol | $Ar-O\mathbf{H}$ | 4.5–7.0 |
| carboxylic acid | $RCOO\mathbf{H}$ | 9.0–13.0 |

Use Table 8.1 to complete Table 8.2 and state:

- the typical proton ($^1H$) chemical shift values (δ) for the protons
- the splitting pattern (singlet, doublet, triplet, quartet or multiplet) shown by each peak
- the explanation for the splitting patterns of the $CH_3$ protons and the CH proton.

**Table 8.2**

| environment | δ / ppm | splitting pattern | explanation for splitting pattern |
|---|---|---|---|
| $CH_3$ | | | |
| CH | | | |
| COOH | | | |

[3]

**3.** Nov/2023/Paper_9701/42/No.7

Benzene can be used to make benzoic acid in the two-step process shown in Fig. 7.1.

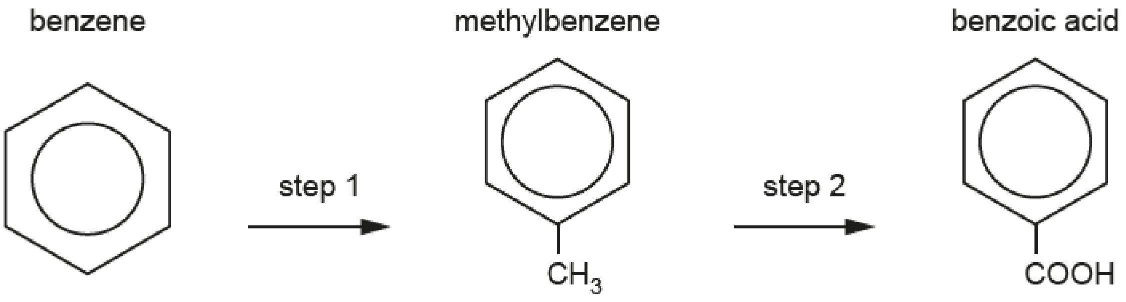


**Fig. 7.1**

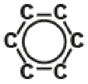
**(a)** Give the reagents and conditions for step 1 and step 2.

step 1 ..............................................................................................................................

step 2 ..............................................................................................................................
[2]

**(b)** Methylbenzene and benzoic acid each have five different peaks in the carbon ($^{13}C$) NMR spectrum.

**Table 7.1**

| hybridisation of the carbon atom | environment of carbon atom | example | chemical shift range / ppm |
|---|---|---|---|
| $sp^3$ | alkyl | $\mathbf{C}H_3$–, –$\mathbf{C}H_2$–, –**C**H<, >**C**< | 0–50 |
| $sp^3$ | next to alkene/arene | –**C**–C=C, –**C**–Ar | 25–50 |
| $sp^3$ | next to carbonyl/carboxyl | **C**–COR, **C**–$O_2$R | 30–65 |
| $sp^3$ | next to halogen | **C**–X | 30–60 |
| $sp^3$ | next to oxygen | **C**–O | 50–70 |
| $sp^2$ | alkene or arene | >**C**=**C**<,  | 110–160 |
| $sp^2$ | carboxyl | R–**C**OOH, R–**C**OOR | 160–185 |
| $sp^2$ | carbonyl | R–**C**HO, R–**C**O–R | 190–220 |
| sp | nitrile | R–**C**≡N | 100–125 |

Use Table 7.1 to complete the two sentences to suggest descriptions of these two spectra.

The carbon ($^{13}C$) NMR spectrum of methylbenzene:

- has ................ peak(s) in the chemical shift range of ..................... and
- has ................ peak(s) in the chemical shift range of ..................... .

The carbon ($^{13}C$) NMR spectrum of benzoic acid:

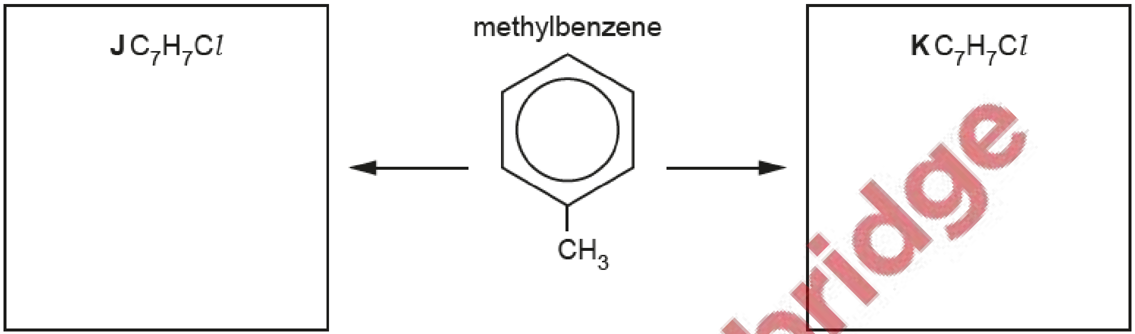
- has ................ peak(s) in the chemical shift range of .................... and
- has ................ peak(s) in the chemical shift range of .................... .

[2]

**(c)** **(i)** When treated with $Cl_2$ under suitable conditions, methylbenzene forms compound **J**.

When treated with $Cl_2$ under **different** conditions with **different** reagents, methylbenzene forms compound **K**.

Suggest and draw structures of compounds **J** and **K** in the boxes. The molecular formula of each compound is given.



State the reagents and conditions required to form each product.

to form compound **J** ..........................................................................................................

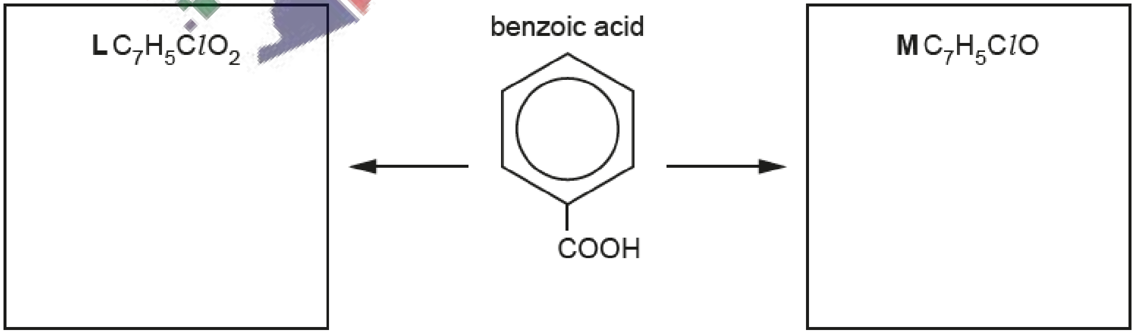
to form compound **K** ..........................................................................................................

[4]

**(ii)** When treated with a chlorine-containing reagent under suitable conditions, benzoic acid forms compound **L**.

When treated with a **different** chlorine-containing reagent under **different** conditions, benzoic acid forms compound **M**.

Suggest and draw structures of compounds **L** and **M** in the boxes. The molecular formula of each product is given.



State the reagents and conditions to form compound **M** from benzoic acid.

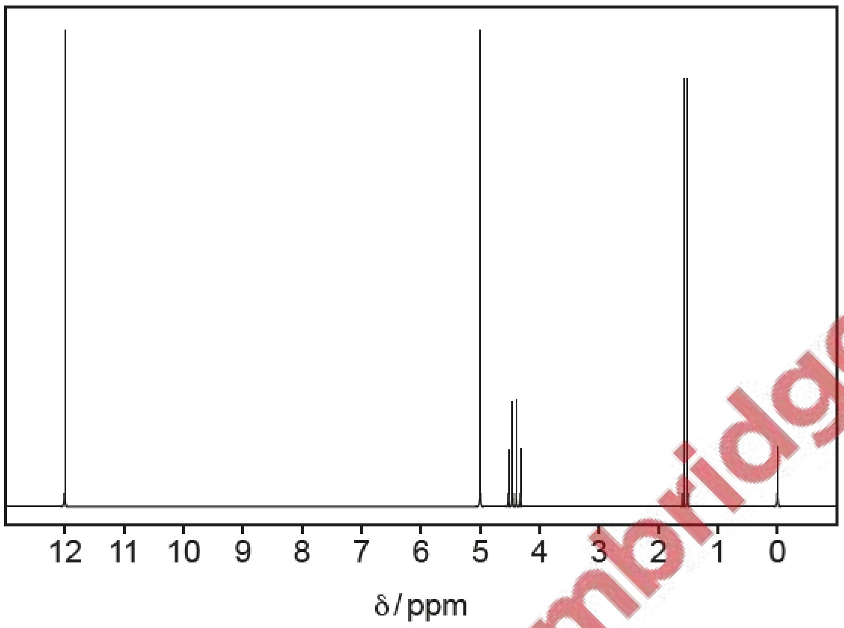
.......................................................................................................................... [3]

[Total: 11]

**4.** Nov/2023/Paper_9701/42/No.8(b, c)

Lactic acid, $CH_3CH(OH)COOH$, is the only monomer needed to form the polymer polylactic acid, PLA.

**(b)** The proton ($^1H$) NMR spectrum of $CH_3CH(OH)COOH$ in $CDCl_3$ is shown in Fig. 8.1. The proton NMR chemical shift ranges are shown in Table 8.1.



Lactic acid

**Fig. 8.1**

**Table 8.1**

| environment of proton | example | chemical shift range δ / ppm |
|---|---|---|
| alkane | $-CH_3$, $-CH_2-$, $>CH-$ | 0.9–1.7 |
| alkyl next to C=O | $CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$ | 2.2–3.0 |
| alkyl next to aromatic ring | $CH_3-Ar$, $-CH_2-Ar$, $>CH-Ar$ | 2.3–3.0 |
| alkyl next to electronegative atom | $CH_3-O$, $-CH_2-O$, $-CH_2-Cl$ | 3.2–4.0 |
| attached to alkene | =C**H**R | 4.5–6.0 |
| attached to aromatic ring | **H**–Ar | 6.0–9.0 |
| aldehyde | **H**COR | 9.3–10.5 |
| alcohol | RO**H** | 0.5–6.0 |
| phenol | Ar–O**H** | 4.5–7.0 |
| carboxylic acid | RCOO**H** | 9.0–13.0 |

(i) Use Fig. 8.1 and Table 8.1 to complete Table 8.2.

**Table 8.2**

| proton environment | chemical shift (δ) | name of splitting pattern |
|---|---|---|
| –COOH | | |
| $>\!\!\!-CH$ | | |
| –OH | | |
| $-CH_3$ | | |

[3]

(ii) Name the substance responsible for the peak at δ = 0.0.

.......................................................................................................................... [1]

(iii) Explain why $CDCl_3$ is a better solvent than $CHCl_3$ for use in proton NMR.

..........................................................................................................................

.......................................................................................................................... [1]

**(c)** An impure sample of $CH_3CH(OH)COOH$ contains pentan-3-one as the only contaminant. The mixture is analysed using gas/liquid chromatography. The pentan-3-one is found to have a longer retention time than the lactic acid.

**(i)** Explain what is meant by retention time.

..................................................................................................................................

.......................................................................................................................... [1]

**(ii)** Suggest suitable substances, or types of substances, that could be used as the mobile and stationary phases.

mobile phase ..................................................................................................................

stationary phase ............................................................................................................
[1]

**(iii)** Describe how the percentage composition of the mixture can be determined from the gas/liquid chromatogram.

..................................................................................................................................

.......................................................................................................................... [1]

**5.** June/2023/Paper_9701/41/No.4(d)

**W**

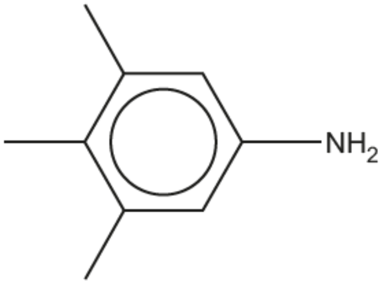


**Fig. 4.2**

Give the systematic name of **W**.

.................................................................................................................................... [1]

**(d)** Complete Table 4.1 to show the number of peaks observed in the carbon-13 NMR spectrum for **W** and **Z**.

**Table 4.1**

| compound | number of peaks observed |
|---|---|
| **W** | |
| **Z** | |

[1]

**6.** June/2023/Paper_9701/41/No.7(e)

**(e)** Alanine, $H_2NCH(CH_3)COOH$, reacts with methanol to form the ester **G** under certain conditions.

The proton ($^1H$) NMR spectrum of **G** dissolved in $D_2O$ is shown in Fig. 7.3.

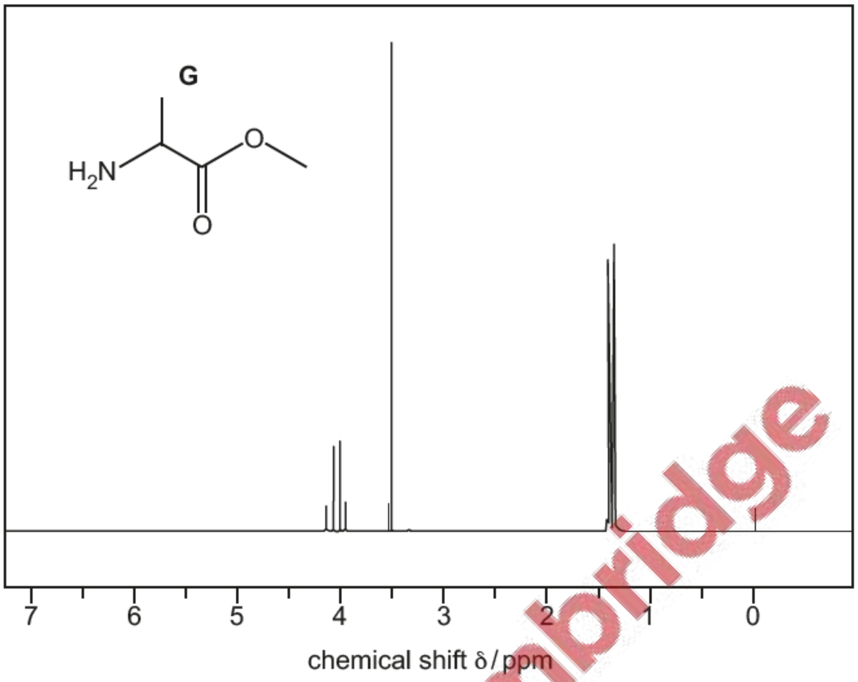


**Fig. 7.3**

**Table 7.1**

| environment of proton | example | chemical shift range, δ / ppm |
|---|---|---|
| alkane | $-CH_3$, $-CH_2-$, $>CH-$ | 0.9–1.7 |
| alkyl next to C=O | $CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$ | 2.2–3.0 |
| alkyl next to aromatic ring | $CH_3-Ar$, $-CH_2-Ar$, $>CH-Ar$ | 2.3–3.0 |
| alkyl next to electronegative atom | $CH_3-O$, $-CH_2-O$, $-CH_2-Cl$ | 3.2–4.0 |
| attached to alkene | =C**H**R | 4.5–6.0 |
| attached to aromatic ring | **H**–Ar | 6.0–9.0 |
| aldehyde | **H**COR | 9.3–10.5 |
| alcohol | RO**H** | 0.5–6.0 |
| phenol | Ar–O**H** | 4.5–7.0 |
| carboxylic acid | RCOO**H** | 9.0–13.0 |
| alkyl amine | R–N**H**– | 1.0–5.0 |
| aryl amine | Ar–N**H**$_2$ | 3.0–6.0 |
| amide | RCON**H**R | 5.0–12.0 |

**(i)** Complete Table 7.2 for the proton ($^1H$) NMR spectrum of **G**.

**Table 7.2**

| chemical shift (δ) | splitting pattern | number of $^1H$ atoms responsible for the peak | number of protons on adjacent carbon atoms |
|---|---|---|---|
| 1.4 | | | |
| 3.5 | | | |
| 4.0 | | | |

[3]

**(ii)** The proton ($^1H$) NMR spectrum of **G** dissolved in $CDCl_3$ is obtained.

Describe the difference observed between this spectrum and the proton NMR spectrum in $D_2O$ shown in Fig 7.3.

Explain your answer.

..................................................................................................................................................

..................................................................................................................................................

.................................................................................................................................................. [1]

**7.** June/2023/Paper_9701/42/No.8(c)

**(c)** The proton ($^1$H) NMR spectrum of compound **T**, $C_5H_9O_2Cl$, in $CDCl_3$ is shown in Fig. 8.2.

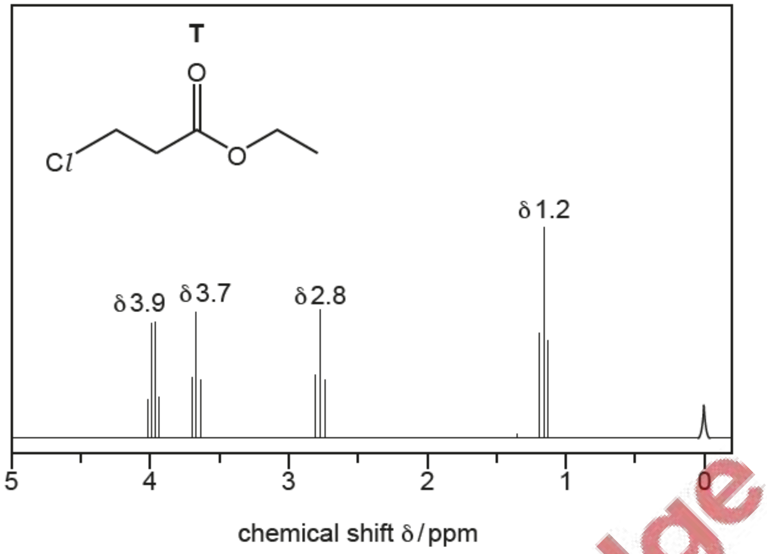


**Fig. 8.2**

**Table 8.1**

| environment of proton | example | chemical shift range δ / ppm |
|---|---|---|
| alkane | $-CH_3$, $-CH_2-$, $>CH-$ | 0.9–1.7 |
| alkyl next to C=O | $CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$ | 2.2–3.0 |
| alkyl next to aromatic ring | $CH_3-Ar$, $-CH_2-Ar$, $>CH-Ar$ | 2.3–3.0 |
| alkyl next to electronegative atom | $CH_3-O$, $-CH_2-O$, $-CH_2-Cl$ | 3.2–4.0 |
| attached to alkene | =CHR | 4.5–6.0 |
| attached to aromatic ring | H–Ar | 6.0–9.0 |
| aldehyde | HCOR | 9.3–10.5 |
| alcohol | ROH | 0.5–6.0 |
| phenol | Ar–OH | 4.5–7.0 |
| carboxylic acid | RCOOH | 9.0–13.0 |
| alkyl amine | R–NH– | 1.0–5.0 |
| aryl amine | $Ar-NH_2$ | 3.0–6.0 |
| amide | RCONHR | 5.0–12.0 |

**(i)** Suggest why $CDCl_3$ is used as a solvent instead of $CHCl_3$ for the proton ($^1H$) NMR spectrum.

..........................................................................................................................................

.................................................................................................................................... [1]

**(ii)** Complete Table 8.2 for the proton ($^1H$) NMR spectrum of **T**.

**Table 8.2**

| chemical shift δ / ppm | environment of proton | splitting pattern | number of $^1H$ atoms responsible for the peak |
|---|---|---|---|
| 1.2 | | | |
| 2.8 | | | |
| 3.7 | | | |
| 3.9 | | | |

[4]

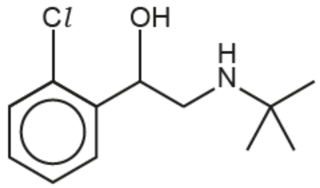
**(iii)** Explain the splitting pattern of the peak at δ 3.9 ppm.

..........................................................................................................................................

.................................................................................................................................... [1]

**8.** March/2023/Paper_9701/42/No.5(f)

tulobuterol



**(f)** **(i)** Predict the number of peaks that would be seen in the carbon-13 NMR spectrum of tulobuterol.

.............................................................................................................................................. [1]

**(ii)** The proton ($^1H$) NMR spectrum of tulobuterol dissolved in $D_2O$ shows peaks in four different types of proton environment.

The peak for the —$CH_2N$— environment is a doublet in the chemical shift range $\delta = 2.0–3.0$ ppm.

Give details for each of the other **three** peaks in the proton NMR spectrum of tulobuterol, to include:

- chemical shift
- environment of the proton
- splitting pattern
- number of $^1H$ atoms responsible.

Table 5.1 gives information about typical chemical shift values.

..............................................................................................................................................

..............................................................................................................................................

..............................................................................................................................................

..............................................................................................................................................

..............................................................................................................................................

..............................................................................................................................................

.............................................................................................................................................. [3]

## Table 5.1

| environment of proton | example | chemical shift range δ / ppm |
|---|---|---|
| alkane | $-\mathbf{CH}_3$, $-\mathbf{CH}_2-$, $>\mathbf{CH}-$ | 0.9–1.7 |
| alkyl next to C=O | $\mathbf{CH}_3-C{=}O$, $-\mathbf{CH}_2-C{=}O$,<br>$>\mathbf{CH}-C{=}O$ | 2.2–3.0 |
| alkyl next to aromatic ring | $\mathbf{CH}_3-Ar$, $-\mathbf{CH}_2-Ar$,<br>$>\mathbf{CH}-Ar$ | 2.3–3.0 |
| alkyl next to electronegative atom | $\mathbf{CH}_3-O$, $-\mathbf{CH}_2-O$,<br>$-\mathbf{CH}_2-Cl$ | 3.2–4.0 |
| attached to alkene | $=\mathbf{CH}R$ | 4.5–6.0 |
| attached to aromatic ring | $\mathbf{H}-Ar$ | 6.0–9.0 |
| aldehyde | $\mathbf{H}COR$ | 9.3–10.5 |
| alcohol | $RO\mathbf{H}$ | 0.5–6.0 |
| phenol | $Ar-O\mathbf{H}$ | 4.5–7.0 |
| carboxylic acid | $RCOO\mathbf{H}$ | 9.0–13.0 |
| alkyl amine | $R-N\mathbf{H}-$ | 1.0–5.0 |
| aryl amine | $Ar-N\mathbf{H}_2$ | 3.0–6.0 |
| amide | $RCON\mathbf{H}R$ | 5.0–12.0 |

**9.** March/2023/Paper_9701/42/No.6(a _ c)

A student uses thin-layer chromatography (TLC) to analyse a mixture containing different metal cations. The student repeats the experiment using different solvents.

Fig. 6.1 shows the chromatogram obtained by the student using water as a solvent.

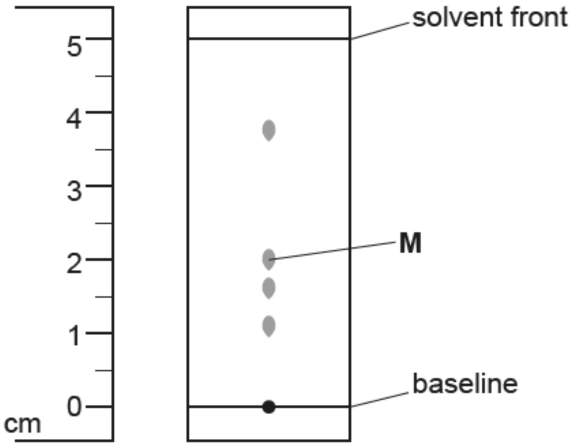


**Fig. 6.1**

**(a)** **(i)** Suggest a compound that could be used as the stationary phase in this experiment.

........................................................................................................................ [1]

**(ii)** Table 6.1 shows the $R_f$ values for different metal cations when separated by TLC using water as a solvent.

**Table 6.1**

| cation | $R_f$ value (water) |
|---|---|
| $Cd^{2+}(aq)$ | 0.40 |
| $Co^{2+}(aq)$ | 0.77 |
| $Cu^{2+}(aq)$ | 0.32 |
| $Fe^{3+}(aq)$ | 0.12 |
| $Hg^{2+}(aq)$ | 0.23 |
| $Ni^{2+}(aq)$ | 0.75 |

Suggest the identity of the cation that causes the spot at **M** in Fig. 6.1.

Explain your answer.

........................................................................................................................

........................................................................................................................ [1]

**(b)** The student repeats the experiment using butan-1-ol as a solvent.

The metal cations do **not** travel as far up the TLC plate in this experiment.

Suggest why the metal cations do not move as far up the TLC plate with butan-1-ol as a solvent.

..........................................................................................................................................

.................................................................................................................................... [1]

**(c)** The student sprays the TLC plate in Fig. 6.1 with KSCN(aq).

The colour of some of the spots changes, as some of the metal cations undergo a ligand exchange reaction.

Identify the ligands involved in the ligand exchange reaction.

........................................................ exchanges with ........................................................ [1]