## Organic problem solving: Deducing structures of organic molecules

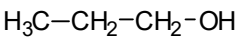
Organic problem solving is one of the best bits of A-level Chemistry but it can be a challenge. It does require you to bring lots of knowledge and understanding from across the syllabus and also involves a fair bit of trial and error. This set of notes and questions attempts to cover some of the important aspects. Often you have several pieces of information that you need to fit together. We shall first look at some of the different pieces of information that you might need to use.

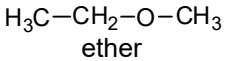
### Looking at the molecular formula

The molecular formula is often the starting point to a question and you should use it to start your questioning about the identity of a compound.
Look at:

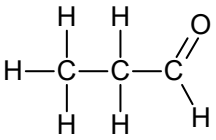
- How many atoms of oxygen, nitrogen or chlorine there are? This will point you towards possible functional groups.
- What is the number of hydrogen atoms relative to carbon atoms? This will point you towards whether the compound is saturated, unsaturated, cyclic or aromatic.

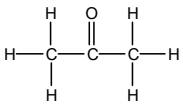
e.g. $C_3H_{\mathbf{8}}\mathbf{O}$ ($C_nH_{2n+2}O$) is saturated and cannot contain any double bonds or be cyclic. It is most likely to be an alcohol (possibly the functional group isomer ether)


alcohol

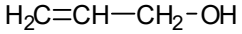

ether

e.g. $C_3H_{\mathbf{6}}\mathbf{O}$ ($C_nH_{2n}O$) - is unsaturated and either contains a double bond (C=O or C=C) or it could be cyclic.
The functional group isomers could be an aldehyde, a ketone, a cyclic alcohol, or a combination of a C=C bond with an O-H bond.

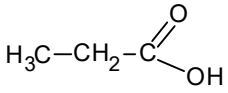

aldehyde

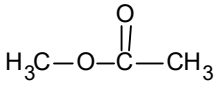

ketone

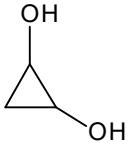

cyclic alcohol

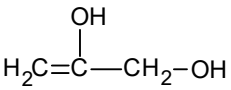


e.g. $C_3H_{\mathbf{6}}\mathbf{O_2}$ ($C_nH_{2n}O_2$) - is unsaturated and either contains a double bond (C=O or C=C) or it could be cyclic.
The two oxygen atoms suggest a carboxylic acid or an ester but it could be various other things.

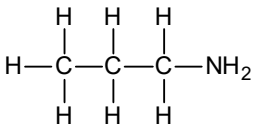

carboxylic acid

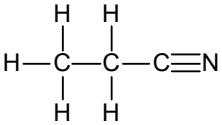

ester



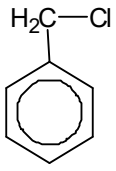


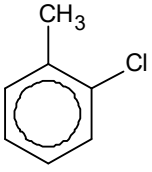
e.g. compare $C_3H_{\mathbf{9}}\mathbf{N}$ and $C_3H_{\mathbf{5}}\mathbf{N}$ – $C_3H_{\mathbf{9}}\mathbf{N}$ is saturated and suggests an amine functional group.
$C_3H_{\mathbf{5}}\mathbf{N}$ is unsaturated and suggests the nitrile functional group





e.g. $C_7H_{\mathbf{7}}Cl$ – if the formula has ≥ six carbons and a low carbon to hydrogen ratio then it is likely to contain a benzene ring.





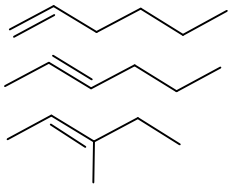
## Using functional group tests

The following tests are often used to identify the presence of a particular functional group

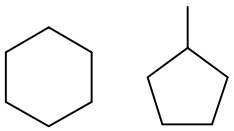
| Functional group | Reagent | Result |
|---|---|---|
| Alkene | Bromine water | Orange colour decolourises |
| Aldehyde | Fehling's solution | Blue solution to red precipitate |
| Aldehyde | Tollens' reagent | Silver mirror formed |
| Carboxylic acid | Sodium carbonate | Effervescence of $CO_2$ evolved |
| 1° 2° alcohol and aldehyde | potassium dichromate and sulfuric acid | Orange to green colour change |
| Chloroalkane | Warm with silver nitrate | Slow formation of white precipitate of AgCl |
| Acyl chloride | Silver nitrate | Vigorous reaction- steamy fumes of HCl- rapid white precipitate of AgCl |

**Example 1**. Compounds **A and B** have the molecular formula $C_6H_{12}$.
Compound **A** changes bromine water from orange to colourless.
Compound **B** does not react with bromine water.
Draw possible structures for compounds **A** and **B.**

**A** must be an alkene. (There are many possible structures).



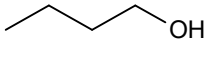
**B** must be an cycloalkane. (There are several possible structures).



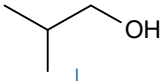
**Example 2**. Compounds **C and D** are alcohols with the molecular formula $C_4H_9O$.
Compound **C** reacts with acidified potassium dichromate to form compound **E** with a molecular formula $C_4H_8O_2$.
Compound **D** does not react with acidified potassium dichromate.
Draw possible structures for **C, D** and **E.**

Primary and secondary alcohols react with acidified potassium dichromate. But only primary would form a compound **E** with two oxygens (carboxylic acid). **C** must be a primary alcohol

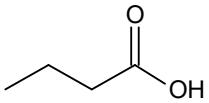
**C**




or




**E**

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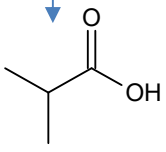
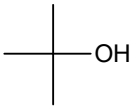
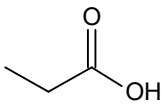



Tertiary alcohols do not react with acidified potassium dichromate. **D** must be a tertiary alcohol

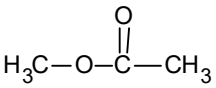


**Example 3** Compounds **F** and **G** have the molecular formula $C_3H_6O_2$
**F** reacts with aqueous sodium carbonate to produce bubbles of carbon dioxide gas and **G** does not.
Draw possible structures for compounds **F** and **G.**

**F** must be a carboxylic acid.




**G** is not a carboxylic acid. It could be several things but most commonly will be an ester. Other information could be given to narrow down the options.

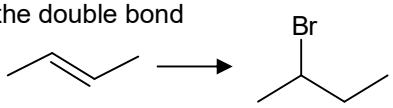



### Other reactions that can give information about the structure

Other organic reactions can be used to help give more information about the structure.
For example: alkene addition reactions, alcohol dehydration reactions and halogenoalkane elimination reactions.

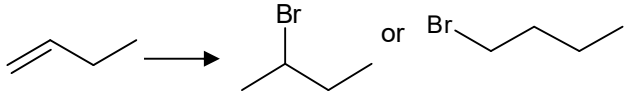
**Example 4**. Compounds **H and I** have the molecular formula $C_4H_8$.
Compound **H** reacts with HBr to form only one compound
Compound **I** reacts with HBr to form two structural isomers.
Draw possible structures for compounds **H** and **I.**

**H** must be a symmetrical alkene around the double bond




But-2-ene can only form 2-bromobutane

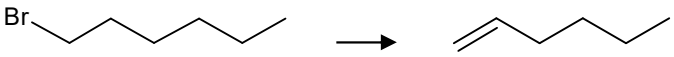
**I** must be a unsymmetrical alkene around the double bond



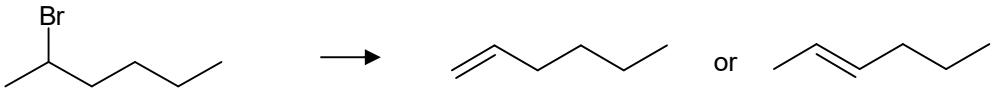

But-1-ene can form 2-bromobutane (major product) and 1-bromobutane (minor product

**I** could also be methylpropene

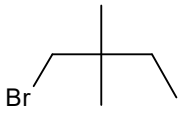
The alcohol dehydration reaction (reaction with concentrated sulfuric acid) and halogenoalkane elimination reaction (reaction with ethanolic potassium hydroxide) can help give information about the structure.
**Example 5** Consider the reactions of some isomers of $C_6H_{13}Br$ with ethanolic potassium hydroxide.




1-bromohexane can only form hex-1-ene




2-bromohexane can form hex-1-ene and hex-2-ene . Hex-2-ene exists as two E-Z isomers.



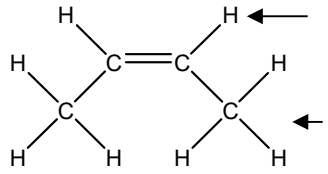

1-bromo-2,2-dimethylbutane does not react with ethanolic KOH because the carbon next to the one attached to the Br does not have any hydrogen atoms.

**Stereoisomerism**

Stereoisomers have the same structural formulae but have a different spatial arrangement of atoms. Stereoisomerism can be either **E-Z stereoisomerism** or **optical isomerism.** Information about existence of stereoisomerism can help identify the structure.

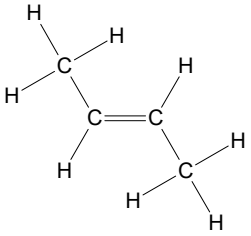
## E-Z stereoisomerism

E-Z stereoisomers arise when:
(a) There is **restricted rotation** around the C=C double bond.
(b) There are **two different groups/atoms** attached both ends of the double bond.



*two different groups* attached either end of the restricted double bond- leads to EZ isomers

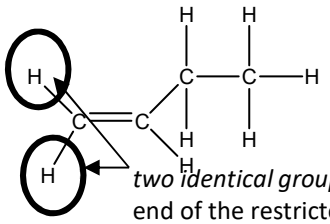
***Z*- but-2-ene**



These are two isomers as the lack of rotation around the double bonds means one cannot be switched to the other.

***E* -but-2-ene**

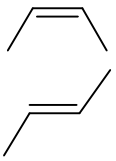
But-1-ene is a structural isomer of but-2-ene but does not show E-Z isomerism.



**But-1-ene**

*two identical groups* attached to one end of the restricted double bond – no E-Z isomers

Skeletal formulae can also represent E-Z isomerism

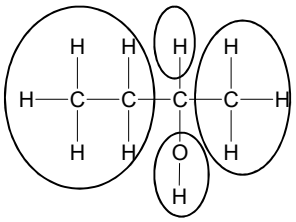


Z-but-2-ene

E-but-2-ene

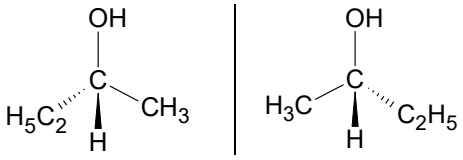
## Optical isomerism

Optical isomerism occurs in carbon compounds with 4 different groups of atoms attached to a carbon (called an **asymmetric carbon**).



A carbon atom that has four different groups attached is called a **chiral** (asymmetric) carbon atom

These four groups are arranged tetrahedrally around the carbon.



This causes two different isomers that are not superimposable to be formed. They are mirror images

Two compounds that are optical isomers of each other are called **enantiomers**.

## Section A: Questions using reactions and stereoisomerism

**1** Isomers **A** and **B** have the molecular formula $C_4H_8O$
When warmed with Tollens' reagent:
A gives a silver mirror
B does not give a silver mirror
Draw a possible structure for compounds **A** and **B**

**2** Compounds **C, D** and **E** have the molecular formula $C_4H_8$
**C** and **D** decolourise bromine water but **E** does not.
**D** exists as two stereoisomers but **C** does **not** show stereoisomerism.
Draw a possible structure for each of compounds **C**, **D** and **E.**

**3** Compound **F** is a straight chain halogenoalkane with the molecular formula $C_5H_{11}Br$.
When compound **F** reacts with hot, ethanolic sodium hydroxide a mixture of three alkenes **G**,**H** and **I** can be formed. **G** and **H** are a pair of E-Z stereoisomers.
**I** does not show stereoisomerism.
Draw a possible structure for each of compounds **F**,**G**, **H** and **I.**

**4** Compound **J** is an ester with the molecular formula $C_5H_8O_2$ that shows E-Z stereoisomerism.
Draw a possible structure for compound **J**

**5** Compounds **K** and **L** have the molecular formula $C_3H_6Br_2$
**K** shows optical activity but **L** does not.
Draw a possible structure for compounds **K** and **L.**

**6** Compounds **M**, **N** and **O** have the molecular formula $C_6H_{12}$
All three are branched-chain molecules and none is cyclic.
**M** can represent a pair of optical isomers.
**N** can represent a pair of E-Z stereoisomers.
**O** can represent another pair of E-Z stereoisomers different from **N**.
Draw a possible structure for each of compounds **M**, **N** and **O.**

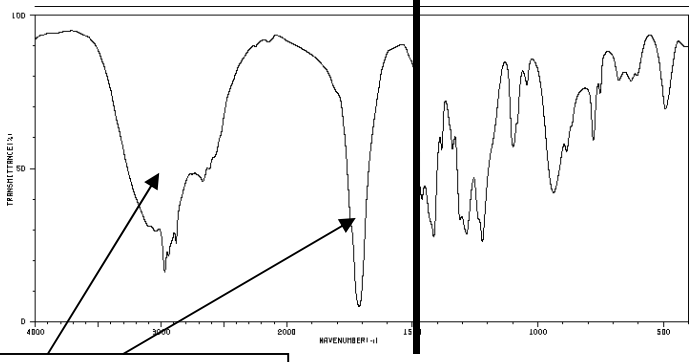
**7** Compounds **P** and **Q** have the molecular formula $C_5H_8O_2$
Both **P** and **Q** react with aqueous sodium carbonate to produce bubbles of carbon dioxide gas
**P** has a branched carbon chain and does **not** show stereoisomerism.
**Q** is an optically active.
Draw a possible structure for compounds **P** and **Q.**

**8** Compounds **R, S** and **T** are all isomers with the molecular formula $C_6H_{12}O_2$
They all react with aqueous sodium carbonate to produce carbon dioxide.
They all have asymmetric carbon atom.
Draw a possible structure for each of compounds **R, S** and **T**

## Using infrared spectroscopy

Use an IR absorption table provided in exam to deduce presence or absence of particular bonds or functional groups

Above 1500 $cm^{-1}$ – "Functional group identification"



e.g. C=O 1680 – 1750 $cm^{-1}$

O-H (acid) 2500- 3000 $cm^{-1}$

Infrared absorption data

| Bond | Wavenumber /$cm^{-1}$ |
|---|---|
| N – H (amines) | 3300 – 3500 |
| O – H (alcohols) | 3230 – 3550 |
| C – H | 2850 – 3300 |
| O – H (acids) | 2500 – 3000 |
| C ≡ N | 2220 – 2260 |
| C = O | 1680 – 1750 |
| C = C | 1620 – 1680 |
| C – O | 1000 – 1300 |
| C – C | 750 – 1100 |

### Section B: Questions using IR data

**1** Compounds **A** and **B** have the molecular formula $C_2H_4O_2$

Each has an absorption in its infra-red spectrum at about 1700 $cm^{-1}$ but only **B** has a broad absorption at 3350 $cm^{-1}$
Draw a possible structure for compounds **A** and **B**

**2** Compounds **C** and **D** have the molecular formula $C_6H_{12}O$

Each exists as a pair of optical isomers and each has an absorption at about 1700 $cm^{-1}$ in its infrared spectrum. **C** forms a silver mirror with Tollens' reagent but **D** does not.

Draw a possible structure for compounds **C** and **D.**

**3** Compound **E**, $C_6H_{12}O_2$, is a neutral compound and is formed by the reaction between compounds **F** and **G** in the presence of a small amount of concentrated sulfuric acid.
**F** and **G** can both be formed from propanal by different redox reactions.
**F** has an absorption in its infra-red spectrum at 1750 $cm^{-1}$.
Draw a possible structure for compounds **E**, **F** and **G**.

**4** Isomers **H** and **I** have the molecular formula $C_5H_{12}O$
Both **H** and **I** have broad absorptions in the region 3230 - 3550 $cm^{-1}$
**H** reacts with acidified potassium dichromate but does **not** react with concentrated sulfuric acid
**I** does **not** react with acidified potassium dichromate but reacts with concentrated sulfuric acid
Draw a possible structure for compounds **H** and **I**

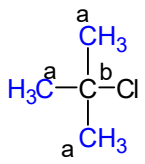
# Using NMR spectroscopy

There are two main types of NMR
1. $C^{13}$ NMR
2. H (proton) NMR

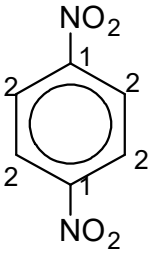
**Equivalent carbon atoms.**

In a $C^{13}$ NMR spectrum, there is one signal (peak) for each **set of equivalent C atoms.**

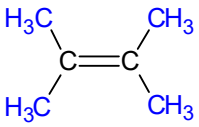
Often in questions the compounds will have a low number of peaks- this should lead you towards symmetrical molecules, like the ones below.
The $(CH_3)_3C$ structure is also common in questions




2 peaks

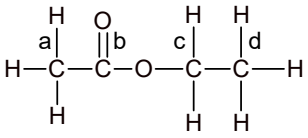



2 peaks




2 peaks

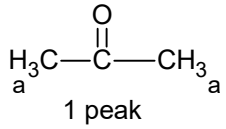
Non- symmetrical



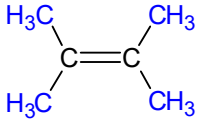

4 peaks

**Equivalent hydrogen atoms.**

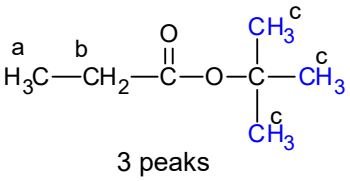
In proton $^1H$ NMR spectrum, there is one peak for each set of equivalent H atoms.
Again questions will often refer to a low number of peaks relative to the number of carbons- so look for symmetry.



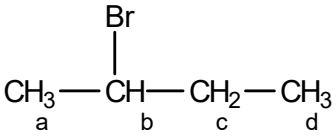

1 peak




1 peak




3 peaks

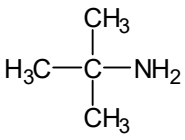



4 peaks

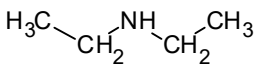
Non- symmetrical

**Amines**

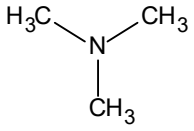
Questions about amines will often combine $^1H$ NMR or $^{13}C$ NMR data with information about whether the amine is primary, secondary or tertiary.




A primary amine with two $^1H$ NMR peaks and two $^{13}C$ NMR peaks



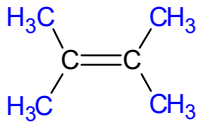

A secondary amine with three $^1H$ NMR peaks and two $^{13}C$ NMR peaks



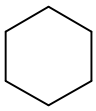

A tertiary amine with one $^1H$ NMR peak and one $^{13}C$ NMR peaks

**Revisiting this earlier example with some extra NMR data**
**Example 1**. Compounds **A and B** have the molecular formula $C_6H_{12}$.
Compound **A** changes bromine water from orange to colourless.
Compound **B** does not react with bromine water.
Both compounds **A and B** have one peak in their $^1$H NMR spectra
Draw possible structures for compounds **A** and **B.**

All the straight chain alkenes with six carbons have at least 3 peaks.
Need to look for something branched and symmetrical for **A.**

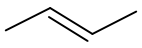



All the hydrogens are the same environment in this cyclic alkane.
This is **B.**



**Revisiting this earlier example with some extra NMR data**
**Example 4**. Compounds **H** and **I** have the molecular formula $C_4H_8$.
Compound **H** reacts with HBr to form only one compound
Compound **I** reacts with HBr to form two structural isomers.
Both compounds **H and I** have two peaks in their $^1$H NMR spectra
Draw possible structures for compounds **H** and **I.**

**H** must be a symmetrical alkene around the double bond



but-2-ene can only form 2-bromobutane

But-2-ene has two peaks in its $^1$H NMR spectra.

**I** must be a unsymmetrical alkene around the double bond. Previously there were two options, but but-1-ene has four peaks- so we are left with methylpropene which does have two peaks in its $^1$H NMR spectra.

## Section C: Questions using NMR data – number of peaks

**1** Compounds **A** and **B** have the molecular formula $C_5H_{12}$
In their $^1$H NMR spectra, **A** has three peaks and **B** has only one.
Draw the structures for compounds **A** and **B.**

**2** Compounds **C** and **D** both have the molecular formula $C_6H_3Cl_3$
**C** has two peaks in its $^{13}$C NMR spectrum
**D** has four peaks in its $^{13}$C NMR spectrum
Draw the structures for compounds **C** and **D.**

**3** Compounds **E** and F have the molecular formula $C_6H_4N_2O_4$ and both are dinitrobenzenes.
**E** has two peaks in its $^{13}$C NMR spectrum.
**F** has three peaks in its $^{13}$C NMR spectrum.
Draw the structures for compounds **E** and **F.**

**4 G** and **H** are cyclic compounds with the molecular formula $C_6H_{10}O$.
Both have four peaks in their $^{13}$C NMR spectra.
Each has an absorption at about 1700 $cm^{-1}$ in their infrared spectrums.
**G** forms a silver mirror with Tollens' reagent but **H** does not.
Draw the structures for compounds **G** and **H.**

**5** Compounds **I** and **J** have the molecular formula $C_5H_{10}O$.
Both have two peaks in their $^1$H NMR spectra.
**I** forms a silver mirror with Tollens' reagent but **J** does not.
Draw the structures for compounds **I** and **J.**

**6** Compounds **K** and **L** have the molecular formula $C_4H_8O$
**K** gives a silver mirror with Tollens' reagent but **L** does not
**K** and **L** both have an absorption at about 1700 $cm^{-1}$ in their infrared spectra
**K** has three peaks and **L** has four peaks in their $^{13}$C NMR spectra:
Draw the structures for compounds **K** and **L**.

**7** Compounds **M** and **N** are alcohols with the molecular formula $C_6H_{14}O$
**M** as four peaks and **N** has six peaks in their $^1H$ NMR spectra
**M** does not react with acidified potassium dichromate(VI)
**N** exists as optical isomers.
Draw the structures for compounds **M** and **N.**

**8** Compound **O** has the molecular formula $C_5H_8O_2$
**O** is a cyclic compound.
**O** has an absorption at about 1700 $cm^{-1}$ in its infrared spectrums and has two peaks in its $^1H$ NMR spectrum.
Draw the structure for compound **O.**

**9** Compound **P** is a cyclic compound with the molecular formula $C_6H_{12}O_2$
The infrared spectrum of compound **P** does not show an absorption in the region 1680–1750 $cm^{-1}$ but does have an absorption at 3270 $cm^{-1}$
Compound **P** has two peaks in its $^{13}C$ NMR spectrum and three peaks in its $^1H$ NMR spectrum.
Draw the structure of compound **P**.

**10** Compound **Q** has the molecular formula $C_6H_{12}O_2$
Compound **Q** reacts with aqueous sodium carbonate to produce carbon dioxide.
Compound **Q** has a chiral centre and has five peaks in its $^{13}C$ NMR spectrum.
Draw the structure for compound **Q.**

**11** Compounds **R** and **S** have the molecular formula $C_6H_{12}$.
Both have only one peak in their $^1H$ NMR spectra.
**R** reacts with aqueous bromine but **S** does not.
Draw the structures for compounds **R** and **S**.

**12** Isomers **T** and **U** have the molecular formula $C_3H_9N$
**T** has absorptions in the 3350–3450 $cm^{-1}$ region of their infrared spectra but **U** has no absorptions at wavenumbers greater than 3100 $cm^{-1}$
Compound **T** has three peaks in its $^1H$ NMR spectra and **U** has one peak.
Draw the structures for compounds **T** and **U**.

**13** Compounds **W, X, Y,** and **Z** have the molecular formula $C_4H_{11}N$
**W** is a primary amine and has two peaks in its $^1H$ NMR spectrum.
**X** and **Y** are secondary amines. In their $^{13}C$ NMR spectra, **X** has two peaks and **Y** has three.
**Z** is a tertiary amine.
Draw a possible structure for compounds **W, X, Y,** and **Z**.

**14** Compounds **A** and **B** have the molecular formula $C_6H_{15}N$
**A** is a tertiary amine with two peaks in its $^1H$ NMR spectrum.
**B** is a secondary amine with three peaks in its $^1H$ NMR spectrum.
Draw the structures of **A** and **B**.

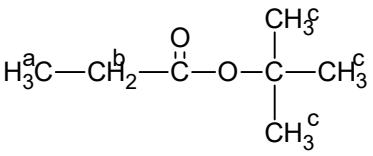
**15** Compounds **C** and **D** have the molecular formula $C_6H_{16}N_2$
**C** contains two primary amine groups and has two peaks in its $^{13}C$ NMR spectrum.
**D** contains two tertiary amine groups and has two peaks in its $^{13}C$ NMR spectrum.
Draw a structure for compounds **C** and **D.**

**16** Compounds **E** and **F** have the molecular formula $C_3H_6O$
**E** has an absorption at 1715 $cm^{-1}$ in its infrared spectrum and has one peak in its $^1H$ NMR. spectrum.
**F** has absorptions at 3300 $cm^{-1}$ and at 1645 $cm^{-1}$ in its infrared spectrum and does **not** show *E*–*Z* isomerism.
Draw a possible structure for compounds **E** and **F.**

**17** Compound **G** has molecular formula $C_7H_{12}O_4$
1 mol of **G** reacts exactly with 2 mol of sodium hydroxide.
**G** has four peaks in its $^{13}C$ NMR spectrum and three peaks in its $^1H$ NMR spectrum.
Suggest a structure for **G**

## Using NMR shift data, integration ratios and splitting data

The **intensity (integration value)** of each signal in the $^1$H NMR spectra is proportional to the **number of equivalent H atoms** it represents.

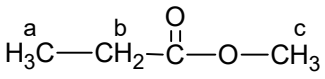


3 sets of equivalent H's: ratio 3:2:9

## Splitting

In high resolution $^1$H NMR each signal in the spectrum can be split into further lines due to inequivalent H's on neighbouring C atoms.

Splitting of peak = number of inequivalent H's on neighbouring C atoms + 1



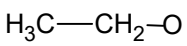
The peak due to group **a** will be a **triplet** as it is next to **b** (a carbon with 2 H's)

The peak due to group **b** will be a **quartet** as it is next to **a** (a carbon with 3H's)

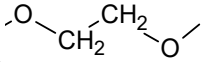
The peak due to group **c** will be a **singlet** as it is next to a carbon with no H's)

### Common fragments of molecules

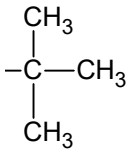
An ethyl group will give a combination of a triplet and a quartet



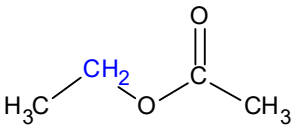
An isolated -$CH_2$-$CH_2$- group will give a combination of two triplets



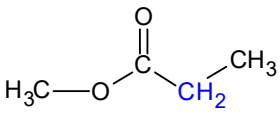
The $(CH_3)_3C$- group will give just one singlet



**Example 6** Compounds **J** and **K** are esters with the molecular formula $C_4H_8O_2$.
Both **J** and **K** have 3 peaks in their $^1$H NMR spectra with integration ratios of 3:2:3. Both $^1$H NMR spectra also contain one singlet, one triplet and one quartet.
The quartet for **J** occurs at a shift of δ 2.3 ppm



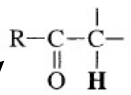
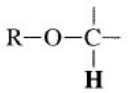
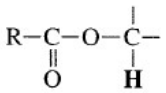
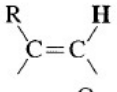
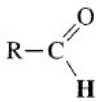
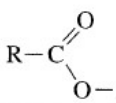
ethyl ethanoate



methyl propanoate

Both ethyl ethanoate and methyl propanoate have 3 peaks in their $^1$H NMR spectra with integration ratios of 3:2:3. Both $^1$H NMR spectra contain one singlet, one triplet and one quartet.
The final bit of information about shift will differentiate between the two.
The $CH_2$ group next to the $CH_3$ will be the quartet. A shift of δ 2.3 ppm suggests the $CH_2$ is next to a C=O
So compound **J** must be methyl propanoate

$^1$H n.m.r. chemical shift data

| Type of proton | δ/ppm |
|---|---|
| ROH | 0.5 – 5.0 |
| $RCH_3$ | 0.7 – 1.2 |
| $RNH_2$ | 1.0 – 4.5 |
| $R_2CH_2$ | 1.2 – 1.4 |
| $R_3CH$ | 1.4 – 1.6 |
|  | 2.1 – 2.6 |
|  | 3.1 – 3.9 |
| $RCH_2Cl$ or Br | 3.1 – 4.2 |
|  | 3.7 – 4.1 |
|  | 4.5 – 6.0 |
|  | 9.0 – 10.0 |
|  | 10.0 – 12.0 |

**Section D: Questions with $^1$H HMR splitting, integration ratio and shift data**

**1** Compound **A** has the molecular formula $C_6H_{12}O_2$
Compound **A** reacts with aqueous sodium carbonate to produce carbon dioxide.
Compound **A** has three singlet peaks in its $^1$H HMR spectrum.
Draw the structure for compound **A.**

**2** Compounds **B** and **C** are esters with the molecular formula $C_6H_{12}O_2$ .
Both **B** and **C** have only two peaks in their $^1$H NMR spectrum.
The integration ratio for both **B** and **C** is 3:1
Draw possible structures for compounds **B** and **C.**

**3** Compounds **D** and **E** both have the molecular formula $C_4H_8Br_2$
**D** has a singlet, a triplet and a quartet in its $^1$H NMR spectrum.
**E** has two singlets in its $^1$H NMR spectrum.
Draw the structures for compounds **D** and **E**.

**4** Compounds **F**, **G**, **H** and **I** have the molecular formula $C_5H_{13}N$.
**F**, **G**, and **H** all have 3 peaks in their $^{13}$C NMR spectrums.
**F** and **G** are primary amines
**H** is a secondary amine.
**I** is a tertiary amine. Its $^1$H NMR spectrum has three peaks. One of the peaks is a doublet.

Draw a possible structure for compounds **F**, **G**, **H** and **I**.

**5** Compounds **J** and **K** have the molecular formula $C_6H_{11}OCl$
**J** and **K** both have an absorption at about 1700 $cm^{-1}$ in their infrared spectra.
**J** and **K** each have two singlet peaks only in their $^1$H NMR spectra.
In both spectra the integration ratio for the two peaks is 2:9

Draw the structures for compounds **J** and **K**.
Suggest which compound would react more vigorously with water.

**6** Compounds **L** and **M** have the molecular formula $C_3H_6O_2$
**L** effervesces with aqueous sodium hydrogencarbonate but **M** does not.
**L** and **M** both have a quartet, a triplet and a singlet peak in their $^1$H NMR spectra.
Draw the structures of compounds **L** and **M.**

**7** Compounds **N** and **O** have the molecular formula $C_4H_8Cl_2$
Compound **N** has a $^1$H NMR spectrum which only contains a singlet, a triplet and a quartet with an integration ratio of 3:3:2 respectively.
Compound **O** has a $^1$H NMR spectrum which only contains two singlets with an integration ratio of 3:1.
Draw the structures of compounds **N** and **O**.

**8** Compounds **P** and **Q** have the molecular formula $C_4H_8O_2$
**P** and **Q** both have strong absorptions in the 1700–1750 $cm^{-1}$ region.
Neither **P** and **Q** react with aqueous sodium carbonate.
In their $^1H$ NMR spectra, **P** has a quartet at δ= 2.3 ppm and **Q** has a quartet at δ = 4.1 ppm.
Draw the structures of compounds **P** and **Q**

**9** Compounds **R** and **S** have the molecular formula $C_5H_{10}O_2$
**R** and **S** both have strong absorptions in the 1700–1750 $cm^{-1}$ region
**R** effervesces with aqueous sodium hydrogencarbonate but **S** does not.
Compound **R** has a $^1H$ NMR spectrum which has two singlets with an integration ratio 9:1
Compound **S** has a $^1H$ NMR spectrum which has two triplets and two quartets with integration ratio 3:3:2:2
Draw the structures of compounds **R** and **S**

**10** Compounds **T** and **U** have the molecular formula $C_5H_{10}O_2$
**T** and **U** both have strong absorptions in the 1700–1750 $cm^{-1}$ region.
Neither **T** and **U** react with aqueous sodium carbonate.
The $^1H$ NMR spectrum of **T** consists of two singlets
The $^1H$ NMR spectrum of **U** consists of two quartets and two triplets.
Draw the structures of compounds **T** and **U**

**11** Compounds **V, W** and **X** have the molecular formula $C_6H_{12}$
**V** and **W** have an absorption in their infra-red spectrum at about 1650 $cm^{-1}$ and neither shows E-Z stereoisomerism.
**X** has no absorptions between 1500 and 2900 $cm^{-1}$
The $^1H$ NMR spectrum of **V** consists of one singlet.
The $^1H$ NMR spectrum of **W** consists of a singlet, a triplet and a quartet.
The $^1H$ NMR spectrum of **X** only has one peak
Draw a structure for compounds **V, W** and **X**

## Section E: Questions where reasoning is needed

**1** Compound **A** has the molecular formula of $C_6H_{12}O_2$
The table shows information about the $^1H$ NMR spectrum for compound **A**

| Chemical shift δ / ppm | 3.8 | 3.5 | 2.6 | 2.2 | 1.2 |
|---|---|---|---|---|---|
| Integration ratio | 2 | 2 | 2 | 3 | 3 |
| Splitting pattern | triplet | quartet | triplet | singlet | triplet |

Deduce the structure of compound **A and** explain your reasoning

**2** Compound **B** has the molecular formula $C_4H_7ClO$.
It does not produce misty fumes when added to water.
The infra-red spectrum of **B** contains a major absorption at 1724 $cm^{-1}$.
The $^1H$ NMR spectrum of **B** shows 3 peaks. Information about the 3 peaks is given in the table.

| | Peak 1 | Peak 2 | Peak 3 |
|---|---|---|---|
| Integration value | 3 | 3 | 1 |
| Splitting pattern | doublet | singlet | quartet |

Deduce the structure of compound **B and** explain your reasoning

**3** The molecular formula of compound **C** is $C_6H_{14}O_2$
**C** has a peak at wavenumber 3500 $cm^{-1}$ in its infra red spectrum. It does not have a peak in the range 1680 to 1750 $cm^{-1}$
When **C** is warmed with acidified potassium dichromate(VI) a green solution is formed.
The $^1H$ NMR spectrum of **C** contains five peaks.
Information about the 5 peaks is given in the table.

| Chemical shift δ/ppm | 3.8 | 3.2 | 3.1 | 1.4 | 1.1 |
|---|---|---|---|---|---|
| Integration ratio | 2 | 3 | 1 | 2 | 6 |
| Splitting patterns | triplet | singlet | singlet | triplet | singlet |

Deduce the structure of compound **C and** explain your reasoning

**4** The molecular formula of compound **D** is $C_6H_{14}O$
**D** has a peak at wavenumber 3400 $cm^{-1}$ in its infra red spectrum. It does not have a peak in the range 1680 to 1750 $cm^{-1}$
The $^1H$ NMR spectrum of **D** contains four peaks.
Information about the four peaks is given in the table.

| Chemical shift δ/ppm | 1.5 | 1.2 | 1.1 | 0.9 |
|---|---|---|---|---|
| Integration ratio | 4 | 1 | 3 | 6 |
| Splitting patterns | quartet | singlet | singlet | triplet |

Deduce the structure of compound **D and** explain your reasoning.

**5** The molecular formula of compound **E** is $C_6H_{14}O_2$
The $^1H$ NMR spectrum of **E** contains five peaks.
Information about the five peaks is given in the table.

| Chemical shift, δ/ppm | 3.7 | 3.5 | 2.6 | 2.2 | 1.1 |
|---|---|---|---|---|---|
| Integration value | 2 | 2 | 2 | 3 | 3 |
| Splitting pattern | triplet | quartet | triplet | singlet | triplet |

Deduce the structure of compound **E and** explain your reasoning.

**6** The molecular formula of an ester compound **F** is $C_4H_8O_2$
The $^1H$ NMR spectrum of **F** contains three peaks.
Information about the three peaks is given in the table.

| Chemical shift, δ/ppm | 4.1 | 2 | 1.2 |
|---|---|---|---|
| Integration ratio | 2 | 3 | 3 |
| Splitting patterns | quartet | singlet | triplet |

Deduce the structure of compound **F and** explain your reasoning.

**7** Compound **G** has molecular formula $C_7H_{12}O_4$
Compound **G** does not react with acidified potassium dichromate.
Compound **G** reacts with sodium hydroxide to produce ethanol as one of the products.
Compound **G** has four peaks in its $^{13}C$ NMR spectrum.
The $^1H$ NMR spectrum of **G** contains three peaks.
Information about the three peaks is given in the table.

| Chemical shift, δ/ppm | 3.9 | 3.4 | 1.3 |
|---|---|---|---|
| Integration ratio | 4 | 2 | 6 |
| Splitting patterns | quartet | singlet | triplet |

Deduce the structure of compound **G and** explain your reasoning.