Solving a puzzle using spectroscopy (question 4, 2011 paper)

Video transcript

This question is all about solving a puzzle using spectroscopy, specifically ^{13}C and ^{1}H NMR spectroscopy. You really need to have studied NMR before tackling the question. However, if you haven't, some extra information is provided on the next page of the question paper to help you with your answer.

The question begins by telling you that compounds **1–7** all have a molecular formula of $C_4H_{10}O$. You will be aware of four types of compound that contain a single oxygen atom. These are:

- *Alcohols* which contain an O-H, hydroxyl group.
- *Ethers* which have a central oxygen atom splitting two carbon chains.
- *Aldehydes* which contain a terminal C=O group with a hydrogen atom attached to the carbonyl carbon.
- *Ketones* which contain a C=O group in the middle of a carbon chain and therefore has two carbon atoms bonded either side of the carbonyl carbon.

Since the formula of the compounds is $C_4H_{10}O$, this means that they contains the same number of hydrogen atoms as a straight chain alkane with an equivalent number of carbon atoms; they fit the general formula of C_nH_{2n+2}. Therefore our compounds can't contain any double bonds; they must be fully saturated. This rules out the possibility of our compounds being either aldehydes or ketones. Therefore compounds **1**–**7** must be either alcohols or ethers.

To help identify each of the possible compounds, the best step now is to draw out all possible structures with a formula $C_4H_{10}O$. If we do this we find that there are four possible alcohols and three possible ethers.

If we now look at the second bullet point, this tells us that compounds **5**–**7** have lower boiling points than compounds **1**–**4**. From our chemical knowledge, we know that alcohols generally have higher boiling points than molecules with a similar relative molecular mass owing to hydrogen bonding between the molecules. Therefore we can expect the alcohols to be compounds **1**–**4** and the ethers to be compounds **5**–**7**. This is supported by the information given in the third bullet point where we are told that compounds **1**–**4** have a broad absorption at 3300 cm^{-1} in their infra-red spectra. This corresponds to the stretching frequency of an O-H group in an alcohol.

So we now know that **compounds 1–4 are the alcohols** and **compounds 5–7 are the ethers**. We must now work through the details given for the individual compounds and match them to the possible structures.

Let us now look at the identification of the alcohols, compounds **1**–**4**.

The fourth bullet point tells us that **compound 2** can exist as optical isomers. For a molecule to be able to exist as optical isomers it must have four different groups attached to any one carbon atom. Looking through our possible alcohol structures, only one of the structures matches this requirement. If we look at the structure on the top right we can see that the carbon atom highlighted with an asterisk has a methyl group, a single hydrogen atom, a hydroxyl group and an

ethyl group coming from it. Therefore this is a chiral carbon atom and hence this alcohol can exist as optical isomers and so must be compound 2. Looking back at the start of the question, we see that we need to draw the skeletal formula of each compound identified and give the systematic name of compounds **1**–**4**. If you have not come across skeletal formulae before, the skeletal formula of a molecule is a drawing of the molecule in which all the hydrogen atoms are removed from carbon chains, leaving just a carbon skeleton with functional groups attached to it. The carbon atoms are not drawn in. Instead, it is assumed that there is a carbon atom at each junction between bonds in a chain and at the end of each bond unless there is something else already there eg a hydroxyl group, OH. Therefore we can draw compound 2 as shown. **Compound 2** can be named as **butan-2-ol** as the longest carbon chain contains four carbon atoms and the hydroxyl group is on carbon-2.

The fifth bullet point shows us the ^{1}H NMR of **compound 3.** From the spectrum, we can identify four different peaks, three of which are labelled as A, B and C. Since there are four different peaks in the ^{1}H NMR spectrum, this alcohol must have hydrogen atoms in four different environments. This is only true for one of the possible alcohol structures, the one at the bottom right. We can confirm this identification by looking further at the integration and splitting patterns for the peaks. If peak B has an integration of one proton, then peak C corresponds to two protons and peak A to six protons. If we now look at the, peak C must be due to the two protons on carbon atom, *C*-1, split into a doublet by the single proton on *C*-2. Peak A must be due to the six equivalent protons on the two *C*-3 carbon atoms. This peak is again split into a doublet by the single proton on carbon atom *C*-2. Finally, peak B is due to the single proton on *C*-2. This is split into a triplet by the two protons on *C*-1 and a septet by the six equivalent protons on *C*-3. As a result, it appears as a nonet with a peak ratio 1:8:28:56:70:56:28:8:1. Therefore we can confirm the identification of compound 3 and draw its skeletal structure. **Compound 3** can be named, **2-methylpropan-1-ol**. Notice that the hydroxyl group takes preference in the numbering.

The next bullet point down, tells us that the ^{1}H NMR spectra of **compound 4** consist of two distinct signals meaning that compound 4 must contain only two types of non-equivalent protons. Therefore compound 4 must be the alcohol in the bottom left, one signal due to the hydroxyl group proton and one signal a result of the nine equivalent protons on the methyl groups. Therefore we can confirm the identification of **compound 4 as 2-methylpropan-2-ol**. By a process of elimination this then allows us to identify **compound 1 as butan-1-ol**.

Finally, we need to identify the ethers, which we know to be compounds **5–7**, and we can do this using the last two bullet points in the question.

The ^{1}H NMR spectrum of **compound 5** only has two distinct signals and we can see that these two signals have a relative intensity of 2:3. Looking at our possible ether structures, the only ether which would match this data is the first symmetrical ether, **diethyl ether**, and so we can identify this as **compound 5**. We can confirm this identification by looking at the ^{1}H NMR data in more detail. The CH_2 next to the ether oxygen atom appears as a quartet, split by the neighbouring CH_3 group, with a chemical shift of δ_H 3.47 ppm as a result of the deshielding effect of the electronegative oxygen atom. The CH_3 group appears as a triplet, split by the neighbouring CH_2 group, with a chemical shift of δ_H 1.21 ppm. We are not required to name this ether but must draw its skeletal formula to get the full marks.

Finally we are provided with some ^{13}C NMR data to help distinguish between the last two ethers corresponding to **compounds 6** and **7**. The ^{13}C NMR spectrum of compound 6 contains four distinct

signals whereas the ^{13}C NMR spectrum of compound 7 shows only 3. Therefore **compound 6** must be **methyl propyl ether (or methoxypropane**), the four non-equivalent carbon atoms highlighted here in pink, yellow, blue and green and **compound 7** must be **methyl isopropyl ether (or 2-methoxypropane)** in this case. All that remains now to complete the question is to correctly draw out the skeletal formulae of each of these compounds.