

17.11: SPECTROSCOPY OF ALCOHOLS AND PHENOLS

OBJECTIVES

After completing this section, you should be able to

1. identify the two most prominent absorptions seen in the infrared spectra of alcohols and phenols.
2. describe the characteristic feature of the proton NMR spectra of alcohols and phenols.
 - a. explain how deuterium oxide (D_2O) can be used to assist in the identification of the signal caused by the presence of the O-H proton in the 1H NMR spectrum of an alcohol.
 - b. predict the general form (i.e., number of peaks, approximate chemical shifts, and splitting pattern) of the proton NMR of a given alcohol or phenol.
3. describe the two most common initial fragmentations in the mass spectra of alcohols.
4. use spectral data (infrared, NMR, mass spectroscopy) to assist in the identification of an unknown alcohol or phenols. You may use tables of characteristic absorptions as an aid to accomplishing this objective.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- alpha cleavage
- dehydration

STUDY NOTES

The 1H NMR chemical shifts for phenols are not particularly distinctive. However, one expects the $-OH$ signal to be in the 4–7 ppm range, while the aromatic protons (see Section 15.7) are expected to be found at 7–8 ppm.

In a mass spectrometer, alcohols fragment in two characteristic ways: alpha cleavage and dehydration. From the equation showing H-Y elimination, you can see that the dehydration of an alcohol in a mass spectrometer is essentially the same as the dehydration of an alcohol in a normal chemical reaction. “Alpha cleavage” refers to the breaking of the bond between the oxygen-bearing carbon atom and one of the neighboring carbons.

INFRARED SPECTROSCOPY

The IR spectrum of aliphatic alcohols have a distinctive O-H stretch in the range of 3300 to 3400 cm^{-1} . This peak tends to be very strong and very broad. This exact position of the peak is dependent on the amount of hydrogen bonding in the alcohol. In addition alcohol have a strong C-O stretch near 1000 cm^{-1} . In the IR spectra of 1-butanol, show below, the O-H stretch appears at 3300 cm^{-1} and the C-O stretch appears at 1073 cm^{-1} .

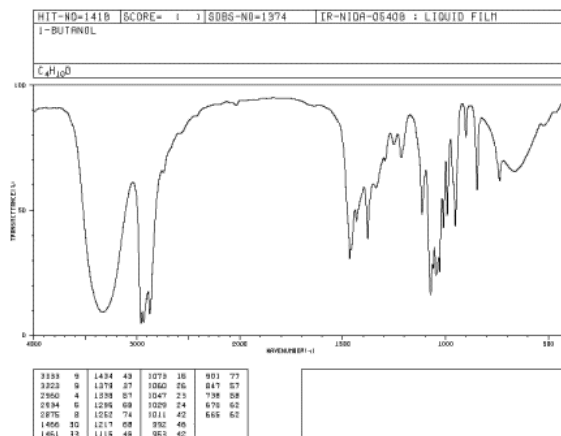
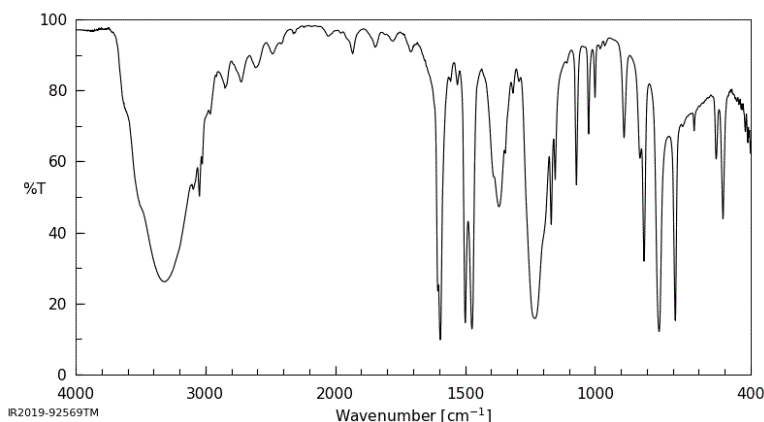


Figure IR8. IR spectrum of 1-butanol. Source: SDBSWeb : <http://riodb01.ibase.aist.go.jp/sdbs/> (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

Peak shapes are sometimes very useful in recognizing what kind of bond is present. The rounded shape of most O-H stretching modes occurs because of hydrogen bonding between different hydroxy groups. Because protons are shared to varying extent with neighboring

oxygen, the covalent O-H bonds in a sample of alcohol all vibrate at slightly different frequencies and show up at slightly different positions in the IR spectrum. Instead of seeing one sharp peak, you see a broad set of multiple overlapping peaks. The broadness of the O-H peak makes it very easy to distinguish in an IR spectrum.

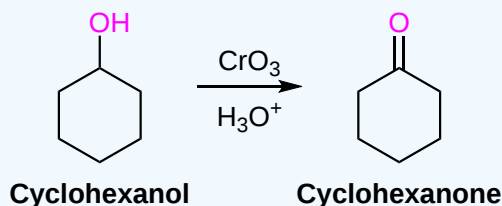
The IR spectrum of phenols the O-H stretch appears at roughly 3500 cm^{-1} . In addition, the IR spectra will show the bands typical for aromatic compounds in the region of $1500\text{--}1600\text{ cm}^{-1}$.



The IR Spectrum of Phenol

? EXERCISE 17.11.1

Assume that you have just converted cyclohexanol into cyclohexanone. How would you use IR spectroscopy to tell if the conversion was successful? What changes would you expect to see between the starting material and the product?



Answer

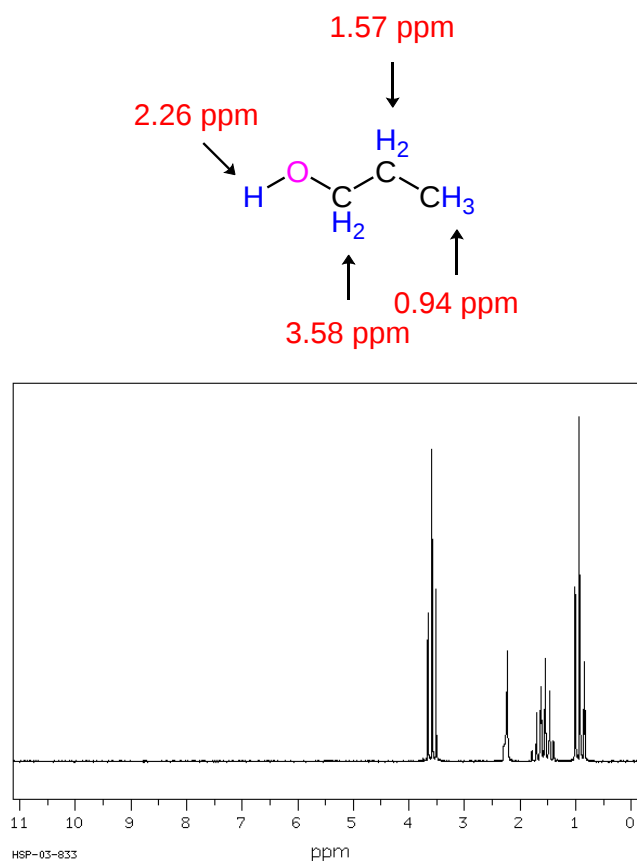
The cyclohexanol starting material would have a distinctive O-H stretch between $3300\text{ and }3400\text{ cm}^{-1}$. If the conversion were successful this peak would not be present in the product. Also, the IR spectrum of the product would have a strong C=O stretch between $1700\text{ and }1800\text{ cm}^{-1}$.

^1H NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

ALCOHOLS

- Protons on carbon adjacent to the alcohol oxygen show up in the region of 3.4–4.5 ppm. The electronegativity of the alcohol oxygen deshields these protons causing them to appear downfield when compared to alkane protons.
- Protons directly attached to the alcohol oxygen often appear in the region of 2.0 to 2.5 ppm. These peaks tend to appear as short, broad singlets. The position of the -OH peak can vary depending on the conditions, such as the NMR solvent used, the concentration of the alcohol, the purity of the alcohol, temperature, and if any water is present in the sample.

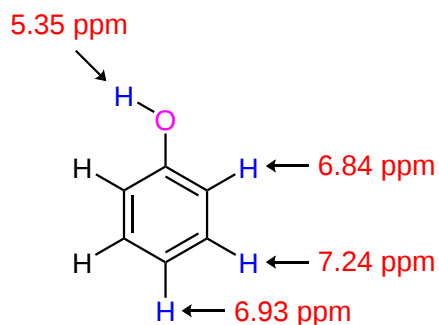
Notice that the alcohol proton is not involved in spin-spin splitting. This is usually true unless the alcohol is exceptionally pure. Most samples of alcohols contain minute amounts of acidic impurities which catalyze the exchange of protons causing the splitting effects to be removed. This is why alcohol protons typically appears as a singlet in NMR spectrum. The ^1H NMR spectrum of propanol shows the -CH₂- attached to the alcohol as a triplet at 3.58 ppm. This shows that the signal is being split by the adjacent -CH₂- group and not the alcohol -OH. The signal for the proton attached to the oxygen appears as a singlet at 2.26 ppm. If this signal was involved in spin-spin splitting with the adjacent -CH₂- group it would appear as a triplet.

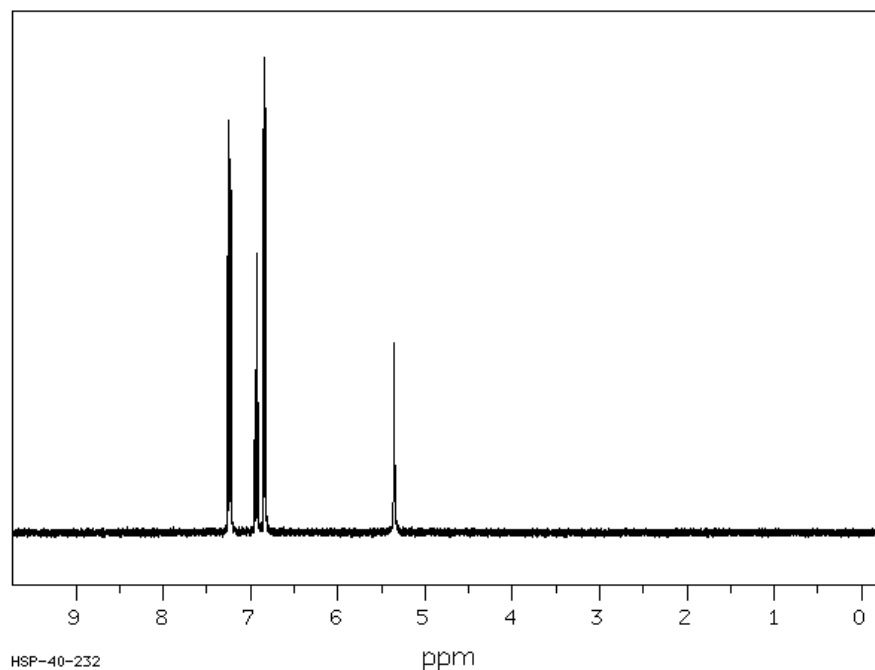


Source: SDBSWeb : <http://sdbb.db.aist.go.jp> (National Institute of Advanced Industrial Science and Technology, 28 June 2017)

PHENOL

- Protons attached to the aromatic ring in phenols show up near the aromatic region of an NMR spectrum (7-8 ppm). These peaks will have splitting typical for aromatic protons.
- The protons directly attached to the alcohol oxygen of phenols appear in the region of 3 to 8 ppm. These peaks tend to appear as short, broad singlets similarly to other alcohols.

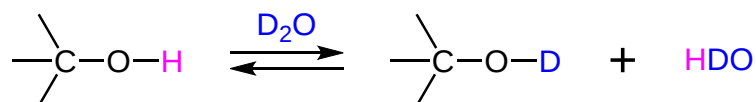




DETERMINING THE POSITION OF AN -OH PEAK IN ^1H NMR

The position of the -OH absorption for alcohols and phenols can be easily determined through the addition a few drops of deuterium oxide, D_2O to the NMR sample tube.

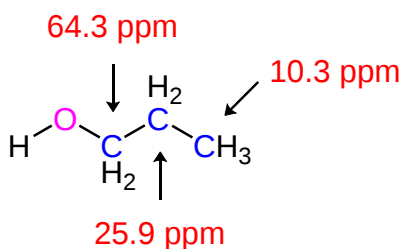
After addition, the OH proton will be rapidly exchanged for a deuterium. Because deuterium atoms do not produce peaks in a typical NMR spectrum the original -OH peak will disappear. This technique is sometimes called a " **D_2O shake**" due to the mixing required after D_2O has been added to the NMR sample tube.

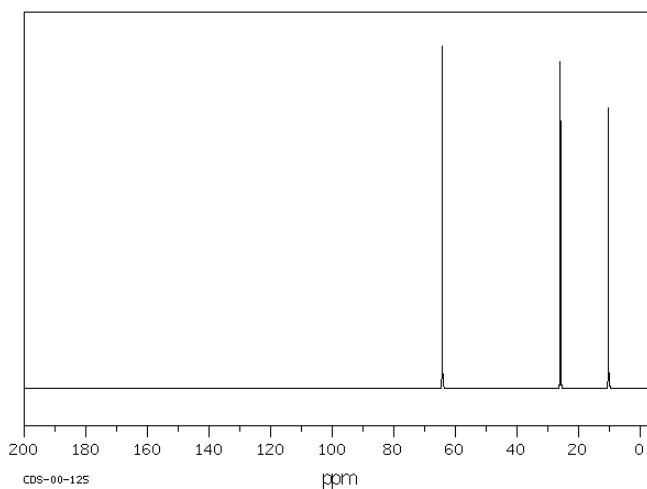


^{13}C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

ALCOHOLS

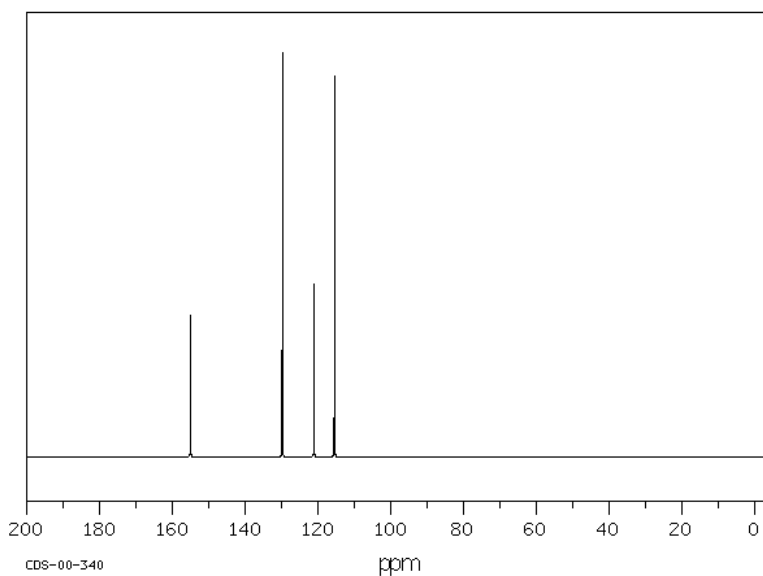
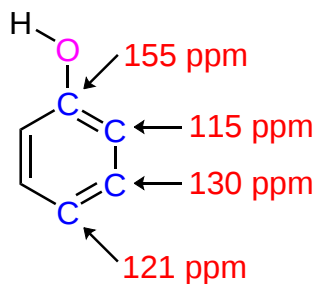
- Carbons adjacent to the alcohol oxygen show up in the distinctive region of 50-65 ppm in ^{13}C NMR spectrum.





PHENOLS

- Due to the electronegative oxygen, the aromatic carbon attached to the -OH group is shifted downfield to 155 ppm.
- The other carbons in the phenol ring appear in the region typical for aromatic carbons of 125-150 ppm.



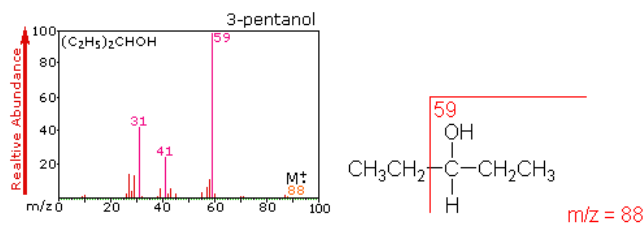
MASS SPECTRA

ALCOHOLS

An alcohol's molecular ion is small or non-existent. Alpha-cleavage of the C-C bond next to the oxygen usually occurs. A loss of H₂O may occur as in the spectra below.

3-Pentanol (C₅H₁₂O) with MW = 88.15

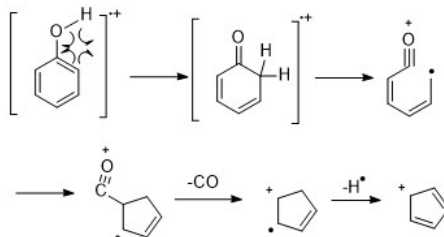
3-Pentanol shows three significant fragment ions. Alpha-fragmentation (loss of an ethyl radical) forms the m/z=59 base peak. Loss of water from this gives a m/z=41 fragment, and loss of ethene from m/z=59 gives a m/z=31 fragment.



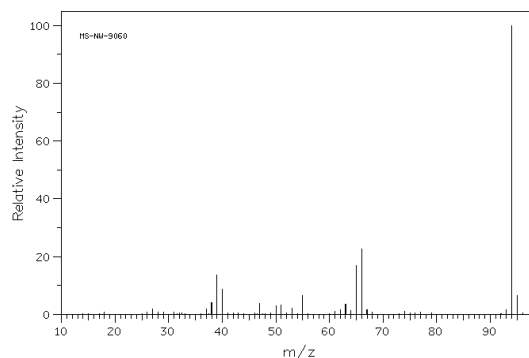
PHENOL

Phenol (C₆H₆O) with MW = 94.11

Phenol exhibits a strong molecular ion peak. The presence of an aromatic ring and an OH gives phenol a unique fragmentation pattern. In particular loss of CO (M - 28) and loss of a formyl radical (HCO•, M - 29) are common observed.

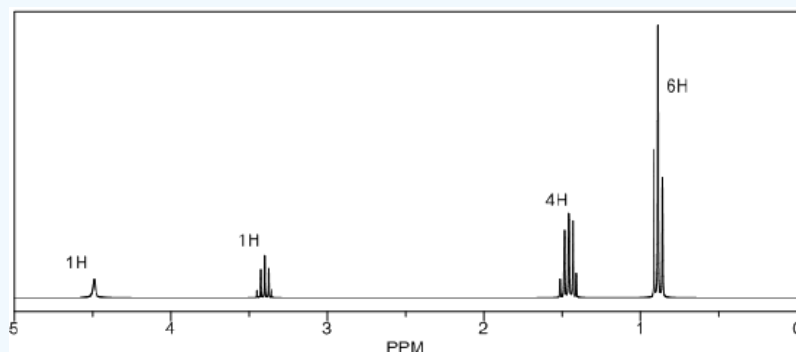


From an outside source

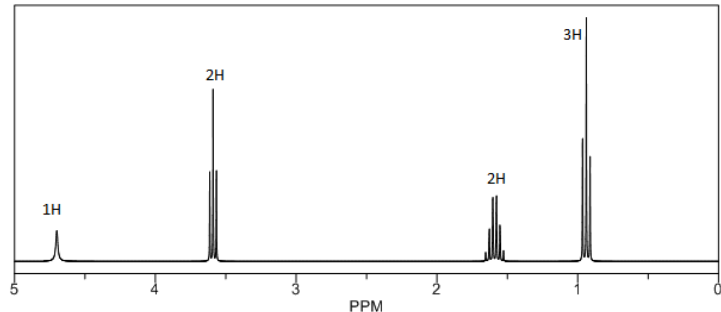


? EXERCISE 17.11.1

1) From mass spectroscopy analysis it was determined that a compound has the general formula C₅H₁₂O. Given the following ¹H NMR spectrum, draw the structure. The integration values of each group of signals is given on the spectrum.

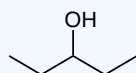


- 2) How would you expect the NMR spectrum shown in question one to change if D₂O was added to the NMR sample tube.
- 3) From mass spectroscopy analysis it was determined that a compound has the general formula C₃H₈O. Given the following ¹H NMR spectrum, draw the structure. The integration values of each group of signals is given on the spectrum.



Answer

1) 3-Pentanol



? EXERCISE 17.11.2

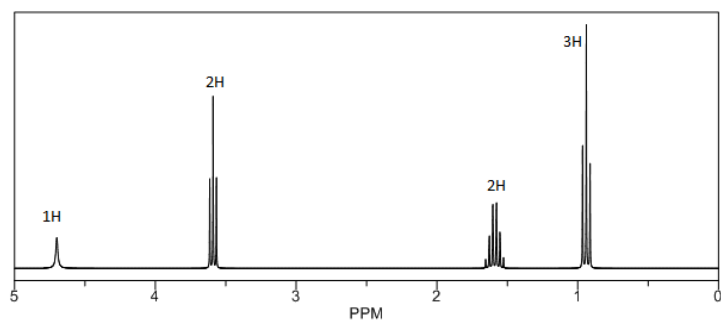
How would you expect the NMR spectrum shown in Exercise 1 to change if D₂O was added to the NMR sample tube.

Answer

The -OH peak at 4.5 ppm would disappear due to deuterium exchange.

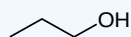
? EXERCISE 17.11.3

From mass spectroscopy analysis it was determined that a compound has the general formula C₃H₈O. Given the following ¹H NMR spectrum, draw the structure. The integration values of each group of signals is given on the spectrum.



Answer

1-Propanol



CONTRIBUTORS AND ATTRIBUTIONS

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- William Reusch, Professor Emeritus ([Michigan State U.](https://www.libretexts.org/@go/page/474117)), [Virtual Textbook of Organic Chemistry](https://www.libretexts.org/@go/page/474117)
- James Kabrhel (University of Wisconsin - Green Bay, Sheboygan Campus)

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