EXPERIMENT 8

CHARACTERIZATION OF ACETATE ESTERS BY CARBON NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Materials Needed

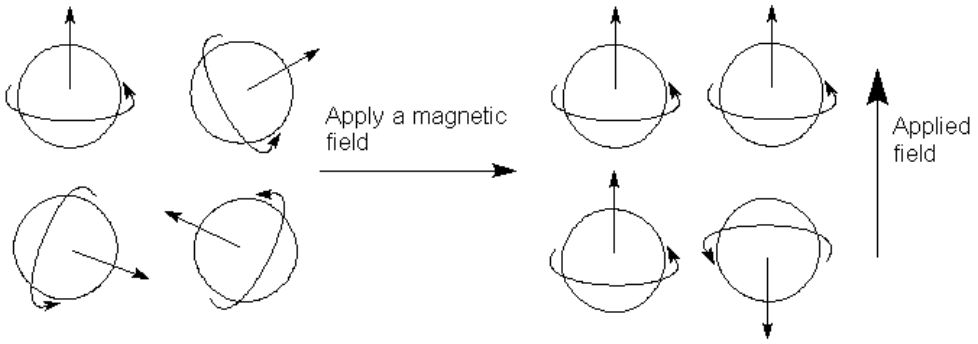
- approx 100 mg of an ester synthesized in Expt #5 - (octyl acetate, propyl acetate, benzyl acetate, or isopentyl acetate)
- approx 1 mL NMR solvent $CDCl_3$
- 1 NMR tube with cap, Pasteur pipet

Relevant Reading Assignment – Bettelheim, review chapter 2.4 on isotopes. Also see the box on MRI on p 81.

INTRODUCTION

The nuclei of some atoms behave as if they were spinning similar to the way a top spins about its axis. The number of neutrons in the nucleus is critical to its ability to exhibit such behavior. Hence, only the nuclei of certain isotopes of an atom can spin. Important examples of spinning nuclei are ^{1}H, ^{13}C. ^{19}F, and ^{31}P, whereas ^{12}C and ^{16}O are two nuclei that do not spin. It is important to realize that, much like a top, nuclei that spin have at least two possible *spin states*, i.e., they can spin either in a clockwise or a counterclockwise direction.

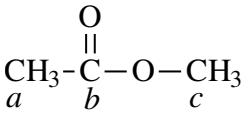
Because a nucleus is positively charged, its spinning generates a small magnetic field. One can thus view a spinning nucleus as a small magnet with north and south poles. When such a nucleus is placed inside a magnetic field the different spin states available to it will correspond to different energy levels for the nucleus. Nuclear magnetic resonance (NMR) describes the fact that such a nucleus will absorb radio waves that have a frequency that is equal to the energy difference between the spin states. This absorption of energy causes the nucleus to be excited to the



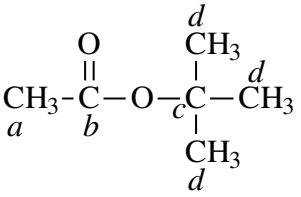
higher energy spin state. In simpler terms, the nucleus reverses the direction in which it is spinning. (The spinning nuclei at right in the diagram above become like the one at bottom right.) A nucleus inside a magnetic field that is flipping its spin due to its absorption of radio waves is said to be *resonating*.

The exact resonance frequency of a nucleus depends on its chemical environment. In other words, the presence of other nearby atoms in the same molecule affects it. One way this happens is through an electronegativity difference that causes the atom to become more electron rich or electron poor. A greater electron density around a nucleus tends to shield it from the magnetic field of the NMR instrument (it doesn't feel the full impact of the magnetic field) and, hence, it resonates at a lower frequency. Conversely, an electron-poor nucleus (an atom with a partial positive charge) resonates at a relatively higher frequency.

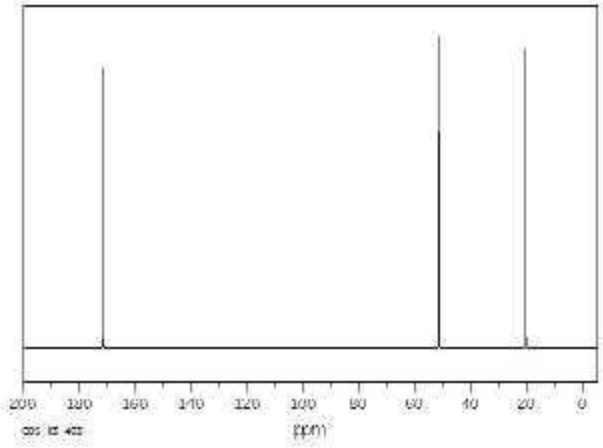
In this experiment we will obtain carbon NMR spectra of the esters from experiment #7. A carbon NMR spectrum shows all of the different frequencies absorbed by the carbon atoms in a molecule. These frequencies show up as *peaks* on a graph of intensity vs frequency. (Frequency is given in units of parts per million or ppm for reasons we won't go into here.) The number of peaks in a carbon NMR spectrum tells you how many distinct carbon atoms there are in the molecule. Often two or more carbon atoms in a molecule have the same chemical environment and, thus, give only one peak and are considered equivalent. Two illustrative examples are given below.

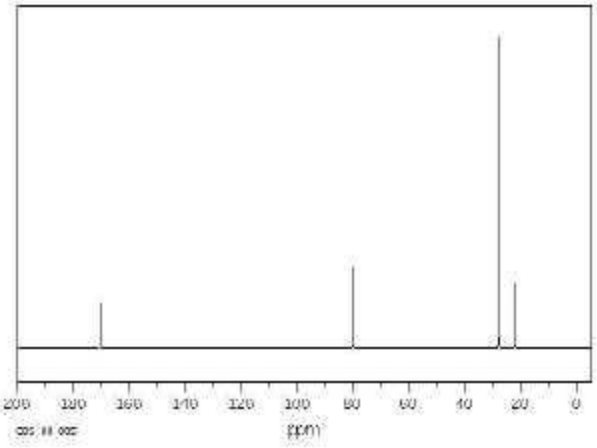


methyl acetate



tert-butyl acetate





Methyl acetate gives 3 peaks in its carbon NMR spectrum. (None of the carbons are equivalent, thus we see one peak for each carbon in the molecule). The *b* carbon is the most electron poor (partially positive) so it resonates (gives a peak) at the highest frequency of the three. Similar reasoning leads to the conclusion that the *a* carbon will resonate at the lowest frequency. *tert*-Butyl acetate, on the other hand, has only four peaks in its NMR spectrum even though there are six total carbons in the molecule. This is because the three methyl group carbons are all equivalent to each other. Also note that carbon *a* in *tert*-butyl acetate will have a very similar resonance frequency to that of carbon *a* in methyl acetate and ditto for the *b* carbons in the two molecules.

PROCEDURE

Safety Precautions - $CDCl_3$ has harmful fumes avoid breathing it and dispense it in a fume hood.

General - Come together in groups of four to six for this experiment. Team up with the other group in the lab that synthesized the same ester as you. Each group will be assigned a fume hood to work in. First each group will prepare a sample for NMR analysis. Then the instructor will demonstrate the operation of the NMR spectrometer and print out a spectrum for each ester analyzed.

Preparing the Sample. NMR tubes and solvents are very costly so please be very careful with the tubes and do not waste the solvent. Also, be very careful when capping and uncapping your NMR tube. The tubes are fragile and the caps are tight so it is easy to break a tube in the process of capping it. Use a Pasteur pipet to add the ester to the NMR tube to a height of approximately 2-3 mm. Now add the $CDCl_3$ solvent carefully to a height in the tube of approximately 5 cm. Cap the tube with the plastic cap provided and label your tube by writing on the side of the cap with a permanent felt tip marker.

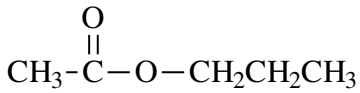
PRELABORATORY QUESTIONS

EXPERIMENT 8

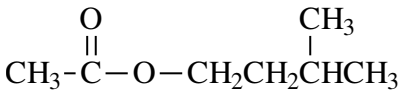
CHARACTERIZATION OF ACETATE ESTERS BY CARBON NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Name _____ Section _____ Date _____

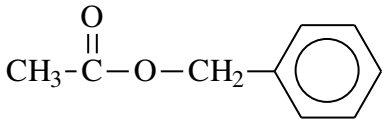
Predict the number of peaks in the carbon NMR of the compounds to be examined in today's lab.



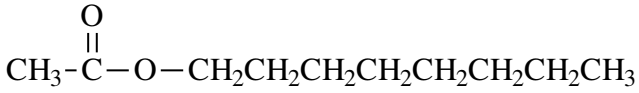
propyl acetate



isopentyl acetate



benzyl acetate



octyl acetate

IN-LAB OBSERVATIONS/DATA

EXPT 8 - CHARACTERIZATION OF ACETATE ESTERS BY CARBON NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Names_____ Section _____ Date _____

Ester analyzed _____

Observations

ester _____$CDCl_3$_____

NMR sample solution_____

Mass Data

NMR tube and cap (g) _____ NMR tube, cap, and ester (g) _____ ester (g) _____

Results

Structure of the ester with carbons labeled as in the examples on page 2 of this lab handout. (Label equivalent carbons, if there are any, with the same letter.)

resonance frequencies observed in spectrum (ppm)	**carbon(s) resonating at this frequency** (*a,b,c*,.. from labeled structure above)

QUESTIONS

1. Explain how the carbon NMR spectrum obtained provides evidence for the structure of the ester you prepared.

2. Why does the C=O carbon resonate at nearly the same frequency in all of the esters analyzed as well as in the example esters discussed on page 2? Also explain why its resonance frequency is so high compared to the other carbons in the molecules.

3. Carbon is not the best nucleus to use for NMR experiments partly because ^{12}C, a nucleus with no net spin and therefore unable to do NMR, is the main isotope of carbon that occurs on earth. The experiment we did only looked at the ^{13}C atoms in the sample. Look up the natural abundances of C-12 and C-13 isotopes. What percent of the carbons in your sample were you actually seeing in your spectrum?