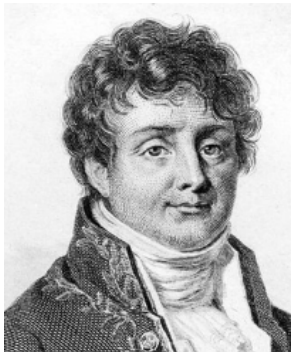
Experiment 25

IDENTIFICATION OF ORGANIC UNKNOWNS. III

Fig. 25-1



Jean Baptiste Joseph Fourier (1768-1830) worked for Napoleon. As a result of his studies of heat transfer, he developed expansion of functions as trigonometric series now called Fourier series or transforms. Modern ir and nmr instruments use Fourier transforms to convert signals to spectra.
http://en.wikipedia.org/wiki/Joseph_Fourier

Text Topics and New Techniques

Infrared spectroscopy of solids.

Discussion

Experiments 7 and ***10*** included the use of the physical properties (density, boiling point, refractive index) and infrared and nmr spectroscopy to determine the identity of unknowns. Today's experiment will differ in two key ways from the earlier experiments. First, a list of possible unknowns was provided for ***Experiments 7*** and ***10***. A list will not be provided for this experiment. This affords a much more interesting challenge. Second, you will be given two unknowns and at least one of them will be a solid. Obtaining the ir and nmr spectra of solids is not necessarily as straightforward as it is for liquids. For H-nmr, a solvent or host must be found that dissolves the unknown and doesn't absorb in the spectrum near the region of interest.

Since this experiment does not contain a list of possible unknowns, it will be even more important than before to extract as much information as possible from the spectra. The ir and nmr spectra should enable you to determine the primary functional groups that are present. The nmr spectra should enable you to determine at least some information about the structure of the carbon skeleton present. Then, using the Knovel Critical Tables (free registration required) that has tables with compounds that can be arranged [http://www.knovel.com/web/portal/browse/display?_EXT_KNOVEL_DISPLAY_bookid=761]
according to increasing melting point, boiling point, density and refractive index, you should be able to use the physical properties to narrow down the list of possible substances to a very few choices. Now, you can compare the properties much more closely and should be able to make an identification by comparing spectra. There is a very small possibility that your unknown is not included in the Knovel Critical Tables. This eventuality will be more challenging but more satisfying when you are able to find matches for the spectra.

For access to physical property data of organic compounds, see pages 7 and 8 of this text. For collections of ir and nmr spectra, refer to pages 9 and 10 of this text. Additional help is offered by web sites on page 10 of this text that enable you to input some experimental information. These sites then give you possible matches with compounds that are included in their libraries. These libraries are generally limited and may not include your unknown.

Techniques

The most commonly use techniques for obtaining infrared spectra of solids is to run them either in a KBr pellet or in a nujol mull. Preparation of a KBr pellet requires the use of dry KBr and a high pressure press. First using an agate mortar and pestle, thoroughly grind about 0.01 g of your compound. Add

about 0.09 g of the dry KBr to it to make a 10% mixture and thoroughly mix and grind again. Depending on the type of press you will use, use about half of the sample to prepare a pellet. Ask your instructor for more specific instructions. This procedure should be performed as rapidly as possible as KBr absorbs moisture from the air. As water absorbs strongly in the ir, this will interfere with the spectrum of your unknown. After you gain some experience, you will probably be able to prepare pellets without weighing the sample.

For nujol mulls, grind about 5 mg of the unknown in an agate mortar and pestle. Add a couple of drops of white mineral oil and grind to form an even suspension. Apply to a salt plate and run the spectrum as you would for a pure liquid. As the oil has C-H bonds, this method will not be useful in the C-H stretch and bending regions.

Another alternative for solids if you have access to an FTIR is to prepare as concentrated a solution as possible in dichloromethane. Apply a few drops of the solution to a salt plate and allow it to dry. Then run the ir.

For ^{1}H-nmr, determine if the solid has sufficient solubility in carbon tetrachloride. If not, try chloroform. If it dissolves sufficiently, prepare a solution in $CDCl_3$. The use of other deuterated solvents is also possible. However, except for D_2O and $CDCl_3$, most are expensive. For liquids, if the unknown is not sufficiently soluble in carbon tetrachloride, run the liquid pure (termed neat) unless it is viscous. In that event, try chloroform.

For ^{13}C, you will need to prepare a solution in carbon tetrachloride or deuterochloroform that is as concentrated as possible. ^{13}Cnmr is substantially less sensitive than ^{1}H-nmr (only 1% of the carbons are ^{13}C) and it may be necessary to average many scans to attain an adequate spectrum.

Procedure

This experiment involves the analysis of two unknowns. Using the instructions in the *Techniques* section of this experiment and ***Experiments 7*** and ***10***, determine the melting or boiling point, density (if liquid), refractive index (if liquid), ir and nmr (^{1}H and if available ^{13}C) spectra of your unknowns. Use the spectra coupled with the physical properties and chemical resources to deduce the identity of your unknowns.

Prelaboratory Preparation - *Experiment 25*

List all the goals of the experiment.

Observations

Report all relevant observations.

Conclusions

This section should include the following:
1. Were the goals of the experiment achieved? Explain your answer.
2. What were the identities of your unknowns. Carefully explain the evidence.