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Mulls of Deuterated Solid Samples for Infrared Spectrometry

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Interpretation of the infrared spectra of complex molecules can be facilitated by recording the spectra of the deuterated, as well as of the hydrogen form, of the compound. In most cases, deuterium–hydrogen exchange occurs very rapidly for the active proton in compounds. Techniques for achieving deuterium–hydrogen exchange in carbon tetrachloride soluble compounds (*1*, *2*) or in cyclohexane soluble compounds (*3*) have been reported. However, these techniques are not suitable for the wide variety of compounds which are not soluble in carbon tetrachloride, cyclohexane, or other infrared-transparent solvents. The preparation of KBr pellets of compounds deuterated at their active sites is very difficult unless one resorts to drybox techniques, otherwise the substituted deuterium can readily undergo exchange with the protons from atmospheric moisture during the mixing and pelletizing process. In this paper we develop a method for preparing mulls of deuterated compounds which can be routinely used as a bench-top technique in any laboratory, without resorting to the added delay and expense of a drybox. The conventional method for preparing mulls is described in ref 4.

EXPERIMENTAL SECTION

Equipment. The apparatus consists of a round-bottom flask with side tube (Kimax No. 25323, 250 mL, 19/22 ground glass neck). The flask is connected to a vacuum line through a 19/22 ground glass connector and a segment of heavy duty Tygon tubing, sufficiently long to allow swirling of the flask while attached to the vacuum line. The vacuum line has two vapor traps placed in Dewar flasks containing dry ice. A three-way valve allows the flask to be connected to the vacuum or released to the atmosphere. A septum is attached to the side tube.

Other items required are safety goggles and/or safety screen, syringes (3-mL capacity) and needles (22 gauge), ball bearings or Pyrex glass beads (6 mm diameter), rubber policeman, NaCl infrared windows and cell holders, lens tissue, hot air gun, mortar and pestle or Wig'l'bug vibrator, and grinding vials. Spectra were measured on a Model 700 Perkin-Elmer spectrophotometer.

Chemicals. In addition to the compounds for deuteration, the following chemicals are required: D_2O (99.8 atom %), CH_3OD (99.5 atom %), CH_3OH, and toluene (all four purchased from Aldrich Chemical Co., Metuchen, NJ); mineral oil and perfluorohydrocarbon (purchased from Beckman Instruments, Inc., Fullerton, CA); dry ice, and toluene.

Procedure. CAUTION: Caution should be exercised in swirling the flask to prevent the ball bearings from striking and cracking the flask. We encountered no implosions in carrying out 147 experimental runs; in five cases a slight crack was detected in the flask. In those cases, the experiment was aborted and restarted with a new flask. Protective goggles should be worn as an added precaution.

The compound is first ground to a very fine consistency with a mortar and pestle or Wig'l'bug vibrator. Approximately 100 mg of the compound is added to the round-bottom flask containing five ball bearings or Pyrex glass beads. The flask is connected to the vacuum line and approximately 0.8 mL of D_2O or CH_3OD is injected through the septum by means of a syringe; D_2O is used for water-soluble compounds and CH_3OD is used for methanol-soluble compounds. The flask is then swirled gently to dissolve the compound. Vacuum is applied and the D_2O or CH_3OD evaporates. After the sample is dry, the vacuum is slowly released by means of the three-way valve and the complete procedure is repeated for a second aliquot of deuterating solvent. After the second aliquot of solvent has been evaporated, the vacuum is released and approximately 0.2 mL of mineral oil or perfluorohydrocarbon is added from a syringe. The flask is swirled to generate a mull from the oil–compound mixture. The ball bearings or glass beads cause effective mixing of the oil and compound. If the consistency of the mull is considered to be satisfactory, a third aliquot of D_2O or CH_3OD is added and the flask is again swirled. This third aliquot of deuterating solvent compensates for any moisture which may be present in the mineral oil or perfluorohydrocarbon. At this stage the compound generally dissolves in the D_2O or CH_3OD phase, resulting in two clear layers. Vacuum is then applied, while continuing to swirl the flask, and the D_2O or CH_3OD gradually evaporates, resulting again in a mull with cloudy appearance. Evaporation of the D_2O is complete in 7–8 min; evaporation of CH_3OD is considerably faster. The volatilization of solvent can be expedited somewhat by gentle heating of the flask by means of the hot-air gun; however, care must be exercised so as not to lose more volatile compounds by sublimation. After the third aliquot of deuterating solvent has been removed, the vacuum is released, a portion of the deuterated mull is removed from the flask by means of a rubber policeman and applied to the infrared windows, and its spectrum is recorded.

The mull of the undeuterated compound may be prepared in the conventional manner. However, in order to avoid potential complications resulting from the undeuterated and deuterated forms of the compound existing in different crystalline modifications it is advisable to first dissolve the compound in the corresponding hydrogen form of the solvent (H_2O or CH_3OH). In fact, we have found that the spectra of both forms of the compound can be conveniently obtained in a single sequence of operations: H_2O or CH_3OH is first added to the mull of oil-plus-compound in the round-bottom flask; after evaporation of solvent a portion of the mull is removed and its spectrum is recorded; the compound in the residual mull is then deuterated by successive additions of three aliquots of D_2O or CH_3OD, after which the spectrum of the deuterated compound is recorded. The complete procedure can be readily carried out in a 1-h period.

Some workers may prefer to avoid the use of Tygon tubing and to use an all-glass vacuum line. For this type of arrangement the ball bearings can be rotated around the inside of the flask by means of a magnetic stirring bar contained within the flask and driven by a magnetic stirrer.

The D_2O or CH_3OD which is removed is retained in the vapor traps. It is good practice to clean the vapor traps after each experimental run, particularly when deuteriomethanol is used, as this solvent does not freeze at dry ice temperatures. The rubber septum is replaced by a new one after each experimental run.

RESULTS AND DISCUSSION

We have applied the above deuteration technique to all of the following compounds with very satisfactory results: 2-hydroxybenzyl alcohol, *p*-hydroxybenzaldehyde, dimethylglyoxime, *p*-toluic acid, *p*-aminobenzoic acid, pyrogallol, sorbitol, 3,5-dimethylbenzoic acid, phenylacetic acid, and *p*-nitrophenylhydrazine. Typical results are illustrated in Figure 1. The wavenumber axis in Figure 1 is linear between 800 and 2000 cm^{-1}; it is also linear, but with a different scale, between 2000 and 4000 cm^{-1}. Perfluorohydrocarbon is essentially opaque to infrared radiation below $\sim$1350 cm^{-1}, and mineral oil has absorption bands at about 2900, 1460, and 1380 cm^{-1}. A combination of these two media provides an infrared window from 650 to 4000 cm^{-1}. The changes in the position of absorption bands, resulting from deuteration, are clearly illustrated. For example, the two OH stretching bands of 2-hydroxybenzyl alcohol at $\sim$3420 and $\sim$3140 cm^{-1} are replaced by OD absorption bands at $\sim$2570 and $\sim$2370 cm^{-1}, respectively. The aliphatic CH stretching bands at 2900 and

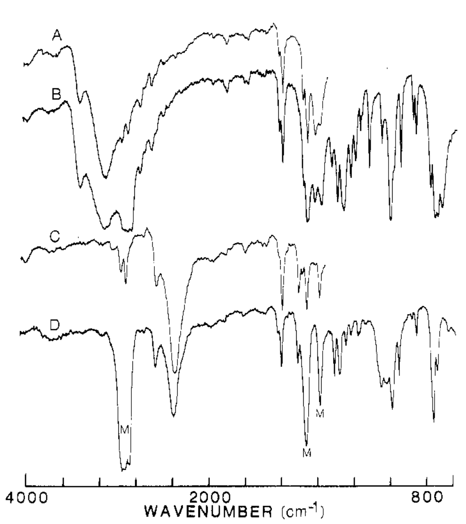

Figure 1. Infrared spectra of: 2-hydroxybenzyl alcohol (a) in perfluorohydrocarbon, (b) in mineral oil; deuterated 2-hydroxybenzyl alcohol (c) in perfluorohydrocarbon, (d) in mineral oil. Deuterating solvent was CH_3OD. The absorption bands of the mineral oil in (d) are designated by M.

2950 cm^{-1}, which are normally obscured by the OH absorption band at ~3140 cm^{-1} (Figure 1a), are clearly revealed in the spectrum of the deuterated compound (Figure 1c). Similarly, the aromatic CH stretching band, which is concealed in the spectrum of the hydrogen form of the compound, is evident at ~3050 cm^{-1} in the deuterated material (Figure 1c). Other spectral changes resulting from deuteration are evident in the spectra of Figure 1. The spectra of the deuterated samples show little or no evidence of residual OH bands.

Broomhead (*5*) has previously mentioned the preparation of mulls of deuterated compounds by the conventional mortar and pestle technique. We applied the conventional mulling technique to a selection of the compounds listed above. In those experiments, three aliquots of the deuterating solvent were successively added to the mull contained on the mortar; after mixing, each aliquot was evaporated by placing the mortar and contents in an oven for a short period. This technique resulted in only partial deuteration in all cases. On the other hand, the evacuated flask technique is a highly reproducible and effective method of deuteration. We also found that, once the mull of the deuterated compound had been prepared inside the evacuated flask, it could subsequently be exposed to a relatively high humidity atmosphere for extended periods of time without deteriorating significantly. Presumably, the oil forms an effective coating which excludes atmospheric moisture from contacting the deuterated compounds.

One should be aware of the possibility of certain compounds becoming methylated through contact with CH_3OD. This was the case with phenylboric acid which undergoes a facile methylation reaction (*6*).

Finally, the method of deuteration as described here requires the use of 100 mg of compound. However, the method can be readily scaled down to deal with smaller quantities of material.

LITERATURE CITED

(1) Fales, H. M.; Robertson, A. V. *Tetrahedron Lett.* **1962**, 111.
(2) Worley, J. D.; Garteiz, D. A. *J. Chem. Educ.* **1969**, *46*, 608.
(3) Carlson, G. L.; Fateley, W. G.; Bentley, F. F. *Spectrochim. Acta, Part A* **1972**, *28A*, 177.
(4) Potts, W. J., Jr.; "Chemical Infrared Spectroscopy"; Wiley: New York, 1963; Vol. I, pp 141–148.
(5) Broomhead, J. A. *J. Am. Chem. Soc.* **1968**, *90*, 4480.
(6) MacCarthy, P.; Bowman, S. J. *J. Chem. Educ.*, in press.

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