Application of Lanthanide Shift Reagents to Alkyl Fluorides[1]

Sir:

The utility of certain lanthanide β-diketoenolate complexes in NMR studies of organic compounds, first demonstrated by Hinckley,[2] has been expanded on by others.[3] In practice, the use of these complexes has been restricted to systems containing relatively basic heteroatom centers, such as oxygen, nitrogen, and, to a lesser extent, phosphorus and sulfur. Here we wish to report the application of these reagents to the study of the ^{1}H NMR spectra of alkyl fluorides.

Figure 1 illustrates the influence of Yb(fod)$_3$ on the ^{1}H NMR spectrum of *n*-propyl fluoride.[4,5] Several features about these and related data are revealing. First, it is apparent that the induced chemical shift differences decrease as the average distance from the fluorine atom to the nucleus under observation increases. Second, resolution of shifted resonances is poorest for nuclei closest to the fluorine center and improves as the distance increases. Initial addition of Yb(fod)$_3$ eliminates the spin-spin coupling between adjacent methylene protons as well as remote proton-fluorine coupling. Further addition ultimately removes both the more remote proton-proton coupling and the large geminal proton-fluorine coupling. Third, successive observations carried out over a range of concentrations indicate that the observed chemical shift displacements increase monotonically with increasing lanthanide concentration. Fourth, under equivalent conditions, Yb(fod)$_3$ provides significantly greater chemical shift displacements (ca. an order of magnitude) than Eu(fod)$_3$. However, this advantage is partially offset by decreased spectral resolution (increased line widths), a characteristic of Yb(III) shift reagents that is presumably a reflection of the relatively longer spin-lattice relaxation time of the unpaired electrons on ytterbium compared to europium. Nonetheless, complimentary application of Eu(fod)$_3$ and Yb(fod)$_3$ provides a useful means of separating the resonances of alkyl fluorides: proximal protons can be shifted by Eu(fod)$_3$ without significant line width broadening while similar results can be achieved for more remote protons using Yb(fod)$_3$.[6] The dramatic effect which Yb(fod)$_3$ can have on the ^{1}H NMR spectrum of an alkyl fluoride is manifest in the spectrum of *n*-octyl fluoride (Figure 2) in which all eight nonequivalent protons are clearly visible. Equivalent results were obtained with *sec*-octyl fluoride. Induced shifts were not observed in the ^{1}H NMR spectrum of *n*-octyl chloride, bromide, or iodide under similar conditions.

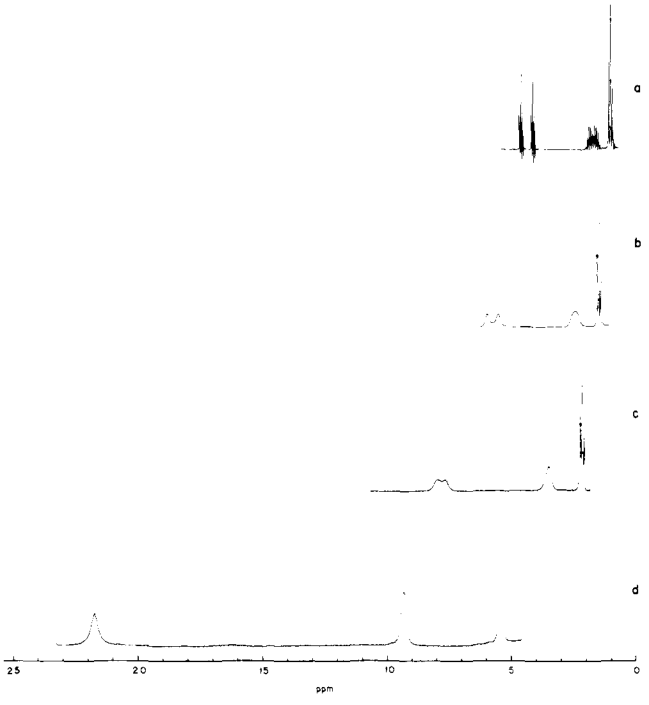

Figure 1. Spectra (100 MHz) of *n*-propyl fluoride (~0.3 *M*) in the presence of increasing concentrations of Yb(fod)$_3$ in CCl$_4$. The concentration of Yb(fod)$_3$ in these spectra is ca. (a) 0.0 *M*, (b) 0.1 *M*, (c) 0.2 *M*, and (d) 0.5 *M*.

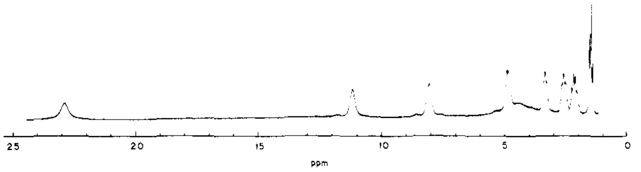

Figure 2. The influence of Yb(fod)$_3$ (ca. 0.5 *M*) on the ^{1}H NMR spectrum (100 MHz) of *n*-octyl fluoride (ca. 0.3 *M*) in CCl$_4$. The asterisk (*) denotes water impurity.

The nature of the interactions between an alkyl fluoride and a lanthanide shift reagent remains unclear. One possibility involves the formation of a fluorine-coordinated lanthanide-fluoroalkane complex accompanied by basically the same magnetic interactions responsible for the induced shifts witnessed in organic substrates containing much more basic heteroatom centers.[3] An alternative mechanism in which the lanthanide-substrate complex results from a purely electrostatic interaction between the highly polar C-F bond and the electropositive lanthanide center cannot at present be dismissed. A fuller discussion of these and related studies will be presented in other papers.

References and Notes

(1) Supported by the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) C. C. Hinckley, *J. Am. Chem. Soc.*, **91**, 5160 (1969).

(3) R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents", Academic, New York, N.Y., 1973, and references therein.

(4) A detailed analysis of the ^{1}H NMR spectrum of *n*-propyl fluoride at room temperature has been carried out: D. L. Hooper, N. Sheppard, and C. M. Woodman, *J. Mol. Spectrosc.*, **24**, 277 (1967).

(5) Both Yb(fod)$_3$ and Eu(fod)$_3$ are commercially available from several sources.

(6) NOTE ADDED IN PROOF. Under comparable conditions, tris(1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedionate)europium(III), Eu(dfhd)$_3$,[7] produces substantially greater chemical shift displacements (~4 ppm for the α-methylene protons in *n*-octyl fluoride) than does Eu(fod)$_3$.

(7) W. G. Scribner, B. H. Smith, R. W. Moshier, and R. E. Sievers, *J. Org. Chem.*, **35**, 1696 (1970); M. F. Richardson, W. F. Wagner, and D. E. Sands, *J. Inorg. Nucl. Chem.*, **30**, 1275 (1968); M. F. Richardson and R. E. Sievers, *Inorg. Chem.*, **10**, 498 (1971).

Joseph San Filippo, Jr.,* Ralph G. Nuzzo, Louis J. Romano
School of Chemistry, Rutgers University
New Brunswick, New Jersey 08903

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Electroorganic Chemistry. XXII. Novel Anodic Cleavage of Glycols to Carbonyl Compounds

Sir:

Although the cleavage of 1,2-diols by oxidizing agents such as chromic acid,[1] lead tetraacetate,[2,3] or periodic acid[2,3] has been well studied, these cleavages are not necessarily useful because of the troublesome work-up. However, in the present study, the anodic oxidation[4] of 1,2-glycols