The stereochemical results[7] (Table II) indicate a high per cent retention which is approximately the same as that reported for the nitrosoamide decompositions of 1-phenylethylamine[5] and 3$\beta$-cholestanylamine[8] in acetic acid (OH and OD). Note that the solvent-derived products were formed with net retention of configuration (Table II).[9] The mechanism for the decomposition of III is presumably the same as that outlined for 1-phenylethylamine.[5]

(7) Using values of G. H. Green and J. Kenyon (*J. Chem. Soc.*, 751 (1950)) for benzhydrol, values of G. R. Clemo, C. Gardner, and R. Raper (*ibid.*, 1958 (1939)) for the amine, and the fact that all previous nitrosoamide reactions in polar solvents have proceeded with retention of configuration. Suitable controls were run to ensure the validity of the O-18 and stereochemical results.

(8) E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 77 (1965).

(9) For a related example, see E. H. White and J. E. Stuber, *J. Am. Chem. Soc.*, **85**, 2168 (1963), and for an example of retention observed in the solvolysis of a benzhydryl ester, see H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, **85**, 3059 (1963).

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## Anomalous Rotatory Dispersion of 1-Butyl-1-*d* Acetate

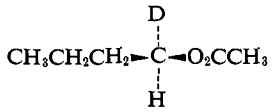
*Sir:*

It is now established, both theoretically[1] and experimentally,[2] that molecules which are optically active because of hydrogen–deuterium asymmetry[3] do not differ in principle from normally asymmetric molecules.

Investigation of the optical rotatory dispersion (ORD) of several deuterium compounds, $R_1CHDR_2$, resulted in the observation of plain dispersion curves.[2] However, measurements could not be carried out in the region of electronic absorption due to the small optical activity and high absorptivity exhibited by these compounds. Since the Cotton effect is observed only in the vicinity of an absorption band, it was not possible to demonstrate experimentally whether molecules which are optically active because of H–D asymmetry are capable of exhibiting measurable Cotton effects.

We wish to report what we believe to be the first observation of a Cotton effect in a molecule which owes its optical activity solely to isotopic substitution.

(*R*)-(+)-1-Butyl-1-*d* acetate, (+)-**1**, $[\alpha]^{27}D$ +0.687°,



$$CH_3CH_2CH_2-\overset{D}{\underset{H}{C}}-O_2CCH_3$$

(+)-**1**

was prepared from (*R*)-(−)-butanol-1-*d*[4] by treatment with acetyl chloride and pyridine. Since preparation of the ester does not involve the asymmetric center, (+)-**1** is also 59% of optical purity.

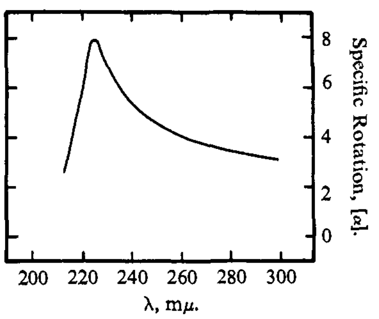


Figure 1. Optical rotatory dispersion curve of (*R*)-(+)-1-butyl-1-*d* acetate in isooctane solution.

The ultraviolet ORD curve of (+)-**1** in isooctane solution is shown in Figure 1. The first extremum of a positive Cotton effect is observed with a peak at 226 mμ. Because of a decreasing rotation:absorption ratio, measurements were possible only to 212 mμ.[6] The results of the ORD data for (+)-**1** indicate that optically active deuterium compounds can be expected to exhibit weak but measurable Cotton effects.

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(1) W. Fickett, *J. Am. Chem. Soc.*, **74**, 4204 (1952).

(2) A. Streitwieser, Jr., L. Verbit, and S. Andreades, *J. Org. Chem.*, 30, 2078 (1965); M. Sprecher, R. Berger, and D. B. Sprinson, *J. Biol. Chem.*, **239**, 4268 (1964); J. W. Cornforth, G. Ryback, G. Popjak, C. Donninger, and G. Schroepfer, Jr., *Biochem. Biophys. Res. Commun.*, **9**, 371 (1962). Professor H. S. Mosher, Stanford University, has very kindly communicated the results of some preliminary ORD measurements of derivatives of neopentyl alcohol-1-*d* made in 1960: H. S. Mosher and V. E. Althouse, unpublished work.

(3) A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959).

(4) The 1-butanol-1-*d* was prepared *via* the asymmetric hydroboration reaction (A. Streitwieser, Jr., and L. Verbit, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Abstracts, p 50N) and was 59% optically pure.[5] Nmr analysis indicated the presence of 0.97 ± 0.05 D per molecule.

(5) V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *ibid.*, **88**, 3595 (1966), report $[\alpha]^{27.5}D$ 0.471° for 1-butanol-1-*d* prepared enzymatically.

(6) A JASCO recording spectropolarimeter was used. Measurements were carried out under constant nitrogen flush using the ±30 millidegree scale. In order to guard against instrument artifacts such as stray light, the sample absorbance was kept below 2. Base-line measurements were taken using unlabeled (thus inactive) *n*-butyl acetate in isooctane at the same concentration at which the optically active sample was run. A 450-w high-pressure xenon arc with less than 50 lamp-hr was used as the source.

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## Fluorescence and Room-Temperature Laser Action of Trivalent Neodymium in an Organic Liquid Solution

*Sir:*

In two recent communications, we reported fluorescence and laser action of trivalent neodymium in an aprotic inorganic solvent.[1,2] The present communication extends this study to organic liquid systems.

Excited neodymium undergoes radiationless relaxation by two mechanisms: direct energy transfer to a vibration of the environment[3] and self-quenching.[4] Both the choice of the solvent and the design of the solute for the present system were aimed to reduce these.

(1) A. Heller, *Appl. Phys. Letters*, **9**, 106 (1966).

(2) A. Lempicki and A. Heller, *ibid.*, **9**, 108 (1966).

(3) A. Heller, *J. Am. Chem. Soc.*, **88**, 2058 (1966).

(4) G. E. Peterson and P. M. Brindenbaugh, *J. Opt. Soc. Am.*, **54**, 644 (1964).