resonances were observed to shift dramatically downfield, to which we assign the hydrogens flanking the carbonyl, H_1 and H_{10}, respectively. One of the three relatively unshifted bridgehead hydrogens appears as a quartet (J = 5 Hz) and is coupled to H_2, the hydrogen β to the carbonyl, and both of the remaining bridgehead hydrogens, H_4 and H_7. Only ketone 1 is consistent with these observations.[16]

The most likely mechanism for the **3 → 1** transformation appears to be silver-assisted ionization of **3**, ring opening to give the homobullvalenyl cation, **8a**, subsequent rearrangement to give **8b**, and hydrolysis to afford **9**.[16] The **9 → 1** conversion may proceed *via* 1,3-alkyl shift or through intermediate **10**, isoelectronic with
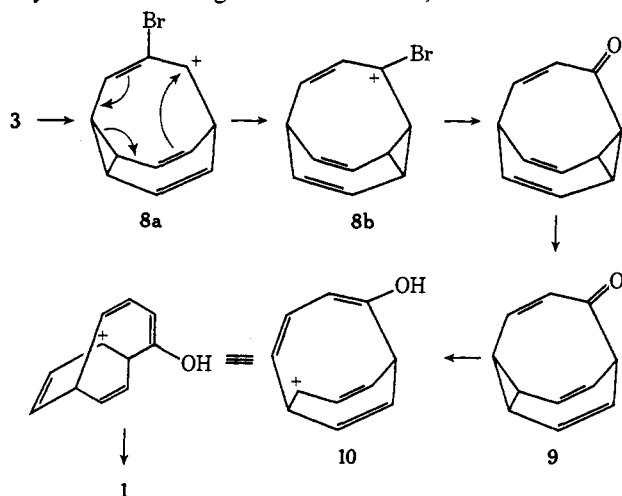
2. The relative ease with which this **3 → 1** transformation occurs may be indicative of substantial strain relief in passing from **9** to **1** or electronic stabilization of **10**. It is also possible that the orbital symmetry expectations in this rearrangement are affected by mediating silver ion.[17] We are currently studying these and other aspects of this reaction.

(16) The synthesis and interconversions of the higher homologous enones of bullvalene have recently been described; **9** is clearly inconsistent with the lack of symmetry in the nmr spectrum of 1; see M. J. Goldstein, *et al.*, ref 8.
(17) (a) L. A. Paquette, *Accounts Chem., Res.*, 4, 280 (1971), and references therein; (b) P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, 92, 763 (1970).

John T. Groves,* **Beverly S. Packard**
Department of Chemistry, The University of Michigan
Ann Arbor, Michigan 48104
Received November 24, 1971

Separation of Nuclear Magnetic Resonance Signals of Internally Enantiotropic Protons Using a Chiral Shift Reagent. The Deuterium Isotope Effect on Geminal Proton–Proton Coupling Constants

Sir:

Recent studies[1] on a variety of chiral shift reagents have shown that such compounds are capable of induc-

(1) (a) G. M. Whitesides and D. W. Lewis, *J. Amer. Chem. Soc.*, 92, 6979 (1970); (b) G. M. Whitesides and D. W. Lewis, *ibid.*, 93, 5914
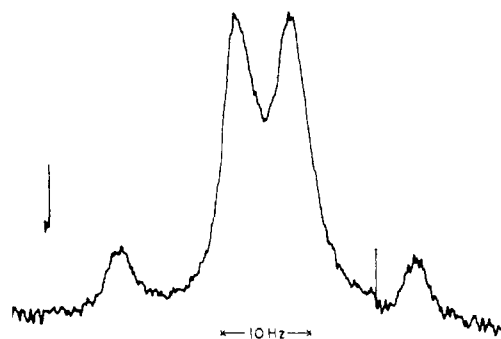
Figure 1. The methylene proton absorption of a 0.2 M solution of benzyl alcohol in CCl_4 in the presence of 0.15 mol equiv of 1.

ing differential pseudocontact shifts[2] for corresponding protons in the R and S enantiomers of certain organic Lewis bases. Their ability to differentiate enantiotropic[3] protons at a prochiral[3] center was recognized but not observed experimentally.[1c] We wish to report that tris[3-heptafluoropropylhydroxymethylene-*d*-camphorato]praseodymium(III) (**1**) possesses the ability to induce a chemical-shift difference of up to 0.8 ppm (per molar equivalent[4] of added shift reagent) between the benzylic protons of benzyl alcohol and its derivatives. Such resolution of signals for enantiotropic protons provides an alternative to the isotopic substitution method for the determination of geminal coupling constants. In addition, the latter method will be shown to be in error due to a small isotope effect on the geminal coupling constant, and relaxation effects.

When a 0.2 M solution of benzyl alcohol in CCl_4 was treated with 0.15 mol equiv[4] of **1**, the CH_2 protons were shifted 6.63 ppm to higher field and appeared as an AB quartet having J_{AB} = 13.0 ± 0.2 Hz[5] and $\Delta\nu_{AB}$ = 0.13 ppm (see Figure 1). This resolution of the benzylic protons must result from their shift nonequivalence as diastereotopic protons in the complex of benzyl alcohol with **1**. The possibility exists that J_{AB} may also contain a significant contribution from this complex. We therefore determined J_{AB} at three other concentrations of **1**. As shown in Table I, J_{AB} does not vary measurably until more than 0.3 equiv of **1** has been added. We therefore conclude that J_{AB} = 13.0 ± 0.2 Hz in benzyl alcohol. To confirm this value, J_{H-D} for O-α-dideuteriobenzyl alcohol in chloroform at 39 and at 49° was found[6] to be 1.91 ± 0.01, in fair agreement (0.6 Hz) with the direct measurement using **1**. The data for six para-substituted benzyl alcohols[7] and neopentanol are given in Table I.

(1971); (c) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *ibid.*, 93, 5913 (1971); (d) R. R. Fraser, M. Petit, and J. K. Saunders, *Chem. Commun.*, 1450 (1971).
(2) Recent evidence indicates that lanthanide-induced shifts are produced primarily by a pseudocontact mechanism; see (a) J. K. M. Saunders and D. M. Williams, *Tetrahedron Lett.*, 2812 (1971); (b) H. Huber and C. Pascal, *Helv. Chim. Acta*, 54, 913 (1971); for a recent compilation of references on shift reagents see W. DeW. Horrocks, Jr., J. P. Sipe III, and J. R. Luber, *J. Amer. Chem. Soc.*, 93, 5258 (1971).
(3) M. Raban and K. Mislow, *Top. Stereochem.*, 1, 1 (1967).
(4) Information regarding the stoichiometry of this donor–lanthanide complex in solution is not available.
(5) All geminal coupling constants discussed in this paper are assumed to be negative as has been established for other benzylic protons; see R. R. Fraser, *Can. J. Chem.*, 40, 1483 (1962).
(6) All other protons were spin decoupled during measurement of the spectra.
(7) A plot of ^2J *vs.* Hammett σ constants for the seven benzyl alcohols gives a slope (ρ) = −1.53 (r = 0.960). The magnitude of ρ in compari-

Table I. Effect of 1 on Enantiotropic Protons of RCH₂OH[a]

R	PS,[b] ppm	Mole ratio (1/ RCH₂OH)	J_{AB}, Hz	$\Delta\nu_{AB}$,[c] ppm
Ph	6.63	0.15	13.0 ± 0.2	0.13
Ph	10.03	0.21	13.0 ± 0.2	0.19
Ph	11.72	0.28	12.9 ± 0.2	0.22
Ph	15.29	0.38	12.5 ± 0.3	0.26
4-CNPh	12.18	0.30	14.5 ± 0.5	0.12
4-CF₃Ph	10.58	0.27	14.0 ± 0.2	0.15
4-FPh	10.21	0.26	13.2 ± 0.2	0.08
4-CH₃Ph	9.48	0.23	12.8 ± 0.2	0.15
4-CH₃OPh	11.31	0.22	13.0 ± 0.4	0.11
4-N(CH₃)₂Ph	8.74	0.22	12.5 ± 0.4	0.09
t-Bu	11.06	0.27	12.0 ± 0.5	0.12

[a] All spectra were measured on a Varian HA-100 spectrometer at 26° using 0.2 M solutions of the alcohol in CCl₄. Coupling constants are reported as the average of at least eight determinations with the quoted uncertainty representing the standard deviation. [b] PS represents the upfield shift induced by addition of 1. [c] $\Delta\nu_{AB}$ represents the nonequivalence of the enantiotropic protons.

The 12.0-Hz geminal coupling constant in neopentanol is 1.6 Hz larger than the value of 10.4 Hz calculated[3] from the 1.6-Hz H–D coupling constant in α-deuterioneopentanol.[9] This descrepancy can result from residual effects of deuterium relaxation,[10] an isotope effect on $J_{H–D}$,[8] or both. From the line width (>1 Hz) in the published spectra it appears likely that relaxation effects are influencing their measurement of $J_{H–D}$.

In order to determine the isotope effect of deuterium substitution on ^2J, we have examined the nmr spectrum of a 1:3 mixture of benzyl methyl sulfoxide and its stereoselectively labeled[11] α-deuterio derivative in acetone. The effect of nuclear quadrupole relaxation on the H–D splittings was shown to be nil by measuring[6] $J_{H–D}$ at 34 and 45°. At both temperatures the line widths for the triplet were 0.6 Hz and $J_{H–D}$ was 1.92 ± 0.01 Hz. The value for $J_{H–H}$ was 12.97 ± 0.02 Hz. Thus, the discrepancy between $J_{H–H}$ (measured) and $J_{H–H}$ (calculated, i.e. 1.92 × 6.514 = 12.51 Hz) is 0.46 Hz. This value represents an accurate assessment (±0.2 Hz) of the isotope effect on $J_{H–H}$. This effect, though probably constant, must be investigated further.

Addition of 1 to solutions of benzylamine, dibenzylnitrosamine, and allyl alcohol failed to effect a resolution of the signals for the enantiotropic protons. However, in the only two cases studied, enantiotropic methyl groups were distinguishable. The methyl groups of dimethyl sulfoxide showed a nonequivalence of 0.17 ppm in the presence of 0.34 equiv of 1 while those of 2-

propanol possessed a nonequivalence of 0.04 ppm in the presence of 0.27 equiv of 1, both measured in CCl₄. It can be concluded from the above results that chiral shift reagents offer a potent method for distinguishing nmr signals of internally enantiotropic groups.

It seems likely that 1 and future chiral reagents of improved potency will be of great use in the determination of geminal coupling constants and in the solution of complex stereochemical problems.

Robert R. Fraser,* Michel A. Petit, Maurice Miskow
Department of Chemistry, University of Ottawa
Ottawa, Canada K1N 6N5

Nitrogen-Centered Free Radicals. IV. An Electron Spin Resonance Study of Transient Dialkylaminium Radical Cations[1]

Sir:

Transient dialkylaminium radical cations, $R_2\dot{N}H^+$, are of interest to chemists not only because they are isoelectronic with alkyl radicals but also because these species are finding increasing use as chain-carrying intermediates in novel synthetic applications.[2–5] We presently wish to report the high-resolution electron spin resonance (esr) spectra of several dialkylaminium radical cations generated by photolysis of sulfuric acid solutions of the corresponding N-chloramines directly in the cavity of the esr spectrometer.[6,7] Re-

$$R_2NCl \xrightarrow[H_2SO_4]{h\nu} R_2\dot{N}H^+$$
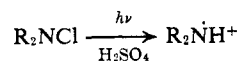
sults are reported in Table I along with the corresponding neutral dialkylamino radicals which we have reported previously.[9] Representative spectra are shown in Figure 1; satisfactory computer simulations have been obtained for all radicals.

(1) Part III: W. C. Danen and C. T. West, J. Amer. Chem. Soc., 93, 5582 (1971).
(2) (a) N. C. Deno, W. E. Billings, R. Fishbein, C. Pierson, R. Whalen, and J. C. Wyckoff, ibid., 93, 438 (1971); (b) N. C. Deno, R. Fishbein, and J. C. Wyckoff, ibid., 93, 2065 (1971).
(3) (a) R. S. Neale, J. Org. Chem., 32, 3263 (1967); (b) R. S. Neale and N. L. Marcus, ibid., 32, 3273 (1967); (c) R. S. Neale and M. R. Walsh, ibid., 30, 3683 (1967); (d) R. S. Neale, M. R. Walsh, and N. L. Marcus, J. Amer. Chem. Soc., 87, 1255 (1965).
(4) M. E. Wolff, Chem. Rev., 63, 55 (1963).
(5) (a) F. Minisci, R. Galli, and G. Pollina, Chim. Ind. (Milan), 47, 736 (1965); (b) F. Minisci, ibid., 49, 705 (1967); (c) F. Minisci, R. Galli, and M. Cecere, Tetrahedron Lett., 3163 (1966).
(6) A PEK AH6-2B, 2000-W, high-pressure mercury capillary lamp was utilized in conjunction with a suitable lens system.
(7) Neta and Fessenden have recently postulated the formation of dimethylaminium and aziridinium radical cations by high-energy electron irradiation of acidic solutions of trimethylamine and dimethylamine, respectively.[8] Although the coupling constants attributed to (CH₃)₂NH⁺ differ considerably from the values herein reported, subsequent investigations by these workers revealed a misinterpretation of spectra and that (CH₃)₃N⁺ and (CH₃)₂NH⁺ were instead being produced from the respective amines (private communication from R. W. Fessenden).
(8) P. Neta and R. W. Fessenden, J. Phys. Chem., 75, 738 (1971).
(9) W. C. Danen and T. T. Kensler, J. Amer. Chem. Soc., 92, 5235 (1970).

son with those previously measured in conformationally fixed benzyl ethers [R. R. Fraser and R. Renaud, Can. J. Chem., 49, 755 (1971)] is evidence that the dominant conformation about the CH₂–Ph bond is the one in which the oxygen atom lies in or nearly in the plane of the benzene ring.
(8) It has generally been assumed that a geminal $J_{H–H}$ can be determined by isotopic substitution of one H by D in which case the measurable $J_{H–D}$ multiplied by γ_H/γ_D (6.514) equals $J_{H–H}$ (see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 188). This assumption neglects changes in electron distribution resulting from the isotopic substitution.
(9) R. M. Moriarty, J. P. Kim, S. J. Druck, and E. Lustig, Tetrahedron, 25, 1261 (1969).
(10) Ch. Brevard, J. P. Kintzinger, and J. M. Lehn, Chem. Commun., 1193 (1969).
(11) (a) T. Durst, R. Viau, and M. R. McClory, J. Amer. Chem. Soc., 93, 3077 (1971); (b) T. Durst, R. R. Fraser, M. R. McClory, R. B. Swingle, R. Viau, and Y. Y. Wigfield, Can. J. Chem., 48, 2148 (1970). We wish to thank Mr. Viau for samples of the deuterated sulfoxide.