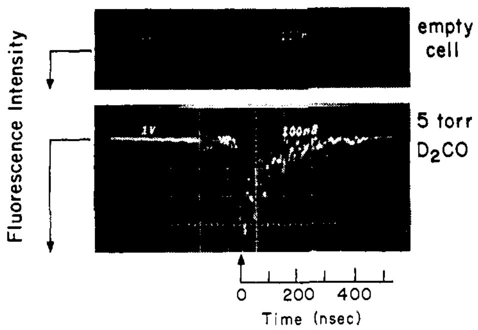

Figure 2. Fluorescence decay of D_2CO excited at 3139 Å.

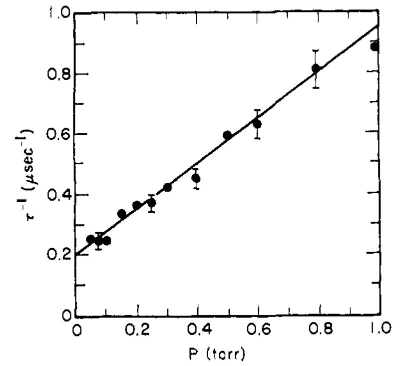

Figure 3. Stern–Volmer plot of inverse lifetimes of D_2CO excited at 3471 Å.

sary to further put a polarizing element in the dye cavity to obtain properly polarized laser output.

The dye laser output (ω_D) is 1 Å wide and can be tuned by suitable choice of dye, dye concentration, and grating position. Typically, for a 10^{-4} *M* solution of Rhodamine-6G in ethanol, the output at 5730 Å is 800 kW and 10 nsec wide, as measured on an Eppley bismuth–silver 16-junction thermopile. The dye laser is reflected by M2 through M5 onto the summing crystal. Meanwhile, the ruby fundamental is reflected by M4 and made collinear with the dye laser by M5. Summing is achieved by a 2-in. long KDP crystal (KDP2) rotated to the phase-matching angle of 56° 26′ for summing 6943 and 5730 Å to give 3139 Å. A tunable uv output of 200 kW has been measured by comparison with an attenuated beam of 3471 Å on a photomultiplier tube.

The uv radiation is separated from the visible radiation by M6 and passes into a 0.75-in. diameter Pyrex sample cell. Fluorescence is observed through a Spex 1400 double monochromator with slits parallel to the cell and detected by an Amperex 56AVP photomultiplier on a Tektronix 7704 oscilloscope. A typical trace is shown in Figure 2. It should be noted that one photon has a height of one-tenth of a vertical division. The trace shows the intrinsic photon counting fluctuation.

We have excited D_2CO with 3139-Å light, corresponding to 3 quanta of C=O stretching excitation[5] (3544 cm^{-1}). A lifetime for 4220-Å fluorescence emission (20-Å band width) of 103 ± 15 nsec was found. No observable pressure dependence was found from 3 to 10 Torr, corresponding to 3–10 collisions per lifetime.

We have also excited the 1 − level of the inversion[5] (501 cm^{-1}) of D_2CO with 3471-Å radiation and obtained an extrapolated zero-pressure lifetime of 5.0 ± 0.6 μsec. The Stern–Volmer plot of inverse lifetimes for observation at 4220 Å is shown in Figure 3. The plot is linear over the range of 0.05–10 Torr. The slope is 0.74 μsec^{-1} Torr^{-1}, corresponding to a quenching cross section of 1.2 Å^2.

With this experimental technique we hope to be able to study predissociation or intersystem crossing as a function of vibrational excitation of each normal mode. Experiments are under way with formaldehyde and its mono- and dideuterated species. The tuned-laser excitation method can easily be extended to study other molecules as well.

Acknowledgment. We wish to thank the National Science Foundation for a grant which supported this work.

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[6] University of California Science Fellow.

[7] Alfred P. Sloan Fellow.

An Alternative to Donor–Acceptor Pseudocontact-Shift Nuclear Magnetic Resonance Shift Reagents[1]

Sir:

Recently a group of nmr shift reagents based on donor–acceptor bonds and the pseudocontact-shift effect have received much favorable and deserved attention.[2–8] The success of this group of shift reagents leads to an interest in other groups of reagents which can serve in complementary roles. This report describes one such group.

The reagents of this group rely on the ring-current effect of certain germanium–porphyrin systems for field asymmetry and on covalent bonds between the germanium atom of the porphyrin and the compound of interest for holding the reagent in place. The covalent bonds are formed by the reaction of appropriate functional groups on the macrocyclic germanium atom (halo or hydroxy groups) with appropriate groups on the compounds. Serving among the latter are ordinary organometallic groups (*e.g.*, the groups of organolithium and Grignard compounds) and both weakly acidic hydroxyl groups and strongly acidic hydroxyl groups (*e.g.*, the groups of alcohols, phenols, and carboxylic acids).[9] The utility of the reagents with

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[1] Support for this work was provided by the National Science Foundation through Grant No. GP-8368 and through a Traineeship.

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[7] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *ibid.*, **92**, 5737 (1970).

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[9] The ground work for the use of porphyrins as shift reagents with hydroxylic compounds has been laid clearly in previous work, par-

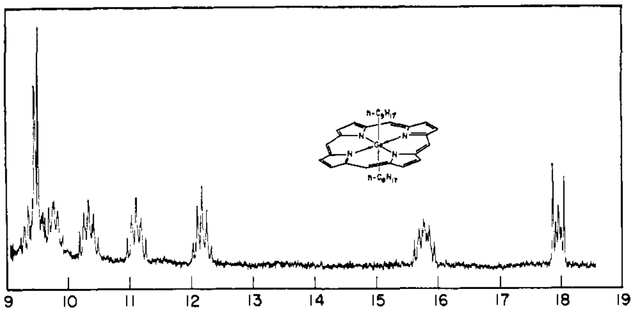

Figure 1. The upfield portion of the 100-MHz spectrum of dioctylgermanium porphin in $CDCl_3$.

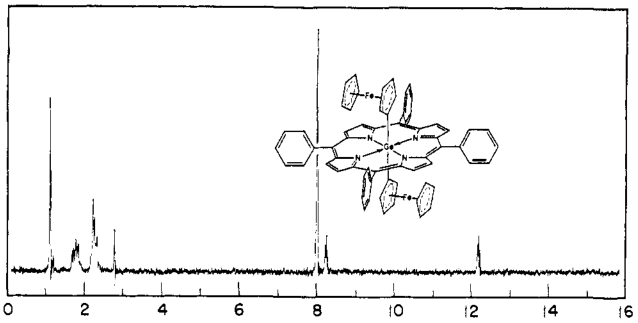

Figure 2. The 60-MHz spectrum of bis(ferrocenyl)germanium tetraphenylporphin in $CDCl_3$.

organometallic groups is of particular importance because the pseudocontact shift reagents are not applicable to such groups and because many compounds containing them (or convertible to compounds containing them) are of interest. The utility of the reagents with carboxylic acid and phenolic groups is also of importance since such acidic groups are reported to decompose the europium contact-shift reagent.[3] In addition the new reagents offer, where this may be desired, the option of nonlability of the reagent–compound bond.

The application of the reagents to compounds carrying organometallic functional groups is illustrated by work done with methyl and *n*-octyl Grignard reagents. For the methyl Grignard reagent the germanium–porphin system was used. An ether solution of methylmagnesium bromide (0.5 mmol) was added to a stirred refluxing mixture of dichlorogermanium porphin[10] (26 mg, 0.057 mmol) in benzene (25 ml) under nitrogen. The resulting red solution was refluxed for 10 min and cooled, and water (0.5 ml) was added. After a minute, the benzene layer was separated, dried over anhydrous sodium sulfate, centrifuged free of solids, and taken to dryness under vacuum. The resulting purple reflecting crystalline product was washed with pentane (23 mg, an essentially quantitative yield), and then was recrystallized from chloroform by the incremental addition of pentane.

A solution of the recrystallized product in deuteriochloroform gave sharp singlets at τ -0.43, 0.41, and 17.98 (Varian HA-100 data). These resonances are attributable respectively to the meso, β, and methyl protons. The position of the latter resonance is 8.11 ppm above that reported for the methyl resonance of tetramethylgermane.[11] Such a shift is approximately the maximum ordinarily to be obtained with porphyrin ring-current shift reagents.

For work with the octyl Grignard reagent again the germanium–porphin system was used. An ether solution of *n*-octylmagnesium bromide (0.5 mmol) was stirred with a mixture of dichlorogermanium porphin (26 mg, 0.057 mmol) in benzene (15 ml) under nitrogen. After 15 min, water (0.5 ml) was added to the resulting red solution and the mixture was worked up as above. The red product, upon being dried at 80° under vacuum, washed with pentane, and redried (24 mg), gave the spectrum shown in Figure 1.[12] The spectrum can be compared to those for the *n*-pentyl alcohol complex of tris(dipivalomethanato)praseodymium[4] and the *n*-hexyl alcohol complex of tris(dipivalomethanato)europium[3] (although, of course, the present spectrum pertains to the organic group derived from a Grignard reagent while the latter pertain to the organic groups of coordinated alcohols).

Studies carried out with bromoferrocene provide an example of the application of a porphyrin reagent to a compound with a group convertible to an organolithium group. Under nitrogen a hexane solution of *n*-butyllithium (0.5 mmol) was added with stirring to a solution of bromoferrocene[13] (153 mg, 0.58 mmol) in ether (3 ml) over 10 min. After 40 min, benzene (35 ml) was added followed by dichlorogermanium tetraphenylporphin[14] (100 mg, 0.13 mmol). Water (0.5 ml) was mixed with the resulting intensely green solution after 90 min. Work-up in the usual manner yielded blue reflecting crystals (65 mg). These were recrystallized from chloroform by the incremental addition of pentane.

The shifted and separated ferrocenyl portion of the spectrum of this compound, Figure 2, provides direct information about ring–ring rotation in the stereochemically nonrigid ferrocenyl group. The inner cyclopentadienyl ring is fixed with respect to the macrocycle[15] and thus gives an AA′BB′ multiplet. The outer ring is referenced to the macrocycle by the field gradients of the macrocycle and could give either a singlet or a complex multiplet. Since it gives a singlet at magnet temperature (*ca.* 27°) and down to $-100°$ (CS_2), it is clear that this ring rotates freely with respect to the other ferrocenyl ring in the temperature range studied.

To illustrate the use of a porphyrin shift reagent with a carboxylic acid, bis(acetoxy)germanium tetraphenylporphin was synthesized and studied. A mixture of dihydroxygermanium tetraphenylporphin (prepared

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ticularly that with silanols and the silicon phthalocyanine system; see, for example, A. R. Kane, J. F. Sullivan, D. H. Kenny, and M. E. Kenney, *Inorg. Chem.*, 9, 1445 (1970).

(10) A. R. Kane, R. G. Yalman, and M. E. Kenney, *ibid.*, 7, 2588 (1968); available from M and J Chemical Co., Cleveland Heights, Ohio 44118.

(11) R. Drago and N. Matwiyoff, *J. Organometal. Chem.*, 3, 62 (1965).

(12) Integration of the full spectrum of the compound gave the expected ratios.

(13) R. W. Fish and M. Rosenblum, *J. Org. Chem.*, 30, 1253 (1965).

(14) Prepared by a route analogous to that used for the corresponding porphin; available from M and J Chemical Co.

(15) It is presumed that the inner cyclopentadienyl ring is not perpendicular to the ring plane, but it is difficult to estimate how much it is tipped. It is also presumed that the two cyclopentadienyl rings are not parallel to each other.

by the hydrolysis of dichlorogermanium tetraphenylporphin, 300 mg, 0.42 mmol), acetic acid (238 mg, 4.0 mmol), and benzene (25 ml) was refluxed 1 hr. The resulting red solution was taken to dryness under vacuum and the red solid obtained washed with pentane. This product (334 mg) was recrystallized from benzene. *Anal.* Calcd for $C_{48}H_{34}N_4O_4Ge$: C, 71.76; H, 4.27; Ge, 9.04; OAc, 14.70. Found: C, 71.62; H, 4.25; Ge, 8.88; OAc, 14.65.

The nmr spectrum of this acetate in $CDCl_3$ showed a singlet at τ 11.08 together with the usual ligand multiplets (and two small impurity singlets, one attributable to hydrolytically formed free acetic acid and the other, of equal methyl intensity, attributable to hydrolytically formed monoacetoxy derivative). The position of the acetoxy singlet in the compound corresponds to a shift of 3.17 ppm from the analogous singlet of dilute acetic acid in $CDCl_3$.

Examples of the application of the reagents to alcohols (*e.g.*, *cis*-4-*tert*-butylcyclohexanol) and to phenols (*e.g.*, the highly hindered phenol 2,6-diisopropylphenol) have been worked out and will be reported later. An advantage of these reagents kindly pointed out by one of the referees is that, because of their diamagnetic nature, these reagents cannot lead to the paramagnetic broadening effects which sometimes become significant with the rare earth reagents.

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Electron Spin Resonance Spectra from Ultraviolet Irradiation in an Adamantane Matrix. The Primary Process for Aliphatic Amines

Sir:

In recent letters, Wood, *et al.*,[1,2] have reported a method for the preparation and esr study of free radicals in adamantane. The technique offers advantages over low-temperature isolation methods in that the samples are easy to prepare, the spectra are isotropic, and the radicals may have appreciable lifetimes at ambient temperature. The compounds studied were aliphatic amines. Radical species were formed by exposure to X-rays[1] and by dual irradiation, exposure to X-rays followed by exposure to uv.[2] Attempts to obtain spectra by exposure to uv only were unsuccessful.[2] This observation may lead to the conclusion that the method has severely limited usefulness for the study of photochemical processes in the uv region. We wish to report a simple extension of the technique which makes uv studies practical and results with some aliphatic amines.

The results obtained by the dual-radiation method indicate that failure to observe free radicals by uv irradiation alone was due to an intensity effect, since uv irradiation of free radicals, X-ray produced, induced formation of secondary radicals. Presumably, the initial radicals had much greater absorptivity than the parent compound. In the method used, adamantane was crystallized from solution, thereby trapping some of the solvent. The resulting small white crystals would be expected to scatter the incident uv light. To obviate this problem, we have made cylindrical pellets, 1.1 cm in diameter, of the crystallized adamantane at a pressure of 10.0×10^3 bars. The pellets present a milky translucent appearance. Esr spectra of uv-irradiated inclusions were readily obtained with the compounds studied, amines and chloro olefins.

For the compounds which both Wood, Lloyd, and Pratt,[2] and we have studied, analogous results were obtained. Using a mercury resonance arc housed in quartz, predominantly a source of a mixture of 185- and 254-nm light, the spectrum shown in Figure 1A was obtained from *n*-butylamine at ambient temperature. From the results with primary amines containing three or more carbon atoms, Wood, *et al.*,[2] suggest the reaction sequence

$$(R_1)(R_2)HC{-}NH_2 \xrightarrow{\text{X-ray}} \underset{\text{I}}{R_1R_2\dot{C}{-}NH_2} \xrightarrow{h\nu} \underset{\text{II}}{R_1R_2C{=}N\cdot}$$

where R_1 is an alkyl radical and R_2 is an alkyl radical or H. The computer fit, Figure 1B, was made using the reported coupling constants.[3] As the amines are virtually transparent at wavelengths greater than 240 nm, I may be attributed to absorption at 185 nm, while II may come from absorption of uv radiation by I. Subsequent irradiation with light from a high-pressure mercury arc gave the spectrum shown in Figure 1C. The central portion, radical I, has diminished, while the wings, radical II, have increased in intensity. Since radical II decays more rapidly than radical I, without this second radiation the central portion would have remained virtually unchanged while the wings would have diminished in intensity by some 15% in the elapsed time. Similar results were obtained with *n*-propylamine.

Preliminary results obtained with ethylamine, which was not included in the report of Wood, *et al.*,[2] are shown in Figure 2A. This system is more difficult to work with because of fast radical decay rates. The spectrum was not reproducible on the assumption of a mixture of I, $(CH_3)H\dot{C}{-}NH_2$, and II, $(CH_3)HC{=}N\cdot$. A better computer fit was obtained if III, $CH_3CH_2\dot{N}H$, was included, but even this was not completely successful.[4] Although additional work is required to completely elucidate the spectrum, evidence for ethylidenimino, II, is clear. The computer simulation, Figure 2B, of ethylidenimino was made using the following coupling constants: $a_\alpha{}^H$, 76.0; $a_\beta{}^H$, 3.1; a^N, 9.6 G. The fit is quite good in view of the interference from the other radicals present, the effect of which is expected to be most noticeable on the inner portions of the spectrum. The coupling constants are in reasonable agreement with values from INDO calculations:[5] $a_\alpha{}^H$, 60.0; a^N, 9.2; $a_\beta{}^{H(1)}$, 0.5; $a_\beta{}^{H(2)}$ =

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[1] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **52**, 3840 (1970).

[2] D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Amer. Chem. Soc.*, **92**, 4115 (1970).

[3] For radical I, from ref 1: $a_\alpha{}^H = a_\beta{}^H$, 14.8; $a_N{}^H$, 5.0; a^N, 4.8 G. For radical II, from ref 2: $a_\alpha{}^H$ 79.5; $a_\beta{}^H$, 2.8; a^N, 9.5 G.

[4] (a) A range of probable coupling constants was used to attempt a computer fit. The values were: $a_\alpha{}^H = 32.0 \pm 4.0$; $a_\beta{}^H = 32.0 \pm 4.0$; $a^N = 15.0 \pm 3.0$ G. These values are based on those given by (b) W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970), for isotropic N coupling and for β-proton coupling in dimethyl- and diethylamino radicals, and by (c) S. G. Hadley and D. H. Volman, *ibid.*, **89**, 1053 (1967), for β-proton coupling in methyl- and dimethylamino radicals.

[5] P. Svejda and D. H. Volman, *J. Phys. Chem.*, 74, 1872 (1970).