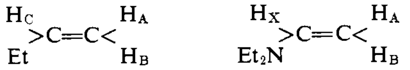
In Figure 1.3, the bands at b, d, and e are the characteristic remnants of 1-butene raser action;[1] the ABC pattern here is broken down into an absorption and an emission peak for each of the protons with the negative peak downfield from the positive peak. Thus e con-

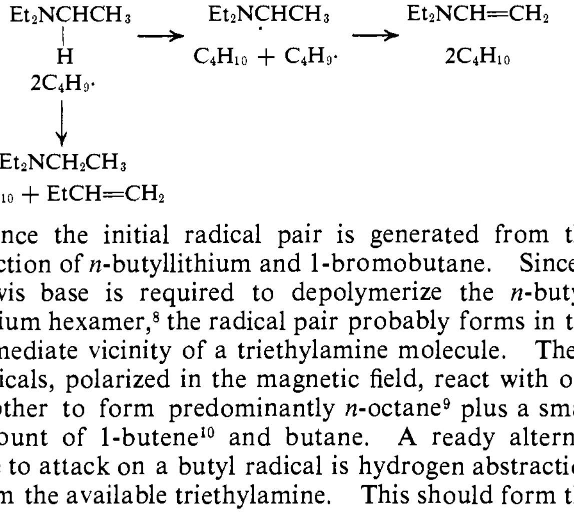


$$\overset{H_C}{\underset{Et}{>}}C{=}C\overset{H_A}{\underset{H_B}{<}} \qquad \overset{H_X}{\underset{Et_2N}{>}}C{=}C\overset{H_A}{\underset{H_B}{<}}$$

tains all the peaks of H_A and H_B, which have overlapping positive bands coupled by J_{AC} and J_{BC} with the two downfield negative multiplets. The chemical shift for H_C accounts for both b and d, but net cancelation of two of the normal triplets leaves only the outside emission and absorption pair. The other immediately assigned band was h, which, aside from the distortion of g, was obviously the unreacted 1-bromobutane H_X band.

The remaining bands, a, c, f, and g, showed the reverse relationship of absorption to emission pairs, *i.e.*, negative peak upfield from the positive peak, the inverse of b, d, and e. However, the same basic, if somewhat simplified, relationships hold for splitting, indicating an ABX system. H_A (upfield band of f, and g) is at δ 3.43 ppm, H_B (downfield band of f, and g) is at δ 3.49 ppm, and H_X (a and c) is at δ 5.92 ppm, with coupling constants of $J_{AB} = 0$ cps, $J_{AX} = 9.5$ cps, and $J_{BX} = 15$ cps. Although the pmr spectrum of the simplest vinylamine which might be anticipated in this system has not been reported,[6] it is possible from data on related amines[7] to justify the assignment of these bands to N,N-diethylvinylamine.

Chemically the origin of these compounds can be postulated by the reaction sequence 1. In this se-



$$\underset{2C_4H_9\cdot}{Et_2N\underset{\underset{H}{|}}{C}HCH_3} \longrightarrow \underset{C_4H_{10} + C_4H_9\cdot}{Et_2N\dot{C}HCH_3} \longrightarrow \underset{2C_4H_{10}}{Et_2NCH{=}CH_2}$$
$$\downarrow$$
$$\underset{C_4H_{10} + EtCH{=}CH_2}{Et_2NCH_2CH_3} \qquad (1)$$

quence the initial radical pair is generated from the reaction of *n*-butyllithium and 1-bromobutane. Since a Lewis base is required to depolymerize the *n*-butyllithium hexamer,[8] the radical pair probably forms in the immediate vicinity of a triethylamine molecule. These radicals, polarized in the magnetic field, react with one another to form predominantly *n*-octane[9] plus a small amount of 1-butene[10] and butane. A ready alternative to attack on a butyl radical is hydrogen abstraction from the available triethylamine. This should form the more stable α-amine radical, which undergoes subsequent loss of a second hydrogen to give the vinylamine observed in Figure 1.3. The absence of an emission band in the characteristic triplet of h confirms[11] the negligible amount of halogen–metal interchange, at least by radical processes.

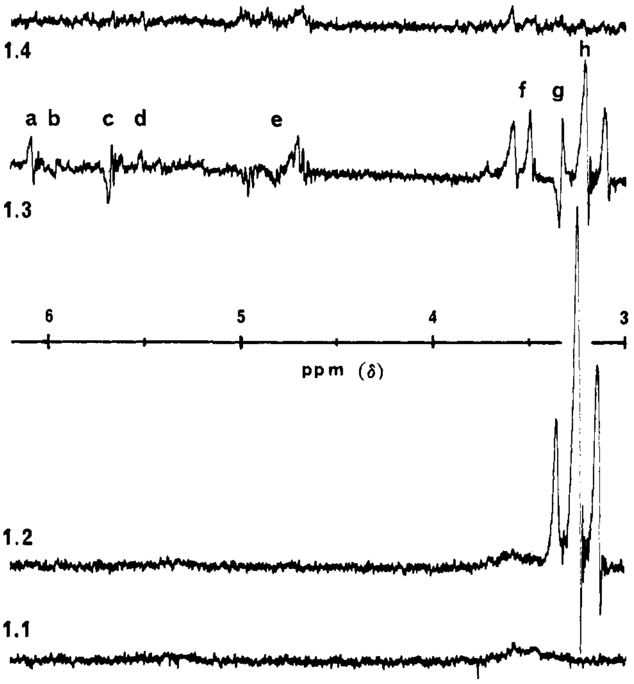


Figure 1. Proton magnetic resonance in the range δ 3–6.3 ppm for 0.5 ml of 1.5 *M n*-butyllithium in hexane (1.1), the addition of 0.07 ml of 1-bromobutane to this solution (1.2), and time scans (1.3 at 0.8 min and 1.4 at 10 min) after the addition of 0.25 ml of triethylamine.

Two mechanisms might account for the emission as well as absorption bands in the vinylamine produced. Either the intermediate amine radical is formed in an unpolarized state, but with a lifetime in the range necessary to allow its polarization,[2,12] or the polarization of the original butyl radical, which abstracts the hydrogen, is transmitted in the process of forming the amine radical. However, until more is known about the stabilities of such radicals and the emission–absorption relationships in the spectra, it is not possible to differentiate between these routes to polarization.[13]

Other amines tested as radical-generation initiators were either so efficient that they could not be used in significant quantities[14] or so inefficient[15] that a more reactive halide was required.

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(6) For a recent summary of data on this compound see: L. Spailter and J. A. Pappalardo, "The Acyclic Aliphatic Tertiary Amines," The Macmillan Co., New York, N. Y., 1965, p 130.

(7) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, 30, 3141 (1965); M. L. Farmer, W. E. Billups, R. B. Greenlee, and A. N. Kurtz, *ibid.*, 31, 2885 (1966).

(8) G. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **87**, 3276 (1965), and references cited therein.

(9) A. R. Lepley and W. A. Khan, unpublished work.

(10) 2-Butene was not detected.[9]

(11) D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963).

(12) R. G. Lawler, *ibid.*, **89**, 5519 (1967).

(13) The formation of this radical from the butyl radical and the increased radical stability with chain branching in simple hydrocarbon systems may support the first of these, but the characteristics of the last step in the reaction are unknown.

(14) Comparable reaction times to those reported here were encountered with 25 μl of tetramethylethylenediamine.

(15) N,N-Dimethylaniline.

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Received February 5, 1968

The Nuclear Magnetic Resonance Spectrum of a Phenoxy Radical. Di-*t*-butyl Nitroxide as a Spin Relaxer

Sir:

The nmr spectra of organic radicals provides a means of determining both the sign and magnitude of electron–nuclei coupling constants.[1] One observes single

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(1) R. W. Kreilick, *J. Chem. Phys.*, **46**, 4260 (1967); **45**, 1922 (1966); H. H. Hausser, H. Brunner, and J. C. Jochims, *Mol. Phys.*, **10**, 253 (1966).

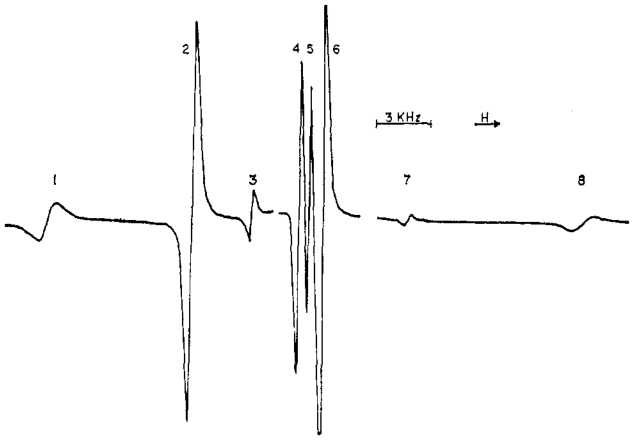


Figure 1. 100-MHz nmr spectrum of radical I in DBNO. The center lines are recorded at lower gain. Peaks 5 and 6 are the *t*-butyl line from the diamagnetic phenol and DBNO, respectively. Other assignments are given in Table I.

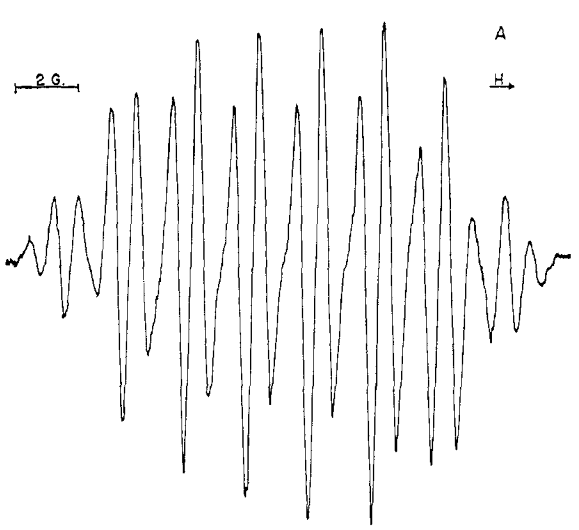


Figure 2A. Low-resolution esr spectrum of radical I.

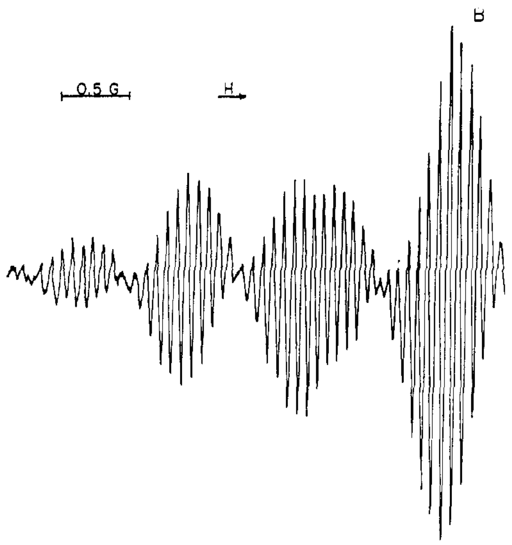


Figure 2B. High-resolution spectrum showing the first four low-field groups.

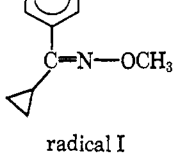
shifted lines from each group of equivalent nuclei when a mechanism for rapidly averaging the two electron spin states is present. The relation between the magnitude of the shifts (ΔH) and the electron–nuclei coupling constant (a_i) is

$$a_i = -\Delta H/\left(\frac{\gamma_e}{\gamma_n}\right)\left(\frac{gBH}{4kT}\right) \qquad (1)$$

In concentrated solutions of organic radicals, spin exchange may be rapid enough so that some of the shifted lines may be observed. The width of the lines increases with the magnitude of their shift, and lines from protons with large coupling constants are generally impossible to detect. In cases in which the radicals have moderate or poor solubility the nmr lines are very broad and cannot be observed.

We have conducted experiments in which the liquid free radical di-*t*-butyl nitroxide (DBNO) was used as a solvent for a second radical. Spin exchange between the solvent and solute molecules rapidly averages the electron spin levels of the solute molecules, and one is able to observe the nmr spectrum of the solute in dilute solutions. Under these experimental conditions we have also been able to observe lines from protons with relatively large coupling constants.

When nmr spectra of saturated solutions of radical I[2] in $CDCl_3$ or benzene-*d* were taken, we could only observe a peak from the *t*-butyl protons along with small peaks from unoxidized phenol. When the phenoxy radical was dissolved in DBNO, the spectrum shown in Figure 1 was observed. This spectrum shows lines from all of the protons in the molecule except the four methylene protons on the cyclopropyl ring. The line from these protons may be hidden under another peak, or the coupling may be very small. The spectrum may be readily analyzed to yield the coupling constants given in Table I. The shift of the phenoxy ring protons to low field shows that these protons have a positive coupling constant. This positive coupling results from negative spin density at the *m*-carbon atoms which is predicted for phenoxy radicals.



radical I

This phenoxy radical can exist in a *syn* or an *anti* conformation. One might expect different coupling constants for the methoxy protons and the α proton on the cyclopropyl ring in the two conformations. The nmr spectrum shows peaks from both conformations. The favored conformation is probably the one in which the methoxy group is *anti* to the phenoxy ring. The larger peaks at positions 2 and 8 were assigned to the methoxy and cyclopropyl protons in molecules with the favored conformation. The lines at positions 3 and 7 have less than 10% of the area of peaks 2 and 8. These lines were assigned to the methoxy and cyclopropyl protons in the other isomer.

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[2] The starting phenol and the radical were made by techniques previously described: R. W. Kreilick, *J. Amer. Chem. Soc.*, **88**, 5284 (1966). The nmr spectra were taken on a JEOLCO 4H-100 nmr spectrometer equipped with a broad-line unit with 35-Hz field modulation.

Table I. Shifts and Coupling Constants for the Various Protons in Radical I

Spectral position	Assignment	Shift,[a] kHz	a_i, G
1	Phenoxy ring protons	13.75	+1.85
2	Methoxy protons, *anti* conformation	6.09	+0.82
3	Methoxy protons, *syn* conformation	2.90	+0.39
4	*t*-Butyl protons	0.54	+0.074
7	α-Cyclopropyl proton, *syn* conformation	5.43	−0.73
8	α-Cyclopropyl proton, *anti* conformation	14.98	−2.02

[a] The shifts are from the corresponding peak in the spectrum of the diamagnetic phenol.

The esr spectrum of radical I is given in Figure 2. This spectrum could be computer simulated with the proton coupling constants given in Table I and a nitrogen splitting of 3.78 G. This spectrum results from the isomer with the favored conformation. The spectrum from the other isomer has less than 10% of the intensity of this spectrum and cannot be observed.

Through the use of a free-radical solvent such as DBNO, one should be able to observe the nmr spectra of many organic radicals. With this technique one can unambiguously determine both the sign and magnitude of electron–nuclei coupling constants. Analysis of the nmr spectra is much simpler than analysis of the esr spectra. Couplings too small to be detected by esr may be observed and information about species in low concentration in mixtures of paramagnetic compounds may be obtained.

Acknowledgment. This work was supported in part by National Science Foundation Grant GP 5482.

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Received February 28, 1968

Observation of Electron-Impact-Induced Anion of Dodecamethylcyclohexasilane

Sir:

The preparation of the radical anion of dodecamethylcyclohexasilane in a solution of tetrahydrofuran–1,2-dimethoxyethane has been described.[1] We wish to report that the negative ion mass spectrum of dodecamethylcyclohexasilane exhibits an ion which occurs at *m/e* 348[2] and which was shown to be $C_{12}H_{36}Si_6$ by examination of the ion abundance of *m/e* 349 and 350. This observation provides unequivocal evidence for the existence of the radical anion of dodecamethylcyclohexasilane as a stable species in the gas phase.

This ion must be formed by electron capture—as opposed to an ion pair or a dissociative attachment process—and hence the ion yield should be sensitive to the energy (velocity) of the electrons which produce it and should exhibit a maximum at relatively low electron energy.[3] This behavior is confirmed as shown in Figure 1, which indicates an approximately 20-fold increase in the *m/e* 348 ion signal at an electron bombardment energy of 4 V as compared to the 80 V usually used. We do not fix the position of maximum ion yield because of instrumental instability below 4 eV. Such a point does occur, however.

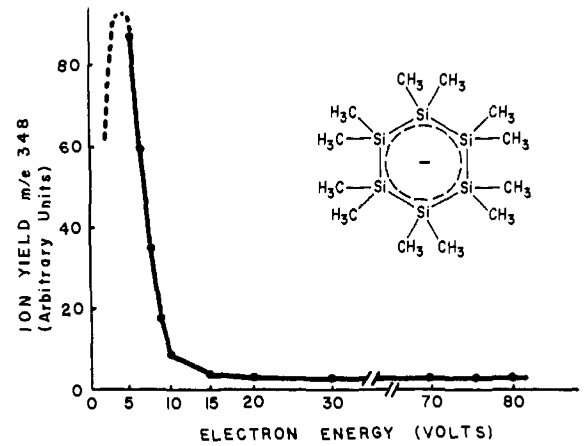

Figure 1. Effect of variation of electron energy on intensity of molecular anion of dodecamethylcyclohexasilane.

The existence of this species indicates that delocalization of the added electron (probably in the 3d orbitals of adjacent silicon atoms) imparts an unusual degree of stability to the radical anion. The negative ion mass spectrum of hexamethyldisilane also exhibits a molecular radical anion (*m/e* 146) which is produced by electron capture, although its abundance is approximately 100 times less than the molecular ion observed for dodecamethylcyclohexasilane. The mass spectrum of hexamethyldisiloxane, however, does not indicate a molecular anion under any conditions available to us. Stabilizing 3d orbital delocalization is, in this case, apparently prevented by the presence of the intervening oxygen atom, and only ion fragments are observed. The negative ion mass spectra of other polysilanes are being investigated.

Experimental Conditions. Mass spectrometer Type MS-12, manufactured by Associated Electrical Industries, Ltd., was used in this investigation. The ion source and analyzer pressure were 1×10^{-6} torr and 2×10^{-7} torr, respectively. The width of the collector slit and the ion source slit was 0.020 in. The temperature of the sample reservoir was 85 ± 2°, the leak line was 100 ± 5°, and the ion source was 140 ± 10°. An all-glass (Pyrex) inlet system was employed. An electron multiplier containing 11 Cu–Be dynodes operated at an estimated gain of 10^5 (3000-V potential difference across dynodes) was used as the ion detector. The absolute magnitude of the ion current was not determined. The signal:noise ratio was, in the worst case, better than 100:1. The electron beam current was 20 μA (trap regulated) for a filament (tungsten) current which ranged between 3.2 and 4.4 A. The ion accelerating potential was 6000 V. The mass spectrometer was electrically refocused (ion repeller, beam centering, Y deflection) at each experimental point to ensure that the

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(1) G. R. Husk and R. West, *J. Amer. Chem. Soc.*, **87**, 3993 (1965).

(2) Verification of mass was carried out by using previously characterized perfluorokerosene as an internal mass standard in mixture with the dodecamethylcyclohexasilane.

(3) C. E. Melton in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 4, provides a good general discussion on negative ion mass spectrometry.