field splitting parameters are listed in Table I. The magnitude of D in these spectra suggests a mean separation of the two nonbonding electrons of 5.0–5.5 Å,[4] in agreement with a formal 1,5 diradical in conformations as shown in V, in which the two trivalent carbon atoms assume the greatest possible distance from each other. As shown in Table I, D is dependent upon structural variations of both the initial 3H-indazole and the trapping olefin, indicating the incorporation of both molecular components in the new triplet-state molecules. A comparison of the D values of Va, Vd, and Ve with those of IIa, IIb, and IIc[2] shows that cyano, carbomethoxy, and methoxy substituents give the same sequence of increasing D in both II and V. The most compelling evidence for structures Va–e as the carriers of the triplet-state spectra comes from the observed carbon-13 hyperfine interaction obtained when Ia was photolyzed in a matrix of 1,1-diphenylethylene-1-^{13}C-2,2-d_2. Although the line width did not allow complete resolution of the hyperfine splitting, the observed line broadening for the z and x,y transitions gave an isotropic hyperfine constant of approximately 30 MHz. This value corresponds to a spin density of 0.25 (when normalized to 1 or 0.5 of *one* electron), in excellent agreement with the reported value for the benzhydryl radical.[5,6]

Table I. Zero-Field Splitting Parameters of Biradicals V

	D/hc, cm^{-1}	E/hc, cm^{-1}
Va	0.0156 ± 0.0002^a	$< 0.0008^a$
Vb	0.0181 ± 0.0003	< 0.001
Vc	0.0151 ± 0.0005	< 0.001
Vd	0.0169 ± 0.0003	< 0.001
Ve	0.0177 ± 0.0003	< 0.001

[a] Values were determined from the adduct obtained from IIa and 1,1-diphenylethylene-2,2-d_2.

Warm-up experiments to 140°K showed that the disappearance rate of the 1,3 diradical II and the 1,5 diradical V differ by an order of magnitude, with the 1,5 diradical being the slower reacting species. It should be noted that the identification of V constitutes the first example of a physical identification of what might be regarded as a "Skell intermediate," in analogy to the postulated 1,3 diradical assumed to be an intermediate in the addition of triplet carbenes to olefins.[7]

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(4) Computed by using the point-dipole approximation $D \cong 3\beta r_{1,2}^{-3}$, where β = Bohr magneton and $r_{1,2}$ is the mean distance of the two electrons.

(5) N. M. Atherton and R. S. F. Hardong, *J. Chem. Soc.*, 5587 (1964).

(6) The trapping products of IIa with styrene, butadiene, and 1,1-diphenylethylene were formed in solution in excellent yields and were characterized as indan derivatives by conventional spectroscopic and analytical means.

(7) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(8) National Institute of Health, Predoctoral Fellow, 1965–1968.

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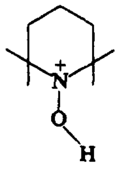
Protonated Nitroxide Free Radical

Sir:

In the course of investigating the interactions between organic free radicals and Lewis acids we have discovered that it is possible to protonate an aliphatic nitroxide without destroying the paramagnetic center. A strong Lewis acid can coordinate with residual water in an organic solvent, giving a complex which acts as a strong Brønsted acid and protonates the nitroxide. The nitroxide 2,2,6,6-tetramethylpiperidine-N-oxyl (I) gives rise to the protonated species



II

This species is stable at room temperature in aluminum chloride–methylene chloride solutions despite the fact that di-*t*-butyl nitroxide (DTBN) is converted to di-*t*-butylhydroxylammonium chloride upon treatment with anhydrous HCl.[1] Several nitroxides have survived in aqueous media, pH 1, for moderate lengths of time,[2] but we have observed that they are not protonated under these conditions. We have further observed that the paramagnetic center of I is destroyed by anhydrous HCl, concentrated sulfuric acid, and aqueous trifluoroacetic acid (TFA) at concentrations greater than 20% acid. We find, in particular, that I is rapidly destroyed by TFA without being protonated, although di(*p*-methoxyphenyl) nitroxide has been observed to protonate in 100% TFA.[3]

The solution electron spin resonance spectrum of I consists of three lines produced by interaction of the unpaired electron with a single ^{14}N nucleus (Figure 1A). In degassed methylene chloride, $a_N(I) = 15.87 \pm 0.10$ G and $g = 2.0059 \pm 0.0002$. Species II exhibits a six-line spectrum (Figure 1B) in which each of the three ^{14}N lines is split into a doublet by interaction with the additional proton; $a_H(II) = 3.3 \pm 0.1$ G. The ^{14}N hyperfine coupling has increased by a factor of 1.37 to a value of $a_N(II)$ of 21.8 ± 0.2 G, and the g value has decreased to $g = 2.0042 \pm 0.0002$. The esr spectrum of II can be computer simulated using coupling constants $a_N(II)$ and $a_H(II)$ and gaussian component line widths of 1.28 G.

Several Lewis acids have been used to form II from the parent nitroxide I. Solutions of I containing BX_3 ($X = F, Cl$) are prepared by condensing BX_3 on a vacuum line onto a degassed, frozen solution of I in a sample tube and freezing. Solutions containing $AlCl_3$ are prepared by condensing I, which though solid can be readily transferred on a vacuum line, onto the frozen solvent which has been previously saturated with $AlCl_3$, and then filtering under vacuum to remove the solid. The resulting esr spectra are independent of the Lewis acid. Species II is

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(1) A. K. Hoffman and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).

(2) C. L. Hamilton and H. M. McConnell in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968, p 115.

(3) H. Hogeveen, H. R. Gersmann, and A. P. Praat, *Rec. Trav. Chim.*, **86**, 1063 (1967).

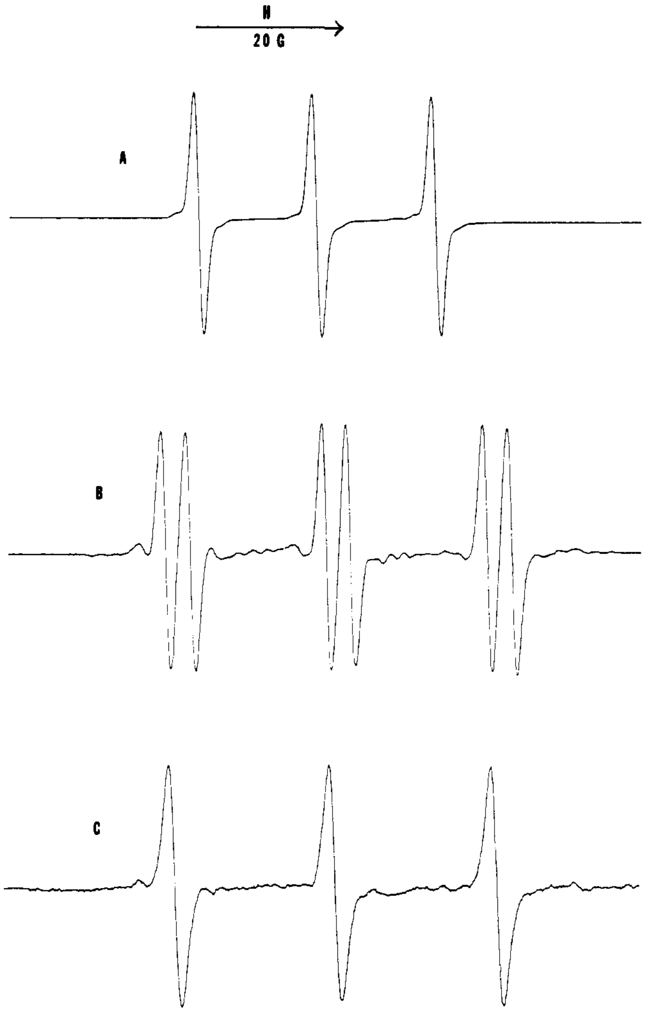

Figure 1. Room-temperature esr spectra of (A) 2,2,6,6-tetramethylpiperidine-N-oxyl (I), (B) protonated nitroxide (II), (C) deuterated nitroxide (III) in methylene chloride solutions.

destroyed by the BX_3 if allowed to remain at room temperature, but it is stable in $AlCl_3$ solutions for long periods of time.

If dried methylene chloride solutions are first shaken with D_2O before addition of the Lewis acid, the spectrum shown in Figure 1C is observed. The ^{14}N splitting constant is $a_N(III) = 21.9 \pm 0.2$ G, and within experimental error $a_N(II) = a_N(III)$. However, the component lines no longer show resolvable splittings. Spectrum 1C may be computer simulated using the same gaussian component line shape and line width as for spectrum 1B and assuming that the unpaired electron interacts with one ^{14}N nucleus, coupling constant $a_N(III)$, and one deuteron. Satisfactory agreement is obtained by assuming that $a_D(III) = 0.507$ G, as derived from $a_H(II)$ by assuming $a_H(II)/a_D(III) = \gamma_H/\gamma_D = \alpha = 6.514$,[4] the ratio of proton to deuteron gyromagnetic ratios. However, values of α between 6.18 and 6.514 give essentially indistinguishable computer-simulated spectra.[5] Thus, saturating the dried solvent with D_2O replaces the proton involved in the formation of II with a deuteron.

The increase of the ^{14}N hyperfine splitting and the decrease of the g value upon protonation indicate that the site of protonation is the oxygen atom, as drawn above. Attaching a proton to the oxygen atom draws the bonding π electrons toward the oxygen but shifts the unpaired antibonding π electron toward the nitrogen atom. This process increases the nitrogen atom spin density (ρ_N) and therefore the nitrogen hyperfine splitting. Decrease in the spin density on oxygen and a blue shift in the n–π^* transition are responsible for the decrease in g.[6] The signs of the change in nitrogen coupling constant and g factor upon protonation are consistent with those found in previous studies of solvent effects on DTBN. The magnitudes of the changes, although far larger than any previously observed, correlate well with an extension of a plot of nitrogen splitting *vs.* g value as these parameters vary with solvent.[6]

These results also allow us to make an observation about the magnitude of ρ_N in the parent nitroxides, which has been estimated to be from 0.2 to 0.3,[7] to as high as 0.8 to 0.9.[2]

A recent analysis[8] shows that nitroxide ^{14}N coupling constants obey a simple McConnell relationship,[9] $a_N = Q_N\rho_N$. If we assume that Q_N is unchanged by protonation, then using the ratio $a_N(I)/a_N(II)$ leads to a value for the parent compound of $\rho_N(I) \leq 0.73$.

In aluminum chloride solutions, the spectrum of II is observed only after the sample has been warmed above *ca.* 0°. If the sample has not been warmed above this temperature, we observe a complicated spectrum which is apparently due to two species, at least one of which appears to demonstrate coupling with both ^{14}N and ^{27}Al. These complexes are presently being investigated.

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(4) T. F. Wimett, *Phys. Rev.*, **91**, 499 (1953).

(5) Substitution of D for H in molecules where splittings from either nucleus are resolvable generally leads to values $a_H/a_D < 6.514$, and values varying from 6.18 to 6.45 have been observed. See R. G. Lawler and G. K. Fraenkel, *J. Chem. Phys.*, **49**, 1126 (1968).

(6) T. Kawamura, S. Matsunomi, and T. Yonezawa, *Bull. Chem. Soc. Japan*, **40**, 1111 (1966).

(7) G. Berthier, H. Lemaire, A. Rassat, and A. Veillard, *Theoret. Chim. Acta*, **3**, 23 (1965).

(8) A. M. Vasserman and A. L. Buchachenko, *J. Struct. Chem. USSR*, **7**, 633 (1966).

(9) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

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Novel Acid-Catalyzed Sigmatropic Migrations in the Dienone–Phenol Rearrangement

Sir:

This communication reports the observation of two novel types of sigmatropic shifts of a substituted allyl group in a linearly conjugated cyclohexadienone: an acid-catalyzed "reverse Claisen" rearrangement and a formal [1,5] shift of the migrating group from C-6 of the dienone to C-2.

It was previously reported that rearrangement of dienone **1** in dilute methanolic HCl gives phenol **2** as the