The mechanism of this reduction of Hi by NO is not known. However, the known hydrolysis[17,18] of the nitroprusside to $[Fe(CN)_5NO_2]^{4-}$ suggests the possible reaction mechanism[19,20] given by eq 1–3.

$$(\text{heme Fe})^{3+} + NO \rightarrow (\text{heme FeNO})^{3+} \quad (1)$$

$$(\text{heme FeNO})^{3+} + 2OH^- \rightarrow (\text{heme FeNO}_2)^+ + H_2O \quad (2)$$

$$(\text{heme FeNO}_2)^+ + NO \rightarrow (\text{heme FeNO})^{2+} + NO_2^- \quad (3)$$

The relative photostability of HbNO as compared to HbCO can be attributed to the dissimilar nature of the metal–ligand bonds. The ligand in HbCO is axially bonded.[11] Photodissociation could result from the excitation of an electron in the e_g ($d\pi$) to the strongly metal–ligand antibonding $A_{1g}(d_{z^2})$ orbital.[21] However, HbNO has a bent Fe–N–O bond with an angle of 110°.[9] Therefore, this d–d transition in HbNO is shifted to the infrared region and has much lower oscillator strength. Instead there is expected to be a $d_{xz} \rightarrow NO(\pi^*)$ charge-transfer band in the visible wavelengths. The photoinitiated ligand exchange observed here may be represented by eq 4, where HbNO* could be the excited charge-transfer doublet state.

$$\text{HbNO} \xrightarrow{h\nu} \text{HbNO*} \xrightarrow{CO} \text{HbCO} + \text{NO} \quad (4)$$

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[17] L. Cambi and L. Szego, *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis. Mat. Nat.*, **5**, 737 (1927).

[18] K. A. Hofmann, *Ann.*, **312**, 1 (1900).

[19] We thank the referee for calling our attention to the paper on cytochrome *c*.[20]

[20] A. Ehrenberg and T. W. Szczepkowski, *Acta Chem. Scand.*, **14**, 1684 (1960). These authors proposed a similar mechanism for the autoreduction of the stable ferricytochrome *c*–NO complex in neutral and alkaline media. They postulated a dissociation equilibrium which could also be involved in our system, *i.e.*

$$(\text{heme Fe NO})^{3+} \rightleftharpoons (\text{heme Fe})^{2+} + NO^+$$

[21] This transition has been estimated[22] to lie between 13,600 and 23,200 cm^{-1}.

[22] M. Zerner, M. Gouterman, and H. Kobayashi, *Theoret. Chim. Acta*, **6**, 363 (1966).

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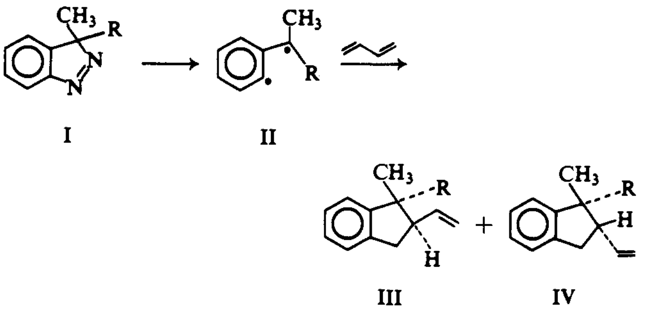
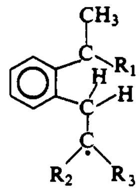
Electron Spin Resonance Identification of Diradicals Generated by Addition of Triplet Ground State Molecules to Olefins[1]

Sir:

In a previous communication we reported that irradiation of dilute solutions of 3H-indazoles (I) at 77°K produced molecules identified by esr spectroscopy to have triplet ground states.[2,3] Based on the magnitude of the zero-field splitting parameters, *D* and *E*, and on the observed chemistry, these paramagnetic species were assigned the 1,3-diradical structures II. The intermediates were trapped in solution by reaction with butadiene, giving the stereoisomeric indan derivatives III and IV. This trapping reaction is of mechanistic interest because II as a triplet molecule can be expected to react with the diene in a two-step reaction, if spin conservation is assumed in the initial addition process. Therefore, a new diradical V, also in a triplet state, should be the reaction intermediate in the formation of the indan derivatives. In this communication we wish to report the successful identification of diradicals of structure V by esr spectroscopy.



a, R = CN; b, R = COOCH$_3$; c, R = OCH$_3$



Va, $R_1 = CN$; $R_2 = R_3 = C_6H_5$
b, $R_1 = CN$; $R_2 = H$; $R_3 = C_6H_5$
c, $R_1 = CN$; $R_2 = H$; $R_3 = -CH{=}CH_2$
d, $R_1 = COOCH_3$; $R_2 = R_3 = C_6H_5$
e, $R_1 = OCH_3$; $R_2 = R_3 = C_6H_5$

Ultraviolet irradiation (3–20 sec) of a 0.1–1.0% solution of Ia in 1,1-diphenylethylene frozen to a glass at 77°K and subsequent examination by esr gave a superposition of two triplet-state spectra with approximately equal intensities. The first spectrum was identical with that obtained from IIa as previously reported, while the second extended over a much narrower range of the external magnetic field. The observed $\Delta m = 1$ transitions were fitted to the usual triplet-state spin Hamiltonian, $\mathscr{H} = \beta H \cdot g \cdot S + DS_z^2 + E(S_x^2 - S_y^2)$, $S = 1$, yielding the zero-field splitting parameters as listed in the first entry of Table I. The spectra persisted unchanged for several hours after irradiation was ceased, indicating a triplet ground state or a triplet state very close to the ground state and populated by *kT*.

Similar results were obtained upon irradiation of Ia in styrene and butadiene glasses and of Ib and Ic in 1,1-diphenylethylene. In each case, the spectrum of the corresponding triplet molecule II was obtained, in addition to new spectral features which should be attributed to triplet-state molecules of structures Va–e. The zero-

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[1] Work supported by National Science Foundation Grant GP-7043.

[2] G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Am. Chem. Soc.*, **89**, 3376 (1967).

[3] For similar intermediates see G. Baum, R. Bernard, and H. Shechter, *ibid.*, **89**, 5307 (1967).

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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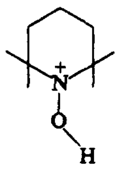
Protonated Nitroxide Free Radical

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).