H, 7.81). Hydrolysis in the usual way gave an oil which decomposed on attempted distillation.

Similarly 1,2-bis(2-phenyl-1,3-dithianyl)tetramethyldisilane was prepared from phenyldithiane anion in 77% yield, mp 274–275° from benzene (*Anal.* Calcd for $C_{24}H_{34}S_4Si_2$: C, 56.86; H, 6.76. Found: C, 57.09; H, 6.73). Attempted hydrolysis gave a yellow oil (C=O stretch 6.19 μ) which could not be completely purified and which decomposed to benzaldehyde on attempted glpc separation.

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[21] Dow Corning Silicones of Canada Fellow, 1966–1967.

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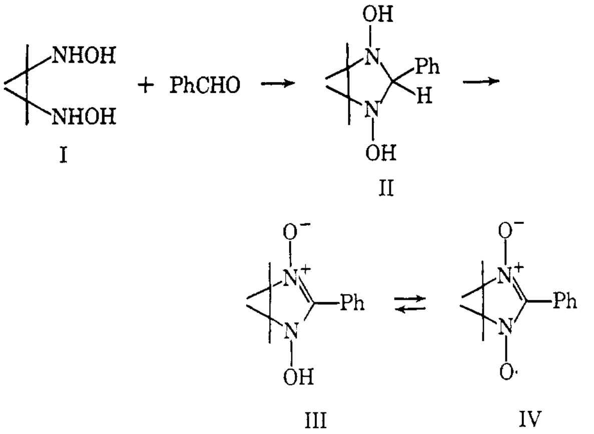
Studies of Free Radicals. I. α-Nitronyl Nitroxides, a New Class of Stable Radicals

Sir:

Although a sizable number of relatively stable free radicals have been described, those classes which are sufficiently stable for isolation and characterization in the presence of oxygen remain quite limited.[1] Notable among these are the nitroxides,[1,2] verdazyls,[3] and phenylhydrazyls[1] together with several individual radicals that owe their stability to exceptional structural relationships (*e.g.*, *peri*-naphthenyl,[4] Koelsch's radical,[5] and galvinoxyl[6]). We now wish to report on the first members of a large new class of radicals of exceptional stability that may find use in spin-labeling techniques[7] and possibly as primary esr standards.

On treatment of the previously known, 2,3-bis(hydroxylamino)-2,3-dimethylbutane[8] (I) with benzaldehyde in benzene solution at room temperature, a product was obtained in 74% yield that was identified as 1,3-dihydroxy-4,4,5,5-tetramethyl-2-phenyltetrahydroimidazole (II) by its analytical and spectral data [ν^{KBr} 3330 cm^{-1} (OH); τ 2.29 (2-NOH), 2.7 (5-ArH), 5.49 (singlet, CH), and 8.93 and 8.97 (2 singlets, 4-CH$_3$) (DMSO); *m/e* 236 (molecular ion)]. Treatment of a benzene solution of II with excess lead dioxide at room temperature produced an intense blue color. The product IV, isolated quantitatively as blue-black crystals by evaporation of the solvent and recrystallization from ether, displayed an esr spectrum in benzene of five lines in the ratio 1:2:3:2:1, $g = 2.00651 \pm 0.00003$, indicative of two equivalent nitrogen nuclei, $a_N = 7.5$ gauss (benzene). At higher resolution each of the five lines was further split by 0.22 gauss into at least 16 lines due to long-range coupling with the methyl and aromatic hydrogens. As anticipated, solutions of IV showed no nmr signal. Its mass spectrum displayed intense molecular ion, benzoyl, and tetramethylethylene peaks, together with minor fragments at *m/e* 145 and 162; it had characteristic maxima in the infrared (CHCl$_3$) at 1371,[9] 1140, and 873 (w) cm^{-1} and electronic absorption (EtOH) at 238 mμ (ε 9400), 263 (12,200), 360 (13,300), and 588 (685).



(1)

If oxidation of II with lead dioxide was not carried to completion, a highly reactive intermediate could be isolated. This compound was identified as III by its analytical and spectral data [ν^{KBr} 2610 cm^{-1} (hydrogen-bonded OH); $\lambda_{\text{max}}^{\text{EtOH}}$ 239 mμ (ε 11,500) and 317 (ε 6000); *m/e* 234 (molecular ion) and peaks identical with those of IV] and by its formation from IV either by reduction of a dimethoxyethane solution of IV with sodium dispersion or by catalytic hydrogenation. This reduced form III of the radical IV was exceptionally susceptible to oxidizing agents. Thus air, di-*t*-butyl nitroxide, Fremy's salt, and manganese dioxide all yielded IV. The hydrogen affinity of IV must therefore be less than that of the simple nitroxides.

Although solid samples of IV stored in air partially deteriorated during storage for several weeks near a window, samples stored in the darkness appeared to be indefinitely stable. The radical was not decomposed at its melting point (85°) and was unaffected by hot aqueous alkali. Treatment of the radical in benzene with trifluoroacetic acid led to a color change from blue to orange. The resulting solution displayed a 12-line esr spectrum consistent with the asymmetric protonated radical V (R = H), $a_N = 5.7$ gauss, $a_{N'} = 4.5$ gauss, and $a_H = 4.7$ gauss. In agreement with this interpretation, addition of triethylamine to this solution regenerated the blue color and the original five-line esr pattern. By contrast, when trifluoroacetic anhydride was added to a benzene solution of IV a diamagnetic orange solution was obtained. Similarly, an orange solution of IV, which was obtained in 1 *N* aqueous hydrochloric acid, displayed

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[1] Reviews on stable radicals include (a) A. L. Buchachenko, "Stable Radicals," Consultants Bureau, New York, N. Y., 1965; (b) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p 381 ff; (c) W. E. Bachmann, "Organic Chemistry, An Advanced Treatise," H. Gilman, Ed., Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1943, Chapter 6.

[2] (a) A. K. Hoffmann and A. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961); (b) E. G. Rosantzev and M. B. Neiman, *Tetrahedron*, **20**, 131 (1964); (c) R. Dupeyre and A. Rassat, *J. Am. Chem. Soc.*, **88**, 3180 (1966).

[3] R. Kuhn, F. A. Neugebauer, and H. Trischmann, *Monatsch.*, **97**, 525 (1966), and earlier references cited.

[4] D. H. Reid, *Chem. Ind.* (London), 1504 (1956).

[5] C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957).

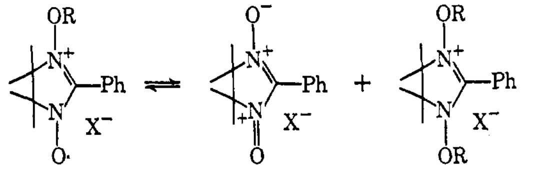
[6] (a) G. Coppinger, *ibid.*, **79**, 501 (1957); (b) G. Coppinger, *Tetrahedron*, **18**, 61 (1962).

[7] (a) H. M. McConnell and J. C. A. Boeyans, *J. Phys. Chem.*, **71**, 12 (1967); (b) G. A. Russell, E. T. Strom, E. R. Talaty, K. Y. Chang, R. D. Stephans, and M. C. Young, *Record Chem. Progr.*, **27**, 3 (1966); (c) S. F. Nelson and E. D. Seppanen, *J. Am. Chem. Soc.*, **89**, 5740 (1967).

[8] M. Lamchen and T. W. Mittag, *J. Chem. Soc., Sect. C*, 2300 (1966).

[9] Probable N–O stretching peak (*cf.* ref 2a).

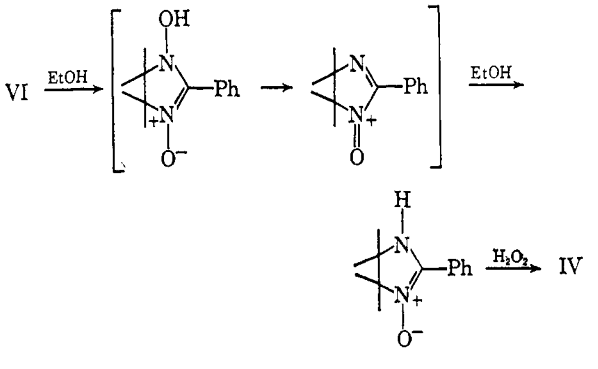
only a reduced-intensity esr signal identical with that of an aqueous solution of the starting radical IV rather than the protonated species V (R = H). Since neutralization of these solutions in each case quantitatively regenerated radical IV, these observations suggest a disproportionation process such as (2) (R = H or $COCF_3$) which is favored with trifluoroacetic anhydride or aqueous acid but not with nonaqueous acid.



(2)

V VI VII

Further evidence for the disproportionation reaction was found by comparison of the properties of acidic solutions of IV with those of the reaction product of IV with chlorine. Thus, solutions of IV in carbon tetrachloride after treatment with chlorine gas and evaporation of the solvent yielded an orange solid, VI (X = Cl) [τ 2.34 (5-ArH) and 8.17 (singlet, 4-CH_3) (SO_2Cl_2); ν^{KBr} 1600 (w), 1580 (w), and 1140 cm^{-1}]. Both this compound and strongly acidic solutions of IV were exceptionally powerful oxidants. They not only readily oxidized aqueous iodide or bromide with liberation of the free halogens but also attacked many organic compounds and most solvents. Indeed, VI was even reduced slowly by water, and it was also found to oxidize aqueous alkali to hydrogen peroxide, although acidic solutions of IV failed to do this, apparently because of the rapid reversal of the disproportionation process (2) on neutralization. Parallel reactions of VI in neutral ethanol and of the radical IV in 1 *N* ethanolic hydrochloric acid were also observed. Both solutions became colorless on boiling for a few minutes, and good yields (60–80%) of a new product, VIII, were obtained. Structure VIII is supported by its spectral data which suggest the existence of intermolecular association even in dilute solutions [ν^{CHCl_3} 3380, 3130, 2500, 2350, 1600 (w), 1572 (w), and 1150 cm^{-1}; τ 1.72 (2 *o*-ArH), 2.2 (3 ArH), 6.08 (1 NH, broad), 8.67 (2-CH_3), and 8.72 (2-CH_3) (EtOH); λ_{max}^{EtOH} 238 mμ (ϵ ~15,000) and 325 (~5000) (concentration dependent)] and by its oxidation by hydrogen peroxide and phosphotungstic acid back to the radical IV.



(3)

VIII

Condensation of the bishydroxylamine I has also been found to proceed with other aromatic aldehydes as, for example, *p*-hydroxy- and *p*-nitrobenzaldehydes. The corresponding nitronyl nitroxide radicals had esr spectra in benzene that were very similar to that of IV (a_N = 7.5 gauss, g = 2.00660 and 2.00645 ± 0.00003, respectively) and their mass spectra likewise showed intense molecular ion peaks. Aliphatic derivatives of IV are also readily prepared, and future communications will deal with the chemistry of these and related radicals.

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Lewis Acid Adducts of Planar Four-Coordinated d^8 Complexes. BF_3–[$IrClCO(P(C_6H_5)_3)_2$] and Related Systems

Sir:

Although the basicity of certain metal complexes toward molecular Lewis acids is now recognized,[1,2] unequivocal examples are lacking for adducts of four-coordinated planar d^8 complexes with σ Lewis acids like BF_3.[3] Schrauzer published the first attempt to bring about donor–acceptor interaction between BF_3 and a planar d^8 complex.[4] This work with a Ni(II) complex and other studies with Ni(II) and Pd(II) complexes led to no observable metal basicity.[5]

Rapid tensimetric titration of the planar d^8 complex [$IrClCO(P(C_6H_5)_3)_2$][6] (**1**), in benzene solution at 5.5°, led to a break in the pressure–composition curve at $2BF_3$:1Ir complex. Also, a slow secondary reaction was observed which resulted in uptake beyond the 2:1 stoichiometry. Cryoscopic molecular weight determinations for *ca.* 5 m*M* solutions of the 2:1 complex in benzene gave an average molecular weight of 1150 as compared with the formula weight of 916 (the experimental value is thought to be slightly high because of traces of precipitate which formed even at these low concentrations). The solid 2:1 adduct has a single CO stretching frequency at 2063 cm^{-1} which is 107 cm^{-1} higher than ν_{CO} of the parent complex; it also contains BF stretching bands characteristic of tetrahedrally coordinated boron (1138, 931, and 960 cm^{-1}) but none in the region expected for three-coordinated boron (1200–1450 cm^{-1}). The BF_3 stretches are quite different from those of $(C_6H_5)_3PBF_3$ (1150–1000, 915, 888 cm^{-1}). The Ir–Cl stretching frequency is 325 cm^{-1}, a value which is very slightly higher than in the parent complex (321 cm^{-1}).

Attempts to isolate a solid 1:1 complex by mixing stoichiometric quantities of BF_3 and **1**, followed by removal of the benzene solvent, always resulted in a product displaying sharp absorptions of nearly equal intensities at 1956 and 2063 cm^{-1}, attributable to

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(1) M. P. Johnson and D. F. Shriver, *J. Am. Chem. Soc.*, **88**, 301 (1966), and references therein.

(2) L. Vaska and D. L. Catone, *ibid.*, **88**, 5324 (1966).

(3) A possible exception is the report that BCl_3 and BBr_3 adducts of a Rh(I) complex may be prepared: P. Powell and H. Nöth, *Chem. Commun.*, 637 (1966).

(4) G. N. Schrauzer, *Ber.*, **95**, 1438 (1962).

(5) D. F. Shriver, *J. Am. Chem. Soc.*, **84**, 4610 (1962); **85**, 1405 (1963); D. F. Shriver, A. Luntz, and J. J. Rupp, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, Sept 1964.

(6) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).