

chlorite by a 1,2 shift of chlorine from C₂ to oxygen also exists. As has been argued previously,¹³ we believe that such an intermediate might then decompose to the α -ketocarbonium ion-chloride tight ion pair with Wagner-Meerwein rearrangement competing with C₃-chloride bond formation leading to the major products, **2** and **3**. Intermediacy of the enol hypochlorite offers a convenient way to move the chlorine from the *endo* face to the *exo* face of the norbornyl system.

It is also noteworthy that the CD curve of (+)-**3** is not that expected for the 1*R*,2*R* configuration by application of the octant rule; the CD curve in ethanol exhibits a single maxima, $[\theta]_{295} +280^\circ$. It is difficult to envision how the 1*S*,2*S* configuration could be produced in this rearrangement. Professor Djerassi has informed us¹⁹ that our configuration may be correct and that we are "encountering another example of an unusual effect of a β -halogen atom on a carbonyl group." This same type of effect has recently been observed in the β -haloadamantanones when the halogen has an axial relationship to the carbonyl group.²⁰ The geometric relationships of the halogen and the carbonyl groups in these axial- β -haloadamantanones and **3** are extremely similar; thus the halogens give "antioctant" contributions to the Cotton effect.

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(19) Private communication.

(20) G. Sznatzke and G. Eckhardt, *Tetrahedron*, **24**, 4543 (1968). We wish to thank Dr. Sznatzke for informing us of certain of his data and conclusions prior to publication.

(21) NDEA Fellow, 1964-1967; National Science Foundation Cooperative Fellow, 1967-1968; taken from the Ph.D. thesis of R. N. Steppel.

Richard N. McDonald, Richard N. Steppel²¹

Department of Chemistry, Kansas State University
Manhattan, Kansas 66502

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The Triplet Electron Spin Resonance Signal of 1,3-Diradicals from Bicyclic Azo Compounds

Sir:

The spectroscopic characterization of 1,3-diradicals is a topic of considerable current interest since they are postulated intermediates in several reactions, such as the photochemical and thermal isomerization of cyclopropanes,^{1a} the photochemical and thermal decomposition of pyrazolines,^{1b} the photolysis of cyclopentene ozonide,^{1c} and the addition of carbenoid species to olefins.^{1d} Furthermore, the chemistry of 1,3-diradicals may depend on whether the ground state is singlet or

(1) (a) J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962); M. J. Jorgenson, *ibid.*, **88**, 3463 (1966); P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 85 (1968); H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966); W. R. Roth and M. Martin, *Ann.*, **702**, 1 (1967); E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **89**, 7133 (1967); (c) P. R. Story, W. H. Morrison, III, T. K. Hall, J.-C. Farine, and C. E. Bishop, *Tetrahedron Letters*, 3291 (1968); (d) P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 235.

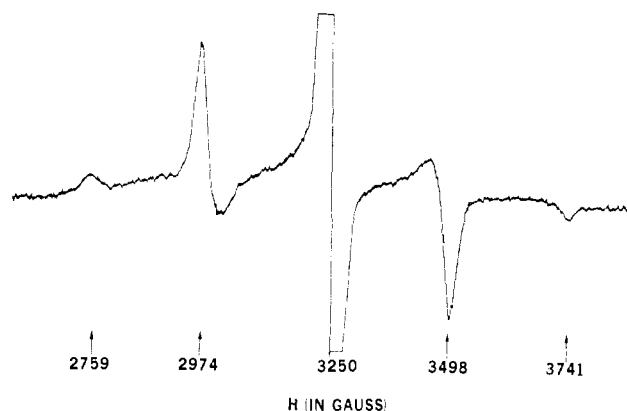
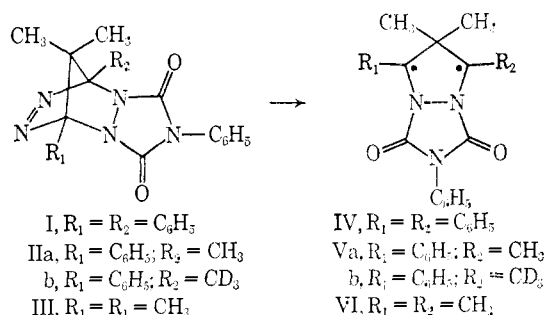


Figure 1. ESR spectrum from irradiation of I.

triplet.² We report here the electron spin resonance (esr) spectra (Figure 1) observed when the azo compounds I-III are irradiated at low temperatures. We assign the spectra to triplet 1,3-diradicals of the form IV-VI.



Compounds I-III³ were prepared by the Diels-Alder reactions of the corresponding isopyrazole with 4-phenyl-1,2,4-triazoline-3,5-dione.⁴ When I⁵ was irradiated in a quartz tube at 77°K with a 450-W Hanovia medium-pressure mercury arc through a uv filter (Corning 7-54), the pale yellow sample became green and gave the esr spectrum shown in Figure 1. Absorptions at 2759 and 3741 and at 2974 and 3498 G can be assigned, respectively, to the parallel and perpendicular signals of randomly oriented triplet molecules with axially symmetric spin-spin interaction terms. The $\Delta M = \pm 2$ transition for the triplet was observable at 1590 G. The strong absorption near the center of the triplet pattern (~ 3250 G) is due to other radical specie(s) produced in the irradiation. The spectrum remained unchanged after a period of several hours at 77°K. Upon annealing at 190°K for a few minutes, however, the green color disappeared along with the triplet signal, leaving a canary yellow sample which gave only the central signal in the esr. Further

(2) R. Hoffman, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(3) Satisfactory combustion analyses were obtained on all new compounds.

(4) A. B. Evinin and D. R. Arnold, *J. Amer. Chem. Soc.*, **90**, 5330 (1968).

(5) The sample was ca. 0.1 M in dry pyridine and crystallized upon cooling to 77°K. I-III were not appreciably soluble in other suitable solvents (acetonitrile, perfluorolube, perfluoromethylcyclohexane); however, the same signal was obtained in these media.

Table I. Zero Field Splitting Parameters of Triplet Species

Assigned structure	g	D, cm^{-1}	E, cm^{-1}
IV	2.000 ± 0.002	0.048 ± 0.002	<0.001
Va	2.000 ± 0.002	0.055 ± 0.002	0.0020 ± 0.0005
Vb	2.000 ± 0.002	0.055 ± 0.002	0.0020 ± 0.0005
VI	2.000 ± 0.002	0.068 ± 0.002	0.0030 ± 0.0005
VII ⁷	2	0.024	<0.001
VIIIa ⁸	~ 2.002	0.1069 ± 0.0005	0.0058 ± 0.0003
VIIIb ⁸	~ 2.002	0.1110 ± 0.0005	0.0069 ± 0.0003
VIIIc ⁸	~ 2.002	0.1217 ± 0.0008	0.0066 ± 0.0003

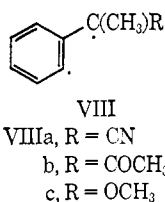
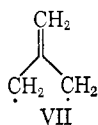
warming to room temperature discharged both the yellow color and the central signal.

Irradiation of samples of IIa,b gave similar spectra. No triplet signal could be observed from III at 77°K; however, we were able to detect the triplet from III when the irradiation and scan were carried out at 4°K.

The assignment of the observed peaks to the usual triplet-state spin Hamiltonian⁶ gave the g values and the zero-field splitting parameters shown in Table I.

In terms of a point-dipole approximation, the coupling constant of 0.048 cm^{-1} observed from I corresponds to an average separation of 3.8 \AA , in reasonable agreement with the proposed structure IV. The observed increase in coupling constants (IV < V < VI) is also consistent with the structure, since the delocalization of the spin(s) into the benzene π system, with a greater average separation of the electrons, is possible with IV and V. We have also observed that the apparent line width of the triplet signals increased in the order IV < Vb < Va < VI. This is additional support for the proposed structures if this increase is due to hyperfine splitting by the methyl protons.

Triplet signals have been reported for trimethyl-ene methane (VII)⁷ and VIII.⁸ In these diradicals the observed spin-spin interaction constants cannot be



attributed to a simple dipole-dipole interaction across the 1,3 positions because of the contribution of other resonance structures. The importance of electron delocalization to the urazole moiety in IV-VI has not been assessed.

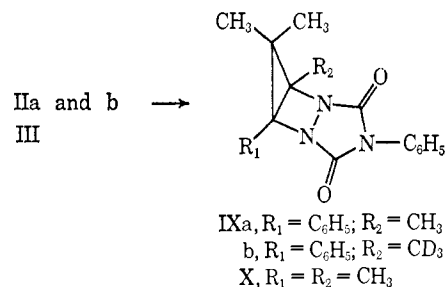
Much of the chemistry of I-III, IX, and X can be rationalized assuming the intermediacy of a diradical, either singlet or triplet.⁴ The role of the triplet is difficult to assign because of uncertainties as to the

(6) For a discussion of esr signals from the triplet state see: (a) M. Bersohn and J. C. Baird, "An Introduction to Electron Paramagnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 8; (b) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(7) P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **90**, 2715 (1968), and previous papers of this series.

(8) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *ibid.*, **89**, 3376 (1967).

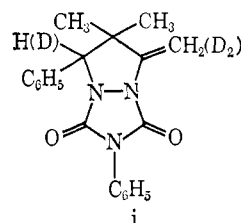
difference in energy between it and the singlet and the probability of spin inversion. Irradiation, both direct and sensitized,⁹ of IIa,b and III at -35° results in loss of nitrogen and formation of IXa,b¹⁰ and X.^{4,11} We



believe the triplet is an intermediate in this reaction, giving the product upon spin inversion. The stability of the triplet at lower temperatures suggests that this requires activation energy. The lack of N-N bond cleavage in reactions involving the diradical⁴ may indicate a strengthening beyond that expected for a diacylhydrazine¹² due to the contribution of ionic resonance structures of the urazole. A study of analogous compounds now in progress should answer these questions.

(9) Direct irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc external to a cooled irradiation vessel. The sensitized runs used acetone as the sensitizer (solvent), irradiating at 2537 Å using low-pressure mercury lamps in a Rayonet reactor.

(10) IXa,b were too unstable to isolate. IXa was characterized by nmr (CH₂Cl₂): 1.78 (s), 1.64 (s), 0.88 (s), 7.4-7.6 ppm (m); IXb lacked the resonance at 1.78 ppm. IXa,b are converted cleanly to the olefin i upon warming to ca. 50°.



(11) We had tentatively assigned *syn* stereochemistry to X based on analogy to carbocyclic systems.⁴ We now believe that this and other urazole derivatives are planar or rapidly inverting at the hydrazine nitrogens (unpublished work with E. B. Whipple).

(12) E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropoulos, and L. M. Kyle, *J. Amer. Chem. Soc.*, **89**, 4875 (1967).

D. R. Arnold, A. B. Evin, P. H. Kasai
Union Carbide Research Institute
Tarrytown, New York 10591
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