

When 1,2-dimethoxybenzene (veratrole) (0.5 mole) in turn electrochemically methoxylated (4.0 amp., 7.3–8.6 v., 22 hr.) a mixture of four products resulted. Fractional distillation afforded the already known ketal V (15% yield) as established by direct comparison with a sample secured as described above. The second component consisted of 1,2,4-trimethoxybenzene and appeared to result from the decomposition of a labile precursor during the process of distillation. A third component (15% yield; homogeneous by v.p.c. analysis), b.p. 108–111° (25 mm.), n_D^{27} 1.4766, was shown to consist of 5,5,6,6-tetramethoxy-1,3-cyclohexadiene (*o*-benzoquinone tetramethyl ketal) (IX). *Anal.* Calcd. for $C_{10}H_{16}O_4$: C, 59.95; H, 8.05. Found: C, 59.77; H, 7.85. The n.m.r. spectrum (in CCl_4) showed peaks at 6.72 and 4.27 τ (unresolved multiplet), the areas under which were in the ratio of 3:1 in agreement with the structure. The diene chromophore of IX was revealed as a peak in the ultraviolet at 265 $m\mu$ (ϵ 2500).¹² Acid hydrolysis in the presence of zinc produced catechol (25% yield) as ascertained by v.p.c. analysis.

Of special interest was the fourth component (10% yield), a crystalline substance m.p. 100°, the structure of which was established as hexamethyl *cis,cis*-orthomuconate (VIII). *Anal.* Calcd. for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C, 55.59; H, 8.43. The n.m.r. spectrum showed a single peak at 6.92 τ and two symmetrical octets (A_2B_2 system) between 4.8 and 3.0 τ . The area ratio of the two characteristic regions was 4.5:1 in agreement with the structure. It exhibited a peak in the ultraviolet at 234 $m\mu$ (ϵ 10,200) as expected and was quantitatively converted in cold dilute mineral acid to dimethyl *cis,cis*-muconate, m.p. 74°, which proved identical in every respect with an authentic specimen. That the ketal IX is a precursor of the bis-ortho ester VIII was confirmed by electrochemical methoxylation (4.0 amp.; 6 v.; 6 hr.) of IX (0.026 mole), which was transformed into VIII in 77% yield.

The formation of the bis-ortho ester VIII deserves special comment because the mechanisms involved appear to be unique. The presence of four vicinal oxygen atoms in the intermediate ketal IX ought to be energetically unfavorable¹² and thus may facilitate fission to the triene X which would then accept two methoxyl radicals from the electrode to give the final product VIII. The fact that the *cis,cis* isomer is actually formed rules out the participation of long-lived free radicals as intermediates since delocalization of the unpaired electrons would allow isomerization to the thermodynamically more stable *trans,trans* isomers of VIII. It is clear that IX must undergo fission on the electrode surface so that the process leading to VIII may involve species that are stabilized by adsorption on it. The mechanisms and scope of these novel electrochemical syntheses are under investigation.

Acknowledgments.—The authors are grateful to Miss E. Busk and Dr. L. Hall for the determination of the n.m.r. spectra and to Dr. R. R. Fraser, Bristol Laboratories, for valuable comments.

(12) Unexpectedly, a second peak at 235 $m\mu$ (ϵ 2500) was also observed. Another similar structure to be described in our full paper also shows this anomalous band. It seems probable that the appearance of this peak marks a $\pi \rightarrow \pi^*$ transition of lower energy than normal for a single double bond; oxygen-oxygen interactions in IX can be more effectively relieved if one C–C bond is free to twist. This effect should tend to stabilize the $\pi \rightarrow \pi^*$ transition.

(13) Predoctoral fellow of the National Cancer Institute of Canada.

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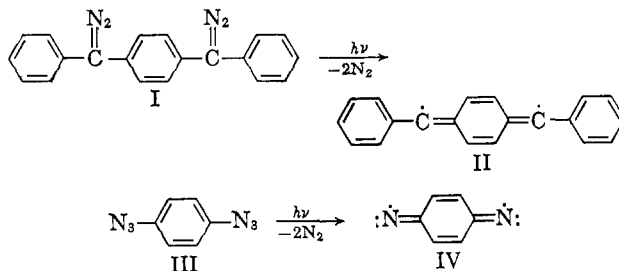
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The E.p.r. of Dicarbene and Dinitrene Derivatives

Sir:

Recently we reported the electron paramagnetic resonance (e.p.r.) of several methylenes^{1,2} and nitrenes³ which demonstrated the triplet ground state of these species. Each of the previously reported ground-state triplet molecules^{1–4} contained only one electron-deficient atom. We now report the e.p.r. of *p*-phenylenebis-(phenylmethylene) (II) and *p*-phenylenedinitrene (IV), ground-state triplet species containing two electron-deficient atoms. This constitutes the first physical evidence for species of this type.

The intermediates II and IV were formed by the photolytic expulsion of two molecules of nitrogen from 1,4-bis-(α -diazobenzyl)-benzene (I)⁵ and 1,4-diazidobenzene (III), respectively.⁶



Preliminary e.p.r. experiments⁵ as well as chemical evidence had indicated that a radical species was produced in the thermal decomposition of I, but these data gave no information regarding the existence of II. In addition, evidence for the simultaneous or near-simultaneous loss of both molecules of nitrogen in the photolytic decomposition of crystals of I had been obtained from microscopic studies.⁷ The e.p.r. experiments were undertaken to provide further evidence as to the existence of II.

A modification of the experimental technique previously described¹ was employed. A finely ground 5% solid solution of I in 1,4-dibenzoylbenzene was irradiated at 77°K.^{8,9} in the quartz dewar insert of a Varian V-4500 e.p.r. spectrometer with 100-kc. field modulation. The r.f. energy employed was 0.3030 cm^{-1} ($\nu = 9080$ Mc.

(1) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962).

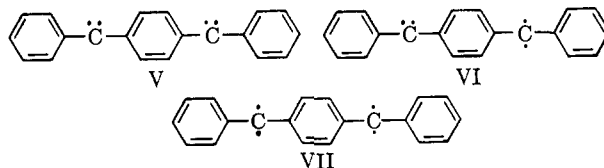
(2) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

(3) G. Smolinsky, E. Wasserman, and W. A. Yager, *ibid.*, **84**, 3220 (1962).

(4) R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962).

(5) R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).

(6) A number of other possible electronic states can be envisaged for II: (a) a singlet electronic state containing no unpaired electrons (ν); (b) a triplet configuration in which only one of the electron-deficient atoms has



its two unshared electrons unpaired and in separate orbitals (VI); and (c) a quintet state containing four unpaired electrons (VII). Analogous alternatives are possible for IV. However, the e.p.r. data are most satisfactorily explained by II and IV, triplet states containing a quinoid structure.³ Also, geometrical isomers are possible for II, but these would not be expected to differ greatly in the e.p.r. absorption spectrum.

(7) R. W. Murray and A. M. Trozzolo, "Proceedings, 1961 International Symposium on Microchemical Techniques," N. D. Cheronis, Ed., Interscience, New York, N. Y., 1962, pp. 233–242.

(8) A Hanovia 140-w. mercury arc with Pyrex filter was used. Irradiation times were 5–10 min.

(9) A detailed description of the advantages of the *random crystal* method will be published shortly. In experiments where a glass matrix was used, additional e.p.r. absorptions were detected which probably were due to a species in which only one molecule of nitrogen had been lost from I.

sec.⁻¹). The sample tube was rotated (10 r.p.m.) during the irradiation and absorption measurement periods. A series of e.p.r. absorptions were recorded which did not diminish in intensity for at least 8 hr. after cessation of irradiation. The persistence of these lines is interpreted as evidence for a ground-state species.¹⁰

The e.p.r. spectrum of II consisted of a comparatively sharp line at 1587 gauss (peak-to-peak width of 11 gauss) and a pair of absorptions occurring at 2973 and 3481 gauss. These absorptions are consistent with a spin Hamiltonian description¹¹

$$\mathcal{H} = g\beta H \cdot S + DS_z^2 + E(S_x^2 - S_y^2)$$

in which $|D| = 0.0521 \text{ cm.}^{-1}$ and $|E| < 0.002 \text{ cm.}^{-1}$.^{12,13}

The e.p.r. of the photolysis product of 1,4-diazidobenzene¹⁴ in fluorolube was obtained in a similar manner. A series of absorptions at 1578 (= H_{\min}), 2500, 3852, 3566, and 3972 gauss were recorded which can be described by the above spin Hamiltonian with $|D| = 0.0675 \text{ cm.}^{-1}$ and $E \approx 0$.¹⁵

The e.p.r. spectrum of both II and IV were quite different from that which would be expected of a species in which only one molecule of nitrogen had been expelled from I or III. If this process had occurred, the e.p.r. spectrum would have resembled that of diphenylmethylene¹ or phenylnitrene,³ respectively.

The close similarity between the e.p.r. absorption spectrum and the magnitude of the zero-field parameters for the two species suggests a common structural feature which is responsible for the low spin-spin interaction. The observed zero-field splittings for II¹⁶ correspond to a value of $(1/\tau^3)^{-1/3}$ of approximately 4 Å. The most reasonable structures which explain this low spin-spin interaction are II and IV where the two electron-deficient atoms are approximately 5.6 Å. apart. The fact that the observed values of $|D|$ are somewhat larger than expected may be due to a spin polarization through the benzene ring, causing an increased spin-spin interaction. The larger value of $|D|$ for IV as compared to II is partly explained by the absence of spin delocalization onto the end phenyl rings which can occur in II.

In II and IV where the two electron-deficient atoms are *para* to each other, it is not unexpected that the triplet states II and IV are of lower energy than the quintet states. In *m*-phenylene-bis-(phenylmethylene), and *m*-phenylenedinitrene, one might anticipate that the quintet would be of lower energy. The e.p.r. spectra of the photolytic products of 1,3-bis-(α -diazobenzyl)-benzene and 1,3-diazidobenzene have been obtained. The spectra are quite complex and are currently being analyzed. However, it is of interest that the spectra are quite similar to each other and quite distinct from those of II and IV.

Acknowledgment.—The authors wish to acknowledge the assistance of Richard M. R. Cramer and to thank

(10) Since experiments at 4°K. gave similar absorption lines, it is inferred that the observed species is probably the ground state, although the possibility that the e.p.r. is derived from a species only a few cm.⁻¹ above the ground state cannot be completely excluded.

(11) K. W. H. Stevens, *Proc. Roy. Soc. (London)*, **A214**, 237 (1952); C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961).

(12) In the calculation of D and E the 1587 gauss line was employed as " H_{\min} " or half-field line¹²; the other two lines were principal axis lines (when $E = 0$, the x - and y -axis lines are degenerate). The z -axis lines whose intensity would be expected to be weak were not observed in II but were seen in IV at 2500 and 3972 gauss.

(13) M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **3**, 190 (1960).

(14) Prepared from 1,4-diaminobenzene by the method of M. O. Ferster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1953 (1907).

(15) An additional set of absorptions were recorded at 1227 (= H_{\min}), 1473, 2062, and 4115 gauss which can be fitted to the spin Hamiltonian where $|D| = 0.171 \text{ cm.}^{-1}$ and $E \approx 0$.

(16) For a recent theoretical calculation of the zero-field splittings based on this structure, see J. Higuchi, *J. Chem. Phys.*, **38**, 1237 (1963).

Drs. L. C. Snyder and J. Higuchi for stimulating discussions.

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Metal Nitrosyl Derivatives with Bridging Nitrosyl Groups

Sir:

No clear examples of metal nitrosyl derivatives with bridging nitrosyl groups have been reported. The cyclopentadienylmanganese nitrosyl derivative, $(C_5H_5)_3Mn_2(NO)_3$, claimed to have bridging nitrosyl groups on the basis of a band in the infrared spectrum at 1510 cm^{-1} , was prepared several years ago.¹ However, this manganese compound apparently has not been investigated since its original discovery, and its relationship to other known metal nitrosyl, cyclopentadienyl, and carbonyl derivatives is not clear. Its structure therefore must be regarded as still uncertain.

This communication describes new nitrosyl derivatives of chromium and manganese where not only the presence of bridging nitrosyl groups is clearly indicated from the infrared spectrum, but also the relationship between the new compounds and well established metal carbonyl derivatives is quite clear.

For the preparation of the chromium derivative, an aqueous solution of $C_5H_5Cr(NO)_2Cl^{1,2}$ was reduced with sodium borohydride. The product was extracted with benzene and purified by chromatography on alumina to give dark violet crystals of $[C_5H_5Cr(NO)_2]_2$, m.p. 158–159°, in 5–6% yield. *Anal.* Calcd. for $C_{10}H_{10}N_4O_4Cr_2$: C, 33.9; H, 2.8; N, 15.8; Cr, 29.4; O, 18.1; mol. wt., 354. Found: C, 34.0, 34.4; H, 2.8, 3.4; N, 16.1, 16.1; Cr, 28.2, 28.7; O, 18.1, 18.1; mol. wt., 347 (Mechrolab vapor pressure osmometer in benzene solution). This chromium derivative exhibited a single sharp cyclopentadienyl resonance at 4.82 τ demonstrating its diamagnetism.

For the preparation of the manganese derivative, a similar sodium borohydride reduction of an aqueous solution of the cation $[C_5H_5Mn(CO)_2NO]^+$ was carried out.³ The product was extracted from the reaction mixture with benzene. After evaporating the benzene solution at $\sim 30 \text{ mm.}$, the resulting purple-brown crystalline residue was purified by recrystallization from a dichloromethane–hexane mixture to give violet crystals of $[C_5H_5MnCONO]_2$ dec. $>200^\circ$, in yields up to 60%. *Anal.* Calcd. for $C_{12}H_{10}N_2O_4Mn_2$: C, 40.4; H, 2.8; N, 7.9; Mn, 30.9; O, 18.0. Found: C, 39.6, 40.3; H, 2.9, 2.7; N, 8.0, 8.1; Mn, 31.2, 31.1; O, 18.1. The manganese derivative appeared to be too unstable in benzene solution for molecular weight determinations or for sharp n.m.r. spectra.

The new compounds $[C_5H_5Cr(NO)_2]_2$ and $[C_5H_5MnCONO]_2$ have physical properties very similar to the well known isoelectronic^{3,4} $[C_5H_5Fe(CO)_2]_2$, demonstrated to have structure I with two bridging carbonyl groups and two terminal carbonyl groups.⁵ The terminal carbonyl groups in the iron carbonyl derivative exhibit infrared bands⁶ at 1940 and 1955 cm^{-1} ,

(1) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

(2) E. O. Fischer and P. Kuzel, *Z. anorg. allgem. Chem.*, **317**, 226 (1962).

(3) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(4) B. F. Hallam, O. S. Mills, and P. L. Pauson, *ibid.*, **1**, 313 (1955).

(5) O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

(6) The infrared spectra described here were taken either on the Beckman