

methanol. The ratio of total P:acid labile P:guanosine was 1.92:0.94:1.00, and the compound was chromatographically identical with an authentic sample.

**P<sup>1</sup>-(Guanosine-5') P<sup>2</sup>-(4-Morpholine) Pyrophosphate (V).** The GDP directly obtained above (1.5 mmoles) was passed through a column containing 25 ml of Dowex-50 (morpholine form) resin, and the eluates were concentrated to a volume of 20 ml. Morpholine (0.52 ml, 6 mmoles) and *t*-butyl alcohol (20 ml) were added and the mixture was gently refluxed while a solution of dicyclohexylcarbodiimide (2.15 g, 10.5 mmoles) in *t*-butyl alcohol (30 ml) was added dropwise over 4 hr. After a further hour under reflux, the solvent was evaporated to roughly half its volume and the aqueous residue was extracted twice with ether with an intermediate filtration of dicyclohexylurea. The aqueous layer was then applied to a 2.2 × 42 cm column of DEAE cellulose (HCO<sub>3</sub><sup>-</sup>), and the column was eluted with a linear gradient of triethylammonium bicarbonate (4 l. from 0.005 to 0.20 *M*). Two peaks resulted; the first (3600 ODU at 252 m $\mu$ , 18%) was GMP-morpholidate, while the second (10,800 ODU 53%) was GDP-morpholidate. Some of the early fractions in the second peak were contaminated by a little orthophosphate and these were separately rechromatographed as above. The chromatographically homogeneous GDP-morpholidate was evaporated to dryness and freed from residual bicarbonate by four evaporations with 25-ml portions of methanol. The residue was dissolved in methanol (10 ml) together with free base 4-morpholine-N,N'-dicyclohexylcarboxamidine<sup>9</sup> (600 mg), and the solution was evaporated to dryness. The residue was dissolved in methanol (5 ml), and dry ether (25 ml) was added. The resulting precipitate was washed several times with ether and dried *in vacuo*, giving the di(4-morpholine-N,N'-dicyclohexylcarboxamidine) salt

of P<sup>1</sup>-(guanosine-5') P<sup>2</sup>-(4-morpholine) pyrophosphate (V) as the tetrahydrate.

*Anal.* Calcd for C<sub>48</sub>H<sub>84</sub>N<sub>12</sub>O<sub>13</sub>P<sub>2</sub>·4H<sub>2</sub>O: C, 49.21; H, 7.91; N, 14.35; P, 5.28; total P:guanosine, 2.00:1.00. Found: C, 49.07; H, 7.79; N, 14.24; P, 5.23; total P:guanosine, 1.95:1.00.<sup>23</sup>

**Condensation of GDP-Morpholidate with GMP.** GDP-morpholidate (V, 0.1 mmole) was carefully dried by three evaporations with 10-ml portions of anhydrous pyridine, followed by two evaporations with benzene. Separately tributylammonium guanosine 5'-phosphate (0.4 mmole) was dried by evaporations with pyridine and benzene as above. The two were then combined in anhydrous dimethyl sulfoxide and stored at room temperature for 4 days. Water (25 ml) was then added and the mixture was directly applied to a 2 × 35 cm column of DEAE cellulose (HCO<sub>3</sub><sup>-</sup>). After a thorough water wash the column was eluted with a linear gradient of 3.5 l. of triethylammonium bicarbonate (0.005 to 0.5 *M*). Three main peaks were obtained. The first (4600 ODU) was unreacted GDP-morpholidate and excess GMP, the second (665 ODU) was GDP, and the third (640 ODU 23%) was GP<sub>2</sub>G. The latter was isolated as its sodium salt in the usual way and was indistinguishable from GP<sub>2</sub>G obtained by the other routes above.

(23) Determination of acid labile phosphate was complicated by precipitation of the 4-morpholine-N,N'-dicyclohexylcarboxamidine. The triethylamine salt of GDP-morpholidate directly obtained from the ion-exchange column showed total P:labile P:guanosine = 1.95:0.98:1.00. The guanosine content had to be determined from the ultraviolet absorption at 280 m $\mu$  in view of some slight absorption by the carboxamidine salt at the  $\lambda_{\max}$  of 252 m $\mu$ .

## Communications to the Editor

### Organic Nitrenes in Single Crystals. Observation of Hyperfine Structure in the Electron Spin Resonance<sup>1</sup>

Sir:

Photolysis of organic azides may be considered to proceed with loss of molecular nitrogen and formation of a monovalent nitrogen radical known as a nitrene. Numerous chemical reactions have been rationalized in terms of this description.<sup>2</sup> Direct physical evidence has been obtained for the existence of alkyl<sup>3</sup> and aryl nitrenes<sup>4</sup> as well as a dinitrene.<sup>5</sup> This was accomplished by observation of the electron spin resonance spectra of their ground-state triplets at -269 and -196°. The nitrenes were generated photochemically in dilute frozen glassy solutions.

In this communication we report the observation by means of esr of triplet nitrenes in single crystals. Also, for the first time, hyperfine structure in nitrenes has been observed. Furthermore, single-crystal nitrenes display unusual thermal stability. As representative materials,

(1) Support of this work by the U. S. Army Engineer Research and Development Laboratories under Contract DA44-009-AMC-861(T) is gratefully acknowledged.

(2) For reviews see L. Horner and A. Christmann, *Angew. Chem. Intern. Ed. Engl.*, **2**, 599 (1963); R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(3) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

(4) E. Wasserman, G. Smolinsky, and W. A. Yager, *ibid.*, **86**, 3166 (1964).

(5) A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *ibid.*, **85**, 2526 (1963).

*p*-fluorobenzenesulfonyl azide,<sup>6</sup> triphenyltin azide,<sup>7</sup> cyanuric triazide (2,4,6-triazido-*s*-triazine),<sup>8</sup> phenyl azide, and methanesulfonyl azide<sup>9</sup> were photolyzed.

Single crystals of *p*-fluorobenzenesulfonyl azide, triphenyltin azide, and cyanuric triazide were photolyzed at -160° with a medium-pressure mercury arc and the esr spectra were determined using a Varian X-band spectrometer or a Strand Labs K-band spectrometer. Figure 1 shows the spectrum of *p*-fluorobenzenesulfonyl nitrene at a perpendicular orientation of the magnetic field with respect to the sulfur-nitrogen bond axis. Three nitrogen nuclear hyperfine interactions split the electronic line into three equal lines with spacing of about 18 gauss. The single-crystal spectrum exhibited the proper orientational variation for a triplet *S* = 1 nitrene spectrum at 9.2 (and 24.2) kMc/sec. Also the resolved hyperfine interactions showed characteristic intensity variations with orientation in the magnetic field. The zero-field splitting parameters determined for *p*-fluorobenzenesulfonyl nitrene are *D* = 1.555, *E* = <0.005 cm<sup>-1</sup>. The observation of hyperfine structure agrees with the model assumed by Smolinsky, *et al.*<sup>3</sup>

(6) This compound was prepared by treatment of *p*-fluorobenzenesulfonyl chloride with sodium azide in ethanol.

(7) J. G. A. Luijten, J. J. Jansen, and G. J. M. vander Kirk, *Rec. Trav. Chim.*, **81**, 202 (1962).

(8) E. Ott and E. Ohse, *Ber.*, **54**, 179 (1921).

(9) J. H. Boyer, C. H. Mack, N. Goebel, and L. H. Morgan, Jr., *J. Org. Chem.*, **23**, 1051 (1958).

Photolysis of triphenyltin azide at  $-160^\circ$  gave the corresponding nitrene which was observed by esr and may be a ground-state triplet with  $D = 1.54$  and  $E = <0.01 \text{ cm}^{-1}$ . This is the first direct physical evidence for the existence of a nitrene derived from a metal-azide type molecule. In contrast to the other pure azides studied, a strong  $S = 1/2$  resonance signal was also observed in the crystal. Repeated unsuccessful attempts were made to observe the triplet signal at  $-160^\circ$  for the pure powdered triphenyltin azide and also for dilute solid solutions of the azide in several solvents.

The resonance signals for both *p*-fluorobenzenesulfonyl nitrene and triphenyltin nitrene bleached at about  $-35^\circ$ .<sup>10</sup>

Photolysis of cyanuric triazide<sup>11</sup> at  $-160^\circ$  yielded a ground-state triplet nitrene for which  $D = 1.440$ ,  $E = 0.005 \text{ cm}^{-1}$ . This nitrene displayed remarkable thermal stability. The resonance signal for the nitrene persisted with only slightly diminished intensity for 1 week at room temperature.

Pure phenyl azide and methanesulfonyl azide were photolyzed in the glassy state at  $-160^\circ$ . Strong nitrene resonance signals were observed which developed complicated sharp line structure upon increasing temperature; however, the integrated intensities remained nearly constant up to about  $-35^\circ$ . In this temperature range rapid bleaching occurred for both these nitrenes. The measured  $D$  values (phenyl nitrene,  $D = 0.999$ ,  $E = 0 \text{ cm}^{-1}$ , and methanesulfonyl nitrene,  $D = 1.569$ ,  $E = 0 \text{ cm}^{-1}$ ) were in substantial agreement with previously reported values.<sup>4</sup> Related bleaching experiments were performed on dilute randomly oriented glassy solutions of the azides.<sup>4</sup> We found that the bleaching temperatures for such solutions were invariably in the range of  $-120^\circ$ . The relatively high bleaching temperatures for nitrenes in single crystals probably result from the fact that the nitrene is locked in a highly oriented environment in the crystalline lattice.

Comparison of variations in line width with increasing temperature is also instructive. The esr lines in the *p*-fluorobenzenesulfonyl nitrene and triphenyltin nitrene spectra were approximately 5 gauss wide (peak to peak derivative) at  $-160^\circ$ . The triplet lines in the cyanuric nitrene spectra were only 1 gauss wide for a comparable crystal orientation. Thermal line broadening made esr measurements difficult above  $-100^\circ$  for the hydrogen-containing single crystals and glasses, but the cyanuric nitrene esr lines were only 2 gauss wide at room temperature. This remarkable difference in both line width and thermal line width variation can be best ascribed to dipolar line-broadening effects of hydrogen. The dramatic line broadening above  $-100^\circ$  in the hydrogen-containing materials is probably a preliminary to a nitrene-hydrogen abstraction reaction. The line broadening may result from motional effects due to hydrogen or may reflect some real conformational changes occurring in the materials.

The zero-field splitting parameter  $D$  is proportional to the magnitude of dipolar spin interaction between the two spin-unpaired electrons from the nitrogen atom

(10) In order to eliminate errors introduced by spin lattice broadening all esr measurements on the thermally bleached samples were made after recooling the sample to  $-160^\circ$ .

(11) G. J. King, F. F. Carlson, and B. S. Miller, *Bull. Am. Phys. Soc.*, **10**, 373 (1965).



Figure 1. Derivative of the absorption ( $dX^{11}/dH$ ) for *p*-fluorobenzenesulfonyl nitrene. The center of the three lines is at 8089 gauss for a microwave frequency of 9213 kMc/sec for the stated angle.

of the nitrene.<sup>12</sup> In the case of phenyl nitrene one electron may occupy a  $\pi$ -molecular orbital involving the aromatic  $\pi$ -system; the other electron is localized in an orthogonal *p*-orbital on nitrogen.  $\pi$  delocalization reduces the spin density on nitrogen, and a decrease in the  $D$  value results.

For the highly delocalized dinitrene derived from 1,4-diazidobenzene, a  $D$  value of  $0.0675 \text{ cm}^{-1}$  has been obtained. The  $D$  value for cyanuric nitrene,  $1.440 \text{ cm}^{-1}$ , is not particularly small. Delocalization of the  $\pi$  electrons on nitrogen between adjacent nitrene nitrogens is not possible due to their *meta* relationship.<sup>13</sup> The possibility of decomposition into simpler nitrenes such as cyanonitrene which might possess a large  $D$  value cannot be excluded.<sup>14</sup>

(12) J. Higuchi, *J. Chem. Phys.*, **39**, 1847 (1963).

(13) A calculation is in progress to determine the extent of  $\pi$  delocalization in the cyanuric nitrene. The bond alternation for the ring is 1.31 and 1.38 Å.

(14) We wish to thank a referee for calling our attention to this possibility.

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### Electron Paramagnetic Resonance Spectra. III. Coupling Constants for Protons in Bicyclic Derivatives of Semiquinones<sup>1</sup>

Sir:

We have examined the epr spectra<sup>2,3</sup> of some unsaturated bicyclic semiquinone derivatives. Russell and Chang recently observed long-range stereoselective couplings for the saturated protons of bicyclic semidiones and pointed out that the vinyl protons of the semidione prepared from 3-ketobicyclo[3.2.1]octene-6 were coupled.<sup>4</sup> In this communication we report other long-range couplings to the protons bonded to unsaturated carbon atoms in bicyclic radicals.

(1) Supported in part by the Petroleum Research Fund of the American Chemical Society (2325A4) and in part by the National Science Foundation (G25190).

(2) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 183 (1963).

(3) A. Carrington, *Quart. Rev. (London)*, **17**, 67 (1963).

(4) G. A. Russell and K. Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965); G. A. Russell, K. Y. Chang, and C. W. Jefford, *ibid.*, 4383 (1965). We have also detected long-range couplings in the semiquinones of 3',6'-dihydroxybenzobicyclo[2.2.1]heptene-2 and 3',6'-dihydroxybenzobicyclo[2.2.2]octene-2. Our results are similar to the observations of Russell and Chang and will be discussed in a forthcoming publication.