

to clarification of the electronic structure of thiabenzene 1-oxides would be of considerable theoretical interest.

Studies on the synthetic utility of the reaction of acetylenic compounds with sulfur ylides as a general route to thiabenzene derivatives are being continued; the chemical reactivity and photochemistry of **5** are also being investigated.⁸

(8) This work was supported by a grant to Washington University from the National Aeronautics and Space Administration. Thanks are accorded to Mr. Daniel Schiffer for the n.m.r. spectra.

Alfred G. Hortmann

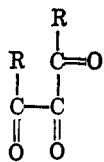
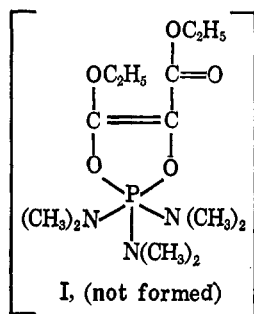
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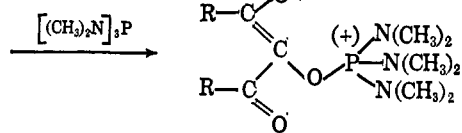
Reaction of Triaminophosphines with Oxomalonic Esters, Vicinal Triketones, and *o*-Quinones. Triaminoxyphosphonium Dipolar Ions¹

Sir:

Burgada² has assigned structure I, with pentavalent phosphorus, to the adduct formed in the reaction of trisdimethylaminophosphine with diethyl oxomalonate in tetrahydrofuran solution. We wish to report that this adduct is, actually, a dipolar ion, IV, with quadruply connected phosphorus.



II, R = OC₂H₅
III, R = C₆H₅



IV, R = OC₂H₅; $\delta P^{31} = -38.2$ p.p.m.
V, R = C₆H₅; $\delta P^{31} = -35.9$ p.p.m.

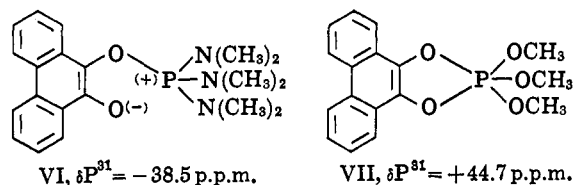
A similar, although more stable adduct, V, was obtained from diphenylpropanetrione and the triaminophosphine. Interestingly enough, the adduct derived from 9,10-phenanthrenequinone and the aminophosphine was also an open dipolar adduct, VI. This *o*-quinone,³ as well as the triketone,⁴ III, formed rather stable 1,3,2-dioxaphospholones, VII and VIII, with trimethyl phosphite.

(1) This investigation was supported by Public Health Service Research Grant No. CA-04769-06 from the National Cancer Institute and National Science Foundation Grant GP 3341.

(2) R. Burgada, *Compt. rend.*, **258**, 4789 (1964); *Chem. Abstr.*, **61**, 2958 (1964).

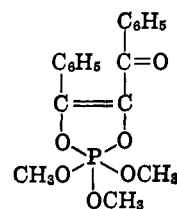
(3) The literature to 1964 has been reviewed by F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

(4) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **30**, 2575 (1965).



VI, $\delta P^{31} = -38.5$ p.p.m.

VII, $\delta P^{31} = +44.7$ p.p.m.



VIII, $\delta P^{31} = +49.3$ p.p.m.

The pale yellow 1:1 adduct,⁵ IV, precipitated out of solution when the reagents were mixed in hexane at 0° (2 *M* solutions; 1.5 mole equiv. of the aminophosphine). In benzene, the adduct remained in solution; the P³¹ n.m.r. spectrum is described in Table I. The negative value of the shift is inconsistent with the oxyphosphorane structure I.^{3-6,6a} The adduct was soluble in methylene chloride; the shift was also negative, as shown in Table I. From these solvents, yellow adduct⁶

Table I. P³¹ N.m.r. Shifts^a in the Reaction of Trisdimethylaminophosphine with Diethyl Oxomalonate (DEOM), Diphenylpropanetrione (DPT), and Phenanthrenequinone (PQ)^b

Compd.	Solvent	After 1 hr.	After ~24 hr.
DEOM	Benzene	-38.0	-38.3
DEOM	CH ₂ Cl ₂	-38.2	-38.4
DEOM	THF	-38.8	-38.8 ^c
DPT	CH ₂ Cl ₂	-35.9	
PQ	CH ₂ Cl ₂	-38.6	

^a In p.p.m. vs. 85% H₃PO₄ at 40.5 Mc.p.s.; see ref. 6. ^b A 2 *M* solution of the carbonyl compound was added to a 2 *M* solution of the triaminophosphine, slowly, at 0°, under N₂. The mixture was allowed to warm to 20°; the infrared and P³¹ and H¹ n.m.r. spectra were examined. ^c A weak signal at -24 p.p.m. due to [(CH₃)₂N]₃PO began to appear.

IV, m.p. 112–113° (from benzene-hexane), could be obtained in about 90% yield upon evaporation at reduced pressure.

The reaction of the keto ester and the aminophosphine was carried out in tetrahydrofuran, the solvent employed by Burgada.² The P³¹ n.m.r. shift was similar (Table I), but the adduct showed more tendency to decompose in this solvent than in benzene or methylene chloride.

The infrared spectrum⁵ of the adduct, IV, had a strong band at 6.30 μ , which is consistent with the di-

(5) Satisfactory elemental analyses and molecular weights (in benzene) were obtained for the crystalline adducts. The infrared spectra and the P³¹ n.m.r. spectra were determined in CH₂Cl₂, the H¹ n.m.r. spectra in CDCl₃. The adducts reacted with CCl₄ and were very sensitive to moisture.

(6) (a) F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, and S. R. Heller, *J. Am. Chem. Soc.*, **87**, 543 (1965); (b) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *ibid.*, **87**, 127 (1965); (c) F. Ramirez, O. P. Madan, and S. R. Heller, *ibid.*, **87**, 731 (1965).

(6a) NOTE ADDED IN PROOF. The P³¹ n.m.r. shifts (in p.p.m.) of some pertinent compounds are: (CH₃O)₃P, -140.0; (CH₃O)₃PCRR', -56.2; (CH₃O)₃PO, -2.4; [(CH₃)₂N]₃P, -122.0; [(CH₃)₂N]₃PCRR', -63.2; [(CH₃)₂N]₃PO, -23.2; R = COC₆H₅, R' = CH₂COC₆H₅. F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, in press.

polar structure.⁷ The 18 H¹ of the six methyl groups attached to nitrogen gave a doublet, $J_{\text{HP}} = 9.7$ c.p.s., at τ 7.17, when the H¹ n.m.r. spectrum was examined in CDCl₃.

The DEOM-TA 1:1 adduct, IV, reacted further with a second molecule of the keto ester II. Consequently, when the aminophosphine was added slowly to the ester, even in a 1:1 mole ratio, little 1:1 adduct IV resulted, in particular in THF² solution at 20°. The details of this reaction³ will be given in the final paper of this series.

The orange triketone-TA adduct⁵ V, m.p. 119–120°, was insoluble in hexane and sparingly soluble in benzene. It was soluble in methylene chloride and gave, in this solvent, a strongly negative P³¹ n.m.r. shift (Table I). The infrared spectrum⁵ had a strong band at 6.76 μ , ascribed to the “enolate” carbonyl.⁷ The 18 H¹ of the dimethylamino groups gave a doublet, $J_{\text{HP}} = 10.0$ c.p.s., at τ 7.08.

The yellow *o*-quinone-TA adduct⁵ VI, m.p. 101° (benzene-hexane), was insoluble in hexane and in cold benzene. It was obtained unchanged from hot benzene. The P³¹ n.m.r. shift was negative, as shown in Table I. The infrared spectrum⁷ had a strong band at 6.78 μ , and the 18 H¹ gave a doublet, $J_{\text{HP}} = 10.2$ c.p.s., at τ 7.42.

It seems clear that the relative stability of compounds with quintuply and quadruply connected phosphorus, derived from the reaction of trivalent phosphorus compounds with polycarbonyl compounds, may vary significantly with the structure of *both* reagents.^{3,8} Therefore, each case must be examined on its own merits until all the factors responsible for the difference are ascertained.

(7) The absence of the infrared bands due to the stretching of normal carbonyl functions is one argument against adducts having a phosphorus-carbon bond. Other arguments are based on chemical reactions to be presented in the final paper of this series.

(8) For reactions of aldehydes with triaminophosphine see: (a) V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963); (b) M. S. Newman and S. Blum, *ibid.*, **86**, 5598 (1964).

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Electron Paramagnetic Resonance and Geometry of Perfluoroalkylmethylenes. A Chemiluminescent Reaction with Oxygen

Sir:

We have observed the electron paramagnetic resonance spectra of several ground-state triplet perfluoroalkylmethylenes, R- $\dot{\text{C}}\text{-H}$, R = CF₃ (I), R = CF₃CF₂CF₂ (II), R = CF₃(CF₂)₆ (III), and CF_{3 $\dot{\text{C}}\text{CF}_3$ (IV), including the fluorine hyperfine structure in IV. This is the first direct physical evidence for alkylmethylenes. I–IV are bent at the divalent carbon, *i.e.*, $\theta < 180^\circ$. As such, they are similar to the aromatic methylenes (*e.g.*, diphenylmethylene) which have $\theta \approx 140\text{--}150^\circ$ and which are approximately planar.^{1,2} However, the values of θ for the monosubstituted I–III are signifi-}

(1) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964).

(2) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965).

cantly greater than that of disubstituted IV. Extrapolation to the unsubstituted CH₂ indicates a linear geometry. Thus, although all the substituted methylenes that have been observed by e.p.r. are bent, the observations are compatible with Herzberg's conclusion, from the ultraviolet spectrum, of a “linear or nearly linear” structure for the lowest triplet state of CH₂.³

Dilute “solid solutions” of the diazo precursors^{4,5} were irradiated at 4°K. and the spectra were obtained and analyzed as described previously.^{1,6} The values of the zero-field parameters were $D_{\text{I}} = 0.712$, $E_{\text{I}} = 0.021$, $D_{\text{II}} = 0.723$, $E_{\text{II}} = 0.027$, $D_{\text{III}} = 0.72$, $E_{\text{III}} = 0.024$, and $D_{\text{IV}} = 0.7444$, $E_{\text{IV}} = 0.0437$ cm.⁻¹. The spectrum of IV in CFC1₃ exhibited the hyperfine pattern expected for six equivalent fluorine nuclei. The magnitudes of the splittings along the *x*, *y*, and *z* principal axes were 85.9, 37.6, and 115.6 Mc.p.s., respectively, where *x* is the bisector of θ and *y* is perpendicular to the C–C–C plane.¹ The splittings are probably all positive although the *y* value could be negative. The magnitudes of the isotropic (average) and anisotropic components indicate $\sim 0.2\%$ s and $\sim 2\%$ p character, respectively, for the unpaired electrons in the fluorine orbitals.⁷ These values are similar to those found for β -fluorines in the radical from sodium perfluorosuccinate.⁸

Assuming that $D_{\text{IV}} - D_{\text{I}} = D_{\text{I}} - D_{\text{CH}_2}$, we obtain $D_{\text{CH}_2} = 0.69\text{--}0.70$ cm.⁻¹, which (*vide infra*) should be appropriate for the linear molecule. If one of the hydrogens is replaced by an aromatic system the resulting value of *D* is approximately proportional to the π spin density remaining at the divalent carbon after delocalization, since *D* is a measure of $1/r^3$ with *r* the distance between the unpaired electrons. The proportionality of the observed *D* values with the theoretical spin densities for several aromatic methylenes² leads to an extrapolated $D_{\text{CH}_2} = 0.69\text{--}0.72$ cm.⁻¹, in good agreement with the value obtained above.

E measures the difference of the magnetic dipole interaction along the *x* and *y* axes. It would vanish for the 3-fold symmetry of linear structures in I and IV in which these two axes would be equivalent. The nonzero values of E_{I} and E_{IV} thus indicate bent structures. The angle may be determined from the E/D ratios^{1,9} which give $\theta_{\text{I}} \approx 160^\circ$ and $\theta_{\text{IV}} \approx 140^\circ$. The ratios also indicate that $\theta_{\text{I}} \approx \theta_{\text{II}} \approx \theta_{\text{III}}$.

Empirically, $\theta_{\text{IV}} < \theta_{\text{I}}$ indicates that an attached CF₃ group reduces the angle at a divalent carbon. The same effect may be observed in a comparison of phenylmethylene, $D = 0.5150$ cm.⁻¹, $E = 0.0251$ cm.⁻¹,¹ and phenyltrifluoromethylmethylene, $D = 0.5183$ cm.⁻¹, $E = 0.0313$ cm.⁻¹.¹⁰ If a similar effect occurs in

(3) G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961).

(4) The monosubstituted diazo compounds were prepared by decomposition of the sodium salts of the corresponding tosylhydrazones.

(5) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965), describe the preparation of the precursor of IV. We are grateful to Drs. Middleton, Krespan, and H. E. Simmons of the Central Research Department, Experimental Station, E. I. du Pont de Nemours, for making available the experimental details for the preparation of the bis(trifluoromethyl)diazomethane.

(6) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964); P. Kottis and R. Lefebvre, *ibid.*, **41**, 379 (1964).

(7) The anisotropic components indicate that the axis of the p orbital on each fluorine is well displaced from any of the principal axes of the electron spin-spin interaction, *i.e.*, the *x*, *y*, *z* system mentioned above.

(8) M. T. Rogers and D. H. Whiffen, *J. Chem. Phys.*, **40**, 2662 (1964).

(9) J. Higuchi, *ibid.*, **39**, 1339 (1963).

(10) In a previous publication (E. Wasserman, *ibid.*, **42**, 3739 (1965)),