

**Table I.** Rate Constants  $k_1$  and  $k_2$  for Conversion of **5** to **7** at 40°<sup>a</sup>

Acid concn. <sup>b</sup>	$k_1 \times 10^2$ , min. <sup>-1</sup> <sup>c</sup>	$k_2 \times 10^2$ , min. <sup>-1</sup> <sup>c</sup>	$k_1/k_2$
0.303	27	1.31	21
0.152	13	0.58	22
0.0303	2.9	0.139	21
0.000 <sup>d</sup>		3	

<sup>a</sup> 0.4 M **5** and 0.15 M methanol (used for internal reference) in aqueous solution. <sup>b</sup> Molarity of sulfuric acid. <sup>c</sup>  $\pm 15\%$ . <sup>d</sup> Neutral unbuffered aqueous solution of **1**.

neutral aqueous solution relative to the rates in moderately acidic solutions. This latter result demonstrates a small and probably negligible contribution to  $k_2$  from catalysis by water ( $k_0$ ) and suggests a large specific hydroxide ion catalytic constant ( $k_{OH^-}$ ).<sup>8</sup>

**Acknowledgment.** The author is appreciative of support of this work by the National Science Foundation (Grant No. GP 3589).

(8) R. P. Bell, "The Proton in Chemistry," Methuen & Co., Ltd., London, 1959, Chapter IX.

(9) A. P. Sloan Foundation Research Fellow.

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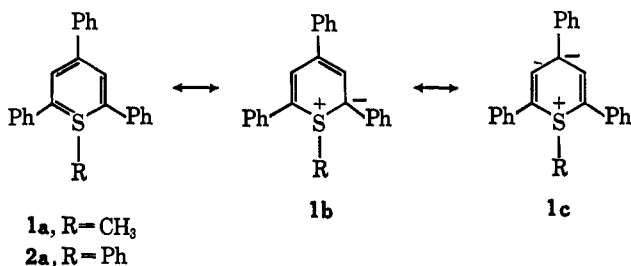
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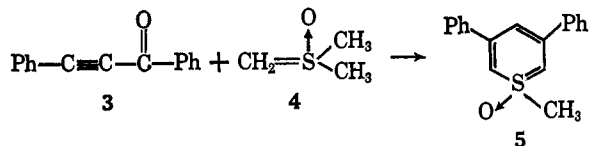
## Thiabenzenes. A Stable Thiabenzene 1-Oxide

Sir:

Several thiabenzene derivatives (**1a**, **2a**) have been reported recently<sup>1</sup>; of current interest is the question of



whether these structures are ylene-like and possess appreciable cyclic aromatic conjugation or whether they are more accurately represented as hybrid structures principally composed of ylide-like contributing structures such as **1b** and **1c**. In this communication the novel synthesis of a related heterocycle, 1-methyl-3,5-diphenylthiabenzene 1-oxide, is reported.



In a typical preparation a solution of 3-phenylpropiophenone (**3**, 8.0 g., 0.039 mole) in 20 ml. of dry dimethyl sulfoxide was added rapidly under nitrogen to a solution of dimethyloxosulfonium methylide (**4**,<sup>2</sup> 0.082

(1) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961); **84**, 2094 (1962); C. C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963).

mole) in 80 ml. of dimethyl sulfoxide at 20°. After 20 hr. at room temperature the resulting red-orange solution was poured into water; the precipitated solid was crystallized from ethyl acetate-petroleum ether (b.p. 63–69°) to yield 6.75 g. (62%) of 1-methyl-3,5-diphenylthiabenzene 1-oxide (**5**) as yellow needles, m.p. 147–148.5°. A purified sample of **5** (sublimed at 140° (0.05 mm.)) melted at 148–148.5°; ultraviolet<sup>3</sup>  $\lambda_{max}^{MeOH}$  240 m $\mu$  ( $\epsilon$  26,200), 364 m $\mu$  ( $\epsilon$  10,000); infrared  $\nu_{max}^{CHCl_3}$  1527, 1490, 1385, 1371, 1130, and 697 cm.<sup>-1</sup>; n.m.r. (CDCl<sub>3</sub>) signals at  $\delta$  7.15–7.65 (10 H, multiplet), 6.19 (1 H, triplet,  $J = 1.1$  c.p.s.), 5.75 (2 H, doublet,  $J = 1.1$  c.p.s.), and 3.50 (3 H, singlet). *Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>SO: C, 77.12; H, 5.75; S, 11.42; mol. wt., 280.4. Found: C, 77.15; H, 5.76; S, 11.60; mol. wt., 276 (osmometer), 323 (Rast).<sup>4</sup>

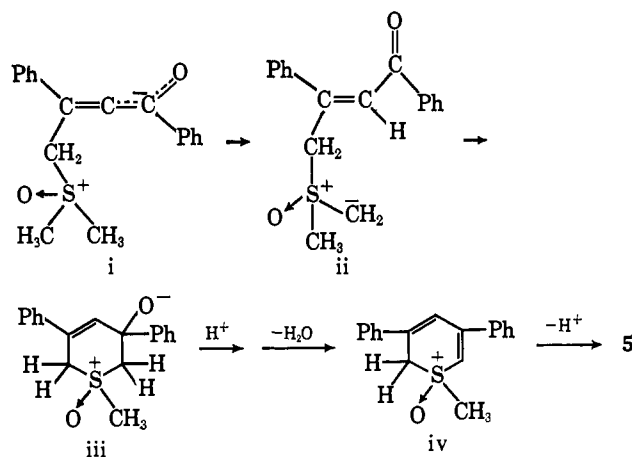
Refluxing **5** with D<sub>2</sub>O–CH<sub>3</sub>OD–NaOD (21 hr.) followed by aqueous workup gave **5-d<sub>3</sub>** in which the methyl hydrogens were exchanged (absence of 3 H singlet at  $\delta$  3.50); a solution of **5** in deuterioacetic acid (containing a trace of D<sub>2</sub>O) showed disappearance of the signals at  $\delta$  5.75 and 6.19 and appearance of a broad singlet (*ca.* 3 H) at  $\delta$  8.0 due to rapid exchange of the S-ring protons.<sup>5</sup>

The remarkable stability of **5** when compared with that of **1a** and **2a** is particularly noteworthy.<sup>6</sup> A similar relationship has been observed between dimethyloxosulfonium methylide and dimethylsulfonium methylide.<sup>2</sup> The behavior of **5** in acidic media taken with the n.m.r. peak positions (in CDCl<sub>3</sub>) for the S-ring protons suggests ylide-like character for **5**. However, the possibility of some cyclic aromatic conjugation involving the use of 3d orbitals by sulfur<sup>7</sup> cannot be discounted on this basis alone; further work leading

(2) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965); **84**, 867 (1962).

(3) The ultraviolet spectrum was unchanged when measured in dilute methanolic sodium hydroxide; addition of hydrochloric acid to a neutral solution of **5** effected appearance of a new band at 313 m $\mu$ . No pK values have been obtained as yet.

(4) A reasonable route for the formation of **5** might involve initial Michael addition of **4** to **3** to give **i**, proton exchange to yield **ii**, followed by the transformations **ii**  $\rightarrow$  **iii**  $\rightarrow$  **iv**  $\rightarrow$  **5**.



(5) Facile protonation has been reported for the somewhat similar 1,1-diphenylphosphabenzene system: G. Märkl, *Angew. Chem.*, **75**, 669 (1963).

(6) Whereas **1a** and **2a** rearrange readily at 25° to yield thiapyrans, **5** can be evaporatively distilled at 160° (0.05 mm.) without decomposition; compound **5** is stable to air whereas **2a** reacts rapidly with oxygen to yield a "peroxide" (see ref. 1).

(7) See, however, R. Breslow and E. Mohacsy, *J. Am. Chem. Soc.*, **84**, 684 (1962), and references cited therein.

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.<sup>8</sup>

(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.

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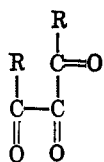
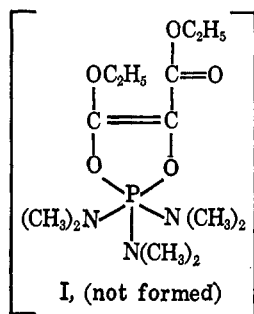
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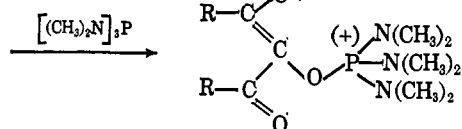
### Reaction of Triaminophosphines with Oxomalic Esters, Vicinal Triketones, and *o*-Quinones. Triaminoxophosphonium Dipolar Ions<sup>1</sup>

Sir:

Burgada<sup>2</sup> 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 = OC<sub>2</sub>H<sub>5</sub>  
III, R = C<sub>6</sub>H<sub>5</sub>



IV, R = OC<sub>2</sub>H<sub>5</sub>;  $\delta P^{31} = -38.2$  p.p.m.  
V, R = C<sub>6</sub>H<sub>5</sub>;  $\delta P^{31} = -35.9$  p.p.m.

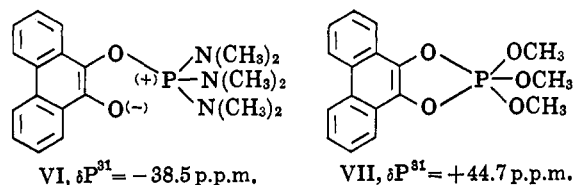
A similar, although more stable adduct, V, was obtained from diphenylpropanetrione and the triaminophosphine. Interestingly enough, the adduct derived from 9,10-phenanthrenequinone and the aminophosphine was also an open dipolar adduct, VI. This *o*-quinone,<sup>3</sup> as well as the triketone,<sup>4</sup> III, formed rather stable 1,3,2-dioxaphospholenes, 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).

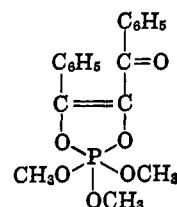
(3) The literature to 1964 has been reviewed by F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

(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,<sup>5</sup> 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 P<sup>31</sup> n.m.r. spectrum is described in Table I. The negative value of the shift is inconsistent with the oxyphosphorane structure I.<sup>3-6,6a</sup> The adduct was soluble in methylene chloride; the shift was also negative, as shown in Table I. From these solvents, yellow adduct<sup>5</sup>

Table I. P<sup>31</sup> N.m.r. Shifts<sup>a</sup> in the Reaction of Trisdimethylaminophosphine with Diethyl Oxomalonate (DEOM), Diphenylpropanetrione (DPT), and Phenanthrenequinone (PQ)<sup>b</sup>

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

<sup>a</sup> In p.p.m. vs. 85% H<sub>3</sub>PO<sub>4</sub> at 40.5 Mc.p.s.; see ref. 6. <sup>b</sup> A 2 M solution of the carbonyl compound was added to a 2 M solution of the triaminophosphine, slowly, at 0°, under N<sub>2</sub>. The mixture was allowed to warm to 20°; the infrared and P<sup>31</sup> and H<sup>1</sup> n.m.r. spectra were examined. <sup>c</sup> A weak signal at -24 p.p.m. due to [(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>PO 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.<sup>2</sup> The P<sup>31</sup> 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 spectrum<sup>5</sup> 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 P<sup>31</sup> n.m.r. spectra were determined in CH<sub>2</sub>Cl<sub>2</sub>, the H<sup>1</sup> n.m.r. spectra in CDCl<sub>3</sub>. The adducts reacted with CCl<sub>4</sub> 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 P<sup>31</sup> n.m.r. shifts (in p.p.m.) of some pertinent compounds are: (CH<sub>3</sub>O)<sub>3</sub>P, -140.0; (CH<sub>3</sub>O)<sub>3</sub>PCRR', -56.2; (CH<sub>3</sub>O)<sub>3</sub>PO, -2.4; [(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>P, -122.0; [(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>PCRR', -63.2; [(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>PO, -23.2; R = COC<sub>6</sub>H<sub>5</sub>, R' = CH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>. F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, in press.