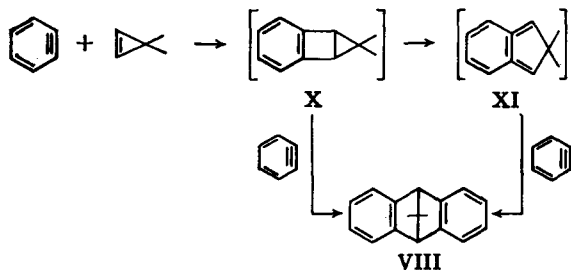


and 333  $m\mu$ ;  $\log \epsilon$  4.52, 4.32, 4.36, and 4.32; compare IV,  $\lambda_{\max}$  228, 305 sh, 314, and 331  $m\mu$ ;  $\log \epsilon$  4.44, 4.37, 4.45, and 4.33; infrared spectrum:  $\lambda_{\max}$  (carbon tetrachloride) 5.5  $\mu$ ; compare IV,  $\lambda_{\max}$  5.5  $\mu$ ; 60 Mc. n.m.r. (carbon tetrachloride): only aromatically bound protons,  $\delta \sim 7.3$  and 7.7 p.p.m. relative to tetramethylsilane as internal standard. The only reasonable alternative structure, tetraphenylallene, m.p. 164–165°, is a known compound<sup>11</sup> and has properties quite different from those of VI.

Although the possibility of substitutive addition now was precluded, tetraphenylcyclopropane (VI) nevertheless still failed to add benzyne; it was recovered unchanged in >95% yield after exposure to decomposing *o*-benzenediazonium carboxylate in ethylene chloride. Under the same conditions, the same batch of *o*-benzenediazonium carboxylate reacted with anthracene in a parallel experiment to give a 66% yield of triptycene.

Blocking the 3,3 positions and leaving the 1,2 positions of the cyclopropane unsubstituted had a fruitful result. When a cold suspension of  $\sim 7$  mmoles of *o*-benzenediazonium carboxylate in a solution of 3 mmoles of 3,3-dimethylcyclopropane<sup>12</sup> in ethylene chloride was gradually warmed to 55°, there was obtained a complex mixture of products, from which was isolated biphenylene (m.p. 110–110.5°, ultraviolet and infrared spectra identical with those reported<sup>13</sup>) and, as the major component of the volatile fraction, an approximately 5% yield of a new hydrocarbon, 7,7-dimethyldibenzonorbornadiene (VIII), m.p. 127.8–128°. *Anal.* Calcd. for  $C_{17}H_{16}$ : C, 92.68; H, 7.32;



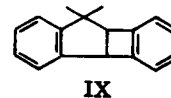
mol. wt., 220. Found: C, 92.90; H, 7.25; mol. wt., 219 (osmometric incarb on tetrachloride). Spectral peaks appeared at: n.m.r., symmetrical pattern centered

(11) (a) D. Vorländer and C. Siebert, *Ber.*, **39**, 1027 (1906); (b) W. Otting, *ibid.*, **87**, 611 (1954).

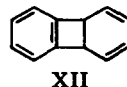
(12) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

(13) W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954); C. G. Cannon and G. B. M. Sutherland, *Spectrochim. Acta*, **4**, 373 (1951).

about  $\delta \sim 6.9$  p.p.m. (aromatic protons, area 8); sharp singlet at  $\delta$  3.63 p.p.m. (bridgehead protons, area 2); sharp singlet at  $\delta$  0.90 p.p.m. (methyl protons, area 6); ultraviolet  $\lambda_{\max}$  (95% ethanol) 274 and 281  $m\mu$ ;  $\log \epsilon$  3.25 and 3.37; compare dibenzonorbornadiene,  $\lambda_{\max}$  272 and 278  $m\mu$ ;  $\log \epsilon$  3.30 and 3.41.<sup>14</sup> The extreme simplicity of the n.m.r. spectrum precludes assignment to the new substance of an unsymmetrical structure such as IX.



The formation of VIII is most simply explained as a cycloaddition of benzyne to 3,3-dimethylcyclopropane to give 2,2-dimethylpseudoindene (X), followed by reaction with a second mole of benzyne, either directly on X or after a preliminary isomerization of X to 2,2-dimethylisoidene (XI). The latter isomerization is only formally analogous to that proposed<sup>15</sup> for the presumed dihydrobiphenylene intermediate (XII) in the benzene-benzyne reaction that leads to benzocyclooctatetraene. Closer analogies are the thermolyses of benzocyclobutene (XIII) in the presence of



diene acceptors. These processes, which seem to proceed *via* *o*-xylylene (XIV) or a closely related species, are quite slow at 150°,<sup>3,16,17</sup> in sharp contrast to the hypothetical X  $\rightarrow$  XI reaction which, if it occurs, must be rapid at 55°.

A remarkable feature of the present results is the apparent capture of an extremely reactive substance (X and/or XI) by a trapping agent (very probably benzyne<sup>18</sup>) which itself has only a fleeting existence.

(14) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 7 (1957).

(15) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963).

(16) M. P. Cava and D. R. Napier, *ibid.*, **80**, 2255 (1958).

(17) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, No. 1, 15 (1962).

(18) It is conceivable that the reactive entity is not benzyne but some other transient species derived from *o*-benzenediazonium carboxylate. Experiments like those reported<sup>9</sup> for other additions using substituted *o*-benzenediazonium carboxylates might clarify this point.

(19) National Science Foundation Postdoctoral Fellow, 1963–1964.

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### Pentaethoxyphosphorus

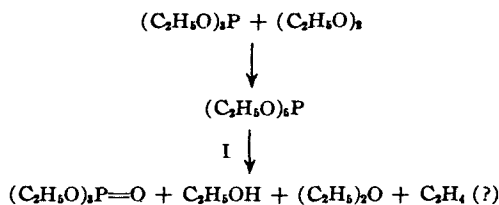
Sir:

Compounds containing five atoms bonded to phosphorus are relatively rare. During the past few years Ramirez and co-workers<sup>1</sup> have described the preparation of substances containing five oxygens bonded to phosphorus. Because of the method of preparation two of these oxygen atoms always comprise part of a five-membered ring. Materials without a ring are generally unknown.<sup>2</sup> We wish to report the prepara-

(1) (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **85**, 3252 (1963); (b) F. Ramirez, N. B. Desai, and N. Ramanathan, *ibid.*, **85**, 1874 (1963); (c) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); and references cited in these papers.

(2) I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **29**, 1687 (1959); *Chem. Abstr.*, **54**, 8689 (1960). have reported briefly on penta-phenoxyphosphorus.

tion of a substance which is believed to be pentaethoxyphosphorus (I).



Triethyl phosphite and diethyl peroxide were allowed to react at room temperature for 15 days. Periodic inspection in the n.m.r. showed the disappearance of starting material.<sup>3</sup> The absorptions of the starting materials were replaced by a distorted quintet ( $J = 7$  c.p.s.) at  $\tau$  6.18 and a triplet ( $J = 7$  c.p.s.) at  $\tau$  8.87; each line of the triplet was split into a doublet ( $J = 2$  c.p.s.). Minor absorptions which were most probably due to triethyl phosphate, ethanol, and diethyl ether were also present. After standing 17 months the spectrum of the mixture was completely in accord with that expected for a mixture of these three materials. Furthermore, g.l.p.c. analysis showed them to be present and to constitute the bulk of the sample.<sup>4</sup> Interestingly, g.l.p.c. analysis, under the same conditions, of a sample after a 21-day reaction time showed only triethyl phosphate, ethanol, and diethyl ether.

Changes in the infrared spectrum were also observed over a 15-day reaction period. These changes indicated that the triethyl phosphite was being consumed but that triethyl phosphate was not being produced at the same rate.

In another experiment triethyl phosphite labeled with deuterium in the methyl group (63.6% deuterium) was allowed to react with unlabeled diethyl peroxide. After 20 days triethyl phosphate was isolated by g.l.p.c. It was found to contain 40.7% deuterium in the methyl groups. This result shows that essentially complete equivalence of all of the ethoxy groups has been obtained.

Investigation of a reaction mixture (21 days after reaction started) in the phosphorus-31 n.m.r. showed three absorptions,  $-139.6$ ,  $+1.1$ , and  $+70.9$  p.p.m., relative to 85% phosphoric acid as external standard. The areas indicated relative percentages of 19, 23, and 58%. The first two components are clearly triethyl phosphite ( $-138$  p.p.m.) and triethyl phosphate ( $+1$  p.p.m.). The material absorbing at  $+70.9$  p.p.m. is unique in that such large positive shifts are diagnostic for substances having five oxygens or chlorines bonded to phosphorus.<sup>5</sup>

The most reasonable interpretation of these data is that initial reaction occurs to give pentaethoxyphosphorus (I). This material slowly decomposes at room temperature to give triethyl phosphate, ethanol, diethyl ether, and presumably ethylene. Attempts to analyze by g.l.p.c. undoubtedly caused decomposi-

(3) Triethyl phosphite has a quintet at  $\tau$  6.18 and a triplet at  $\tau$  8.80. Diethyl peroxide has a quartet at  $\tau$  6.05 and a triplet at  $\tau$  8.85.

(4) Analyses were performed with an F and M 500 gas chromatograph, using a 2-ft. silicone gum rubber column, helium flow 68 ml./min., programmed from  $55^\circ$  at  $21^\circ/\text{min.}$ , and a 10-ft. Carbowax 20M column, helium flow 59 ml./min. at  $60^\circ$ . The injection port temperature was  $ca.$   $235^\circ$ .

(5) For example Ramirez and Desai (ref. 1a) report  $+53$  p.p.m. for the biacetyl-trimethyl phosphite adduct.

tion of I to give the same products. Acceptance of this interpretation leads to the conclusion that a wide variety of pentaalkoxyphosphorus compounds can be prepared by this general technique.<sup>6</sup> The mechanism of the formation is under investigation but it seems reasonable to suggest that it involves a displacement process with phosphorus acting as the nucleophilic atom. The reaction probably leads to I without the intervention of ions.<sup>7</sup>

**Acknowledgment.**—We wish to thank Dr. John R. Van Wazer and the Monsanto Company for their determination of the  $\text{P}^{31}$  n.m.r. spectrum. Special thanks are due to Prof. Fausto Ramirez for discussions concerning these problems and for aid in obtaining  $\text{P}^{31}$  n.m.r. spectra which led to clarification of the nature of this and other reactions.

(6) More recent work by S. T. D. Gough indicates that this is the case. A number of phosphites have been allowed to react with diethyl and dimethyl peroxides. In most cases good evidence has been obtained for the formation of relatively stable pentaalkoxy compounds. It is hoped that a preliminary report on these materials can be submitted in the near future.

(7) D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Am. Chem. Soc.*, **83**, 1726 (1961).

(8) National Science Foundation Cooperative Graduate Fellow, 1962–1963; Public Health Service Fellow, 1963–1964.

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RECEIVED JULY 16, 1964

#### Paracyclophanes. IV. A Multilayered [2.2]Paracyclophane<sup>1</sup>

Sir:

Intramolecular reactions and interactions define the chemical and physical properties of certain many-membered rings. Such transannular effects stem from a variety of geometric characteristics unique to specific macrocyclic systems. In the  $[m.n]$ paracyclophane series (e.g., I,  $m = n = 2$ ) transannular effects become pronounced in the lower homologs as the separation between the aromatic rings decreases.<sup>2</sup> The [2.2]-paracyclophane system (I), with nonplanar benzenoid rings<sup>3</sup> at a maximum separation of only 3.1 Å., has been extensively examined in this regard. In addition to ring-current effects in I, transannular effects of substituents on  $\pi$ -base strengths, n.m.r. spectra, and electrophilic substitutions have been clearly demonstrated.<sup>4</sup>

There exists the intriguing possibility that electronic effects could be transmitted over long distances through a "tight" multilayered paracyclophane structure. We wish to report the synthesis and characterization of the first example of such a multilayered system.

Pyrolysis of the quaternary ammonium hydroxide V affords, presumably *via* VI, tetramethyl[2.2]paracyclophane (II). This dimer is identical with the one we obtained<sup>5</sup> from 1,2,4,5-tetramethylenecyclohexane, also *via* VI. The methyl groups in the dimer are

(1) Previous paper in this series: D. T. Longone and L. H. Simanyi, *J. Org. Chem.*, in press.

(2) D. J. Cram, *Record Chem. Progr.*, **20**, 71 (1959); D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963), and previous papers in this series.

(3) K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc. (London)*, **A255**, 82 (1960).

(4) L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963), and ref. 2.

(5) D. T. Longone and C. L. Warren, *ibid.*, **84**, 1507 (1962); D. T. Longone and F. P. Boettcher, *ibid.*, **85**, 3436 (1963).