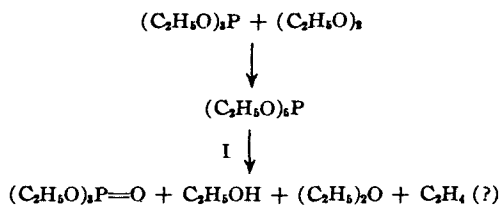


tion of a substance which is believed to be pentaethoxyphosphorus (I).



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.³ The absorptions of the starting materials were replaced by a distorted quintet ($J = 7$ c.p.s.) at τ 6.18 and a triplet ($J = 7$ c.p.s.) at τ 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.⁴ 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.⁵

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-

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.⁶ 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.⁷

Acknowledgment.—We wish to thank Dr. John R. Van Wazer and the Monsanto Company for their determination of the P^{31} n.m.r. spectrum. Special thanks are due to Prof. Fausto Ramirez for discussions concerning these problems and for aid in obtaining 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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Paracyclophanes. IV. A Multilayered [2.2]Paracyclophane¹

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.² The [2.2]-paracyclophane system (I), with nonplanar benzenoid rings³ 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 π -base strengths, n.m.r. spectra, and electrophilic substitutions have been clearly demonstrated.⁴

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 obtained⁵ 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).

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

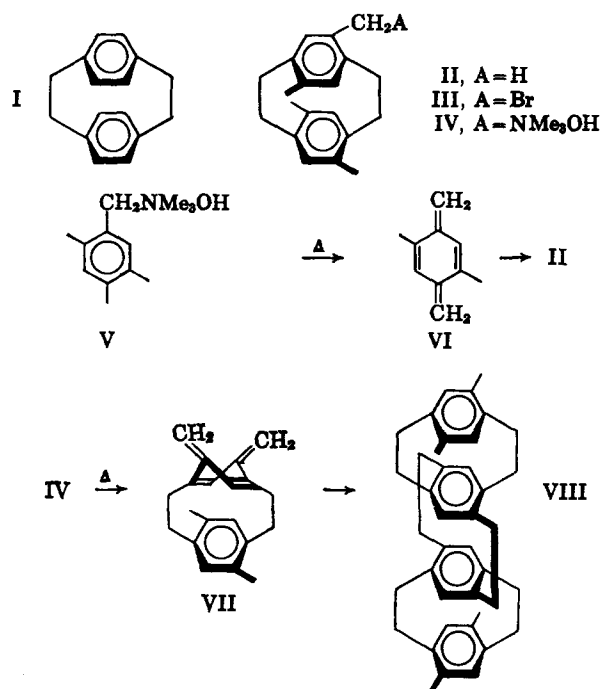
(4) Analyses were performed with an F and M 500 gas chromatograph, using a 2-ft. silicone gum rubber column, helium flow 68 ml./min., programmed from 55° at 21°/min., and a 10-ft. Carbowax 20M column, helium flow 59 ml./min. at 60°. The injection port temperature was ca. 235°.

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

structurally equivalent and bear the necessary *para* relationship for subsequent conversion of II to a higher arylog. Reaction of II with N-bromosuccinimide yields the bromomethyl⁶ compound III which is converted to the Hofmann base IV in the usual manner. Pyrolysis of IV in a toluene-water medium⁷ results in the smooth evolution of trimethylamine. The resulting reaction filtrate readily yields a microcrystalline hydrocarbon (m.p. *ca.* 265° dec.⁸) which analyzes correctly for a dimer of the *p*-xylylene-cyclophane VII.

Anal. Calcd. for C₄₀H₄₄: C, 91.55; H, 8.45; mol. wt., 525. Found: C, 91.63, 91.71; H, 8.36, 8.32; osmometric mol. wt., 528 (C₈H₈).

The dimer, isolated in 10% yield, is inert to permanganate and bromine solutions. Its infrared spectrum displays only aromatic unsaturation and is virtually identical with that of II. On the basis of chemical genesis and its chemical and physical properties, structure VIII can be assigned to the product. A structure which involves two isolated (noninteracting) paracyclophane moieties can be rejected on spectral grounds.



It would be premature to report the existence of long range (*ca.* 9 Å.) electronic interactions between the first and fourth rings of VIII; however, the spectral properties give some insight into the electronic nature of the system. The ultraviolet spectrum, devoid of fine structure, is similar to that of II at shorter wave lengths. At longer wave lengths VIII exhibits a marked hyperchromic effect.⁹ Compound VIII has $\lambda_{\text{max}}^{\text{isooctane}}$ 228 (log ϵ 4.30), 258 sh (3.84), 294 (3.45),

(6) The reduced reactivity of the bridge-methylene hydrogens allows selective bromination of the methyl groups: K. C. Dewhirst and D. J. Cram, *J. Am. Chem. Soc.*, **80**, 3115 (1958).

(7) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960).

(8) Analytically pure material fuses instantly when placed on a heated block at or above the recorded temperature; below this temperature the sample is rapidly converted to a high-melting (>300°) polymer.

(9) We have noted a similar hyperchromic effect in the spectrum of the overcrowded octamethyl[2.2]paracyclophane and have attributed it to aromatic ring distortions (ref. 1).

and 330 sh (2.65) $m\mu$ while II has $\lambda_{\text{max}}^{\text{isooctane}}$ 226 (4.20), 248 sh (3.53), 287 sh (2.38), and 300 sh (2.31) $m\mu$.

The n.m.r. spectrum¹⁰ of VIII is noteworthy. Much like II, the bridge-methylene protons appear as an A₂B₂ multiplet centered at τ 7.4 and the methyl protons as a singlet at τ 8.19. While the aromatic protons in II appear as a singlet at characteristically² high field (τ 3.77), in VIII *both sets* of aromatic protons (inner and outer rings) appear as singlets at very high fields, τ 4.38 and 4.48. These chemical shifts are concentration insensitive. With II as a model, we had anticipated that the two structurally equivalent pairs of protons on the inner rings of VIII (each shielded by two adjacent aromatic rings) would be found at *ca.* τ 4.5 while the protons on the outer rings would appear close to τ 3.8. Clearly, transannular shielding due to induced ring currents cannot alone account for the nearly identical chemical shifts of the two types of aromatic protons. A qualitative explanation might be offered by simply assuming disruption of ring currents brought about by severe puckering of all aromatic rings; however, this argument does not appear attractive to us. Until a crystallographic structure analysis becomes available we cannot adequately explain the observed chemical shifts.

Compound VIII forms an insoluble, blue-black 1:1 complex with tetracyanoethylene. The complex has $\lambda_{\text{max}}^{\text{KBr}}$ 680 $m\mu$ while the tetracyanoethylene complex of II absorbs at 565 $m\mu$ in the same medium and at 580 $m\mu$ in methylene chloride solution. The relative positions⁴ of the absorption maxima reflect a significant enhancement in π -basicity of VIII with respect to II.

The properties of VIII will be discussed in detail in a subsequent publication.

(10) Varian A-60 instrument, *ca.* 10% solutions in carbon tetrachloride. Integrated peak areas correct for the assigned structures.

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Regulation of Structural Isomerism in Simple Diels-Alder Adducts

Sir:

A few years ago, two research groups reported the very pronounced catalytic effect of Lewis acids on the Diels-Alder reaction.^{1,2} We now wish to report that Lewis acids not only accelerate the Diels-Alder reaction, but also regulate the structural isomerism of the adducts.

It is well known that two structural isomeric adducts are obtained from the reaction of an unsymmetrical diene with an unsymmetrical dienophile. Nazarov, *et al.*,³ have shown that when 1- or 2-alkyl-1,3-butadienes are allowed to react with esters of α -alkylacrylic acids, two structural adducts are formed in which the predominant isomer is the one that has the greatest separation between bulky groups.⁴

(1) P. Yates and P. Eaton, *J. Am. Chem. Soc.*, **82**, 4436 (1960).

(2) G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961).

(3) I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Dokl. Akad. Nauk SSSR*, **124**, 586 (1959); *Chem. Abstr.*, **53**, 11,268f (1959).

(4) H. B. Hennis, *J. Org. Chem.*, **28**, 2570 (1963), has found in the Diels-Alder reaction of isoprene with methyl acrylate that methyl 4-methyl-3-cyclohexene-1-carboxylate accounts for 70% of the two isomeric adducts formed and that the reaction is temperature independent.