

afforded the pure material: mp 103–105°; $\nu_{\text{max}}^{\text{KBr}}$ 3020, 1168, 1140, 1098, 1066, 1057, and 1042 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{O}_4$: C, 69.19; H, 10.32. Found: C, 69.09; H, 10.56.

cis,cis-4,4,9,9-Bis(ethylenedioxy)cyclodeca-1,6-diene (1e). Diketone **1a** (162 mg, 1 mmol) was partially dissolved in 20 ml of ethylene glycol and 0.5 ml of boron trifluoride etherate was added. The resulting solution was sealed, stirred at ambient temperature for 2.5 hr, and cooled to 0°, and the resulting precipitate was collected by suction filtration to give 227 mg (91%) of diketal, mp 187°. Recrystallization from carbon tetrachloride afforded the analytical sample as fluffy, colorless crystals: mp 185.5–186.0° subl; $\nu_{\text{max}}^{\text{CHCl}_3}$ 1200–1230 (b), 1140, 1060, and 1030 cm^{-1} .

Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$: C, 66.65; H, 7.99. Found: C, 66.76; H, 7.99.

cis,cis-4,4,9,9-Bis(thioethylenedioxy)cyclodeca-1,6-diene (1f). Diketone **1a** (1.0 g, 6.1 mmol) was dissolved in 100 ml of chloroform containing 20 ml of 1,2-ethanedithiol and 1.0 ml of boron trifluoride etherate. The reaction mixture was then sealed and allowed to stand at ambient temperature for 2 hr. Solvent was then removed with the aid of a rotary evaporator and the resulting precipitate was collected by suction filtration to give 1.92 g (99.5%) of colorless crystals, mp 239–240°. Recrystallization from chloroform afforded 1.62 g (84%) of pure dithioketal, mp 240.5–242.0° subl (lit.^{10c} mp 244–245°).

cis,cis-4,4,9,9-Tetracarboethoxycyclodeca-1,6-diene (1g). The

tetraester was prepared in 2.1% yield by condensation of diethyl malonate with *cis*-1,4-dichloro-2-butene according to the procedure of Gipson;^{10c,22} colorless plates, mp 158–160° (lit.^{10c} mp 161–162°).

cis,cis-4,4,9,9-Tetrakis(hydroxymethyl)cyclodeca-1,6-diene (1h). The tetraol was prepared by the method of Gipson.^{10c} A solution of 216 mg (5.7 mmol) of lithium aluminum hydride in 50 ml of dry tetrahydrofuran was prepared in a 100-ml, three-necked, round-bottomed flask equipped with a condenser, a magnetic stirrer, and an addition funnel. The system was placed under a nitrogen atmosphere, and a solution of 385 mg (0.91 mmol) of tetraester **1g** in 20 ml of dry tetrahydrofuran was added through the dropping funnel. The resulting mixture was then refluxed with stirring for 24 hr. After cooling to room temperature and cautious addition of 3 ml of absolute ethanol, the mixture was stirred for 15 min. Then 20 ml of 2 *N* hydrochloric acid was added and the mixture refluxed for 1 hr. After the mixture was cooled to room temperature and concentrated to about one-half the original volume on a rotary evaporator, 230 mg of a white precipitate was collected by suction filtration. Recrystallization from methanol and drying over phosphorus pentoxide under vacuum afforded 110 mg (48%) of the tetraol as colorless crystals, mp 254–257° (lit.^{10c} mp 261–262°).

Acknowledgment. We thank the National Science Foundation for support of this research.

(22) A similar procedure for making this compound may be found in ref 10a.

Phosphorus Large Membered Ring Molecules. 12- and 18-Membered Ring Phosphonites and the Corresponding Phosphonothioates

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Abstract: 2,5,5-Trimethyl-1,3,2-dioxaphosphorinane exists in equilibrium with its dimeric and trimeric forms which are 12- and 18-membered rings, respectively. The corresponding 2-thiono derivatives have been prepared and isolated. These large membered rings exist in different diastereomeric forms which display distinct ³¹P nmr signals. The two diastereoisomers of the 12-membered ring thiono derivatives have been separated.

The tendency of cyclic phosphonites to polymerize has been noted by different authors.¹ In particular, in a study of six-membered cyclic phosphonites,² White reported some experimental features concerning the polymerization process of 2,5,5-trimethyl-1,3,2-dioxaphosphorinane (**1**) and showed that this process is a reversible one. He also suggested that the polymeric species observed are phosphonites, but did not further elucidate their structure (long chain or macrocyclic).

As part of our studies on six-membered cyclic phosphorus compounds,³ we report here data which show the existence of dimeric (12-membered ring) and trimeric (18-membered ring) phosphonite molecules

among the polymeric species obtained in the polymerization process of **1**. The corresponding phosphonothioates have been isolated and characterized.

Results

Our observations on the evolution of pure samples of **1**, on standing, are very close to those reported by White. For samples of very good purity, sealed off under vacuum, the polymerization may be a very slow process since some of our samples remained quite mobile liquids after several months at room temperature. As reported previously,² the redistillation *in vacuo* of polymerized samples allows a nearly quantitative recovery of pure mobile **1**.

A freshly prepared benzene solution of **1** (sample I) shows only the nmr features expected for **1** (Figure 1a). In particular, the ¹H noise-decoupled ³¹P spectrum is a sharp singlet (δ –163 ppm). When such a benzene solution of **1** is left for a few days in a tube sealed under vacuum, additional nmr lines appear in the proton and phosphorus spectra in addition to the lines of species **1**.

(1) T. Mukaiyama, T. Fujisawa, Y. Tamura, and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964); A. N. Pudovik and G. I. Evstaf'ev, *Vysokomol. Soedin.*, **6** (12), 2139 (1964); A. Zwierzak, *Can. J. Chem.*, **45**, 2501 (1967); H. J. Harwood and N. K. Patel, *Macromolecules*, **1**, 233 (1968); J. E. Newbery, R. Woodcock, and R. F. Hudson, *Chem. Commun.*, 22 (1969); W. G. Bentrude, K. G. Yee, R. D. Bertrand, and D. M. Grant, *J. Amer. Chem. Soc.*, **93**, 797 (1971).

(2) D. W. White, *Phosphorus*, **1**, 33 (1971).

(3) R. O. Hutchins, B. E. Maryanoff, J. P. Albrand, A. Cogne, D. Gagnaire, and J. B. Robert, *J. Amer. Chem. Soc.*, **94**, 9151 (1972).

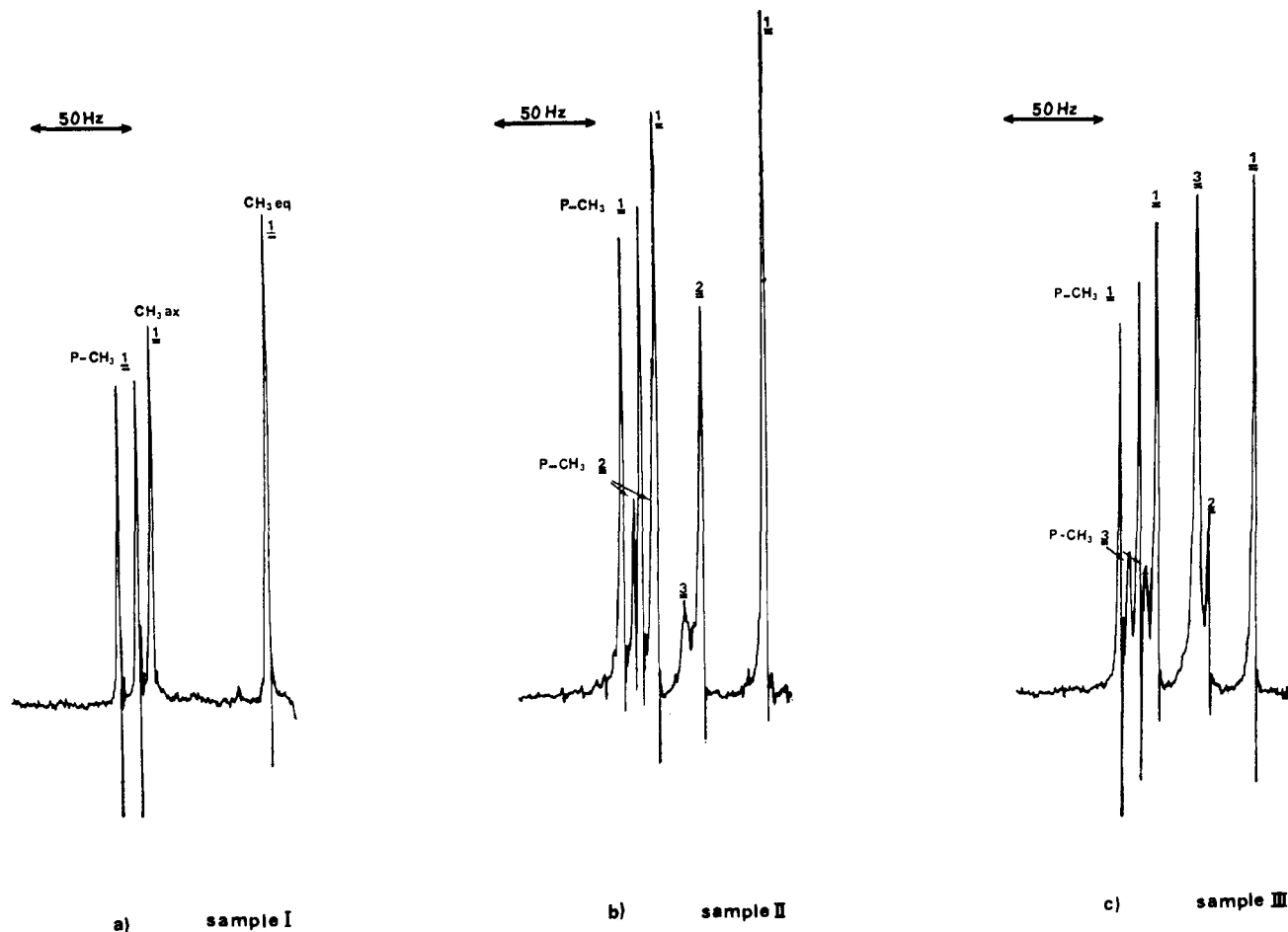


Figure 1. Modifications of the proton nmr methyl signal (P-CH_3 and $\text{C}(\text{CH}_3)_2$) of a benzene solution of 2,5,5-trimethyl-1,3,2-dioxaphosphorinane (**1**) left in a tube sealed under vacuum. The spectra are recorded at 100 MHz: (a) freshly prepared sample of **1**; (b) 25% by volume solution after 5 months at room temperature; (c) 50% by volume solution after 5 months at room temperature. The lines belonging to each species **1**, **2**, and **3** (see text) are shown by the corresponding numbers.

The changes from the initial spectrum (compound **1**) depend upon the starting concentration of compound **1** in the solution.

In the ^1H nmr spectrum of a dilute solution of **1** (25% v/v), sample II, the additional nmr lines appear in the methyl region (Figure 1b) (broad singlet δ 0.83 ppm; doublet P-CH_3 δ 1.12 ppm, $J_{\text{P-CH}_3} = 9.25$ Hz) and in the methylene region (a complex pattern overlapping with the AA'BB'X system of **1**). The proton-decoupled ^{31}P spectrum exhibits two additional sharp lines of equal intensity ($\delta -165.5$ ppm and -169.0 ppm). The presence of these two lines suggested the existence of two distinct species of similar structure. As expected on this basis, the P-CH_3 doublet at 1.12 ppm in the ^1H spectrum consists of two superimposed doublets which are selectively collapsed by selective decoupling of the phosphorus resonances at -165.5 and -169.0 ppm, respectively. The mass spectrum of sample II shows a peak at m/e 296 with an intensity of ca. 10% with respect to the molecular peak of **1** at m/e 148 ($\text{C}_6\text{H}_{13}\text{O}_2\text{P}$).

The above nmr and mass spectrometry data are consistent with the presence, in sample II, of a cyclic dimeric structure of **1**. The two additional lines in the ^{31}P nmr spectrum should correspond to two diastereoisomers *cis*-**2** and *trans*-**2** of such a dimeric structure. These isomers will differ by the relative orientation of the P-CH_3 bonds with respect to the mean plane of the molecule, as depicted on Figure 2.

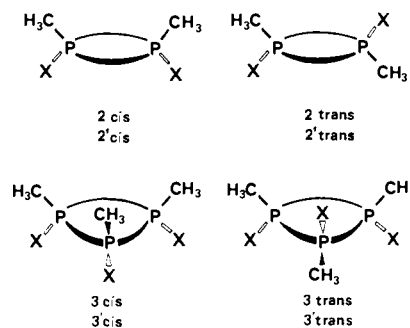


Figure 2. Schematic representation of the stereoisomers of the dimeric **2**, and trimeric **3** species obtained by polymerization of molecule **1**. **2'** and **3'** are the corresponding thiono derivatives: **2**, **3**, X = lone pair; **2'**, **3'**, X = S.

In the ^1H nmr spectrum of a more concentrated solution of **1** (50% v/v), sample III, the additional lines appear in the methyl region (Figure 1c) (broad singlet δ 0.86 ppm; doublet P-CH_3 δ 1.16 ppm, $J_{\text{P-CH}_3} = 8.5$ Hz) and in the methylene region (a complex pattern overlapping with the AA'BB'X system of **1**). In the proton-decoupled ^{31}P spectrum, one observes essentially three sharp lines in an approximate intensity ratio 1:2:2 ($\delta -180.01$ ppm, -180.0 ppm, and -179.5 ppm) and two broad lines with an intensity ratio 2:1 ($\delta -180.5$, -179.9). The mass spectrum of sample III shows some

Table I. Nmr Data of the Phosphonothioates 1', 2'a, 2'b, 3'a, and 3'b

Compd	C(CH ₃) ₂		—P—CH ₃ —		O—CH _a H _b —				P δ(³¹ P) ^b	
	δ(CH ₃) ^a		δ(PCH ₃)	² J(PCH ₃) ^a	δ(H _a)	δ(H _b)	² J(H _a H _b)	³ J(PH _A)		³ J(PH _B)
1'(C ₆ D ₆)	0.44; 0.99		1.72	15.5	3.40	4.42	11.0	21.0	7.0	-95.8 (s)
2'a(C ₆ D ₆)	0.59		1.46	15.8	3.47	4.04	10.0	4.5	8.5	-93.6 (s)
2'b(CDCl ₃)	0.95; 1.02		1.87	15.0	3.72	3.84	9.5	5.5	6.5	-91.8 (s)
3'a(C ₆ D ₆)	0.99		1.86	15.5	3.72	3.95	9.8	6.4	7.2	-96.2 (t)
3'b(C ₆ D ₆)	0.99		1.86	15.5	3.74	3.92	9.8	6.4	7.2	-96.2 (t)

^a The proton chemical shifts are in parts per million with respect to TMS; the *J* values are in hertz (Hz). ^b The δ(P) values are in parts per million downfield from external 85% H₃PO₄; s stands for singlet and t for triplet line.

fragments of small intensity (<1% of the parent peak *m/e* 69) which may derive from a species of mass 444 (C₆H₁₃O₂P)₃: *m/e* 359 (loss of C₃H₉O) and 375 (loss of C₃H₉). Very weak peaks were also detected above the mass 500. The above data may be explained by the presence of a trimeric structure of 1 in sample III, along with higher polymeric species. However, the main clues for the existence of a cyclic trimer proceed from the sulfurization of sample III (*vide infra*).

As explained for the dimeric species, the trimeric molecules may exist in two diastereomeric forms *cis*-3 and *trans*-3 as shown on Figure 2. Each isomer should exhibit distinct signals in the proton-decoupled ³¹P spectrum: a single line for *cis*-3 and a 1:2 doublet for *trans*-3. The sharp lines observed in the ³¹P nmr spectrum may be explained on this basis.

It must be pointed out that sample III is not completely free of the new species appearing in sample II and *vice versa*.

Samples of intermediate concentration (25% < C < 50%) show the methyl and methylene nmr lines observed in both samples II and III. The changes in the position lines observed in going from sample II to sample III are thus not due to a solvent effect, but clearly indicate that in addition to 1 different species exist in samples II and III depending upon the starting concentration.

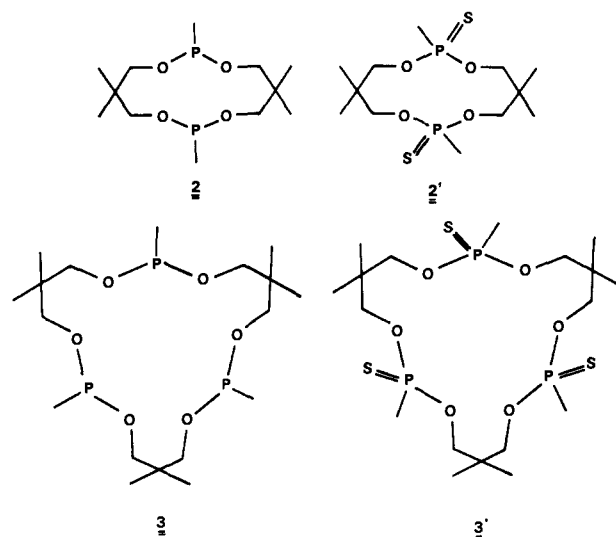
At room temperature, the additional lines appearing in samples II and III reached a maximum intensity after 5 months for II and a few days for III. The amounts of the new species with respect to 1 as defined by the intensity ratio of the corresponding nmr methyl signals are respectively 12% for II and 30% for III. When an equilibrated sample of II or III is maintained at 160° for 3 days, the additional nmr lines which increased with time in samples II and III disappear, and one gets back the nmr spectrum of compound 1. These experiments show that the extra species appearing in samples II and III are in equilibrium with molecule 1.

Sulfurization Reactions

Due to the fact that the species 2 and 3 are in equilibrium with 1, no attempt was made to isolate them. However, isolation of the corresponding phosphonothioates derivatives has been made.

The addition of elemental sulfur⁴ to sample I gives rise to the expected 2,5,5-trimethyl-2-thiono-1,3,2-dioxaphosphorinane (1') which has been identified by elemental analysis, mass spectrum (molecular peak at M' 180), and nmr (see Table I).

Reaction of elemental sulfur with sample II gave rise in addition to compound 1' to additional species 2'a



and 2'b. 2'a (mp 250°) and 2'b (mp 280°) are crystalline compounds which have been separated and isolated and which are characterized by elemental analysis (C₆H₁₃O₂PS)_n, mass spectrum (molecular peak at 2 M'), and the nmr data quoted in Table I. These analytical data allow us to assign without any ambiguity the cyclic formula shown above to compounds 2'a and 2'b. 2'a and 2'b should be isomeric molecules differing by the relative orientation of the bonds attached to the phosphorus atoms. In these two molecules the phosphorus atoms are equivalent and each of these molecules shows a single line in the proton-decoupled ³¹P spectrum (Figure 3).

By reaction of sulfur with sample III, one obtains in addition to 1' a highly viscous oil which is characterized by elemental analysis (C₆H₁₃O₂PS)_n and mass spectrum (molecular peak at 3 M'). These analytical data can only be explained by considering a cyclic trimeric formula for this species. The ³¹P proton-decoupled nmr spectrum shows clearly the existence of two isomeric molecules 3'a and 3'b. As explained before for 2'a and 2'b, these molecules will differ by the relative orientation of the methyl groups attached to the phosphorus atoms (Figure 2). In the molecule *cis*-3' the ³¹P nmr spectrum displays a single line. In the molecule *trans*-3', the phosphorus atoms are not all equivalent and the ³¹P spectrum shows a 2:1 doublet (Figure 3). According to the line intensities, the relative abundance of *cis*-3 to *trans*-3 is close to 1:3.

Discussion

It can be concluded from the present study that the polymeric species which are in equilibrium in solution with the 2,5,5-trimethyl-1,3,2-dioxaphosphorinane (1)² are the dimeric (12-membered ring) and the trimeric

(4) R. S. Edmundson, *Chem. Ind. (London)*, 1770 (1962).

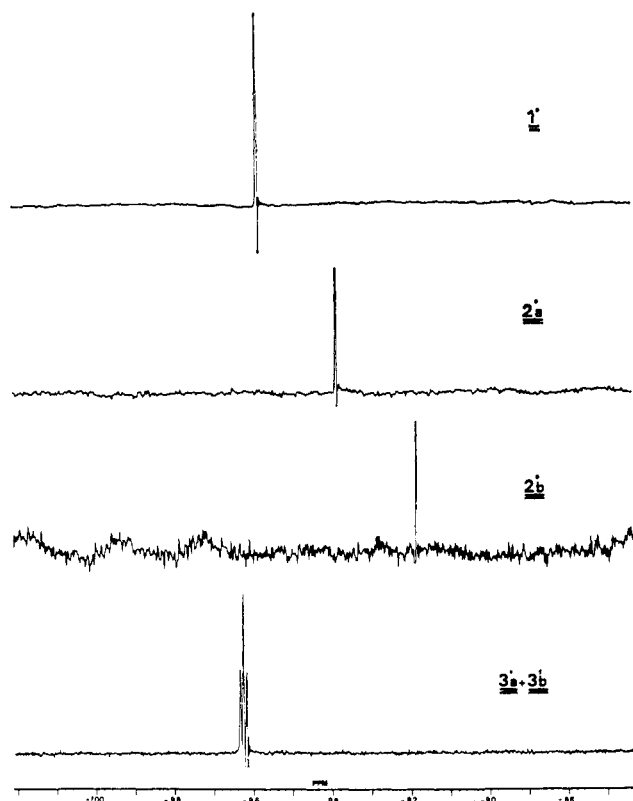


Figure 3. The 40-MHz proton-decoupled ^{31}P nmr spectra of 2,5,5-trimethyl-2-thiono-1,3,2-dioxaphosphorinane (**1'**) and of the corresponding dimeric **2'a** and **2'b** and trimeric **3'a** and **3'b** species.

forms (18-membered ring) of the phosphonite **1**. At a given temperature, the relative abundance of the monomeric, dimeric, and trimeric species in the equilibrium mixture depends on the starting concentration of molecule **1**.

If the formation of the diastereoisomers is statistical, one would expect a 1:1 ratio for the relative population of **2a** and **2b**. The two single lines of equal intensity observed in the ^{31}P [^1H] nmr spectrum of sample II are in agreement with such an interpretation. On the same statistical basis, one would expect a 1:3 ratio between **3a** and **3b**. By sulfurization of sample III, one would get a 1:3 ratio between species **3'a** and **3'b**, a ratio which may reasonably be assumed to be equal to the relative population of the nonsulfurized molecules **3a** and **3b** in the initial solution. It must, however, be pointed out that the ^{31}P [^1H] spectrum of sample III is not showing the expected 1:2:1 triplet for a 1:3 relative abundance ratio of molecule *cis*-**3** to *trans*-**3**; one observes a sharp 1:2:2 triplet and two broader additional lines. Such a discrepancy with the expected 1:2:1 triplet is probably due to the existence of higher polymeric species which have not been recovered after sulfurization. The 1:1 ratio observed for the two AB methylene proton spectra in the ^1H [^{31}P] spectrum of the mixture **3'a** + **3'b** (Figure 4) can also be accounted for by considering a 1:3 ratio between species **3'a** and **3'b** and two kinds of AB subspectra. One is due to protons which are located between two P=S bonds which have a *cis* relationship with respect to the mean plane of the 18-membered ring. The other one is due to protons

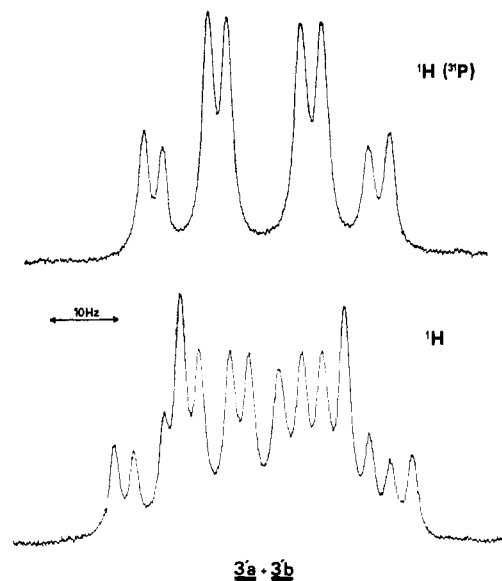


Figure 4. Methylene signal of the ^1H nmr spectrum of the mixture of the trimeric species **3'a** + **3'b**: upper part with phosphorus decoupling, lower part without phosphorus decoupling.

located between P=S bonds which have a *trans* relationship with respect to this mean plane.

The polymeric species which have been isolated, and the corresponding phosphonites, may have some interesting properties as chelating agents, a possibility which is presently under investigation.

Experimental Section

2,5,5-Trimethyl-1,3,2-dioxaphosphorinane (1). The synthesis of this compound was performed as reported previously.²

Sulfurization Experiments. A solution of elemental sulfur in benzene was added slowly under nitrogen to a stirred solution of **1**, **1** + **2**, or **1** + **3** in benzene cooled to 5°. The reaction takes place instantaneously. Sulfurization of **1** (sample I) gave the 2,5,5-trimethyl-2-thiono-1,3,2-dioxaphosphorinane (**1'**), which is recrystallized from benzene; mp 60°. *Anal.* Calcd for $\text{C}_6\text{H}_{13}\text{O}_2\text{PS}$: C, 39.99; H, 7.27; P, 17.19; S, 17.79. Found: C, 40.07; H, 7.13; P, 16.87; S, 17.88.

Sulfurization of sample II (**1** + **2**) gave a mixture of **1'**, **2'a**, and **2'b**. **2'b** which precipitates was recovered by filtration and recrystallized from *o*-dichlorobenzene, mp 280°. *Anal.* Calcd for $\text{C}_6\text{H}_{13}\text{O}_2\text{PS}$: C, 39.99; H, 7.27; P, 17.19; S, 17.79. Found: C, 40.25; H, 7.28; P, 16.62; S, 17.81.

The mixture of **1'** and **2'a** was chromatographed on silica with the following sequence of solvents: hexane, hexane-benzene, benzene. **2'a** eluted with benzene was recrystallized from benzene, mp 250°. *Anal.* Calcd for $\text{C}_6\text{H}_{13}\text{O}_2\text{PS}$: C, 39.99; H, 7.27; P, 17.19; S, 17.79. Found: C, 40.03; H, 7.22; P, 16.92; S, 17.61.

Sulfurization of sample III (**1** + **3**) gave a mixture of **1'** and **3'a** + **3'b**. The mixture of the two trimeric molecules was separated from **1'** by silica column chromatography. The mixture of **3'a** + **3'b** eluted by chloroform is a highly viscous oil; the two isomers have not been separated. Attempted recrystallization was unsuccessful. *Anal.* Calcd for $\text{C}_6\text{H}_{13}\text{O}_2\text{PS}$: C, 39.99; H, 7.27; P, 17.19; S, 17.79. Found: C, 40.89; H, 7.23; P, 15.69; S, 16.60.

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