A Thermolysis Study of Poly(trimethylene phenylphosphinate) and Poly(2,2-dimethyltrimethylene phenylphosphinate). NMR and X-ray Structure of 2-Oxo-2-phenyl-4,4-dimethyl-1,2-oxaphospholane[1a]

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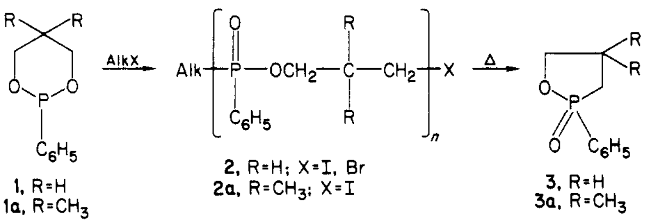
Thermal decomposition of poly(trimethylene phenylphosphinate) (**2**) and poly(2,2-dimethyltrimethylene phenylphosphinate) (**2a**) to 2-oxo-2-phenyl-1,2-oxaphospholane (**3**) and 2-oxo-2-phenyl-4,4-dimethyl-1,2-oxaphospholane (**3a**), respectively, has been described and the mechanism of their formation discussed. The X-ray crystal structure of oxaphospholane **3a** has been determined and compared to its preferred conformation in solution inferred from ^1H and ^{13}C NMR data. Compound **3a** crystallized in the monoclinic space group $C2/c$ with eight molecules per unit cell of dimensions a = 26.688 (5) Å, b = 7.612 (1) Å, c = 11.305 (3) Å, and β = 98.88 (2)°. The stereochemistry of another decomposition product of **2a**, namely, 4,4-dimethyl-2,6-diphenyl-1,2,6-oxadiphosphorinane 2,6-dioxide (**4a**), has also been deduced from its NMR data, and the mechanism of its formation is discussed.

The syntheses of poly(trimethylene phenylphosphinate) (**2**)[2-4] and poly(2,2-dimethyltrimethylene phenylphosphinate) (**2a**)[5] by the ring-opening polymerization of the corresponding 1,3,2-dioxaphosphorinanes **1** and **1a** using CH_3I initiator have been reported previously. We have found that these polymers thermally decompose to eliminate 1,2-oxaphospholanes **3** and **3a**. In this paper, we have studied the mechanism of their decomposition based on model compounds and the nature of the decomposition products. The stereochemistry of some of the decomposition products is examined by proton and carbon-13 NMR spectroscopy and single-crystal X-ray diffraction.



Results and Discussion

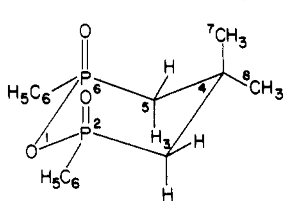
Poly(trimethylene phenylphosphinate) (**2**) was prepared by using CH_3I and n-C_3H_7Br as initiators. The polymer obtained with CH_3I had brown color presumably due to some HI elimination. n-Propyl bromide gave a colorless polymer and was used in this study. In the case of poly(2,2-dimethyltrimethylene phenylphosphinate), however, the iodide initiator had to be used to enhance the reactivity of the sterically hindered neopentyl-type propagating end with dioxaphosphorinane **1a**.

Polymers **2** and **2a** thermally decomposed to eliminate oxaphospholanes **3** and **3a**, respectively, depending on the temperature. For example, **2** made by using a 100:1 mol ratio of the monomer to n-PrBr at 160, 180, and 200 °C for 6 h contained 3.3%, 9.4% and 23.5%, respectively, of **3** as determined from its ^{31}P NMR spectrum (δ 58.5 ppm). On the other hand, **2a** made at 180–185 °C for 24 h had only a very small amount (<1%) of oxaphospholane **3a** (δ 59.5 ppm). However, at 195–200 °C the polymer formation and decomposition occurred simultaneously, giving 89% of 3a. It may be mentioned here that dioxaphosphorinanes **1** and **1a** did not isomerize directly to the oxaphospholanes at these polymerization temperatures.

We previously reported that 3-iodopropyl methylphenylphosphinate (**2**·I, n = 1) thermally decomposed at 160 °C to give 1.3-diiodopropane and 1,3-propanediyl bis(methylphenylphosphinate) presumably via a bimolecular reaction involving S_N2 displacement of the halide by phosphinate group.[5] Likewise, 3-iodo-2,2-dimethylpropyl methylphenylphosphinate (**2a**·I, n = 1), when heated at 200 °C for 8 h, liberated 1,3-diiodo-2,2-dimethylpropane. From these results, the elimination of oxaphospholanes **3** and **3a** from their polymers can be rationalized as an unzipping process following first the rearrangement of the terminal phosphinate group as shown in Scheme I. In the case of polymer **2a**, once the phosphinate end group is rearranged, the elimination of oxaphospholanes **3a** by the unzipping process would be relatively easy because of the *gem*-dimethyl effect.

Some phosphinate groups in the interior of the polymer chain are also rearranged. This was evident particularly from the ^{31}P NMR spectrum of polymer **2**. For example, the polymer made at 160 °C showed three absorptions at 45.06, 44.62, and 44.55 ppm, presumably due to the chiral phosphorus. However, the polymer made at 200 °C had several peaks upfield at 40.3–41.5 ppm which were attributed to the rearranged groups in the polymer chain. The phosphinate group rearrangement in aliphatic polyphosphinate has also been reported by others.[4,6,7]

The thermolysis of polymer **2a** also gave a small amount (~3%) of 4,4-dimethyl-2,6-diphenyl-1,2,6-oxadiphosphorinane 2,6-dioxide (**4a**). Its structure was established by elemental analysis and hydrolysis to 2,2-dimethyl-1,3-propanediyl bis(phenylphosphinic acid) (**5a**). From ^1H and ^{13}C NMR, it was assigned the following stereochemistry:



4a

^1H NMR data
CH_3 (axial) = 1.80 ppm
CH_3 (equatorial) = 1.24 ppm, triplet ($^4J_{PH}$ = 3.0 Hz)
CH_2's appeared as an unresolved multiplet at 2.10–2.33 ppm

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[1] (a) Presented at the International Conference on Phosphorus Chemistry, Nice, France, Sept 1983. (b) Central Research and Development Department.

[2] Petrov, K. A.; Nefantev, E. A.; Sopikova, I. I. *Vysokmol. Soedin.* **1960**, *2*, 685; *Chem. Abstr.* **1961**, *55*, 9935.

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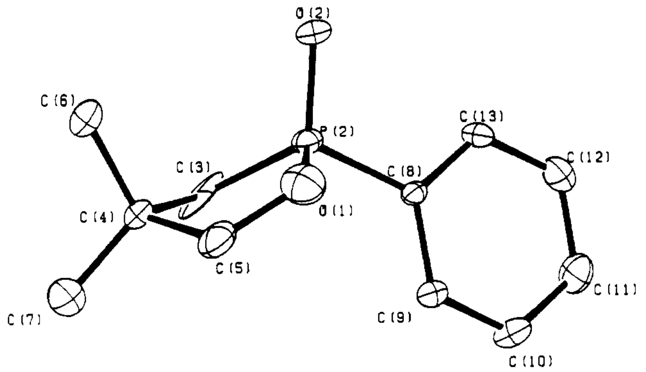


Figure 1. Perspective view of 2-oxo-2-phenyl-4,4-dimethyl-1,2-oxaphospholane (**3a**) with numbering of atoms.

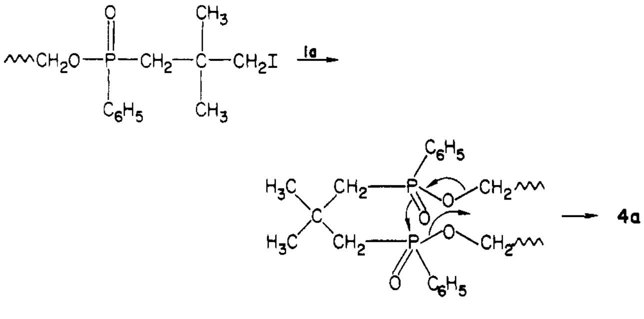
The axial CH_3 appears downfield because of the very strong deshielding effect of the P=O groups.[8,9] The upfield assignment to the equatorial CH_3 is consistent with previous observations.[10] Further, it showed a strong W-type long-range $^{31}P-C-C-C-^{1}H$ coupling of 3.0 Hz which is quite consistent with what Benezra[11] has reported over four σ bonds (3.0–5.0 Hz) in molecules with rigid geometry.

The importance of dihedral angle dependence of vicinal PCCC coupling is well established[12-15] and has been often used in determining the stereochemistry of phosphorus compounds.[16-18] In **4a**, the vicinal coupling constants of phosphorus with C_7, C_8, and C_5 (or C_3) are 0.0, 16.9, and 5.2 Hz, respectively. The corresponding dihedral angles (ϕ) calculated from these coupling constants by using the relationship[17a] in eq 1 are 75.5°, 176.5°, and 48.6°. These

$$^{3}J_{PC} = 7.35 - 1.76 \cos \phi + 7.86 \cos 2\phi \qquad (1)$$

angles are quite in line with the stereochemistry of **4a**.

The formation of **4a** provides further evidence for the rearrangement of the phosphinate group. The rearranged phosphinate end group of the polymer presumably reacts with the cyclic monomer **1a** forming a linkage that would eliminate **4a**.


$$\sim CH_2O-\overset{O}{\underset{C_6H_5}{\overset{\|}{\underset{|}{P}}}}-CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2I \xrightarrow{1a}$$

X-ray Structure and NMR Data of Oxaphospholane 3a.

X-ray Structure and NMR Data of Oxaphospholane 3a. The single-crystal X-ray analysis shows that the five-membered ring is puckered at C(4), making an angle of 36.8° between the plane C(3)–C(4)–C(5) and the mean plane of C(5)–O(1)–P(2)–C(3) (Figure 1). Atom C(4) is 0.59 Å out of the mean plane of the ring. Pertinent bond distances and angles, dihedral angles between selected planes, and deviations of atoms from the mean plane of the ring are listed in Table II.[19]

The ^{13}C and ^{1}H NMR data (Tables I and III), however, indicate that in solution **3a** exists in somewhat different conformations depending on the solvent. For example, in $CDCl_3$ the dihedral angles P(2)–C(3)–C(4)–C(6) and P(2)–C(3)–C(4)–C(7) calculated from the observed PC vicinal coupling constants of 4.1 and 9.9 Hz by using eq 1 are approximately 119.4° and 139.5°, respectively, vs. 82.1° and 153° in the crystal. These NMR angles would require moving C(4) more into the plane of the ring; and any bond eclipsing that might occur as a result of this can be minimized by an anticlockwise rotation around the P–C bond which, in turn, will move O(1) out of the plane of the ring. The anticlockwise (vs. clockwise) rotation around the P–C bond will give a less sterically hindered conformer and will position H(3) gauche and H(3′) trans to the P=O bond consistent with the large differences in the chemical shifts of these protons and their geminal coupling constants with phosphorus.

Further, these changes would decrease dihedral angle POCH(5) and increase POCH(5′) from their X-ray values of 142.7° and 101.5°, respectively. The dihedral angle relationship is also supposed to hold for vicinal POCH coupling constants[25] and, therefore, can be used to monitor conformational changes of **3a** in solution. H(5) is more deshielded than H(5′) due to the proximity to the P=O bond and is also more strongly coupled to phosphorus. From the phosphorus coupling constants with vicinal H(5), H(5′), C(6), and C(7), the maximum effect on their dihedral angles seems to occur in $CDCl_3$ solution. In more polar acetone-d_6 and Me_2SO-d_6, the couplings PH(5) and PC(7) increase while PH(5′) and PC(6) decrease vs. those in $CDCl_3$, indicating the dihedral changes more in the direction of the X-ray structure. This is possible if these solvents were associating with the phosphorus of **3a** from the opposite side of P=O bond. At higher temperatures in MeSO-d_6, due to the molecular dissociation from the solvent, the vicinal PH coupling constants approach those in nonpolar benzene-d_6 (Table III).

It is interesting to note that $CDCl_3$ not only has the greatest effect on the conformation of **3a** but it is in the opposite direction from that due to acetone-d_6 and MeSO-d_6. This can be rationalized if $CDCl_3$ was associating from the top side of the molecule possibly via a C—D···O=P bond. Its infrared spectrum, run on a 0.5 M solution in CCl_4 containing 5% $CDCl_3$, provided some evidence for the existence of this bond. The C–D absorption of $CDCl_3$ shifted from 2253 to 2238 cm^{-1} and was accompanied by an increase in intensity.[26]

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(19) Supplementary material on final positional and thermal parameters along with their standard deviations is available. See paragraph at end of paper.

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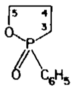
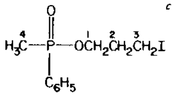
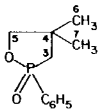
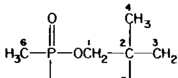
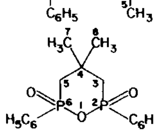
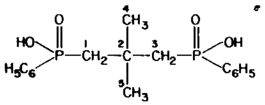
Table I. Carbon-13 NMR Data

no.	compound[a]	solvent	chemical shifts, ppm[b] (PC coupling constants, Hz)							
			C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
3		$CDCl_3$			25.54 (82.3)	24.25 (~0.0)	70.36 (4.6)			
2 (*n* = 1)	 [c]	$CDCl_3$	63.60 (6.3)	33.72 (6.7)	1.26	15.48 (102.6)				
3a		$CDCl_3$			40.25 (82.1)	38.70 (1.8)	81.45 (3.9)	27.06 (4.1)	27.19 (9.9)	
		C_6D_6			40.22 (82.2)	38.24 (~2)	81.21 (3.3)	26.90 (2.8)	26.68 (10.7)	
		$(CD_3)_2CO$			40.38 (82.4)	39.00 (2.0)	81.87 (3.3)	27.25 (2.0)	26.71 (11.8)	
		$(CD_3)_2SO$			39.03 (81.9)	38.05 (2.0)	80.69 (3.3)	26.60 (1.8)	25.94 (11.7)	
2a (*n* = 1)		$CDCl_3$	69.95 (5.9)	34.78 (7.1)	18.56	23.66	23.89	15.44 (102.1)		
4a		$CDCl_3$			40.37 ($^1J_{PC}$ = 96.4) ($^3J_{PC}$ = 5.2)	33.42 (6.1 t)[d]			28.06 (~0.0)	36.55 (16.9 t)[d]
5a	 [e]	$CDCl_3$	42.39 ($^1J_{PC}$ = 94.0) ($^3J_{PC}$ = 6.6)	33.18 (3.7 t)[d]	42.39 ($^1J_{PC}$ = 94.0) ($^3J_{PC}$ = 6.6)	30.71 (7.8 t)[d]				

[a] Carbon atoms are numbered as in the text. [b] Downfield from internal Me_4Si. [c] Prepared as described in ref 5. [d] t = triplet. [e] In Me_2SO-d_6.

Scheme I

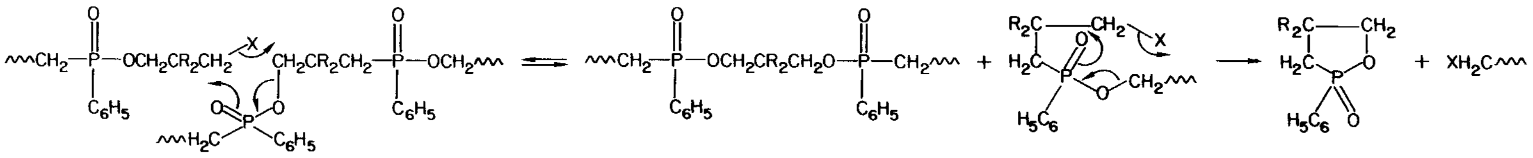


Table II. X-ray Structure Data of 3a[a]

Bond Distances (Å)			
P(2)-O(1)	1.599 (6)	C(3)-C(4)	1.659 (13)
P(2)-O(2)	1.472 (5)	C(4)-C(5)	1.501 (11)
P(2)-C(3)	1.785 (10)	C(4)-C(6)	1.549 (10)
P(2)-C(8)	1.772 (7)	C(4)-C(7)	1.498 (11)
O(1)-C(5)	1.411 (10)		
Bond Angles (deg)			
O(1)-P(2)-O(2)	111.8 (3)	O(1)-C(5)-C(4)	112.7 (8)
O(1)-P(2)-C(3)	100.5 (5)	C(3)-C(4)-C(5)	102.7 (6)
O(1)-P(2)-C(8)	104.7 (3)	C(3)-C(4)-C(6)	108.7 (6)
O(2)-P(2)-C(3)	117.4 (4)	C(3)-C(4)-C(7)	116.7 (7)
O(2)-P(2)-C(8)	110.8 (3)	C(5)-C(4)-C(6)	110.9 (7)
C(3)-P(2)-C(8)	110.5 (3)	C(5)-C(4)-C(7)	107.7 (7)
P(2)-O(1)-C(5)	111.0 (6)	C(6)-C(4)-C(7)	109.9 (6)
P(2)-C(3)-C(4)	98.8 (5)		

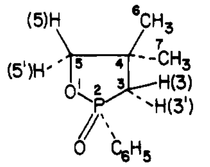
Dihedral Angles (deg)	
P(2)-C(3)-C(4)-C(6)	82.1
P(2)-C(3)-C(4)-C(7)	153.0
P(2)-O(1)-C(5)-H(5)	142.7
P(2)-O(1)-C(5)-H(5′)	101.5
O(2)-P(2)-C(3)-H(3)	16.9
O(2)-P(2)-C(3)-H(3′)	148.4

Deviations of Atoms from the Mean Plane O(1)-P(2)-C(3)-C(5) (Å)

O(1)	0.028	P(2)	−0.025	C(3)	0.015	C(5)	−0.019		
O(2)	−1.179	C(4)	−0.590	C(6)	−2.136	C(7)	−0.177	C(8)	1.488

[a] Esds in units of the least significant figure in parentheses.

Table III. Solvent and Temperature Dependence of Phosphorus-Proton and Proton-Proton Coupling Constants in Oxaphospholane 3a



	proton chemical shifts, ppm (coupling constants, Hz)[a]							
	24 °C				Me_2SO-d_6			
	$CDCl_3$	C_6D_6	CD_3COCD_3	Me_2SO-d_6	60 °C	100 °C	150 °C	neat 80 °C
PH(3)	2.12 (13.6)[a]	1.76(12.4)						(12.5 ± 0.5)[b]
PH(3′)	1.92 (6.0)[a]	1.41 (6.4)						(6.5 ± 0.5)[b]
HH(3,3′)	(15.0)	(14.8)						(14.9)
PH(5)	4.27 (13.3)	3.85 (14.3)	4.20 (15.7)	4.16 (16.2)	(15.5)	(15.0)	(14.5)	(14.5)[c]
PH(5′)	3.97 (9.6)	3.48 (8.6)	4.05 (6.6)	4.01 (6.1)	(7.0)	(8.0)	(9.0)	(9.0)[c]
HH(5,5′)	(9.1)	(8.8)	(8.9)	(8.9)				(9.0)[c]
CH_3(6)	1.41	1.23	1.38	1.31				
CH_3(7)	1.21	0.65	1.22	1.16				

[a] H(3) is more deshielded because of its gauche position to P=O bond and more strongly coupled to phosphorus than the trans H(3′), consistent with reports on similar other compounds.[20-24] Our previous assignments of these protons[5] were in error. [b] Because of the closeness of the chemical shifts of H(3) and H(3′) and since ^{31}P spectrum did not yield the resolution due to couplings with H(5), H(5′), and all the aromatic protons, $J_{PH(3)}$ and $J_{PH(3')}$ reported here for neat liquid at 80 °C may have an uncertainty of ±0.5 Hz. In all cases H(5) and H(5′) were well separated and the couplings involving these protons to phosphorus are accurate. [c] These coupling constants did not change between 80 and 180 °C in neat liquid.

Experimental Section

Melting points were determined by interactive DSC. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Proton, ^{13}C, and ^{31}P NMR spectra were recorded on a Nicolet NT-300 spectrometer equipped with a Fourier transform accessory. The spectrometer was operated at 75.46 and 121.47 MHz for ^{13}C and ^{31}P, respectively, with a time-shared deuterium lock on $CDCl_3$. A broad-band noise decoupler was used to eliminate the $^{13}C-^1H$ and $^{31}P-^1H$ couplings. The spectra were run on 0.5 M solutions in $CDCl_3$ unless mentioned otherwise. The variable-temperature ^1H spectra of oxaphospholane **3a** were run on a wide-bore Nicolet NT-360 spectrometer. The ^1H and ^{13}C chemical shifts are reported downfield from internal standard of Me_4Si; and ^{31}P chemical shifts are downfield from the external reference of 85% H_3PO_4.

2-Phenyl-1,3,2-dioxaphosphorinane (1) and 4,4-Dimethyl-2-phenyl-1,3,2-dioxaphosphorinane (1a). They were prepared as described previously[5] and purified by vacuum distillation; **1** distilled at 92–95 °C (0.4–0.6 mmHg) and **1a** at 114 °C (0.3 mmHg) as colorless liquids. On cooling to room temperature, **1a** solidified to a white solid, mp 75 °C. Their ^{31}P chemical shifts were at 153.65 ppm and 145.84 ppm, respectively.

Preparation of Poly(trimethylene phenylphosphinate) (2) Using *n*-Propyl Bromide as Initiator. A mixture of 36.4 g (0.2 mol) of **1** and 0.246 g (0.002 mL) of freshly distilled *n*-PrBr was taken in a heavy-walled glass tube. The contents of the tube were thoroughly flushed by using an alternating N_2/vacuum cycle and sealed under vacuum. Three tubes were prepared by this procedure and heated at 160, 180, and 200 °C for 6 h in a Wood's metal bath. They were broken while still warm and the colorless,

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(26) For bonding of C–D with strong deuterium acceptors, see: Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 1715.

clear polymer was poured out. The polymer turned into a hard solid on standing at room temperature. Its ^{31}P NMR analysis showed complete conversion of the monomer (disappearance of its absorption at 153.65 ppm) and that the polymer made at 160, 180, and 200 °C had 3.3% 9.4% and 23.5%, respectively, of oxaphospholan **3** (δ 58.5). The oxaphospholane was distilled from the polymer at 120 °C (0.1 mmHg) (lit.[27] bp 142 °C (0.2 mmHg)). It supercooled at room temperature and then suddenly solidified, liberating a large amount of heat; mp 69 °C. Anal. Calcd for $C_{17}H_{20}O_3P$: C, 59.3; H, 6.0; P, 17.0. Found: C, 59.4; H, 6.2; P, 16.9

Preparation and in Situ Decomposition of Poly(2,2-dimethyltrimethylene phenylphosphinate) (2a). A mixture of 84.0 g (0.4 mol) of 4,4-dimethyl-2-phenyl-1,3,2-dioxaphosphorinane (**1a**) and 5.3 g (0.0152 mol) of 3-iodo-2,2-dimethylpropyl methylphenylphosphinate (**2a**·I, *n* = 1)[5] was shaken in a heavy-walled glass tube. The mixture was thoroughly flushed by using an alternating N_2/vacuum cycle, sealed under vacuum, and heated at 195–200 °C for 24 h. It first got viscous, indicating the formation of the polymer, and then became quite fluid due to decomposition to oxaphospholane **3a**. The tube was broken and the oxaphospholan distilled at 152–153 °C (0.5 mmHg) as a colorless liquid, 75 g (89%). It supercooled at room temperature and then quickly solidified, giving a large amount of heat; mp 67 °C.

The viscous residue (12 g) left behind was dissolved in 25 mL of refluxing acetone and filtered. On cooling, a white solid separated which was collected by filtration and washed with 10 mL of acetone, 2.2 g (3%). Its analytical sample, prepared by recrystallization from acetone, had mp 198 °C. Anal. Calcd. for $C_{17}H_{20}O_3P_2$ (**4a**): C, 61.1; H, 6.0; P, 18.6. Found: C, 61.1; H, 6.0; P, 18.2. Its IR spectrum (KBr) showed P=O stretch at 1238 (s) and P—O—P asymmetric stretch at 912 cm^{-1} (s);[28] NMR ^{31}P δ 39.1. Refluxing in 20 mL of aqueous acetone for 2 h completely hydrolyzed it to 2,2-dimethyl-1,3-propanediyl bis(phenylphosphinic acid (**5a**) which separated as white solid and was collected by filtration, mp 175 °C. Anal. Calcd for $C_{17}H_{22}O_4P_2$: P, 17.6. Found: P, 17.4. Its ^{1}H NMR Me_2SO-d_6) δ 1.07 (2 CH_3), 2.13 (2 CH_2, d, J_{PH} = 13.7 Hz), 9.54 (2 OH, br); ^{31}P NMR δ 36.77.

X-ray Structure Determination of 3a. A colorless rectangular plate with dimensions 0.35 × 0.20 × 0.70 mm obtained by crystallization from cyclohexane/petroleum ether (bp 38–54 °C) was mounted on a glass fiber and placed on an Enraf-Nonius CAD4 diffractometer equipped with a Mo K_α source, graphite monochromator, and an FTS low-temperature refrigeration unit operating at −70 °C. The CAD4 routines indicated a monoclinic unit cell space group *C*2/*c* with dimensions a = 26.688 (5) Å, b = 7.612 (1) Å, c = 11.305 (3) Å, β = 98.88 (2)°. With Z = 8 the calculated density of $P_1O_2C_{11}H_{15}$ is 1.231 g/cm^{-1}. A total of 1096 independent reflections with $I \geq 2\sigma(I)$ were obtained from $2° \leq \theta \leq 25°$ using the ω-scan mode with $\omega = 0.7 + 0.35(\tan\theta)$. The structure was solved with direct methods (MULTAN)[29] and refined by using full matrix anisotropic least squares with 127 variables to a conventional R = 8.8% and R_w = 8.6%. Hydrogens were both located from difference electron density maps and calculated and included as fixed atom contributors in idealized positions with isotropic temperature factors. All atoms refined satisfactorily with the exception of ring atom C(3) which showed an elongated thermal ellipsoid. The largest peak on a final difference map was 0.3 e/Å near atom C(3).

Thermolysis of 3-Iodo-2,2-dimethylpropyl Methylphenylphosphinate (2a·I, *n* = 1). A 3.0-g sample was taken in a heavy-walled glass tube, purged thoroughly by using alternating an N_2/vacuum cycle, and sealed under vacuum. It was heated at 200 °C in a Wood's metal bath for 8 h. The material turned brown and was isolated by breaking the tube. Bulb-to-bulb distillation at 104 °C (0.2 mmHg) gave 2 drops of a colorless liquid. ^{1}H NMR showed two sharp singlets at 1.24 and 3.27 ppm in 2:3 ratio, consistent with the structure of 1,3-diiodo-2,2-dimethylpropane; and its mass of 324 was confirmed by GC/mass spectrum.

Registry No. 1, 7526-32-1; **1a**, 7526-31-0; 2 (n = 1), 68900-54-9; **2a** (n = 1), 68900-52-7; **3**, 16324-19-9; **3a**, 68900-53-8; **4a**, 93454-13-8; **5a**, 93454-14-9; *n*-PrBr, 106-94-5; 1,3-diiodo-2,2-dimethylpropane, 66688-49-1.

Supplementary Material Available: Table of fractional atomic coordinates and anisotropic thermal parameters for compound **3a** (1 page). Ordering information is given on any current masthead page.

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Thiopyranothiopyran Chemistry. 1. Synthesis of 1,3,5,7-Tetraphenylthiopyrano[4,3-*c*]thiopyran 2,2,6,6-Tetraoxide

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During a synthetic study aimed at the hitherto unknown thiopyrano[4,3-*c*]thiopyran system, the disulfone derivative 1,3,5,7-tetraphenylthiopyrano[4,3-*c*]thiopyran 2,2,6,6-tetraoxide (**4**) was synthesized. The approach starting from 2,6-diphenyl-3-formylthiopyran-4-one (**11**) via the key intermediate 3-[2(*Z*)-(benzylthio)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one (**12**), whose absolute configuration was confirmed by X-ray analysis, is described in detail. Cyclization of the corresponding sulfoxide 3-[2(*Z*)-(benzylsulfinyl)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one (**15**) with LDA/THF at −78 °C gives 2,6,7,9-tetraphenyl-1,8-dithiaspiro[4,5]deca-2,6,9-trien-4-one (**18**), which is rationalized by a basic Pummerer rearrangement. The corresponding sulfone (*Z*)-**16**, under similar conditions, annulates to give a new, rearranged dihydrothiopyrano[3,4-*b*]thiopyran (**20**), whose formation is explained by a double Michael addition of the lithiated anion of (*Z*)-**16**. A cyclic voltammogram of **4**, which shows characteristics of an organic acceptor, is included.

The novel 12π thiopyrano[4,3-*c*]thiopyran system **1**, which is isoelectronic with heptalene,[1] has been proposed as a new class of donors on the basis of the concept of "intermolecular migration of aromaticity" in the mixed-

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