

- 27, 231 (1969).
- (6) C. A. Maryanoff, B. E. Maryanoff, R. Tang, and K. Mislow, *J. Am. Chem. Soc.*, **95**, 5839 (1973).
- (7) T. Svinning, F. Mo, and T. Bruun, *Acta Crystallogr., Sect. B*, **32**, 759 (1976).
- (8) Comments concerning these analyses should be directed to Professor Chu at Southern Methodist University.
- (9) C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report, ORNL-3794, 1974.
- (10) S. S. C. Chu and B. Chung, *Acta Crystallogr., Sect. B*, **30**, 235 (1974).
- (11) S. S. C. Chu, *Acta Crystallogr., Sect. B*, **31**, 1082 (1975).
- (12) S. S. C. Chu, *Acta Crystallogr., Sect. B*, **32**, 1583 (1976).
- (13) The numbering shown in Figure 1 is used throughout the discussion of the x-ray results.
- (14) Assignment of configuration to such compounds will be presented in a future communication.
- (15) We have observed that both *meso*- and *dl*-1,4-dimesityl-1,4-dithiabutane 1,4-dioxides exhibit complex ethano regions under all of the conditions employed (-20 to $+60$ °C in CDCl_3 , C_6D_6 , and $\text{C}_6\text{D}_5\text{N}$). The x-ray and NMR studies of these will be discussed in a future communication. Asymmetric synthesis⁵ has been used to prepare the enantiomerically enriched (+)-*R,R* diastereomer.¹⁶
- (16) J. Lin, M.A. Dissertation, The University of Texas at Arlington, 1975.
- (17) M. Raban, *Tetrahedron Lett.*, 3105 (1966).
- (18) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).
- (19) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964).
- (20) The higher melting isomer in such compounds traditionally has been labeled α and the lower melting one β .
- (21) D. Jung and A. A. Bothner-By, *J. Am. Chem. Soc.*, **86**, 4025 (1964).
- (22) K. Higasi, *Rikagaku Kenkyusho Iho*, **22**, 805 (1943); *Chem. Abstr.*, **43**, 7764a (1949).
- (23) B. Krishna and K. K. Sirvastava, *J. Chem. Phys.*, **27**, 835 (1957).
- (24) C. Altona, Ph.D. Dissertation, Leiden, The Netherlands, 1964.
- (25) Determined: Me_2SO , 4.07 D; $(\text{C}_6\text{H}_5)_2\text{SO}$, 3.87 D. Literature: 4.03 and 3.9 D, respectively.²⁶
- (26) Because of their polarity, sulfoxides have been studied extensively by this technique. For example: C. R. Johnson and N. J. Leonard, *J. Am. Chem. Soc.*, **84**, 3701 (1962); H. L. Lumbruso and G. Montaudo, *Bull. Soc. Chim. Fr.*, 2119 (1964); C. W. N. Cumper and A. G. Vogel, *J. Chem. Soc.*, 3521 (1959); C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956); A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.
- (27) It does not follow of course that *all* diastereomers of this type should be distinguishable by this method. Highly polar aryl substrates may lead to alterations in this pattern. However, the diastereomers of 1,4-di-*tert*-butyl-1,4-dithiabutane 1,4-dioxides differ in dipole moment by 1.05 D (1.83 vs. 2.88 D), and we have tentatively assigned the *meso* configuration to the former (unpublished results).
- (28) The absence of starting material was established by TLC (Kieselgel, 0.25 mm; on glass column; chloroform-ethyl acetate (3:1) eluent; iodine visualization). The NMR spectrum (CDCl_3) was distinctive and exhibited in the ethano region a singlet at δ 3.02 and a symmetric two-winged multiplet centered at δ 3.02.
- (29) L. J. Bellamy, *Org. Sulfur Compd.*, **1**, Chapter 6 (1961).
- (30) The ethano region appeared as a singlet.
- (31) E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1798 (1927).
- (32) R. J. W. LeFevre and C. Y. Chen, *Aust. J. Chem.*, **16**, 917 (1963).
- (33) E. Fromm, H. Benzinger, and F. Schafer, *Justus Liebigs Ann. Chem.*, **394**, 325 (1912).
- (34) N. A. Milas and A. McAlvey, *J. Am. Chem. Soc.*, **55**, 349 (1933).
- (35) L. Katz, L. S. Karger, W. Schroeder, and M. S. Cohen, *J. Org. Chem.*, **18**, 1380 (1953).
- (36) Kahl Scientific Instrument Corp.
- (37) *Natl. Bur. Stand. (U.S.)*, *Circ.*, No. 514 (1951).
- (38) N. F. M. Henry and K. Lonsdale, Eds., "International Tables for X-ray Crystallography", Vol III, Kynoch Press, Birmingham, England, 1962, pp 201-207.
- (39) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Ten-Membered Ring Heterocyclic Molecules Containing Phosphorus, Oxygen, and Nitrogen

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Received January 18, 1978

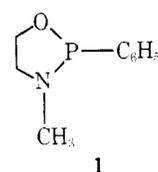
The five-membered ring 2-phenyl-1,3,2-oxazaphospholidine exists in solution in equilibrium with its ten-membered ring dimers and polymeric species of high molecular weight. The corresponding 2-thiono derivatives have been prepared by direct addition of elemental sulfur. The ¹H, ¹³C, and ³¹P NMR spectral parameters are reported along with a discussion concerning the five-membered ring conformation.

In previous papers we described spontaneous dimerization from various 1,3,2-dioxo and 1,3,2-dithia organophosphorus molecules. Thus, ten-membered rings have been obtained from 2-phenyl-1,3,2-dioxaphospholane,^{2a} 12-membered rings from 2-methyl-1,3,2-dioxaphosphorinane^{2b} and from 2-*tert*-butyl-1,3,2-dithiaphosphorinane,³ 14-membered rings from 2-*tert*-butyl-1,3,2-dioxaphosphepane,⁴ and 16-membered rings from 2-methyl-1,3,6,2-trioxaphosphocane.⁵

In those reactions, besides dimers one observes the formation of polymeric species which are under investigation and whose structure (cyclic or not cyclic) has not yet been established.

Such a dimerization has not been observed starting from 1,3,2-diazaphospholidines or 1,3,2-diazaphosphorinanes. However, due to the influence of minor experimental factors (moisture, nature of the storing vessel) on the evolution of the reaction when it takes place, we cannot conclude that this reaction does not take place with 1,3-diaza compounds. Thus, it seemed interesting to investigate the behavior of 1,3-oxaza compounds ($-\text{O}-\text{P}-\text{N}-$). As according to our previous results, the dimerization is more easily observed in dioxaphospholanes

than in dioxaphosphorinanes or dioxaphosphepanes, and as this reaction goes easily with the 2-phenyl-1,3,2-dioxaphos-



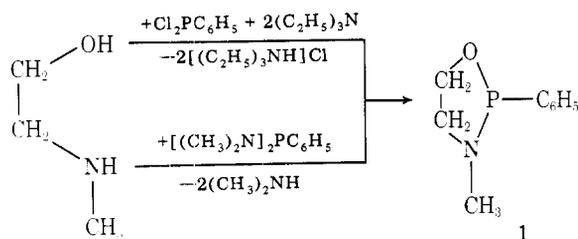
pholane, the 2-phenyl-1,3,2-oxazaphospholidine **1** appeared to be a good candidate for a possible ring-expansion reaction.

Some results have been previously reported on the behavior of 2-substituted 1,3,2-oxazaphospholidines. 2-Phenyl-3-methyl-1,3,2-oxazaphospholidine (**1**) is an interesting compound, since, at room temperature, it polymerizes into a solid in a reversible reaction. The polymer formula was written as a linear chain $[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{P}(\text{C}_6\text{H}_5)-]_n$.⁶ In another study, the 2,3-dimethyl-1,3,2-oxazaphospholidine was said to exist as a dimer but no details concerning the dimer identification or stereochemical discussions were given.⁷

We wish to report here on the identification of the compounds which are obtained by evolution of the oxazaphospholidine 1. They are two cyclic ten-membered ring dimers and polymeric species of higher molecular weight. The NMR spectral parameters (^1H , ^{13}C , and ^{31}P) of these different species are also discussed.

Oxazaphospholidine Dimerization and Polymerization.

(a) **2-Phenyl-3-methyl-1,3,2-oxazaphospholidine.** 2-Phenyl-3-methyl-1,3,2-oxazaphospholidine (1) can be pre-



pared by reaction of 2-(methylamino)ethanol with dichlorophenylphosphine or in better yield and higher purity with bis(dimethylamino)phenylphosphine.⁸

When neat or in benzene solution (I), 1 undergoes a reaction which has been followed via changes observed in its proton noise-decoupled ^{31}P NMR spectrum.

Immediately after preparation (by dissolving a freshly distilled sample of compound 1 in benzene), solution I shows only one line (M) at 142 ppm in the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum.³⁰ When the benzene solution (I) is left in an NMR tube sealed under vacuum, additional lines appear in the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum. The first new lines which appear consist of a four-line pattern (P) of the same intensity and of equal spacing, located between 134 and 135 ppm³⁰ (Figure 1, A and B). By recording the spectrum at two different frequencies (24 and 40 MHz), the line spacing is shown to be due to a chemical shift and not to spin-spin couplings. Simultaneous with the appearance of the line system P, the viscosity of the solution increases suggesting that a polymerization process takes place, and one observes the formation of compact colorless crystals, whose existence has already been noticed by Hudson and co-workers.⁶ Finally, the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum of solution I shows, in addition to the lines previously described [single peak at 142 ppm (M), four line pattern (P) between 134 and 135 ppm], two lines at 136.5³⁰ (D_1) and 134.9 ppm³⁰ (D_2), respectively (Figure 1, C). The rate of these changes can be increased in the first step (appearance of the four-line pattern denoted P) by addition of a catalytic amount of *p*-toluenesulfonic acid to the solution. The appearance of peaks D_1 and D_2 is accelerated by heating the solution for a few hours at 80 °C.

The compounds corresponding to the different lines observed in the $\{^1\text{H}\}^{31}\text{P}$ NMR spectra of solution I have been characterized, either as the three-coordinate phosphorus compounds or as the corresponding thiono derivatives.

(b) **Identification of the Compounds.** Compound 1 which shows peak M in its $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum (Figure 1, A) is a nonviscous liquid which remains stable for several days at 0 °C. Reaction with elemental sulfur in benzene gives rise to a stable crystalline compound 1' (mp 67 °C). By elemental analysis, mass spectrometry (molecular peak at m/e 181 and 218 for 1 and 1', respectively), and ^1H , ^{13}C , and ^{31}P NMR spectroscopy (Tables I and II) 1 and 1' are identified as 2-phenyl-3-methyl-1,3,2-oxazaphospholidine (1) and the corresponding 2-thiono derivative 1'.

The crystalline compound which appears in solution I was isolated by filtration and recrystallization from hot benzene (mp 191–193 °C). This compound, denoted 3, was characterized by elemental analysis ($\text{C}_9\text{H}_{12}\text{ONP}$)_n, mass spectrometry (molecular peak at m/e 362, $n = 2$), and ^1H , ^{13}C , and ^{31}P NMR

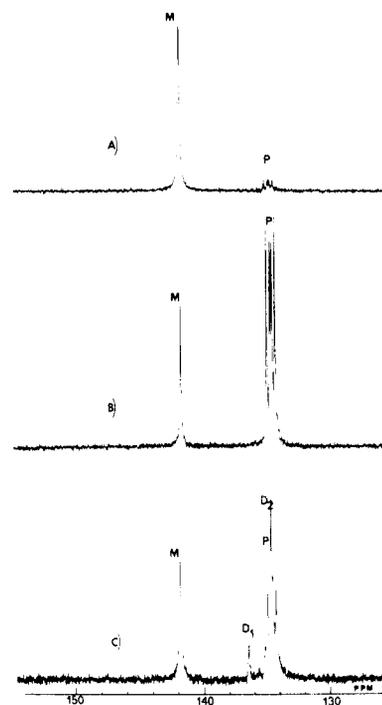
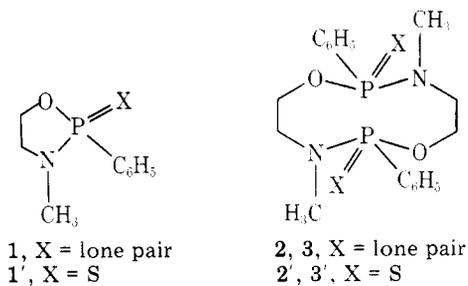


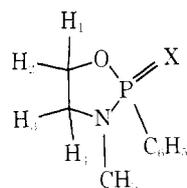
Figure 1. $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum of a benzene solution of 3-methyl-2-phenyl-1,3,2-oxazaphospholidine.

spectroscopy (Table III). All the data are in agreement with a ten-membered ring structure for compound 3, a dimer of 2-phenyl-3-methyl-1,3,2-oxazaphospholidine (1). The $\{^1\text{H}\}^{31}\text{P}$ NMR peak of compound 3 (134.9 ppm) corresponds to the peak denoted D_2 in solution I.



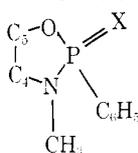
Addition of elemental sulfur to compound 3 gives the expected ten-membered ring cyclic dimer of 2-thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine (3', mp 274–275 °C). The elemental analysis is in agreement with the ($\text{C}_9\text{H}_{12}\text{NOP}$)_n formula, and the mass spectrum exhibits a molecular peak at m/e 426, $n = 2$. Unfortunately, compound 3' is nearly insoluble in all common solvents and only the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum has been obtained (sharp peak at 81.1 ppm).

The ten-membered ring dimer of 2-phenyl-3-methyl-1,3,2-oxazaphospholidine (1) may exist in two diastereomeric forms, depending upon the relative orientation of the phenyl groups attached to the phosphorus to the mean plane of the ten-membered ring. The isolation of a second ten-membered ring dimer, with the phosphorus three-coordinate state, has not been possible. However, after sulfurization and chromatography of a reaction mixture which shows in its $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum the peaks denoted M (142 ppm), D_1 (136.5 ppm), D_2 (134.9 ppm), and P (134–135 ppm) (Figure 1, C), one can isolate a second dimer of 2-thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine (2'). 2' is a crystalline compound (mp 186–187 °C) and is identified by elemental analysis ($\text{C}_9\text{H}_{12}\text{NOP}$)_n, mass spectrometry (molecular peak at m/e

Table I. ^1H NMR Data of 2-Phenyl-3-methyl-1,3,2-oxazaphospholidine^a and of 2-Thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine^b in C_6D_6 

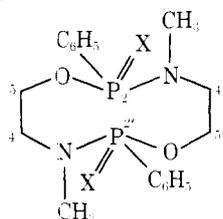
	chemical shift, ppm, from Me_4Si					spin-spin coupling constants, Hz					
	CH_3	H_1	H_2	H_3	H_4	$^2J_{\text{H}_1\text{H}_2}$	$^2J_{\text{H}_3\text{H}_4}$	$^3J_{\text{H}_1\text{H}_3}$	$^3J_{\text{H}_1\text{H}_4}$	$^3J_{\text{H}_2\text{H}_3}$	$^3J_{\text{H}_2\text{H}_4}$
1, X = lone pair	2.54	3.70	3.76	2.61	2.28	-8.7	-10.4	7.0	7.0	7.7	5.3
1', X = S	2.30	3.90	3.73	2.90	2.83	-8.8	-8.6	6.6	4.4	7.4	6.7

^a Registry no.: 1885-79-6. ^b Registry no.: 1885-80-9.

Table II. ^{13}C and ^{31}P NMR Data of 2-Phenyl-3-methyl-1,3,2-oxazaphospholidine and of 2-Thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine in C_6D_6 

	chemical shift, ppm				spin-spin coupling constants, Hz						
	C_4^a	C_5	CH_3	$^{31}\text{P}^b$	$^2J_{\text{PC}_4}$	$^2J_{\text{PC}_5}$	$^2J_{\text{PCH}_3}$	$^3J_{\text{PH}_1}$	$^3J_{\text{PH}_2}$	$^3J_{\text{PH}_3}$	$^3J_{\text{PH}_4}$
1, X = lone pair	50.9	67.4	37.9	141.8	5.6	10.5	26.8	7.0	1.0	2.7	7.0
1', X = S	50.1	66.2	31.8	94.3	6.3	9.5	3.8	10.0	14.3	6.0	16.8

^a ^{13}C chemical shifts are in parts per million downfield from internal Me_4Si . ^b ^{31}P chemical shifts are in parts per million downfield from external 85% H_3PO_4 .

Table III. Partial ^{13}C and ^{31}P NMR Data of Dimeric Forms of 2-Phenyl-3-methyl-1,3,2-oxazaphospholidine and of 2-Thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine in C_6D_6 

	^{31}P	chemical shift, ppm ^a			phosphorus carbon spin-spin coupling, Hz				
		$\text{C}_{4,4'}$	$\text{C}_{5,5'}$	CH_3	$^2J_{\text{P}_2\text{C}_4}$	$^3J_{\text{P}_2\text{C}_4}$	$^2J_{\text{P}_2\text{C}_5}$	$^3J_{\text{P}_2\text{C}_5}$	$^2J_{\text{PNCH}_3}$
2, X = lone pair, D_1^b	136.5								
3, X = lone pair, D_2	134.9	50.9	67.2	37.2	17.4	2	24.1	0	9.8
2', X = S, D_1'	80.9	50.5	62.9	35.6	2.5	2.5	7.3	2.1	6.9
3', X = S, D_2' ^c	81.1								

^a See Table II for the references. ^b The dimer D_1 has not been isolated in the three-coordinate phosphorus valence state. ^c The very low solubility of dimer D_2' precluded the recording of ^{13}C NMR spectra.

426, $n = 2$), and ^1H , ^{13}C , and ^{31}P NMR spectroscopy (Table III).

It has been verified that compound 2' can be obtained only from the chromatography of a sulfurized mixture if peak D_1 (136.5 ppm; Figure 1, C) is present in the mixture of three-coordinate phosphorus compounds. Thus, we conclude that peak D_1 corresponds to one of the two possible dimeric forms of 2-phenyl-3-methyl-1,3,2-oxazaphospholidine.

The first additional peaks which appear in the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum of a freshly prepared sample of compound 1 dissolved in benzene (solution I) are a quartet (Figure 1, A-C). The peaks corresponding to dimers 2 and 3 appear only later on. After sulfurization, the species corresponding to the quartet observed in the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum can be isolated

by column chromatography on silica, with a 7:3 benzene-acetone mixture as eluent. This compound is a solid white powder, 4'. The elemental analysis indicates the formula $(\text{C}_9\text{H}_{12}\text{NOP})_n$, which corresponds to a polymer of the 2-thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine.

A gel permeation chromatography study³¹ on compound 4' shows that it corresponds to a highly polydispersed polymer. The number average molecular weight, $M_n = \Sigma(n_i M_i / n_i)$, and the weight average molecular weight, $M_w = \Sigma n_i M_i^2 / \Sigma n_i M_i$, are equal to 6000 and 17 000, respectively. This corresponds to a polydispersity index $M_w/M_n = 2.9$. The highest molecular weights are around 70 000 and the molecular weight distribution is bimodal and shows two maxima around 2000 and 8000, respectively.

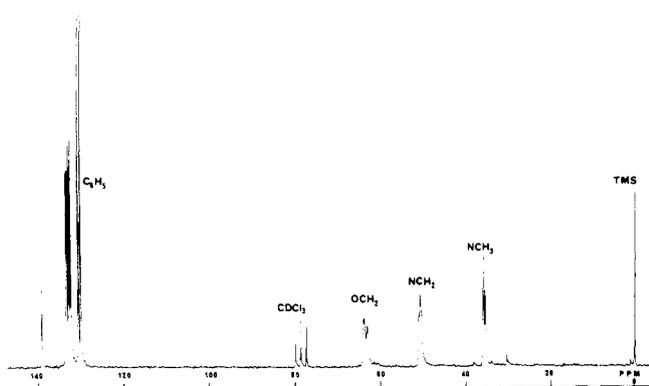


Figure 2. ^1H - ^{13}C NMR spectrum of the sulfurized polymeric species obtained by evolution of a benzene solution of 3-methyl-2-phenyl-1,3,2-oxazaphospholidine.

The ^1H and ^{13}C NMR spectra of the polymeric species **4'** show signals only in the NCH_3 , OCH_2 , NCH_2 , and phenyl regions (Figure 2). The $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum corresponds to a complex multiplet spread over 20 Hz. The phosphorus chemical shift (~ 81.0 ppm) corresponds unambiguously to a $\text{OP}(\text{S})(\text{C}_6\text{H}_5)\text{N}$ - group. Although it was not possible to locate in the ^1H , ^{13}C , and ^{31}P spectra peaks which correspond to end groups, we cannot conclude at present whether the polymeric species **4'** corresponds to linear chains or to macrocyclic molecules.

The quartet observed in the $\{^1\text{H}\}^{13}\text{C}$ NMR spectrum of the three-coordinate phosphorus polymer **4** can easily be explained by assuming that a phosphorus nucleus is sensitive only to the stereochemistry of its two nearest phosphorus neighbors. As the phosphorus atom is an asymmetric center, one observes four different sequences depending upon the phosphorus absolute configuration (*RRR*, *RRS*, *RSR*, *RSS*) and their enantiomeric configurations. In the $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum of the tetracoordinate phosphorus polymer, one does not observe such a regular pattern.

By heating at 80°C a sealed tube which, at room temperature, shows a $\{^1\text{H}\}^{31}\text{P}$ NMR spectrum similar to the one observed on Figure 1, C (i.e., containing the monomeric species **1**, the dimers **2** and **3**, and the polymer **4**), one reaches a new equilibrium in which the signal corresponding to the polymer disappears almost completely. Going back to room temperature, one obtains again the initial ratio of the different species. A quantitative analysis is difficult as one of the dimer has a low solubility and is present at a greater amount than the one corresponding to its NMR signal.

Thus, the evolution of a benzene solution of 2-phenyl-3-methyl-1,3,2-oxazaphospholidine (**1**) leads to the formation of the two corresponding ten-membered ring dimers by a ring-expansion reaction similar to what has been observed with dioxaphospholanes, dioxaphosphorinanes, dioxaphosphepanes, and dithiaphosphorinanes. In addition to the ten-membered ring dimers, one observes the formation of polymeric species. The different species are in equilibrium at room temperature.

NMR spectral data. In the ten-membered rings, monomer **1** and **1'**, the proton and phosphorus nuclei form an ABCDX system (X, phosphorus) which results in an ABCD system after phosphorus decoupling. For the first step, the $\{^{31}\text{P}\}^1\text{H}$ spectra have been analyzed. The final results quoted in Tables I and II have been obtained by use of the LAOCOON III iterative computer program. The ^1H NMR spectra of the dimeric ten-membered rings are much more complicated and have not been analyzed.

In the five-membered ring compounds **1** and **1'**, the low-field protons are assigned to those attached to the carbon in the α -position of the oxygen atom (H_1, H_2). In 2-R-1,3,2-

dioxaphospholanes, the high-field proton which has the highest coupling constant with the phosphorus atom (10 Hz) corresponds to the proton which is on the same side as the R group with respect to the mean plane of the ring.⁹ Thus, one can assign the H_1 proton of compound **1** ($^3J_{\text{PH}} = 7$ Hz) to the CH bond which has a syn relationship with respect to the phenyl group. In the case of the 2-R-1,3,2-diazaphospholanes, the difference between the two $^3J(\text{PNCH})$ NMR coupling is small¹⁰ and the stereochemical assignment of the ring proton of the $\text{NCH}_2\text{CH}_2\text{N}$ fragment is difficult on the basis of the NMR data.

The conformational analysis of five-membered rings is always a complex problem due to the possible existence of several conformations close in energy.¹¹ The proton-proton and phosphorus-proton NMR coupling constants could be used in order to obtain information concerning the oxazaphospholidine ring shape.¹² However, care must be exercised in such studies for two main reasons. Firstly, there exist two pathways joining the phosphorus and hydrogen nuclei; thus, the J_{PH} NMR coupling must be considered as 3J and 4J at the same time. Secondly, the $^3J_{\text{HH}}$ couplings depend upon the heteroatoms' lone pair orientation, resulting in a complex angular dependence. Here, the $^2J_{\text{PC}}$ NMR coupling constants provide some insight into the five-membered ring conformation.

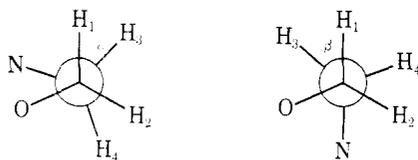
The most interesting point in examining the NMR data of Tables I and II comes from the exocyclic (NCH_3) and intracyclic (NCH_2) $^2J_{\text{PC}}$ NMR couplings which are significantly different in the three-coordinate compounds.

Such a difference can be explained in two different ways: change of the phosphorus bond angles between the intra- and extracyclic groups or influence of the lone pair orientation. From X-ray structural data, it has been found in the five-membered ring dioxaphospholanes that the O-P-O ring angle is about 5° smaller than the normal average bond angle measured in six-membered rings.¹³⁻¹⁵ A similar trend is observed in going from six- to seven-¹⁶ or ten-membered¹⁷ ring organophosphorus compounds. However, as one observes both increase and decrease of the $^2J_{\text{PC}}$ values on increasing the ring size (increase for $^2J_{\text{PNCH}_2}$ and decrease for $^2J_{\text{PNCH}_3}$) in going from the five-membered ring to the ten-membered ring (Tables II and III), we think that the O-P-N bond angle difference which must certainly exist between the five- and ten-membered rings cannot account for the $^2J_{\text{PC}}$ differences found in the five-membered ring. The second factor which plays an important role on the $^2J_{\text{PNC}}$ coupling is the phosphorus lone pair orientation in three-coordinate derivatives.

As a general rule, it appears that in a P-Y-X fragment, where X and Y represent first or second row atoms, the $^2J_{\text{PX}}$ NMR coupling is larger when the phosphorus lone pair and the Y-X bond adopt a cis relationship.¹⁸⁻²⁴ Such an influence is clearly illustrated by the low-temperature study of *N,N*-dimethylaminophosphines (when the P-N rotation barrier becomes slow on the NMR time scale). From the low-temperature study of $\text{C}_6\text{H}_5\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$, one obtains two very different $^2J_{\text{PNC}}$ values: 33.9 and 11.4 Hz, respectively.²⁴ As one expects a decrease for $^2J_{\text{PNC}}$, when the phosphorus atom bears less electronegative substituents, the extracyclic $^2J_{\text{PNC}}$ value (26.8 Hz) observed in compound **1** must correspond to a conformation in which the phosphorus lone pair and the extracyclic N-C bond are close to a cis relationship. Conversely, the small value observed for the intracyclic $^2J_{\text{PNC}}$ (5.6 Hz) coupling, which is of unknown sign, indicates that the phosphorus lone pair and the N-C bond and phosphorus lone pair orientation would be in agreement with a half-chair conformation of the ring with a nitrogen edge. Moreover, the close values found for the $^3J_{\text{HH}}$ coupling would not disagree with such a conformation.

In the case of compound **1'**, the $^2J_{\text{PNC}}$ NMR coupling con-

Chart I. Newman Projection Representation of the Torsional Angle around the C₄-C₅ Bond in Compound 1'



stants, which are quite similar for the extra- and intracyclic carbon atoms, cannot be used for stereochemical information, because in tetracoordinate phosphorus molecules the $^2J_{\text{PXC}}$ values are virtually insensitive to the bond orientation around the phosphorus atom. The absence of large $^3J_{\text{HH}}$ coupling suggests the presence of at least two conformations which will correspond to different torsional angles (α and β) around the C-C bond. Evidence that the torsional angles α and β are different is given by the large difference which exists between the two $^3J_{\text{POCH}}$ couplings (10.0 and 14.3 Hz) and the two $^3J_{\text{PNCH}}$ couplings (16.8 and 6.0 Hz). The existence of such a difference contrasts with what has been observed in other unsubstituted 1,3,2-oxazaphospholidines¹² rings. On the other hand, the absence of a precise knowledge of the angular dependence of the $^3J_{\text{POCH}}$, $^3J_{\text{PNCH}}$, and $^3J_{\text{HCCH}}$ NMR coupling does not allow us to check if the ring conformation of compound 1' is in agreement with the recently reported solid-state ring shape of the 2-thiono-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine.²⁷

Experimental Section

General Data. ^{31}P NMR spectra were recorded on a Bruker WP-60, ^1H NMR spectra on a Varian HA-100, and the ^{13}C NMR spectra on a Varian XL-100(15). Elemental analyses were carried out by Service Central de Microanalyse, Villeurbanne. Melting points were obtained with a Büchi melting point apparatus and are uncorrected.

The preparation of the three-coordinate phosphorus compounds was conducted in an atmosphere of dry argon using the Schlenk technique. Ether and benzene were dried over sodium and freshly distilled before use. 2-(Methylamino)ethanol (Baker Co.) was dried with about 5% weight of sodium and distilled under reduced pressure. Triethylamine (Prolabo) was refluxed over sodium 12 h before distillation. Bis(dimethylamino)phenylphosphine was prepared by treatment of dichlorophenylphosphine (Aldrich) with dimethylamine in presence of triethylamine.²⁸

2-Phenyl-3-methyl-1,3,2-oxazaphospholidine (1). 1 was prepared as described previously⁸ but, instead of bis(diethylamino)phenylphosphine as starting material, bis(dimethylamino)phenylphosphine was used: yield 85–90%.

2-Thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine (1'). To a 2.9-g (16 mmol) solution of 1 in 30 mL of benzene, 0.6 g of elemental sulfur (19 mmol) was added under stirring.²⁹ The reaction took place instantaneously. After evaporation of the solvent, the resulting product was recrystallized from cyclohexane: mp 67 °C; yield 2.7 g; ^1H NMR (CDCl_3) 2.7 (NCH₃, $^2J_{\text{PCH}_3}$ = 12.6 Hz), 3.30–3.60 (NCH₂), 4.20–4.75 (OCH₂), 7.3–8.1 (ArH), 94.3 ppm (^{31}P). Anal. Calcd for C₉H₁₂NOPS: C, 50.70; H, 5.67; N, 6.57; P, 14.52; S, 15.04. Found: C, 50.74; H, 5.66; N, 6.58; P, 14.45; S, 15.16.

Dimer of 2-Phenyl-3-methyl-1,3,2-oxazaphospholidine (3). A solution of 1 in benzene (50% v/v) containing a catalytic amount (1 mol %) of *p*-toluenesulfonic acid was allowed to stand for several days at room temperature and then heated for some hours at 80 °C. After cooling, the resulting colorless crystals were separated and recrystallized from benzene: mp 191–193 °C; ^1H NMR (C_6D_6) 2.7 (NCH₃, $^2J_{\text{PCH}_3}$ = 7 Hz), 2.9 (NCH₂), 3.6–4.3 (OCH₂ and NCH₂), 7.2–7.8 (ArH), 134.9 ppm (^{31}P). Anal. Calcd for C₉H₁₂NOP: C, 59.67; H, 6.68; N, 7.73; P, 17.09. Found: C, 59.64; H, 6.69; N, 7.48; P, 16.91.

Dimer of 2-Thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine (3'). A suspension of 0.5 g (1.3 mmol) of 3 and of 0.13 g (4 mmol) of sulfur in 20 mL of benzene was refluxed for 2–3 h. The resulting fine crystalline product was separated by filtration and recrystallized from hot pyridine: mp 274–275 °C. 3' is nearly insoluble in all common solvents: δ 81.1 ppm (^{31}P). Anal. Calcd for C₉H₁₂NOPS: C, 50.70; H,

5.67; N, 6.57; P, 14.52; S, 15.04. Found: C, 50.62; H, 5.62; N, 6.49; P, 14.52; S, 14.90.

Dimer of 2-Thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine (2') and Polymer 4'. A 1:1 vol benzene solution of a freshly distilled sample of 1 was allowed to stand for several days at room temperature. When the ^1H ^{31}P NMR spectrum showed a figure similar to Figure 1, C (see the text), an excess of elemental sulfur was added to the solution. The insoluble dimer 3' was separated by filtration. The remaining solution was chromatographed on a silica column. The monomer 1' and the dimer 2' were eluted together with benzene and then separated by fractionated crystallization from cyclohexane. 2': mp 186–187 °C; NMR (CDCl_3) 3.2 (NCH₃, $^2J_{\text{PCH}_3}$ = 11.8 Hz), 2.8–3.6 (NCH₂), 3.9 and 5.1 (OCH₂), 7.4–7.9 ppm (ArH).

The polymer 4' was eluted with a 7:3 benzene-acetone mixture. After removal of the solvent and drying, one obtains a white powder. Anal. Calcd for C₉H₁₂NOPS: C, 50.70; H, 5.67; N, 6.57; P, 14.52; S, 15.04. Found: C, 51.58; H, 5.85; N, 6.17; P, 13.74; S, 14.70.

Acknowledgments. We wish to thank Dr. A. C. Guimaraes who made the preliminary observations concerning the work and J. P. Dutasta and J. Martin for helpful discussion during the completion of this work.

Registry No.—4', 66357-77-5; 2-phenyl-3-methyl-1,3,2-oxazaphospholidine isomer 1, 66358-45-0; 2-phenyl-3-methyl-1,3,2-oxazaphospholidine isomer 2, 66511-12-4; 2-thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine isomer 1, 66358-46-1; 2-thiono-2-phenyl-3-methyl-1,3,2-oxazaphospholidine isomer 2, 66511-13-5; bis(dimethylamino)phenylphosphine, 6143-71-1.

References and Notes

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- (a) J. P. Dutasta, A. C. Guimaraes, J. Martin, and J. B. Robert, *Tetrahedron Lett.*, 1519 (1975); (b) J. P. Albrand, J. P. Dutasta, and J. B. Robert, *J. Am. Chem. Soc.*, **96**, 4584 (1974).
- J. P. Dutasta, J. Martin, and J. B. Robert, *J. Org. Chem.*, **42**, 1662 (1977).
- J. P. Dutasta, A. C. Guimaraes, and J. B. Robert, *Tetrahedron Lett.*, 801 (1977).
- J. P. Dutasta and J. B. Robert, *J. Am. Chem. Soc.*, **100**, 1925 (1978).
- R. Greenhalgh, J. E. Newbery, R. Woodcock, and R. F. Hudson, *Chem. Commun.*, 22 (1969).
- E. E. Nifante'ev, A. P. Touceev, and V. V. Tarasov, *J. Obshch. Khim.*, 1124 (1965).
- O. Mitsunobu, T. Ohashi, M. Kikuchi, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **39**, 214 (1966).
- D. Gagnaire, J. B. Robert, J. Verrier, and R. Wolf, *Bull. Soc. Chim. Fr.*, 3719 (1968); P. Haake, J. P. McNeal, and E. Goldsmith, *J. Am. Chem. Soc.*, **90**, 715 (1968).
- J. P. Albrand, A. Cogne, D. Gagnaire, and J. B. Robert, *Tetrahedron*, **28**, 819 (1972).
- C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1969).
- J. Devillers, J. Navech, and J. P. Albrand, *Org. Magn. Reson.*, **3**, 177 (1971).
- T. A. Steitz and W. N. Lipscomb, *J. Am. Chem. Soc.*, **87**, 2488 (1965); Y. H. Chui and W. N. Lipscomb, *ibid.*, **91**, 4150 (1969).
- M. G. Newton, J. R. Cox, and J. A. Bertrand, *J. Am. Chem. Soc.*, **88**, 1503 (1966); M. G. Newton and B. S. Campbell, *ibid.*, **96**, 7790 (1974).
- F. P. Boer, *Acta Crystallogr., Sect. B*, **28**, 1201 (1972).
- A. Grand and J. B. Robert, *Acta Crystallogr., Sect. B*, **34**, 199 (1978).
- A. Grand, unpublished results.
- R. Wasilychen in "Nuclear Magnetic Resonance Spectroscopy of Nuclei Other than Protons", T. Axenrod and G. A. Webb, Ed., Wiley, New York, N.Y., 1974.
- W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Grandley, and D. M. Jerina, *J. Am. Chem. Soc.*, **94**, 8501 (1972), and references cited therein.
- S. Sorensen and H. J. Jakobsen, *Org. Magn. Reson.*, **9**, 101 (1977).
- J. P. Albrand, D. Gagnaire, M. Picard, and J. B. Robert, *Tetrahedron Lett.*, 4593 (1970).
- M. Haemers, R. Ottinger, J. Reisse, and D. Zimmerman, *Tetrahedron Lett.*, 2241 (1973).
- J. P. Dutasta and J. B. Robert, *Chem. Commun.*, 747 (1975).
- G. A. Gray and S. E. Cremer, *Chem. Commun.*, 367 (1972).
- J. J. Breen, S. I. Faetherman, L. D. Quin, and R. G. Stocks, *Chem. Commun.*, 657 (1972).
- M. P. Simonin, R. M. Lequan, and F. W. Wehrli, *Chem. Commun.*, 1204 (1972).
- T. Prange, C. Pascard, J. Devillers, and J. Navech, *Bull. Soc. Chim. Fr.*, 185 (1977).
- R. H. Cragg and M. F. Lappert, *J. Chem. Soc. A*, 82 (1966).
- R. S. Edmundson, *Chem. Ind. (London)*, 1770 (1962).
- All the ^{31}P NMR chemical shifts are given in parts per million with the positive value downfield from external 85% H₃PO₄.
- We wish to thank Dr. J. Brossas at the C.R.M. (Strasbourg) for the gel permeation chromatography measurements.