Synthesis, Fragmentation, and Photorearrangement of Neopentyl and Adamantyl Phosphonates in the 2,3-Oxaphosphabicyclo[2.2.2]octene System

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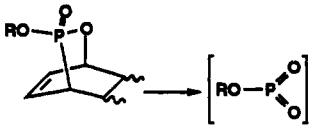
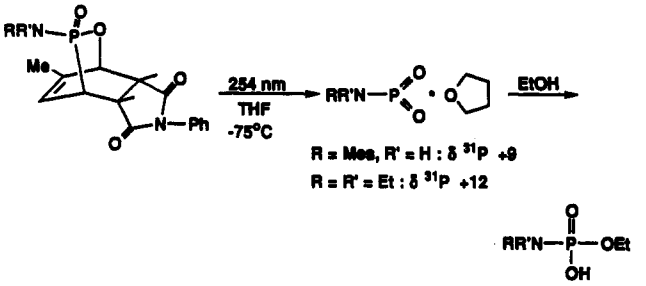
Precursors for the generation of neopentyl and 1-adamantyl metaphosphates were prepared by the insertion of oxygen into a ring carbon–phosphorus bond of some 7-phosphanorbornene derivatives. The stereochemistry of the resulting products, which possess the 2,3-oxaphosphabicyclo[2.2.2]octene ring system, was established by NMR spectroscopy, and by X-ray analysis in one case. The O-insertion (by MCPBA) generally proceeds with retention of phosphorus configuration, but in one precursor with a *syn*-neopentoxy group a minor product from an inversion process was isolated. The 7-phosphanorbornene isomer with the uncommon *anti* neopentoxy structure was synthesized by rearrangement of the *syn* isomer; O-insertion gave exclusively the product of retention, identical to the minor product from the *syn* isomer. Conditions were developed for the photochemical fragmentation of the precursors at room temperature to release the metaphosphates; these highly reactive species were trapped as phosphates when alcohols were included in the medium. Thermal fragmentation also was effective for generating the neopentyl ester. Irradiation was also performed at −75 °C in an attempt to stabilize the metaphosphates so as to allow their spectral characterization, but a rearrangement occurred to give a novel tricyclic compound. In this rearrangement, the ring oxygen shifted stereospecifically to the adjacent sp^2 carbon, and a cyclopropane ring was formed.

In earlier studies, we have demonstrated that both thermolysis[1,2] and photolysis[2,3] of phosphonates in the 2,3-oxaphosphabicyclo[2.2.2]octene ring system occur readily with the extrusion of the bridging P–O unit and formation of an ester of metaphosphoric acid. Metaphosphates are



unstable at room temperature, and there is no report in the literature on the direct observation of such species.[4] Our technique for generating the esters from a bridged heterocyclic phosphonate offers considerable versatility in the nature of the O-substituent, and it occurred to us that with the proper combination of a large bulky O-substituent and generation by the photochemical method at low temperatures, we might be able to achieve sufficient stabilization of a metaphosphate so as to characterize it by spectroscopic techniques. We have already had some success in attempts to preserve the three-coordinate phosphoramide that is released on photolysis at −75 °C of N-substituted phosphonamides in the 2,3-oxaphosphabicyclo[2.2.2]octene ring system.[5] The desired fragment is indeed extruded and gives ^{31}P NMR signals in the range δ +9 to +12 in THF solution. The species giving these signals, however, is more likely a THF solvate of the phosphoramide than the free phosphoramide. Nevertheless, the extruded fragment has the chemical properties expected for the three-coordinate phosphoramide (intermolecular condensations at room temperature to form P–O–P derivatives; reaction with ethanol at −75 °C to form phosphoramidates).



We selected three species with large O-substituents for study in the present project: neopentyl, 1-adamantyl, and 2,4,6-tri-*tert*-butylphenyl. The synthesis of the bicyclic precursor for the latter species could not be realized because of a strong steric effect in a critical step (O-insertion in a C–P bond). Precursors for the other two were successfully prepared and indeed released the corresponding metaphosphates on thermolysis or on photolysis at room temperature. A remarkable rearrangement has been encountered on photolysis at −75 °C, however, which seriously interferes with the release of the three-coordinate species. These new results are discussed in this paper.[6]

Neopentyl metaphosphate has been the subject of investigations elsewhere,[7] where it has presumably been generated in the gas phase, by pyrolysis (800 °C; 0.001

• Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) Quin, L. D.; Marsi, B. G. *J. Am. Chem. Soc.* **1985**, *107*, 3389.

(2) Jankowski, S.; Quin, L. D. *J. Am. Chem. Soc.* **1991**, *113*, 7011.

(3) Quin, L. D.; Péte, B.; Szewczyk, J.; Hughes, A. N. *Tetrahedron Lett.* **1988**, *29*, 2627.

(4) Recently reviewed: Meisel, M. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990; Chapter E6.

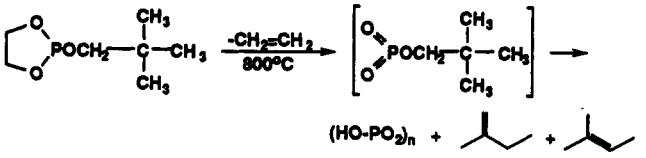
(5) Quin, L. D.; Bourdieu, C.; Quin, G. S. *Phosphorus, Sulfur, Silicon* **1991**, *63*, 349.

(6) Preliminary communication: Quin, L. D.; Wu, X.-P.; Lukes, I.; Day, R. O. *Tetrahedron Lett.* **1992**, *33*, 3975.

(7) Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Jack, A. G. C.; Rodger, D. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1033.

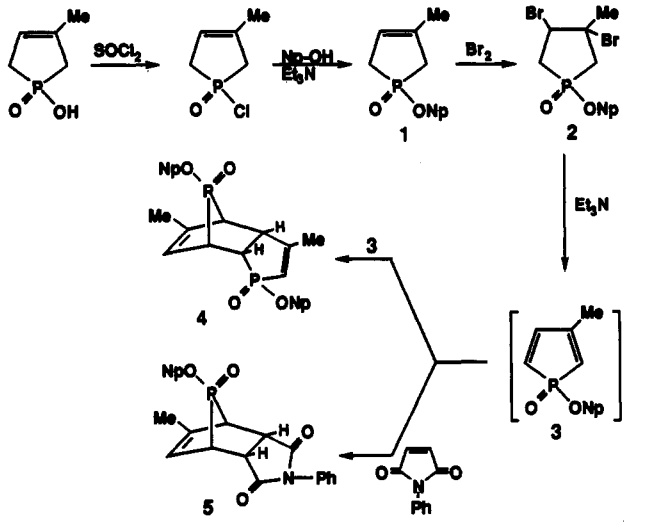
0022-3263/94/1959-0120$04.50/0

mm) of 2-neopentoxy-1,3,2-dioxaphospholane. The products observed, however, were those arising from a presumed subsequent HO–PO_2 elimination from the initially formed neopentyl metaphosphate, involving a methyl shift familiar in neopentyl chemistry to give pentenes with rearranged carbon skeleton:



This raises the question of whether neopentyl metaphosphate will behave similarly in solution and thus undergo elimination rather than P=O condensation to P–O–P derivatives that is normally encountered for metaphosphates. Our techniques would allow the generation of neopentyl metaphosphate in solution under milder conditions, thereby allowing us to examine the relative tendency to self-condense or to eliminate with rearrangement.

Scheme 1

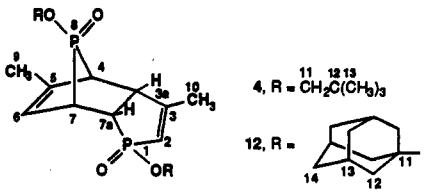


Synthesis and Stereochemistry of Metaphosphate Precursors. Two types of precursors with the 2,3-oxaphosphabicyclo[2.2.2]octene ring system have been synthesized to serve as generators of neopentyl metaphosphate. As in our previous work,[1-3,5] the general approach was to construct the 7-phosphanorbornene framework by a suitable Diels–Alder reaction on a phosphole oxide and then perform an insertion of oxygen in one of the C–P bonds to generate the desired 2,3-oxaphosphabicyclo[2.2.2]octene ring system. In Scheme 1 (Np = neopentyl) are shown the reactions used to synthesize the requisite phosphole oxide **3**. The phosphole oxide is itself unstable and rapidly undergoes an intermolecular Diels–Alder dimerization. The dimer **4** constitutes one of the 7-phosphanorbornene derivatives needed for the oxygen insertion reaction with *m*-chloroperbenzoic acid. The other Diels–Alder adduct **5** is obtained when the phosphole oxide is generated in the presence of *N*-phenylmaleimide (preferred over other dienophiles[8]).

As is characteristic of phosphole oxides,[8] both the dimer (**4**, ^{13}C NMR Table 1) and the Diels–Alder adduct (**5**, ^{13}C NMR Table 2) were formed as single diastereoisomers, even though many other isomers are possible. We proceeded to confirm structure **4** for the dimer by X-ray diffraction analysis.[9] As in other structural determinations,[10,11] a strongly contracted C–P–C bond angle (to 82.8°) was found in the 7-phosphanorbornene unit and this is responsible for the ready insertion of oxygen when

(8) Quin, L. D. *Rev. Heteroatom Chem.* **1990**, *3*, 39.

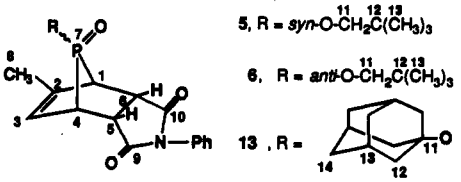
Table 1. ^{13}C NMR Spectra of Phosphole Oxide Dimers 4 and 12 in $CDCl_3$



	4			12		
carbon	δ	J_{P_1C}	J_{P_8C}	δ	J_{P_1C}	J_{P_8C}
2	122.4	128.5	6.0	125.5	129.9	6.1
3	160.1	11.3	31.5	158.1	11.4	31.5
3a	48.5	16.6[a]	18.9[a]	49.0	19.1[a]	16.7[a]
4	45.1	–	86.6	47.0	–	82.5
5	136.4	–	8.5	136.5	–	8.3
6	124.1	2.5	2.5	124.7	5.5	5.5
7	40.2	–	81.6	42.0	–	87.9
7a	36.7	104.3	16.4	39.4	104.4	16.3
9	19.64	–	7.2	19.76	–	4.5
10	19.55	5.0	–	19.52	20.5	–
11[b]	76.59	(7.6)		82.23	(10.0)	
	74.17	(7.2)		81.82	(8.7)	
12[b]	32.18	(5.3)		44.36	(3.6)	
	31.94	(6.2)		43.74	(3.9)	
13[b]	26.05	–		31.16	–	
	25.87	–		31.11	–	
14[b]	–	–		35.82	–	
				35.67		

[a] Could be reversed. [b] Groups on P_3 and P_8 cannot be distinguished.

Table 2. ^{13}C NMR Spectra of *N*-phenylmaleimide adducts 5, 6, and 13 of Phosphole Oxides



	5 (*syn* NpO)		6 (*anti* NpO)		13 (*syn* AdO)	
carbon	δ	$^1J_{PC}$	δ	$^1J_{PC}$	δ	$^1J_{PC}$
1	44.7	86.8	46.1	86.0	46.4	87.0
2	141.1	7.9	143.1	9.9	141.3	8.0
3	121.7	5.5	123.8	6.9	122.2	5.4
4	41.9	86.5	43.1	86.3	43.4	85.1
5	43.4[a]	21.1	43.6[a]	16.9	43.7	20.9
6	42.1[a]	19.3	44.8[a]	18.8	42.4	18.9
8	19.5	4.1	21.2	3.9	19.6	3.7
9	175.3[a]	17.2	176.2[a]	14.9	175.7[a]	17.2
10	174.9[a]	18.5	176.5[a]	15.7	175.3[a]	16.8
11	77.0	7.6	78.1	8.0	83.6	9.6
12	32.3	5.4	33.5	5.1	43.7	3.7
13	25.9	–	27.4	–	31.1	–
14					35.6	–

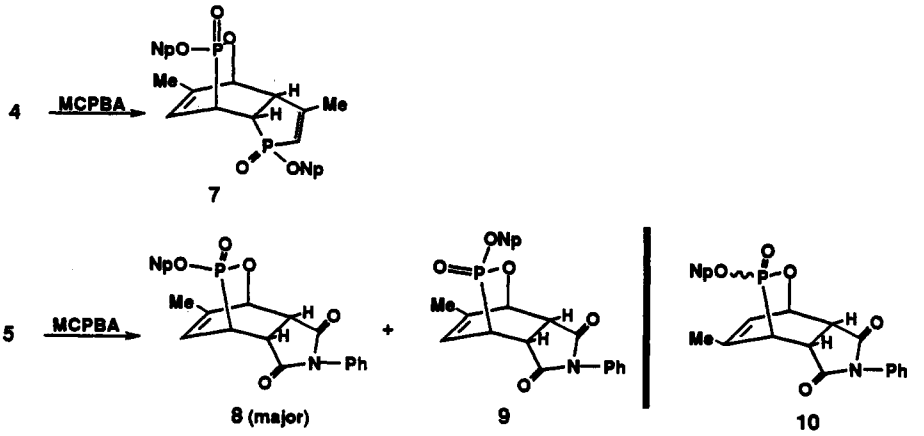
[a] Could be reversed.

(9) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

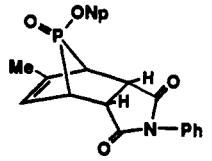
(10) (a) Chiu, Y.-Y. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1969**, *91*, 4150. (b) Hocking, M. B.; Bushnell, G. W. *Can. J. Chem.* **1990**, *68*, 1020.

(11) Quin, L. D.; Szewczyk, J.; Szewczyk, K. M.; McPhail, A. T. *J. Org. Chem.* **1986**, *51*, 3341.

Scheme 2



the compound is treated with *m*-chloroperbenzoic acid.[12] We then noticed that aged solutions of Diels–Alder adduct **5** developed a second ^{31}P NMR signal at δ 71.0 ($CDCl_3$); this compound was isolated by chromatography and found to be the *anti*-neopentoxy isomer **6**. This is the first instance of the observation of isomerization at P in a phosphinate in the 7-PBN series. Isomerization by protic reagents has been observed in phosphine oxides in this series[8] and is believed to proceed through a five-coordinate addition product. We therefore attempted the intentional isomerization of the *syn* compound **5** to the *anti* **6** and found that this was easily accomplished by simply stirring a sample in a hexane–methanol solution for a few days. Compound **6** was isolated in pure form.



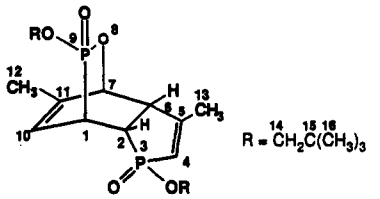
6

In the O-insertion reaction (Scheme 2) on phosphole oxide dimers, it is possible to obtain two position isomers from the attack at the two nonequivalent C–P bonds. Each of these may have syn (from retention) and anti (from inversion) geometry at phosphorus, but only position isomers have been noted in our other studies.[12] In the case of dimer **4**, the product obtained after purification by chromatography followed by recrystallization consisted of a single isomer; since the major isomer has always[12] been that from O-insertion in the C–P bond nearest to the ring C-methyl group, structure **7** was proposed and was confirmed by X-ray analysis.[9] The angle at phosphorus was expanded to 99.6° in the O-insertion product. The ^{13}C NMR spectrum (Table 3) was interpreted on this basis.

The Diels–Alder adduct **5**, on the other hand, gave an O-insertion reaction product which after the workup procedure contained two isomers (^{31}P δ 25.6 and 22.6, signal ratio 15:1). The standard isolation procedure of chromatography with 3% methanol in chloroform followed by recrystallization provided a pure sample of the major isomer (Scheme 2, **8**), but with the solvent system hexane–chloroform (3:7) the first fraction on chromatography consisted only of the minor isomer with ^{31}P NMR δ 22.6. Both of the isolated isomers were obtained in reasonably pure form, but neither could be induced to form crystals

(12) Quin, L. D.; Kisalus, J. C.; Mesch, K. A. *J. Org. Chem.* **1983**, *48*, 4466.

Table 3. ^{13}C NMR Spectrum of Compound 7

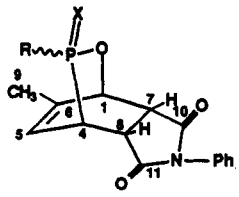


carbon	δ	J_{P_3C}	J_{P_8C}
1	31.16	123.9	–
2	31.16	–	123.9
4	123.9	–	117.9
5	159.0	–	30.5
6	52.3	8.9	15.9
7	79.6	7.5	2.7
10	125.2	9.2	–
11	136.6	12.8	–
12	19.70	4.6	–
13	19.47	–	14.0
14[a]	76.63	(7.3)	
	74.66	(7.3)	
15[a]	32.06	(4.1)	
	30.44	(5.6)	
16[a]	26.11	–	
	25.99	–	

[a] Groups on P_3 and P_8 cannot be distinguished.

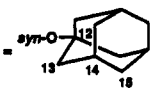
suitable for structure determination by X-ray analysis. However, the major isomer had strong similarities in its ^{13}C NMR spectrum (Table 4) to that for a phosphonamide of related structure that had been characterized by X-ray analysis[11] as being the 6-methyl position isomer with *syn*-alkoxy. Structure **8** was therefore assigned. The minor product, whose ^{13}C NMR spectrum is also recorded in Table 4, was the *anti* isomer (**9**) of **8**, rather than the expected 5-methyl position isomer **10**. This structure was indicated by features of the ^{13}C NMR spectrum. There were almost no differences in the signals for the ring carbon attached to O in the isomers, nor in the signals for C attached to P; yet in known cases of isomerism due to the position of the ring methyl, differences of several ppm are common for both types of carbon.[5] Furthermore, the 2D ^1H NMR spectrum conclusively showed coupling of the olefinic H with the ring CH attached to P in both isomers (Table 5). This is the first recorded case of the detection of a stereoisomer at P from the O-insertion process. However, the isomer **9** may arise not from a lack of stereospecificity in the MCPBA reaction, but rather from the presence in the reaction medium of a small amount of the *anti* isomer **6** of the starting material. This could be formed by the isomerization of **5** promoted by the acids present in the solution. A sample of compound **6** in fact

Table 4. ^{13}C NMR Spectra of Bicyclic Phosphonates 8, 9, 15, and 16 in $CDCl_3$



8, X = O, R = *syn*-O-$CH_2C(CH_3)_3$ (C-12, C-13, C-14)

9, X = O, R = *anti*-O-$CH_2C(CH_3)_2$ (C-12, C-13, C-14)



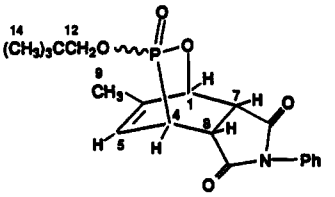
15, X = O, R = *syn*-O- (C-12, C-13, C-14, C-15, C-16)

16, X = S, R = *syn*-O-$CH_2C(CH_3)_3$ (C-12, C-13, C-14)

	8		9		15		16	
carbon	δ	$^1J_{PC}$	δ	$^1J_{PC}$	δ	$^1J_{PC}$	δ	$^1J_{PC}$
1	77.3	4.6	77.2	6	77.1	8.1	77.7	10.4
4	33.1	125.8	32.7	126.3	34.7	125.2	39.6	95.1
5	123.1	12.1	122.2	11.7	123.5	12.1	122.8	13.0
6	140.5	12.8	143.2	12.9	139.4	11.9	140.2	13.2
7	46.2	9.5	45.7	9.7	46.2	9.9	45.9	8.4
8	37.9	4.3	39.0	6.2	38.0	4.6	38.3	–
9	19.6	<1	20.0	<1	19.7	–	19.8	–
10	172.9	–	172.7	–	173.1	–	173.0	–
11	175.1	20.7	175.0	17.3	175.2	20.9	175.3	22.9
12	76.9	7.1	74.9	7.2	84.1	8.3	77.1	–
13	32.1	6.5	*a*		43.9	3.4	32.0	7.3
14	25.9	–	26.0	–	31.2	–	26.1	–
15	–	–	–	–	35.6	–		

[a] Not clearly observed.

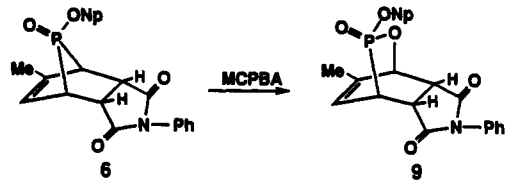
Table 5. ^1H NMR Spectra of Diastereoisomers 8 and 9



	8[a]		9[b]	
	δ	*J*	δ	*J*
H-1	5.17	ddd, 23.3 (P), 2.2 (H-5), 4.4 (H-7)	5.17	ddd, 23.4 (P), 2.2 (H-5), 4.2 (H-7)
H-4	3.57	ddd, 14.8 (P), 7.1, 2.6	3.66–3.72	m
H-5	6.09	m	6.18	m
H-7	3.96	dd, 4.4 (H-1), 8.1 (H-8)	3.79–3.87[d]	
H-8	3.7-3.8[c]		3.5–3.63	m
H-9	1.93	dd, 1.7 and 5.0	1.93	dd, 1.7 and 5.2
H-12	3.76[c]	d, 6.5 (P)	3.79–3.87[d]	
H-14	0.91	s	0.99	s

[a] Some connections from 2D: H-1 with H-7; H-4 with H-5; H-5 with H-4 and H-9; H-7 with H-8; H-8 with H-7; H-9 with H-5. [b] Some connections from 2D: H-1 with H-5 and H-7; H-4 with H-5; H-5 with H-4, H-1, and H-9; H-7 with H-1 and H-8; H-8 with H-7; H-9 with H-5. [c] H-12 and H-8 overlap. [d] H-7 and H-12 overlap.

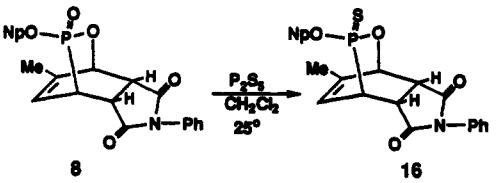
underwent the O-insertion reaction with complete retention of configuration, giving **9** as the only product. This product was spectrally identical to the minor product isolated from the O-insertion on the *syn* neopentoxy isomer **5**.



6 **9**

The same approaches were used to synthesize precursors for 1-adamantyl metaphosphate (Scheme 3). The presence of the significantly larger O-substituent caused no difficulties in the reactions leading to the phosphole oxide monomer, its dimerization to **12** (^{13}C NMR, Table 1), and Diels–Alder reaction with *N*-phenylmaleimide to give adduct **13** (^{13}C NMR, Table 2). However, the steric size of the adamantyl substituent strongly hindered the O-insertion reaction on the dimer **12**, which required a reaction period of 6 weeks in a refrigerator (to prevent premature fragmentation) for completion. Adduct **13** required 7 days at room temperature; the normal reaction period is a few hours.[8] The insertion products (^{13}C NMR, Tables 3 and 4) were obtained as single isomers after isolation and by analogy with other insertion products were assigned structures **14** and **15**, respectively.

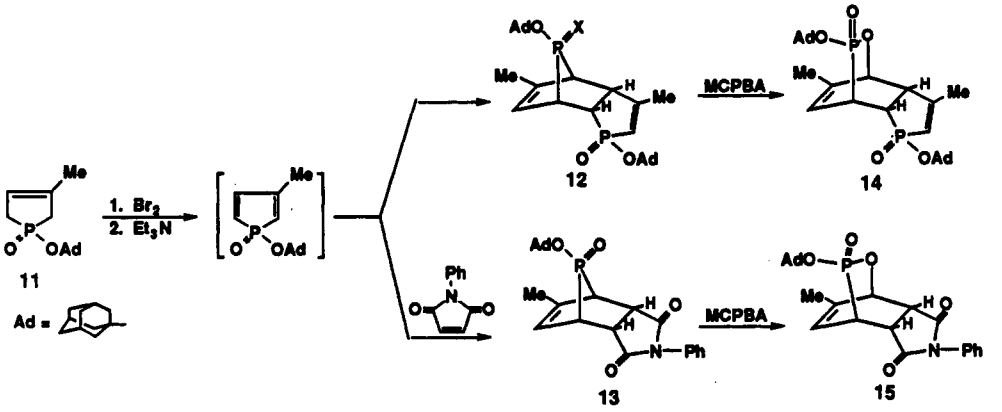
The phosphoryl oxygen of **8** was replaced by sulfur using the reaction with P_2S_5 as employed in some other cases.[13] This provided compound **16** (^{13}C NMR, Table 4) to serve as a precursor of neopentyl metathiophosphate (NpOP(S)O).



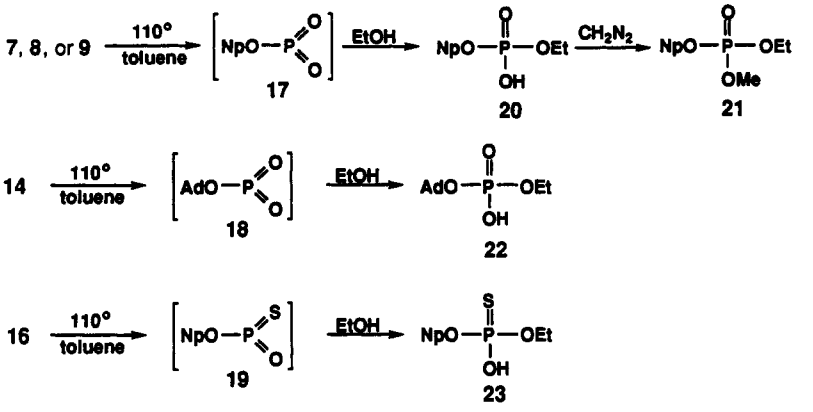
8 **16**

(13) Quin, L. D.; Sadanani, N. D.; Wu, X.-P. *J. Am. Chem. Soc.* **1989**, *111*, 6852.

Scheme 3



Scheme 4

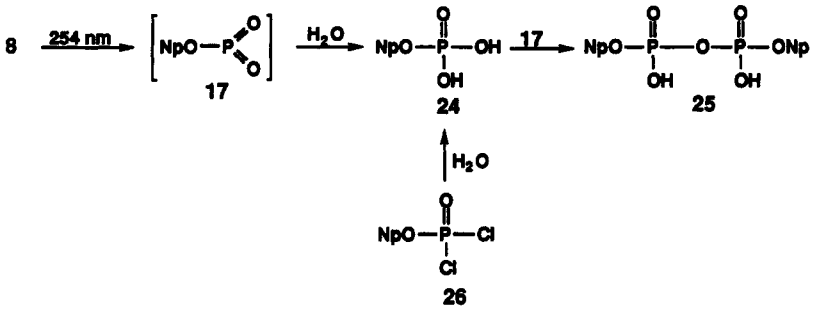


Generation of Neopentyl and 1-Adamantyl Metaphosphate by the Thermolysis Method. The conditions we have employed in previous studies for metaphosphate generation consist of heating the bicyclic precursor in toluene solution at 110 °C, in a closed tube to prevent entry of water. In the absence of a trapping reagent, the formation of the metaphosphate is indicated by the presence of ^{31}P NMR signals due to P–O–P links (typically at around δ −10 and −20). With an alcohol present in the reaction mixture as a trapping reagent, all phosphorus appears as a dialkyl phosphate, with a ^{31}P NMR shift around δ 0. Fragmentation experiments (Scheme 4) were performed with ethanol as the trapping agent on precursors 7, 8, and 9 of neopentyl metaphosphate; the only phosphorus signal then appeared in the expected phosphate region (δ 1). This is taken to mean, as established for related compounds by kinetics measurements,[2] that the free metaphosphate 17 was indeed generated. The identity of the dialkyl phosphate product 20 from the trapping reaction was confirmed by ^{1}H and ^{13}C NMR spectroscopy on a sample purified by chromatography. Further confirmation of 20 was obtained by methylating its free OH with diazomethane to give 21 and then performing GC-MS. The metathiophosphate 19 was similarly generated from 16; ethyl alcohol trapping gave the thiono ester 23 (δ ^{31}P 61.9), rather than the thiolo ester. This result is consistent with other observations on metathiophosphates.[2,13] The fragmentation of adamantyl ester 14 was much more complicated and gave barely a trace of the expected trapping product 22 with numerous unidentified ^{31}P NMR signals. This is the only failure we have yet experienced in our study of the thermal fragmentation process. As will be seen, photolysis did give a clean fragmentation to 18.

The results for the neopentyl case are especially important, since there was no indication of the elimination–rearrangement reaction observed in the flash vacuum pyrolytic generation of the species.[7] At least under the thermal conditions we have employed, then, neopentyl metaphosphate exhibits the same behavior on generation in a solvent as seen for other alkyl metaphosphates.

Photochemical Generation of Neopentyl and 1-Adamantyl Metaphosphates at Room Temperature. Again the same conditions developed in previous studies were employed. Irradiation with a 450 W medium-pressure Hanovia lamp was performed on neopentyl metaphosphate precursor 8 and adamantyl metaphosphate precursor 15 in quartz vessels, using acetonitrile, dioxane, or ethylene dichloride as solvents. Ethanol was included in the medium as a trapping reagent. After photolysis all phosphorus was found in the expected form of a dialkyl phosphate. The ^{31}P NMR shifts (as well as ^{13}C and ^{1}H NMR) were the same as for the phosphates when formed by the thermal process. Thus it is seen that the formation of the bulky metaphosphates 17 and 18 proceeds smoothly. The trapping agent was then omitted from the media to determine if the metaphosphates could be detected by ^{31}P NMR, but no signals other than those for P–O–P products were present. In the case of the generation of neopentyl metaphosphate (17), a pronounced sharp signal was present at δ −13.3 ($C_2H_4Cl_2$). This suggested a single symmetrical pyrophosphate rather than a more complex polymeric product as usually observed. It was established that this signal arose from the pyrophosphate 25, presumably formed from the reaction of neopentyl metaphosphate first with the water inevitably present to form neopentyl phosphate (24), followed by its reaction with neopentyl metaphosphate. This proof was accomplished

Scheme 5



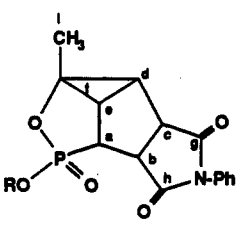
by preparing neopentyl phosphate from the reaction of neopentyl alcohol with phosphorus oxychloride to form chlorophosphate **26**, followed by hydrolysis, and then using this substance as a trapping agent for neopentyl metaphosphate when generated by photolysis of **8**. All phosphorus appeared in the form of the pyrophosphate with δ -13.3.

That metaphosphates **17** and **18** were successfully formed by the photochemical fragmentation of the bicyclic precursors provided encouragement to attempt their generation at low temperatures to improve the chances for direct detection.

Photolysis at −75 °C: Rearrangement vs Metaphosphate Extrusion. The choice of inert solvent for photolysis at the temperatures conveniently provided by dry ice chilling is severely limited. In previous work on photolysis of bicyclic phosphonamides,[5] we had employed tetrahydrofuran, but this solvent is itself somewhat photosensitive. The only other solvent of sufficient polarity to dissolve the precursors, yet having a freezing point below about −75 °C, that we have encountered is propionitrile (mp −93 °C), and this was employed in the present study.[6] O-Adamantyl phosphonate **15** was nearly completely consumed on irradiation in this solvent in a quartz tube chilled by a dry ice-hexane mixture (nominally −75 °C). The ^{31}P NMR spectrum, however, contained only a moderate signal in the pyrophosphate region (δ −15); the major signal appeared at δ 48.7. This signal was not observed in the room temperature photolysis, but it was immediately apparent that it was not due to the desired 1-adamantyl metaphosphate **18**. Thus, the signal did not diminish in size when the solution was warmed to room temperature, and indeed persisted unchanged over a several-day period. Furthermore, addition of ethanol either at −75 °C or at room temperature had no effect on the signal, and the signal was found when the photolysis was conducted in the presence of ethanol (3 equiv). It was then observed that the compound giving this signal survived passage through chromatography columns, thus allowing its separation from other products of the photolysis. The yield of recovered product was 51.6%. The new compound was a white solid that could be crystallized from benzene–hexane. Elemental analysis showed that it was isomeric with the starting bicyclic compound **15**, but its NMR spectral properties were completely different, and a rearrangement more deep-seated than mere inversion of configuration at phosphorus was indicated. Thus, the ^{31}P NMR signal was at the extreme downfield end of the phosphonate region, populated uniquely by five-membered cyclic phosphonates or bridged phosphonates with a five-membered ring component.[14] The ^{13}C NMR spectrum showed the absence of a C=C unit and that the oxygen atom was no longer attached to a CH unit but to a quaternary carbon. This was also apparent in the ^{1}H NMR spectrum, which additionally indicated that the methyl group was attached to the quaternary carbon. To account for these features, it was considered that the O–C bond had been disconnected and that an oxygen atom had become attached to an sp^2 C, requiring the creation of a cyclopropane unit in the new molecule (structure **27**). This structure was conclusively established by single-crystal X-ray diffraction analysis,[6,15] which also revealed the stereochemistry at phosphorus to be the same as in the starting **15**. Therefore, it is the original ring oxygen that has become attached to the sp^2 carbon. The opposite configuration at phosphorus would have resulted had the phosphoryl oxygen participated in the rearrangement, very likely leading to a mixture of diastereoisomeric products. ^{13}C NMR spectral data for **27** are given in Table 6 (for ^{1}H NMR data, see ref 6).

Exactly the same results were obtained[6] when the bicyclic *O*-neopentyl phosphonate **8** was irradiated at −75

Table 6. ^{13}C NMR Spectra of Rearrangement Products 27, 28 and 30



27, R =  (*exo* [a])

28, R = -CH$_2$C(CH$_3$)$_3$ (*exo* [a])

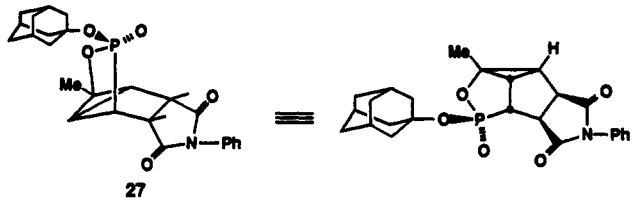
30, R = -CH$_2$C(CH$_3$)$_3$ (*endo* [a])

	27[b]		28[c]		30[c]	
carbon	δ	J_{PC}, Hz	δ	J_{PC}, Hz	δ	J_{PC}, Hz
a	39.8	133.8	38.2	131.0	38.9	131.7
b	52.7[d]	4.2	52.8[d]	3.9	53.8	~0
c	45.7[d]	–	45.7[d]	–	45.6	–
d	27.8	–	27.5	–	27.2	–
e	37.3	7.1	37.5	6.8	37.5	7.6
f	62.1	4.0	62.3	7.1	62.8	7.2
g	176.3	–	176.2	–	176.0	–
h	176.4	5.4	176.0	6.0	175.9	5.9
i	20.2	4.5	20.1	4	20.2	4.4
j	84.4	10.0	76	*e*	76.3	8.0
k	44.1	3.5	29.7	–	29.7	–
l	31.2	–	26.0	–	26.0	–
m	35.6	–				

[a] *Exo* refers to OR *syn*, and *endo anti*, with respect to H on Ca, Ce. [b] In C_6H_6 (D_2O as lock). [c] In $CDCl_3$. [d] May be reversed. [e] Overlaps with $CDCl_3$.

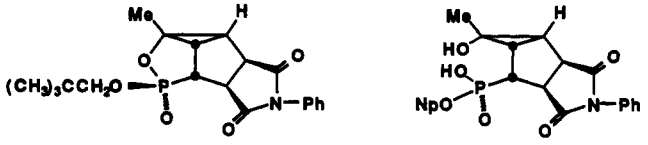
(14) Edmundson, R. S. In *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; CRC Press, Inc.: Boca Raton, FL, 1991; Chapter 11.

(15) Atomic coordinates are available as specified in ref. 9.



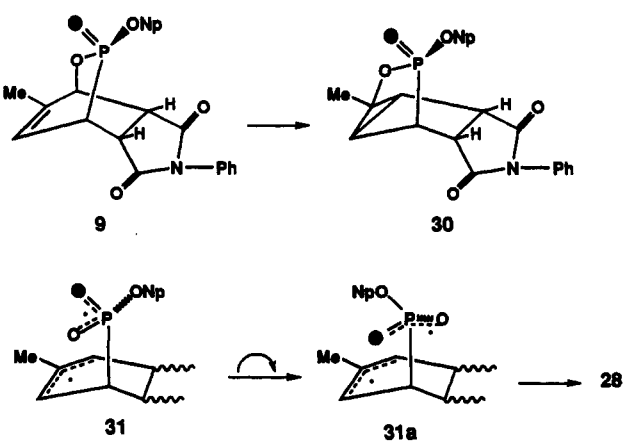
27

°C; the major product 28 had δ ^{31}P NMR 53.2 and could be isolated by column chromatography. However, a new product with ^{31}P NMR δ 31.1 developed during the procedure, preventing the procurement of a sample of sufficient purity for elemental analysis. The new compound appears to arise from sensitivity to moisture in the media and is tentatively assigned a structure (29) from



28 29

opening of the cyclic phosphonate ring, thus accounting for the upfield shift of the ^{31}P NMR signal. Another technique for minimizing the hydrolysis reaction involved chromatography on silica gel at −55 °C and on cellulose at 25 °C. ^{13}C and ^{1}H NMR data have been reported;[6] the former are reproduced in Table 6 from comparison with the spectrum of the diastereoisomer (*vide infra*). These spectra confirmed that the ring structure was the same as established for the adamantyl ester 27. The availability of the diastereomer 9 of neopentyl phosphonate 8 allowed further consideration of the stereospecificity of the rearrangement process, indicated to proceed with retention by the X-ray analysis of adamantyl ester 27. The photolysis of 9 at −75 °C gave a product whose major ^{31}P NMR signal appeared at δ 44.3. This compound was isolated as a crystalline, analytically pure solid in 71% yield and proved to be the stereoisomer 30 of the product 28 from 8. The ^{13}C NMR spectra (Table 6) of the two stereoisomers were very similar. Since none of the compound with δ 53 was observed in the photolysis product from 9 and none with δ 44 in the product from 8, the photorearrangement is established to proceed with complete stereospecificity. This probably means that the oxygen atom that is to become detached from the ring carbon must start bonding to the adjacent sp^2 carbon before rotation around the P–C bond can occur; if a full disconnection to form a radical intermediate (31) occurred

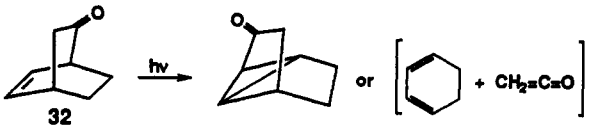


9 30

31 31a 28

as was originally considered,[6] rotation might be possible that would place the original phosphoryl oxygen in position to participate (31a) and thus give the product of inverted configuration. Stereospecificity is common in some other types of photochemical rearrangements, notably of the di-π-methane type,[16] to which the present rearrangement bears some superficial resemblance (*vide infra*).

It is remarkable that the rearrangement took precedence over metaphosphate extrusion when the photolysis of the bridged compounds 8, 9, and 15 was conducted at −75 °C. That some metaphosphate extrusion probably did occur is indicated by the presence of an alkyl phosphate in the photolysis medium; this could have been formed from the reaction of released metaphosphate with the traces of water that always seem to be present in spite of strenuous efforts to eliminate it. When the photolysis was performed in the same solvent at room temperature, none of the rearrangement product was observed for 8 or 15, and only a trace for 9. It was established that, once formed, the photorearrangement product (e.g., 27) was stable on irradiation at room temperature and did not function as a precursor for elimination of the metaphosphate. This dual pathway of fragmentation–rearrangement has been reported in the photolysis of bicyclic ketones bearing some resemblance to the oxaphosphabicyclic system we have employed; ketone 32 and some derivatives either can undergo the oxadi-π-methane rearrangement to give a cyclopropane structure,[17] or it can undergo a second type of C–C cleavage to extrude ketene. The possible impor-



32

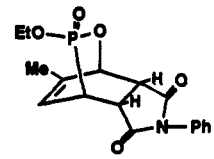
tance of reaction temperature in determining the outcome of the photolysis was not reported in these papers, however.

A small ^{31}P NMR signal at δ 53 was observed in the room temperature photolysis product of *O*-neopentyl phosphonate 8 in acetonitrile that had been rigorously dried (two distillations from P_2O_5 on a vacuum line). The signal was also observed in a photolysis in 1,2-dichloroethane, which is more readily freed of water. However, when a trace of water was purposely present in dichloroethane, none of the rearrangement product was observed in the room temperature photolysis product. Any role that water may play in inhibiting the rearrangement is not known at this time.

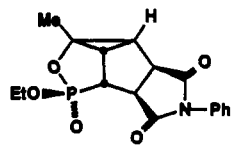
Although the rearrangement reaction was discovered for bridged phosphonates bearing sterically demanding O-substituents, we have noted[6] that there is no requirement for special structure in the O-substituent. Thus, the *O*-ethyl phosphonate 33 gave exactly the same results. The major product 34 had ^{31}P NMR δ 53.2, which by itself is sufficient to show that the rearrangement to a five-membered cyclic phosphonate had occurred. The rearrangement reaction does not, however, occur when amino groups take the place of alkoxy on phosphorus. Two bicyclic phosphonamides were photolyzed at -75 °C in earlier studies[5] and there were no signals in the downfield

(16) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; Chapter 12.

(17) Parker, S. D.; Rogers, N. A. J. *Tetrahedron Lett.* **1976**, 4389. Eckersley, T.; Parker, S. D.; Roger, N. A. J. *Tetrahedron Lett.* **1976**, 4393.



33



34

region expected for the rearrangement product. As noted earlier, the evidence is strong that metaphosphoramide extrusion has occurred in these cases.

Finally, we considered the effect of replacing phosphoryl oxygen with sulfur by photolyzing ester **16** in propionitrile at −75 °C. The product was a very complex mixture with numerous broad ^{31}P NMR signals. The most downfield signal appeared at δ 49. If the rearrangement had occurred to place either oxygen or sulfur in the five-membered ring component, a signal significantly downfield from that of the oxygen counterpart (**27**, δ 53) would be expected. Thionophosphonate **16** therefore does not seem to follow the same readily recognized pathway on low-temperature photolysis as seen for **27** and gives no indication of undergoing the rearrangement reaction.

Experimental Section

General. 1-Chloro-3-methyl-3-phospholene 1-oxide was prepared as described previously.[5] Solvents for thermal or UV fragmentations were dried as follows: CH_3CN and CH_3CH_2CN, distillation from P_2O_5; toluene, distillation over K; dioxane, distillation over CaH_2. Spectroscopic measurements were made as reported recently.[2]

3-Methyl-1-neopentoxy-3-phospholene 1-Oxide (1). A solution of 14.97 g (0.170 mol) of neopentyl alcohol and 42.2 mL (0.319 mol) of triethylamine in 45 mL of benzene was cooled with an ice bath to about 5 °C. To the stirred solution was added dropwise a solution of 19.2 g (0.128 mol) of 1-chloro-3-methyl-3-phospholene 1-oxide in 55 mL of dry benzene. After 14 h the precipitate was filtered from the mixture and the filtrate concentrated on a rotoevaporator to give a pale yellow liquid. Distillation gave 21.93 g (85.0%) of **1** as a colorless liquid: bp 130 °C at 0.4 mm; ^{31}P NMR ($CDCl_3$) δ 76.0; ^{13}C NMR, Table 7; ^1H NMR ($CDCl_3$) δ 0.95 (s, 9H), 1.81 (s, 3H), 2.43 (m, 4H), 3.68 (d, $^3J_{HH}$ = 5.7, 2H), 5.54 (ddd, $^3J_{PH}$ = 35.8, $^3J_{HH}$ = 3.0, $^4J_{HH}$ = 1.5, 1H). Anal. Calcd for $C_{10}H_{19}O_2P$: C, 59.39; H, 9.47. Found: C, 59.41; H, 9.56.

3,4-Dibromo-3-methyl-1-neopentoxyphospholane 1-Oxide (2). A solution of 18.0 g (0.089 mol) of **1** in 60 mL of $CHCl_3$ was placed under nitrogen and cooled to 0 °C. To the mixture was added dropwise a solution of 4.6 mL (0.089 mol) of bromine dissolved in 20 mL of $CHCl_3$. Concentration by rotoevaporation and then high vacuum gave 30.6 g (95%) of **2** as a yellow oil consisting of a 1:1 mixture of stereoisomers: ^{31}P NMR ($CDCl_3$) δ 68.30, 67.44. This crude dibromide was used directly in the preparation of the phosphole oxide dimer **4**.

Dimer (4) of 3-Methyl-1-neopentoxyphosphole 1-Oxide (3). To a solution of 25.8 g (0.071 mol) of **2** in 70 mL of dry benzene was added dropwise 37 mL (0.27 mol) of triethylamine. After the mixture had been stirred under nitrogen for 16 h, it was filtered to remove the precipitate. The filtrate was concentrated by rotoevaporation to give 33.0 g of thick oil. Chromatography on silica gel (3% methanol in chloroform) afforded 25.8 g of yellow solid. Crystallization from benzene gave 6.64 g (46.6%) of **4** as a white solid: mp 158–159 °C; ^{31}P NMR ($CDCl_3$) δ 81.04 (d, $^3J_{PP}$ = 48.8 Hz) and 71.87 (d, $^3J_{PP}$ = 48.8 Hz); ^{13}C NMR, Table 1; ^1H NMR δ 0.87 (s, 9H), 0.91 (s, 9H), 1.79 (s, 3H), 1.95 (s, 3H), 2.85–3.04 (m, 5H), 5.85 (dd, $^3J_{PH}$ = 20.0, $^3J_{HH}$ = 5.5, 1H), 6.15 (dd, $^3J_{PH}$ = 15.0, $^3J_{HH}$ = 5.0, 1H). Anal. Calcd for $C_{20}H_{34}O_4P_2$: C, 59.99; H, 8.56; P, 15.47. Found: C, 60.09; H, 8.84; P, 15.68.

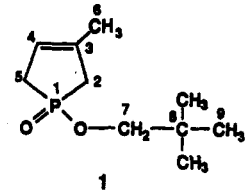
5,11-Dimethyl-3,9-dineopentoxy-3,9-diphospha-8-oxatricyclo[5.2.2.0^{2,6}]undeca-4,10-diene 3,9-Dioxide (7). A mixture of phosphole oxide dimer **4** (20 g, 5 mmol) and *m*-chloroperbenzoic acid (1.73 g, 10 mmol) in 50 mL of dry chloroform was allowed to stand for 40 h at room temperature. To remove the *m*-chlorobenzoic acid formed, the mixture was treated with 2.2 g of anhydrous potassium fluoride and stirred for 3 h to form a solid complex. The solid was removed by filtration, and the filtrate was evaporated under reduced pressure at room temperature. The residual oil was flash-chromatographed on Florisil using methylene dichloride, which removed residual *m*-chlorobenzoic acid. Elution with 50% methanol–chloroform then removed the product from the column. The eluate was evaporated to dryness; 1.89 g (90.0%) of white solid was obtained. A sample for analysis was twice recrystallized from a 1:1 mixture of benzene and petroleum ether (40–50 °C). The crystals that formed on chilling the solution were filtered to give **7**: mp 139–140 °C; ^{31}P NMR ($CDCl_3$) δ 68.41 and 28.38 (both d, $^3J_{PP}$ = 63.1 Hz); ^{13}C NMR, Table 3; ^1H NMR ($CDCl_3$), δ 0.89 (s, 9H), 0.91 (s, 9H), 1.77 (dd, $^5J_{PH}$ = 4.8, $^4J_{HH}$ = 1.8, 3H), 1.99 (s, 3H), 2.80–2.93 (m, 1H), 3.25–3.34 (m, 1H), 3.56–3.79 (m, 5H), 4.93 (dm, $^3J_{PH}$ = 22.5, 1H), 5.92 (d, $^2J_{PH}$ = 32.1, 1H), 6.17 (tm, $^3J_{PH}$ = $^3J_{HH}$ = 8.4, 1H). Anal. Calcd for $C_{20}H_{34}O_4P_2$: C, 57.68; H, 8.23. Found: C, 57.28; H, 8.24.

2-Methyl-*syn*-7-neopentoxy-*N*-phenyl-7-phosphabicyclo-[2.2.1]hept-2-ene-*endo*-5,6-dicarboximide 7-Oxide (5). To a solution of 32.0 g (0.0884 mol) of dibromophospholane-1-oxide **2** and 15.4 g (0.0889 mol) of *N*-phenylmaleimide in 500 mL of dry benzene was added 29.6 mL (0.2124 mol) of triethylamine. After the reaction mixture had been stirred under nitrogen for 5 days at room temperature, it was filtered to remove the precipitate. The filtrate was concentrated by rotoevaporation to give a dark-brown semisolid. Chromatography on silica gel (3% methanol in chloroform) afforded 21.8 g (66.1%) of **5** as a white solid, mp 129-130 °C; ^{31}P NMR ($CDCl_3$) δ 81.4; ^{13}C NMR, Table 2; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.91 (s, 9H), 1.94 (s, 3H), 3.4 (m, 2H), 3.8 (d, $^3J_{PH}$ = 8 Hz, 2H), 3.9 (apparent t, 2H), 6.02 (d, $^3J_{PH}$ = 12 Hz). Anal. Calcd for $C_{20}H_{24}NO_4P$: C, 64.33; H, 6.47; N, 3.75. Found: C, 64.31; H, 6.38; N, 3.73.

2-Methyl-*anti*-7-neopentoxy-*N*-phenyl-7-phosphabicyclo-[2.2.1]hept-2-ene-5,6-dicarboximide 7-Oxide (6). A solution of *syn* isomer **5** (3.1 g, 8.3 mmol) in 15 mL of hexane–methanol (2:1) was stirred for 1 week at room temperature. Analysis by ^{31}P NMR showed the complete conversion of **5** to a new product with a shift of δ 71. The product was recovered as a solid after evaporation of the solvent and was twice recrystallized from methanol to yield 2.3 g (76%) of **6**: mp 197-198 °C; ^{31}P NMR ($CDCl_3$) δ 71.0; ^{13}C NMR, Table 2; ^1H NMR (80 MHz, $CDCl_3$) δ 0.99 (s, 9H), 2.01 (s, 3H), 3.3–4.1 (m, 6H), 5.95–6.40 (m, 1H). Anal. Calcd for $C_{20}H_{24}NO_4P$: C, 64.34; H, 6.43; N, 3.75. Found: C, 64.10; H, 6.35; N, 3.84.

6-Methyl-3-*syn*-neopentoxy-*N*-phenyl-2,3-oxaphosphabicyclo[2.2.2]oct-5-ene-*endo*-7,8-dicarboximide 3-Oxide (8). A mixture of 14.4 g (0.0354 mol) of **5**, 20.0 g (0.116 mol) of *m*-chloroperbenzoic acid, and 300 mL of

Table 7. ^{13}C NMR Spectra of 1-Alkoxyphospholene Oxides 1 and 11



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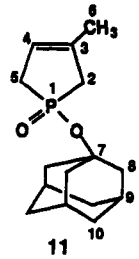

11

	1		11	
carbon	δ	J_{PC}, Hz	δ	J_{PC}, Hz
2	30.4	88.5	36.5	93.7
3	136.1	17.1	136.2	17.3
4	120.2	10.9	120.4	11.1
5	33.1	92.5	34.0	90.0
6	20.6	12.8	20.8	12.9
7	73.9	7.3	81.8	9.0
8	38.5	0	44.3	3.7
9	25.9	0	31.2	0
10	–	–	35.8	0

chloroform was stirred at room temperature for 2 days. Anhydrous potassium fluoride (20.2 g, 0.348 mol) was added to the reaction mixture and stirred at room temperature for 6 h; it was filtered to remove the precipitate of complexed benzoic acids. The filtrate was concentrated by rotoevaporation to give 11.6 g (77.8%) of crude 8 as a light yellow solid. Chromatography on Florisil (100–200 mesh; 3% methanol in chloroform) afforded 7.69 g (51.5%) of 8. Recrystallization (CH_2Cl_2/*n*-hexane) gave a white crystalline solid: mp 140.2–140.7 °C; ^{31}P NMR ($CDCl_3$) δ 25.6; ^{13}C NMR, Table 4; ^1H NMR, Table 5. Anal. Calcd for $C_{20}H_{24}NO_5P$: C, 61.69; H, 6.21; N, 3.60; P, 7.95. Found: C, 61.41; H, 6.05; N, 3.57; P, 7.85.

Another sample of the MCPBA insertion product was analyzed by ^{31}P NMR before chromatographic purification and had δ 25.6 and 22.6 (15:1). The mixture was partially separated by chromatography on Florisil. The compound with δ 22.6 was eluted in the first fraction with 30% hexane–chloroform. The second fraction was a 1:1 mixture with the compound having δ 25.6, which was then obtained cleanly on continued elution with chloroform. The minor reaction product 9 with δ 22.6 was obtained as a solid, in adequate purity to allow the recordings of its ^{13}C NMR (Table 4) and ^1H NMR spectra (Table 5). The sample was identical to that obtained separately from O-insertion on 5A.

6-Methyl-3-*anti*-neopentoxy-*N*-phenyl-2,3-oxaphosphabicyclo[2.2.2]oct-5-ene-*endo*-7,8-dicarboximide 3-Oxide (9). A solution of 0.1 g (0.27 mmol) of 6 and 0.15 g (0.87 mmol) of *m*-chloroperbenzoic acid in 10 mL of chloroform was stirred for 24 h at room temperature. To the mixture was added 55 mg of anhydrous KF, which was removed by filtration after 3 h. Evaporation of the solvent left solid 9 that was recrystallized from hexane to yield 0.06 g (60%); ^{31}P, ^1H, and ^{13}C NMR identical to those obtained for 9 isolated from O-insertion on 5. Anal. Calcd for $C_{20}H_{24}NO_5P$: C, 61.69; H, 6.21; N, 3.60. Found: C, 61.82; H, 5.94; N, 3.69.

6-Methyl-3-neopentoxy-*N*-phenyl-2,3-oxaphospha[2.2.2]-oct-5-ene-*endo*-7,8-dicarboximide 3-Sulfide (16). A mixture of 3.5 g (0.009 mol) of 8, 12.0 g (0.027 mol) of phosphorus pentasulfide, and 60 mL of dry dichloromethane was stirred at room temperature for 6 days. It was filtered and the residue washed with two 30-mL portions of dry CH_2Cl_2. The filtrate was concentrated by rotoevaporation to give a yellow-brown crude product (16). Chromatography on silica gel (grade 60, CH_2Cl_2) afforded 1.10 g (30.2%) of 16. Recrystallization (CH_2Cl_2, *n*-hexane) gave a white crystalline solid with indistinct mp; ^{31}P NMR ($CDCl_3$, 121.4 MHz) δ 85.9; ^{13}C NMR (Table 4). Anal. Calcd for $C_{20}H_{24}NO_4PS$: C, 59.24; H, 5.97; N, 3.45; P, 7.64; S, 7.89. Found: C, 59.15; H, 6.01; N, 3.43; P, 7.43; S, 7.98.

1-(1-Adamantoxy)-3-methyl-3-phospholene 1-Oxide (11). A solution of 3.2 g (0.021 mol) of 1-adamantanol and 5.6 mL (0.04 mol) of dry triethylamine in 20 mL of dry benzene was cooled with an ice bath. To the stirred solution was added dropwise a solution of 3.0 g (0.02 mol) of 1-chloro-3-methyl-3-phospholene 1-oxide in 10 mL of dry benzene. After 24 h the precipitate was filtered from the mixture and the filtrate concentrated on a rotoevaporator to give a yellow liquid. A mixture of this liquid with 30 mL of benzene was treated with 50 mL of 5% $NaHCO_3$. The water layer was extracted with benzene (3 × 40 mL). The combined organic fractions were concentrated by rotoevaporation to give 6.87 g of brown liquid, which afforded 4.77 g (89.8%) of white solid (11) after chromatography on silica gel (ethyl acetate). Crystallization from ethyl acetate gave white crystals: mp 68.5–69.5 °C; ^{31}P NMR ($CDCl_3$) δ 69.07; ^{13}C NMR, Table 7; ^1H NMR ($CDCl_3$) δ 1.67 (s, 6H), 1.78 (s, 3H), 2.12 (s, 6H), 2.18 (s, 3H), 2.38 (d, $^2J_{PH}$ = 15.0, 2H), 2.48 (d, $^2J_{PH}$ = 15.0), 5.50 (d, $^3J_{PH}$ = 39.0, 1H). Anal. Calcd for $C_{15}H_{23}O_2P$: C, 67.65; H, 8.70; P, 11.63. Found: C, 67.41; H, 8.58; P, 11.41.

1-(1-Adamantoxy)-3,4-dibromo-3-methylphospholane 1-Oxide. A solution of 2.90 g (0.011 mol) of 11 in 8 mL of $CHCl_3$ was placed under nitrogen and cooled to 0 °C. To the mixture was added dropwise a solution of 0.7 mL (0.014 mol) of bromine dissolved in 3 mL of $CHCl_3$. Concentration by rotoevaporation and then high vacuum gave 2.75 g (95%) of the dibromide as a yellow oil consisting of a 1:1 mixture of diastereoisomers: ^{31}P NMR ($CDCl_3$) δ 60.63, 59.83. The crude dibromide was used directly in the preparation of the dimer (12) or the Diels–Alder adduct (13) with *N*-phenylmaleimide.

Synthesis of the Dimer of 1-(1-Adamantoxy)-3-methylphosphole 1-Oxide (12). To a solution of 4.63 g (0.011 mol) of 1-(1-adamantoxy)-3,4-dibromo-3-methylphospholane-1-oxide in 30 mL of dry benzene was added dropwise 5.7 mL (0.041 mol) of triethylamine. After the solution had been stirred and warmed at 45 °C for 16 h, it was filtered to remove the precipitate. The filtrate was concentrated by rotoevaporation to give 5.4 g of thick oil. Fractional recrystallization with ethyl acetate afforded 2.0 g (69.4%) of white solid 12: mp 166–168 °C; ^{31}P NMR ($CDCl_3$) δ 78.56 (d, $^3J_{PP}$ = 50.0 Hz) and 67.39 (d, $^3J_{PP}$ = 50.0 Hz); ^{13}C NMR, Table 1; ^1H NMR ($CDCl_3$), 1.63 (d, $^3J_{HH}$ = 2.1, 6H), 1.72 (d, $^3J_{HH}$ = 2.7, 6H), 1.91 (s, 3H), 1.98 (d, $^3J_{HH}$ = 2.4), 2.04–2.22 (m, 6H), 2.85–3.01 (m, 2H), 3.12–3.27 (m, 1H), 3.65 (t, $^3J_{PH}$ = $^3J_{HH}$ = 7.7, 1H), 5.82 (dd, $^3J_{PH}$ = 22.6, $^3J_{HH}$ = 5.2, 1H), 6.09 (dm, $^3J_{PH}$ = 14.4, 1H). Anal. Calcd for $C_{30}H_{42}O_4P_2 \cdot H_2O$: C, 65.93; H, 8.06; P, 11.36. Found: C, 66.29; H, 8.11; P, 11.12.

3,9-Di(1-adamantoxy)-5,11-dimethyl-3,9-diphospha-8-oxatricyclo[5.2.2.0^{2,6}]undeca-4,10-diene 3,9-Dioxide (14). A mixture of 0.4 g (0.757 mmol) of the dimer 12 and MCPBA (0.96 g, 5.58 mmol) in 13 mL of dry $CHCl_3$ was allowed to stand for 6 weeks at 0 °C in a refrigerator. The ^{31}P NMR showed that the reaction was complete. The reaction mixture was treated with 1.8 g of anhydrous potassium fluoride and stirred for 3 h. The solid was removed by filtration, and the filtrate was evaporated under reduced pressure at room temperature. The residual oil was flash-chromatographed twice on Florisil using methylene dichloride, which removed residual *m*-chlorobenzoic acid. Elution with 50% methanol–chloroform removed the product 14 from the column. The eluate was evaporated to dryness and 0.207 g (50.5%) of 14 was obtained as a clear oil: ^{13}C NMR, Table 1; ^{31}P NMR ($CDCl_3$), δ 26.23 and 66.26 (both d, $^3J_{PP}$ = 65.8 Hz); ^1H NMR ($CDCl_3$), 1.65–2.20 (m, 36H), 2.88–3.04 (m, 1H), 3.18–3.38 (m, 1H), 3.64–3.80 (m, 1H), 4.91 (dm, $^3J_{PH}$ = 22.6), 5.98 (d, $^2J_{PH}$ = 22.4, 1H), 6.16 (t, $^3J_{PH}$ = $^3J_{HH}$ = 9.1, 1H).

Synthesis of 7-syn-(1-Adamantoxy)-2-methyl-*N*-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*endo*-5,6-dicarboximide 7-Oxide (13). To a solution of 28.4 g (0.067 mol) of 1-adamantoxy-3,4-dibromo-3-methylphospholane 1-oxide and 15.26 g (0.088 mol) of *N*-phenylmaleimide in 200 mL of dry benzene in an ice-bath (5 °C) was added dropwise 45 mL (0.32 mol) of triethylamine (dried with potassium hydroxide). After the mixture was stirred under nitrogen for 5 days at 25 °C, it was filtered to remove the precipitated salt. The filtrate was concentrated by rotoevaporation to give a maroon oil. Crystallization from dichloromethane–hexane gave 17.77 g (61.1%) of white solid 13: mp 236–237 °C; ^{31}P NMR ($CHCl_3$ with D_2O lock) δ 76.1; ^{13}C NMR, Table 2; ^1H NMR ($CDCl_3$), 1.61 (s), 1.89 (s, 3H), 1.99 (d, $^3J_{HH}$ = 2.1), 2.18 (s), 3.30 (d, $^2J_{PH}$ = 9.0, 1H), 3.38–3.48 (m, 1H), 3.82 (m, 2H), 5.93 (dd, $^3J_{PH}$ = 12.8, $^3J_{HH}$ = 4.1, 1H), 7.02–7.49 (m, 5H). Anal. Calcd for $C_{25}H_{28}O_4NP$: C, 68.64; H, 6.45. Found: C, 68.59; H, 6.46.

Synthesis of 3-(1-Adamantoxy)-6-methyl-*N*-phenyl-2,3-oxaphosphabicyclo[2.2.2]oct-5-ene-*endo*-7,8-dicarboximide 3-Oxide (15). A mixture of phosphinate 13 (1.10 g, 0.0025 mol) and MCPBA (3.47 g, 0.020 mol) in 140 mL of dry methylene chloride was allowed to stand for 7 days at room temperature. To complex the excess MCPBA and MCBA formed, the mixture was treated with 9.45 g of anhydrous potassium fluoride and stirred for 5 h. The solid was removed by filtration through Celite, and the filtrate was concentrated by rotoevaporation. The residual yellowish solid was flash-chromatographed on Florisil with chloroform–methanol as eluants. The eluate was evaporated to dryness leaving 0.56 g (50.0%) of white solid. Recrystallization from dichloromethane–hexane gave 15: mp 166–167 °C; ^{31}P NMR ($CDCl_3$) δ 20.7; ^1H NMR ($CDCl_3$) δ 1.62 (s, 6H), 1.90 (dd, $^5J_{PH}$ = 4.8, $^4J_{HH}$ = 1.6, 3H), 2.05 (d, $^4J_{PH}$ = 2.6, 6H), 2.18 (br, 3H), 3.49 (ddd, $^2J_{PH}$ = 14.6, $^3J_{HH}$ = 7.1, $^3J_{HH}$ = 2.7, 1H), 3.74 (dt, $^3J_{PH}$ = $^3J_{HH}$ = 8.1, $^3J_{HH}$ = 2.7, 1H), 3.96 (dd, $^3J_{HH}$ = 8.1, $^3J_{HH}$ = 4.3, 1H), 5.14 (ddd, $^3J_{PH}$ = 23.4, $^3J_{HH}$ = 4.3, J = 2.2, 1H), 6.06 (tm, $^3J_{PH}$ = $^3J_{HH}$ = 7.5, 1H), 7.10–7.48 (m, 5H). Anal. Calcd for $C_{25}H_{28}NO_5P$: C, 66.21; H, 6.22. Found: C, 65.93; H, 6.15.

Photolysis of Adamantyl Phosphonate 15 at −75 °C. Rearrangement Product 27. A solution of 15 (153 mg, 0.334 mmol) in 4 mL of dry propiononitrile in a quartz NMR tube was

irradiated at −75 °C for 16.5 h, using a Hanovia medium-pressure lamp (254 nm). The yellow solution from the reaction was evaporated to dryness and a brown oil was obtained. Chromatography on Florisil using methanol–dichloromethane as eluants gave 79 mg (51.6%) of **27**. The sample was recrystallized from benzene–hexane: white, mp 241–242 °C; ^{31}P NMR (C_6H_6, with D_2O lock) δ 48.7; ^{13}C NMR ($CDCl_3$), Table 6; ^{1}H NMR, ref 6. Anal. Calcd for $C_{25}H_{28}NO_5P$: C, 66.21; H, 6.22; N, 3.09. Found: C, 65.91; H, 6.09; N, 3.16.

Photolysis of Neopentyl Phosphonates 8 and 9 and Ethyl Phosphonate 33 at −75 °C. A 0.39-g sample of phosphonate **8** in 1.5 mL of dry propiononitrile was photolyzed at −75 °C as for **15**. After 28 h, no starting material remained; the major signal appeared at δ 53 (**28**), with smaller peaks at δ 1 and −13 (broad). The solution was evaporated to leave an oil that was treated with ether. The non-phosphorus byproduct was insoluble and was removed by filtration. The ether was evaporated and the residue was flash-chromatographed on silica gel with $CHCl_3$. The only ^{31}P NMR signal appeared at δ 53; the ^{13}C (Table 6) and ^{1}H NMR[6] spectra similarly indicated no significant impurities. The sample could not be recrystallized or analyzed successfully; further purification attempts led to formation of a decomposition product **29** with ^{31}P NMR δ 31, not further characterized.

Neopentyl phosphonate **9** (0.06 g, 0.15 mmol) in 3 mL of propionitrile was photolyzed similarly for 4 h. The major product had ^{31}P NMR δ 44; there was no signal at δ 53 corresponding to rearrangement product **28**. The new product **30** was isolated in the same way as **28**, except that elution was accomplished with a hexane–chloroform (1:1) mixture. Unlike **28**, this compound (0.043 g, 71%) crystallized on standing: mp 177–178 °C; ^{31}P NMR 44.8 ($CDCl_3$), ^{13}C NMR, Table 6. Anal. Calcd for $C_{20}H_{24}NO_5P$: C, 61.70; H, 6.17; N, 3.60. Found: C, 61.51; H, 5.38, N, 3.73.

In a similar manner, the photolytic rearrangement of the O-ethyl analogue **33**[2] gave **34**, with ^{31}P NMR δ 53.2; attempts to purify **34** for further characterization were hampered by its sensitivity to water.

Photochemical Generation and Trapping of Metaphosphates 17 from 8 and 9, and 18 from 15. A sample of neopentyl phosphonate **8** (195 mg, 0.50 mmol) and 5 mmol of ethanol in 5 mL of $C_2H_4Cl_2$ was placed in a quartz NMR tube and photolyzed with a 450-W medium pressure Hanovia lamp (254 nm). Analysis by ^{31}P NMR showed that after 0.5 h, no **8** remained, and all phosphorus appeared as ethyl neopentyl phosphate (**20**), ^{31}P NMR δ 1.1. The compound was isolated by chromatography on silica gel with elution by 30% hexane in $CHCl_3$: ^{31}P ($CDCl_3$) δ 1.0; ^{13}C NMR ($CDCl_3$) δ 16.2 (d, J_{PC} = 6.8 Hz), 26.4, 31.8 (d, J_{PC} = 7.6), 61.6 (d, J_{PC} = 4.6), 75.3 (d, J_{PC} = 10); ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 9H), 1.23 (t, J = 7.1 Hz), 3.5–3.77 and 3.77–3.96 (both m, 2H). A sample was methylated with diazomethane, prepared in the usual way from Diazald (Aldrich), to form ester **21**: ^{1}H NMR ($CDCl_3$) δ 0.94 (9H), 1.34 (t, J = 7.1 Hz, 3H), 3.68 (d, J_{PH} = 2.7 Hz, 2H), 3.75 (d, J_{PH} = 2.6 Hz, 3H), 4.12 (m, 2H); GC-MS showed no M^+ peak as is typical of phosphates, but gave m/z 127 (100%, $EtPO_4H_2^+$), 195 (9.8%, M^+ − Me), 154 (59%, $C_4H_{11}PO_4^+$), 74 (73.8%, $CH_6PO_4^+$).

Similarly, adamantyl phosphonate **15** (30 mg, 0.066 mmol) in 2 mL of acetonitrile containing 31 mg (0.66 mmol) of ethanol was irradiated for 1.5 h; ^{31}P NMR showed that all **15** had been consumed and the only signal, attributed to phosphate **22**, appeared at δ −4.8 (CH_3CN, D_2O lock).

Photolysis of neopentyl phosphonate **8** in the absence of ethanol in $C_2H_4Cl_2$ gave only a trace of **27**; the major product had ^{31}P NMR δ −13.3 and was identified as pyrophosphate **25** by comparison with a known sample prepared as follows. Neopentyl phosphorodichloridate **26** was prepared by treating a solution of neopentyl alcohol (4.41 g, 0.050 mol) in 30 mL of toluene with a solution of 7.66 g (0.050 mol) of $POCl_3$ and 5.06 g (0.050 mol) of triethylamine in 40 mL of toluene. The precipitated salt was removed by filtration, and the filtrate was evaporated to leave a solid. This was dissolved in acetone and aqueous NaOH added to pH 8. Some precipitated NaCl was filtered off, and the solution was evaporated to dryness, the residue taken up in MeOH, and additional NaCl removed by filtration. The filtrate was passed through a column of Dowex 50 (H^+). Evaporation of the eluate gave a solid residue with a major ^{31}P NMR ($CDCl_3$) peak at δ 0.10 for neopentyl phosphate (**24**) and a minor peak at δ −13 for a pyrophosphate, presumably **25**. Recrystallization from toluene gave pure **24**; mp 129–130 °C; ^{31}P NMR δ 0.50 ($CDCl_3$). Anal. Calcd for $C_5H_{13}O_4P$: C, 35.72; H, 7.79. Found: C, 35.98; H, 7.84. This compound was used as a trapping agent for neopentyl metaphosphate (**17**) when released by photolysis of phosphonate **8**. The major product from the photolysis had ^{31}P NMR δ −13.3 ($C_2H_4Cl_2$) and is assigned pyrophosphate structure **25**. Spiking showed that this pyrophosphate was identical to the minor product obtained in the synthesis of neopentyl phosphate (**24**).

Photolysis of **9** (0.1 g) in 3 mL of propiononitrile was complete in 8 h; the major products were P–O–P materials but a small signal (~5%) was noted at δ 44 (**30**).

The quantum yield in the photolysis of **8** in the presence of ethanol was determined by the method previously reported[2] and found to be 0.30. The same value was found when neopentyl phosphate **24** was present as a trap.

Thermal Generation and Trapping of Metaphosphate 17 and Metathiophosphate 19. To generate and trap **17**, a solution of neopentyl phosphonate **8** (40 mg, 0.096 mol) and ethanol (0.05 mL) in 2 mL of dry chlorobenzene in a closed tube was heated at 130 °C for 2 h (or in toluene at 110 °C for 9 h). The solvent was evaporated and the ^{31}P NMR spectrum of the residue in $CDCl_3$ showed that all **8** had been decomposed; the only signal was at δ 1.0. This was confirmed as arising from **20** by isolating the compound by silica gel chromatography (methanol–chloroform, 1:4). The product had the same ^{13}C and ^{1}H NMR spectra as obtained for **20** when prepared by the photolytic procedure. Similar results were obtained in the thermolysis of **9**, which required 7.5 h for completion. Compound **6** gave the same results, decomposing in only about 1 h.

Similarly, thermolysis of **16** (10 h) released metathiophosphate **19** which in the presence of ethanol gave thionophosphate **23**, isolated by chromatography but not obtainable in analytically pure form: ^{31}P NMR ($CDCl_3$) δ 61.9; ^{13}C NMR ($CDCl_3$) δ 16.1 (d, J_{PC} = 7.5 Hz), 26.4 , 32.0 (d, J_{PC} = 8.7), 43.5 (d, J_{PC} = 5.1,), 76.6 (d, J_{PC} = 7.3); ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 9H), 1.33 (t, J = 6.9, 3H), 3.6–3.8 and 3.9–4.3 (both m, 2H).

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