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Products Derived from Oxidations of 3,4-Dimethyl-1-phenylphosphole-1-oxide: A 3-Phenyl-5,6-dimethyl-2,3-oxaphosphabicyclo[2.2.2]octene-3-oxide Derivative as a Precursor of Phenyl Metaphosphonic Anhydride

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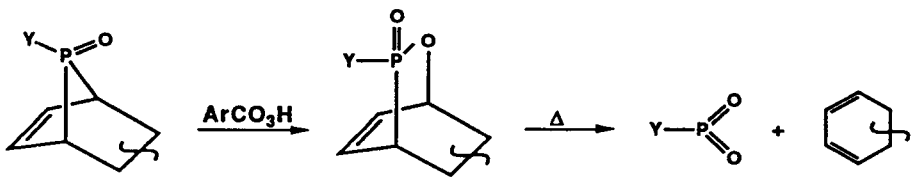
ABSTRACT

Oxidation of 3,4-dimethyl-1-phenylphosphole with peracids or peroxides gives a relatively stable P-*oxide, which can be used in Diels-Alder reactions to give derivatives with the 7-phosphanorbornene framework. Oxygen insertion into a C–P bond of this framework occurs smoothly with* m-*chloroperbenzoic acid (MCPBA) providing derivatives of the 2,3-oxaphosphabicyclo[2.2.2]octene ring system. The phosphole can be converted to this system in a one-pot synthesis by reaction with excess MCPBA in the presence of* N-*phenylmaleimide as dienophile. The phosphole oxide undergoes mono-epoxidation with MCPBA. Thermal or photochemical fragmentation of the 2,3-oxaphosphabicyclo[2.2.2]ocetene is a useful source of the 3-coordinate species Ph–PO_2, a meta-anhydride of phenylphosphonic acid. This species was trapped successfully with a variety of alcohols.*

RESULTS AND DISCUSSION

In 1985, we demonstrated that the fragmentation of the 2,3-oxaphosphabicyclo[2.2.2]octene ring system could serve as a useful source of low-coordination species of phosphorus [1]. The ring system was created by the insertion of oxygen with a peracid into a C–P bond of a 7-phosphanorbornene derivative [2, 3], a reaction bearing some resemblance to the well-known Baeyer-Villiger conversion of ketones to lactones (Reaction 1). We included one example where the species eliminated was the meta-anhydride (Ph–PO_2) of phenylphosphonic acid (Ph–$PO(OH)_2$), and we proved its existence as a transient intermediate by trapping it with *N*-methylpyrrole through an electrophilic substitution reaction [1] (Reaction 2). Meta-anhydrides are of great current interest as rare examples of low-coordination phosphorus species. Neither the anhydrides of phosphoric acid derivatives (metaphosphates) nor of phosphonic acids have sufficient



REACTION 1

Dedicated to Professor Dr. Marianne Baudler on the occasion of her seventieth birthday.

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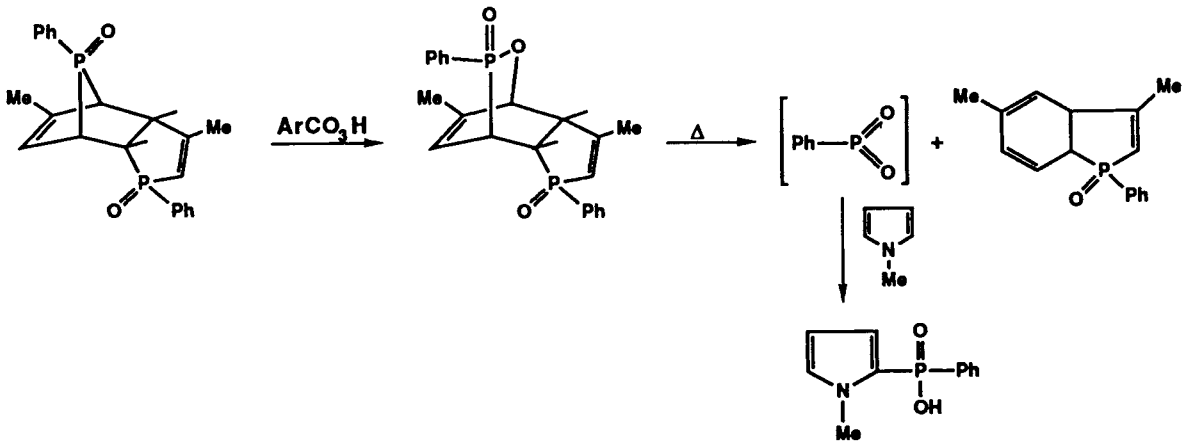


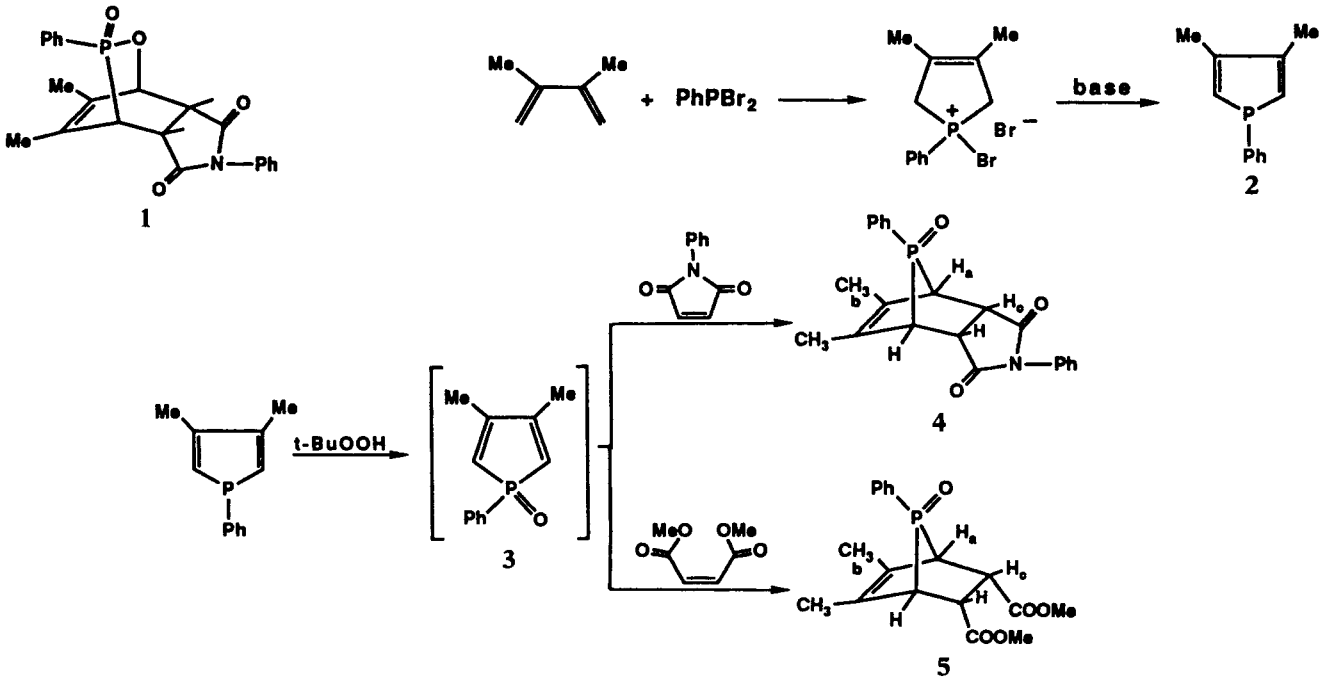
REACTION 2

stability to allow isolation or even direct detection in solution at room temperature by spectroscopic means.

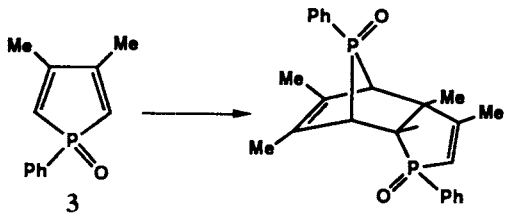
We now have developed a superior, easily synthesized precursor for Ph–PO_2 and have demonstrated its utility for the phosphonylation of some representative alcohols. The new precursor has the structure **1**. The starting material for its synthesis is 3,4-dimethyl-1-phenylphosphole (**2**), which is easily prepared by the Mathey method of dehydrohalogenation of the McCormack cycloadduct of 2,3-dimethylbutadiene and phenylphosphonous dibromide. The intermediate McCormack adduct is simply crushed and filtered from the reaction mixture; without further purification it is dispersed in the solvent and treated with a tertiary amine base (α-picoline is preferred). The literature reports a yield of 85% [4]; we have achieved 80.1%.

We have employed phosphole **2** in several ways that lead to the Ph–PO_2 precursor **1**. In our first experiment on the synthesis of the requisite 7-phosphanorbornene structure, we found that the phosphole could be oxidized with *t*-butyl hydroperoxide in the presence of a dienophile (*N*-phenylmaleimide or the less reactive dimethyl maleate), whereupon the initially-formed phosphole oxide (**3**) underwent Diels-Alder cycloaddition to give derivatives with the 7-phosphanorbornene framework. The yields were 88.5% for **4** and 72.8% for **5**. These products were easily purified; crystallization was used for **4** and column chromatography for **5**. Their identity was confirmed by NMR measurements. Most revealing were the ^{31}P NMR shifts; as is characteristic for oxides of 7-phosphanorbornenes [5], these shifts (**4**, δ 77.5; **5**, δ 66.8) were more downfield than unbridged monocyclic models (e.g., δ 46 for 3,4-dimethyl-1-phenyl-3-phospholene-1-oxide [6]).

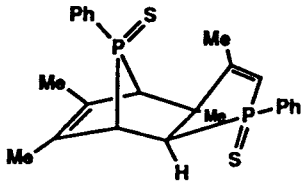
We later found that phosphole oxide **3** has un-



expected stability, allowing detection at room temperature. Solutions of **3** prepared from the phosphole and *t*-butyl hydroperoxide were stable for several days in the refrigerator. With only the exceptions of 1,2,5-triphenylphosphole oxide and pentaphenylphosphole oxide, *P*-aryl or *P*-alkyl phosphole oxides dimerize rapidly upon formation [7]. Oxide **3** was detected by its ^{31}P NMR signal of δ 42.3, which diminished on long standing or on heating and was replaced by the characteristic doublet of doublets for the dimer (**6**, reported previously [8]), at δ 74.3 and δ 53.6, $^{3}J_{PP}$ = 38.8 Hz. It was also possible to obtain the ^{13}C and ^{1}H NMR spectra for phosphole oxide **3**. The former had signals for the ring carbons at δ 121.5 (C-2,5) and δ 155.2 (C-3,4), with coupling constants to ^{31}P of 100.0 Hz and 21.7 Hz, respectively. The methyl signal was a doublet (18.6 Hz) at δ 17.4. The ^{1}H NMR spectrum simply showed the α-proton doublet at δ 5.95 ($^{2}J_{PH}$ = 26.9 Hz) and the methyl signal at δ 2.05. Addition of *N*-phenylmaleimide or dimethyl maleate to the solution gave the cycloadducts **4** and **5**, respectively.



Diels-Alder adducts of phosphole oxides are well known in the literature and are always found to have the endo configuration, with the singly bonded substituent on phosphorus syn to the carbon–carbon double bond [9]. Several properties support this structural assignment to the adducts of the present study. The endo configuration is revealed by the magnitude of the 3-bond coupling of ^{31}P to the carbonyl carbons; the values are relatively large (**4**, 15.9 Hz; **5**, 17.1 Hz), as expected for the dihedral angle approaching 180° imposed by this structure [10]. The exo configuration would have dihedral angles near 90°, where little coupling is expected. Indeed, there is one phosphine sulfide known with the exo configuration (**7**), and it shows no 3-bond coupling to the carbon in the exo position [11]. The syn configuration is revealed by deoxygenation of the phosphine oxides with trichlorosilane-pyridine; it is well established [5] that 7-phosphanorbornene derivatives are reduced with retention, and when this reaction was performed on oxide **4**, a phosphine (**8**) was formed that clearly had the syn structure, as evidenced by the far-downfield, highly characteristic ^{31}P NMR shift of δ 126.4. Furthermore, the 2-bond coupling of ^{31}P to the sp^3 carbons was quite large (29.8 Hz); this indicates close proximity of the lone pair to the coupled carbon as in structure **8**



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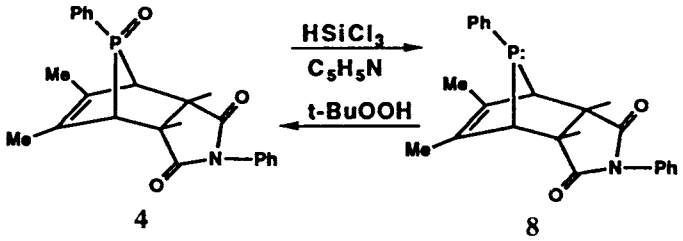
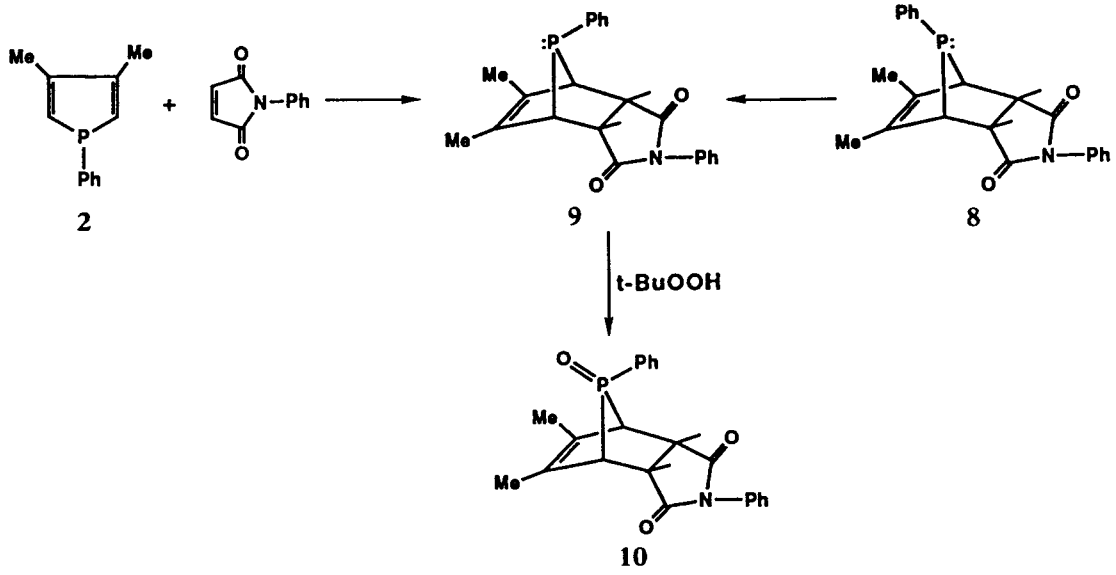


[5] (the sp^2 carbons could not be distinguished from the aromatic carbon signals). Peroxide oxidation of **8**, a process also known to occur with retention of configuration [12], regenerated the starting oxide **4**.

On studying the phosphine **8**, an unusual property was noted; on standing at room temperature in $CDCl_3$ solution, inversion of the configuration at phosphorus occurred to give the anti phosphine **9**. This transformation was easily followed by ^{31}P NMR spectroscopy, since the anti phosphine has a ^{31}P NMR shift (δ 47.5) quite far upfield of that of the syn. The anti phosphine **9** has, in fact, been reported before [13], and has essentially the same shift (δ 45.5) that we have observed. It was formed in the direct Diels-Alder reaction of phosphole **2** with *N*-phenylmaleimide. The syn to anti conversion has been observed before among phosphines of the 7-phosphanorbornene system, but has been brought about by action of hydroxy species [14, 15] possibly through formation of a P(V) intermediate that isomerizes before collapse to the phosphine. No information exists on a noncatalyzed inversion, however, and many syn phosphines are known to have quite good stability at room temperature, with some even surviving distillation without isomerization. Oxidation of anti phosphine **9** gave an oxide (**10**, δ ^{31}P 81.4) that was isomeric with oxide **4** (δ 77.5).

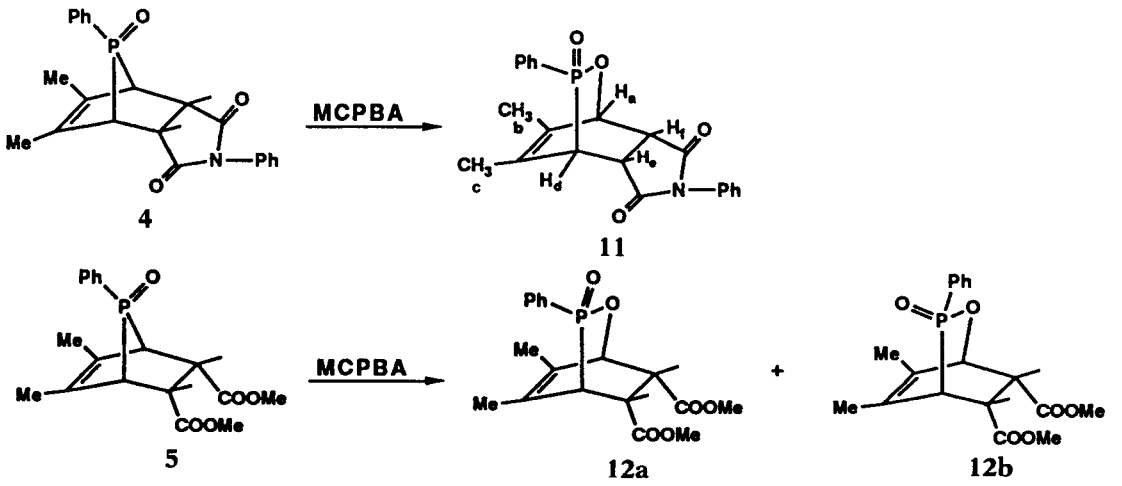
The 7-phosphanorbornene oxides **4** and **5** were found to undergo the O-insertion [2, 3] with *m*-chloroperbenzoic acid at room temperature, without attack on the carbon–carbon double bond. The single product (**11**) from **4** (69.7%) was a crystalline solid, but attempts to recrystallize it caused decomposition. Product **12** from **5** has not yet been crystallized. The ^{31}P NMR properties left no doubt about their structures, however; the downfield signals were replaced by new signals in the region of the bridged unstrained phosphonates (**11**, δ 36.2; **12**, 32.8 and 33.1). For **11**, the CH unit attached to the bridging oxygen was easily recognized in both the ^{13}C NMR spectrum (δ 78.5) and the ^{1}H NMR spectrum (δ 5.32).

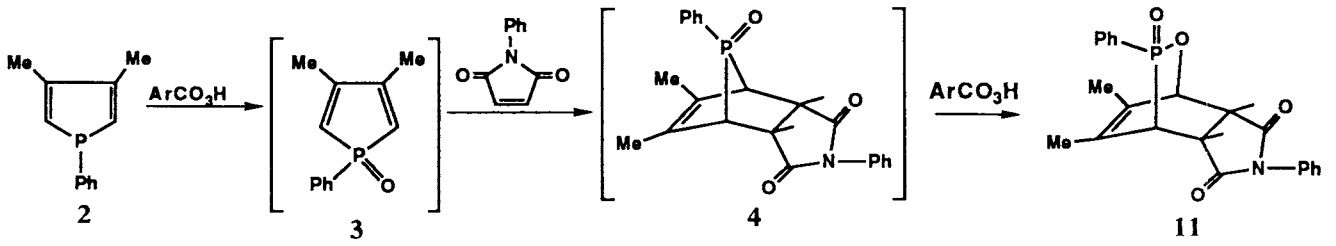


Two diastereomeric products are possible from the O-insertion reaction, with phenyl syn (from retention) or anti (inversion), but only one product is usually isolated [9]. In studies (including X-ray analysis) of insertions on related esters [16], we have found that the isolated product is that from retention of configuration, and by analogy we are assigning the syn structure **11** to the product from **4**. However, two insertion products (**12a, 12b**) were detected in the crude product from **5**, in nearly equal amounts. Since the mixture has not been successfully separated, no structural assignments have been made.

We have also developed a one-pot method for the conversion of phosphole **2** to the 2,3-oxaphosphabicyclo[2.2.2]octene derivative **11**, and this is clearly the preferred method for the synthesis of this compound. The method simply consists of the use of excess (3 equiv) of *m*-chloroperbenzoic acid when the phosphole is being oxidized in the presence of *N*-phenylmaleimide. Three reactions occur consecutively in the flask to give the bridged product. The yield of **11** is 83.9% from phosphole **2**. Compound **11** is therefore the most easily and directly synthesized derivative of the bridged ring system that we have encountered, and its availability makes it most attractive as a precursor of a metaphosphonic acid anhydride.

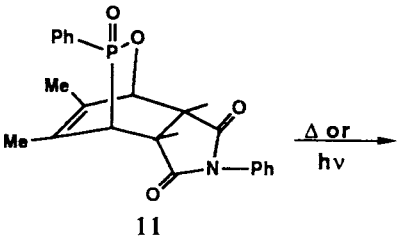
For generation of Ph–PO_2, we have devised both thermal and photochemical methods. When **11** is heated in inert solvents, it is rapidly decomposed (e.g., after 15 min in toluene at 110°C). ^{31}P NMR is useful in monitoring this process; the signal at δ 36.2 disappears, and a new signal appears at δ 11.8. This is in the expected position for a polymer of Ph–PO_2 with P–O–P links, possibly a cyclic trimer, but it has not been further studied. Similarly, when **11** is irradiated at 254 nm in dioxane (conditions we have used for generation of metaphosphates from bridged systems [17]), it is decomposed after 2 h, again with formation of the material with δ 11.8. From both the thermal and photochemical reaction media, we





2 3 4 11

have isolated the dihydrophthalimide derivative **14**. When an alcohol (5.5 equiv) is included in the medium of thermolysis, the Ph–PO_2 polymer is not formed; instead, a phenylphosphonate from trapping of the intermediate **13** is the sole product. Several alcohols have been used in this process. We have proceeded to isolate three (**15a–c**) of these products as sodium salts and have further characterized them by ^1H and ^{13}C NMR. Data are provided in the Experimental Section.



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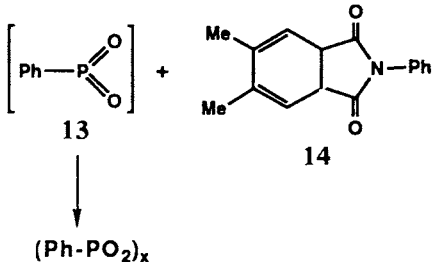
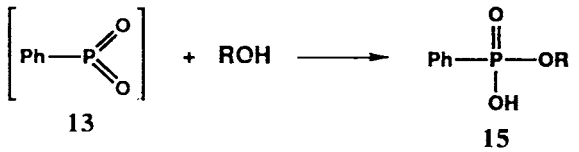


13 14 $(Ph\text{-}PO_2)_x$

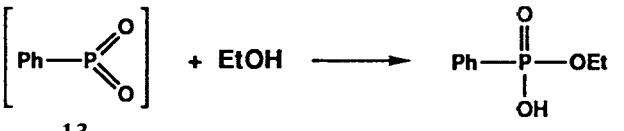
Similarly, when the photolysis is performed in the presence of an alcohol, intermediate **13** is trapped and the polymeric product is not formed. The only ^{31}P NMR signal in the product is that for the ester **16** (δ 20.5).



13 15

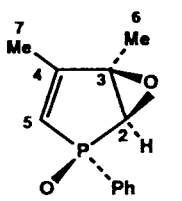
	R	δ ^{31}P ($CDCl_3$)	Na salt, δ ^{31}P (D_2O)
15a	t-BuMeCH	19.9	13.9
15b	n-C_7H_{15}	20.9	15.8
15c	cyclo-C_6H_{11}	17.4	14.7
15d	p-MeC_6H_4	18.1	15.8
15e	cholesteryl	20.8	13.5
15f	$PhCH_2$	21.7	18.5

Finally, we must consider if the species Ph–PO_2 is ever present in the reaction media in free form. Evidence has been accumulated that this is the case for alkyl metaphosphates when generated by these methods. Thus, from kinetic studies [18], it is known that the thermal reaction is first-order and its rate is not accelerated when the trapping alcohol is present, ruling out the possible alternative explanation of a P(V) intermediate product forming between the precursor and the alcohol that then decomposes to the phosphate. For metathiophosphates with a chiral alkyl substituent, it has been shown from the formation of two diastereomers in equal intensity that a planar (hence metaphosphate) intermediate is involved [19]. We therefore feel it is reasonable to assume that Ph–PO_2 is also a free species in the thermolysis and photolysis media, and as noted we interpret the reaction of electrophilic substitution on *N*-methylpyrrole [1] in this way. However, further explorations of this point would be desirable.

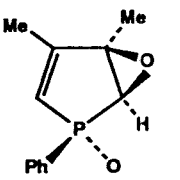


13 16

We have made the surprising discovery that one of the double bonds in 3,4-dimethyl-1-phenylphosphole oxide can be epoxidized with ease by *m*-chloroperbenzoic acid. The reaction takes place in refluxing chloroform and is best performed by starting with the phosphole and reacting it with excess (3 equiv) of the peracid. The product, which is of an unprecedented type, consists of two diastereoisomers (**17a** and **17b**) in the ratio 2:3. Separation of the mixture has not yet been successful, and all NMR data as well as the elemental analysis were performed on the crystalline mixture. Signals were adequately separated to allow full acquisiton of ^{31}P, ^{13}C, and ^1H NMR spectra for both isomers (Table



17a (δ ^{31}P 38.76)



17b (δ ^{31}P 38.37)

TABLE 1 Spectral Data for the Epoxide Isomers **17a, 17b**.

	$^{13}CNMR^a$		$^{1}HNMR^b$	
Position	**17a**[c]	**17b**[d]	**17a**	**17b**
2	55.24(100.0)	59.34(103.5)	3.28[33.3](2.5)	3.59[27.3](2.6)
3	63.51(14.3)	65.84(18.0)		
4	161.80(7.7)	162.30(7.5)		
5	120.67(100.5)	123.16(98.4)	5.77[22.2](2.5, 1.6)	5.90[22.5](1.52)
6	15.06—	15.71—	1.65[1.2]	1.69
7	17.73(15.4)	17.94(15.4)	2.143(1.71)	2.136(1.63)

[a] $^{13}C-^{31}P$ coupling constants (Hertz) are given in parentheses.
[b] $^{1}H-^{31}P$ coupling constants (Hertz) in square brackets; $^{1}H-^{1}H$ coupling constants are in parentheses.
[c] *ortho*-C 131.0(10.3); *meta*-C 128.9(12.1); *para*-C 132.6; *ipso* not observed.
[d] *ortho*-C 132.0(10.0); *meta*-C 128.3(12.2); *para*-C 132.5(2.6); *ipso* not observed.

1). The epoxide structure was revealed by the characteristic ^{13}C signals for two carbons bearing oxygen and by the single ^{1}H signal in the downfield region also associated with the attachment of oxygen. The best indicator for assignment of the structure of the diastereoisomers is probably provided by the phosphoryl oxgyen deshielding effect [20] on the adjacent proton (at C-2). The difference in shifts is 0.31 ppm. There are also significant differences (3–4 ppm) in the ^{13}C signals for ring carbons 2 and 3, but it is not as obvious why the isomers have these differences.

EXPERIMENTAL

General

FT ^{31}P NMR measurements were made with IBM NR-80 and Varian XL-300 spectrometers, using 85% H_3PO_4 as external standard. Downfield shifts are positive. FT ^{13}C and ^{1}H NMR spectra were obtained with Varian XL-200 and 300 spectrometers. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37950.

Synthesis of **4** *by Oxidation of Phosphole* **2** *in the Presence of* N*-Phenylmaleimide*

A stirred solution of 6.8 g (0.039 mol) of *N*-phenylmaleimide and 3.5 g (0.039 mol) of *tert*-butyl hydroperoxide in 200 mL of chloroform was cooled in an ice bath and treated dropwise with a solution of 6.0 g (0.032 mol) of 3,4-dimethyl-1-phenylphosphole (**2**) in 100 mL of chloroform. The solution was stirred at room temperature for 3 h and then evaporated to dryness on a rotary evaporator. The residue was recrystallized from methylene chloride–hexane (4:1) to give 10.6 g (88.5%) of **4**, mp 259–260°C; δ ^{31}P NMR ($CDCl_3$) 77.5; ^{13}C NMR, Table 2; ^{1}H NMR δ 1.65 (d, J = 1.65, 6H, H-b), 3.57 (apparent d of t, 2H, H-c), 4.15 (d, J_{PH} = 1.65, 2H, H-a), 7.1–7.7 (10H, ArH).

Anal. Calcd. for $C_{22}H_{20}O_3NP$: C, 70.02; H, 5.34; N, 3.71; P, 8.20. Found: C, 70.09; H, 5.16; N, 3.57; P, 8.34.

Synthesis of **5** *by Oxidation of Phosphole* **2** *in the Presence of Dimethyl Maleate*

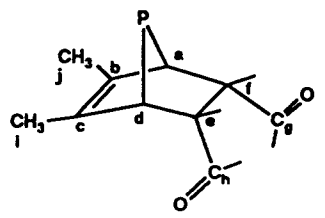
To a stirred solution of dimethyl maleate (77.8 g, 0.54 mol) and 3.6 g (0.040 mol) of *tert*-butyl hydroperoxide in 600 mL of chloroform in an ice bath was added 6.8 g (0.036 mol) of phosphole **2** in 800 mL of chloroform. The solution was stirred at room temperature for one week, and then evaporated to dryness on a rotary evaporator. The residue was chromatographed on a silica gel column with ethyl acetate as eluent. The eluate was evaporated to dryness, leaving a white solid that on recrystallization from chloroform–benzene gave 9.13 g (72.8%) of **5**, mp 161–162°C; δ ^{31}P NMR ($CDCl_3$) 66.8; ^{13}C NMR, Table 2; ^{1}H NMR 1.68 (d, J = 1.8 , 6H, H-b), 3.22 (apparent d of t, 2H, H-c), 3.67 (s, OCH_3), 4.09 (t, J_{PH} = J_{HH} = 1.3, 2H, H-a), 7.3–7.7 (5H, ArH).

Anal. Calcd. for $C_{18}H_{21}O_5P$: C, 62.07; H, 6.08; P, 8.89. Found: C, 61.90; H, 6.00; P, 8.67.

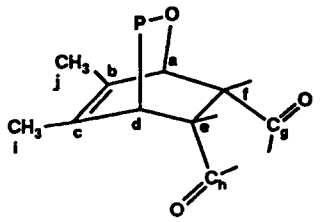
Synthesis of 3,4-Dimethyl-1-phenylphosphole-1-oxide (**3**)

A solution of 0.1 g (0.533 mmol) of phosphole **2** in 1 mL of $CDCl_3$ was cooled in an ice bath and treated dropwise with 0.1 g (1.114 mmol) of *tert*-butyl hydroperoxide. The ^{31}P NMR spectrum was recorded immediately after the addition was complete; all phosphole had been oxidized and the only signal appeared at δ 42.3. The ^{1}H and ^{13}C NMR spectra were also taken on a fresh solution; ^{1}H ($CDCl_3$) δ 2.05 (s, CH_3), 5.95 (d, J_{PH} = 26.9 Hz, CH); ^{13}C ($CDCl_3$) δ 17.4 (J_{PC} = 18.6 Hz, CH_3), 121.5 (J_{PC} = 100.0, C-2), 155.2 (J_{PC} = 21.7, C-3). The solution of **3** was stable at room temperature for a few hours but then noticeable amounts of the dimer of **3** began to form. After 6 days, the dimerization was complete. The ^{31}P signals for the dimer appeared at δ 74.3 and 53.6, $^{3}J_{PP}$ = 38.8 Hz. Attempts to isolate phosphole

TABLE 2 ^{13}C NMR Spectral Data of Bridged Compounds[a]



4, 5, 8, 9, 10



11

Position	4	5	8	9	10[c]	11
a	47.9(64.3)	48.6(63.5)	49.2(14.4)	52.4(10.1)	—[d]	78.5(8.2)
b	131.2(9.5)	131.1(8.8)	—[b]	—[b]	—[d]	—[b]
c	131.2(9.5)	131.1(8.8)	—[b]	—[b]	—[d]	—[b]
d	47.9(64.3)	48.6(63.5)	49.2(14.4)	52.4(10.1)	—[d]	41.8(79.7)
e	44.8(13.7)	45.6(13.2)	46.0(29.8)	48.7(2.6)	—[d]	36.7(6.6)
f	44.8(13.7)	45.6(13.2)	46.0(29.8)	48.7(2.6)	—[d]	46.7(11.6)
g	175.3(15.9)	171.6(17.1)	177.5(37.8)	176.4(16.3)	175.7(5.4)	173.2(0)
h	175.3(15.9)	171.6(17.1)	177.5(37.8)	176.5(16.3)	175.7(5.4)	175.7(15.5)
i	15.3(3.9)	15.5(3.5)	—[b]	—[b]	14.1(0)	16.4(1.8)
j	15.3(3.9)	15.5(3.5)	—[b]	—[b]	14.1(0)	17.9(0)

[a] $CDCl_3$ solutions. ^{13}C–^{31}P coupling constants (Hertz) are given in parentheses.
[b] Signal overlap prevented assignments.
[c] Mixed with isomer **4**.
[d] Unresolved from isomer **4** signals.

oxide **3** by evaporating the chloroform solution to dryness gave a residue that on dissolution in $CDCl_3$ proved to be only the dimer. Addition of *N*-phenylmaleimide or dimethyl maleate in chloroform solutions caused removal of the ^{31}P NMR signal for **3** and formation of the respective adducts **4** and **5**.

Deoxygenation of Phosphine Oxide **4** *to Form Phosphine* **8**

A solution of 0.359 g (2.65 mmol) of trichlorosilane in 50 mL of dry benzene was mixed with a solution of 0.628 g (7.93 mmol) of pyridine in 10 mL of benzene, followed by a solution of 0.2 g (0.53 mmol) of phosphine oxide **4** in 5 mL of benzene. The vessel was flushed with nitrogen and the mixture refluxed for 2 h. It was then chilled in an ice bath and treated slowly with 30 mL of 30% NaOH. The mixture was stirred for 15 min, and the layers were then separated. The water layer was washed with two 30-mL portions of benzene. The combined benzene layers were dried ($MgSO_4$) and evaporated to leave a clear oily residue of **8** (0.162 g, 84.8%; ^{31}P NMR δ 126.4; ^{13}C NMR, Table 2; ^1H NMR δ 1.57 (s, 6H, H-b), 3.41 (d, J_{PH} = 12, 2H, H-c), 3.95 (d, J = 1.1, 2H, H-a), 7.01–7.48 (10H, ArH).

Isomerization of Phosphine **8** *to* **9**

A sample of neat **8** was allowed to stand for 12 days at room temperature. It was then dissolved in $CDCl_3$ and found to have completely isomerized to form a different phosphine (**9**) with δ ^{31}P NMR 47.5 ($CDCl_3$); ^{13}C NMR spectral data Table 2 (confirming the anti structure); ^1H NMR δ 1.89 (s, 6H, H-b), 3.49 (d, J = 2.8, 2H, H-c), 3.78 (d, J_{PH} = 1.0, 2H, H-a), 6.98–7.50 (10H, ArH).

Oxidation of Phosphine **9** *to Phosphine Oxide* **10**

To a stirred solution of 0.162 (0.45 mmol) of phosphine **9** in 20 mL of dry chloroform in an ice bath was added dropwise a solution of 0.0477 g (0.53 mmol) of *tert*-butyl hydroperoxide in 5 mL of dry $CHCl_3$. The ^{31}P NMR spectrum indicated that complete oxidation to form phosphine oxide **10** had occurred; δ ^{31}P 81.4; ^1H NMR δ 1.46 (s, 6H, H-b), 3.23 (d, J = 0.8, 2H, H-c), 3.73 (d, J = 1.24, 2H, H-a), 7.01–7.83 (10H, ArH).

*Synthesis of 5,6-Dimethyl-3-phenyl-2,3-oxaphosphabicyclo[2.2.2]oct-5-ene-*N*-phenyl-7,8-dicarboximide-3-oxide* (**11**)

A mixture of 2.0 g (0.0053 mol) of phosphine oxide **4** and 1.8 g (0.0106 mol) of *m*-chloroperbenzoic acid was stirred for 2 h at room temperature. The ^{31}P NMR spectrum showed that all of the starting oxide had been converted to the product **11**. The remaining perbenzoic acid and its reduction product *m*-chlorobenzoic acid were removed from the solution by complexation on the surface of solid anhydrous KF (3.6 g). After a 4-h stirring period, the mixture

was filtered and the filtrate was evaporated under reduced pressure almost to dryness. The residual material was placed in the refrigerator; the crystals of **11** that formed after 20 h were removed by filtration (1.45 g, 69.7%); mp 124.5–127°C; ^{31}P NMR δ 3.62; ^{13}C NMR spectrum, Table 2; ^{1}H NMR ($CDCl_3$) δ 1.47 (s, CH_3-b), 1.88 (m, CH_3-c), 3.48 (d of d, J_{PH} = 7.5, J_{HH} = 2.7, H-d), 3.99 (d of d, J_{PH} = 7.4, J_{HH} = 2.8, H-e), 4.3 (d of d, J_{PH} = 8.0 Hz), J_{HH} = 4.2 Hz, H-f), 5.32 (d of d, J_{PH} = 22, J_{HH} = 4.0, H-a), 7.0–7.6 (10H, ArH). The compound could not be adequately purified by crystallization for elemental analysis.

One-Flask Conversion of Phosphole **2** *to Phosphonate* **11**

A solution of 3.4 g (0.0197 mol) of *N*-phenylmaleimide and 8.8 g (0.0512 mol) of *m*-chloroperbenzoic acid in 280 mL of dry chloroform in an ice bath was treated dropwise with a solution of 3.6 g (0.0191 mol) of phosphole **2** in 125 mL of chloroform. The solution was stirred for 5 h in the ice bath, and then 24 g of solid KF was added to complex the benzoic acids. The mixture was stirred for 3 h and then filtered through Celite. Concentration of the filtrate on a rotary evaporator gave 13.22 g of oily residue. This was recrystallized from chloroform–hexane (4:1) to give 6.31 g (83.9%) of phosphonate **11**, having the same mp (124.5–127°C) and ^{31}P NMR shift (δ 36.2) as found for the product from O-insertion into phosphine oxide **4**. The ^{1}H and ^{13}C NMR spectra were also identical for the two samples.

Thermal Fragmentation of Phosphonate **11**

A suspension of 0.07 g of phosphonate **11** in 1.5 mL of dry toluene was stirred in a closed tube for 15 min at 110°C. During this time, solids dissolved to give a clear solution. The ^{31}P NMR spectrum was recorded for this solution; all starting **11** had been destroyed, and the only signal appeared at δ 11.8 as a sharp line. This may be attributed to a cyclic trimer from $PhPO_2$.

Thermal Fragmentation of Phosphonate **11** *in the Presence of Alcohols*

The following procedure is illustrative of that applied to the use of alcohols as trapping agents for $PhPO_2$ generated thermally from **11**. A solution of 0.189 g (0.48 mmol) of **11** and pinacolyl alcohol (0.271 g, 2.65 mmol) in 10 mL of dry toluene was heated at 100°C for 1 h in a closed tube filled with nitrogen. Analysis by ^{31}P NMR showed that all **11** had been destroyed, and the only signal was due to the pinacolyl ester of phenylphosphonic acid (**15a**), δ ^{31}P 19.9 ($CDCl_3$). To isolate this product, the solution was treated with 0.139 g (1.07 mmol) of *N,N*-diisopropylethylamine to form the salt. The mixture was shaken well and then evaporated to dryness in vacuo at room temperature. The residue was taken up in ether and a small amount of precipitate was filtered off. The solution was extracted 3 times with 5 mL each of water. The water extracts were combined and evaporated to dryness. The amine salt was converted to the sodium salt by ion-exchange on the Na^+ form of Bio-Rad AG 50WX8. Evaporation of the water left 0.108 g (84.6%) of the sodium salt of half-ester **15a**; ^{31}P NMR (D_2O) δ 13.9; ^{13}C NMR 16.7 ($\underline{C}H_3CH$), 25.5 ($\underline{C}H_3CMe_2$), 34.2 (J = 6.5 Hz, $\underline{C}Me_3$), 79.7 (J = 6.0 Hz, CH–O), 128–135 (Ar); ^{1}H NMR 0.63 (s, $(\underline{H}_3C)_3C$), 0.88 (d, J = 6.4 Hz, $\underline{H}_3C$–CH), 3.80 (H–C, t, $^{3}J_{HH}$ = 6.4 Hz), 7.5–7.6 (Ar-H).

From the use of *n*-heptyl alcohol as a trapping agent was obtained phosphonate **15b** with δ ^{31}P 20.9 ($CDCl_3$). Isolation as the sodium salt gave a product with δ ^{31}P 15.8 in 76.4% yield; ^{1}H NMR δ 0.6 (t, J = 8.0 Hz, CH_3), 1.22 (M, $-C\underline{H}_2CH_2O-$), 0.92 (m, 8H for CH_2), 3.5 (m, $-CH_2O-$); ^{13}C NMR δ 13.5 (C-7), 22.1 (C-6), 24.9 (C-3), 28.1 (C-4), 29.9 (C-2), 31.1 (C-5), 65.2 (J = 5.5 Hz, C-1), 128–131 (Ar).

From cyclohexyl alcohol was obtained phosphonate **15c** with ^{31}P NMR δ 17.4 ($CDCl_3$). Isolation as the sodium salt gave 72.5% of product with ^{31}P NMR (D_2O) 14.7; ^{1}H NMR δ 0.92–1.75 (m, 10H, overlapping), 3.8 (m, 1H, CHO), 7.3–7.7 (ArH); ^{13}C NMR δ 24.0 (C-3), 25.0 (C-4), 33.8 (J = 8.3 Hz, C-2), 74.9 (J = 6.9 Hz, C-1), 128.5 (J = 14.3 Hz, *meta*-C), 131.1 (J = 11.2 Hz, *ortho*-C), 134.3 (J = 178.6 Hz, *ipso*-C), *para*-C not clearly observed.

Fragmentation of **11** *by Photolysis*

A solution of compound **11** (50 mg, 0.86 mmol) in 50 mL of dry dioxane containing 39 mg (0.86 mmol) of ethanol in a nitrogen atmosphere was irradiated for 2 h at 254 nm using a Hanovia medium-pressure lamp. The reactor (quartz) was cooled with water and the solution stirred magnetically. The ^{31}P NMR spectrum on a sample after concentration showed that all **11** had been decomposed; the only signal (δ 20.5) was attributed to monoethyl phenylphosphonate (**16**).

Synthesis of 4,5-Dimethyl-2-phenyl-6-oxa-2-phosphabicyclo[3.1.0]hex-3-ene-1-oxide (**17a, 17b**)

A solution of 2.7 g (0.0144 mol) of 3,4-dimethyl-1-phenylphosphole in 210 mL of $CHCl_3$ was treated with 8.25 g (0.0477 mol) of *m*-chloroperbenzoic acid, and the mixture refluxed for 3 h. It was stirred vigorously for 2 h with a solution of 10.9 g (0.13 mol) of $NaHCO_3$ in 110 mL of water. The organic layer was then separated and extracted with 100 mL of water. It was dried ($MgSO_4$) and concentrated to leave 4.7 g of a greenish oil that was mixed with 4 g (0.0690 mol) of solid KF in 100 mL of CH_2Cl_2

and stirred for 3 h. The solid was filtered through Celite. Concentration of the filtrate gave 3.5 g of a yellowish oil. Recrystallization with toluene-hexane gave 0.95 g of **17a, 17b**. The mother liquid was concentrated and then chromatographed on silica gel with $CHCl_3$ and 3% methanol in chloroform. Concentration of the eluent by rotoevaporation gave an additional 1.12 g of yellowish oil. Crystallization of this oil with toluene-hexane gave 0.34 g of very pure, white product. The total yield in the synthesis was 40.8%; mp 123–124°C; ^{31}P NMR ($CHCl_3$ with D_2O lock), δ 38.76 (**17a**), 38.37 (**17b**), ratio 2:3.

Anal. Calcd. for $C_{12}H_{13}O_2P$: C, 65.45; H, 5.95. Found: C, 65.20; H, 5.90.

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