17.0 (CH_3), 0.16 (CH_3); MS, *m/e* 184 (M^+), 169, 75, 73 (base), M^+ found 184.1280, $C_{10}H_{20}OSi$ requires 184.1283; IR ν_{max} (neat) 3100 (w), 2950 (s), 1620 (s), 1300 (s), 1250 (s), 1225 (s), 1130 (m), 1100 (s), 1010 (s), 840 (s), 745 (m).

For **4f**: ^1H NMR (100 MHz, $CDCl_3$) 4.76 (1 H, d, J = 4 Hz), 2.6–1.8 (4 H, m), 1.92 (3 H, s), 1.65 (3 H, s), 1.35–1.1 (1 H, m), 0.92 (3 H, d, J = 7 Hz), 0.11 (9 H, s); MS, *m/e* (relative intensity) 224 (M^+, 23), 209 (100), 75 (9), 73 (24), M^+ found 224.1584, $C_{13}H_{24}OSi$ requires 224.1596.

Procedure C was performed for the ketones **1a** and **1b** using a method derived from that described by Danishefsky.[19]

Procedure C. In a dried flask was placed $ZnCl_2$ (anhydrous, 0.026 g) and Et_3N (2.0 mL). The mixture was stirred under a dry nitrogen atmosphere for 1 h before 3-penten-2-one, **1b**, (0.517 g) in C_6H_6 (1 mL) was added followed by $ClSiMe_3$ (1.60 mL). The mixture was stirred for 2 h and then heated in an oil bath maintained at a temperature of 80 °C for 9 h. The cooled reaction mixture was filtered through a plug of glass wool into a dropping funnel and worked up as described under procedure B to give a mixture of **2b**, **3b**, and **4b** in the ratio 9:7:84 as determined by ^1H NMR. The reaction was performed similarly for ketone **1a**, except that the mixture was not heated, to give **2a**, **3a**, and **4a** in the ratio 14:1:85.

Procedure D was performed on ketone **1d** only.

Procedure D. In a dried flask, under an atmosphere of dry nitrogen, were placed dry THF (4 mL) and a crystal of 2,2'-bipyridyl indicator. The solution was cooled in an ice bath and diisopropylamine (0.62 mL) was added followed by a hexane solution of butyllithium (5.5 mL of a 0.73 M solution). After 5 min, 3,5-dimethyl-3-penten-2-one, **1d**, (0.54 mL) in dry THF (2 mL) was added dropwise to the well-stirred purple solution. Excess $ClSiMe_3$ (2.0 mL) was then added to the reaction mixture, and after 30 min of further stirring the reaction mixture was worked up as described for procedure B to give 1.24 g of a yellow oil. The GC of the product indicated that the yield was in excess of 90%. A sample of the product was purified by preparative GC to give **4d** identical with a sample prepared by procedure C.

***E–Z* Isomerization of Siloxy Dienes. *E–Z* Isomerization of 2c.** The siloxy diene **2c** (0.12 g) was dissolved in benzene (10 mL) in a quartz tube and irradiated with a low pressure mercury lamp (254-nm light). The reaction was followed by GC and after 2 h approximately half of **2c** had been converted to the geometrical isomer **3c**. The benzene was evaporated and the residue purified by GC to give a mixture of **2c** and **3c**. The ^1H NMR of the mixture in C_6D_6 indicated similar quantities of **2c** and **3c**. For **3c**: ^1H NMR (C_6D_6) 6.69 (1 H, X of ABX, J = 17, 11 Hz), 5.11, 4.97 (2 H, AB of ABX, J = 17, 11, 1.5 Hz), 1.86 (3 H, s), 1.75 (3 H, s), 0.07 (9 H, s).

***E–Z* Isomerization of 2b.** The siloxy diene **2b** (0.0112 g) was dissolved in C_6D_6 (ca. $^1/_3$ mL) in a quartz NMR tube containing biphenyl (0.1105 g) and the tube was suspended adjacent to a low pressure mercury lamp. Under these conditions the lamp emits mainly at 254 nm and the biphenyl absorbs all the light. The progress of the reaction was followed by ^1H NMR which indicated that after 4 h **2b** and **3b** were present in the ratio 9:8. The mixture of isomers was stable in the absence of light (i.e., their ratio remained unchanged) over a period of 380 h at room temperature and they survived preparative GC at 80 °C. For **2c**: ^1H NMR (200 MHz, C_6D_6) 6.40 (1 H, ddd, J = 17.3, 10.9, 10.3 Hz), 6.67 (1 H, double sextuplet, J = 10.9, 0.7), 5.08 (1 H, dd, J = 17.3, 2.2 Hz), 4.90 (1 H, double doublet of sextuplets, J = 10.3, 2.2, 0.7 Hz), 1.75 (3 H, t, J = 0.7 Hz).

***E–Z* Isomerization of (*E*)-4b.** The (*E*)-siloxy diene **4b** (0.0195 g) was dissolved in C_6D_6 (ca. $^1/_3$ mL) in a quartz NMR tube and irradiated with a low pressure mercury lamp for 5 h as described for **2b**. In this reaction the solvent served as the sensitiser. The 200-MHz ^1H NMR spectrum of the mixture of (*E*)- and (*Z*)-**4b** indicated that they were present in the ratio 70:30, respectively. The mixture of *E* and *Z* isomers was stable (i.e., their ratio remained unchanged) over a period of 22 h at 80 °C (the NMR tube was suspended in the vapors of boiling benzene and the ^1H NMR spectrum rerecorded). For (*Z*)-**4b**: ^1H NMR (200 MHz, $CDCl_3$) 6.25 (1 H, dq, J = 16, 7 Hz), 5.80 (1 H, dq, J = 16, 1.5 Hz), 4.29 (1 H, s), 4.23 (1 H, s), 1.29 (3 H, dd, J = 7, 1.5 Hz).

Registry No. **1a**, 141-79-7; **1b**, 78-94-4; **1c**, 1567-73-3; **1d**, 684-94-6; **1e**, 22573-24-6; **1f**, 15932-80-6; **2a**, 76915-32-7; **2b**, 103322-97-0; **2c**, 103322-98-1; **2d**, 103322-99-2; **2e**, 103323-00-8; **2f**, 76430-27-8; **3a**, 99884-75-0; **3b**, 103323-05-3; **3c**, 103323-01-9; **3e**, 103323-02-0; **4a**, 6651-46-3; (*E*)-**4b**, 81802-34-8; (*Z*)-**4b**, 103323-06-4; (*E*)-**4c**, 103323-03-1; **4d**, 103323-04-2; **4f**, 58898-35-4; 8, 81459-09-8.

Synthesis of Phosphinamides in the 5,6-Oxaphosphabicyclo[2.2.2]octene Series as Possible Precursors of Metaphosphoramidates[1]

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The readily dimerizable 1-aminophosphole oxides were found to function as dienes in the Diels–Alder reaction with *N*-phenylmaleimide, thereby providing phosphinamides with the 7-phosphanorbornene structure. The dimers also possess this structural feature, which has been subjected to the oxygen-insertion reaction with *m*-chloroperbenzoic acid. The Diels–Alder adducts react cleanly to provide the insertion product at the P–C bond, providing the 5,6-oxaphosphabicyclo[2.2.2]octene ring system; the dimers undergo reaction first at the phosphinamide nitrogen of the 2-phospholene ring and then at the 7-phosphanorbornene P–C bond. Stereochemical features of an aminophosphole oxide dimer and of the O-insertion product of a Diels–Alder adduct were unequivocally established by X-ray crystal structure analyses. The O-insertion occurred with retention of the configuration at phosphorus. ^{31}P and ^{13}C NMR spectra were also of value in structure assignments. The 5,6-oxaphosphabicyclo[2.2.2]octene prepared from the Diels–Alder adduct was completely decomposed by loss of the bridging phosphorus on heating in toluene at 100 °C for 30 h. On the assumption that the fragment may be a metaphosphoramidate, trapping experiments with cyclohexanol and benzylamine were attempted. Only the latter gave a phosphorylation product, but since it greatly increased the rate of phosphorus debridging, it must be directly involved in a process that causes the ejection of the bridge. Intermediates in this process were detected by ^{31}P NMR.

Ring strain in the 7-phosphanorbornene (7-PNB) system is of such magnitude that special chemical properties, not found in simpler systems, can arise. Among these properties is the insertion of oxygen by peracids into a C–P bond, a process reminiscent of the Baeyer–Villiger reaction with ketones. This reaction was first demonstrated with phosphine oxides[2,3] in the 7-PNB system and then with

(1) Supported by a grant from the Army Research Office.

(2) Kashman, V.; Awerbouch, O. *Tetrahedron Lett.* **1975**, *31*, 53.

0022-3263/86/1951-3341$01.50/0

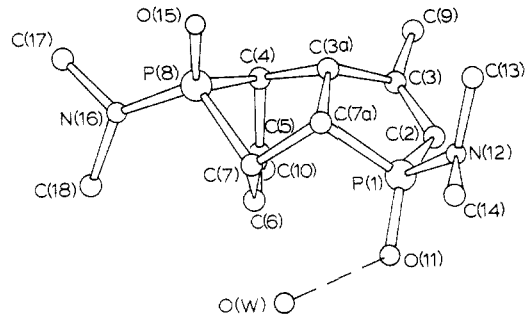
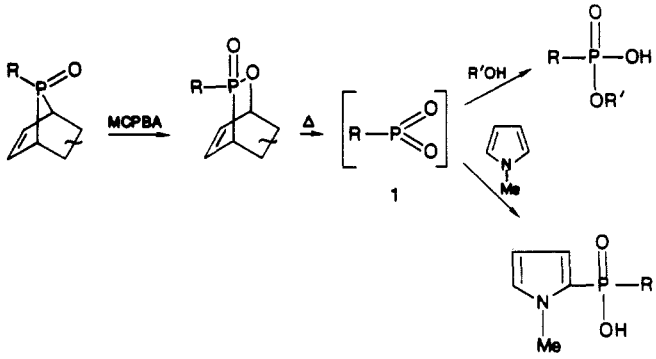
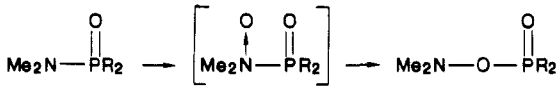


Figure 1. Structure and solid-state conformation of **3a** in crystals of the monohydrate; hydrogen atoms have been omitted for clarity.

phosphinates.[4] The ring-expanded products proved of value as precursors on thermolysis of the highly reactive metaphosphate 1 (R = MeO) species, which can be detected by trapping reactions with alcohols, amines, and *N*-methylpyrrole. It is presumed that the thermolysis proceeds by a retro[4 + 2]cycloaddition, since the other product from the elimination of RPO_2 is a diene.

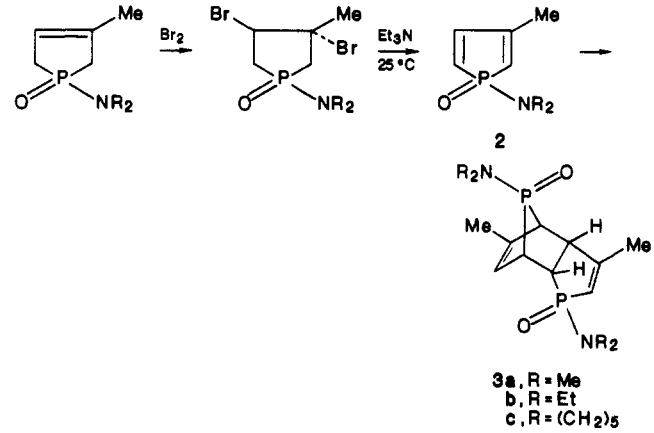


In principle, phosphinamides in the 7-PNB series could undergo the O-insertion process and then serve as precursors of the metaphosphoramidate species, R_2NPO_2. However, a competing reaction is known for phosphorus amides with peracids, namely, N-oxidation and rearrangement with O-insertion into the P–N bond[5], followed by further reactions. Nevertheless, since the R_2NPO_2



species has been included in research on low-coordination derivatives of phosphorus,[6] an investigation of the peracid reaction with phosphinamides of the 7-PNB ring system has been conducted. In this paper, it will be shown that O-insertion into a C–P bond can indeed predominate over N-oxidation and rearrangement and that the products do undergo elimination of the bridging phosphorus atom on thermolysis. The mechanism of this elimination has received attention.

Synthesis and Characterization of Phosphinamides. Two different types of compounds with the 7-PNB skeleton were prepared for this study, the dimers **3** of phosphole oxides **2** and Diels–Alder adducts **4** of phosphole oxides with *N*-phenylmaleimide. Both processes start with 1-amino-3-phospholene oxides, prepared as earlier described,[7] which serve as precursors of the highly reactive phosphole oxide system by bromine addition followed by dehydrohalogenation. This procedure is



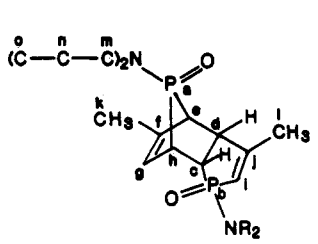
useful also for phosphinates.[4,8] In the absence of a trapping agent, dimerization occurs to give a readily isolated, crystalline product. On occasion, when monitoring the course of the reaction with ^{31}P NMR spectroscopy, signals have been observed in the region where the monomeric phosphole oxide should absorb (e.g., δ +39.4 for **2**). These signals soon disappear, and no attempts at preserving this species have been made. The yields of the dimers from the dibromo derivatives fall in the range 65–73%.

The dimeric character of the products is immediately recognizable from their ^{31}P NMR spectra, which possess two doublets with a large $^3J_{PP}$ value (41.5 Hz) such as is observed for the related phosphine oxides[9] and phosphinates.[4] The bridging phosphorus experiences a significant deshielding effect (e.g., δ +82.0 in **3a**) in all of these derivatives, and its signal is easily distinguished from that of the 2-phospholene moiety (e.g., **3a**, δ +63.0). The ^{13}C NMR spectra of the dimers are recorded in Table I. The magnitude (9.9 Hz) of the three-bond ^{31}P–^{13}C coupling of the bridging P to C_3 of the 2-phospholene ring (C_j in Table I) is indicative of endo fusion of the rings, by analogy to dimers with the tertiary phosphine oxide function.[9] With exo fusion, a dihedral angle close to that giving minimal coupling would be present. Dimers of phosphole sulfides illustrate this effect: endo,[9] $^3J_{PC}$ = 9.8 Hz; exo,[10] $^3J_{PC} \sim$ 0 Hz. However, neither the ^{13}C NMR spectra nor the ^1H NMR spectra[11] of the amides provide the details needed to establish the complete stereochemistry at the two phosphorus centers, although structure **3** expresses the most likely stereochemical assignment based on related systems.[8,9]

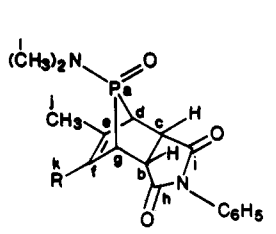
Because of the importance of stereochemistry in this program, these assignments were placed on a firm basis via a single-crystal X-ray analysis of **3a** in crystals of its monohydrate. The crystal structure was solved by the heavy-atom approach. Full-matrix least-squares refinement of atomic parameters[12] converged to R = 0.045[13] over

(3) Quin, L. D.; Kisalus, J. C.; Mesch, K. A. *J. Org. Chem.* **1983**, *48*, 4466.
(4) Quin, L. D.; Marsi, B. G. *J. Am. Chem. Soc.* **1985**, *107*, 3389.
(5) Holden, I.; Segall, Y.; Kimmel, E. C.; Casida, J. E. *Tetrahedron Lett.* **1982**, *23*, 5107.
(6) Regitz, M. *Methoden der Organischen Chemie (Houben-Weyl)*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1982; Band E1, pp 583–615.
(7) Szewczyk, J.; Lloyd, J. R.; Quin, L. D. *Phosphorus Sulfur* **1984**, *21*, 155.
(8) Usher, D. A.; Westheimer, F. H. *J. Am. Chem. Soc.* **1964**, *86*, 4732.
(9) Quin, L. D.; Mesch, K. A.; Bodalski, R.; Pietrusiewicz, K. M. *Org. Magn. Reson.* **1982**, *20*, 83.
(10) Synthesis: Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809. *Selected ^{13}C Nuclear Magnetic Resonance Spectral Data*; Thermodynamics Research Center, Texas A&M University: College Station, TX, 1982; Supplementary Volume G-12, ^{13}C NMR Spectrum 805.
(11) We have found these spectra to have little structural value, and therefore they are not reported in this paper.

Table I. ^{13}C NMR and ^{31}P NMR Spectra[a]



3a-c



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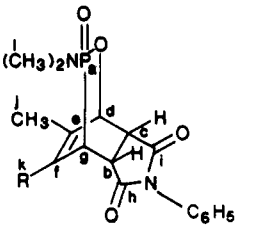


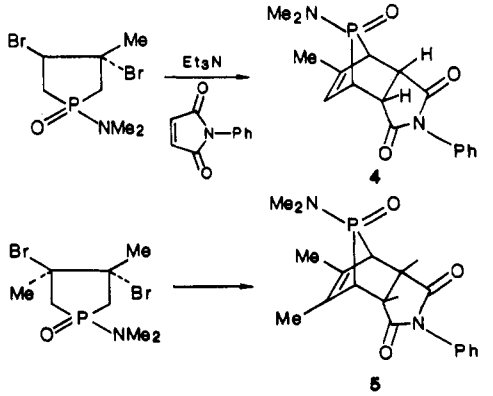
6,7

	^{31}P NMR			^{13}C NMR, C													
compd	δP_a	δP_b	J_{PP}	b	c	d	e	f	g	h	i	j	k	l	m	n	o
3a	64.8	83.0	41.5														
δ					36.1	50.8	45.8	134.8	124.6	40.6	123.2	160.7	19.3	19.2	38.73		
J_{CP_b}					91.2	15.4	0	0	6.6	2.2	118.6	28.6	0	18.7	0		
J_{CP_a}					13.2	15.4	80.2	9.9	5.5	74.7	5.5	9.9	4.4	0	0		
3b	62.0	82.5	41.5														
δ					38.7	51.3	46.4	134.8	125.3	41.1	124.5	160.5	19.2	18.9	41.4	13.5	
J_{CP_b}					92.8	15.3	0	0	6.7	2.2	117.2	28.1	0	18.4			
J_{CP_a}					13.4	15.3	81.8	9.9	4.3	75.7	4.9	9.8	4.4	0	1.2	2.2	
3c	61.4	80.6	41.5														
δ					37.0	50.8	45.8	134.0	124.6	40.3	123.5	160.0	19.4	19.1	47.2	25.7	23.7
J_{CP_b}					92.3	15.5	0	0	6.6	2.0	116.5	27.5	0	17.6	0	0	0
J_{CP_a}					12.1	15.5	80.2	9.9	4.4	72.5	4.4	10.1	4.4	0	0	4.4	0
4	82.7																
δ				43.3	44.5	45.17	140.2	121.4	42.3	175.4	175.0	19.3		38.7			
J_{CP}				15.9	17.1	79.2	9.8	6.1	79.4	15.9	14.6	3.6		0			
5	76.9																
δ				44.2	44.2	46.3	130.5	130.5	46.3	175.1	175.1	15.0	15.0	38.2			
J_{CP}				16.5	16.5	80.2	7.7	7.7	80.2	15.4	15.4	5.5	5.5	0			
6	25.0																
δ				46.0	39.0	76.7	141.1	124.0	35.0	175.3	173.0	19.5		37.6			
J_{CP}				11.9	6.6	7.7	11.0	9.9	111.3	18.7	0	2.2		4.4			
7	25.0																
δ				46.5	68.9	78.3	133.2	131.4	40.2	175.2	173.0	15.8	17.7	37.4			
J_{CP}				12.1	6.6	7.7	11.0	9.9	111.0	17.6	0	3.3	4.4	4.4			

[a] All J in hertz.

1076 reflections. A view of the structure and solid-state conformation is provided in Figure 1. The crystals comprise **3a** molecules linked by P=O···O(W) hydrogen bonds.[14] Elongation of C–C single bonds between trisubstituted carbon centers, similar to those found[15] in dimers of 1-phenyl-3-methylphosphole and of its oxide, occurs in the 7-PNB unit of **3a**. Other bond lengths are in accord with expected values. In this unit, the C_4–P_8–C_7 bond angle is highly contracted at 82.3 (3)° and is not significantly different from the corresponding angle of 83.0 (1)° in the phosphole oxide dimer.[15] The geometry around each of the nitrogen centers differs somewhat according to the local environment. Thus, N_{16} on the 7-PNB phosphorus lies close (Δ = 0.039 Å) to the P_8,C_{17},C_{18} plane and has an approximately trigonal planar bonding geometry. Nonbonded interactions associated with an approximately eclipsing arrangement about the P_8–N_{16} bond (torsion angle C_7–P_8–N_{16}–C_{18} = −3.5°) are accommodated by a significant increase in the P_8–N_{16}–C_{18} bond angle [127.7 (6)° vs. 119.3 (7)° for P_8–N_{16}–C_{17}]. In contrast, N_{12} is displaced by 0.229 Å from the P_1,C_{13},C_{14} plane, and thus the bonding geometry is distorted from trigonal planar toward pyramidal. There are no severe eclipsing interactions involving the N_{12}-methyl groups in the conformation adopted around the P_1–N_{12} bond and consequently the P_1–N_{12}–C_{13} and P_1–N_{12}–C_{14} bond angles are essentially equal [119.0 (5)°; 120.1 (5)°]. The differences in the two *N*-methyl groups at the 7-PNB position vanish when **3a** is placed in solution; both the ^{13}C and the ^1H NMR spectra show a single signal for these methyls.

When the monomeric 1-aminophosphole oxides are generated under the same conditions but in the presence of the dienophile *N*-phenylmaleimide, the dimerization process is retarded and a single Diels–Alder cycloadduct is obtained. The adducts **4** and **5** are crystalline solids, and are formed in yields of 65% and 54%, respectively. ^{13}C NMR spectra are recorded in Table I. That the orienta-



(12) Supplementary material; see the paragraph at the end of the paper.

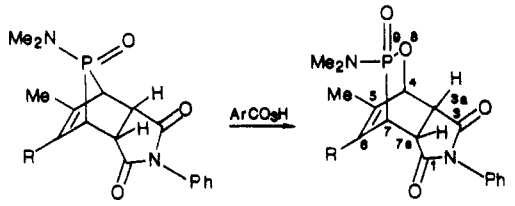
(13) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(14) Hydrogen-bonded distances follow: O(11)···(O(W) 2.957 (8) Å, O(W)···O(15) 2.837 (6) Å.

(15) Bond lengths (Å) in **3a** follow: C_{3a}–C_4 = 1.562 (7), C_{3a}–C_{7a} = 1.548 (10), C_7–C_{7a} = 1.554 (8). Corresponding distances (Å) in the dimer of *O*-phenyl-3-methylphosphole oxide[15] are 1.565 (3), 1.559 (3), and 1.564 (3), while in the *dimer* of 1-phenyl-3-methylphosphole[15] they are 1.562 (5), 1.551 (4), and 1.558 (4). McPhail, A. T.; Mesch, K. A.; Quin, L. D., unpublished results.

tion of the amino substituents on phosphorus may be the same as established for the dimers is suggested by similarities in their spectra. The endo ring fusion was indicated by the size[9] of the $^3J_{PC}$ value to the carbonyl carbons (15.4 Hz).

Oxygen-Insertion into Phosphinamides. The Diels–Alder adducts **4** and **5** were subjected to the reaction with MCPBA under conditions used for phosphinates.[4] ^{31}P NMR was used to monitor the course of the reactions, since a substantial upfield shift would occur on ring expansion to the bicyclo[2.2.2]octene framework in the O-insertion product, a cyclic phosphonamide. With adduct **4**, the ^{31}P shift changed from δ +82.7 to +25.0, while for **5** the shifts were δ +76.9 and +25.0. After 2 days, no starting material remained, and the products were then isolated as crystalline solids. The ^{31}P shifts alone confirm that the peracid had not attacked the nitrogen atom, since this would not lead to a change in the 7-PNB framework and no strong upfield shift would result. The upfield ^{31}P signals are similar to those found on O-insertion into 7-PNB phosphinates.[4] The ^{13}C NMR spectra (Table I) confirmed the structure, since they possessed ring carbon signals appropriately downfield from an oxygen substituent (**6**, δ 76.7; **7**, δ 78.3). In the case of O-insertion into **5**, there is no uncertainty about the identity of the carbon being attacked, but **4** has two possible sites for attack. Analysis of the reaction product just after completion showed the presence of isomeric products, but one was lost in the workup. The NMR spectra alone are not adequate for determining the structure of this isomer. A single-crystal X-ray analysis of the product was therefore performed. The results showed that in this isomer the oxygen had attacked ring carbon 4 to form product **6**. Solution of the



4, R = H
5, R = Me

6, R = H
7, R = Me

crystal structure of **6** was effected by direct methods.[16] Full-matrix least-squares adjustment of atomic parameters[12] converged to $R = 0.045$[13] over 2609 reflections. The structure and solid-state conformation of **6** are illustrated in Figure 2. Bond lengths are generally close to expected values, but strain is still evident in the rather long C_7–C_{7a} bond [1.560 (2) Å]. The phosphonamide nitrogen atom, N_{14}, is only 0.050 Å out of the P_9,C_{15},C_{16} plane, and thus its bonding geometry is approximately trigonal planar. Here, as at N_{16} in **3a**, the small O_8–P_9–N_{14}–C_{16} torsion angle (22.2°) is associated with the larger P–N–C bond angle [P_9–N_{14}–C_{16} = 125.1 (1)°, P_9–N_{14}–C_{15} = 119.1 (1)°].

The configuration at phosphorus was of course revealed by the X-ray analysis and was the same as in the starting phosphinamide; this provides the first determination of the stereochemical pathway for the O-insertion reaction, but the result is consistent with the mechanism proposed for this process. A P(V) intermediate such as **8** has been proposed;[2,3] with the ring in the apical–equatorial position, the angle (90°) is more compatible with that imposed by the 7-PNB structure (82.3° in **3**). This intermediate would form with the peroxy group apical (as in general structure **8**), but one pseudorotation is required to place this group

(16) Main, P. MULTAN11/82; University of York, England, 1982.

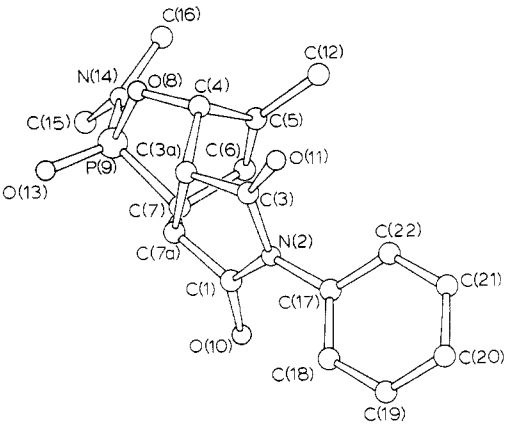
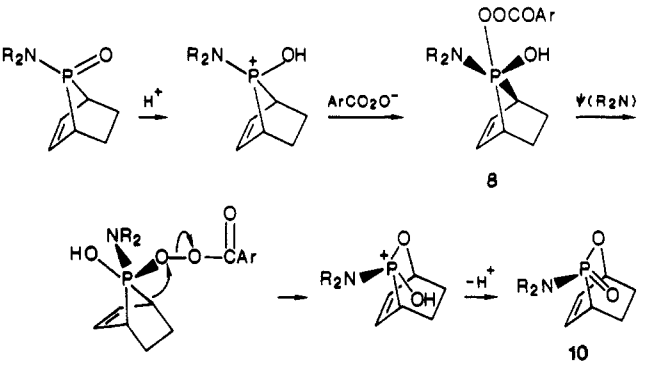


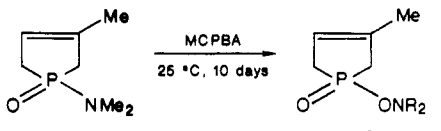
Figure 2. Structure and solid-state conformation of **6**; hydrogen atoms have been omitted for clarity.

in position (equatorial, as in **9**) for migration of the P–C bond. This leads to retention of the original phosphorus configuration in the P(IV) product **10**. With this new



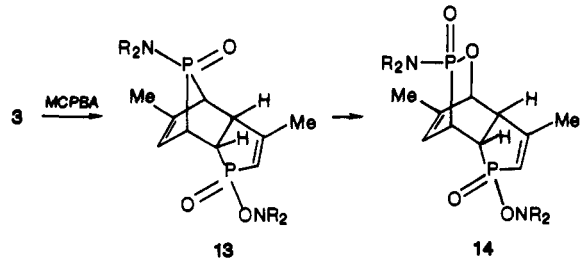
knowledge of the course of the O-insertion process, it can now be proposed that the previously reported phosphinates resulting from insertions into strained phosphine oxides[2,3] and of phosphonates resulting from strained phosphinates[4] also have the retained phosphorus configuration.

The above experiments show that, in the attack of MCPBA at a 7-PNB phosphinamide group, O-insertion into a C–P bond occurs before any reaction on nitrogen. The dimers of 1-aminophospholes have a second phosphinamide group that could present another site for attack by MCPBA.[5] To test for the sensitivity of the cyclic phosphinamide nitrogen to MCPBA, as observed for acyclic phosphoramidates,[5] the reaction of oxide **11** with MCPBA was performed as a model. The changes in ^{31}P and ^{13}C NMR (see Experimental Section) were consistent with the replacement of the *P*-amino group by a *P*-oxy group (**12**) as expected from results with acyclic phosphorus amides.[4] The ^{13}C NMR spectra were especially indicative of this chemical change, since the PC coupling in **11** was lost in the final product **12**. When the MCPBA



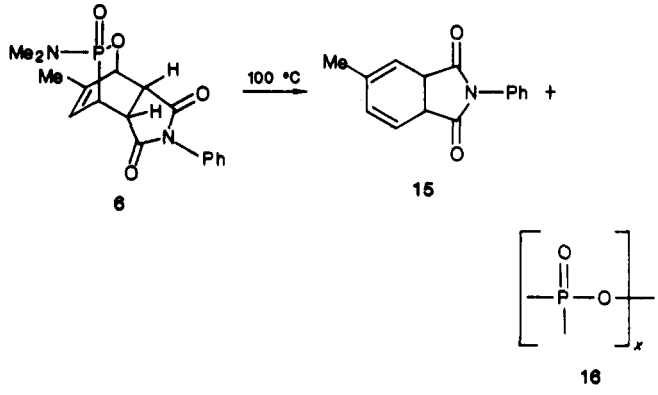
11 **12**

reaction was applied to dimer **3**, the first point of attack proved to be the amino group of the 2-phospholene moiety. This was clearly revealed by the ^{31}P NMR changes accompanying the reaction; the bridging P signal remained in position, but the signal for the 2-phospholene P shifted from δ +64.8 to +73.6. The product is probably **13**. On



continued reaction, the bridging P signal δ +83 decreased in size as a new signal at δ +28.2 appeared from oxygen insertion into the ring (14). These products proved to be unstable, however, and attempts to isolate them were not successful. Thus, although O-insertion into the strained C–P bond of the dimer structure can occur, the product is less useful for further study than is the Diels–Alder structural type (4 or 5).

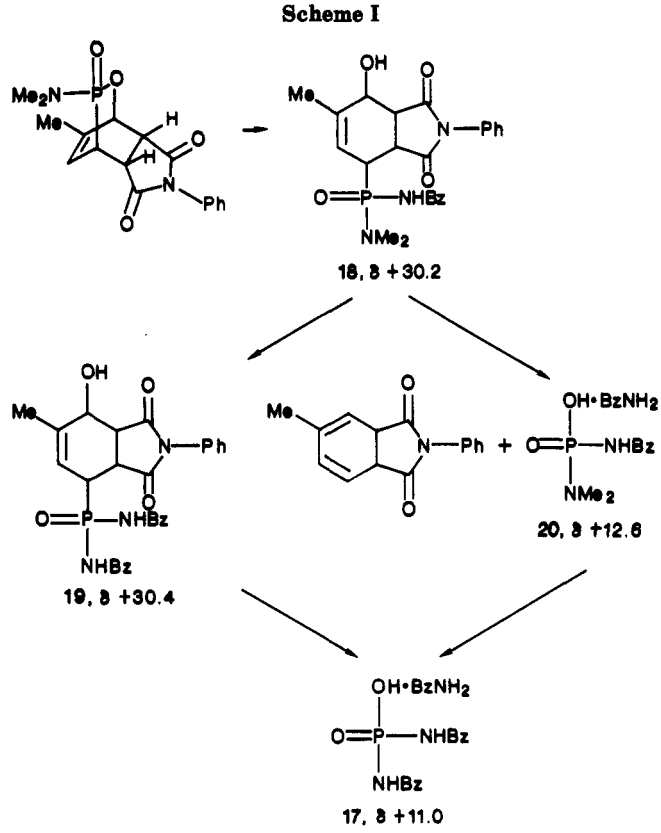
Chemical Properties of the Oxaphosphabicyclo[2.2.2]octene System. The Diels–Alder adduct 6 is especially suitable for examining the properties of this ring system, since it is stable at room temperature and soluble in common solvents. The critical property of thermal stability was first tested by heating it in toluene at 100 °C. Decomposition was complete after 30 h (monitored with ^{31}P NMR). All phosphorus appeared in forms with P–O–P links, which was indicated by complex NMR signals in the region δ −10 to −22. The organic product was identified as the known compound 15.[12] Diels–Alder adduct 7 was



much less stable; none remained after standing at room temperature for 3 days or on heating for 2 h at 40 °C in $CDCl_3$. The products resembled those from adduct 6. These results show that the elimination of the phosphorus fragment indeed occurs under relatively mild conditions, but the mechanism (concerted retro[4+2]cycloaddition to form R_2NPO_2 or step-wise unimolecular or intermolecular processes) needs to be considered.

To determine if the decomposition occurred by elimination of the R_2NPO_2 species, attempts were made to perform trapping reactions with cyclohexanol, which had been used successfully to trap $ROPO_2$ and RPO_2 from the related esters.[4] The thermolysis of 6 was therefore conducted in the presence of cyclohexanol (1:1 or 8:1 excess) at 100 °C. ^{31}P NMR analysis revealed that none of the expected trapping product, $C_6H_{11}OP(O)(OH)NMe_2$, was formed. Some modification of the complex pyrophosphate signals did occur, however, especially in enhancement of a signal suggestive of a diphosphate species at δ −10.2. Similarly, *N*-methylpyrrole was ineffective in trapping the postulated Me_2NPO_2 fragment, although it is highly effective[4] for trapping $ROPO_2$ or RPO_2. These results indicate that either the fragment was not released as such or that if released it is of quite low electrophilic reactivity on comparison to the species $ROPO_2$ and RPO_2 as generated by ester thermolysis.[4] On the other hand, a trapping product was successfully obtained when the thermolysis of 6 was conducted in the presence of excess benzylamine. When an eightfold molar excess of the amine was used, ^{31}P NMR measurements showed that the decomposition at 100 °C was greatly expedited and was complete after only 75 min. The only phosphorus product, δ +11.0, was isolated as a solid and found by analysis and NMR studies to have structure 17, which could be viewed as a derivative of the R_2NPO_2–benzylamine product. When only a fourfold

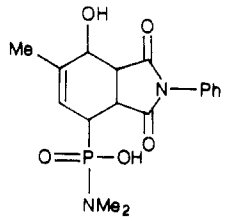
Scheme I



$$6 \xrightarrow{PhCH_2NH_2} \underset{17}{(PhCH_2NH)_2POO^-\overset{+}{N}H_3CH_2Ph}$$

amine excess was used, the process was incomplete. These observations are of considerable importance, for they suggest that the amine is directly involved in promoting the decomposition of 6 and not just in the trapping of a thermally produced fragment. It seemed possible that intermediates from the attack of benzylamine might survive at room temperature and be detectable by ^{31}P NMR. Accordingly, a 1:8 molar mixture of 6 and benzylamine was allowed to stand at room temperature while being monitored by ^{31}P NMR. After 14 days, all starting material was consumed, and the only phosphorus product was the phosphorodiamidate salt 17. However, other signals did develop during the course of the reaction, two of which fell in the phosphonamide region (δ +30.2 and +30.4) while the other (δ +12.6) appeared to be a phosphorodiamidate, possibly 20. The phosphonamide intermediates, which would be derived from ring opening, could not be isolated but structures 18 and 19 seem reasonable postulates. By observing changes in the relative signal intensities, the relations in Scheme I were suggested. With the detection of intermediates of possible structures 18 and 19, further evidence is provided that, at least in the presence of a nucleophilic species such as benzylamine, the degradation of the Diels–Alder adducts does not occur by a retrocycloaddition to release R_2NPO_2. The degradation of 6

in the presence of some other nucleophilic species (*N,N*-dimethylhydrazine or NaOMe in MeOH) failed to give their phosphorylation products, and for the present the reaction experienced with benzylamine appears to be of limited scope. In another attempt to form the suspected ring-opened intermediates such as **18** or **19**, an acid hydrolysis of **6** was performed with 6 N HCl at room temperature. Indeed, **6** was slowly converted to another species with δ_{31P} +25.2 which could be a ring-opened phosphonamide (e.g., **22**) but its instability (leading to H_3PO_4) again prevented isolation. The suspected instability of the organization HOCC=CCP(O) needs further consideration; the construction of an appropriate model system for a test of the pathway proposed for degradation of adduct **6** may be informative.



22

Experimental Section[17]

Preparation of 1-(*N,N*-Dialkylamino)-3-methyl-3-phospholene 1-Oxide. 1-(*N,N*-Dimethylamino)- and 1-(*N,N*-diethylamino)-3-methyl-3-phospholene 1-oxide were prepared as previously reported[6] by amidation of the phosphinic acid. 1-Piperidyl-3-methyl-3-phospholene 1-oxide was prepared in the same manner. Anal. Calcd for $C_{10}H_{20}NOP$: C, 60.30; H, 9.04; P, 15.58. Found: C, 60.14; H, 8.93; P, 15.34.

3,4-Dibromo-1-(*N,N*-dialkylamino)-3-methylphospholane 1-Oxides. A solution of 0.10 mol of the 1-(*N,N*-dialkylamino)-3-methyl-3-phospholene 1-oxide in 200 mL of chloroform was cooled to 0 °C, and 0.10 mol of bromine dissolved in 10 mL of chloroform was added slowly. The mixture was then stirred at room temperature for 2 h. Chloroform was evaporated, and the product was purified on a silica gel column by using chloroform and then 5% methanol in chloroform as eluants. The fractions containing the desired product were evaporated under reduced pressure, and the product was isolated as a semicrystalline white solid, consisting of two isomers as seen by ^{31}P NMR. These products were used without further purification for the next reaction. Yields were as follows: *N,N*-dimethyl, 86%; *N,N*-diethyl, 76%; piperidyl, 78%.

Dimers of 1-(Dialkylamino)-3-methylphosphole 1-Oxides. The general procedure involved reaction of 0.05 mol of 3,4-dibromo-1-(*N,N*-dialkylamino)-3-methylphospholane 1-oxides in 300 mL of benzene (or a mixture of 300 mL of benzene and 150 mL of chloroform) and 0.20 mol of triethylamine at room temperature for 4 days. The progress of reaction was monitored by means of ^{31}P NMR. The precipitated triethylamine hydrochloride was filtered off, and solvent was removed under reduced pressure. The residual dimer was purified on a silica gel column and then recrystallized as indicated. Specral data are given in Table I.

3a: 73%; mp 116–118 °C (benzene–hexane). Anal. Calcd. for $C_{19}H_{24}N_2O_2P_2$: C, 53.50; H, 7.64; P, 19.75. Found: C, 53.28; H, 7.89; P, 20.03.

3a monohydrate: mp 136–138 °C. Anal. Calcd for $C_{19}H_{24}N_2O_2P_2 \cdot H_2O$; C, 50.60; H, 7.83; P, 18.67. Found: C, 50.77; H, 7.99; P, 18.59.

3b: 65%, mp 78–79 °C (pentane). Anal. Calcd. for $C_{18}H_{32}N_2O_2P_2$: C, 58.38; H, 8.65; P, 16.76. Found: C, 58.12; H, 8.68; P, 16.66.

3b monohydrate: mp 88–89 °C. Anal. Calcd for $C_{18}H_{32}N_2O_2P_2 \cdot H_2O$: C, 55.67; H, 8.76; P, 15.98. Found: C, 55.42; H, 8.74; P, 15.81.

3c monohydrate: 65%, mp 116–118 °C (benzene–pentane). Anal. Calcd for $C_{20}H_{32}N_2O_2P_2 \cdot H_2O$: C, 58.25; H, 8.25; P, 15.04. Found: C, 58.42; H, 8.31; P, 15.17.

Reaction of 1-(*N,N*-Dimethylamino)-3-methyl- or 1-(*N,N*-Dimethylamino)-3,4-dimethylphosphole 1-Oxide and *N*-Phenylmaleimide. A solution of 0.10 mol of 3,4-dibromo-1-(*N,N*-dimethylamino)-3-methyl- or 1-*N,N*-dimethylamino-3,4-dimethylphospholane 1-oxide in 500 mL of benzene and 100 mL of chloroform was treated with 0.130 mol of *N*-phenylmaleimide and then 0.250 mol of triethylamine. The reaction mixture was allowed to stand at room temperature for a few days. The progress of the reaction was monitored by means of ^{31}P NMR. The precipitated triethylamine hydrobromide was removed by filtration, and solvent was evaporated from the filtrate under reduced pressure. The product was purified by chromatography on silica gel, using benzene and then benzene–acetone (3:2) as eluants. Spectral data for the products **4** and **5** are given in Table I.

4: 65%; mp 193–194 °C. Anal. Calcd for $C_{17}H_{19}N_2O_3P$: C, 61.82; H, 5.76; N, 8.24; P, 9.39. Found: C, 61.88; H, 5.77; N, 8.53; P, 9.63.

5: 54%; mp 195–197 °C. Anal. Calcd for $C_{18}H_{21}N_2O_3P$: C, 62.79; H, 6.10; P, 9.01. Found: C, 62.83; H, 6.24; P, 8.79.

Oxidation of Phosphole Cycloadducts 4 and 5 with *m*-Chloroperbenzoic Acid. A solution of 0.007 mol of cycloadducts **4** or **5** was dissolved in 100 mL of chloroform containing 0.012 mol of *m*-chloroperbenzoic acid. The mixture was allowed to stand overnight, and then solvent was removed under reduced pressure. The product was isolated by column chromatography on silica gel 230–400 mesh, with elution by ethyl acetate–hexane (5:2) and then ethyl acetate. Products **6** and **7**, respectively, were recrystallized from benzene–hexane.

6: 40%; mp 162–163 °C. Anal. Calcd for $C_{17}H_{19}N_2O_4P$: C, 58.96; H, 5.49; P, 8.95. Found: C, 58.83; H, 5.54; P, 8.86.

7: 23%; mp 116–118 °C. Anal. Calcd for $C_{18}H_{21}N_2O_4P$: C, 60.00; H, 5.83; P, 8.61. Found: C, 59.81; H, 5.77; P, 8.43.

Oxidation of 1-(*N,N*-Diethylamino)-3-methyl-3-phospholene 1-Oxide (11) with *m*-Chloroperbenzoic Acid. Compound **11** (0.50 g, 0.00267 mol) was added to 5 mL of $CDCl_3$ containing 0.65 g (80% purity, 0.0030 mol) of *m*-chloroperbenzoic acid. The progress of the reaction at room temperature was monitored by ^{31}P NMR analysis. Pure **11** had δ_{31P} +63.2 but in MCPBA gave signals at δ_{31P} +73.8 and +70.8. After 30 min, a new signal was detected at δ_{31P} +69.5 (possibly the *N*-oxide); this peak later disappeared as a new signal appeared at δ_{31P} +64.1. After 10 days, this was the only phosphorus species in the solution. The ^{13}C NMR spectrum was obtained directly on this solution: δ_{13C} 11.3 (s, CH_2CH_3), 21.0 (J = 13.2 Hz, C_5), 33.1 (J = 87.9 Hz, C_5), 35.7 (J = 91.2 Hz, C_2), 42.0 (s, NCH_2), 120.8 (J = 11.0 Hz, C_4), 136.5 (J = 17.0 Hz, C_3). For reference, the ^{13}C spectrum of **11** was obtained: δ_{13C} 14.3 (J = 2.0 Hz, CH_2CH_3), 20.6 (J = 11.7 Hz, C_6), 32.6 (J = 80.1 Hz, C_5), 35.0 (J = 83.0 Hz, C_2), 38.1 (J = 3.9 Hz, NCH_2), 121.7 (J = 9.6 Hz, C_4), 137.1 (J = 15.6 Hz, C_3).

Oxidation of Aminophosphole Oxide Dimer 3a with *m*-Chloroperbenzoic Acid. A sample of 0.628 g (0.002 mol) of dimer **3a** was added to a chloroform (4 mL) solution containing 1.1 g (80% purity, 0.005 mol) of *m*-chloroperbenzoic acid. After 30 min, the ^{31}P NMR signal for the 2-phospholene phosphorus (initially δ +64.8, a doublet of 41.5 Hz from coupling to the bridging P, δ +83.0) was replaced by a new signal at δ +73.7 (J = 46.4 Hz), with little change at the bridging P, δ +83.5. Also present was a second compound presumed to be **13** (δ +71.0 and +28.3, J = 58.6 Hz), which became the major product after 20 h. Other signals at δ +44.4, +74.1, and +74 are probably phosphindole derivatives; the product was not isolated due to the complexity of the mixture.

Thermal Decomposition of 5,6-Oxaphosphabicyclo[2.2.2]octene Derivative 6. A suspension of **6** (0.10 g) in 1 mL

(17) Proton NMR spectra were obtained on an IBM NR-80 spectrometer at 80 MHz, with tetramethylsilane (Me_4Si) as an internal standard. Phosphorus-31 spectra (FT) were obtained on a JEOL-FX 90Q spectrometer at 36.2 MHz, with 85% H_3PO_4 as an external standard with an internal deuterium lock. Negative shifts are upfield and positive shifts downfield of the reference. Carbon-13 spectra (FT) were obtained on a JEOL-FX 90Q spectrometer at 22.5 MHz, with Me_4Si as an internal standard. Broad-band proton noise-decoupling was employed on all carbon-13 and phosphorus-31 NMR spectra. Melting points were taken on a Mel-Temp apparatus and are corrected; boiling points are uncorrected. Combustion analyses were performed by MHW Laboratories, Phoenix, AZ.

of toluene was heated at 100 °C in an NMR tube. The progress of the reaction was followed by ^{31}P NMR. After 30 h, all **6** had disappeared, and the only phosphorus species gave complex signals in the pyrophosphate region (δ −10 and −21). The dihydrophthalimide derivative **15**[4] was identified in the solution by ^1H and ^{13}C NMR spectroscopy.

Reaction of 5,6-Oxaphosphabicyclo[2.2.2]octene Derivative 6 with Benzylamine. A solution of 0.10 g (0.29 mmol) of benzylamine in 0.75 mL of toluene was heated at 100 °C for 75 min, by which time all **6** had disappeared (^{31}P NMR analysis) and only one phosphorus product (δ about +11) was present. On cooling, a crystalline product precipitated; it was collected by filtration and recrystallized from ethanol–ether to yield 0.075 g of **17** (66%); mp 128–130 °C dec; $\delta_{^{31}P}$ ($CDCl_3$) +11.6. Anal. Calcd for $C_{21}H_{26}N_3O_2P\cdot{}^1/_2H_2O$: C, 64.28; H, 6.88; P, 7.90. Found: C, 64.18; H, 6.78; P, 7.71.

The reaction was also conducted at room temperature; after 14 days, all **6** had disappeared, and the only phosphorus product was **17**, isolated in 69% yield.

X-ray Crystal Structure Analyses of 3a·H₂O and 6. Crystal data: $C_{14}H_{24}N_2O_2P_2\cdot H_2O$ (**3a**·H_2O), M_r 332.32, monoclinic, a = 6.333 (1) Å, b = 17.220 (3) Å, c = 9.585 (1) Å, β = 125.19 (1)°, V = 854.3 Å^3, Z = 2, D_{calcd} = 1.292 g cm^{-3}, μ (Cu Kα radiation, λ = 1.5418 Å) = 24.3 cm^{-1}. Space group $Pc(C_s^2)$ or $P2/c(C_{2h}^4)$ from the systematic absences $h0l$ when $l \neq 2n$, with Z = 2, an ordered structure demands the former as **3a** lacks either a center or twofold axis of symmetry. Sample dimensions: 0.07 × 0.12 × 0.70 mm (sealed inside a thin-walled glass capillary to prevent loss of water of crystallization).

$C_{17}H_{19}N_2O_4P$ (**6**), M_r 346.33, triclinic, a = 8.013 (1) Å, b = 15.480 (1) Å, c = 7.084 (1) Å, α = 91.26 (1)°, β = 108.30 (1)°, γ = 100.05 (1)°, V = 818.7 Å^3, Z = 2, D_{calcd} = 1.405 g cm^{-3}, μ(Cu Kα radiation) = 16.9 cm^{-1}. Space group $P\bar{1}(C_1^1)$ or $P\bar{1}(C_i^1)$ from Laue symmetry; shown to be the latter by structure solution. Sample dimensions: 0.08 × 0.30 × 0.60 mm (mounted on the end of a thin glass fiber).

Oscillation, Weissenberg, and precession photographs yielded preliminary unit-cell parameters and space group information. Intensity data $hk\pm l$ for **3a**·H_2O; $\pm h\pm kl$ for **6**) were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, incident-beam graphite monochromator; ω–2θ scans, θ_{max} = 67°). From totals of 1554 and 2941 unique forms for **3a**·H_2O and **6**, respectively, those 1076 and 2609 with $I > 3.0\sigma(I)$ were retained for the structure analyses. In addition to the usual Lorentz and polarization corrections, empirical absorption corrections, based on the ϕ dependence of the intensities of several reflections with χ ca. 90°, were also applied to the data. Refined unit-cell parameters were derived by least-squares treatment of the diffractometer setting angles for 25 reflections (39° < θ < 65° for **3a**·H_2O; 60° < θ < 67° for **6**) widely separated in reciprocal space.

The crystal structure of **3a**·H_2O was solved by the heavy-atom approach. Initial coordinates for the phosphorus atoms were derived from the three-dimensional Patterson map, and remaining non-hydrogen atom positions were obtained from a weighted F_o Fourier synthesis phased by the phosphorus atoms. Full-matrix least-squares adjustment of non-hydrogen atom positional and anisotropic thermal parameters, with hydrogen atoms included at their calculated positions in the later iterations, converged to R = 0.045 (R_w = 0.059).[13] For **6**, the crystal structure was solved by use of direct methods.[16] Approximate positions for all non-hydrogen atoms were obtained from an E-map. Hydrogen atoms were located in a difference Fourier synthesis evaluated at a late stage in the analysis. Full-matrix least-squares adjustment of atomic positional and thermal (anisotropic C, N, O, P; isotropic H) parameters converged to R = 0.045 (R_w = 0.073).[13]

Neutral atom scattering factors used in the structure-factor calculations were taken from ref 18. In the least-squares iterations, $\sum w\Delta^2[w = 1/\sigma^2(|F_o|), \Delta = ||F_o| - |F_c||]$ was minimized. All calculations were performed on a PDP11/44 computer by use of the Enraf-Nonius SDP suite of programs.

Registry No. **3a**·H_2O, 103003-07-2; **3b**, 96548-52-6; **3c**, 103003-08-3; **4**, 103003-10-7; **5**, 103003-11-8; **6**, 103003-12-9; **7**, 103003-13-0; **11**, 92063-25-7; **12**, 103003-14-1; **13**, 103003-15-2; **14**, 103003-16-3; **15**, 75581-74-7; **17**, 103003-17-4; 1-(*N*,*N*-diethylamino)-3-methyl-3-phospholene 1-oxide, 3105-70-2; 1-piperidyl-3-methyl-3-phospholene 1-oxide, 7563-20-4; 3,4-dibromo-1-(*N*,*N*-dimethylamino)-3-methylphospholane 1-oxide, 103003-04-9; 3,4-dibromo-1-(*N*,*N*-diethylamino)-3-methylphospholane 1-oxide, 103003-05-0; 3,4-dibromo-1-piperidinyl-3-methylphospholane 1-oxide, 103003-06-1; 1-(*N*,*N*-dimethylamino)-3,4-dimethylphospholane 1-oxide, 103003-09-4; *N*-phenylmaleimide, 941-69-5; benzylamine, 100-46-9.

Supplementary Material Available: Tables of non-hydrogen atom positional and anisotropic thermal parameters, hydrogen atom parameters, interatomic distances and angles, torsion angles, and displacements of atoms from least-squares planes for **3a**·H_2O and **6** (16 pages). Ordering information is given on any current masthead page.

(18) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Synthesis of a Precursor to Quassimarin

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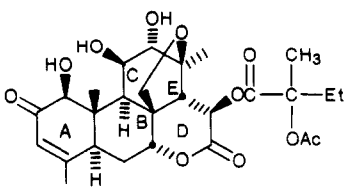
An intermediate containing the ACE ring system of quassimarin was prepared. The isopropylidene malonate **8** reacted with diene **2** to afford two Diels–Alder adducts. The major adduct was converted into lactone **11** by a sequence involving epoxidation followed by acid-mediated epoxide opening and lactonization.

The quassinoids are a diverse class of diterpenes that exhibit useful biological activity.[1] This fact, combined with their challenging structure, has made them frequent synthetic objectives. This is evidenced by the significant number of recent approaches. Grieco's elegant studies on quassinoid synthesis have led to total syntheses of quassin and castelanolide and the synthesis of an isomer of the pentacyclic quassinoid quassimarin.[2] Ganem has reported



quassimarin

a clever approach to the pentacyclic member.[3] Fuchs,[4] Weller,[5] Watt,[6] and Heathcock[7] have also reported very

(1) Polonsky, J. *Fortschr. Chem. Org. Naturst.* **1973**, *30*, 102.

0022-3263/86/1951-3347$01.50/0