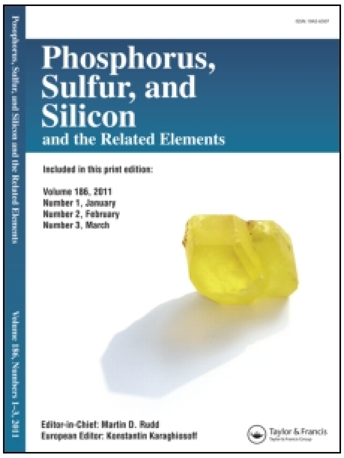

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SOLID-STATE CONFORMATIONS OF MEDIUM-SIZED-RING PHOSPHORUS HETEROCYCLES: X-RAY CRYSTAL STRUCTURES OF TWO NORBORNENE-FUSED 1,3,2-DIOXAPHOSPHEPANES WITH EQUATORIALLY DISPOSED SUBSTITUENTS ON PHOSPHORUS

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SOLID-STATE CONFORMATIONS OF MEDIUM-SIZED-RING PHOSPHORUS HETEROCYCLES: X-RAY CRYSTAL STRUCTURES OF TWO NORBORNENE-FUSED 1,3,2-DIOXAPHOSPHEPANES WITH EQUATORIALLY DISPOSED SUBSTITUENTS ON PHOSPHORUS

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The seven-membered-ring phosphorus heterocycles, *trans*-5,6-(*endo*,*endo*-2′,3′-bicyclo[2.2.1]hept-5′-eno)-2-oxo-2-phenoxy-1,3,2-dioxaphosphepane, *trans*-**1**, and *trans*-5,6-(*endo*,*endo*-2′,3′-bicyclo-[2.2.1]hept-5′-eno)-2-oxo-2-phenyl-1,3,2-dioxaphosphepane, *trans*-**2**, have been synthesized and the crystal and molecular structures of the compounds determined from single-crystal X-ray studies. Compound *trans*-**1** crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell of dimensions $a = 6.275(2)$ Å, $b = 19.419(7)$ Å, $c = 11.363(2)$ Å, and $\beta = 90.89(2)°$. Full-matrix least-squares refinement using 2317 unique reflections having $2.5° \leq 2\theta \leq 49.0°$ and $I \geq 3\ \sigma(I)$ converged at $R = 0.0543$ and $R_w = 0.0650$. Compound *trans*-**2** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell of dimensions $a = 9.702(3)$ Å, $b = 11.296(4)$ Å, and $c = 12.605(4)$ Å. Full-matrix least-squares refinement using 1862 unique reflections having $4.0° \leq 2\theta \leq 50.0°$ and $I \geq 2.5\ \sigma(I)$ converged at $R = 0.040$ and $R_w = 0.036$. In both of these structures, the seven-membered ring heterocycle adopts a chair conformation with the substituent on phosphorus equatorial.

Key words: dioxaphosphepane; conformation; solid-state; crystal structure; norbornene; bicyclo-[2.2.1]heptene.

INTRODUCTION

We have been interested in the conformational consequences of heteroatom substitution for carbon atoms in cycloalkanes. More specifically, we have studied the conformational properties of phosphorus heterocycles, including the five-membered 1,3,2-oxazaphospholanes[2] and the six-membered 1,3,2-oxazaphosphori-

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nanes.[3] We are currently extending our conformational studies to include medium-sized ring phosphorus heterocycles.

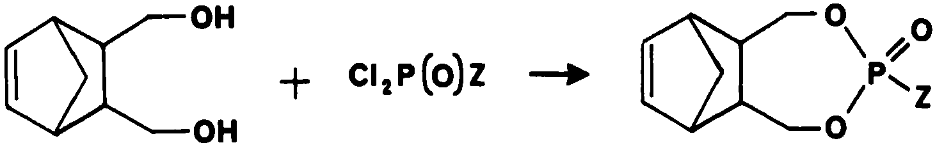
The 1,3,2-dioxaphosphepane ring system affords the opportunity to study the effect on the conformational properties of cycloheptane of replacing ring carbon atoms with heteroatoms. Heteroatom replacement results in (a) different bond lengths and bond angles, (b) replacement of ring hydrogens by heteroatom lone pairs, and (c) introduction of bond and molecular dipoles.

There are two conformational families available to cycloheptane: One family consists of the chair and twist-chair, and intermediate forms; the other family consists of the boat and twist-boat.[4] Introduction of a torsional constraint such as unsaturation or ring fusion reduces the conformational possibilities. Thus cycloheptene and analogous compounds can adopt rigid chair or flexible boat-family conformations.[5]

In this paper we report the synthesis and the crystal and molecular structure of the norbornene-fused seven-membered-ring phosphorus heterocycles, *trans*-5,6-(*endo*,*endo*-2′,3′-bicyclo[2.2.1]hept-5′-eno)-2-oxo-2-phenoxy-1,3,2-dioxaphosphepane, *trans*-**1**, and *trans*-5,6-(*endo*,*endo*-2′,3′-bicyclo[2.2.1]hept-5′-eno)-2-oxo-2-phenyl-1,3,2-dioxaphosphepane, *trans*-**2**.

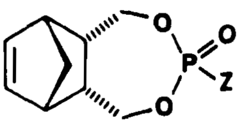
RESULTS AND DISCUSSION

The 1,3,2-dioxaphosphepane **1** and **2** are conveniently prepared by reaction of 5-norbornene-*endo*,*endo*-2,3-dimethanol with phenyl dichlorophosphate, PhOP(O)Cl_2 or phenylphosphonic dichloride, PhP(O)Cl_2, respectively. The two diastereomers which resulted from each cyclization were separated by preparative HPLC on silica gel.



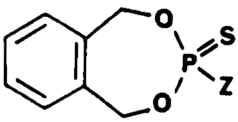
The crystal data for *trans*-**1** and *trans*-**2** are listed in Table I. The final atomic parameters for the compounds are compiled in Tables II and III, respectively. Perspective views of the molecules, along with the labeling schemes, are given in Figures 1 and 2. Selected bond lengths, bond angles, and torsion angles for the compounds are listed in Tables IV, V, and VI, respectively.[6]

X-ray crystal structures have previously been carried out on 2-thio-2-methyl-5,6-benzo-1,3,2-dioxaphosphepane, **3**, and 2-thio-2-(dimethylamino)-5,6-benzo-1,3,2-dioxaphosphepane, **4**.[7] The conformation adopted by the seven-membered ring in each of these four crystal structures is a chair with approximate C_s symmetry. The gross structural features for these four 1,3,2-dioxaphosphepane rings are similar. The geometry at the phosphorus atom in both *trans*-**1** and *trans*-**2**, as expected, is a distorted tetrahedron. The structural features of the norbornene ring in *trans*-**1** and *trans*-**2** appear to be completely regular and do not differ appreciably from those seen in other structures of compounds containing the bicyclo[3.3.1]heptane ring system.[8]



1, Z = OPh

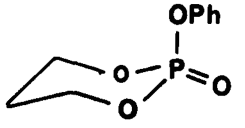
2, Z = Ph



3, Z = Me

4, Z = NMe$_2$

An interesting feature of the crystal structure of *trans*-**1** is that the phenoxy substituent is *equatorial*. In X-ray crystal structures of the six-membered ring analogs, 1,3,2-dioxaphosphorinanes,[9–11] the phenoxy substituent is found to be axially disposed. It is apparent from NMR equilibrium studies that alkoxy substituents are axial seeking in 1,3,2-dioxaphosphorinanes[12] presumably due to the anomeric effect[13] (more specifically, the *endo*-anomeric effect) in this ring system. Indeed, X-ray crystal structures of 1,3,2-dioxaphosphorinanes containing aryloxy substituents on phosphorus show these substituents to be axial[14] unless precluded by geometrical constraints such as ring fusion.[15] Although the phenoxy substituent is equatorial in *trans*-**1** and axial in the 1,3,2-dioxaphosphorinanes **5**,[9] **6**,[10] and **7**,[11] the geometrical features about the phosphorus atom are comparable. That is, the exocyclic P—O(4) and P=O(1) bond lengths, the endocyclic P—O(2) and P—O(3) bond lengths, and the bond angles around the phosphorus atom, are similar to the corresponding bond lengths and angles in the 1,3,2-dioxaphosphorinane crystal structures.



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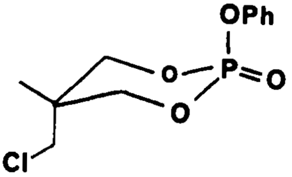

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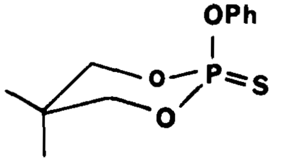

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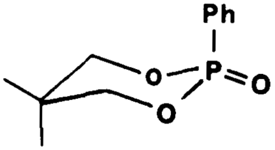

8

Although NMR studies have shown the phenyl substituent on phosphorus in 1,3,2-dioxaphosphorinanes to generally show little axial preference,[12] the X-ray crystal structure of 2-oxo-2-phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane, **8**,[16] shows this phenyl substituent to be axial. In *trans*-**2**, on the other hand, the phenyl substituent is equatorial. The geometrical parameters about the phosphorus atom in **8** and in *trans*-**2** are, again, comparable. There is apparently little, if any, manifestation of the *endo*-anomeric effect in the geometries of *trans*-**1** and *trans*-**2**. That is, the bond lengths of the endocyclic P—O bonds and the exocyclic P═O and P—Z are comparable (within experimental error) to those for the corresponding six-membered-ring analogs, despite the phosphorus substituents being axial in the six-membered rings and equatorial in these seven-membered rings.

TABLE I

Crystal data for 1,3,2-dioxaphosphepanes 1 and 2

Compound	*trans*-**1**	*trans*-**2**
Molecular formula	$C_{15}H_{17}O_4P$	$C_{15}H_{17}O_3P$
Molecular weight	292.27	276.18
Space group	P_1/c(No. 14)[a]	$P2_12_12_1$(No. 19)[b]
Cell dimensions		
a, Å	6.275(2)	9.702(3)
b, Å	19.419(7)	11.296(4)
c, Å	11.363(2)	12.605(4)
β, deg	90.89(2)	
V, Å^3	1384.57	1381.43
Z	4	4
D_{calcd}, g cm^{-3}	1.402	1.328
Crystal dimensions, mm	0.32 × 0.29 × 0.26	0.54 × 0.44 × 0.37
No. of unique data	2317	2287
No. of obsd. data	1850	1862
absorption coeff., cm^{-1}	2.0	1.9

[a] The space group was unambiguously determined by the systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$.

[b] The space group was unambiguously determined by the systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$.

TABLE II

Final atomic parameters for *trans*-**1**

Atom	x	y	z	B_{iso}(Å^2)
P	0.8193(2)	0.13491(6)	0.54343(9)	2.74(2)
O1	0.7298(5)	0.2035(2)	0.5441(3)	3.62(7)
O2	1.0059(5)	0.1253(2)	0.4546(2)	3.23(6)
O3	0.6561(5)	0.0759(2)	0.5194(3)	3.43(6)
O4	0.9181(5)	0.1085(2)	0.6629(3)	3.70(7)
C1	0.9597(7)	0.1348(2)	0.3303(4)	3.31(9)
C2	0.8932(7)	0.0672(2)	0.2747(4)	3.19(9)
C3	0.8595(7)	0.0733(2)	0.1389(4)	3.40(9)
C4	0.6876(8)	0.1266(3)	0.1159(4)	3.9(1)
C5	0.5059(8)	0.0989(3)	0.1490(4)	4.0(1)
C6	0.5540(8)	0.0270(2)	0.1936(4)	3.9(1)
C7	0.7352(9)	0.0071(3)	0.1145(4)	4.2(1)
C8	0.6781(7)	0.0353(2)	0.3138(4)	3.31(9)
C9	0.5489(7)	0.0745(2)	0.4035(4)	3.27(9)
C10	1.0521(7)	0.1502(2)	0.7347(4)	3.15(9)
C11	0.9840(7)	0.1655(2)	0.8450(4)	3.41(9)
C12	1.1213(8)	0.2004(2)	0.9206(4)	3.7(1)
C13	1.3210(8)	0.2200(3)	0.8838(4)	3.9(1)
C14	1.3832(8)	0.2055(3)	0.7707(5)	4.2(1)
C15	1.2470(8)	0.1700(3)	0.6952(4)	3.8(1)

B_{iso} is the mean of the principal axes of the thermal ellipsoid.

TABLE III

Final atomic parameters for *trans*-**2**

Atom	x	y	z	$B_{\text{iso}}(\text{Å}^2)$
P	0.05536(9)	0.07308(8)	0.09327(6)	3.43(4)
O1	0.1599(2)	−0.0194(2)	0.1043(2)	5.0(1)
O2	−0.0957(2)	0.0330(2)	0.1207(2)	4.07(9)
O3	0.0839(2)	0.1866(2)	0.1630(2)	3.5(1)
C1	−0.1330(3)	−0.0008(3)	0.2289(3)	4.1(2)
C2	−0.1709(3)	0.1056(3)	0.2952(2)	3.3(1)
C3	−0.2255(3)	0.0680(3)	0.4071(3)	4.1(2)
C4	−0.1138(4)	−0.0036(3)	0.4596(3)	4.7(2)
C5	−0.0121(4)	0.0680(4)	0.4826(2)	4.4(2)
C6	−0.0527(4)	0.1914(3)	0.4487(2)	3.9(2)
C7	−0.2082(4)	0.1838(3)	0.4669(3)	4.4(2)
C8	−0.0550(3)	0.1947(3)	0.3249(2)	3.3(1)
C9	0.0877(3)	0.1701(3)	0.2784(3)	3.7(1)
C10	0.0360(3)	0.1312(3)	−0.0367(2)	3.5(2)
C11	−0.0524(3)	0.2247(3)	−0.0571(2)	4.2(2)
C12	−0.0693(4)	0.2662(4)	−0.1588(3)	5.0(2)
C13	0.0057(4)	0.2152(4)	−0.2408(3)	5.5(2)
C14	0.0938(4)	0.1239(4)	−0.2217(3)	5.8(2)
C15	0.1128(4)	0.0818(3)	−0.1175(2)	4.7(2)

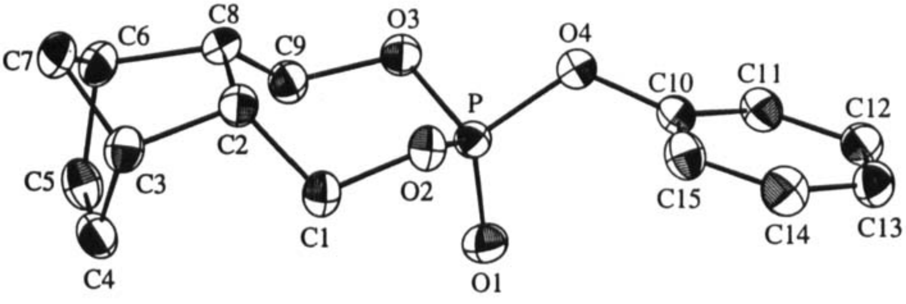

FIGURE 1 ORTEP Perspective Drawing of *trans*-**1**.

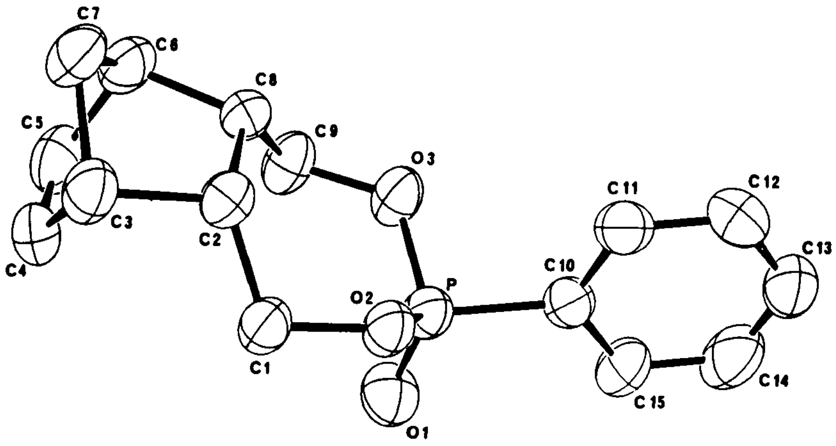

FIGURE 2 ORTEP Perspective Drawing of *trans*-**2**.

TABLE IV

Selected bond lengths (Å) for *trans*-**1** and *trans*-**2**

Atoms	*trans*-**1**	*trans*-**2**
P-O1	1.447(3)	1.463(2)
P-O2	1.569(3)	1.573(2)
P-O3	1.559(3)	1.579(2)
P-O4	1.570(3)	—
P-C10	—	1.775(3)
O2-C1	1.450(5)	1.462(4)
O3-C9	1.469(5)	1.467(4)
C1-C2	1.512(6)	1.510(5)
C2-C3	1.559(6)	1.565(4)
C2-C8	1.556(6)	1.554(4)
C3-C4	1.514(6)	1.506(5)
C3-C7	1.526(6)	1.519(5)
C4-C5	1.321(6)	1.308(6)
C5-C6	1.514(6)	1.510(5)
C6-C7	1.511(7)	1.528(5)
C6-C8	1.570(6)	1.561(4)
C8-C9	1.518(6)	1.529(5)

TABLE V

Selected bond angles (deg) for *trans*-**1** and *trans*-**2**

Atoms	*trans*-**1**	*trans*-**2**
O1-P-O2	114.1(2)	114.8(1)
O1-P-O3	114.9(2)	113.9(1)
O1-P-O4	116.5(2)	—
O1-P-C10	—	115.2(2)
O2-P-O3	107.1(1)	106.0(1)
O2-P-O4	103.2(2)	—
O2-P-C10	—	102.2(1)
O3-P-O4	99.2(2)	—
O3-P-C10	—	103.4(1)
P-O2-C1	118.2(2)	120.7(2)
P-O3-C9	117.4(2)	116.9(2)
P-O4-C10	122.3(2)	—
O2-C1-C2	110.3(3)	111.7(3)
C1-C2-C3	112.4(3)	111.4(3)
C1-C2-C8	117.5(3)	118.3(3)
C3-C2-C8	102.0(3)	101.8(2)
C2-C3-C4	107.9(3)	107.4(3)
C2-C3-C7	100.2(4)	100.1(3)
C4-C3-C7	100.5(4)	99.5(3)
C3-C4-C5	106.8(4)	107.9(3)
C4-C5-C6	107.6(4)	108.2(3)
C5-C6-C7	100.6(4)	99.4(3)
C5-C6-C8	106.9(3)	107.9(3)
C7-C6-C8	100.1(4)	97.8(3)
C3-C7-C6	93.7(3)	94.8(3)
C2-C8-C6	102.3(3)	103.7(2)
C2-C8-C9	117.8(3)	116.4(3)
C6-C8-C9	111.9(4)	111.5(3)
O3-C9-C8	111.7(3)	109.6(3)

TABLE VI

Selected torsion angles (deg) for *trans*-**1** and *trans*-**2**

Atoms	*trans*-**1**	*trans*-**2**
C1-C2-C8-C9	0.8(6)	3.4(2)
C2-C8-C9-O3	−67.8(5)	−67.5(2)
C8-C9-O3-P	87.3(4)	93.5(2)
C9-O3-P-O2	−63.5(3)	−65.5(2)
O3-P-O2-C1	66.4(3)	60.7(2)
P-O2-C1-C2	−90.3(4)	−85.0(2)
O2-C1-C2-C8	66.8(5)	68.7(2)
O1-P-O4-C10	−44.8(4)	—
O1-P-C10-C11	—	175.5(3)

The 1,3,2-dioxaphosphepane rings **3** and **4** have been shown to exhibit a greater degree of ring pucker than do the analogous six-membered rings.[7] Ring pucker is also greater in *trans*-**1** and *trans*-**2** than in 1,3,2-dioxaphosphorinanes. Thus, the dihedral angles about the endocyclic P—O bonds average 65° and 63° in *trans*-**1** and *trans*-**2**, respectively, while the analogous angles in **5** average 43°. Similarly, the dihedral angles about the ring C—O bonds average 89° for both *trans*-**1** and -**2**, but 53° in **5**. Of course, the C1—C2—C8—C9 torsion angles in *trans*-**1** and *trans*-**2** are nearly 0° due to the *cis* fusion with the norbornene ring.

The phenoxy group in *trans*-**1** bisects the O1—P—O2 bond angle as seen in the Newman projection along the P—O4 bond (Figure 3). (The O1—P—O4—C10 torsion angle is −44.8°.) This conformation is also seen in the 1,3,2-dioxaphosphorinane **5** (O═P—O—C = −56°) and may be attributed to the *exo*-anomeric effect.[12] That is, the lone pair on the exocyclic oxygen (O4) is nearly coplanar with the P—O2 bond. This results in a favorable orbital interaction between the lone pair on O4 and the P—O2 antibonding orbital. Evidence for such an interaction is seen in the P—O2 bond length (1.569(3) Å) as compared to the P—O3 bond

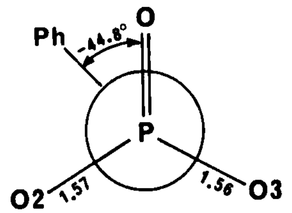

FIGURE 3 Newman Projection Down the P—O4 Bond in *trans*-**1**.

(1.559(3) Å). The *exo*-anomeric effect would be expected to result in a lengthened P—O2 bond, as observed.

The phenyl substituent in *trans*-**2** is nearly coplanar with the phosphoryl, P=O, allowing for conjugation with that group. This seems to be the preferred conformation of an aryl substituent on phosphorus when that substituent is equatorial; a coplanar mesityl and phosphoryl have been seen in an X-ray structure of a 1,3,2-oxazaphosphorinane.[3c] When an aryl substituent is axial, on the other hand, the substituent adopts a conformation perpendicular to P=O, presumably to avoid axial 1,3 steric interactions.

EXPERIMENTAL SECTION

Methods and Materials. All reagents were obtained from Aldrich Chemical Company, Milwaukee, WI. Solvents were dried using standard techniques. Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN. Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 1330 spectrophotometer. Proton NMR spectra were obtained on an IBM/Bruker AF 200 spectrometer, operated in the FT mode. Coupling constants were measured at 200 MHz on 100 Hz SW expansions, 32K data base, 9.044-s acquisition times, and are probably accurate to ± 0.2 Hz. Phosphorus-31 NMR spectra were made at 81.015 MHz on an IBM/Bruker AF 200 spectrometer under proton noise decoupling conditions. Positive phosphorus-31 chemical shifts are in δ parts per million downfield from external 85% H_3PO_4. Diastereomeric products were separated on an ISCO Model 2300 HPLC equipped with an ISCO Model UA-5 UV detector, ISCO FOXY fraction collector, and a Rainin DYNAMAX silica gel column (21.4 mm i.d. × 25 cm length).

5-Norbornene-endo,endo-2,3-dimethanol. A solution of 5-norbornene-*endo,endo*-2,3-dicarboxylic anhydride[17] (16.5 g; 100 mmol) in anhydrous tetrahydrofuran (100 mL) was added slowly to a stirred suspension of lithium aluminum hydride (4.0 g, 105 mmol) in tetrahydrofuran (200 mL). The reaction mixture was heated to gentle reflux for 48 h, allowed to cool to room temperature, quenched with a solution of tetrahydrofuran (100 mL) and water (6.0 mL), and stirred for an additional hour. Anhydrous magnesium sulfate was added and stirring continued for 20 min. The reaction mixture was filtered and the solids washed with tetrahydrofuran (4 ×). The solvent was removed from the filtrate under reduced pressure leaving a crystalline solid residue which was recrystallized from ether/pentane to give 6.07 g (39.4% yield) norbornenedimethanol as a colorless crystalline solid.

5,6-(endo,endo-2',3'-bicyclo[2.2.1]hept-5'-eno)-2-oxo-2-phenoxy-1,3,2-dioxaphosphepane, **1**. A solution of 5-norbornene-*endo,endo*-2,3-dimethanol (2.00 g, 13.0 mmol), triethylamine (3.10 mL, 22.4 mmol), and sufficient ethyl acetate to dilute to 100 mL; and a solution of 1.66 mL phenyl dichlorophosphate (1.66 mL, 11.1 mmol) and sufficient ethyl acetate to dilute to 100 mL were added simultaneously by dropwise addition to 200 mL of ethyl acetate under anhydrous conditions. The reaction mixture was stirred for 48 h, the triethylamine hydrochloride filtered off, the solid washed with ethyl acetate, and the solvent removed from the filtrate under reduced pressure to give 4.04 g of a pale yellow oil which solidified upon standing. A 2.00-g sample of the crude product was chromatographed by a gravity column (2.5 × 60 cm) on silica gel, eluting with ethyl acetate/hexane (60:40), to give 1.67 g (88.7% yield) pure **1** as a mixture of diastereomers. Anal. Calcd for $C_{15}H_{17}O_4P$: C, 61.64; H, 5.87; P, 10.59. Found: C, 61.81; H, 5.87; P, 10.14. The diastereomers were separated by preparative HPLC on silica gel, eluting with ethyl acetate/hexane (60:40) to give pure *cis*-**1** as a colorless crystalline solid: mp 134.5°; ^1H NMR (acetone-d_6) δ 1.44–1.57 (m, 2H, norbornyl), 2.78–2.91 (m, 4H, norbornyl), 3.96 (ddd, 2H, -CH_2O-, J_{HH} = 12.0 Hz, J_{HH} = 12.2 Hz, J_{PH} = 7.0 Hz), 4.26 (ddd, 2H, -CH_2O-, J_{HH} = 12.0 Hz, J_{HH} = 3.7 Hz, J_{PH} = 26.5 Hz), 6.21 (m, 2H, vinyl), 7.21–7.44 (m, 5H, aryl); ^{31}P NMR (acetone-d_6) δ −9.34; IR (KBr) 3160, 2972(s), 2940(s), 2870, 1735, 1598, 1580, 1487(s), 1450, 1352, 1335, 1313, 1300(s), 1290(s), 1260, 1249, 1210(s), 1169(s), 1139, 1090, 1050(s), 1020, 1010, 995, 979, 930(s), 903, 870, 845, 827, 800, 758, 738, 722, 690, 614, 582, 563, 498, 439 cm^{-1}; and pure *trans*-**1** as a colorless crystalline solid: mp 122°C; ^{1}H NMR (acetone-d_6) δ 1.43–1.55 (m, 2H, norbornyl), 2.78–2.91 (m, 4H, norbornyl), 3.98 (ddd, 2H, -CH_2O-, J_{HH} = 12.3 Hz, J_{HH} = 11.7 Hz, J_{PH} = 8.2 Hz), 4.27 (ddd, 2H, -CH_2O-, J_{HH} = 12.3 Hz, J_{HH} = 4.1 Hz, J_{PH} = 23.3 Hz), 6.20 (m, 2H, vinyl), 7.20–7.44 (m, 5H, aryl); ^{31}P NMR (acetone-d_6) δ − 1.29; IR (KBr) 3070, 2980(s), 2965(s), 2935, 2920, 2900, 1586, 1486(s), 1459, 1377, 1348, 1337, 1290, 1264(s), 1250, 1200(s), 1172, 1164, 1137, 1120, 1073, 1041(s), 1025, 1015, 993, 970, 964(s), 935, 922, 900, 875(s), 845, 835, 806, 780, 746, 730, 696, 577, 547, 510, 472 cm^{-1}.

*X-ray Single Crystal Structure Study of trans-***1**.[18] Clear colorless crystals of *trans*-**1** were obtained by vapor diffusion of a solution of the compound in ethyl acetate with hexane. A well formed prism was mounted on a Syntex $P\bar{1}$ auto diffractometer equipped with a scintillation counter and graphite-monochromated MoKα radiation. The automatic centering, indexing, and least-squares routines were carried out on 15 reflections to obtain the cell dimensions which are given in Table I. The data were reduced to F_o^2 and $\sigma(F_o^2)$. Lorenz and polarization factors were applied to all reflections. The θ-2θ scan technique over the range 2.5° $\leq 2\theta \leq$ 49° was used to collect the data of which those with $I \geq 3\ \sigma\ (I)$ were considered observed and were used in the calculations.

The structure was solved by direct methods and refined by full-matrix least-squares techniques.[18] Hydrogen atoms were added to the model in geometrically ideal positions and refined isotropically. Refinement converged at

$$R = \Sigma\,|F_o - F_c|/\Sigma\,|F_o| = 0.054$$

$$R_w = \mathrm{SQRT}(\Sigma w(F_o - F_c)^2/\Sigma w F_o^2) = 0.065$$

and

$$\mathrm{GOF} = \mathrm{SQRT}(\Sigma w(F_o - F_c)^2(\text{no. of refls.} - \text{no. of parms.}) = 1.27.$$

In the last difference map, the highest peak was 0.285 $e^-/Å^3$.

5,6-(endo,endo-2',3'-bicyclo[2.2.1]hept-5'-eno)-2-oxy-2-phenyl-1,3,2-dioxaphosphepane, **2**. A solution of 5-norbornene-*endo,endo*-2,3-dimethanol (2.00 g, 13.0 mmol), triethylamine (3.10 mL, 30.0 mmol), and sufficient ethyl acetate to dilute to 100 mL; and a solution of phenylphosphonic dichloride (1.95 mL, 13.0 mmol) and sufficient ethyl acetate to dilute to 100 mL were added simultaneously by dropwise addition to 200 mL of ethyl acetate under anhydrous conditions. The reaction mixture was stirred for 24 h, the triethylamine hydrochloride filtered off, the solid washed with ethyl acetate, and the solvent removed from the filtrate under reduced pressure to give 5.27 g of a yellow solid residue. A 2.00-g sample of the crude product was chromatographed by a gravity column (2.5 × 60 cm) on silica gel, eluting with ethyl acetate/hexane (90:10), to give 1.56 g (58.6% yield) pure **2** as a mixture to diastereomers. Anal. Calcd for $C_{15}H_{17}O_3P$: C, 65.22; H, 6.20; P, 11.20. Found: C, 65.37; H, 6.40; P, 11.05. The diastereomers were separated by preparative HPLC on silica gel, eluting with ethyl acetate/hexane (90:10) to give pure *cis*-**2** as a thick paste: ^{1}H NMR (acetone-d_6) δ 1.08–1.55 (m, 2H, norbornyl), 3.30–3.61 (m, 4H, norbornyl), 4.06 (ddd, 2H, -CH_2O-, J_{HH} = 11.9 Hz, J_{HH} = 11.8 Hz, J_{PH} = 7.1 Hz), 4.27 (ddd, 2H, -CH_2O-, J_{HH} = 11.9 Hz, J_{HH} = 2.5 Hz, J_{PH} = 25.2 Hz), 6.23 (t, 2H, vinyl, J_{HH} = 1.6 Hz), 7.47–7.87 (m, 9H, aromatic); ^{31}P NMR (acetone-d_6) δ 18.08; IR (thin film) 2960-2850, 1400, 1255 (s, P=O), 1100-1020, 795, 700-660 cm^{-1}; and pure *trans*-**2** as a colorless crystalline solid: mp 131–136°C; ^{1}H NMR (C_6D_6) δ 1.00 (dt, 1H, norbornyl bridge, J_{HH} = 8.3 Hz, J_{HH} = 1.4 Hz), 1.20 (dt, 1H, norbornyl bridge, J_{HH} = 8.3 Hz, J_{HH} = 1.9 Hz), 2.18 (m, 2H, norbornyl), 2.42 (m, 2H, norbornyl), 3.70 (ddd, 2H, -CH_2O-, J_{HH} = 12.3 Hz, J_{HH} = 3.8 Hz, J_{PH} = 20.5 Hz), 4.25 (ddd, 2H, -CH_2O-, J_{HH} = 12.3 Hz, J_{HH} = 12.3 Hz, J_{PH} = 8.4 Hz); ^{31}P NMR (acetone-d_6) δ 22.90; IR (KBr) 3050, 2990, 2965(s), 2940, 2900, 2870, 1595, 1568, 1494, 1475, 1453, 1439, 1382, 1339, 1268, 1254, 1230(s), 1177, 1137(s), 1057(s), 1020, 1000, 982, 968, 906, 860(s), 840, 825, 806(s), 746, 730, 711, 693(s), 593, 546, 498, 457, 430 cm^{-1}.

*X-ray Single Crystal Structure Study of trans-***2**.[19] Clear colorless crystals of *trans*-**2** were obtained by vapor diffusion of a solution of the compound in ethyl acetate with hexane. A well formed prism was mounted on a Syntex $P2_1$ auto diffractometer equipped with a scintillation counter and graphite-monochromated MoKα radiation. The automatic centering, indexing, and least-squares routines were carried out on 15 reflections in the range 12.81° $\leq 2\theta \leq$ 29.87° to obtain the cell dimensions which are given in Table I. The data were reduced to F_o and $\sigma(F_o)$. Lorenz and polarization factors were applied to all reflections. The ω-scan technique over the range 4.0° $\leq 2\theta \leq$ 50.0° was used to collect the data of which those with $I \geq 2.5\ \sigma\ (I)$ were considered observed and were used in the calculations.

The structure was solved by the heavy atom method. The phosphorus atom was located from a three-dimensional Patterson map. The remaining atoms were located by subsequent structure factor calculations and difference electron density maps. The structure was refined by full-matrix least-squares techniques.[19] The hydrogen atoms were located by electron density difference maps and added to the model but were not refined. Anisotropic refinement converged at

$$R = \Sigma\,|F_o - F_c|/\Sigma\,|F_o| = 0.040$$

$$R_w = \mathrm{SQRT}(\Sigma w(F_o - F_c)^2/\Sigma w F_o^2) = 0.036$$

and

$$\mathrm{GOF} = \mathrm{SQRT}(\Sigma w(F_o - F_c)^2(\text{no. of refls.} - \text{no. of parms.}) = 2.112.$$

In the last difference map, the deepest hole was −0.210 e⁻/Å³, and the highest peak was 0.240 e⁻/Å³.

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