Heteroatom Chemistry
Volume 4, Number 4, 1993

P-Substituted 3-Phosphabicyclo[3.1.0]hexane 3-Oxides from Diastereoselective Substitution at Phosphorus

György Keglevich,* Attila Kovács, and László Tőke

Department of Organic Chemical Technology, Technical University of Budapest, 1521 Budapest, Hungary

Kálmán Újszászy

EGIS Pharmaceuticals, 1475 Budapest, Hungary

Gyula Argay, Mátyás Czugler, and Alajos Kálmán

Central Research Institute of Chemistry for Hungarian Academy of Sciences, 1525 Budapest, Hungary

Received 6 October 1992

ABSTRACT

Preparation of P-amino-3-phosphabicyclo[3.1.0]-hexane 3-oxides either by addition of dichlorocarbene to the double bond of 1-amino-2,5-dihydro-1H-phosphole 1-oxides or by substitution of the P-chloro derivative of the bicyclic system was accomplished. Two different diastereomers are obtained by the two approaches; their ^{13}C NMR spectra were interpreted on the basis of the P-ethoxy isomers, whose structures were confirmed by X-ray analysis. The P-hydroxy adduct was also prepared, and it was found that intermolecular O–H . . . O hydrogen bonding connects the molecules together in the solid phase. This effect eliminates the possibility of diastereoisomerism, as was also observed in the case of P-hydroxy tetrahydrophosphinine oxides. Thermolysis of the P-hydroxy adduct is a better way to synthesize 1-hydroxy-1,2-dihydrophosphinine oxides than by hydrolysis of the phosphinic chlorides.

INTRODUCTION

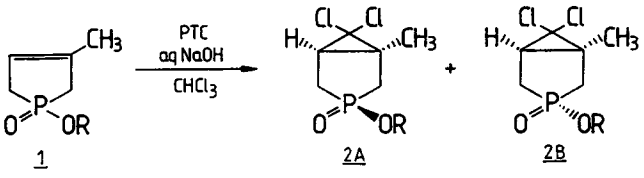
We have recently developed a convenient two-step method for the ring enlargement of P-alkyl- and P-alkoxy-3-phospholene 1-oxides to di- and tetrahydrophosphinine oxides through adducts with dichlorocarbene [1–3]. This article shows how the P-amino, P-chloro, and P-hydroxy derivatives can be prepared by applying this method, as well as by other approaches.

RESULTS AND DISCUSSION

As was shown earlier [2], the addition of dichlorocarbene to the double bond of P-alkoxy-2,5-dihydro-1H-phosphole 1-oxides (**1**) provided the adducts (**2**) as the mixture of two diastereomers (Scheme 1). The two sets of ^{13}C NMR signals could only be assigned tentatively to the two diastereomers [4]. Now we have been successful in obtaining one of the isomers of adduct **2a** in crystalline form suitable for single-crystal X-ray analysis. It turned out that we had diastereoisomer **2Ba** in hand, where the phosphoryl oxygen and the dichlorocyclopropane ring are in the *cis* disposition (Figure 1; positional parameters are listed in Table 1, while selected bond parameters can be found in Table 2). The ^{13}C NMR spectrum of known struc-

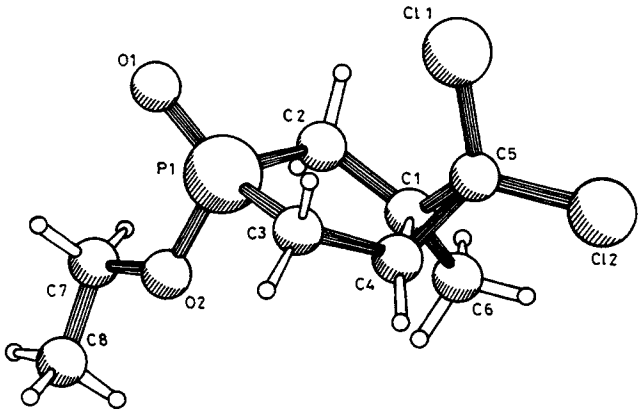
*To whom correspondence should be addressed.

1042-7163/93/$5.00 + .25



1 2A 2B

SCHEME 1



2B a

FIGURE 1 Perspective view of **2Ba**; hydrogen atoms are shown but not labeled.

TABLE 1 Positional Parameters for **2Ba** with Estimated Standard Deviations

Atom	*x*	*y*	*z*	*B* (Å²)
CL1	0.4001(3)	0.1587(3)	0.0541(1)	5.38(5)
CL2	0.2385(4)	0.5016(4)	0.0091(1)	6.45(6)
P1	0.4904(2)	0.2440(3)	0.2398(1)	3.73(4)
O1	0.5707(7)	0.0628(9)	0.2573(4)	5.3(1)
O2	0.4755(6)	0.3775(9)	0.3052(3)	4.4(1)
C1	0.4372(9)	0.492(1)	0.1358(4)	3.7(2)
C2	0.577(1)	0.383(1)	0.1746(5)	4.6(2)
C3	0.2817(9)	0.246(1)	0.2032(5)	4.3(2)
C4	0.2701(9)	0.406(1)	0.1497(4)	3.6(2)
C5	0.335(1)	0.381(1)	0.0800(5)	4.0(2)
C6	0.455(1)	0.699(1)	0.1287(5)	5.6(2)
C7	0.615(1)	0.426(2)	0.3521(6)	7.0(3)
C8	0.579(1)	0.559(2)	0.4036(6)	8.4(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3) * [*a*2 * *B*(1,1) + *b*2 * *B*(2,2) + *c*2 * *B*(3,3) + *ab*(cos gamma) * *B*(1,2) + *ac*(cos beta) * *B*(1,3) + *bc*(cos alpha) * *B*(2,3)]

TABLE 2 Selected Bond Lengths and Angles for **2Ba** and **6** with Their Estimated Standard Deviations

Atoms	*2Ba*	*6*
C1-C2	1.53(1)	1.53(1)
C1-C4	1.56(1)	1.534(8)
C1-C5	1.52(1)	1.47(1)
C3-C4	1.53(1)	1.51(1)
C4-C5	1.49(1)	1.486(8)
P1-C2	1.79(1)	1.791(6)
P1-C3	1.809(8)	1.786(7)
P1-O1	1.474(7)	1.516(5)
P1-O2	1.585(6)	1.520(5)
O1-P1-O2	114.1(4)	113.5(3)
O1-P1-C2	116.0(4)	113.5(3)
O1-P1-C3	119.4(4)	112.0(3)
O2-P1-C2	106.5(4)	109.5(3)
O2-P1-C3	99.4(4)	109.3(3)
C2-P1-C3	99.0(4)	97.9(3)

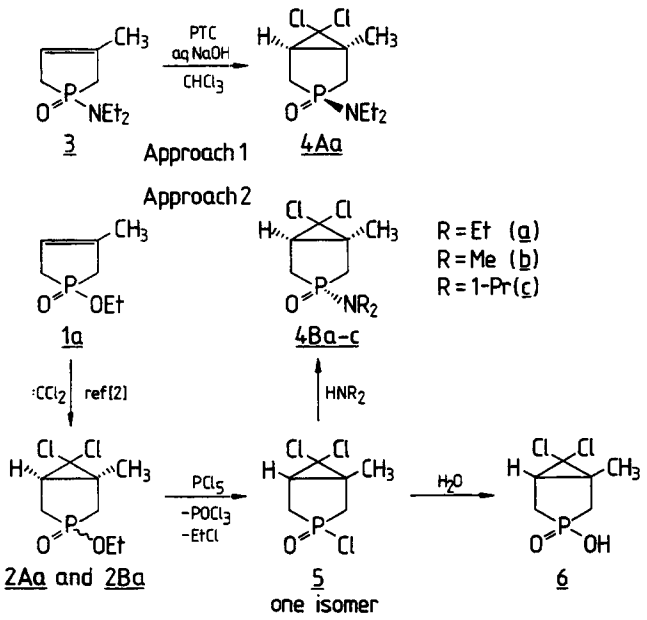
ture **2Ba** made possible the correct characterization of both isomers (Table 3) and showed that the earlier tentative assignment [4] should be reversed. As will be shown below, correct assignment of the isomers can be well utilized in the structure elucidation of other P-substituted derivatives.

We tried to extend our method to the preparation of P-amino adducts. The reaction of 1-diethylamino-3-methyl- 2, 5 -dihydro-1H-phosphole 1-oxide **3** with dichlorocarbene generated from chloroform by sodium hydroxide under phase transfer catalytic conditions [5] afforded the expected adduct (**4a**) as a single isomer (**A**) in poor yield (14%) (Approach 1/Scheme 2). Hopefully, to improve the yields, another approach was also tried. Diastereoisomeric adduct **2a** obtained from **1a** by dichlorocarbene addition was converted to the P-chloro intermediate **5** by reaction with phosphorus pentachloride. The intermediate **5** proved to be a single isomer on the basis of its ^{13}C NMR spectrum (Table 3). The reason for the disappearance of the diastereoisomerism during the reaction with phosphorus pentachloride must be due to the higher stability of one of the isomers. Reaction of **5** with secondary amines, including diethylamine, afforded the expected products (**4a–c**) in better overall yields (~37%) after column chromatography. Again, single diastereomers were found to have been formed. ^{13}C NMR spectra (Table 3) showed, however, that the isomer formed was not identical with that formed by the direct dichlorocarbene addition reaction. Hence, it must be assumed that the other diastereomer (**B**) is the result of the second approach (Approach 2/Scheme 2) and both approaches are diastereoselective. Structures **4A** and **4B** were assigned by comparing the ^{13}C NMR data with those of the isomers (**A** and **B**) of the P-ethoxy adduct (**2a**) (Table 3). Due to the unknown ster-

TABLE 3 ^{13}C NMR Spectral Data for the **A** and **B** Diastereoisomers of P-Substituted 6,6-Dichloro-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-Oxides (**2**, **4a–c**, **5**, and **6**) in $CDCl_3$ Solutions

	δ ^{13}C NMR (J_{PC} in Hz)								
Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
2Aa[a]	[b]	31.7 (96.6)	25.7 (91.6)	32.6 (12.4)	71.0 (12.4)	21.3 (8.1)	61.6 (7.3)	15.9 (4.4)	—
2Ba[a]	30.9 (12.4)	30.3 (90.2)	24.5 (90.1)	31.9 (10.3)	71.6 (12.4)	21.1 (8.1)	60.2 (6.6)	16.1 (5.9)	—
4Aa	32.5 (11.7)	32.7 (82.8)	26.5 (82.0)	34.4 (9.6)	72.0 (10.2)	21.4 (7.4)	38.6 (2.9)	14.2 (3.0)	—
4Ba	31.4 (12.5)	31.5 (82.8)	25.5 (82.8)	32.6 (11.0)	73.2 (16.9)	21.2 (5.8)	38.2 (3.7)	13.7 (2.2)	—
4Bb	31.4 (12.5)	30.2 (83.6)	24.2 (83.5)	32.6 (11.0)	72.9 (16.1)	21.3 (5.9)	35.5 (2.9)	—	—
4Bc	31.4 (12.4)	31.5 (83.5)	25.5 (82.7)	32.7 (11.7)	73.5 (16.8)	21.3 (6.6)	45.8 (3.7)	21.3 (1.5)	10.7
5	31.6 (13.2)	32.2 (93.0)	26.4 (92.4)	33.0 (11.7)	72.0 (13.2)	21.4 (8.1)	—	—	—
6	30.4 (16.9)	37.8 (74.7)	32.5 (74.8)	31.4 (15.4)	71.2 (19.1)	21.1 (8.0)	—	—	—

[a]From Ref. [4].
[b]Not resolved.



SCHEME 2

eostructure of the chloride (**5**), we cannot interpret the direction of the substitution at phosphorus. It should be mentioned, however, that diastereoselective substitution at the tetracoordinate phosphorus of a five-ring species is not unknown: hydrolysis of a cyclic phosphinate ester was found to proceed with inversion of configuration [6].

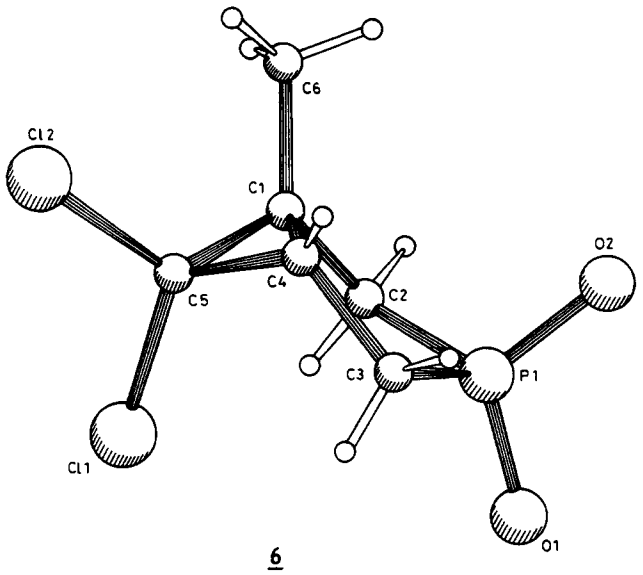
Hydrolysis of the chloro-intermediate provided again a single product, phosphinic acid **6**,

TABLE 4 Positional Parameters for **6** with Estimated Standard Deviations

Atom	*x*	*y*	*z*	$B(Å^2)$
CL1	0.6138(2)	0.1583(3)	0.1181(2)	5.81(4)
CL2	0.5771(2)	0.5239(4)	0.2090(2)	7.64(5)
P1	0.9061(1)	0.2523(2)	0.0768(1)	3.31(3)
O1	0.9215(4)	0.0524(6)	0.0359(4)	4.6(1)
O2	1.0078(4)	0.3852(7)	0.0815(4)	4.8(1)
C1	0.7348(5)	0.4830(9)	0.0798(6)	4.1(1)
C2	0.7658(5)	0.359(1)	−0.0139(5)	4.2(1)
C3	0.8870(5)	0.255(1)	0.2240(5)	4.3(1)
C4	0.8023(5)	0.419(1)	0.2143(5)	4.2(1)
C5	0.6709(6)	0.392(1)	0.1532(6)	4.6(2)
C6	0.7212(7)	0.694(1)	0.0523(9)	7.3(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3) * [*a2* * *B*(1,1) + *b2* * *B*(2,2) + *c2* * *B*(3,3) + *ab*(cos gamma) * *B*(1,2) + *ac*(cos beta) * *B*(1,3) + *bc*(cos alpha) * *B*(2,3)]

exhibiting only one series of signals in the ^{13}C NMR spectrum (Table 3). Single-crystal X-ray analysis shows the five-membered ring to be puckered in an envelope form with the P atom on the flap (Figure 2; positional parameters are listed in Table 4). Equidistant positions of both oxygen atoms from the phosphorus one are also shown (Table 2). This, together with the obvious atomic assignment conflicts of the symmetry center related 0 atoms, suggests the $P2_1/c$ structure model to be acceptable only as a disordered one. Such a disordered structure can be visualized as if centers of symmetries were lacking between the center related pairs of



6

FIGURE 2 Perspective view of **6**; hydrogen atoms are shown but not labeled.

molecules of the $P2_1/c$ space group, thus enabling these molecules to form ordinary hydrogen-bonded spirals along the crystallographic *b* axis (Figure 3). The $\vartheta_{P=O}$ and ϑ_{P-O} stretching vibrations in the IR spectrum of **6** at 1200 and 965 cm^{-1}, respectively, refer also to the hydrogen bonding [7]. Dimeric [8] or linear (chain) [9] associations were also pointed out earlier for several dialkylphosphinic acids.

Products **4Aa**, **4Ba–c**, and **6** were also characterized by ^1H NMR and mass spectral parameters (see the Experimental section).

Two approaches have been tried to prepare double-bond isomers of the P-hydroxy dihydrophosphinine oxide (**7** and **8**). In the first approach, the mixture of products **7** and **8** was obtained by the thermolysis of adduct **6** (Scheme 3). In the other route, the isomers of the 1-ethoxy dihidrophosphinine oxides (**9** and **10**) were transformed to the chlorides (**11** and **12**) [10] which gave the phosphinic acids (**7** and **8**) on hydrolysis (Scheme 3). Being a neat reaction without side-products, the preparation by thermolysis is more advantageous than that by substitution.

We were not, however, successful in synthesizing the P-aminodihydrophosphinine oxides. The thermolysis procedure led to decomposition products, while reaction of P-chloro-intermediates **11** and **12** with dialkylamines was complicated by addition to the conjugated double bond and displacement of chlorine from the carbon atom in position 4.

Finally, it seemed to be of interest to synthesize another cyclic phosphinic acid with two chiral centers. Double-bond isomers of the 1-ethoxy-3-methoxy tetrahydrophosphinine oxides (**13** and **14**) [3] were transformed to the mixture of phosphinic acids **15** and **16** by conversion to the chlorides followed by hydrolysis (Scheme 4). Although the starting esters were used as a diastereomeric mixture, the acids proved to be of uniform composition. The lack of the stereoisomerism must be due to the intermolecular hydrogen bonding, which causes equivalence of the two oxygen functions.

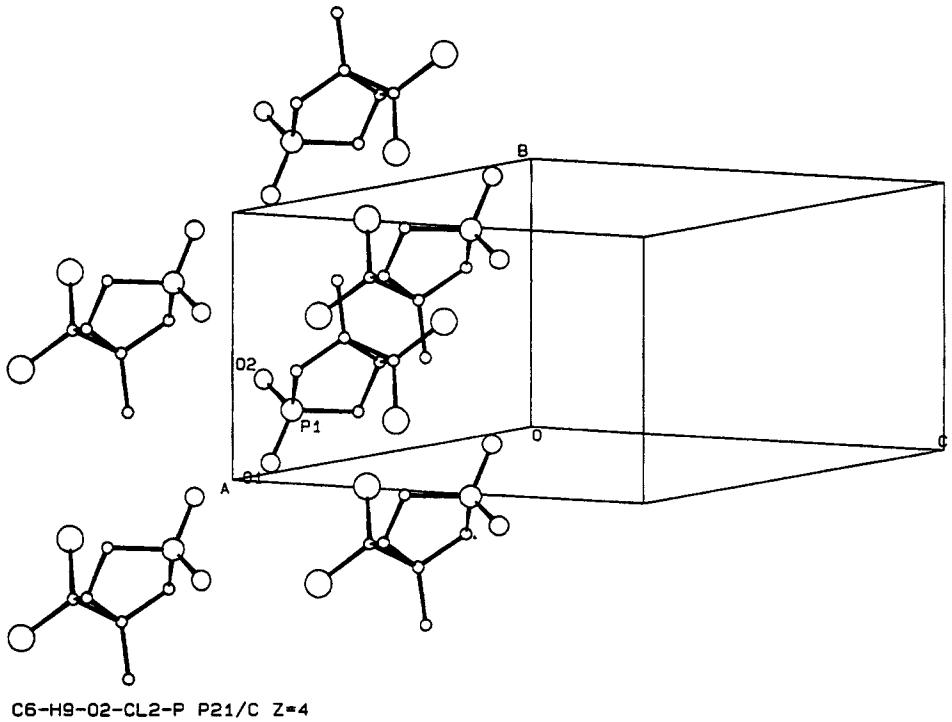
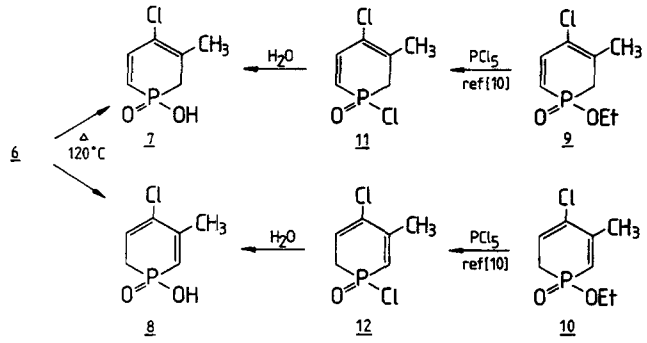
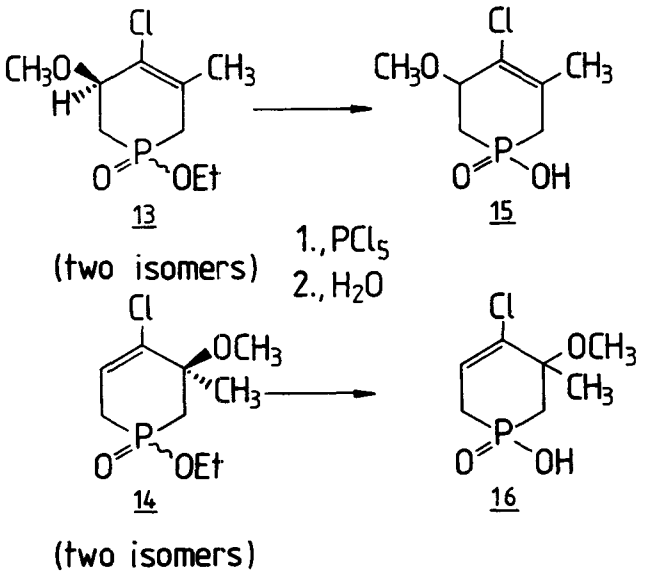


FIGURE 3 Perspective view of a portion of the crystal structure of **6** showing symmetry center related molecules in the $P2_1/c$ space group (molecules are hydrogen bonded along the *b* axis in a disordered crystal such that centers of symmetries must not exist in a presumably lower symmetry space group).



SCHEME 3



SCHEME 4

EXPERIMENTAL

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were taken on a JEOL FX 100 spectrometer operating at 40.26, 25.0, and 100 MHz, respectively. Chemical shifts are downfield relative to 85% phosphoric acid and to tetramethylsilane for both ^{1}H and ^{13}C NMR spectra. Infrared spectra were recorded on a SPECORD 75 spectrometer. Mass spectra were obtained on an MS 25-RFA instrument at 70 eV.

6.6-Dichloro-3-diethylamino-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-Oxide (**4Aa**)

A solution of sodium hydroxide (25.2 g, 0.63 mol) in water (25 mL) was added dropwise to a mixture of 1-diethylamino-3-methyl-2.5-dihydro-1H-phosphole 1-oxide (**3**) (3.9 g, 20.9 mmol) [11], triethylbenzylammonium chloride (0.9 g, 3.96 mmol), and alcohol-free chloroform (80 mL), which was stirred in an ice bath. After completion of the addition, the cooling bath was removed and the temperature of the mixture rose gradually to reflux. After stirring for 7 hours, the content of the flask was filtered. The oily residue obtained after removing the solvent of the organic phase in vacuo was purified by repeated column chromatography (silica gel, 3% methanol in chloroform, and benzene-acetone 8:2) to give the **A** diastereomer of **4a** (0.8 g, 14%); ^{13}C NMR. Table 1; ^{1}H NMR ($CDCl_3$) δ 1.14 (t, 6H, $CH_2C\underline{H}_3$, J = 7 Hz), 1.55 (s, 3H, C_1–CH_3), 1.65–2.65 (m, 5H, PCH_2, CH), 3.05 (dq, 4H, $C\underline{H}_2CH_3$, $^{3}J_{PH}$ = 11 Hz); MS, m/z (relative intensity) 269 (M^+, 13), 254 (10), 234 (100), 118 (52), 72 (88); IR (neat) 2950, 1440, 1370, 1210, 800 cm^{-1}; M^+_{found} = 269.0534, $C_{10}H_{18}Cl_2NOP$ requires 269.0503 for the isotope having two ^{35}Cl atoms.

6.6-Dichloro-3-diethylamino-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-Oxide (**4Ba**)

Phosphorus pentachloride (3.61 g, 17.3 mmol) was added to 4.0 g (16.5 mmol) of the mixture of **2Aa** (42%) and **2Ba** (58%) [2,4] in dichloromethane (50 mL). The content of the flask was stirred for 30 minutes at room temperature and for 3 hours at reflux. Evaporation of the volatile components in vacuo gave phosphinic chloride **5** (3.85 g) in a form suitable for further transformation; ^{31}P NMR ($CDCl_3$) δ + 96.3; ^{13}C NMR, Table 2; MS, m/z (relative intensity) 232 (M^+, 11), 217 (6), 197 (100), 79 (79). Diethylamine (3.5 mL, 33.8 mmol) in benzene (20 mL) was added dropwise at 0°C to the benzene (40 mL) solution of **5** (3.85 g, 16.5 mmol) from the previous reaction. After completion of the addition, the cooling bath was removed and the mixture stirred for 2 hours at room temperature. The amine hydrochloride was filtered off and washed with benzene. Solvent of the combined benzene solutions was removed under reduced pressure, and the residue was purified by repeated column chromatography (silica gel, 3% methanol in chloroform, and benzene-acetone 4:6) to give the **B** diastereomer of **4a** (1.6 g, 36%); ^{31}P NMR ($CDCl_3$) δ + 74.4; ^{13}C NMR, Table 3; ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 6H, $CH_2C\underline{H}_3$, J = 7 Hz), 1.56 (s, 3H, C_1–CH_3), 1.7–2.7 (m, 5H, PCH_2, CH), 2.98 (dq, 4H, $C\underline{H}_2CH_3$, $^{3}J_{PH}$ = 11 Hz); MS, m/z (relative intensity) 269 (M^+, 2), 254 (4), 234 (94), 118 (48), 72 (100); M^+_{found} = 269.0525, $C_{10}H_{18}Cl_2NOP$ requires 269.0503 for the isotope having two ^{35}Cl atoms.

6.6-Dichloro-3-dimethylamino-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-Oxide (**4Bb**)

4Bb was prepared by the procedure described for **4Ba** using dimethylamine in the second step; yield 41%; mp 84–86°C; ^{31}P NMR ($CDCl_3$) δ + 77.5; ^{13}C NMR, Table 3; ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 3H, C_1–CH_3), 1.6–2.2 (m, 5H, PCH_2, CH), 2.58 (d, 6H, PCH_3, $^{3}J_{PH}$ = 10 Hz); MS, m/z (relative intensity) 241 (M^+, 2), 206 (63), 90 (50), 44 (100).

6.6-Dichloro-3-di-n-propylamino-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-Oxide (**4Bc**)

4Bc was prepared by the procedure described for **4Ba** using di-*n*-propylamine in the second step; yield 34%; ^{13}C NMR, Table 3; ^{1}H NMR ($CDCl_3$) δ 0.79 (t, 6H, $CH_2C\underline{H}_3$, J = 7 Hz), 1.44 (m, 4H, $C\underline{H}_2CH_3$), 1.56 (s, 3H, C_1–CH_3), 1.6–2.4 (m, 5H, PCH_2, CH), 2.85 (dt, 4H, NCH_2, $^{3}J_{PH}$ = 10 Hz); MS, *m/z* (relative intensity) 297 (M^+, 4), 268 (74), 262 (63), 232 (48), 118 (88), 100 (59), 72 (100).

6.6-Dichloro-3-hydroxy-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-Oxide (**6**)

To 3.85 g (16.5 mmol) of **5** obtained as described above was added acetone (20 mL) and water (10 mL), and the mixture was stirred at room temperature for 4 hours. Volatile components were removed in vacuo to give a semicrystalline residue. Purification by column chromatography (silica gel, 4% methanol in chloroform) afforded **6** (2.2 g, 62%); mp. 125–126°C dec (from chloroform); ^{31}P NMR ($CDCl_3$) δ + 85.4; ^{13}C NMR, Table 3; ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 3H, CH_3), 1.6–2.6 (m, 5H, PCH_2, CH), 11.8 (s, 1H, POH); MS, *m/z* (relative intensity) 214 (M^+, 7), 199 (2), 179 (60), 79 (100); IR (KBr disc) 1200, 965, 805 cm^{-1}; Anal. calcd for $C_6H_9Cl_2O_2P$: C, 33.52; H, 4.22. Found: C, 33.83; H, 4.44.

5-and 3-Methyl-4-chloro-1,2-dihydro-1-hydroxyphosphinine (**7** *and* **8**)

By the Thermolysis Procedure. Compound **6** (0.3 g, 1.4 mmol) in a small vial was heated at 135°C for 4.5 minutes. The crude product was purified by flash column chromatography on silica gel using 4% methanol in chloroform as the eluant to give a mixture (0.13 g, 52%) containing 80% of **7** and 20% of **8**; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 2.4H, CH_3 of **7**), 2.05 (d, 0.6H, CH_3 of **8**, $^{4}J_{PH}$ = 1.2 Hz), 2.52–2.90 (m, 2H, CH_2), 6.0 (t, P–CH= of **7**, $^{2}J_{PH}$= $^{3}J_{HH}$ = 11), overlapping the signals of the olefinic protons in **8**, total intensity 1.20H, 6.62 (dd, 0.80H, P–CH=C$\underline{H}$, $^{3}J_{PH}$ = 40 Hz, $^{3}J_{HH}$ = 13 Hz), 10.8 (s, 1H, OH); MS, *m/z* (relative intensity) 178 (M^+, 62), 160 (13), 114 (18), 79 (100); M^+_{found} = 177.9915, $C_6H_8ClO_2P$ requires 177.9950 for the isotope having two ^{35}Cl atoms.

7: ^{31}P NMR ($CDCl_3$) δ + 33.1; ^{13}C NMR ($CDCl_3$) δ 24.6 ($^{3}J_{PC}$ = 14.7 Hz, C–CH_3), 28.8 ($^{1}J_{PC}$ = 99.7 Hz, C_2), 119.3 ($^{1}J_{PC}$ = 129.7 Hz, C_6), 123.3 ($^{2}J_{PC}$ ~ 10 Hz, C_3), 131.6 ($^{3}J_{PC}$ ~ 20 Hz, C_4), 150.3 (C_5).

8: ^{31}P NMR ($CDCl_3$) δ + 32.4; ^{13}C NMR ($CDCl_3$) δ 23.3 ($^{3}J_{PC}$ = 10.3 Hz, C–CH_3), 34.5 ($^{1}J_{PC}$ = 100.4 Hz, C_2), 120.0 ($^{1}J_{PC}$ = 126.0 Hz, C_6), 123.5 ($^{3}J_{PC}$ = 22.7 Hz, C_4), 131.8 ($^{2}J_{PC}$ = 8.8 Hz, C_3), 144.3 (C_5).

By Substitution at Phosphorus. Isomers of the P-ethoxy dihydrophosphinine oxides (**9** and **10**) were transformed to the chlorides (**11** and **12**), as described in Ref. [10]. Hydrolysis of **11** and **12** and the work-up procedure were performed, as shown for the hydrolysis of **5** (above). The mixture of **7A** and **7B** was isolated in a purity of ~90%; yield 27%.

5- and 3-Methyl-4-chloro-1-hydroxy-3-methoxy-1,2,3,6-tetrahydrophosphinine 1-Oxide (**15** *and* **16**)

Phosphorus pentachloride (0.77 g, 3.69 mmol) was added to the dichloromethane solution (20 mL) of the mixture of **13** and **14** (0.84 g, 3.52 mmol) [3]. The mixture was stirred for 15 minutes at room temperature and for 3 hours at reflux. Evaporation of the volatile components in vacuo gave the P-chloro compound, which was hydrolyzed with water (5 mL) in acetone (10 mL), as shown for **5** (above) to give a 55:45 mixture of **15** and **16** (0.36 g, 49%); ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 1.35H, C–CH_3 of **16**), 1.96 (s, 1.65H, CH_3 of **15**), 2.0–3.0 (m, 4H, CH_2), 3.17 (s, 1.35H, OCH_3 of **16**), 3.39 (s, 1.65H, OCH_3 of **15**), 4.20 (dt, 0.55H, OCH, $^{3}J_{PH}$ = 19.2 Hz), 6.03 (dt, 0.45H, CH=, $^{3}J_{PH}$ = 30.0 Hz), 11.7 (bs, 1H, OH); MS, *m/z* (relative intensity) 210 (M^+, 4), 195 (51), 179 (26), 178 (78), 175 (22), 114 (13), 79 (100); M^+_{found} = 210.0186, $C_7H_{12}ClO_3P$ requires 210.0212 for the isotope having two ^{35}Cl atoms.

15: ^{13}C NMR ($CDCl_3$) δ 23.1 ($^{3}J_{PC}$ = 11.0 Hz, C–CH_3), 31.0 ($^{1}J_{PC}$ ~ 90 Hz, C_6), 33.3 ($^{1}J_{PC}$ = 92.3 Hz, C_2), 56.6 (OCH_3), 79.3 (C_3), 128.3 ($^{3}J_{PC}$ ~ 10 Hz, C_4), 128.8 ($^{3}J_{PC}$ = 5.9 Hz, C_5).

16: ^{13}C NMR ($CDCl_3$) δ 26.2 (C–CH_3), 28.0 ($^{1}J_{PC}$ = 87.9 Hz, C_6), 34.6 ($^{1}J_{PC}$ ~ 85 Hz, C_2), 50.3 (OCH_3), 122.0 ($^{2}J_{PC}$ = 4.4 Hz, C_5), 138.4 ($^{3}J_{PC}$ = 10.3 Hz, C_4).

X-ray Crystal Structure Determination for **2Ba**

Crystals of $C_8H_{13}O_2Cl_2P$ (M_w = 243.07) are monoclinic, space group $P2_1/n$, a = 8.292(1), b = 7.107(1), c = 19.150(2) Å, β = 95.04(1)°, V = 1124.1(3) Å^3, Z = 4, D_c = 1.440 gcm^{-3}. X-ray data were collected from a crystal, having dimensions of 0.25 × 0.30 × 0.30 mm^3, by an Enraf-Nonius CAD4 diffractometer using graphite monochromated CuK_α radiation (λ = 1.54184 Å, ω – 2θ scan range 2 < 2θ < 148°, scan width 0.6 + 0.14 tg θ). A total of 2394 unique, not systematically absent reflections were collected. For the structure analysis and refinement, 1663 reflections taken with $F_0 > 3\sigma(F_0)$ were applied. Linear decay correction (from 1.0 to 1.246 on I) was used. The structure was solved by direct methods and refined anisotropic mode for 118 variables to a final R = 0.087 (R_w = 0.103, S = 2.368). The highest residual peak in the final difference electron density map was 0.47(14) eÅ^{-3}. The hydrogen positions were generated from assumed geometries. All calculations have been done by the aid of MolEN [12].

X-ray Crystal Structure Determination for **6**

Crystals of $C_6H_9O_2Cl_2P$ (M_w = 215.02) are monoclinic, space group $P2_1/c$, a = 11.952(3), b = 7.042(1), c = 11.495(3) Å, β = 110.92(2)°, V = 903.7(2) Å^3, Z = 4, D_c = 1.580 gcm^{-3}. X-ray data were collected from a crystal, having dimensions of 0.08 × 0.14 × 0.30 mm^3 as above (graphite monochromated CuK_α radiation, λ = 1.54184 Å, $\omega - 2\theta$ scan range $3 < 2\theta < 146°$, scan width 0.8 + 0.26 tg θ). Out of 1913 observations, 1804 were unique and nonzero. For the structure analysis and refinement, 1260 reflections taken with $F_0 > 3\sigma(F_0)$ were applied. Linear decay correction (from 1.0 to 1.06 on I) was used. The structure was solved and refined in the same way as for **2Ba** (for 100 variables to a final R = 0.066 R_w = 0.083, R_{tot} = 0.089, S = 2.32). The highest residual peak in the final difference electron density map was 0.64(9) eÅ^{-3}. The hydrogen positions were generated from assumed geometries and were not refined. No hydrogen position for the OH group could be suggested from this model. All calculations were performed as above.

ACKNOWLEDGMENTS

Gy. Keglevich is indebted to Prof. Louis D. Quin (University of Massachusetts, Amherst, MA) for his advice. The OTKA support of this work is gratefully acknowledged (Grant No. 1170).

Supplementary Material Available

List of bond distances, bond angles, torsion angles, and displacement parameters for **2Ba** and **6**. Ordering information is given on any current masthead page.

REFERENCES

[1] Gy. Keglevich, I. Petneházy, P. Miklós, A. Almásy, G. Tóth, L. Tőke, L. D. Quin, *J. Org. Chem., 52*, 1987, 3983; Gy. Keglevich, G. Tóth, I. Petneházy, P. Miklós, L. Tőke, *J. Org. Chem., 52*, 1987, 5721; Gy. Keglevich, B. Androsits, L. Tőke, *J. Org. Chem., 53*, 1988, 4106.

[2] Gy. Keglevich, J. Brlik, F. Janke, L. Tőke, *Heteroatom Chem., 1*, 1990, 419.

[3] Gy. Keglevich, L. Tőke, A. Kovács, G. Tóth, K. Újszászy, *Heteroatom Chem.*, in press.

[4] Gy. Keglevich, F. Janke, V. Fülöp, A. Kálmán, G. Tóth, L. Tőke, *Phosphorus Surfur, 54*, 1990, 73.

[5] W. P. Weber, G. W. Gokel: *Phase Transfer Catalysis in Organic Synthesis*, Springer-Verlag, Berlin, p. 18 (1977).

[6] P. M. Cullis, A. D. Kaye, *J. Chem. Soc. Chem. Comm.*, 1992, 346.

[7] S. T. King, *J. Phys. Chem., 74*, 1970, 2133.

[8] A. V. Nikolaev, L. N. Mazalov, E. A. Gal'tsova, Yu. A. Dyadin, A. P. Zeif, N. I. Yakovleva, V. V. Murakhtanov, *Dokl. Akad. Nauk SSSR, 181*, 1968, 119.

[9] F. Giordano, A. Ripomonti, *Acta Crystallogr., 22*, 1967, 678.

[10] Gy. Keglevich, K. Újszászy, A. Kovács, L. Tőke, *J. Org. Chem.*, in press.

[11] L. D. Quin, J. Szewczyk, *Phosphorus Sulfur, 21*, 1984, 161.

[12] MolEN, An Interactive Structure Solution Procedure, Enraf-Nonius Delft, The Netherlands, 1990.