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A New P-Heterocyclic Family: A Variety of Six-Membered and Bridged P-Heterocycles with 1-Benzyl Substituent

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ABSTRACT: *The ring enlargement of 1-benzyl-2,5-dihydro-1H-phosphole oxide (***1***) via the corresponding 2-phosphabicyclo[3.1.0]hexane 2-oxide (***2***) afforded, depending on the conditions, the double bond isomers (***A*** and* ***B***) *of 1,2-dihydrophosphinine oxide* **4** *or that of 3-substituted 1,2,3,6-tetrahydrophosphinine oxides* **5** *and* **6**. *Dihydrophosphinine oxides (***4***) were suitable starting materials for 1,2,3,4,5,6-hexahydrophosphinine oxide* **7** *and 1,2,3,6-tetrahydrophosphinine oxide* **8** *obtained by reductive approaches and for the double bond isomers (***A*** and* ***B***) *of 2-phosphabicyclo[2.2.2]octadiene 2-oxide* **9** *and phosphabicyclooctene oxide* **10** *prepared in Diels–Alder cycloaddition. Precursor* **9** *was utilized in the fragmentation-related phosphorylation of alcohols.*

The paper is dedicated to Professor Dr. Csaba Szántay on the occasion of his 80th birthday.

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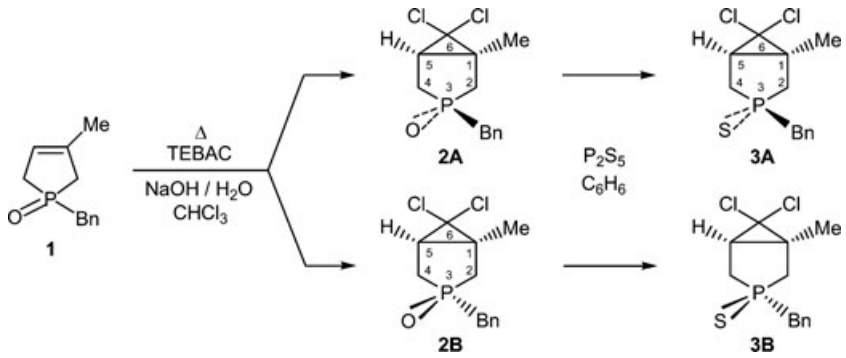
INTRODUCTION

P-Heterocycles have attracted much attention recently and represent a growing field mainly from the point of view of their use as P-ligands [1]. In our laboratory, a ring enlargement method was developed making available a variety of 2-phosphabicyclo[3.1.0]hexane oxides, 1,2- and 1,4-dihydrophosphinine oxides, different 1,2,3,6-tetrahydrophosphinine oxides, 1,2,3,4,5,6-hexahydrophosphinine oxides, phosphepine oxides, and bridged phosphabicyclo[2.2.2]octene derivatives [2–6], the latter being precursors of low-coordinate fragments useful in the phosphorylation of nucleophiles [6]. The intermediates of the above P-heterocycles are the suitably substituted 2,5-dihydro-1*H*-phosphole 1-oxides available easily. The 1-benzyl-P-heterocycles form a relatively less studied group; only simple derivatives,



SCHEME 1

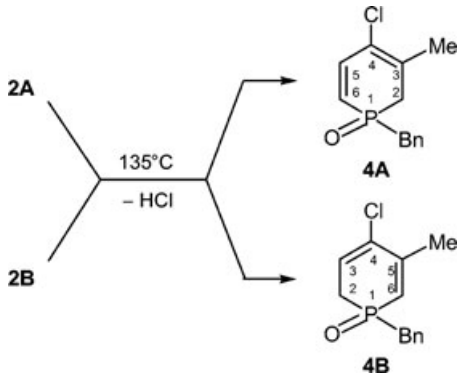
such as the corresponding 1*H*-phosphole [7], 2,5-dihydro- and 2,3,4,5-tetrahydro-1*H*-phosphole oxides [8,9], as well as some other species including 7-phosphanorbornene 7-oxides [10] have been described. In this paper, the 1-benzyl derivatives of a variety of six-membered P-heterocycles, mainly phosphinines, as well as bridged P-heterocycles, such as phosphabicyclooctenes, are discussed.

RESULTS AND DISCUSSION

1-Benzyl-2,5-dihydro-1*H*-phosphole 1-oxide **1** was subjected to dichlorocyclopropanation reaction using dichlorocarbene generated from chloroform by aqueous sodium hydroxide under phase transfer catalytic conditions, as described for other cases [2]. 2-Phosphabicyclo[3.1.0]hexane 3-oxide **2** was obtained as a 3:1 mixture of two (**A** and **B**) diastereomers (Scheme 1). The stereochemical assignment was justified by earlier arguments [11]. The isomeric mixture of phosphabicyclohexane oxide (**2**) was converted to the corresponding sulfide **3** with phosphorus pentasulfide (Scheme 1).

The second step of the ring enlargement involved opening of the dichlorocyclopropane ring, which was carried out thermally to afford a 3:1 mixture of the double bond isomers (**A** and **B**) of dihydrophosphinine oxide **4** (Scheme 2) or was done under solvolytic conditions applying silver nitrate and methanol or water to give a mixture of the double bond isomers (**A** and **B**) of 3-methoxy- or 3-hydroxy-1,2,3,6-tetrahydrophosphinine oxides **5** and **6**, respectively (Scheme 3). The double bond isomer (**A** and **B**) of compounds **5** and **6** consisted of diastereomers.

In the next part of our project, 1,2-dihydrophosphinine oxide (**4**) was utilized in the synthesis of other P-heterocycles. Catalytic hydrogenation of the isomeric mixture of **4** furnished 1,2,3,4,5,6-hexahydrophosphinine oxide **7**

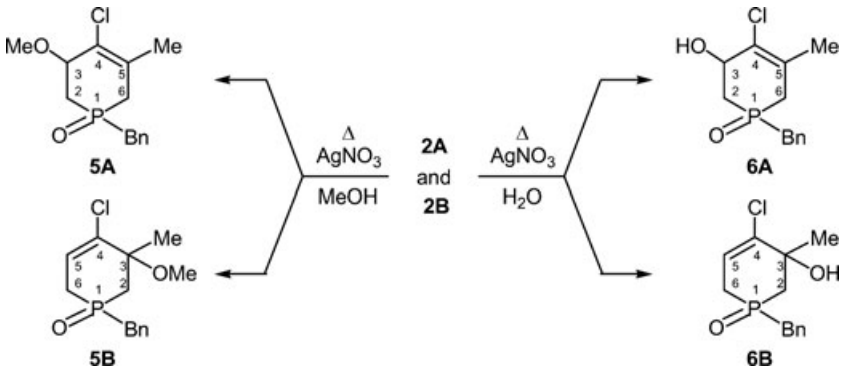


SCHEME 2

as a mixture of two diastereomers (Scheme 4). It was found earlier that the hydrogenation of 2-phosphabicyclo[3.1.0]hexane oxides at somewhat more forcing conditions may also lead to the corresponding hexahydrophosphinine oxides [12]. However, transformation of the isomeric mixture of phospabicyclohexane **2** to **7** was not too efficient. The reason for this experience may stem the sensitivity of the P-benzyl moiety under hydrogenation.

A selective reduction of the electron-poor double bond of the isomers **A** and **B** of dihydrophosphinine oxide **4** was achieved by dimethylsulfide borane. The reduction of isomer **4A** was found to be more efficient than that of **4B**. Hence, the 3:1 isomeric ratio of starting isomers **4A** and **4B** was shifted to 9:1 in regard to products **8A** and **8B** (Scheme 5).

Finally, 1,2-dihydrophosphinine oxides **4A** and **4B** were used as dienes in the Diels–Alder reaction. In cycloaddition with dimethyl acetylenedicarboxylate (DMAD) and *N*-phenylmaleimide (NPMI), the double bond isomers (**A** and **B**) of 2-phosphabicyclo[2.2.2]octadiene **9** and phosphabicyclooctene **10** were formed, respectively (Scheme 6). Isomers **9A** and **9B** consisted of two diasteromers.



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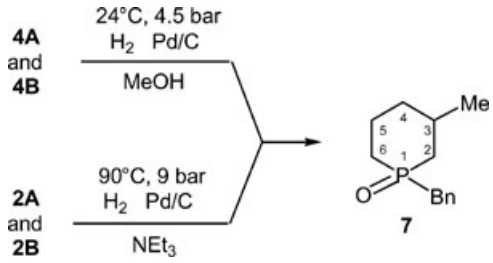


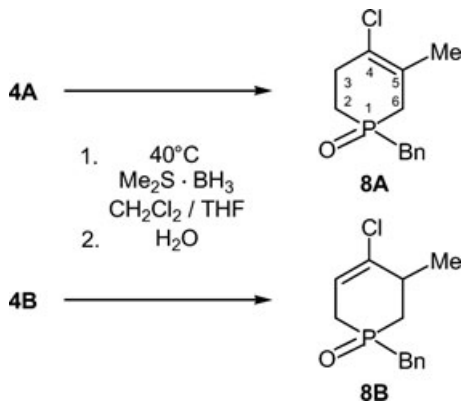
SCHEME 4

The bridged P-heterocycles **9** and **10** were tested in the UV light mediated fragmentation-related phosphorylation of simple alcohols. Irradiation of the acetonitrile solution of the isomeric mixture of phosphabicyclooctadiene **9** in the presence of methanol, ethanol, propanol, and butanol at 254 nm led to phosphinates **11a–d** (Scheme 7). Surprisingly, precursor **10** was not found to be useful in similar phosphorylations due to intensive decomposition in UV light. In the presence of methanol, the photolysis of **10** led to by products, revealing ^{31}P NMR shifts at 39.2 and 40.5 ppm that could not be identified yet. The expected phosphinate (**11a**) was formed only in small proportion (less than 5%).

It is recalled that in the case of phenyl substitution, the use of the corresponding dihydrophosphinine oxide–NPMI cycloadduct was more appropriate in photoinduced phosphorylation than that of the DMAD cycloadduct [13].

P-Heterocycles **2–8**, mostly as isomeric pairs, were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass spectral data. At the same time, the spectral parameters of precursors **9** and **10** were compared with those of authentic samples prepared in the meantime under microwave conditions and to be published elsewhere [14].

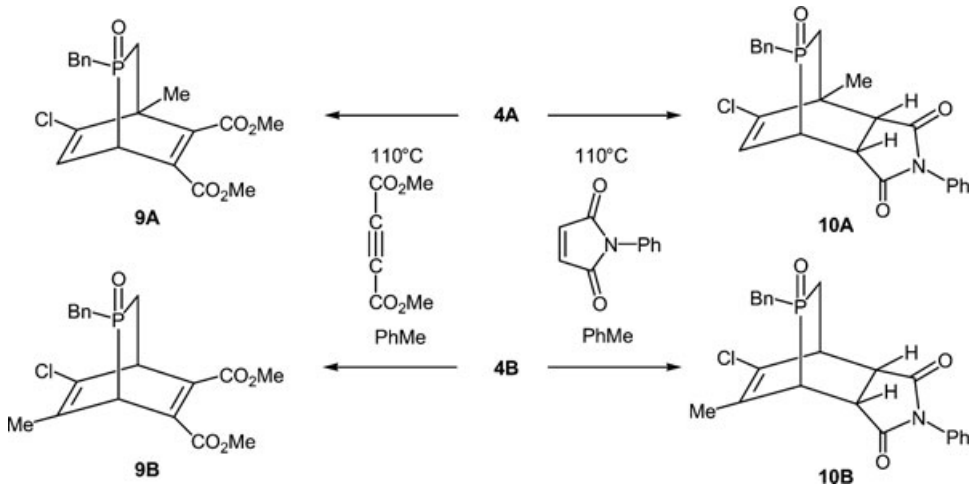
In summary, new benzyl-substituted P-heterocycles including 2-phosphabicyclo[3.1.0]hexane oxide and sulfide, 1,2-dihydro-, 1,2,3,6.tetrahydro- and 1,2,3,4,5,6-hexahydrophosphinine oxides, as well as 2-phosphabicyclo[2.2.2]octadiene derivatives were obtained and characterized. One of the bridged P-heterocycles proved to be an efficient reagent in the photoinduced phosphorylation of alcohols.



SCHEME 5

EXPERIMENTAL

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 and TMS. The couplings are given in hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument. Isomeric ratios were determined on the basis of relative ^{31}P NMR intensities. Photolyses were conducted in a photochemical reactor equipped with a quartz, water-cooled immersion well with a high-pressure mercury lamp (125 W). The starting 1-benzyl-3-



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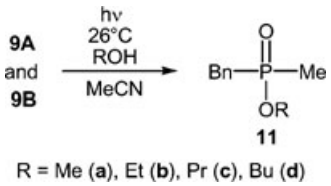

SCHEME 7

methyl-2,5-dihydro-1*H*-phosphole oxide (**1**) was prepared as described earlier [15].

3-Benzyl-6,6-dichloro-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-oxide **2**

To 21.4 g (100 mmol) of dihydrophosphole oxide **1** and 5.0 g (22.0 mmol) of triethylbenzylammonium chloride (TEBAC) in 200 mL of chloroform, 125 g (3.13 mol) of sodium hydroxide in 125 mL of water was added dropwise and the mixture was stirred until it cooled down to room temperature. After filtration and separation, the organic phase was made up to its original volume and 1.7 g (7.5 mmol) of TEBAC was added. The reaction mixture was treated with three more times with aqueous sodium hydroxide (125 g/125 mL, 150 g/150 mL, 150 g/150 mL $NaOH/H_2O$, respectively) as mentioned above. The solution obtained after filtration and separation was concentrated in vacuo, and the residue so obtained was purified by chromatography (2% methanol in chloroform, silica gel) to give 22 g (75%) of a 3:1 mixture of **2A** and **2B**; HRMS, $[M + H]^+_{found} = 289.0310$, $C_{13}H_{16}Cl_2OP$ requires 289.0316.

2A. ^{31}P NMR ($CDCl_3$) δ: 85.6; ^{13}C NMR ($CDCl_3$) δ: 21.0 ($J = 6.0$, CH_3), 28.5 ($J = 64.6$, C4), 34.3 ($J = 65.0$, CPh), 35.3 ($J = 7.5$, C_1), 36.1 ($J = 6.0$, C_5), 36.9 ($J = 55.1$, C2), 71.7 ($J = 8.7$, C_6), 126.6 ($J = 3.0$, $C_{4'}$), 128.4 ($J = 2.5$, $C_{3'}$), 128.9 ($J = 5.3$, $C_{2'}$), 131.3 ($J = 8.1$, $C_{1'}$), C_{ipso}, C_{ortho}, C_{meta}, and C_{para} are marked by $C_{1'}$, $C_{2'}$, $C_{3'}$ and $C_{4'}$, respectively; ^1H NMR ($CDCl_3$) δ: 1.63 (s, 3H, CH_3), 2.03–2.22 (m, 1H, C_5-H), 2.25–2.45 (m, 2H, CH_2), 2.52–2.80 (m, 2H, CH_2), 3.31 (d, 2H, $J = 12.8$, CH_2Ph), 7.15–7.45 (m, 5H, Ar).

2B. ^{31}P NMR ($CDCl_3$) δ: 82.4; ^{13}C NMR ($CDCl_3$) δ: 20.3 ($J = 7.0$, CH_3), 27.0 ($J = 63.6$, C_4), 33.1 ($J = 63.8$, CPh), 35.4 ($J = 7.3$, C_1), 36.0 ($J = 6.5$, C_5), 37.0 ($J = 54.2$, C2), 71.8 ($J = 11.6$, C_6), 126.8 ($J = 2.9$, $C_{4'}$), 128.5 ($J = 2.4$, $C_{3'}$), 129.0 ($J = 5.1$, $C_{2'}$), 130.7 ($J = 7.2$, $C_{1'}$); ^1H NMR ($CDCl_3$) δ: 1.50 (s, 3H, CH_3).

3-Benzyl-6,6-dichloro-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-sulfide **3**

To 0.30 g (1.0 mmol) of phosphabicyclohexane oxide **2** consisting of isomers **A** (75%) and **B** (25%) in 5 mL of degassed benzene, 0.16 g (0.7 mmol) of P_2S_5 was added and the mixture was refluxed for 20 h under nitrogen. The suspension was filtered, the solvent of the filtrate evaporated, and the residue purified by column chromatography (3% methanol in chloroform, silica gel) to give 0.29 g (91%) of **3** as a 4:1 mixture of diastereoisomers **A** and **B**. HRMS, $[M + H]^+_{found} = 305.0069$, $C_{13}H_{15}Cl_2SP$ requires 305.0087.

3A. ^{31}P NMR ($CDCl_3$) δ: 88.4; ^{13}C NMR ($CDCl_3$) δ: 21.0 ($J = 6.5$, CH_3), 33.3 ($J = 51.7$, C_4), 37.0 ($J = 7.3$, C_1), 38.0 ($J = 6.2$, C_5), 38.5 ($J = 51.2$, CPh), 41.0 ($J = 40.0$, C2), 72.5 ($J = 11.9$, C_6), 127.9 ($J = 3.4$, $C_{4'}$), 129.0 ($J = 2.9$, $C_{3'}$), 129.9 ($J = 5.1$, $C_{2'}$), 131.4 ($J = 7.9$, $C_{1'}$); ^1H NMR ($CDCl_3$) δ: 1.35 (s, 3H, CH_3), 1.75 (ddd,

1H, $J_1 = 18.1$, $J_2 = 8.3$, $J_3 = 2.2$, CH_2), 1.23 (ddd, 1H, $J_1 = 16.0$, $J_2 = 7.6$, $J_3 = 2.0$, CH_2), 2.29–2.43 (m, 2H, CH_2 and CH), 2.65–2.75 (m, 1H, CH_2), 3.36 (dt, 2H, $J = 28.8$, 13.5, CH_2Ph), 7.22–7.40 (m, 5H, Ar).

3B. ^{31}P NMR ($CDCl_3$) δ: 88.6.

1-Benzyl-4-chloro-3-methyl-1,2-dihydrophosphinine 1-oxide **4**

A 0.50 g (1.73 mmol) sample of phosphabicyclohexane oxide **2** consisting of isomers **A** (75%) and **B** (25%) was heated at 135°C in a vial for 4 min (the evolution of hydrochloride acid started after 1 min). The crude product was purified by column chromatography (2% methanol in chloroform, silica gel) to give 0.38 g (87%) of dihydrophosphinine 1-oxide **4** as a 3:1 mixture of **4A** and **4B**. MS, 253 (100, $[M+H]^+$), 154 (68), 136 (67), 91 (93), 69 (82); HRMS, $[M+H]^+_{found} = 253.0555$, $C_{13}H_{15}ClOP$ requires 253.0549.

4A. ^{31}P NMR ($CDCl_3$) δ: 23.9; ^{13}C NMR ($CDCl_3$) δ: 22.2 ($J = 8.4$, CH_3), 31.6 ($J = 69.3$,C_2), 37.0 ($J = 68.1$, C7), 118.0 ($J = 89.9$, C_6), 122.7 ($J = 18.8$, C_3), 126.0 ($J = 3.3$, C_4), 126.1 ($J = 3.3$, $C_{4'}$), 127.8 ($J = 2.8$, $C_{3'}$), 128.6 ($J = 5.3$, $C_{2'}$), 130.0 ($J = 7.9$, $C_{1'}$), 142.4 ($J = 1.2$, C_5); ^1H NMR ($CDCl_3$) δ: 1.96 (s, 3H, CH_3), 2.58 (dd, 1H, $J = 18.6$, 11.3, CH_2), 2.76 (t, 1H, $J = 19.5$, CH_2), 3.26 (dd, 2H, $J = 15.5$, 4.2, CH_2Ph), 6.08 (t, 1H, $J = 12.7$, C_6H), 6.67 (dd, 1H, $J = 34.1$, 12.9, C_5H), 7.22–7.38 (m, 5H, Ar).

4B. ^{31}P NMR ($CDCl_3$) δ: 22.5; ^{13}C NMR ($CDCl_3$) δ: 23.6 ($J = 12.5$, CH_3), 30.2 ($J = 68.0$, C_2), 36.6 ($J = 68.4$, CPh), 117.5 ($J = 93.6$, C_6), 122.2 ($J = 10.2$, C_3), 125.8 ($J = 3.1$, C_4), 126.1 ($J = 3.3$, $C_{4'}$), 127.8 ($J = 2.8$, $C_{3'}$), 128.7 ($J = 5.3$, $C_{2'}$), 130.2 ($J = 8.0$, $C_{1'}$), 143.7 ($J = 1.6$, C_5); ^1H NMR ($CDCl_3$) δ: 2.12 (s, 3H, CH_3).

5- and 3-Methyl-1-benzyl-4-chloro-3-methoxy-1,2,3,6-tetrahydrophosphinine 1-oxide **5**

A solution of 0.40 g (1.38 mmol) of phosphabicyclohexane oxide **2** consisting of isomers **A** (75%) and **B** (25%) and 4.2 g (25.0 mmol) of silver nitrate in 15 mL of methanol was refluxed for 24 h. After filtration, the mixture was extracted with chloroform and the organic phase was dried over sodium sulfate and concentrated. The crude product was purified by column chromatography (3% methanol in chloroform, silica gel) to give 0.29 g (70%) of compound **5** as a 40:28:21:10 mixture of four isomers with a purity of 95%. A further refinement by chromatography led to a 1:1.1:1.2:1 mixture of the isomers. MS, 285 (88, $[M+H]^+$), 253 (64), 137 (100); HRMS, $[M+H]^+_{found} = 285.0799$, $C_{14}H_{19}ClO_2P$ requires 285.0811.

5-1^A.* ^{31}P NMR ($CDCl_3$) δ: 37.8; ^{13}C NMR ($CDCl_3$) δ: 22.5 ($J = 8.5$, CH_3), 29.8 ($J = 63.2$, C_6),[a] 33.1 ($J = 59.5$, C_2),[a] 36.4 ($J = 63.0$, CPh),[b] 55.8 (CH_3O), 78.5 ($J = 4.2$, C_3), 126.7 ($C_{4'}$),[c] 128.6 ($J = 5.3$, C_5), 128.4 ($C_{3'}$),[d] 129.0 ($J = 5.1$, $C_{2'}$),[e] 130.6 ($J = 11.1$, $C_{1'}$),[f] 137.3 ($J = 11.4$, C_4); ^1H NMR ($CDCl_3$) δ: 1.88 (s, 3H, CH_3), 2.00–2.72 (m, 4H, $P(CH_2)2$), 3.21 (d, 2H, $J = 15.0$, CH_2Ph), 3.43 (s, 3H, OCH_3),[g] 4.00–4.30 (m, 1H, CH), 7.10–7.42 (m, 5H, Ar).

5-2^A. ^{31}P NMR ($CDCl_3$) δ: 35.0; ^{13}C NMR ($CDCl_3$) δ: 22.9 ($J = 8.5$, CH_3), 28.9 ($J = 62.5$, C_6),[h] 31.3 ($J = 62.0$, C_2),[h] 37.5 ($J = 62.8$, CPh),[b] 57.3 (CH_3O), 79.1 ($J = 5.3$, C_3), 126.7 ($C_{4'}$),[c] 128.4 ($C_{3'}$),[d] 129.4 ($J = 5.1$, $C_{2'}$),[e] 131.0 ($J = 8.5$, $C_{1'}$),[f] 137.5 ($J = 9.6$, C_4); ^1H NMR ($CDCl_3$) δ: 1.94 (s, 3H, CH_3), 2.00–2.72 (m, 4H, $P(CH_2)_2$), 3.21 (d, 2H, $J = 15.0$, CH_2Ph), 3.37 (s, 3H, OCH_3),[g] 4.00–4.30 (m, 1H, CH), 7.10–7.42 (m, 5H, Ar).

5-3^B. ^{31}P NMR ($CDCl_3$) δ: 35.8; ^{13}C NMR ($CDCl_3$) δ: 25.8 ($J = 63.5$, C_6), 26.9 ($J = 5.6$, CH_3), 35.7 ($J = 60.7$, C_2), 36.4 ($J = 63.5$, CPh),[b] 50.4 (CH_3O), 77.0 ($J = 3.1$, C_3), 122.4 ($J = 6.2$, C_5), 126.7 ($C_{4'}$),[c] 127.9 ($J = 10.9$, C_4), 128.4 ($C_{3'}$),[d] 129.1 ($J = 4.9$, $C_{2'}$),[e] 130.7 ($J = 8.1$, $C_{1'}$)[f]; ^1H NMR ($CDCl_3$) δ: 1.52 (s, 3H, CH_3), 2.00–2.72 (m, 4H, $P(CH_2)_2$), 3.21 (d, 2H, $J = 15.0$, CH_2Ph), 3.22 (s, 3H, OCH_3),[g] 6.06 (bdt, 1H, $J^1 = 23.0$, $J^2 = 10.0$, CH=), 7.10–7.42 (m, 5H, Ar).

5-4^B. ^{31}P NMR ($CDCl_3$) δ: 36.1; ^{13}C NMR ($CDCl_3$) δ: 25.5 ($J = 2.8$, CH_3), 26.1 ($J = 64.2$, C_6), 31.7 ($J = 63.4$, C_2), 37.8 ($J = 63.7$, CPh),[b] 49.9 (CH_3O), 76.7 ($J = 3.1$, C_3), 121.5 ($J = 7.0$, C_5), 126.5 ($J = 2.0$, $C_{4'}$),[c] 127.4 ($J = 11.4$, C_4), 128.2 ($C_{3'}$),[d] 129.1 ($J = 5.0$, $C_{2'}$),[e] 130.7 ($J = 7.5$, $C_{1'}$)[f]; ^1H NMR ($CDCl_3$) δ: 1.59 (s, 3H, CH_3), 2.00–2.72 (m, 4H, $P(CH_2)_2$), 3.21 (d, 2H, $J = 15.0$, CH_2Ph), 3.16 (s, 3H, OCH_3),[g] 6.06 (bdt, 1H, $J_1 = 23.0$, $J_2 = 10.0$, CH), 7.10–7.42 (m, 5H, Ar).

5- and 3-Methyl-1-benzyl-4-chloro-3-hydroxy-1,2,3,6-tetrahydrophosphinine 1-Oxide **6**

A solution of 0.40 g (1.38 mmol) of phosphabicyclohexane oxide **2** consisting of isomers **A** (75%) and **B** (25%) and 2.4 g (13.8 mmol) of silver nitrate in 10 mL of water was refluxed for 2 h. After filtration, the mixture was extracted with chloroform and the organic phase was dried over sodium sulfate and concentrated. The crude product was purified by column chromatography (3% methanol in chloroform, silica gel) to give 0.22 g (60%) of compound **6** as a 5.5:2.4:1.4:1 mixture of four isomers. MS, 271 (100, $[M+H]^+$), 253 (82), 154 (91), 136 (90), 91

*[A,B]the corresponding signals within the isomer pairs may be reversed. [a–h]tentative assignment.

(92); HRMS, $[M+H]^+_{found}$ = 271.0641, $C_{13}H_{17}ClO_2P$ requires 271.0655.

6-1. ^{31}P NMR ($CDCl_3$) δ: 37.9; ^{13}C NMR ($CDCl_3$) δ: 23.3 ($J=9.6$, CH_3), 31.3 ($J=64.3$, C_6),[a] 31.8 ($J=61.4$, C_2),[a†] 36.2 ($J=61.6$, CPh), 69.5 (C_3), 125.7 ($J=4.8$, C_5), 127.2 ($J=2.9$, $C_{4'}$), 128.8 ($J=2.4$, $C_{3'}$), 129.2 ($J=5.1$, $C_{2'}$), 130.4 ($J=8.0$, $C_{1'}$), 131.1 ($J=10.3$, C_4); ^1H NMR ($CDCl_3$) δ: 1.92 (s, 3H, CH_3), 2.00–2.65 (m, 4H, $P(CH_2)_2$), 3.25 (d, 2H, $J=15.0$, CH_2Ph), 3.90 (bs, 1H, OH), 4.50 (bd, 1H, $J=19.0$, CH), 7.10–7.42 (m, 5H, Ar).

6-2. ^{31}P NMR ($CDCl_3$) δ: 35.0; ^{13}C NMR ($CDCl_3$) δ: 23.3 ($J=9.6$, CH_3), 31.3 ($J=64.3$, C_6),[b] 32.3 ($J=61.6$, C_2),[b] 37.0 ($J=61.9$, CPh), 69.1 ($J=4.5$, C_3), 126.4 ($J=4.9$, C_5), 126.9 ($J=3.0$, $C_{4'}$), 128.5 ($J=2.6$, $C_{3'}$), 129.7 ($J=5.3$, $C_{2'}$), 130.5 ($J=11.0$, $C_{1'}$), 131.3 ($J=8.8$, C_4); ^1H NMR ($CDCl_3$) δ: 1.91 (s, 3H, CH_3), 2.00–2.65 (m, 4H, $P(CH_2)_2$), 3.25 (d, 2H, $J=15.0$, CH_2Ph), 3.90 (bs, 1H, OH), 4.69 (bd, 1H, $J=20.4$, CH), 7.10–7.42 (m, 5H, Ar).

6-3. ^{31}P NMR ($CDCl_3$) δ: 35.3; ^{13}C NMR ($CDCl_3$) δ: 26.0 ($J=64.4$, C_6), 29.5 ($J=5.6$, CH_3), 30.2 ($J=63.4$, C_2), 36.4 ($J=63.2$, CPh), 71.9 ($J=5.3$, C_3), 118.3 ($J=6.0$, C_5), 126.9 ($J=3.1$, $C_{4'}$), 128.6 ($J=2.9$, $C_{3'}$), 129.5 ($J=5.2$, $C_{2'}$), 131.0 ($J=8.5$, $C_{1'}$), 140.4 ($J=12.4$, C_4); ^1H NMR ($CDCl_3$) δ: 1.63 (s, 3H, CH_3), 2.00–2.65 (m, 4H, $P(CH_2)_2$), 3.25 (d, 2H, $J=15.0$, CH_2Ph), 3.90 (bs, 1H, OH), 5.84 (bdt, 1H, $J_1=24.8$, $J_2=4.6$, CH=), 7.10–7.42 (m, 5H, Ar).

6-4: ^{31}P NMR ($CDCl_3$) δ: 38.4.

3-Benzyl-3-methyl-1,2,3,4,5,6-hexahydrophosphinine 1-oxide **7** *(from 1-benzyl-4-chloro-3-methyl-1,2-dihydrophosphinine 1-oxide* **4***)*

To 0.30 g (1.19 mmol) of dihydrophosphinine oxide **4** consisting of isomers **A** (75%) and **B** (25%) in 20 mL of ethanol 0.06 g of a 5% Pd—C was added and the mixture was stirred in an autoclave under a 4.5-bar atmosphere of hydrogen at 23°C for 24 h. The suspension was filtered, the solvent of the filtrate was evaporated, and the residue purified by column chromatography (2% methanol in chloroform, silica gel) to give 0.21 g (80%) of compound **7** as a 9:1 mixture of diastereoisomers **A** and **B**; MS, 223 (100, $[M+H]^+$), 191 (25), 136 (35), 91 (28); HRMS, $[M+H]^+_{found}$ = 223.1241, $C_{13}H_{19}OP$ requires 223.1252.

7A. ^{31}P NMR ($CDCl_3$) δ: 39.8; ^{13}C NMR ($CDCl_3$) δ: 22.9 ($J=3.7$, C_5), 24.2 ($J=15.1$, CH_3), 26.0 ($J=62.1$, C_6), 31.7 ($J=3.6$, C_3), 33.9 ($J=59.6$, CPh), 34.5 ($J=5.4$, C_4), 35.2 ($J=60.0$, C_2), 126.8 ($J=2.8$, $C_{4'}$), 128.7 ($J=2.5$, $C_{3'}$), 129.5 ($J=4.9$, $C_{2'}$), 131.7 ($J=8.0$, $C_{1'}$); ^1H NMR ($CDCl_3$) δ: 1.04 (dd, 3H, $J=6.3$, 2.6, CH_3), 1.39–2.22 (m, 9H, $4\times CH_2$ + CH), 3.17 (d, 2H, $J=12.6$, CH_2Ph), 7.19–7.41 (m, 5H, Ar).

7B. ^{31}P NMR ($CDCl_3$) δ: 39.9; ^{13}C NMR ($CDCl_3$) δ: 20.5 ($J=5.7$, C_5), 24.6 ($J=14.3$,CH_3), 25.1 ($J=62.2$, C_6), 28.1 ($J=4.8$, C_3), 34.2 ($J=62.4$, CPh), 35.4 ($J=4.6$, C_4), 38.8 ($J=60.0$, C_2), 128.8 ($J=2.8$, $C_{4'}$), 128.7 ($J=2.5$, $C_{3'}$), 129.4 ($J=4.9$, $C_{2'}$), 132.0 ($J=7.3$, $C_{1'}$); ^1H NMR ($CDCl_3$) δ: 0.98 (dd, 3H, $J=6.6$, 2.1, CH_3), 1.39–2.22 (m, 9H, $4\times CH_2$ and CH), 3.14 (d, 2H, $J=15.5$, CH_2Ph), 7.19–7.41 (m, 5H, Ar).

1-Benzyl-3-methyl-1,2,3,4,5,6-hexahydrophosphinine 1-oxide **7***(from 3-Benzyl-6,6-dichloro-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-oxide* **2***)*

The hydrogenation of phosphabicyclohexane oxide **2** consisting of isomers **A** (75%) and **B** (25%) was performed according to the procedure described above except the mixture was kept under a 9-bar atmosphere of hydrogen at 90°C for 16 h. Workup and purification by column chromatography (2% methanol in chloroform, silica gel) afforded 0.11 g (48%) of **7** as a 2:1 mixture of diastereoisomers **A** and **B**.

1-Benzyl-4-chloro-5-methyl-1,2,3,6-tetrahydrophosphinine 1-oxide **8**

To 0.50 g (2.0 mmol) of dihydrophosphinine oxide **4** consisting of isomers **A** (75%) and **B** (25%) in 10 mL of CH_2Cl_2, 1.5 mL of a 2 M solution of borane–dimethyl sulfide in THF was added and the mixture was stirred for 24 h. The reaction mixture was treated with 0.5 mL of water, stirred for 10 min, and the organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography (3% methanol in chloroform, silica gel) to give 0.36 g (70%) of compound **8** as a 9:1 mixture of two double bond isomers **A** and **B**. HRMS, $[M+H]^+_{found}$ = 255.0689, $C_{13}H_{17}ClOP$ requires 255.0706.

8A. ^{31}P NMR ($CDCl_3$) δ: 34.7; ^{13}C NMR ($CDCl_3$) δ: 23.2 (CH_3), 23.6 ($J=74.1$, C_2), 31.2 (d, $J=64.1$, C_6), 31.4 ($J=5,56$, C_3), 35.4 ($J=63.0$, CPh), 124.4 ($J=5.3$, C_4), 126.6 ($J=12,6$, C_3), 127,1 ($J=3.1$, $C_{4'}$), 128.9 ($J=2.6$, $C_{3'}$), 129.4 ($J=5.2$, $C_{2'}$), 131.2 ($J=7.9$, $C_{1'}$); ^1H NMR ($CDCl_3$) δ: 1.86 (s, 3H, CH_3), 1.85–2.20 (m, 2H, CH_2), 2.28–2.55 (m, 2H, CH_2), 2.58–2.80 (m, 1H, CH_2), 2.80–3.02 (m, 1H, CH_2), 3.19 (dd, 2H, $J=14.3$, 1.46, CH_2Ph), 7.20–7.40 (m, 5H, Ar).

8B. ^{31}P NMR ($CDCl_3$) δ: 36.3.

4- and 6-Methyl-5-chloro-2-oxo-2-benzyl-2λ^5-phosphabicyclo[2.2.2]octa-5,7-diene-7,8-dicarbonic Acid Dimethyl Ester **9**

To 60.0 mg (0.24 mmol) of dihydrophosphinine oxide **4** consisting of isomers **A** (75%) and **B** (25%) in

[†] [a,b] tentative assignment.

3 mL of toluene, 0.15 mL (1.20 mmol) of dimethyl acetylenedicarboxylate was added and the mixture was refluxed for 12 h. The volatiles were evaporated, and the residue was purified by column chromatography (3% methanol in chloroform, silica gel) to give 60.0 mg (66%) of compound **9** as a 37:27:18:18 mixture of four isomers. The spectroscopic data of the four isomers were similar to those published previously (δ_P: ($CDCl_3$) δ: 55.2, 54.3, 51.0, and 50.0, δ_P lit [13]: 55.3, 54.3, 51.1, and 50.1).

4- and 6-Methyl-2-benzyl-5-chloro-10-phenyl-10-aza-2 λ^5-phosphatricyclo[5.2.2.0^{7,8}]undec-5-ene-9,11-dion-2-oxide **10**

To 60.0 mg (0.24 mmol) of dihydrophosphinine oxide **4** consisting of isomers **A** (75%) and **B** (25%) in 3 mL of toluene, 0.12 g (0.69 mmol) of *N*-phenylmaleimide was added and the mixture was refluxed for 8 h. The volatiles were evaporated, and the residue was purified by column chromatography (3% methanol in chloroform, silica gel) to give 50.0 mg (50%) of compound **10** as a 55:45 mixture of diastereomers **A** and **B**. The spectroscopic data of **10A** and **10B** were similar to those published previously (δ_P ($CDCl_3$) δ: 47.7 and 47.4, δ_P: lit [13] 47.5 and 47.0).

O-Alkyl-benzyl-methylphosphinates **11**

The solution of 40.0 mg (0.10 mmol) of benzylphosphabicyclooctadiene **9** consisting of isomers (37:27:18:18) and 4 mL of the corresponding alcohol in 45 mL of acetonitrile was irradiated in a photochemical reactor with a mercury lamp (125 W) for 1 h. Volatile components were removed, and the residue so obtained was purified by flash chromatography (3% methanol in chloroform, silica gel) to give the corresponding phosphinates **11**.

O-Methyl-benzyl-methylphosphinate **11a**. Yield: 75%; ^{31}P NMR ($CDCl_3$) δ: 53.5; HRMS, $[M+H]^+_{found}$ = 185.0741, $C_9H_{14}O_2P$ requires 185.0731.

O-Ethyl-benzyl-methylphosphinate **11b** [16]. Yield: 75%; ^{31}P NMR ($CDCl_3$) δ: 51.8; HRMS, $[M+H]^+_{found}$ = 199.0871, $C_{10}H_{16}O_2P$ requires 199.0881.

O-Propyl-benzyl-methylphosphinate **11c**. Yield: 83%, ^{31}P NMR ($CDCl_3$) δ: 51.3; HRMS, $[M+H]^+_{found}$ = 213.1029, $C_{11}H_{18}O_2P$ requires 213.1044.

O-Butyl-benzyl-methylphosphinate **11d**. Yield: 85%; ^{31}P NMR ($CDCl_3$) δ: 51.4; HRMS, $[M+H]^+_{found}$ = 227.1191, $C_{12}H_{20}O_2P$ requires 227.1201.

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