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New P-Ligands: 3-(Ethyl-phenylphosphinato-) 1,2,3,6-Tetrahydro- and 1,2,3,4,5,6-Hexahydrophosphinine Derivatives

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ABSTRACT: *The trimethylaluminum-mediated Michael addition of ethyl phenyl-H-phosphinate to 1,2-dihydrophosphinine oxides (***1A***) yielded 3-(EtOPhP(O))-1,2,3,6-tetrahydrophosphinine oxides (***4***) in a selective manner, as a mixture of only two diastereomers. In the above type of reactions (e.g., in that of* **1Aa** *and $Ph_2P(O)H$), Me_3Al could not be substituted by microwave irradiation due to low efficiency. Catalytic hydrogenation of the Michael adducts (***4***) led to 3-(EtOPhP(O)-1,2,3,4,5,6-hexahydrophosphinine oxides* **5**, *in the case of P-phenyl substituent (***5a***), as a mixture of only two diastereomers, while in the instance of the P-ethoxy derivative (***5b***), as a mixture of four isomers. Stereostructure of the products (***5***) was substantiated on the basis of analogies and stereospecific NMR couplings. The predominant conformations of compounds* **4a**, **4b**, **5a**, *and* **5b-1** *were determined by HF/6-31G* calculations. Reduction of P(1)–Ph heterocycles* **4a** *and* **5a** *by phenylsilane resulted in monodeoxygenation to afford P-ligands* **6** *and* **8**, *respectively, that were protected as the corresponding phosphine boranes (***7** *and* **9**, *respectively).* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:747–753, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20365

INTRODUCTION

The six-membered P-heterocycles, phosphinine derivatives form a representative class of P-ring compounds [1–3]. Recently, 3-phosphinoxido- and 3-phosphono-1,2,3,6-tetrahydro- [4,5], and 1,2,3,4,5,6-hexahydrophosphinine oxides [6,7] have been introduced by us. After double deoxygenation,

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bis(phosphine oxides) served as bidental P-ligands in transition metal complexes [8,9]. In this paper, we describe new 3-P-derivatives with mixed substituents in the exocyclic moiety that are potential P-ligands after deoxygenation.

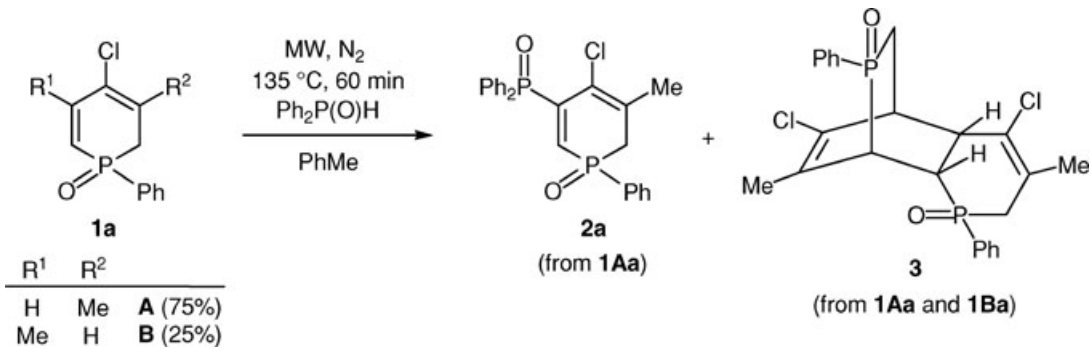
RESULTS AND DISCUSSION

For the synthesis of 1,2,3,6-tetrahydrophosphinine oxides with exocyclic P-function, the trimethylaluminum-promoted addition of the >P(O)H species on the α,β-double bond of the 1,2-dihydrophosphinine oxides was found to be the method of choice [4,5]. More trivial approaches were applied only in simpler phospha-Michael reactions involving, e.g. methylvinylketone [10]. First, we investigated whether the addition of the quite reactive diphenylphosphine oxide on the electron-poor double bond of dihydrophosphinine oxide **1a** can be accomplished under "greener" conditions involving microwave (MW) irradiation of the toluene solution of the reactants at 135°C. It was found that the reaction afforded a ca. 6:4 mixture of the desired product (**2a**) and the [4+2] cycloadduct (**3**) of the double bond isomers (**A** and **B**) of the starting P-cycle (**1a**) in a conversion of ca. 40% related to $Ph_2P(O)H$. A major part of **2a** was polymerized on MW irradiation. A threefold excess of dihydrophosphinine oxide **1a** promoted a more complete conversion of $Ph_2P(O)H$, the formation of dimer **3** became, however, the predominant route (Scheme 1).

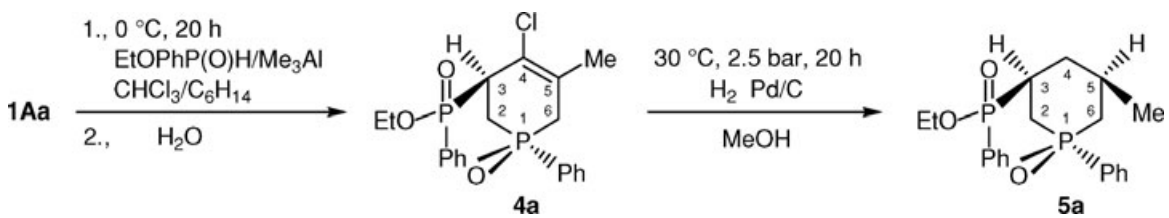
In order to activate the $Ph_2P(O)H$ reagent, *n*-butyllithium and sodium hydride were also tried (in THF); the use of these reagents led, however, to complex mixtures.

After the above experiences, the Me_3Al-mediated Michael addition remained for the preparation of the new 3-*P*-tetrahydrophosphinine oxides we aimed at. Hence, *P*-phenyl (**1Aa**) and the *P*-ethoxy (**1Ab**) 1,2-dihydrophosphinine oxides were reacted with ethyl phenyl-*H*-phosphinate in the presence of Me_3Al to give 3-*P*-1,2,3,6-tetrahydrophosphinine oxides (**4a** and **4b**, respectively) in a diastereoselective manner. Although both starting materials (**1a** and EtOPhP(O)H) were used as racemate, and a stereogenic center C(3) is also constructed during the reaction, the products (**4**) were formed as a mixture of only a major (79/84%) and a minor (21/16%) diastereomer (Schemes 2 and 3).

It is noted that dihydrophosphinine oxides (**1**) were used as a ca. 3:1 mixture of double bond isomers (**A** and **B**), but only isomer **A** was reacted. The stereostructure of 3-*P*-tetrahydrophopshinine oxides **4a** and **4b** was substantiated by HF/6-31G* calculations revealing that **4a** and **4b** may exist in the twist-boat conformations shown in Figs. 1 and 2, respectively. For both **4a** and **4b**, an intramolecular interaction between the suitable proton of the $C(6)H_2$ moiety and the oxygen atom of the P(2)OEt unit was found to stabilize the molecule. The corresponding O···H distance was found to be 2.508 and 2.577 Å, respectively. For **4b**, there was an additional H-bonding (2.675 Å) between the P(1)=O and a suitable proton of the phenyl ring. The abovementioned H-bonds were justified by the Bondi



SCHEME 1



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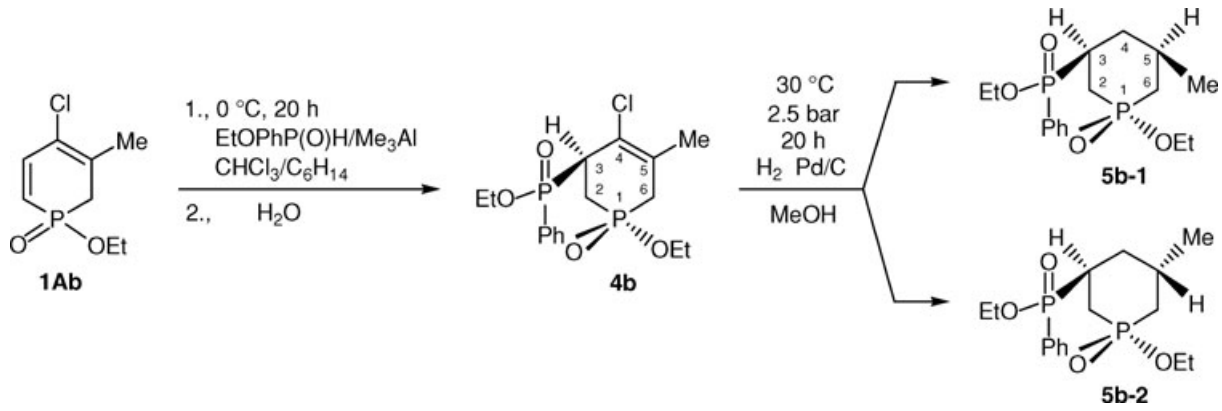


SCHEME 3

criteria [11]. This means that the distance between the heavy (pilar) atoms fell within the sum of their van der Waals radii (i.e., 3.22 Å for the carbon and oxygen atoms involved), and the angle defined by the pilar atoms and the hydrogen atom (donor atom–H atom–acceptor atom) was larger than 90°. Similar type of H-bonds was also observed by us for other 3-*P*-tetrahydrophosphinine oxides [5]. The conformation of 1,2,3,6-tetrahydrophosphinine oxides was found to be governed by both substitution effects and intramolecular interactions [3].

Then, 3-(EtOPhP(O))-1,2,3,6-tetrahydrophosphinine oxides (**4a** and **4b**) consisting of two diastereomers were subjected to catalytic hydrogenation. Saturation of the double bond and hydrogenolysis of the C—Cl unit took place under mild conditions to furnish 3-P-1,2,3,4,5,6-hexahydrophosphinine oxides (**5a** and **5b**). The isomeric composition depended on the P-substituent in the starting material (Schemes 2 and 3). According to this, hydrogenation of the isomeric mixture of the 1-phenyl starting material (**4a**) provided the 3-P-hexahydrophosphinine oxide **5a** in a diastereoselective manner, as a 74:26 mixture of two isomers, meaning that the new stereogenic center C(5) was established fully selectively. Close analogies [6] suggested that the C(5)–Me may

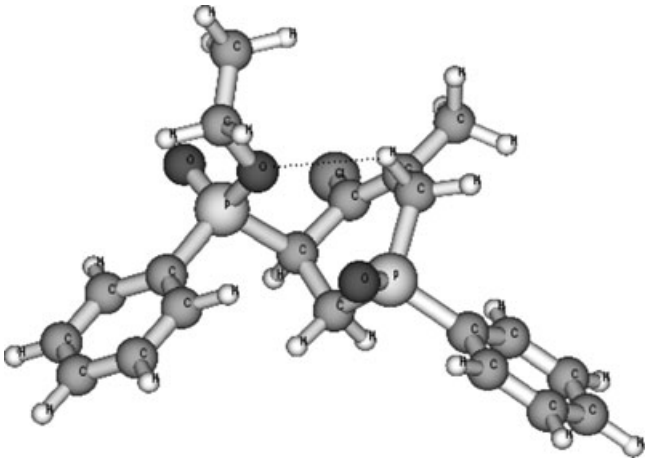


FIGURE 1 Stereostructure of the twist-boat conformer of **4a** with bond lengths (Å), bond angles (°), and torsion angles (°) obtained at the HF/6-31G* level of theory. P(1)–C(2) 1.827, C(2)–C(3) 1.543, C(3)–C(4) 1.521, C(4)–C(5) 1.327, C(5)–C(6) 1.521, C(6)–P(1) 1.832, O–P(1)–C(2) 114.9, O–P(1)–C(6) 114.4, O–P–C(1′) 111.4, C(2)–P(1)–C(6) 102.4, P(1)–C(2)–C(3)–P −76.3, P(1)–C(2)–C(3)–C(4) 58.8, P(1)–C(6)–C(5)–CH(3) −150.0, P(1)–C(6)–C(5)–C(4) 32.5, C(6)–C(5)–C(4)–C(3) −3.0, C(6)–P(1)–C(2)–C(3) −25.8.

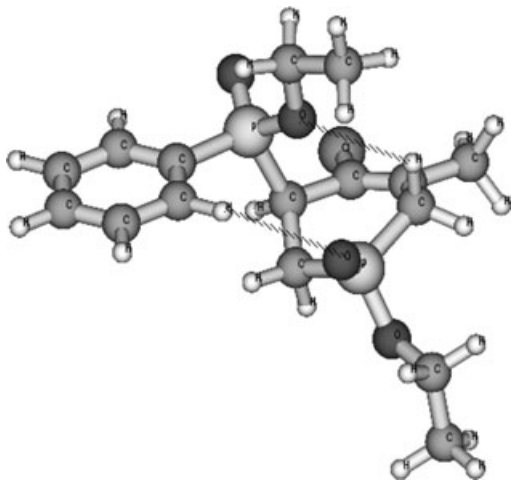


FIGURE 2 Stereostructure of the twist-boat conformer of **4b** with bond lengths (Å), bond angles (°), and torsion angles (°) obtained at the HF/6-31G* level of theory. P(1)–C(2) 1.812, C(2)–C(3) 1.542, C(3)–C(4) 1.522, C(4)–C(5) 1.326, C(5)–C(6) 1.522, C(6)–P(1) 1.822, O–P(1)–C(2) 117.1, O–P(1)–C(6) 114.2, O–P(1)–O 113.6, C(2)–P(1)–C(6) 104.7, P(1)–C(2)–C(3)–P −77.0, P(1)–C(2)–C(3)–C(4) 53.4, P(1)–C(6)–C(5)–CH(3) −150.1, P(1)–C(6)–C(5)–C(4) 32.3, C(6)–C(5)–C(4)–C(3) −3.5, C(6)–P(1)–C(2)–C(3) −25.9.

be cis with the C(3)–P group. At the same time, hydrogenation of the two diastereomers of the 1-ethoxy-dihydrophosphinine oxide **4b** resulted in the product (**5b**) as a 59:26:9:6 mixture of four isomers. Both the major (>59%, **5b-1**) and the minor (>26%, **5b-2**) isomers consisted of two diasteromers. **5b-1** and **5b-2** differ in the configuration of the sp^3 C(5) atom formed on reduction. As stereospecific NMR couplings, multiplicity of the C(5)–Me group in the ^{13}C NMR spectra of **5a** and **5b-1** is doublet ($J = 15$ Hz) or doublet of doublets (J_1 ~15 Hz, J_2 ~4 Hz) at ca. δ_C 24.2. At the same time, C(5)–Me of **5b-2** appears as a singlet at δ_C 18.6. The multiplicity of C(5)–Me in the ^1H NMR spectra of **5a**, **5b-1**, and **5b-2** was also of diagnostic value (see Experimental). The above experiences were in full agreement with earlier observations [6]. HF/6-31G* calculations revealed that compounds **5a** and **5b-1** adopt the chair conformations with equatorial 3-P(O)Ph(EtO) and 5-Me substituents and with axial P(1) groups. The perspective views of **5a** and **5b-1** are shown in Figs. 3 and 4, respectively.

The major isomers of the 3-*P*-tetra- and hexahydrophosphinine oxides (**4a,b** and **5a,b**, respectively) were identified and characterized by ^{31}P, ^{13}C and ^1H NMR, as well as FAB-MS data.

In the next stage of our work, the P(1)-phenyl 3-*P*(O)<-tetra- and hexahydrophosphinine oxides (**4a** and **5a**, respectively) were reacted with 2 equivalents of phenylsilane at 80°C without any solvent under nitrogen in a sealed tube. Because of the sensitivity of the P(III) products, they were immediately treated with 2.5 equivalents of dimethylsulfide borane. ^{31}P and ^{11}B NMR spectra of the purified products suggested that only one of the P(O) functions was deoxygenated. On the basis of the ^{13}C NMR spectra, we had P-heterocycles **7** and **9** with a P–BH_3 function in the ring in hand (Schemes 4 and 5).

We found that under the same conditions (using phenylsilane), 3-Ph_2P(O)-1-phenyltetrahydrophosphinine oxide **2a** smoothly underwent double deoxygenation to afford, after reaction with 2 equivalents of dimethylsulfide borane, the corresponding diborane (δ_P ($CDCl_3$) 7.0 and 30.4; δ_P lit. [8] 7.7 and 30.8). The phosphine boranes (e.g., **7** and **9**) can be regarded as protected P-ligands from which phosphine can be liberated by a standard procedure involving heating with a *sec*-amine in benzene or toluene [12].

In summary, new 3-(ethyl-phenylphosphinato-) 1,2,3,6-tetrahydro- and 1,2,3,4,5,6-hexahydrophos-

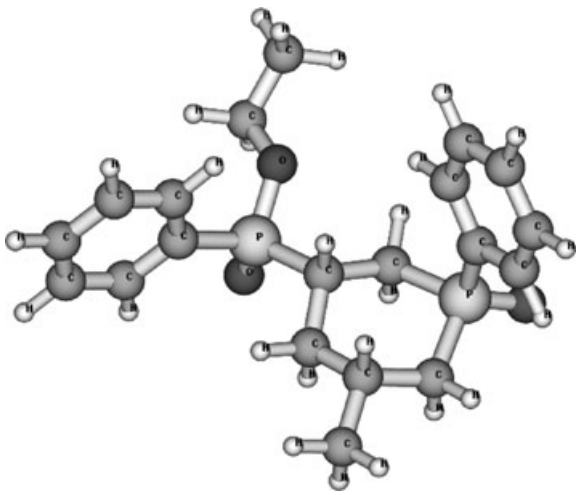


FIGURE 3 Stereostructure of the chair conformer of hexahydrophosphinine oxide **5a** with bond lengths (Å), bond angles (°), and torsion angles (°) obtained at the HF/6-31G* level of theory. P(1)–C(2) 1.824, C(2)–C(3) 1.541, C(3)–C(4) 1.541, C(4)–C(5) 1.536, C(5)–C(6) 1.540, C(6)–P(1) 1.821, O–P(1)–C(2) 113.3, O–P(1)–C(6) 114.1, O–P–C(1′) 113.2, C(2)–P(1)–C(6) 101.8, P(1)–C(2)–C(3)–P 179.8, P(1)–C(2)–C(3)–C(4) −57.5, P(1)–C(6)–C(5)–CH(3) −176.8, P(1)–C(6)–C(5)–C(4) 53.3, C(6)–C(5)–C(4)–C(3) −61.0, C(6)–P(1)–C(2)–C(3) 45.4.

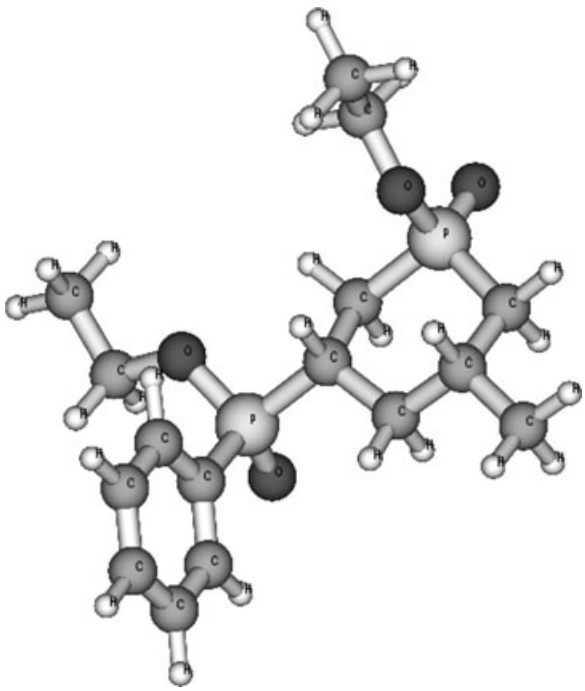
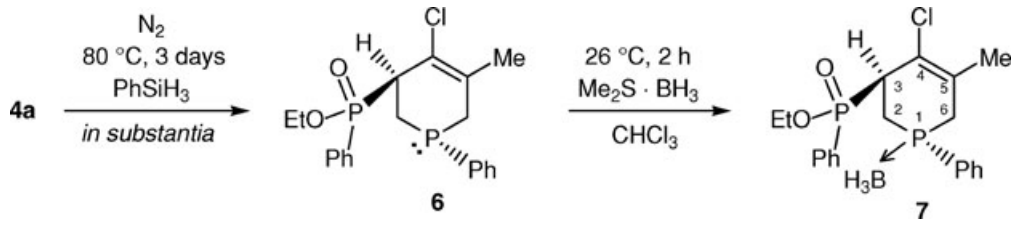
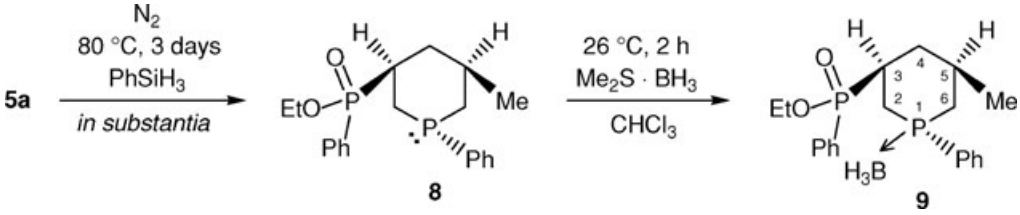


FIGURE 4 Stereostructure of the chair conformer of hexahydrophosphinine oxide **5b-1** with bond lengths (Å), bond angles (°), and torsion angles (°) obtained at the HF/6-31G* level of theory. P(1)–C(2) 1.814, C(2)–C(3) 1.543, C(3)–C(4) 1.542, C(4)–C(5) 1.538, C(5)–C(6) 1.540, C(6)–P(1) 1.806, O–P(1)–C(2) 114.4, O–P(1)–C(6) 116.7, O–P(1)–O 114.4, C(2)–P(1)–C(6) 103.8, P(1)–C(2)–C(3)–P −179.1, P(1)–C(2)–C(3)-C(4) −56.2, P(1)–C(6)–C(5)–CH(3) 178.3, P(1)–C(6)–C(5)–C(4) 54.9, C(6)–C(5)–C(4)–C(3) −62.1, C(6)–P(1)–C(2)–C(3) 46.1.



SCHEME 4



SCHEME 5

phinine oxides were synthesized mostly in a diasteroselective manner, utilizing the phospha-Michael reaction and catalytic hydrogenation. The tetrahydrophosphinine oxides were found to exist in the twist-boat conformation, whereas the hexahydrophosphinine oxides in the chair conformation. In the former case, intramolecular interactions were found to stabilize the molecules. The reaction of the 3-P(O)<-cyclic phosphine oxides with phenylsilane led to monodeoxygenation, yielding 3-P(O)<-cyclic phosphines that can be protected as P-boranes.

EXPERIMENTAL

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were obtained in $CDCl_3$ solution on a Bruker DRX-300 spectrometer operating at 121.5, 75.5, and 300 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. The coupling constants are given in hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument. The 1,2-dihydrophosphinine 1-oxides (**1a,b**) were prepared as described earlier [13].

Attempted Synthesis of 3-Diphenylphosphinoxido-1,2,3,6-tetrahydrophosphinine Oxide **2a**

A mixture of 0.05 g (0.21 mmol) of the double bond isomers 1,2-dihydrophosphinine oxide **1a** and 0.04 g (0.21 mmol) of diphenylphosphine oxide in 1 mL of toluene was heated at 135°C under N_2 atmosphere in a CEM Discovery microwave reactor (applying ca. 50 W) for 1 h. The crude product obtained after filtration from the polymer of **1a**, and concentration in vacuo was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford a 65:35 mixture of 3-*P*-tetrahydrophosphinine oxide **2a** (^{31}P NMR ($CDCl_3$) δ 33.8 and 34.6, δ lit. [4] 34.0 and 34.8) and dimer **3** (^{31}P NMR ($CDCl_3$) δ 28.5 and 37.4, δ lit. [14] 28.6 and 37.5). The conversion in respect of $Ph_2P(O)H$ was ca. 40%.

*General Procedure for the Synthesis of 3-(Ethyl-phenylphosphinato-)1,2,3,6-tetrahydrophosphinine Oxides (***4a,b***)*

To 0.13 mL (0.84 mmol) of the ethyl phenylphosphinate in 5 mL of dry chloroform was added 0.42 mL (0.84 mmol) of 2 M trimethylaluminum in hexane at 0°C was added. After 20 min, 0.84 mmol of the corresponding dihydrophosphinine oxide (**1Aa** or **1Ab**) in 5 mL of chloroform was added dropwise. The cooling bath was removed, and the solution was stirred for 20 h. Then, the reaction was hydrolyzed by the addition of 1.4 mL of conc. hydrochloric acid in 13 mL of water. The organic phase was separated, dried (Na_2SO_4), and concentrated, and the crude product so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford compounds **4a** and **4b**.

*4-Chloro-3-(ethyl-phenylphosphinato-)5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine 1-Oxide (***4a***).* Yield: 0.26 g (76%), $(M+H)^+_{found}$ = 409.0869, $C_{20}H_{24}ClO_3P_2$ requires 409.0889 for the ^{35}Cl isotope.

Major: 79%; δ_{P2} 32.0 (d), δ_{P1} 39.5 (d), $^3J_{PP} = 16.8$; δ_C 16.5 (d, $^2J = 6.2$, CH_3CH_2), 23.8 (dd, $^1J = 6.9$, $^2J = 2.7$, C_5—CH_3), 25.5 (dd, $^1J = 71.6$, $^2J = 3.7$, C_2), 34.6 (dd, $^1J = 61.9$, $^2J = 2.5$, C_6), 44.5 (dd, $^1J = 5.7$,

$^2J = 97.4$, C_3), 61.8 (d, $^2J = 6.7$, CH_2O), 123.1 (dd, $^1J = 6.8$, $^2J = 16.2$, C_5), 128.6 (d, $^2J = 12.7$, $C_{3''}$),[a] 128.8 (d, $^1J = 11.5$, $C_{3'}$),[a] 129.8 (d, $^1J = 8.9$, $C_{2'}$),[a] 130.6 (dd $^1J = 9.5$, $^2J = 7.1$, C_4), 132.0 (d, $^1J = 2.6$, $C_{4'}$),[b] 132.7 (d, $^2J = 9.7$, $C_{2''}$),[a] 133.0 (d, $^2J = 2.7$, $C_{4''}$),[b] 133.9 (d, $^1J = 99.6$, $C_{1'}$), [a,b]may be reversed; δ_H 1.38 (t, $J = 7.1$, 3H, CH_2CH_3), 1.75 (d, $J = 5.4$, 3H, C_5—CH_3), 2.43–2.91 (m, 3H, C(3)H and P—CH_2), 3.08–3.25 (m, 1H, P—CH), 3.32–3.55 (m, 1H, P—CH), 3.95–4.32 (m, 2H, CH_2O), 7.43–7.67 and 7.81–7.90 (m, 10H, Ar).

Minor: 21%; δ_{P2} 32.4 (d), δ_{P1} 41.3 (d), $^3J_{PP} = 15.3$; δ_C 16.6 (d, $^2J = 6.2$, CH_3CH_2), 23.9 (dd, overlapped, C_5—CH_3), 25.6 (d, $^1J = 71.8$, C_2), 35.0 (dd, $^1J = 61.6$, $^2J = 2.5$, C_6), 45.9 (dd, $^1J = 5.8$, $^2J = 96.2$, C_3), 62.1 (d, $^2J = 6.8$, CH_2O).

*4-Chloro-3-(ethyl-phenylphosphinato-)5-methyl-1-ethoxy-1,2,3,6-tetrahydrophosphinine 1-Oxide (***4b***).* Yield: 0.16 g (49%); $(M+H)^+_{found} = 377.0821$, $C_{16}H_{25}ClO_4P_2$ requires 377.0838 for the ^{35}Cl isotope.

Major: 84%; δ_{P2} 39.7 (d), δ_{P1} 50.5 (d), $^3J_{PP} = 18.7$; δ_C 16.4 (d, $J = 6.3$, CH_3CH_2), 16.6 (d, $J = 5.8$, CH_3CH_2), 23.3 (dd, $^1J = 97.5$, $^2J = 4.1$, C_2), 23.8 (dd, $^1J = 7.9$, $^2J = 2.6$, C_5—CH_3), 31.8 (dd, $^1J = 85.0$, $^2J = 2.2$, C_6), 44.9 (dd, $^1J = 5.0$, $^2J = 98.4$, C_3), 60.6 (d, $J = 6.2$, CH_2O), 61.7 (d, $J = 6.6$, CH_2O), 121.5 (dd, $^1J = 6.5$, $^2J = 17.5$, C_5), 128.6 (d, $^2J = 12.7$, $C_{3'}$),* 128.9 (d, $^1J = 126.3$, $C_{1'}$), 130.6 (dd $^1J = {}^2J = 8.8$, C_4), 132.6 (d, $^1J = 9.8$, $C_{2'}$),* 132.9 (d, $^1J = 2.8$, $C_{4'}$), *may be reversed; δ_H 1.30 (t, $J = 7.1$, 3H, CH_2CH_3), 1.34 (t, $J = 6.9$, 3H, CH_2CH_3), 1.86 (d, $J = 5.1$, 3H, C_5—CH_3), 2.12–2.58 (m, 3H, C(3)H és P—CH_2), 2.88 (dt, $^1J = 19.8$, $^2J = 6.5$, 1H, P—CH), 3.20–3.52 (m, 1H, P—CH), 3.89–4.26 (m, 4H, CH_2O), 7.45–7.62 and 7.76–7.85 (m, 5H, Ar).

Minor: 16%; δ_{P2} 41.7 (d), δ_{P1} 51.2 (d), $^3J_{PP} = 16.6$.

*General Procedure for the Synthesis of 3-(Ethyl-phenylphosphinato-)1,2,3,4,5,6-hexahydrophosphinine Oxides (***5a,b***)*

A solution of 0.49 mmol of tetrahydrophosphinine oxide **4a** or **4b** in 30 mL of methanol and 0.10 g of 10% Pd/C was measured in an autoclave equipped with a magnetic stirrer. The hydrogenation was carried out at 30°C and 2.5 bar for 24 h. The suspension was filtered, and the solvent evaporated. Purification of the crude product by column chromatography (silica gel, 3% methanol in chloroform) furnished hexahydrophosphinine oxide **5a** or **5b**.

*3-(Ethyl-phenylphosphinato-)5-methyl-1-phenyl-1,2,3,4,5,6-hexahydrophosphinine 1-Oxide (***5a***).* Yield: 0.14 g (76%), $(M+H)^+_{found} = 377.1419$, $C_{20}H_{27}O_3P_2$ requires 377.1435.

Major: 74%; δ_{P2} 35.3, δ_{P1} 43.8 (d), $^3J_{PP} = 57.5$; δ_C 16.5 (d, $^2J = 6.0$, CH_3CH_2), 24.2 (d, $^1J = 16.0$, C_5—CH_3), 24.9 (dd, $^1J = 63.7$, $^2J = 3.3$, C_2), 31.3 (dd, $^1J = 3.0$, $^2J = 17.7$, C_5), 33.3 (d, $^1J = 2.7$, C_4), 35.0 (d, $^1J = 64.4$, C_6), 35.8 (dd, $^1J = 2.4$, $^2J = 99.4$, C_3), 61.4 (d, $^2J = 6.7$, CH_2O), 128.0 (d, $^2J \sim 115$, $C_{1''}$), 128.9 (d, $^2J = 12.3$, $C_{3''}$),[a] 129.2 (d, $^1J = 11.3$, $C_{3'}$),[a] 129.6 (d, $^1J = 9.1$, $C_{2'}$),[a] 130.9 (d, $^1J = 95.4$, $C_{1'}$), 132.2 (d, $^1J \sim 4.0$, $C_{4'}$),[b] 132.3 (d, $^2J = 9.7$, $C_{2''}$),[a] 132.8 (d, $^2J = 2.6$, $C_{4''}$),[b] [a,b]may be reversed; δ_H 1.05 (dd, $^1J = 6.0$, $^2J = 3.0$, 3H, C_5—CH_3), 1.35 (t, $J = 7.0$, 3H, CH_2CH_3), 3.90–4.00 and 4.08–4.19 (m, 2H, CH_2O), 7.46–7.75 (m, 10H, Ar).

Minor: 26%; δ_{P2} 35.4 (d), δ_{P1} 43.9 (d), $^3J_{PP} = 59.3$; δ_C 16.5 (d, $^2J = 6.0$, CH_3CH_2), 24.2 (d, $^1J = 16.0$, C_5—CH_3), 25.4 (d, $^1J = 63.3$, C_2), 31.4 (dd, $^1J = 3.4$, $^2J = 17.3$, C_5), 33.0 (d, $^1J = 2.7$ C_4), 34.9 (d, $^1J = 64.1$, C_6), 35.6 (dd, $^1J = 2.0$, $^2J = 100.2$, C_3); δ_H 1.06 (dd, $^1J = 6.0$, $^2J = 3.0$, 3H, C_5—CH_3), 1.33 (t, $J = 4.2$, 3H, CH_2CH_3).

*3-(Ethyl-phenylphosphinato-)5-methyl-1-ethoxy-1,2,3,4,5,6-hexahydrophosphinine 1-Oxide (***5b***).* Yield: 0.07 g (90%), $(M+H)^+_{found} = 345.1365$, $C_{16}H_{26}O_4P_2$ requires 345.1385.

Isomer$_1$: 59%; δ_{P2} 40.0 (d), δ_{P1} 44.9 (d), $^3J_{PP} = 58.1$; δ_C 16.5 (d, $J = 6.1$, CH_3CH_2), 16.7 (d, $J = 5.6$, CH_3CH_2), 24.2 (dd, $^1J = 14.8$, $^2J = 4.1$, C_5—CH_3), 24.5 (dd, $^1J = 85.3$, $^2J = 4.4$, C_2), 31.4 (dd, $^1J = 4.4$, $^2J = 17.8$, C_5), 33.2 (dd, $^1J = 5.7$ $^2J = 1.9$, C_4), 34.7 (d, $^1J = 85.7$, C_6), 35.9 (dd, $^1J = 4.2$, $^2J = 100.6$, C_3), 60.1 (d, $J = 6.2$, CH_2O), 61.3 (d, $J = 6.7$, CH_2O), 128.5 (d, $^1J = 121.4$, $C_{1'}$), 128.9 (d, $^2J = 12.1$, $C_{3'}$),* 132.3 (d, $^2J = 9.3$, $C_{2'}$),* 132.8 (d, $^2J = 2.5$, $C_{4'}$), *may be reversed; δ_H 1.00 (dd, $^1J = 6.4$, $^2J = 3.1$, 3H, C_5—CH_3), 1.29 (t, $J = 7.0$, 3H, CH_2CH_3), 1.34 (t, $J = 6.9$, 3H, CH_2CH_3), 1.80–1.96 (m, 4H, CH_2), 2.13–2.22 (m, 1H, C(5)H), 2.36–2.54 (m, 1H, C(3)H), 3.85–4.20 (m, 4H, CH_2O), 7.46–7.80 (m, 5H, Ar).

Isomer$_2$: 26%; δ_{P2} 40.8 (d), δ_{P1} 44.8 (d) $^3J_{PP} = 56.9$; δ_C 18.6 (s, C_5—CH_3); δ_H 1.08 (d, $^1J = 7.5$, 3H, C_5—CH_3).

Isomer$_3$: 9%; δ_{P2} 40.3 (d), δ_{P1} 44.7 (d) $^3J_{PP} = 60.6$.

Isomer$_4$: 6%; δ_{P2} 41.2 (d), δ_{P1} 44.8 (d) $^3J_{PP} = 59.0$.

*General Procedure for the Preparation of 3-(Ethyl-phenylphosphinato)-5-methyl-1-phenyl-1,2,3,6-tetrahydro- and 3-(Ethyl-phenylphosphinato)-5-methyl-1-phenyl-1,2,3,4,5,6-hexahydrophosphinine 1-Borane Complexes (***7***) and (***9***)*

0.24 mmol of P-heterocycle **4a** or **5a** and 60 μL (0.48 mmol) of phenylsilane was kept at 80°C

under nitrogen for 3 days. Then, the mixture was taken up in 5 mL of degassed dichloromethane and the phosphine (**6** or **8**) formed was immediately reacted with 0.31 mL of 2 M tetrahydrofuran solution of $BH_3{\cdot}SMe_2$ (0.6 mmol) at 26°C, under nitrogen. After stirring for 3 h, 1 mL of water was added and the mixture was stirred further for 10 min. Filtration of the boric acid and evaporation of the filtrate led to phosphine borane **7** or **9**.

*3-(Ethyl-phenylphosphinato)-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine 1-Borane Complex (**7**).* Yield: 71%; FAB: $(M - BH_3)^+ = 405$.

Major: 82%; δ_{P2} 40.0 (d), $^3J_{PP} = 13.0$, δ_{P1} 7.8 (broad); δ_B –35.7; δ_C 16.7 (d, $^2J = 6.2$, CH_3CH_2), 21.4 (dd, $^1J = 35.1$, $^2J = 2.8$, C_2), 24.1 (dd, $^1J = 4.0$, $^2J = 2.7$, C_5—CH_3), 29.2 (dd, $^1J = 31.0$, $^2J = 2.8$, C_6), 43.9 (dd, $^1J = 7.7$, $^2J = 98.6$, C_3), 62.1 (d, $^2J = 6.7$, CH_2O), 123.4 (dd, $^1J = 7.6$, $^2J = 13.5$, C_5), 128.8 (d, $^2J = 12.7$, $C_{3''}$),[a] 128.9 (d, $^1J = 84.1$, $C_{1'}$), 129.1 (d, $^1J = 9.8$, $C_{3'}$),[a] 130.0 (d, $^1J = 7.9$, C_4), 131.4 (d, $^1J = 9.1$, $C_{2'}$),[a] 131.6 (d, $^1J = 2.3$, $C_{4'}$),[b] 132.8 (d, $^2J = 9.7$, $C_{2''}$),[a] 133.2 (d, $^2J = 2.9$, $C_{4''}$),[b] [a,b]may be reversed; δ_H 1.37 (t, $J = 7.1$, 3H, CH_2CH_3), 1.76 (d, $J = 5.4$, 3H, C_5—CH_3), 2.28–2.40 and 2.52–2.66 (m, 3H, C(3)H and P—CH_2), 2.73–2.90 (m, 1H, P—CH), 3.36–3.54 (m, 1H, P—CH), 3.97–4.28 (m, 2H, CH_2O), 7.38–7.64 and 7.77–7.87 (m, 10H, Ar).

Minor: 18%; δ_{P2} 41.6 (d), $^3J_{PP} = 11.2$, δ_{P1} 7.8 (broad).

*3-(Ethyl-phenylphosphinato)-5-methyl-1-phenyl-1,2,3,4,5,6-hexahydrophosphinine 1-Borane Complex (**9**).* Yield: 0.09 g (83%); FAB: $(M - BH_3)^+ = 373$.

Major: 60%; δ_{P2} 43.40 (d), $^3J_{PP} = 32.8$, δ_{P1} 9.2 (broad); $\delta_B = -33.6$; δ_C 16.7 (d, $^2J = 6.1$, CH_3CH_2), 20.0 (dd, $^1J = 31.6$, $^2J = 3.3$, C_2), 24.6 (d, $^1J = 16.5$, C_5—CH_3), 28.6 (dd, $^1J = 7.2$, $^2J = 15.2$, C_5), 29.4 (d, $^1J = 32.7$, C_6), 33.4 (dd, $^1J = {}^2J = 2.5$, C_4), 34.4 (dd, $^1J = 7.6$, $^2J = 99.2$, C_3), 61.6 (d, $^2J = 6.6$, CH_2O), 129.0 (d, $^2J = 12.2$, $C_{3''}$),[a] 129.5 (d, $^1J = 9.4$, $C_{3'}$),[a] 130.6 (d, $^1J = 8.1$, $C_{2'}$),[a] 130.9 (d, $^1J = 2.7$, $C_{4'}$),[b] 132.4 (d, $^2J = 9.3$, $C_{2''}$),[a] 133.0 (d, $^2J = 2.8$, $C_{4''}$),[b] [a,b]may be reversed; δ_H 1.02 (dd, $^1J = 6.5$, $^2J = 1.0$, 3H, C_5—CH_3), 1.35 (t, $J = 7.0$, 3H, CH_2CH_3), 3.88–3.98 and 4.08–4.17 (m, 2H, CH_2O), 7.36–7.75 (m, 10H, Ar).

Minor: 40%; δ_{P2} 43.38 (d), $^3J_{PP} = 33.8$, δ_{P1} 9.2 (broad); $\delta_B = -33.6$; δ_C 16.6 (d, $^2J = 5.9$, CH_3CH_2), 20.5 (dd, $^1J = 31.6$, $^2J = 1.4$, C_2), 28.7 (dd, $^1J = 7.0$, $^2J = 14.8$, C_5), 29.2 (d, $^1J = 34.4$, C_6), 33.1 (dd, $^1J = {}^2J = 2.7$, C_4), 34.3 (dd, $^1J = 7.7$, $^2J = 99.8$, C_3), 61.5 (d, $^2J = 5.0$, CH_2O), 129.1 (d, $^2J = 12.4$, $C_{3''}$),* 129.4 (d, $^1J = 9.3$, $C_{3'}$),* 130.5 (d, $^1J = 8.9$, $C_{2'}$),* 132.5 (d, $^2J = 9.3$, $C_{2''}$),* *may be reversed; δ_H 1.04 (dd, $^1J = 6.5$, $^2J = 1.0$, 3H, C_5—CH_3).

Quantum Chemical Calculations

The geometry optimization of different conformers of molecules was performed by ab initio calculations by Gaussian 03 [15] with HF/6-31G* basis. In the ab initio calculations, the force matrices of the fully optimized molecules had no negative eigenvalues. The factor of 0.8929 was used as a scaling factor for the ZPVEs. The initial conformations were chosen on the basis of earlier literature data [5,6].

REFERENCES

[1] Hewitt, D. G. In Comprehensive Heterocyclic Chemistry II; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V., (Eds.); Pergamon: Oxford, 1996; Vol. 5. Ch. 12.

[2] Gallagher, M. J. In Phosphorus–Carbon Heterocyclic Chemistry: The Rise of a New Domain; Mathey, F. (Ed.); Pergamon: Amsterdam, 2001; Ch. 5.1.

[3] Keglevich, Gy. Current Org Chem 2006, 10, 93.

[4] Keglevich, Gy.; Sipos, M.; Imre, T.; Ludányi, K.; Szieberth, D.; Tóke, L. Tetrahedron Lett 2002, 43, 8515.

[5] Keglevich, Gy.; Sipos, M.; Szieberth, D.; Nyulászi, L.; Imre, T.; Ludányi, K.; Tóke, L. Tetrahedron 2004, 60, 6619.

[6] Keglevich, Gy.; Sipos, M.; Körtvélyesi, T.; Imre, T.; Tóke, L. Tetrahedron Lett 2005, 46, 1655.

[7] Körtvélyesi, T.; Sipos, M.; Keglevich, Gy. Heteroatom Chem 2005, 16, 520.

[8] Keglevich, Gy.; Sipos, M.; Szieberth, D.; Petőcz, Gy.; Kollár, L. J Organomet Chem 2004, 689, 3158.

[9] Keglevich, Gy.; Sipos, M.; Ujj, V.; Körtvélyesi, T. Lett Org Chem 2005, 2, 608.

[10] Keglevich, Gy.; Sipos, M.; Takács, D.; Greiner, I. Heteroatom Chem 2007, 18, 226.

[11] Bondi, A. J Phys Chem 1964, 68, 441.

[12] Pellon, P. Teterahedron Lett 1992, 33, 4451.

[13] Keglevich, Gy. Synthesis 1993, 931.

[14] Keglevich, Gy.; Kovács, J.; Ludányi, K.; Tóke, L. Heterocyclic Commun 2002, 8, 31.

[15] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian 03, Revision B.01, Gaussian, Inc., Pittsburgh PA, 2003.