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1,2,3,4,5,6-Hexahydrophosphinine 1-oxides with an exocyclic P-function at position 3: diastereoselective synthesis, stereostructure and conformation

György Keglevich,[a,*] Melinda Sipos,[a] Tamás Körtvélyesi,[b] Tímea Imre[c] and László Tőke[a]

[a]*Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary*
[b]*University of Szeged, Department of Physical Chemistry, 6701 Szeged, Hungary*
[c]*Hungarian Academy of Sciences, Chemical Research Center, 1525 Budapest, Hungary*

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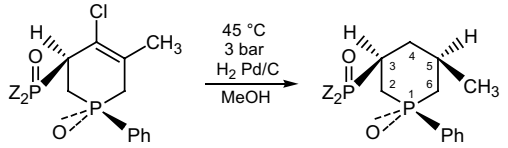
Abstract—Catalytic hydrogenation of the corresponding tetrahydrophosphinine oxides afforded the title compounds (**4**–**6**) as exclusive or major diastereomers the stereostructure and conformation of which were evaluated by stereospecific ^{3}J couplings, as well as HF/6-31G* ab initio calculations.

The six-membered ring compounds, dihydro-, tetrahydro- and hexahydrophosphinine oxides form a representative group of P-heterocycles.[1,2]

We have recently introduced 1,2,3,6-tetrahydrophosphinine-derivatives with a P-function in position 3.[3] The dioxides and disulfides were found to exist as the twist-boat conformers stabilised by novel intramolecular interactions.[4] In addition, the corresponding diphosphine behaved as a suitable bidentate P-ligand to form a *cis*-chelate platinum complex.[5]

It was a logical continuation to prepare the fully saturated 3-substituted 1,2,3,4,5,6-hexahydrophosphinine oxides and to study their properties in comparison with the corresponding 1,2,3,6-tetrahydrophosphinine derivatives.

The starting 3-diphenylphosphinoxido- and 3-dialkylphosphono-4-chloro-5-methyl-1,2,3,6-tetrahydrophosphinine oxides (**1a**, **2a**,**b** and **3a**,**b**) were subjected to catalytic hydrogenation to afford the corresponding 1,2,3,4,5,6-hexahydrophosphinine oxides **4a**, **5a**,**b** and **6a**,**b**, respectively, in 83–92% yields after chromatography.[6] Saturation of the double bond and hydrogenolysis of the C–Cl bond took place under unusually mild conditions at 25–45 °C and ca. 3 bar, as compared to analogous cases.[7] Moreover, the reductions were stereoselective; the 1-phenylhexahydrophosphinine oxides **4a**,[8] **5a**[9] and **6a**[10] were formed as single diastereomers (Scheme 1), whereas the 1-ethoxy products **5b**[11] and **6b**[12] were obtained as mixtures of major (~80%) and minor (~20%) isomers (Scheme 2). The configuration at the P-1 and C-3 centres of the starting tetrahydrophosphinine oxides **1**–**3** was assumed to have been preserved in the corresponding hexahydrophosphinine oxides **4**–**6**, while the stereogenic sp^2 C-5 centre of **1**–**3** was transformed to an sp^3 carbon atom in a selective manner during the reduction. On the basis of the stereospecific NMR couplings (see below), we had to assume



	Z		yield [%]
1a	Ph	**4a**	92
2a	MeO	**5a**	90
3a	EtO	**6a**	85

Scheme 1.

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* Corresponding author. Tel.: +36 1 4631111x5883; fax: +36 1 4633648; e-mail: keglevich@mail.bme.hu

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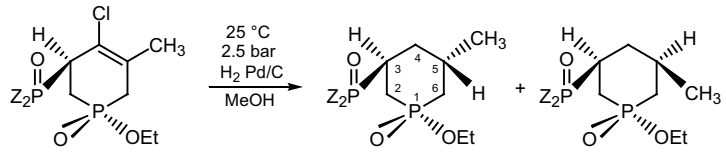


	Z			yield [%]
2b	MeO	**5b-1** (78%)	**5b-2** (22%)	87
3b	EtO	**6b-1** (75%)	**6b-2** (25%)	83

Scheme 2.

that the configuration at the C-5 centre was different in **4–6/a** and in the predominating diastereomers of **5b** and **6b** (Schemes 1 and 2).

The hexahydrophosphinine oxides **4–6** were characterised by ^{31}P, ^{13}C and ^{1}H NMR as well as by mass spectroscopic data. It was of diagnostic value that the chemical shift and the multiplicity of the skeletal methyl group was significantly different for the P-1–Ph products **4a**, **5a** and **6a** and for the major isomer of the P-1–OEt compounds **5b-1** and **6b-1** in the ^{13}C NMR spectra. In the former cases, the methyl group at C-5 appeared at $\delta_C \sim 24.1$ as a doublet of doublets ($^1J \sim 16$, $^2J \sim 2$), while in the latter instances it occurred at $\delta_C \sim 18.2$ as a singlet (Table 1). Based on analogies, a $^3J_{PC}$ coupling of ~17 Hz can be expected for an equatorial C-3 methyl group of a hexahydrophosphinine oxide.[13] According to this, the C-5 methyl of **4a**, **5a** and **6a** with a $^3J_{PC}$ of ~16 Hz must be equatorial, while that of **5b-1** and **6b-1** with no observable $^3J_{PC}$ is probably axial. Without going into details, analysis of the ^1H NMR data of the C-5 methyl group led to the same conclusion (see Table 1). Moreover, it could also be seen that spectral parameters of the minor isomers **5b-2** and **6b-2** showed resemblance to those of **4a**, **5a** and **6a**.

Due to the preserved configuration of the C-3 centre, the sterically demanding 3-P moiety occupies the more favourable equatorial position. Hence, the relative position of the 3-P substituent and the skeletal methyl group is *cis* in **4–6/a** and is *trans* in **5b-1** and **6b-1**.

In order to evaluate the conformational situation of the products **4–6**, HF/6-31G* ab initio calculations were carried out on the relevant chair conformers.[14,15] Relative energies for the selected conformers of **4a** and **6b-1** are listed in Table 2. It can be seen that for **4a**, the chair conformation is the most favourable form in which besides the C-5–Me and the C-3–P(O)Ph_2 groups, the P-1–Ph substituent is also equatorial (**A**). If the methyl group were in the axial position, the conformer (**B**) would be 2.4 kcal/mol less stable. For **6b-1**, the chair with an axial P-1–OEt (**C**) seems to be the most favourable. If the C-5–Me group is placed in the axial position,

Table 1. ^{13}C and ^{1}H NMR data of the skeletal methyl group in the exclusive or predominating form of hexahydrophosphinine oxides **4–6** ($CDCl_3$)

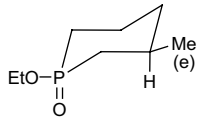
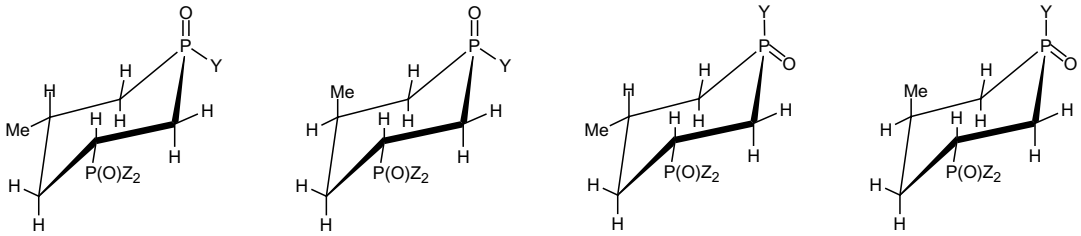
	δ_C (C_5–CH_3)	Multipl.	J_1 (Hz)	J_2 (Hz)	δ_H (C_5–CH_3)	Multipl.	J_1 (Hz)	J_2 (Hz)	Reference
4a	24.4	dd	15.4	1.5	1.05	dd	5.7	2.7	
5a	23.8	dd	15.8	2.4	1.10	dd	6.0	3.0	
6a	24.3	dd	15.9	2.6	1.12	dd	6.3	2.8	
5b-1	17.8	s			1.15	d	7.5		
6b-1	18.5	s			1.15	d	7.0		
	22.9	d	16.9			dd			7

Table 2. Relative energies (kcal/mol) for some chair conformers of hexahydrophosphinine oxides **4a** and **6b-1** calculated at the HF/6-31G* level



Y	Z	A	B	C	D
Ph	Ph	0	2.4	5.1	8.9
EtO	EtO	0.3	2.7	0	2.3

the conformer (**D**) becomes 2.3 kcal/mol less stable. Taking into account the stereospecific $^3J_{PC}$ couplings (see above), it is predicted that, in this case, major component **6b-1** adopts conformation **D**, while conformation **C** is adopted by the minor component **6b-2**. This situation seems to be allowed by a difference of ca. 2 kcal/mol. Rotation of the 3-P(O)$(OEt)_2$ moiety around the C-3-P bond may further decrease the difference in the energy content. Our experience is that the energy of the species is sensitive towards the rotation position of the exocyclic moiety. This phenomenon is being studied further.

Calculations also suggested that orientation of the C-3–P substituent into the axial position has a dramatic impact on the energy content of the species. A relative energy of 9.2 kcal/mol was calculated for the chair conformer of **4a** with an axial $Ph_2P(O)$ group. Moreover, the chair conformation becomes deformed if the $Ph_2P(O)$ moiety is axial.

Perspective views of the **A** conformer of **4a** and the **D** conformer of **6b-1** are shown in Figures 1 and 2, respectively. According to the Karplus relationship,[16] a dihedral angle of 165° can be attributed to the $^3J_{PC}$ coupling of 15.4 Hz measured on the C-5–Me group of **4a**. In comparison, the stereostructure of **4a** obtained from HF/6-31G* calculations reveals a torsion angle of 182.1°. Similarly, the lack of an observable $^3J_{PC}$ coupling on the C-5–Me group of **6b-1** predicts a torsion angle of 85° which is comparable with the value of −79.1° suggested by the calculations. It can be seen that the experimental and the theoretical data are in quite good agreement.

The 1,3-disubstituted hexahydrophosphinine oxides are of interest as, on the one hand, they can become bidentate P-ligands after deoxygenation. On the other hand, they are of potential interest as biologically active molecules, as they can be regarded as bisphosphine oxides

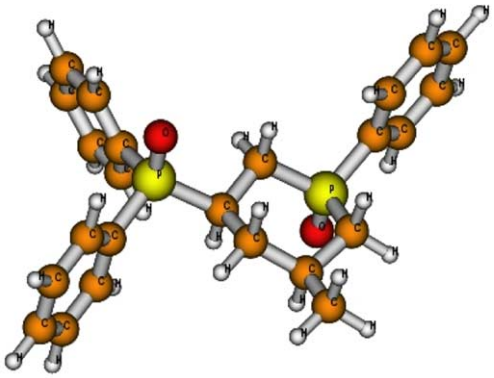


Figure 1. Stereostructure of the stable chair conformer of hexahydrophosphinine oxide **4a** obtained at the HF/6-31G* level of theory;[14] P(1)–C(2): 1.820 Å, C(2)–C(3): 1.544 Å, C(3)–C(4): 1.544 Å, C(4)–C(5): 1.539 Å, C(5)–C(6): 1.541 Å, C(6)–P(1): 1.819 Å, O–P(1)–C(2): 113.1°, O–P(1)–C(6): 113.7°, O–P(1)–C(1′): 112.5°, C(2)–P(1)–C(6): 101.6°, P(1)–C(2)–C(3)–P(2): 176.8°, P(1)–C(2)–C(3)–C(4): −61.2°, P(1)–C(6)–C(5)–CH_3: −177.8°, P(1)–C(6)–C(5)–C(4): 58.7°, C(6)–C(5)–C(4)–C(3): −60.9°, C(6)–P(1)–C(2)–C(3): 55.5°.

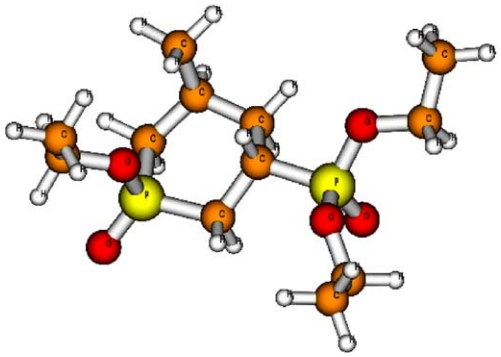


Figure 2. Stereostructure of the stable *chair* conformer of hexahydrophosphinine oxide **6b-1** obtained at the HF/6-31G* level of theory;[14] P(1)–C(2): 1.809 Å, C(2)–C(3): 1.543 Å, C(3)–C(4): 1.543 Å, C(4)–C(5): 1.541 Å, C(5)–C(6): 1.545 Å, C(6)–P(1): 1.815 Å, O–P(1)–C(2): 116.1°, O–P(1)–C(6): 113.7°, O–P(1)–O: 114.2°, C(2)–P(1)–C(6): 103.9°, P(1)–C(2)–C(3)–P(2): 179.5°, P(1)–C(2)–C(3)–C(4): −57.0°, P(1)–C(6)–C(5)–CH_3: −79.1°, P(1)–C(6)–C(5)–C(4): 49.6°, C(6)–C(5)–C(4)–C(3): −59.3°, C(6)–P(1)–C(2)–C(3): 44.4°.

(**4a**), phosphinoxido-phosphonates (**5a** and **6a**) or phosphinato-phosphonates (**5b** and **6b**).

In summary, a selective reduction for the preparation of a series of 1,2,3,4,5,6-hexahydrophosphinine oxides with an exocyclic P-function in position 3 has been described and the stereostructures of the products has been evaluated by stereospecific NMR couplings and quantum chemical calculations. The theory and practice are in good agreement.

Acknowledgements

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6. General procedure for the preparation of 3-substituted-5-methyl-1-phenyl or 1-alkoxy-1,2,3,4,5,6-hexahydrophosphinine 1-oxides (**4a**, **5a**,**b** and **6a**,**b**): A solution of 0.10 g of the 3-substituted-1,2,3,6-tetrahydrophosphinine 1-oxide (**1a**, **2a**,**b**, **3a**,**b**) in 30 ml of methanol was measured in an

autoclave equipped with a magnetic stirrer and 0.10 g of 10% Pd/C was added. The hydrogenation was carried out at 45 °C and at 3 bar for 14 h for **1a** and at 25 °C and 2.5 bar for 14 h for the other starting materials (**2a**,**b** and **3a**,**b**). The resulting suspension was filtered and the solvent was evaporated. Purification of the crude product by column chromatography (silica gel, 3% methanol in chloroform) afforded the hexahydrophosphinine oxide in the cases of **4a**, **5a** and **6a** as a single isomer, or in the cases of **5b** and **6b**, as a mixture of diastereomers.

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8. 3-Diphenylphosphinoxido-5-methyl-1-phenyl-1,2,3,4,5,6-hexahydrophosphinine 1-oxide (**4a**): Yield: 0.085 g (92%); δ_{P_2} 33.8, δ_{P_1} 35.0 (d, $^3J_{PP}$ = 51.4); δ_C 24.4 (dd, ^1J = 15.4, ^2J = 1.5, C-5–*C*H$_3$), 25.3 (d, ^1J = 61.6, C-2), 31.8 (dd, ^1J = 2.9, ^2J = 15.2, C-5), 33.1 (br s, C-4), 34.7 (d, ^1J = 62.3, C-6), 34.8 (d, ^2J = 67.0, C-3), 129.0 (d, ^2J = 11.2, C-3″),[a] 129.1 (d, ^2J = 11.3, C-3″),[a] 129.4 (d, ^1J = 11.0, C-3′),[b] 129.8 (d, ^1J = 9.0, C-2′),[b] 131.2 (d, ^2J = 8.8, C-2″),[a] 131.3 (d, ^2J = 8.5, C-2″),[a] 132.3 (d, ^1J = 2.5, C-4′), 132.5 (br s, C-4″),[a,b] may be reversed; δ_H 1.05 (dd, ^1J = 5.7, ^2J = 2.7, 3H, C-5–CH$_3$), 1.21–1.36, 1.72–1.86 (m, 4H, CH$_2$), 2.02–2.20 (m, 1H, C-5–H), 2.20–2.53 (m, 2H, CH$_2$), 2.54–2.68 (m, 1H, C-3–H), 7.43–7.76 (m, 15H, Ar); $(M+H)^+_{found}$ = 409.1433, $C_{24}H_{27}O_2P_2$ requires 409.1486.
9. 3-Dimethylphosphono-5-methyl-1-phenyl-1,2,3,4,5,6-hexahydrophosphinine 1-oxide (**5a**): Yield: 0.08 g (90%); δ_{P_2} 30.8, δ_{P_1} 33.9 (d, $^3J_{PP}$ = 65.5); δ_C 23.8 (dd, ^1J = 15.8, ^2J = 2.4, C-5–*C*H$_3$), 25.2 (dd, ^1J = 64.0, ^2J = 5.1 C-2), 30.9 (dd, ^1J = 3.3, ^2J = 18.5, C-5), 31.9 (bd, ^2J = 143.7, C-3), 33.3 (d, ^1J = 4.1, C-4), 34.4 (d, ^1J = 63.7, C-6), 52.6 (d, ^2J = 6.9, CH$_3$O), 52.7 (d, ^2J = 6.9, CH$_3$O), 128.9 (d, ^1J = 11.2, C-3′),[a] 129.2 (d, ^1J = 9.2, C-2′),[a] 130.1 (d, ^1J = 94.9, C-1′), 131.9 (d, ^1J = 2.3, C-4′),[a] may be reversed; δ_H 1.10 (dd, ^1J = 6.0, ^2J = 3.0, 3H, C-5–CH$_3$), 1.18–1.27, 1.66–1.74 (m, 2H, CH$_2$), 1.77–1.84 (m, 2H, CH$_2$), 1.96–2.07 (m, 1H, C-5–H), 2.29–2.42, 2.72–2.83 (m, 2H, CH$_2$), 2.53–2.61 (m, 1H, C-3–H), 3.77 (d, J = 10.5, 3H, CH$_3$O), 3.78 (d, J = 10.5, 3H, CH$_3$O), 7.48–7.78 (m, 5H, Ar); $(M+H)^+_{found}$ = 317.1049, $C_{14}H_{23}O_4P_2$ requires 317.1072.
10. 3-Diethylphosphono-5-methyl-1-phenyl-1,2,3,4,5,6-hexahydrophosphinine 1-oxide (**6a**): Yield: 0.08 g (85%); δ_{P_2} 28.5, δ_{P_1} 33.9 (d, $^3J_{PP}$ = 64.8); δ_C 16.6 (d, ^2J = 5.4, *C*H$_3$CH$_2$), 24.3 (dd, ^1J = 15.9, ^2J = 2.6, C-5–*C*H$_3$), 26.0 (dd, ^1J = 64.4, ^2J = 5.7, C-2), 31.4 (dd, ^1J = 3.4, ^2J = 19.8, C-5), 33.0 (dd, ^1J = 2.4, ^2J = 146.2, C-3), 34.0 (d, ^1J = 4.3, C-4), 35.1 (d, ^1J = 63.9, C-6), 62.2 (d, ^2J = 7.0, CH$_2$O), 62.3 (d, ^2J = 6.8, CH$_2$O), 129.3 (d, ^1J = 11.2, C-3′),[a] 129.7 (d, ^1J = 9.2, C-2′),[a] 131.1 (d, ^1J = 95.1, C-1′), 132.3 (d, ^1J = 2.4, C-4′),[a] may be reversed; δ_H 1.12 (dd, ^1J = 6.3, ^2J = 2.8, 3H, C-5–CH$_3$), 1.17–1.27, 1.68–1.91 (m, 4H, CH$_2$), 1.34 (t, J = 7.0, 3H, CH$_2$C*H*$_3$), 1.35 (t, J = 7.0, 3H, CH$_2$C*H*$_3$), 1.99–2.08 (m, 1H, C-5–H), 2.10–2.22, 2.75–2.85 (m, 2H, CH$_2$), 2.54–2.63 (m, 1H, C-3–H), 4.12 (q, J = 3.5, 2H, *CH*$_2$O), 4.15 (q, J = 3.5, 2H, *CH*$_2$O), 7.48–7.77 (m, 5H, Ar); $(M+H)^+_{found}$ = 345.1354, $C_{16}H_{27}O_4P_2$ requires 345.1384.
11. 3-Dimethylphosphono-5-methyl-1-ethoxy-1,2,3,4,5,6-hexahydrophosphinine 1-oxide (**5b**): Yield: 0.08 g (87%) as a 78:22 mixture of two diastereomers; $(M+H)^+_{found}$ = 285.0996, $C_{10}H_{23}O_5P_2$ requires 285.1021; for the major diastereomer: δ_{P_2} 32.2, δ_{P_1} 47.2 (d, $^3J_{PP}$ = 63.9); δ_C 15.8 (d, J = 5.6, *C*H$_3$CH$_2$O), 17.8 (C-5–*C*H$_3$), 25.2 (dd, ^1J = 85.8, ^2J = 5.13 C-2), 26.9 (dd, ^1J = 5.0, ^2J = 17.9, C-5), 26.9 (dd, ^1J = 4.1, ^2J = 149.0, C-3), 30.3 (dd, ^1J = 8.8, ^2J = 4.1, C-4), 30.5 (d, ^1J = 84.9, C-6), 52.2 (d, J = 6.9, CH$_3$O), 59.4 (d, J = 6.1, CH$_3$*C*H$_2$); δ_H 1.15 (d, J = 7.5, 3H, C-5–CH$_3$), 1.36 (t, J = 6.9, 3H, CH$_2$C*H*$_3$), 3.78 (d, J = 10.4, 6H, OCH$_3$), 4.08 (q, J = 7.2, 2H, *CH*$_2$O); for the minor diastereomer: δ_{P_2} 31.3, δ_{P_1} 47.3 (d, $^3J_{PP}$ = 66.4); δ_H 1.06 (dd, ^1J = 6.5, ^2J = 3.0, C-5-CH$_3$).
12. 3-Diethylphosphono-5-methyl-1-ethoxy-1,2,3,4,5,6-hexahydrophosphinine 1-oxide (**6b**): Yield: 0.075 g (83%) as a 75:25 mixture of two diastereomers; $(M+H)^+_{found}$ = 313.1307, $C_{12}H_{27}O_5P_2$ requires 313.1334; for the major diastereomer: δ_{P_2} 29.9, δ_{P_1} 47.5 (d, $^3J_{PP}$ = 63.5); δ_C 16.3 (d, J = 5.7, *C*H$_3$CH$_2$OP–C-3), 16.4 (d, J = 8.1, *C*H$_3$CH$_2$OP–C-3), 18.5 (C-5–*C*H$_3$), 26.3 (dd, ^1J = 86.3, ^2J = 6.1, C-2), 27.6 (dd, ^1J = 5.1, ^2J = 17.9, C-5), 28.1 (dd, ^1J = 4.8, ^2J = 145.4, C-3), 31.1 (dd, ^1J = 9.1, ^2J = 4.4, C-4), 31.4 (d, ^1J = 84.6, C-6), 60.0 (d, J = 6.3, CH$_2$OPC-3), 62.0 (d, J = 6.9, CH$_2$OP–C-3); δ_H 1.15 (d, J = 7.0, 3H, C-5–CH$_3$), 1.33 (t, J = 7.0, 6H, CH$_2$C*H*$_3$), 1.34 (t, J = 7.0, 3H, CH$_2$C*H*$_3$), 4.02–4.09 (m, 2H, *CH*$_2$O), 4.13 (q, J = 7.0, 4H, *CH*$_2$O); for the minor diastereomer: δ_{P_2} 29.1, δ_{P_1} 47.5 (d, $^3J_{PP}$ = 63.5); δ_H 1.06 (dd, ^1J = 6.5, ^2J = 3.5, C-5–CH$_3$).
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