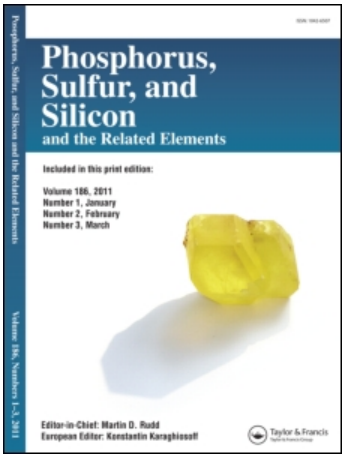

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FACILE SYNTHESIS OF 1,2,3,4,5,6-HEXAHYDROPHOSPHININE 1-OXIDES BY THE HYDROGENATION OF 1,2-DIHYDROPHOSPHININE 1-OXIDES

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FACILE SYNTHESIS OF 1,2,3,4,5,6-HEXAHYDROPHOSPHININE 1-OXIDES BY THE HYDROGENATION OF 1,2-DIHYDROPHOSPHININE 1-OXIDES

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The hydrogenation of the dihydrophosphinine oxides obtained from 3-methyl- or 3,5-dimethyl-1-alkoxy-2,5-dihydro-1H-phosphole oxides on ring enlargement gives the diastereoisomers of new hexahydrophosphinine oxides. Conformational analysis of the 3-methyl-products suggests the equilibria to be strongly biased toward structures with an equatorial C-methyl substituent. In contrast, the predominant diastereoisomer of the 3,5-dimethyl-product exists as an equilibrium of two conformers. A new P-chloro-hexahydrdophosphinine has also been prepared from the ethoxy-derivative which is useful in the synthesis of the amino-product. The hexahydrophosphinine oxides are characterized by ^{31}P, ^{13}C and ^{1}H NMR and mass spectroscopic methods.

Key words: Dihydrophosphinine oxide; hydrogenation; hexahydrophosphinine oxide; diastereoisomer; conformer; stereospecific coupling.

INTRODUCTION

We have recently described a two-step method for the ring enlargement of P-alkyl-, P-phenyl- and P-alkoxy-substituted 2,5-dihydro-1H-phosphole 1-oxides to 1,2-dihydrophosphinine oxides.[1–3] Dichlorocarbene is added to the double bond of the dihydro-1H-phosphole oxide in the first step,[1,3] and the cyclopropane ring so formed is opened up thermally in the second step[2,3] to give the products in good yields. This method offers easier access to valuable dihydrophosphinines than the four-step procedure[4] involving ozonolysis of the dihydro-1H-phosphole oxide, intramolecular aldol-condensation of the intermediate dioxo-compound, reduction of the carbonyl function of the resultant tetrahydrophosphinine and dehydration.

1,2-Dihydrophosphinine oxides are excellent starting materials for other P-heterocycles: their ring can be enlarged to a seven-membered phosphepine oxide,[5] or they can be used as dienes in the Diels-Alder reaction to produce new derivatives of the 2-phosphabicyclo[2.2.2]octa-5,7-diene ring system. These are of importance after P-deoxygenation, as precursors of low-coordinate phosphorus fragments.[4,6,7]

In this paper we show, how dihydrophosphinine oxides can be further utilized to afford hexahydrophosphinine oxides by a new approach.

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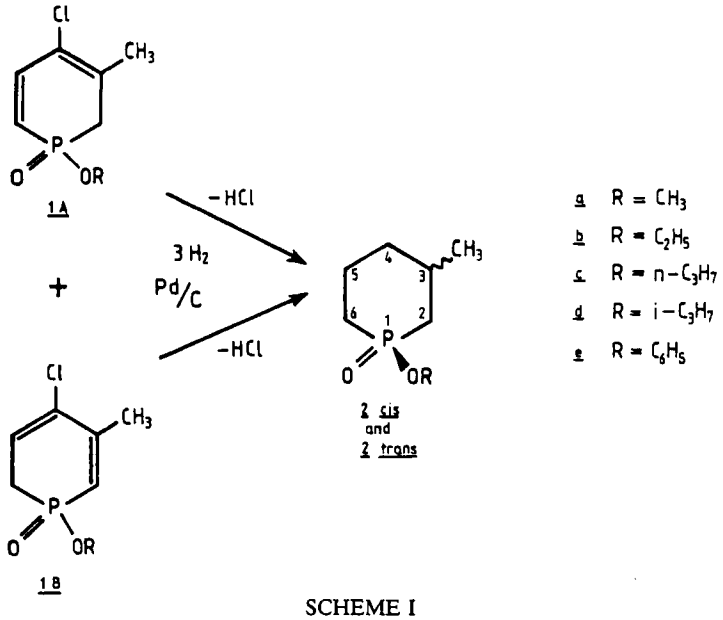
RESULTS AND DISCUSSION

A number of substituted hexahydrophosphinine oxides (phosphorinane oxides)[8-12] including also P-hydroxy,[10] P-alkoxy[11] and P-amino[12] derivatives are known from the literature. To prepare new derivatives the alkoxy-dihydrophosphinine oxides (**1a–d**) together with the newly synthesized phenoxy-compound (**1e**) were subjected to hydrogenation. The mixtures containing the regioisomers (**A** and **B**) of **1** absorbed three equivalents of hydrogen at 450 kPa and room temperature in the presence of 5% palladium on carbon to give the desired hexahydrophospinine oxides **2a–d** in a 41–52% yield after fractional distillation (Scheme I).



SCHEME I

Product **2e** was purified by column chromatography. The two sets of signals in the ^{31}P, ^{13}C and ^{1}H NMR spectra of the products (**2a–e**) reveal the presence of two diastereoisomers (*cis* and *trans*). The product compositions together with the ^{31}P and ^{1}H NMR data are listed in Table I, while the ^{13}C NMR spectral parameters are provided in Table II. The ^{13}C NMR assignments were performed on the basis of an earlier example[9] and were confirmed by spectra obtained by the "Attached Proton Test" technique.

The mass spectra of the hexahydrophosphinine oxides (**2a–e**) exhibit the appropriate molecular ion and the absence of the chlorine atom. In the case of products **2a** and **2b** the $P(O)OR+H^{+}$ fragment is the base peak and characteristic fragmentation of the methyl-substituted hetero ring, like the loss of $C_2H_4(28)$, $C_3H_6(42)$ or $C_3H_7(43)$, $C_4H_6(54)$ and $C_5H_8(68)$ can also be observed. This kind of behavior is also displayed by other saturated phosphinine oxides.[13] The mass spectra of the propoxy-products (**2c** and **2d**) contain only a few signals; the loss of the propenyl group (C_3H_5, 41) gave the base peak. Product **2e** gives a spectrum similar to that of **2a** and **2b**. Mass spectral data have been gathered in Table III.

TABLE I

^{31}P and ^{1}H NMR data for 3-methyl-1,2,3,4,5,6-hexahydrophosphinine 1-oxides (**2a–e**, **4** and **5**) in $CDCl_3$

			^{31}P δ	^{1}H δ (J_{PH})				
		isomeric ratio (%)		C_3-CH_3	H_2,	H_3,	H_4,	others
2a	*cis*	63[a,b]	51.9	1.04,dd (2.7)	3.69,d (10.7)	-	-	1.1-2.4,m
	trans	37	50.6	1.04,dd (2.7)	3.68,d (10.8)	-	-	1.1-2.4,m
2b	*cis*	62[a,b]	50.7	1.02,dd (2.7)	4.00,m	1.31,t		1.4-2.2,m
	trans	38	49.4	1.02,dd (2.7)	4.06,m	1.34,t		1.4-2.2,m
2c	*cis*	63[a,c]	51.1		3.63,m		0.68,t	0.8-2.0,m
	trans	37	49.7		3.59,m		0.62,t	0.8-2.0,m
2d	*cis*	69[a,b]	50.0	1.02,dd (2.9)	4.64,m	1.30,d		1.2-2.3,m
	trans	31	48.6	1.02,dd (2.9)	4.61,m	1.32,d		1.2-2.3,m
2e	*cis*	55[a,c]		1.07,dd (3.0)				1.0-2.4,m 6.8-7.3,m
	trans	45		1.07,dd (3.0)				1.0-2.4,m 6.8-7.3,m
4	e			1.04,dd (3.7)				1.4-2.6,m
5	*cis*	74[a,c]		1.04,dd (2.7)	2.45,d (10.0)			1.2-2.4,m
	trans	26		1.04,d (2.7)	2.42,d (10.5)			1.2-2.4,m

[a] tentatively assigned as the *cis* isomer
[b] determined on the basis of the ^{31}P NMR intensities
[c] determined on the basis of the ^{1}H NMR intensities
[e] only one set of signals could be detected

TABLE II

^{13}C NMR data for 3-methyl-1,2,3,4,5,6-hexahydrophosphinine 1-oxides (**2a–e**, **4** and **5**) in $CDCl_3$

		^{13}C δ (J_{PC})									
		C_2	C_3	C_4	C_5	C_6	C_3-CH_3	C_2'	C_3'	C_4'	C_5'
2a	*cis*[a]	33.8	29.4	34.0	20.8	24.9	22.8	49.3	-	-	-
		(83.5)	(2.9)	(6.6)	(3.6)	(85.7)	(14.7)	(6.6)			-
	trans[a]	33.7	30.4	33.7	21.8	24.3	23.1	48.9	-	-	-
		(83.5)	(4.4)	(6.5)	(5.1)	(87.2)	(16.9)	(6.6)			-
2b	*cis*[a]	34.5	29.3	34.0	20.8	25.5	22.9	58.6	15.6	-	-
		(83.1)	(2.9)	(6.6)	(3.6)	(85.7)	(16.9)	(6.6)	(5.2)		
	trans[a]	34.3	30.3	33.7	21.8	25.0	23.1	58.2	15.5	-	-
		(84.3)	(5.1)	(6.5)	(5.2)	(86.4)	(16.1)	(5.8)	(5.9)		
2c	*cis*[a]	35.1	30.1	34.7	21.5	26.1	23.5	65.2	23.8[b]	9.5	-
		(84.3)	(3.7)	(6.6)	(3.7)	(86.5)	(16.1)	(6.6)	(6)		
	trans[a]	35.0	31.0	34.3	22.4	25.6	23.7	64.7	23.8[b]	9.6	-
		(83.5)	(5.1)	(7)	(5.1)	(87.9)	(16.1)	(5.8)	(6)		
2d	*cis*[a]	35.6	29.9	34.4	21.4	26.5	23.4	68.0	23.7	-	-
		(84.3)	(3.0)	(5.9)	(3.7)	(86.5)	(16.8)	(6.6)	(3.6)		
	trans[a]	35.4	30.7	34.1	22.3	26.0	23.3	67.7	23.7	-	-
		(84.2)	(4.4)	(6.5)	(5.1)	(85.7)	(15.4)	(7.3)	(3.6)		
2e	*cis*[a]	35.0	29.9	34.4	21.3	26.1	23.4	150.4	120.0	129.1	124.0
		(83.5)	(3.0)	(6.6)	(3.6)	(85.7)	(15.3)	(8.8)	(8.8)		
	trans[a]	34.7	30.9	34.0	22.3	25.4	23.5	150.4	120.0	129.1	124.0
		(82.8)	(5.1)	(7.3)	(5.1)	(84.3)	(16.8)	(8.8)			
4	c	41.8	31.7	34.1[b]	22.9	33.0	23.7	-	-	-	-
		(66.7)	(4.2)	(6)	(5.2)	(68.1)	(19.1)				
5	*cis*[a]	33.4	29.3	34.9[b]	21.1	24.0	23.7	34.6[b]	-	-	-
		(77.0)	(2.9)	(6)	(4.4)	(81.3)	(15.4)	(4)			
	trans[a]	33.3	30.3	34.3	21.9	24.5	23.1	36.0	-	-	-
		(73.3)	(4.4)	(5.1)	(5.2)	(83.3)	(14.2)	(3.7)			

[a] tentative assignment
[b] one part of the doublet is overlapped
[c] only one set of signals could be detected

TABLE III

Mass spectroscopic data for hexahydrophosphinine oxides **2a–e**, **4**, and **5**

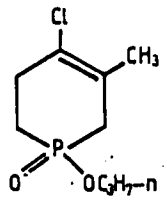
Compound	M^{+a}	M-15	M-28	M-29	M-41	M-42	M-43	M-54	M-68	P(O)YH	68	69	55	56	41
	Relative Intensity %														
2a	40	25	15			20		37	35	100		6		42	50
2b	49	30	28	32[b]			33	33	32	100		20		42	91
2c	3	4			100							5		9	33
2d	3	9			100							6		15	37
2e	80	45		12			18	15	12	60	100		20		64
4	33	15		26		30		75	16		58		71		100
5[c]	9	1					12			23		2	4		13

a m/e values for the molecular ions are: 162, 176, 190, 190, 224, 166, 175 respectively

b from the loss of the ethyl group

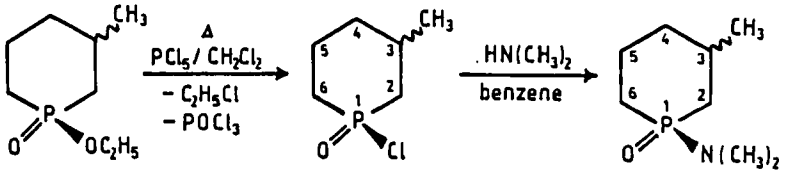
c base peak: m/z 44

To obtain information on the course of the reduction, an experiment was conducted in which the hydrogenation of **1c** was interrupted before completion. After the work-up procedure a mixture was obtained which, according to its ^{31}P NMR spectrum, contained an intermediate along with the isomers of the reduced product (**2c**). On the basis of the mass spectrum obtained by GC-MS, the structure of the intermediate can be formulated as **3**. The m/z value for the molecular ion is 222 with one chlorine atom present. The ^{13}C NMR spectrum also supports the structure as no CH signal is present in the sp^2 region. It can be concluded that the hydrogenation of the disubstituted double bond is the slowest process.



3

A new P-chloro-hexahydrophosphinine oxide (**4**) was also prepared from the ethoxy-compound (**2b**) which gave the amide **5** on reaction with two equivalents of dimethylamine in benzene at 0°C (Scheme II). Intermediate **4** was identified as

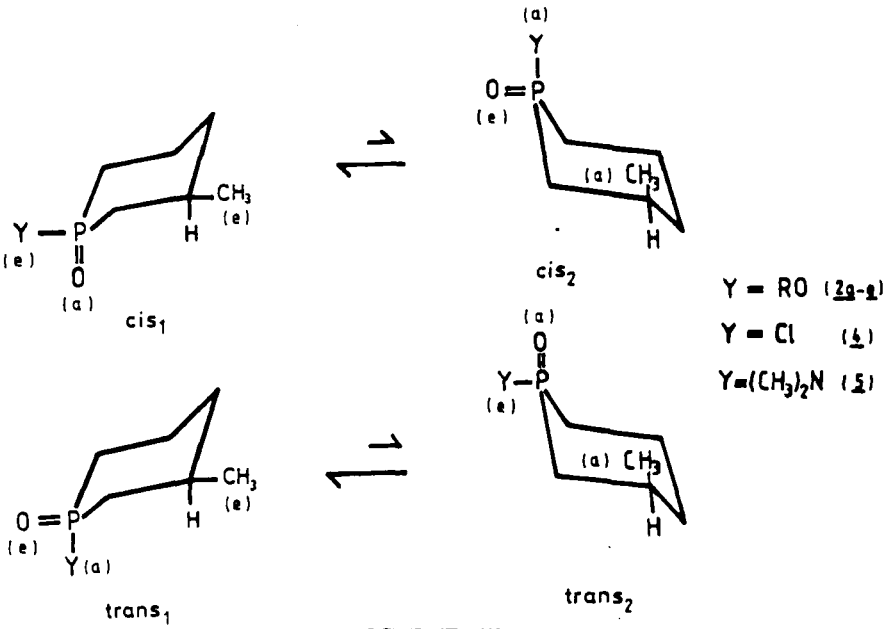


2b **4** **5**

SCHEME II

a crude product, while the amide (**5**) could be obtained in pure form on distillation. Spectral parameters for both **4** and **5** resemble those for the alkoxy-hexahydrophosphinines (**2a–e**). Isomeric composition and ^1H NMR data for products **4** and **5** can be found in Table I, while the ^{13}C NMR and mass spectral features are listed in Tables II and III, respectively.

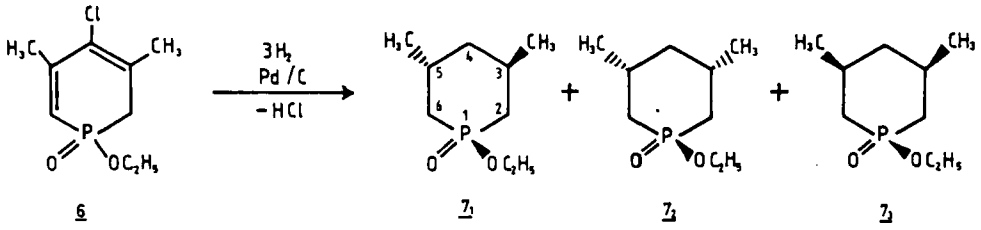
A $cis_1 \rightleftharpoons cis_2$ and a $trans_1 \rightleftharpoons trans_2$ type of equilibrium can be visualized for both diastereoisomers of the hexahydrophosphinine oxides prepared (**2**, **4** and **5**) (Scheme III). A conformational assignment can be made, if the values of the $^3J_{PC}$ coupling



SCHEME III

constants are considered. A coupling of ~18 Hz is expected[14] for the cis_1 and $trans_1$ forms where the P—C_2—C_3—CH_3 dihedral angle is 180°, while a coupling of ~3 Hz is predicted for the cis_2 and $trans_2$ forms with a dihedral angle of ~60°. The measured $^3J_{PC}$ couplings of 14–19 Hz suggest the predominance of the cis_1 and $trans_1$ forms where the methyl group is in the equatorial position. The lack of the special γ-upfield effect in the ^{13}C NMR spectra of the products (**2**, **4** and **5**) also confirms the above conclusion, as such effect should be present if the skeleton methyl group was in the axial position.[9] A similar conformational situation was described for the P-methyl substituted hexahydrophosphinine derivatives.[9] With respect to products **2** and **5** the assignment of the cis_1 and $trans_1$ structures to the two series of data is tentative.

Finally, the 3,5-dimethyl-dihydrophosphinine oxide (**6**) was subjected to hydrogenation. The expected hexahydrophosphinine oxide was formed as a 75–15–10% mixture of three diastereoisomers (7_1, 7_2 and 7_3) (Scheme IV). The methyl groups in the predominant diastereoisomer (7_1) are not equivalent as shown by the ^{13}C NMR spectrum of the product (δ_C = 20.5 and 22.1 for the two methyl groups). The measured $^3J_{PC}$ couplings of 6.7 and 11.6 Hz for the two methyl groups in 7_1



SCHEME IV

suggest the existence of a conformational equilibrium with a ~2:3 participation of the two (possible) conformers.

The skeletal methyl groups are equivalent in both of the minor diastereoisomers (δ_C = 23.9 for 7_2 and δ_C = 23.7 for 7_3, tentative assignment) and occupy equatorial positions ($^3J_{PC}$ = 17.9 and 16.4 Hz, respectively).

EXPERIMENTAL

^{31}P, ^1H and ^{13}C NMR spectra were taken on a JEOL FX 100 instrument operating at 40.26, 100.0 and 25.0 MHz, respectively. Chemical shifts are downfield relative to 85% phosphoric acid (for ^{31}P NMR) and to tetramethylsilane (for ^1H and ^{13}C NMR) and have a positive sign. All coupling constants are given in Hertz. Infrared spectra were recorded on a Specord 75 spectrometer. Mass spectra were obtained on an MS 25-RFA instrument at 70 eV.

The regioisomeric mixtures of the alkoxy-dihydrophosphinine oxides (**1a–d**) were prepared as described earlier.[3] The phenoxy-compound (**1e**) was prepared similarly (vide infra) from the 2,5-dihydro-3-methyl-1-phenoxy-1H-phosphole 1-oxide (**8**).

6,6-Dichloro-1-methyl-3-phenoxy-3-phosphabicyclo[3.1.0]hexane 3-oxide (**9**). A mixture of 3.0 g (14.4 mmol) of **8**[15], 80 ml of alcohol-free chloroform, 33.0 g (0.178 mol) of sodium trichloroacetate and 0.4 g (1.76 mmol) of triethylbenzylammonium chloride was stirred at reflux for 24 h, then the solid phase was filtered off and the solvent evaporated. The residue was purified by column chromatography on silica gel using chloroform as the eluant to give 1.8 g (43%) of **9**: ^{31}P NMR ($CDCL_3$) δ +85.7; ^1H NMR ($CDCl_3$) δ 1.57 (s, 3H, CH_3), 7.0–7.5 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ 20.6 ($^3J_{PC}$ = 7.3, CH_3), 24.1 ($^1J_{PC}$ = 89.4, C_4), 29.7 ($^1J_{PC}$ = 90.1, C_2), 30.3 ($^2J_{PC}$ = 13.2, C_1), 31.4 ($^2J_{PC}$ = 11.0, C_5), 71.3 ($^3J_{PC}$ = 12.5, C_6), 119.6 ($^3J_{PC}$ = 4.6, $C_{2'}$), 124.3 ($C_{4'}$), 129.3 ($C_{3'}$), 149.7 ($^2J_{PC}$ = 9.5, $C_{1'}$); MS, m/e (relative intensity) 290 (M^+, 40), 225 (100), 197 (24), 141 (35), 140 (32), 94 (52), 77 (75).
Anal. Calc. for $C_{12}H_{13}Cl_2O_2P$: C, 49.49; H, 4.50.
Found: C, 49.71; H, 4.65.

3- and 5-Methyl-4-chloro-1,2-dihydro-1-phenoxyphosphinine 1-Oxide (**1Ae** *and* **1Be**) were prepared by the thermolysis of **9** performed as described for the alkoxy-substituted adducts.[3] Reaction time: 16 h, yield: 44%, ^{31}P NMR ($CDCl_3$) δ +32.4 for the major isomer (72%) and +31.5 for the minor isomer (28%); ^1H NMR ($CDCl_3$) δ 2.03 and 2.13 (s, total intensity 3H, CH_3), 2.90 (d, $^2J_{PH}$ = 18) and 2.88 (dd, $^2J_{PH}$ = 18, $^3J_{HH}$ = 5) total intensity 2H, CH_2), 7.0–7.5 (m, 5H, Ar); MS, m/e (relative intensity) 254 (M^+, 47), 219 (6), 161 (18), 160 (28), 94 (100), 77 (38).
Anal. Calc. for $C_{12}H_{12}ClO_2P$: C, 56.58; H, 4.75.
Found: C, 56.74; H, 4,89.

1-Ethoxy-1,2,3,4,5,6-hexahydro-3-methylphosphinine 1-Oxide (**2b**). To the mixture of 7.1 g (34.5 mmol) of **1Ab** and **1Bb** in 150 ml of absolute ethanol was added 1.0 g of 5% palladium on carbon and the suspension then hydrogenated at 450 kPa and room temperature until 3 equivalents of hydrogen were absorbed. The mixture was filtered, the solvent evaporated and the residue distilled *in vacuo* to yield 2.5 g (41%) of **2b** as a 62–38% mixture of two diastereoisomers; bp 82–84°C (0.1 mm Hg) IR (neat) 2940, 1460, 1410, 1250, 1210, 1040 cm^{-1}.
Anal. Calc. for $C_8H_{17}O_2P$: C, 54.51; H, 9.73.
Found: C, 54.75; H, 9.86.

The other *P*-substituted hexahydrophosphinine oxides (**2a**, **c–e**) were prepared similarly from the regioisomeric mixture (**A** and **B**) of the dihydrophosphinine oxides (**1a**, **c–e**) using the appropriate alcohol as the solvent.

1,2,3,4,5,6-Hexahydro-1-methoxy-3-methylphosphinine 1-Oxide (**2a**). Yield 50%; bp 92–94°C (0.1 mm Hg); IR (neat) 2930, 1440, 1390, 1230, 1190, 1020 cm^{-1}; M^{+}_{found} = 162.0832, $C_7H_{15}O_2P$ requires 162.0810.

1,2,3,4,5,6-Hexahydro-3-methyl-1-(1-propoxy)phosphinine 1-Oxide (**2c**). Yield 43%; bp 82–86°C (0.1 mm Hg); IR (neat) 2980, 1480, 1430, 1270, 1220, 1020 cm^{-1}.
Anal. Calc. for $C_9H_{19}O_2P$: C, 56.81; H, 10.07.
Found: C, 57.11; H, 10.18.
Interrupting the hydrogenation (of **1c**) at ~50% conversion the fraction collected in the range of 92–120°C (0.1 mm Hg) contained ~70% of **3**; ^{31}P NMR ($CDCl_3$) δ +44.3; GC-MS, m/e (relative intensity) 222 (M^+, 13), 180 (48), 43 (72), 41 (100).

1,2,3,4,5,6-Hexahydro-3-methyl-1-(2-propoxy)phosphinine 1-Oxide (**2d**). Yield 52%; bp 88–94°C (0.1 mm Hg); IR (neat) 2940, 1460, 1390, 1250, 1200, 1000 cm^{-1}.
Anal. Calc. for $C_9H_{19}O_2P$: C, 56.81; H, 10.07.
Found: C, 56.62; H, 9.90

1,2,3,4,5,6-Hexahydro-3-methyl-1-phenoxyphosphinine 1-Oxide (**2e**). Ethanol was used as the solvent and the product purified by column chromatography (silica gel, 3% methanol in chloroform); yield, 73%; IR (neat) 2950, 1610, 1510, 1470, 1220, 940 cm^{-1}.
Anal. Calc. for $C_{12}H_{17}O_2P$: C, 64.26; H, 7.65.
Found: C, 64.06; H, 7.75.

The isomeric composition, ^{31}P and ^1H NMR data for products **2a–e** are listed in Table I, while the ^{13}C NMR and mass spectral parameters can be found in Table II and Table III, respectively.

1-Chloro-1,2,3,4,5,6-hexahydro-3-methylphosphinine 1-Oxide (**4**). To the 15 ml dichloromethane solution of 1.96 g (11.1 mmol) of **2b** was added 2.67 g (12.8 mmol) of phosphorus pentachloride. The mixture was stirred for 30 min at room temperature and for 3.5 h at reflux. Evaporation of the volatile components *in vacuo* provided 1.75 g of crude **4**; ^{13}C NMR, Table II; MS, Table III. M^{+}_{found} = 166.0333, $C_6H_{12}ClOP$ requires 166.0314.

1-Dimethylamino-1,2,3,4,5,6-hexahydro-3-methylphosphinine 1-Oxide (**5**). The mixture of 2.1 ml (31.7 mmol) of dimethylamine and 10 ml of benzene was added dropwise to the solution of 1.75 g (~10.5 mmol) of crude **4** in 10 ml of benzene with external ice cooling and stirring. On completion of the addition, the cooling bath was removed and the mixture was stirred at room temperature for 3 h. Then the precipitate was filtered off and the solvent evaporated. Fractional distillation of the residue *in vacuo* gave 1.4 g (76%) of **5**; bp 92–98°C (0.1 mm Hg); IR (neat) 2930, 1460, 1400, 1290, 1190, 980 cm^{-1}.
Anal. Calc. for $C_8H_{18}NOP$: C, 54.82, H, 10.36.
Found: C, 54.55, H, 10.12

3,5-Dimethyl-1-ethoxy-1,2,3,4,5,6-hexahydrophosphinine 1-Oxide (**7**). 4-Chloro-1,2-dihydro-3,4-dimethyl-1-ethoxyphosphinine 1-oxide (**6**)[16] was hydrogenated as the monomethyl-derivative (**1b**) and gave a mixture of three diastereoisomers of **7**. Yield 65%; bp 87–92°C (0.15 mm Hg); IR (neat) 2940, 1440, 1390, 1240, 1180, 1020 cm^{-1}; MS, m/z (relative intensity) 190 (M^+, 39), 175 (40), 161 (18), 148 (32), 147 (26), 122 (38), 108 (20), 93 (100), 65 (70), 55 (56), 41 (94).

7_1: (75%) ^{13}C NMR ($CDCl_3$) δ 16.2 ($^3J_{PC}$ = 5.6, $C_{3'}$), 20.5 ($^3J_{PC}$ = 6.7, C_3—CH_3), 22.1 ($^3J_{PC}$ = 11.6, C_5—CH_3), 25.6 ($^2J_{PC}$ = 3.6, C_3), 26.1 ($^2J_{PC}$ = 3.4, C_5), 32.0 ($^1J_{PC}$ = 83.5, C_2), 33.5 ($^1J_{PC}$ = 84.7, C_6), 40.2 ($^3J_{PC}$ = 7.6, C_4), 59.2 ($^2J_{PC}$ = 6.1, $C_{2'}$); ^1H NMR ($CDCl_3$) δ 1.33 (*t*, 3H, CH_2—$C\underline{H}_3$), 1.12 (dd, $^3J_{HH}$ = 6.9, $^4J_{PH}$ = 3.3, C_3—CH_3), 1.08 (dd, $^3J_{HH}$ = 6.9, $^4J_{PH}$ = 2.0, C_5—CH_3) total intensity 6H, 4.06 (m, 2H, OCH_2).

7_2: (15%) ^{13}C NMR ($CDCl_3$) δ 15.3 ($^3J_{PC}$ = 9.1, $C_{3'}$), 23.9 ($^3J_{PC}$ = 17.9, C—CH_3), 29.2 ($^2J_{PC}$ = 1.4, C_3), 33.9 ($^1J_{PC}$ = 85.2, C_2), 43.7 ($^3J_{PC}$ = 4.6, C_4), 59.6 ($^2J_{PC}$ = 6.6, $C_{2'}$).

7_3: (10%) ^{13}C NMR ($CDCl_3$) δ 15.5 ($^3J_{PC}$ = 9.5, $C_{3'}$), 23.7 ($^3J_{PC}$ = 16.4, C—CH_3), 29.8 ($^2J_{PC}$ = 3.0, C_3), 33.5 ($^1J_{PC}$ = ~85, C_2), 43.1 ($^3J_{PC}$ = 5.6, C_4), 60.0 ($^2J_{PC}$ = 6.5, $C_{2'}$).

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