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Synthesis of the P-Sulfide Derivatives of 3-Phosphabicyclo[3.1.0]hexanes and 1,2-Dihydrophosphinines

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ABSTRACT

Several 3-phosphabicyclo[3.1.0]hexane 3-oxides have been transformed into the corresponding sulfides by reaction with phosphorus pentasulfide. The 3-phenyl derivative could also be prepared by deoxygenation of the oxide followed by reaction with elemental sulfur. Opening of the cyclopropane ring in phosphabicyclohexane sulfides afforded mixtures of 3- and 5-methyl-1,2-dihydro-phosphinine-1-sulfides. Because of better yields, preparation of these products by thionation of the dihydrophosphinine oxides is more appropriate. The new phosphorus heterocycles have been characterized by ^{31}P, ^{13}C, and ^{1}H NMR and mass spectral data.

INTRODUCTION

A number of methods are known for the synthesis of sulfide derivatives of organophosphorus compounds [1]. One of the most often used procedures is the transformation of P=O compounds to P=S derivatives. Change in the functionality can be accomplished with reagents such as phosphorus pentasulfide (P_2S_5) [2,3], 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide [Lawesson's reagent (LR)] [4], and elemental sulfur [5]. The other widely used approach involves the addition of sulfur to tertiary phosphines. The sulfur atom may be donated by elemental sulfur or by a variety of sulfur-transfer agents [1]. Perhaps, the most important sulfur-transfer reagent is the LR [6], but the use of dibenzoyl tetrasulfide also has certain advantages [7].

The sulfide derivatives of phosphorus heterocycles (mainly tertiary phosphine sulfides) are well-known [1]. Six-membered ring compounds including dihydrophosphinines have also been described [8,9], which are of importance, as they can be utilized in the preparation of phosphinines [9]. Phosphabicyclo[2.2.2]octadienes, prepared by the Diels–Alder reactions of dihydrophosphinines, form the other useful group of sulfide-functionalized phosphorus heterocycles, as they can be used as precursors of reactive methylene-phosphine-sulfides [10,11].

We have recently developed a method for the synthesis of 1,2-dihydrophosphinine oxides from 2,5-dihydro-1H-phosphole 1-oxides. According to this

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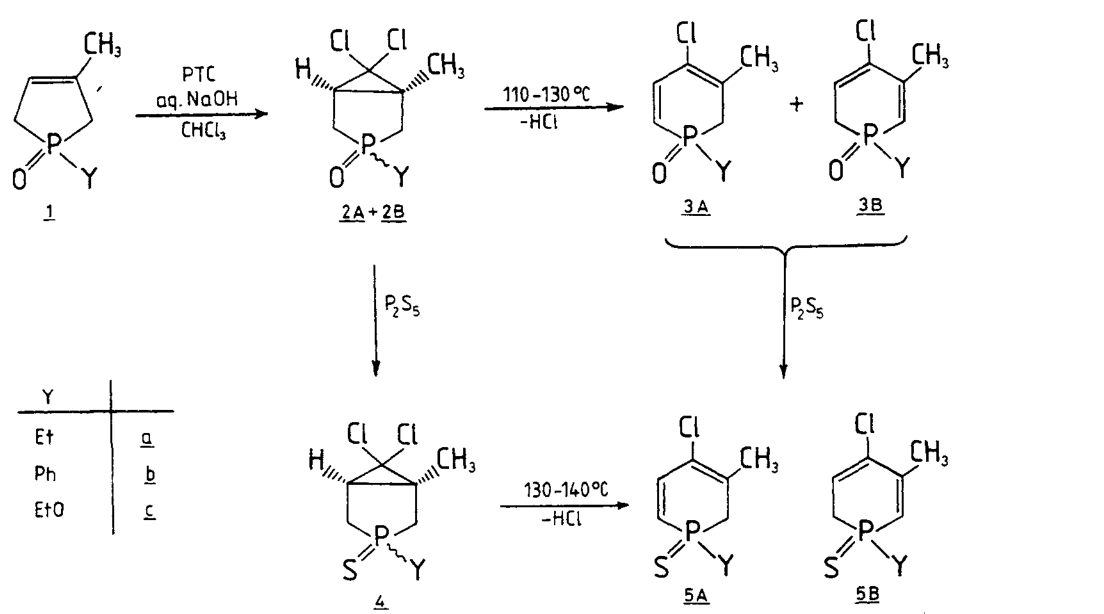
method, the ring of the starting material is enlarged by the "dichlorocarbene method" (Scheme 1) [12–15]. In this article, preparations of the sulfide analogues of the intermediates (3-phosphabicyclo[3.1.0]hexane derivatives) and ring-expanded products are shown.

RESULTS AND DISCUSSION

First, the preparation of sulfide derivatives bearing a phenyl or an ethyl substituent on the P atom was attempted. With regard to the 3-phosphabicyclo[3.1.0]hexane 3-sulfides (**4**), synthesis by the exchange of the oxygen atom in **2** with sulfur seemed to be more appropriate than that by dichlorocarbene addition to 2,5-dihydro-1H-phosphole 1-sulfides. Thionation of the oxides (**2**) was accomplished by reaction with P_2S_5 (Scheme 1). To avoid the opening of the dichlorocyclopropane ring in adduct **2**, the reaction was carried out at a temperature under 100°C. From the oxides (**2a,b**) of uniform composition (isomer **A**, where the dichlorocyclopropane ring and the P=O group are in the *trans* disposition) [12,16], the sulfides (**4a,b**) were also formed in each case as a single diastereomer. Since thionation of the P=O, compounds takes place with retention of configuration [17], it had to be assumed that sulfides **4a** and **4b** also had structure **A**. The products (**4a,b**) were obtained in ca. 65% yield and, together with the newly synthesized starting material **2a**, were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass and IR spectral data. ^{13}C NMR chemical shifts for the C_1, C_2, C_4, and C_5 atoms of the sulfides (**4a,b**) are downfield with respect to the corresponding shifts of the oxides (**2**) [12,16]. The sulfides (**4a,b**) have smaller $^1J_{PC}$ couplings than the oxides (**2**) (≈50 Hz vs. ≈64 Hz [12,16]) (Table 1). Mass spectral fragmentation of the products (**4a,b**) is similar to that of the oxides (**2**): loss of the chloro-substituent and the P(S)Y moiety can be observed in the mass spectra. Moreover, a fragment formed by the loss of a chlorine atom and hydrogen sulfide could also be identified in the spectra (Table 2). The peak with m/z = 181 in the mass spectrum of **4b** could be assigned to the fragment $PhP(S)CH_2CH{=}CH_2 \urcorner^{+}$ (see footnote *b* in Table 2). The molecular ions and the fragments containing chlorine atom(s) had the correct isotopic distribution. Absorption at ca. 620 cm^{-1} in the IR spectra of the products also proves that P=S functionalized species (**4a,b**) had been produced.

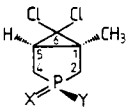
Another method was also tried for the conversion of oxides **2** to sulfides **4**. According to this, compound **2b** was deoxygenated with trichlorosilane, and phosphine **6** so obtained was then treated with elemental sulfur (Scheme 2). The yield of sulfide **4b** was comparable with the outcome of the direct oxygen-sulfur exchange reaction.

In the first approach, synthesis of the dihydrophosphinine sulfides (**5**) was also attempted by oxygen-sulfur exchange. To avoid the decomposition of dihydrophosphinines, the mixture of the oxides (**3a,b**) and P_2S_5 was heated at a temperature under 100°C. From the mixture of the double bond isomers (**A** and **B**) of the oxides (**3a,b**) [13], the isomers (**A** and **B**) of the products (**5a,b**) were formed in a similar ratio (ca. 76:24) (Scheme 1). The dihydrophosphinine sulfides (**5a,b**) were obtained in ca. 58% yield. Structures of the products (**5a,b**) were confirmed by ^{31}P and ^{1}H NMR, as well as MS, GC–

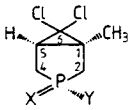


SCHEME 1

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



A



B

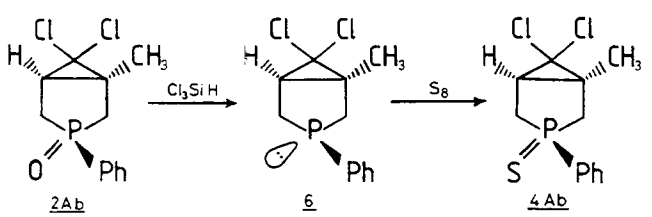
			$\delta^{13}C$ NMR(J_{PC} in Hz)									
Compound	*X*	*Y*	C_1	C_2	C_4	C_5	C_6	C_1–CH_3	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$
2Aa	O	Et	36.3 (6.6)	35.6 (63.7)	29.4[a] (63.7)	37.1 (5.1)	72.6 (8.8)	21.7 (5.8)	22.8[a] (61.0)	6.5 (5.8)		
4Aa	S	Et	*b*	38.5 (47.9)	32.6 (51.3)	*b*	72.6 (13.2)	21.3 (5.8)	25.1 (46.9)	6.2 (3.6)		
4Ab	S	Ph	37.6 (6.6)	43.0 (52.8)	35.8 (54.2)	39.5 (5.9)	72.7 (11.8)	21.1 (6.6)	134.3 (68.9)	129.0 (11)	129.7 (10)	*b*
4Ac	S	EtO	*b*	41.5 (71.8)	*b*	*b*	72.6 (16.8)	22.0 (6.6)		62.3 (7.3)	16.3 (4.4)	
4Bc	S	EtO	36.0 (8.0)	41.0 (69.6)	35.2 (70.0)	37.0 (7.3)	72.8 (14.7)	21.5 (6.6)		60.8 (5.8)	16.4 (6.6)	

[a]May be reversed.
[b]Not resolved.

TABLE 2 Mass Spectral Data for 6,6-Dichloro-1-methyl-3-phosphabicyclo[3.1.0]hexane Derivatives **2a** and **4a–c**

	Relative Intensity (%)			
Fragment (*m/z*)	**2a**[a]	**4a**[a]	**4b**[b]	**4c**[c]
M^{+d}	6	54	37	45
$M-Cl^{+}$	100	76	100	75
$M-Cl-H_2S^{+}$	–	12	47	–
M–Cl–P(O)Et or $P(S)Y^{+}$(115)	8	24	16	34
$P(S)Y^{+}$	–	20	30	–
$C_6H_7^{+}$(79)	50	100	37	100
$C_6H_5^{+}$(77)	35	47	46	52

[a]*m/z* = 156 (11%); *m/z* = 127 (10%).
[b]*m/z* = 91 (76%); *m/z* = 181 (52%) (m/z_{found} = 181.0245, $C_9H_{10}PS$ requires 181.0241).
[c]*m/z* = 195 (52%); *m/z* = 161 (17%); *m/z* = 149 (79%).
[d]*m/z* values for the molecular ions of **2a**, **4a**, **4b**, and **4c** are 226, 242, 290, and 258, respectively.



2Ab 6 4Ab

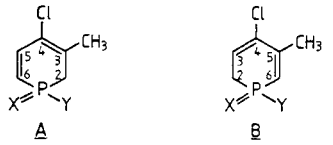
SCHEME 2

MS, and HRMS methods. Product **5b** was also characterized by ^{13}C NMR spectroscopy. These data, together with those of the newly prepared starting material **3a**, are listed in Table 3, while mass spectral characterizations of the dihydrophosphinines (**3a**, **5a**, and **5b**) are shown in Table 4.

Then, of course, we wanted to prepare the dihydrophosphinine sulfides (**5**) by thermolysis of the 3-phosphabicyclo[3.1.0]hexane 3-sulfides (**4**). TG and DTG examinations showed that the dichlorocyclopropane ring of **4a** opened in the range of 125–160°C. From this, it can be concluded that the sulfides of the phosphabicyclohexanes (**4**) are somewhat more resistant to the thermal process than are the oxides (**2**) [13]. Experiments also demonstrated this, as under the conditions appropriate for the transformation of the oxides (a 7 hour boiling period in toluene in the presence of one equivalent of triethylamine) [14], sulfide **4a** underwent only partial cyclopropane ring opening. In the next experiment, the thermolysis of adduct **4a** was carried out at 140°C without solvent (Scheme 1). The reaction was complete after 10 minutes, but due to the instability of dihydrophosphinine **5a**, side products (including polymers) were also formed. The yield of **5a** was poor as determined when it was isolated by flash column chromatography. It can be concluded that thionation of the oxides (**3a,b**) is the better method for the preparation of dihydrophosphinine sulfides (**5a,b**).

After preparing the tertiary phosphine sulfide derivatives (**4** and **5**), we desired to synthesize monothiophosphinic esters **4c** and **5c**. Based on our experiences discussed above, preparation by thion-

TABLE 3 ^{13}C NMR Spectral Data for the Double Bond Isomers (**A** and **B**) of 4-Chloro-1,2-dihydrophosphinine Derivatives **3a** and **5a–c**, in $CDCl_3$ Solutions



A B

Compound	X	Y	$\delta^{13}C$ NMR(J_{PC} in Hz)									
			C_2	C_3	C_4	C_5	C_6	C–CH_3	C_1'	C_2'	C_3'	C_4'
3Aa			32.7	130.4	123.4	142.6	118.6	22.8	22.7	5.0		
			(67.4)	(9.6)	(19.0)	—	(88.7)	(8.0)	(74.7)	(5.1)		
	O	Et										
3Ba			26.8	122.4	131.4	148.1	118.1	*a*	22.4	5.0		
			(68.2)	(8.8)	(19.1)	—	(92.3)		(75.5)	(5.1)		
5Ab			40.4	121.5	123.8	140.7	119.2	23.0	131.8	130.8	128.6	132.0
			(56.4)	(12.3)	(21.8)	(4.0)	(77.7)	(8.5)	(83.5)	(11.1)	(12.6)	(3.2)
	S	Ph										
5Bb			34.4	*a*	*a*	146.6	118.6	24.4	*a*	130.9	128.5	131.9
			(56.7)			(3.5)	(80.4)	(13.0)		(11.1)	(12.6)	(3.2)
5Ac			41.0	131.6	123.6	140.2	122.3	23.0		60.8	16.5	
			(77.0)	(11.7)	(21.2)	—	(96.7)	(9.5)		(6.6)	(5.9)	
	S	EtO										
5Bc			35.2	*a*	*a*	146.2	121.8	23.9		60.8	16.5	
			(77.7)			—	(93.0)	(13.2)		(6.6)	(5.9)	

[a]Not resolved.

TABLE 4 Mass Spectral Data for 3- and 5-Methyl-4-chloro-1,2-dihydrophosphinine Derivatives **3a** and **5a–c**

Fragment (m/z)	Relative Intensity (%)			
	3a[a]	**5a**[b]	**5b**	**5c**[c]
M^{+d}	100	84	69	100
M–SH⌐⌐$^+$	—	100[e]	40	22
M–Cl–P(O)Et or P(S)Y⌐⌐$^+$ (79)	92	58	16	59
$C_6H_5^+$ (77)	63	43	100	50

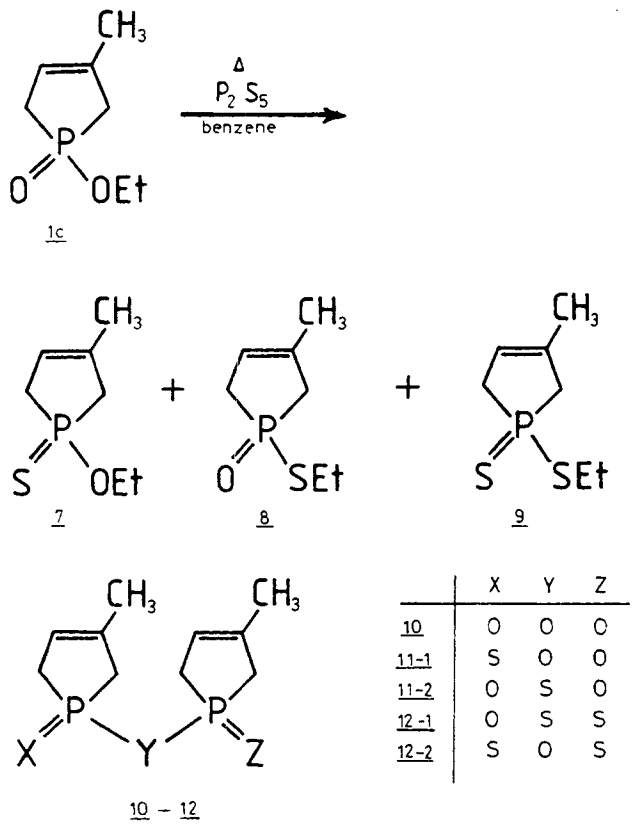
[a]m/z = 161 (41%); m/z = 155 (17%); m/z = 114 (16%).
[b]m/z = 145 (26%).
[c]m/z = 176 (29%); m/z = 161 (71%).
[d]m/z values for the molecular ions of **3a**, **5a**, **5b**, and **5c** are 190, 206, 254, and 222, respectively.
[e]m/z_{found} = 173.0268; $C_8H_{11}PCl$ requires 173.0287 for the ^{35}Cl isotope.

ation of the corresponding P=O derivatives (**2c** and **3c**) with P_2S_5 seemed to be the most appropriate procedure. To avoid the formation of dithio-derivatives, the reaction conditions first had to be optimized.

Dihydrophosphole oxide **1c** was chosen as the starting material in the optimization. Application of the procedure used for the thionation of compounds **2** and **3** (a 24 hour boiling period in benzene in the presence of 0.66 equivalent of P_2S_5) was not suitable, as it led to the formation of a mixture consisting of the desired product (**7**, m/z = 176, δ_p = +114.5, 24%; preparation of an authentic sample is described below), a compound which may be the isomer of **7** (**8**, m/z = 176, δ_p = +114.0, 14%), dithio-phosphole **9** (m/z = 192, δ_p = +81.1, 32%), and a mixture of diphosphinate **10** (m/z = 246, for HRMS see Ref. [18]) and its monothio- and dithio-derivatives (**11**, m/z = 262 and **12**, m/z = 278, respectively) (altogether 30%) (Scheme 3). The presence of the isomers of the monothio- and dithio products (**11** and **12**) was assumed on the basis of GC–MS measurements and the number of signals found in the ^{31}P and ^{13}C NMR spectra. Partial separation of the components of the mixture was achieved by column chromatography. This permitted ^{13}C NMR characterization of phospholes **7** and **9** (Table 5; for the comparison, data of **1c** were also included).

To avoid the side reactions, the thionation was carried out at room temperature. After the working up procedure following 5 days of stirring, dihydrophosphole sulfide **7** could be isolated in 84% yield and with a high purity. (For ^{13}C NMR and other spectral data of **7**, see Table 5 and Ref. [19], respectively).

Thionation of phosphabicyclohexane oxide **2c** and dihydrophosphinine oxide **3c** in the above manner provided the desired products (**4c** and **5c**, respectively). Due to the isomeric composition of



	X	Y	Z
10	O	O	O
11-1	S	O	O
11-2	O	S	O
12-1	O	S	S
12-2	S	O	S

SCHEME 3

the starting materials (**2c** [20] and **3c** [14]), the sulfides (**4c** and **5c**) obtained from them were also isomeric: **4c** consisted of two diastereomers (**A** and **B** with a ratio of 20:80), while **5c** consisted of a mixture of two double bond isomers (**A** and **B** in the ratio of 74:26) (Scheme 1). After the working up procedure, the sulfides (**4c** and **5c**) were obtained in ca. 55% yield. Products **4c** and **5c** were characterized by ^{31}P, ^{13}C, and ^{1}H NMR, as well as mass and IR spectroscopy. ^{13}C NMR spectral data for the isomers of sulfides **4c** and **5c** are listed in Tables 1 and 3, respectively, while mass spectral features of the products (**4c** and **5c**) can be found in Tables 2 and 4, respectively. Regarding **5c**, the loss of SH was confirmed by HRMS (see footnote *e* in Table 4). The loss of SH was also observed during the fragmentation of dihydro-1H-phosphole sulfides [3].

EXPERIMENTAL

The ^{13}C NMR spectra were taken on a JEOL FX 100 instrument with Me_4Si as internal standard. The ^{31}P and ^{1}H NMR spectra were recorded with a Varian UNITY 300 and a Bruker AW-80 spectrometer using 85% H_3PO_4 as external and Me_4Si as internal standards, respectively. Downfield shifts have positive signs. Coupling constants are given in hertz. Mass spectra were recorded with a MS 25-RFA instrument at 70 eV. Infrared spectra were obtained by use of a SPECORD 75 spectrometer. 3-Phosphabicyclo[3.1.0]hexane 3-oxides **2b** and **2c** were prepared as described earlier [12,14].

3-Ethyl-3-phosphabicyclo[3.1.0]hexane 3-Oxide (**2Aa**)

A 9 g quantity (62.5 mmol) of 1-ethyl-2,5-dihydro-1H-phosphole 1-oxide (**1a**) [bp 110–130°C/0.27 mb (Ref. [21], 116–117°C/0.80 mb); ^{31}P NMR ($CDCl_3$), δ + 78.4] and 3.2 g (14.1 mmol) of triethylbenzylammonium chloride in 150 mL of alcohol-free $CHCl_3$ was treated with four portions of aqueous NaOH (1. 90 g/90 mL, 2. 90 g/90 mL, 3. 72 g/72 mL, and 4. 72 g/80 mL) as described for the preparation of other dihydro-1H-phosphole oxides [12]. Yield, 7.7 g (54%); ^{31}P NMR ($CDCl_3$), δ +92.5; ^{13}C NMR, Table 1; ^{1}H NMR ($CDCl_3$), δ 1.22 (dt, CH_2–$C\underline{H}_3$, $^{3}J_{PH}$ = 17, $^{3}J_{HH}$ = 8), 1.65 (s, C_1–CH_3); MS, Table 2; IR (neat), 2940, 1440, 1390, 1160, 800 cm^{-1}.

3-Ethyl-3-phosphabicyclo[3.1.0]hexane 3-Sulfide (**4Aa**)

A mixture of 2.5 g (11.0 mmol) of adduct **2Aa** and 1.6 g (7.21 mmol) of P_2S_5 in 25 mL of C_6H_6 was deoxygenated and stirred at the boiling point under N_2 for 20 hours. The contents of the flask were filtered and the filtrate evaporated. The crude product so obtained was purified by column chromatography (silica gel, 1% MeOH in $CHCl_3$ eluant)

TABLE 5 ^{13}C NMR Spectral Data for 2,5-Dihydro-1H-phosphole Derivatives **1c**, **7**, and **9** in $CDCl_3$ Solutions

	δ ^{13}C NMR(J_{PC} in Hz)						
Compound	C_2	C_3	C_4	C_5	C_3–CH_3	$\underline{C}H_2CH_3$	$CH_2\underline{C}H_3$
1c	33.2	135.9	120.0	30.5	20.4	60.4	16.2
	(92.1)	(16.4)	(10.9)	(88.2)	(12.5)	(7.0)	(5.5)
7	43.1	136.4	120.4	40.2	19.7	60.8	16.1
	(72.6)	(13.3)	(7.8)	(67.9)	(12.5)	(7.0)	(7.0)
9	47.5	136.7	120.7	44.6	19.5	29.5	16.3
	(54.9)	(11.5)	(8.6)	(52.1)	(11.6)	(4.3)	(4.5)

to give 1.4 g (53%) of **4Aa**. Mp 125–126°C (acetone-n-C_5H_{12}); ^{31}P NMR ($CDCl_3$) δ + 91.7; ^{13}C NMR, Table 1; ^1H NMR ($CDCl_3$), δ 1.20 (dt, CH_2–C$\underline{H}_3$, $^3J_{PH}$ = 17, $^3J_{HH}$ = 8), 1.54 (s, C_1–CH_3); MS, Table 2; IR (KBr disc), 2940, 1440, 1390, 810, 680, 600 cm^{-1}. Anal. calcd for $C_8H_{13}Cl_2PS$: C, 39.52; H, 5.38. Found: C, 39.83; H, 5.59.

3-Phenyl-3-phosphabicyclo[3.1.0]hexane 3-Sulfide (**4Ab**)

Method 1. The reaction of 0.5 g (1.82 mmol) of **2Ab** with 0.27 g (1.22 mmol) of P_2S_5 in 5 mL of C_6H_6 and the working-up procedure were carried out as shown for the thionation of **2Aa**. Yield: 0.4 g (76%) of **4b**. ^{31}P NMR ($CDCl_3$), δ +83.7; ^{13}C NMR, Table 1; M^+_{found} = 289.9832, $C_{12}H_{13}Cl_2PS$ requires 289.9853 for the ^{35}Cl isotope; ^1H NMR ($CDCl_3$), δ 1.48 (s, C_1–CH_3); MS, Table 2; IR (neat) 2900, 1420, 1390, 720, 630 cm^{-1}.

Method 2. To 0.6 g (2.18 mmol) of **2Ab** in 5 mL of CH_2Cl_2 was added 0.33 mL (3.27 mmol) of Cl_3SiH. After a 5 hour stirring period, the volatile components were removed in vacuum. The 0.56 g (≈100%) of phosphine **6** so obtained was suitable for further transformation. ^{31}P NMR ($CDCl_3$), δ +25.2; ^{13}C NMR ($CDCl_3$), δ 21.2 (CH_3, $^3J_{PC}$ = 2.9), 27.0 (C_4, $^1J_{PC}$ = 18.6), 32.8 (C_2, $^1J_{PC}$ = 17.6), 40.5 (C_5, $^2J_{PC}$ = 4.9), 40.9 (C_1); MS, m/z (relative intensity), 258 (M^+, 23), 223 (85), 222 (44), 187 (19), 115 (60), 91 (84), 79 (100), 77 (93).

To 0.56 g (≈2.18 mmol) of phosphine **6** from the previous reaction was added 2.5 mL of CH_2Cl_2, 2.5 mL of acetone, and 0.091 g (2.83 mmol) of sulfur. Following a 2 day stirring period at room temperature, the mixture was filtered and the solvent of the filtrate evaporated. The crude product so obtained was purified by flash chromatography (silica gel, C_6H_6-acetone 4:6 eluant) to give 0.49 g (77%) of **4Ab**.

1-Ethoxy-3-phosphabicyclo[3.1.0]hexane 3-Sulfide (**4c**)

A mixture of 1.0 g (4.12 mmol) of **2c** (consisting of isomers **A** and **B**), 0.60 g (2.70 mmol) of P_2S_5, and 10 mL of CH_2Cl_2 was stirred at room temperature under N_2 for 5 days. The crude product obtained after filtration and evaporation of the solvent of the filtrate was purified by column chromatography (silica gel, 3% MeOH in $CHCl_3$ eluant) to give 0.58 g (54%) of **4c** consisting of 20% of the **A** and 80% of the **B** isomer. ^{31}P NMR, ($CDCl_3$), δ +128.1 (**A**) and +135.6 (**B**); ^{13}C NMR, Table 1; ^1H NMR ($CDCl_3$), δ 1.28 (t, CH_2–C$\underline{H}_3$ (**A**), $^3J_{HH}$ = 7), 1.31 (t, CH_2–C$\underline{H}_3$ (**B**), $^3J_{HH}$ = 7) total intensity 3H, 1.58 (s, C_1–CH_3 (**B**)), 1.62 (s, C_1–CH_3 (**A**)) total intensity 3H, 1.74–2.96 (m, 5H, PCH_2, CH), 3.82–4.32 (m, C$\underline{H}_2$–CH_3); MS, Table 2; IR (neat), 2960, 1440, 1390, 1020, 640 cm^{-1}. Anal. calcd for $C_8H_{13}Cl_2OPS$: C, 37.08; H, 5.05. Found: C, 37.49; H, 5.35.

Double bond isomers (**A** and **B**) of dihydrophosphinine oxides **3b** and **3c** were prepared as described earlier [13,14].

3- and 5-Methyl-4-chloro-1,2-dihydro-1-ethylphosphinine 1-Oxide (**3Aa** *and* **3Ba**)

A mixture of 5.9 g (2.60 mmol) of adduct **2Aa** and 3.6 mL (26.0 mmol) of NEt_3 in 70 mL of toluene was stirred at the boiling point for 8 hours. The precipitate was filtered off and the solvent of the filtrate evaporated. The crude product so obtained was purified by column chromatography (silica gel, $CHCl_3$–MeOH 98:2 eluant) to give 2.5 g (50%) of **3a** as a 74:26 mixture of double bond isomers **A** and **B**. ^{31}P NMR ($CDCl_3$) δ +27.9 (**A**) and +26.9 (**B**); ^{13}C NMR, Table 3; ^1H NMR ($CDCl_3$), δ 1.18 (dt, 3H, $CH_2C\underline{H}_3$, $^3J_{PH}$ = 19, $^3J_{HH}$ = 8), 2.02 (s, CH_3 (**A**)), 2.17 (s, CH_3 (**B**)), 2.30–3.16 (m, 2H, P–CH_2), 6.10 (t, P–CH=C$\underline{H}$(**A**), $^3J_{PH}$ = $^3J_{HH}$ = 13), 6.76 (dd, 0.74H, P–CH=(**A**), $^2J_{PH}$ = 32, $^3J_{HH}$ = 12); MS, Table 4; IR (neat), 2940, 1610, 1560, 1450, 1360, 1160, 720 cm^{-1}.

3- and 5-Methyl-4-chloro-1,2-dihydro-1-ethylphosphinine 1-Sulfide (**5Aa** *and* **5Ba**)

Method 1. By the thionation of dihydrophosphinine **3a**. The reaction of 0.7 g (3.68 mmol) of **3a** with 0.54 g (2.43 mmol) of P_2S_5 in 15 mL of C_6H_6 and the working-up procedure were carried out as described for the thionation of **2Aa**. Yield: 0.35 g (42%) of **5a** as the mixture of 77% of the **A** and 23% of the **B** isomer with a purity of 90%. ^{31}P NMR ($CDCl_3$) δ +27.2 (**A**) and +26.7 (**B**); ^1H NMR ($CDCl_3$, 300 MHz), δ 5.46 (d, 0.23H, P–CH=(**B**), $^2J_{PH}$ = 31.0), 5.96 (dd, 0.77H, P–CH=C$\underline{H}$(**A**), $^3J_{PH}$ = 18.0, $^3J_{HH}$ = 12.1), 6.18 (dt, 0.23H, P–C$\underline{H}_2$–C$\underline{H}$=(**B**), $^3J_{PH}$ = 20.8 $^3J_{HH}$ = 5.2), 6.55 (dd, 0.77H, P–C$\underline{H}$=(**A**), $^2J_{PH}$ = 33.8, $^3J_{HH}$ = 12.1); MS, Table 4; M^+_{found} = 206.0115, $C_8H_{12}SPCl$ requires 206.0130 for the ^{35}Cl isotope; (neat), 660 cm^{-1}.

Method 2: by the thermolysis of adduct **4Aa**. A 0.3 g quantity (1.24 mmol) of **4Aa** was heated at 140°C for 10 minutes. Flash chromatography (silica gel, 1% MeOH in $CHCl_3$ eluant) of the resulting mixture afforded 0.12 g (28%) of **5a** with a purity of ≈60%.

3- and 5-Methyl-4-chloro-1,2-dihydro-1-phenylphosphinine 1-Sulfide (**5b**)

The reaction of 0.50 g (2.10 mmol) of **3b** with 0.31 g (1.41 mmol) of P_2S_5 in 10 mL of C_6H_6 and the working-up procedure were carried out as described for the thionation of **2Aa**. Yield: 0.39 g (73%) of **5b** as the mixture of 75% of the **A** and 25% of the **B** isomer. ^{31}P NMR ($CDCl_3$) δ +19.9 (**A**) and

+19.1 (**B**); ^{1}H NMR ($CDCl_3$, 300 MHz), δ 2.04 (s, 2.25H, C_3–CH_3 (**A**)), 2.20 (s, 075H, C_5–CH_3 (**B**)), 3.02–3.33 (m, 2H, P–CH_2), 6.08 (dd, 0.75H, P–CH=C<u>H</u>–(**A**), $^3J_{PH}$ = 17.7, $^3J_{HH}$ = 12.3), 6.2 (dt, 0.25H, P–C<u>H</u>$_2$–C<u>H</u>=(**B**), $^3J_{PH}$ = 21.8, $^3J_{HH}$ = 5.5), 6.75 (dd, 0.75H P–CH=(**A**), $^2J_{PH}$ = 35.5, $^3J_{HH}$ = 12.3), 7.47–7.97 (m, 5H, Ar); ^{13}C NMR, Table 3; MS, Table 4; M^+_{found} = 254.0108, $C_{12}H_{12}SPCl$ requires 254.0130 for the ^{35}Cl isotope; IR (neat), 3050, 1620, 1560, 1440, 1380, 740, 690 cm^{-1}.

3- and 5-Methyl-4-chloro-1,2-dihydro-1-ethoxyphosphine 1-Sulfide (**5c**)

A 1.0 g quantity (4.84 mmol) of **5c** was thionated with 0.71 g (3.20 mmol) of P_2S_5 in 10 mL of CH_2Cl_2 as shown above for the **2c** → **4c** transformation. A similar working-up procedure provided 0.6 g (56%) of **5c** containing 74% of the **A** and 26% of the **B** isomer. ^{31}P NMR ($CDCl_3$) δ +70.2 (**A**) and +69.2 (**B**); ^{13}C NMR, Table 3; ^{1}H NMR ($CDCl_3$), δ 1.28 (t, 3H, $CH_2C\underline{H}_3$, $^3J_{HH}$ = 16.5), 2.01 (s, C_3–CH_3 (**A**)), 2.13 (s, C_5–CH_3 (**B**)) total intensity 3H, 2.60–3.18 (m, 2H, P–CH_2), 3.84–4.29 (m, 2H, C<u>H</u>$_2$–CH_3), ~6.1 (m, P–CH=C<u>H</u>(**A**)), 6.55 (dd, P–CH=(**A**), $^2J_{PH}$ = 43, $^3J_{HH}$ = 15); MS, Table 4; IR (neat), 2940, 1605, 1540, 1420, 1360, 1010, 680 cm^{-1}; Anal. calcd for $C_8H_{12}ClOPS$: C, 43.15; H, 5.43. Found: C, 43.59; H, 5.78.

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[18] m/z_{found} = 246.0575; $C_{10}H_{16}O_3P_2$ requires 246.0579.

[19] ^{31}P NMR ($CDCl_3$), δ +115.3; ^{1}H NMR ($CDCl_3$), δ1.29 (t, 3H, $CH_2C\underline{H}_3$, $^3J_{HH}$ = 7), 1.86 (s, 3H, C–CH_3), 2.43–3.15 (m, 4H, P–CH_2), 3.85–4.32 (m, 2H, C<u>H</u>$_2$CH$_3$), 5.48 (d, 1H, =CH, $^3J_{PH}$ = 37); MS, *m/z* (relative intensity), 176 (M+, 100), 148 (13), 132 (40); IR(neat) 2950, 1630, 1420, 1380, 1020, 640 cm^{-1}.

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