

# Convenient Synthesis of 1-Alkoxy-Di- and Tetrahydrophosphinine 1-Oxides by Ring Enlargement

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## ABSTRACT

*The double bond of the P-alkoxy 3,4-dimethyl-2,5-dihydro-1H-phosphole 1-oxides reacts easily with dichlorocarbene to give two diastereomers of an unstable adduct useful in the synthesis of ring expanded products, such as 1,2-dihydrophosphinine oxides or 1,2,3,6-tetrahydrophosphinine oxides. The former can be prepared by thermolysis of the adducts, while the latter are obtained by cyclopropane ring opening effected by silver nitrate in an alcoholic solvent. The preparation of the double-bond isomers of 1-alkoxy-tetrahydrophosphinine oxides containing only one methyl substituent in the ring is also described. The reaction of dihydro-1H-phosphole oxides with dichlorocarbene can be modified to give P-alkoxy 1,4-dihydrophosphinine oxides in an unexpected reaction.*

## INTRODUCTION

We have recently described the ring enlargement of 1-alkyl-, 1-phenyl-, and 1-alkoxy-3-methyl-2,5-

dihydro-1H-phosphole 1-oxides to the double-bond isomers of 1,2-dihydrophosphinine 1-oxides [1-3]. The adduct of the dihydro-1H-phosphole oxide with dichlorocarbene is prepared in the first step [1,3] to give the dihydrophosphinine oxide in the second, thermolysis step [2,3]. The adducts can also be utilized in the synthesis of 1,2,3,6-tetrahydrophosphinine 1-oxides [4].

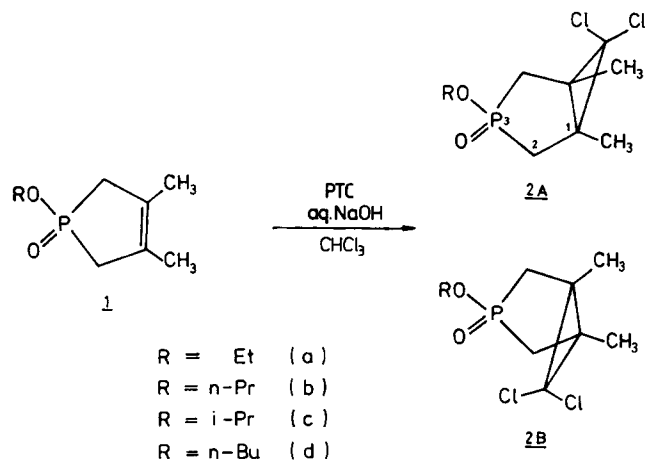
The ring of 3- and 5-methyl-dihydrophosphinine oxides can be further enlarged to afford phosphepine oxides [5], while the P-phenyl- and P-alkyl 3,5-dimethyl-dihydrophosphinine oxides, intermediates in the ring expansion of 3,4-dimethyl-dihydro-1H-phosphole oxides, yield, surprisingly, the 4-dichloromethylene-1,4-dihydrophosphinine oxides by reaction with a second unit of dichlorocarbene [6].

The simple, two-step ring enlargement method developed by us is now applied to the synthesis of new 1-alkoxy-3,5-dimethyl-1,2- and 1,4-dihydrophosphinine oxides and of 3- and 5-methyl- and 3,5-dimethyl-1,2,3,6-tetrahydrophosphinine oxides.

## RESULTS AND DISCUSSION

The 1-alkoxy-3,4-dimethyl-2,5-dihydro-1H-phosphole 1-oxides (**1a-d**) obtained by the alcoholysis of the cycloadduct of 2,3-dimethyl-1,3-butadiene,

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SCHEME 1

and phosphorus tribromide were reacted with dichlorocarbene generated from chloroform with aqueous sodium hydroxide under phase transfer catalytic conditions [7]. The  $^1\text{H}$  NMR spectra of the crude products showed that the adducts (**2a–d**) were formed as a mixture of two diastereoisomers (**A** and **B**) (Scheme 1).

As in the case of the corresponding monomethyl derivatives [8] diastereoisomer **2A**, in which the phosphoryl oxygen and the dichlorocyclopropane ring are in a *trans* disposition, was presumed to be the component in slight excess (~56%). This arrangement was confirmed in the case of the sin-

gle diastereomer of the P-phenyl derivative [8]. While we succeeded in preparing diastereomers **2Ab–d** in pure form, diastereomers **2Bb,d** could be obtained with a purity of only about 94%. The diastereomers (**A** and **B**) of adducts **2a–d** were characterized by  $^{13}\text{C}$  and  $^1\text{H}$  NMR. The NMR spectral data (Tables 1 and 2) resemble those for the monomethyl adducts described earlier [8]. Hydrogen atoms of the P—CH<sub>2</sub> moiety in **2** were distinguished by NOE measurements. The molecular weights of products **2** were confirmed in all cases by chemical ionization mass spectra. Isotopic distribution for the molecular ions supported the presence of two chlorine atoms in the products (**2**).

Adducts **2a–d** are thermally unstable and undergo cyclopropane ring opening even at room temperature. While the completion of this reaction requires 3 weeks at 24°C, the reaction time is reduced to 2.5 hours at 80°C. The instability of adducts **2** relative to the monomethyl derivatives which undergo cyclopropane ring opening only at ~120°C [2,3] is due to the presence of the second methyl group in the ring, stabilizing the cationic intermediate involved in the ring opening reaction [2]. Ring expansion of the P-alkoxy derivatives (**2a–d**) provides the corresponding P-alkoxy-dihydrophosphinine oxides (**3a–d**) together with the P-hydroxy product (**3**, R=H); e.g., a mixture containing ~45% of **3a–d** and ~55% of the phosphinic acid ( $\delta_{\text{p}} = +33.1$ ; Ref. [1]  $\delta_{\text{p}} = +32.5$ ) is formed at room temperature.

Cleavage of the esters to phosphinic acid by the hydrogen chloride evolved can be avoided by carrying out the thermolysis in the presence of one

**TABLE 1**  $^{13}\text{C}$  NMR Data for the Diastereoisomers (**A** and **B**) of 6,6-Dichloro-1,5-dimethyl-3-phospha-bicyclo[3.1.0]hexane 3-Oxides (**2a–d**) in  $\text{CDCl}_3$  Solutions at 62.5 MHz

Product	$\delta^{13}\text{C}$ ( $J_{\text{PC}}$ in Hz)							
	$C_1$	$C_2$	$C_6$	$C-\text{CH}_3$	$C_\alpha$	$C_\beta$	$C_\gamma$	$C_\delta$
<b>2Aa</b>	31.5 (12.4)	32.2 (91.0)	76.3 (15) <sup>b</sup>	16.5 (9.6)	60.2 (6.5)	16.3 (5.7)		
<b>2Ba<sup>a</sup></b>	32.3 (13.6)	33.8 (92.5)	75.9 (12.0)	16.8 (10.1)	61.6 (6.7)	16.0 (5.3)		
<b>2Ab</b>	31.1 (12.4)	31.7 (91.3)	76.0 (15.2)	16.1 (9.6)	65.4 (6.5)	23.2 (6.0)	9.4	
<b>2Bb<sup>a</sup></b>	31.8 (13.6)	33.2 (92.6)	75.5 (12.2)	16.4 (10.2)	66.7 (7.0)	23.0 (5.4)	9.3	
<b>2Ac</b>	31.7 (12.7)	33.2 (91.2)	<sup>c</sup>	16.9 (9.2)	69.5 (6.6)	24.4 (3.4)		
<b>2Bc<sup>a</sup></b>	32.3 (13.0)	34.3 (92.6)	76.2 (11.2)	16.8 (10.1)	70.4 (6.8)	23.5 (3.7)		
<b>2Ad</b>	31.5 (13) <sup>b</sup>	32.2 (90.8)	76.4 (15) <sup>b</sup>	16.6 (9.3)	64.0 (6.6)	32.3 (6.0)	18.5	13.3
<b>2Bd<sup>a</sup></b>	32.5 (13.7)	33.8 (92.5)	76.1 (12.0)	16.9 (10.2)	65.6 (6.9)	32.2 (5.2)	18.5	13.3

<sup>a</sup>Tentative assignment to isomers **A** and **B**.

<sup>b</sup>One part of the doublet is overlapped.

<sup>c</sup>Not resolved.

**TABLE 2**  $^1\text{H}$  NMR Data for the Diastereoisomers (**A** and **B**) of 6,6-Dichloro-1,5-dimethyl-3-phosfabicyclo[3.1.0]hexane 3-Oxides (**2a-d**) in  $\text{CDCl}_3$  Solutions at 250 MHz

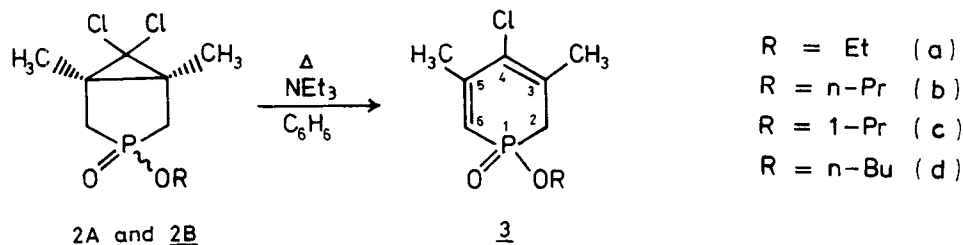
Product	$\delta$ $^1\text{H}$ (Multiplicity, $J_{\text{PH}}$ in Hz)						
	C—CH <sub>3</sub>	P—CH <sub>2</sub>		$H_\alpha$	$H_\beta$	$H_\gamma$	$H_\delta$
		ax	eq				
<b>2Aa</b>	1.42 (s)	2.0–2.5 (m)		4.05–4.20 (m)	1.40 <sup>b</sup> (t)		
<b>2Ba</b> <sup>a</sup>	1.48 (s)	2.0–2.5 (m)		4.05–4.20 (m)	1.35 <sup>b</sup> (t)		
<b>2Ab</b>	1.38 (s)	2.32 (dd, 4.4)	2.07 (t, 15.9)	3.96 (q, 6.7)	1.71 (m)	0.99 (t)	
<b>2Bb</b> <sup>a</sup>	1.41 (s)	2.32 (dd, 7.0)	2.07 (dd, 18.9)	3.92 (q, 6.6)	1.64 (m)	0.89 (t)	
<b>2Ac</b> <sup>c</sup>	1.34 (s)	2.32 (dd, 5)	2.11 (t, 15)	4.62 (m)	1.31 (d)		
<b>2Bc</b> <sup>a</sup>	1.45 (s)	1.9–2.4 (m)		4.68 (m)	1.32 (d)		
<b>2Ad</b> <sup>a</sup>	1.38 (s)	2.32 (dd, 4.7)	2.03 (dd, 18.4)	4.00 (q, 6.5)	1.68 (qui)	1.42 (m)	0.96 (t)
<b>2Bd</b>	1.45 (s)	2.37 (dd, 7.1)	2.13 (dd, 19.0)	4.01 (q, 6.6)	1.64 (qui)	1.38 (m)	0.93 (t)

<sup>a</sup>Tentative assignment to isomers **A** and **B**.<sup>b</sup>May be reversed.<sup>c</sup>At 100 MHz.

equivalent of triethylamine. Starting with the diastereomeric mixtures of the adducts (**2a-d**), the dihydrophosphinine oxides (**3a-d**) could be obtained in 62% overall yield after heating under reflux for 2.5 hours in benzene followed by column chromatography (Scheme 2). Products **3a-d** were characterized by  $^{13}\text{C}$  and  $^1\text{H}$  NMR and mass spectral parameters (Tables 3, 4, and 5, respectively). Spectral features of the products (**3**) are similar to those of the 3- and 5-methyl-dihydrophosphinine oxides described earlier [3]. Isotopic distribution for the molecular ions confirms the presence of one chlorine atom in the product (**3**).

The dichlorocyclopropane ring can also be opened by the action of electrophiles in protic solvents [4]. Thermolysis of the adducts in methanol or ethanol in the presence of silver nitrate affords

the expected 1,2,3,6-tetrahydrophosphinine oxides (**4a-d**) as an ~8:2 mixture of two diastereomers (Scheme 3). The major diastereomer of **4a-d** could be isolated in pure form by column chromatography. In the case of **4c**, the minor isomer could also be isolated in pure form. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR data (Tables 6 and 7, respectively) were assigned tentatively to the diastereomers of products **4a-d**. (The minor isomer of **4a** was characterized by the  $^{13}\text{C}$  NMR spectrum of the diastereomeric mixture.) Characteristic fragmentations like the loss of Me,  $\text{CH}_2\text{O}$  (or  $\text{C}_2\text{H}_4\text{O}$ ),  $\text{R}'\text{OH}$ , R, and the  $\text{P}(\text{O})\text{OR}$  moiety or their superposition can be observed in the mass spectra of the tetrahydrophosphinine oxides (**4**) (Table 8). Isotopic distribution of the molecular ions is in accord with the presence of a chlorine atom in products **4**.

**SCHEME 2**

**TABLE 3**  $^{13}\text{C}$  NMR Data for 4-Chloro-1,2-dihydro-3,5-dimethylphosphinine 1-Oxides (**3a–d**) in  $\text{CDCl}_3$  Solutions at 62.5 MHz

Product	$\delta^{13}\text{C}$ ( $J_{\text{PC}}$ in Hz)										
	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$	$\text{C}_5$	$\text{C}_6$	$\text{C}_3\text{—CH}_3$	$\text{C}_5\text{—CH}_3$	$\text{C}_\alpha$	$\text{C}_\beta$	$\text{C}_\gamma$	$\text{C}_\delta$
<b>3a</b>	33.2 (97.9)	131.5 (8.4)	126.0 (18.4)	151.3 (2.6)	115.4 (126.7)	23.5 (11.0)	24.9 (16.2)	59.7 (5.9)	16.0 (5.8)		
<b>3b</b>	32.9 (98.0)	131.4 (8.3)	125.8 (18.5)	151.0 (2.5)	115.3 (126.6)	23.3 (11.0)	24.7 (16.3)	65.0 (6.3)	23.1 (6.0)	9.12	
<b>3c</b>	33.7 (98.3)	131.4 (8.3)	125.8 (18.5)	150.7 (2.5)	116.2 (127.1)	23.5 (10.8)	24.7 (16.2)	68.5 (5.8)	23.5 (6) <sup>a</sup>		
<b>3d</b>	32.9 (98.0)	131.4 (8.2)	125.8 (18.5)	151.1 (2.5)	115.3 (126.5)	23.3 (11.0)	24.7 (16.2)	63.3 (6.1)	31.8 (5.8)	17.8	12.7

<sup>a</sup>Overlapped**TABLE 4**  $^1\text{H}$  NMR Data for 4-Chloro-1,2-dihydro-3,5-dimethylphosphinine 1-Oxides (**3a–d**) in  $\text{CDCl}_3$  Solutions at 250 MHz

Product	$\delta^1\text{H}$ (Multiplicity, $J_{\text{PH}}$ in Hz)								
	$\text{H}_2$	$\text{H}_6$	$\text{C}_3\text{—CH}_3$	$\text{C}_5\text{—CH}_3$	$\text{H}_\alpha$	$\text{H}_\beta$	$\text{H}_\gamma$	$\text{H}_\delta$	
<b>3a</b>	2.38 (dd, 19.2)	2.51 (ddq, 18.4)	5.66 (d, 8.5)	1.83 (d)	1.77 (s)	3.75 (m)	1.00 (t)		
<b>3b</b>	2.38 (dd, 19.3)	2.50 (ddq, 18.3)	5.64 (d, 8.4)	1.85 (d)	1.78 (s)	3.66 (m)	1.37 (m)	0.62 (t)	
<b>3c<sup>a</sup></b>	2.44 (dd, 19.5)	2.48 (dd, 18.6)	5.67 (d, 8.5)	1.88 (s)	1.82 (s)	4.40 (m)	1.04 (d)		
<b>3d<sup>a</sup></b>	2.41 (dd, 19.3)	2.45 (dd, 18.3)	5.65 (d, 8.3)	1.86 (d)	1.79 (s)	3.70 (q, 6.6)	1.32 (qui)	1.10 (m)	0.63 (t)

<sup>a</sup>At 100 MHz.**TABLE 5** MS Data for 4-Chloro-1,2-dihydro-3,5-dimethylphosphinine 1-Oxides (**3a–d**)

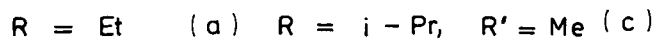
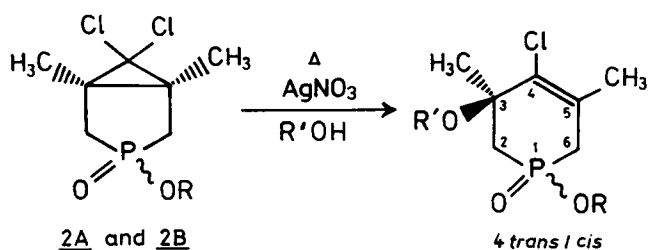
Fragment ( $m/z$ )	Relative Intensity (%)			
	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>
$\text{M}^{+\text{a}}$	61	23	12	19
$[\text{M}-(\text{R}-\text{H})]^+$ (192)	85	100	100	100
$[\text{M}-\text{ROH}]^+$ (174)	21	6	8	5
$[\text{M}-\text{P}(\text{O})\text{OR}]^+$ (128)	17	15	11	12
$[\text{M}-\text{P}(\text{O})\text{OR}-\text{Cl}]^+$ (93)	100	80	57	50

<sup>a</sup> $m/z$  values for the molecular ions of **3a**, **3b**, **3c**, and **3d** are 220, 234, 234, and 248, respectively.

It is worth mentioning that a dimer ( $\text{M}^+ = 533$ ) could be formed from tetrahydrophosphinine oxide **4a** in the mass spectrometer by the high pressure self-chemical ionization technique.

Use of the adducts of dimethyl-dihydro-1H-phosphole 1-oxides with dichlorocarbene (**2**) in the preparation of ring expanded products is more advantageous than that of the monomethyl derivatives, because the di- and tetrahydrophosphinine oxides are provided as a single product and not as the mixture of double-bond isomers [2–4].

To prepare additional P-alkoxy-tetrahydro-

**SCHEME 3**

phosphinine oxides, the known 3-methyl derivatives **5a**, **b** [3] were also subjected to thermolysis in alcohols and even in water in the presence of silver nitrate. The mixtures containing the diastereomers of the two double bond isomers (**A** and **B**) of 3-alkoxy- and 3-hydroxy-1,2,3,6-tetrahydrophosphinine oxides (**6a–e**) were obtained in good

**TABLE 6**  $^{13}\text{C}$  NMR Data for the Diastereoisomers of 3-Alkoxy-4-chloro-3,5-dimethyl-1,2,3,6-tetrahydrophosphinine 1-Oxides (**4a–d**) in  $\text{CDCl}_3$  Solutions at 62.5 MHz

Product	$\delta^{13}\text{C}$ ( $J_{\text{PC}}$ in Hz)												
	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$	$\text{C}_5$	$\text{C}_6$	$\text{C}_3\text{-CH}_3$	$\text{C}_5\text{-CH}_3$	$\text{C}_\alpha$	$\text{C}_\beta$	$\text{C}_\gamma$	$\text{C}_\delta$	$\text{C}_{\alpha'}$	$\text{C}_{\beta'}$
<b>4a trans</b>	34.6 (83.9)	78.6	132.6 (7.4)	127.7 (5) <sup>a</sup> (88.8)	32.3 (88.8)	24.1 (11) <sup>a</sup>	27.1	60.5 (6.7)	20.0 (6) <sup>a</sup>	—	—	58.0	15.3
<b>4a cis</b>	34.9 (87.4)	78.3	133.1 (7.5)	127.7 (5) <sup>a</sup> (89) <sup>a</sup>	33.5 (89) <sup>a</sup>	23.9 (12) <sup>a</sup>	26.8	60.6 (7.5)	19.8 (6) <sup>a</sup>	—	—	58.0	15.3
<b>4b trans<sup>b</sup></b>	34.5 (85.7)	78.8	131.9 (8.0)	128.5 (4.4) (87.9)	32.4 (87.9)	23.6 (11) <sup>a</sup> (3.7)	26.6	65.7 (6.6)	23.5 (6) <sup>a</sup>	9.5	—	49.7	—
<b>4c trans</b>	34.7 (86.0)	78.7	131.6 (7.7)	128.3 (4.5) (87.4)	32.7 (87.4)	23.6 (12.0)	26.6 (3.6)	69.4 (6.3)	23.8 (3.9) 23.7 (4.1)	—	—	49.7	—
<b>4c cis<sup>b</sup></b>	35.2 (84.3)	78.7	132.6 (7.3)	128.3 (3.0) (90.1)	34.3 (90.1)	23.9 (12.4)	26.5 (2.9)	69.5 (6.6)	24.0 (4.3)	—	—	49.9	—
<b>4d trans</b>	33.8 (85.0)	78.7	131.6 (7.6)	128.4 (4.4) (88.5)	31.9 (88.5)	23.7 (12.2)	26.5 (3.3)	63.9 (6.5)	32.1 (6.2)	18.3	13.1	49.8	—

<sup>a</sup>One part of the doublet is overlapped.<sup>b</sup>At 25 MHz.**TABLE 7**  $^1\text{H}$  NMR Data for the Diastereoisomers of 3-Alkoxy-4-chloro-3,5-dimethyl-1,2,3,6-tetrahydrophosphinine 1-Oxides (**4a–d**) in  $\text{CDCl}_3$  Solutions at 250 MHz

Product	$\delta^1\text{H}$ (Multiplicity $J_{\text{PH}}$ in Hz)											
	$\text{H}_2$		$\text{H}_6$		$\text{C}_3\text{-CH}_3$	$\text{C}_5\text{-CH}_3$	$\text{H}_\alpha$	$\text{H}_\beta$	$\text{H}_\gamma$	$\text{H}_\delta$	$\text{H}_{\alpha'}$	$\text{H}_{\beta'}$
	<i>ax</i>	<i>eq</i>	<i>ax</i>	<i>eq</i>								
<b>4a trans<sup>a</sup></b>	2.51 (t, 14)	1.95 (m)	2.68 (dd, 14.2)	2.25 (m)	1.45 (s)	1.91 (s)	3.24 (qd, 3.0)	1.26 (t)	—	—	4.01 (qui)	1.11 (t)
<b>4a cis</b>	—	—	1.9–2.8 (m)	—	1.63 (s)	2.00 (s)	3.30 (m)	1.20 (t)	—	—	4.10 (m)	1.35 (t)
<b>4b trans<sup>a</sup></b>	2.37 (t, 14)	2.00 (m)	2.73 (dd, 13.0)	2.28 (m)	1.50 (s)	1.98 (s)	3.94 (q)	1.67 (m)	0.91 (t)	—	—	3.11 (s)
<b>4c trans</b>	2.37 (t, 14.6)	1.98 (ddd, 20.5)	2.69 (ddd, 13.1)	2.32 (ddd, 20.3)	1.48 (s)	1.94 (t, 1)	4.66 (m, 8.3)	1.23 (d) 1.29 (d)	—	—	—	3.08 (s)
<b>4c cis<sup>a</sup></b>	2.25 (m)	2.01 (m)	2.54 (m)	2.25 (m)	1.63 (s)	2.01 (s)	4.76 (m)	1.34 (d)	—	—	—	3.15 (s)
<b>4d trans</b>	2.46 (t, 14.4)	2.09 (ddd, 20.2)	2.75 (ddd, 13.0)	2.43 (ddd, 20.7)	1.54 (s)	2.01 (s)	4.03 (q, 6.7)	1.67 (qui)	1.39 (m)	0.94 (t)	—	3.15 (s)

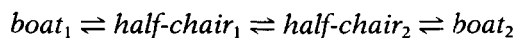
<sup>a</sup>At 100 MHz.**TABLE 8** MS Data for 3-Alkoxy-4-chloro-3,5-dimethyl-1,2,3,6-tetrahydrophosphinine 1-Oxides (**4a–d**)

Fragment	$m/z$ (Relative Intensity, %)			
	<b>4a<sup>a</sup></b>	<b>4b</b>	<b>4c</b>	<b>4d</b>
$\text{M}^+$	266 (6)	266 (6)	266 (1)	280 (1)
$[\text{M}-\text{Me}]^+$	251 (15)	251 (14)	251 (4)	265 (7)
$[\text{M}-\text{CH}_2\text{O}]^+$	222 <sup>b</sup> (100)	236 (41)	236 (20)	250 (47)
$[\text{M}-\text{R}'\text{OH}]^+$	220 (73)	234 (29)	234 (9)	248 (23)
$[\text{M}-\text{Me}-(\text{R}-\text{H})]^+$	223 (51)	209 (67)	209 (46)	209 (47)
$[\text{M}-\text{CH}_2\text{O}-(\text{R}-\text{H})]^+$	194 <sup>c</sup> (54)	194 (77)	194 (100)	194 (100)
$[\text{M}-\text{R}'\text{OH}-(\text{R}-\text{H})]^+$	192 (68)	192 (100)	192 (77)	192 (84)
$[\text{M}-\text{P}(\text{O})\text{OR}-\text{Cl}-\text{R}'\text{OH}]^+$	93 (74)	93 (59)	93 (41)	93 (55)

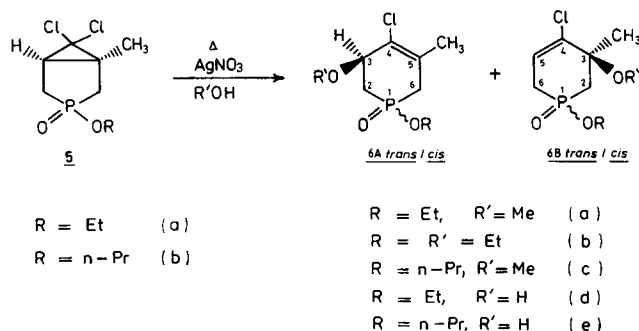
<sup>a</sup>195 (91), 193 (93); <sup>b</sup> $\text{M}-\text{C}_2\text{H}_4\text{O}$ ; <sup>c</sup> $\text{M}-\text{C}_2\text{H}_4\text{O}-(\text{Et}-\text{H})$ .

yields after column chromatography (Scheme 4). Products **6a** and **6b** were formed as mixtures of four isomers (**A trans**, **A cis**, **B trans**, and **B cis**), while products **6c–e** were formed as mixtures of only three isomers (**A trans**, **A cis**, and **B trans**). As reported before [4], the sets of  $^{13}\text{C}$  NMR signals were assigned tentatively to the individual diastereomers (Table 9). The  $^1\text{H}$  NMR and mass spectral data (Tables 10 and 11, respectively) also supported the structural assignments of products **6**.

The flexible six-membered ring of tetrahydrophosphinine oxides **4** and **6** may exist as a



equilibrium (Scheme 5). Because of the eclipsed position of the P-substituent and the R'O group, the *half-chair*<sub>1</sub> conformer can be ruled out. The NOE measured on the  $\text{C}(2)\text{H}_2$  protons in **4** when irradiating the  $\text{C}(3)\text{CH}_3$  is consistent only with the *boat*<sub>1</sub> conformer. This conclusion is also supported by the



SCHEME 4

measured values of some  $^3J_{\text{PC}}$  constants; e.g.,  $^3J_{\text{PC}}$  is  $\sim 12$  Hz for the P—C(3)CH<sub>3</sub> group, where the dihedral angle is  $\sim 180^\circ$ , and  $^3J_{\text{PC}}$  is  $< 4$  Hz for the P—C(5)CH<sub>3</sub> group, where the torsion angle is  $\sim 120^\circ$  (Table 6 vs. Dreiding model) [9]. Regarding tetrahydrophosphinine oxides **6A**, the  $^3J_{\text{PC}}$  couplings of  $\sim 11$  Hz measured for the C—CH<sub>3</sub> group are consistent with a dihedral angle of  $\sim 180^\circ$  and suggest the involvement of the *half-chair*<sub>2</sub> conformer [9]. In the case of the other double-bond isomer (**6B**),  $^3J_{\text{PC}}$  couplings of 0–4 Hz and  $^3J_{\text{PH}}$  couplings of  $\sim 31$  Hz were measured for the C—CH<sub>3</sub> and C(5)H groups, respectively, suggesting again the predominance

**TABLE 9**  $^{13}\text{C}$  NMR Data for the Diastereoisomers of 5- and 3-Methyl-3-alkoxy (or hydroxy)-4-chloro-1,2,3,6-tetrahydrophosphinine 1-Oxides (**6Aa–e** and **6Ba–e**) in CDCl<sub>3</sub> Solutions at 62.5 MHz

Product	C	$\delta^{13}\text{C}$ ( $J_{\text{PC}}$ in Hz)						Other Unresolved Signals
		A trans		A cis		B trans		
<b>6a</b>	C <sub>2</sub>	30.8 (87.1)	31.6 (91.2)	32.3 (82.3)	32.5 (81.3)	C <sub>α</sub> 59.2 (6.1), 59.5 (6.8), 59.6 (6.6)		
	C <sub>3</sub>	77.8 (4.1)	78.4 (4.9)	77.1 (6)	77.1 (6)	C <sub>β</sub> 15.4 (5)		
	C <sub>4</sub>	127.0 (11.6)	126.8 (13.3)	136.6 (9.6)	137.1 (9.4)			
	C <sub>5</sub>	127.8 (5.1)	127.8 (5.1)	121.5 (6.1)	121.2 (4.3)			
	C <sub>6</sub>	29.2 (89.3)	28.0 (86.7)	25.3 (88.7)	26.6 (89.0)			
	C—CH <sub>3</sub>	22.0 (10.5)	22.2 (11.0)	25.4	25.0			
	C <sub>α'</sub>	55.1	56.1	49.2	49.2			
<b>6b</b>	C <sub>2</sub>	31.1 (87.0)	31.9 (91.7)	33.4 (82.1)	33.8 (81.4)	C <sub>α</sub> 59.8 (6), 59.9 (5)		
	C <sub>3</sub>	76.7 (3.5)	77.1 (5) <sup>a</sup>	77.4 (5)	77.3 (5)	C <sub>β</sub> 15.8		
	C <sub>4</sub>	127.8 (10.2)	127.5 (11.4)	137.7 (9.6)	138.1 (9.5)			
	C <sub>5</sub>	127.6 (5.8)	127.6 (5)	121.0 (5.9)	120.8 (4.2)			
	C <sub>6</sub>	30.2 (89.0)	28.9 (86.7)	25.7 (88.6)	27.0 (90.3)			
	C—CH <sub>3</sub>	22.4 (10.4)	22.6 (11.4)	26.1	25.7			
	C <sub>α'</sub>	63.7	64.7	57.5	59.9			
<b>6c<sup>b</sup></b>	C <sub>2</sub>	14.4	14.5	14.6	14.4			
	C <sub>3</sub>	31.3 (87.2)	32.0 (90.1)	33.3 (82.8)		C <sub>α</sub> 65.4 (6.6), 65.3 (6.6), 65.1 (6)		
	C <sub>4</sub>	78.4 (4) <sup>a</sup>	78.8 (5.1)	77.7 (2.2)				
	C <sub>5</sub>	127.6 (11.0)	127.4 (13.2)	137.2 (10.3)				
	C <sub>6</sub>	128.0 (5.8)	128.0 (5.8)	121.6 (5.8)				
	C <sub>β</sub>	29.7 (89.3)	28.9 (87.9)	25.8 (88.6)				
	C—CH <sub>3</sub>	22.2 (9.5)	22.4 (11.0)	25.8				
<b>6d</b>	C <sub>β</sub>	23.0 (6.6)	23.0 (6.6)	23.0 (6.6)				
	C <sub>γ</sub>	9.0	9.0	9.0				
	C <sub>α'</sub>	55.3	56.1	49.4				
	C <sub>2</sub>	32.6 (85.1)	32.0 (92.1) <sup>c</sup>	38.4 (82.8)		C <sub>α</sub> 60.6 (6.3), 61.0 (6.0)		
	C <sub>3</sub>	69.3	69.7	72.5				
	C <sub>4</sub>	131.0 (9.3)	130.3 (11.9)	140.4 (11.0)				
	C <sub>5</sub>	125.9 (3.9)	126.7 (3.7)	118.1 (5.1)				
<b>6e<sup>b</sup></b>	C <sub>6</sub>	31.8 (89.4)	32.1 (84.0) <sup>c</sup>	26.6 (89.2)				
	C—CH <sub>3</sub>	23.1 (12.2)	23.2 (11.7)	27.9 (4.0)				
	C <sub>β</sub>	16.2	16.3	16.3				
	C <sub>2</sub>	32.7 (85.0)	32.0 (90.9) <sup>c</sup>	38.6 (83.5)		C <sub>α</sub> 66.2 (6), 65.8 (6.6)		
	C <sub>3</sub>	69.3 (2.9)	69.4 (5) <sup>a</sup>	72.4 (2.2)				
	C <sub>4</sub>	131.0 (10.3)	130.5 (11.7)	140.5 (11.0)				
	C <sub>5</sub>	125.7 (4.4)	126.3 (4.3)	117.9 (6.6)				
<b>6e<sup>b</sup></b>	C <sub>6</sub>	31.7 (88.7)	32.3 (85.7) <sup>c</sup>	26.5 (89.4)				
	C—CH <sub>3</sub>	22.8 (11.7)	23.0 (12) <sup>a</sup>	27.9 (3.6)				
	C <sub>β</sub>	23.4 (5.9)	23.4 (5.9)	23.4 (5.9)				
	C <sub>γ</sub>	9.4	9.4					

<sup>a</sup>One part of the doublet overlapped.

<sup>b</sup>At 25 MHz.

<sup>c</sup>Tentative assignment.

**TABLE 10**  $^1\text{H}$  NMR Data for the Diastereoisomers of 5- and 3-Methyl-3-alkoxy (or hydroxy)-4-chloro-1,2,3,6-tetrahydrophosphinine 1-Oxides (**6Aa-e** and **6Ba-e**) in  $\text{CDCl}_3$  Solutions at 250 MHz

Product	$\delta$ $^1\text{H}$ (Multiplicity, Integral, $J_{\text{PH}}$ in Hz)				
	A trans	A cis	B trans	B cis	Unresolved
<b>6a</b>	C—CH <sub>3</sub> 1.82 (s, 2.1H)		1.37 (s, 0.45H)	1.46 (s, 0.45H)	3.75–4.05 (m, 2.7H, OCH <sub>2</sub> , OCH); 1.75–2.65 (m, 4H, PCH <sub>2</sub> ); 1.0–1.2 (m, 3H, OCH <sub>2</sub> CH <sub>3</sub> )
	O—CH <sub>3</sub> 3.25 (s, 1.05H)	3.28 (s, 1.05H)		3.04 (s, 0.9H)	
	HC=	—		5.8–6.05 (m, 0.3H, 30.1)	
<b>6b</b>	C—CH <sub>3</sub> 1.88 (s, 1.95H)		1.44 (s, 0.75H)	1.53 (s, 0.3H)	2.8–4.0 (m, 4.5H, OCH <sub>2</sub> , OCH); 1.55–2.5 (m, 4H, PCH <sub>2</sub> ); 0.75–1.0 (m, 6H, OCH <sub>2</sub> CH <sub>3</sub> )
	HC=	—	5.94 (ddd, 0.25H, 30.2)	5.99 (dm, 0.1H, 31)	
<b>6c<sup>a</sup></b>	C—CH <sub>3</sub> 1.96 (s, 2.2H)		1.53 (s, 0.8H)		3.8–4.4 (m, 2.75H, OCH <sub>2</sub> , OCH); 1.6–2.8 (m, 4H, PCH <sub>2</sub> ); 1.5–1.8 (m, 2H, OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ); 0.96 (t, 3H, OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )
	O—CH <sub>3</sub> 3.40 (s, 1.1H)	3.42 (s, 1.1H)	3.20 (s, 0.8H)		
	HC=	—	6.04 (ddd, 0.25H, 30.0)		
<b>6d</b>	C—CH <sub>3</sub> 1.99 (s, 2.5H)		1.57 (s, 0.5H)		4.25–4.55 (m, 1.85H, OH, OCH); 3.85–4.1 (m, 2H, OCH <sub>2</sub> ); 1.95–2.6 (m, 4H, PCH <sub>2</sub> ); 1.15–1.25 (m, 3H, OCH <sub>2</sub> CH <sub>3</sub> )
	HC=	—	5.88 (dt, 0.15H, 30.8)		
<b>6e<sup>a</sup></b>	C—CH <sub>3</sub> 1.95 (s, 2.4H)		1.56 (s, 0.6H)		4.3–4.8 (m, 0.8H, OCH); 3.8–4.2 (m, 2H, OCH <sub>2</sub> ); 3.61 (broad, 1H, OH); 1.9–2.8 (m, 4H, PCH <sub>2</sub> ); 1.5–1.9 (m, 2H, OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ); 0.95 (t, 3H, OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )
	HC=	—	5.86 (dt, 0.2H, 30.0)		

<sup>a</sup>At 100 MHz.**TABLE 11** MS Data for 5- and 3-Methyl-3-alkoxy (or hydroxy)-4-chloro-1,2,3,6-tetrahydrophosphinine 1-Oxides **6a-e**

Fragment	$m/z$ (Relative Intensity, %)				
	6a	6b <sup>a</sup>	6c	6d <sup>b</sup>	6e <sup>c</sup>
M <sup>+</sup>	238 (7)	252 (6)	252 (10)	224 (9)	238 (10)
[M—Me] <sup>+</sup>	223 (29)	237 (7)	237 (13)	209 (6)	223 (4)
[M—CH <sub>2</sub> O] <sup>+</sup>	208 (38)	208 <sup>d</sup> (82)	222 (44)		
[M—R'OH] <sup>+</sup>	206 (30)	206 (36)	220 (17)	206 (25)	220 (17)
[M—R'—(R—H)] <sup>+</sup>	195 (44)	195 (48)	195 (61)	195 (17)	195 (19)
[M—CH <sub>2</sub> O—R] <sup>+</sup>	179 (7)	179 <sup>e</sup> (66)	180 <sup>f</sup> (74)		
[M—ROH] <sup>+</sup>				178 (23)	178 (48)
[M—P(O)OR—Cl—R'OH] <sup>+</sup>	79 (100)	79 (100)	79 (100)	79 (100)	79 (77)

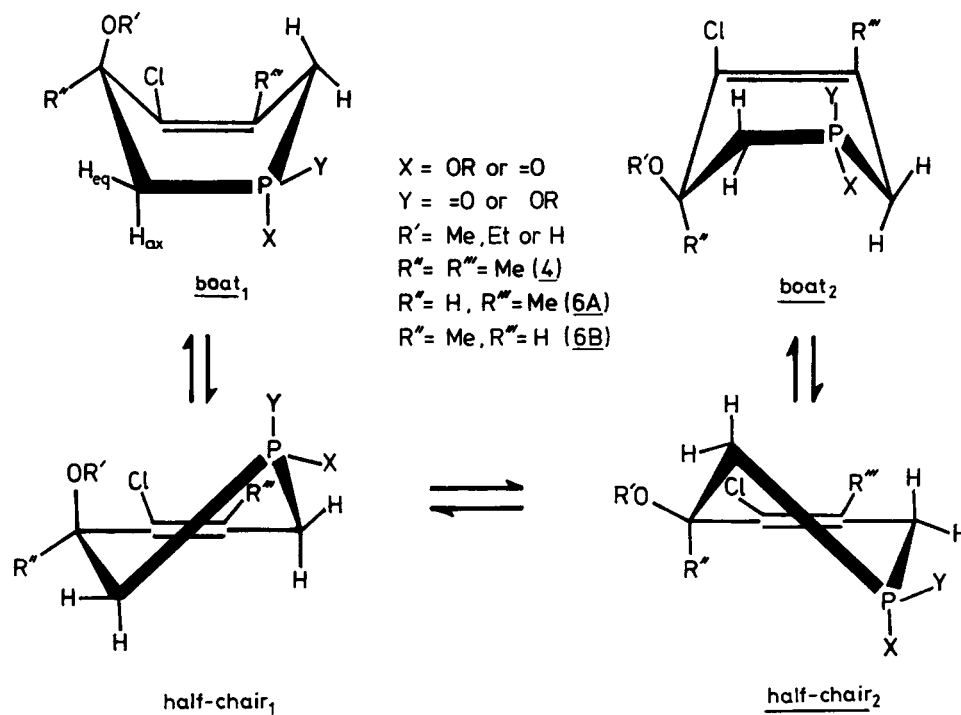
<sup>a</sup>M-29 (32); <sup>b</sup>M-Cl (36), M—H<sub>2</sub>O—EtO(69); <sup>c</sup>M-Cl (14), M—H<sub>2</sub>O—PrO (100); <sup>d</sup>M—C<sub>2</sub>H<sub>4</sub>O; <sup>e</sup>M—C<sub>2</sub>H<sub>4</sub>O—Et; <sup>f</sup>M—CH<sub>2</sub>O—(Et—H).

of the *half-chair*<sub>2</sub> conformer, where the appropriate dihedral angles are  $\sim 60^\circ$  and  $\sim 180^\circ$ , respectively [9,10]. Thus, tetrahydrophosphinine oxides **4** and **6** have different predominant conformers.

Comparing these results with the earlier observation that the P—C substituted tetrahydrophosphinine oxides exist as the equilibrium mixture of half-chair conformers [4], it can be concluded that the substitution pattern has a dramatic effect on the conformation of the products.

Finally, we examined whether the outcome of the reaction of 3,4-dimethyl-2,5-dihydro-1H-phosphole 1-oxides (**1a-d**) with dichlorocarbene changed if the dichlorocarbene was used in larger excess and under more forcing conditions. We observed that, if twice as much dichlorocarbene were generated as originally, and if a reaction temperature of  $\sim 60^\circ$  was maintained, 4-dichloromethylene-1,4-dihydrophosphinine 1-oxide **8** was the product instead of adduct **2**.

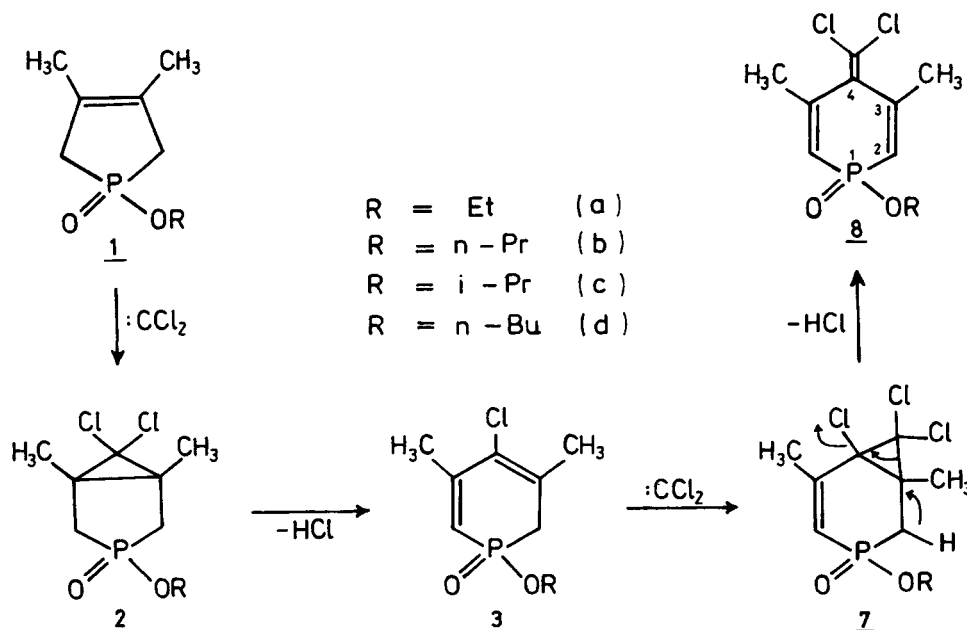
The formation of these unexpected products at first sight (**8a-d**) can be explained assuming a series of consecutive reactions. Adduct **2** is formed



SCHEME 5

in the first step which undergoes in situ cyclopropane ring opening to yield dihydrophosphinine **3**. This intermediate gives a second adduct (**7**) by reaction with an additional unit of dichlorocarbene. Adduct **7** is then the subject of an unusual and rarely occurring cyclopropane ring opening [11] to afford an exocyclic dichloromethylene group in position 4

of the original six-membered ring (Scheme 6). To confirm the suggested route for the formation of product **8**, dihydrophosphinine oxide **3d** was reacted with dichlorocarbene. As expected, 1,4-dihydrophosphinine oxide **8d** could be isolated. The formation of P-phenyl- and P-alkyl 4-dichloromethylene-1,4-dihydrophosphinine oxides in similar



SCHEME 6



**TABLE 12**  $^{13}\text{C}$  NMR Data for 4-Dichloromethylene-1,4-dihydro-3,5-dimethylphosphinine 1-Oxides **8a-d** in  $\text{CDCl}_3$  Solutions at 25 MHz

Product	$\delta^{13}\text{C}$ ( $J_{\text{PC}}$ in Hz)								
	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$	$=\text{CCl}_2$	$\text{C}-\text{CH}_3$	$\text{C}_\alpha$	$\text{C}_\beta$	$\text{C}_\gamma$	$\text{C}_\delta$
<b>8a</b>	122.1 (128.9)	155.1	136.6 (25.0)	123.6	23.3 (16.1)	61.2 (6.6)	16.3 (5.9)	—	—
<b>8b</b>	121.5 (128.9)	155.0	136.4 (24.2)	123.4	23.0 (16.1)	66.5 (6.6)	23.3 (5.8)	9.4	—
<b>8c</b>	122.5 (129.7)	154.4	136.6 (24.9)	123.0	23.0 (16.1)	70.0 (6.6)	23.8 (4.4)	—	—
<b>8d<sup>a</sup></b>	121.8 (128.6)	155.5 (1)	136.5 (24.0)	123.7	23.5 (16.4)	65.1 (6.5)	32.4 (6.5)	18.6	13.5

<sup>a</sup>Measured at 62.5 MHz.

reactions has also been observed by us [6]. We failed, however, to isolate the unstable intermediates in these instances. The P-alkoxy 1,4-dihydrophosphinine oxides (**8a-d**) were obtained in 30% overall yield after column chromatography and recrystallization. They exhibited NMR and mass spectral parameters (Tables 12–14) similar to the P—C substituted spectral derivatives described [6].

**TABLE 13**  $^1\text{H}$  NMR Data for 4-Dichloromethylene-1,4-dihydro-3,5-dimethylphosphinine 1-Oxides **8a-d** in  $\text{CDCl}_3$  Solutions at 100 MHz

Product	$\delta^1\text{H}$ ( $J_{\text{PH}}$ in Hz)					
	$\text{H}_2$	$\text{C}-\text{CH}_3$	$\text{H}_\alpha$	$\text{H}_\beta$	$\text{H}_\gamma$	$\text{H}_\delta$
<b>8a</b>	5.86 (11.5)	2.24	3.91 (8.8)	1.22	—	—
<b>8b</b>	5.88 (11.2)	2.23	3.76 (7.8)	1.4–1.7	0.93	—
<b>8c</b>	5.91 (11.6)	2.23	4.44 (9.4)	1.22	—	—
<b>8d<sup>a</sup></b>	6.00 (11.0)	2.33	3.95 (7.4)	1.62	1.39	0.91

<sup>a</sup>Measured at 250 MHz.**TABLE 14** MS Data for 4-Dichloromethylene-1,4-dihydro-3,5-dimethylphosphinine 1-Oxides **8a-d**

Fragment ( $m/z$ )	Relative Intensity (%)			
	<b>8a</b>	<b>8b<sup>b</sup></b>	<b>8c</b>	<b>8d</b>
$\text{M}^{+a}$	2	3	3	3
$[\text{M}-\text{Cl}]^+$	14	90	30	100
$[\text{M}-\text{RO}]^+$ (221)	6	26	25	26
$[\text{M}-\text{P}(\text{O})\text{OR}]^+$ (174)	100	100	100	72
$[\text{M}-\text{P}(\text{O})\text{OR}-\text{Me}]^+$ (159)	60	73	50	57
$[\text{M}-\text{P}(\text{O})\text{OR}-\text{Cl}]^+$ (139)	40	53	42	52

<sup>a</sup> $m/z$  values for the molecular ions are 266, 280, 280, and 294, respectively; <sup>b</sup>M-41 (25).

## EXPERIMENTAL

The FT  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken on a Bruker AC-250 spectrometer or on a JEOL FX 100 instrument with  $\text{Me}_4\text{Si}$  as internal standard. The FT  $^{31}\text{P}$  NMR spectra were recorded with an IBM NR-80 spectrometer using 85%  $\text{H}_3\text{PO}_4$  as external standard. 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 a SPECORD 75 spectrometer.

The 1-alkoxy-2,5-dihydro-3,4-dimethyl-1H-phosphole 1-oxides (**1a-d**) were prepared by the alcoholysis of the 2,3-dimethylbutadiene-phosphorus tribromide-cycloadduct as described for other derivatives [3].

The following compounds were thus prepared.

### 2,5-Dihydro-3,4-dimethyl-1-ethoxy-1H-phosphole 1-Oxide (**1a**)

Yield 60%; bp 85–90°C/0.27 mb (Ref. [12] 85–87°C/0.27 mb).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (t, 3H,  $\text{CH}_2\text{CH}_3$ ,  $J = 7$ ), 1.72 (s, 6H,  $=\text{C}-\text{CH}_3$ ), 2.42 (d, 4H, P— $\text{CH}_2$ ,  $^2J_{\text{PH}} = 13$ ), 4.07 (m, 2H,  $\text{OCH}_2$ ).

### 2,5-Dihydro-3,4-dimethyl-1-(1-propoxy)-1H-phosphole 1-Oxide (**1b**)

Yield 92%; bp 91–96°C/0.27 mb (Ref. [12] 135–136°C/12 mb).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.94 (t, 3H,  $\text{CH}_2\text{CH}_3$ ,  $J = 7$ ), 1.72 (s,  $=\text{C}-\text{CH}_3$ ) overlapped by 1.40–2.05 (m,  $\text{CH}_2\text{CH}_3$ ) total intensity 8H, 2.42 (d, 4H, P— $\text{CH}_2$ ,  $^2J_{\text{PH}} = 12$ ), 3.97 (m, 2H,  $\text{OCH}_2$ ). MS,  $m/z$  (relative intensity): 188 ( $\text{M}^+$ , 15), 146 (31), 82 (100). IR (neat): 2960, 1640, 1440, 1390, 1230, 990  $\text{cm}^{-1}$ .

**2,5-Dihydro-3,4-dimethyl-1-(2-propoxy)-1H-phosphole 1-Oxide (1c)**

Yield 87%; bp 90–95°C/0.27 mb.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.34 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ,  $J = 6$ ), 1.72 (s, 6H,  $=\text{C}-\text{CH}_3$ ), 2.43 (d, 4H,  $\text{P}-\text{CH}_2$ ,  $^2J_{\text{PH}} = 13$ ), 4.69 (m, 1H, OCH). MS,  $m/z$  (relative intensity): 188 ( $\text{M}^+$ , 12), 146 (37), 82 (100). IR (neat): 2970, 1630, 1440, 1370, 1230, 980  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_9\text{H}_{17}\text{O}_2\text{P}$ : C, 57.41; H, 9.11. Found: C, 57.66; H, 9.31.

**1-(1-Butoxy)-2,5-dihydro-3,4-dimethyl-1H-phosphole 1-Oxide (1d)**

Yield 85%; bp 106–110°C/0.27 mb.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.73 (s, 3H,  $=\text{C}-\text{CH}_3$ ), 2.44 (d, 4H,  $\text{P}-\text{CH}_2$ ,  $^2J_{\text{PH}} = 13$ ), 4.01 (m, 2H, OCH<sub>2</sub>). MS,  $m/z$  (relative intensity): 202 ( $\text{M}^+$ , 19), 146 (45), 82 (100). IR (neat): 2950, 1610, 1430, 1390, 1230, 1020  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{10}\text{H}_{19}\text{O}_2\text{P}$ : C, 59.37; H, 9.48. Found: C, 59.58; H, 9.38.

**General Procedure for the Preparation of 3-Alkoxy-6,6-dichloro-1,5-dimethyl-3-phosphabicyclo[3.1.0]hexane 3-Oxides (2a–d)**

A solution of sodium hydroxide (14.4 g, 0.36 mol) in water (18 mL) was added dropwise to a mixture of 1-alkoxy-2,5-dihydro-3,4-dimethyl-1H-phosphole 1-oxide (**1a–d**; 15.0 mmol), TEBAC (0.24 g, 1.06 mmol), and alcohol-free chloroform (50 mL) with stirring over a 15-minute period. The temperature of the mixture gradually rose to reflux. After having been stirred for 7 hours, the mixture was filtered and the chloroform phase was dried ( $\text{Na}_2\text{SO}_4$ ). The crude product obtained after evaporating the solvent was chromatographed on silica gel, using 2% methanol in chloroform as the eluant to give **2a–d** as a mixture of two diastereoisomers (**A** and **B**). The isomeric mixture so obtained could be used in the next step. (If necessary, the diastereoisomers of **2b,d** could be separated by repeated column chromatography.) Important notice: The adducts can only be stored under refrigeration at  $\sim 0^\circ\text{C}$ .

The following products were thus prepared.

**6,6-Dichloro-1,5-dimethyl-3-ethoxy-3-phosphabicyclo[3.1.0]hexane 3-Oxide (2a)**

Yield 65%; the ratio of **A** and **B** was  $\sim 55:45$ .  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +80.4 and +77.4;  $^{13}\text{C}$  NMR, Table 1;  $^1\text{H}$  NMR, Table 2. MS,  $m/z$  (relative intensity): 257 ( $\text{M}^+$ +1, 87), 221 (100), 187 (51), 193 (11).

**6,6-Dichloro-1,5-dimethyl-3-(1-propoxy)-3-phosphabicyclo[3.1.0]hexane 3-Oxide (2b)**

Yield 70%; the ratio of **A** and **B** was  $\sim 59:41$ .  $^{13}\text{C}$  NMR, Table 1;  $^1\text{H}$  NMR, Table 2. Anal. calcd for  $\text{C}_{10}\text{H}_{17}\text{Cl}_2\text{O}_2\text{P}$ : C, 44.30; H, 6.32. Found: C, 44.52; H, 6.22. Repeated column chromatography resulted

in 21% of **2Ab** (MS,  $m/z$  (relative intensity): 271 ( $\text{M}^+$ +1, 68), 235 (97), 201 (4), 193 (100)) and 19% of **2Bb**.

**6,6-Dichloro-1,5-dimethyl-3-(2-propoxy)-3-phosphabicyclo[3.1.0]hexane 3-Oxide (2c)**

Yield 72%; the ratio of **A** to **B** was  $\sim 55:45$ .  $^{13}\text{C}$  NMR, Table 1;  $^1\text{H}$  NMR, Table 2. MS,  $m/z$  (relative intensity): 271 ( $\text{M}^+$ +1, 100), 235 (83), 201 (54), 193 (67). IR (neat): 2980, 1440, 1380, 1230, 980  $\text{cm}^{-1}$ . Repeated column chromatography resulted in 26% of **2Ac**.

**3-(1-Butoxy)-6,6-dichloro-1,5-dimethyl-3-phosphabicyclo[3.1.0]hexane 3-Oxide (2d)**

Yield 62%; the ratio of **A** to **B** was  $\sim 58:42$ .  $^{13}\text{C}$  NMR, Table 1;  $^1\text{H}$  NMR, Table 2. MS,  $m/z$  (relative intensity): 285 ( $\text{M}^+$ +1, 53), 249 (100), 215 (40), 193 (21). IR (neat): 2970, 1460, 1400, 1240, 1030  $\text{cm}^{-1}$ . Repeated column chromatography resulted in 16% of **2Ad** and 17% of **2Bd**.

**General Procedure for the Preparation of 1-Alkoxy-4-chloro-1,2-dihydro-3,5-dimethylphosphinine 1-Oxides (3a–d)**

The mixture of the adduct (**2a–d**; 15 mmol) and triethylamine (2.1 mL, 15 mmol) in benzene (40 mL) was stirred at reflux for 3 hours. Then the precipitate was filtered off and the solvent of the filtrate was evaporated. The residue so obtained was chromatographed on silica gel (3% methanol in chloroform) to give **3a–d** as an oil.

The following products were thus prepared.

**4-Chloro-1,2-dihydro-3,5-dimethyl-1-ethoxyphosphinine 1-Oxide (3a)**

Yield 59%.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +34.6;  $^{13}\text{C}$  NMR, Table 3;  $^1\text{H}$  NMR, Table 4; MS, Table 5. IR (neat): 3000, 1630, 1580, 1450, 1390, 1230, 1050  $\text{cm}^{-1}$ .

**4-Chloro-1,2-dihydro-3,5-dimethyl-1-(1-propoxy)phosphinine 1-Oxide (3b)**

Yield 68%.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +29.4;  $^{13}\text{C}$  NMR, Table 3;  $^1\text{H}$  NMR, Table 4; MS, Table 5.  $M_{\text{found}}^+ = 234.0557$ ,  $\text{C}_{10}\text{H}_{16}\text{ClO}_2\text{P}$  requires 234.0577 for the  $^{35}\text{Cl}$  isotope. IR (neat): 2970, 1620, 1570, 1440, 1370, 1220, 970  $\text{cm}^{-1}$ .

**4-Chloro-1,2-dihydro-3,5-dimethyl-1-(2-propoxy)phosphinine 1-Oxide (3c)**

Yield 67%; mp 68–72°C (ethyl acetate-1-pentane).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +38.2;  $^{13}\text{C}$  NMR, Table 3;  $^1\text{H}$  NMR, Table 4; MS, Table 5. IR (KBr disc): 2950,

1600, 1550, 1430, 1380, 1190, 950  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{10}\text{H}_{16}\text{ClO}_2\text{P}$ : C, 51.18; H, 6.87. Found: C, 51.33; H, 7.0.

*1-(1-Butoxy)-4-chloro-1,2-dihydro-3,5-dimethylphosphinine 1-Oxide (3d)*

Yield 54%.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +37.0;  $^{13}\text{C}$  NMR, Table 3;  $^1\text{H}$  NMR, Table 4; MS, Table 5. IR (neat): 2960, 1610, 1560, 1430, 1370, 1210, 960  $\text{cm}^{-1}$ .

*General Procedure for the Preparation of 1-Alkoxy-4-chloro-3,5-dimethyl-3-methoxy-(or ethoxy)-1,2,3,6-tetrahydrophosphinine 1-Oxides (4a–d)*

The mixture of the adduct (**2a–d**; 15 mmol) and silver nitrate (24 g, 0.14 mmol) in methanol or ethanol (60 mL) was stirred at the boiling point for 4 hours. Then the solid components were removed by filtration and the filtrate was evaporated. The residue so obtained was purified by repeated column chromatography (silica gel, 3% methanol in chloroform (a) and benzene-acetone 4:6 (b) to give **4a–d**.

The following products were thus prepared.

*4-Chloro-1,3-diethoxy-3,5-dimethyl-1,2,3,6-tetrahydrophosphinine 1-Oxide (4a)*

The alcohol: ethanol; purification: a,b; yield 31% (one diastereoisomer).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  + 43.8;  $^{13}\text{C}$  NMR, Table 6;  $^1\text{H}$  NMR, Table 7; MS, Table 8.  $M_{\text{found}}^+$  = 250.0868,  $\text{C}_{11}\text{H}_{20}\text{ClO}_2\text{P}$  requires 250.0890 for the  $^{35}\text{Cl}$  isotope.

*4-Chloro-3,5-dimethyl-3-methoxy-1-(1-propoxy)-1,2,3,6-tetrahydrophosphinine 1-Oxide (4b)*

The alcohol: methanol; purification: a; yield 42% (one diastereoisomer).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +43.9;  $^{13}\text{C}$  NMR, Table 6;  $^1\text{H}$  NMR, Table 7; MS, Table 8.

*1-(1-Butoxy)-4-chloro-3,5-dimethyl-3-methoxy-1,2,3,6-tetrahydrophosphinine 1-Oxide (4d)*

The alcohol: methanol; purification: a; yield 44% (one diastereoisomer).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +44.3;  $^{13}\text{C}$  NMR, Table 6;  $^1\text{H}$  NMR, Table 7; MS, Table 8. IR (neat): 2960, 1630, 1550, 1460, 1370, 1210, 1020  $\text{cm}^{-1}$ .

*4-Chloro-3,5-dimethyl-3-methoxy-1-(2-propoxy)-1,2,3,6-tetrahydrophosphinine 1-Oxide (4c)*

The alcohol: methanol; purification: a,b; yield 27% and 18% for the two diastereoisomers.  $^{13}\text{C}$  NMR, Table 6;  $^1\text{H}$  NMR, Table 7; MS, Table 8.

The mixtures of 5- and 3-methyl-3-alkoxy- or hydroxy-1-alkoxy-4-chloro-1,2,3,6-tetrahydro-

phosphinine 1-oxides (**6Aa–e** and **6Ba–e**) were prepared similarly from the 3-alkoxy-6,6-dichloro-1-methyl-3-phosphabicyclo[3.1.0]hexane 3-oxides (**5a,b**)[3].

The following products were prepared.

*5- and 3-Methyl-4-chloro-1-ethoxy-3-methoxy-1,2,3,6-tetrahydrophosphinine 1-Oxide (6Aa and 6Ba)*

Protic species: methanol; reaction time: 8 hours; purification: a; yield 58%.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +46.5, 44.9, 44.5, and 43.7 for the four diastereoisomers;  $^{13}\text{C}$  NMR, Table 9;  $^1\text{H}$  NMR, Table 10; MS, Table 11. IR (neat): 2980, 1730, 1640, 1440, 1380, 1210, 1030, 950  $\text{cm}^{-1}$ .

*5- and 3-Methyl-4-chloro-1,3-diethoxy-1,2,3,6-tetrahydrophosphinine 1-Oxide (6Ab and 6Bb)*

Protic species: ethanol; reaction time: 8 hours; purification: a; yield 73%.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  + 47.3, 45.7, 45.1, and 44.4 for the four diastereoisomers;  $^{13}\text{C}$  NMR, Table 9;  $^1\text{H}$  NMR, Table 10; MS, Table 11. IR (neat): 2970, 1710, 1640, 1430, 1380, 1220, 1020, 940  $\text{cm}^{-1}$ .

*5- and 3-Methyl-4-chloro-methoxy-1-(1-propoxy)-1,2,3,6-tetrahydrophosphinine 1-Oxide (6Ac and 6Bc)*

Protic species: methanol; reaction time: 8 hours; purification: a,b; yield 66%.  $^{13}\text{C}$  NMR, Table 9;  $^1\text{H}$  NMR, Table 10; MS, Table 11. IR (neat): 2970, 1680, 1640, 1450, 1380, 1200, 1000, 920  $\text{cm}^{-1}$ .

*5- and 3-Methyl-4-chloro-1-ethoxy-3-hydroxy-1,2,3,6-tetrahydrophosphinine 1-Oxide (6Ad and 6Bd)*

Protic species: water; reaction time: 6 hours; purification after extraction with chloroform: a; yield 36%; mp 103–109°C.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  +44.3, 43.0, and 44.3 for the three diastereoisomers;  $^{13}\text{C}$  NMR, Table 9;  $^1\text{H}$  NMR, Table 10; MS, Table 11. IR (KBr disc): 3240, 2960, 1630, 1410, 1380, 1190, 1030, 950  $\text{cm}^{-1}$ .

*5- and 3-Methyl-4-chloro-3-hydroxy-1-(1-propoxy)-1,2,3,6-tetrahydrophosphinine 1-Oxide (6Ae and 6Be)*

Protic species: water; reaction time: 6 hours; purification after extraction with chloroform: a; yield 74%.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  + 45.5, 46.3, and 45.5 for the three diastereoisomers;  $^{13}\text{C}$  NMR, Table 9;  $^1\text{H}$  NMR, Table 10; MS, Table 11. IR (neat): 3310, 2970, 1640, 1450, 1380, 1200, 1000, 920  $\text{cm}^{-1}$ .

*General Procedure for the Preparation of 1-Alkoxy-4-dichloromethylene-1,4-dihydro-3,5-dimethylphosphinine 1-Oxides (8a–d)*

A vigorously stirred solution of the dihydro-1H-phosphole 1-oxide (**1a–d**; 15.0 mmol) and triethylbenzylammonium chloride (0.19 g, 0.86 mmol) in alcohol-free chloroform (150 mL) was treated with sodium hydroxide (33 g, 0.83 mol) in water (33 mL) at 50°C over a period of 15 minutes. The mixture was stirred at the boiling point for 3 hours. The chloroform phase obtained after filtration was evaporated to give **8a–d** on purification by repeated column chromatography (silica gel, 3% methanol in chloroform).

The following products were thus prepared.

*4-Dichloromethylene-1,4-dihydro-3,5-dimethyl-1-ethoxyphosphinine 1-Oxide (8a)*

Yield 31%; mp 79–81°C (from ether-1-pentane 1:9). <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ +19.1; <sup>13</sup>C NMR, Table 12; <sup>1</sup>H NMR, Table 13; MS, Table 14. IR (KBr disk): 3010, 1650, 1480, 1400, 1250, 1010 cm<sup>-1</sup>. Anal. calcd for C<sub>10</sub>H<sub>13</sub>Cl<sub>2</sub>O<sub>2</sub>P: C, 44.95; H, 4.91. Found: C, 44.70; H, 4.76.

*4-Dichloromethylene-1,4-dihydro-3,5-dimethyl-1-(1-propoxy)-phosphinine 1-Oxide (8b)*

Yield 25%; mp 72–74°C. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ +19.6; <sup>13</sup>C NMR, Table 12; <sup>1</sup>H NMR, Table 13; MS, Table 14. IR (KBr disk): 2980, 1670, 1480, 1420, 1260, 1040 cm<sup>-1</sup>. Anal. calcd for C<sub>11</sub>H<sub>15</sub>Cl<sub>2</sub>O<sub>2</sub>P: C, 46.98; H, 5.38. Found: C, 46.84; H, 5.57.

*4-Dichloromethylene-1,4-dihydro-3,5-dimethyl-1-(2-propoxy)phosphinine 1-Oxide (8c)*

Yield 24%; mp 76–78°C. <sup>13</sup>C NMR, Table 12; <sup>1</sup>H NMR, Table 13; MS, Table 14. IR (KBr disk): 3020, 1660, 1490, 1420, 1270, 1020 cm<sup>-1</sup>. Anal. calcd for C<sub>11</sub>H<sub>15</sub>Cl<sub>2</sub>O<sub>2</sub>P: C, 46.98; H, 5.38. Found C, 46.78; H, 5.48.

*1-(1-Butoxy)-4-dichloromethylene-1,4-dihydro-3,5-dimethyl-phosphinine 1-Oxide (8d)*

Yield 27%; mp 64–66°C. <sup>13</sup>C NMR, Table 12; <sup>1</sup>H NMR, Table 13; MS, Table 14. IR (KBr disk): 3000, 1670, 1490, 1420, 1260 cm<sup>-1</sup>.

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