Notes

Formation of the 4-Methylene-1,4-dihydrophosphinine Ring System in the Reaction of 2,5-Dihydro-3,4-dimethyl-1*H*-phosphole 1-Oxides with Dichlorocarbene

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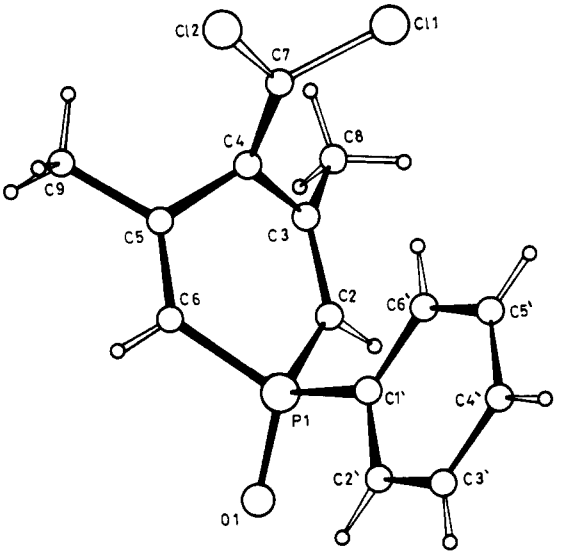
Earlier we reported on the two-step ring enlargement of 1-substituted 2,5-dihydro-3-methyl-1*H*-phosphole 1-oxides. The first step involves the addition of dichlorocarbene to the double bond of the starting material,[1] while the cyclopropane ring so formed is opened in the second step to give dihydrophosphinine oxides.[2] Further reaction with dichlorocarbene followed by ring expansion in a similar manner affords phosphepine oxides.[3]

When an additional methyl group is present in the starting dihydrophosphole oxide at positon 4, the primary adduct formed rapidly undergoes further transformations under the conditions of the reaction[4] to yield products resulting from the attack of 1 or 2 equiv of dichlorocarbene.[1]

With the phenyl-substituted compound **1a**, a single product was obtained, for which structure **2a** was proposed. The product has now been subjected to single-crystal X-ray diffraction analysis and found to have a structure (**3a**) isomeric with that originally proposed (**2a**). Compound **3a** is a derivative of the 4-methylene-1,4-dihydrophosphinine ring system (Figure 1, Scheme I).[5] On the basis of the ^1H and ^{13}C NMR, MS, and IR spectra, **2a** was previously proposed for the structure of the product.[1] ^1H NMR, MS, and IR spectroscopic data, however, do not allow proper assignment, because one cannot easily differentiate a phosphepine oxide and a 4-methylene-1,4-dihydrophosphinine oxide on the basis of these spectra. In the ^{13}C NMR spectrum of the product, a weak doublet can be found, which was previously ignored because of its very low intensity, but now on the basis of repeated measurements it has turned out to be an important signal. This additional doublet of 2.9 Hz at 123.9 ppm belongs to the dichloromethylene group and is decisive as such (Table I). The assignment has been confirmed also by the attached proton test technique.

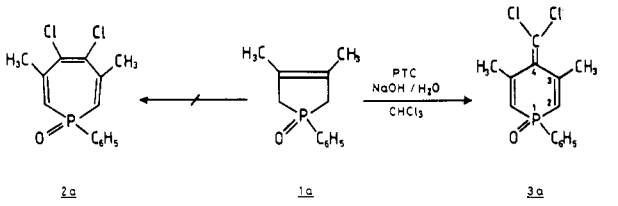
The reaction of the 1-methoxydihydrodimethylphosphole oxide **1b** with dichlorocarbene leads to the formation of several products,[1] including the one resulting from the attack of 2 equiv of dichlorocarbene. In the ^{13}C NMR spectrum of the latter compound, the weak but characteristic doublet at 123.9 ppm (J = 3.7 Hz) can again be found, and the other shifts and couplings are also sim-



3a

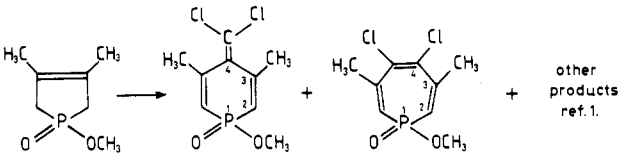
Figure 1. Perspective view of **3a**; hydrogen atoms are shown but not labeled.

Scheme I



2a 1a 3a

Scheme II



1b 3b 2b

(1) Keglevich, Gy.; Petneházy, I.; Miklós, P.; Almásy, A.; Tóth, G.; Töke, L.; Quin, L. D. *J. Org. Chem.* **1987**, *52*, 3983.

(2) Keglevich, Gy.; Androsits, B.; Töke, L. *J. Org. Chem.* **1988**, *53*, 4106.

(3) Keglevich, Gy.; Janke, F.; Brlik, J.; Petneházy, I.; Tóth, G.; Töke, L. *Phosphorus Sulfur*, **1989**, *46*, 69.

(4) Makosza, M.; Wawrzyniewicz, M. *Tetrahedron Lett.* **1969**, 4659.

(5) The six-membered hetero ring possessing two parallel double bonds of 1.334 (3) and 1.322 (3) Å assumes an asymmetric boat shape with P(1) and C(4) on the bows situated at a distance of 0.371 (1) and 0.493 (2) Å, respectively, from the best plane of the other four atoms. The puckering parameters (Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354) are Q = 0.508 (2) Å, φ = 360.0 (2)°, θ = 95.1(2)°, whereas the corresponding lowest asymmetry factors (Kálmán, A., Czugler, M., Simon, K. In *Molecular Structure and Biological Activity*; Griffith, F. J., Duax, W. L., Eds.; Elsevier Biomedical: New York, 1982; pp 367-376) fC_S(P1) = 0, fC_S(C_5-C_6) = 3.7 pm, indicating a perfect mirror plane bisecting P(1) and C(4) and a second less perfect mirror plane perpendicular to the first one. The phenyl ring is bound to P(1) pseudoaxially, while O(1) occupies a pseudoequatorial orientation. The torsion angles C(7)-C(4)-C(3)-C(2) = 126.8 (4)° and C(7)-C(4)-C(5)-C(6) = -126.8 (4)° indicate a transitional position of the dichloromethylene moiety bound to C(4) atom by the third C-C double bond of 1.331 (3) Å.

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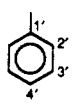
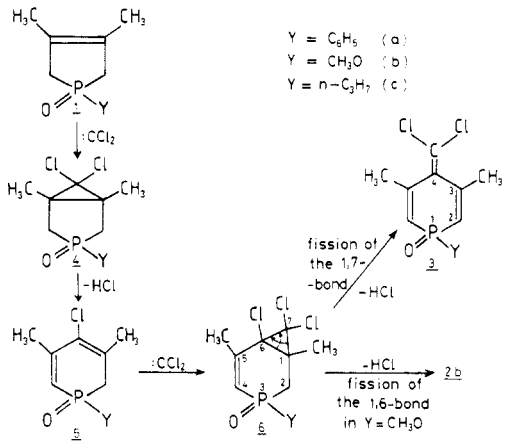
Table I. ^{13}C NMR Spectral Data for 4-(Dichloromethylene)-1,4-dihydro-3,5-dimethylphosphinine 1-Oxides 3a–c[a]

compd	Y	^{13}C δ (J_{PC})								
		C_2	C_3	C_4	CCH_3	$=CCl_2$	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$
3a		124.1 (96.7)	152.1	136.6 (21.3)	23.3 (14.7)	123.9 (2.9)	131.9 (112.1)	128.2 (12.5)	129.4 (10.3)	131.5 (1.5)
3b	2' 1' CH_3O	121.0 (129.0)	155.4	136.2 (24.2)	23.4 (16.1)	123.9 (3.7)		51.3 (6.6)		
3c	3' 2' 1' $CH_3CH_2CH_2$	124.1 (90.9)	151.5	136.6 (21.3)	23.1 (13.9)	123.1 (2.9)	32.5 (70.7)	15.0 (3.6)	15.2 (15.7)	

[a] $CDCl_3$ solutions; J_{PC} given in hertz.

Scheme III



ilar to those of **3a** (Table I). The structure is therefore consistent with **3b** rather than **2b**. At the same time, we were successful isolating a product in a small quantity from the reaction mixture, which can be assigned structure **2b**. Structure **2b** is supported by high-resolution mass spectroscopic measurement, and the ^{13}C NMR spectrum of the product contains characteristic shifts and couplings for carbon atoms 2 and 3 (see Experimental Section, Scheme II).

The reaction was repeated with the *P*-*n*-propyl compound in order to see if the formation of 1,4-dihydrophosphinine oxides is general in the reaction of the dihydrodimethylphosphole oxides with dichlorocarbene. As expected, again a 1,4-dihydrophosphinine oxide, **3c**, was observed to form. The structure of **3c** isolated in 15% yield after column chromatography was substantiated as above.

As shown earlier, in the reaction of dihydrodimethylphosphole oxides **1** with dichlorocarbene, first a ring expansion takes place through the adduct **4** to give the dihydrophosphinine oxide **5**. Compound **5** may then be subjected to another similar ring expansion, yielding phospepine oxide **2b**.[1] The cyclopropane ring in intermediate **6** involved in this second ring enlargement step can open, however, an alternative manner with the fission of the C_1–C_7 bond leading to the formation of methylenedihydrophosphinine oxide **3** after loss of a proton (Scheme III).

Experimental Section[6]

2,5-Dihydro-3,4-dimethyl-1-*n*-propyl-1*H*-phosphole 1-oxide (1c) was prepared by the Grignard reaction as published for other dihydro-1*H*-phosphole oxides:[1] yield 79%; bp 110–2 °C (0.1 Torr); ^{31}P NMR ($CDCl_3$) δ +63.6; ^1H NMR ($CDCl_3$) δ 1.06 (m, 3 H, CH_2CH_3), 1.70 (s, $=CCH_3$), overlapped by 1.50–2.0 (m, $(CH_2)_2$) (total intensity 10 H), 2.54 (d, 4 H, PCH_2, $^2J_{PH}$ = 11 Hz); MS *m/e* (rel intensity) 172 (M^+, 96), 144 (49), 130 (83), 82 (39), 67 (100); IR (neat) 2920, 1640, 1450, 1400, 1230 cm^{-1}. Anal. Calcd for $C_9H_{17}OP$: C, 62.81; H, 9.89. Found: C, 62.61; H, 9.77.

4-(Dichloromethylene)-1,4-dihydro-3,5-dimethyl-2-phenylphosphinine 1-Oxide (3a). Compound **1a** was reacted with dichlorocarbene and the mixture worked up as described earlier[1] to give **3a**: yield 10%; mp 148 °C; ^{31}P NMR ($CDCl_3$) δ +9.2; ^{13}C NMR, Table I; ^1H NMR ($CDCl_3$) δ 2.35 (s, 6 H, CH_3), 6.27 (d, 2 H, HC=, $^2J_{PH}$ = 11 Hz), 7.41–7.97 (m, 5 H, Ar); MS, *m/e* (rel intensity) 298 (M^+, 12), 263 (9), 174 (100), 159 (57), 139 (46); IR (KBr disk) 2970, 1605, 1430, 1180, 840 cm^{-1}. Anal. Calcd for $C_{14}H_{13}Cl_2OP$: C, 56.21; H, 4.35. Found: C, 56.06; H, 4.25.

4-(Dichloromethylene)-1,4-dihydro-3,5-dimethyl-1-*n*-propylphosphinine 1-oxide (3c) was prepared by the procedure as used for **3a**: yield 15%; mp 116–8 °C; ^{31}P NMR ($CDCl_3$) δ +20.7; ^{13}C NMR, Table I; ^1H NMR ($CDCl_3$) δ 0.74–1.24 (m, 3 H, CH_2CH_3), 1.24–1.97 (m, 4 H, $(CH_2)_2$), 2.24 (s, 6 H, $=CCH_3$), 6.04 (d, 2 H, HC=, $^2J_{PH}$ = 11); MS, *m/e* (rel intensity) 264 (M^+, 15), 229 (100), 174 (60), 159 (26), 139 (32); IR (KBr disk) 2960, 1620, 1440, 1190, 860 cm^{-1}. Anal. Calcd for $C_{11}H_{15}Cl_2OP$: C, 49.84; H, 5.66. Found: C, 49.54; H, 5.51.

4-(Dichloromethylene)-1,4-dihydro-3,5-dimethyl-1-methoxyphosphinine 1-Oxide (3b). Compound **1b** was reacted with dichlorocarbene as reported earlier[1] to give **3b** (instead of **2b**): yield 5%; ^{31}P NMR ($CDCl_3$) δ +20.9; ^{13}C NMR, Table I; ^1H NMR ($CDCl_3$) δ 2.33 (s, 6 H, CH_3), 3.65 (d, 3 H, OCH_3, $^3J_{PH}$ = 12), 5.99 (d, 2 H, HC=, $^2J_{PH}$ = 11); MS, *m/e* (rel intensity) 252 (M^+, 16), 174 (100), 159 (52), 139 (35); exact mass found M^+ 251.9861, $C_9H_{11}Cl_2O_2P$ requires 251.9874; IR (neat) 2960, 1620, 1440, 1380, 1220, 1030, 850 cm^{-1}.

4,5-Dichloro-3,6-dimethyl-1-methoxyphosphepine 1-Oxide (2b). From the previous reaction a fraction containing product **2b** was also obtained: yield 0.5%; ^{31}P NMR ($CDCl_3$) δ +19.0; ^{13}C NMR ($CDCl_3$) δ 23.3 ($^3J_{PC}$ = 16.1 Hz, CCH_3), 51.3 ($^2J_{PC}$ = 6.6, OCH_3), 121.6 ($^1J_{PC}$ = 129.0 Hz, C_2), 155.1 (C_3); exact mass found M^+ 251.9859, $C_9H_{11}Cl_2O_2P$ requires 251.9874.

X-ray Crystal Structure Analyses of 3a. X-ray data were collected from a triclinic crystal of dimensions 0.3 × 0.3 × 0.4 mm^3 by an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu K_α radiation (ω–2θ scan, $3 < 2\theta < 150°$, scan width (ω) 0.6 + 0.14 tan θ): $C_{14}H_{13}Cl_2OP$ (MW = 299.14); space group $P\bar{1}$; lattice parameters a = 7.339 (1), b = 8.105 (1), and c = 12.116 (2) Å; α = 96.17 (1)°, β = 91.14 (1)°, γ = 100.23 (1)°; V = 704.5 (3) A^3; Z = 2; D_x = 1.41 $g \cdot cm^{-3}$. The structure was solved by direct methods (SHELXS-86) and refined for 163 variables against 2641 observations taken with $I > 3\sigma(I)$. Final R was 0.051 (H positions were not refined). All calculations have been done with SDP-PLUS.[7]

Acknowledgment. We thank Prof. Louis D. Quin (University of Massachusetts, Amherst, MA) for his advice.

Supplementary Material Available: List of atomic positions, bond distances, bond angles, and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

(6) The same instruments have been used as in ref 1.

(7) Structure Determination Package: Frenz, B. A., and Associates Inc.: College Station, TX, and Enraf-Nonius: Delft, 1983.