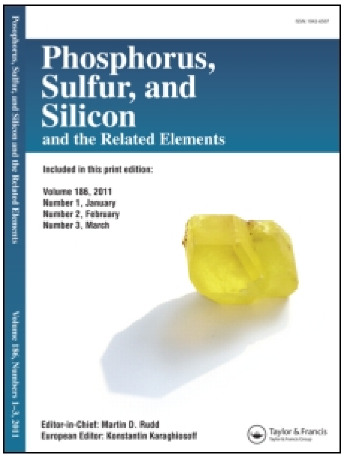

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DIPHENYLBORYLDIPIVALOYLPHOSPHIDE—THE FIRST EXAMPLE OF BORYLATED 2-PHOSPHA-1,3-DIONATE

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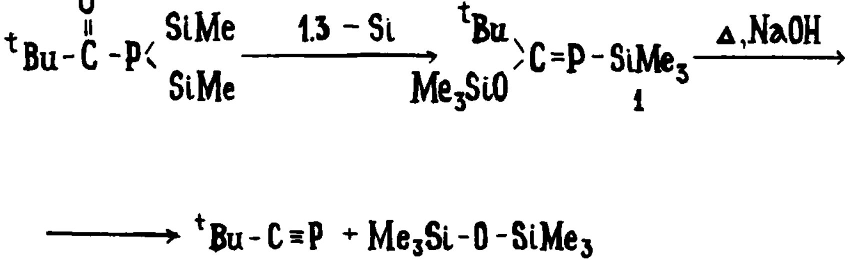
C-Trimethylsiloxy substituted phosphaalkene **1** reacts exothermically with diphenylchloroborane. The expected spontaneous 1,3-elimination of trimethylsiloxydiphenylborane took place to give phosphaalkyne **3** in 1–2% yield only. The symmetrization of intermediately formed C-diphenylboroxysubstituted phosphaalkene **2** into (diphenylboryl)dipivaloylphosphide **4** was found to be the main way of the reaction.

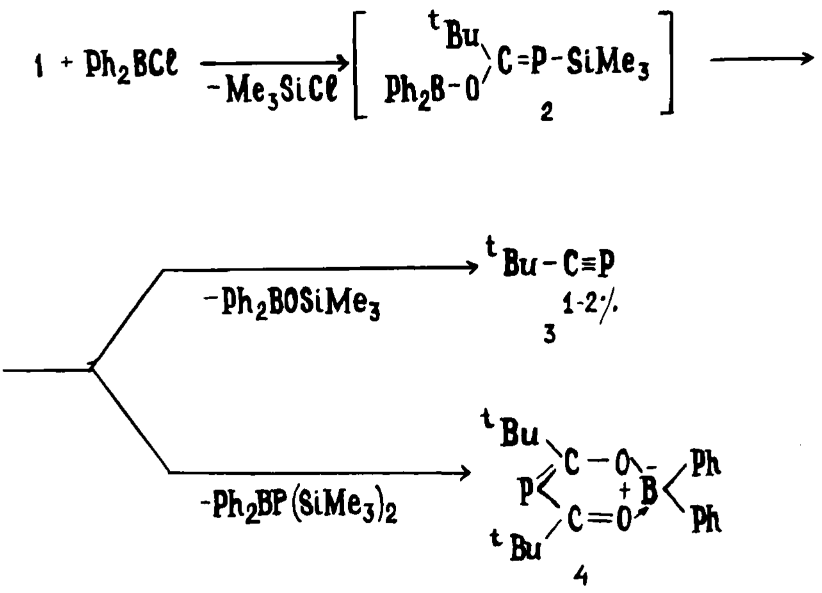
Key words: Phosphaalkene; phosphaalkyne; diphenylchloroborane.

1,3-Migration of the trimethylsilyl group is known to be used in two-coordinated phosphorus synthesis.[1] Such a migration is also used in the synthesis of three-coordinated silicone compounds.[2]

The one-coordinated phosphorus (phosphaalkynes) synthesis does not proceed through 1,3-migration but via 1,3-elimination of trimethylsilyl group. However, 1,3-elimination does not proceed readily in such a system and more rigid conditions (alkaline or F^- catalysis) are required. Lutsenko, Foss et al. showed that silicon replacement by boron atom in acylsilylphosphines accelerates 1,3-migration which effects the acylphosphine conversion into phosphaalkenes.[3] As it was shown earlier, 1,3-elimination of diorganylboron groups i.e. R_2BX ($X{=}NR_2$, SR, OR) takes place spontaneously in many cases to give phosphaalkenes.[4–6] So, we attempted to replace siloxy groups in **1** with diphenylboroxy ones and thus to induce 1,3 spontaneous elimination resulting in phosphaalkynes (one-coordinated phosphorus compounds).

Such a replacement has been recently described for C-trimethylsiloxy substituted phosphaalkenes.[7] By contrast, diphenylchloroborane reacted with **1** exothermically at room temperature. The expected 1,3-spontaneous elimination of trimethylsiloxydiphenylborane took place to give phosphaalkyne **3** in 1–2% yield only. The ^{31}P





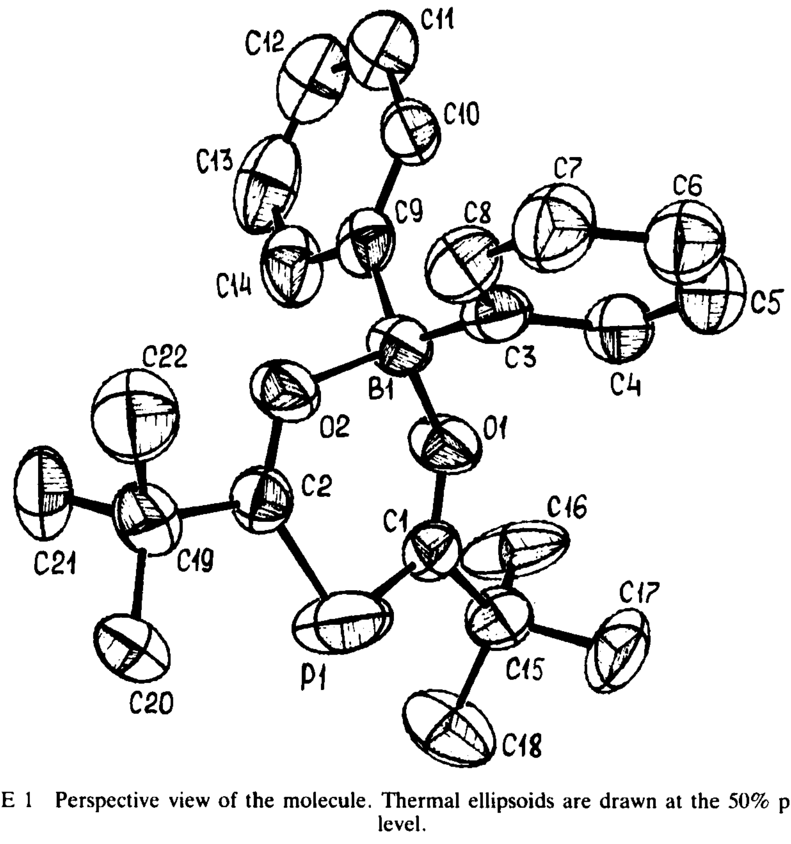


FIGURE 1 Perspective view of the molecule. Thermal ellipsoids are drawn at the 50% probability level.

NMR spectrum of the reaction mixture included a signal at −70 ppm (−69.2 ppm in Reference 8) which may be ascribed to phosphaalkyne **3**.

The symmetrization of intermediately formed C-diphenylborooxysubstituted phosphaalkene **2** into diphenylboryldipivaloylphosphide **4** was found to be the main way of the reaction. Such 2-phospha-1,3-dionate complexes are known for Li, Al, Cr, and Ni. This fact gives evidence of the great stability of this type of phosphorus compounds; it is due to chelating effects in these compounds.

The structure of **4** has been confirmed by ^1H and ^{31}P NMR, mass-spectrometry, and X-ray analysis. The ^{31}P NMR spectrum shows a signal at 63 ppm, which is within the interval for such chelate phosphaalkenes.[9,10] The resonances of the phenyl groups in boron vicinity with $\delta = 6.93-7.70$ ppm, and of tert-butyl ones with $\delta = 1.3$ ppm and $^4J_{PH} = 0.6$ Hz are observed in the ^1H NMR spectrum. The electron impact mass-spectrum indicates a molecular ion peak with M/e = 366, as well as $P(C(^tBu)\text{-}O)_2$, Ph_2B, C_4H_9 fragment ion peaks.

A three dimensional view of the molecule investigated and the atom numbering are shown in Figure 1. Fractional atomic parameters are presented in Table 1. The

TABLE I

Fractional atomic co-ordinates with estimated standard deviations in parentheses.

Atom	x/a	y/b	z/c	B_{iso}, Å
P^1	0.1266(1)	0.2848(2)	−0.22753(7)	9.81(6)
O^1	0.1449(2)	0.2365(3)	−0.1122(1)	5.14(7)
O^2	0.1558(2)	0.0256(3)	−0.1762(1)	5.31(7)
C^1	0.1263(2)	0.3229(4)	−0.1533(2)	4.12(9)
C^2	0.1405(2)	0.0972(5)	−0.2234(2)	4.17(9)
C^3	0.2557(2)	0.1103(4)	−0.1059(2)	4.3(1)
C^4	0.2867(2)	0.2233(5)	−0.0707(2)	4.4(1)
C^5	0.3536(2)	0.2371(5)	−0.0605(2)	5.4(1)
C^6	0.3924(2)	0.1436(5)	−0.0851(2)	5.9(1)
C^7	0.3642(2)	0.0310(5)	−0.1208(3)	6.5(1)
C^8	0.2964(2)	0.0164(5)	−0.1312(2)	5.4(1)
C^9	0.1493(2)	−0.0146(4)	−0.0696(2)	4.14(9)
C^{10}	0.1870(2)	−0.0827(5)	−0.0236(2)	4.6(1)
C^{11}	0.1615(2)	−0.1677(5)	0.0174(2)	5.9(1)
C^{12}	0.0959(3)	−0.1842(6)	0.0121(2)	7.2(1)
C^{13}	0.0543(3)	−0.1190(6)	−0.0334(3)	7.5(1)
C^{14}	0.0821(2)	−0.0362(5)	−0.0730(3)	6.2(1)
C^{15}	0.1030(2)	0.4695(5)	−0.1340(2)	5.3(1)
C^{16}	0.0717(7)	0.460(1)	−0.0757(5)	9.4(4)
C^{16*}	0.0477(6)	0.421(1)	−0.0976(8)	15.7(4)
C^{17}	0.1603(5)	0.579(1)	−0.1229(7)	9.7(4)
C^{17*}	0.1605(7)	0.528(1)	−0.0927(6)	10.0(4)
C^{18}	0.0500(5)	0.550(1)	−0.1756(5)	7.1(3)
C^{18*}	0.0760(g)	0.555(1)	−0.1919(8)	15.7(5)
C^{19}	0.1343(2)	0.0071(5)	−0.2791(2)	5.4(1)
C^{20}	0.1322(8)	0.093(1)	0.3330(5)	9.3(4)
C^{20*}	0.1985(6)	0.052(2)	−0.3066(5)	10.5(4)
C^{21}	0.0664(5)	−0.078(1)	−0.2826(5)	6.8(3)
C^{21*}	0.0801(7)	0.068(2)	−0.3265(5)	12.3(4)
C^{22}	0.1879(5)	−0.112(1)	−0.2741(5)	7.4(3)
C^{22*}	0.131(1)	−0.152(1)	−0.2685(6)	12.9(5)
B^1	0.1792(2)	0.0877(5)	−0.1152(2)	4.1(1)

*Half occupied sites for disorded atoms.

six-membered phosphorus-boron containing heterocycle with two B—O bonds is formed.

The six-membered heterocycle in **4** has a boot conformation. The boron atom is at a distance of 0.45 Å from the least squares plane P1C1C2O1O2 atoms. The angles in the chelate ring are compared with corresponding values of dipivaloyl phosphide.[9,10] The interatomic P—C distances are shortened (1.745 Å), and C—O (1.260 Å) are similar to those of other dipivaloyl phosphides.[9,10] The intramolecular P—B distance equals 3.2 Å.

EXPERIMENTAL

4.05 g (0.02 mol) of diphenylchloroborane were added to 5.29 g (0.02 mol) of **1**. An exothermic reaction was observed. After 24 hours, the precipitated crystals were filtered and recrystallized from MeCN. Yield 2.29 g (62%), mp 158–159°C. Anal. Calcd. for $C_{22}H_{28}BO_2P$: P 8.47. Found: P 8.64. ^{31}P NMR spectra were recorded with KGY-4 and Bruker M-250 instrument, and ^{1}H NMR—with Varian T-60 at 34.6°C. Mass spectra were obtained on a MX-1310 spectrometer with an exact ion masses determination and elemental analysis, $\mu = 60V$.

Crystal data $C_{22}H_{28}B_1O_2P_1$ M = 366.03. Monoclinic space group C2/c, a = 20.727(7), b = 9.146(4), c = 23.075(5) Å, $\beta = 98.74(4)°$, V = 4323.7Å^3, z = 8.$D_{calc.}$ = 1.125 gcm^{-3}, MoK_α-radiation (monochromatic), $\delta = 0.71069$ Å. Crystallographic measurements and structure analysis. Single crystals of **4**, mp 158–159°C, were grown from MeCN solution. The space group and cell parameters were determined by least-squares refinement from values of 25 reflections accurately measured on a Ennraf Nonius CAD-4 diffractometer using MoK_α radiation. The intensity data were collected in $\Theta/2\Theta$ with Θ in range 3–50°). The space group was found to be C2/c of the 2899 independent reflections measured, 2637 were considered as significant ($J>3\sigma(J)$). Apart from the usual Lorentz and polarisation correction no further corrections were made. Absorption effects could be neglected because of the small size and the low value of the linear absorption coefficient ($\mu = 1.34$ cm^{-1}). The structure was solved by direct method and refined by full-matrix least-squares, with anisotropic thermal parameters for all the non-hydrogen atoms.

The methyl groups are disordered about two positions. The hydrogen atoms of the phenyl groups were located from a Δ F map and their coordinates were introduced in the last cycle. Methyl H atoms were placed at calculated positions and their positional and thermal parameters being fixed. Convergence was reached at R = 0.085, R_{vw} = 0.117.

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