REACTION OF 1-BORYL-2-PHOSPHINOETHENES WITH CARBON DISULFIDE

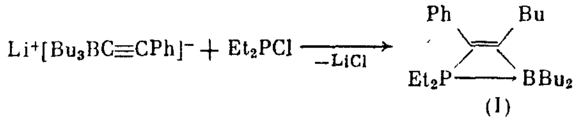
A. S. Balueva, G. N. Nikonov, S. G. Vul'fson,
N. N. Sarvarova, and B. A. Arbuzov

UDC 542.91:541.49:547.
1'127'118:546.265.14

1-Butyl-1-dibutylboryl-2-diethylphosphino-2-phenylethene reacts with chloral and oxygen in a manner similar to 1-butyl-1-dibutylboryl-2-dipheylphosphino-2-phenylethene but, unlike the former, can also react with carbon disulfide to form a cyclic complex through an intramolecular S → B coordination bond; charge density transfer from sulfur to boron consisted of about 0.3 e.

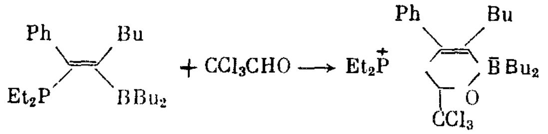
Investigation of the reactivity of 1-boryl-2-phosphinoethenes such as 1-butyl-1-dibutylboryl-2-diphenylphosphino-2-phenylethene (BBDPE) showed that the reaction is characterized by the introduction of aldehydes along the intramolecular P → B coordination bond [1, 2]. However, this reaction could not be extended to compounds with $>C{=}N-$ and $>C{=}S$ double bonds. Quantum-chemical calculations [3] as well a reaction of BBDPE with electrophilic and nucleophilic reagents [4] show that the UEP of phosphorus and the vacant orbital of boron are preserved to a large extent. Thus we might anticipate an increase in the nucleophilicity of the phosphorus atom when its phenyl groups are substituted by alkyl groups.

On the other hand, introduction of alkyl substituents at the phosphorus atom could increase the strength of the P → B coordination bond and decrease the compound's reactivity. For this reason 1-butyl-1-dibutylboryl-2-diethylphosphino-2-phenylethene (I), a new borylphosphinoethene comopund obtained from the rearrangement of lithium tributyl(2-phenylethenyl) borate in the presence of diethylchlorophosphine, was introduced into familar reactions: addition of aldehydes and oxidation in the presence of amines.



(I)

Compound (I) is a viscous liquid, distillable under high vacuum; the chemical shift (CS) of its signal in the ^{31}P NMR spectrum is at 13 ppm, which indicates the presence of an intramolecular P → B coordination bond. The compound reacts exothermally with chloral at about 20°C to form 2,2,3-tributyl-4-phenyl-5,5-diethyl-6-trichloromethyl-1-oxa-2-borata-5-phosphoniocyclohexene-3 (II).



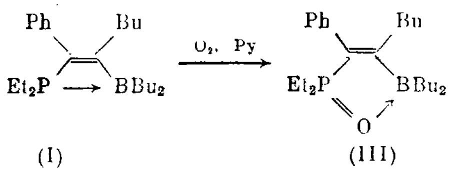
(I) (II)

Compound (II) is a stable crystalline substance; the CS of its signal in the ^{31}P NMR is at 6 ppm. A similar upfield signal shift, indicating the formation of a six-membered cyclic betaine, was observed when aldehydes were added to BBDPE [2]. The PMR spectrum of compound (II) contains three groups of signals with an integral intensity ratio of 5:1:37 [a phenyl proton multiplet; a doublet at 5.33 ppm (SSIC $^2J_{PH}$ = 6 Hz), corresponding to a ring methine proton; and an alkyl proton multiplet].

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2613-2616, November, 1990. Original article submitted November 28, 1989.

0568-5230/90/3911-2367$12.50

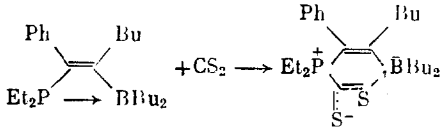
The oxidation of compound (I) by atmospheric oxygen in pyridine was somewhat faster than the oxidation of BBDPE [5]; after 1 h, the ^{31}P NMR spectrum showed only one signal with a CS of 82 ppm. It is in the same region as the signal of (2-butyl-2-dibutylboryl-1-phenylethenyl) diphenylphosphine oxide and represents (2-butyl-2-dibutylboryl-1-phenylethenyl)diethylphosphine oxide (III).



(I) (III)

Compound (III) is a viscous, distillable liquid. The downfield position of its signal in the ^{31}P NMR spectrum and the shift of the phosphoryl group vibration band to lower frequencies (1110 cm^{-1}) are indicative of the presence of an intramolecular O → B coordination bond. The structure of compound (III) was also confirmed by PMR spectral data.

The exchange of phenyl for alkyl groups at the phosphorus atom of borylphosphinoethene changed its reactivity with respect to carbon disulfide. BBDPE did not react with it. After one day's reaction at about 20°C, compound (I) added one carbon disulfide molecule, as shown by elemental analysis. Adduct (IV), a crystalline, bright red substance, is stable both in the solid state and in solutions. Its ^{31}P NMR spectrum shows a CS of 6 ppm (C_6H_6). The IR spectrum of compound (IV) in the solid state contains a C=S vibration band at 1075 cm^{-1}; spectra of its benzene solutions do not contain a cumulative carbon disulfide double-bond band, which indicates the absence of dissociation with evolution of CS_2. Compound (IV) is isolated from solution in unchanged form. The CS δP for compound (IV) coincides with the CS of compound (II), which is a six-membered cyclic betaine. Comparison of these values with the chemical shifts of two model compounds – the acyclic tributylphosphine–carbon disulfide complex [6] (20 ppm) and acyclic BBDPE iodomethylate (19 ppm) [4] – indicates that compound (IV) has a cyclic structure. However, the dipole moment of compound (IV) is only 5.7 D, which is insufficient for a betaine structure with a negative charge on boron. This suggests an incomplete charge transfer from one of the sulfur atoms to boron and the existence of an S → B coordination bond. This was confirmed by x-ray diffraction analysis, which showed that the complex of 1-butyl-1-dibutylboryl-2-diethylphosphino-2-phenylethene with carbon disulfide (IV) is indeed a six-membered ring: the boron atom is tetracoordinated, and there is a short contact between it and one of the sulfur atoms. However, the large S → B bond length (2.01 Å) and the small difference in the C–S bond lengths (0.06 Å) indicates that S → B is a coordination bond and that the negative charge is not centered on boron but is delocalized over the system $S \cdots C \cdots S \cdots B$



(I) (IV)

These results prompted us to determine the charge transfer density from S to B. Since the polarity of $R_3P^+{-}CS_2^-$ was previously unknown, we equated it with the experimental dipole moment of the tributylphosphine–carbon disulfide complex (6.9 D). Assuming that the experimental dipole moment of compound (IV) is the vector sum of the dipoles of $R_3P^+{-}CS_2^-$ and the S → B coordination bond (the geometry of molecule (IV) was obtained from x-ray diffraction analysis*), the dipole moment of the latter was calculated as m (S → B) = 2.9 D, which corresponds to a transfer of 0.3 e from S to B.

For 1-oxa-2-borata-5-phosphoniacyclohexenes-3 it was shown that a –CHR–O– fragment can be inserted between phosphorus and boron during reaction with chloral [2]. However, carbon disulfide could not be displaced from compound (IV) by chloral even upon boiling in benzene, which is evidence of the high stability of the complex.

---

*The x-ray diffraction data will be pubished later.

The difference in reactivities between BBDPE and comopund (I) is typical for regular tertiary phosphines: replacement of phenyl by alkyl substituents increases the nucleophilicity of phosphorus. At the same time, there is no increase in the strength of the P → B coordination bond, which might have compensated for the higher charge density on phosphorus. This shows that the UEP of phosphorus in borylphosphinoethenes is largely preserved.

EXPERIMENTAL

^{31}P NMR spectra were recorded on a NMR KGU-4 instrument at a frequency of 10.2 MHz with proton noise suppression (25.2 MHz); the internal standard was 85% H_3PO_4. PMR spectra were recorded on a Varian T-60 spectrometer at 34.5°C with TMS as internal standard. IR spectra were recorded on a UR-20 spectrometer as emulsions in petrolatum oil and as 10-15% solutions in C_6H_6.

The dipole moment of compound (IV) was determined at 25°C in C_6H_6; the dipole moment of the model complex $Bu_3P{\cdot}CS_2$ [6] was determined at 25°C in $C_6H_6{:}CS_2$ (10:1), since IR spectra have shown that the complex is partially dissociated in the given concentration range. The calculation of orientational polarities and dipole moments is described in [5].

All procedures with compound (I) were performed in an argon atmosphere.

1-Butyl-1-dibutylboryl-2-diethylphosphino-2-phenylethene (I). A solution of 3.03 g (0.036 mole) phenyllithium in 30 ml ether was added, with mixing at 0°C, to 3.67 g (0.036 mole) phenylacetylene, and the mixture was kept for 30 min at 20°C. It was then cooled to 0°C, 6.55 g (0.036 mole) of tributylborane in 7 ml ether was added, and the mixture was kept for 1 h at 20°C. Then a solution of 4.48 g (0.036 mole) diethylchlorophosphine in 5 ml ether was added, and the reaction mixture was boiled for 3 h. After removal of ether in a vacuum, the lithium chloride precipitate was filtered. Fractionation of the filtrate in a vacuum afforded 4.61 g (34%) of compound (I), a viscous liquid with a bp of 147-150°C (0.001 mm), δP 13 ppm. PMR spectrum ($CDCl_3$, δ, ppm): 7.63-7.10 m (5H, $C_6\underline{H}_5$), 2.77-0.57 m (37 H, C_2H_5 + C_4H_9). Found: C 77.33; H 11.34; P 8.45%. $C_{24}H_{42}BP$. Calculated C 77.41; H 11.29; P 8.33%.

2,2,3-Tributyl-4-phenyl-5,5-diethyl-6-trichloromethyl-1-oxa-2-borata-5-phosphoniacyclohexene-3 (II). A 1-ml portion of chloral was added to 1 g (3 mmoles) of compound (I) in 3 ml benzene. After 30 min the volatile components of the reaction mixture were removed in a vacuum, and the residue was crystallized from acetonitrile. Yield of compound (II), 0.93 g (67%); mp 95-98°C; δP 6 ppm (acetone). PMR spectrum ($CDCl_3$, δ, ppm): 7.43-6.87 m (5H, C_6H_5), 5.33 d (1H, $CCl_3{-}\overset{|}{\underset{|}{C}}{-}\underline{H}$, $^2J_{PH}$ = 6 Hz). 2.47-0.33 m (37H, $C_2\underline{H}_5$ + $C_4\underline{H}_9$). Found: C 59.89; H 8.57; P 6.15%. $C_{26}H_{43}BCl_3OP$. Calculated: C 60.06; H 8.27; P 5.97%.

(2-Butyl-2-dibutylboryl-1-phenylethenyl)diethylphosphine Oxide (III). Dry air was bubbled for 24 h through 1.4 g (4 mmoles) of compound (I) in 3 ml pyridine. After removal of pyridine in a vacuum, compound (III), a viscous, yellow liquid, was obtained in a yield of 1.37 g (94%), δP 82 ppm. IR spectrum (ν, cm^{-1}): 1110 (P=O, film). PMR spectrum ($CDCl_3$, δ, ppm): 7.50-6.83 m (5 H, C_6H_5), 2.40-0.31 m (37 H, C_2H_5 + C_4H_9). Found: C 74.61; H 10.36; P 7, 83%. $C_{24}H_{42}BOP$. Calculated: C 74.22; H 10.82; P 7.99%.

Complex of 1-Butyl-1-dibutylboryl-2-diethylphosphino-2-phenylethene with Carbon Disulfide (IV). A 0.92-g (2.5 mmoles) portion of compound (I) was dissolved in 5 ml carbon disulfide. The following day excess carbon disulfide was removed in a vacuum, and the residue crystallized. The bright red crystals were filtered and washed with acetonitrile. Yield of compound (IV), 0.83 g (75%); mp 96-98°C: δP 6 ppm (C_6H_6). PMR spectrum ($CDCl_3$, δ, ppm): 7.50-6.90 m (5 H, C_6H_5), 2.66-0.37 m (37 H, $C_2\underline{H}_5$ + C_6H_9). IR spectrum (ν, cm^{-1}): 1075 (C=S, oil). Found: C 66.48; H 9.31; P 6.91; S 14.14%. $C_{25}H_{42}BPS_2$. Calculated: C 66.94; H 9.37; P 6.92; S 14.28%.

LITERATURE CITED

1. A. S. Balueva and O. A. Erastov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1119 (1987).
2. A. S. Balueva and O. A. Erastov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 163 (1988).
3. L. V. Ermolaeva, S. G. Vul'fson, and A. N. Vereshchagin, Dokl. Akad. Nauk SSSR, 304, No. 5, 1170 (1989).
4. A. S. Balueva, Yu. Ya. Efremov, V. M. Nekhoroshkov, and O. A. Erastov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2793 (1990).

5. L. V. Ermolaeva, A. S. Balueva, O. A. Erastov, et al., Zh. Obshch. Khim., 60, No. 4, 755 (1990).
6. G. M. Kosolapoff and Z. Maier, Organic Phosphorus Compounds, Vol. 1, Wiley-Interscience, New York (1972), p. 128.