REACTION OF 1-BUTYL-1-DIBUTYLBORYL-2-DIPHENYLPHOSPHINO-2-PHENYLETHENE WITH TERT-BUTYL ISOCYANIDE

A. S. Balueva, A. A. Karasik,
G. N. Nikonov, and B. A. Arbuzov

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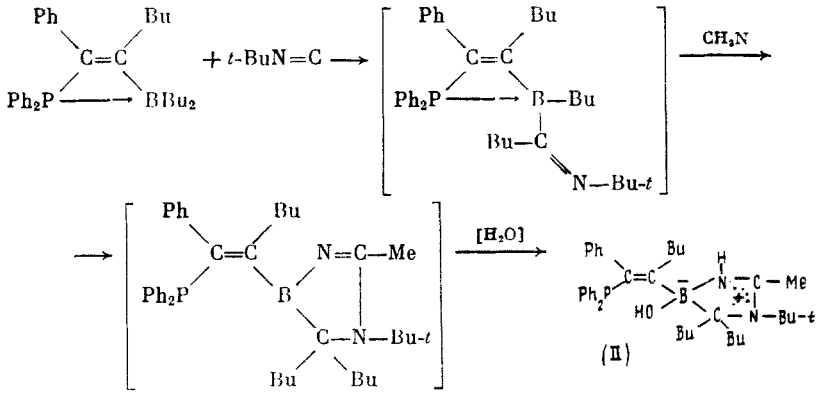
1-Butyl-1-dibutylboryl-2-diphenylphosphino-2-phenylethene reacts with tert-butyl isocyanide to give the corresponding α-iminoborane, which reacts with acetonitrile and benzalaniline to give B,N-containing heterocycles.

The reactivity of 1-butyl-1-dibutylboryl-2-diphenylphosphino-2-phenylethene (I) is largely determined by the system of elements with an unshared electron pair (UEP) (the phosphorus atom) and a vacant orbital (the boron atom). In previous work [1-3], we described syntheses for a series with different substituents at the phosphorus atom (I), which indicates the retention of activity of the UEP of this atom. Of the derivatives with substituents at the boron atom, only the stable complex with pyridine could be detected. On the other hand, the capacity of trialkylborane complexes to undergo anionotropic intramolecular rearrangements is well known.

Indeed, (I) reacts with excess tert-butyl isocyanide under mild conditions both without solvent and in THF. The course of the reaction was monitored by ^{31}P NMR spectroscopy. The signal for (I) disappeared after only 1 h and was replaced by a signal at −2 ppm. Removal of the volatile components of the reaction mixture gave a viscous, nondistilling liquid. α-Iminoboranes dimerize irreversibly to give diazadiboracyclohexanes [4]. However, the phosphorus-containing α-iminoborane obtained reacts under mild conditions with acetonitrile. A ^{31}P NMR signal arises in the reaction mixture at +2 ppm and slow crystallization occurs. The ^{31}P NMR spectrum of the filtered crystals show a signal at −4 ppm (in DMF). The IR spectra show stretching bands for C=N, N-H, and O-H bonds. The elemental analysis indicated the presence of two nitrogen atoms and one phosphorus atom, while the PMR spectra showed only one tert-butyl group, indicating the participation of acetonitrile in the reaction. These results do not permit a rigorous selection among the various isomeric structures. An x-ray diffraction structural analysis* permitted unequivocal establishment of the structure as 4-hydroxy-4-[1'-butyl-2'-phenyl-2'-(diphenylphosphino)ethenyl]-2-methyl-5,5-dibutyl-1-tert-butyl-1-aza-3-azonia-4-borata-2-cyclopentene (II).



Apparently, the nucleophilic attack of the isocyanide on the boron atom of (I) is followed by the rapid migration of one butyl group to the α-carbon atom. The coordination bond between

*The x-ray diffraction structural analysis data will be published later.

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. 9, pp. 2147-2149, September, 1990. Original article submitted November 28, 1989.

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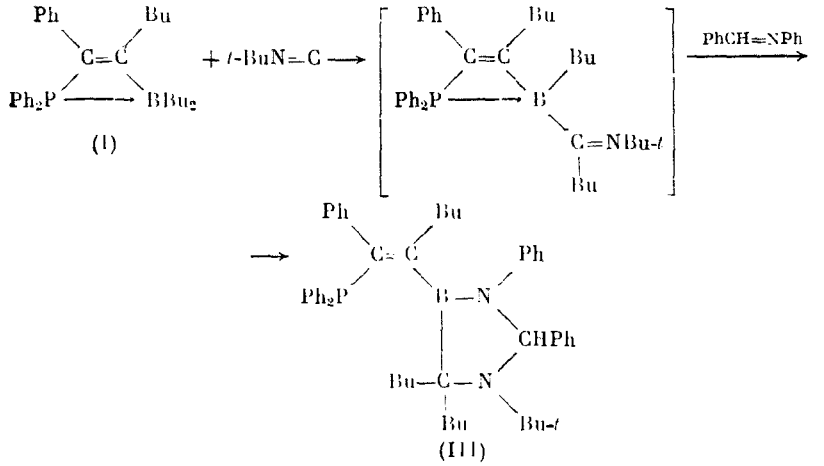
the phosphorus and boron atoms in the iminoborane formed hinders its dimerization. The addition of an acetonitrile molecule at the B-C-N system is accompanied by the migration of the second butyl group. The heterocycles with a B-N=C bond are unstable and are readily hydrolyzed even by traces of moisture.

The phosphorus-containing iminoborane reacts analogously with benzalaniline. The reaction is accompanied by the migration of two butyl groups to the α-carbon atom. However, in this case, the cyclization product is stable to hydrolysis and the reaction terminates with the formation of 4-(1′-butyl-2′-diphenylphosphino-2′-phenylethenyl)-5,5-dibutyl-1-tert-butyl-2,3-diphenyl-1,3-diaza-4-boratacyclopentane (III). The structure of this product was established by IR, PMR, and ^{31}P NMR spectroscopy.



We should note that the starting borylphosphinoethene (I) does not react with acetonitrile and benzalaniline, as might have been expected by analogy to the reaction with aldehydes [1]. On the other hand, the P→B coordination bond in the borylphosphinoethene does not hinder the formation of a tert-butyl isocyanide complex at the boron atom, which undergoes subsequent anionotropic rearrangements. This again indicates the insignificance of the electron transfer from the phosphorus atom to the boron atom [5].

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The PMR spectra were taken on a Varian T-60 spectrometer at 60 MHz at 34.5°C for 10% solutions. The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz with proton noise suppression (25.2 MHz) for 30-50% solutions. The external standard was 85% H_3PO_4.

4-Hydroxy-4-(1′-butyl-2′-phenyl-2′-diphenylphosphinoethenyl)-2-methyl-5,5-dibutyl-1-tert-butyl-1-aza-3-azonia-4-borata-2-cyclopentene (II). A sample of 0.74 g (9 mmoles) tert-butyl isocyanide was added to 1.5 g (3 mmoles) (I) in 5 ml THF. On the following day, the volatile components of the reaction mixture were removed in vacuum and the residue was recrystallized from acetonitrile at 0°C. The crystals were filtered off and washed with ether to give 0.45 g (23%) (II), mp 155-158°C. An analytical sample was recrystallized from 1:2 benzene-acetonitrile, mp 161-163°C, $\delta P = -4$ ppm (in DMF). IR spectrum (ν, cm^{-1}): 1600 (C=N), 3360 (N-H), 3560 (O-H) (vaseline mull). Found: C, 76.58; H, 9.18; N, 4.32; P, 4.80%. Calculated for $C_{39}H_{56}BN_2OP$: C, 76.72; H, 9.18; N, 4.59; P, 5.08%.

5,5-Dibutyl-1-tert-butyl-2,3-diphenyl-4-(1′-butyl-2′-phenyl-2′-diphenylphosphinoethenyl)-1,3-diaza-4-boracyclopentane (III). A sample of 0.83 g (9 mmoles) tert-butyl isocyanide was added to a solution of 1.57 g (3 mmoles) (I) in 5 ml THF. On the following day, the volatile components were removed in vacuum and a solution of 0.6 g (3 mmoles) benzalaniline in 6 ml benzene was added to the residue. On the following day, the solvent was removed and the residue was crystallized from ether at 0°C to give 0.3 g (13%) (III), mp 122-124°C. An analytical sample was recrystallized from 2:3 benzene-acetonitrile, mp 124-125°C, $\delta P = 0$ ppm (in DMF). PMR spectrum in DMF-d_7 (δ, ppm): 7.47-6.60 m (26H, C_6H_5 + NCHN), 2.40-0.50 m (36H, n-C_4H_9 + t-C_4H_9). IR spectrum (ν, cm^{-1}): bands corresponding to C=N, N-H, and O-H bonds are absent (mull). Found: C, 81.99; H, 8.79; N, 4.01; P, 3.99%. Calculated for $C_{50}H_{62}BN_2P$: C, 81.96; H, 8.46; N, 3.82; P, 4.23%.

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REACTION OF AMINOSULFENATES WITH CHLORAMINE B

B. M. Musin, P. V. Yudina, and V. B. Ivanov

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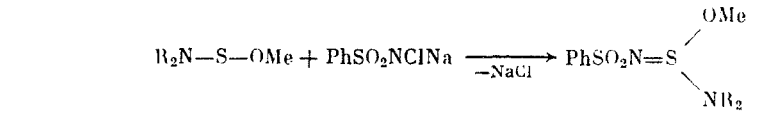
The reaction of aminosulfenates with the sodium chloramide of benzenesulfonic acid gives S-methoxy-S-dialkylamino-N-benzenesulfonyl sulfimides.

Sodium chloramides of arenesulfonic acids iminize the sulfenyl sulfur atom of sulfenamides [1] and N,N′-thiobisamines [2].

We studied the reaction of aminosulfenates (I) with the sodium chloramide of benzenesulfonic acid (Chloramine B) (II) and showed that the heating (I) with (II) in acetone at reflux for 2 h gives the expected corresponding S-methoxy-S-dialkylamino-N-benzenesulfonyl sulfimides (III).



(I) (II) (III)

R = Et (a), R + R = $(CH_2)_5$ (b), $(CH_2)_2O(CH_2)_2$ (c).

The structure of (III) was indicated by IR and PMR spectroscopy and elemental analysis.

Sulfimide (IIIa) decomposes upon distillation in high vacuum and, thus, this product was purified by chromatography on a silica gel column. Crude (IIIb) crystallized upon prolonged standing. This product was recrystallized from ether. Various attempts to crystallize (IIIc) were unsuccessful.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer. The PMR spectra were obtained on a Varian T-60 spectrometer at 60 MHz in CCl_4 with HMDS as the internal standard. Aminosulfenates were synthesized according to a procedure analogous to that proposed by Almasi and Hantz [3]. A sample of chemically pure Chloramine B trihydrate (II) was first dried in vacuum at 50°C to constant weight. The use of previously evacuated (II) leads to extensive tar formation.

Silica gel L 100/160 was used for the column chromatography. Ethyl acetate served as the eluent. The R_f values are given for Silufol thin-layer chromatography plates manufactured in Czechoslovakia with ethyl acetate as the eluent.

General Procedure for the Preparation of (III). A mixture of 0.02 mole (I) and 0.02 mole (II) in 75 ml acetone was heated at reflux with stirring for 2 h. Upon cooling the NaCl precipitate was filtered off and washed with acetone. The filtrate was evaporated in vacuum. Products (IIIa) and (IIIc) were purified by column chromatography. Product (IIIb) was recrystallized from ether.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR.

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