ORGANOBORON COMPOUNDS.

374.* CYCLIC COMPOUNDS OF THE CHELATE TYPE FROM 2-PYRIDYL- AND 2-PYRIMIDINYLAMINOBORANES AND DICYCLOHEXYLCARBODIIMIDE

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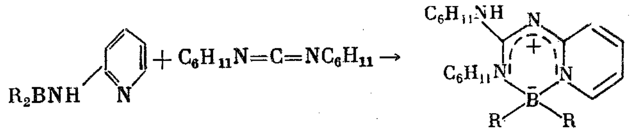
UDC 542.91:547.1'127

Among aminoboranes 2-pyridylaminoboranes are distinguished by their ability to form heterocyclic (chelate) compounds by means of addition over the multiple bonds [2, 3]. For example, 2-pyridylaminodialkyl- and 2-pyridylaminodiphenylborane are added as 1,2-dipolar reagents across the C =O bond of aldehydes, ketones, and CO_2 [4-6] to form chelates with the corresponding derivatives of 2-aminopyridine as ligands. 2-Pyridylaminoboranes react with isocyanates as 1,4-dipolar systems, and the addition across the C =N bond results in the formation of chelates in which the ligands are 1-carbamoylpyridone-2-imines [7]. (The structure of chelates of the N-diphenylboryl-N'-(2-pyridyl)urea type was erroneously assigned to the products of the reaction of 2-pyridylaminodiphenylborane with isocyanates in [8].) In this context it seemed of interest to ascertain the behavior of 2-pyridylaminoboranes with carbodiimides, which are heterocumulene systems of a similar type. In the present work we investigated the action of 2-pyridylaminodiorganylboranes (I) on dicyclohexylcarbodiimide (II) (for the preliminary report see [1]).

The exothermic reaction of I with II in benzene or petroleum ether results in the formation of yellowish crystalline compounds of type III. Compounds of type I with alkyl substituents on the boron atom are easily synthesized from 2-aminopyridine and trialkylboranes; therefore, the synthesis of the corresponding compounds of type III can be carried out by boiling a mixture of aminopyridine, the trialkylborane, and II in benzene without a step involving the isolation of I:



(I) (II) (III-IIId)

R=Et (a), Pr (b), Bu (c), Ph (d).

The compounds obtained (IIIa-IIId) are stable in the air and are not decomposed by water or alcohols. Their cyclic (chelate) structure was confirmed by ^{11}B NMR, the observed signals being located in the region of four-coordinate boron. The compounds are monomeric according to the determinations of the molecular weights by cryoscopy in benzene. The formation of III may be represented as the addition of the compounds of type I as 1,2-dipolar reagents to the carbodiimide across a C =N bond (the aminoboration of di-p-tolylcarbodiimide yields the corresponding guanidines [9]) followed by prototropic 1,3(N →N)-rearrangement of the adducts of type IV to form chelates of type III. If the compounds of type I reacted as 1,4-dipolar reagents (see the addition of I to isocyanates in [7], we would have expected the formation of compounds of type V or VI:

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*For the preceding report see [1].

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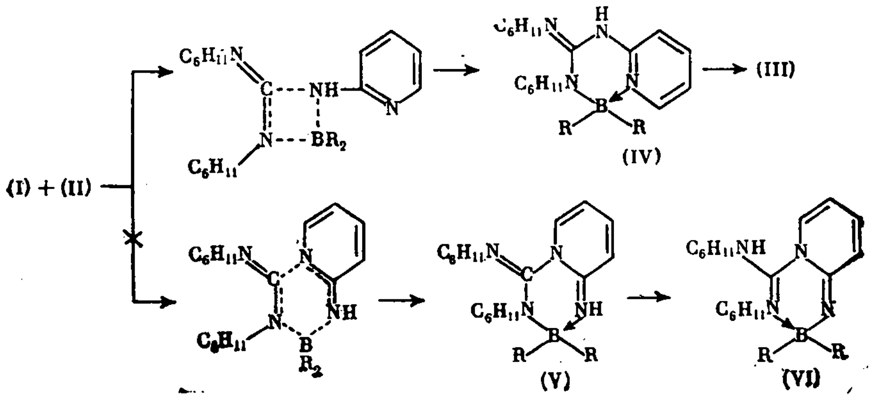
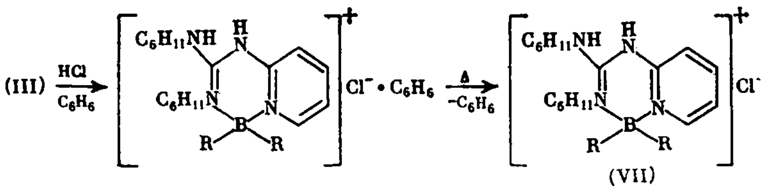
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 659-663, March, 1980. Original article submitted January 4, 1979.



However, the data obtained allow us to choose between possible structures III-VI in favor of III with the delocalized system of π electrons in the chelate ring. It is known that chelates of such a type are distinguished by their high chemical and thermal stability. For example, dialkylborylimidoylamidinates are not decomposed by dilute HCl, but they form boronium salts [10]. The treatment of benzene solutions of IIIb and IIIc with etheral HCl also made it possible to obtain salts with a similar structure (VII), which precipitate in the form of molecular complexes with C_6H_6 (1:1), and after prolonged heating in a vacuum, they are released from the C_6H_6 and isolated in the free form:

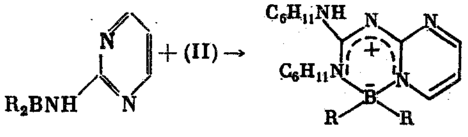


The IR spectra of the chelates obtained also correspond to structure III, since the intense bands at 1470, 1505, and 1580 cm^{-1} indicate delocalization of the π electrons in the chelate ring (six π electrons in five orbitals [11]). At the same time, in the 1600-1700-cm^{-1} region there is only one band of moderate intensity at 1635 cm^{-1}, which is typical of derivatives of 2-aminopyridine coordinated to boron at the ring N atom [3, 4]. The band of the C =N group coordinated to boron in V would have to have been more intense and found at a higher frequency (~1660 cm^{-1}) [7, 12]). For similar reasons the spectrum in the region of the multiple bonds does not correspond to structures IV-VI. The position of the band of the stretching vibrations of NH in the high-frequency region at 3500 cm^{-1} also contradicts IV and V, since on the basis of the previously obtained data, absorption in the 3350-3450-cm^{-1} region would have been expected for chelate systems of this type [3, 4, 7].

The mass spectra of the compounds synthesized are characterized by the presence of intense peaks of the $(M - R)^+$ ions (>30% of the total ion current). The high stability of the $(M - R)^+$ ions, which is attributed to their aromaticity (see [13]), is consistent with structure III. Finally, the PMR spectra also correspond completely to structure III.

Thus, 2-pyridylaminodiorganylboranes are added to dicyclohexylcarbodiimide across a C =N bond differently than to isocyanates or isothiocyanates [7](i.e., they react as 1,2-dipolar, rather than 1,4-dipolar, systems). In the compounds of type III obtained the chelate-forming ligand is N,N'-dicyclohexyl-N''-(2-pyridyl)guanidine, which can also be called (N,N'-dicyclohexylamidino)aminopyridine. According to the nomenclature used for the previously described chelate systems based on 2-aminopyridine [4, 7], the compounds of type III should be named diorganylboryl-[2-(N,N'-dicyclohexylamidino)aminopyridinates].

Like the compounds of type I, 2-pyrimidinylaminodiorganylboranes (VIII) react smoothly with II to form crystalline chelates (IX):



(VIII) (IXa-IXc)

R = i-Pr (a), Bu (b), Ph (c)

Compounds IXa-IXc are the first representatives of chelate compounds of boron based on 2-aminopyrimidine. Their structure is clearly similar to the structure of III, as indicated by the great similarity between the IR and NMR spectra, the mass spectra, and the chemical properties of both groups of chelates. It should be noted that both 2-aminopyridine and 2-aminopyrimidine do not react with II in boiling benzene or toluene.

EXPERIMENTAL

The operations were carried out in an atmosphere of dry Ar. The ^{11}B NMR spectra were recorded on a Bruker SXP 4-100 spectrometer, the PMR spectra were recorded on a Varian DA-60-IL instrument, and the UV spectra were recorded in heptane on a Specord UV-VIS instrument. The mass spectra were obtained on a Varian MAT CH-6 instrument.

The original 2-pyridylamino- and 2-pyrimidinylaminoboranes (I and VIII) were synthesized according to [3, 14].

Dipropylboryl[2-(N,N'-dicyclohexylamidino)aminopyridinate] (IIIb). A 7.0-g portion of 2-pyridylaminodipropylborane was given an addition of a solution of 7.6 g of II in 15 ml of abs. hexane. The mixture was left to stand for 25 h, and the precipitating crystals were filtered and washed with hexane. This yielded 12.75 g (87%) of IIIb, mp 122-124°C (from abs. EtOH). Found: C 72.64; H 10.46; B 2.64; N 14.09%. Calculated for $C_{24}H_{41}BN_4$; C 72.71; H 10.43; B 2.73; N 14.13%. ^{11}B NMR spectrum (in THF): −1.5 ppm (relative to $Et_2O \cdot BF_3$). PMR spectrum (in CCl_4, δ, ppm): 6.97-7.45 (m, $H^6 + H^4$ of pyridine ring), 6.13-6.60 (m, $H^3 + H^5$), 4.12 (broadened singlet, NH), 4.05 (m, CHN), 3.07 (m, $\rangle$CH—N). UV spectrum (λ_{max}, nm): 213 (ε 14,200), 294 (ε 14,000), 370 (ε 6150). Mass spectrum (m/e): 353 $(M - C_3H_7)^+$.

Dibutylboryl-[2-(N,N'-dicyclohexylamidino)aminopyridinate] (IIIc). Compound IIIc was obtained in analogy to the preceding compound. The yield was 85%, and the mp was 96-98°C (from abs. EtOH). Found: C 73.46; H 10.76; B 2.47; N 13.34%; mol. wt. 417 (cryoscopy in benzene). Calculated for $C_{26}H_{45}BN_4$: C 73.57; H 10.68; B 2.55; N 13.20%; mol. wt. 424. ^{11}B NMR spectrum (in THF): −1.5 ppm. PMR spectrum in CCl_4 (δ, ppm): 6.93-7.42 (m, $H^6 + H^4$), 6.10-6.58 (m, $H^3 + H^5$), 4.08 (broadened s, NH), 4.02 (m, CHN), 3.07 (m, $\rangle$CH—N). Mass spectrum: 367 $(M - C_4H_9)^+$. UV spectrum (λ_{max}, nm): 213 (ε 11,200), 294 (ε 14,800), 368 (ε 6500).

Diphenylboryl[2-(N,N'-dicyclohexylamidino)aminopyridinate] (IIId). A suspension of 2.5 g of 2-pyridylaminodiphenylborane in 30 ml of abs. C_6H_6 was given an addition of a solution of 2 g of II in 5 ml of abs. C_6H_6. The mixture was heated (60°C) until the original borane dissolved, the benzene was distilled in a vacuum, and the syrupy residue was treated with hexane. The crystals formed were filtered and washed with hexane. This yielded 3.27 g (71%) of chelate IIId, mp 129-130°C (from abs. EtOH). Found: C 77.65; H 8.12; B 2.30; N 12.05%. Calculated for $C_{30}H_{37}BN_4$: C 77.58; H 8.03; B 2.33; N 12.06%. Mass spectrum (m/e): 387 $(M - C_6H_5)^+$. IR spectrum (CCl_4, ν, cm^{-1}): 3495 (NH).

Diethylboryl[2-(N,N'-dicyclohexylamidino)aminopyridinate] (IIIa). A mixture of 4.1 g of 2-aminopyridine, 6 g of Et_3B, and 9.5 g of II in 30 ml of benzene was boiled until 1 eq of ethane was evolved, and the benzene was distilled off. The crystallized residue was treated with hexane. This yielded 12.1 g (75% relative to 2-aminopyridine) of chelate IIIa, mp 103-105°C (from abs. EtOH). Found: C 71.60; H 10.09; B 2.90; N 15.29%. Calculated for $C_{22}H_{37}BN_4$: C 71.73; H 10.13; B 2.93; N 15.21%. Mass spectrum (m/e): 339 $(M - C_2H_5)^+$.

Chloride Salt of Dipropylboryl[2-(N,N'-dicyclohexylamidino)aminopyridinate] (VII) (R = Pr). A solution of 2 g of IIIb in 10 ml of benzene was given an addition of an etheral solution of 5.5 M HCl. The precipitated colorless crystals were filtered, washed with benzene, and dried in a vacuum. This yielded 2.36 g of $VII \cdot C_6H_6$ (R = Pr), 92% yield. Found: C 70.74; H 9.49; B 2.05; Cl 7.16; N 11.60%. Calculated for $C_{30}H_{48}BClN_4$: C 70.51; H 9.47; B 2.12; Cl

6.94; N 10.96%. Heating of the product for 8 h at 100°C in a vacuum (~1 mm) yielded the free salt VII (R =Pr), which decomposes at >130°C. Found: C 66.92; H 9.96; B 2.46; Cl 8.72; N 13.56%. Calculated for $C_{24}H_{42}BClN_4$: C 66.59; H 9.78; B 2.50; Cl 8.19; N 12.94%. IR spectrum (KBr, ν, cm^{-1}): 1650 (C =N), 3400 (NH).

A mixture of 1 g of $VII \cdot C_6H_6$ (R =Pr) in 3 ml of ether and a solution of 0.2 g of NaOH in 5 ml of water was shaken over the course of several minutes, the etheral solution was separated, and the aqueous layer was extracted with ether (three 2-ml portions). The etheral extracts were dried over Na_2SO_4, and the ether was distilled off. This yielded 0.67 g (84%) of chelate IIIb.

Chloride Salt of Dibutylboryl[2-N,N'-(dicyclohexylamidino)aminopyridinate] (VII) (R =Bu). The salt $VII \cdot C_6H_6$ (R =Bu) was isolated in analogy to the preceding procedure. The yield was 84%. Found: C 71.17; H 9.56; B 1.79; Cl 6.93%. Calculated for $C_{32}H_{52}BClN_4$: C 71.30; H 9.72; B 2.00; Cl 6.58%.

Diisopropylboryl[2-(N,N'-dicyclohexylamidino)aminopyrimidinate] (IXa). Compound IXa was obtained from 2-pyrimidinylaminodiisopropylborane and II in analogy to IIIb. The yield was 82%, and the mp was 140-142°C (from hexane). Found: C 69.54; H 10.22; B 2.72; N 17.81%; mol. wt. 382 (cryoscopy in benzene). Calculated for $C_{23}H_{40}BN_5$: C 69.51; H 10.15; B 2.72; N 17.62%; mol. wt. 397.4. Mass spectrum (m/e): 354 $(M - C_3H_7)^+$. IR spectrum (KBr, ν, cm^{-1}): 3500 (NH). PMR spectrum (in CCl_4, δ, ppm): 8.35 (m), 7.45 (m), 6.36 (m, protons of pyrimidine ring), 4.36 (broadened s, NH), 4.19 (m), 3.12 (m, NCH). UV spectrum (λ_{max}, nm): 244 (ε 12,600), 302 (ε 13,400), 370 (ε 1980).

Dibutylboryl[2-(N,N'-dicyclohexylamidino)aminopyrimidinate] (IXb). Compound IXb was obtained in analogy to IXa. The yield was 88%, and the mp was 118-121°C (from hexane). Found: C 70.63; H 10.45; B 2.62; N 16.95%. mol. wt. 409 (cryoscopy in benzene). Calculated for $C_{25}H_{44}BN_5$: C 70.57; H 10.43; B 2.54; N 16.46%; mol. wt. 425.45. Mass spectrum (m/e): 368 $(M - C_4H_9)^+$. IR spectrum (KBr, ν, cm^{-1}): 3491 (NH).

Diphenylboryl[2-(N,N'-dicyclohexylamidino)aminopyrimidinate] (IXc). Compound IXc was obtained in analogy to IIId from 2-pyrimidinylaminodiphenylborane and II. The yield was 63%, and the mp was 183-187°C (from hexane). Found: C 75.02; H 7.85; B 2.37; N 15.43%. Calculated for $C_{29}H_{36}BN_5$: C 74.83; H 7.80; B 2.32; N 15.05%. Mass spectrum (m/e): 388 $(M - C_6H_5)^+$. IR spectrum (CCl_4, ν, cm^{-1}): 3490 (NH).

CONCLUSIONS

New chelate compounds of boron, in which the chelating agents are, respectively, N,N'-dicyclohexyl-N"-(2-pyridyl)guanidine and N,N'-dicyclohexyl-N"-(2-pyrimidinyl)guanidine, have been synthesized by adding 2-pyridylaminodiorganylboranes and 2-pyrimidinylaminodiorganylboranes to dicyclohexylcarbodiimide.

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ORGANOBORON COMPOUNDS.

375. N^2-DIALKYLBORYL-N^1-ALKYLBENZAMIDINES

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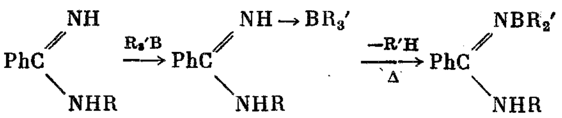
UDC 542.91:547.1'127

We had previously investigated certain dialkylborylamidines that were synthesized from N,N- or N,N'-dialkylamidines [1-3]. From N-monosubstituted amidines, it is also possible to obtain dialkylboryl derivatives [1] that are regarded as intermediates in the synthesis of chelate compounds of boron from amidines and organoboranes [4]. Here we are reporting on a more detailed study of the synthesis of dialkylborylamidines from N-alkylbenzamidines, and also the structure and certain chemical properties of these compounds.

Trialkylboranes react smoothly with N-alkylbenzamidines (I) upon refluxing in THF, benzene, or other aprotic solvents with boiling points in the 50-60° range or higher. The complexes (II) that are formed upon mixing the reactants [5] decompose upon heating to form N^2-dialkylboryl-N^1-alkylbenzamidines (III) and saturated hydrocarbons.



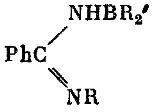
(I) (II) (III)

The isolation of some of the compounds (III) in pure form proved to be difficult, as they are thermally unstable. For example, when the product from the reaction of N-methylbenzamidine with Bu_3B was distilled, it decomposed to a considerable degree. It had been noted previously that thermal instability is also typical for dialkylboryl derivatives of amidines without any N-substitution [4].

Therefore, in order to obtain compounds (III) that would be thermally stable, we used certain N-alkylbenzamidines and trialkylboranes with branched substituents (i-Pr, i-Bu, t-Bu, etc.). The synthesized N^2-dialkylboryl-N^1-alkylbenzamidines (IIIa-IIIe) can be vacuum-distilled without decomposition and can be isolated in pure form (Table 1). One of these, (IIIb), was described in an earlier communication [1].

The freshly distilled compounds (IIIa-IIIc) are colorless, rather mobile liquids, whereas (IIId) and especially (IIIe) are viscous substances. In the presence of traces of moisture (IIIa-IIIe) are readily hydrolyzed to the original N-alkylbenzamidines.

In establishing the structure of the dialkylborylalkylbenzamidines (DABAB) that we have synthesized, we must consider not only the structure (III), but also the possible isomeric structures (IV)-(VI):



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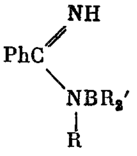
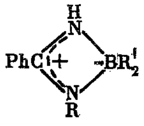


(V)



(VI)

The prototropic [6] and metallotropic [7] rearrangements that are characteristic of amidines should be taken into account. Determination of the DABAB structure is difficult be-

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 663-669, March, 1980. Original article submitted January 4, 1979.

0568-5230/80/2903-0485$07.50