Direct Synthesis of (IIc) from 2-Phenylaminopyridine, $Pr_3B$, and $o-CH_3C_6H_4NCO$. A mixture of 3.65 g of 2-phenylaminopyridine, 5.2 g of $Pr_3B$, and 3.25 g of $o-CH_3C_6H_4NCO$ in 14 ml of $C_6H_6$ was boiled for 6 h, and the precipitate which separated on cooling was filtered and washed with benzene. Yield, 8.2 g (96%) of (IIc).

Direct Synthesis of (IId) from 2-Phenylaminopyridine, $Pr_3B$, and PhNCO. Compound (IId) was obtained in the same way as (IIc) by boiling the reagents in toluene for 5 h, yield of (IId) 88%.

## CONCLUSIONS

1. The ability of diorganylboryl-[1-(N-organyl)carbamoylpyrid-2-one-iminates] (III) to undergo thermal isomerization into N-diorganylboryl-[2-(N-organyl)carbamoylaminopyridinates] (II) was discovered.

2. On heating, 2-diorganylborylaminopyridines can add to isocyanates at the C=O group to form O-diorganylboryl-[2-(N-organyl)carbamoylaminopyridinates] (I).

## LITERATURE CITED

1. V. A. Dorokhov, L. I. Lavrinovich, M. N.Bochkareva, B. M. Zolotarev, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 253 (1978).
2. V. A. Dorokhov, L. I. Lavrinovich, M. N. Bochkareva, B. M. Zolotarev, V. A. Petukhov, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 1340 (1979).
3. V. A. Dorokhov, L. I. Lavrinovich, and B. M. Mikhailov, Dokl. Akad. Nauk SSSR, 245, 121 (1979).
4. V. A. Dorokhov, L. I. Lavrinovich, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 1085 (1979).
5. V. I. Minkin, L. P. Olekhnovich, and Yu. A. Zhdanov, Molecular Design of Tautomeric Systems [in Russian], Izd. Rostovsk. Univ., Rostov (1977).

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# ORGANOBORON COMPOUNDS.

# COMMUNICATION 421. BORON–NITROGEN HETEROCYCLES FROM 2-DIALKYLBORYLAMINOTHIAZOLES AND ISOCYANATES

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UDC 542.91:547.1'127

Cyclic systems with a tetracoordinated boron atom, with a structure that depends on the sequence of transformations of the initial compounds and selection of the organoborane, can be produced from 2-aminothiazole, isocyanates, and organoboranes in analogy with the syntheses from 2-aminopyridine [1-3]. One of the possible paths previously studied [4] includes the preparation from 2-aminothiazole of N'-organyl-N-(thiazol-2-yl)ureas and the reaction of the latter with trialkylboranes or alkylthiodialkylboranes with the formation of O- and N-dialkylboryl-[2-(N-organyl)carbamoylaminothiazolates] (I) and (II), respectively. In the present work, we discuss another path – the synthesis of dialkylboryl-[3-(N-organyl)carbamoylthiazol-2-one-iminates] (IV) by the reaction of 2-dialkylborylaminothiazoles (III) with isocyanates.

The borylation of 2-aminothiazole by trialkylboranes proceeds smoothly in boiling benzene [5], and the compounds (III) formed can be used without a further isolation. Addition of (III) at the C=N bond of the isocyanate should be considered as a reaction of (4 + 2)-cyclo-

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*Deceased.

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2570-2575, November, 1985. Original article submitted April 25, 1984.

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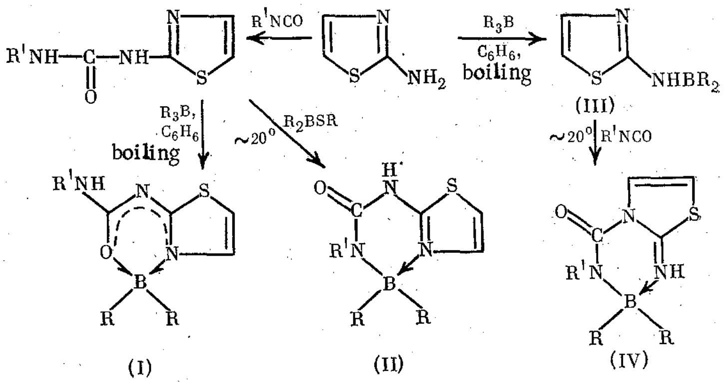
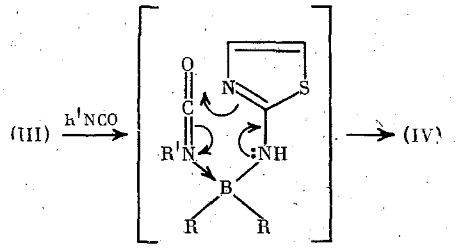


R = Pr, R' = Ph (IVa); R = Bu, R' = Ph (IVb); R = Pr, R' = β-$C_{10}H_7$ (IVc); R = Pr, R' = Me (IVd); R = Bu, R' = Me (IVe).

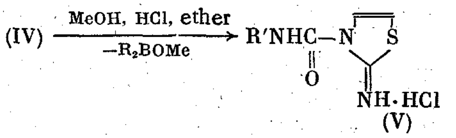
Fig. 1.

addition, proceeding with change in the valence state of the B atoms and the exocyclic N atom of the aminothiazole system:



The yield of the crystalline compounds (IVa-e) is 62-69% based on the initial 2-aminothiazole. These compounds differ from their isomeric (I) and (II) as they contain a thiazolone-imine and not an aminothiazole fragment. In the IR spectra of (IVa-e) (in KBr), besides the intense absorption band of the C=O group (1670-1690 $cm^{-1}$), a C=N band is also observed (1630 $cm^{-1}$); the intense peaks of the $(M - R)^+$ and $(M - R - R'NCO)^+$ ions are characteristic in the mass spectra.

Compounds (IVa-e) are stable in air and are not decomposed by water in the absence of acids. However, they can be split by the action of alcohol in an ethereal solution of HCl. The previously unknown 3-arylcarbamoylthiazol-2-one-imine hydrochlorides (Va, b) are thus obtained:



R' = Ph (Va); R' = β-$C_{10}H_7$ (Vb).

The structure of salts (Va, b) was confirmed by spectral methods. These compounds are thermally unstable and are decomposed at >100°C, in the same way as the salts of 1-organylcarbamoylpyrid-2-one-imines, decomposing into isocyanates and 2-aminopyridine hydrochloride [2].

An x-ray diffraction study of the compound (IVa) was carried out. A schematic view with numeration of the atoms in the molecule of (IVa) is as follows.

The interatomic distances and valence angles are given in Tables 1 and 2, and the atom coordinates in Table 3 (the anisotropic temperature factors of the nonhydrogen atoms and the isotropic factors for the hydrogen atoms can be obtained from the authors).

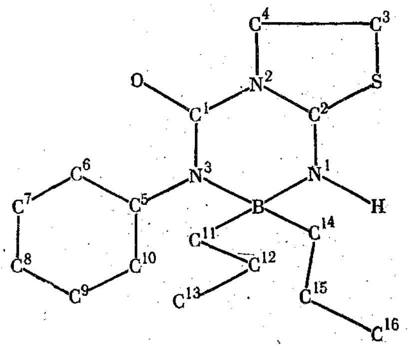
The bicyclic part of the molecule of (IVa) is nonplanar, the inflection angles on the $N^1N^2$, $N^2B$, and $N^3N^2$ lines are 9.1, 30.5, and 14.8°, respectively. The configuration of the atoms is weakly pyramidal with different degrees of deviation (Δ) from the plane of the three nearest substituents: $\Delta N^1 = 0.036(2)$ Å, $\Delta N^2 = 0.093(2)$, $\Delta N^3 = 0.123(2)$ Å. The phenyl group

TABLE 1. Interatomic Distances in (IVa)

| Bond | d, Å | Bond | d, Å |
|---|---|---|---|
| $B-N^1$ | 1,570(5) | $C^6-C^7$ | 1,382(5) |
| $B-N^3$ | 1,608(4) | $C^7-C^8$ | 1,376(6) |
| $B-C^{11}$ | 1,612(5) | $C^8-C^9$ | 1,358(6) |
| $B-C^{14}$ | 1,607(5) | $C^9-C^{10}$ | 1,391(5) |
| $N^1-C^2$ | 1,281(4) | $C^{10}-C^5$ | 1,372(5) |
| $N^2-C^2$ | 1,367(4) | $C^{11}-C^{12}$ | 1,525(5) |
| $N^2-C^1$ | 1,444(4) | $C^{12}-C^{13}$ | 1,509(7) |
| $N^3-C^1$ | 1,327(4) | $C^{14}-C^{15}$ | 1,513(5) |
| $N^3-C^5$ | 1,449(4) | $C^{15}-C^{16}$ | 1,508(6) |
| $C^1-O$ | 1,223(4) | $N^1-H^3$ | 0,86(4) |
| $C^2-S$ | 1,736(3) | $C^3-H^1$ | 0,91(4) |
| $C^3-S$ | 1,732(5) | $C^4-H^2$ | 0,94(4) |
| $C^4-N^2$ | 1,394(4) | $C_{Ph}-H_{av}$ | 0,94(4) |
| $C^3-C^4$ | 1,316(6) | $C_{Pr}-H_{av}$ | 0,97(6) |
| $C^5-C^6$ | 1,377(5) | | |

TABLE 2. Valence Angles in (IVa)

| Angle | ω, deg | Angle | ω, deg |
|---|---|---|---|
| $N^1BN^3$ | 103,0(2) | $C^4C^3S$ | 112,5(3) |
| $N^1BC^{14}$ | 108,3(3) | $C^3SC^2$ | 90,4(2) |
| $N^1BC^{11}$ | 109,4(3) | $SC^2N^1$ | 127,7(2) |
| $N^3BC^{11}$ | 108,2(3) | $SC^2N^2$ | 110,3(2) |
| $N^3BC^{14}$ | 111,8(3) | $N^1C^2N^2$ | 122,0(3) |
| $C^{11}BC^{14}$ | 115,4(3) | $C^2N^1B$ | 122,4(3) |
| $BN^3C^5$ | 118,3(2) | $C^2N^1H^3$ | 115(2) |
| $BN^3C^1$ | 124,5(3) | $BN^1H^3$ | 122(2) |
| $C^5N^3C^1$ | 115,1(3) | $BC^{11}C^{12}$ | 117,8(3) |
| $N^3C^1O$ | 129,7(3) | $C^{11}C^{12}C^{13}$ | 114,3(4) |
| $N^2C^1O$ | 116,1(3) | $BC^{14}C^{15}$ | 116,8(3) |
| $N^3C^1N^2$ | 114,2(3) | $C^{14}C^{15}C^{16}$ | 114,0(4) |
| $C^1N^2C^4$ | 122,0(3) | $N^3C^5C^6$ | 120,2(3) |
| $C^1N^2C^2$ | 123,4(3) | $N^3C^5C^{10}$ | 120,2(3) |
| $C^2N^2C^4$ | 113,3(3) | $C^6C^5C^{10}$ | 119,6(3) |
| $N^2C^4C^3$ | 113,5(4) | $C^5C^6C^7$ | 120,3(4) |
| $C^8C^9C^{10}$ | 120,9(4) | $C^6C^7C^8$ | 120,1(4) |
| $C^9C^{10}C^5$ | 119,6(4) | $C^7C^8C^9$ | 119,5(4) |



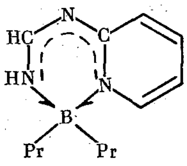
is almost perpendicular to the bicyclic part; the torsional angle $C^6C^5N^3C^1$ = 71.7°. The B atom has a distorted tetrahedral configuration.

It has been somewhat unexpectedly found that the original donor—acceptor $B-N^1$ bond is shorter than the $B-N^3$ bond [1.570(5) and 1.608(4) Å, respectively]. Thus, the distances $C^1-N^3$ (1.327 Å) and $C^2-N^2$ (1.367 Å) are characteristic of bonds with a partially double bond character. The length of the $C^2-N^1$ bond (1.281 Å) somewhat exceeds the value for the double bond, while the $C^1-N^2$ distance (1.444 Å) practically corresponds to the value of the ordinary $C_{sp^2}-N$ bond. These data show the presence of partial delocalization of the π electrons on the three-centered orbitals of the $OC^1N^3$ and $N^1C^2N^2$ fragments. As a result, the $B-N^1$ and $B-N^3$ bonds are similar in character, and coincide in value with the " semicoordinational" bonds in heterocycles of type (VI) ($B-N_{av}$ = 1.585 Å) [6] or (VII) ($B-N_{av}$ = 1.587 Å [7]) with a delocalized sys-

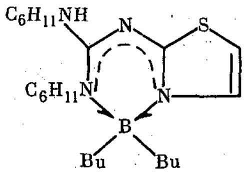
TABLE 3. Atom Coordinates in (IVa)

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| B | 0,3580(2) | 0,2138(2) | −0,0356(2) | $H^1$ | 0,065(2) | 0,221(2) | 0,184(2) |
| S | 0,15565(6) | 0,11219(6) | 0,11168(6) | $H^2$ | 0,133(2) | 0,367(2) | 0,125(2) |
| O | 0,2219(1) | 0,4364(1) | 0,0157(1) | $H^3$ | 0,289(2) | 0,082(2) | 0,000(2) |
| $N^1$ | 0,2870(2) | 0,1455(2) | 0,0041(1) | $H^4$ | 0,277(2) | 0,347(2) | −0,198(2) |
| $N^2$ | 0,2129(1) | 0,2782(2) | 0,0603(1) | $H^5$ | 0,342(2) | 0,451(2) | −0,293(2) |
| $N^3$ | 0,3079(1) | 0,3175(2) | −0,0456(1) | $H^6$ | 0,443(2) | 0,560(2) | −0,252(2) |
| $C^1$ | 0,2494(2) | 0,3522(2) | 0,0068(2) | $H^7$ | 0,485(2) | 0,565(3) | −0,112(2) |
| $C^2$ | 0,2273(2) | 0,1792(2) | 0,0511(2) | $H^8$ | 0,415(2) | 0,465(2) | −0,017(2) |
| $C^3$ | 0,1103(2) | 0,2209(3) | 0,1479(2) | $H^9$ | 0,418(2) | 0,257(2) | 0,077(2) |
| $C^4$ | 0,1457(2) | 0,2998(2) | 0,1147(2) | $H^{10}$ | 0,480(2) | 0,277(2) | 0,003(2) |
| $C^5$ | 0,3437(2) | 0,3901(2) | −0,1013(2) | $H^{11}$ | 0,446(2) | 0,087(2) | 0,071(2) |
| $C^6$ | 0,3208(2) | 0,3885(2) | −0,1825(2) | $H^{12}$ | 0,518(2) | 0,110(2) | 0,007(2) |
| $C^7$ | 0,3594(2) | 0,4530(3) | −0,2370(2) | $H^{13}$ | 0,580(2) | 0,100(2) | 0,135(2) |
| $C^8$ | 0,4202(2) | 0,5203(3) | −0,2100(2) | $H^{14}$ | 0,597(2) | 0,209(3) | 0,104(2) |
| $C^9$ | 0,4412(2) | 0,5234(3) | −0,1295(2) | $H^{15}$ | 0,522(3) | 0,178(4) | 0,170(3) |
| $C^{10}$ | 0,4041(2) | 0,4574(2) | −0,0744(2) | $H^{16}$ | 0,426(2) | 0,116(2) | −0,111(2) |
| $C^{11}$ | 0,4373(2) | 0,2291(2) | 0,0276(2) | $H^{17}$ | 0,418(2) | 0,216(2) | −0,152(2) |
| $C^{12}$ | 0,4872(2) | 0,1376(2) | 0,0553(2) | $H^{18}$ | 0,285(2) | 0,073(2) | −0,156(2) |
| $C^{13}$ | 0,5533(3) | 0,1568(3) | 0,1217(2) | $H^{19}$ | 0,261(2) | 0,178(2) | −0,177(2) |
| $C^{14}$ | 0,3845(2) | 0,1676(2) | −0,1225(2) | $H^{20}$ | 0,291(2) | 0,089(3) | −0,297(2) |
| $C^{15}$ | 0,3108(2) | 0,1311(2) | −0,1760(2) | $H^{21}$ | 0,387(3) | 0,060(3) | −0,265(3) |
| $C^{16}$ | 0,3372(3) | 0,1113(3) | −0,2631(2) | $H^{22}$ | 0,365(2) | 0,170(3) | −0,286(2) |

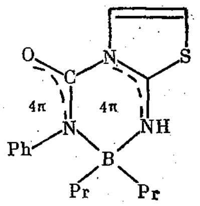
tem of π electrons. Accordingly, in a more accurate approximation, the structure of the heterocycle (IVa) can be expressed by the structural formula (VIII)



(VI)



(VII)



(VIII)

In the crystal, the molecules of (IVa) are bound by an intermolecular H-bond $N^1$–H...O [O...$N^1$ = 2.841, O...H = 2.00 Å, ∠$N^1$HO = 166(2)°], into chains stretching along the b axis. The interaction between the chains is Van der Waals in character

## EXPERIMENTAL

The operations were carried out in a dry argon atmosphere. The PMR spectra were recorded on a Tesla BS-497 spectrometer with reference to HMDS (δ, ppm), and the $^{11}$B NMR spectra on a Bruker SXP4-100 spectrometer (external standard $Et_2O \cdot BF_3$). The IR spectra were recorded on a UR-20 spectrophotometer (ν, $cm^{-1}$), and the UV spectra on a Specord UV-VIS spectrophotometer [$\lambda_{max}$, nm (ε)]. The mass spectra were run on a Varian MAT CH-6 mass spectrometer with direct introduction of the samples into the ion source (m/z).

Dialkylboryl-[3-(N-organyl)carbamoylthiazol-2-one-iminates] (IVa-e). A solution of 0.03-0.06 mole of 2-aminothiazole and 0.04-0.08 mole of trialkylborane in 15-20 ml of $C_6H_6$ was boiled to cessation of gas evolution (5-6 h). It was then cooled to ~20°C, and 0.03-0.06 mole of isocyanate was added. The crystals of (IV) that separated on standing (up to 2 days) were filtered and washed with $C_6H_6$ or hexane.

Dipropylboryl-[3-(N-phenyl)carbamoylthiazol-2-one-iminate] (IVa), yield 66%, mp 134-136°C (dec., from EtOH). Found: C 61.10; h 7.17; B 3.47; N 13.45; S 10.25%. $C_{16}H_{22}BN_3OS$. Calculated: C 60.96; H 7.03; B 3.43; N 13.33; S 10.17%. Mass spectrum: 272 $(M - Pr)^+$, 153 $(M - Pr - PhNCO)^+$. $^{11}$B NMR spectrum (in THF): 1.3 ppm. PMR spectrum (in $CDCl_3$): 7.37 d and 6.00 d ($H^4$, $H^5$ of dihydrothiazole ring), 7.47-6.97 m (Ph, NH). UV spectrum (in EtOH): 203 (18605), 245 (11395), 294 (1655). IR spectrum (in KBr): 1630 (C=N), 1681 (C=O), 3235 (NH). IR spectrum (in $CHCl_3$): 3410 (NH)

Dibutylboryl-[3-(N-phenyl)carbamoylthiazol-2-one-iminate] (IVb), yield 69%, mp 140-142°C (dec., from EtOH). Found: C 63.35; H 7.58; B 3.04; S 9.22%. $C_{18}H_{26}BN_3OS$. Calculated: C

62.97; H 7.63; B 3.15; S 9.34%. Mass spectrum: 286 $(M - Bu)^+$, 167 $(M - Bu - PhNCO)^+$. $^{11}B$ NMR (in MeOH): 1.3 ppm. PMR spectrum (in $CDCl_3$): 7.40 d ($H^4$), 6.03 d ($H^5$). IR spectrum (in KBr): 1630 (C=N), 1667 (C=O), 3217 (NH).

Dipropylboryl-[3-(N-β-naphthyl)carbamoylthiazol-2-one-iminate] (IVc), yield 67%, mp 138-141°C (dec., from EtOH). Found: C 65.90; H 6.63; B 2.89; N 11.55; S 8.75%. $C_{20}H_{24}BN_3OS$. Calculated: C 65.75; H 6.62; B 2.96; N 11.50; S 8.78%. Mass spectrum: 322 $(M - Pr)^+$, 153 $(M - C_{10}N_7NCO)^+$. IR spectrum (in KBr): 1630 (C=N), 1670 (C=O), 3275 (NH).

Dipropylboryl-[3-(N-methyl)carbamoylthiazol-2-one-iminate] (IVd) yield 69%, mp 156-159°C (dec., from $C_6H_6$). Found: C 52.33; H 7.89; B 4.33; N 16.27; S 12.53%. $C_{11}H_{20}BN_3OS$. Calculated: C 52.18; H 7.96; B 4.27; N 16.60; S 12.67%. Mass spectrum: 210 $(M - Pr)^+$, 153 $(M - Pr - MeNCO)^+$. PMR spectrum (in $CDCl_3$): 7.30 d ($H^4$), 5.94 ($H^5$), 6.90 br.s (NH), 2.66 s (Me). IR spectrum (in KBr): 1631 (C=N), 1690 (C=O), 3210 (NH)

Dibutylboryl-[3-(N-methyl)carbamoylthiazol-2-one-iminate] (IVe), yield 62%, mp 176-179°C (dec., from MeCN). Found: C 55.68; H 8.64; B 3.84; N 14.78; S 11.50%. $C_{13}H_{24}BN_3OS$. Calculated: C 55.52; H 8.60; B 3.85; N 14.94; S 11.40%. Mass spectrum: 224 $(M - Bu)^+$, 167 $(M - Bu - MeNCO)^+$. IR spectrum (in KBr): 1631 (C=N), 1690 (C=O), 3200 (NH)

3-(N-phenyl)carbamoylthiazol-2-one-imine Hydrochloride (Va). A 3-ml portion of MeOH and 12 ml of an ethereal solution of HCl (N = 1.6) were added to a solution of 1.56 g of (IIIa) in 8 ml of THF. The precipitate was filtered and washed with ether. Yield, 1.12 g (96%) of salt (Va), mp 90-94°C (dec.). Found: C 46.99; H 3.97; Cl 14.00; N 16.65; S 12.65%. $C_{10}H_{10}ClN_3OS$. Calculated: C 46.97; H 3.94; Cl 13.86; N 16.43; S 12.54%. IR spectrum (in KBr): 1722 (C=O), 3330, 3365 sh (NH). UV spectrum (in EtOH): 237 (19,545), 260 (9773).

3-(N-β-Naphthyl)carbamoylthiazol-2-one-imine Hydrochloride (Vb). Salt (Vb) was obtained in the same way as (Va), yield 94%, mp 94-98°C (dec.). Found: C 54.83; H 4.13%. $C_{14}H_{12}ClN_3OS$. Calculated: C 54.99; H 3.96%. IR spectrum (in KBr): 1715 (C=O), 3270 (NH).

X-Ray Diffraction Analysis of (IVa). The colorless prismatic crystals were obtained by recrystallization from $C_6H_6$. A single crystal 0.45 × 0.45 × 0.9 mm in size, was used for the investigation. Space group Pbc$a$, Z = 8, $a$ = 15.336(3), b = 13.536(3), c = 16.388(4) Å. The experimental data were obtained on a SAD-4 autodiffractometer (Mo $K_\alpha$ radiation, ω-scanning, $\theta < \theta < 27.5°$, 3890 reflections; 1844 of these reflections with $I > 3\sigma(I)$. All the calculations were carried out using the ENX-SDP programs on a RDR-11/55t computer. The structure was resolved by the direct method (MULTAN). All the H atoms were localized after a few cycles of anisotropic refinement of the nonhydrogen atoms in differential syntheses. The final refinement (anisotropic — for nonhydrogen atoms, isotropic — for H atoms), taking into account secondary extinction, led to R = 0.046, $R_w$ = 0.063 (weighted scheme $W_i = 1/[\sigma(F)^2 + (0.05 \cdot F^2_{exp})^2]$, S = 0.862, c = $10.1(3) \cdot 10^{-7}$.

## CONCLUSIONS

1. A (4 + 2)-cycloaddition reaction of 2-dialkylborylaminothiazoles to isocyanates led to the formation of cyclic compounds of tetracoordinated boron, dialkylboryl-[3-(N-organyl)-carbamoylthiazol-2-one-iminates].

2. The crystal and molecular structures of dipropylboryl-[3-(N-(phenyl)carbamoylthiazol-2-one-iminate] were determined by the x-ray diffraction method.

## LITERATURE CITED

1. V. A. Dorokhov, L. I. Lavrinovich, and B. M. Mikhailov, Dokl. Akad. Nauk SSSR, 245, 121 (1979).
2. V. A. Dorokhov, L. I. Lavrinovich, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 1085 (1979).
3. V. A. Dorokhov, L. I. Lavrinovich, M. N. Bochkareva, B. M. Zolotarev, V. A. Petukhov, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 1340 (1979).
4. V. A. Dorokhov, O. G. Bol'dyreva, B. M. Mikhailov, Z. A. Starikova, and I. A. Tesla, Izv. Akad. Nauk SSSR, Ser. Khim., 431 (1985).
5. V. A. Dorokhov, B. M. Zolotarev, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 869 (1981).

6. I. A. Tesla, Z. A. Starikova, V. K. Trunov, T. N. Kukina, V. A. Dorokhov, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 2730 (1981).
7. I. A. Tesla, Z. A. Starikova, V. A. Dorokhov, and B. M. Mikhailov, Koordinats. Khim., 8, 1546 (1982).

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# ORGANOBORON COMPOUNDS.

## COMMUNICATION 422. PROBLEM OF BROMINATION OF 9-ISOPROPYL-9-BORABICYCLO[3.3.1]NONANE

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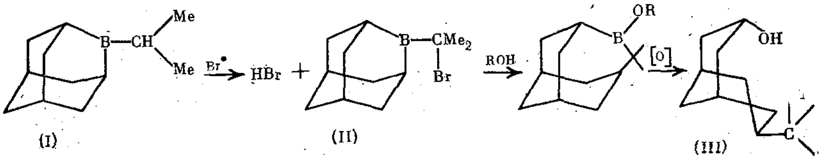
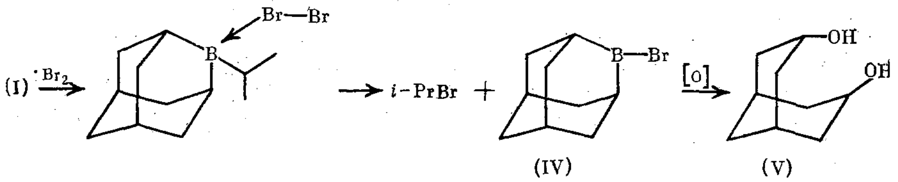
UDC 542.944:547.1'127

In the course of a study of chemical properties of 2-boraadamantane [1], we found that, depending on the conditions, bromination of 2-isopropyl-2-boraadamantane (I) proceeds preferentially by one of the following paths. If the bromination of (I) is carried out with illumination by a 200-W lamp, then a radical process of substitution of the α-H atom of the isopropyl group takes place. Bromide (II) thus formed, by the action of nucleophilic reagents, can undergo a Matteson–Pastor rearrangement [2] with ring expansion. As a result of subsequent oxidation, 3α-hydroxy-7α-(2-hydroxy-2-propyl)bicyclo[3.3.1]nonane (III) is formed:



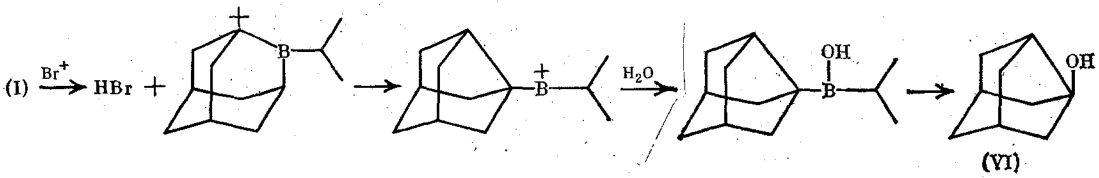
(1)

During normal illumination, the splitting of the B—$C_{i-Pr}$ bond predominates; it proceeds as a nucleophilic coordination of the $Br_2$ molecule to the B atom, followed by an electrophilic attack at the α-C atom, resulting in formation of i-PrBr and 2-bromo-2-boraadamantane (IV). On oxidation, this gives 3α,7α-dihydroxybicyclo[3,3.1]nonane (V):



(2)

Lastly, in the bromination of (I) in the presence of water, there is an ionic attack of a solvated $Br^+$ ion at the junction α-H atom of (I) and then the Matteson–Pastor rearrangement, proceeding with ring contraction. As a result of subsequent oxidation, 3-noradamantanol (VI) is formed:



(3)

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