CONCLUSIONS

1. Iodine atoms in any position of the pyrrole ring are capable of being replaced by acetylenic groups under the conditions of palladium complex and copper catalysis. We accomplished the acetylenic condensation of a number of α - and β -iodopyrroles.

2. The alkaline cleavage of the thus-synthesized tertiary pyrrolylacetylenic alcohols leads to ethynylpyrroles.

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ORGANOBORON COMPOUNDS.

378. SYNTHESIS OF CYCLIC TETRACOORDINATED BORON COMPOUNDS FROM

ENAMINOBORANES, PHENYL ISOCYANATE, AND PHENYL ISOTHIOCYANATE

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Previously it was shown that vinylaminodialkylboranes, not completely substituted on the B-C atom of the vinyl group, add to nitriles [1-3] and isonitriles [4] to give heterocyclic tetracoordinated boron compounds.

In the present paper, in order to further study the reactivity of organoboron enamines, we studied the reaction of N-substituted cyclohexenylaminodialkylboranes (I) with phenyl isocyanate (PIC) and phenyl isothiocyanate (PITC). Although it is characteristic for compounds with a B-N bond to undergo 1,2-addition to isocyanates and isothiocyanates to give the corresponding urea and thiourea derivatives [5-8], it could be reasoned that under certain conditions the enaminoboranes (I) will behave like ordinary enamies [9-12] and enter into nucleophilic C-addition reactions. Here the formation of cyclic (chelate) compounds, containing a tetracoordinated B atom in the ring, could be expected.

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The reaction of (I) with PIC (in a 1:1 ratio) begins even at $\sim 20^{\circ}$ C, but it proceeds slowly and is ended only after several months (the reaction course can be judged by the decrease in the absorption band of the NCO group in the IR spectrum). Based on the IR and PMR spectral data, the reaction products are dialkylborylureas (II) and dialkylborylbiurets (III). Consequently, the 1,2-addition of (I) to the C=N bond of PIC (aminoborination) proceeds under the given conditions:



 $R = C_4H_9$, K' = Ph(a); $R = C_3H_7$, $K' = i-C_4H_9(b)$; $R = C_3H_7$, R' = Ph(c).

The analytically pure (II) and (III) compounds could not be isolated due to their heat and the hydrolytic instability. Alcoholysis of the reaction mixture, obtained from (N-phenylcyclohexenylamino)dibutylborane (Ia) and PIC, gave a mixture of the corresponding urea (IV) and biuret (V), which were identified via the IR, PMR, and mass spectra



 $\mathbf{R'} = \mathbf{Ph}(\mathbf{a}).$

As a result, under mild conditions the (I) compounds behave toward PIC like the simple aminoboranes. However, during further study we were able to establish that crystalline chelates (VIa-c) are obtained when (II) and (III) were heated. Compounds (VIa-c) were obtained in 76-85% yield by heating PIC with (I) at $130-180^{\circ}$



 $\begin{array}{l} R = C_4H_9, \ R' = Ph(VIa); \ R = C_3H_7, \ R' = i - C_4H_9(VIb); \\ R = C_3H_7, \ R' = Ph(VI \ c). \end{array}$

The formation of (VIa-c) can be depicted as being due to the heat decomposition of (II) and (III) to the starting (I) and PIC, i.e., to assume that the processes, depicted in scheme (1), are reversible and on heating the equilibrium is shifted toward the starting compounds. Under these conditions the (I) compounds are probably capable of reacting with PIC on the type of the nucleophilic C-addition of enamines [9-12], with the difference that the (VI) compounds are stabilized due to inner coordination and do not undergo further transformations (isomerization, addition of a second molecule of isocyanate, etc.). Here the reaction mechanism can include the formation of donor-acceptor complex between (I) and PIC. It is also possible to assume another reaction mechanism, by which either the (II) or (III) compounds are converted directly to the (VI) compounds by migration (N+C) of the carbamoyl group on the type of acylotropic rearrangements. The chelate structure of (VIa-c) was confirmed by the ¹¹B NMR spectral data (signal in the upfield region), and also by the mass spectra, which are characterized by having intense peaks of the $(M-R)^+$ ions, typical for cyclic compounds with a dialkylboryl group [13].

In the synthesized compounds the chelating ligands are the anilides of a 2-alkyl (or aryl)iminocyclohexanecarboxylic acid (VII). However, for chelates with these ligands it is possible to have, besides (VI), the alternate structures (VIII)-(XI):



The IR and PMR spectral data make it possible to unequivocally select structure (VI). Thus, they show the presence of the NH group, which excludes structure (VIII)-(X) for the obtained chelates. The NH absorption frequency in the IR spectra is too high $(3455-3460 \text{ cm}^{-1})$ to assume that this group takes part in the coordination, as is represented by structure (XI). Finally, in the region of multiple bonds the IR spectra have intense bands at 1475, 1528, and 1618 cm⁻¹, while absorption above 1618 cm⁻¹ is absent. These data testify to the presence of a developed system of delocalized π -electrons and are found in complete agreement with structure (VI).

The yellow crystalline chelates (VIa-c) are readily soluble in most organic solvents. In their chemical stability they are noticeably inferior to a number of related chelate systems (for example, the diorganylboryl- β -diiminates [1, 2, 14]). When refluxed in ethanol the (VIa-c) compounds decompose with liberation of the free ligand. Thus, from (VIb) was obtained the crystalline anilide of 2-isobutyliminocyclohexanecarboxylic acid (VIIa, R' = i-C₄H₉), whose structure was confirmed by the IR, PMR, and mass spectral data

 $(\text{VIb}) \xrightarrow{+C_2H_5\text{OH}}_{-(C H_7)_2\text{BOC}_2H_5} (\text{VII})$ $\text{R'}=i-C_4H_9(\text{VIIa}).$

It is known that compounds of the (VII) type can be synthesized from cyclohexanone anils and aryl isocyanates by refluxing in toluene. However, only the corresponding cyclohexenylureas were obtained from the N-alkyliminocyclohexanes (XII) under analogous conditions [15]. By using the dialkylboryl derivatives of the (XII) compounds, i.e., the (I) enamines, it is possible, in contrast, to synthesize the (VII) anilides by the scheme:



Thus, for example, the yield of compound (VIIa, $R' = i-C_4H_9$) by the indicated scheme is $\sim 60\%$ (when based on N-isobutyliminocyclohexane).

Six-membered cyclic compounds with a tetracoordinated B atom in the ring were also synthesized by the reaction of (Ia, c) with PITC. More moderate heating $(90-100^{\circ})$ than in the case of PIC is needed for (Ia, c) to add as enamines to the C=N bond of PITC. In the formed chelates (XIIIa, b) the ligand is the anilide of 2-(N-phenylimino)cyclohexanethiocarboxylic acid (XIV). However, it is coordinated with the B atom in a different manner than its oxygen analog (VII) in the (VI) chelates.

The structure of the compounds (XIIIa, b) was confirmed by the IR, NMR, and mass spectra. The ¹¹B NMR spectra of (XIIIa, b) have signals in the region of a tetracoordinated B atom. Their mass spectra have the peak of the $(M-R)^+$ ion. Important information on the structure of (XIIIa, b) is furnished by their IR spectra, which lack absorption in the region of the NH stretching vibrations, but have a band at 1652 cm⁻¹ (C=N). These data, like the PMR spectral data, are in agreement with the structure assigned to (XIIIa, b) and make it possible to reject the alternate structure (XV).

Compounds (XIIIa, b) represent yellow crystals that are readily soluble in THF, CHCl₃, or CCl₄. Like the (VI) chelates, they are decomposed by boiling alcohol.



 $R = C_4 H_9(XIIIa); C_3 H_7(XIIIb).$

In harmony with the nomenclature adopted by us for boron chelates [16], it is expedient to regard the (VII) ligands as being 2-phenylcarbamoylcyclohexanonimines, and, for example, to name the chelates (VI, R = Ph) as O-dialkylboryl-[2-phenylcarbamoylcyclohexanone(N-phenyl)-iminates]. In like manner, the (XIII) compounds should be named N-dialkylboryl[2-phenylthio-carbamoylcyclohexanone(N-phenyl)iminates].

EXPERIMENTAL

The operations were run in an argon atmosphere. The starting cyclohexenylaminodialkylboranes were obtained from cyclohexanone imines and alkylmercaptodialkylboranes [1, 17]. The ¹¹B NMR spectra were recorded on a Bruker SXP 4-100 instrument, the PMR spectra were recorded on a Varian DA-60-IL instrument, and the IR spectra were recorded on a UR-20 spectrometer. The mass spectra were taken on a Varian MAT CH-6 mass spectrometer, with direct insertion of the sample into the ion source.

Reaction of (N-Phenylcyclohexenylamino)dibutylborane (Ia) with Phenyl Isocyanate in a 1:1 Ratio at $\sim 20^{\circ}$. A mixture of 4 g of (Ia) and 1.6 g of PhNCO was kept for 18 months at $\sim 20^{\circ}$ until the ν NCO band in the 2280 cm⁻¹ region disappeared in the IR spectrum. The obtained viscous mass is a mixture of (IIa) and (IIIa). Infrared spectrum: 1719 cm⁻¹ (ν C=0). PMR spectrum (CCl₄, δ , ppm): 5.45 m (HC=C). ¹¹B NMR spectrum (CH₂Cl₂): -52.2 ppm relative to Et₂O·BF₃.

Excess abs. MeOH was added to the obtained mixture, and the obtained crystals were filtered and washed with abs. ether to give 2.4 g of biuret (Va), contaminated with urea (IVa). Found: C 76.75; H 6.32; N 10.18%. $C_{26}H_{25}N_3O_2$. Calculated: C 75.88; H 6.12; N 10.21%. Infrared spectrum (CCl₄, v, cm⁻¹): 1665 (C=C), 1729 (C=O), 3300 (NH). PMR spectrum (CCl₄, δ , ppm): 10.52 s (NH), 7.36-6.28 m (3C₆H₅), 5.59 br.s (HC=C). Ratio of intensities = 1:15:1. Mass spectrum: m/e 411 (M⁴).

O-Dibutylboryl-[2-phenylcarbamoylcyclohexanone(N-phenyl)iminate]or 6-Phenylamino-3-phenyl-4,5-tetramethylene-2,2-dibutyl-1,3,2-oxaazoniaborata-3,5-cyclohexadiene (VIa). A mixture of 9.7 g of (Ia) and 3.9 g of PhNCO was heated for 4 h at 130-150°, cooled to \sim 20°, 1-2 ml of abs. hexane was added, and the mixture was rubbed until crystals were formed, which were transferred to a filter and washed with chilled hexane. We obtained 10.4 g (76%) of chelate (VIa), mp 80-84° (from hexane). Found: C 77.52; H 9.11; B 2.49; N 6.80%. C₂₇H₃₇BN₂O. Calculated: C 77.87; H 8.96; B 2.60; N 6.73%. Infrared spectrum (CCl₄, \vee , cm⁻¹): 1475, 1530, 1595, 1615, 3460 (NH). PMR spectrum (CCl₄, δ , ppm): 8.73-7.69 m (2C₆H₅), 7.51 br.s (NH), 2.37 m (2CH₂), m/e 359 (M-R)⁺.

O-Dipropylboryl-[2-phenylcarbamoylcyclohexanone(N-isobutyl)iminate] (VIb). A mixture of 9.4 g of (lb) and 4.7 g of PhNCO was heated for 3 h at 150-180°. The obtained crystals were washed on the filter with cold hexane. We obtained 12.15 g (85%) of (VIb), mp 64-68°. Found: C 74.54; H 10.01; B 2.86; N 7.76%. $C_{23}H_{37}BN_2O$. Calculated: C 74.99; N 10.12; B 2.94; N 7.61%. Infrared spectrum (CCl₄, v, cm⁻¹): 1530, 1590, 1617, 3460 (NH). PMR spectrum (CCl₄, δ , ppm): 7.45-6.75 m (C_6H_5), 6.30 s (NH), 2.96 m (N-CH₂), m/e 325 (M-R)⁺.

<u>O-Dipropylboryl-[2-phenylcarbamoylcyclohexanone(N-phenyl)iminate]</u> (VIc). Compound (VIc) was synthesized in a similar manner: yield 78%, mp 68-73° (from hexane). Found: C 77.36; H 8.94; B 2.61; N 7.10%. $C_{25}H_{33}BN_2O$. Calculated: C 77.31; H 8.57; B 2.79; N 7.21%. Infrared spectrum (CHCl₃, v, cm⁻¹): 1475, 1528, 1615, 3455 (NH). PMR spectrum (CCl₄, δ , ppm): 7.54-

 $6.82 \text{ m} (2C_6H_5)$, 6.54 s (NH), $2.18 \text{ m} (2CH_2)$, $1.94 \text{ m} (2CH_2)$. ¹¹B NMR spectrum (THF): -6.4 ppm, m/e 345 (M-R)⁺.

Alcoholysis of O-Dipropylboryl-[2-phenylcarbamoylcyclohexanone(N-isobutyl)iminate (VIb). Chelate (VIb) (6.3 g) was refluxed in abs. ethanol for 1 h. The alcohol and volatile substances were vacuum-distilled, abs. ether was added to the residue and the crystals were filtered. We obtained 3.2 g of 2-phenylcarbamoylcyclohexanonimine (VIIa) with mp 91-93°. (Yield 59%, when based on starting N-isobutyliminocyclohexane.) Found: C 75.04; H 9.15; N 10.35%. C₁₇H₂₄N₂O. Calculated: C 74.96; H 8.88; N 10.29%. Infrared spectrum (CCl₄, ν , cm⁻¹): 1640, 3470 (NH). PMR spectrum (CCl₄, δ , ppm): 10.0 br.s (NH), 7.56-6.68 (C₆H₅), 2.92 m (NCH₂), 2.26 m (2CH₂), 1.62 m (2CH₂); m/e 272 (M⁺).

<u>N-Dibutylboryl-[2-phenylthiocarbamoylcyclohexanone(N-phenyl)iminate]</u> or 6-Thio-1,3-diphenyl-4,5-tetramethylene-2,2-dibutyl-1,3,2-azaazoniaborata-3-cyclohexene (XIIIa). A mixture of 16.1 g of (Ia) and 7.2 g of PhNCS was heated for 11 h at 90-100°. The obtained crystals were washed on a filter with abs. hexane and then ether. We obtained 13.5 g (60%) of (XIIIa), mp 124-126°. Found: C 75.19; H 8.75; B 2.53; N 6.58; S 7.46%. $C_{22}H_{37}BN_2S$. Calculated: C 74.98; H 8.62; B 2.49; N 6.47; S 7.41%. Infrared spectrum (CCl₄, ν , cm⁻¹): 1655 (C=N). ¹¹B NMR spectrum (in C_6H_6): -2.2 ppm, m/e 375 (M-R)⁺.

<u>N-Dipropylboryl-[2-phenylthiocarbamoylcyclohexanone(N-phenyl)iminate]</u> (XIIIb). In a similar manner, from (Ic) and PhNCS we obtained compound (XIIIb) in 78% yield, mp 170-174°. Found: C 74.40; H 8.57; B 2.46; N 7.29; S 8.05%. $C_{25}H_{33}BN_2S$. Calculated: C 74.24; H 8.23; B 2.68; N 6.93; S 7.93%. Infrared spectrum (CHCl₃, \vee , cm⁻¹): 1652 (C=N). m/e 361 (M-R)⁺.

CONCLUSIONS

1. When N-substituted cyclohexenylaminodialkylboranes are reacted with phenyl isocyanate under mild conditions ($\sim 20^{\circ}$) the C=N bond undergoes aminoborination, whereas under heating (90-180°) the reaction with phenyl isocyanate and phenyl isothiocyanate proceeds on the type of nucleophilic C-addition to respectively give dialkylboryl-[2-phenylcarbamoylcyclohexanoniminates] and dialkylboryl-[2-phenylthiocarbamoylcyclohexanoniminates].

2. A method was proposed for the synthesis of the anilides of a 2-alkyliminocyclohexanecarboxylic acid from cyclohexanone imines and phenyl isocyanate via boron chelates.

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