BORON CHELATES WITH 5,5,5-TRIFLUORO- AND 5,5,5-TRICHLORO-4-AMINOPENT-3-EN-2-ONES

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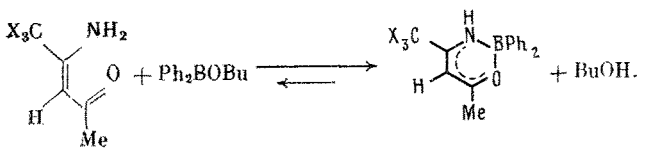
Boron chelates were obtained by the reaction of butoxy(butylthio)diphenylborane with 5,5,5-trifluoro(trichloro)-4-aminopent-3-en-2-one, and their reactions with primary amines were investigated. β-Diiminate complexes of boron with trifluoro- and trichloromethyl groups were synthesized.

Keywords: *boron chelate complexes, synthesis, aminovinyl ketones, boron β-ketoiminates and diiminates.*

Aminovinyl ketones are widely used in organic synthesis and also as ligands in complexation with various metals [1-5]. However, their boron complexes have been studied relatively little [6-8]. Recently we described chelates of boron with S,N- and N,N-acetals of diacylketenes, which are functionalized aminovinyl ketones [9-11]. The purpose of the present paper is the preparation of chelate complexes of boron with aminovinyl ketones (**1**) containing strong electron-acceptor substituents, i.e., CF_3 or CCl_3, because unique reactivity and the exhibition of biological activity can be expected from compounds of such a type.

We have found that 5,5,5-trichloro- or 5,5,5-trifluoro-4-aminopent-3-en-2-ones (**1a, b**) react with butoxydiphenylborane (**2**) with the formation of chelates (**3a, b**):



(1a, b) (2) (3a, b) X=Cl(a), F(b). (1)

The course of the process can be followed conveniently by ^{11}B NMR: the appearance and gradual increase of the signal in a strong field with a chemical shift of 4.7 ppm with a simultaneous decrease of the signal of the starting compound **2** (45.5 ppm) indicates the formation of chelate **3**. On the other hand, with addition of a large excess of butanol to **3**, a weak signal of **2** appeared in the ^{11}B NMR spectrum, which indicates an equilibrium nature of reaction (1). However, because of complexation, the equilibrium was strongly shifted toward chelate **3**. Thus, in a 0.5 *M* ether solution, ~25% of chelate **3a** formed from **1a** and **2** after 15 min, and its content in the reaction material reached ~95% after 4.5 h. During evaporation of the resulting butanol *in vacuo*, the equilibrium of (1) shifted virtually completely toward **3a**.

Butylthiodiphenylborane (**4**) can also be used as a borylating agent. In that case, the reaction is irreversible and occurs with significant heating. However, the use of compound **2** for the synthesis of chelates of the type of **3** seems preferable because they are probably more readily available than **4**.

$$\underset{(4)}{1a+Ph_2BSBu} \rightarrow 3a+BuSH \qquad (2)$$

Chelates **3a** and **3b** are yellow crystalline substances soluble in benzene, chloroform, and acetone. They are sparingly soluble in hexane and insoluble in water. They are stable in air at ~20°C, but it is better to carry out reactions involving them

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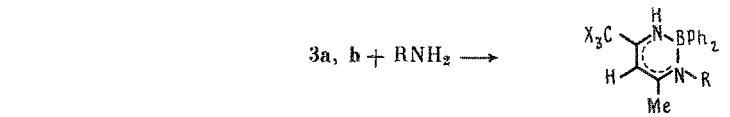
in an inert-gas atmosphere. An NH band was observed in the IR spectra of compounds **3a** and **3b** (3380 cm^{-1} for **3b** and 3360 cm^{-1} for **3a**), and there were characteristic absorption bands of a coordinated ligand in the region of multiple bonds (1614 and 1533 cm^{-1} for **3a** and 1627 and 1564 cm^{-1} for **3b**).

The presence of the trihalomethyl group in **3a** and **3b** strongly increases the reactivity of the coordinated carbonyl group with respect to primary amines. Thus, whereas our attempts to introduce boron chelates with aminovinyl ketones (**1**, where X = H) into a reaction with primary amines (at 20-100°C) were unsuccessful (which also corresponds to the data of [6] and [7]), compounds **3a** and **3b** did react with amines (except for weak bases such as aniline and 2-aminopyridine) even at ~20°C; here complexes of corresponding β-aminovinylimines **5a-d** formed in high yields.



(3)

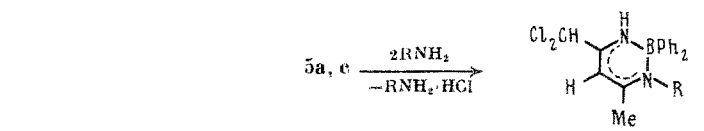
(5a — d)

X = Cl, R = Bn (a), *i*-Bu (b), *n*-Bu (c); F, R = *i*-Bu (d).

In this regard, it should be noted that free ligands **1a** and **1b** behave completely differently with respect to primary amines: transamination of **1b** occurs in the reaction of aliphatic amines with **1b** [12, 13]; the reaction of **1a** with amines occurs very complexly, and only an amine hydrochloride could be recovered from its products [14].

Chelates **5a-d** are yellow crystalline substances, soluble in benzene, $CHCl_3$, acetone, and DMSO, sparingly soluble in hexane, and insoluble in water.

In boiling benzene, chelates **5a-c** react with amines, with reduction of CCl_3 to the $CHCl_2$ group. Replacement of CCl_3 by an amino group was not observed.



(6a, b)

R=Bn (a); *n*-Bu (b).

Complexes **5a-d, 6a**, and **6b** do not decompose during boiling with alcohol and water.

Thus, the reaction of diphenylboryl complexes of aminovinyl ketones with amines is a novel method for preparation of boron β-diiminates with high thermal and chemical stability [16].

EXPERIMENTAL

The NMR spectra of all the obtained compounds were recorded in $CDCl_3$: the PMR spectra (δ, ppm) were recorded with a Bruker WM-250 instrument; the ^{13}C NMR spectra (δ, ppm, $J_{C,H}$, Hz) were recorded with a Bruker AM-300 spectrometer; and the ^{11}B NMR spectra (δ, ppm) were recorded with a Bruker AM-200 P instrument. The IR spectra (ν, cm^{-1}) in CH_2Cl_2 were recorded with a UR-20 instrument. The mass spectra (*m/z*) were recorded with a Varian MAT CH-6 instrument.

5,5,5-Trifluoro-4-aminopent-3-en-2-one (1b) was obtained according to [15], and **5,5,5-trichloro-4-aminopent-3-en-2-one** was obtained according to [14]. Pre-dehydrated solvents were used.

Diphenylboryl Complex of 5,5,5-Trichloro-4-aminopent-3-en-2-one (3a). a) A solution of 4.2 g (20 mmoles) of **1a** was added to a solution of 5.25 g (20 mmoles) of **4** in 40 ml of ether for 15 min with stirring (here a yellow color appeared immediately, and the temperature rose by 7-8°C); the reaction mixture was left for 12 h. The solvent was evaporated *in vacuo*, 30 ml of pentane was added to the residue, the precipitate was filtered and washed with pentane (3 × 15 ml), and 6.9 g (92%) of **3a**, with mp 112.5-113.5°C, was obtained. IR spectrum: 3360 (NH), 1614, 1533. PMR spectrum ($(CD_3)_2CO$, δ, ppm): 2.28 s (3H, Me); 6.02 d (1H, $^4J_{H,NH}$ = 2.5, CH); 7.1-7.42 m (10H, Ph); 8.95 br.s (1H, NH). ^{13}C NMR spectrum: 24.7 q (129, Me); 91.6 d (174, C^3); 92.8 s (C^5); 126.8, 127.5, 131.7, 148.4 (Ph); 165.8 d (4, C^4); 186.3 m (CO). ^{11}B NMR spectrum: 4.7. Mass spectrum, *m/z*: 288 $[M - Ph]^+$. Found, %: C 55.32; H 4.04; B 3.08; Cl 28.77; N 3.91. $C_{17}H_{15}BCl_3NO$. Calculated, %: C 55.71; H 4.11; B 2.95; Cl 29.06; N 3.84.

b) To a solution of 7.95 g (33 mmoles) of **2** in 30 ml of ether was added 6.39 g (32 mmoles) of **1a** in 5 ml of ether, and the whole was stirred for 1 h and left for 12 h. The solvent was evaporated *in vacuo* (for more complete removal of *n*-BuOH, the bath temperature was raised to 50-60°C, and the vacuum was brought to 2 mm Hg). To the residue was added 70 ml of pentane, the precipitate was filtered and washed with pentane (3 × 15 ml), and 10.85 g (94.5%) of **3a** was obtained.

Diphenylboryl Complex of 5,5,5-Trifluoro-4-aminopent-3-en-2-one (3b). A mixture of 9.5 g (63 mmoles) of **1b** and 16.4 g (69 mmoles) of **2** in 100 ml of pentane was stirred for 1 h and left for 12 h. The reaction material was evaporated to a half of the volume and cooled (in a Dewar flask with solid CO_2), and the precipitated crystals of **3b** (10.3 g) were filtered in a funnel that was cooled with solid CO_2 and were washed with cold pentane. The filtrate was evaporated *in vacuo*, the residue was washed with pentane, and an additional 5.1 g of **3b** was obtained. The total yield of chelate **3b**, with mp 99-100°C (from hexane), was 15.4 g (75%). IR spectrum: 3380 (NH), 1627, 1565, 1170-1210. PMR spectrum: 2.30 s (3H, Me); 5.56 d (1H, $^4J_{NH,H}$ = 2.5, CH); 7.05 br.s (1H, NH); 7.25-7.45 m (10H, 2Ph). ^{13}C NMR spectrum: 24.7 q (129, Me); 91.5 d (174, C^3); 118.7 q (279, C^5); 127.1, 127.5, 131.6 (Ph); 156.8 q (C^4, $^2J_{C,F}$ = 33); 188.3 s (CO). ^{11}B NMR spectrum: 4.5. Mass spectrum: 240 [M — Ph]$^+$. Found, %: C 64.55; H 4.72; N 4.69; F 17.87. $C_{17}H_{15}BF_3NO$. Calculated, %: C 64.39; H 4.77; F 17.97; N 4.42.

Diphenylboryl Complex of 1,1,1-Trichloro-2-amino-4-(benzylimino)pent-2-ene (5a). A mixture of 9.13 g (25 mmoles) of **3a**, 10.7 g (100 mmoles) of $BnNH_2$, and 30 ml of ether was boiled for 3 h, and the resulting precipitate (8.13 g) of **5a** was filtered and washed with pentane (3 × 25 ml). To the filtrate was added 50 ml of pentane, and an additional 1.27 g of **5a** precipitated; the total yield of **5a**, with mp 157-157.5°C, was 9.4 g (83%). IR spectrum: 3390 (NH), 1602, 1533, 1487. PMR spectrum: 2.11 s (3H, Me); 4.68 s (2H, NCH_2); 5.52 d (1H, $^4J_{H,NH}$ = 2.5, CH); 6.16 br.s (1H, NH); 6.75-7.40 m (15H, 3Ph). ^{13}C NMR spectrum: 22.3 q (127, Me); 53.2 t (139, NCH_2); 90.3 d (170, C^3); 126.0, 126.4, 126.7, 127.2, 128.3, 133.3, 137.1, 149.3 (3Ph); 159.5 d ($5C^2$); 169.2 m (C^4). ^{11}B NMR spectrum: 0.7. Mass spectrum: 377 [M — Ph]$^+$. Found, %: C 63.74; H 5.20; B 2.53; Cl 22.44; N 6.33. $C_{24}H_{22}BCl_3N_2$. Calculated, %: C 63.26; H 4.87; B 2.37; Cl 23.34; N 6.15.

Diphenylboryl Complex of 1,1,1-Trichloro-2-amino-4-(isobutylimino)pent-2-ene (5b). A solution of 1.62 g (4.4 mmoles) of **3a** and 3 ml of *i*-$BuNH_2$ in 10 ml of ether was stirred for 1 h and then boiled for 0.5 h, the solvent and excess amine were evaporated *in vacuo*, 15 ml of pentane was added to the residue, the whole was cooled to −78°C, the precipitated lemon-yellow crystals were filtered and washed with cold pentane (2 × 5 ml), and 1.2 g (64.5%) of **5b**, with mp 112-113°C, was obtained. IR spectrum: 3400 (NH), 1605, 1532, 1492. PMR spectrum: 0.59 d (6H, J = 6.5, 2Me); 1.15 m (1H, CH); 2.30 s (3H, Me); 3.2 d (2H, J = 7, NCH_2); 5.48 d (1H, $^4J_{H,NH}$ = 3.3, CH); 6.05 br.s (1H, NH); 7.20-7.40 m (10H, 2Ph). ^{13}C NMR spectrum: 20.4 q ($CH\underline{Me}_2$); 22.1 q (128, Me); 28.4 d (127, $Me_2\underline{C}H$); 56.8 t (137, NCH_2); 90.9 d (172, C^3); 94.3 s (C^1); 126.4, 127.2, 133.3, 150.1 (Ph); 159.8 s (C^2); 167.9 br.s (C^4). ^{11}B NMR spectrum: 0.3. Mass spectrum: 343 [M — Ph]$^+$.

Diphenylboryl Complex of 1,1,1-Trichloro-2-amino-4-(*n*-butylimino)pent-2-ene (5c). Similarly to the preceding experiment, from 1.88 g (5.1 mmoles) of **3a** and 5 ml of *n*-$BuNH_2$ was obtained 1.64 g (76%) of **5c**, with mp 113.5-114.5°C. IR spectrum: 3397 (NH), 1609, 1537, 1497. PMR spectrum: 0.6 t (3H, Me); 0.97 m (4H, $2CH_2$); 2.29 s (3H, Me); 3.28 t (2H, NCH_2); 5.43 d (1H, $^4J_{H,NH}$ = 2.5, CH); 5.92 br.s (1H, NH); 7.20-7.50 m (10H, 2Ph). ^{13}C NMR spectrum: 13.3 q (124); 20.1 t (130); 31.0 t (130); 49.9 t (139, *n*-Bu); 21.0 q (130, Me); 89.6 d (171, C^3); 94.3 d (C^1); 126.3, 127.2, 133.4, 150.5 (2Ph); 158.6 (C^2); 166.8 br.s (C^4). ^{11}B NMR spectrum: 0.1. Mass spectrum: 343 [M — Ph]$^+$. Found, %: C 59.50; H 5.84; B 2.61; Cl 25.34; N 6.99. $C_{21}H_{24}BCl_3N_2$. Calculated, %: C 59.82; H 5.74; B 2.57; Cl 25.23; N 6.65.

Diphenylboryl Complex of 1,1,1-Trifluoro-2-amino-4-(isobutylimino)pent-2-ene (5d). A mixture of 1.13 g (3.6 mmoles) of **3b** and 2.5 ml of *i*-$BuNH_2$ in 10 ml of ether was stirred for 1 h at ~20°C, the high volatile substances were evaporated *in vacuo*, 15 ml of pentane was added to the residue, the precipitate was filtered and washed with pentane, and 0.76 g of **5d** was obtained. The filtrate was evaporated to two-thirds of the volume and cooled to −78°C, and an additional 0.54 g of **5d** was obtained; the total yield of **5d**, with mp 141-141.5°C, was 1.3 g (98.5%). IR spectrum: 3401 (NH), 1614, 1567, 1498, 1309-1147. PMR spectrum: 0.43 d (6H, 2Me); 0.87-1.04 m (1H, CH); 2.12 s (3H, Me); 3.07 d (2H, NCH_2); 4.96 d (1H, $^4J_{H,NH}$ = 2.5, CH); 5.57 br.s (1H, NH); 7.03-7.20 m (10H, 2Ph). ^{13}C NMR spectrum: 20.2 q ($\underline{Me}_2CH$); 21.7 q (128, Me); 28.3 d ($\underline{C}HMe_2$); 58.8 t (136, NCH_2); 91.1 d (171, C^3); 123.3 q (275, C^1); 126.4; 127.1; 133.2; 149.9 (Ph); 148.9 q ($^2J_{C,F}$ = 34, C^2); 168.0 s (C^4). Mass spectrum: 295 [M — Ph]$^+$. Found, %: C 67.56; H 6.37; F 15.39; N 7.70. $C_{21}H_{24}BF_3N_2$. Calculated, %: C 67.76; H 6.50; F 15.34; N 7.53.

Diphenylboryl Complex of 1,1-Dichloro-2-amino-4-(benzylimino)pent-2-ene (6a). A mixture of 2.62 g (5.8 mmoles) of **5a** and 3.21 g (30 mmoles) of $BnNH_2$ in 10 ml of benzene was boiled for 7 h, the precipitate ($BnNH_2 \cdot HCl$) was filtered and washed with pentane, the filtrate was evaporated *in vacuo*, the residue, a dark oil, was chromatographed on a column with SiO_2 (the eluents were hexane and then hexane−benzene), and 1.6 g (69%) of **6a**, with mp 141-142°C, was obtained. IR

spectrum: 3388 (NH), 1603, 1555, 1490. PMR spectrum: 2.04 s (3H, Me); 4.67 s (2H, NCH_2); 4.96 d (1H, J = 2.5, CH); 6.13 br.s (2H, NH, Cl_2CH-); 6.75-7.45 m (15H, 3Ph). ^{13}C NMR spectrum: 21.8 q (132, Me); 53.2 t (137, NCH_2); 68.8 d (178, C^1); 91.0 d (168, C^3); 126.1, 126.3, 126,6, 127.2, 128.3, 133.4, 137.5, 150.0 (Ph); 158.1 (C^2); 168.6 (C^4). Mass spectrum: 343 [M — Ph]$^+$. Found, %: C 68.33; H 5.64; B 2.75; Cl 16.98; N 6.36. $C_{24}H_{23}BCl_2N_2$. Calculated, %: C 68.44; H 5.51; B 2.57; Cl 16.84; N 6.65.

Diphenylboryl Complex of 1,1-Dichloro-2-amino-4-(*n*-butylimino)pent-2-ene (6b). Similarly to the preceding experiment, a mixture of 1.0 g (2.4 mmoles) of **5b** and 1.8 g (24 mmoles) of *n*-$BuNH_2$ in 5 ml of benzene was boiled for 9.5 h. The residue was chromatographed on a column with SiO_2 (the eluents were first petroleum ether and then petroleum ether—benzene). We recovered 0.3 g (30%) of the starting **5b** and 0.28 g (30.2%) of **6b**, with mp 128.5-129.5°C. PMR spectrum: 0.59 t (3H, Me); 0.92 m (4H, $2CH_2$); 2.21 s (2H, Me); 3.25 t (2H, $N-CH_2$); 4.85 d (1H, $^4J_{H,NH}$ = 2.5, CH); 5.85 br.s (1H, NH); 6.04 s (1H, Cl_2CH-); 7.2-7.45 m (10H, 2Ph). ^{11}B NMR spectrum: −0.3. Mass spectrum: 309 [M — Ph]$^+$. Found, %: C 65.80; H 6.75; B 2.58; Cl 18.40. $C_{21}H_{25}BCl_2N_2$. Calculated, %: C 65.14; H 6.51; B 2.79; Cl 18.32.

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