Nitrones and oximes of bifunctional carbonyl compounds and their reaction products with diarylborinic acids. Crystal and molecular structure of examples of five-, six-, and seven-membered boron chelates[1]

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Abstract: Synthesis has been carried out of diarylboron chelates of 2- and 3-hydroxynitrones, of 2- and 3-hydroxyoximes, and of 2-carboxynitrones and a 2-carboxyoxime. The structures have been determined from spectroscopic data and from X-ray analyses of **5*d***, **9*a***, **11*b***, and **19**. Crystals (at 180 K) of **5*d*** are monoclinic, a = 10.543(2), b = 19.085(4), c = 10.2667(3) Å, β = 90.4978(7)°, Z = 4, space group $P2_1/c$; those of **9*a*** are orthorhombic, a = 10.9913(5), b = 14.9329(7), c = 10.2460(13) Å, Z = 4, space group $P2_12_12_1$; those of **11*b*** are monoclinic, a = 11.227(2), b = 9.967(2), c = 17.0537(4) Å, β = 105.4179(5)°, Z = 4, space group $P2_1/n$; those of **19** are monoclinic, a = 11.1847(15), b = 13.715(3), c = 11.5559(5) Å, β = 104.8730(10)°, Z = 4, space group $P2_1/n$. The structures were solved by direct methods and refined by full-matrix least-squares procedures to $R(F, I \geq 3\sigma(I))$ = 0.049, 0.047, 0.042, and 0.047, respectively, for CCD data for **5*d***, **9*a***, **11*b***, and **19**. The four molecules contain five-, seven-, six-, and five-membered rings, respectively, with O-B-N groups in the **5*d***, **11*b***, and **19**, and O-B-O in **9*a***; the rings exhibit various deviations from planarity, particularly the seven-membered ring.

Key words: diarylboron chelates, hydroxyoximes, hydroxynitrones, carboxyoximes, carboxynitrones, organoboron compounds, crystal structure.

Resumé : On a réalisé la synthèse de chélates du diarylbore avec de 2- et 3-hydroxynitrones, de 2- et 3-hydroxyoximes, de 2-carboxynitrones et d'une 2-carboxyoxime. On a déterminé les structures à partir de données spectroscopiques et d'analyses par diffraction des rayons X des composés **5*d***, **9*a***, **11*b*** et **19**. Les cristaux du composé **5d** sont monocliniques (à 180 K), groupe d'espace $P2_1$/c avec a = 10,543(2), b = 19,085(4) et c = 10,2667(3) Å, β = 90,4978(7)° et Z = 4; ceux du composé **9*a*** sont orthorhombiques, groupe d'espace $P2_12_12_1$, avec a = 10,9913(5), b = 14,9329(7) et c = 10,2460(13) Å et Z = 4; ceux du composé **11*b*** sont monocliniques, groupe d'espace $P2_1/n$ avec a = 11,227(2), b = 9,967(2) et c = 17,0537(4) Å, β = 105,4179(5)° et Z = 4 et ceux du composé **19** sont monocliniques, groupe d'espace $P2_1/n$ avec a = 11,1847(15), b = 13,715(3) et c = 11,5559(5) Å, β = 104,8730(10)° et Z = 4. On a résolu les structures par des méthodes directes et on les a affinées par la méthode des moindres carrés (matrices entières) jusqu'à des valeurs de $R(F, I \geq 3\sigma(I))$ = 0,049, 0,047, 0,042 et 0,047 respectivement pour les données pour les molécules **5*d*, 9*a*, 11*b*** et **19**. Les quatre molécules comportent respectivement des cycles à cinq, sept, six et cinq chaînons et des groupes O-B-N dans les molécules **5*d*, 11*b*** et **19** et O-B-O pour la molécule **9*a***; les cycles présentent des déviations diverses par rapport à la planéité, en particulier pour le cycle à sept chaînons.

Mots Clés : chélates de dialkylbores, hydroxyoximes, hydroxynitrones, carboxyoximes, carboxynitrones, composés organiques du bore, structure cristalline.

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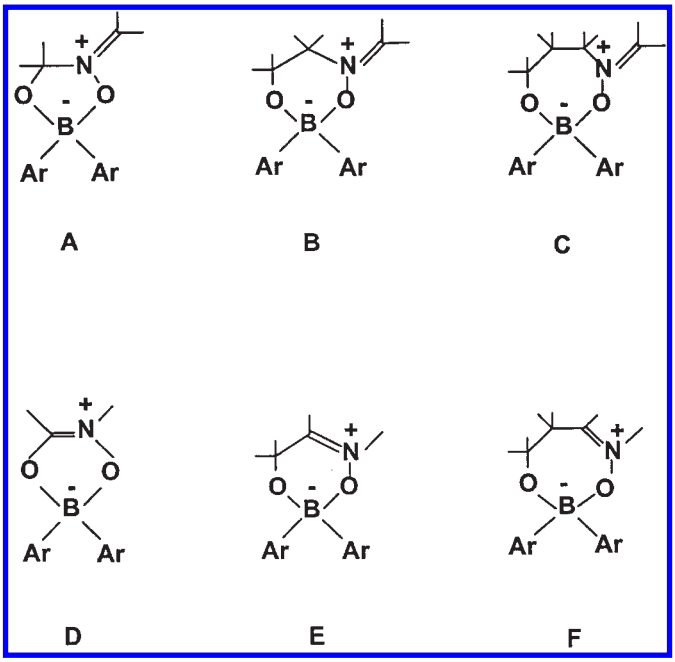
Introduction

In the course of our investigations on cyclic boron nitrogen betaines (1) we synthesized a series of five-, six-, and seven-membered boron chelates containing bidentate nitrone ligands with an *N*-(1-hydroxyalkyl) group (2) (ring system **A**), an *N*-(2-hydroxylalkyl) group (3) or *N*-(1-carboxyalkyl) group (4) (ring system **B**), and an *N*-(3-hydroxylalkyl) group (5) (ring system **C**), all having the nitrone C=N bond located outside of the chelate ring ("exocyclic" or "semicyclic" (6, see footnote for exocyclic double bonds, p. 954)). As an extension of our work in this area we investigated comparable chelate ring structures with an "endocyclic" C=N double bond, as depicted in the ring systems **D**, **E**, and **F**. Five-membered boron chelates of type **D** had been obtained previously from various hydroxamic acid derivatives (7). We now report, continuing and completing this series, the synthesis and structural characteristics of six- and seven-membered boron chelates, type **E** and **F**, derived from the corresponding bidentate nitrones. In connection with these compounds we describe also the synthesis and structural features of several boron chelates of analogous bifunctional oximes. Unambiguous proof of coordination sites and ring geometries is furnished by X-ray crystallographic analyses in selected cases.



Experimental

General procedures

Oxybis(diphenylborane) was prepared according to literature methods (8). All reactions were carried out under normal conditions, without protective gas atmosphere. Melting points (uncorrected): Linström apparatus and Büchi SMP 20. IR: PYE-Unicam SP 3-200, Philips PU 9800 FT-IR-Spectrometer, V 3.00, and ATI Mattson Genesis Series FT-IR™ Rev. I. ^{1}H NMR: Varian EM 390 and Bruker AM 400. ^{11}B NMR: Bruker AC 200. Elemental analyses: Carlo Erba CHNO elemental analyzer 1106; boron and chlorine titrimetrically after Schöniger-oxidation with Metrohm Potentiograph E 536/Dosimat 655.

2-(Methylimino)ethanol *N*-oxide (2*a*)

Hydroxyacetaldehyde (1.20 g, 20 mmol) and *N*-methylhydroxylamine hydrochloride (1.67 g, 20 mmol) are dissolved in 20 mL of ethanol (96%) and mixed with a solution of K_2CO_3 (1.38 g, 10 mmol) in 5 mL of water under stirring. After 48 h, KCl is filtered off, the solvent removed in vacuo, and the residue taken up in 50 mL of absolute ethanol. After filtration the solvent is distilled off in vacuo. The remaining oil is not purified further, and is characterized only with NMR data. ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 3.65 (s, N-CH_3), 4.15 (s, broad, exchangeable, OH), 4.35 (d, J = 4 Hz, O-CH_2), 6.92 (t, J = 4 Hz, N=CH).

N-(Benzylimino)ethanol *N*-oxide (2*b*)

Hydroxyacetaldehyde (1.20 g, 20 mmol), *N*-benzylhydroxylamine hydrochloride (3.19 g, 20 mmol), and K_2CO_3 (1.38 g, 10 mmol) are reacted as described above for **2*a***. The remaining solid is recrystallized from ethanol–ether. Yield: 2.30 g (70%) of colorless plates, mp 82–84°C. IR (KBr, cm^{-1}): 3 300 and 3 170 (broad, O-H), 1610 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 4–5 (s, very broad, exchangeable, OH), 4.35 (d, J = 4 Hz, O-CH_2), 4.83 (s, N-CH_2), 6.88 (t, J = 4 Hz, N=CH), 7.37 (s, C_6H_5). Anal. calcd. for $C_9H_{11}NO$: C 65.44, H 6.71, N 8.48; found: C 65.41, H 6.71, N 8.57.

1-(Methylimino)-2-propanol *N*-oxide (2*c*)[3]

This compound was prepared as described previously (9).

1-(*tert*-Butylimino)-2-propanol *N*-oxide (2*d*)

2-Hydroxypropanal (1.48 g, 20 mmol) and *N*-*tert*-butylhydroxylamine (1.80 g, 20 mmol) are dissolved in 20 mL of absolute ethanol and stirred for 48 h at room temperature. The solvent is distilled off in vacuo. The remaining oily residue is not purified further, and is characterized only with NMR data. ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.37 (d, J = 7 Hz, OC-CH_3), 1.51 (s, $C(CH_3)_3$), 4.68 (m, 1 H exchangeable, OH and O-CH), 6.93 (d, J = 5 Hz, N=CH).

1-(Cyclohexylimino)-2-propanol *N*-oxide (2*e*)

2-Hydroxypropanal (2.22 g, 30 mmol) and *N*-cyclohexylhydroxylamine (3.45 g, 30 mmol) are reacted as described above for **2*d***. The remaining solid is recrystallized from absolute ethanol. Yield: 4.42 g (86%) of colorless needles, mp 129°C. IR (KBr, cm^{-1}): 3 210 (broad, O-H), 1 600 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.04–2.20 (m, $(CH_2)_5$), 1.39 (d, J = 7 Hz, CH_3), 3.64 (m, N-CH), 4.71 (m, O-CH), 5.61 (s, exchangeable, OH), 6.85 (d, J = 5 Hz, N=CH). Anal. calcd. for $C_9H_{17}NO_2$: C 63.13, H 10.01, N 8.18; found: C 63.09, H 10.15, N 7.97.

1-(Benzylimino)-2-propanol *N*-oxide (2*f*)

This compound was prepared as described previously (9).

[3] Alternative nomenclature for the compounds of type **2** (generally): *N*-(2-hydroxyalkylidene) alkanamine *N*-oxide, as used in ref. 9.

1-(Benzhydrylimino)-2-propanol *N*-oxide (2*g*)

2-Hydroxypropanal (1.48 g, 20 mmol) and *N*-benzhydrylhydroxylamine (3.98 g, 20 mmol) are reacted as described above for **2*d***. The remaining solid is recrystallized from ethanol–ether. Yield: 4.21 g (82%) of colorless crystals, mp 110–111°C. IR (KBr, cm^{-1}): 3 290 (broad, O-H), 1 590 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.34 (d, J = 7 Hz, CH_3), 4.71 (m, O-CH), 5.47 (s, broad, exchangeable, OH), 6.15 (s, N-CH), 6.82 (d, J = 5 Hz, N=CH), 7.32 (s, $C(C_6H_5)_2$). Anal. calcd. for $C_{16}H_{17}NO_2$: C 75.27, H 6.71, N 5.49; found: C 75.47, H 6.71, N 5.64.

3-(Cyclohexylimino)-2-butanol *N*-oxide (2*h*)

3-Hydroxy-2-butanone (0.88 g, 10 mmol) and *N*-cyclohexylhydroxylamine (1.15 g, 10 mmol) are dissolved in 30 mL of benzene and refluxed for 5 h using a Dean–Stark trap for continuous removal of water. The solution is evaporated down to one-quarter of the initial volume. After addition of 10 mL of hexane and cooling down to –18°C crystallization starts after 48 h. The air-sensitive compound can be recrystallized carefully from chloroform–ether. Yield: 0.90 g (49%) of colorless crystals, mp 118°C. IR (KBr, cm^{-1}): 3 221 (broad, O-H), 1 587 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.67–2.67 (m, $(CH_2)_5$), 1.37 (d, J = 6 Hz, OC-CH_3), 2.13 (s, NC-CH_3), 3.93 (m, N-CH), 4.67 (q, J = 6 Hz, O-CH), 6.53 (s, broad, exchangeable, OH). Anal. calcd. for $C_{10}H_{19}NO_2$: C 64.83, H 10.34, N 7.56; found: C 64.92, H 10.41, N 7.46.

4-Methyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*a*)

2*a* (0.2 g of the crude product) in 1 mL of ethanol and oxybis(diphenylborane) (0.35 g, 1 mmol) in 1 mL ethanol are mixed under stirring. After 5 h at room temperature, the analytically pure crystals are filtered off and washed with ether.[4] Yield: 0.31 g (61%) of colorless crystals[6], mp 104–105°C (decomp.). IR (KBr, cm^{-1}): 1 665 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 3.14 (s, CH_3), 4.23 (m, O-CH_2), 6.25 (s, N=CH), 6.87–7.40 (m, $B(C_6H_5)_2$). Anal. calcd. for $C_{15}H_{16}BNO_2$: C 71.18, H 6.37, N 5.53; found: C 71.17, H 6.37, N 5.49. (Boron elemental analyses and NMR data were obtained only for some of the examples of compounds of type **3**.)

4-Cyclohexyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*b*)

Hydroxyacetaldehyde (0.12 g, 2 mmol) and *N*-cyclohexylhydroxylamine (0.23 g, 2 mmol) are dissolved in 5 mL of ethanol. After addition of oxybis(diphenylborane) (0.35 g, 1 mmol) in 1 mL of ethanol the crystallization commences at room temperature or after several hours of cooling. The analytically pure crystals are filtered off and washed with ether.[4] Yield: 0.43 g (77%) of colorless crystals[6], mp 131°C (decomp.). IR (KBr, cm^{-1}): 1 653 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.80–2.47 (m, $(CH_2)_5$), 3.53 (m, N-CH), 4.47 (s, O-CH_2), 6.90 (s, N=CH), 6.97–7.67 (m, $B(C_6H_5)_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 7.1 ($w_{1/2}$ = 300 Hz). Anal. calcd. for $C_{20}H_{24}BNO_2$: C 74.78, H 7.53, B 3.37, N 4.36; found: C 74.84, H 7.84, B 3.35, N 4.15.

4-Benzyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*c*)

2*b* (0.33 g, 2 mmol) and oxybis(diphenylborane) (0.35 g, 1 mmol) are reacted as described above for **3*a***. Yield: 0.53 g (80%) of colorless needles[6], mp 125°C (decomp.). IR (KBr, cm^{-1}): 1 655 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 4.49 (m, O-CH_2), 4.84 (s, N-CH_2), 6.92 (s, N=CH), 7.02–7.45 (m, 15 aromatic H). Anal. calcd. for $C_{21}H_{20}BNO_2$: C 76.62, H 6.12, N 4.26; found: C 76.60, H 6.15, N 4.19.

4-Benzhydryl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*d*)

Hydroxyacetaldehyde (0.30 g, 5 mmol), *N*-benzhydrylhydroxylamine (1.00 g, 5 mmol), and oxybis (diphenylborane) (0.87 g, 2.5 mmol) are reacted as described for **3*b***. Yield: 1.05 g (52%) of colorless crystals[6], mp 126°C. IR (KBr, cm^{-1}): 1 638 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 4.60 (s, CH_2), 6.30 (s, N-CH), 7.00–7.67 (m, 20 aromatic H and N=CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.4 ($w_{1/2}$ = 257 Hz), 26.0, ratio of peak areas 20:1.[7] Anal. calcd. for $C_{27}H_{24}BNO_2$: C 80.00, H 5.97, B 2.67, N 3.46; found: C 80.08, H 6.04, B 2.68, N 3.34.

4-Cyclohexyl-2,2-di(4-chlorophenyl)-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*e*)

Hydroxyacetaldehyde (0.12 g, 2 mmol), *N*-cyclohexylhydroxylamine (0.23 g, 2 mmol), and di(4-chlorophenyl)borinic acid (11) (0.50 g, 2 mmol) are reacted as described for **3*b***. Yield: 0.55 g (71%) of colorless crystals[6], mp 141°C (decomp.). IR (KBr, cm^{-1}): 1 650 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.93–2.43 (m, $(CH_2)_5$), 3.73 (m, N-CH), 4.60 (s, CH_2), 7.00–7.53 (m, aromatic H and N=CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.7 ($w_{1/2}$ = 300 Hz). Anal. calcd. for $C_{20}H_{22}BCl_2NO_2$: C 61.58, H 5.68, B 2.77, N 3.59; found: C 61.58, H 5.71, B 2.80, N 3.37.

4-Cyclohexyl-2,2-di(1′-naphthyl)-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*f*)

Hydroxyacetaldehyde (0.12 g, 2 mmol), *N*-cyclohexylhydroxylamine (0.23 g, 2 mmol), and di(1′-naphthyl)borinic acid (12) (0.56 g, 2 mmol) are reacted as described for **3*b***. Yield: 0.66 g (78%) of colorless crystals[6], mp 153°C (decomp.). IR (KBr, cm^{-1}): 1 640 (C=N). ^{1}H NMR

[4] Recrystallization should be avoided because of a thermally induced rearrangement reaction with an aryl 1,4-shift leading to heterocyclic arylboronates.[5] Very careful recrystallization without thermal stress or reprecipitation from chloroform with petroleum ether at mild temperature is possible in some cases.

[5] W. Kliegel, G. Lubkowitz, J.O. Pokriefke, S.J. Rettig, and J. Trotter. To be published.

[6] The product gives a blue-colored solution upon the addition of diphenylcarbazone in ethanol, indicating the presence of the chelated diarylborenium (Ar_2B^+) ion (10).

[7] The signals with very small peak areas originate from impurities caused by thermally induced rearrangement of the type **3** compounds, resulting in heterocyclic arylboronates **3**′ (see discussion below).

(90 MHz, $CDCl_3$–TMS) δ (ppm): 0.87–2.27 (m, $(CH_2)_5$), 3.33 (m, N-CH), 4.17 (s, O-CH_2), 6.63 (s, N=CH), 7.00–8.13 (m, 12 aromatic H), 8.33–8.70 (m, 2 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 9.1 ($w_{1/2}$ = 514 Hz). Anal. calcd. for $C_{28}H_{28}BNO_2$: C 79.82, H 6.70, B 2.57, N 3.32; found: C 79.64, H 6.51, B 2.63, N 3.02.

4-Cyclohexyl-2,2-di[(2′, 2″-ethylene)phenyl]-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*g*)

Hydroxyacetaldehyde (0.24 g, 4 mmol), *N*-cyclohexylhydroxylamine (0.46 g, 4 mmol), and 5,5′-oxybis(10,11-dihydro-5*H*-dibenzo[b,f]borepin) (12) (0.18 g, 2 mmol) are reacted as described for **3*b***. Yield: 1.10 g (79%) of colorless crystals[6], mp 132°C. IR (KBr, cm^{-1}): 1 643 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.90–2.33 (m, $(CH_2)_5$), 3.23 (s, ar-CH_2CH_2-ar), 3.67 (m, N-CH), 4.43 (s, O-CH_2), 6.67–7.67 (m, 8 aromatic H and N=CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 3.6 ($w_{1/2}$ = 342 Hz). Anal. calcd. for $C_{22}H_{26}BNO_2$: C 76.09, H 7.55, B 3.11, N 4.03; found: C 76.27, H 7.58, B 3.22, N 3.77.

4,6-Dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*h*)

2*c* (0.41 g of the crude product, about 4 mmol) and oxybi(diphenylborane) (0.69 g, 2 mmol) are reacted as described for **3*a***. Yield: 0.80 g (75%) of colorless crystals[6], mp 113–114°C (decomp.). IR (KBr, cm^{-1}): 1 660 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.36 (d, J = 7 Hz, C-CH_3), 3.27 (s, N-CH_3), 4.40 (m, O-CH), 6.51 (s, N=CH), 6.88–7.40 (m, $B(C_6H_5)_2$). Anal. calcd. for $C_{16}H_{18}BNO_2$: C 71.94, H 6.79, B 4.05, N 5.24; found: C 71.99, H 6.82, B 4.05, N 5.21.

4-*tert*-Butyl-6-methyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*i*)

2*d* (0.58 g of the crude product, about 4 mmol) and oxybis(diphenylborane) (0.69 g, 2 mmol) are reacted as described for **3*a***. Yield: 1.10 g (89%) of colorless crystals[6], mp 106–107°C (decomp.). IR (KBr, cm^{-1}): 1 620 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.38 (d, J = 7 Hz, OC-CH_3), 1.56 (s, $C(CH_3)_3$), 4.72 (m, O-CH), 7.00–7.50 (m, $B(C_6H_5)_2$ and N=CH). Anal. calcd. for $C_{19}H_{24}BNO_2$: C 73.80, H 7.82, B 3.50, N 4.53; found: C 73.97, H 7.92, B 3.52, N 4.50.

4-Cyclohexyl-6-methyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*j*)

2*e* (0.34 g, 2 mmol) and oxybis(diphenylborane) (0.35 g, 1 mmol) are reacted as described for **3*a***. Yield: 0.51 g (76%) of colorless crystals[6], mp 117–118°C (decomp.). IR (KBr, cm^{-1}): 1 625 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.00–2.17 (m, $(CH_2)_5$), 1.44 (d, J = 7 Hz, CH_3), 3.57 (m, N-CH), 4.60 (q, J = 7 Hz, O-CH), 6.95 (s, N=CH), 7.00–7.53 (m, $B(C_6H_5)_2$). Anal. calcd. for $C_{21}H_{26}BNO_2$: C 75.24, H 7.82, N 4.18; found: C 75.03, H 7.87, N 4.32.

4-Benzyl-6-methyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*k*)

2*f* (0.36 g, 2 mmol) and oxybis(diphenylborane) (0.35 g, 1 mmol) are reacted as described for **3*a***. Yield: 0.59 g (86%) of slightly yellow crystals[6], mp 107–108°C (decomp.). IR (KBr, cm^{-1}): 1 635 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.38 (d, J = 7 Hz, CH_3), 4.53 (q, J = 7 Hz, O-CH), 4.74 (s, N-CH_2), 6.82 (s, N=CH), 6.97–7.44 (m, 15 aromatic H). ^1H NMR (400 MHz, $CDCl_3$–TMS) δ (ppm): 1.39 (d, J = 7 Hz, CH_3), 4.59 (q, J = 7 Hz, O-CH), 4.81 (q, AB system, N-CH_2), 6.88 (d, J = 1 Hz, N=CH), 7.07–7.49 (m, 15 aromatic H). Anal. calcd. for $C_{22}H_{22}BNO_2$: C 76.99, H 6.46, N 4.08; found: C 77.09, H 6.45, N 4.19.

4-Benzhydryl-6-methyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*l*) (·EtOH)

2*g* (0.51 g, 2 mmol) and oxybis(diphenylborane) (0.35 g, 1 mmol) are reacted as described for **3*a***. Yield: 0.85 g (91%) of slightly yellow plates[6], mp 86–90°C (decomp.). IR (KBr, cm^{-1}): 3 390 (broad, O-H), 1 650 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.22 (t, J = 7 Hz, CH_3 of ethanol), 1.48 (d, J = 7 Hz, CH_3), 3.66 (q, J = 7 Hz, O-CH_2 of ethanol), 4.73 (m, O-CH), 6.31 (s, N-CH), 7.06–7.50 (m, 20 aromatic H, N=CH, and OH of ethanol). Anal. calcd. for $C_{28}H_{26}BNO_2$ + C_2H_5OH: C 77.42, H 6.93, N 3.01; found: C 77.30, H 6.94, N 3.22.

4-Cyclohexyl-5-methyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*m*)

Hydroxyacetone (0.37 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are dissolved in 5 mL of absolute ethanol, if necessary under slight warming. A solution of *N*-cyclohexylhydroxylamine (0.58 g, 5 mmol) in 5 mL of ethanol is added without stirring, after precooling of both solutions. At –18°C, crystallization starts spontaneously or after rubbing with a glass stick. The crystals are filtered off and are washed rapidly with a small amount of ethanol and small portions of ether.[4] Yield: 0.52 g (32%) of colorless crystals[6], mp 156°C (decomp.). IR (KBr, cm^{-1}): 1 647 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.90–2.67 (m, $(CH_2)_5$), 1.83 (s, CH_3), 3.90 (m, N-CH), 4.50 (s, O-CH_2), 6.9 7.73 (m, $B(C_6H_5)_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.4 ($w_{1/2}$ = 257 Hz). Anal. calcd. for $C_{21}H_{26}BNO_2$: C 75.24, H 7.82, B 3.22, N 4.18; found: C 75.24, H 7.96, B 3.22, N 3.98.

4-Benzyl-5-methyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*n*)

Hydroxyacetone (0.37 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are dissolved in 5 mL of absolute ethanol, if necessary under slight warming. To a solution of *N*-benzylhydroxylamine hydrochloride (0.80 g, 5 mmol), triethylamine (0.51 g, 5 mmol) is added. Both solutions are cooled and mixed without stirring. Crystallization starts during storage at –18°C spontaneously or upon rubbing with a glass stick. The crystals are filtered off and washed rapidly with a small amount of ethanol and small portions of ether.[4] Yield: 1.3 g (66%) of colorless crystals[6], mp 118°C. IR (KBr, cm^{-1}): 1 654 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.93 (s, CH_3), 4.53 (s, O-CH_2), 5.07 (s, N-CH_2), 6.90–7.90 (m, 15 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.9 ($w_{1/2}$ = 257 Hz), 27.0, ratio of peak areas 10:1.[7] Anal. calcd. for $C_{22}H_{22}BNO_2$: C 76.99, H 6.46, B 3.15, N 4.08; found: C 76.48, H 6.31, B 3.07, N 3.88.

5-Methyl-4-(4′-methylphenyl)-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*o*)

Hydroxyacetone (0.37 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), and *N*-(4-methylphenyl)hydroxylamine (0.62 g, 5 mmol) are reacted as described for **3*m***. Yield: 0.85 g (50%) of colorless crystals[6], mp 113°C. IR (KBr, cm^{-1}): 1 636 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.70 (s, N=C-CH_3), 2.43 (s, aryl-CH_3), 4.73 (s, O-CH_2), 6.77–8.03 (m, 14 aromatic H)[8]. ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 7.6 ($w_{1/2}$ = 257 Hz), 29.2, ratio of peak areas 20:1.[7] Anal. calcd. for $C_{22}H_{22}BNO_2$: C 76.99, H 6.46, B 3.15, N 4.08; found: C 77.12, H 6.63, B 3.28, N 3.93.

4-Benzhydryl-5-ethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*p*)

1-Hydroxy-2-butanone (0.44 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), and *N*-benzhydrylhydroxylamine (1.00 g, 5 mmol) are reacted as described for **3*m***. Yield: 1.23 g (57%) of colorless crystals[6], mp 120°C. IR (KBr, cm^{-1}): 1 626 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.97 (t, J = 7 Hz, CH_3), 2.33 (q, J = 7 Hz, N=C-CH_2), 4.67 (s, O-CH_2), 6.50 (d, N-CH), 6.83–7.90 (m, 20 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 7.4 ($w_{1/2}$ = 257 Hz). Anal. calcd. for $C_{29}H_{28}BNO_2$: C 80.38, H 6.51, B 2.49, N 3.23; found: C 80.58, H 6.57, B 2.55, N 2.96.

4,5,6-Trimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*q*)

3-Hydroxy-2-butanone (0.44 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), *N*-methylhydroxylamine hydrochloride (0.42 g, 5 mmol), and triethylamine (0.51 g, 5 mmol) are reacted as described for **3*n***. Yield: 0.79 g (56%) of colorless crystals[6], mp 120°C. IR (KBr, cm^{-1}): 1 655 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.57 (t, J = 7 Hz, O-C-CH_3), 1.67 (s, N=C-CH_3), 3.47 (s, N-CH_3), 4.53 (q, J = 7 Hz, O-CH), 6.90–8.03 (m, B(C_6H_5)$_2$)[9]. ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.6 ($w_{1/2}$ = 214 Hz), 27.0, ratio of peak areas 20:1.[7] Anal. calcd. for $C_{17}H_{20}BNO_2$: C 72.62, H 7.17, B 3.85, N 4.98; found: C 72.65, H 7.28, B 3.86, N 4.84.

5,6-Dimethyl-2,2-diphenyl-4-propyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*r*)

3-Hydroxy-2-butanone (0.44 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), *N*-propylhydroxylamine hydrochloride (0.56 g, 5 mmol), and triethylamine (0.51 g, 5 mmol) are reacted as described for **3*n***. Yield: 0.79 g (51%) of colorless crystals[6], mp 115°C. IR (KBr, cm^{-1}): 1 637 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.97 (t, J = 7 Hz, N-C-C-CH_3), 1.57 (d, J = 7 Hz, O-C-CH_3), 1.63–2.30 (m, N-C-CH_2-C), 1.83 (s, N=C-CH_3), 3.73 (t, J = 7 Hz, N-CH_2), 4.33–4.60 (m, O-CH), 6.80–8.03 (m, B(C_6H_5)$_2$)[10]. ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 7.0 ($w_{1/2}$ = 214 Hz), 27.0, ratio of peak areas 20:1.[7] Anal. calcd. for $C_{19}H_{24}BNO_2$: C 73.80, H 7.82, B 3.50, N 4.53; found: C 73.84, H 7.99, B 3.53, N 4.40.

4-Isopropyl-5,6-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*s*)

3-Hydroxy-2-butanone (0.44 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), *N*-isopropylhydroxylamine hydrochloride (0.56 g, 5 mmol), and triethylamine (0.51 g, 5 mmol) are reacted as described for **3*n***. Yield: 0.99 g (64%) of colorless crystals[6], mp 133°C. IR (KBr, cm^{-1}): 1 625 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.30–1.67 (m, N-C(CH_3)$_2$ and O-C-CH_3), 1.83 (s, N=C-CH_3), 4.20 (sept, J = 7 Hz, N-CH), 4.36 (q, J = 7 Hz, O-CH), 6.80–7.70 (m, B(C_6H_5)$_2$)[10]. ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.2 ($w_{1/2}$ = 171 Hz). Anal. calcd. for $C_{19}H_{24}BNO_2$: C 73.80, H 7.82, B 3.50, N 4.53; found: C 73.86, H 7.98, B 3.49, N 4.80.

4-Cyclohexyl-5,6-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*t*)

Method A

2*h* (0.19 g, 1 mmol) and oxybis(diphenylborane) (0.17 g, 0.5 mmol) are reacted as described for **3*a***. Yield: 0.14 g (40%).

Method B

3-Hydroxy-2-butanone (0.44 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), and *N*-cyclohexylhydroxylamine (0.55 g, 5 mmol) are reacted as described for **3*m***. Yield: 1.10 g (63%) of colorless crystals[6], mp 132°C. IR (KBr, cm^{-1}): 1 614 (C=N). ^{1}H NMR 90 MHz, $CDCl_3$–TMS) δ (ppm): 0.93–2.57 (m, $(CH_2)_5$), 1.53 (d, J = 7 Hz, O-C-CH_3), 1.93 (s, N=C-CH_3), 3.87 (m, N-CH), 4.63 (q, J = 7 Hz, O-CH), 6.90–7.70 (m, B(C_6H_5)$_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.4 ($w_{1/2}$ = 257 Hz). Anal. calcd. for $C_{22}H_{28}BNO_2$: C 75.65, H 8.08, B 3.10, N 4.01; found: C 75.64, H 8.16, B 3.05, N 3.84.

4-Benzyl-5,6-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*u*)

3-Hydroxy-2-butanone (0.44 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), *N*-benzylhydroxylamine hydrochloride (0.80 g, 5 mmol), and triethylamine (0.51 g, 5 mmol) are reacted as described for **3*n***. Yield: 1.21 g (68%) of colorless crystals[6], mp 120°C. IR (KBr, cm^{-1}): 1 630 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.50 (d, J = 7 Hz, O-C-CH_3), 1.83 (s, N=C-CH_3), 4.40–4.70 (m, O-CH), 4.87/5.07 (d/d, AB system, J = 15 Hz, N-CH $_2$), 7.00–7.90 (m, 15 aromatic H)[11]. ^{1}H NMR (400 MHz, CD_3Cl_2–TMS, –17°C) δ (ppm): 1.53 (d, J = 7 Hz, O-C-CH_3), 1.93 (s, N=C-CH_3), 4.65 (q, J = 7 Hz, O-CH), 5.02/5.12 (d/d, AB system, J = 15 Hz, N-CH_2), 7.03–7.96 (m, 15 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 7.1 ($w_{1/2}$ = 214 Hz), 27.8, ratio of peak areas 5:1. Anal. calcd. for $C_{23}H_{24}BNO_2$: C 77.33, H 6.77, B 3.03, N 3.92; found: C 77.48, H 6.91, B 2.99, N 3.72.

[8] Additional small peaks at: 1.47 (s, N-C-CH_3), 2.77 (s, aryl-CH_3).[7]
[9] Additional small peaks at: 1.03 (d, J = 7 Hz, O-C-CH_3), 1.43 (s, N-C-CH_3), 2.50 (s, N-CH_3).[7]
[10] Additional small peaks at: 0.83 (t?, J = 7 Hz, N-C-C-CH_3), 1.40 (s, N-C-CH_3).[7]
[11] Additional small peaks at: 1.00 (d, J = 7 Hz, O-C-CH_3), 1.53 (s, N-C-CH_3), 3.63 (s, N- CH_2).[7]

4-Benzhydryl-5,6-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*v*)

3-Hydroxy-2-butanone (0.44 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), and *N*-benzhydrylhydroxylamine (1.00 g, 5 mmol) are reacted as described for **3*m***. Yield: 1.05 g (49%) of colorless crystals[6], mp 105°C (rearr.). MS (CI, NH_3, pos. mode, 90°C) *m/z*: 433 (26%, M^+), 434 (100%, $M^+ + H$). IR (KBr, cm^{-1}): 1 607 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.57 (d, *J* = 7 Hz, O-C-CH_3), 1.97 (s, N=C-CH_3), 4.37 (q, *J* = 7 Hz, O-CH), 6.40 (s, N-CH), 6.67–7.97 (m, $B(C_6H_5)_2$)[12]. ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.4 ($w_{1/2}$ = 257 Hz), 27.0, ratio of peak areas 10:1. Anal. calcd. for $C_{29}H_{28}BNO_2$: C 80.38, H 6.51, B 2.49, N 3.23; found: C 80.07, H 6.74, B 2.47, N 3.02.

2,2-Di(4′-chlorophenyl)-4-cyclohexyl-5,6-dimethyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*w*)

3-Hydroxy-2-butanone (0.18 g, 2 mmol), di(4-chlorophenyl)borinic acid (11) (0.5 g, 2 mmol), and *N*-cyclohexylhydroxylamine (0.23 g, 2 mmol) are reacted as described for **3*m***. Yield: 0.39 g (47%) of colorless crystals[6], mp 150°C. IR (KBr, cm^{-1}): 1 579 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.90–2.50 (m, $(CH_2)_5$), 1.50 (d, *J* = 7 Hz, O-C-CH_3), 1.97 (s, N=C-CH_3), 3.90 (m, N-CH), 4.57 (q, *J* = 7 Hz, O-C-CH_3), 7.00–7.50 (m, 8 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 5.7 ($w_{1/2}$ = 258 Hz). Anal. calcd. for $C_{22}H_{26}BCl_2NO_2$: C 63.19, H 6.27, B 2.59, N 3.35; found: C 63.21, H 7.03, B 2.64, N 3.14.

4-Benzhydryl-2,2-di(4-chlorophenyl)-5,6-dimethyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*x*)

3-Hydroxy-2-butanone (0.88 g, 10 mmol), di(4-chlorophenyl)borinic acid (11) (2.50 g, 10 mmol), and *N*-benzhydrylhydroxylamine (1.99 g, 10 mmol) are reacted as described for **3*m***. Yield: 2.42 g (48%) of colorless crystals[6], mp 130°C (rearr.). MS (CI, NH_3, pos. mode, 100°C) *m/z*: 502 (2%, M^+). IR (KBr, cm^{-1}): 1 578 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.57 (d, *J* = 7 Hz, O-C-CH_3), 2.10 (s, N=C-CH_3), 4.67 (q, *J* = 7 Hz, O-C-CH), 6.43 (s, N-CH), 6.63–7.90 (m, 18 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.9 ($w_{1/2}$ = 342 Hz). Anal. calcd. for $C_{29}H_{26}BCl_2NO_2$: C 69.35, H 5.22, B 2.15, Cl 14.12, N 2.79; found: C 69.29, H 5.20, B 2.28, Cl 14.22, N 2.71.

4-Cyclohexyl-5,6-dimethyl-2,2-di(1′-naphthyl)-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*y*)

3-Hydroxy-2-butanone (0.18 g, 2 mmol), di(1-naphthyl)borinic acid (11) (0.56 g, 2 mmol), and *N*-cyclohexylhydroxylamine (0.23 g, 2 mmol) are reacted as described for **3*m***. Yield: 0.51 g (57%) of colorless crystals[6], mp 157°C. IR (KBr, cm^{-1}): 1 625 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.87–2.42 (m, $(CH_2)_5$), 1.47 (d, *J* = 7 Hz, O-C-CH_3), 1.87 (s, N=C-CH_3), 3.93 (m, N-CH), 4.37 (q, *J* = 7 Hz, O-CH), 7.00–8.00 (m, 12 aromatic H), 8.43–8.87 (m, 2 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 9.2 ($w_{1/2}$ = 342 Hz). Anal. calcd. for $C_{30}H_{32}BNO_2$: C 80.18, H 7.18, B 2.41, N 3.12; found: C 80.21, H 7.25, B 2.45, N 3.00.

4-Cyclohexyl-5,6-tetramethylene-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*z*)

2-Hydroxycyclohexanone (0.57 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are dissolved in 10 mL of absolute ethanol under slight heating and stirring for a further 10 min. After cooling down to room temperature, a solution of *N*-cyclohexylhydroxylamine (0.58 g, 5 mmol) in 5 mL of absolute ethanol is added, and the mixture stored at room temperature. Crystallization starts spontaneously or upon cooling. The usually analytically pure crystals are filtered off after 1 h and can be recrystallized from ethanol. Yield: 1.20 g (64%) of colorless crystals[6], mp 151°C. IR (KBr, cm^{-1}): 1 619 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.00–2.90 (m, $(CH_2)_4$ and $(CH_2)_5$), 4.10 (m, N-CH), 4.47 (dd, *J* = 12 Hz, *J* = 7 Hz, O-CH), 6.83–7.67 (m, $B(C_6H_5)_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.1 ($w_{1/2}$ = 214 Hz). Anal. calcd. for $C_{24}H_{30}BNO_2$: C 76.81, H 8.06, B 2.88, N 3.73; found: C 76.87, H 8.24, B 2.87, N 3.56.

4-Benzyl-5,6-tetramethylene-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*aa*)

2-Hydroxycyclohexanone (0.57 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) in 10 mL of ethanol are reacted with *N*-benzylhydroxylamine hydrochloride (0.80 g, 5 mmol) and triethylamine (0.51 g, 5 mmol) in 5 mL of ethanol as described for **3*z***. Yield: 1.50 g (78%) of colorless crystals[6], mp 138°C. IR (KBr, cm^{-1}): 1 632 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.87–2.83 (m, $(CH_2)_4$), 4.40 (dd, *J* = 12 Hz, *J* = 6 Hz, O-CH), 5.03/5.17 (d/d, AB system, *J* = 15 Hz, N-CH_2), 6.87–7.87 (m, 15 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.1 ($w_{1/2}$ = 257 Hz). Anal. calcd. for $C_{25}H_{26}BNO_2$: C 78.34, H 6.84, B 2.82, N 3.65; found: C 78.31, H 6.88, B 2.88, N 3.48.

4-Benzhydryl-5,6-tetramethylene-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*bb*)

2-Hydroxycyclohexanone (0.57 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), and *N*-benzhydrylhydroxylamine (1.00 g, 5 mmol) are reacted as described for **3*z***. Yield: 1.50 g (65%) of colorless crystals[6], mp 144°C. IR (KBr, cm^{-1}): 1 610 (C=N/C=C). ^1H NMR (400 MHz, $CDCl_3$–TMS) δ (ppm): 0.94–2.91 (m, $(CH_2)_4$), 4.57 (dd, *J* = 12 Hz, *J* = 6 Hz, O-CH), 6.66 (s, N-CH), 6.90–7.82 (m, 20 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.9 ($w_{1/2}$ = 257 Hz). Anal. calcd. for $C_{31}H_{30}BNO_2$: C 81.05, H 6.58, B 2.35, N 3.05; found: C 81.08, H 6.63, B 2.39, N 2.79.

5,5-Tetramethylene-4-(4′-methylphenyl)-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexene (3*cc*)

2-Hydroxycyclohexanone (0.57 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), and *N*-(4-methylphenyl)hydroxylamine (0.62 g, 5 mmol) are reacted as described for **3*z***. Yield: 1.28 g (67%) of colorless crystals[6], mp 140°C. IR (KBr, cm^{-1}): 1 657 (C=N), 1625 (C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.00–2.90 (m, $(CH_2)_4$), 2.40 (s, CH_3), 4.63 (dd, *J* = 12 Hz, *J* = 6 Hz, O-CH), 6.90–7.80 (m, 14 aromatic

[12]Additional small peaks at: 0.90 (d, *J* = 7 Hz, O-C-CH_3), 0.97 (s, N-C-CH_3), 4.97 (s, N-CH)[7].

H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.3 ($w_{1/2}$ = 299 Hz). Anal. calcd. for $C_{25}H_{26}BNO_2$: C 78.34, H 6.84, B 2.82, N 3.65; found: C 78.87, H 7.01, B 2.89, N 3.48.

4,5-Dimethyl-2,2-diphenyl-1-oxa-3-azonia-2-borata-3-cyclopenten-3-ol (5*a*)

3-Hydroxy-2-butanonoxime (13) (0.52 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are dissolved separately in 5 mL of absolute ethanol each. The solutions are mixed at room temperature under continuous stirring. Crystallization commences after a few minutes, if necessary after slight cooling or addition of petroleum ether. The usually analytically pure substance can be recrystallized from ethanol. Yield: 1.02 g (76%) of colorless crystals[6], mp 170°C. IR (KBr, cm^{-1}): 2 598 (broad, O-H), 1 664 (C=N). ^{1}H NMR (90 MHz, DMSO-d_6–TMS) δ (ppm): 1.40 (d, J = 7 Hz, O-C-CH_3), 2.10 (s, N=C-CH_3), 4.83 (q, J = 7 Hz, O-CH), 6.80–7.80 (m, B(C_6H_5)$_2$), 11.93 (s, exchangeable, OH). ^{11}B NMR (64 MHz, DMSO-d_6–Et_2OBF_3) δ (ppm): 9.7 ($w_{1/2}$ = 385 Hz). Anal. calcd. for $C_{16}H_{18}BNO_2$: C 71.94, H 6.79, B 4.05, N 5.24; found: C 71.92, H 6.80, B 4.02, N 5.22.

4-Ethyl-2,2-diphenyl-1-oxa-3-azonia-2-borata-3-cyclopenten-3-ol (5*b*)

1-Hydroxy-2-butanonoxime (14) (0.52 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are reacted as described for **5*a***. Yield: 0.35 g (26%) of colorless crystals[6], mp 145°C. IR (KBr, cm^{-1}): 2 775 (broad, O-H), 1 668 (C=N). ^{1}H NMR (90 MHz, DMSO-d_6–TMS) δ (ppm): 1.10 (t, J = 7 Hz, CH_3), 2.57 (q, J = 7 Hz, N=C-CH_2), 4.73 (s, O-CH_2), 7.00–8.00 (m, B(C_6H_5)$_2$), 11.9 (s, exchangeable, OH). ^{11}B NMR (64 MHz, DMSO-d_6–Et_2OBF_3) δ (ppm): 10.1 ($w_{1/2}$ = 470 Hz). Anal. calcd. for $C_{16}H_{18}BNO_2$: C 71.94, H 6.79, B 4.05, N 5.24; found: C 71.98, H 6.90, B 3.99, N 5.20.

4,5-Tetramethylene-2,2-diphenyl-1-oxa-3-azonia-2-borata-3-cyclopenten-3-ol (5*c*)

2-Hydroxycyclohexanonoxime (15) (0.39 g, 3 mmol) and oxybis(diphenylborane) (0.52 g, 1.5 mmol) are reacted as described for **5*a***. Yield: 0.71 g (81%) of colorless crystals[6], mp 180°C. IR (KBr, cm^{-1}): 2 472 (broad, O-H), 1 674 (C=N). ^{1}H NMR (90 MHz, DMSO-d_6–TMS) δ (ppm): 1.00–3.23 (m, $(CH_2)_4$), 4.60 (m, O-CH), 7.00–7.83 (m, B(C_6H_5)$_2$), 11.83 (s, exchangeable, OH). ^{11}B NMR (64 MHz, DMSO-d_6–Et_2OBF_3) δ (ppm): 10.2 ($w_{1/2}$ = 470 Hz). Anal. calcd. for $C_{18}H_{20}BNO_2$: C 73.75, H 6.88, B 3.69, N 4.78; found: C 73.67, H 6.99, B 3.69, N 4.74.

2,2,4,5-Tetraphenyl-1-oxa-3-azonia-2-borata-3-cyclopenten-3-ol (5*d*)

α-Benzoinoxime (commercial product "Cupron") (0.23 g, 1 mmol) and oxybis(diphenylborane) (0.17 g, 0.5 mmol) are reacted as described for **5*a***. Yield: 0.32 g (82%) of colorless crystals[6], mp 170°C. IR (KBr, cm^{-1}): 2 734 (broad, O-H), 1 637 (C=N), 1596 (C=C). ^{1}H NMR (90 MHz, DMSO-d_6–TMS) δ (ppm): 6.53 (s, O-CH), 6.93–7.90 (m, 20 aromatic H), 12.77 (s, exchangeable, OH). ^{11}B NMR (64 MHz, DMSO-d_6–Et_2OBF_3) δ (ppm): 8.0. Anal. calcd. for $C_{26}H_{22}BNO_2$: C 79.81, H 5.67, B 2.76, N 3.58; found: C 97.91, H 5.70, B 2.89, N 3.42. Single crystals suitable for X-ray crystallographic analysis were obtained by very slow crystallization from absolute ethanol.

3-(Methylimino)-2,2-dimethylpropanol *N*-oxide (8*a*)

3-Hydroxy-2,2-dimethylpropanal (16) (1.02 g, 10 mmol), *N*-methylhydroxylamine hydrochloride (0.84 g, 10 mmol), and K_2CO_3 (0.7 g) are suspended in 10 mol of water and stirred for 10 min. After addition of 20 mL of benzene the mixture is refluxed using a Dean–Stark trap for continuous removal of water. After 5 h, the precipitated KCl is filtered off and the solvents removed in vacuo. The oily residue is purified by destillation in vacuo. Yield: 0.61 g (47%) of slightly orange oil, bp 135°C/5 torr (1 torr = 133 Pa). MS (CI, NH_3, pos. mode) *m*/*z*: 132 (100%, M^+ + H). IR (NaCl, film, cm^{-1}): 3 323 (broad, O-H), 1 606 (C=N). ^{1}H NMR ($CDCl_3$–TMS) δ (ppm): 1.23 (s, C(CH_3)$_2$), 3.63 (s, O-CH_2), 3.70 (s, N-CH_3), 4.57 (s, broad, exchangeable, OH), 6.53 (s, N=CH). Anal. calcd. for $C_6H_{13}NO_2$: C 54.94, H 9.99, N 10.86; found: C 54.92, H 9.84, N 10.10.

3-(Propylimino)-2,2-dimethylpropanol *N*-oxide (8*b*)

3-Hydroxy-2,2-dimethylpropanol (1.02 g, 10 mmol), *N*-propylhydroxylamine hydrochloride (0.12 g, 10 mmol), and K_2CO_3 (0.7 g) are reacted as described for **8*a***. Yield: 0.75 g (47%) of a slightly yellow oil, bp 142°C/10 torr (1 torr = 133 Pa). MS (CI, NH_3, pos. mode) *m*/*z*: 160 (100%, M^+ + H). IR (NaCl, film, cm^{-1}): 3 338 (broad, O-H), 1 595 (C=N). ^{1}H NMR ($CDCl_3$–TMS) δ (ppm): 0.97 (t, J = 6 Hz, N-C-C-CH_3), 1.27 (s, C(CH_3)$_2$), 1.67–2.20 (m, N-C-CH_2), 3.57 (s, O-CH_2), 3.73 (t, J = 6 Hz, N-CH_2), 6.00 (s, broad, exchangeable, OH), 6.60 (s, N=CH). Anal. calcd. for $C_8H_{17}NO_2$: C 60.35, H 10.76, N 8.80; found: C 60.42, H 10.26, N 8.49.

3-(Cyclohexylimino)-2,2-dimethylpropanol *N*-oxide (8*c*)

3-Hydroxy-2,2-dimethylpropanal (1.02 g, 10 mmol) and *N*-cyclohexylhydroxylamine are refluxed in 20 mL of benzene using a Dean–Stark trap for continuous removal of water. After 5 h, the solvent is distilled off and the remaining orange-colored oil is dissolved in a small amount of ethanol. Crystallization is achieved upon cooling and addition of *n*-hexane. Yield: 1.30 g (66%) of colorless crystals, mp 72°C (from EtOH–hexane). IR (KBr, cm^{-1}): 3 284 (broad, O-H), 1 595 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.57–2.33 (m, $(CH_2)_5$), 1.23 (s, C(CH_3)$_2$), 3.40–3.87 (m, N-CH), 3.60 (d, J = 6 Hz, O-CH_2), 6.07 (t, J = 6 Hz, broad, exchangeable, OH), 6.53 (s, N=CH). Anal. calcd. for $C_{11}H_{21}NO_2$: C 66.30, H 10.62, N 7.03; found: C 66.29, H 10.61, N 6.82.

3-(Benzylimino)-2,2-dimethylpropanol *N*-oxide (8*d*)

3-Hydroxy-2,2-dimethylpropanal (2.04 g, 20 mmol), *N*-benzylhydroxylamine hydrochloride (3.19 g, 20 mmol), and K_2CO_3 (1.40 g) are reacted as described for **8*a***. After the refluxing, about two-thirds of the benzene is distilled off and crystallization is achieved by addition of ether. Yield: 1.77 g (43%) of colorless crystals, mp 98°C (from benzene–ether). IR (KBr, cm^{-1}): 3 243 (broad, O-H), 1 600 (C=N/C=C). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.23

(s, $C(CH_3)_2$), 3.63 (d, J = 6 Hz, O-CH_2), 4.87 (s, N-CH_2), 5.70 (t, J = 6 Hz, exchangeable, OH), 6.53 (s, N=CH), 7.43 (s, C_6H_5). Anal. calcd. for $C_{12}H_{17}NO_2$: C 69.54, H 8.27, N 6.76; found: C 69.52, H 8.27, N 6.67.

3-(Benzhydrylimino)-2,2-dimethylpropanol *N*-oxide (8*e*)

3-Hydroxy-2,2-dimethylpropanal (1.02 g, 10 mmol) and *N*-benzhydrylhydroxylamine (1.99 g, 10 mmol) are reacted as described for **8*c***. After the refluxing about two-thirds of the benzene is distilled off and crystallization is achieved upon cooling and addition of petroleum ether. Yield: 1.84 g (65%) of colorless crystals, mp 123°C (from abs ethanol–petroleum ether). IR (KBr, cm^{-1}): 3 400 (broad, O-H), 1 587 (C=N/C=C). ^{1}H NMR (90 MHz, $CDCl_3$-TMS), δ (ppm): 1.20 (s, $C(CH_3)_2$), 3.63 (d, J = 6 Hz, O-CH_2), 5.67 (t, J = 6 Hz, exchangeable, OH), 6.20 (s, N-CH), 6.57 (s, N=CH), 7.37 (s, $C(C_6H_5)_2$). Anal. calcd. for $C_{18}H_{21}NO_2$: C 76.30, H 7.47, N 4.94; found: C 76.31, H 7.46, N 4.71.

4,6,6-Trimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cycloheptene (9*a*)

Solutions of **8*a*** (0.13 g, 1 mmol) in 1 mL of ethanol and of oxybis(diphenylborane) (0.17 g, 0.5 mmol) in 1 mL of ethanol are mixed under stirring at room temperature. Crystallization commences usually after a few minutes or upon cooling and rubbing with a glass stick. If necessary the substance can be recrystallized from absolute ethanol. Yield: 0.21 g (71%) of colorless crystals[6], mp 176°C. IR (KBr, cm^{-1}): 1 664 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.27 (s, $C(CH_3)_2$), 3.03 (s, N-CH_3), 3.70 (s, O-CH_2), 6.80 (s, N=CH), 7.00–7.97 (m, $B(C_6H_5)_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 10.6 ($w_{1/2}$ = 257 Hz). Anal. calcd. for $C_{18}H_{22}BNO_2$: C 73.24, H 7.51, B 3.66, N 4.57; found: C 73.37, H 7.53, B 3.77, N 4.67. Single crystals suitable for X-ray crystallographic analysis were obtained by very slow crystallization from ethanol.

6,6-Dimethyl-2,2-diphenyl-4-propyl-1,3-dioxa-4-azonia-2-borata-4-cycloheptene (9*b*)

8*b* (0.16 g, 1 mmol) and oxybis(diphenylborane) (0.17 g, 0.5 mmol) are reacted as described for **9*a***. Yield: 0.22 g (68%) of colorless crystals[6], mp 170°C. IR (KBr, cm^{-1}): 1 655 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.77 (t, J = 6 Hz, N-C-C_3), 1.27 (s, $C(CH_3)_2$), 1.47–1.97 (m, N-C-CH_2), 3.10 (t, J = 6 Hz, N-CH_2), 3.73 (s, O-CH), 6.90 (s, N=CH), 7.00–7.90 (m, $B(C_6H_5)_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 10.3 ($w_{1/2}$ = 257 Hz), 44.6, ratio of peak areas 10:1.[13] Anal. calcd. for $C_{20}H_{26}BNO_2$: C 74.32, H 8.11, B 3.34, N 4.33; found: C 74.20, H 8.10, B 3.40, N 4.17.

4-Cyclohexyl-6,6-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cycloheptene (9*c*)

8*c* (0.20 g, 2 mmol) and oxybis(diphenylborane) (0.35 g, 1 mmol) are reacted as described for **9*a***. Yield: 0.64 g (88%) of colorless crystals[6], mp 178°C. IR (KBr, cm^{-1}): 1 636 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.67–2.27 (m, $(CH_2)_5$), 1.30 (s, $C(CH_3)_2$), 2.97 (m, N-CH), 3.77 (s, O-CH_2), 6.93 (s, N=CH), 7.07–8.00 (m, $B(C_6H_5)_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 10.6 ($w_{1/2}$ = 342 Hz), 46.7, ratio of peak areas 10:1.[13] Anal. calcd. for $C_{23}H_{30}BNO_2$: C 76.06, H 8.32, B 2.98, N 3.86; found: C 76.22, H 8.36, B 3.05, N 3.66.

4-Benzyl-6,6-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cycloheptene (9*d*)

8*d* (0.42 g, 2 mmol) and oxybis(diphenylborane) (0.35 g, 1 mmol) are reacted as described for **9*a***. Yield: 0.73 g (98%) of colorless crystals[6], mp 174°C. IR (KBr, cm^{-1}): 1 652 (C=N), 1 605 (C=C). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.23 (s, $C(CH_3)_2$), 3.77 (s, O-CH_2), 4.27 (s, N-CH_2), 6.73 (s, N=CH), 6.93–8.00 (m, 15 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 10.7 ($w_{1/2}$ = 258 Hz), 47.3, ratio of peak areas 10:1.[13] Anal. calcd. for $C_{24}H_{26}BNO_2$: C 77.64, H 7.06, B 2.91, N 3.77; found: C 77.75, H 7.21, B 3.01, N 3.69.

4-Benzhydryl-6,6-dimethyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cycloheptene (9*e*)

8*e* (0.57 g, 2 mmol) and oxybis(diphenylborane) (0.35 g, 1 mmol) are reacted as described for **9*a***. Yield: 0.76 g (85%) of colorless crystals[6], mp 168°C. IR (KBr, cm^{-1}): 1 664 (C=N), 1 586 (C=C). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.30 (s, $C(CH_3)_2$), 3.83 (s, O-CH_2), 5.60 (s, N-CH), 6.67–8.00 (m, 20 aromatic H and N=CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 10.5 ($w_{1/2}$ = 342 Hz), 46.0, ratio of peak areas 10:1.[13] Anal. calcd. for $C_{30}H_{30}BNO_2$: C 80.54, H 6.76, B 2.42, N 3.13; found: C 80.37, H 6.80, B 2.49, N 2.91.

5,5-Dimethyl-2,2-diphenyl-1-oxa-3-azonia-2-borata-3-cyclohexen-3-ol (11*a*)

3-Hydroxy-2,2-dimethylpropionaldoxime (16) (0.12 g, 1 mmol) and oxybis(diphenylborane) (0.17 g, 0.5 mmol) are reacted as described for **5*a***. Yield: 0.25 g (89%) of colorless crystals[6], mp 165°C (from ethanol). IR (KBr, cm^{-1}): 2 566 (broad, O-H), 1 638 (C=N). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.30 (s, $C(CH_3)_2$), 3.57 (s, O-CH_2), 7.13–7.67 (m, 1 H exchangeable, OH and $B(C_6H_5)_2$, and N=CH). ^{1}H NMR (400 MHz, $CDCl_3$–TMS) δ (ppm): 1.30 (s, $C(CH_3)_2$), 3.53 (s, O-CH_2), 7.13 (m, exchangeable, OH), 7.23–7.57 (m, $B(C_6H_5)_2$), 7.60 (s, N=CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 4.00 ($w_{1/2}$ = 257 Hz). Anal. calcd. for $C_{17}H_{20}BNO_2$: C 72.62, H 7.17, B 3.84, N 4.98; found: C 72.67, H 7.22, B 3.98, N 4.84.

2,2-Di(4′-methoxyphenyl)-5,5-dimethyl-1-oxa-3-azonia-2-borata-3-cyclohexen-3-ol (11*b*)

3-Hydroxy-2,2-dimethylpropionaldoxime (16) (0.23 g, 2 mmol) and di(4-methoxyphenyl)-borinic acid (obtained from the 2-aminoethyl ester (19) by hydrolysis (11)) (0.48 g, 2 mmol) are reacted as described for **5*a***. Yield: 0.33 g (49%)

[13]Side signals with a small peak area at about 46 ppm have also been observed in the ^{11}B NMR spectra of diphenylboron chelates from other nitrone ligands (17) indicating a trivalent (sp^2) boron atom of a Ph_2B-O-R species (18). It is not yet clear whether the signal originates from an open-chain diphenylborinate (scission of the nitrone O-B coordination in **9**), or from free diphenylborinic acid caused by partial solvolysis.

of colorless crystals[6], mp 128°C (from ethanol). IR (KBr, cm^{-1}): 2 517 (broad, O-H), 1 640 (C=N), 1 599 (C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.27 (s, $C(CH_3)_2$), 3.60 (s, O-CH_2-C), 6.67–8.00 (m, 1 H exchangeable, OH and N=CH, and 8 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 9.9 ($w_{1/2}$ = 342 Hz). Anal. calcd. for $C_{19}H_{24}BNO_4$: C 66.88, H 7.09, B 3.17, N 4.11; found: C 66.81, H 7.15, B 3.28, N 3.95. Single crystals suitable for X-ray crystallography were obtained by very slow crystallization from absolute ethanol.

4,5-Dimethyl-2,2-diphenyl-1-oxa-3-azonia-2-borata-3-cyclohexen-3-ol (11*c*)

4-Hydroxy-3-methyl-2-butanonoxime (15) (0.59 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are reacted as described for **5*a***. Instead of petroleum ether, diethyl ether is added to initiate the crystallization. Yield: 0.85 g (58%) of colorless crystals[6], mp 151°C (from ethanol–ether). IR (KBr, cm^{-1}): 2 691 (broad, O-H), 1 638 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.40 (d, J = 7 Hz, N=C-C-CH_3), 2.23 (s, N=C-CH_3), 2.40–3.00 (m, X of ABX system, N=C-CH), 3.47/3.90 (m/m, AB of ABX system, O-CH_2), 7.07 (s, broad, exchangeable, OH), 7.20–7.67 (m, $B(C_6H_5)_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.6 ($w_{1/2}$ = 235 Hz). Anal. calcd. for $C_{17}H_{20}BNO_2$: C 72.62, H 7.17, B 3.84, N 4.98; found: C 72.66, H 7.16, B 3.87, N 4.85.

4,6,6-Trimethyl-2,2-diphenyl-1-oxa-3-azonia-2-borata-3-cyclohexen-3-ol (11*d*)

4-Hydroxy-4-methyl-2-pentanonoxime (20) (0.66 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are reacted as described for **5*a***. Yield: 0.60 g (41%) of colorless crystals[6], mp 124°C (from ethanol). IR (KBr, cm^{-1}): 2 702 (broad, O-H), 1 650 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.37 (s, $C(CH_3)_2$), 2.30 (s, N=C-CH_3), 2.50 (s, N=C-CH_2-C), 7.10–7.90 (m, 1 H exchangeable, OH and $B(C_6H_5)_2$). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 6.2 ($w_{1/2}$ = 128 Hz). Anal. calcd. for $C_{18}H_{22}BNO_2$: C 73.24, H 7.51, B 3.66, N 4.75; found: C 73.27, H 7.65, B 3.71, N 4.58.

(Methylimino)acetic acid *N*-oxide (16*a*)

Method A

Glyoxylic acid monohydrate (0.46 g, 5 mmol), dried $MgSO_4$ (0.60 g), *N*-methylhydroxylamine hydrochloride (0.42 g, 5 mmol), and triethylamine (0.51 g, 5 mmol) are refluxed in 50 mL of ether for 5 min. The solid residue is filtered off and extracted several times with boiling ether. The combined ether solutions are partially evaporated and, if necessary, cooled for crystallization. Yield: 0.12 g (24%) of colorless crystals, mp 78°C (from ether). IR (KBr, cm^{-1}): 2 600–2 000 ("curtain," O-H assoc.), 1 711 (C=O), 1 580 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 3.93 (s, CH_3), 7.43 (s, N=CH), 14.67 (s, very broad, exchangeable, OH). Anal. calcd. for $C_3H_5NO_3$: C 34.96, H 4.89, N 13.59; found: C 34.72, H 4.87, N 13.32.

Method B

Large quantities (up to 40 mmol) can be prepared advantageously also by the procedure described in the literature (21) for **16*d*** (see below), which gives better yields, but requires more time.

(*tert*-Butylimino)acetic acid *N*-oxide (16*b*)

Method A, as described above for **16*a***, is applied for *N*-*tert*-butylhydroxylamine (0.45 g, 5 mmol), without triethylamine in *n*-hexane as the solvent. Yield: 0.58 g (68%) of colorless crystals, mp 62°C (from hexane). IR (KBr, cm^{-1}): 2 600–2 170 (curtain, O-H assoc.), 1 703 (C=O), C=N band not identified. ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.60 (s, $C(CH_3)_3$), 7.47 (s, N=CH), 14.63 (s, broad, exchangeable, OH). Anal. calcd. for $C_6H_{11}NO_3$: C 49.65, H 7.64, N 9.65; found: C 49.42, H 7.73, N 9.42.

(Cyclohexylimino)acetic acid *N*-oxide (16*c*)

Method A, as described above for **16*b***, is applied for *N*-cyclohexylhydroxylamine (0.58 g, 5 mmol). Yield: 0.46 g (54%) of colorless crystals, mp 87°C (from hexane). IR (KBr, cm^{-1}): 2 500–2 340 (curtain, OH assoc.), 1 727/1 699 (C=O), 1 609 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.00–2.37 (m, $(CH_2)_5$), 3.90 (m, N=CH), 7.43 (s, N=CH), 14.77 (s, broad, exchangeable, OH). Anal. calcd. for $C_8H_{13}NO_3$: C 56.13, H 7.65, N 8.18; found: C 56.02, H 7.80, N 8.05.

(Benzylimino)acetic acid *N*-oxide (16*d*)

The compound was prepared as described in the literature (21), using *N*-benzylhydroxylamine hydrochloride and triethylamine in equimolar amounts.

4-Methyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*a*)

Method A

16*a* (0.21 g, 2 mmol) in 5 mL of absolute ethanol and oxybis(diphenylborane) (0.35 g, 1 mmol) in 5 mL of absolute ethanol are mixed. Under stirring at room temperature crystallization commences. After complete precipitation, the crystals are washed with 3 × 5 mL of warm ether. Yield: 0.40 g (75%) of colorless crystals[6], mp 114°C.[14] IR (KBr, cm^{-1}): 1 719/1 705 (C=O), 1 602 (C=N/C=C). ^1H NMR (90 MHz, DMSO-d_6–TMS) δ (ppm): 3.97 (s, CH_3), 7.00–8.00 (m, $B(C_6H_5)_2$), 8.53 (s, N=CH). A ^{11}B NMR spectrum could not be obtained because of poor solubility. Anal. calcd. for $C_{15}H_{14}BNO_3$: C 67.45, H 5.28, B 4.05, N 5.24; found: C 67.26, H 5.26, B 4.06, N 5.03.

Method B

Glyoxylic acid monohydrate (0.46 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are dissolved in 5 mL of absolute ethanol under stirring at room temperature for 5 min. A solution of *N*-methylhydroxylamine hydrochloride (0.42 g, 5 mmol) and triethylamine (0.51 g, 5 mmol) in 5–10 mL of ethanol is added and stirred briefly for homogenization. Yield: 1.00 g (75%) of colorless crystals as described for method A.

[14]The usually analytical pure compound rearranges under thermal stress in solution[5]; therefore, recrystallization was not possible.

4-*tert*-Butyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*b*)

16*b* (0.58 g, 4 mmol) and oxybis(diphenylborane) (0.70 g, 2 mmol) are reacted as described for **17*a*** (method A). Yield: 0.95 g, (77%) of colorless crystals[6], mp 132°C[14]. IR (KBr, cm^{-1}): 1 703 (C=O), 1 605 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 1.47 (s, $C(CH_3)_3$), 7.00 – 7.60 (m, $B(C_6H_5)_2$), 7.70 (s, N=CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 10.5 ($w_{1/2}$ = 300 Hz), 30.0, ratio of peak areas 40:1.[15] Anal. calcd. for $C_{18}H_{20}BNO_3$: C 69.93, H 6.52, B 3.50, N 4.53; found: C 69.93, H 6.50, B 3.60, N 4.36. The compound is also available by a three component reaction of equimolar amounts of glyoxylic acid, *N*-*tert*-butylhydroxylamine, and diphenylborinic acid (method B as described for **17*a***, omitting triethylamine).

4-Cyclohexyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*c*)

16*c* (0.34 g, 2 mmol) and oxybis(diphenylborane) (0.35 g, 1 mmol) are reacted as described for **17*a*** (method A). Yield: 0.21 g, (32%) of colorless crystals[6], mp 121°C[14]. IR (KBr, cm^{-1}): 1 706 (C=O), 1 603 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.80–2.33 (m, $(CH_2)_5$), 3.73 (m, N-CH), 7.00–7.67 (m, $B(C_6H_5)_2$ and N=CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 10.3 ($w_{1/2}$ = 385 Hz), 30.1, ratio of peak areas 40:1[15]. Anal. calcd. for $C_{20}H_{22}BNO_3$: C 71.66, H 6.62, B 3.23, N 4.18; found: C 71.69, H 6.64, B 3.35, N 4.00. The compound is also available by a three component reaction of equimolar amounts of glyoxylic acid, *N*-cyclohexylhydroxylamine, and diphenylborinic acid (method B as described for **17*a***, omitting triethylamine).

4-Benzyl-2,2-diphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*d*)

16*d* (0.18 g, 1 mmol) and oxybis(diphenylborane) (0.17 g, 0.5 mmol) are reacted analogous as described for **17*a*** (method A). Yield: 0.16 g, (47%) of colorless crystals[6], mp 199°C[13]. IR (KBr, cm^{-1}): 1 719 (C=O), 1 615 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 4.87 (s, N-CH_2), 6.67–7.73 (m, aromatic H and N=CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ: C 73.50, H 5.29, B 3.15, N 4.08; found: C 73.20, H 5.39, B 3.16, N 4.12. The compound is also available by a three component reaction of equimolar amounts of glyoxylic acid, *N*-benzylhydroxylamine (hydrochloride + triethylamine), and diphenylborinic acid (method B as described for **17*a***).

4-Benzyl-2,2-di(4′-chlorophenyl)-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*e*)

16*d* (0.36 g, 2 mmol) and di(4-chlorophenyl)borinic acid (11) (0.50 g, 2 mmol) are reacted as described for **17*a*** (method A). Yield: 0.45 g, (55%) of colorless crystals[6], mp 113°C[14]. IR (KBr, cm^{-1}): 1 709 (C=O), 1 616 (C=N). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 4.93/5.13 (d/d, J = 15 Hz, AB system, N-CH_2), 6.67–8.00 (m, 13 aromatic H and N-CH). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 11.6 ($w_{1/2}$ = 684 Hz), 31.3, ratio of peak areas 50:1.[15] Anal. calcd. for $C_{21}H_{16}BCl_2NO_3$: C 61.21, H 3.91, B 2.62, N 3.40; found: C 61.13, H 3.85, B 2.90, N 3.30. The compound is also available by a three component reaction of glyoxylic acid, *N*-benzylhydroxylamine (hydrochloride + triethylamine), and di(4-chlorophenyl)borinic acid (method B as described for **17*a***).

4-Methyl-2,2,5-triphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*f*)

Phenylglyoxylic acid (0.75 g, 5 mmol) and oxybis(diphenylborane) (0.87 g, 2.5 mmol) are dissolved in 5 mL of absolute ethanol under stirring. After addition of a solution of *N*-methylhydroxylamine hydrochloride (0.42 g, 5 mmol) and triethylamine (0.51 g, 5 mmol) in 5 mL of ethanol and short heating, crystallization of the analytically pure product starts, at room temperature, eventually after cooling. Yield: 1.52 g, (89%) of colorless crystals[6], mp 132°C (from ethanol). IR (KBr, cm^{-1}): 1 711 (C=O), 1 594 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 3.60 (s, CH_3), 6.80–7.83 (m, 15 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 10.2 ($w_{1/2}$ = 214 Hz). Anal. calcd. for $C_{21}H_{18}BNO_3$: C 73.50, H 5.29, B 3.15, N 4.08; found: C 73.45, H 5.36, B 3.33, N 3.90.

2,2,5-Triphenyl-4-propyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*g*)

Phenylglyoxylic acid (0.75 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), *N*-propylhydroxylamine hydrochloride (0.56 g, 5 mmol), and triethylamine (0.51 g, 5 mmol) are reacted as described for **17*f***. Yield: 0.66 g, (36%) of colorless crystals[6], mp 117°C (from ethanol). IR (KBr, cm^{-1}): 1 717 (C=O), 1 594 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.80 (t, J = 7 Hz, CH_3), 1.67–2.17 (m, N-C-CH_2), 3.70 (t, J = 7 Hz, N-CH_2), 6.80–7.73 (m, 15 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 11.1 ($w_{1/2}$ = 257 Hz). Anal. calcd. for $C_{23}H_{22}BNO_3$: C 74.41, H 5.97, B 2.91, N 3.77; found: C 74.33, H 5.97, B 2.96, N 3.80.

4-Cyclohexyl-2,2,5-triphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*h*)

Phenylglyoxylic acid (0.75 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), and *N*-cyclohexylhydroxylamine (0.58 g, 5 mmol) are reacted as described for **17*f***, omitting triethylamine. Yield: 1.34 g, (65%) of colorless crystals[6], mp 139°C (from ethanol). IR (KBr, cm^{-1}): 1 719 (C=O), 1 586 (C=N/C=C). ^1H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 0.83–2.67 (m, $(CH_2)_5$), 3.73 (m, N-CH), 6.70–7.87 (m, 15 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 9.2 ($w_{1/2}$ = 342 Hz). Anal. calcd. for $C_{26}H_{26}BNO_3$: C 75.93, H 6.37, B 2.63, N 3.41; found: C 75.82, H 6.36, B 2.57, N 3.27.

4-Benzyl-2,2,5-triphenyl-1,3-dioxa-4-azonia-2-borata-4-cyclohexen-6-one (17*i*)

Phenylglyoxylic acid (0.75 g, 5 mmol), oxybis(diphenylborane) (0.87 g, 2.5 mmol), *N*-benzyhlhydroxylamine hydrochloride (0.80 g, 5 mmol), and triethylamine (0.51 g, 5 mmol) are reacted as described for **17*f***. Yield: 1.31 g, (63%) of colorless crystals[6], mp 112°C (from ethanol). IR (KBr, cm^{-1}): 1 713 (C=O), 1 596 (C=N/C=C). ^1H NMR

[15]The signal with very small peak area originates from impurities caused by a thermally induced rearrangement reaction.[5]

Table 1. Crystallographic data.[a]

Compound	**5*d***	**9*a***	11***b***	19
Formula	$C_{26}H_{22}BNO_2$	$C_{18}H_{22}BNO_2$	$C_{19}H_{24}BNO_4$	$C_{20}H_{16}BNO_3$
fw	391.28	295.19	341.21	329.16
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a (Å)	10.543(2)	10.9913(5)	11.227(2)	11.1847(15)
b (Å)	19.085(4)	14.9329(7)	9.967(2)	13.715(3)
c (Å)	10.2667(3)	10.2460(13)	17.0537(4)	11.5559(5)
β (°)	90.4978(7)	90	105.4179(5)	104.8730(10)
V (Å^3)	2065.6(4)	1681.7(2)	1839.7(3)	1713.2(3)
Z	4	4	4	4
ρ_{calc} (g/cm^3)	1.258	1.166	1.232	1.276
F(000)	824	632	728	688
Radiation	Mo	Mo	Mo	Mo
μ (cm^{-1})	0.78	0.74	0.85	0.85
Size (mm)	0.25 0.3 0.4	0.25 0.35 0.4	0.3 0.35 0.4	0.35 0.4 0.5
Corr. factors[b]	0.83–1.00	0.79–1.00	0.86–1.00	0.84–1.00
φ range (χ = –90°)	0–190	0–190	0–190	0–190
ω range (χ = –90°)	–23–18	–23–18	–22–18	–22–18
Osc. width (deg)	0.5	0.5	0.5	0.5
Images, time	462, 80 s	462, 80 s	460, 60 s	460, 90 s
$2\theta_{max}$ (deg)	60.1	60.1	60.0	60.4
Total reflections	19617	15953	17151	15767
Unique reflections	5150	4438 [c]	4331	3996
R_{merge}	0.069	0.069	0.040	0.025
No. with $I \geq 3\sigma(I)$	3392	3338	2807	2739
No. of variables	359	287	322	287
R (F) ($I \geq 3\sigma(I)$)	0.049	0.047	0.042	0.047
R_w (F^2) (all data)	0.128	0.111	0.085	0.095
gof	1.27	1.16	2.07	2.72
Max Δ/σ (final cycle)	0.0003	0.006	0.0003	0.0004
Residual density (e/Å^3)	–0.50–0.46	–0.49–0.46	–0.34–0.36	–0.29–0.32

[a]Temperature 180 K, Rigaku/ADSC CCD diffractometer, Mo K_a (l = 0.71069 Å), graphite monochromator, takeoff angle 6.0°, aperture 94.0 × 94.0 mm at a distance of 39.2 mm from the crystal, $\sigma^2(F^2) = (C + B)/Lp^2$ (C = scan count, B = background count), function minimized $\sum w(|F_o^2| - |F_c^2|)^2$ where $w = 1/\sigma^2(F_o^2)$, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w(F^2) = (\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2)^{1/2}$, and gof = $[\sum w(|F_o^2| - |F_c^2|)^2/(m - n)]^{1/2}$.

[b]Includes crystal decay (if any), absorption, and scaling corrections performed in a single step.

[c]Includes Friedel pairs, 3 144 are unique.

(90 MHz, $CDCl_3$–TMS) δ (ppm): 4.90 (s, N-CH_2), 6.80–7.70 (m, 15 aromatic H). ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 11.5 ($w_{1/2}$ = 385 Hz). Anal. calcd. for $C_{27}H_{22}BNO_3$: C 77.35, H 5.29, B 2.58, N 3.34; found: C 77.36, H 5.33, B 2.63, N 3.17.

3-Hydroxy-2,2,4-triphenyl-1-oxa-3-azonia-2-borata-3-cyclopenten-5-one (19)

2-(Hydroxyimino)phenylacetic acid (22) (0.83 g, 5 mmol) is dissolved in 50 mL of refluxing $CHCl_3$. After the addition of oxybis(diphenylborane) (0.87 g, 2.5 mmol), dissolved in 2 mL of $CHCl_3$, the mixture is refluxed briefly. The solvent is distilled off until the volume is reduced to 10 mL. Crystallization is achieved after addition of small amount of petroleum ether and cooling to –18°C for 1 h. Yield: 1.16 g (70%) of colorless crystals[6], mp 181°C (from $CHCl_3$–petroleum ether). IR (KBr, cm^{-1}): 3 156–2 737 (curtain, O-H assoc.), 1 725 (C=O), 1 657 (C=N), 1597 (C=C). ^{1}H NMR (90 MHz, $CDCl_3$–TMS) δ (ppm): 7.23–7.73 (m, 13 aromatic H), 8.90 (d, J = 7 Hz, 2 aromatic H), signal for OH not detectable. ^{11}B NMR (64 MHz, $CDCl_3$–Et_2OBF_3) δ (ppm): 9.3 ($w_{1/2}$ = 300 Hz). Anal. calcd. for $C_{20}H_{16}BNO_3$: C 72.98, H 4.90, B 3.28, N 4.26; found: C 73.03, H 4.89, B 3.21, N 4.25. Single crystals suitable for X-ray crystallography were obtained by very slow crystallization from chloroform–petroleum ether (bp 30–70°C) using the liquid diffusion method (23).

X-ray crystallographic analyses of 5*d*, 9*a*, 11*b*, 19

Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares based on 12 693, 12 078, 8 118, and 9 840 reflections with 2θ = 4–64° for **5*d***, **9*a***, **11*b***, and **19**, respectively. The data were processed,[16] corrected for Lorentz and polarization effects, and absorption (based on analysis of symmetry-equivalent data).

The structures were solved by direct methods, the coordinates of the atoms being determined from *E*-maps or from

[16]teXsan: Crystal structure analysis package. Unix version 1.7. Molecular Structure Corp. The Woodlands, TX, U.S.A. 1995; and d*TREK: Area Detector Software. Molecular Structure Corp. The Woodlands, TX, U.S.A. 1997.

Table 2. Selected bond lengths (Å, σ = 0.002 Å) and angles (deg, σ = 0.1°).

Structure	**5*d***	**9*a***	**11*b***	**19**
Ring size	5	7	6	5
(A) Bond lengths (Å)				
B—N	1.613	—	1.626	1.608
B—O	1.503	1.464, 1.593	1.491	1.517
B—C	1.604, 1.612	1.616, 1.621	1.605, 1.612	1.601, 1.608
N=C	1.289	1.284	1.275	1.294
N—O	1.380	1.357 (ring)	1.394	1.360
O—C	1.427	1.417	1.430	1.311
C—C (ring)	1.518	1.498, 1.536	1.498, 1.528	1.512
(B) Angles (deg)				
O-B-N	94.9	107.0 (OBO)	102.8	95.3
C-B-C	115.7	117.0	117.6	118.5
B-N=C	114.1	112.4 (BON)	126.1	115.3
B-O-C	112.0	113.6	113.8	113.3

subsequent difference Fourier syntheses. The non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were refined with isotropic thermal parameters. No corrections for secondary extinction were necessary. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for X-Ray Crystallography*. For **9a**, the absolute configuration for the crystal used could not be determined from the small anomalous scattering effect. Selected bond lengths and angles are listed in Table 2. Complete tables of atomic coordinates and equivalent isotropic thermal parameters, bond lengths and angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least squares planes are included as supplementary material.[17]

Results and discussion

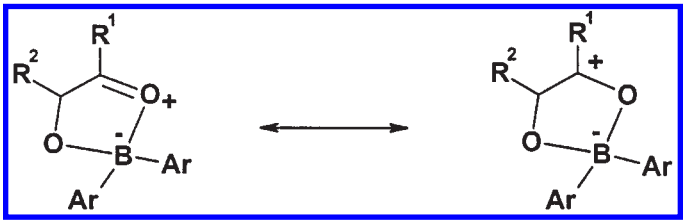
Nitrones 2

The *N*-alkylnitrones **2** which were required as intermediates for the synthesis of the six-membered boron chelates **3** could be prepared in the case of the aldonitrone species by condensation of *N*-alkylhydroxylamines with 2-hydroxycarbaldehydes **1** (R^1 = H) (9). The preparation of ketonitrones from 2-hydroxyketones (R^1 = alkyl) by condensation with *N*-alkylhydroxylamines appeared ineffective and led to some nitrone only in the case of **2*h***.

Since it has been recognized that the (*Z*)-configuration of aldonitrones is generally favored (24), it can be assumed that the aldonitrones **2** exist entirely in the (*Z*)-form which should be stabilized additionally by the intramolecular O-H···O bond in this case. The ready formation of **3**, described below, might corroborate this supposition.

Typical for the nitrones **2** are infrared spectra showing a C=N absorption band between 1 587 and 1 600 cm^{-1} and a broadened band of the associated O-H group at about 3 250 cm^{-1}. The ^1H NMR spectra of the aldonitrones **2** are characterized by the signals for the N=CH methine proton between 6.76 and 6.93 ppm and signals for an exchangeable OH proton which is present also in the spectrum of the ketonitrone **2*h***.

Scheme 1.



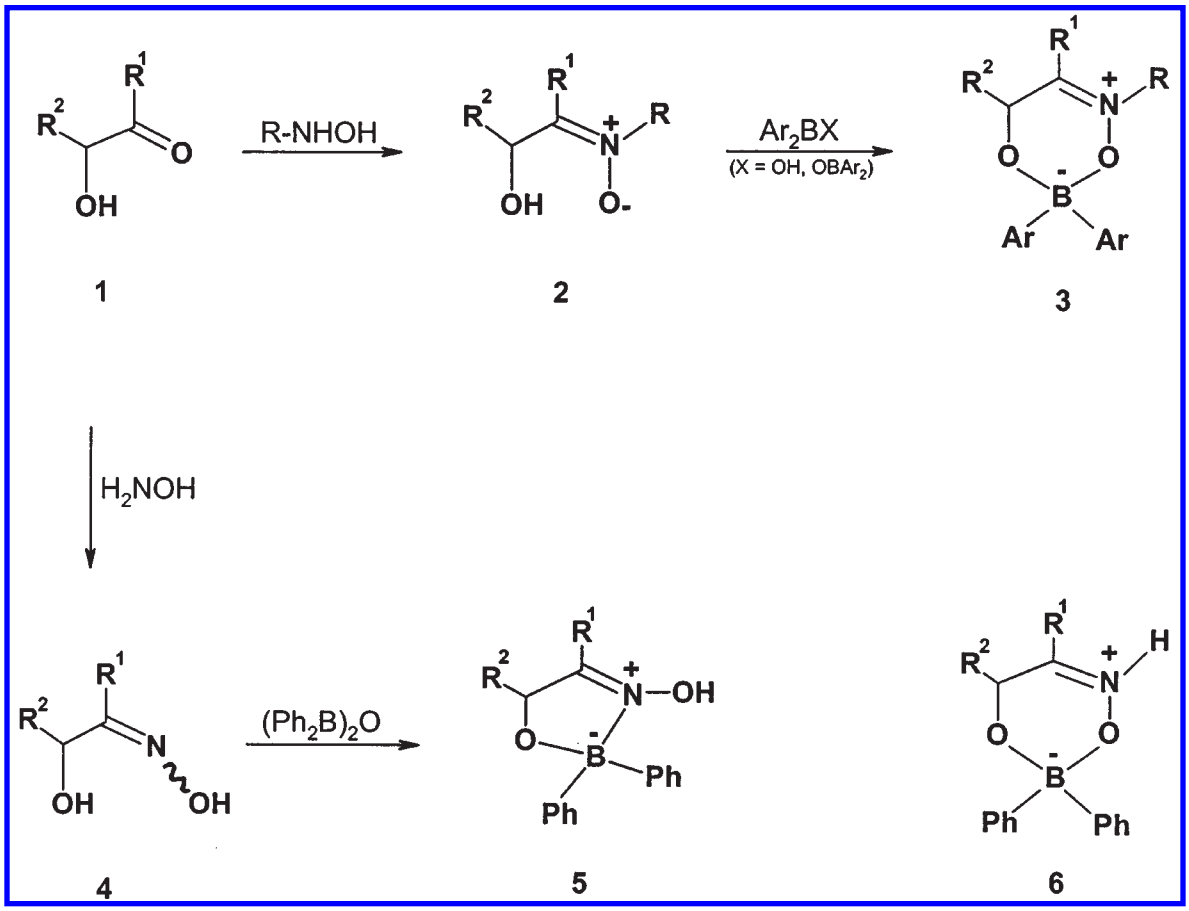
Nitrone complexes 3

Reaction of **2** with a diarylborinic acid or anhydride gave the diarylboron chelates **3** readily and in good yields. However, the preformation of the nitrone **2**, which is quite difficult with ketones, could be avoided by a three-component one-pot reaction of **1**, a diarylborinic acid, and an *N*-alkylhydroxylamine, which proved an advantage for the synthesis of ketonitrone derivatives applying the 2-hydroxyketones **1** (R^1 = alkyl). In the latter case, a preceding complex formation between the 2-hydroxyketone and the Lewis-acid boron compound (see Scheme 1)[18] might facilitate the nucleophilic attack of the hydroxylamine at the carbonyl carbon atom. Thus, only one of the ketonitrones (**2*h***) could be isolated in a satisfying yield and applied as an educt for the diphenylboron complex (**3*t***). All the other ketonitrone chelates **3** were prepared by the one-pot method without isolation of an intermediate **2**.

The infrared spectra of **3** are characterized by the disappearance of the stretching vibration of the O-H group of the free ligand **2**, and display an N=C band between 1 578 and 1 665 cm^{-1}, generally shifted to higher wave numbers

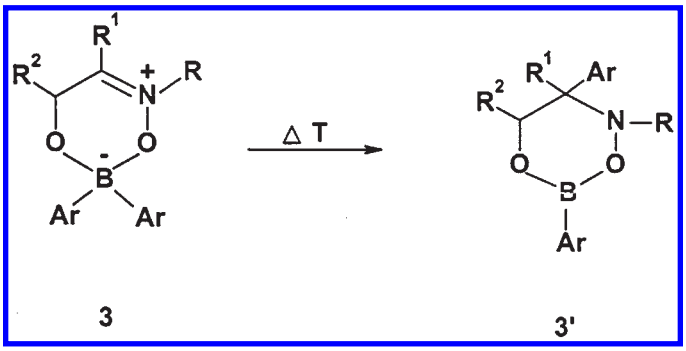
[17]Copies of material on deposit may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2 (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).

[18]Diarylboron complexes of this type could not be isolated as crystalline products or intermediates in the reactions of the various 2-hydroxycarbonyl compounds used in this investigation.



		R	R^1	R^2
2	*a*	CH_3	H	H
	b	$PhCH_2$	H	H
	c	CH_3	H	CH_3
	d	$(CH_3)_3C$	H	CH_3
	e	C_6H_{11}	H	CH_3
	f	$PhCH_2$	H	CH_3
	g	Ph_2CH	H	CH_3
	h	C_6H_{11}	CH_3	CH_3

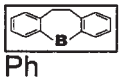
Scheme 2.



compared to the N=C bands of the corresponding educts **2**. In the ^{1}H NMR spectra of the aldonitrone derivatives (**3*a*–*l***), the N=CH methine proton shows a signal between 6 and 7 ppm. The ^{11}B NMR spectra of **3** indicate the tetracoordinate boron nucleus with signals between 3.6 and 9.2 ppm. In some of the spectra a second signal with very small peak area appears between 26.0 and 29.2 ppm, pointing to a trivalent boron atom in the trigonal arrangement of an arylboronate derivative (18). Small additional peaks were also observed in some of the ^{1}H NMR spectra and originate from impurities caused by a thermally induced rearrangement reaction (Scheme 2), leading to the isomeric arylboronates **3′**.[5] The isomerization can be retarded mostly by avoiding thermal stress during the preparation, recrystallization, and spectroscopy of **3**. The thermal stability of **3** depends on the substitution pattern. Thus the compounds **3*f*, *g*, *y*** can be recrystallized from the boiling solvent, and especially **3*z*–*cc*** show a high stability at all temperatures in various solvents.

Oxime complexes 5

Several 2-hydroxyketoximes **4** were reacted with diphenylborinic acid anhydride and gave readily crystalline compounds which show an elemental analysis consistent with both of the isomeric structures, **5** and **6**. An intact diphenylboron moiety is proved by the color reaction with

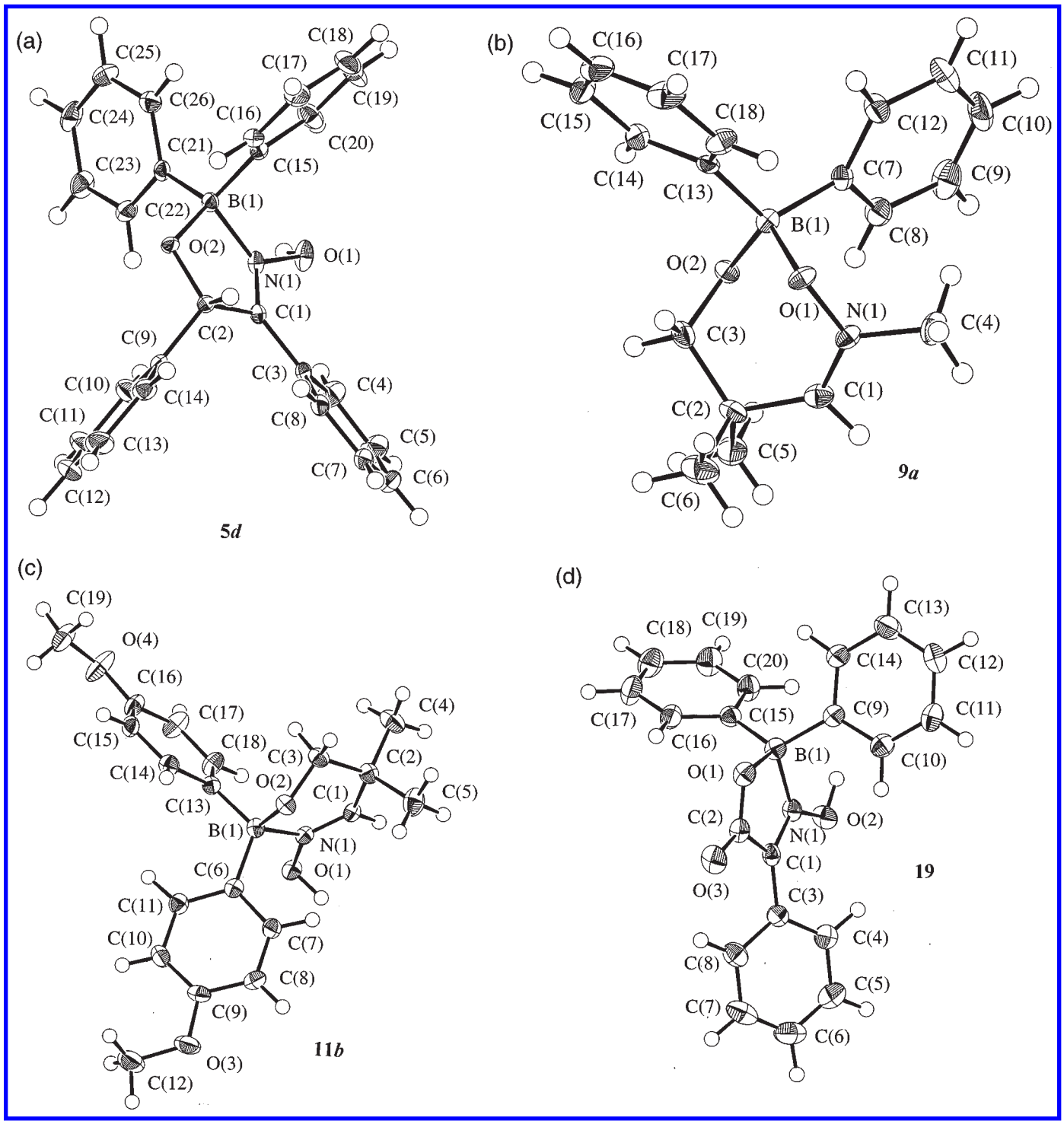
		R	R^1	R^2	Ar
3	***a***	CH_3	H	H	Ph
	b	C_6H_{11}	H	H	Ph
	c	$PhCH_2$	H	H	Ph
	d	Ph_2CH	H	H	Ph
	e	C_6H_{11}	H	J	4-ClC_6H_4
	f	C_6H_{11}	H	H	1-naphthyl
	g	C_6H_{11}	H	H	Ar_2B= 
	h	CH_3	H	CH_3	Ph
	i	$(CH_3)_3C$	H	CH_3	Ph
	j	C_6H_{11}	H	CH_3	Ph
	k	$PhCH_2$	H	CH_3	Ph
	l	Ph_2CH	H	CH_3	Ph
	m	C_6H_{11}	CH_3	H	Ph
	n	$PhCH_2$	CH_3	H	Ph
	o	4-$CH_3C_6H_4$	CH_3	H	Ph
	p	Ph_2CH	C_2H_5	H	Ph
	q	CH_3	CH_3	CH_3	Ph
	r	n-C_3H_7	CH_3	CH_3	Ph
	s	i-C_3H_7	CH_3	CH_3	Ph
	t	C_6H_{11}	CH_3	CH_3	Ph
	u	$PhCH_2$	CH_3	CH_3	Ph
	v	Ph_2CH	CH_3	CH_3	Ph
	w	C_6H_{11}	CH_3	CH_3	4-ClC_6H_4
	x	Ph_2CH	CH_3	CH_3	4-ClC_6H_4
	y	C_6H_{11}	CH_3	CH_3	1-naphthyl
	z	C_6H_{11}	—— $(CH_2)_4$ ——		Ph
	aa	$PhCH_2$	—— $(CH_2)_4$ ——		Ph
	bb	Ph_2CH	—— $(CH_2)_4$ ——		Ph
	cc	4-$CH_3C_6H_4$	—— $(CH_2)_4$ ——		Ph

diphenylcarbazone (10). The infrared spectra, displaying a C=N absorption between 1 637 and 1 674 cm^{-1} and a broad band in the region of stretching vibrations of associated N-H/O-H groups (2 400–2 800 cm^{-1}), do not allow an unambiguous assignment to the five-membered ring system **5** with N-B coordination, or to the six-membered O-B-O chelate **6**, which is an *N*-unsubstituted derivative of **3**. From the ^1H NMR spectra, as well as from ^{11}B NMR spectra, no positive proof for one of the ring systems can be obtained. One exchangeable proton giving a ^1H signal about 12 ppm for acidic N-H or O-H, and a ^{11}B signal between 8.0 and 10.2 ppm, indicating the tetracoordinate boron nucleus (18), might characterize either of the structures **5** and **6**. For most of the metal complexes of 2-hydroxyoximes a five-membered O-*M*-N chelate structure is assumed (25), but evidence is presented also for six-membered O-*M*-O ring systems (26), even from the stereochemically defined (*E*)-benzoinoxime (α-benzoinoxime) as an educt (26*b*). The geometrical isomerism of the educt seems to be of minor significance, anyway, because *E*/*Z*-isomerization of oximes (inversion and (or) rotation) can take place easily, especially in the presence of an acid (27) or Lewis acid like a boron compound (28). Of the ketoximes **4** used in this work only α-benzoinoxime ((*E*)-**4**) (R^1 = R^2 = Ph), was stereochemically defined. An X-ray crystallographic analysis of **5*d*** proves the five-membered chelate ring structure presenting the oxime ligand in the (*E*)-conformation. Since the spectroscopic data of the other derivatives, **5*a*–*c***, are very similar, this structure should be applicable to all of the compounds **5**. To the best of our knowledge, **5*d*** is the first X-ray structurally characterized boron (or any other element) chelate of α-benzoinoxime.

The crystal structure of **5*d*** consists of discrete molecules (Fig. 1), linked by NO-H···O hydrogen bonds, the acceptor oxygen atom being the O(2) ring member:

O (1)···O (2) = 2.583(1), O(1)-H = 0.90(2),
H···O(2) = 1.71(2) Å, O(1)-H···O(2) = 162(2)°

Fig. 1. Views of the molecules of (*a*) ***5d***, (*b*) ***9a***, (*c*) ***11b***, and (*d*) **19**; 50% probability thermal ellipsoids are shown for the non-hydrogen atoms.



The C-C=N-B system in the five-membered ring in ***5d*** shows some deviation from exact planarity, torsion angle 9.6(2)°, and the ring conformation is best described as a half-chair, with B and O displaced on opposite sides of the C-C=N plane. A relatively narrow "bite" of the oxime ligand leads to a compressed O-B-N angle of 94.9(1)° (Table 2), thus distorting the tetrahedral grouping around the boron atom slightly. This angle is even smaller than the O-B-N angle between 98.2 and 99.9° in other five-membered COBNC rings derived from 2-aminoethanols and diarylborinic acids (29). The O-B, B-N, and N=C bond lengths are of the same order as those found in the diphenylboron chelate of

salicylaldoxime (cf. formula **13** below), which represents a six-membered analogue (30):

5*d*: 1.503, 1.613, and 1.289(2) Å, respectively.

13: 1.516, 1.609, and 1.284(2) Å, respectively.

The B—C (phenyl) bond lengths (1.604 and 1.612 Å) are about normal.

Nitrones 8

The 3-hydroxyaldehyde nitrones **8** were prepared by condensation of 3-hydroxy-2,2-dimethylpropanal with various *N*-alkylhydroxylamines to obtain bidentate ligands for the synthesis of the seven-membered boron chelate type **9**. Depending on the *N*-alkyl residue the nitrones **8** are high boil-

		R^1	R^2	Ar
5	*a*	CH_3	CH_3	Ph
	b	C_2H_5	H	Ph
	c	— $(CH_2)_4$ —		Ph
	d	Ph	Ph	Ph

ing liquids or crystalline substances under normal conditions. In the IR spectra the most characteristic absorptions are found in the 3 400–3 200 cm^{-1} region where stretching modes of hydrogen bonded O-H groups appear, and between 1 587 and 1 606 cm^{-1} where the C=N group of the nitrone function absorbs. The ^1H NMR spectra of **8** display some typical signals, common to all of the samples, such as the resonance of the N=CH methine proton between 6.53 and 6.60 ppm and a signal for the hydroxyl proton between 4.57 and 6.07 (in $CDCl_3$), as well as from the singlet of the 2,2-dimethyl grouping at about 1.23 ppm. As mentioned above for the aldonitrones **2**, it can be assumed that **8** exists in the (*Z*)-form and thus presents a suitable ligand for the diphenylborenium (Ph_2B^+) ion to form the chelate **9**.

Nitrone complexes 9

From the reaction of **8** with diphenylborinic acid anhydride the diphenylboron chelates **9** resulted as crystalline compounds in high yields, favored by larger *N*-alkyl substituents. The IR spectra of **9** show C=N absorptions be-

		R
8, 9	*a*	CH_3
	b	n-C_3H_7
	c	C_6H_{11}
	d	$PhCH_2$
	e	Ph_2CH

tween 1 636 and 1 664 cm^{-1}, a shift of 30–60 cm^{-1} to higher frequencies compared to the free ligand **8**. Similar observations have been made from the IR spectra of **2** and **3** and of other boron chelates and their nitrone ligands (31). In the ^1H NMR spectra of **9** the most significant signal is that of the N=CH methine proton between 6.73 and 6.93 ppm, shifted to lower field by 0.2–0.4 ppm compared to the ligand nitrone **8**. The ^{11}B NMR spectra of **9** show the expected signals of a tetravalent boron nucleus at about 10.5 ppm. A thermally induced 1,4-phenyl shift (from the diphenylboron group to the N=CH methine carbon), as observed from the spectra of **3**, obviously does not occur in **9**, even in boiling ethanol.

To prove the molecular structure, an X-ray crystallographic analysis of **9*a*** was carried out and confirmed the seven-membered ring structure derived from the (*Z*)-form of the nitrone ligand (Fig. 1). This is a new crystallographic example of a boron chelate with a stable seven-membered ring system. Similar chelate rings (**14**) containing a bidentate ligand with an *N*-oxide and a phenolate donor group have been described by X-ray crystallographic analyses in earlier work (17*c*, 32, 33). Two of these are derivatives of salicylaldehyde nitrones (**14**, X = Y = H, *R* = Me (32); X = NEt_2, Y = H, *R* = CH_2-C_6H_4-2-OH (17*c*)). Unlike the boron chelate rings of the salicylaldehyde nitrones **14**, which possess a somewhat distorted envelope (or sofa) conformation with the boron atom on the flap displaced by 0.8–1 Å from the mean plane formed by the remaining ring atoms, the seven-membered ring of **9*a*** has a distorted half-chair conformation (Fig. 1). The ring contains a planar segment, O(1)-N(1) = C(1)-C(2) of the nitrone moiety (torsion angle 0.1°), with the other three ring atoms considerably displaced from this plane (torsion angles as large as 95.5(2)°). This ring conformation places the B-phenyl groups quite far from the nitrone carbon atom C(1), the distance between the nearest boron-bound phenyl carbon atom C(7) and the nitrone carbon atom C (1) being 3.75 Å (with C(13)···C(1) = 4.40 Å). These distances are probably too long to facilitate the 1,4-migration of the phenyl group as observed in the diphenylboron chelate of *N*-methylsalicylaldonitrone (32). The higher thermal stability of the compounds **9** could be explained at least partially by that structural difference. As in other diphenylboron chelates with an *N*-oxide and an alcoholate or phenolate ligand (ref. 32 and refs. therein), the O—B bond between the nitrone oxygen atom and boron in **9*a*** (O(1)—B(1) = 1.593(2) Å) is longer than the O—B bond from the alcoholate (O(2)—B(1) = 1.464(2) Å). The mean O—B (1.528(2) Å) and C—B (1.619(2) Å) distances are similar to the average O—B and C—B bonds lengths in **14** (*R* = Me, X = Y = H) of 1.528 and 1.610 Å, respectively, (32), and the mean C—B:O—B bond length ratio of 1.059 for **9*a*** is only slightly larger than the value of 1.054 for **14** (*R* = Me, X = Y = H), indicating a minor increase of overall binding strength (34) of the ligand to the Ph_2B^+ nucleus in both of the seven-membered diphenylboron chelates. **9*a*** has no hydrogen-bond donating functional group, and the molecules in the crystal are linked by van der Waals forces, with a possibly significant C-H···O interaction: C···O = 3.235(2), C-H = 0.93(2), H···O = 2.33(2) Å, C-H···O = 153(2)°.

Oxime complexes 11

The stability of the nitrone chelates **9** led us to investigate diarylboron complexes of 3-hydroxyoxime which might have a six-membered ring structure **11** with N-B coordination or the seven-membered isomeric structure **12** corresponding to the nitrone O-B-O chelates **9**. The reaction of 3-hydroxyaldoximes (**10**, R^1 = H) and ketoximes (**10**, R^1 = alkyl)

		R^1	R^2	R^3	R^4	R^5	Ar
11	***a***	H	CH_3	CH_3	H	H	Ph
	b	H	CH_3	CH_3	H	H	4-$CH_3OC_6H_4$
	c	CH_3	CH_3	H	H	H	Ph
	d	CH_3	H	H	CH_3	CH_3	Ph

(which were prepared according to the literature (15, 16, 20) without regard to geometrical isomerism) with a diarylborinic acid or anhydride gave crystalline compounds in quite good yields. The elemental analyses and the spectroscopic data confirm the 1:1 condensation of oxime and diarylborinic acid. In the IR spectra distinct C=N stretching modes at about 1 640 cm^{-1} and broad absorption bands between 2 700 and 2 400 cm^{-1} in the N-H/O-H region are characteristic but do not allow an unambiguous assignment to either **11** or **12**. The same holds for the ^1H NMR spectra, which give no specific indication of one of the two isomeric structures. The ^{11}B NMR spectra show the expected signals in the shift region of tetracoordinate boron nuclei between 4.0 and 9.9 ppm. An intact diphenylboron grouping was proved by the color reaction with diphenylcarbazone (10). Positive evidence of the molecular structure however, was furnished by an X-ray crystallographic analysis of **11*b*** (Fig. 1) which gave the best single crystals. The six-membered O-B-N chelate structure **11** based upon the (*E*)-form of the oxime ligand **10** corresponds to the structure of the salicylaldoximediphenylboron chelate **13** (30). Like **13** and also like **5*d*** (see above), the crystal structure of **11*b*** consists of discrete molecules (Fig. 1) linked by strong O-H···O hydrogen bonds:

O(1)···O(2) = 2.569(1), O (1)-H = 0.98(2),
H···O (2) = 1.59(2) Å; O(1)-H···O = 175(2)°

Compared to **13** and **5*d*** the hydrogen bond in **11*b*** is the shortest with the least bent angle:

	11*b*	**13**	**5*d***
O···O	2.569	2.737	2.583 Å
O-H···O	175	167	162°

A half-chair conformation, with a nearly planar B(1)-N(1) = C(1)-C(2) segment (torsion angle = 0.9(2)°), and O(2) and C(3) displaced on opposite sides of the six-membered ring, characterizes the overall structure, as a result of the presence of the C=N double bond within the otherwise saturated ring skeleton of **11**. The O-B-N angle in **11*b*** (102.8(1)°, Table 2) is less compressed than the O-B-N angle in **5*d*** (94.9°), allowing a less distorted tetrahedral arrangement around the boron atom. Compared to **13** and also to **5*d***, the oxime C=N bond in **11*b*** (1.275(2) Å) is slightly shorter by about 0.01 Å, which is in accordance with a lengthened (by 0.01 Å) N—B bond.

Nitrones 16

As described in the literature (21), the aldonitrones **16** (R^1 = H) can be obtained by condensation of glyoxylic acid with an *N*-alkylhydroxlamine. The IR spectra of **16** show a broadened band of low intensity (curtain) in the region of associated O-H groups between 2 700 and 2 000 cm^{-1}, carboxyl-C=O stretching modes at about 1 700, and C=N vibrations at about 1 600 cm^{-1}, often hidden by aromatic C=C vibrations. In the ^1H NMR spectra, a typical N=CH methine proton signal between 7.43 and 8.13 ppm and a broad low field singlet (13–14 ppm) of the carboxyl-OH identify the nitrone and the carboxylic acid functions of **16**. It can be assumed that the aldonitrones **16** exist in the (*Z*)-form, stabilized additionally by an intramolecular O-H···O hydrogen bridge, as has been discussed above for the nitrones **2**.

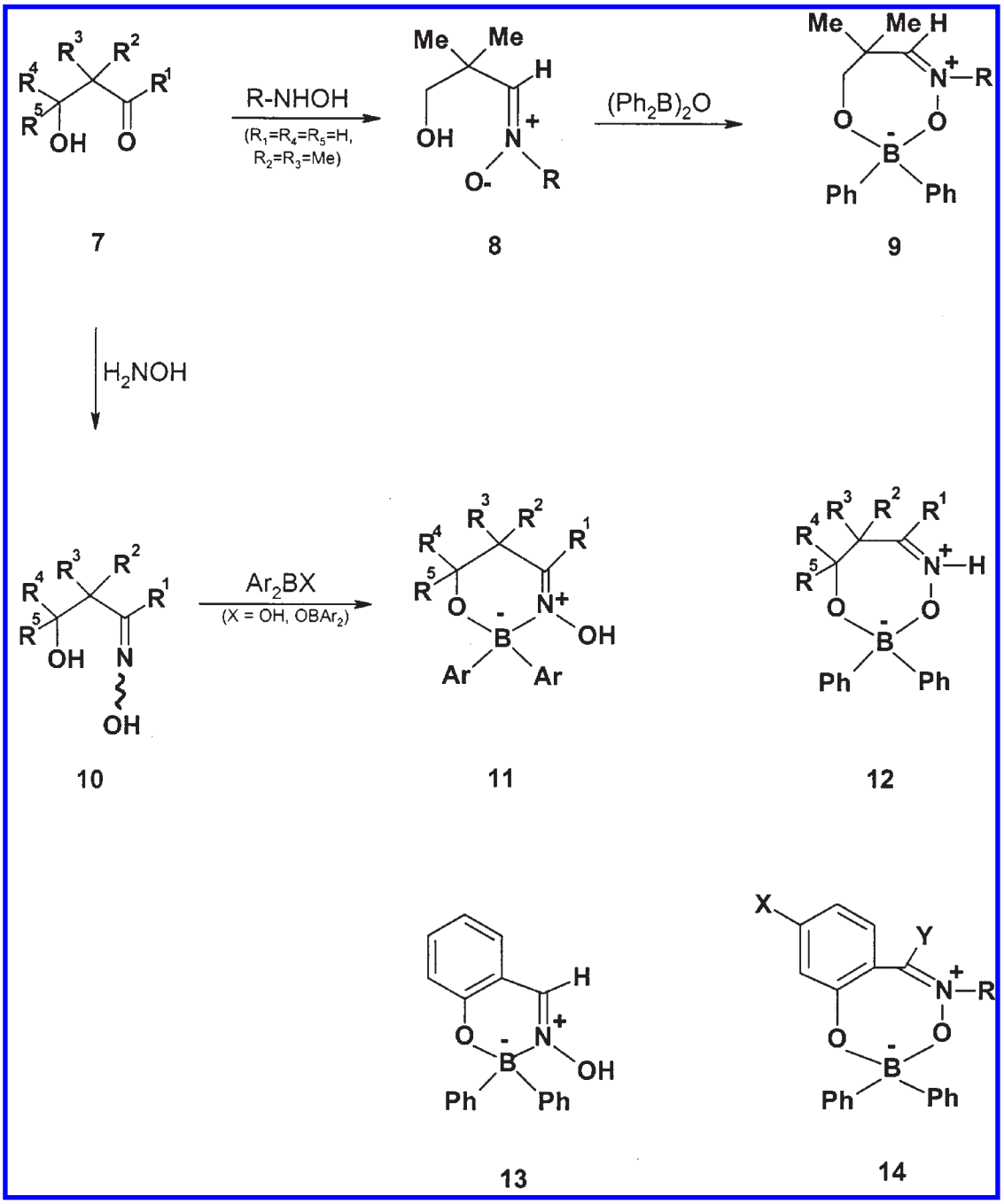
		R	R^1
16	***a***	CH_3	H
	b	$(CH_3)_3C$	H
	c	C_6H_{11}	H
	d	$PhCH_2$	H

Nitrone complexes 17

Reaction of the aldonitrones **16** (R^1 = H) with a diarylborinic acid (or anhydride) resulted in the crystalline diarylboron chelates **17*a*–*e*** which can be isolated under avoidance of thermal stress leading to isomerization similar to that mentioned above for some type **3** nitrones.[5] For the synthesis of ketonitrone chelates **17**, the difficulties of preparing the nitrone of an α-ketocarbonic acid **16** could be avoided by a three-component one-pot reaction of **15** (R^1 = Ph), diarylborinic acid, and *N*-alkylhydroxylamine, with the advantage of a Lewis acid catalysis of the nitrone formation, as described above for the ketonitrone complexes **3**. The ketonitrone derivatives **17*f*–*i*** turned out to be thermally more stable, which suggests that they are less susceptible to an isomerization by 1,4-phenyl migration. In the IR spectra of the chelates **17** there is not much change as compared with the free ligands **16**, except for the absence of the O-H absorption. The disappearance of the OH signal is also the most significant change in the ^1H NMR spectra of the chelates **17** compared to the nitrone ligand **16**. In the ^{11}B NMR spectra of **17** the typical signals for tetracoordinate boron appear between 9.2 and 11.6 ppm. The compounds **17** are functionally related to the six-membered boron chelates of *N*-carboxymethylnitrones (4), with the difference of an *endo*cyclic nitrone-C=N group.

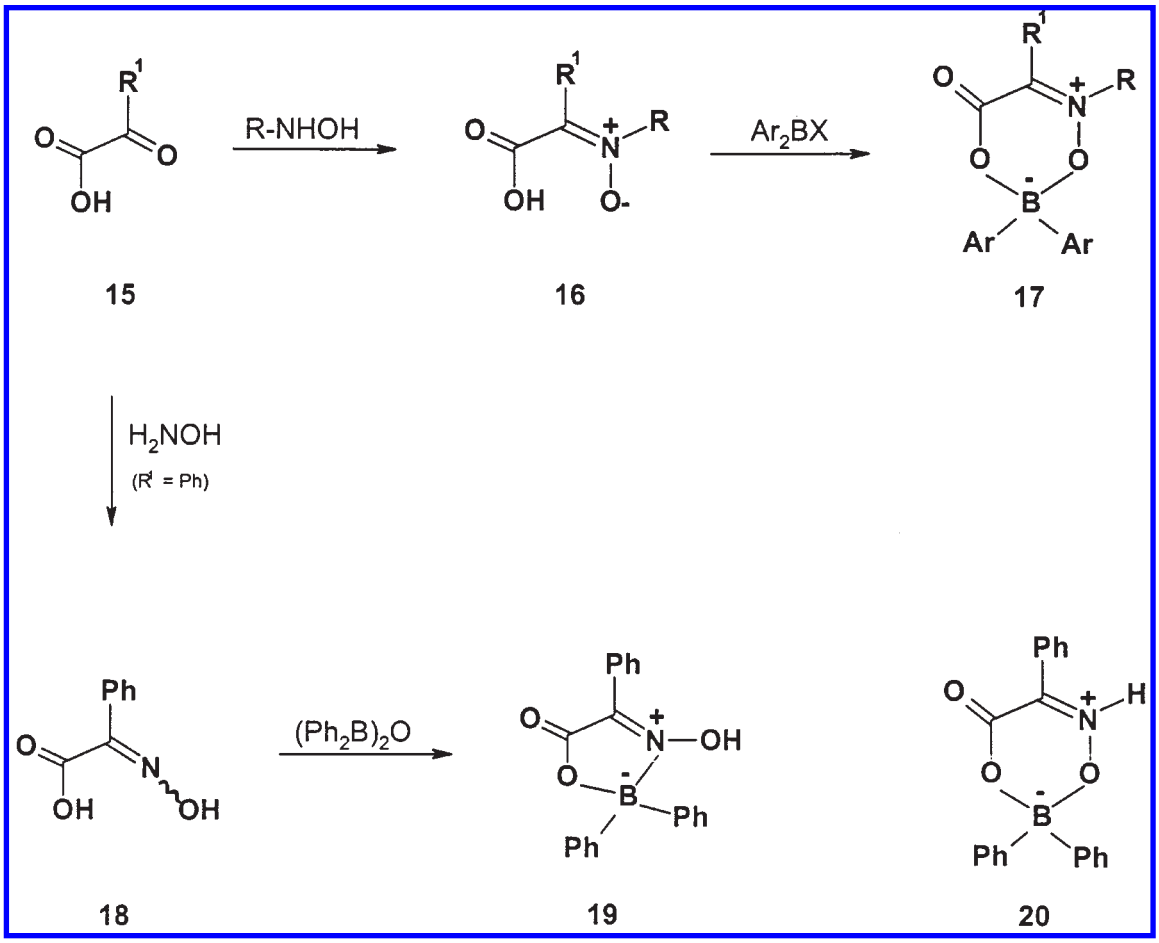
Oxime complex 19

To obtain at least one reaction product of an oxime of a 2-oxocarbonic acid and diphenylborinic acid, the phenylglyoxylic acid oxime **18** (22) was chosen. Because of the easy isomerization, even at room temperature in aqueous



solution (22*a*, *b*), the oxime was applied without separation of the *E*/*Z*-isomers. The high-melting crystalline product is obtained in good yield and has an elemental analysis corresponding to the isomeric molecular structures **19** and **20**. The IR spectrum shows the expected bands in the N-H/O-H region between 2 737 and 3 156 cm^{-1}, as well as the carboxylate C=O and the oxime C=N absorptions at 1 725 and 1 657 cm^{-1}, respectively. An ^{11}B NMR signal for tetracoordinate boron at 9.3 ppm and the blue color reaction with diphenylcarbazone indicate the diphenylboron–chelate character of the compound. The unambiguous discrimination between the five-membered ring **19** with N-B coordination, and the six-membered O-B-O chelate system **20** representing an *N*-unsubstituted derivative of **17**, was made possible by an X-ray crystallographic analysis. The X-ray analysis confirms the five-membered boron chelate structure **19** incorporating the (*E*)-form of the ligand **18**. The ring dimensions are similar to that of **5**, with the ring conformation being more near planar (B-N=C-C torsion angle = 2.7(2)°). As in **5*d***, the O-B-N angle in **19** is distinctly compressed (to 95.3(1)°). The ring C(2)-O(1) distance in **19** (1.311(2) Å, Fig. 1, Table 2), part of the carboxylate function, is shorter than the ring alcoholate-C(2)-O(2) distance in **5*d*** (1.427(2) Å), according to expectation. The crystal structure of **19** consists of discrete molecules linked by N-O-H···O=C hydrogen bonds:

O(2)···O(3) = 2.600(1), O(2)-H = 0.96(2),
H···O (3) = 1.76(2) Å; O-H···O = 144(2)°



		R	R^1	Ar
17	*a*	CH_3	H	Ph
	b	$(CH_3)_3C$	H	Ph
	c	C_6H_{11}	H	Ph
	d	$PhCH_2$	H	Ph
	e	$PhCH_2$	H	4-ClC_6H_4
	f	CH_3	Ph	Ph
	g	n-C_3H_7	Ph	Ph
	h	C_6H_{11}	Ph	Ph
	i	$PhCH_2$	Ph	Ph

To the best of our knowledge **19** is the first boron complex of a 2-(hydroxyimino)carboxylic acid reported on and structurally established. The coordination chemistry of 2-(hydroxyimino)carboxylic acids has not been a subject of extensive investigation until recently (35). Previous reviews (25) do not mention this species of ligand. However, a cobalt complex of phenylglyoxylate oxime is described by NMR data earlier (36). Structural details of 2-(hydroxyimino)propionate complexes of different metals have been determined by X-ray analyses (35). All of these complexes possess five-membered O-*M*-N chelate moieties with a near planar ring conformation like **19**.

The large number of compounds of type **3** with various substituents has been synthesized for a broader investigation of the thermal rearrangement reaction of these materials, and for the interest in new boron compounds with potentially herbicidal, insecticidal, and other biological effects (37).

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References

1. W. Kliegel. Organomet. Chem. Rev. Sect. A: **8**, 153 (1972).
2. W. Kliegel, U. Riebe, S.J. Rettig, and J. Trotter. Can. J. Chem. **73**, 835 (1995).
3. (*a*) W. Kliegel. Tetrahedron Lett. 223 (1969); (*b*) W. Kliegel and H. Becker. Chem. Ber. **110**, 2067 (1977); (*c*) Chem. Ber. **110**, 2090 (1977); (*d*) W. Kliegel, B. Enders, and H. Becker. Liebigs Ann. Chem. 1712 (1982); (*e*) Chem. Ber. **116**, 27 (1983).
4. W. Kliegel and J. Graumann. Liebigs Ann. Chem. 1545 (1984).
5. (*a*) W. Kliegel and L. Preu. Liebigs Ann. Chem. 1937 (1983); (*b*) Chem. Ztg. **108**, 283 (1984).
6. (*a*) G. Zinner. Chem. Ztg. **109**, 436 (1985); (*b*) H. Hopf and G. Maas. Angew. Chem. **104**, 953 (1992).

7. (*a*) S.J. Rettig, J. Trotter, W. Kliegel, and D. Nanninga. Can. J. Chem. **55**, 1 (1977); (*b*) Can. J. Chem. **56**, 1676 (1978); (*c*) W. Kliegel and D. Nanninga. Chem. Ber. **116**, 2616 (1983); and refs. therein.
8. (*a*) R. Neu. Chem. Ber. **87**, 802 (1954); (*b*) G.N. Chremos, H. Weidmann, and H.K. Zimmerman. J. Org. Chem. **26**, 1683 (1961).
9. W. Kliegel, G. Lubkowitz, S.J. Rettig, and J. Trotter. Can. J. Chem. **70**, 2809 (1992).
10. (*a*) R. Neu. Z. Anal. Chem. **176**, 334 (1960); (*b*) B. Friese and F. Umland. Anal. Chim. Acta **96**, 303 (1978).
11. G.E. Coates and J.G. Livingstone. J. Chem. Soc. 4909 (1961).
12. R.L. Letsinger and I.H. Skoog. J. Am. Chem. Soc. **77**, 5176 (1955).
13. G. Rindorf. Acta Chem. Scand. **25**, 774 (1971).
14. A. Dornow and A. Müller. Chem. Ber. **93**, 26 (1960).
15. A. Balsamo, D. Gentili, A. Lapucci, M. Macchia, and A. Martinelli. Farmaco (Pavia), **49**, 759 (1994).
16. (*a*) L. Wessely. Monatsh. Chem. **21**, 216 (1900); (*b*) J.M. Kern and P. Ferlin. Bull. Soc. Chim. Fr. 4379 (1972).
17. (*a*) W. Kliegel, J. Metge, S.J. Rettig, and J. Trotter. Can. J. Chem. **75**, 1830 (1997); (*b*) Can. J. Chem. **76**, 389 (1998); (*c*) Can. J. Chem. **76**, 1082 (1998).
18. (*a*) H. Nöth and B. Wrackmeyer. Nuclear magnetic resonance spectroscopy of boron compounds. Springer, Berlin. 1978; (*b*) R. Köster (*Editor*). Houben-Weyl: Organobor-Verbindungen III. Vol. XIII/3c. Georg Thieme, Stuttgart. 1984.
19. T.P. Povlock and W.T. Lippincott. J. Am. Chem. Soc. **80**, 5409 (1958).
20. M. Kohn and G. Lindauer. Monatsh. Chem. **23**, 755 (1902).
21. D. Keirs and K. Overton. Heterocycles, **28**, 841 (1989).
22. (*a*) A. Hantzsch. Ber. Dtsch. Chem. Ges. **24**, 36 (1891); (*b*) A. Ahmad and I.D. Spenser. Can. J. Chem. **39**, 1340 (1961); (*c*) J. Armand and J.-P. Guetté. Bull. Soc. Chim. Fr. 2849 (1969).
23. P.G. Jones. Chem. Ber. **17**, 222 (1981).
24. (*a*) H. Stamm. *In* Methodicum Chimicum. Vol. 6. *Edited by* F. Zymalkowski. Georg Thieme, Stuttgart. 1974. p. 337; (*b*) E. Breuer. *In* The chemistry of amino, nitroso and nitro compounds and their derivatives. Part 1. *Edited by* S. Patai. Wiley, Chichester. 1982. p. 459; (*c*) E. Breuer. *In* Nitrones, nitronates, and nitroxides. *Edited by* S. Patai and Z. Rapoport. Wiley, Chichester. 1989. p. 245; (*d*) D. Döpp and H. Döpp. *In* Houben-Weyl, Organische Stickstoff-Verbindungen mit C,N-Doppelbindungen.. Vol. E 14b. *Edited by* D. Klamann and H. Hagemann. Georg Thieme, Stuttgart. 1990. p. 1372.
25. (*a*) A. Chakravorty. Coord. Chem. Rev. **13**, 1 (1974); (*b*) R.C. Mehrotra, A.K. Rai, A. Singh, and R. Bohra. Inorg. Chim. Acta, **13**, 91 (1975); (*c*) M.E. Keeney, K. Osseo-Asare, and K.A. Woode. Coord. Chem. Rev. **59**, 141 (1984); (*d*) R.C. Mehrotra. *In* Comprehensive coordination Chemistry. Vol. 2. *Edited by* G. Wilkinson. Pergamon, Oxford. 1987. p. 269; (*e*) J. Szymanowski and A. Borowiak-Resterna. Crit. Rev. Anal. Chem. **22**, 65 (1991); (*f*) A. Borowiak-Resterna and J. Szymanowski. J. Radioanal. Nucl. Chem. **150**, 235 (1991).
26. (*a*) J.S. Fritz, D.R. Beuerman, and J.J. Richard. Talanta, **18**, 1095 (1971); (*b*) N.S. Biradar, V.B. Mahale, and V.H. Kulkarni. J. Inorg. Nucl. Chem. **35**, 2565 (1973).
27. (*a*) C.G. McCarthy. *In* The chemistry of the carbon–nitrogen double bond. *Edited by* S. Patai. Interscience, London. 1970. p. 363; (*b*) W.B. Jennings and V.E. Wilson. *In* Acyclic organonitrogen stereodynamics. *Edited by* J.B. Lambert and Y. Takeuchi. VCH, Weinheim. 1992. p. 191.
28. C.E. Hauser and D.S. Hoffenberg. J. Org. Chem. **20**, 1491 (1955).
29. S.J. Rettig and J. Trotter. Can. J. Chem. **51**, 1288 (1973); Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **B30**, 2139 (1974); Can. J. Chem. **54**, 3130 (1976); Can. J. Chem. **61**, 2334 (1983).
30. W. Kliegel, S.J. Rettig, and J. Trotter. Can. J. Chem. **62**, 1363 (1984).
31. W. Kliegel, J. Metge, S.J. Rettig, and J. Trotter. Can. J. Chem. **75**, 1830 (1997) and refs. therein.
32. W. Kliegel, U. Lauterbach, S.J. Rettig, and J. Trotter. Can. J. Chem. **65**, 1457 (1987).
33. W. Kliegel, M. Tajerbashi, S.J. Rettig, and J. Trotter. Can. J. Chem. **66**, 2621 (1988).
34. W.R. Cullen, S.J. Rettig, J. Trotter, and E.B. Wickenheiser. Can. J. Chem. **66**, 2007 (1988).
35. (*a*) Yu.A. Simonov, T.Yu. Sliva, M.D. Mazus, A.A. Dvorkin, and R.D. Lampeka. Russ. J. Inorg. Chem. **34**, 489 (1989); (*b*) A.A. Dvorkin, Yu.A. Simonov, T.Yu. Sliva, R.D. Lampeka, M.D. Mazus, V.V. Skopenko, and T.I. Malinovskii. Russ. J. Inorg. Chem. **34**, 1475 (1989); (*c*) V.V. Skopenko, T.Yu. Sliva, Yu.A. Simonov, A.A. Dorkin, N.D. Mazus, R.D. Lampeka, and T.I. Malinovskii. Russ. J. Inorg. Chem. **35**, 993 (1990); (*d*) R.D. Lampeka, Z.D. Uzakbergenova, and V.V. Skopenko. Z. Naturforsch. B: Chem. Sci. **48 b**, 409 (1993); (*e*) R.D. Lampeka, R. Bergs, R. Krämer, K. Polborn, and W. Beck. Z. Naturforsch. B: Chem. Sci. **49 b**, 225 (1994) and refs. therein.
36. G. Occupati and L. Pratt. J. Chem. Soc. Dalton Trans. 1699 (1973).
37. (*a*) W. Kliegel. Bor in Biologie, Medizin und Pharmazie. Springer, Berlin. 1980; (*b*) M.F. Hawthorne. Angew. Chem. **105**, 997 (1993); Angew. Chem. Int. Ed. Engl. **105**, 950 (1993); (*c*) C. Morin. Tetrahedron, **50**, 12521 (1994); (*d*) R.F. Schinazi and R.F. Lesnikowski. Nucleosides Nucleotides, **17**, 635 (1998); (*e*) A.H. Solway, W. Tjarks, B.A. Barnum, F.G. Rong, R.F. Barth, I.M. Codogni, and G. Wilson. Chem. Rev. **98**, 1515 (1998); (*f*) M.P. Groziak. Prog. Heterocycl. Chem. **12**, (2000), in press.
38. W. Kliegel, J.O. Pokriefke, S.J. Rettig, and J. Trotter. Can. J. Chem. **78**, 546 (2000).