Reaction of 2,3-Dihydro-1*H*-1,3,2-diazaboroles and Diphenylketene: A Novel Synthesis of 1,3,2-Oxazaborolidines

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*Summary: Reaction of equimolar amounts of diphenylketene with a series of 1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazaboroles tBuNCH=CH−N(tBu)BX [X = Br (**1a**), F (**1b**), NH_2 (**1c**), NMe_2 (**1d**), Me (**1e**), $SnMe_3$ (**1f**), $CH=C(SnMe_3)C_6H_4$-4-Cl (**1g**)] regioselectively afforded good yields of the 1,3,2-oxazaborolidines tBuN−CH(CH=NtBu)C(=CPh_2)OBX (**2a**−**g**). The X-ray structure analysis of **2d** revealed an essentially planar five-membered heterocycle with a long B−O bond and a strong exocyclic BN−π bond.*

Introduction

The chemistry of 1,3,2-oxazaborolidines originated in the 1970s with the first studies by Cragg.[1] Interest in these heterocycles increased markedly in the past decade with the recognition that compounds of this type are efficient catalysts in a series of chemical transformations. Usually oxazaborolidines were prepared from boranes RBX_2 (X = leaving group) and 1,2-amino alcohols.[1,2] The employment of chiral amino alcohols such as (*S*)-(−)-2-(diphenylhydroxymethyl)pyrrolidine,[3,4] ephedrine,[4−7] and pseudoephedrine[8a] or others[8b] furnished chiral oxazaborolidines[8] which enantioselectively catalyzed borane reduction of prochiral ketones to give chiral secondary alcohols[3,8,9] and the enantioselective addition of diethylzinc to aldehydes to afford secondary alcohols.[5,6]

A series of 1,3,2-oxazaborolidin-5-ones were obtained by the borylation of (*S*)-alanine, (*S*)-valine, (*S*)-leucine, (*S*)-isoleucine, and (*S*,*R*)-*tert*-leucine with (*tert*-butylimino)-(2,2,6,6-tetramethylpiperidino)borane.[10] Amino acid derived oxazaborolidin-5-ones are excellent catalysts for highly enantioselective Diels−Alder reactions,[11−13] the Mukaiyama aldol reaction of aldehydes and silyl enol ethers,[14,15] and asymmetric aldol reactions of silyl ketene acetals.[16,17]

In a program on functionalized 2,3-dihydro-1*H*-1,3,2-diazaboroles it was demonstrated that the 2-haloderivatives[18,19] can easily be converted into 2-cyano-,[19] 2-isocyanato-,[19] 2-isothiocyanato-,[19] 2-hydro-,[20] 2-alkyl-,[20] 2-alkynyl-,[20] 2-amino-,[21] and 2-stannyl-2,3-dihydro-1*H*-1,3,2-diazaboroles[20] by halide substitution with the respective nucleophile. Various alkynes were inserted into the B−Sn bond of the latter compound to afford highly functionalized 2-alkenyl-2,3-dihydro-1*H*-1,3,2-

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diazaboroles.[22] Almost all transformations occur at the periphery of the heterocycle, and little information on processes involving the core of the ring system is available.[23]

The aim of the work described herein was to provide a novel synthesis of 1,3,2-oxazaborolidines from 1,3,2-diazaboroles by treatment with diphenylketene.

Experimental Section

All operations were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under nitrogen prior to use. ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra were recorded in C_6D_6 with Bruker AC 100 (^{1}H, 100.13 MHz, ^{11}B, 32.13 MHz) and Bruker Avance DRX 500 (^{1}H, 500.13 MHz, ^{11}B, 160.46 MHz, ^{13}C, 125.75 MHz, ^{19}F, 470.60 MHz, ^{119}Sn, 186.51 MHz). References: $SiMe_4$ (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), $CFCl_3$ (^{19}F), $SnMe_4$ (^{119}Sn).

Compounds *t*BuN−CH=CH−N(*t*Bu)BBr (**1a**),[18] *t*BuN−CH=CH−N(*t*Bu)BF (**1b**),[19] *t*BuN−CH=CH−N(*t*Bu)BNH$_2$ (**1c**),[21] *t*BuN−CH=CH−N(*t*Bu)B−CH$_3$ (**1e**),[24] *t*BuN−CH=CH−N(*t*-Bu)BSnMe$_3$ (**1f**),[20] *t*BuN−CH=CH−N(*t*Bu)B−CH=C(SnMe$_3$)-(C$_6$H$_4$-4-Cl) (**1g**),[22] and Ph$_2$C=C=O[25] were synthesized according to literature procedures.

***t*BuN−CH=CH−N(*t*Bu)BNMe$_2$ (1d)**. Gaseous dimethylamine was bubbled into a solution of 1,3-di-*tert*-butyl-2-bromo-2,3-dihydro-1*H*-1,3,2-diazaborole (**1a**) (3.00 g, 11.6 mmol) in 60 mL of *n*-hexane at 20 °C during a period of 15 min. Excess amine was removed by a flow of argon. It was filtered, and the filtrate was liberated from solvent and volatile components in vacuo. Compound **1d** was obtained as a yellow oil (1.88 g, 72% yield). ^{1}H NMR: δ 1.33 [s, 18H, C(CH$_3$)$_3$], 2.46 [s, 6H, N(CH$_3$)$_2$], 6.25 (s, 2H, NCH). ^{13}C{^{1}H} NMR: δ 31.6 [s, C(*C*H$_3$)$_3$], 41.2 (s, NCH$_3$), 51.8 [s, *C*(CH$_3$)$_3$], 111.4 (s, NCH). ^{11}B{^{1}H} NMR: δ 22.8 s. MS/EI: *m*/*z* (relative intensity) 223 (63) [M$^+$]. Anal. Calcd for $C_{12}H_{26}BN_3$ (223.17): C, 64.58; H, 11.74; N, 18.83. Found: C, 64.37; H, 12.08; N, 18.52.

***t*BuN−CH(CH=N*t*Bu)C(=CPh$_2$)OBBr (2a)**. A solution of diphenylketene (0.62 g, 3.2 mmol) in 10 mL of *n*-hexane was added dropwise to a chilled solution (−20 °C) of **1a** (0.83 g, 3.2 mmol) in *n*-hexane (40 mL). The mixture was warmed to ambient temperature. After 2 h of stirring it was filtered, and the light yellow filtrate was concentrated in vacuo until it became cloudy. After storing for 24 h at −30 °C **2a** precipitated as a yellow solid (yield: 0.97 g, 67%). ^{1}H NMR: δ 0.87 [s, 9H, C(CH$_3$)$_3$], 1.21 [s, 9H, C(CH$_3$)$_3$], 5.13 (d, $^{3}J_{HH}$ = 6.6 Hz, 1H, CH$_{ring}$), 7.00−7.13 (m, 9H, Ph + CH=N), 7.66 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H, Ph). ^{13}C{^{1}H} NMR: δ 28.9 [s, C(*C*H$_3$)$_3$], 31.0 [s, C(*C*H$_3$)$_3$], 52.6 [s, *C*(CH$_3$)$_3$], 56.7 [s, *C*(CH$_3$)$_3$], 67.3 (s, CH$_{ring}$), 119.4 (s, *C*Ph$_2$), 126.6, 127.3, 128.9, 129.8, 131.1, 139.0, 139.1 (Ph), 149.1 (s, *C*=CPh$_2$), 153.9 (s, CH=N). ^{11}B{^{1}H} NMR: δ 26.0 s. Anal. Calcd for $C_{24}H_{30}BBrN_2O$ (453.22): C, 63.60; H, 6.67; N, 6.18. Found: C, 63.48; H, 6.82; N, 6.08.

***t*BuN−CH(CH=N*t*Bu)C(=CPh$_2$)OBF (2b)**. Analogously, a sample of diphenylketene (0.37 g, 1.90 mmol) was reacted with **1b** (0.38 g, 1.90 mmol) to afford 0.47 g (64%) of **2b** as a light yellow solid. ^{1}H NMR: δ 0.87 [s, 9H, C(CH$_3$)$_3$], 1.07 [s, 9H, C(CH$_3$)$_3$], 5.10 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H, CH$_{ring}$), 7.02−7.19 (m, 9H, Ph + CH=N), 7.62 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ph). ^{13}C{^{1}H} NMR: δ 28.9 [s, C(*C*H$_3$)$_3$], 30.5 [s, C(*C*H$_3$)$_3$], 51.3 [s, *C*(CH$_3$)$_3$], 56.2 [s, *C*(CH$_3$)$_3$], 65.4 (s, CH$_{ring}$), 119.7 (s, *C*Ph$_2$), 126.7, 127.2, 128.9, 129.0, 131.2, 139.0, 139.6 (Ph), 147.1 (s, *C*=CPh$_2$), 154.4 (s, CH=N). ^{11}B{^{1}H} NMR: δ 22.3 s. ^{19}F{^{1}H} NMR: δ 176.9 s. Anal. Calcd for $C_{24}H_{30}BFN_2O$ (392.32): C, 73.48; H, 7.71; N, 7.14. Found: C, 73.56; H, 7.64; N, 7.14.

***t*BuN−CH(CH=N*t*Bu)C(=CPh$_2$)OBNH$_2$ (2c)**. Colorless **2c** (0.28 g, 64%) precipitated from the reaction mixture of diphenylketene (0.22 g, 1.13 mmol) and **1c** (0.22 g, 1.13 mmol) in *n*-hexane (40 mL) at −40 °C. IR (KBr): $\tilde{\nu}$ 3511 s (νNH), 3417 s (νNH) cm^{-1}. ^{1}H NMR: δ 0.91 [s, 9H, C(CH$_3$)$_3$], 1.06 [s, 9H, C(CH$_3$)$_3$], 1.81 (s, 2H, NH$_2$), 5.10 (d, $^{3}J_{HH}$ = 7.0 Hz, 1H, CH$_{ring}$), 7.00−7.24 (m, 9H, Ph + CH=N), 7.75 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ph). ^{13}C{^{1}H} NMR: δ 29.1 [s, C(*C*H$_3$)$_3$], 31.0 [s, C(*C*H$_3$)$_3$], 50.8 [s, *C*(CH$_3$)$_3$], 56.3 [s, *C*(CH$_3$)$_3$], 66.1 (s, CH$_{ring}$), 116.7 (s, *C*Ph$_2$), 126.1, 126.8, 128.0, 128.7, 130.0, 131.5, 140.1, 140.8 (Ph), 150.8 (s, *C*=CPh$_2$), 155.8 (s, CH=N). ^{11}B{^{1}H} NMR (d_6-DMSO): δ 25.2 s. Anal. Calcd for $C_{24}H_{32}BN_3O$ (389.35): C, 74.04; H, 8.28; N, 10.79. Found: C, 73.86; H, 8.54; N, 10.50.

***t*BuN−CH(CH=N*t*Bu)C(=CPh$_2$)OBNMe$_2$ (2d)**. Analogously, reaction of **1d** (0.66 g, 3.0 mmol) and 0.57 g (3.0 mmol) of diphenylketene resulted in the formation of yellow microcrystalline **2d** (0.90 g, 73%). Recrystallization from toluene at −30 °C afforded crystals suitable for an X-ray structural analysis. ^{1}H NMR: δ 0.94 [s, 9H, C(CH$_3$)$_3$], 1.23 [s, 9H, C(CH$_3$)$_3$], 2.68 (s, 6H, NMe$_2$), 5.18 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H, CH$_{ring}$), 7.06−7.25 (m, 9H, Ph + CH=N), 7.81 (d, $^{3}J_{HH}$ = 6.9 Hz, 2H, Ph). ^{13}C{^{1}H} NMR: δ 28.9 [s, C(*C*H$_3$)$_3$], 31.7 [s, C(*C*H$_3$)$_3$], 39.7 (s, NCH$_3$), 50.9 [s, *C*(CH$_3$)$_3$], 56.1 [s, *C*(CH$_3$)$_3$], 66.6 (s, CH$_{ring}$), 115.5 (s, *C*Ph$_2$), 125.6, 126.6, 128.1, 128.6, 129.4, 130.0, 131.4, 140.0, 140.4 (Ph), 149.7 (s, *C*=CPh$_2$), 155.4 (s, CH=N). ^{11}B{^{1}H} NMR: δ 24.8 s. Anal. Calcd for $C_{26}H_{36}BN_3O$ (417.39): C, 74.82; H, 8.69; N, 10.07. Found: C, 74.76; H, 8.76; N, 9.89.

***t*BuN−CH(CH=N*t*Bu)C(=CPh$_2$)OBMe (2e)**. Analogously, reaction of 0.55 g (2.8 mmol) of **1e** with 0.54 g (2.8 mmol) of diphenylketene in 50 mL of *n*-hexane afforded 0.76 g (70%) of colorless microcrystalline **2e**. ^{1}H NMR: δ 0.56 (s, 3H, BCH$_3$), 0.92 [s, 9H, C(CH$_3$)$_3$], 1.10 [s, 9H, C(CH$_3$)$_3$], 5.14 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H, CH$_{ring}$), 7.02−7.22 (m, 9H, Ph + CH=N), 7.77 (d, $^{3}J_{HH}$ = 6.9 Hz, 2H, Ph). ^{13}C{^{1}H} NMR: δ 29.0 [s, C(*C*H$_3$)$_3$], 31.4 [s, C(*C*H$_3$)$_3$], 51.2 [s, *C*(CH$_3$)$_3$], 56.5 [s, *C*(CH$_3$)$_3$], 66.6 (s, CH$_{ring}$), 117.3 (s, *C*Ph$_2$), 126.3, 126.9, 128.3, 128.8, 129.9, 131.4, 140.0, 140.4 (Ph), 151.6 (s, *C*=CPh$_2$), 155.2 (s, CH=N). ^{11}B-{^{1}H} NMR: δ 34.5 s. Anal. Calcd for $C_{25}H_{33}BN_2O$ (388.35): C, 77.32; H, 8.56; N, 7.21. Found: C, 77.19; H, 8.46; N, 7.28.

***t*BuN−CH(CH=N*t*Bu)C(=CPh$_2$)OBSnMe$_3$ (2f)**. A sample of diphenylketene (0.33 g, 1.7 mmol) was slowly added at room temperature to the solution of **1f** (0.55 g, 1.6 mmol) in 5 mL of benzene. After stirring for 3 h solvent was removed in vacuo, and the residue was dissolved in 2 mL of benzene. Product **2f** separated as colorless needles (yield: 0.59 g, 69%). ^{1}H NMR: δ 0.31 [s, 9H, $^{2}J_{SnH}$ = 49.9 Hz, Sn(CH$_3$)$_3$], 0.87 [s, 9H, C(CH$_3$)$_3$], 1.17 [s, 9H, C(CH$_3$)$_3$], 5.20 (d, $^{3}J_{HH}$ = 7.0 Hz, 1H, CH$_{ring}$), 7.04−7.23 (m, 9H, Ph + CH=N), 7.22 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H, Ph). ^{13}C{^{1}H} NMR: δ −10.5 [s, $^{1}J_{SnC}$ = 289.2 Hz, Sn(CH$_3$)$_3$], 28.9 [s, C(*C*H$_3$)$_3$], 32.4 [s, C(*C*H$_3$)$_3$], 52.3 [s, *C*(CH$_3$)$_3$], 56.9 [s, *C*(CH$_3$)$_3$], 66.0 (s, CH$_{ring}$), 118.2 (s, *C*Ph$_2$), 126.5, 127.0, 128.9, 129.9, 131.2, 139.7, 140.0 (Ph), 152.9 (s, $^{3}J_{SnC}$ = 49.4 Hz, *C*=CPh$_2$), 154.7 (s, CH=N). ^{11}B{^{1}H} NMR: δ 38.2 s. ^{119}Sn-{^{1}H} NMR: δ −110.7. MS/EI *m*/*z* (relative intensity): 538 (75) [M$^+$]. Anal. Calcd for $C_{27}H_{39}BN_2OSn$ (537.14): C, 60.37; H, 7.32; N, 5.22. Found: C, 60.45; H, 7.40; N, 5.47.

***t*BuN−CH(CH=N*t*Bu)C(=CPh$_2$)OB−CH=C(SnMe$_3$)C$_6$H$_4$-4-Cl (2g)**. Analogously reaction of **1g** (0.56 g, 1.2 mmol) and 0.25 g of diphenylketene (1.3 mmol) in 5 mL of benzene for 6 h afforded colorless crystalline **2g** (yield: 0.49 g, 62%) ^{1}H

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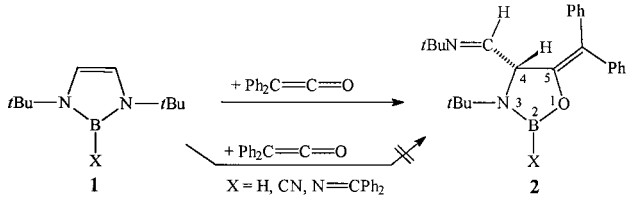
Scheme 1



1,2	X	1,2	X
a	Br	e	CH_3
b	F	f	$SnMe_3$
c	NH_2	g	HC=C($SnMe_3$)(C_6H_4-4-Cl)
d	NMe_2		

NMR: δ 0.13 [s, 9H, $^2J_{SnH}$ = 55.3 Hz, $Sn(CH_3)_3$], 0.93 [s, 9H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$], 5.38 (d, $^3J_{HH}$ = 6.3 Hz, 1H, CH_{ring}), 6.82 (s, 1H, BCH), 6.93−7.24 (m, 13H, Ph + CH=N + *p*-ClC_6H_4), 7.54 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR: δ −7.3 [s, $^1J_{SnC}$ = 347.1 Hz, $Sn(CH_3)_3$], 29.1 [s, $C(CH_3)_3$], 31.9 [s, $C(CH_3)_3$], 52.2 [s, $C(CH_3)_3$], 56.5 [s, $C(CH_3)_3$], 66.1 (s, CH_{ring}), 119.2 (s, CPh_2), 127.6, 128.3, 128.7, 128.8, 129.8, 130.3, 131.0, 132.4, 140.4, 148.0 (Ph), 138.5 (s, br, BC), 151.2 (s, C=CPh_2), 154.7 (s, CH=N), 163.8 (s, =C−Sn). $^{11}B\{^1H\}$ NMR: δ 30.9 s br. $^{119}Sn\{^1H\}$ NMR: δ −38.8 s. MS/EI *m/z* (relative intensity): 674 (6) [M^+], 559 (33), 167 (100). Anal. Calcd for $C_{35}H_{44}BClN_2OSn$ (673.72): C, 62.40; H, 6.58; N, 4.16. Found: C, 62.58; H, 6.69; N, 4.14.

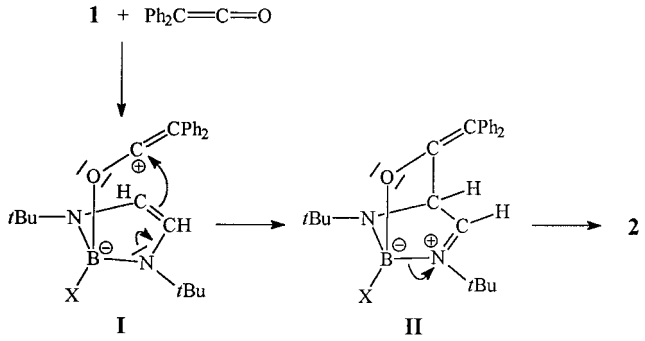
Results and Discussions

Reaction of diphenylketene and equimolar amounts of the 2,3-dihydro-1*H*-1,3,2-diazaboroles **1a**−**e** in *n*-hexane in the temperature range between −20 and +20 °C led to the formation of the 1,3,2-oxazaborolidines **2a**−**e** in 64−70% yield. Similarly, the 1,3,2-diazaboroles **1f** and **1g** were converted into the corresponding 1,3,2-oxazaborolidines **2f** and **2g** by treatment with Ph_2C=C=O in benzene at room temperature. The progress of this transformation was monitored by ^{11}B NMR spectroscopy, and products **2a**−**e** were obtained as light yellow to colorless crystals from *n*-pentane. The derivatives **2f** and **2g** were isolated as colorless deliquescent crystals from benzene (Scheme 1).

The 1,3,2-oxazaborolidines **2a**−**g** are less soluble than the starting materials **1a**−**g**. It is obvious that the ring transformation reaction tolerates halide substituents, amino groups, the Me_3Sn unit, and alkenyl groups at the boron atom. No reactions were observed with the 2-hydro-, 2-cyano-, and 2-diphenylketimino derivatives and 1,3,2-diazaboroles bearing 2,6-dimethylphenyl substituents at both nitrogen atoms.

The IR spectra of the products confirmed the absence of a ν(C=O) vibration, which implies a reaction involving the carbonyl unit of the ketene. From the ^1H and ^{13}C NMR spectra of the products **2** it is obvious that the vertical mirror plane of the precursor molecules **1** is no longer present. Thus the singlet for the 18 protons of the *tert*-butyl groups, ranging from δ 1.24 to 1.43, in **1** is replaced by two singlet resonances at δ 0.87−0.94 and δ 1.06−1.23, which are attributed to the chemically and nonequivalent *tert*-butyl groups at the ring nitrogen atom and at the exocyclic methane imino group in **2**. A

Scheme 2



doublet for the proton at the ring carbon atom in **2** was observed at δ 5.10−5.38 ($^3J_{HH}$ = 6.3−7.0 Hz). In the precursors **1** the two equivalent ring protons gave rise to singlets at δ 5.99−6.50. The second CH group in **1** was converted into the exocyclic methane imino functionality in **2**, the proton signal of which is obscured by the phenyl hydrogens. The ^{13}C carbon atom of the CH=N group gives rise to singlets at δ 153.9−155.8 in the $^{13}C\{^1H\}$ NMR spectra of the products, whereas the ring carbon atom is assigned to a singlet at δ 65.4−67.3. A singlet in the range δ 147.1−152.9 is due to the sp^2-hybridized ring carbon atom introduced by the ketene building block. The exocyclic carbon atom of the double bond in **2** was observed as a singlet at δ 115.5−119.7. In **2b** (X = F), **2c** (X = NH_2), and **2d** (X = NMe_2), where the boron atoms are linked to π-donating groups X the ^{11}B NMR resonances (δ 22.3−25.2) are deshielded by only δ 2.0−3.1 on going from **1** to **2**. For comparison 1,3,2-oxazaborolidin-5-ones derived from α-amino acids and an amino-iminoborane display ^{11}B resonances at δ 27.0−27.4.[10] In the remaining products **2a** (X = Br, δ 26.0), **2e** (X = Me, δ 34.5), **2f** (X = $SnMe_3$, δ 38.2), and **2g** (X = alkenyl, δ 30.9) a more pronounced deshielding ($\Delta\delta$ 8.3−12.4) of the boron nuclei relative to the corresponding 1,3,2-diazaborole precursors is observed.

In the $^{19}F\{^1H\}$ NMR spectrum of **2b** a singlet was registered at δ 176.9. This resonance compares well with the one in the nonaromatic heterocycle $MeNCH_2CH_2N(Me)BF$ (δ 168)[26] but is markedly deshielded with respect to precursor **1b** (δ 56.57).

In line with Zweifel's[27] and Herberich's[28] results on the reaction of 3-borolenes with aldehydes, ketones, and ketenes to give 1,2-oxaborolane derivatives it is conceivable that the formation of **2** is initiated by a nucleophilic attack of the ketene oxygen atom at the boron atom of the ring to give zwitterion **I**. Attack of the electron-deficient ketene carbon center at the C=C bond of the ring leads to **II**. Fission of the BN bond of **II** eventually afforded **2** as a pair of enantiomers. The reaction between a 2,3-dihydro-1*H*-1,3,2-diazaborole and a ketene constitutes a novel synthetic approach to oxazaborolidines with a stereogenic center at the ring carbon atom. Experiments focusing on the asymmetric synthesis of such heterocycles are underway.

(26) Fussstetter, H.; Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1977**, *110*, 3172−3182.
(27) Zweifel, G.; Shoup, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 5578.
(28) Herberich, G. E.; Englert, U.; Wang, S. *Chem. Ber.* **1993**, *126*, 297.

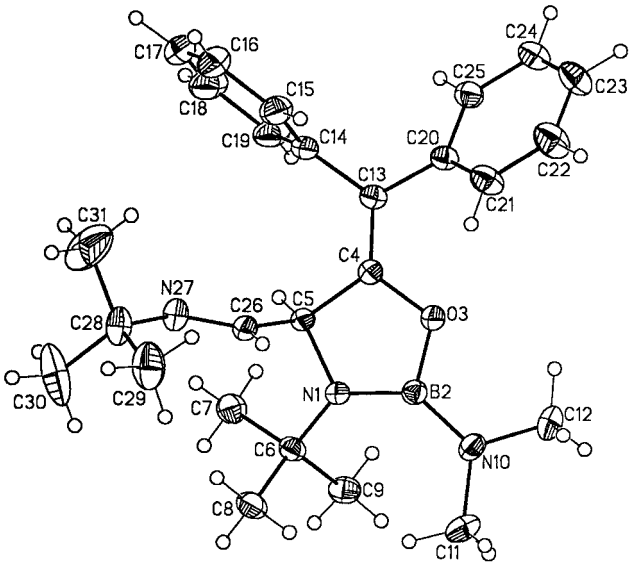


Figure 1. Molecular structure of **2d** in the crystal. The thermal ellipsoids correspond to 50% probability.

X-ray Structural Analysis of 2d. The structure of **2d** was confirmed by an X-ray analysis (Figure 1)[29]

Single crystals of the compound were grown from toluene at −30 °C. An essential structural feature is an almost planar five-membered heterocycle (the largest deviation from the best plane is 0.065 Å). The sum of the endocyclic angles is 538.68°; which is close to the theoretical value of 540°. The endocyclic bonds N(1)−B(2) [1.429(2) Å] and B(2)−O(3) [1.411(2) Å] are comparable. The BO bond is markedly elongated when compared with the BO distances in {*t*BuNCH=CHN(*t*Bu)B}$_2$O (**III**) [1.365(4), 1.354(4) Å], whereas the BN bond lengths in **III** are similar [1.439(4), 1.434(4), 1.442(3) Å]. The C_2N plane of the dimethylamino substituent and the plane of the oxazaborolidine ring possess an interplanar angle of 22°, which allows for a relatively strong exocyclic BN−π-bond of 1.405(2) Å. The bond length C(4)−C(13) of 1.334(2) Å is that of a localized double bond, as it is observed for the C=N bond [1.251(2) Å] of the exocyclic *N*-*tert*-butylmethane imino group. Due to steric congestion the exocyclic angles B(2)−N(1)−C(6) [133.13(12)°] and N(1)−B(2)−N(10) [134.88(14)°] are markedly widened, when compared with angles C(6)−N(1)−C(5) [118.96(11)°] and O(3)−B(2)−N(10) [116.06(13)°]. The same strain is obvious from the angles at the planar dimethylamino group [B(2)−N(10)−C(11) 127.40(14)° and B(2)−N(10)−C(12) 119.91(13)°].

(29) The crystallographic data for **2d** (atomic coordinates and bonding parameters) have been placed in the Supporting Information.

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Supporting Information Available: Table of X-ray data, atomic coordinates, thermal parameters, and complete bond distances and angles and thermal ellipsoid plots for compound **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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