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Straightforward access to oxazaborines, diazaborinones and triazaborines by reactions of β-enaminoamides with 4-methylbenzenediazonium tetraphenylborate

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ABSTRACT

The reaction of substituted β-enaminoamides with 4-methylbenzenediazonium tetraphenylborate in dichloromethane produces besides the primary products of azo coupling reaction at the α-carbon atom of β-enaminoamides, also mixtures of heterocyclic compounds of boron: 1,3,2λ^4-oxazaborines, 1*H*-1,3,2λ^4-diazaborine-4-ones and 4*H*-1,2,4,3λ^4-triazaborines. Proportions of the products change depending on the reaction conditions, particularly depending on the presence or absence of base (sodium acetate) in the reaction mixture. The heterocyclic compounds were separated chromatographically and identified by means of X-ray, ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR spectra and elemental analyses.

1. Introduction

Boron together with carbon, oxygen and nitrogen forms a number of types of heterocyclic compounds: oxazaborolidines, oxazaborines, oxazaborinanes etc. Some representatives of this group of substances exhibit miscellaneous types of biological activity [1–4]: antibacterial, fungicidal, insecticidal, and herbicidal.

Some of them have been considered as potential BNCT agents for targeting brain tumors [5]. In organic synthesis, heterocyclic compounds of boron have been adopted for protection of amino acids [6], in the synthesis of isoquinoline [7], isoindole [7]. They are used in asymmetrical hydroborations [8], to separate diastereomeric and racemic methoxyborolane mixtures [9], as the catalysts for enantioselective reduction of ketones [10], or in the Diels–Alder reaction [11]. Literature describes application of 1,3,2-oxazaborinides to dyeing of polyester, polyamide and polypropylene fibres [12].

The most common methods for preparing heterocycles with O–B–N grouping are reactions of 1,2- and 1,3-aminoalcohols with alkyl- and arylboronic acids [10e,13] or dialkyl- and diarylborinic acids [14], boronate [15] or borane [16] and borane-dimethylsulfide [17]. Another method [18] consists in aminoboration of ketene with dialkyl(dimethylamino)boranes or bromodimethylborane and amine, or reactions of substituted vinyloxyboranes with nitriles [19,20]. Another possibility is the synthesis from β-enaminones and various derivatives of boron containing compounds (e.g. diphenylborinic acid or its ester, boron trifluoride or triphenylborane) [21].

Recently we published a new method of preparation of substituted 1,3,2λ^4-oxazaborines by reaction of the corresponding β-enaminones with 4-substituted benzenediazonium tetraphenylborates in dichloromethane at room temperature [22]. We also suggested a mechanism of formation of oxazaborines. Thermal rearrangement of the mentioned oxazaborines leads to substituted 4*H*-1,2,4,3λ^4-triazaborines [22].

Various polarized ethylenes were applied in the development of novel synthetic methodologies in our laboratory. In this paper, we report on novel synthetic transformations leading to N–B–O and N–B–N heterocyclic systems using reactions of β-enaminoamides and diazonium salts.

2. Results and discussion

The reaction of equimolar amounts of substituted benzenediazonium tetraphenylborates with β-enaminoamides in anhydrous dichloromethane at room temperature gives a mixture of boron containing heterocyclic compounds. The decisive factor affecting the composition of this mixture is the presence or absence of base – anhydrous sodium acetate. If sodium acetate is present, then the reaction products contain (in two cases; **1c**,**d**), besides the heterocyclic compounds, also the primary product **5** of azo coupling reaction with β-enaminoamide. The presence of this base also changes the proportion of heterocyclic compounds in the reaction mixture (Scheme 1).

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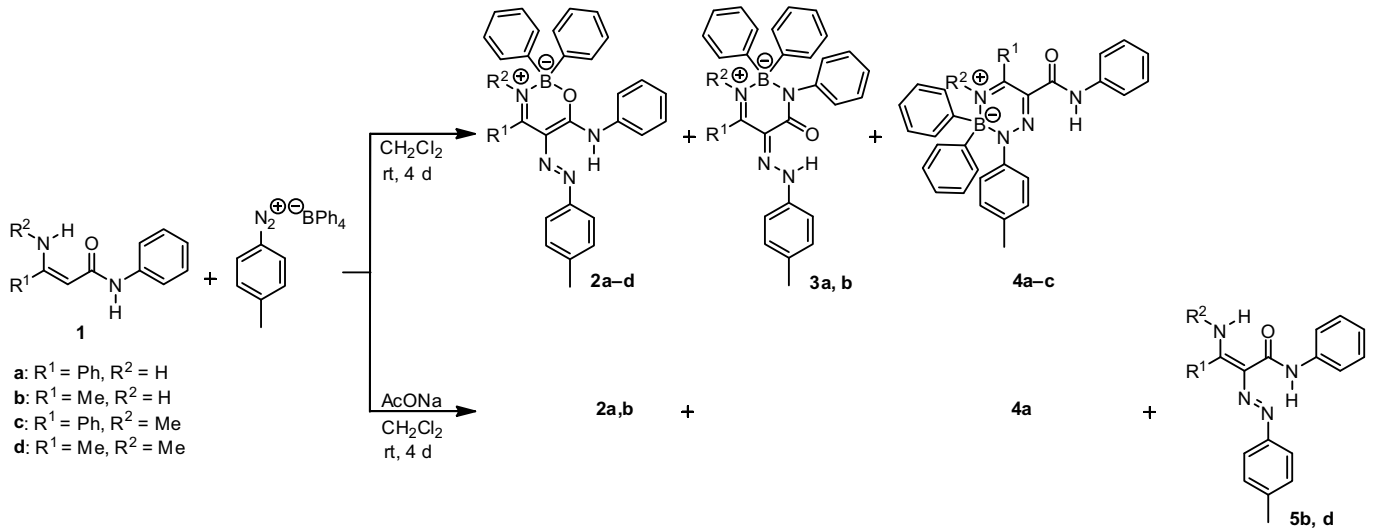


Scheme 1. Reaction of β-enaminoamides **1** with 4-methylbenzenediazonium tetraphenylborate.

In the case of the reaction of 3-amino-*N*,3-diphenylprop-2-enamide (**1a**) with 4-methylbenzenediazonium tetraphenylborate without the presence of sodium acetate the reaction products include oxazaborine (**2a**), diazaborinone (**3a**) and triazaborine (**4a**) in the molar ratio of 5:2:1 (determined from integration of ^{1}H NMR spectrum of the crude reaction mixture). The ratios of the products obtained with other combinations of substituents are presented in Table 1. The reaction products were separated chromatographically on a silica gel (dichloromethane as the mobile phase) and further purified by recrystallization.

The products were identified by ^{1}H, ^{13}C, ^{11}B and ^{15}N NMR, and in several cases also by means of X-ray diffraction. The ^{1}H NMR spectra of the compounds **2a**, **3a** and **4a** are shown in Fig. 1. The proton spectra of these compounds are of similar character. In the aromatic part, there are multiplets belonging to three types of monosubstituted benzene rings, one 1,4-disubstituted ring, and broadened signals of N–H groups. In the aliphatic part, there is only a singlet of methyl group from the starting diazonium salt. The protons of the *N*-phenyl group were identified by measuring the substances prepared from partially deuterated amide **1a** (using aniline D_5). The multiplets of the phenyl groups linked with the boron atom exhibit a twofold intensity.

Table 1
Proportions of products **2**, **3**, **4** and **5** in a crude reaction mixture.

Starting compound	Products	The ratio of the products[a,b]	Yield[c] (%)	The ratio of the products[a,d]	Yield[c] (%)
1a	**2a**	5	54	10	86
	3a	2	21	traces	–
	4a	1	8	0.7	4
1b	**2b**	10	43	1	64
	3b	7	28	–	–
	4b	4	11	–	–
1c	**2c**	10	41	1	15
	3c	–	–	–	–
	4c	13	45	–	–
	5c	–	–	5	51
1d	**2d**	10	74	1	20
	3d	Traces	–	–	–
	4d	Traces	–	–	–
	5d	Traces	–	5	57

[a] From integration of ^{1}H NMR.
[b] Without the presence of sodium acetate.
[c] Isolated yield (after column chromatography).
[d] In the presence of sodium acetate.

When suggesting the structure of compounds **2a**, **3a**, **4a**, we started from the previously described mechanism of the reaction of β-enaminones with diazonium tetraphenylborates [22]: the primary product of the azo coupling reaction reacts with tetraphenylborate anion with gradual splitting off of two molecules of benzene and ring closure giving the heterocycle. The primary product of the azo coupling reaction can exist in several forms stabilised by the formation of intramolecular hydrogen bonds. These forms were observed spectroscopically in the case of azo coupling reaction products obtained from β-enaminones [23]. Theoretically, the coordination between boron atom and the atoms originally linked by means of the intramolecular hydrogen bond can lead to five structures with six-membered rings: **A**–**E** (Scheme 2).

In the case of compound **2a** we rejected triazaborines **B** and **C**, because the positive value of $\delta(^{11}B)$ corresponds to the arrangement N–B–O (Ref. [22]) (Table 2). ^{1}H–^{15}N *gs*HMBC spectrum of the compound **2a** is presented in Fig. 1 (top); the values of chemical shifts of nitrogen atoms are given in Table 2. The positive values of $\delta(^{15}N)$ 12.2 and 86.9 ppm indicate the presence of an azo group [23,24], which is not present in the suggested structures **D** and **E**. Hence, the compound **2a** has structure **A**.

With regard to the positive values of $\delta(^{15}N)$, a potential tautomeric equilibrium of this compound is shifted in favour of the azo compound (Scheme 3), which is also in accordance with the found value of the coupling constant $^{1}J(^{15}N1,^{1}H) = 84.3$ Hz [25] (for notation of nitrogen atoms, see the structure **X** in Scheme 2). The structure of the compound **2a** suggested on the basis of NMR parameters was confirmed by X-ray diffraction (Fig. 2).

In the ^{11}B NMR spectrum of the compound **3a**, the boron atom exhibits a negative chemical shift (Table 2), which excludes structures **A** and **E** (Scheme 2). The measured value of coupling constant $^{1}J(^{15}N4,\ ^{1}H) = 93.7$ Hz corresponds to the presence of pure hydrazone form. The ^{1}H–^{15}N *gs*HMBC spectrum of the compound **3a** is given in Fig. 1 (middle); the values of chemical shifts of nitrogen atoms are presented in Table 2. The ORTEP view is in Fig. 3.

The chemical shift of boron atom in the compound **4a** ($\delta(^{11}B) = -1.46$ ppm (Table 2)) is comparable with the measured values for the earlier-studied triazaborines [22] prepared from β-enaminones. Scheme 2 suggests two possible structures for triazaborines, namely **B** and **C**. Fig. 1 (bottom right) presents the ^{1}H–^{15}N HMBC spectrum of this compound, wherefrom it is obvious that the triazaborine prepared possesses two different nitrogen atoms with directly linked hydrogen atoms (single-bond interac-

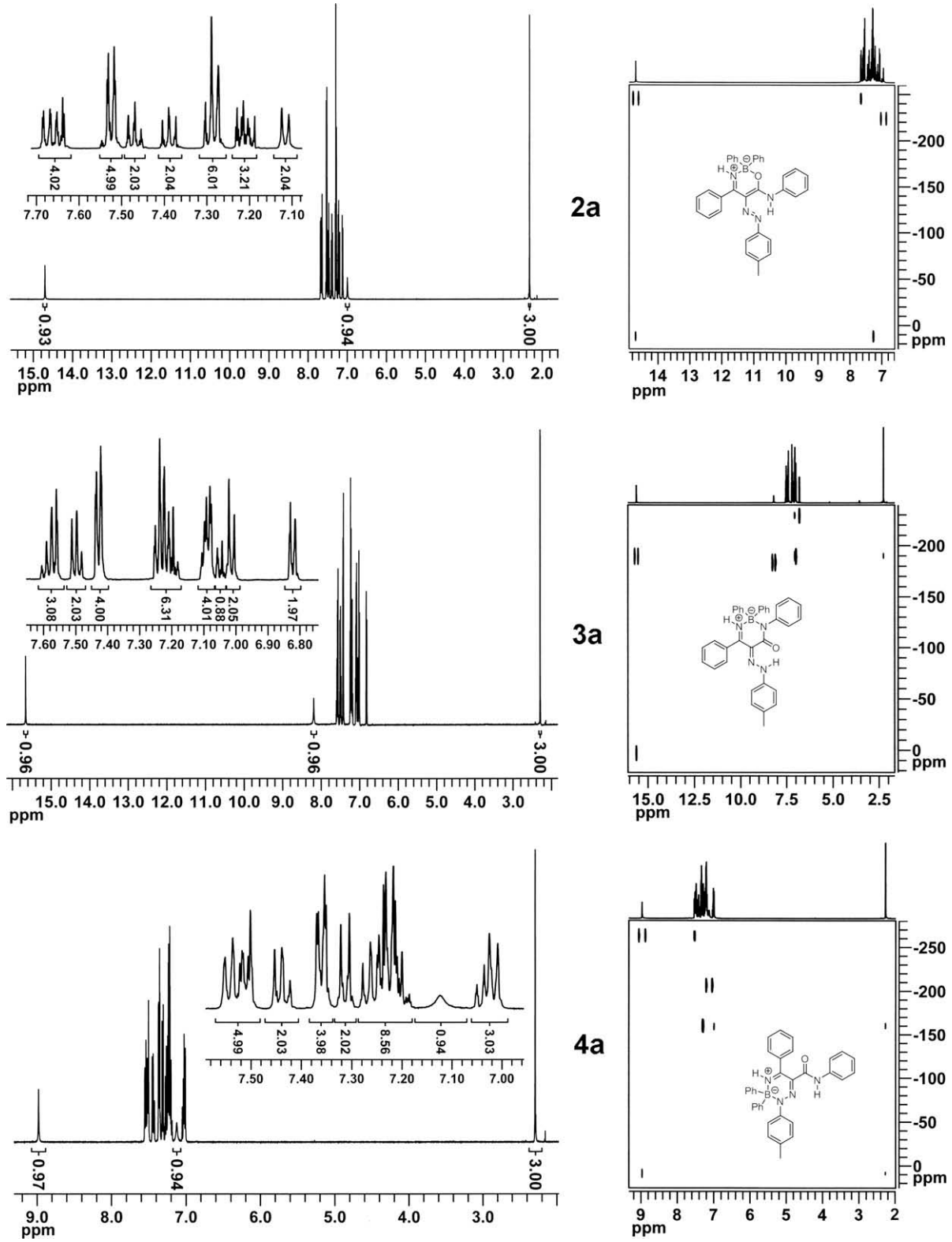
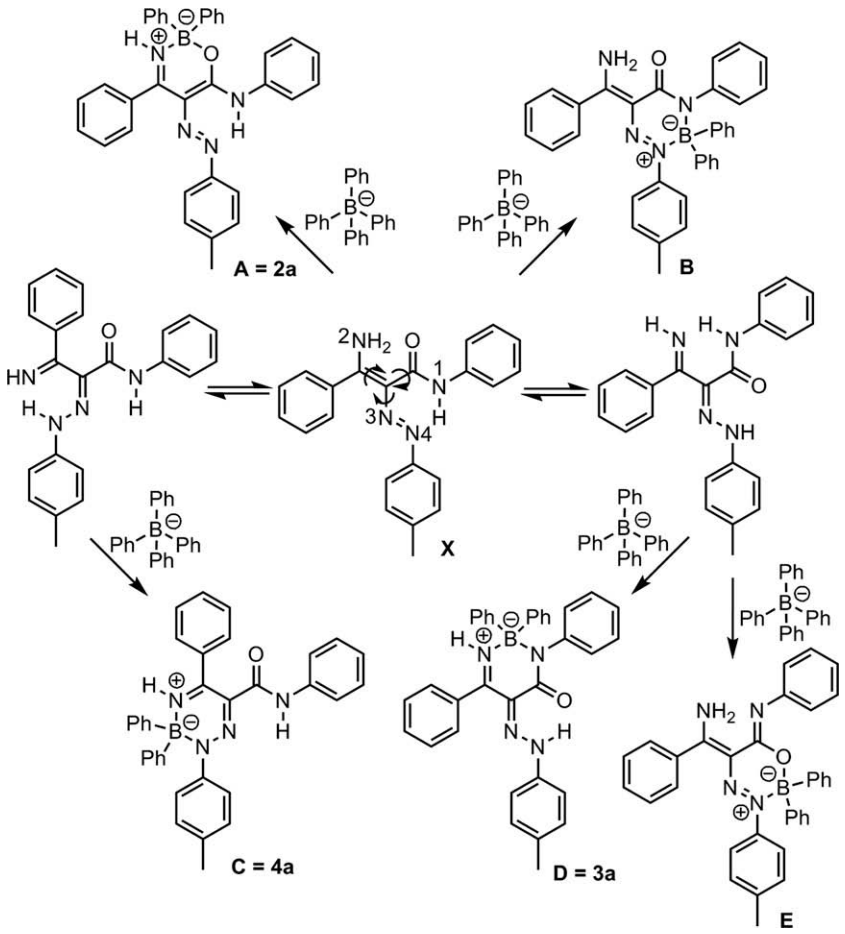


Fig. 1. 500.13 MHz ^{1}H a $^{1}H–^{15}N$ *gs*HMBC spectra of compounds **2a, 3a** and **4a** in $CDCl_3$.

tion N–H). This does not correspond with the suggested structure **B**, whose $^{1}H–^{15}N$ HMBC spectrum would exhibit the single-bond interaction N–H belonging to one nitrogen atom only. We also measured the $^{1}H–^{13}C$ HMBC spectrum (Fig. 4), which shows a two-bond interaction C–H of amidic group that is not present in structure **B**.

The reaction of β-enaminoamide **1a** with equimolar amount of diazonium salt in the presence of sodium acetate gave only two (isolable) products: the major product – oxazaborine **2a** (yield 68% after recrystallization) and the minor product – triazaborine **4a** (yield 3% after recrystallization) (Scheme 1). Diazaborinone **3a** was only formed in a non-isolable amount. Its



Scheme 2. The possibility of the coordination of BPh_4^- to the azo compound **X**.

presence in the reaction mixture was confirmed by the ^{1}H NMR spectrum.

Similar results were also obtained from the reaction of β-enaminoamide **1b**: if no sodium acetate was present, then three product were isolated: **2b**, **3b** and **4b**; if the reaction took place in the presence of sodium acetate, then the major product obtained was oxazaborine **2b**. The ^{11}B a ^{15}N chemical shifts of these compounds are presented in Table 2.

β-Enaminoamides **1c** and **1d** differ from the previous ones by the presence of secondary *N*-methyl enamino group (C=C–NHMe) in the molecule. When the reaction of these enaminoamides took place without the presence of sodium acetate, then two products (from β-enaminoamide **1c**) or one product (from β-enaminoamide **1d**) were obtained. Whereas 3-methylaminobut-2-enamide (**1d**) reacts with 4-methylbenzenediazonium tetraphenylborate to give oxazaborine **2d** only, the reaction of the same diazonium salt with 3-methylamino-*N*,3-diphenylprop-2-enamide (**1c**) produces both oxazaborine **2c** and triazaborine **4c** (for the ORTEP diagram, see Fig. 5). Diazaborinone was not formed under these reaction conditions.

The primary products **5** of the azo coupling reactions of 4-methylbenzenediazonium tetraphenylborate were identified in the case of the reactions with enaminoamides **1c** and **1d**. In $CDCl_3$ solution, these products exist as mixtures of *E*- and *Z*-isomers differing in the arrangement of intramolecular hydrogen bond. The tautomeric form of the major *E*-isomer is opposite to that of the minor *Z*-isomer (Fig. 6). The positions of tautomeric equilibria were determined on the basis of the ^{15}N NMR parameters (Table 2) [23] The ^{1}H–^{15}N HMBC spectrum of the compound **5c** exhibits a signal with chemical shift $\delta(^{15}N) = -220.4$, which does not correspond to any of the structures suggested. This signal is present in the spectrum even if the substance was twice recrystallized before the measurement. It could belong to the third isomer, whose possible structure is presented in Fig. 6 (bottom). However, this is only hypothesis whose confirmation would need more experimental data.

2.1. X-ray diffraction study

ORTEP [26] views of the compounds **2a**, **3a** and **4c** are shown in Figs. 2, 3 and 5. ORTEP views of the compounds **2b**, **2c** and **3b** are shown in Figs. S42–44. The oxazaborines **2a–c** display intramolecular short N–H···N resonance assisted hydrogen bonds [27] (Table S3) between an enamino and a diazenyl group [28]. The ···HN2–C3=C2–N3=N4··· heterodienic systems exhibit extended conjugation within the C2=C3–N2–H enamino moiety and weaker delocalisation within the C2–N3=N4 diazenyl one. In both compounds **2a** and **2b** the N–H groups are not involved in any intermolecular H-bond.

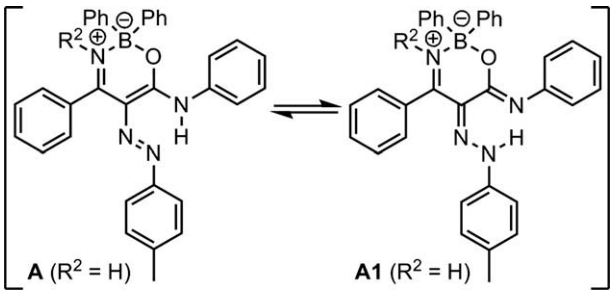
The diazaborinones **3a** and **3b** exhibit intramolecular H-bond assisted by resonance between a keto and a hydrazone group [29]. The HN4–N3=C2–C3=O1 heterodienic systems display a good delocalisation within both the C3=O1 keto and HN4–N3=C2 hydrazone groups. In both compounds the N1–H moiety forms intermolecular H-bond with O1 oxygen.

Triazaborine **4c** contains an amidic substituent at C2 which does not form the usual intermolecular N–H···O hydrogen bonded chain but only N4–H···N2 intramolecular H-bond which can be rather considered, owing to the narrow H-bond angle of 112(1)°, as a short intramolecular contact.

Table 2
^{15}N and ^{11}B chemical shifts of compounds **2a–d, 3a–b, 4a–c and 5c,d** in $CDCl_3$ (for notation of nitrogens see Scheme 2).

Product	$^{15}N1$	$^{15}N2$	$^{15}N3$	$^{15}N4$	^{11}B
2a[a]	−245.2	−223.5	85.9	12.3	2.51
2b[b]	−246.8	−219.9	78.9	5.4	2.37
2c[c]	−244.8	−218.9	84.3	0.5	4.41
2d[d]	−243.4	−216.0	133.9	−11.4	4.08
3a[e]	−228.8	−183.1	3.3	−189.1	−0.50
3b[f]	−228.0	−179.3	−4.9	−194.0	−0.93
3c[g]	−226.7	−178.4	1.9	−193.8	−2.54
3d[h]	−225.6	−177.6	−8.2	−197.8	−2.78
4a[i]	−262.7	−206.1	9.3	−159.9	−1.46
4b[j]	−262.9	−199.3	5.4	−163.4	−1.20
4c[k]	−262.8	−200.3	3.7	−167.7	−3.32
4d[l]	−262.0	−195.5	1.0	−171.3	−3.65
5c[m]					
Major[*]	−246.4	−265.1	96.1	14.1	–
Minor[#]	[o]	−92.4	−7.3	−212.3	
5d[n]					
Major[*]	−247.2	−260.5	85.3	3.4	–
Minor[#]	−239.5	−93.4	−17.7	−215.3	

[a] $^1J(^{15}N1,^1H) = 84.3$ Hz, $^1J(^{15}N2,^1H) = 81.8$ Hz.
[b] $^1J(^{15}N2,^1H) = 80.1$ Hz.
[c] $^1J(^{15}N1,^1H) = 81.4$ Hz.
[d] $^1J(^{15}N1,^1H) = 79.5$ Hz.
[e] $^1J(^{15}N4,^1H) = 93.7$ Hz, $^1J(^{15}N2,^1H) = 78.9$ Hz.
[f] $^1J(^{15}N4,^1H) = 94.2$ Hz, $^1J(^{15}N2,^1H) = 79.8$ Hz.
[g] $^1J(^{15}N4,^1H) = 96.4$ Hz.
[h] $^1J(^{15}N4,^1H) = 96.4$ Hz.
[i] $^1J(^{15}N1,^1H) = 89.3$ Hz, $^1J(^{15}N2,^1H) = 81.5$ Hz.
[j] $^1J(^{15}N1,^1H) = 89.6$ Hz, $^1J(^{15}N2,^1H) = 80.3$ Hz.
[k] $^1J(^{15}N1,^1H) = 89.4$ Hz.
[l] $^1J(^{15}N1,^1H) = 89.3$ Hz.
[m*] $J(^{15}N1,^1H) = 85$ Hz, $^1J(^{15}N2,^1H) = 92$ Hz, $^2J(^{15}N2,CH3) = 6.6$ Hz.
[m#] $^1J(^{15}N4,^1H) = 95.2$ Hz.
[n*] $^1J(^{15}N1,^1H) = 86$ Hz, $^1J(^{15}N2,^1H) = 92.6$ Hz, $^2J(^{15}N2,CH_3) = 5.5$ Hz.
[n#] $^1J(^{15}N1,^1H) = 82.7$ Hz, $^1J(^{15}N4,^1H) = 96$ Hz.
[o] Not detected.



Scheme 3. Azo-hydrazone tautomerism of the oxazaborines.

The six boron heterocycles assume quite different conformations, as evidenced by the puckering parameters [30] in Table S4, due to the different atoms forming the cycles and electronic and steric features of the substituents.

2.2. Rearrangement of the oxazaborines

When oxazaborines **2a–d** were refluxed in *N*,*N*-dimethylformamide, a recyclization occurred to give the diazaborinones **3a**,**c**,**d**, triazaborines **4a–d** and unreacted oxazaborines **2a–d** (Scheme 4; reaction conditions and yields are shown in Table 3). Although diazaborinone **3b** was identified in the reaction mixture (^1H NMR), its amount was insufficient for isolation.

It cannot be decided whether the amounts represented an equilibrium proportion of the products or further heating would completely transform the oxazaborines into a mixture of diazaborinones and triazaborines, because the substances undergo decomposition on long-term heating. The hypothesis that the mixture represents an equilibrium between the three products mentioned is supported by the fact that also diazaborinone **3b** is slowly transformed into a mixture of oxazaborine and triazaborine on heating. Hence, by increasing temperature it is possible to obtain

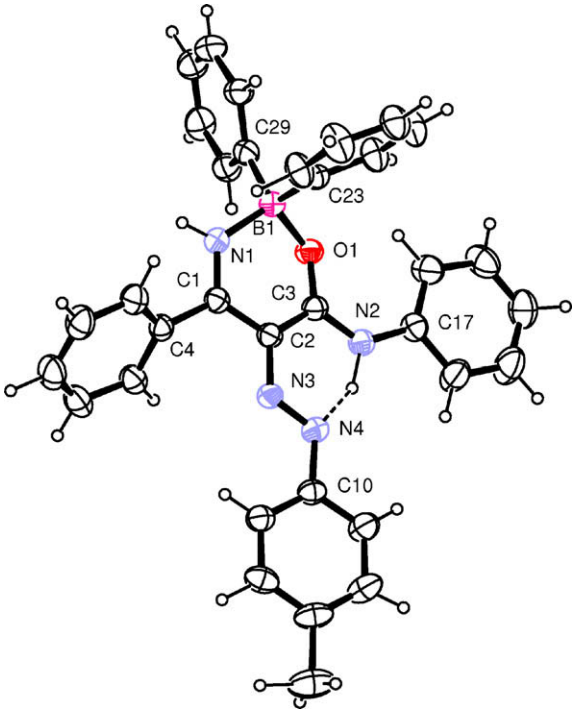


Fig. 2. ORTEP view of compound **2a**. The thermal ellipsoids are drawn at 30% probability level.

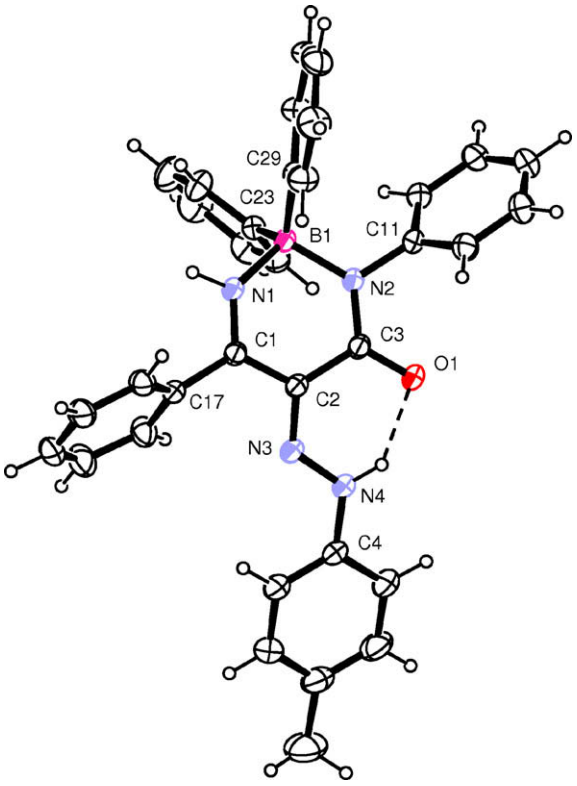


Fig. 3. ORTEP view of compound **3a**. The thermal ellipsoids are drawn at 30% probability level.

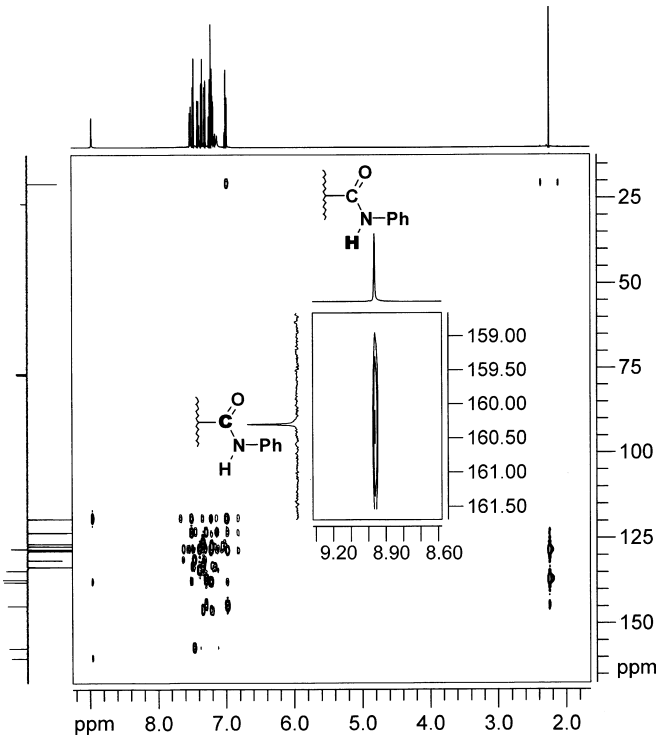


Fig. 4. 500.13 MHz $^{1}H–^{13}C$ *gs*HMBC spectrum of compound **4a** in $CDCl_3$.

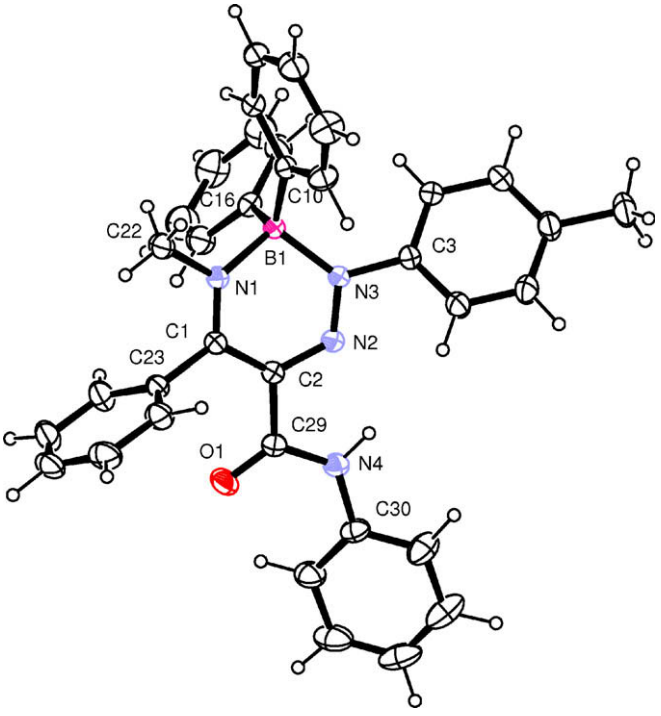


Fig. 5. ORTEP view of compound **4c**. The thermal ellipsoids are drawn at 30% probability level.

diazaborinone also from β-enaminoamides having a secondary enamino group. The difference in thermal rearrangement of oxazaborines **2a–d** as compared with the oxazaborines prepared from β-enaminones [22] lies in the fact that compounds **2c** and **2d** (derived from enamioamides with *N*-methyl group) give triazaborines already at room temperature or at enhanced temperature, while the oxazaborines with *N*-methyl group derived from β-enaminones [22] either do not undergo thermal rearangement at all or undergo it but very unwillingly, the yields of triazaborines being poor.

3. Conclusion

We have described a new, simple method of synthesis of six-membered heterocyclic compounds containing oxygen, nitrogen and boron. Besides the earlier-described reaction of β-enaminones with substituted benzenediazonium tetraphenylborates, here are now described reactions of β-enaminoamides having primary or secondary enamino group with 4-methylbenzenediazonium tetraphenylborate. This reaction at mild conditions (r.t.) produces mixtures of oxazaborines, diazaborinones and triazaborines. The primarily formed oxazaborines can be thermally rearranged to give a mixture of diazaborinones and triazaborines, which is possible even in the cases of the starting β-enaminoamides that have a secondary amino group (C=C–NHR). In the case of the oxazaborines derived from β-enaminones, an analogous rearrangement was only possible in the presence of primary amino group.

4. Experimental

3-Amino-*N*,3-diphenylprop-2-enamide (**1a**) and 3-amino-*N*-phenylbut-2-enamide (**1b**) were synthesized according to the literature procedures [31] from corresponding β-oxoamide and NH_4OAc.

*3-Methylamino-N,3-diphenylprop-2-enamide (**1c**).* To a solution of benzoylacetanilide (6.95 g, 26 mmol) in ethanol (50 mL) was added methylamine (33% solution in ethanol, 30 mL). The resulting solution was refluxed for 7 h and concentrated *in vacuo*. The residue was a yellow oil which solidified on standing overnight at room temperature. Recrystallization of the solid from toluene afforded enaminoamide **1c** as a white powder (4.61 g, 63%): m.p. 110–113 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.66 (d, J = 5 Hz, 3H), 4.54 (s, 1H), 6.95–6.99 (m, 1H), 7.03 (br s, 1H), 7.20–7.23 (m, 2H), 7.28–7.30 (m, 2H), 7.34–7.36 (m, 3H), 7.44–7.45 (m, 2H), 9.07 (q, J = 5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 87.4, 119.6, 122.7, 127.6, 128.1, 128.6, 128.8, 136.0, 138.9, 164.0, 168.7. Anal. Calc. for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.16; H, 6.43; N, 11.07%.

*3-Methylamino-N-phenylbut-2-enamide (**1d**).* This compound was prepared from acetoacetanilide according to the same procedure as **1c**. Recrystallization of the crude product from ethanol gave white solid (4.42 g, 45%): m.p. 142.5–144 °C (Ref. [32] 145 °C).

4.1. General procedures for the synthesis of oxazaborines, diazaborinones and triazaborines

Method A. A stoichiometric amount of freshly prepared 4-methylbenzenediazonium tetraphenylborate [22] (4.38 g, 10 mmol) was added to a stirred solution of β-enaminoamide (10 mmol) in dry dichloromethane (70 mL). The reaction mixture was stirred at room temperature for 96 h. Then it was filtered and the solvent was removed *in vacuo*. The crude residue containing one to three compounds was separated by column chromatography over silica gel (dichloromethane) and the fractions containing the individual compounds were recrystallised. The following compounds were prepared according to the procedure described.

*5-(4-Methylphenyldiazenyl)-2,2,4-triphenyl-6-phenylamino-3H-1,3,2λ⁴-oxazaborine (**2a**).* Recrystallization from toluene, yellow crystals (2.23 g, 43%): m.p. 199–201 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 6.99 (s, 1H), 7.11–7.12 (m, 2H), 7.19–7.23 (m, 3H), 7.27–7.30 (m, 6H), 7.37–7.40 (m, 2H), 7.45–7.48 (m, 2H), 7.51–7.55 (m, 5H), 7.64–7.69 (m, 4H), 14.70 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 114.9, 120.4, 121.9, 125.6, 126.3, 127.3,

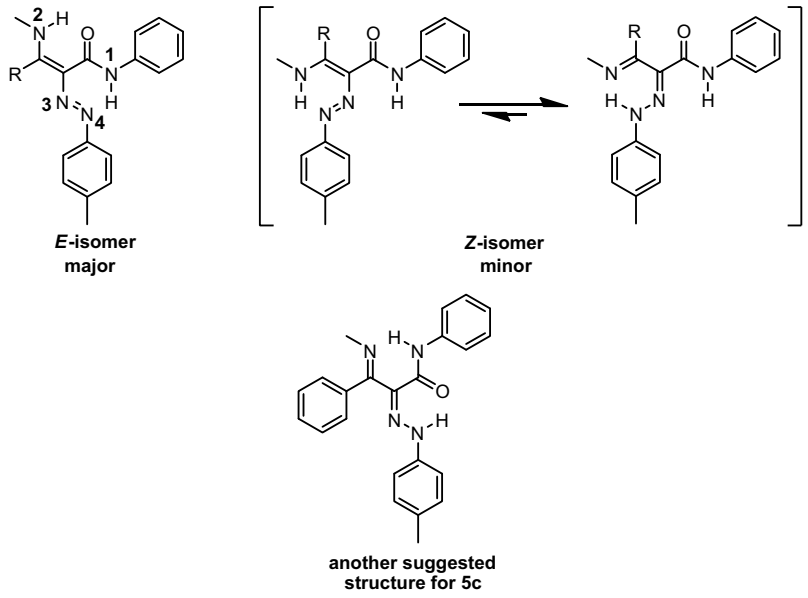
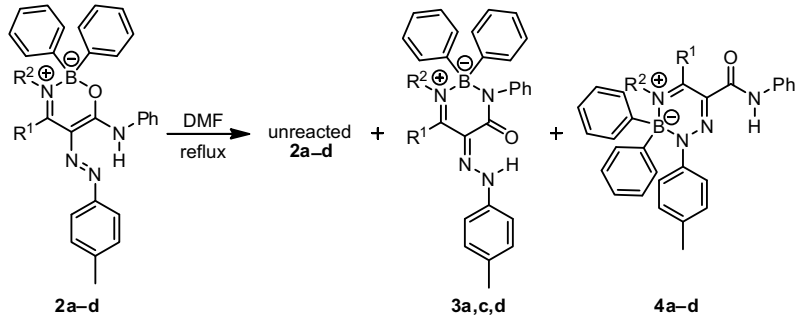


Fig. 6. The structure of compounds **5c** and **5d**.



Scheme 4. Rearrangement of oxazaborines **2a–d**.

127.9, 129.2, 129.4, 129.5, 130.9, 131.7, 135.5, 136.4, 137.6, 148.9, 149.2, 159.4, 169.3. Anal. Calc. for $C_{34}H_{29}BN_4O$: C, 78.47; H, 5.62; N, 10.77. Found: C, 78.61; H, 5.61; N, 10.65%.

*4-Methyl-5-(4-methylphenyldiazenyl)-2,2-diphenyl-6-phenylamino-3H-1,3,2λ⁴-oxazaborine (**2b**).* Recrystallization from toluene, yellow crystals (1.32 g, 29%): m.p. 206–208 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.58 (s, 3H), 6.96 (br s, 1H), 7.15–7.22 (m, 5H), 7.26–7.29 (m, 4H), 7.33–7.36 (m, 2H), 7.43–7.45 (m, 4H), 7.48–7.50 (m, 2H), 7.59–7.61 (m, 2H), 14.58 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 21.2, 114.9, 120.1, 121.9, 125.5, 126.3, 127.3, 129.1, 129.6, 131.6, 136.5, 137.5, 148.9, 149.2, 157.9, 170.0. Anal. Calc. for $C_{29}H_{27}BN_4O$: C, 75.99; H, 5.94; N, 12.22. Found: C, 75.93; H, 6.11; N, 12.29%.

*3-Methyl-5-(4-methylphenyldiazenyl)-2,2,4-triphenyl-6-phenylamino-1,3,2λ⁴-oxazaborine (**2c**).* Recrystallization from cyclohexane, yellow crystals (1.67 g, 31%): m.p. 204–207 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.81 (s, 3H), 6.70–7,04 (m, 4H), 7.12–7.15 (m, 1H), 7.24–7.27 (m, 2H), 7.29–7.33 (m, 6H), 7.35–7.37 (m, 2H), 7.45–7.53 (m, 7H), 7.55–7.57 (m, 2H), 14.67 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 39.3, 116.9, 119.9, 121.8, 125.3, 126.5, 127.2, 127.8, 128.0, 128.7, 129.1, 129.4, 132.9, 134.1, 136.9, 136.9, 147.3, 149.1, 158.2, 171.7. Anal. Calc. for $C_{35}H_{31}BN_4O$: C, 78.65; H, 5.85; N, 10.48. Found: C, 78.56; H, 5.97; N, 10.52%.

*3,4-Dimethyl-5-(4-methylphenyldiazenyl)-2,2-diphenyl-6-phenylamino-1,3,2λ⁴-oxazaborine (**2d**).* Recrystallization from cyclohexane, yellow crystals (2.08 g, 44%): m.p. 175.5–178.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.54 (s, 3H), 2.93 (s, 3H), 6.98–7.02 (m, 1H), 7.12–7.14 (m, 2H), 7.18–7.23 (m, 4H), 7.26–7.28 (m, 4H), 7.41–7.48 (m, 8H), 14.99 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1, 21.0, 37.5, 116.1, 119.8, 121.9, 125.1, 126.4, 127.1, 129.0, 129.6, 132.9, 136.8, 137.0, 147.4, 149.0, 157.3, 170.5. Anal. Calc. for $C_{30}H_{29}BN_4O$: C, 76.28; H, 6.19; N, 11.86. Found: C, 76.50; H, 6.25; N, 11.78%.

*5-[(4-Methylphenyl)hydrazono]-2,2,3,6-tetraphenyl-1H-1,3,2λ⁴-diazaborine-4-one (**3a**).* Recrystallization from ethanol, yellow crystals (0.84 g, 16%): m.p. 216–219 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 6.81–6.83 (m, 2H), 6.00–7.02 (m, 2H), 7.04–7.06 (m, 1H), 7.08–7.11 (m, 4H), 7.18–7.25 (m, 6H), 7.42–7.44 (m, 4H), 7.48–7.51 (m, 2H), 7.56–7.61 (m, 3H), 8.19 (s, 1H), 15.66 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 115.7, 121.8, 125.6, 126.2, 127.1, 127.9, 128.1, 128.2, 129.0, 129.9, 131.7, 133.4, 133.7, 135.4, 139.1, 141.1, 147.5, 164.3, 169.1. Anal. Calc. for $C_{34}H_{29}BN_4O$: C, 78.47; H, 5.62; N, 10.77. Found: C, 78.47; H, 5.69; N, 10.71%.

*6-Methyl-5-[(4-methylphenyl)hydrazono]-2,2,3-triphenyl-1H-1,3,2λ⁴-diazaborine-4-one (**3b**).* Recrystallization from ethanol, yellow crystals (0.91 g, 20%): m.p. 212–215 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.44 (s, 3H), 6.66–6.68 (m, 2H), 6.98–7.04 (m, 3H), 7.13–7.21 (m, 10H), 7.32–7.33 (m, 4H), 8.19 (br s, 1H), 15.46 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 20.9, 115.6, 122.4, 125.6, 126.2, 127.0, 127.9, 128.3, 130.0, 133.5, 135.2, 139.1, 141.0, 147.3, 163.6, 170.2. Anal. Calc. for $C_{29}H_{27}BN_4O$: C, 75.99; H, 5.94; N, 12.22. Found: C, 76.05; H, 6.14; N, 12.38%.

Table 3
Reaction times, products and yields of the rearrangement of oxazaborines **2a–d** in DMF at reflux.

	Reaction time (min)	Products of the rearrangement	The ratio of the product in the reaction mixture[a]	Yield after chromatography (%)	Yield after crystallization (%)
2a	140	**2a**	3	17	10
		3a	2	10	5
		4a	10	54	35
2b	140	**2b**	2	10	7
		3b	0.1	–	–
		4b	10	64	47
2c	370	**2c**	10	28	20
		3c	10	31	17
		4c	7	14	7
2d	400	**2d**	10	25	20
		3d	15	39	28
		4d	8	18	14

[a] From integration of ^{1}H NMR.

*2-(4-Methylphenyl)-3,3,5-triphenyl-4H-1,2,4,3λ^4-triazaborine-6-carboxanilide (**4a**).* Recrystallization from cyclohexane-toluene, yellow crystals (0.21 g, 4%): m.p. 201–204 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.01–7.05 (m, 3H), 7.12 (br s, 1H), 7.19–7.28 (m, 8H), 7.30–7.32 (m, 2H), 7.35–7.37 (m, 4H), 7.42–7.45 (m, 2H), 7.50–7.55 (m, 5H), 8.98 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 119.4, 123.4, 123.5, 126.7, 127.4, 128.1, 128.3, 128.4, 128.7, 128.8, 131.4, 133.4, 134.5, 137.1, 137.9, 144.8, 146.1, 157.3, 160.3. Anal. Calc. for $C_{34}H_{29}BN_4O$: C, 78.47; H, 5.62; N, 10.77. Found: C, 78.47; H, 5.87; N, 10.57%.

*5-Methyl-2-(4-methylphenyl)-3,3-diphenyl-4H-1,2,4,3λ^4-triazaborine-6-carboxanilide (**4b**).* Recrystallization from toluene, orange crystals (0.17 g, 4%): m.p. 215–218.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (s, 3H), 2.49 (s, 3H), 6.91–6.93 (m, 2H), 7.01–7.04 (m, 1H), 7.13–7.21 (m, 8H), 7.24–7.27 (m, 2H), 7.31–7.33 (m, 4H), 7.38 (br s, 1H), 7.50–7.52 (m, 2H), 8.91 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 23.6, 119.7, 122.7, 123.6, 126.6, 126.7, 127.3, 128.6, 128.8, 133.4, 136.6, 137.8, 145.0, 146.5, 159.1, 161.8. Anal. Calc. for $C_{29}H_{27}BN_4O$: C, 75.99; H, 5.94; N, 12.22. Found: C, 76.07; H, 6.06; N, 12.18%.

*4-Methyl-2-(4-methylphenyl)-3,3,5-triphenyl-4H-1,2,4,3λ^4-triazaborine-6-carboxanilide (**4c**).* Recrystallization from toluene, orange crystals (1.24 g, 23%): m.p. 225–229 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.80 (s, 3H), 6.94–6.97 (m, 3H), 7.14–7.24 (m, 12H), 7.35–7.36 (m, 4H), 7.40–7.45 (m, 5H), 8.93 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 40.4, 119.4, 123.2, 123.6, 126.3, 126.6, 127.4, 128.4, 128.6, 128.9, 129.3, 133.8, 134.0, 136.4, 138.0, 144.8, 145.4, 159.1, 160.6. Anal. Calc. for $C_{35}H_{31}BN_4O$: C, 78.65; H, 5.85; N, 10.48. Found: C, 78.63; H, 6.05; N, 10.47%.

Method B. The procedure was the same as for the method A, excepting re-melted and finally grounded sodium acetate (2.46 g, 30 mmol) was added to a stirred solution of β-enaminoamide and 4-methylbenzenediazonium tetraphenylborate. The following compounds were prepared by the procedure described.

*Compound **2a**.* Yellow crystals; 3.54 g (68%).

*Compound **2b**.* Yellow crystals; 2 g (44%).

*Compound **2c**.* Yellow crystals; 0.23 g (4%).

*Compound **2d**.* Yellow crystals; 0.6 g (13%).

*Compound **4a**.* Yellow crystals; 0.17 g (3%).

*3-Methylamino-2-(4-methylphenyldiazenyl)-N,3-diphenylprop-2-enamide (**5c**).* The title compound was obtained chromatographically as yellow crystals from the same reaction mixture as the compound **2c** (1.13 g, 31%): recrystallization from ethanol, m.p. 123.5–127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (s, 0.87H, min.), 2.22 (s, 3H, maj.), 2.81 (d, 3H, ^3J = 5.2 Hz, maj.), 3.12 (s, 0.83H, min.), 6.61–6.66 (m, 0.52H, min.), 6.88–6.90 (m, 0.69H, min.), 6.96–7.08 (m, 6.18H, maj. + min.), 7.17–7.20 (m, 2.3H, maj. + min.), 7.29–7.33 (m, 3H, maj.), 7.36–7.39 (m, 4H, maj.), 7.64–7.67 (m, 2.72H, maj. + min.), 11.84 (br q, 1H, ^3J = 5.1 Hz, maj.), 13.36 (br s, 1H, maj.), 13.63 (s, 0.26 H, min.), 14.08 (s, 0.26 H, min.); ^{13}C NMR (125 MHz, $CDCl_3$) major form δ 20.8, 31.9, 114.2, 120.1, 120.2, 120.6, 123.3, 127.5, 128.1, 128.6, 129.1, 133.2, 136.5, 138.6, 150.0, 164.3, 172.8; minor form δ 20.4, 39.7, 115.7, 120.5, 123.9, 125.8, 127.3, 127.5, 128.4, 128.7, 129.4, 132.4, 135.9, 137.8, 140.3, 163.7, 171.2. Anal. Calc. for $C_{23}H_{22}N_4O$: C, 74.57; H, 5.99; N, 15.12. Found: C, 74.40; H, 6.20; N, 15.20%.

*3-Methylamino-2-(4-methylphenyldiazenyl)-N-phenylbut-2-enamide (**5d**).* The title compound was obtained (1.2 g, 39%) as yellow crystals: recrystallization from cyclohexane, m.p. 154–155.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) major form δ 2.30 (s, 3H), 2.34 (s, 3H), 2.88 (d, 3H, ^3J = 5.2 Hz), 6.99–7.04 (m, 1.38H (maj. + min.)), 7.10–7.12 (m, 2H), 7.26–7.30 (m, 2.32H (maj. + min.)), 7.41–7.43 (m, 2H), 7.59–7.61 (m, 2H), 12.00 (q, 1H, ^3J = 5.2 Hz), 13.59 (s, 1 H); minor form δ 2.07 (s, 0.37H), 2.24 (s, 0.41H), 3.16 (s, 0.42H), 6.99–7.04 (m, 1.38H (maj. + min.)), 7.07–7.09 (m, 0.26H), 7.26–7.30 (m, 2.32H (maj. + min.)), 7.54–7.55 (m, 0.35H), 13.86 (s, 1H), 14.14 (s, 1 H); ^{13}C NMR (125.77 MHz, $CDCl_3$) major form δ 14.0, 20.9, 30.5, 119.5, 120.1, 122.8, 123.2, 128.6, 129.4, 136.4, 138.8, 150.3, 164.0, 172.2; minor form δ 13.6, 20.6, 37.9, 120.5, 123.8, 128.7, 129.8, 132.4, 139.0, 140.6, 163.9, 169.6. Anal. Calc. for $C_{18}H_{20}N_4O$: C, 70.11; H, 6.54; N, 18.17. Found: C, 70.36; H, 6.44; N, 18.13%.

*5-(4-Methylphenyldiazenyl)-2,2,4-triphenyl-6-[$^2H_5$]phenylamino-3H-1,3,2λ^4-oxazaborine (**2a**).* The title compound was prepared according to the procedure B. 3-Amino-*N*-[$^2H_5$]phenyl-3-phenylprop-2-enamide was used instead of enamide **1a**. It was obtained as yellow crystals (1.32 g, 63%): recrystallization from cyclohexane-toluene, m.p. 200.5–202.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (s, 3H), 6.93 (s, 1H), 7.04–7.06 (m, 2H), 7.16–7.20 (m, 2H), 7.23–7.28 (m, 6H), 7.37–7.40 (m, 2H), 7.42–7.45 (m, 1H), 7.50–7.52 (m, 4H), 7.57–7.58 (m, 2H), 14.67 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 121.6 (t, ^1J(^{13}C, ^{2}H) = 25 Hz), 125.2 (t, ^1J(^{13}C, ^{2}H) = 25 Hz), 126.3, 127.3, 127.9, 128.7 (t, ^1J(^{13}C, ^{2}H) = 25 Hz),129.4, 129.5, 131.0, 131.7, 135.6, 136.3, 137.7, 148.9, 149.2, 159.5, 169.3. Anal. Calc. for $C_{34}H_{24}D_5BN_4O$: C, 77.72; H, 6.52; N, 10.66. Found: C, 77.95; H, 6.81; N, 10.57%.

4.2. Rearrangement of oxazaborines

The appropriate oxazaborines (3 mmol) was dissolved in DMF (8 mL) and the solution was refluxed (the reaction times and resulting yields are shown in Table 3). DMF was evaporated *in vacuo* and the residue was subjected to the column chromatography over silica gel (dichloromethane).

4.2.1. 2,2,3,6-Tetraphenyl-1-methyl-5-[(4-methylphenyl)hydrazono]-1H-1,3,2λ^4-diazaborine-4-one (**3c**)

Recrystallization from cyclohexane-toluene, yellow crystals: m.p. 232–235 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.80 (s, 3H), 6.55–6.56 (m, 2H), 6.70–6.72 (m, 2H), 6.95–6.96 (m, 2H), 6.98–7.00 (m, 3H), 7.20–7.26 (m, 8H), 7.48–7.50 (m, 7H), 15.27 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 41.0, 115.3, 124.3, 125.6, 127.0, 127.1, 127.9, 128.3, 128.5, 129.3, 129.8, 132.9, 133.9, 134.6, 139.4, 141.0, 145.9, 163.1, 171.8. Anal. Calc. for $C_{35}H_{31}BN_4O$: C, 78.65; H, 5.85; N, 10.48. Found: C, 78.91; H, 6.13; N, 10.49%.

4.2.2. 1,6-Dimethyl-5-[(4-methylphenyl)hydrazono]-2,2,3-triphenyl-1H-1,3,2λ^4-diazaborine-4-one (**3d**)

Recrystallization from ethanol, yellow crystals: m.p. 205.5–208 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.56 (s, 3H), 3.00 (s, 3H), 6.48–6.50 (m, 2H), 6.95–6.96 (m, 3H), 7.12–7.14 (m,

2H), 7.16–7.21 (m, 8H), 7.37–7.38 (m, 4H), 15.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.2, 20.8, 39.8, 115.3, 123.2, 125.5, 126.1, 127.0, 127.8, 128.4, 130.0, 133.9, 134.5, 139.5, 141.0, 145.9, 162.8, 170.9. Anal. Calc. for $C_{30}H_{29}BN_4O$: C, 76.28; H, 6.19; N, 11.86. Found: C, 76.42; H, 6.41; N, 11.82%.

*4.2.3. 4,5-Dimethyl-2-(4-methylphenyl)-3,3-diphenyl-4H-1,2,4,3λ^4-triazaborine-6-carboxanilide (**4d**)*

Recrystallization from cyclohexane, orange crystals: m.p. 180–182.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.67 (s, 3H), 3.00 (s, 1H), 6.88–6.89 (m, 2H), 7.03–7.06 (m, 3H), 7.15–7.22 (m, 6H), 7.27–7.33 (m, 6H), 7.54–7.56 (m, 2H), 9.03 (s, 1H); ^{13}C NMR (125.77 MHz, $CDCl_3$) δ 17.7, 20.8, 39.0, 119.6, 123.1, 123.4, 126.5, 127.4, 128.2, 128.3, 128.8, 133.7, 135.8, 145.0, 145.5, 159.8, 162.1. Anal. Calc. for $C_{30}H_{29}BN_4O$: C, 76.28; H, 6.19; N, 11.86. Found: C, 76.24; H, 6.34; N, 11.89%.

Acknowledgments

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Appendix A. Supplementary material

Experimental section such as NMR, crystallography and general, copies of ^{1}H and ^{13}C NMR for all new compounds, ^{15}N NMR spectra for selected compounds (**2b**–**d**, **3b**–**d**, **4b**–**d**, **5c**,**d**), ORTEP views for **2b**,**c** and **3b**, X-ray tables and crystalographic information files. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.004.

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