Novel 5-(4-Substituted-phenyldiazenyl)-1,3,2λ^4-oxazaborines and Their Rearrangement to 1,2,4,3λ^4-Triazaborines

Markéta Pešková,[†] Petr Šimůnek,*[,†] Valerio Bertolasi,[‡] Vladimír Macháček,[†] and Antonín Lyčka[§]

Department of Organic Chemistry, Faculty of Chemical Technology, University of Pardubice, Nám Čs. Legií 565, CZ-532 10 Pardubice, Czech Republic, Dipartimento di Chimica and Centro di Strutturistica Diffrattometrica, Università di Ferrara, Via L. Borsari 46, I-441 00 Ferrara, Italy, and Research Institute for Organic Syntheses (VUOS), Rybitví 296, CZ-532 18 Pardubice 20, Czech Republic

Received December 19, 2005

The reaction of substituted benzenediazonium tetraphenylborates with the β-enaminones derived from pentane-2,4-dione, 1-phenylbutane-1,3-dione, and 1,4-diphenylbutane-1,3-dione with a primary or secondary (*N*-methyl, *N*-phenyl) amino group in CH_2Cl_2 gives 5-(substituted-phenyldiazenyl)-2,2-diphenyl-4,6-disubstituted-1,3,2λ^4-oxazaborines or 5-(substituted-phenyldiazenyl)-2,2-diphenyl-3,4,6-trisubstituted-1,3,2λ^4-oxazaborines, respectively. The reaction intermediate of these compounds has been identified, and a mechanism for the reaction has been suggested. Substituted 1,3,2λ^4-oxazaborines gradually rearrange into 1,2,4,3λ^4-triazaborines at temperatures above 100 °C.

Introduction

In earlier communications[1−7] we published results on the reactions of substituted benzenediazonium tetrafluoroborates and hexafluorophosphates with β-enaminones.

Depending on the structure of the starting enaminone and substitution in the benzenediazonium used, three situations have been described so far.

1. The reaction takes place between only one molecule of diazonium and one molecule of enaminone at the methine α-carbon atom (the tautomeric form of the azo coupling product depends particularly upon the structure of enaminone).[1−3]

2. The reaction takes place between two molecules of diazonium and one molecule of enaminone at its two different carbon atoms.[4,5]

3. The reaction takes place between two molecules of diazonium and one molecule of enaminone at its two different carbon atoms, and subsequently, the substituted pyridazinium salt is formed[6,7] via intramolecular cyclization.

The pyridazinium salts are formed in good yields, particularly from substituted benzenediazonium hexafluorophosphates. We wanted to find out what effect upon the reaction result would be observed after replacing the hexafluorophosphate counterion by another noncoordinating anion. We have found that tetraphenylborates react with β-enaminones in an entirely different way. The aim of this work is to study this reaction.

Results and Discussion

We have found that the reaction of 4-(methylamino)pent-3-en-2-one (**1**) with 4-methoxybenzenediazonium tetraphenylborate in CH_2Cl_2 in the presence of remelted sodium acetate gives a 58% yield of 5-((4-methoxyphenyl)diazenyl)-3,4,6-trimethyl-2,2-diphenyl-1,3,2λ^4-oxazaborine (**9**). The structure of compound **9** was proved by means of X-ray diffraction (Figure 1). The formation of oxazaborines is not limited to the aforementioned starting compounds: substituted 5-(phenyldiazenyl)-2,2-diphenyl-1,3,2λ^4-oxazaborines are also formed by the reaction of β-enaminones **2**−**6** with 4-(dimethylamino)-, 4-methoxy-, and 4-methylbenzenediazonium tetraphenylborate as the only isolated products (Scheme 1). Benzenediazonium tetraphenylborates are relatively stable only if the benzenediazonium ion carries an electron-donor substituent or hydrogen. The literature[8] also describes the preparation of 4-(ethoxycarbonyl)benzenediazonium tetraphenylborate, which is stable for a period of 2 min at 0 °C. Our attempt at preparing the 4-nitro derivative failed. The molecules of starting β-enaminones can be varied: the amino group present can be primary or secondary (*N*-methyl, *N*-phenyl), the acetyl group can be replaced by benzoyl, and the 5-methyl group can be replaced by benzyl. The oxazaborines prepared were identified by means of X-ray diffraction and ^{1}H, ^{13}C, ^{15}N, and ^{11}B NMR spectra.

The ^{1}H and ^{13}C NMR parameters are given in the Supporting Information, and selected ^{11}B and ^{15}N NMR data of compounds **8**−**16** are presented in Table 1.

The phenyl groups attached to boron in oxazaborines **8**−**10** and **12**−**16** are chemically equivalent, at least on the NMR time scale in $CDCl_3$. In the case of oxazaborine **11**, which is substituted at nitrogen N3 with the 2,4-dimethoxyphenyl group, the two phenyl groups are chemically nonequivalent on the NMR time scale, due probably to steric reasons. The nonequiva-

* To whom correspondence should be addressed. E-mail: petr.simunek@upce.cz. Tel: +420 466 037 039. Fax: +420 466 037 068.
† University of Pardubice.
‡ Università di Ferrara.
§ Research Institute for Organic Syntheses (VUOS).

(1) Macháček, V.; Lyčka, A.; Šimůnek, P.; Weidlich, T. *Magn. Reson. Chem.* **2000**, *39*, 293.
(2) Šimůnek, P.; Bertolasi, V.; Macháček, V. *J. Mol. Struct.* **2002**, *642*, 41.
(3) Šimůnek, P.; Bertolasi, V.; Pešková, M.; Macháček, V.; Lyčka, A. *Org. Biomol. Chem.* **2005**, *3*, 1217.
(4) Šimůnek, P.; Lyčka, A.; Macháček, V. *Eur. J. Org. Chem.* **2002**, 2764.
(5) Šimůnek, P.; Bertolasi V.; Macháček, V.; Lyčka, A. *Org. Biomol. Chem.* **2003**, *1*, 3250.
(6) Šimůnek, P.; Pešková, M.; Bertolasi, V.; Lyčka, A.; Macháček, V. *Eur. J. Org. Chem.* **2004**, 5055.
(7) Šimůnek, P.; Pešková, M.; Bertolasi, V.; Macháček, V.; Lyčka, A. *Tetrahedron* **2005**, *61*, 8130.
(8) Lindeman, S. V.; Kosynkin, D.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 13268.

10.1021/om051078x CCC: $33.50
Publication on Web 03/14/2006

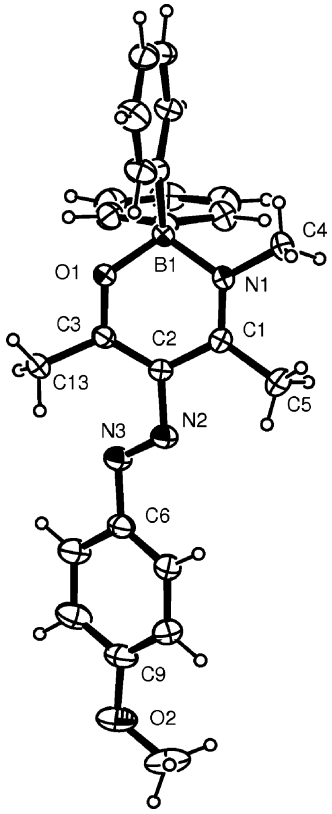


Figure 1. ORTEP view of compound **9** displaying thermal ellipsoids at 30% probability. Selected bond distances (Å): B1−N1 = 1.596(2), N1−C1 = 1.304(2), C1−C2 = 1.442(2), C2−C3 = 1.383(2), O1−C3 = 1.307(2), B1−O1 = 1.522(2). The six-membered ring B1−N1−C1−C2−C3−O1 adopts a mixed boat-twisted conformation, $B_{4,1}/^3T_1$, with the following puckering parameters:[9] $\varphi = 171.9(2)°$, $Q = 0.437(2)$ Å, and $\theta = 107.9(2)°$.

Table 1. ^{11}B and Selected ^{15}N Chemical Shifts of the Compounds 8−18 in $CDCl_3$

	chem shift (ppm)			
compd	N_α	N_β	N_γ	B
8	88.4	not detected	−204.6	1.8
9	85.5	99.5	−200.9	3.7
10	85.6	not detected	−201.6	1.4
11	86.9	not detected	−196.0	3.6
12				3.5
13				3.5
14				4.1
15	not detected	95.3	−208.3	1.9
16				4.0
17	−152.7	27.5	−198.5	−1.9
18	−151.1	27.5	−205.9	−1.5
Im[a,b]	−197.6	−12.8[c]	−157.1	−2.4

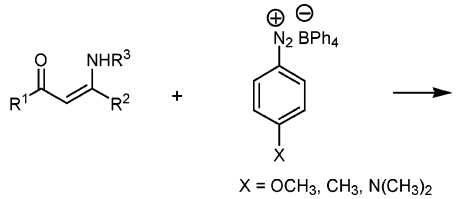
[a] Data measured in CD_2Cl_2 (see Scheme 3). [b] $^1J(^{15}N_\alpha, ^1H) = 96.1$ Hz, $^1J(^{15}N_\gamma, ^1H) = 72.8$ Hz. [c] From the ^{15}N-enriched compound **Im-^{15}N** (see Scheme 3).

lence is manifested by formation of complex multiplets of aromatic protons in the ^{1}H NMR spectra.

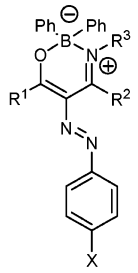
It is known[10] that substituted 1,3,2λ^4-oxazaborines are formed by the reaction of β-enaminones with diphenylborinic acid or its derivatives. The question of whether in our case the first process is formation of 3,4-dimethyl-2,2,6-triphenyl-1,3,2λ^4-oxazaborine (**16**) from 3-(methylamino)-1-phenylbut-2-en-1-one (**4**) (Scheme 2), followed by azo coupling of compound **16**, or

(9) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.
(10) Bally, I.; Ciornei, E.; Vasilescu, A.; Balaban, A. T. *Tetrahedron* **1973**, *29*, 3185.

Scheme 1

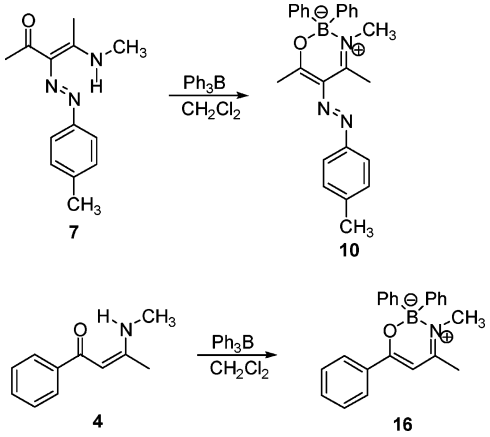


1 $R^1 = R^2 = R^3 = CH_3$
2 $R^1 = R^2 = CH_3$ $R^3 = H$
3 $R^1 = R^2 = CH_3$ $R^3 = 2,4\text{-}(OCH_3)_2C_6H_3$
4 $R^1 = C_6H_5$ $R^2 = R^3 = CH_3$
5 $R^1 = C_6H_5$ $R^2 = C_6H_5CH_2$ $R^3 = CH_3$
6 $R^1 = CH_3$ $R^2 = C_6H_5$ $R^3 = H$



8 $R^1 = R^2 = CH_3$, $R^3 = H$, X = OCH_3
9 $R^1 = R^2 = R^3 = CH_3$, X = OCH_3
10 $R^1 = R^2 = R^3 = CH_3$, X = CH_3
11 $R^1 = R^2 = CH_3$, $R^3 = 2,4\text{-}(OCH_3)_2C_6H_3$ X = OCH_3
12 $R^1 = C_6H_5$, $R^2 = R^3 = CH_3$, X = OCH_3
13 $R^1 = C_6H_5$, $R^2 = R^3 = CH_3$, X = $N(CH_3)_2$
14 $R^1 = C_6H_5$, $R^2 = C_6H_5CH_2$, $R^3 = CH_3$, X = OCH_3
15 $R^1 = CH_3$, $R^2 = C_6H_5$, $R^3 = H$, X = OCH_3

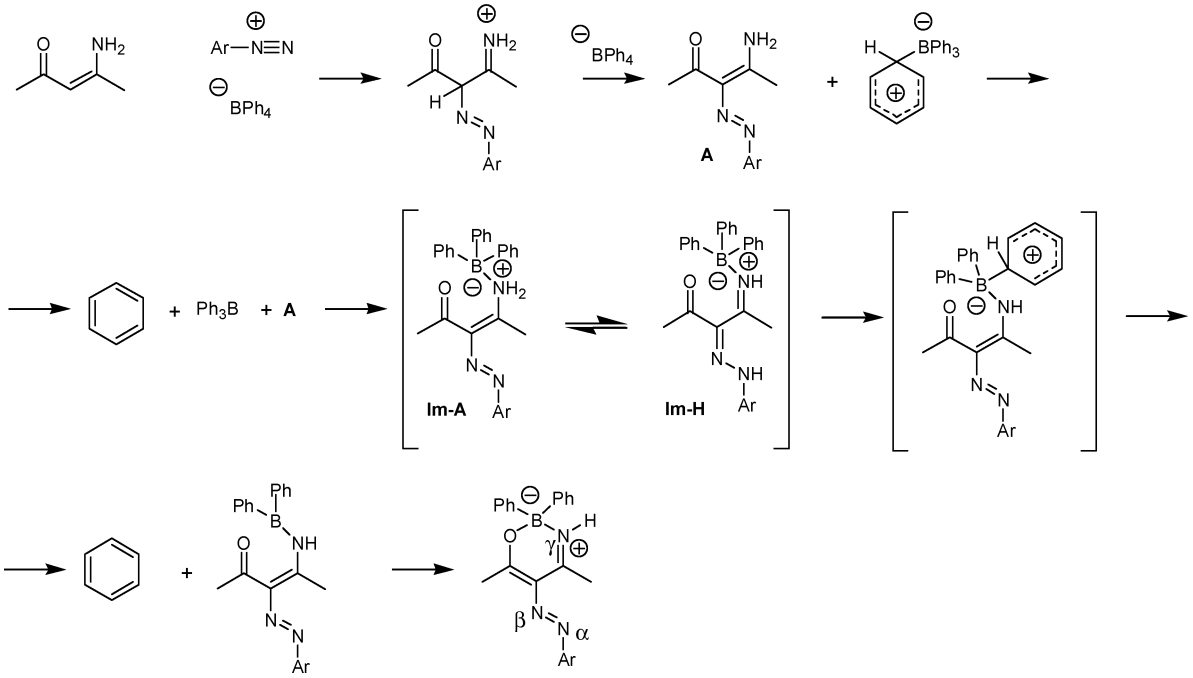
Scheme 2



the reverse sequence of these reaction steps was answered by the finding that 3,4-dimethyl-2,2,6-triphenyl-1,3,2λ^4-oxazaborine (**16**) does not react with diazonium salt.

Hence, the first elementary step is the reaction of β-enaminone with diazonium ion, which produces a protonated species with the character of a Brønsted *N* acid (Scheme 3). The reaction takes place in heterogeneous phases, the base used being sodium acetate, which is virtually insoluble in the reaction medium (CH_2Cl_2). The proton transfer from the nitrogen atom of the *N* acid to the acetate ion through the phase interface is slower than the reaction of this *N* acid with tetraphenylborate. The reaction of tetraphenylborate anion with heterocyclic *N* acids is known;[11] it leads to the formation of stable isolable coordination compounds of the type $HetN^+-B^-Ph_3$ and benzene. The reaction obviously goes through a Wheland-type intermediate,[12] and this is in S_EAr referred to as protodeboronation. An

Scheme 3

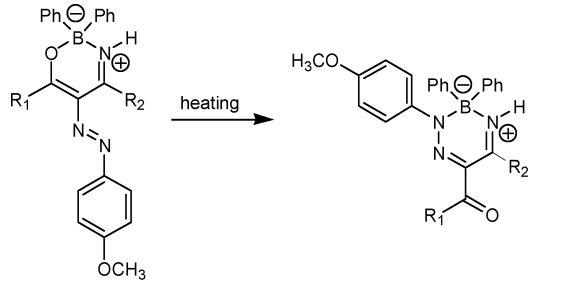


analogous process can also be presumed in the reaction studied by us (Scheme 3).

The reaction between enaminone **2** and 4-methoxybenzenediazonium tetraphenylborate in CD_2Cl_2 at room temperature was followed in an NMR cell. After ca. 50 min, the starting enaminone disappeared from the reaction mixture and the intermediate **Im** was formed. The **Im** molecule contains an acetyl group ($\delta(^{13}C{=}O)$ 193.56), as was proven by means of $^1H-^{13}C$ HMBC. Its boron chemical shift, $\delta(^{11}B)$ −2.4, corresponds to a tetracoordinated boron atom.[13] According to the chemical shifts $\delta(^{15}N)$ (Table 1), this intermediate could exist in CD_2Cl_2 solution in its tautomeric hydrazone form **Im-H** (Scheme 3). This conclusion is also supported by the presence of two different NH protons, whose coupling constants $^1J(^1H-^{15}N)$ agree with the suggested structure of intermediate **Im** (Table 1) as well. This intermediate could be isolated, but its stability was not sufficient for purification and elemental analysis. Within ca. 12 h the intermediate is transformed into oxazaborine **8**, both in solution and in the solid phase. The slow transformation **Im** → **8** could also be monitored in the NMR cell.

If the reaction of enaminones with diazonium tetraphenylborates is carried out in the presence of pyridine as a base instead of sodium acetate (pyridine has comparable basicity, but it is soluble in CH_2Cl_2), then oxazaborines are not formed. This is obviously a consequence of the fact that the proton needed for the protodeboronation is depleted by a far faster acid−base reaction. In these cases the azo coupling reaction produces a substance of type **7**. On the other hand, oxazaborines are formed even if no base is used. (Note: the presence of base is necessary in the preparation of azo coupling products from β-enaminones and diazonium salts, since the acid set free retards the reaction until it finally stops.)[14]

Scheme 4



In the second step, the protodeboronation is repeated and another benzene molecule is produced (Scheme 3). The reaction mechanism suggested is supported also by the fact that 4-(methylamino)-3-((4-methylphenyl)diazenyl)pent-3-en-2-one (**7**) reacts with the triphenylborane added and also gives 3,4,6-trimethyl-5-((4-methylphenyl)diazenyl)-2,2-diphenyl-1,3,2λ⁴-oxazaborine (**10**) and benzene (Scheme 2). The formation of benzene was proved by the method of standard addition in an experiment carried out directly in an NMR cell.

Long-term heating (26 h) of 5-((4-methoxyphenyl)diazenyl)-4,6-dimethyl-2,2-diphenyl-3*H*-1,3,2λ⁴-oxazaborine (**8**) in boiling toluene results in its transformation into 6-acetyl-2-(4-methoxyphenyl)-5-methyl-3,3-diphenyl-4*H*-1,2,4,3λ⁴-triazaborine (**17**) (Scheme 4). The structure of this compound was first suggested on the basis of the presence of an acetyl group in the NMR spectra and was subsequently confirmed by means of X-ray diffraction (Figure 2). The course of rearrangement of the oxazaborine **8** into triazaborine **17** was monitored at a temperature of 200 °C without solvent by the method of taking samples and their analysis by means of ^1H NMR (Figure 3). At enhanced temperatures, oxazaborine **8** probably undergoes reversible B−O

(11) Kiviniemi, S.; Nissinen, M.; Alaviuhkola, T.; Rissanen, K.; Pursiainen, J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 2364.

(12) Meisters, M.; Vandeberg, J. T.; Cassaretto, F. P.; Posvic, H.; Moore, C. E. *Anal. Chim. Acta* **1970**, *49*, 481.

(13) Kennedy, J. D. in *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 8.

(14) Macháček, V.; Čegan, A.; Halama, A.; Rožňavská, O. *Collect. Czech. Chem. Commun.* **1995**, *60*, 1367.

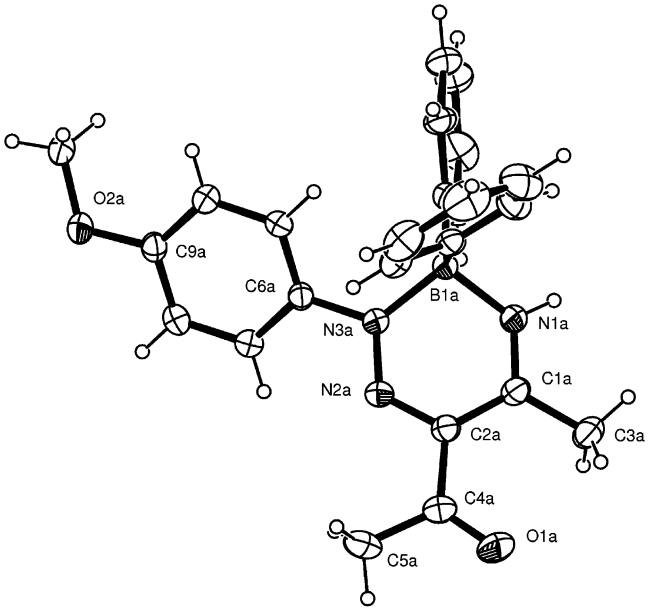


Figure 2. ORTEP view of one molecule of the asymmetric unit of compound **17** displaying thermal ellipsoids at 30% probability. Selected bond distances (Å) for molecules A/B: B1−N1 = 1.567(4)/1.567(4), N1−C1 = 1.300(4)/1.302(4), C1−C2 = 1.436(4)/1.441(4), C2−N2 = 1.338(3)/1.336(3), N2−N3 = 1.307(3)/1.307(3), B1−N3 = 1.588(4)/1.591(3). The six-membered rings B1−N1−C1−C2−N2−N3, for the two independent molecules A and B, adopt boat conformations ^{1,4}B and $B_{4,1}$, respectively, with the following puckering parameters:[9] $\varphi = -1.8(5)/179.8(4)°$, $Q = 0.341(3)/0.408(11)$ Å, and $\theta = 70.5(4)/108.5(6)°$.

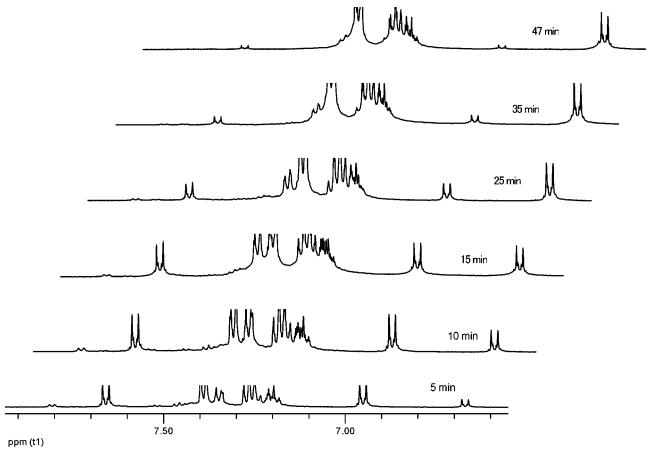


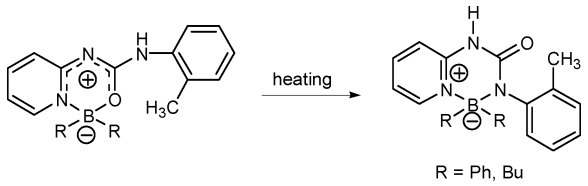
Figure 3. ^{1}H NMR analysis of the thermal rearrangement of **8** in CD_2Cl_2. For details see the Experimental Section.

bond splitting followed by irreversible formation of a B−N bond with the β-nitrogen atom of the azo group (Scheme 4). The thermal rearrangement of a heterocycle with an O−B−N grouping into an N−B−N type is known[15] (Scheme 5). The formation of triazaborine is probably controlled thermodynamically.

In analogy to oxazaborine **8**, also oxazaborine **15** undergoes a rearrangement, giving the triazaborine **18** (Scheme 4). The oxazaborines substituted at the 3-nitrogen give mixtures of products under the same conditions. For the NMR parameters of the triazaborines, see the Supporting Information and Table 1.

(15) Dorokhov, V. A.; Lavrinovich, L. I.; Botchkareva, M. N.; Zolotarev, B. M.; Mikhailov, B. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 253.

Scheme 5



Experimental Section

NMR. The NMR spectra were measured at laboratory temperature with a Bruker Avance 500 spectrometer equipped with a 5 mm broad-band probe with a gradient of magnetic field in the direction of the *z* axis at frequencies of 500.13 MHz (^{1}H), 125.77 MHz (^{13}C), and 50.69 MHz (^{15}N) and with a Bruker AMX 360 spectrometer at frequencies of 360.14 MHz (^{1}H), 90.57 MHz (^{13}C), and 115.55 MHz (^{11}B). The ^{1}H NMR spectra were calibrated in $CDCl_3$ with hexamethyldisiloxane (δ 0.05) and in CD_2Cl_2 with the central signal of the solvent multiplet (δ 5.32). The ^{13}C NMR spectra were calibrated with the central signal of the solvent multiplet (δ 76.9 in $CDCl_3$ and δ 54.0 in CD_2Cl_2). The carbon NMR spectra were measured in the standard way and by means of the APT pulse sequence (spectral width 26.455 kHz, acquisition time 1.238 s, zero filling to 64K, and line broadening 1 Hz prior to Fourier transformation). The ^{15}N NMR spectra were calibrated on external neat ^{15}N nitromethane placed in a coaxial capillary (δ 0.0). The ^{11}B NMR spectra were calibrated on external $B(OCH_3)_3$ placed in a coaxial capillary (δ 18.1). To suppress the signals of ^{11}B nuclei from the NMR tube glass, the measurements were carried out in Teflon sample tube liners (Aldrich) inserted into 5 mm tubes whose bottom part of about 25 mm length was cut off. The $\delta(^{15}N)$ values were measured with the help of techniques with inversion detection (gradient selected 2D ^{1}H−^{15}N HMBC) processed in the magnitude mode. The gradient ratios were 70:30:50.1. Experiments were performed with an NH one-bond coupling of 90 Hz and NH long-range coupling of 5 Hz, with 2k × 160 zero filled to 2k × 1k, sine-bell squared in both dimensions. One-bond coupling constants ^{1}H−^{15}N of the compound **Im-**^{15}N were measured by means of gradient-selected 1D ^{1}H−^{15}N HMBC optimized for 90 Hz. The spectral width was 10 kHz, with acquisition time 3.277 s and line broadening of 3 Hz prior to Fourier transformation. ^{1}H and ^{13}C NMR data of the compounds prepared are given in the Supporting Information.

Crystallography. X-ray diffraction data for compounds **9**−**13** and **17** were collected at room temperature, 295 K, on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The structures were solved by direct methods (SIR97)[16] and were refined (SHELXL-97)[17] using full-matrix least squares. ORTEP[18] views are given in Figures 1 and 2 and in the Supporting Information.

Crystal data for **9**: $C_{25}H_{26}BN_3O_2$, triclinic, space group $P\bar{1}$, a = 7.5283(2) Å, b = 10.7694(4) Å, c = 14.2237(5) Å, α = 91.562(2)°, β = 101.592(1)°, γ = 97.572(2)°, V = 1118.10(6) Å^3, Z = 2, D_c = 1.222 g cm^{-3}, intensity data collected with $\theta \leq 30°$, 6454 independent reflections measured, 3324 observed reflections ($I > 2\sigma(I)$), final R index 0.0539 (observed reflections), R_w = 0.1481 (all reflections), S = 0.993.

Crystal data for **17**: $C_{24}H_{24}BN_3O_2$, monoclinic, space group $P2_1$, a = 10.2803(4) Å, b = 12.4823(5) Å, c = 17.2317(8) Å, β = 96.390(2)°, V = 2197.5(2) Å^3, Z = 4, D_c = 1.201 g cm^{-3}, intensity

(16) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(17) Sheldrick, G. M. SHELXL-97, Program for Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1996.

(18) Burnett, M. N.; Johnson, C. K. ORTEP-III; Report ORNL-6895; Oak Ridge National Laboratory, Oak Ridge, TN, 1996.

data collected with $\theta \leq 28°$, 5416 independent reflections measured, 4026 reflections observed ($I > 2\sigma(I)$), final R index 0.0481 (observed reflections), $R_w = 0.1250$, and $S = 1.022$. The asymmetric unit is built up by the two independent molecules A and B.

Complete crystallographic data (excluding structural factors) for the six structures in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 292282−292287. Copies of the data can be obtained free of charge via WWW.ccdc.cam.ac.uk/conts/retrieving.html or on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44(0)-1223-336033; e-mail, deposit@ccdc.cam.ac.uk).

General Considerations. Melting points were determined with a Kofler hot stage microscope and were not corrected. The elemental analyses were carried out with a FISONS EA 1108 automatic analyzer.

Dichloromethane was predried by treatment with anhydrous calcium chloride and subsequent distillation with phosphorus pentoxide. The anhydrous sodium acetate was fused on a porcelain dish and left to cool in a desiccator.

4-(Methylamino)pent-3-en-2-one[19] (**1**), 4-aminopent-3-en-2-one[20] (**2**), 4-((2,4-dimethoxyphenyl)amino)pent-3-en-2-one[7] (**3**), and 3-(methylamino)-1-phenylbut-2-en-1-one[21] (**4**) were prepared according to the literature procedures.

3-(Methylamino)-1,4-diphenylbut-2-en-1-one (5). 1,4-Diphenylbutane-1,3-dione (6.5 g, 28 mmol) and a 33% solution of methylamine in absolute ethanol (50 mL) was refluxed for 10 h and cooled, and the separated product was collected by suction. After recrystallization from cyclohexane, **5** was obtained: yield 3.74 g (49%); mp 51−55 °C. Anal. Found: C, 81.26; H, 7.08; N, 5.74. Calcd for $C_{17}H_{17}NO$: C, 81.21; H, 6.82; N, 5.57.

1,4-Diphenylbutane-1,3-dione. A 500 mL three-necked flask equipped with a dropping funnel, thermometer, and condenser with calcium chloride drying tube was charged with dry ether (70 mL) and sodium amide (11.7 g, 0.3 mol). The suspension was stirred and, within 10 min, treated with acetophenone (18 g, 0.15 mol) in dry ether (25 mL), added drop by drop. After 5 min, methyl phenylacetate (45 g, 0.3 mol) was added. The reaction mixture was stirred and refluxed on a water bath for another 2 h. The jellylike reaction mixture was poured onto crushed ice (150 g) with concentrated hydrochloric acid (30 mL). The ether phase was separated and extracted first with sodium carbonate solution (3 × 100 mL) and then with water (3 × 100 mL). The organic phase was dried with anhydrous sodium sulfate, and the ether was distilled off. The evaporation residue was dissolved in methanol (60 mL), and a hot solution of copper(II) acetate hydrate (30 g, 0.15 mol) in water (175 mL) was added into it through a filter. After the mixture was cooled to room temperature, the copper(II) salt of the β-diketone was collected by suction, washed with petroleum ether, and dried. The salt was placed in a 500 mL Erlenmeyer flask together with 30% sulfuric acid (250 mL) and ether (100 mL). The mixture was stirred by means of a magnetic stirrer until the salt dissolved. The ether was separated, and the aqueous phase was extracted again with ether (3 × 50 mL). The combined ether phases were shaken with sodium carbonate solution (3 × 50 mL) and dried with anhydrous sodium sulfate. The ether was evaporated, and the separated crystals were recrystallized from ethanol: yield 9.73 g (24%) of β-diketone; mp 48−50 °C (lit.[22] mp 50−51 °C).

4-Amino-4-phenylbut-3-en-2-one (6) was prepared by a known procedure.[3]

4-(Methylamino)-3-((4-methylphenyl)diazenyl)pent-3-en-2-one (7). A 100 mL Erlenmeyer flask was charged with dry diisopropyl ether (30 mL) and the enaminone **1** (5 mmol). The reaction mixture was stirred by means of a magnetic stirrer, and remelted sodium acetate (1.23 g, 15 mmol) was added, followed by 4-methylbenzenediazonium tetrafluoroborate[4] (5 mmol). The mixture was stirred at room temperature for 28 h and then filtered. The filter cake was washed with diisopropyl ether, and the filtrate was evaporated in a vacuum evaporator. After recrystallization from cyclohexane, **7** was obtained: yield 68%; mp 113−115 °C. Anal. Found: C, 67.73; H, 7.69; N, 18.45. Calcd for $C_{13}H_{17}N_3O$: C, 67.51; H, 7.41; N, 18.17.

The substituted benzenediazonium chlorides were prepared by a known way.[4] The diazonium chlorides were transformed into the corresponding diazonium tetraphenylborates by adding a saturated aqueous solution of an equimolar amount of sodium tetraphenylborate. Because of their low stability, the diazonium tetraphenylborates had to be prepared immediately before use.

General Procedure for the Synthesis of 5-Aryldiazenyl-1,3,2λ⁴-oxazaborines. Remelted sodium acetate (1.23 g, 15 mmol) and the respective benzenediazonium tetraphenylborate (5 mmol) were added to a solution of enaminone (5 mmol) in dichloromethane (30 mL) with stirring. The reaction mixture was stirred at room temperature for 24 h, whereupon the solids were collected by suction on a sintered-glass filter and the filter cake was washed with dichloromethane. The filtrate was evaporated under vacuum, and the evaporation residue was either recrystallized or submitted to column chromatography. The following compounds were prepared by the procedure described.

5-((4-Methoxyphenyl)diazenyl)-4,6-dimethyl-2,2-diphenyl-3*H*-1,3,2λ⁴-oxazaborine (8). The title compound was obtained in 58% yield (1.56 g) as yellow crystals after recrystallization in cyclohexane−toluene: mp 160−163 °C. Anal. Found: C, 72.28; H, 5.88; N, 10.59. Calcd for $C_{24}H_{24}BN_3O_2$: C, 72.56; H, 6.09; N, 10.58.

5-((4-Methoxyphenyl)diazenyl)-3,4,6-trimethyl-2,2-diphenyl-1,3,2λ⁴-oxazaborine (9). The title compound was obtained in 50% yield (0.89 g) as yellow crystals after recrystallization in cyclohexane−toluene: mp 185−187 °C. Anal. Found: C, 72.96; H, 6.41; N, 10.03. Calcd for $C_{25}H_{26}BN_3O_2$: C, 73.00; H, 6.37; N, 10.22.

3,4,6-Trimethyl-5-((4-methylphenyl)diazenyl)-2,2-diphenyl-1,3,2λ⁴-oxazaborine (10). Method A (from the Diazonium Salt). This compound was obtained as a yellow crystalline solid after column chromatography (silica gel, chloroform−ethyl acetate 4:1): recrystallization from cyclohexane−toluene; yield 60% (0.94 g); mp 179−182 °C. Anal. Found: C, 76.14; H, 6.71; N, 10.64. Calcd for $C_{25}H_{26}BN_3O$: C, 75.96; H, 6.63; N, 10.63.

Method B (from Triphenylborane). A flask equipped with a calcium chloride drying tube and a dropping funnel was used to dissolve 4-(methylamino)-3-((4-methylphenyl)diazenyl)pent-3-en-2-one (**7**; 0.19 g, 0.82 mmol) in dichloromethane (10 mL) at room temperature. The solution obtained was treated with a solution of triphenylborane (0.2 g, 0.82 mmol) in dichloromethane (10 mL) added from the dropping funnel. The solution was stirred for ca. 24 h, whereupon the solvent was evaporated under vacuum. The crude evaporation residue was recrystallized from ethanol: yield 25% (0.08 g); mp 179−182.5 °C.

3-(2,4-Dimethoxyphenyl)-5-((4-methoxyphenyl)diazenyl)-4,6-dimethyl-2,2-diphenyl-1,3,2λ⁴-oxazaborine (11). This compound was obtained as a yellow crystalline solid after column chromatography (silica gel, chloroform) and recrystallization from cyclohexane: yield 32%; mp 151−154 °C. Anal. Found: C, 71.78; H, 5.85; N, 8.18. Calcd for $C_{32}H_{32}BN_3O_4$: C, 72.05; H, 6.05; N, 7.88.

5-((4-Methoxyphenyl)diazenyl)-3,4-dimethyl-2,2,6-triphenyl-1,3,2λ⁴-oxazaborine (12). The title compound was obtained in 27% yield (0.74 g) as orange crystals after recrystallization (cyclohexane−toluene): mp 211−213 °C. Anal. Found: C, 76.02; H, 5.98; N, 8.80. Calcd for $C_{30}H_{28}BN_3O_2$: C, 76.12; H, 5.96; N, 8.88.

3,4-Dimethyl-5-(4-((dimethylamino)phenyl)diazenyl)-2,2,6-triphenyl-1,3,2λ⁴-oxazaborine (13). This compound was obtained as

(19) Jirkovsky, I. *Can. J. Chem.* **1974**, *52*, 55.
(20) Kazitsina, L. A.; Kupletskaya, N. B.; Polstyanko, L. L.; Kikot, B. S.; Kolesnik, J. A.; Terentev, A. P. *Zh. Obshch. Khim.* **1961**, *31*, 313.
(21) Ribeiro DaSilva, M. A. V.; Ribeiro DaSilva, M. D. M. C.; Paiva, J. P. A.; Nogueira, I. M. C. S.; Daman, A. M.; Barkley, J. V.; Gardiny, M. M.; Akello, M. J.; Pilcher, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1765.
(22) Chen, R.; Wu, H.; Zhang, Y. *J. Chem. Res., Synop.* **1999**, *11*, 666.

an orange crystalline solid after column chromatography (silica gel, chloroform−ethyl acetate 4:1) and recrystallization from toluene−cyclohexane: yield 19% (0.48 g); mp 199.5−203 °C. Anal. Found: C, 76.52; H, 6.49; N, 11.29. Calcd for $C_{31}H_{31}BN_4O$: C, 76.55; H, 6.42; N, 11.52.

4-Benzyl-5-((4-methoxyphenyl)diazenyl)-3-methyl-2,2,6-triphenyl-1,3,2λ^4-oxazaborine (14). This compound was obtained as a sand-colored crystalline solid after heating of the crude reaction mixture in ethanol and recrystallization from a cyclohexane−toluene mixture: yield 14%; mp 198−200 °C. Anal. Found: C, 78.72; H, 5.74; N, 7.63. Calcd for $C_{36}H_{32}BN_3O_2$: C, 78.69; H, 5.87; N, 7.65.

5-((4-Methoxyphenyl)diazenyl)-6-methyl-2,2,4-triphenyl-3*H*-1,3,2λ^4-oxazaborine (15). The title compound was obtained in 43% yield as yellow crystals after column chromatography (silica gel/CH_2Cl_2) and recrystallization (petroleum ether): mp 119−123 °C. Anal. Found: C, 75.92; H, 5.95; N, 9.11. Calcd for $C_{29}H_{26}BN_3O_2$: C, 75.83; H, 5.71; N, 9.15.

3,4-Dimethyl-2,2,6-triphenyl-1,3,2λ^4-oxazaborine (16). This compound was prepared from 3-(methylamino)-1-phenylbut-2-en-1-one (**4**) and triphenylborane by the procedure B for compound **10**. Recrystallization from ethanol gave a yellow crystalline compound: yield 0.32 g (38%); mp 178−184 °C. Anal. Found: C, 81.48; H, 6.71; N, 4.25. Calcd for $C_{23}H_{22}BNO$: C, 81.43; H, 6.54; N, 4.13.

6-Acetyl-2-(4-methoxyphenyl)-5-methyl-3,3-diphenyl-4*H*-1,2,4,3λ^4-triazaborine (17). Method A. Oxazaborine **8** (1.04 g, 2.6 mmol) was heated in boiling toluene (20 mL) for 26 h. The toluene was distilled off, and the evaporation residue was submitted to chromatography (silica gel/CH_2Cl_2). The chromatography gave 31% of the starting material and 52% of the product **17** as an orange crystalline solid: mp 210.5−211 °C. Anal. Found: C, 72.70; H, 6.23; N, 10.52. Calcd for $C_{24}H_{24}BN_3O_2$: C, 72.56; H, 6.09; N, 10.58.

Method B. A 0.55 g portion (1.38 mmol) of oxazaborine **8** was heated in a vial at 200 °C for a period of 60 min. The mixture was submitted to column chromatography (silica gel/CH_2Cl_2) to give 0.46 g (84%) of an orange substance: mp 213−215 °C.

6-Acetyl-2-(4-methoxyphenyl)-3,3,5-triphenyl-4*H*-1,2,4,3λ^4-triazaborine (18). Oxazaborine **15** (0.26 g, 0.57 mmol) was heated in a vial at 200 °C for a period of 40 min. The mixture was submitted to column chromatography (silica gel/CH_2Cl_2) to give 0.18 g (69%) of a dark yellow substance: mp 195−198 °C. Anal. Found: C, 76.08; H, 5.99; N, 8.89. Calcd for $C_{29}H_{26}BN_3O_2$: C, 75.83; H, 5.71; N, 9.15.

Preparation of intermediate Im. The intermediate was prepared immediately before the NMR spectral measurement: enaminone **2** (0.29 g, 2.97 mmol) and 4-methoxybenzenediazonium tetraphenylborate (1.35 g, 2.97 mmol) were stirred with dichloromethane (20 mL) for 55 min. The reaction mixture was filtered with suction, and the solvent was evaporated under vacuum without heating. The evaporation residue was used for the measurements without further purification. For the spectral characteristics see Table 1 and the text.

Preparation of the Intermediate Im-^{15}N. This substance was prepared in the same way as that adopted for **Im**, using the diazonium salt prepared from sodium nitrite (95% ^{15}N).

Acknowledgment. We thank the Czech Science Foundation (Grant No. 203/03/0356) and the Ministry of Education, Youth and Sports of the Czech Republic (Grant No. MSM0021627501) for financial support.

Supporting Information Available: Text and figures giving crystallographic data and ORTEP diagrams of compounds **10**−**13** and NMR data for all the prepared compounds; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051078X