Notiz / Note

Borylation of a Stable Primary Enamine

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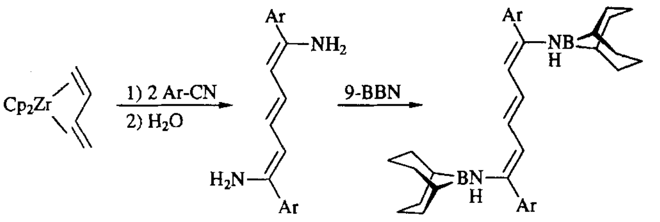
The stable conjugated primary enamine 1,6-diamino-1,6-diphenyl-1,3,5-hexatriene (**2a**) was treated with 9-borabicyclo[3.3.1]nonane. At 40°C in dichloromethane solution (18 h) only borylation at nitrogen was observed. With loss of dihydrogen a 9-BBN substituent became attached to each enamine nitrogen. The *N,N'*-diborylated diaminohexatriene product **3** was characterized by X-ray diffraction.

The reaction of alkenamines $H_2C{=}CH{-}[CH_2]_n{-}NH_2$ ($n \geq 1$) with boranes HBR_2 is often complicated by the competition (or combination) of hydroboration of the carbon–carbon double bond and borylation of the amino functionality (often with concomitant loss of dihydrogen)[1]. To our knowledge this competing situation of the HBR_2 addition sequence has up to now not been investigated by employing simple alkenamines $R{-}CH{=}CR(NH_2)R'$ as substrates. This is probably due to the general problem of obtaining simple primary enamines of sufficient stability without attaching stabilizing electron-withdrawing functional groups[2]. We have recently described a novel synthesis of stable primary enamines. Conjugated primary enamines $R^3CH{=}CH{-}CH{=}C(NH_2)R^1$ (**1**) and $R^1(NH_2)C{=}CH{-}CH{=}CH{-}CH{=}C(NH_2)R^2$ (**2**) have become readily available by means of a metal template reaction by coupling butadiene with two nitriles[3a], or a nitrile and a carbonyl compound[3b], at the bis(η-cyclopentadienyl)zirconium moiety. Subsequent controlled hydrolysis gives the conjugated primary enamines under conditions of thermodynamic control as stable, easily isolated organic products in high yield. We have now used the substituted 1,6-diamino-1,3,5-hexatrienes **2** as substrates to study the outcome of the reaction of a stable primary enamine system with a borane HBR_2. A typical example is described in this paper.

1 $R^3{-}CH{=}CH{-}CH{=}C(NH_2){-}R^1$



2 (Ar = phenyl: **a**)
(Ar = p-tolyl: **b**)

3 (Ar = phenyl)

The conjugated primary enamine **2a** is treated with two molar equivalents of 9-borabicyclo[3.3.1]nonane (9-BBN) in dichloromethane. After 18 h at 40°C the reaction was complete. A single thermally very stable product (**3**) was formed that was isolated in >70% yield. It melts at 205°C (DSC) without decomposition, whereas the conjugated primary enamine starting material **2a** decomposes at the melting point of 140°C with evolution of NH_3. Characterization of the product **3** reveals that only borylation at nitrogen (with elimination of dihydrogen) has taken place. We have not found any indication of hydroboration at the central 1,3,5-hexatriene framework. The ^{1}H-NMR signals of the central olefinic section of **3** appear as an AA'XX' pattern at $\delta = 6.65$ and 6.32. This is at markedly higher δ values as compared to the starting material **2a** ($\delta = 6.28$ and 5.76). The ^{1}H-NMR NH resonance of **3** is at $\delta = 5.45$ (**2a**: $\delta = 3.12$, NH_2). The borylated enamine **3** shows a single sharp IR (NH) band at $\tilde{\nu} = 3350$ cm^{-1} (**2a**: 3450, 3371, NH_2). The maximum of the UV-Vis absorption has shifted from $\lambda_{max} = 403$ (**2a**) to 363 nm (**3**) upon borylation at the enamine nitrogen centers.

Taken together the spectroscopic data indicate a slightly decreased interaction of the nitrogen lone pairs with the central 1,3,5-hexatriene π system on changing from **2a** to **3**. This interpretation is supported by the results of the X-ray crystal structure analysis of **3**.

In the crystal **3** exhibits a planar (1*Z*,3*E*,5*Z*)-configurated 1,3,5-hexatriene framework. As in the related 1,6-diamino-1,3,5-hexatrienes **2a** and **2b**[3a] there is a short-long-short-long-short pattern of carbon–carbon bond lengths of the central conjugated hexatriene portion of the molecule: C3–C2 1.347(4), C2–C1 1.431(4), C1–C1* 1.336(5) Å. The corresponding CC distances in **2a** ( ) and **2b** [ ] are only marginally longer (1.356(2), 1.437(2), 1.349(2) Å), [1.357(2), 1.437(2), 1.353(2) Å]. In **3** the C3–C2–C1 angle is 126.6(3)° (**2a**: 125.7(2)°) [**2b**: 127.3(2)°], the C2–C1–C1* angle is 125.0(3)° (124.4(2)°) [126.5(2)°]. The bonding angles at C3 are 121.9(2)° C2–C3–C31, 121.1(3)° C2–C3–N, and 116.9(1)° C31–C3–N in **3** (**2a**: 115.9(1)°) [**2b**: 115.6(1)°]. In **3** the C3–N bond length is 1.417(4) Å which is slightly larger than the $C(sp^2){-}NH_2$ distance in **2a** (1.385(2) Å) or **2b** [1.397(3) Å] (the $C(sp^2){-}NH_2$ distance in aniline is 1.402(2) Å)[4]. The N–B bond length in **3** is 1.399(4) Å, the C3–N–B angle 131.2(3)°. The substituents at the N–B linkage are arranged coplanarly (dihedral angles C3–N–B–C4: 178.7°, C3–N–B–C8: 1.7°). Orientation and B–N distance are in accord with a boron-nitrogen π interaction[4b,5]. However, the plane of the R_2BNH group is markedly ro-

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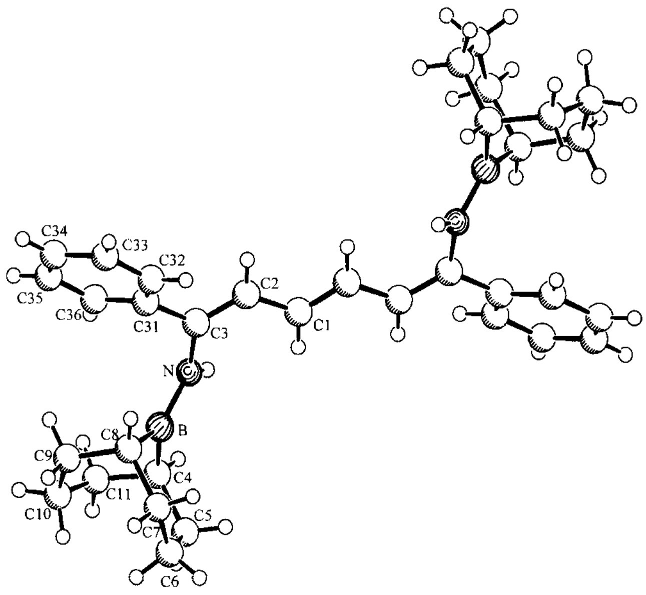

Figure 1. A view of the molecular structure of **3** with (unsystematical) atom numbering scheme

tated away from the conjugated hexatriene σ plane (dihedral angle C2−C3−N−B: 139.4°). Consistently with the observed hypsochromic UV-Vis shift these structural data indicate a decreased interaction of the nitrogen lone pair with the central conjugated polyene π system. As in **2b** the phenyl substituents in **3** are rotated slightly away from the central plane (dihedral angles C2−C3−C31−C32: 39.5°, C2−C3−C31−C36: 137.5°).

We conclude that treatment of the stable conjugated primary enamine **2a** with 9-BBN results in a clean borylation at nitrogen rather than addition of the boron hydride to the carbon-carbon double bond system. This preference for retaining the diaminohexatriene system over other alternatives is a further indication of effective primary enamine stabilization by polyene conjugation.

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Experimental[6]

Preparation of **3**: A mixture of (1*Z*,3*E*,5*Z*)-1,6-diamino-1,6-diphenyl-1,3,5-hexatriene (**2a**, 90 mg, 0.34 mmol) and 9-BBN (90 mg, 0.69 mmol) was dissolved in 30 ml of dry dichloromethane. The solution was stirred for 18 h at 40°C and then cooled. The product crystallized during 12 h at 0°C: yield 0.12 g of **3** (71%), m.p. 205°C (DSC). − IR (KBr): $\tilde{\nu}$ = 3350 (NH), 3032, 1610, 1456 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.55−7.45 and 7.38−7.20 (m, 10H, Ph), 6.65, 6.35 (AA'XX', 4H, olef.), 5.45 (br. s, 2H, NH), 1.0−1.9 (several m, 9-BBN). − UV (CH_2Cl_2): λ_{max} (ε) = 363 nm (26000). − $C_{34}H_{44}B_2N_2$ (502.4): calcd. C 81.29, H 8.83, N 5.58; found C 80.98, H 8.84, N 5.82.

X-Ray Crystal Structure Analysis of **3** *(Data Collection and Structure Solution):* Molecular formula $C_{34}H_{44}B_2N_2$, molecular mass 502.33 g mol^{-1}, crystal color yellow, single crystals from $CDCl_3$, crystal size 0.35 × 0.3 × 0.1 mm, a = 35.025(5), b = 6.515(1), c = 13.510(3) Å, β = 108.12(2)°, V = 2929.9(9) $Å^3$, $d_{calc.}$ = 1.129 g cm^{-3}, μ = 4.8 cm^{-1}, Cu-K_α radiation graphite-monochromated, λ = 1.54178 Å, temperature 293 K, 2θ-range: 5.32−57.34°, space group $C2/c$ (No. 15), Z = 4, Enraf Nonius CAD4 diffractometer, scan speed: variable, 1.6−16.5° min^{-1}, scan-mode: ω-2θ, reflections collected: 2076, independent reflections: 1997, observed reflections with $I \geq 2\sigma(I)$: 1511, R_{int} = 0.010, index ranges: $-38 \leq h \leq 9$, $-7 \leq k \leq 0$, $-14 \leq l \leq 14$, no absorption correction, structure solution: direct methods, hydrogen atoms: placed in calculated positions, non-hydrogen atoms refined anisotropically (177 parameters), refinement based on F^2, final residuals (observed data): R = 0.052, wR^2 = 0.137, extinction coefficient: 0.00075(12), extrema of the final difference Fourier synthesis: +0.56/−0.35 e · $Å^{-3}$, programs used: SHELX-86[7], SHELX-93[8], SCHAKAL92[9]. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58079, the names of the authors, and the journal citation.

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