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[11] To our knowledge, the shortest B–B distance measured previously (156.5(4) pm) was observed in an anionic derivative of **4**.[5] A length of 146.9 pm was calculated for the B–B triple bond in $Li_2B_2H_2$,[12] and the HB–BH distance in **1** and **2** was computed to be 147[1]/148.0[2] and 152.7 pm, respectively.[2]

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[13] In **5a** the planar nature of the B_4 unit is implied by the presence of a symmetry center; deviations from the plane: C1 1.5(2) pm, H –5(2) pm. The "normal", nearly spherical displacement ellipsoids of the B atoms (U_{ii}(max.) $= 0.045(1) \times 10^{-20}$ m^2) show that this is not a result of disorder. In contrast to the experimental planarity of the diamond in **5a**, calculations for the diamond in **5u** show a slight folding (166.6°). Apparently the folding in **5u** is induced by the two trimethylene bridges, and this effect is removed in the presence of the sterically bulky trimethylsilyl substituents in **5a**. In **6a** the deviations from the plane B2-B3-B4 are as follows: C4 –16.4(2), H04 5(2) pm.

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[16] A. Maier, M. Hofmann, H. Pritzkow, W. Siebert, *Angew. Chem.* **2002**, *114*, 1600; *Angew. Chem. Int. Ed.* **2002**, *41*, 1529. Attempts to synthesize tris(dimethylamino)cyclotriborane from 1,3-dichloro-1,2,3-tris(dimethylamino)triborane(5)[17] with K/Na alloy in pentane or with lithium naphthalenide in THF resulted in the formation of **10** in 40–50% yield.[18] **10**: colorless crystals, m.p. 105°C (no decomp), ^{11}B NMR (96 MHz, C_6D_6, 25°C): $\delta = 63, 41, 6$; ^1H NMR (300 MHz, C_6D_6, 25°C): $\delta = 3.4$ (s, 12H; NMe_2), 3.0 (s, 24H; NMe_2); ^{13}C NMR (75 MHz, C_6D_6, 25°C): $\delta = 44.4$ (q, 4C, NMe_2), 42.0 (q, 8C, NMe_2).

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A Planar, Aromatic *bicyclo*-Tetraborane(4)**

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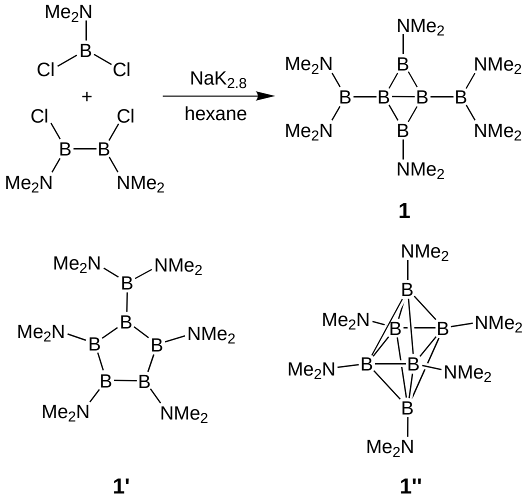
Dedicated to Professor Philipp Gütlich

Recently we demonstrated that the dehalogenation of bis(dialkylamino)dichlorodiboranes(4) provides colorful tetraborane(4) derivatives $(BR)_4$. The blue diisopropylamino derivative displays a folded B_4 ring, whereas a yellow tetrabora-tetrahedrane is formed with the larger 2,2′,6,6′-tetramethylpiperidino substituents.[1] The existence of planar[2] $(BNMe_2)_4$ could not be confirmed.[3] We report here on the *bicyclo*-tetraborane(4) **1**, whose boron atoms form a planar B_4 diamond (Scheme 1).



Scheme 1.

The reaction of a mixture of Me_2NBCl_2 and $(Me_2N)_2B_2Cl_2$[4] with $NaK_{2.8}$ alloy in hexane produced neither the anticipated B_3 nor a B_5 ring. Instead a colorless compound of the composition $B_6(NMe_2)_6$ (EI-MS, m/z 330) was formed in addition to oily products of unknown structure. This new compound is a constitutional isomer of the orange *cyclo*-$(BNMe_2)_6$, a chair-shaped compound that was first obtained in low yields by Nöth and Pommerening[5] upon dehalogenation of $(Me_2N)_2BCl$. The colorless $B_6(NMe_2)_6$ displays three ^{11}B NMR signals at $\delta = 6$, 41, and 63.[6] The pattern of the signals corresponds to a four-membered ring with two different substituents. The isomers **1′** and **1″** can therefore be excluded.

The crystal-structure analysis[7] of **1** displays a planar, diamond-shaped B_4 ring. The short distance across the diagonal (1.633(2) Å) indicates the presence of a B–B bond

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(Figure 1). Even shorter transannular B–B bonds (1.524(3) and 1.511(3) Å)[9] were observed in the diamond-shaped tetraborane(6) **2** and its pyridine adduct (Scheme 2). In **1** the sides of the diamond that are opposite to each other have the same length (1.605(2) and 1.632(2) Å). Remarkably, atoms B3 and B3A of the exocyclic $(Me_2N)_2B$ substituents lie slightly above and below the B_4 plane (0.4 Å), and the planes N2,B3,N3 and N2A,B3A,N3A are nearly perpendicular (78.9°) to the B_4 ring. The N1,C1,C2 plane forms an angle of 11.4° with the plane of the ring. The B–N bond lengths at B2 and B2A (1.381(2) Å) indicate a π interaction between the boron and nitrogen atoms, whereas the B–N bonds of the $(Me_2N)_2B$ substituents are significantly longer (1.430(1) Å). Since atoms B1 and B1A each have connectivities to four boron atoms, and as there are only eight electrons available for the formation of five "bonds" in the B_4 diamond, a nonclassical bonding situation must be present.

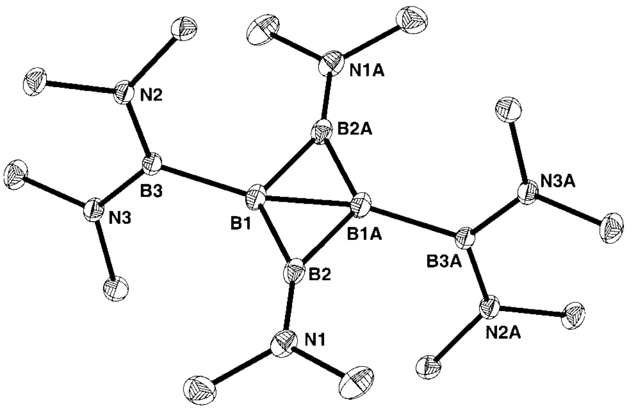
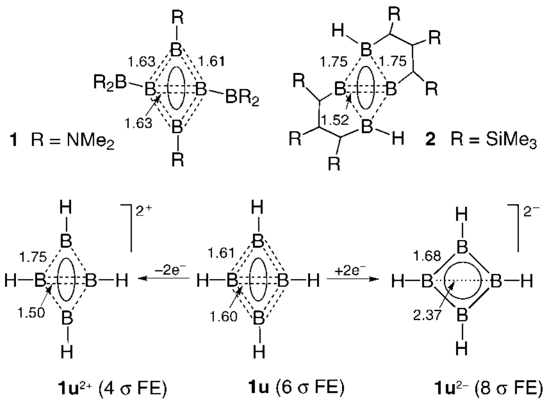


Figure 1. Molecular structure of **1** in the crystal; for reasons of clarity hydrogen atoms are not shown. Selected bond lengths [Å] and angles [°]: B1-B2 1.605(2), B1-B2A 1.632(2), B1-B1A 1.633(2), B1-B3 1.691(2), N1-B2 1.381(2), N2-B3 1.426(1), N3-B3 1.430(1); B1-B2-B1A 60.58(9), B2-B1-B2A 119.42(9), B2-B1-B3 124.05(10), B2A-B1-B3 114.45(9).



Scheme 2.

A density functional calculation was carried out to explain the electronic structure of **1**.[10] In the case of the B_4H_4 parent compound, a D_{4h}-symmetric cycle with classical bonding (Figure 2) does not represent the minimum on the potential energy hypersurface. In fact, it is 65 kcal mol^{-1} higher in energy than the tetrahedrane isomer (T_d, minimum).[11] A more stable structure results when in *cyclo*-$(BH)_4$ the π molecular orbital (π-MO; b_{3u}) made up of four p_z atomic orbitals is occupied with an electron pair (Figure 2) that formally originates from one of the four σ MOs of the B_4 framework. Jahn–Teller distortion lowers the symmetry from D_{4h} to D_{2h}, whereby one of the originally degenerate MOs (e_u) is raised in energy (b_{2u}) but remains unoccupied (Figure 2). In exchange, the second MO (b_{1u}), along with the π MO, is strongly stabilized as a result of favorable 1,3-interactions between B1 and B1A. The third σ MO (b_{3g}) is only slightly higher in energy than in the D_{4h}-symmetric structure and now forms the HOMO. The structure with D_{2h} symmety is 81 kcal mol^{-1} more stable than that with D_{4h} symmetry.

The geometric distortion is accompanied by a rehybridization at B2 and B2A from sp^2 to sp. For these two atoms the increase in the s fraction in the occupied MOs results in a high p character for the unoccupied σ MO, which acts as the acceptor level for the *exo*-σ bonds with B1 and B1A. In the case of B_4H_4 this hyperconjugation interaction leads to the formation of a 3c2e B-H-B bridge.[11] However, in the presence of less effective σ donors there is only a shift of the terminal substituents at B1 and B1A in the molecular plane towards B2 and B2A (Table 1). The deviation of the B_6 framework from planarity observed in **1** cannot be due to crystal packing and steric effects, since calculations predict a nonplanar structure for **1** as well as for model compounds with less sterically bulky substituents. Based on the results presented in Table 1 the amino substituents at B2 and B2A seem to be responsible for the nonplanar structure.

The variations between the frameworks of **1** and **2** result from the differences in the number of framework electrons (FEs). In **1** there are eight FEs (6σ + 2π), but only six are available in **2** since two are required for bonding the two additional H atoms (Scheme 2). These six electrons form two

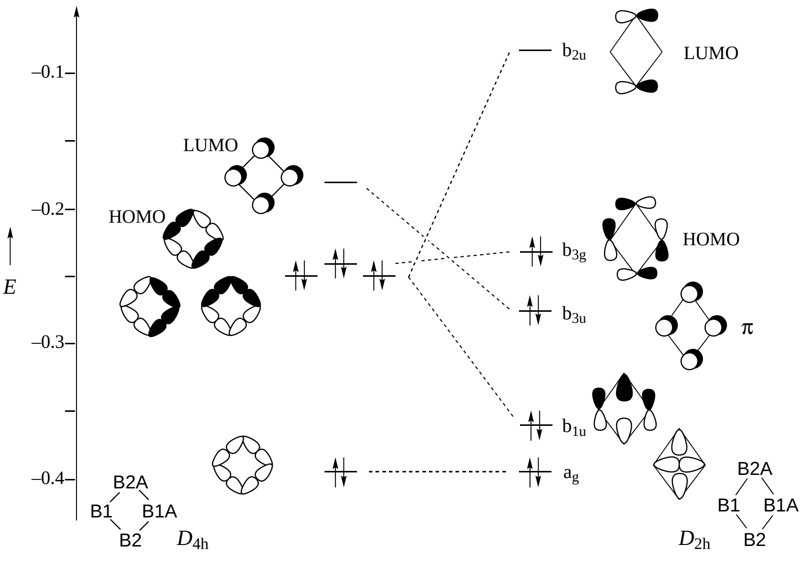
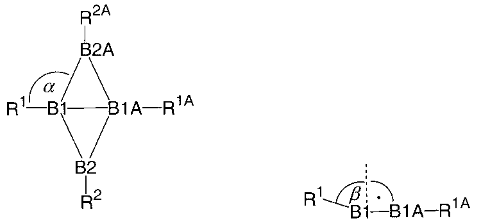


Figure 2. Molecular orbitals relevant for the bonding of the B_4 unit in B_4H_4 with D_{4h} and D_{2h} symmetry.

Table 1. Angles α and β as a measure of the distortion of *bicyclo*-tetraboranes(4) with two different substituents.



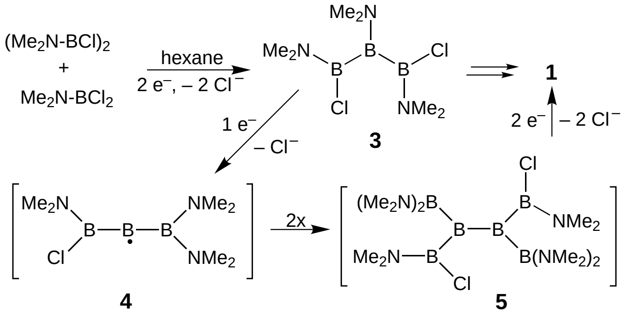
R^1, R^{1A}	R^2, R^{2A}	α	β
H	H	73.4	90.0
BH_2	H	87.2	90.0
$B(NH_2)_2$	H	94.4	90.0
H	NH_2	100.3	52.9
BH_2	NH_2	91.8	73.6
$B(NH_2)_2$	NH_2	95.2	74.7
$B(NMe_2)_2$	NMe_2	113.2	70.4
$B(NMe_2)_2$[a]	NMe_2[a]	114.4[a]	75.7[a]

[a] Experimental results.

3c2e σ bonds (triangles drawn with dashed lines) and one four-center π bond (ellipsoid). Furthermore in **1** there is a 4c2e π bond. In addition to two 3c2e σ bonds (represented in Figure 2 by the a_g and b_{1u} MOs and in Scheme 2 by two triangles with dashed lines) a further σ MO (b_{3g}) is occupied that shows bonding character along the edges (1.61, 1.63 Å in **1** compared to 1.75 Å in **2**) but antibonding character with regard to the shorter diagonals (1.63 Å compared to 1.52 Å in **2**; diamond drawn with dashed lines). The σ bonding in **1** is therefore intermediate to that in **2** and a classical B_4 ring in which eight electrons form four 2c2e σ bonds. The description of the bonding situation and the relationship between **1** and **2** is supported by calculations[12] on $\mathbf{1u}^{2+}$, whose edges (1.75 Å) and short diagonal (1.50 Å) correspond to those of **2**. The results for **1u** (edge length 1.61 Å, diagonal length 1.60 Å) also fit the values for **1**. In the case of $\mathbf{1u}^{2-}$ edge lengths of 1.68 Å and a diagonal length of 2.37 Å were calculated.

McKee reported that a D_{3d}-symmetric B_6 ring is the most stable $B_6(NH_2)_6$ isomer, but in his calculations he did not consider the isomer derived from **1**.[13] Our calculations show that this isomer is 10.3 kcal mol^{-1} lower in energy than the D_{3d}-symmetric structure. However, the relative stabilities are reversed in the case of Me_2N-substituted derivates: The D_{3d}-symmetric $B_6(NMe_2)_6$ ring is 8.0 kcal mol^{-1} more stable than **1** (C_i).

For the formation[14] of **1** we suggest the reaction mechanism shown in Scheme 3, which is supported by recent results from Berndt et al. (the synthesis of **1** in 40–50 % yield by the reaction of **3**[15] with Na/K alloy in pentane or with lithium naphthalenide in THF).[9] It is proposed that dehalogenation of the reagents in hexane provides the triborane **3**, and subsequent chloride elimination and Me_2N migration lead to the radical **4**. After dimerization of **4** to **5** renewed chloride elimination could result in cyclization to form **1**.



Scheme 3. Proposed mechanism for the formation of **1**.

Experimental Section

1: $NaK_{2.8}$ alloy (2 mL) was placed in hexane (100 mL). Then a mixture of 1,2-dichloro-1,2-bis(dimethylamino)diborane(4) (4.17 g, 23 mmol) and dichlorodimethylaminoborane (2.90 g, 23 mmol) was slowly added. The reaction mixture was stirred at room temperature for 6 days and then filtered, and the brown filtrate was concentrated. Compound **1** (20 mg, 0.5 %; m.p. 105 °C) crystallized from a solution of the oily crude product (2.3 g) in hexane at –80 °C.

^{11}B NMR (C_6D_6, 96 MHz): $\delta = 6$ (linewidth 330 Hz), 41 (350 Hz), 63 (350 Hz); HR-EI-MS *m/z* calcd for $^{12}C_{12}{}^{1}H_{36}{}^{11}B_6{}^{14}N_6$: 330.3560, found: 330.3516.

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[6] The chemical shifts in the ^{11}B NMR spectrum that were calculated with GIAO-B3LYP/6-311 + G**//B3LYP/6-31G* correlate well with the experimental values obtained for **1**: $B_6(NH_2)_6$: $\delta = 5.4$ (B1), 37.1 (B3), 63.4 (B2); $B_6(NMe_2)_6$: $\delta = 7.4$ (B1), 38.2 (B2), 63.1 (B3).

[7] Crystal structure analysis of **1**: triclinic, space group $P\bar{1}$, $C_{12}H_{36}B_6N_6$, $a = 7.286(2)$, $b = 8.069(3)$, $c = 9.720(6)$ Å, $\alpha = 85.42(2)°$, $\beta = 72.73(5)°$, $\gamma = 74.16(3)°$, $V = 525.0(4)$ Å^3, $Z = 1$. The crystals investigated were twinned. Intensities were measured with a Bruker-AXS SMART 1000 diffractometer with a CCD area detector ($Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), –83 °C), 11335 reflections ($\theta_{max} = 32°$); structure solution by direct methods, refinement by the method of least square fits against F^2;[8] non-hydrogen atoms were anisotropic, hydrogen atoms were located and isotropically refined; 192 parameters with $R1 = 0.0556$ (observed reflections), $wR2 = 0.1497$ (all reflections). CCDC-167559 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[10] All energies were minimized at the B3LYP/6-31G* level in the given point group and characterized by frequency calculations. Relative energies are based on subsequent energy calculations with B3LYP/6-311 + G**, whereby corrections with unscaled zero-point vibrational energies were taken into account. All calculation were carried out with Gaussian 98: Gaussian 98 (version A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul,

B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

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[12] Compound $\mathbf{1u}^{2-}$ is a transition state in D_{4h} symmetry, $\mathbf{1u}$ and $\mathbf{1u}^{2+}$ (each D_{2h}) are stationary points of the third order. The electronic structure corresponds with the schematic representation.

[13] Calculations were carried out for B_nH_n as well as $B_n(NH_2)_n$ ($n = 3-6$): M. L. McKee, *Inorg. Chem.* **1999**, *38*, 321–330.

[14] We thank one of the referees for suggesting that we propose a mechanism of formation. Owing to the low yield of **1**, which formed instead of the expected *cyclo*-triborane, we had originally not provided a mechanism.

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Synthesis of Enantioenriched 5-Alkylidene-2-cyclopentenones from Chiral Allenyl Carbamates: Generation of a Chiral Lithium Allenolate and Allylic Activation for a Conrotatory 4π-Electrocyclization**

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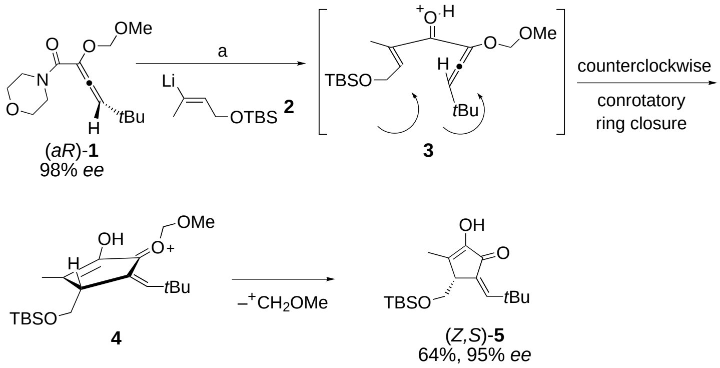
Stefan Grimme,* B. Wibbeling, and Dieter Hoppe*

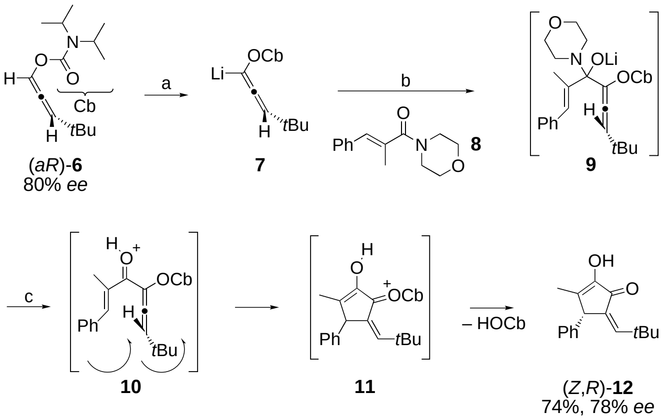
Dedicated to Professor Lutz F. Tietze
on the occasion of his 60th birthday

Chiral allenes have assumed an increasing importance in organic synthesis.[1, 2] A surprising application was reported by Tius et al.:[3] Allenyl alkenyl ketone (*aR*)-**3** cyclized under proton catalysis to form optically active 5-((*Z*)-alkylidene)-2-hydroxy-2-cyclopentenone **5** (Scheme 1). The chirality of the axial unit was transferred to the tetrahedral carbon atom of the cyclopentenone by means of a conrotatory electrocyclization of the 4π-system **3**, in a process that is similar to the Nazarov reaction.[4] The cyclization occurs through a counterclockwise conrotation because of steric demands.[5]



Scheme 1. Cyclization of (*aR*)-**1**. a) 1) **2**, THF, −78 °C, 30 min; 2) saturated aqueous KH_2PO_4. TBS = *tert*-butyldimethylsilyl.

Hoppe and co-workers had developed a simple method for the synthesis of enantiomerically enriched allenyl carbamate **6** (Scheme 2),[6] which initiated a collaboration to utilize **6** in this modified Nazarov reaction. Herein we describe a new stereospecific ring closure, which can be seen as a hybrid of an intramolecular vinylic cycloalkylation of a lithium allenolate and a modified Nazarov cyclization. The lithiation of allene (*aR*)-**6** (80% *ee*)[6] and subsequent acylation with (*E*)-alkenoylmorpholinide **8**, followed by transfer of the reaction mixture into hydrochloric acid in ethanol (5%), occurred as expected for the modified Nazarov cyclization to give hydroxycyclopentenone (*Z*,*R*)-**12**[7] (Scheme 2, 74%, 78% *ee*). The chirality transfer amounted to 98%.



Scheme 2. Cyclization of (*aR*)-**6**. a) *n*BuLi, TMEDA, toluene, −78 °C, 30 min; b) **8**, −78 °C, 2.5 h; c) rapid transfer of the mixture through a cannula into a solution of HCl in ethanol (5%). TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine.

When the reaction mixture was warmed to room temperature after the addition of amide **8** to the lithiated allenyl carbamate **7**, diastereomers of 2-morpholine-2-cyclopentenone (*Z*,*R*)-**14** and (*E*,*S*)-**15** were isolated in 74% yield, with >98% chirality transfer (Scheme 3). We assume that a rearrangement of intermediate **9**, which involves a migration of the *N*,*N*-diisopropylcarbamoyl group (Cb), leads to the formation of a lithium 1,2-dienolate (an "allenolate").[8, 9] The

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