tate was mixed with 20 ml of  $CH_2Cl_2$ , filtered, and the filtrate was concentrated to a thick suspension. The precipitate was filtered off, washed once with  $CH_2Cl_2$ , and air dried. **3e** was obtained in 66% yield, m.p. and IR spectrum are identical with those given above.

The assignment of the NMR spectral signals was carried out on the basis of data of the Table 2. The results obtained are presented in Scheme 3. In addition, the other signals in the NMR spectra were assigned to the following compounds: **2f**. <sup>14</sup>N NMR ( $\Delta_{1/2}$ , Hz): -28.2 (2N, NO<sub>2</sub>). **9a**, **10a**. <sup>13</sup>C NMR: 169.0, 163.8, 150.6, 113.8 ( $\alpha$  -) 123.0 ÷ 124.5 (6 signals, *ipso*), 129.10, 129.06, 128.4, 127.2, 126.3 (*ortho, meta*), 132.3, 131.9, 131.7 (*para*). <sup>14</sup>N NMR: -11.6 br s, -18.5 br s.

Treatment of the reaction mixture  $(1a + N_2O_4)$  with aqueous NaHCO<sub>3</sub>. The reaction of 1a with  $N_2O_4$  was carried out according to the above procedure. After the filtration the reaction mixture was left to stand for 2 min at -10°C, until the green color disappeared; a solution of 0.765 g (9.1 mmol) of NaHCO<sub>3</sub> in 8 ml of water was added, then the mixture was intensively stirred for 5 min at 0°C. The organic phase was separated, dried with MgSO4 for 1 min at 0°C, and filtered into an NMR tube, which was placed into the solid CO<sub>2</sub>-acetone mixture; the NMR spectra were then recorded. The aqueous phase was washed twice with 3 ml of CHCl<sub>3</sub>, and acidified with H<sub>2</sub>SO<sub>4</sub>, until the yellow color disappeared. The precipitated solid was filtered off, washed with water, and dissolved in 1 ml of methanol. 1a was precipitated from this solution by adding 0.21 g (2.1 mmol) of potassium acetate in 1 ml of methanol. The salt was filtered off and washed successively with methanol and ether. The compound was air dried and 0.14 g of 1a was obtained (14% with respect to 1a).

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Received March 17, 1992

# The synthesis of fused benzotriazoles based on hexaaminobenzene derivatives

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New methods for synthesis of hexaaminobenzene are proposed and, based on this compound, previously unknown preparative procedures for obtaining fused benzotriazoles are developed.

Key words: hexaaminobenzene, fused heterocyclic systems, benzotris(triazole), benzo[1,2-d:4,5-d']bis(triazole)-4,8-dione, synthesis methods.

The chemical properties of hexaaminobenzene are currently being extensively explored and on the basis of this compound new types of fused polynitrogeneous heterocyclic systems including derivatives of hexaazacoronene,<sup>1,2</sup> hexaazatriphenylene,<sup>3,6</sup> benzotris(imidazole),<sup>7,8</sup> benzotris[1,2,5]thiadiazole,<sup>9</sup> benzotris[1,2,5]selenodiazole<sup>9</sup>, and aromatic hexaamides with the properties of lyotropic liquid crystals have been obtained.<sup>10</sup>

The known methods for obtaining hexaaminobenzene



are based on the reduction of 1,3,5-triamino-2,4,6trinitrobenzene (TATB) with various reducing agents (phenylhydrazine,<sup>3,11</sup> sodium amide in liquid ammonia,<sup>4</sup> hydrogen in the presence of 10% Pd/C<sup>1,8,12</sup>) and afford a free base which is unstable and decomposes in air within 24 hours.<sup>1,12</sup> Hexaaminobenzene hydrochlorides have been obtained by treatment<sup>11</sup> of an aqueous solution of the free base with concentrated HCl. They were also isolated as a complex with dioxane after reduction<sup>6</sup> of benzotris[1,2,5]thiadiazole in the Sn/HCl system.

The goal of the present work is the search for new methods for obtaining hexaaminobenzene and its derivatives and the synthesis of fused benzotriazoles on the basis of these compounds.

Reduction of benzotrisfuroxan (1) or pentanitroaniline (2) with  $\text{SnCl}_2$  in the presence of HCl in EtOAc affords hexaaminobenzene trihydrochloride (3), which is stable on storage, in 95-98% yield (Scheme 1)<sup>13,14</sup>:

Treatment of compound 3 in AcOH with an aqueous solution of NaNO<sub>2</sub> at low temperature results in formation of a mixture of benzotris(triazole) (4) (~5%) and benzo[1,2-d; 4,5-d']bis(triazole)4,8-dione (5) (~26%) (Scheme 2).

Dione 5 is obtained selectively in 52% yield by treatment of amine 3 with 56%  $HNO_3$ . The yield of product 5 can be increased to 62% by reacting compound 3 with  $HNO_2$  generated *in situ* from aqueous  $NaNO_2$  and  $H_2SO_4$ . Replacement of hexaaminobenzene 3 with 1,3,5triamino-2,4,6-triacetamidobenzene trihydrochloride (6) allows one to obtain benzotris(triazole) 4 in 60% yield. In this case the yield of dione 5 does not exceed 13%. The reaction is carried out in AcOH. Synthesis of 1,3,5triacetyl-substituted compound 6 is accomplished starting with TATB (7) (Scheme 3).

Thus we have developed new methods for obtaining storage-stable hexaaminobenzene derivatives and methods for synthesizing fused benzotriazoles from them, which are simple and preparatively convenient as compared to those reported.<sup>15–17</sup>

# Experimental

Melting points were determined on a Boetius hot-stage. Mass-spectra were obtained on a Varian MAT CH-6 instru-





ment, ionization potential 60 eV.  $^{13}$ C and  $^{1}$ H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz), and IR spectra on a UR-20 instrument in the range 440-4000 cm<sup>-1</sup> in KBr.

# Hexaaminobenzene trihydrochloride (3).

a) From benzotrisfuroxan 1. A solution of 10 g (39,9 mmol) of 1 in 900 ml of EtOAc was added at  $0-10^{\circ}$ C to a stirred solution of 200 g (890 mmol) of SnCl<sub>2</sub> · 2H<sub>2</sub>O in 250 ml of conc. HCl. The temperature was increased gradually to 50°C and the mixture was kept at this temperature for 1 h, cooled to 20°C, the precipitate was filtered off, washed with 50 ml of EtOAc, and dried to give 10.7 g (98%) of hydrochloride 3, m.p. 245-248°C. Found, %: C 25.40; H 5.70; Cl 38.80; N 29.90. C<sub>6</sub>H<sub>12</sub>N<sub>6</sub> · 3HCl. Calculated, %: C 25.95; H 5.40; Cl 38.38; N 30.27. MS (*m/z*): 168 [M-3HCl]<sup>+</sup>. IR spectrum (v, cm<sup>-1</sup>): 3350, 3220, 2900, 2600, 1667, 1620, 1570, 1538, 1470, 1200, 1105, 940.

**b)** From pentanitroaniline **2**. A solution of 3.18 g (10 mmol) of **2** in 150 ml of EtOAc was added at  $0-10^{\circ}$ C to a stirred solution of 67 g (300 mmol) of SnCl<sub>2</sub> · 2H<sub>2</sub>O in 83 ml of conc. HCl. The temperature was increased gradually to 50°C, the mixture was stirred for 1 h, cooled to 20°C, and the precipitate was filtered off, washed with 30 ml of EtOAc, 20 ml of MeOH, 50 ml of Et<sub>2</sub>O, and dried to give 2.64 g (96%) of 3, m.p. 245-248°C. Physical and spectral data of the product obtained were identical with those of the sample described above.

Reaction of the hydrochloride (3) with NaNO<sub>2</sub> in AcOH. A solution of 4.5 g (65 mmol) of NaNO<sub>2</sub> in 20 ml of  $H_2O$  was added to a stirred suspension of 5 g (18 mmol) of 3 in 15 ml of AcOH. The temperature was increased to 95–100°C and the mixture was stirred for 1 h. The precipitate formed was filtered off, the mother liquor was acidified to pH 4.5 with 15% aqueous HCl, the precipitate was filtered off, washed with water and dried to give 1.24 g of a mixture of 4 and 5. The mixture was thoroughly washed with hot Me<sub>2</sub>CO (3×150 ml) and the

### Scheme 3



undissolved residue was dried to give 0.18 g (4.56%) of product 4 as the monohydrate, m.p. 300°C (dec.). This product was purified by precipitation from 10% aqueous NaOH by acidification to pH 3 with HCl. Found, %: C 33.10; H 3.18; N 56.90. C<sub>6</sub>H<sub>3</sub>N<sub>9</sub>·H<sub>2</sub>O. Calculated, %: C 32.88; H 2.28; N 57.53. MS(m/z):  $201[M-H_2O]^+$ . IR (v,cm<sup>-1</sup>): 3467, 3255, 3160, 1639, 1620, 1533, 1481, 1415, 1381, 1315, 1216, 1200, 1169, 1141, 1090, 1053, 1028, 1000, 969, 932, 877, 848, 825. <sup>13</sup>C NMR  $(D_2O+NaOH, \delta)$ : 136.17  $(C_{Ar})$ . Concentrating the mother liquor after separation of **4** gave 1.06 g (26%) of **5** as the dihydrate, m.p.  $305^{\circ}$ C (dec., H<sub>2</sub>O). Lit. <sup>17</sup>:  $300^{\circ}$ C (dec.). Found, %: C 31.70; H 2.41; N 37.40. C<sub>6</sub>H<sub>2</sub>N<sub>6</sub>O<sub>2</sub> · 2H<sub>2</sub>O. Calculated, %: C 31.86; H 2.65; N 37.17. MS(m/z): 190[M-H<sub>2</sub>O]<sup>+</sup>. IR (v, cm<sup>-1</sup>): 3500, 3250, 1700(C=O), 1505, 1485, 1390, 1380, 1120, 1010, 730. <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, δ): 170.724 (CO), 144.834 (C<sub>Ar</sub>). Benzo[1,2-d:4,5-d'']bis(triazole)-4,8-dione (5).

a). Ten grams (36 mmol) of the hydrochloride 3 were added at 5-10°C to 200 ml of 56% HNO<sub>3</sub>. The mixture was stirred, heated to  $95-100^{\circ}$ C and kept for 2-3 h at this temperature under diminished pressure until the volume reduced to ~30 ml. It was then cooled to ~20°C and the precipitate formed was filtered off and washed with cold water. The mother liquor and washings were evaporated to 10 ml, cooled to ~20°C, the precipitate formed was filtered off and washed with cold water. The precipitates were combined and dried in air to afford 4.23 g (53%) of 5 as the dihydrate, m.p. 305°C (dec., H<sub>2</sub>O). Physical and spectral data of the product obtained were identical with those of the sample described above.

b) To 1200 g of finely ground ice were added 60 ml of conc.  $H_2SO_4$ , and at -5 to -2°C with vigorous stirring a solution of 20 g (290 mmol) of NaNO<sub>2</sub> in 60 ml of  $H_2O$  was added. Then under the same conditions were simultaneously added 50 g (180 mmol) of 3 portionwise and a solution of 65 g (949 mmol) of NaNO<sub>2</sub> in 160 m of H<sub>2</sub>O dropwise. After stirring for 1 h at 0-5°C the mixture was gradually heated in 1 h to 95°C and stirred for 1 h at this temperature, then cooled to 20°C. The precipitate was filtered off, washed with water, and dried in air to give 33.37 g of crude product which was treated with 400 ml of boiling Me<sub>2</sub>CO, filtered hot and the mother liquor was concentrated to afford 25.23 g (64%) of 5 as the dihydrate, m.p. 305°C (dec., H<sub>2</sub>O). The product was identical with the sample described above.

1,3,5-Triacetamido-2,4,6-trinitrobenzene (8). To a suspension of 20 g (38.7 mmol) of 1,3,5-triamino-2,4,6-trinitrobenzene 7 in 600 ml of Ac<sub>2</sub>O was added conc.  $H_2SO_4$  (0.5 ml). The mixture was heated to 115-120°C, stirred for 28 h, cooled to 20°C, and poured into 1 liter of cold water. It was stirred for 2 h at 90°C and cooled to 20°C. The precipitate was filtered off, washed with 100 ml of MeOH and dried to give 25.4 g (85.3%) of 8, m.p. 198°C. Found, %: C 37.70; H 3.10; N 21.80.  $C_{12}H_{12}N_6O_9$ . Calculated, %: C 37.50; H 3.13; N 21.88. IR (v,  $cm^{-1}$ ): 3380, 3215, 2966, 2919, 2883, 1688(C=O), 1590, 1541(asNO<sub>2</sub>), 1512, 1495, 1424, 1343(sNO<sub>2</sub>), 1248, 1109, 1029, 1000, 913, 751, 716. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub> $\tilde{S}O$ ,  $\delta$ ): 2.0 (s, 3H, CH<sub>3</sub>), 10.75 (s, 1H, NH).

2,4,6-Triacetamido-1,3,5-triaminobenzene trihydrochloride

(6). 2.6 g (6.8 mmol) of compound 8 in 55 ml of DMF were hydrogenated at 75°C in a glass reactor in the presence of 1 g of 5% Pd/C. After consumption of the theoretical amount of H<sub>2</sub> (the colour of the solution turned from dark-brown to palegreenish, almost colourless), the solution was filtered from the catalyst into a flask containing 2.06 ml of 36% HCl and 10 ml of i-PrOH. Another 40 ml of i-PrOH were added, and the solvent was removed on a rotary evaporator at 50-60°C and 8-10 Torr. After removal of 75-85% of the solvent, 40 ml of *i*-PrOH were added, the precipitate was filtered off and dried in air to give 2.45 g (90%) of 6 m.p. 240°C (dec.). Found, %: C 36.10; H 4.70; N 20.40; Cl 26.51.  $C_{12}H_{21}N_6O_3Cl_3$  Calculated, %: C 35.69; H 5.20; N 20.82; Cl 26.69. IR (v, cm<sup>-1</sup>): 3290, 2940, 2820, 1710(C=O), 1604, 1582, 1484, 1102, 745.

Reaction of hydrochloride (6) with NaNO<sub>2</sub> in AcOH. A solution of 2.15 g (31.25 mmol) of NaNO<sub>2</sub> in 5 ml of H<sub>2</sub>O was added at  $-1-0^{\circ}$ C to a vigorously stirred suspension of 2 g (5.2 mmol) of compound 6 in 50 ml of AcOH. The temperature was increased gradually to 90-95°C and the mixture was stirred for 2 h and cooled to ~20°C. The precipitate was filtered off and washed with  $Me_2CO$  to yield 0.628 g (60%) of 4 as the monohydrate, m.p. 300°C (dec.). Evaporation of the mother liquor afforded 0.12 g (13%) of 5 dihydrate, m.p. 305°C (dec.). Physical and spectral data of the products obtained were identical with those of the samples described above.

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Received March 18, 1992