Synthesis of amino-substituted 1,3-bis(*tert*-butyl-*NNO*-azoxy)benzenes

1. 4-Amino and 4,6-diamino derivatives

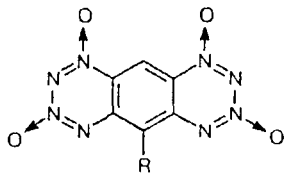
A. E. Frumkin, A. M. Churakov, Yu. A. Strelenko, O. Yu. Smirnov, S. L. Ioffe, and V. A. Tartakovsky*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

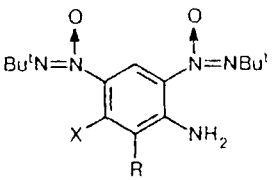
Oxidation of 4,6-dichloro-1,3-phenylenediamine with Caro's acid yields the corresponding dinitrosobenzene, which reacts with *N,N*-dibromo-*tert*-butylamine to give 1,5-bis(*tert*-butyl-*NNO*-azoxy)-2,4-dichlorobenzene. Treatment of the latter with ammonia yields 4-amino- and 4,6-diamino-1,3-bis(*tert*-butyl-*NNO*-azoxy)benzenes.

Key words: amino-, azoxy-, and nitrosoarenes; *m*-nitrosoanilines; *m*-dinitrosobenzenes; *o*-nitrosophenols; oxidation of the amino group; vicarious nucleophilic substitution in arenes.

Earlier,[1] within the framework of a general program for the study of 1,2,3,4-tetrazines, we obtained a novel class of heterocycles in which the benzene ring is fused with the 1,2,3,4-tetrazine-1,3-dioxide ring. The starting compounds for the synthesis of benzo-1,2,3,4-tetrazine-1,3-dioxides are *ortho*-(*tert*-butyl-*NNO*-azoxy)anilines.[1] Anthracene heteroanalogs **A** whose benzene ring is fused with two 1,2,3,4-tetrazine-1,3-dioxide rings would be of obvious interest. The present paper deals with the synthesis of amino-substituted 1,3-bis(*tert*-butyl-*NNO*-azoxy)benzenes **B**, which could be starting compounds for the synthesis of **A**.



A

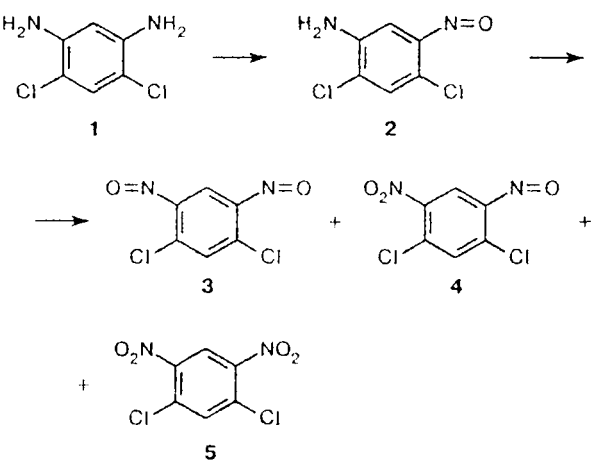


B

X = NH_2, Cl
R = H, Br

Usually, *tert*-butyl-*NNO*-azoxybenzenes are obtained according to the Kovacic method from the corresponding nitroso compounds.[2] Thus, the key compounds in our work were substituted *m*-dinitrosobenzenes. This class of compounds is scarcely reported in the literature. The known procedure for the synthesis of *m*-dinitrosobenzene includes oxidation of the corresponding hydroxylamine, which was obtained by reduction of *m*-dinitrobenzene,[3] but we faced some problems in this way. For this reason, we attempted to synthesize dinitrosobenzene **3** by oxidation of phenylenediamine **1** with Caro's acid, which is often used for oxidation of one aromatic amino group (Scheme 1).[4]

Scheme 1



In our case, however, the reaction products were significantly overoxidized, and we isolated, along with dinitrosobenzene **3** (yield 10%), nitronitroso (**4**) and dinitro derivatives (**5**). Nevertheless, taking into account the availability of the initial phenylenediamine, this method seems to be satisfactory for the synthesis of small amounts of compound **3**.

Compound **3** is formed *via m*-nitrosoaniline **2**, which can be isolated in a small yield (8%), unless the reaction is allowed to be completed. Unlike nitroso compounds **3** and **4**, whose solutions are green, intermediate **2** is dark orange in solution and in the solid state. We could not

Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 7, pp. 1307–1310, July, 1999

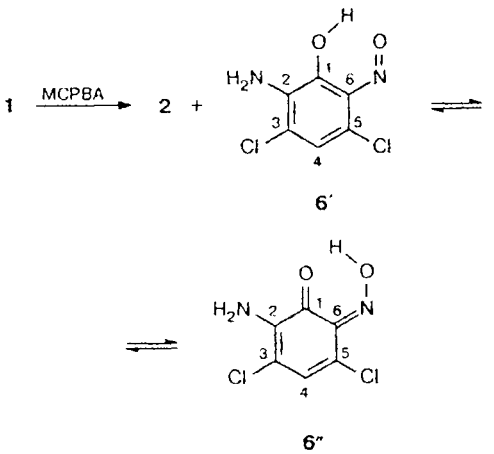
1066-5285/99/4807-1295 $22.00

find reliable literature data on nitroso compounds similar to **2**.

The structures of nitroso compounds **2**, **3**, and **4** were confirmed by ^1H and ^{13}C NMR spectroscopy. At 25 °C, the spectra of these compounds exhibit signals only from a monomeric form with characteristic upfield shifts of the proton and the carbon atom that are *syn*-positioned relative to the nitroso group (see Ref. 5 and references cited therein). This shift is the most pronounced for compound **3** (δ 4.92 (H(3)) and δ 87.63 (C(3))) because of two nitroso groups. At −30 °C, the ^1H NMR spectra of aniline **2** show signals of a dimer (20%), and the ^{13}C NMR spectra of compound **3** contain several additional signals suggesting the formation of a dimer and oligomers (up to 80%). At the same time, nitronitrosobenzene **4** does not dimerize under these conditions. It is noteworthy that the nitroso compounds obtained are stable at room temperature when dissolved in nonpolar solvents and in the solid state, but they rapidly resinify in polar solvents. The half life of dinitrosobenzene **3**, the most unstable compound among them, amounts to *ca.* 1 h in DMSO.

An attempt to increase the yield of aniline **2** by oxidation of phenylenediamine **1** with *m*-chloroperbenzoic acid (MCPBA) gave an insignificant gain (yield 12%), but this procedure facilitated the isolation of the product. In this case, a new interesting reaction was observed. The oxidation of compound **1** resulted in not only aniline **2** but also a violet product, which was assigned the structure of aminonitrosophenol **6** (Scheme 2).

Scheme 2

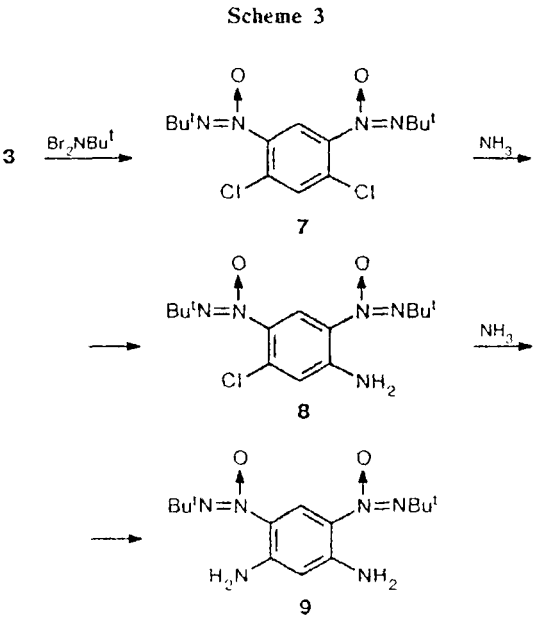


The mass spectrum of compound **6** exhibits a signal corresponding to the molecular ion. In polar solvents, this compound gradually decomposes, but in nonpolar solvents (CH_2Cl_2) it is quite stable enough to be studied by NMR spectroscopy. In ^1H NMR spectra, one can observe not only signals of the ring and NH_2 protons but also a far low-field signal (δ 16.73) of the chelating hydroxyl proton, which correlates with the data for the well-studied *o*-nitrosonaphthols.[6] The signals of the NH_2 and OH protons, which are somewhat broadened at 25 °C, become narrow at −40 °C. ^{13}C NMR signals were assigned with the use of selective polarization transfer from the CH and OH protons. The C(1) shift value (δ 166.9 at −40 °C) suggests that the compound mainly exists in the form of quinone monooxime **6″** because the C(1) shift for the nitrosophenol form **6′** would be δ 123 (with consideration of data for compound **2**) or δ 128 (with consideration of data for *o*-nitrosonaphthols[6]), while that for the quinoid structure **6″** calculated with consideration of data for *o*-naphthoquinone monooximes[6] (δ 172) is close to the experimental value. At the same time, the dark violet color of solutions (the electronic absorption spectrum in CH_2Cl_2 shows a maximum at 560 nm) suggests the presence of the nitrosophenol form.[7] Inasmuch as only one set of signals is observed in the spectra at both 25 °C and −40 °C, it is obvious that a rapid exchange (in the NMR time scale) between tautomers **6′** and **6″** takes place. Note that 2-nitrosophenol, studied earlier by UV spectroscopy,[7] is present in solutions only in the nitrosophenol form.

Current data are insufficient to discuss the mechanism of formation of compound **6**. One can only assume that this compound is formed from aniline **2** upon vicarious nucleophilic substitution of hydrogen with the anion of *m*-chloroperbenzoic acid (for VS_NAr^H reactions, see Refs. 5, 8).

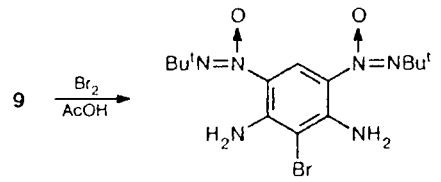
As expected, dinitroso compound **3** reacts with *N,N*-dibromo-*tert*-butylamine to give bis(*tert*-butyl-*NNO*-azoxy)benzene (**7**). The reaction of compound **7** with ammonia in toluene was carried out in an autoclave at 170—180 °C according to the procedure described earlier.[9] Under these conditions, one chlorine atom is

Scheme 3



replaced to form aniline **8**. Under more drastic conditions, the reaction results in replacement of both chlorine atoms, thus yielding diamino derivative **9**.

Scheme 4



10

The structures of compounds **7**—**10** were confirmed by ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectral data (see Experimental). In particular, the ^{14}N NMR spectra exhibit a pronounced signal at δ −48 to −56 with a half width of 100—190 Hz, characteristic of the *N*-oxide nitrogen of an azoxy group (the ^{14}N and ^{15}N NMR spectra of the (*tert*-butyl)azoxy group were previously cited[9,10]).

Bromination of phenylenediamine **9** under the standard conditions results in 2-bromo-substituted derivative **10** in quantitative yield.

Experimental

IR spectra were recorded on a Perkin-Elmer 577 spectrometer. Mass spectra were obtained with a Kratos MS-30 instrument (EI, 70 eV); for chlorine-containing fragments, only signals containing ^{35}Cl are given. ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13, 75.5, 21.5, and 30.4 MHz, respectively). ^{14}N and ^{15}N chemical shifts are given on the δ scale relative to nitromethane. ^{13}C signals were assigned using techniques for recording spectra with selective decoupling of separate protons and selective polarization transfer from protons (SPT) as well as by computational methods. The course of reactions was monitored by TLC (Silufol UV-254). Silica gel was used for column chromatography. 4,6-Dichloro-1,3-phenylenediamine and *N,N*-dibromo-*tert*-butylamine were obtained according to the known procedures.[11,12]

Oxidation of phenylenediamine 1 with Caro's acid. Method *A*. A mixture of ammonium persulfate (41 g, 0.18 mol) and conc. H_2SO_4 (57 g) was stirred at 20 °C for 1 h and then poured into 100 g of ice. To the prepared solution of Caro's acid[4] a solution of compound **1** (4 g, 22.6 mmol) in 22 mL of cold 30% H_2SO_4 was added. The reaction mixture was kept at −3 °C for 1 day and at 6 °C for 2 days. The products were extracted with benzene (3×100 mL) and dried with $MgSO_4$, and the solvent was removed *in vacuo*. The residue was chromatographed in CCl_4 to give dinitrosobenzene **3** (0.47 g, 10%), nitronitrosobenzene **4** (0.35 g, 7%), and dinitrobenzene **5** (0.26 g, 5%).

1,5-Dichloro-2,4-dinitrosobenzene (3), dark green crystals, m.p. 101—102 °C (from CCl_4). Found (%): C, 35.29; H, 1.03; Cl, 34.42; N, 13.74. $C_6H_2Cl_2N_2O_2$. Calculated (%): C, 35.15; H, 0.98; Cl, 34.59; N, 13.67. ^1H NMR (CD_2Cl_2, *c* 0.25 mol L^{-1}), δ: 4.92 (s, 1 H, H(3)); 8.30 (s, 1 H, H(6)). Additional signals for dimers and oligomers appearing at −30 °C, δ: 6.57 (H(3)); 7.98—8.21 (H(6)). ^{13}C NMR (CD_2Cl_2), δ: 87.6 (C(3)); 135.8 (C(6)); 147.8 (C(1), C(5), ^3J = 9.6 Hz, ^2J = 4.2 Hz); 157.1 (C(2), C(4), ^3J = 6.2 Hz, ^2J = 3.1 Hz). MS, *m/z* (I_{rel} (%)): 204 $[M]^+$ (85), 174 $[M - NO]^+$ (33), 144 $[M - 2NO]^+$ (100), 109 $[M - 2NO - Cl]^+$ (95), 74 $[M - 2NO - 2Cl]^+$ (91).

1,5-Dichloro-2-nitro-4-nitrosobenzene (4), m.p. 92—93 °C (from CCl_4). Found (%): C, 32.73; H, 0.92; Cl, 32.25; N, 12.47. $C_6H_2Cl_2N_2O_3$. Calculated (%): C, 32.61; H, 0.91; Cl, 32.08; N, 12.68. ^1H NMR (CD_2Cl_2, *c* 0.25 mol L^{-1}), δ: 6.78 (s, 1 H, H(3)); 8.12 (s, 1 H, H(6)). No dimer was detected at −30 °C. ^{13}C NMR (CD_2Cl_2), δ: 106.4 (C(3)); 134.8 (C(1) or C(5)); 135.7 (C(6)); 145.2 (C(5) or C(1)); 146.2 (br., C(2)); 156.6 (C(4)). ^{14}N NMR (CD_2Cl_2), δ: −18 (NO_2, $\Delta\nu_{1/2}$ = 40 Hz). IR (KBr), ν/cm^{-1}: 1340, 1530 (NO_2). MS, *m/z* (I_{rel} (%)): 220 $[M]^+$ (100), 174 $[M - NO_2]^+$ (11), 144 $[M - NO_2 - NO]^+$ (100), 109 $[M - NO_2 - NO - Cl]^+$ (33), 74 $[M - NO_2 - NO - 2Cl]^+$ (32).

1,5-Dichloro-2,4-dinitrobenzene (5), m.p. 102—103 °C (*cf.* Ref. 13: m.p. 103—104 °C). MS, *m/z* : 236 $[M]^+$.

Method *B*. The reaction mixture obtained by method *A* was kept at −3 °C for 4 h. The products were extracted with benzene and dried with $MgSO_4$, and the solvent was removed *in vacuo*. Chromatography in benzene gave *m*-nitrosoaniline **2** (0.35 g, 8%).

2,4-Dichloro-5-nitrosoaniline (2), dark orange crystals, m.p. 111—112 °C (decomp., from $CHCl_3$). Found (%): C, 37.92; H, 2.17; Cl, 37.02; N, 14.45. $C_6H_4Cl_2N_2O$. Calculated (%): C, 37.73; H, 2.11; Cl, 37.12; N, 14.67. ^1H NMR (CD_2Cl_2, *c* 0.25 mol L^{-1}), δ: 4.01 (br.s, 2 H, NH_2); 5.61 (s, 1 H, H(6)); 7.71 (s, 1 H, H(3)). Additional signals for the dimer appearing at −30 °C, δ: 7.08 (s, 1 H); 7.32 (s, 1 H). ^{13}C NMR (CD_2Cl_2), δ: 93.9 (C(6)); 128.1 (C(2) or C(4), ^3J = 10.6 Hz, ^2J = 4.1 Hz); 131.3 (C(4) or C(2), ^3J = 9.1 Hz, ^2J = 4.8 Hz); 132.0 (C(3)); 142.4 (C(1)); 159.9 (C(5)). ^{14}N NMR (CD_2Cl_2), δ: −328 (NH_2, $\Delta\nu_{1/2}$ = 500 Hz). IR (KBr), ν/cm^{-1}: 3370, 3460 (NH_2). MS, *m/z* (I_{rel} (%)): 190 $[M]^+$ (64), 160 $[M - NO]^+$ (100).

Oxidation of phenylenediamine 1 with *m*-chloroperbenzoic acid. A mixture of phenylenediamine **1** (0.3 g, 1.7 mmol) and MCPBA (1.7 mmol) in 40 mL of CH_2Cl_2 was kept at 6 °C for 12 h. The reaction mixture was filtered, and the filtrate was washed with water (2×100 mL) and a 5% aqueous solution of $NaHCO_3$. The orange solution was dried with $MgSO_4$, and the solvent was removed *in vacuo*. The residue was chromatographed in a 1 : 1 benzene—hexane system to give *m*-nitrosoaniline **2** (0.04 g, 12%). After the extraction, the solutions of $NaHCO_3$ were combined and acidified with 3% HCl to pH 4, and the dark violet solution was extracted with ether. The extract was dried with $MgSO_4$, and the solvent was removed *in vacuo*. Purification of the residue by chromatography in a 1 : 1 benzene—hexane system gave nitrosophenol **6** (0.04 g, 11%).

2-Amino-3,5-dichloro-6-nitrosophenol (6), m.p. 105—108 °C (decomp., from hexane). Found (%): C, 34.68; H, 1.89; Cl, 34.37; N, 13.32. $C_6H_4Cl_2N_2O_2$. Calculated (%): C, 34.81; H, 1.95; Cl, 34.25; N, 13.53. ^1H NMR (CD_2Cl_2), δ: 4.40 (br.s, 2 H, NH_2); 6.85 (s, 1 H, CH); 17.73 (br.s, 1 H, OH). ^1H NMR (CD_2Cl_2, −40 °C), δ: 4.68 (s, 2 H, NH_2); 6.86 (s, 1 H, CH); 17.16 (s, 1 H, OH). ^{13}C NMR (CD_2Cl_2, −40 °C), δ: 121.2 (C(5)); 122.0 (C(3)); 125.9 (C(4)); 137.1 (C(2)); 146.1 (C(6)); 166.9 (C(1)). ^{14}N NMR (CD_2Cl_2), δ: −330 (NH_2, $\Delta\nu_{1/2}$ = 550 Hz). IR (KBr), ν/cm^{-1}: 3375, 3475 (NH_2). MS, *m/z* (I_{rel} (%)): 206 $[M]^+$ (32), 176 $[M - NO]^+$ (100).

1,5-Bis(*tert*-butyl-*NNO*-azoxy)-2,4-dichlorobenzene (7). *N,N*-Dibromo-*tert*-butylamine (0.6 g, 2.6 mmol) was added with stirring at 20 °C to a solution of compound **3** (0.25 g, 1.2 mmol) in 30 mL of CH_2Cl_2, and the reaction mixture was left for ~16 h. The solvent was removed *in vacuo*, and the product was crystallized from MeOH to give compound **7** (0.38 g, 90%), m.p. 114—116 °C. Found (%): C, 48.28; H, 5.77; Cl, 20.62; N, 16.32. $C_{14}H_{20}Cl_2N_4O_2$. Calculated (%): C, 48.43; H, 5.81; Cl, 20.42; N, 16.13. ^{1}H NMR (acetone-d_6), δ: 1.46 (s, 18 H, 6 Me); 7.92 (s, 1 H, H(3)); 8.08 (s, 1 H, H(6)). ^{13}C NMR (acetone-d_6), δ: 25.8 (CH_3); 61.0 ($\underline{C}Me_3$); 121.8 (C(6)); 128.3 (C(2), C(4), ^3J = 9.1 Hz, ^2J = 4.3 Hz); 133.3 (C(3)); 147.4 (br., C(1), C(5)). ^{14}N NMR (acetone-d_6), δ: −56 (N(O), $\Delta\nu_{1/2}$ = 100 Hz). INEPT ^{15}N NMR (acetone-d_6), δ: −55.2 (N(O), ^4J = 2.3 Hz); 1.7 ($\underline{N}$=N(O), ^3J = 5.6 Hz). IR (KBr), ν/cm^{-1}: 1495 (N(O)=N). MS, *m/z*: 346 $[M]^+$.

2,4-Bis(*tert*-butyl-*NNO*-azoxy)-5-chloroaniline (8). A solution of compound **7** (0.6 g, 1.7 mmol) in 17.5 mL of toluene was placed in a 50-mL steel autoclave precooled with liquid nitrogen. After addition of liquid NH_3 (11.5 mL), the reaction mixture was heated at 170—180 °C for 8 h and then cooled. The solvent was removed *in vacuo*, and the residue was purified by chromatography in $CHCl_3$ to give aniline **8** (0.39 g, 69 %), m.p. 97—98 °C (from hexane). Found (%): C, 51.16; H, 6.88; Cl, 10.88; N, 21.25. $C_{14}H_{22}ClN_5O_2$. Calculated (%): C, 51.30; H, 6.76; Cl, 10.81; N, 21.36. ^{1}H NMR ($CDCl_3$), δ: 1.46, 1.47 (both s, 18 H, 6 Me); 6.14 (br.s, 2 H, NH_2); 6.78 (s, 1 H, H(6)); 8.32 (s, 1 H, H(3)). ^{13}C NMR ($CDCl_3$), δ: 25.6, 26.0 (2 CH_3); 59.7, 60.0 (2 $\underline{C}Me_3$); 118.3 (C(6)); 121.8 (C(3)); 129.7 (C(5), ^2J = 4.6 Hz); 130.1 (br, C(2) or C(4), ^3J = 7.7 Hz); 137.7 (br, C(4) or C(2), ^3J = 8.2 Hz); 142.9 (C(1), ^2J = 1.0 Hz). ^{14}N NMR ($CDCl_3$), δ: −53 (N(O), $\Delta\nu_{1/2}$ = 170 Hz). IR (KBr), ν/cm^{-1}: 1495 (N(O)=N); 3325, 3440 (NH_2). MS, *m/z*: 327 $[M]^+$.

4,6-Bis(*tert*-butyl-*NNO*-azoxy)-1,3-phenylenediamine (9). The experiment was carried out analogously, but the amount of liquid ammonia was increased to 24 mL. An autoclave was heated at 190—200 °C and 250 atm. for 12 h. The reaction mixture was cooled, and the solvent was removed *in vacuo*. The residue was crystallized from ether to give phenylenediamine **9** (0.32 g, 60%), m.p. 211—212 °C. Found (%): C, 54.51; H, 7.73; N, 27.44. $C_{14}H_{24}N_6O_2$. Calculated (%): C, 54.53; H, 7.84; N, 27.25. ^{1}H NMR (acetone-d_6), δ: 1.45 (s, 18 H, 6 Me); 6.21 (s, 1 H, H(2)); 6.61 (br.s, 4 H, 2 NH_2); 8.87 (s, 1 H, H(5)). ^{13}C NMR (acetone-d_6), δ: 26.4 (CH_3); 59.2 ($\underline{C}Me_3$); 101.3 (C(2)); 123.3 (C(5)), 124.8 (br, C(4), C(6), ^3J = 9.7 Hz); 146.6 (C(1), C(3), ^3J = 7.1 Hz). ^{14}N NMR (acetone-d_6), δ: −48 (N(O), $\Delta\nu_{1/2}$ = 130 Hz). INEPT ^{15}N NMR (acetone-d_6), δ: −313.5 (NH_2, ^1J = 89 Hz). IR (KBr), ν/cm^{-1}: 1445 (N(O)=N); 3330, 3450 (NH_2). MS, *m/z*: 308 $[M]^+$.

2-Bromo-4,6-bis(*tert*-butyl-*NNO*-azoxy)-1,3-phenylenediamine (10). A solution of bromine (0.15 g, 0.9 mmol) in 1 mL of AcOH was added dropwise with vigorous stirring at 20 °C to a solution of compound **9** (0.3 g, 0.9 mmol) and AcONa (0.03 g, 0.4 mmol) in 3 mL of glacial AcOH. After 5 min, the reaction mixture was poured into 80 mL of water. The precipitate that formed was filtered off, washed with water, and dried to give compound **9** (0.37 g, 98%), m.p. 158—159 °C (from MeOH). Found (%): C, 43.29; H, 5.99; Br, 20.88; N, 21.51. $C_{14}H_{23}BrN_6O_2$. Calculated (%): C, 43.42; H, 5.99; Br, 20.63; N, 21.70. ^{1}H NMR ($CDCl_3$), δ: 1.47 (s, 18 H, 6 Me); 6.72 (br.s, 4 H, 2 NH_2); 8.99 (s, 1 H, CH). ^{13}C NMR ($CDCl_3$), δ: 26.1 (CH_3); 59.3 ($\underline{C}Me_3$); 96.2 (C(2)); 121.7 (C(5)), 123.8 (C(4), C(6)); 142.3 (C(1), C(3)). ^{14}N NMR ($CDCl_3$), δ: −51 (N(O), $\Delta\nu_{1/2}$ = 190 Hz). IR (KBr), ν/cm^{-1}: 1485 (N(O)=N); 3285, 3465 (NH_2). MS, *m/z*: 387, 389 $[M]^+$ (1 : 1).

References

1. A. M. Churakov, S. L. Ioffe, and V. A. Tartakovsky, *Mendeleev Commun.*, 1991, 101.
2. R. C. Zawalski and P. Kovacic, *J. Org. Chem.*, 1979, **44**, 2130.
3. F. J. Alway and R. A. Gortner, *Ber.*, 1905, **38**, 1899.
4. F. B. Mallory, K. E. Schueller, and C. S. Wood, *J. Org. Chem.*, 1961, **26**, 3312.
5. D. L. Lipilin, A. M. Churakov, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Eur. J. Org. Chem.*, 1999, 29.
6. C. F. G. C. Geraldes and M. I. F. Silva, *Opt. Pura Apl.*, 1988, **21**, 71.
7. A. Buraway, M. Cais, J. T. Chamberlain, F. Liversedge, and A. R. Thompson, *J. Chem. Soc.*, 1955, 3727.
8. M. Macosza, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 531 [*Russ. Chem. Bull.*, 1996, **45**, 491 (Engl. Transl.)].
9. A. M. Churakov, O. Yu. Smirnov, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1620 [*Russ. Chem. Bull.*, 1994, **43**, 1532 (Engl. Transl.)].
10. E. T. Apasov, A. M. Churakov, Yu. A. Strelenko, S. L. Ioffe, and V. A. Tartakovsky, *Tetrahedron*, 1995, **51**, 6775.
11. W. S. Emerson and E. L. Ringwald, *J. Am. Chem. Soc.*, 1941, **63**, 2843.
12. W. Gottardi, *Monatsh. Chem.*, 1973, **104**, 1681.
13. J. H. Boyer and R. S. Buriks, *Org. Synth.*, 1960, **40**, 96.

Received November 11, 1998