Organometallic synthesis in the furazan series
4.* Reactions of azofurazans with organolithium compounds

A. B. Sheremetev,[a]★ E. A. Ivanova,[a] E. V. Shatunova,[a] D. E. Dmitriev,[a] and N. E. Kuz´mina[b]

[a]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: sab@ioc.ac.ru
[b]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: arc.sioct@mail.magelan.ru

The reactions of azofurazans, including macrocyclic azofurazans, with Bu^{n}Li and Li derivatives of methylfurazans were studied. Several competitive processes were found to occur: the addition of a Li reagent at the N=N bond, the redox reaction giving rise to hydrazofurazans, and the reaction of the side chain of azofurazan.

Key words: azofurazans, organolithium compounds, electrophilic addition, redox reaction, X-ray diffraction study.

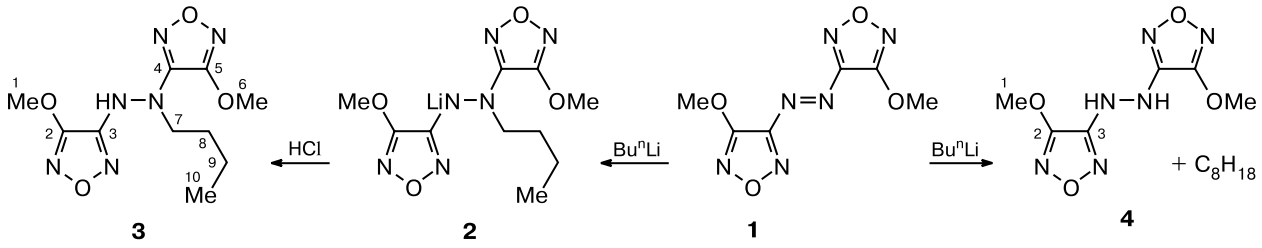
It is known[2] that the reactions of azo compounds with organolithium compounds afforded trisubstituted hydrazine derivatives. This method allows one to prepare hydrazines containing alkyl substituents along with (hetero)aromatic substituents at the nitrogen atoms. Hydrazine as well as its mono-, di-, tri-, and tetrasubstituted derivatives find wide application in various fields of engineering and medicine and also as reagents and substrates in organic synthesis (see, for example, reviews and monographs[3]).

In continuation of investigations on modifications of furazan derivatives using organometallic reagents,[1,4,5] we studied the reactions of organolithium compounds with azofurazans with the aim of preparing hydrazinofurazans. Data on compounds of this type are scarce. The only known procedure for their synthesis involves reduction of the corresponding azo-[7—10] and azoxyfurazans.[11] Trisubstituted hydrazines of the furazan series are unknown.

A strong electron-withdrawing effect of the furazan ring[12] imparts extremely high electrophilicity to the azo group in azofurazans. We chose 4,4´-dimethoxyazofurazan (**1**)[13] as a model compound. In this compound, the electron-releasing methoxy groups partially compensate the effect of the ring.

The slow addition of a solution of Bu^{n}Li in pentane to a solution of compound **1** in THF at −55 °C gives rise to two competitive reactions (Scheme 1). The highly electrophilic azo group is subjected to the attack by Bu^{n}Li to give adduct **2**. Acidification of the latter affords trisubstituted hydrazine **3** in 34% yield. Azo compound **1** acts as a strong oxidant, which initiates the competitive redox reaction resulting in reduction of the azo group to the hydrazo one to form disubstituted hydrazine **4** in 57% yield. The GLC data confirmed that the reaction mixture contained octane, which is a product of oxidation of Bu^{n}Li. Compound **4** was also prepared in 78% yield by

Scheme 1



3 **2** **1** **4**

* For Part 3, see Ref. 1.

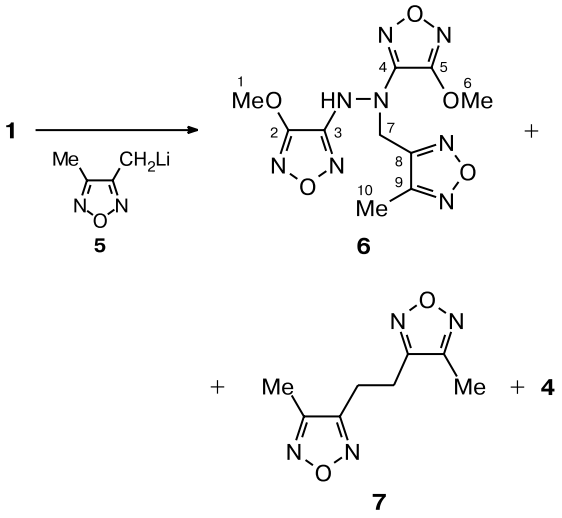
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 587—593, March, 2004.

1066-5285/04/5303-0615

the independent synthesis based on reduction of azo compound **1** with phenylhydrazine.[8]

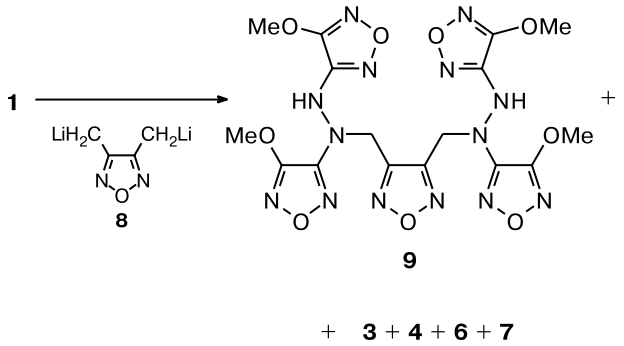
The reaction of azo compound **1** with a monolithium derivative of 3,4-dimethylfurazan (**5**) afforded analogous products (Scheme 2). However, the percentage of addition product **6** generated in this reaction was higher than that of reduction product **4** (48 and 41%, respectively). Oxidation of compound **5** produced symmetrical difurazanylethane **7**.

Scheme 2



Treatment of azofurazan **1** with a dilithium derivative of 3,4-dimethylfurazan (**8**), which was prepared by the reaction of dimethylfurazan with 2 equiv. of Bu^nLi in THF, afforded a mixture containing predominantly products of the redox reaction, *viz.*, disubstituted hydrazine **4** (76% yield) and difurazanylethane **7** (38% yield). The target bis-hydrazine **9** was isolated in a yield of only 1%. In this reaction, trisubstituted hydrazines **3** (6% yield) and **6** (9% yield) were obtained as by-products (Scheme 3).

Scheme 3



Attempts to perform analogous reactions with azofurazans containing electron-withdrawing substituents (such as 4,4-dinitro- and 4,4-dicyanoazofurazan) were unsuccessful. These reactions were accompanied by a strong exothermic effect* and yielded complex mixtures of unseparable products.

Macrocyclic compounds containing the azofurazan fragment are also promising objects of research. From the chemical standpoint, 13-membered macrocycle **10** [14] belonging to this class of compounds is an analog of "linear" azofurazan **1**. These two compounds differ primarily in the orientation of the furazan rings with respect to the azo bond. Linear compound **1** adopts an *ap-ap* conformation[15] (see Scheme 1), whereas the azofurazan fragment in macrocycle **10** has a strictly fixed *ap-sp* conformation[16] (Scheme 4) relative to the Me—O and CH_2—O bonds, respectively. Treatment of macrocycle **10** with *n*-butyllithium, like that of linear azofurazan **1**, afforded trisubstituted hydrazine **13** (33%). However, the expected reduction product **14** was not detected in the reaction mixture (an authentic sample of hydrazine **14** was synthesized by reduction of macrocycle **10** with phenylhydrazine by analogy with a known procedure[8]). We also isolated a mixture of isomeric products **16a** and **16b** formed as a result of cleavage of the macrocycle and addition of two equivalents of Bu^nLi (the yield was 61%). The possible pathways of their formation through salts **11**, **12**, and **15** are shown in Scheme 4.

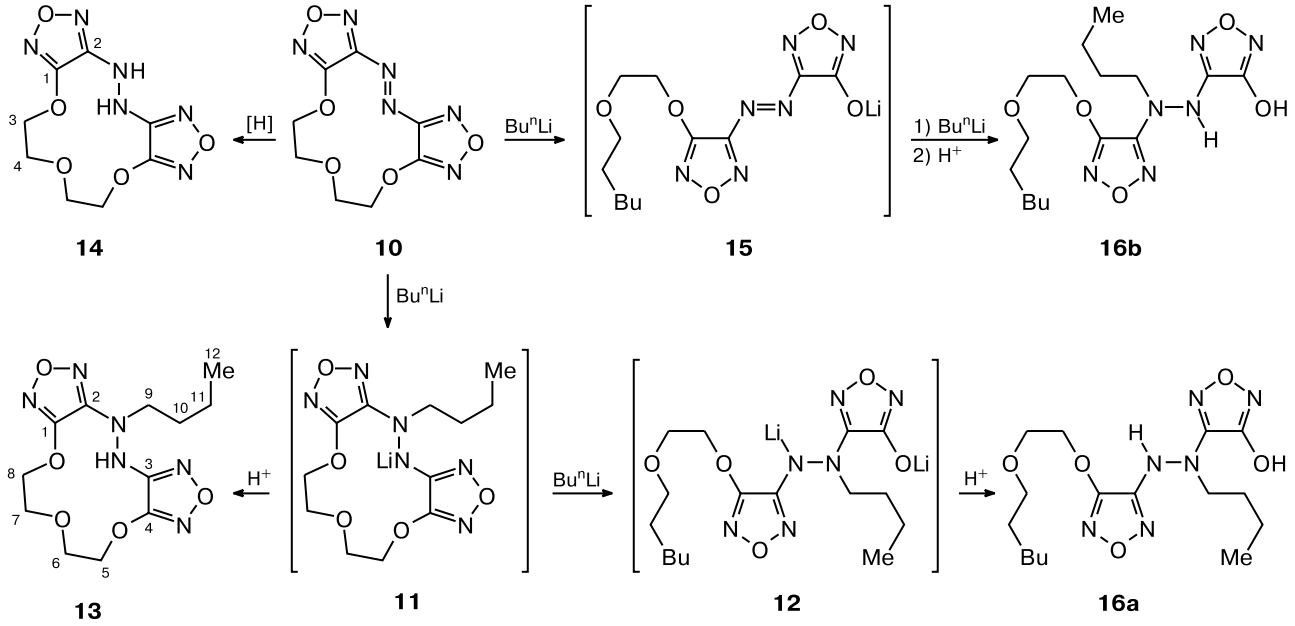
Therefore, a change from linear azo compound **1** to macrocycle **10** leads to a substantial change in the results of the reaction with Bu^nLi. It appeared that the structure of the macrocycle has an equally substantial effect on the ratio and type of products of the reactions of azofurazans with organolithium compounds. For example, 14-membered macrocycle **17**,[17] which has only a slightly larger inner cavity but smaller dentation (only two oxygen atoms can be involved in binding) compared to macrocycle **10**, reacts with Bu^nLi in a different manner (Scheme 5). This reaction afforded trisubstituted hydrazine **18** (67%) as the major product. No other products of reduction or ring opening were detected. The starting macrocycle **17** (31%) was found as the only impurity.

The addition of a monolithium derivative of dimethylfurazan to macrocycle **17** proceeds equally smoothly (see Scheme 5). Trisubstituted hydrazine **19** was prepared in 75% yield. The reaction gave rise to disubstituted difurazanylethane **7** as a by-product (8%).

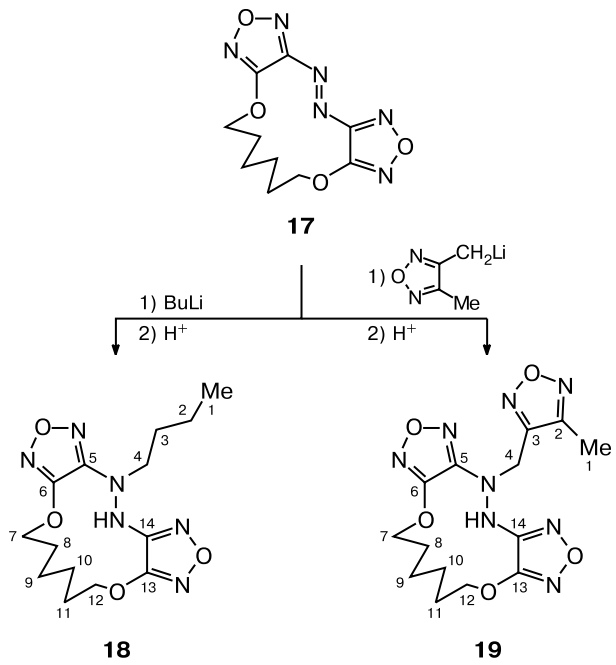
Unlike the starting azo compounds, the trisubstituted hydrazines synthesized are readily soluble not only in organic solvents but also in water, due to which macrocyclic hydrazines can be used as phase transfer catalysts as well as ligands for the formation of coordination compounds.

* With solutions of 4,4-dinitroazofurazan in THF at a concentration higher than 1 g per 100 mL, the exothermic process can lead to ignition of the reaction mixture even at the initial temperature of −70 °C.

Scheme 4



Scheme 5



The structures of the hydrazines synthesized were confirmed by elemental analysis data and the results of ^{1}H and ^{13}C NMR and IR spectroscopy.

The assignment of the signals in the NMR spectra was made taking into account the earlier data on the influence of substituents in the furazan series on the spectroscopic characteristics.[13,18,19] The carbon atoms characterized by similar chemical shifts were identified using double heteronuclear resonance with selective proton decoupling. The signals of the carbon atoms of the furazan ring were assigned by measuring the spin-spin coupling constants between these atoms and the protons of the adjacent hydrogen-containing substituents. The assignment was based on a monotonic decrease in the spin-spin coupling constants with the increasing number of intermediate bonds between the protons and the carbon atoms of the furazan ring.[20] In methylfurazans, the typical spin-spin coupling constant with the carbon atom adjacent to the Me group ($^{2}J_{CH}$ = 7.0—7.5 Hz) is much larger than that with the spatially remote carbon atoms ($^{3}J_{CH}$ = 2.5—3.2 Hz).[19,20] In the spectra of O- and N-alkyl-substituted furazans, only the spin-spin coupling constant with the adjacent carbon atom of the ring ($^{2}J_{CH}$ = 2.0—4.0 Hz) is generally observed.[13] The longer-range spin-spin constants are, as a rule, smaller than 1.5 Hz and are not manifested in the spectrum.

The mass spectra of all the trisubstituted hydrazines synthesized are characterized by the presence of a molecular ion peak as well as a peak corresponding to detachment of the alkyl rather than furazanyl fragment from hydrazine.

The structure of macrocyclic hydrazine **13** was also confirmed by X-ray diffraction analysis (Fig. 1, Table 1). The cavity of the macrocycle has an irregular shape. The average deviation of the atoms of the macrocycle from its mean plane is 0.366 Å. The furazan rings C(1)N(1)O(1)N(2)C(2) (**A**) and C(3)N(5)O(2)N(6)C(5) (**B**) are planar. The average deviation of the atoms from

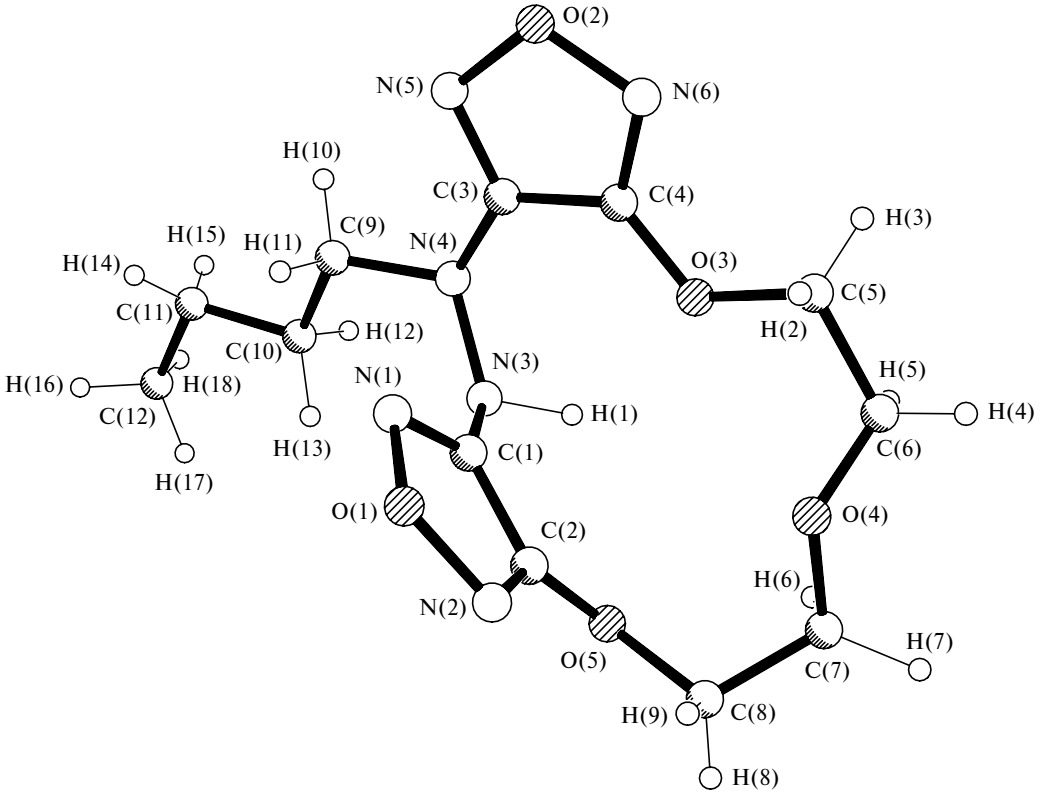


Fig. 1. Molecular structure and the atomic numbering scheme in macrocycle **13**.

the planes of rings **A** and **B** are 0.007 and 0.008 Å, respectively. The dihedral angles between these rings and the mean plane of the macrocycle are 83.3° (for **A**) and 31.1° (for **B**).

The shortest distances characterizing the cavity size are close to the sums of the van der Waals radii of the corresponding atoms (R(O(3)...O(4) = 2.76 Å, R(O(3)...N(3) = 2.86 Å, R(O(4)...O(5) = 2.77 Å, R(O(5)...N(3) = 2.96 Å), which indicates that the proton or an alkali metal atom cannot be incorporated into the cavity.

In the hydrazine fragment, the N atoms have a flattened pyramidal configuration (the sum of the bond angles at N(3) and N(4) are 342.1 and 347.7°, respectively).

In the crystal structure, the molecules are linked only through van der Waals contacts.

Table 1. Geometric parameters of compound **13**

Bond	d/Å	Bond	d/Å	Angle	ω/deg	Angle	ω/deg
O(1)—N(1)	1.409(8)	N(3)—C(1)	1.378(8)	N(1)—O(1)—N(2)	110.4(5)	O(5)—C(2)—N—(2)	127.3(7)
O(1)—N(2)	1.387(9)	N(4)—C(3)	1.380(7)	N(5)—O(2)—N(6)	111.7(4)	O(5)—C(2)—C(1)	122.8(6)
O(2)—N(5)	1.400(6)	N(4)—C(9)	1.467(6)	C(4)—O(3)—C(5)	116.7(4)	N(2)—C(2)—C(1)	109.8(7)
O(2)—N(6)	1.380(6)	N(5)—C(3)	1.313(7)	C(6)—O(4)—C(7)	115.4(5)	N(4)—C(3)—N(5)	122.7(5)
O(3)—C(4)	1.321(6)	N(6)—C(4)	1.312(7)	C(2)—O(5)—C(8)	115.6(5)	N(4)—C(3)—C(4)	128.1(5)
O(3)—C(5)	1.445(6)	C(1)—C(2)	1.436(9)	O(1)—N(1)—C(1)	104.6(6)	N(5)—C(3)—C(4)	109.2(5)
O(4)—C(6)	1.405(9)	C(3)—C(4)	1.424(7)	O(1)—N(2)—C(2)	105.9(6)	O(3)—C(4)—N(6)	125.4(5)
O(4)—C(7)	1.440(8)	C(5)—C(6)	1.501(9)	N(4)—N(3)—C(1)	117.4(5)	O(3)—C(4)—C(3)	124.7(5)
O(5)—C(2)	1.347(9)	C(7)—C(8)	1.48(1)	N(3)—N(4)—C(3)	116.0(4)	N(6)—C(4)—C(3)	109.9(5)
O(5)—C(8)	1.447(7)	C(9)—C(10)	1.518(8)	N(3)—N(4)—C(9)	115.7(4)	O(3)—C(5)—C(6)	105.8(5)
N(1)—C(1)	1.298(9)	C(10)—C(11)	1.499(6)	C(3)—N(4)—C(9)	116.6(4)	O(4)—C(6)—C(5)	107.4(5)
N(2)—C(2)	1.28(1)	C(11)—C(12)	1.52(1)	O(2)—N(5)—C(3)	104.5(5)	O(4)—C(7)—C(8)	106.7(6)
N(3)—N(4)	1.418(7)			O(2)—N(6)—C(4)	104.7(5)	O(5)—C(8)—C(7)	109.6(5)
				N(1)—C(1)—N(3)	125.3(6)	N(4)—C(9)—C(10)	112.8(5)
				N(1)—C(1)—C(2)	109.3(6)	C(9)—C(10)—C(11)	112.1(5)
				N(3)—C(1)—C(2)	125.4(6)	C(10)—C(11)—C(12)	112.8(5)

To summarize, we demonstrated that the reactions of organolithium compounds with azofurazans provide the first approach to trisubstituted hydrazines containing the furazan ring. The efficiency of this reaction depends on the structure of the starting azofurazan.

Experimental

The melting points were determined on a Kofler stage. The ^{1}H and ^{13}C NMR spectra were measured on Bruker AM-300 (300.13 and 75.7 MHz, respectively) and Bruker DRX-500 (500.13 and 125.7 MHz, respectively) spectrometers at natural isotope abundance. The chemical shifts in the NMR spectra are given in the δ scale with respect to the solvent as the internal standard. The mass spectra were obtained on Finnigan MAT INCOS-50 and Varian MAT CH-111 instruments (EI, 70 eV). The IR spectra were measured on a Specord IR-75 spectrometer (in KBr pellets for solids and in a thin layer for liquid samples). The course of the reactions and the purity of the products were monitored by GLC and TLC (on Silufol UV-254 plates, visualization in the UV region). The GLC analysis was carried out on a Biokhrom-1 chromatograph equipped with a flame ionization detector and a quartz capillary column (0.2 mm×20 m, SE-54 phase; helium as the carrier gas).

X-ray diffraction analysis of compound 13. The X-ray diffraction data were collected on an automated Enraf-Nonius CAD-4 diffractometer (graphite monochromator, Mo-Kα radiation, θ scanning technique, $\theta_{max} = 30$). The structure was solved and refined using 1086 observed reflections with $I > 2\sigma(I)$. Calculations were carried out with the use of the SHELX 93 program package.[21] The structure of compound **13** was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. Some hydrogen atoms (H(1), H(5)—H(7), H(12)—H(15), and H(18)) were revealed from difference electron density maps. The coordinates of all other H atoms were calculated geometrically. All H atoms were refined with fixed thermal ($B = 3.948$ Å^2) and positional parameters. The refinement converged to $R = 0.059$, $R_w = 0.155$, GOOF = 0.898.

The crystals of compound **13**, $C_{12}H_{18}N_6O_5$, are monoclinic, at $T = 293$ K, $a = 11.024(2)$ Å, $b = 12.176(2)$ Å, $c = 11.881(2)$ Å, $\beta = 101.59(3)°$, $V = 1562.2(5)$ Å^3, $M_w = 326.3$, $d_{calc} = 1.39$ g cm^{-3}, $\mu_{Mo} = 0.1104$ mm^{-1}, $F(000) = 688.0$, space group $P2_1/c$, $Z = 4$. The atomic coordinates, equivalent isotropic thermal parameters, and complete tables of bond lengths and bond angles were deposited with the Cambridge Structural Database. The selected bond lengths and bond angles are given in Table 1.

Reaction of 4,4′-dimethoxyazofurazan (1) with Bu^{n}Li. A solution of compound **1** [13] (0.6 g, 2.65 mmol) in anhydrous THF (50 mL) was placed in a 200-mL three-neck flask equipped with a thermometer and two dropping funnels with bypasses. Then a solution of Bu^{n}Li (0.169 g, 2.65 mmol, 0.051 g mL^{-1}) in pentane was added dropwise with stirring at −55 °C under a static atmosphere of argon. The reaction mixture was stirred at −55 °C for 30 min. Then cooling was terminated and the mixture was allowed to warm to ~20 °C. The reaction mixture was stirred for 1 h, neutralized with a saturated aqueous solution of NH_4Cl (10 mL), and evaporated to dryness. Water (30 mL) was added to the residue and the mixture was extracted with diethyl ether (3×25 mL). The extract was dried with $MgSO_4$ and the solvent was removed. The products were separated by preparative chromatography (SiO_2 40/100, $CHCl_3$ as the eluent). Two fractions were isolated. Fraction 1 (R_f 0.8), **1-butyl-1,2-di(4-methoxyfurazan-3-yl)hydrazine (3)** (0.25 g, 34%) as an oil, $n_D^{20} = 1.488$. Found (%): C, 42.30; H, 5.69; N, 29.52. $C_{10}H_{16}N_6O_4$ (284.27). Calculated (%): C, 42.25; H, 5.67; N, 29.56. MS, *m/z*: 283 $[M - H]^+$, 227 $[M - BuH]^+$, 185, 170, 153, 143, 129, 100, 99, 84. ^{1}H NMR ($CDCl_3$), δ: 0.83 (t, 3 H, C—Me, $J = 7.1$ Hz); 1.28 (m, 2 H, C$\underline{H}_2$—Me); 1.57 (m, 2 H, CH_2—C$\underline{H}_2$—CH_2); 3.51 (t, 2 H, N—CH_2, $J = 7.1$ Hz); 3.93 and 3.97 (both s, 3 H each, OMe); 6.78 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.4 (C(10)), 19.4 (C(9)), 28.2 (C(8)), 52.3 (C(7)), 59.0 (OCH_3), 59.1 (OCH_3), 147.8 (C(3)), 150.3 (C(4)), 156.9 (C(2)), 157.4 (C(5)). Fraction 2 (R_f 0.32), **1,2-di(4-methoxyfurazan-3-yl)hydrazine (4)** (0.345 g, 57%), m.p. 151—152 °C (from Pr^{i}OH). Found (%): C, 31.61; H, 3.55; N, 36.82. $C_6H_8N_6O_4$ (228.17). Calculated (%): C, 31.58; H, 3.53; N, 36.83. MS, *m/z*: 228 $[M]^+$, 227 $[M - H]^+$, 148, 141, 130, 114, 100, 99, 83. IR, ν/cm^{-1}: 3320, 3117, 1580, 1400, 1345, 1000, 910, 830. ^{1}H NMR (DMSO-d_6), δ: 4.06 (s, 6 H, OMe); 9.07 (br.s, 2 H, 2 NH). ^{13}C NMR (DMSO-d_6), δ: 59.4 (C(1)), 149.0 (C(3)), 157.3 (C(2)).

1,2-Di(4-methoxyfurazan-3-yl)-1-(4-methylfurazan-3-ylmethyl)hydrazine (6). Analogously, a solution of Bu^{n}Li (0.16 g, 2.52 mmol, 0.051 g mL^{-1}) in pentane was added to a solution of 3,4-dimethylfurazan[6] (0.247 g, 2.52 mmol) in anhydrous THF (50 mL). The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of compound **1** (0.57 g, 2.52 mmol) in anhydrous THF (20 mL) was rapidly added. The products were separated by preparative chromatography (SiO_2 40/100, a 2 : 3 CH_2Cl_2—CCl_4 mixture as the eluent). Three fractions were isolated. Fraction 1, 1,2-difurazanylethane **7** (0.1 g, 41.6%), m.p. 98—99 °C (*cf.* lit. data[6]: m.p. 99—101 °C). Fraction 2, **1,2-di(4-methoxyfurazan-3-yl)-1-(4-methylfurazan-3-ylmethyl)hydrazine (6)** (0.21 g, 48%), m.p. 120—121 °C. Found (%): C, 37.06; H, 3.74; N, 34.53. $C_{10}H_{12}N_8O_5$ (324.26). Calculated (%): C, 37.04; H, 3.73; N, 34.56. MS, *m/z*: 324 $[M]^+$, 227, 226, 129, 98, 83. IR, ν/cm^{-1}: 3328, 3088, 3024, 2968, 2952, 2280, 2168, 2080, 1480, 1420, 1376, 1364, 1352, 1256, 1228, 1016, 904, 884. ^{1}H NMR (CD_3CN), δ: 2.45 (s, 3 H, C—Me); 4.03 and 4.07 (both s, 3 H each, OMe); 4.95 (s, 2 H, N—CH_2); 7.49 (s, 1 H, NH). ^{13}C NMR (CD_3CN), δ: 7.5 (C(10)), 45.1 (C(7)), 59.3 (OMe), 59.5 (OMe), 148.1 (C(3)), 150.2 (C(4), $^3J_{CH_2} = 2.3$ Hz), 150.5 (C(8), $^2J_{CH_2} = 5.9$ Hz), 152.1 (C(9), $^3J_{CH_2} = 2.7$ Hz), 157.4 (C(2)), 158.1 (C(5)). Fraction 3, 1,2-difurazanylhydrazine **4** (0.09 g, 15%), m.p. 152 °C. According to the results of TLC and ^{1}H NMR spectroscopy, this compound is identical to the sample described above.

Reaction of 4,4′-dimethoxy-3,3′-azofurazan (1) with a dilithium derivative of 3,4-dimethylfurazan. Analogously to the synthesis of compound **6**, 3,4-dimethylfurazan **1** (2.14 g, 21.8 mol) was lithiated in anhydrous THF (100 mL) with a solution of Bu^{n}Li (2.8 g, 43.6 mol, 0.064 g mL^{-1}) in pentane. The bright-yellow reaction mixture was stirred at −55 °C for 20 min and then a solution of compound **1** (4.9 g, 21.8 mol) in anhydrous THF (30 mL) was added dropwise. The reaction mixture was stirred at −55 °C for 30 min, allowed to warm to ~20 °C, stirred for 1 h, neutralized with a saturated aqueous NH_4Cl solution (10 mL), and concentrated under reduced pressure to dryness. The residue was treated with diethyl ether

(150 mL) and washed with water (3×30 mL). The extract was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The residue was subjected to preparative chromatography (SiO_2 40/100, $CH_2Cl_2 \rightarrow Pr^iOH$ as the eluent). Five fractions were isolated. These fractions contained (in order of decreasing R_f) compounds **7**, **3**, **6**, **4**, and **9**. Fraction 1, compound **7** (1.6 g, 38%), m.p. 99—100 °C (*cf.* lit. data[6]: m.p. 99—101 °C). Fraction 2, hydrazine **3** (0.37 g, 6%); according to the results of TLC and ^{1}H NMR spectroscopy, this compound is identical to the sample described above. Fraction 3, compound **6** (0.64 g, 9%), m.p. 120—121 °C; according to the results of TLC and ^{1}H NMR spectroscopy, this compound is identical to the sample described above. Fraction 4, compound **4** (3.78 g, 76%), m.p. 151—152 °C; according to the results of TLC and ^{1}H NMR spectroscopy, this compound is identical to the sample described above. Fraction 5, **3,4-bis[1,2-(4-methoxyfurazan-3-yl)hydrazinomethyl]furazan (9)** (0.06 g, 1%), m.p. 207—208 °C. $C_{16}H_{18}N_{14}O_9$ (550.41). MS, *m/z*: 550 $[M]^+$, 435, 373, 348, 324, 306, 284, 238, 226, 127. ^{1}H NMR (CD_3CN), δ: 4.04 and 4.07 (both s, 6 H each, OMe); 4.99 (s, 4 H, N—CH_2); 7.48—7.52 (2 H, NH).

Reaction of 8,9,12,13-difurazano-1,4,7-trioxa-10,11-diazacyclotrideca-8,10,12-triene (10) with Bu^{n}Li. A solution of Bu^{n}Li (0.07 g, 1.11 mmol) in pentane was added dropwise with stirring to a solution of macrocycle **10** (0.3 g, 1.11 mmol) in anhydrous THF (50 mL) at −55 °C under a static atmosphere of argon. The reaction mixture was stirred at −55 °C for 30 min. Then the reaction mixture was warmed to ~20 °C and stirred for 1 h. Dilute HCl was added to the reaction mixture to pH 3, the mixture was concentrated to dryness, water (20 mL) was added to the residue, and the mixture was extracted with diethyl ether (3×30 mL). The extract was dried with $MgSO_4$ and the solvent was evaporated. The reaction products were separated on a chromatographic plate (Silufol 40/100, CH_2Cl_2 as the eluent) and two fractions were isolated. Fraction 1 (R_f 0.6), **10-butyl-8,9,12,13-difurazano-1,4,7-trioxa-4,5-diazacyclotrideca-8,12-diene (13)** (0.12 g, 33%), m.p. 121—122 °C. Found (%): C, 44.16; H, 5.59; N, 25.68. $C_{12}H_{18}N_6O_5$ (326.31). Calculated (%): C, 44.17; H, 5.56; N, 25.75. ^{1}H NMR ($CDCl_3$), δ: 0.96 (t, 3 H, C—Me, J = 7.1 Hz); 1.41 (m, 2 H, CH_2—Me); 1.73 (m, 2 H, CH_2—CH_2—CH_2), 3.64 (t, 2 H, N—CH_2, J = 7.2 Hz); 3.77, 3.82, 4.26, and 4.62 (all m, 2 H each, OCH_2); 6.51 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 157.3 (C(4)), 157.1 (C(1)), 150.3 (C(2)), 149.7 (C(3)), 72.7 (OCH_2), 71.1 (OCH_2), 70.1 (OCH_2), 69.7 (OCH_2), 53.5 (C(9)), 28.4 (C(10)), 19.9 (C(11)), 13.8 (C(12)). MS, *m/z*: 327 $[M + H]^+$, 326 $[M]^+$, 283, 270 $[M - Bu + H]^+$, 239, 182, 168, 167, 152, 141, 127, 113, 110, 99, 98, 97, 82, 69. Fraction 2 (R_f 0.2), a mixture of **1-butyl-2-[4-(1,4-dioxadecyl)furazan-3-yl]-1-(4-hydroxyfurazan-3-yl)hydrazine (16a)** and **2-butyl-2-[4-(1,4-dioxadecyl)furazan-3-yl]-1-(4-hydroxy-3-furazanyl)hydrazine (16b)** (0.24 g, 66%), a viscous oil. Found (%): C, 50.13; H, 7.41; N, 21.77. $C_{16}H_{28}N_6O_5$ (384.44). Calculated (%): C, 49.99; H, 7.34; N, 21.86. MS, *m/z*: 384 $[M + H]^+$, 328, 327, 326, 298, 267, 266, 221, 193, 153, 113, 97, 84, 71, 57. ^{1}H NMR ($CDCl_3$), δ: 0.75—0.95 (m, 12 H); 1.40—1.90 (m, 24 H); 3.59 and 3.64 (both t, 2 H each, N—CH_2, J = 7.0 Hz); 3.72—3.76, 4.21—4.23, and 4.62—4.65 (all m, 4 H each, O—CH_2); 6.51 and 7.11 (both s, 1 H each, NH); 10.00—12.00 (br.s, 2 H, OH).

8,9,12,13-Difurazano-1,4,7-trioxa-10,11-diazacyclotrideca-8,12-diene (14). A solution of freshly distilled phenylhydrazine (0.54 g, 5 mmol) in benzene (5 mL) was added dropwise with stirring to a bright-red solution of macrocycle **10** (1.07 g, 4 mmol) in benzene (5 mL) at ~20 °C for 10 min. The color of the solution changed to pale-brown and a precipitate formed. After 1 h, the precipitate was filtered off and recrystallized from ethanol. Colorless amorphous product **14** was obtained in a yield of 0.75 g (69.4%), m.p. 210—211 °C. Found (%): C, 35.59; H, 3.74; N, 31.08. $C_8H_{10}N_6O_5$ (270.20). Calculated (%): C, 35.56; H, 3.73; N, 31.10. MS, *m/z*: 270 $[M]^+$, 240 $[M - NO]^+$. IR, ν/cm^{-1}: 3304, 3264, 2919, 1608, 1568, 1548, 1456, 1368, 1352, 1308, 1256, 1140, 1096, 1056, 1036, 1012, 928, 900. ^{1}H NMR (DMSO-d_6), δ: 3.73 and 4.36 (both m, 4 H each, OCH_2); 9.00 (s, 2 H, NH). ^{13}C NMR (DMSO-d_6), δ: 69.6 (C(4)), 72.1 (C(3)), 150.6 (C(2)), 157.7 (C(1), $^3J_{CH2}$ = 3.0 Hz).

Reaction of 2,3,6,7-difurazano-1,8-dioxa-4,5-diazacyclotetradeca-2,4,6-triene (17) with Bu^{n}Li was carried out analogously to the reaction of macrocycle **10** with the use of compound **17** (0.5 g, 1.8 mmol).[17] Chromatographic separation (SiO_2 40/100, a 3 : 1 CH_2Cl_2—pentane mixture as the eluent) afforded two fractions (**17** > **18**). Fraction 1, red-orange crystals of the starting macrocycle **17** (0.15 g, 31%), m.p. 122—123 °C (*cf.* lit. data[17]: m.p. 123 °C). Fraction 2, **4-butyl-2,3,6,7-difurazano-1,8-dioxa-4,5-diazacyclotetradeca-2,6-diene (18)** (0.41 g, 67%), m.p. 122—125 °C. Found (%): C, 49.73; H, 6.54; N, 24.80. $C_{14}H_{22}N_6O_4$ (338.37). Calculated (%): C, 49.70; H, 6.55; N, 24.84. MS, *m/z*: 338 $[M]^+$, 281 $[M - Bu]^+$, 250. ^{1}H NMR ($CDCl_3$), δ: 0.97 (t, 3 H, Me, J = 7.1 Hz); 1.42 (m, 2 H, C(2)H_2); 1.60 (m, 8 H, C(8)H_2, C(9)H_2, C(10)H_2, C(11)H_2); 1.74 (m, 2 H, C(3)H_2); 3.64 (m, 2 H, C(4)H_2); 4.20 (m, 2 H, C(7)H_2); 4.50 (m, 2 H, C(12)H_2); 6.70 (s, 1 H, NH).

Reaction of macrocycle 17 with a lithium derivative of dimethylfurazan was carried out analogously to the synthesis of compound **6** with the use of compound **17** (0.5 g, 1.8 mmol).[17] Chromatographic separation (SiO_2 40/100, a 3 : 1 CH_2Cl_2—pentane mixture as the eluent) afforded three fractions (**7** > **17** > **19**). Fraction 1, compound **7** (0.012 g, 8%), m.p. 99—100 °C (*cf.* lit. data[6]: m.p. 99—101 °C); according to the results of TLC and ^{1}H NMR spectroscopy, this compound is identical to the authentic sample. Fraction 2, red-orange crystals of the starting macrocycle **17** (0.03 g, 6%), m.p. 122—123 °C (*cf.* lit. data[17]: m.p. 123 °C). Fraction 3: **4-(4-methylfurazan-3-ylmethyl)-2,3,6,7-difurazano-1,8-dioxa-4,5-diazacyclotetradeca-2,6-diene (19)** (0.51 g, 75%), m.p. 156—157 °C. Found (%): C, 44.48; H, 4.82; N, 29.77. $C_{14}H_{18}N_8O_5$ (378.35). Calculated (%): C, 44.44; H, 4.80; N, 29.62. MS, *m/z*: 378 $[M]^+$, 281. ^{1}H NMR ($CDCl_3$), δ: 1.60 (m, 8 H, C(8)H_2, C(9)H_2, C(10)H_2, C(11)H_2); 2.50 (s, 3 H, Me); 4.20 (m, 2 H, C(7)H_2); 4.50 (m, 2 H, C(12)H_2); 4.90 (s, 2 H, C(4)H_2); 6.70 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 8.1 (C(1)), 24.2, 24.9 (C(9), C(10)), 26.9, 27.2 (C(8), C(11)), 46.2 (C(4)), 73.0 (C(7)), 75.1 (C(12)), 148.8 (C(14), $^2J_{C-NH}$ = 7.1 Hz), 149.3 (C(5), $^3J_{CH_2}$ = 2.8 Hz), 150.0 (C(3), $^2J_{CH_2}$ = 6.4 Hz, $^3J_{CH_3}$ = 3.2 Hz), 151.0 (C(2), $^2J_{CH_3}$ = 7.1 Hz, $^3J_{CH_2}$ = 3.6 Hz), 155.7 (C(13), $^3J_{C-NH} \approx 1$ Hz), 157.0 (C(6)).

This study was in part financially supported by the International Science Foundation (Grants MM9000 and MM9300), the Russian Foundation for Basic Research (Project No. 98-03-33024a), and the Federal Target Program "Integration of Science and Higher School of Russia for 2002—2006" (State Contract No. I0667).

References

1. A. B. Sheremetev and E. A. Ivanova, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1910 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2017].
2. *Metody elementoorganicheskoi khimii* [*Methods of Organometallic Chemistry*], Eds. T. V. Talalaev and K. A. Kocheshkov, Nauka, Moscow, 1971, **2**, p. 873 (in Russian).
3. A. P. Grekov, *Organicheskaya khimiya gidrazina* [*Organic Chemistry of Hydrazine*], Tekhnika, Kiev, 1966 (in Russian); C. G. Overberger, J. P. Anselme, and J. G. Lombardino, *Organic Compounds with Nitrogen—Nitrogen Bonds*, Ronald Press, New York, 1966, 115 pp.; *The Chemistry of Hydrazo, Azo and Azoxy Groups* (*The Chemistry of Functional Groups)*, Ed. S. Patai, J. Wiley and Sons, London, 1975, 1100 pp.; B. V. Ioffe, M. A. Kuznetsov, and A. A. Potekhin, *Khimiya organicheskikh proizvodnykh gidrazina* [*Chemistry of Organic Derivatives of Hydrazine*], Khimiya, Leningrad, 1979, 224 pp. (in Russian); N. V. Korovin, *Gidrazin* [*Hydrazine*], Khimiya, Moscow, 1980, 272 pp. (in Russian); U. Jensen-Korte and N. Mueller, in *Methoden der organischen Chemie (Houben-Weyl)*, Ed. D. Klamann, Thieme, Stuttgart, 4th Ed., 1990, **16a**, 425—648; P. R. Huddleston and I. G. C. Coutts, in *Comprehensive Organic Functional Group Transformations*, Eds. A. R. Katritzky, O. Meth-Cohn, and C. W. Rees, Pergamon—Elsevier, Oxford, 1995, **2**, 371—383; U. Ragnarsson, *Chem. Soc. Rev.*, 2001, **30**, 205.
4. A. Yu. Sizov and A. B. Sheremetev, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 365 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 281 (Engl. Transl.)].
5. E. T. Apasov, A. B. Sheremetev, B. A. Dzhetigenov, A. V. Kalinin, and V. A. Tartakovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1916 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1500 (Engl. Transl.)].
6. A. B. Sheremetev, E. A. Ivanova, A. Yu. Sizov, V. O. Kulagina, D. E. Dmitriev, and Yu. A. Strelenko, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 651 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 679].
7. G. Ponzio and G. Ruggeri, *Gazz. Chim. Ital.*, 1923, **53**, 297.
8. G. Ponzio and L. Avogadro, *Gazz. Chim. Ital.*, 1923, **53**, 318.
9. E. Durio and S. Dugone, *Gazz. Chim. Ital.*, 1936, **66**, 139.
10. Pat. US 6388087, 2002; *Chem. Abstr.*, 2002, **136**, 371892.
11. D. Chavez, L. Hill, M. Hiskey, and S. Kinkead, *J. Energetic Materials*, 2000, **18**, 219.
12. A. B. Sheremetev, N. N. Makhova, and W. Friedrichsen, *Adv. Heterocycl. Chem.*, 2001, **78**, 65.
13. A. B. Sheremetev, O. V. Kharitonova, E. V. Mantseva, V. O. Kulagina, E. V. Shatunova, N. S. Aleksandrova, T. M. Mel´nikova, E. A. Ivanova, D. E. Dmitriev, V. A. Eman, I. L. Yudin, V. S. Kuz´min, Yu. A. Strelenko, T. S. Novikova, O. V. Lebedev, and L. I. Khmel´nitskii, *Zh. Org. Khim.*, 1999, **35**, 1555 [*Russ. J. Org. Chem.*, 1999, **35**, 1525 (Engl. Transl.)].
14. A. B. Sheremetev and O. V. Kharitonova, *Mendeleev Commun.*, 1992, 157.
15. A. B. Sheremetev, E. V. Shatunova, B. B. Averkiev, D. E. Dmitriev, V. A. Petukhov, and M. Yu. Antipin, *Heteroatom Chem.*, 2004, **15**, 131.
16. L. Chertanova, C. Pascard, and A. Sheremetev, *Supramolec. Chem.*, 1993, **3**, 71.
17. A. B. Sheremetev and E. V. Shatunova, *Tez. dokl II Moskovskoi konf. po mezhfaznomu katalizu* [*Abstrs. of Papers, II Moscow Conf. on Phase Trasnfer Catalysis*], Moscow, 1994, 70 (in Russian); E. V. Shatunova and A. B. Sheremetev, *IX Eur. Symp. on Organic Chemistry (Warszawa, June 18—23, 1995)*, Warszawa (Poland), PA 115, 184.
18. Yu. A. Strelenko, A. B. Sheremetev, and L. I. Khmel´nitskii, *Khim. Geterotsikl. Soedin.*, 1992, 1101 [*Chem. Heterocycl. Compd.,* 1992, 927 (Engl. Transl.)].
19. D. E. Dmitriev, Yu. A. Strelenko, and A. B. Sheremetev, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 277 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 290].
20. Yu. A. Strelenko, O. A. Rakitin, T. I. Godovikova, and L. I. Khmel´nitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2852 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36** (Engl. Transl.)].
21. G. M. Sheldrick, *SHELX93*, University of Göttingen, Göttingen (Germany), 1993.

Received November 12, 2003;
in revised form December 19, 2003