Organometallic synthesis in the furazan series
2.* Furazanylethanes

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The reactions of Li derivatives of methylfurazans with electrophilic reagents and oxidants were investigated. A series of functionalized furazanylethane derivatives were prepared.

Key words: furazans, furazanylethanes, organolithium synthesis, electrophilic reagents, NMR spectroscopic study.

Organolithium synthons are widely used in the target synthesis of compounds containing heterocyclic fragments.[3,4] Lithiation of the simplest heterocyclic derivatives followed by the reactions of the resulting Li-containing intermediates with electrophiles enables one to substantially complicate the molecular structure in one operation. However, this methodology has found virtually no application in the construction of complex furazan derivatives. At the same time, it is these derivatives that are most attractive as potentially biologically active compounds. The state-of-the-art of chemistry of furazan derivatives has been surveyed in the review.[5]

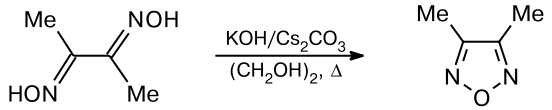
Earlier,[1,2,6] we have demonstrated that the electron-withdrawing nature of the furazan ring is favorable for smooth lithiation of the methyl group bound to this ring. The resulting lithium derivatives reacted with alkyl halides or haloacetic esters to give the corresponding derivatives.

In the present study, we report on the use of Li derivatives of methylfurazans in the synthesis of a series of new functionalized furazanylethanes.

3,4-Dimethylfurazan (**1**) was chosen as the basic precursor. Several procedures have been developed[5] for the synthesis of this compound by dehydration of dimethylglyoxime (**2**) (Scheme 1). However, the procedures described earlier enable one to prepare compound **1** in yields of at most 80% and require large amounts of dehydrating reagents. We optimized dehydration of **2** promoted by bases,[7] which made it possible to increase the yield of **1** to 95%. Thus, slow heating of a suspension of **2** in ethylene glycol to boiling in the presence of catalytic amounts of a mixture of KOH and Cs_2CO_3 ensures smooth distillation of the product and allows one to obtain more than 400 g of furazan **1** in one operation.

* For Part 1, see Ref. 1. Selected results of the present study were submitted to the Conference on Organic Synthesis.[2]

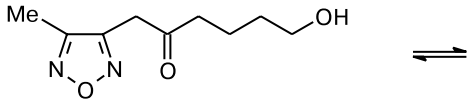
Scheme 1



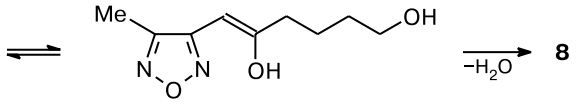
2 **1**

Lithiation of compound **1** with butyllithium was carried out analogously to a procedure described earlier.[1] Treatment of the resulting intermediate **3** with different electrophilic reagents at −50 °C afforded compounds **4—10** (Scheme 2) in 65—85% yields.

The procedure used afforded the expected compounds **4—7**, **9**, and **10a,b**. However, the reaction of intermediate **3** with butyrolactone unexpectedly gave rise to ylidenetetrahydrofuran **8**. Apparently, keto alcohol **11** that initially formed readily underwent enlolization followed by cyclodehydration under the reaction conditions.



11a



11b

Difurazanylethane **6** was also readily prepared in 85—95% yields by oxidative condensation of intermediate **3** under the action of I_2, $CuCl_2$, or dibromoethane. Recently,[8] compound **6** has been synthesized by the reaction of cyclopropyllithium with 3-bromomethyl-4-methylfurazan.

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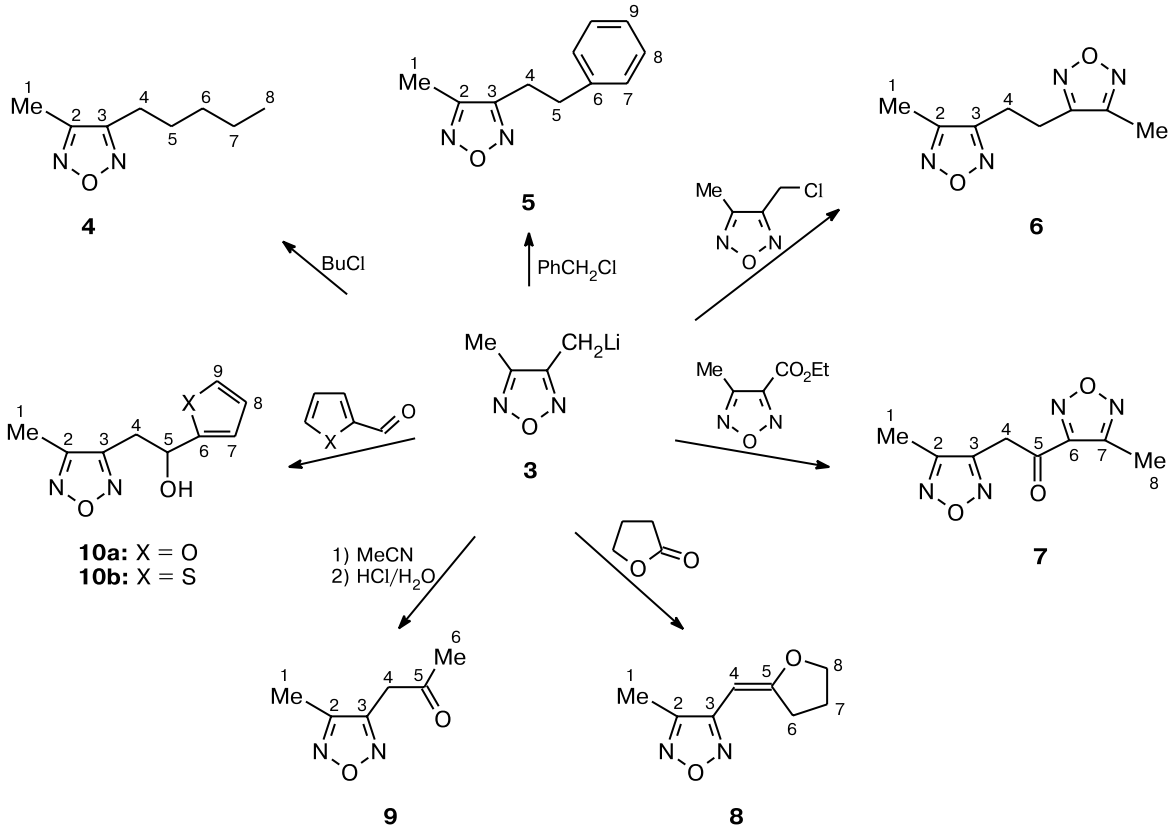
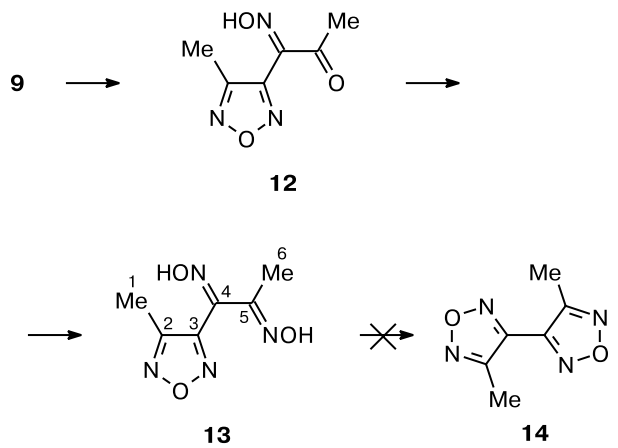
Scheme 2



Ketone **9** was readily nitrosated at the methylene fragment. The resulting ketoxime **12** was transformed into glyoxime **13** (Scheme 3).[9] However, attempts to perform dehydration of glyoxime **13** to produce bifurazan **14** under the conditions used for the synthesis of compound **1** failed.

Scheme 3

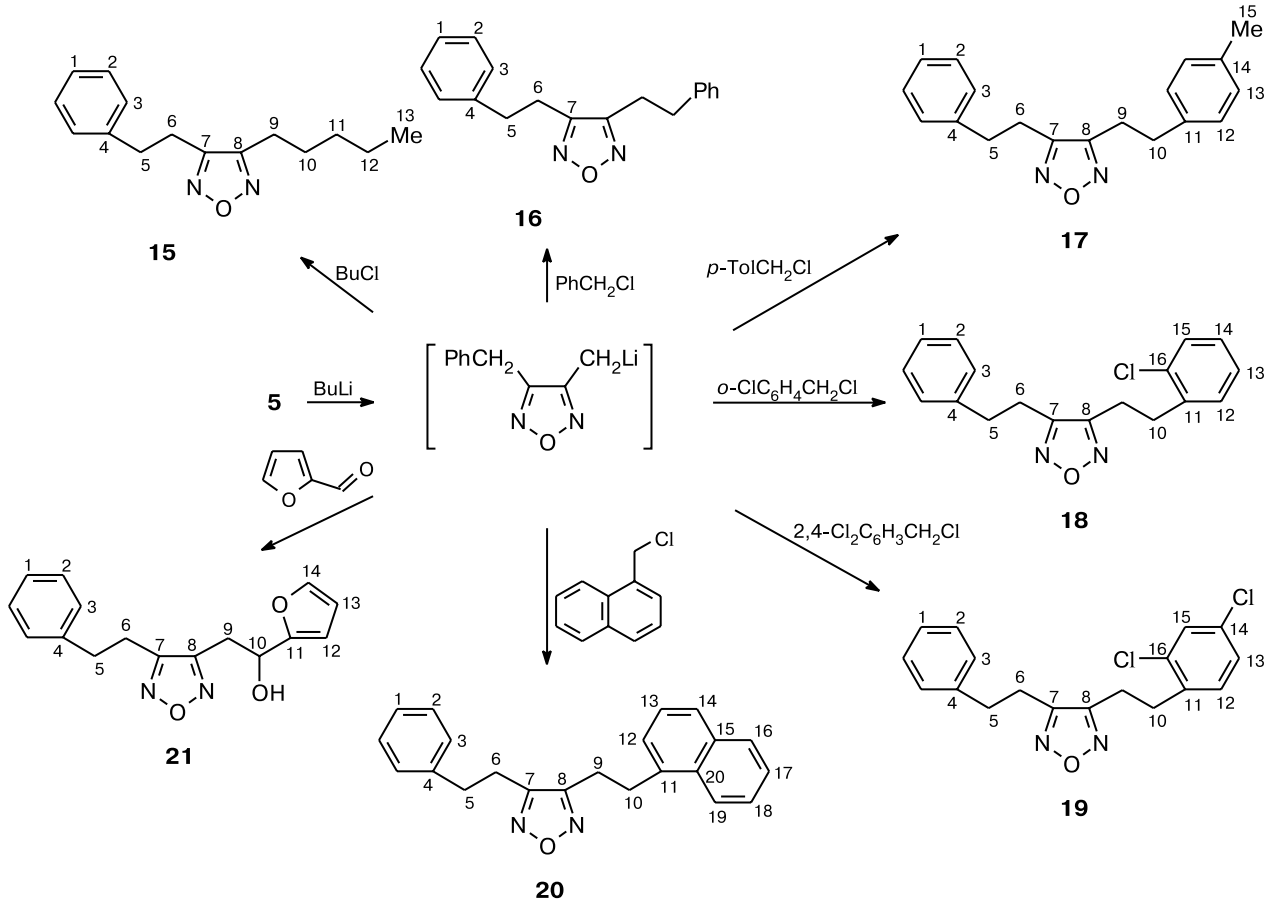


In the next step of investigation, we carried out secondary lithiation of the compounds prepared in the first step and their further modifications. We used compound **5** as a model object. Under the reaction conditions used for lithiation of furazan **1**, compound **5** was lithiated exclusively at the methyl group. Treatment of the intermediate thus formed with electrophiles afforded products **15—21** (Scheme 4). However, the products were prepared in lower yields than those achieved in the reactions of intermediate **3**. The reactions with the use of different benzyl chlorides as electrophiles gave rise to the corresponding stilbenes as by-products. For example, an attempt to synthesize compound **16** by treatment of dimethylfurazan **1** with two equivalents of butyllithium to produce a *C*,*C*′-dilithiated intermediate followed by treatment with two equivalents of benzyl chloride led to the formation of only trace amounts of the target product,[16] stilbene being obtained in 84% yield.

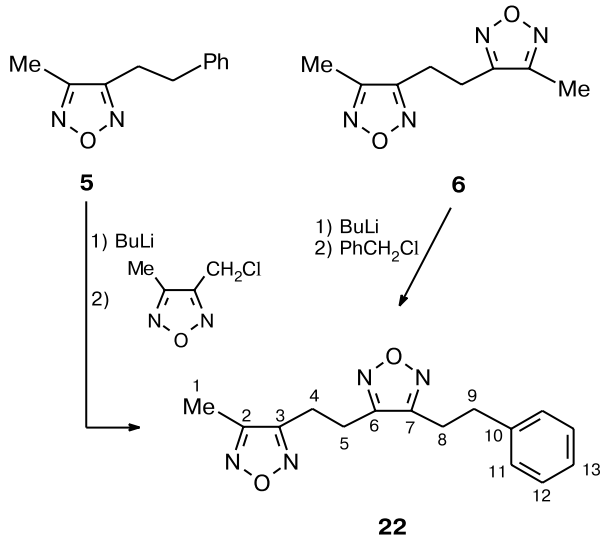
Two approaches to the synthesis of unsymmetrically substituted difurazanylethane **22** were used (Scheme 5). Both approaches gave rise to product **22** in similar yields (66—68%).

Oxidative condensation of the corresponding lithiated derivatives under the action of $CuCl_2$ is an efficient procedure for the synthesis of difurazanylethanes **23** and **24** (Scheme 6), which were isolated in 78 and 85% yields, respectively.

Scheme 4



Scheme 5



The compositions and structures of all compounds were confirmed by elemental analysis, NMR and IR spectroscopy, and mass spectrometry. Thus, an intense molecular ion peak $[M]^+$ was observed in the mass spectra of all compounds. Earlier,[1] we have reported that the $[M^+ - NO]$ fragment is characteristic of furazans containing alkyl substituents. Competitive heterolytic fragmentation of the alkyl chain producing the ions $[M - CH_3]^+$, $[M - C_2H_4]^+$, $[M - NO - CH_3]^+$, *etc.*, was less pronounced.

Taking into account the characteristic features, which have been revealed in the earlier NMR spectroscopic studies of furazan derivatives,[1,10–12] the interpretation of the ^1H and ^{13}C NMR spectra of rather simple compounds, such as **4—16**, **23**, and **24**, presented no problems. However, the assignment of the signals in the spectra of unsymmetrical compounds **17—22** called for a more detailed investigation. Only some of the signals observed in the spectra of the latter compounds can be interpreted by comparing with the spectra of the corresponding symmetrical derivatives. The complete assignment of all signals for the protonated carbon atoms was made based on the assignments of the signals for the corresponding protons with the use of the inversion two-dimensional heteronuclear H,C correlation experiment. The long-range spin-spin coupling constants between the ^1H and

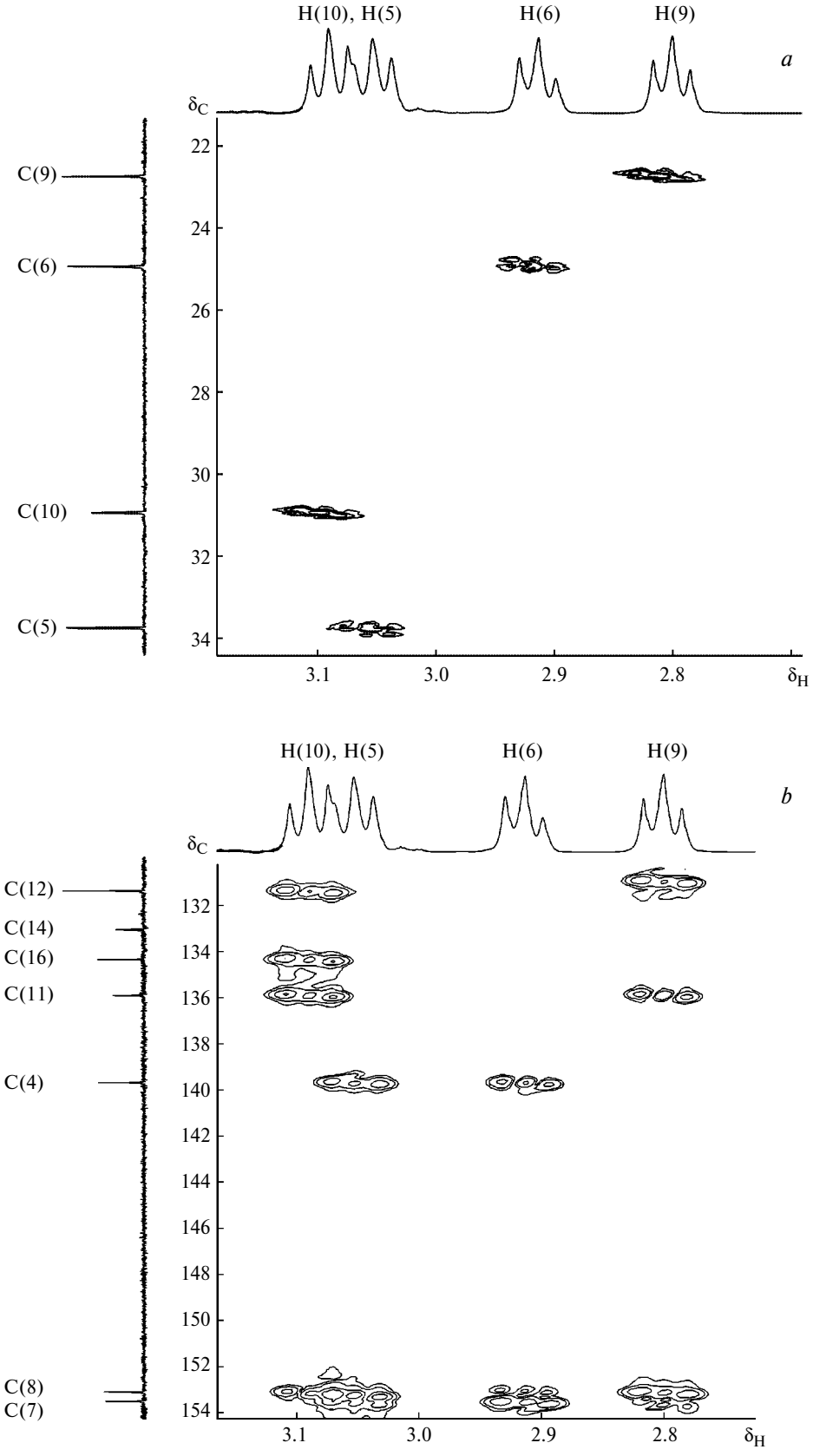
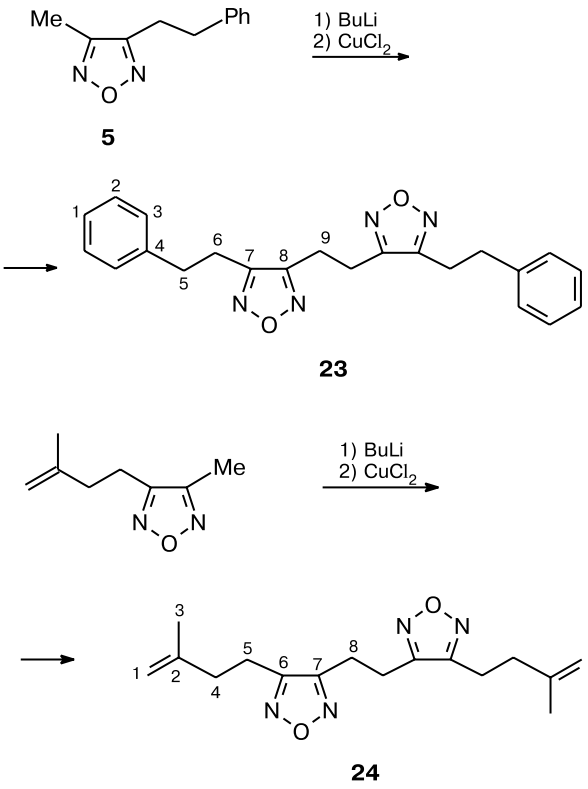


Fig. 1. NMR H,C correlation spectra (*a*) and HMBC spectra (*b*) of the CH_2 groups of compound **19**.

Scheme 6



^{13}C atoms in the HMBC experiment allowed us to complete the analysis of the spectra with the assignment of the signals for the quaternary carbon atoms. As an example, Figure 1 shows the patterns observed in the assignments of the signals in the ^{1}H and ^{13}C NMR spectra of compound **19**.

Since data on the stereochemistry of the difurazanylethylene fragment were lacking, it was of interest to elucidate this question. Calculations by the molecular mechanics with the MM2 force field revealed three low-energy conformations of the ethylene fragment in compound **6**, *viz.*, two equivalent skewed conformations, φ^1 and φ^5, and one transoid conformation φ^3 (Fig. 2).

Since the methylene protons in this symmetrical compound are chemically equivalent and are observed as a singlet in the ^{1}H NMR spectrum, the spin-spin coupling

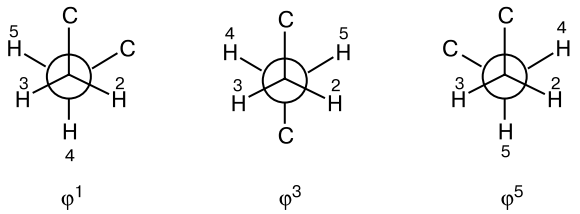


Fig. 2. Conformations of the difurazanylethylene fragment of compound **6**.

Table 1. Calculated and experimental spin-spin coupling constants (J/Hz) of the difurazanylethylene fragment of compound **6**

J	J_{calc}			J_{exp}
	φ^1	φ^3	φ^5	
$J_{2,4}$	1.85	14.82	1.81	8.54
$J_{2,5}$	14.80	2.50	5.25	6.44
$J_{3,4}$	5.25	2.50	14.80	6.44
$J_{3,5}$	1.81	14.82	1.85	8.54
$^{1}J_{C,H}$	—	—	—	132.6
$^{2}J_{C,H}$	—	—	—	5.2

constants $J_{H,H}$ were determined from the analysis of the ^{13}C satellites of this signal. When one of the methylene C atoms is the ^{13}C magnetic isotope, the degeneration is removed giving rise to the AA´BB´X spin system, where A and B are protons and X is the ^{13}C nucleus. The iterative calculations of the ^{1}H and ^{13}C NMR subspectra made it possible to determine all spin-spin coupling constants of the five-spin system. The conformationally dependent vicinal spin-spin coupling constants are given in Table 1. The spin-spin coupling constants for each rotamer were calculated according to the generalized Karplus equation.[13] Assuming that the observed spin-spin coupling constants are the sum of the corresponding spin-spin coupling constants of all conformations with consideration for the proportion of each conformer in the conformational equilibrium, the system of Eqs. (1)—(3) can be written. The solution of these equations gives the proportion of each structure in the dynamic equilibrium and the energy difference (ΔG_{298}) between these structures.

Let us denote the equilibrium fraction of the transoid fragment by A and the fractions of the skewed conformers by B and C. Then:

$$^{3}J_{2,4} = AJ_{2,4} + BJ_{2,4} + CJ_{2,4}, \quad (1)$$

$$^{3}J_{2,5} = AJ_{2,5} + BJ_{2,5} + CJ_{2,5}, \quad (2)$$

$$A + B + C = 1. \quad (3)$$

The solution of these equations gives:

$$A = 0.510,\ B = C = 0.245,$$
$$\Delta G_{298}(A/B) = RT\ln(A/B), \quad (4)$$
$$\Delta G_{298}(A/B) = 1.81 \text{ kJ mol}^{-1}.$$

Hence, the 1,2-di(furazanyl)ethylene fragment in compound **6** occurs predominantly in the transoid conformation.

In conclusion, it should be noted that the possibility of a successive increase in the length of the carbon chain of the substituent opens up an approach to the target synthesis of the previously inaccessible complex furazan derivatives starting from simple methylfurazans.

Experimental

The melting points were determined on a Kofler stage. The ^{1}H and ^{13}C NMR spectra were recorded at natural isotopic

abundance on a Bruker AM-300 spectrometer operating at 300.13 and 75.7 MHz, respectively, and on a Bruker DRX-500 spectrometer operating at 500.13 and 125.7 MHz, respectively. The chemical shifts are given in the δ scale relative 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 purities of the products were monitored by GLC and TLC (Silufol UV-254 plates, detection from UV absorption). Preparative chromatography was carried out with the use of SiO_2 (40—100 μm; Armenia). The GLC analysis was performed on a Biokhrom-1 chromatograph (flame ionization detector, capillary column, helium as the carrier gas). Commercially available dimethylglyoxime was used. 4-Chloromethyl-3-methylfurazan was prepared according to a procedure described earlier.[14]

3,4-Dimethylfurazan (1). Dimethylglyoxime **2** (300 g, 2.5 mol), ethylene glycol (350 mL), KOH (5.6 g, 0.1 mol), and Cs_2CO_3 (6.52 g, 0.02 mol) were placed in a 1-L three-neck flask equipped with a thermometer, a down condenser, and a powerful mechanical stirrer. The resulting viscous substance was rapidly heated to 110 °C with active stirring. Further heating was carried out slowly with a rate of ~1 °C min^{-1}, the dark solution being gradually formed. Once the reaction mixture was heated above 160 °C, distillation of both the product and water that was eliminated in the course of the reaction started and ~300 mL of the distillate were collected, after which the residue was cooled to 80—90 °C and dimethylglyoxime (232 g, 2 mol) was added. Following the above-mentioned recommendations, ~250 mL of the distillate were additionally distilled off, the residue was cooled to 80—90 °C, water (200 mL) was added, and the residue of the product was removed by azeotropic distillation with water. Dichloromethane (100 mL) was added to the combined distillates, and the mixture was washed with water (2×100 mL). The organic layer was dried over $MgSO_4$ and filtered through a layer of silica gel. The dichloromethane was removed on a rotary evaporator at 20 °C. The remaining oil was distilled under atmospheric pressure. Compound **1** was obtained in a yield of 419 g (95%), b.p. 156—158 °C (*cf.* lit. data[7]: b.p. 159—161 °C).

3-Methyl-4-pentylfurazan (4). A solution of compound **1** (0.34 g, 3.47 mmol) in anhydrous THF (150 mL) was placed in a 250-mL three-neck flask equipped with a thermometer and two dropping funnels with pressure-equalization arms and then a solution of BuLi (0.22 g, 3.47 mmol, 0.0255 g mL^{-1}) in pentane was added dropwise with stirring at −55 °C under a static atmosphere of argon. The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of Bu^nCl (0.34 g, 3.67 mmol) in anhydrous THF (30 mL) was rapidly added. The reaction mixture was stirred at −55 °C for 30 min. Then cooling was terminated. The reaction mixture was allowed to warm to ~20 °C, stirred for 1 h, neutralized with a saturated aqueous NH_4Cl solution (10 mL), and concentrated on a rotary evaporator to 20—30 mL. Water (100 mL) was added to the residue and the reaction mixture was extracted with CH_2Cl_2 (3×30 mL). The extract was dried over $MgSO_4$ and filtered through a layer of silica gel, after which the solvent was evaporated. Liquid product **4** was isolated by column chromatography (CH_2Cl_2—pentane, 1 : 1, as the eluent) in a yield of 0.5 g (94%), n_D^{20} 1.499, R_f 0.60 (CH_2Cl_2). Found (%): C, 62.34; H, 9.18; N, 18.14. $C_8H_{14}N_2O$ (154.21). Calculated (%): C, 62.31; H, 9.15; N, 18.17. MS, *m/z*: 154 [M^+], 122 [$M^+ - NO - H_2$], 107, 98, 84. ^1H NMR ($CDCl_3$), δ: 0.95 (t, 3 H, $C(8)H_3$, J = 6.8 Hz); 1.30—1.50 (m, 4 H, $C(6)H_2$, $C(7)H_2$); 1.68 (m, 2 H, $C(5)H_2$); 2.32 (s, 3 H, $C(1)H_3$); 2.54 (t, 2 H, $C(4)H_2$, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 154.2 (C=N); 153.6 (C=N); 31.1 (C(4)); 27.1 (C(5)); 23.0 (C(6)); 22.1 (C(7)); 14.0 (C(8)); 7.9 (C(1)).

3-Methyl-4-(2-phenylethyl)furazan (5). A solution of compound **1** (1.57 g, 0.016 mol) in anhydrous THF (150 mL) was placed in an apparatus used for the synthesis of compound **4** and then a solution of BuLi (1.023 g, 0.016 mol, 0.0472 g mL^{-1}) in pentane was added dropwise with stirring under an atmosphere of argon at −55 °C. The bright-yellow reaction mixture was stirred at −55 °C for 20 min and then a solution of BnCl (2.1 g, 0.0166 mol) in anhydrous THF (20 mL) was rapidly added. The reaction mixture was stirred at −55 °C for 30 min. Then cooling was terminated. The reaction mixture was allowed to warm to ~20 °C, stirred for 1 h, and neutralized with EtOH (3 mL). All volatile components were evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL), washed with water (2×30 mL), dried over $MgSO_4$, and filtered through a SiO_2 layer. The solvent was evaporated. The product was twice purified by preparative chromatography ($CHCl_3$—pentane 1 : 1, as the eluent,). Compound **5** was obtained as an oil in a yield of 2.4 g (80%), b.p. 115 °C (20 Torr), n_D^{20} 1.526. Found (%): C, 70.22; H, 6.47; N, 14.81. $C_{11}H_{12}N_2O$ (188.23). Calculated (%): C, 70.19; H, 6.43; N, 14.88. MS, *m/z*: 188 [M^+], 158 [$M^+ - NO$], 156 [$M^+ - NO - H_2$], 147, 141, 139, 121, 111, 98. IR, ν/cm^{-1}: 3064, 3032, 2936, 2864, 1584, 1496, 1452, 1400, 1216, 1184, 1080, 1036, 888. ^1H NMR ($CDCl_3$), δ: 2.14 (s, 3 H, Me); 2.97—3.12 (m, 4 H, CH_2CH_2); 7.15 (d, 2 H, *m*-Ph, J = 7.2 Hz); 7.22—7.38 (m, 3 H, *o,p*-Ph). ^{13}C NMR ($CDCl_3$), δ: 153.7 (C(3)); 150.6 (C(2)), 139.8 (C(6)); 128.6, 128.3, 128.6, 33.8 (C(5)), 25.1 (C(4)), 7.8 (C(1)).

1,2-Bis(4-methylfurazan-3-yl)ethane (6). ***A.*** The solid compound was prepared analogously to the synthesis of compound **5** starting from 4-chloromethyl-3-methylfurazan (2.2 g, 0.0166 mol) followed by evaporation of the solvent. The resulting compound was purified by recrystallization from CCl_4. Product **6** was obtained as small white crystals in a yield of 2.53 g (79%), m.p. 100—102 °C. Found (%): C, 49.47; H, 5.24; N, 28.78. $C_8H_{10}N_4O_2$ (194.19). Calculated (%): C, 49.48; H, 5.19; N, 28.85. MS, *m/z*: 194 [M^+], 164 [$M^+ - NO$], 153 [$M^+ - MeCN$], 137 [$M^+ - MeCNO$], 111 [$M^+ - MeCNO - CN$]. ^1H NMR ($CDCl_3$), δ: 2.32 (s, 6 H, Me); 3.12 (s, 4 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 153.7 and 150.4 (both C(3)); 20.8 (C(4)); 7.9 (C(1)). IR, ν/cm^{-1}: 2960, 2915, 1585, 1450, 1435, 1385, 1275, 1175, 1040, 980, 890.

B. Analogously to the procedure used for the synthesis of compound **4**, compound **1** (2.2 g, 0.022 mol) was lithiated with a solution of BuLi (1.44 g, 0.022 mol, 0.0511 g mL^{-1}) in pentane. The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of I_2 (2.85 g, 0.044 mol) in anhydrous THF (20 mL) was added. The reaction mixture was stirred at −55 °C for 30 min, heated to ~20 °C for 20 min, stirred for 1 h, and treated with a saturated aqueous NH_4Cl solution (10 mL). Then water (50 mL) was added and the reaction mixture was concentrated under reduced pressure to 70—80 mL.

The residue was extracted with CH_2Cl_2 (3×50 mL). The combined extracts were washed with a 10% sodium hyposulfite solution (30 mL) and water (3×30 mL). The extract was dried over $MgSO_4$ and filtered through a SiO_2 layer. Then the solvent was evaporated and the residue was recrystallized from CCl_4. Compound **6** was obtained in a yield of 1.83 g (84%), m.p. 99—100 °C.

C. Analogously to the procedure used for the synthesis of compound **4**, compound **1** (2.65 g, 0.027 mol) was lithiated with a solution of BuLi (1.728 g, 0.027 mol, 0.043 g mL^{-1}) in pentane. The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of 1,2-dibromoethane (2.538 g, 0.0135 mol) in anhydrous THF (20 mL) was rapidly added. The reaction mixture was stirred at −55 °C for 30 min and treated as described in the method ***A***. The product was obtained in a yield of 2.54 g (97%), m.p. 99—101 °C.

D. Analogously to the procedure used for the synthesis of compound **4**, compound **1** (2.74 g, 0.028 mol) was lithiated with a solution of BuLi (1.79 g, 0.028 mol, 0.025 g mL^{-1}) in pentane. The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of anhydrous $CuCl_2$ (3.78 g, 0.028 mol) in anhydrous THF (20 mL) was rapidly added. The reaction mixture was stirred at −55 °C for 30 min and treated as described in the method ***A***. The product was obtained in a yield of 2.6 g (96%), m.p. 101—102 °C.

1,2-Bis(4-methylfurazan-3-yl)-ethan-1-one (7). Analogously to the synthesis of compound **5**, a solution of BuLi (1.0 g, 0.0156 mol, 0.0224 g mL^{-1}) in pentane was added dropwise with stirring under argon at −55 °C to a solution of compound **1** (1.53 g, 0.0156 mol) in anhydrous THF (100 mL). The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of ethyl 3-methylfurazancarboxylate (2.43 g, 0.0156 mol) in anhydrous THF (10 mL) was rapidly added. The reaction mixture was stirred at −55 °C for 30 min. Then cooling was terminated. The reaction mixture was allowed to warm to ~20 °C, stirred for 1 h, acidified with 20% HCl to pH ~2, and stirred for 10 h. Then volatile components were concentrated under reduced pressure to 15—20 mL. Dichloromethane (80 mL) was added to the residue. The reaction mixture was washed with water (2×30 mL), dried over $MgSO_4$, and filtered through a SiO_2 layer. The solvent was evaporated. The product was purified by preparative chromatography ($CHCl_3$—pentane, 1 : 1, as the eluent). The oily product was obtained in a yield of 1.68 g (52%), n_D^{20} 1.491; R_f = 0.60. Found (%): C, 46.20; H, 3.89; N, 26.84. $C_8H_8N_4O_3$ (208.18). Calculated (%): C, 46.16; H, 3.87; N, 26.91. MS, *m/z*: 208 [M^+], 180, 151, 137, 125, 110, 97. IR, ν/cm^{-1}: 2970, 2940, 1740, 1470, 1400, 1335, 1225, 1050, 920, 900. ^{1}H NMR ($CDCl_3$), δ: 2.32 and 2.54 (both s, 3 H each, Me); 4.62 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 185.8 (C(5)); 150.5 (C(2)); 150.4 (C(6)); 149.7 (C(7)): 147.1 (C(3)); 34.6 (C(4)); 8.2, 7.3.

3-Methyl-4-(tetrahydrofuran-2-ylidenemethyl)furazan (8). Analogously to the synthesis of compound **5**, a solution of compound **1** (2.2 g, 0.0224 mol) in anhydrous THF (100 mL) was lithiated with a solution of BuLi (1.44 g, 0.0224 mol, 0.043 g mL^{-1}) in pentane. The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of γ-butyrolactone (2.0 g, 0.023 mol) in anhydrous THF (15 mL) was rapidly added. After 30 min, cooling was terminated. The reaction mixture was allowed to warm to ~20 °C, stirred for 1 h, treated with a saturated aqueous NH_4Cl solution (10 mL), and concentrated to 15—20 mL. Dichloromethane (100 mL) was added to the residue. The reaction mixture was washed with water (2×40 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was isolated by chromatography on a plate (SiO_2 40/100 μm, $CHCl_3$ as the eluent). Oily compound **8** was obtained in a yield of 1.56 g (42%), n_D^{20} 1.4915, R_f 0.50 ($CHCl_3$). Found (%): C, 57.85; H, 6.08; N, 16.81. $C_8H_{10}N_2O_2$ (166.18). Calculated (%): C, 57.82; H, 6.07; N, 16.86. MS, *m/z*: 166 [M^+], 165, 154, 141, 140, 130, 125, 98, 83. ^{1}H NMR ($CDCl_3$), δ: 2.15 (m, 2 H, C(7)H_2); 2.30 (s, 3 H, Me); 3.05 (t, 2 H, C(6)H_2, J = 6.6 Hz); 4.27 (t, 2 H, C(8)H_2, J = 6.8 Hz); 5.45 (br.s, 1 H, CH). ^{13}C NMR ($CDCl_3$), δ: 151.6, 149.9, 80.9 (C(4)); 71.9 (C(8)); 30.6 (C(6)); 24.3 (C(7)); 9.1 (C(1)).

1-(4-Methylfurazan-3-yl)acetone (9). Analogously to the synthesis of compound **5**, a solution of compound **1** (10 g, 0.102 mol) in anhydrous THF (150 mL) was placed in a 300-mL flask and lithiated with a solution of BuLi (6.53 g, 0.102 mol, 0.0224 g mL^{-1}) in pentane. The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a twofold excess of anhydrous MeCN dissolved in anhydrous THF (50 mL) was added dropwise. The reaction mixture was stirred for 30 min. Then cooling was terminated. The reaction mixture was allowed to warm to ~20 °C and stirred for 1 h. The solvent was evaporated under reduced pressure. The residue was suspended in concentrated HCl (100 mL) and heated at 50—60 °C for 32 h. The product was isolated by azeotropic distillation with a water vapor. The distillate was extracted with CH_2Cl_2 (3×50 mL), dried over $MgSO_4$, and filtered through a layer of silica gel. The solvent was removed under reduced pressure. The liquid product with a characteristic odor was obtained in a yield of 13.56 g (95%). ^{1}H NMR ($CDCl_3$), δ: 2.25 (s, 6 H, Me + Me); 3.55 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$), δ: 201.6 (C(5)); 151.4, 149.2, 37.2 (C(4)); 29.5 (C(6)); 7.8 (C(1)).

1-(4-Methylfurazan-3-yl)acetone oxime was synthesized analogously to compound **9** from compound **1** (2 g, 0.02 mol) (instead of acidification, the residue was dissolved in MeOH (30 mL) followed by treatment with a solution of $NH_2OH \cdot HCl$ (1.39 g, 0.02 mol) in MeOH (20 mL)). The resulting mixture was stirred for 3 h and filtered through a layer of silica gel. The filtrate was concentrated and the residue was recrystallized from Pr^iOH. The product was obtained in a yield of 2 g (64%), m.p. 87—88 °C (cf. lit. data[9]: m.p. 88 °C).

1-(2-Furyl)-2-(4-methylfurazan-3-yl)ethanol (10a). Analogously to the synthesis of compound **5**, a solution of dimethylfurazan **1** (2.14 g, 0.0218 mol) in anhydrous THF (100 mL) was lithiated with a solution of BuLi (1.4 g, 0.0218 mol, 0.064 g mL^{-1}) in pentane. The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of freshly distilled furfurol (2.1 g, 0.0218 mol) in anhydrous THF (30 mL) was rapidly added. The reaction mixture was stirred at −55 °C for 30 min. Then the mixture was allowed to spontaneously warm to ~20 °C, stirred for 1 h, neutralized with a saturated aqueous NH_4Cl solution (10 mL), and concentrated under reduced pressure to 25—30 mL. The residue was treated with ether (150 mL) and washed with water (3×30 mL). The extract was dried over $MgSO_4$ and filtered through a layer of a mixture of silica gel with $NaHSO_3$ (100 : 1). The solvent was removed under reduced pressure. The oily product with 95% purity was

obtained in a yield of 2.7 g (64%). Found (%): C, 55.75; H, 5.18; N, 14.31. $C_9H_{10}N_2O_3$ (194.19). Calculated (%): C, 55.67; H, 5.19; N, 14.43. MS, *m/z*: 194 [M^+], 176 [$M - H_2O]^+$, 164 [$M - NO]^+$, 146 [$M - NO - H_2O]^+$.

Attempts to purify the product on a chromatographic plate (SiO_2 40/100 μm, $CHCl_3$—hexane, 2 : 1, as the eluent) led to its substantial decomposition (apparently, the product was dehydrated followed by the transformation of the resulting vinyl intermediate) to form a mixture of compounds.

2-(4-Methylfurazan-3-yl)-1-(2-thienyl)ethanol (10b) was prepared analogously to compound **10a**. Thienylethanol **10b** was obtained as an amorphous cream-colored compound in 72% yield, m.p. 127—128 °C. Found (%): C, 51.47; H, 4.81; N, 13.31, S, 15.18. $C_9H_{10}N_2O_2S$ (210.25). Calculated (%): C, 51.41; H, 4.79; N, 13.32; S, 15.25. MS, *m/z*: 210 [M^+], 192 [$M - H_2O]^+$, 180 [$M - NO]^+$, 162 [$M - NO - H_2O]^+$. ^{1}H NMR ($CDCl_3$), δ: 2.27 (s, 3 H, Me); 3.20 (d, 2 H, CH_2, J = 6.6 Hz); 5.42 (t, 1 H, C(5)H, J = 6.6 Hz); 6.98 (m, 2 H, C(7)H, C(8)H); 7.29 (br.s, 1 H, C(9)H). ^{13}C NMR ($CDCl_3$), δ: 151.7, 151.4 (C(2), C(3)); 146.3 (C(6)); 126.9, 125.1, 124.4 (C(7)—C(9)); 68.8 (C(5)); 33.3 (C(4)); 6.0 (C(1)).

1-Hydroxyimino-1-(4-methylfurazan-3-yl)acetone (12). A solution of $NaNO_2$ (1.52 g, 0.022 mol) in water (5 mL) was slowly added dropwise with vigorous stirring to a solution of compound **9** (2.8 g, 0.02 mol) in 80% AcOH (5 mL) cooled to 0 °C. The reaction mixture was stirred at 0 °C for 1 h and then a solution of NaOH (2.5 g, 0.0625 mol) in water (20 mL) was added. The reaction mixture was stirred for 2 h and then kept in a refrigerator (+4 °C) for 16 h. The product was filtered off and recrystallized from benzene. Compound **12** was obtained as colorless crystals in a yield of 1.95 g (57%), m.p. 151—153 °C (*cf.* lit. data[9]: m.p. 153 °C).

1-Methyl-2-(4-methylfurazan-3-yl)glyoxime (13). A solution of NH_2OH in MeOH (20 mL) (was prepared from $NH_2OH \cdot HCl$ (1.39 g, 0.02 mol) and sodium (0.46 g, 0.02 mol), NaCl being filtered off) was added to a solution of compound **12** (1.69 g, 0.01 mol) in MeOH (15 mL). The resulting solution was stirred at 50—55 °C for 2 h, concentrated to 1/3 of the initial volume, cooled to 0 °C, and kept for 8 h. The product was filtered off and recrystallized from benzene. The crystalline product was obtained in a yield of 1.63 g (88%), m.p. 171.5—172.5 °C (*cf.* lit. data[9]: m.p. 172 °C). MS, *m/z*: 184 [M^+], 167 [$M^+ - OH$], 154 [$M^+ - NO$], 148, 136, 125, 109, 101, 95, 84. ^{1}H NMR (DMSO-d_6), δ: 2.18 (s, 3 H, C(1)H_3); 2.28 (s, 3 H, C(6)H_3); 11.9 (br.s, 1 H, =N—OH); 12.7 (br.s, 1 H, =N—OH). ^{13}C NMR (DMSO-d_6), δ: 152.8 (C(3)); 151.3 (C(5)); 148.3 (C(4)): 143.6 (C(2)); 9.7 (C(1)); 7.9 (C(6)).

3-Pentyl-4-(2-phenylethyl)furazan (15). Analogously to the synthesis of compound **5**, a solution of compound **5** (0.8 g, 4.25 mmol) in anhydrous THF (150 mL) was placed in a 250-mL flask and lithiated with a solution of BuLi (0.272 g, 4.25 mmol, 0.051 g mL^{-1}) in pentane. The bright-yellow reaction mixture was stirred at −55 °C for 20 min, after which a solution of Bu^nCl (0.4 g, 4.3 mmol) in anhydrous THF (10 mL) was rapidly added at the same temperature. The reaction mixture was stirred for 30 min. Then cooling was terminated. The reaction mixture was allowed to warm to ~20 °C, stirred for 1 h, and neutralized with a saturated aqueous NH_4Cl solution (10 mL). The solvent was removed under reduced pressure. The residue was treated with water (60 mL) and extracted with $CHCl_3$ (2×50 mL). The extract was dried over $CaCl_2$, the solvent was removed, and the residue was passed through a short column with SiO_2 ($CHCl_3$ as the eluent). Oily product **15** was obtained in a yield of 0.97 g (94%), n_D^{20} 1.499, R_f 0.50 (CH_2Cl_2). Found (%): C, 73.79; H, 8.30; N, 11.36. $C_{15}H_{20}N_2O$ (244.34). Calculated (%): C, 73.74; H, 8.25; N, 11.47. MS, *m/z*: 244 [M^+], 188, 187, 171, 130, 123, 109, 105, 84. ^{1}H NMR ($CDCl_3$), δ: 0.95 (t, 3 H, CH_3, J = 6.9 Hz); 1.30—1.50 (m, 4 H, C(11)H_2, C(12)H_2); 1.68 (m, 2 H, C(10)H_2); 2.54 (t, 2 H, C(9)H_2, J = 6.6 Hz); 3.00—3.20 (m, 4 H, C(5)H_2, C(6)H_2); 7.20—7.50 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 154.2 (C(8)); 153.5 (C(7)); 139.9 (C(4)); 128.5, 128.3 (C(2), C(3)); 126.4 (C(1)); 33.7 (C(5)); 31.1 (C(11)); 26.8 (C(10)); 25.2 (C(6)); 22.7 (C(9)); 22.1 (C(12)); 13.8 (C(13)). IR, ν/cm^{-1}: 3064, 3032, 2928, 2888, 2864, 1604, 1592, 1580, 1536, 1496, 1484, 1456, 1408, 1376, 1176, 1080, 1016, 888.

3,4-Bis(2-phenylethyl)furazan (16) was prepared analogously to compound **15** from BnCl (0.63 g, 5 mmol). Chromatographic separation (CH_2Cl_2—pentane, 2 : 1, as the eluent) afforded the product as a colorless oil in a yield of 0.88 g (74%), n_D^{20} 1.565. Found (%): C, 77.70; H, 6.55; N, 10.01. $C_{18}H_{18}N_2O$ (278.35). Calculated (%): C, 77.67; H, 6.52; N, 10.06. MS, *m/z*: 278 [M^+], 261, 248, 201, 187, 172, 157, 143, 130, 105, 91. ^{1}H NMR ($CDCl_3$), δ: 2.80 (t, 2 H, C(6)H_2, J = 7.4 Hz); 3.10 (t, 2 H, C(5)H_2, J = 7.4 Hz); 7.10—7.40 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 153.6 (C(7)); 139.6 (C(4)); 128.2, 128.5 (C(2), C(3)); 126.5 (C(1)); 33.7 (C(5)); 24.9 (C(6)). IR, ν/cm^{-1}: 3060, 3038, 2940, 2875, 1605, 1500, 1465, 1084, 1038, 890.

4-(2-Phenylethyl)-3-[2-(*p*-tolyl)ethyl]furazan (17) was prepared analogously to compound **16** in 87% yield. Oil, n_D^{20} 1.558. MS, *m/z*: 292 [M^+]. Found (%): C, 78.08; H, 6.91; N, 9.52. $C_{19}H_{20}N_2O$ (292.38). Calculated (%): C, 78.05; H, 6.89; N, 9.58. ^{1}H NMR ($CDCl_3$), δ: 2.40 (s, 3 H, Me); 2.85 (m, 4 H, C(6)H_2, C(9)H_2); 3.05 (m, 4 H, C(5)H_2, C(10)H_2); 7.05—7.50 (m, 9 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 153.6 (C(7), C(8)): 139.6 (C(4)); 136.7 (C(11)); 135.9 (C(14)); 129.1 (C(13)); 127.9—128.7 (C(2), C(3), C(12), C(13)); 126.4 (C(1)); 33.2, 33.5 (C(5), C(10)); 24.8, 25.0 (C(6), C(9)); 20.8 (C(15)). IR, ν/cm^{-1}: 3028, 2930, 2867, 1605, 1580, 1518, 1500, 1457, 1187, 1114, 1083, 1028, 895, 818.

4-[2-(2-Chlorophenyl)ethyl]-3-(2-phenylethyl)furazan (18) was prepared analogously to compound **16** in 76% yield. Oil, n_D^{20} 1.569. Found (%): C, 69.18; H, 5.51; N, 8.88. $C_{18}H_{17}ClN_2O$ (312.80). Calculated (%): C, 69.12; H, 5.48; N, 8.96. MS, *m/z*: 313, 311 [M^+], 270, 187, 130, 125, 105, 91. ^{1}H NMR ($CDCl_3$), δ: 2.80—3.30 (m, 8 H, CH_2); 7.00—7.50 (m, 9 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 153.6, 153.4 (C(7), C(8)); 139.7 (C(4)); 137.2 (C(11)); 133.6 (C(16)), 130.6, 129.5, 128.5, 128.4, 128.2, 126.9, 126.4 (Ar); 33.7, 31.8 (C(5), C(10)); 24.9, 22.9 (C(6), C(9)). IR, ν/cm^{-1}: 3066, 3037, 2940, 2400, 1605, 1574, 1495, 1478, 1450, 1170, 1128, 1083, 1060, 900, 765, 710.

3-[2-(2,4-Dichlorophenyl)ethyl]-4-(2-phenylethyl)furazan (19) was prepared analogously to compound **16** in 24% yield. Oil, n_D^{20} 1.577. Found (%): C, 62.31; H, 4.61; N, 8.06. $C_{18}H_{16}Cl_2N_2O$ (347.24). Calculated (%): C, 62.26; H, 4.64; N, 8.07. MS, *m/z*: 347, 345 [M^+], 331, 329, 313, 311, 293, 280, 266, 187, 172, 159, 130, 115, 105, 91, 77. ^{1}H NMR ($CDCl_3$), δ: 2.80 (t, 2 H, C(9)H_2, J = 7.2 Hz); 2.91 (t, 2 H, C(6)H_2, J = 7.2 Hz); 3.06 (t, 2 H, C(10)H_2, J = 7.3 Hz); 3.09 (t, 2 H, C(5)H_2, J = 7.3 Hz); 7.09 (d, 1 H, H(12), J = 7.2 Hz); 7.17 (m,

3 H, H(3), H(13)); 7.25 (t, 1 H, H(1), J = 7.6 Hz); 7.30 (t, 2 H, H(2), J = 7.1 Hz); 7.39 (d, 1 H, H(15), J = 2.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 153.4 (C(7)); 153.0 (C(8)); 139.6 (C(4)); 135.8 (C(11)); 134.2 (C(16)); 133.0 (C(14)); 131.4 (C(12)); 129.3 (C(15)); 128.5 (C(2)); 128.3 (C(3)); 127.2 (C(13)); 126.5 (C(1)); 33.7 (C(5)); 30.9 (C(10)); 24.9 (C(6)); 22.6 (C(9)). IR, ν/cm^{-1}: 3060, 3030, 2938, 2867, 1590, 1560, 1500, 1478, 1458, 1390, 1108, 1084, 1057, 1030, 847, 837, 815, 780, 705.

3-[2-(1-Naphthyl)ethyl]-4-(2-phenylethyl)furazan (20) was prepared analogously to compound **16** in 39% yield as colorless crystals, m.p. 53—54 °C (from hexane). Found (%): C, 80.52; H, 6.20; N, 8.47. $C_{22}H_{20}N_2O$ (328.41). Calculated (%): C, 80.46; H, 6.14; N, 8.53. MS, m/z: 328 [M$^+$], 311, 294, 282, 270, 254, 237, 221, 207, 180, 165, 153, 141, 115, 105, 91, 77. ^{1}H NMR ($CDCl_3$), δ: 2.70 (t, 2 H, C(6)H_2, J = 5.9 Hz); 3.00 (m, 4 H, C(5)H_2, C(9)H_2); 3.55 (t, 2 H, C(10)H_2, J = 6.2 Hz); 7.10 (d, 2 H, H(3), J = 5.6 Hz); 7.35 (m, 4 H, H(1), H(2), H(14)); 7.50 (t, 1 H, H(13), J = 5.2 Hz); 7.65 (m, 2 H, H(17), H(18)); 7.87 (d, 1 H, H(12), J = 4.4 Hz); 7.95 (d, 1 H, H(16), J = 5.4 Hz); 8.10 (d, 1 H, H(19), J = 5.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 153.8 (C(8)); 153.6 (C(7)); 139.6 (C(4)); 135.7 (C(11)); 133.7 (C(15)); 131.2 (C(20)); 128.8 (C(16)); 128.4 (C(2)); 128.1 (C(3)); 127.3 (C(12)); 126.3 (C(14)); 126.2 (C(1)); 126.1 (C(18)); 125.6 (C(17)); 125.4 (C(13)); 123.0 (C(19)); 33.5 (C(5)); 30.9 (C(10)); 24.7 (C(6)); 24.0 (C(9)). IR, ν/cm^{-1}: 3030, 2940, 1600, 1515, 1495, 1455, 1445, 1400, 1170, 1020, 890, 810, 795, 787, 765, 710.

3-[2-Hydroxy-2-(2-furyl)ethyl]-4-(2-phenylethyl)furazan (21) was prepared analogously to compound **10** from compound **5** as an oil in a yield of 2.0 g (35%), n_D^{20} 1.57, R_f 0.50 (CH_2Cl_2). Found (%): C, 67.66; H, 5.69; N, 9.79. $C_{16}H_{16}N_2O_3$ (284.31). Calculated (%): C, 67.59; H, 5.67; N, 9.85. MS, m/z: 284 [M]$^+$, 266 [M – H_2O]$^+$, 254 [M – NO]$^+$, 236 [M – NO – H_2O]$^+$. ^{1}H NMR (DMSO-d_6), δ: 2.90—3.00 (m, 4 H, C(5)H_2, C(6)H_2); 3.05 (d, 2 H, C(9)H_2, J = 6.6 Hz); 4.70 (br.s, 1 H, OH); 4.95 (t, 1 H, C(10)H, J = 6.6 Hz); 6.20—6.30 (m, 2 H, C(12)H, C(13)H); 7.10—7.30 (m, 5 H, Ph); 7.40 (d, 1 H, C(14)H, J = 2.4 Hz). ^{13}C NMR (DMSO-d_6), δ: 157.0 (C(7)); 156.2 (C(8)); 153.3 (C(11)); 143.6 (C(14)); 141.9 (C(4)); 130.4, 129.8 (C(2), C(3)); 127.7 (C(1)); 111.6 (C(13)); 107.7 (C(12)); 67.2 (C(10)); 35.0 (C(5)); 30.7 (C(9)); 28.2 (C(6)). IR, ν/cm^{-1}: 3432, 3032, 2936, 2864, 2528, 1604, 1496, 1456, 1408, 1220, 1176, 1148, 1012, 960.

1-(4-Methylfurazan-3-yl)-2-[4-(2-phenylethyl)furazan-3-yl]ethane (22). ***A.*** Analogously to the synthesis of compound **5**, a solution of compound **6** (0.65 g, 3.35 mmol) in anhydrous THF (50 mL) was placed in a 250-mL flask and lithiated with a solution of BuLi (0.214 g, 3.35 mmol, 0.042 g mL^{-1}) in pentane. The bright-red reaction mixture was stirred at –55 °C for 20 min, after which a solution of BnCl (0.42 g, 3.35 mmol) in anhydrous THF (5 mL) was rapidly added. The reaction mixture was stirred at –55 °C for 30 min, allowed to spontaneously warm to ~20 °C, and stirred for 10 h. The solvent was evaporated and the residue was diluted with CH_2Cl_2 (100 mL). The resulting solution was washed with 10% HCl and water. The organic layer was dried over $MgSO_4$, the solvent was evaporated, and the residue was fractionated on a chromatographic plate (SiO_2, 40/100 μm, $CHCl_3$—pentane, 1 : 1, as the eluent). The oily product was isolated in a yield of 0.63 g (68%), n_D^{20} 1.530. Found (%): C, 63.36; H, 5.73; N, 19.67. $C_{15}H_{16}N_4O_2$ (284.32). Calculated (%): C, 63.37; H, 5.67; N, 19.71. MS, m/z: 284 [M]$^+$, 254 [M – NO]$^+$, 224 [M – 2 NO]$^+$, 188, 187, 130, 117, 103, 98, 91. IR, ν/cm^{-1}: 3065, 3037, 2940, 1605, 1580, 1500, 1450, 1385, 1182, 1085, 1046, 965, 900.

B. Compound **22** was prepared analogously by lithiation of compound **5** followed by treatment with 4-(chloromethyl)-3-methylfurazan. The product was obtained in 66% yield.

1,2-Bis[4-(2-phenylethyl)furazan-3-yl]ethane (23). A solution of compound **5** (2.82 g, 0.015 mol) in anhydrous THF (150 mL) was placed in a 250-mL three-neck flask equipped with a thermometer and two dropping funnels with pressure-equalization arms and then a solution of BuLi (0.96 g, 0.015 mol, 0.024 g mL^{-1}) in pentane was added dropwise with stirring at –55 °C under a static atmosphere of argon. After 20 min, anhydrous CuCl (2.025 g, 0.016 mol) was rapidly added and the reaction mixture was stirred at –55 °C for 30 min. Then cooling was terminated. The reaction mixture was allowed to warm to 20 °C and stirred for 10 h. The solvent was evaporated and the residue was diluted with CH_2Cl_2 (150 mL). The resulting solution was washed with 10% HCl and water. The organic solution was dried over $MgSO_4$ and filtered through a layer of silica gel, after which the solvent was evaporated. The product was recrystallized from $CHCl_3$. Colorless crystals of the product were obtained in a yield of 1.2 g (43%), m.p. 75—76 °C. Found (%): C, 70.61; H, 6.04; N, 14.87. $C_{22}H_{22}N_4O_2$ (374.44). Calculated (%): C, 70.57; H, 5.92; N, 14.96. MS, m/z: 374 [M]$^+$, 344 [M – NO]$^+$, 297, 268, 226, 212, 191, 130, 105, 91, 77. IR, ν/cm^{-1}: 3075, 3037, 2950, 2938, 1605, 1585, 1496, 1455, 1445, 1295, 1170, 1080, 1040, 1030, 1020, 890. ^{1}H NMR ($CDCl_3$), δ: 2.85 (s, 4 H, C(9)H_2); 3.00—3.20 (m, 8 H, C(5)H_2, C(6)H_2); 7.15—7.40 (m, 10 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 153.4 (C(7)); 152.8 (C(8)); 139.6 (C(4)); 128.5 (C(2)); 128.3 (C(3)); 126.5 (C(1)); 33.7 (C(5)); 25.0 (C(6)); 20.6 (C(9)).

1,2-Bis[4-(3-methylbut-3-en-1-yl)furazan-3-yl]ethane (24) was prepared analogously to compound **23** from 3-methyl-4-(3-methylbut-3-en-1-yl)furazan.[1] The yield was 83%. Colorless crystalline compound, m.p. 74—75 °C. Found (%): C, 63.61; H, 7.41; N, 18.48. $C_{16}H_{22}N_4O_2$ (302.38). Calculated (%): C, 63.56; H, 7.33; N, 18.53. MS, m/z: 301 [M – H]$^+$, 285 [M – H – CH_4]$^+$, 272 [M – NO]$^+$, 240, 229, 190, 174. IR, ν/cm^{-1}: 3084, 2995, 2980, 2950, 2920, 2900, 1650, 1590, 1500, 1450, 1377, 1322, 1220, 1250, 1173, 1018, 894, 888. ^{1}H NMR ($CDCl_3$), δ: 1.80 (s, 3 H, CH_3); 2.40 (br.t, 2 H, C(4)H_2, J = 7.6—8.0 Hz); 2.90 (t, 2 H, C(5)H_2, J = 7.6 Hz); 3.20 (s, 2 H, C(8)H_2); 4.70—4.80 (d, 2 H, CH, J = 16.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 153.7 (C(6)); 152.7 (C(7)); 143.2 (C(2)); 111.3 (C(1)); 34.9 (C(4)); 22.2 (C(3)); 21.4 (C(5)); 21.0 (C(8)).

References

1. A. Yu. Sizov and A. B. Sheremetev, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 365 [*Russ. Chem. Bull.*, 1992, **41**, 281 (Engl. Transl.)].
2. A. B. Sheremetev, E. A. Ivanova, and D. E. Dmitriev, *Tez. dokl. konf. "Organicheskii sintez i kombinatornaya khimiya"* [*Abstrs. of Papers, Conf. "Organic Synthesis and Combinatorial Chemistry] (March 4—7, 1999, Suzdal')*, Moscow, 1999, P-64 (in Russian).
3. B. Iddon, *Heterocycles*, 1994, **37**, 1263.

4. B. Iddon, *Heterocycles*, 1995, **38**, 263.
5. A. B. Sheremetev, N. N. Makhova, and W. Friedrichsen, *Adv. Heterocycl. Chem.*, Acad. Press, 2001, **78**, 65.
6. A. Yu. Sizov, Ph. D. (Chem.) Thesis, N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, Moscow, 1992 (in Russian).
7. G. Ohta, T. Takegoshi, K. Ueno, and M. Shimizu, *Chem. Pharm. Bull.,* 1965, **13**, 1445.
8. D. Dielimoriba, S. E. Berezina, L. A. Remizova, and I. N. Domnin, *Vestn. SPbGU, Ser. 4* [*St. Petersburg State Univ. Bull.*, *Ser. 4*], 1999, **4**, 98 (in Russian).
9. T. Asello and S. Cusmano, *Gazz. Chim. Ital.,* 1939, **69**, 391.
10. Yu. A. Strelenko, A. B. Sheremetev, and L. I. Khmel´nitskii, *Khim. Geterotsikl. Soedin.*, 1992, 1101 [*Chem. Heterocycl. Compd.,* 1992, 927 (Engl. Transl.)].
11. 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.)].
12. 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].
13. C. A. G. Haasnoot, F. A. A. M. De Leeuw, and C. Altona, *Tetrahedron*, 1980, **36**, 2783.
14. I. V. Vigalok, A. V. Ostrovskaya, N. V. Svetlakov, T. V. Zykova, and N. A. Zhikhareva, *Khim. Geterotsikl. Soedin.*, 1977, 30 [*Chem. Heterocycl. Compd.,* 1977, 30 (Engl. Transl.)].

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