Synthesis and reactivity of furazanyl- and furoxanyldiazonium salts

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Diazotization of aminofurazans (**1**) and 4-aminofuroxans (**2**) with nitrosylsulfuric acid in a mixture of conc. H_2SO_4 and H_3PO_4 has been studied and offered as a general method for preparing furazanyl- (**3**) and furoxanyldiazonium (**4**) salts. It has been shown that reactions with the retention of the N—N-group (azo coupling, formation of triazenes and azides) are typical of salts **3** and **4**, while elimination of the N_2 molecule (Sandmeyer reaction, hydrolysis, reduction) is not typical.

Key words: diazotization, furazans, furoxans, amines, triazenes, azides, azo compounds, diazonium salts.

Aromatic and heteroaromatic diazonium salts are extensively used in organic synthesis. As a rule, two types of their transformations are considered: reactions with the retention of the N—N moiety (azo coupling, formation of triazenes and azides) and those with liberation of the N_2 molecule (Sandmeyer reaction, hydrolysis, and reduction). The capacity of amino groups to diazotize is known to depend considerably on their basicity, therefore, the preferable and often the only possible condition for the diazotization of weakly basic amines is the use of strongly acidic media.[1]

Among the weakly basic amines are aminofurazans (**1**) and aminofuroxans (**2**). Several examples of diazotization of **1** in a weakly acidic medium (50 % H_2SO_4 or glacial AcOH) have been reported. The resulting diazonium salts were transformed to the corresponding triazenes[2—4] or the products of azo coupling with 2-naphthol.[3] Diazotization of aminofurazans **1**, especially those containing electron-withdrawing substituents, is complicated under these conditions by the opening of the ring and the formation of derivatives of α-oximinonitriles[2,4—5] or the products of their subsequent transformations.[6]

Previously, the diazotization of aminofurazans **1** in strongly acidic media has been carried out only for diaminofurazan and 3-amino-4-(phenylazo)furazan under the action of nitrosylsulfuric acid in concentrated H_2SO_4. The resulting diazonium salts were converted by the reaction with NaN_3 into the corresponding azidofurazans in good yields.[7]

There are no reported data on the diazotization of aminofuroxans **2** and on the reactivity of furoxanyldiazonium salts. In the present work we have developed a general method for the synthesis of furazanyl- (**3**) and furoxanyldiazonium salts (**4**) by the diazotization of aminofurazans **1** or 4-aminofuroxans **2** and have studied the reactions of diazonium salts.

On the basis of previously obtained data[7] and the low basicity of compounds **1** and **2** (the basicity of compound **1** is 7—9 orders of magnitude lower than that of aniline)[8] we have suggested that for their diazotization strongly acidic media are preferable. The most commonly used variants of these media are conc. H_2SO_4,[9] a mixture of conc. H_2SO_4 with H_3PO_4,[10] or a mixture of conc. H_2SO_4 with glacial AcOH.[11]

Previously diazotization of compound **1** was carried out in conc. H_2SO_4. However, when we attempted diazotization of 3-amino-4-nitrofurazan **1a** with nitrosylsulfuric acid under the reported[7] conditions followed by treatment of the reaction mixture with NaN_3 we isolated the starting amine **1a** in a nearly quantitative yield. (The data on the explosiveness of the reaction mixtures in the diazotization of amines in this medium should be taken into account.[12]) In our case, the mixture of conc. H_2SO_4 with glacial AcOH proved to be inconvenient due to its relatively high freezing point which does not allow the reactions to be performed with sufficient cooling.

Nitrosylsulfuric acid in a mixture of conc. H_2SO_4 and H_3PO_4 proved to be the most suitable for diazotization of compounds **1** and **2**. Under these conditions we managed to convert all of the amines **1** and **2** studied into the corresponding diazonium sulfates **3** and **4** (Scheme 1). An attempt to introduce 3-aminofuroxan derivatives into the diazotization reaction proved to be unsuccessful. 3-Amino-4-phenylfuroxan, for example, was completely decomposed under these conditions.

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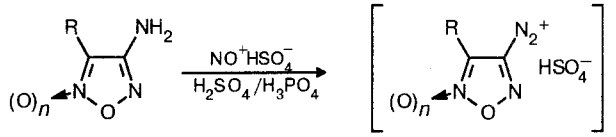
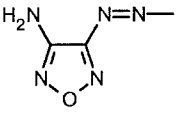
Scheme 1

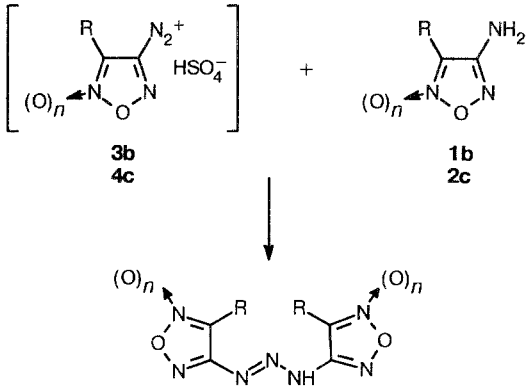


1, 2 **3, 4**

1a, **3a**: R = NO_2, n = 0
1b, **3b**: R = Me, n = 0
1c, **3c**: R = CO_2Me, n = 0
1d, **3d**: R = NH_2, n = 0
1e, **3e**: R = N_3, n = 0
2a, **4a**: R = Me, n = 1
2b, **4b**: R = Ph, n = 1
2c, **4c**: R = CON_3, n = 1

1f, **3f**: R =  , n = 0

Scheme 3

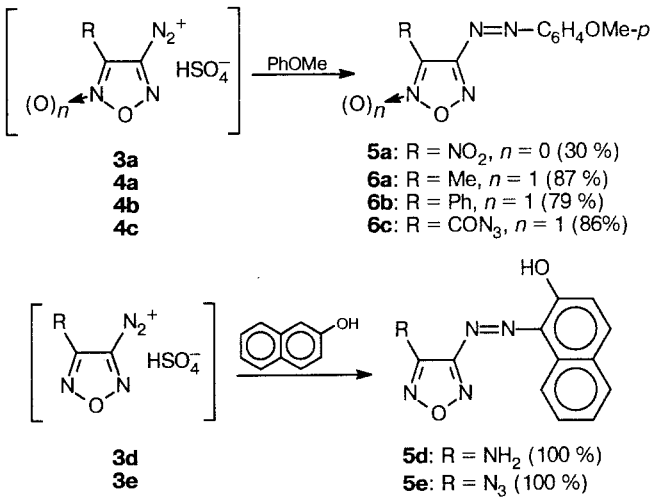


3b
4c

1b
2c

7b: R = Me, n = 0 (100 %)
8c: R = CON_3, n = 1 (34 %)

Scheme 2



3a
4a
4b
4c

5a: R = NO_2, n = 0 (30 %)
6a: R = Me, n = 1 (87 %)
6b: R = Ph, n = 1 (79 %)
6c: R = CON_3, n = 1 (86%)

3d
3e

5d: R = NH_2 (100 %)
5e: R = N_3 (100 %)

Individual salts **3** and **4** are unstable. On attempted isolation by precipitation with ether from the reaction mixture they decompose (*cf.* Ref. 13). The structure of compounds **3** and **4** has been confirmed by the preparation of their derivatives. For this purpose we studied two types of possible transformations of **3** and **4**: reactions with the retention of the N—N group and those with evolution of the N_2 molecule.

Of the former-type reactions we studied the azo coupling with 2-naphthol and anisole, the interaction with the starting amine, and the reaction with NaN_3 to give the corresponding azides. Azo coupling with anisole was carried out using diazonium salts **3a**, **4a**—**4c** as examples, that with 2-naphthol was carried out for salts **3d** and **3e**. The corresponding azo derivatives (**5**) and (**6**) were obtained, as a rule, in high yields (Scheme 2).

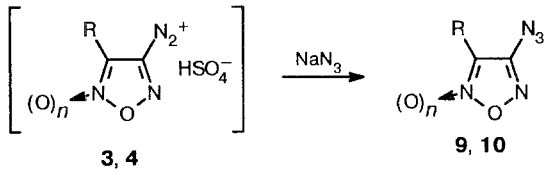
Triazene derivatives (**7b**) and (**8c**) were prepared (Scheme 3) by the reaction of diazonium salts **3b** and **4c** with an excess of the starting amine **1b** or **2c** in water.

The most extensively studied reactions of the latter type are those of compounds **3** and **4** with NaN_3 to prepare azides of the furazan and furoxan series. It has been found that upon treating a reaction mixture containing **3** or **4** with an aqueous solution of NaN_3 (in the case of **4** the reaction mixture was preliminarily diluted with AcOH) or upon pouring the reaction mixture in an aqueous solution of NaN_3 azides **9** and **10** are formed in high yields (Scheme 4). Azidofuroxans were prepared by this method for the first time.

Previously only one example of the preparation of azide **10** has been reported: 4-azido-3-phenylfuroxan **10b** was synthesized by the nucleophilic substitution of the nitro group in 4-nitro-3-phenylfuroxan under the action of NaN_3.

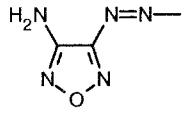
An investigation of the reactions of aryldiazonium salts containing ^{15}N atoms with NaN_3 has shown[15] that they occur by two competing pathways: one of them involves the intermediate formation of linear «pentazene» (~70 %, path **A**), and the other involves cyclic pentazole (~30 %, path **B**) (Scheme 5). Both types of intermediates are unstable and eliminate N_2 to give aryl azides. In the case of the decomposition of the linear intermedi-

Scheme 4



3, 4 **9, 10**

3b, **9b**: R = Me, n = 0 (60 %)
3c, **9c**: R = CO_2Me, n = 0 (89 %)
3d, **9d**: R = NH_2, n = 0 (60 %)

3f, **9f**: R =  , n = 0 (52 %)

4a, **10a**: R = Me, n = 1 (51 %)
4b, **10b**: R = Ph, n = 1 (66 %)
4c, **10c**: R = CON_3, n = 1 (30 %)

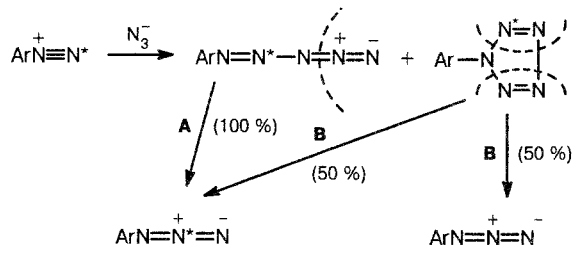
ate, the labeled nitrogen remains entirely in the azide molecule, whereas degradation of the cyclic compound follows two equally probable routes which halves the content of labeled nitrogen in the azide in comparison with that in the starting diazonium salt (Scheme 5).

The experiments on diazotization of furazanylamines **1b** and **1d** with nitrosylsulfuric acid prepared from $Na^{15}NO_2$ followed by the reaction of compounds **3b** and **3d** with NaN_3 and by a mass spectrometric study of the resulting **9b** and **9d** have shown that in the case of furazanyldiazonium salts, path **A** accounts for 15—30 % of the process, while most of the azide is formed according to path **B**.

Using compounds **3b** and **3d** as examples we have demonstrated for the first time the possibility of synthesizing azidofurazans **9** by the reaction of furazanyldiazonium salts **3** with urea, 1,3-dimethylurea, and formamide. The mechanism of this reaction is apparently identical to that of the reactions of aryldiazonium salts with these reactants.[16]

There are practically no data in the literature on the reactions of diazonium salts **3** and **4** involving substitution of a halogen, nitro, or cyano group for the diazonium group or on their hydrolysis or reduction. The only example of a reaction of this type is substitution of chlorine for the diazonium group (in 20 % yield) in the diazotization of 4-amino-3-(3-pyridyl)furazan[17] in the presence of CuCl. Our attempts to carry out these reactions with salts **3c**, **3d**, **4a**, and **4b** resulted in their decomposition, and no individual products could be isolated. Compound **3b** proved to be the sole exception: its reaction with $NaNO_2$ in the presence of $CuSO_4$ gave the substitution product, 4-methyl-3-nitrofurazan (**11**),

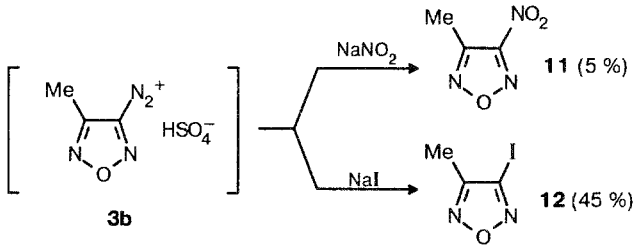
Scheme 5



in a low yield, and the reaction with NaI afforded 3-iodo-4-methylfurazan (**12**) (Scheme 6).

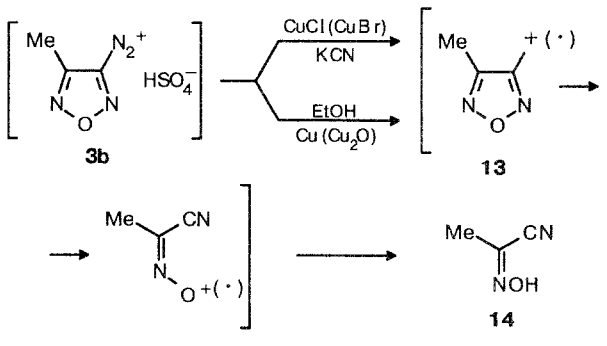
One limitation on the tendency of compounds **3** and **4** to participate in such reactions is obviously due to the instability of the type (**13**) furazanyl and furoxanyl intermediates formed on the abstraction of N_2 owing to the possibility of the opening of the heterocycle. Actually, in the reactions of compound **3b** with copper(I) salts or KCN as well as in the attempts to reduce **3b** with copper in ethanol the product of the ring opening, 2-oximinopropionitrile (**14**), was isolated (Scheme 7).

Scheme 6



3b

Scheme 7



Experimental

IR spectra were obtained on a UR-20 spectrometer for KBr pellets, UV spectra were recorded on a Specord UV VIS spectrophotometer in ethanol; ^1H and ^{13}C NMR spectra were run on a Bruker AM-300 instrument (300 and 75.5 MHz, respectively). Mass spectra were measured on a Varian MAT CH-6 instrument. The TLC analysis was carried out using Silufol UV-254 plates and preparative column chromatography was performed on L 40/100 μ silica gel.

1. Preparation of diazonium salts 3 and 4 (general procedure)

10 mmol of amine **1** or **2** was added with intensive stirring to nitrosylsulfuric acid prepared by dissolving 0.7 g (10 mmol) of $NaNO_2$ in 8 mL of conc. H_2SO_4, according to the known procedure,[18] then 8 mL of conc. H_3PO_4 (d = 1.70 g cm^{-3}) was added dropwise with caution. The reaction mixture was stirred for 1 h at 0—2 °C and used for reactions.

2. Coupling of salts 3 and 4 with 2-naphthol

At 0—2 °C a solution of 1.44 g (10 mmol) of 2-naphthol in 7 mL of pyridine was slowly added dropwise to a solution of **3d** or **3e** prepared by the standard procedure. The reaction mixture was stirred for 1 h at 20 °C and poured into 100 mL of cold water. The precipitate was filtered off, washed with water, and dried in air. The yield was quantitative.

4-Amino-3-(2-hydroxy-1-naphthylazo)furazan (5d), m.p. 221—222 °C (toluene). IR, ν/cm^{-1}: 3500, 3365, 1685, 1580, 1510, 1450, 1390, 1315, 1265, 1220, 1160, 1145, 1110, 1020, 960, 880, 850, 765. Found (%): C, 56.70; H, 3.66; N, 27.75. $C_{12}H_9N_5O_2$. Calculated (%): C, 56.47; H, 3.53; N, 27.45.

4-Azido-3-(2-hydroxy-1-naphthylazo)furazan (5e), m.p. 197—198° C (toluene). IR, ν/cm^{-1}: 3300, 2160, 1635, 1600, 1555, 1510, 1450, 1440, 1380, 1360, 1340, 1290, 1260, 1220, 1195, 1150, 1100, 1060, 985, 850, 820, 770. Found (%): C, 51.47; H, 2.24; N, 35.04. $C_{12}H_7N_7O_2$. Calculated (%): C, 51.25; H, 2.49; N, 34.88.

3. Coupling of salts 3 and 4 with anisole

At 0—2 °C a solution of 1.08 g (10 mmol) of anisole in 7 mL of pyridine was slowly added dropwise to a solution of salt **3a** (**4a**, **4b**, **4c**) prepared by the standard procedure. The reaction mixture was stirred for 1.5 h at 20 °C and poured into 100 mL of cold water (in the case of **3a** the reaction mixture was extracted with 3×25 mL of $AcOC_2H_5$, washed with 2×25 mL of water, dried with $MgSO_4$, and concentrated, and the residue was recrystallized from isopropanol). The precipitate was filtered off, washed with water, and reprecipitated with water from acetone.

3-(4-Methoxyphenylazo)-4-nitrofurazan (5a). Yield 0.74 g (30 %), b.p. 101—102 °C, R_f ($CHCl_3$:CCl_4 = 1:1) 0.49. IR, ν/cm^{-1}: 2940, 2845, 1600, 1560, 1500, 1460, 1400, 1350, 1320, 1300, 1250, 1185, 1140, 1010, 895, 840, 800, 700. ^1H NMR (CD_3NO_2), δ: 3.78 (s, OCH_3), 7.42 (q, 4H-arom.). Mass spectrum, *m/z* (rel. intensity, %): 249[M^+](38), 135(43), 121(71), 107(100), 76(70). Found (%): C, 42.90; H, 2.86; N, 27.89. $C_9H_7N_5O_4$. Calculated (%): C, 43.39; H, 2.83; N, 28.01.

4-(4-Methoxyphenylazo)-3-methylfuroxan (6a). Yield 1.96 g (87 %), b.p. 142—143 °C, R_f ($CHCl_3$) 0.43. IR, ν/cm^{-1}: 3050, 3010, 2920, 2890, 1600, 1560, 1480, 1400, 1310, 1290, 1240, 1165, 1130, 1020, 1010, 830, 800. UV, λ_{max}/nm: 236, 254, 278, 370. ^1H NMR (acetone-d_6), δ: 2.34 (s, CH_3), 3.90 (s, OCH_3), 7.90 (q, 4H-arom.). Mass spectrum, *m/z* (rel. intensity, %): 234[M^+](4), 218(3), 174(80), 135(100), 121(40), 107(83). Found (%): C, 52.30; H, 4.32; N, 23.82. $C_{10}H_{10}N_4O_3$. Calculated (%): C, 51.25; H, 4.32; N, 23.91.

4-(4-Methoxyphenylazo)-3-phenylfuroxan (6b). Yield 2.34 g (79 %), b.p. 150—151 °C, R_f ($CHCl_3$) 0.65. IR, ν/cm^{-1}: 3430, 2645, 2600, 1590, 1500, 1475, 1430, 1385, 1300, 1255, 1210, 1160, 1150, 1120, 1095, 1010, 980, 840, 800. UV, λ_{max}/nm: 249, 365. ^1H NMR (DMSO-d_6), δ: 3.81 (s, OCH_3), 7.52 (q, 4H-arom.). Mass spectrum, *m/z* (rel. intensity, %): 296[M^+](2), 236(31), 135(100), 121(22), 107(78), 77(79), 76(22). Found (%): C, 61.01; H, 4.10, N, 18.85. $C_{15}H_{12}N_4O_3$. Calculated (%): C, 60.92; H, 4.06; N, 18.92.

3-Azidocarbonyl-4-(4-methoxyphenylazo)furoxan (6c). Yield 2.50 g (86 %), b.p. 85—87 °C, R_f ($CHCl_3$:CCl_4, 3:1) 0.32. IR, ν/cm^{-1}: 3100, 3080, 3000, 2840, 2350, 2185, 2130, 1700, 1605, 1580, 1485, 1430, 1390, 1320, 1240, 1180, 1140, 1100, 1010, 990, 910, 850, 815, 790, 700. UV, λ_{max}/nm: 250, 275, 365. ^1H NMR (acetone-d_6), δ: 3.93 (s, OCH_3), 7.59 (q, 4H-arom.). Mass spectrum, *m/z* (rel. intensity, %): 261(2), 201(7), 135(43), 121(100). Found (%): C, 41.66; H, 2.52; N, 33.76. $C_{10}H_7N_7O_4$. Calculated (%): C, 41.51; H, 2.41; N, 33.93.

4. The reaction of salts 3 and 4 with amines

1,3-Bis(4-methylfurazanyl)triazene (7b). A solution of **3b** prepared by the standard procedure was added to a stirred solution of 10 mmol of **1b** in 100 mL of a water-ice mixture. The precipitate was filtered off, washed with water, and dried in air to give 2.09 g of triazene **7b**, m.p. 113—114 °C (*cf.* Ref. 2: 114 °C). IR, ν/cm^{-1}: 3200, 1620, 1585, 1550, 1480, 1450, 1410, 1270, 1230, 1045, 1010, 940, 910, 760, 710.

1,3-Bis(3-azidocarbonylfuroxanyl-4)triazene (8c). ***a.*** A solution of **4c** prepared by the standard procedure and kept for 2 h at −7— −5 °C was cooled to −30 °C, and 16 mL of $CHCl_3$ and 40 mL of water were added to it dropwise in succession. The reaction mixture was held at this temperature for 0.5 h and then the temperature was brought up to −20 °C. The organic phase was separated and the aqueous phase was extracted with $CHCl_3$ (3×40 mL). The combined organic extracts were washed with a dilute aqueous solution of soda (2×60 mL), and the alkaline solution was acidified with dilute H_2SO_4 and extracted with $CHCl_3$ (3×30 mL). The organic fraction was dried with $MgSO_4$ and concentrated *in vacuo*, and the residue was chromatographed on silica gel preliminarily treated with a 3 % solution of CF_3COOH in $CHCl_3$ using $CHCl_3$ as the eluent. Evaporation of the solvent *in vacuo* afforded 0.60 g (34 %) of triazene **8c**. M.p. 98—99 °C, R_f ($CHCl_3$:CH_3OH = 9:1) 0.57. IR, ν/cm^{-1}: 3270, 2190, 2130, 1690, 1670, 1620, 1580, 1550, 1430, 1310, 1220, 1190, 990, 900, 880, 860, 800, 740. ^1H NMR (acetone-d_6), δ: 3.18 (s, NH).

b. A solution of **4c** prepared by the standard procedure was poured into 100 mL of ice water and extracted with $CHCl_3$ (3×60 mL). Then the reaction mixture was treated as described in ***a*** to give 0.14 g (8 %) of **8c**.

5. The synthesis of azidofurazans 9 and azidofuroxans 10

A. The reaction of salts 3 and 4 with NaN_3. ***a.*** At 2—7 °C a solution of 3.25 g (50 mmol) of NaN_3 in 20 mL of water was slowly added dropwise to a solution of diazonium salt **3** or **4** prepared by the standard procedure (in the case of **4** the reaction mixture was preliminarily diluted with 30 mL of AcOH, 3.25 g of NaN_3 in 5 mL of water was added, and the mixture was held for 1 h at 20 °C). When the gas evolution was over, the reaction mixture was diluted with 200 mL of cold water, the precipitate was filtered off, washed with water, and dried in air. If no precipitate was formed, the aqueous phase was extracted with CH_2Cl_2 (3×50 mL), the organic phase was dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue was recrystallized, distilled *in vacuo*, or chromatographed on a column packed with silica gel.

b. A solution of diazonium salt **3** prepared by the standard procedure was poured into a solution of 3.25 g (50 mmol) of NaN_3 in 50 mL of a water—ice mixture. Then the reaction mixture was treated as described in procedure *a*.

3-Azido-4-methylfurazan (9b). Vacuum distillation afforded 0.75 g (60 %) of compound **9b**, b.p. 51 °C (21 Torr), n_D^{21} 1.4717. IR, ν/cm^{-1}: 2960, 2420, 2295, 2160, 1590, 1515, 1465, 1420, 1395, 1300, 1280, 1155, 1050, 1005, 890, 815. UV, λ_{max}/nm: 204, 248. ^{1}H NMR (CCl_4), δ: 2.20 (s, CH_3). ^{13}C NMR (CD_2Cl_2), δ: 6.07 (CH_3), 147.55 (CN_3), 155.07 ($\underline{C}CH_3$). Found (%): C, 28.63; H, 2.59; N, 55.37. $C_3H_3N_5O$. Calculated (%): C, 28.80; H, 2.40; N, 56.00.

3-Azido-4-methoxycarbonylfurazan (9c). Vacuum distillation afforded 1.0 g (60 %) of compound **9c**, b.p. 96—98 °C (12 Torr), n_D^{20} 1.4885. IR, ν/cm^{-1}: 2980, 2300, 2230, 2165, 1770, 1570, 1450, 1360, 1320, 1190, 1040, 965, 920, 900, 835, 800, 780. UV, λ_{max}/nm: 205, 230. ^{1}H NMR (CCl_4), δ: 4.05 (s, CH_3). Found (%): C, 28.75; H, 1.98; N, 41.83. $C_4H_3N_5O_3$. Calculated (%:) C, 28.40; H, 1.78; N, 41.42.

4-Amino-3-azidofurazan (9d) was prepared by procedure *b*. Yield 1.12 g (89 %), m.p. 84—86 °C (*cf.* Ref. 7: 86.5—87.5 °C).

4-Amino-4-azidoazofurazan (9f) was prepared by procedure *b*. The yield of compound **9f** after its purification by column chromatography (elution with $CHCl_3$) amounted to 1.16 g (52 %), R_f ($CHCl_3$) 0.24, m.p. 135—136 °C (CCl_4). IR, ν/cm^{-1}: 3485, 3335, 2260, 2175, 2140, 1630, 1560, 1505, 1480, 1420, 1290, 1135, 1040, 800, 760. Found (%): C, 21.85; H, 0.82; N, 62.73. $C_4H_2N_{10}O_2$. Calculated (%): C, 21.62; H, 0.90; N, 63.06.

4-Azido-3-methylfuroxan (10a). Column chromatography (elution with CCl_4) yielded 0.72 g (51 %) of compound **10a**, m.p. 29—30 °C R_f ($CHCl_3$) 0.60. IR, ν/cm^{-1}: 2910, 2600, 2210, 2140, 1610, 1470, 1380, 1230, 1100, 1015, 840, 790, 715. ^{1}H NMR (CCl_4), δ: 2.06 (s, CH_3). Mass spectrum, *m/z* (rel. intensity, %): 141[M^+](100), 53(47). Found (%): C, 25.62; H, 2.18; N, 49.40. $C_3H_3N_5O_2$. Calculated (%): C, 25.57; H, 2.12; N, 49.60.

4-Azido-3-phenylfuroxan (10b). Column chromatography (elution with CCl_4) yielded 1.34 g (66 %) of compound **10b**, m.p. 92—94 °C (*cf.* Ref. 14: 95 °C), R_f ($CHCl_3$:CCl_4 = 1:1) 0.52. IR, ν/cm^{-1}: 2710, 2650, 2410, 2260, 2150, 1595, 1500, 1465, 1430, 1325, 1315, 1205, 1120, 1100, 1090, 1070, 1050, 980, 850, 770. ^{1}H NMR (CCl_4), δ: 7.56 (m, 3 H *m*- and *p* arom.), 8.00 (m, 2 H *o*-arom.). Mass spectrum, *m/z* (rel. intensity, %): 203[M^+](15), 145(6), 115(100), 99(18), 77(12).

4-Azido-3-azidocarbonylfuroxan (10c). Column chromatography (elution with CCl_4) yielded 0.60 g (30 %) of compound **10c**, m.p. 82—84 °C, R_f ($CHCl_3$) 0.54. IR, ν/cm^{-1}: 2650, 2400, 2260, 2185, 2160, 2130, 1705, 1605, 1505, 1470, 1340, 1215, 1185, 1115, 1095, 985, 885, 840, 790, 750, 740. Mass spectrum, *m/z* (rel. intensity, %): 196[M^+](5), 154(50), 80(53), 66(100). Found (%): C, 18.23; N, 57.13. $C_3N_8O_3$. Calculated (%): C, 18.37; N, 57.20.

B. The reaction of salts 3 with urea derivatives and formamide

3-Azido-4-methylfurazan (9b). At 2—7 °C 30 mmol of urea, 1,3-dimethylurea, or formamide and 15 mL of EtOH were added to a solution of diazonium salt **3b** prepared by the standard procedure. The reaction mixture was carefully heated to 80 °C, held at this temperature for 1 h, cooled to 20 °C, poured into 100 mL of water, extracted with CH_2Cl_2 (3×50 mL), and dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. Distillation yielded 0.20—0.25 g (16—20 %) of **9b**.

3-Amino-4-azidofurazan (9d) was prepared from **3d** in a similar way. Yield 0.20—0.27 g (16—21 %).

6. Sandmeyer reaction

2-Oximinopropionitrile (14). *a.* A solution of 2 g of CuCl in 10 mL of conc. HCl (or 2.87 g of CuBr in 10 mL of conc. HBr) was added dropwise to a solution of diazonium salt **3b** prepared by the standard procedure. The reaction mixture was held for 1 h, poured into 50 mL of water, extracted with CH_2Cl_2 (3×50 mL), and dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. Distillation yielded 0.30—0.35 g (35—42 %) of nitrile **14**, b.p. 58 °C (2 Torr), n_D^{20} 1.4456 (*cf.* Ref. 19: 1.4460).

b. A solution of **3b** prepared by the standard procedure was poured into a solution of 10 g of CuCl in 100 mL of 5 % HCl (or 14.35 g of CuBr in 100 mL of 5 % HBr, or 6.5 g of KCN in 100 mL of water). The reaction mixture was treated as described in procedure *a* to give 0.20—0.30 g (24—35 %) of compound **14**.

4-Methyl-3-nitrofurazan (11). *a.* A solution of diazonium salt **3b** prepared by the standard procedure was poured into a solution of 40 g of $NaNO_2$ and 5 g of $CuSO_4$ in 100 mL of water. When the gas evolution was complete, the reaction mixture was extracted with CH_2Cl_2 (3×50 mL), the extracts were washed with water, and dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. Distillation yielded 0.04 g (3 %) of compound **11**, b.p. 58.8 °C (18 Torr), n_D^{20} 1.4549. ^{1}H NMR (acetone-d_6), δ: 2.72 (s, CH_3) (*cf.* Ref. 20: δ = 2.72).

b. To a solution of **3b** prepared by the standard procedure was added dropwise at 2—5 °C 2 mL of N_2O_4 and then 0.64 g of copper powder. The reaction mixture was allowed to stand for 12 h at a temperature maintained below 10 °C and poured into 100 mL of water. The reaction mixture was treated as described in procedure *a* to afford 0.06 g (5 %) of nitrofurazan **11**.

3-Iodo-4-methylfurazan (12). A solution of diazonium salt **3b** prepared by the standard procedure was poured into a solution of 3.7 g of NaI in 100 mL of water. The reaction mixture was extracted with CH_2Cl_2 (3×50 mL), washed with water, a Na_2SO_4 solution, again with water, and dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. Distillation yielded 0.95 g (45 %) of iodide **12**, b.p. 81.5 °C (22 Torr), n_D^{23} 1.5287. ^{1}H NMR (acetone-d_6), δ: 2.43 (s, CH_3) (*cf.* Ref. 19: δ 2.42).

7. Reduction

2-Oximinopropionitrile (14). At 2—7 °C 10 mL of ethanol and 0.64 g of copper powder (or 1.44 g of Cu_2O) were added to a solution of diazonium salt **3b** prepared by the standard procedure. The reaction mixture was held at this temperature for 1 h, poured into 100 mL of water, and extracted with CH_2Cl_2 (3×50 mL). Evaporation of the solvent and distillation *in vacuo* afforded 0.35 g (42 %) of oximinonitrile **14**.

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