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Synthesis and cascade rearrangement of 3-arylazo-4-(3-ethoxycarbonylureido)furoxans

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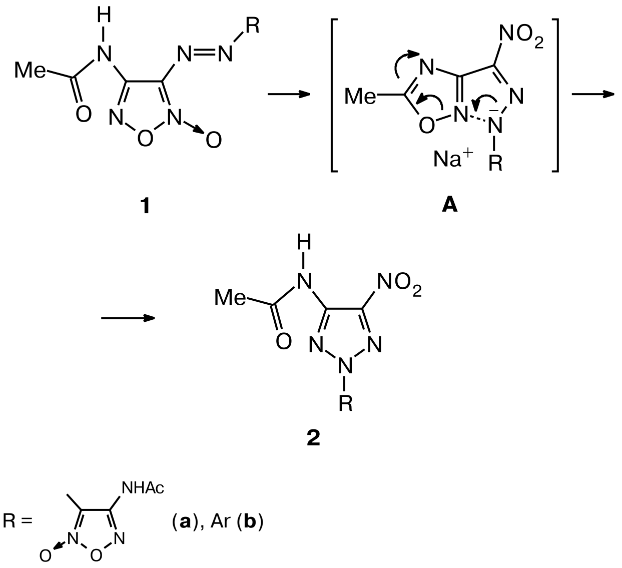
3-Arylazo-4-(3-ethoxycarbonylureido)furoxans, which were synthesized by the reactions of 4-amino-3-arylazofuroxans with ethoxycarbonyl isocyanate, were subjected to cascade rearrangements under the action of potassium *tert*-butoxide in dimethylformamide or by heating in dimethyl sulfoxide to form 4-amino-2-aryl-5-nitro-2*H*-1,2,3-triazoles. X-ray diffraction study and quantum-chemical calculations (B3LYP/6-31G**) of one of ureidofuroxans demonstrated that the intramolecular contact between the carbonyl group and the nitrogen atom of furoxan corresponds to the charge transfer from the lone electron pair of the oxygen atom to the antibonding orbital of the N—O bond.

Key words: cascade heterocycle rearrangements, 3-arylazo-4-(3-ethoxycarbonylureido)furoxans, 4-amino-5-nitro-2*H*-1,2,3-triazoles, X-ray diffraction analysis, quantum-chemical studies.

Heterocycle rearrangements of unfused furoxan derivatives can serve as a convenient procedure for the synthesis of α-nitroalkylazoles.[1] However, these rearrangements, unlike analogous rearrangements of benzofuroxans (Boulton—Katritzky rearrangement[2]), have not been adequately studied.[3,4] Recently,[5—7] we have found several rearrangements in the series of furoxans, including the thermally induced rearrangement of 3,3′-azo-4,4′-bis(acetylamino)furoxan[5] (**1a**) and the base-induced rearrangement of 4-acetylamino-3-arylazofuroxans[7] (**1b**) giving rise to 4-acetylamino-2-furoxanyl- (**2a**) and 4-acetylamino-2-aryl-5-nitro-2*H*-1,2,3-triazoles (**2b**), respectively. We assumed that these reactions involve two successive (cascade) rearrangements. The first step of the reaction affords the 1,2,4-oxadiazole ring (intermediate **A**) followed by its transformation into the 1,2,3-triazole ring involving the azo group (Scheme 1).

Scheme 1



The rearrangement of compounds **1b** into 1,2,3-triazoles derivatives **2b** proceeds in an aqueous solution of alkali and provides a new rather simple approach to completely substituted 1,2,3-triazoles containing the vicinal amino or nitro groups. In the present study, we examined the possibility of performing an analogous rearrangement of 3-arylazo-4-(3-ethoxycarbonylureido)furoxans **4** structurally similar to compounds **1**. Compounds **4** were prepared by the reactions of the corresponding 4-amino-3-arylazofuroxans **3**, which were synthesized according to a known procedure,[7] with ethoxycarbonyl isocyanate (Scheme 2). This isocyanate was chosen due to its high reactivity[8—10] because the amino group in aminofuroxans has very low basicity.[11] The reactions were carried out in dry ethyl acetate at 20 °C for 12 h.

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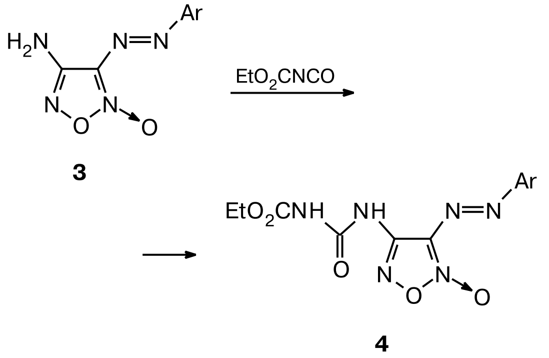
Scheme 2



Ar = 4-$MeOC_6H_4$ (**a**), 4-$EtOC_6H_4$ (**b**), 2,4,6-$Me_3C_6H_2$ (**c**)

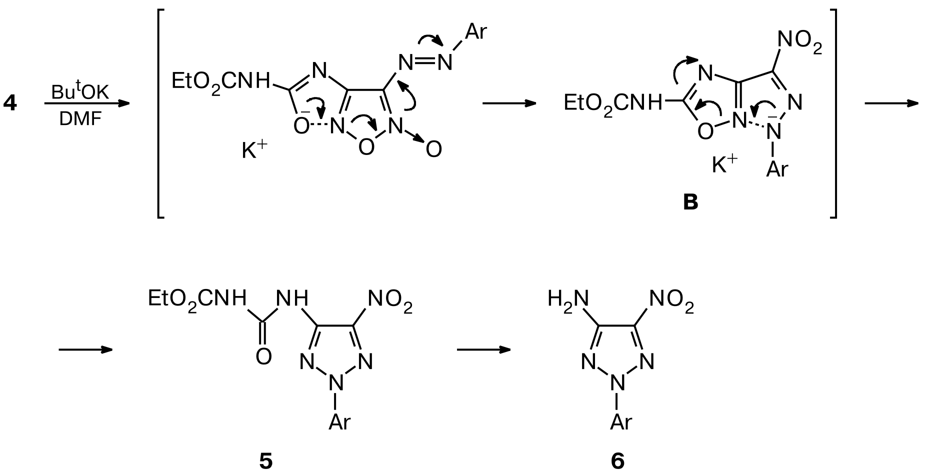
To examine the possibility of subjecting compounds **4a—c** to the heterocycle rearrangement analogous to the cascade rearrangement shown in Scheme 1, we used a 15% aqueous solution of NaOH at 20 °C. However, the starting compounds **4a—c** remained unconsumed under the conditions used. We succeeded in carrying out the desired cascade rearrangement of compounds **4a—c** only with the use of Bu^tOK in anhydrous dimethylformamide as the base, heating at 100 °C for 2 h being necessary for the reaction to proceed. This reaction required much more drastic conditions compared to those, which we have found earlier for the rearrangement of 4-acetylamino-3-arylazofuroxans, due apparently to the fact that the ureido fragment has much lower acidity than the amide group.[12] After completion of the rearrangement, the reaction mixture was cooled, poured into water, and acidified with acetic acid to pH 6.

All reactions yielded compounds containing the unsubstituted amino group, *viz.*, 4-amino-2-aryl-5-nitro-2*H*-1,2,3-triazoles **6a—c**, rather than the target 2-aryl-4-(3-ethoxycarbonylureido)-5-nitro-2*H*-1,2,3-triazoles **5a—c**. Evidently, under the conditions of isolation of the final products, the ethoxycarbamoyl protection is removed and the reaction proceeds through 1,2,4-oxadiazole intermediate **B** (Scheme 3).

In addition to the base-induced rearrangement, we studied the possibility of the thermal rearrangement of ureido derivatives **4** (using **4a,c** as an example) by refluxing their solutions in various solvents (toluene, *m*-xylene, bromobenzene, and DMSO). In the first three solvents, only resinification of the reaction mixture was observed, whereas heating in DMSO at 120 °C for 3 h appeared to be efficient. In spite of the fact that the latter process was also accompanied by resinification, we succeeded in isolating the rearrangement products (column chromatography on SiO_2) in satisfactory yields (Table 1). Interestingly, the latter reaction also afforded compounds **6a,c** rather than the corresponding compounds **5a,c**. Evidently, the ethoxycarbamoyl protection is removed in the course of isolation of the final products, like in the process performed under the base-induced conditions.

The structures of the starting arylazofuroxans **4a—c** and rearrangement products **6a—c** were confirmed by elemental analysis data and spectroscopic characteristics (see Tables 1 and 2). Earlier, ureido derivatives of furoxans have not been known. Hence, the structure of one of these derivatives, *viz.*, compound **4c**, was established by X-ray diffraction analysis (Fig. 1). X-ray diffraction study of **4c** demonstrated[13] that the main bond lengths and bond angles in **4c** (Table 3) are close to the corresponding values in 4-isopropylcarbamoylamino-3-methylfuroxan **7**. In molecule **4c**, the length of the nonbonded intramolecular O(3)...N(2) contact (2.783(3) Å) is only slightly longer than the corresponding contact in molecule **7**

Scheme 3



Ar = 4-$MeOC_6H_4$ (**a**), 4-$EtOC_6H_4$ (**b**), 2,4,6-$Me_3C_6H_2$ (**c**)

Table 1. Yields and selected physicochemical characteristics of the compounds synthesized

Compound	Yield (%)	M.p./°C	R_f ($CHCl_3$: acetone, 1 : 12)	Found/Calculated (%) C	H	N	Molecular formula
4a	86	190—191	0.38	43.70 44.58	3.98 4.03	24.37 23.99	$C_{13}H_{14}N_6O_6$
4b	85	185—186	0.36	46.52 46.16	4.25 4.43	22.92 23.07	$C_{14}H_{16}N_6O_6$
4c	82	172—173	0.48	49.56 49.72	5.12 5.10	23.71 23.19	$C_{15}H_{18}N_6O_5$
6a	50 (32)*	145—146	0.52	46.45 45.96	4.02 3.86	29.42 29.78	$C_9H_9N_5O_3$
6b	65	136—137**	0.64				
6c	45 (42)*	127—128	0.68	52.97 53.43	5.36 5.30	28.77 28.32	$C_{11}H_{13}N_5O_2$

* The yields obtained upon the thermal rearrangement.

** Lit. data[7]: 135—136 °C.

Table 2. Data from ^1H and ^{13}C NMR (DMSO-d_6), ^{14}N NMR (acetone-d_6), and IR spectroscopy and mass spectrometry of the compounds synthesized

Compound	IR, ν/cm^{-1}	^1H NMR (δ, J/Hz)	^{13}C and [^{14}N] NMR (δ, J/Hz)	MS, m/z (I (%))
4a	3480, 3448, 1640, 1572, 1512, 1480, 1452, 1400, 1356, 1332, 1300, 1248, 1168, 1108, 1020, 832	1.32 (t, 3 H, Me, ^3J = 11.7); 3.93 (s, 3 H, MeO); 4.31 (q, 2 H, CH_2, ^3J = 11.7); 7.21, 8.11 (AA´BB´, 4 H, Ar, ^3J = 7.4); 11.09, 11.65 (both s, H, 2 NH)	14.05 ($CH_2\underline{CH_3}$); 55.07 ($\underline{CH_2}CH_3$); 62.30 (OMe); 115.12, 120.91, 125.65, 160.26 (Ar); 126.51 (C(3) of furoxan ring); 154.82 (C(4) of furoxan ring); 148.29, 164.28 (2 C=O)	350 [M]$^+$ (11.90), 261 [M – NH_2CO_2Et]$^+$ (16.67), 219 [M – $HCONHCO_2Et$]$^+$ (14.30), 135 [$MeOC_6H_4N_2$]$^+$ (66.67), 107 [$MeOC_6H_4$]$^+$ (100.00)
4b	3236, 3148, 2984, 1720, 1612, 1504, 372, 1256, 1148, 1112, 1052, 1032, 832, 616	1.35 (m, 6 H, 2 Me); 4.27 (m, 4 H, 2 CH_2); 7.19, 8.09 (AA´BB´, 4 H, Ar, ^3J = 7.5); 11.06, 11.62 (both s, H, 2 NH)	14.09, 14.10 (2 $CH_2\underline{CH_3}$); 53.08, 55.42 (2 $\underline{CH_2}CH_3$); 115.62, 120.68, 125.85, 160.82 (Ar); 126.47 (C(3) of furoxan ring); 154.56 (C(4) of furoxan ring); 148.87, 164.50 (2 C=O)	364 [M]$^+$ (33.82), 275 [M – NH_2CO_2Et]$^+$ (43.24), 247 [M – $CONHCO_2Et$]$^+$ (21.46), 149 [ArN_2]$^+$, (57.82), 121 [Ar]$^+$ (100.00)
4c	3220, 3160, 2980, 1724, 1604, 1558, 1392, 1236, 1100, 1016, 856, 772	1.22 (t, 3 H, Me, ^3J = 11.9); 2.30, 2.35 (both s, 3 H, 6 H, 3 Me, Ar); 4.19 (q, 2 H, CH_2, ^3J = 11.9); 7.07 (s, 2 H, Ar); 11.01 (s, 2 H, 2 NH)	13.97 ($CH_2\underline{CH_3}$); 19.02 (4-Me); 20.77 (2,6-Me); 62.18 ($\underline{CH_2}CH_3$); 122.58 (C(3) of furoxan ring); 130.23, 132.81, 139.0, 145.45 (Ar); 145.10 (C(4) of furoxan ring); 148.40, 154.20 (2 C=O)	362 [M$^+$] (7.02), 346 [M – O]$^+$ (11.62), 274 (M – NH_2CO_2Et]$^+$ (3.82), 147 [2,4,6-$Me_3C_6H_2N_2$]$^+$ (25.6), 119 [$Me_3C_6H_2$]$^+$ (100)
6a	3228, 3144, 2984, 2844, 1744, 1742, 1612, 1580, 1552, 1536, 1504, 1444, 1336, 1308, 1184, 1104, 1032, 848, 632	3.88 (s, 3 H, MeO); 7.02 (s, 2 H, NH_2); 7.15, 7.91 (AA´BB´, 4 H, Ar, ^3J = 7.8);	55.10 (OMe); 114.90, 119.85, 131.30, 158.90 (Ar); 138.5 (C—NO_2); 149.15 (C—NH_2); [−23.13 (NO_2), −138.58 (N(2) of triazole ring)]	235 [M]$^+$ (63.16), 189 (M – NO_2]$^+$ (18.95), 135 [ArN_2]$^+$ (44.21), 107 [Ar]$^+$ (100.00)
6c	3235, 3147, 2950, 2814, 1715, 1700, 1620, 1572, 1540, 1516, 1490, 1430, 1359, 1296, 1188, 1104, 1016, 870, 645	2.10 (s, 3 H, 2 *p*-Me); 2.36 (s, 6 H, *o*-Me); 6.22 (s, 2 H, NH_2); 7.07 (s, 2 H, Ar)	19.62, 20.36 (2 Me); 129.56, 133.19, 134.07, 140.52 (Ar); 149.87 (C—NH_2); 153.54 (C—NO_2) [−22.06 (NO_2), −135.87 (N(2) of triazole ring)]	247 [M]$^+$ (57.86), 201 [M – NO_2]$^+$ (22.34), 147 [ArN_2]$^+$ (39.82), 119 [Ar]$^+$ (100.00)

Table 3. Bond lengths (*d*) and bond angles (ω) in compound **4c**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
O(1)—N(2)	1.392(3)	N(2)—O(1)—N(1)	108.24(17)	N(2)—C(2)—N(3)	126.1(3)
O(1)—N(1)	1.450(3)	O(2)—N(1)—C(1)	134.7(3)	N(2)—C(2)—C(1)	113.3(2)
N(1)—O(2)	1.214(3)	O(2)—N(1)—O(1)	118.5(2)	N(3)—C(2)—C(1)	120.6(2)
N(1)—C(1)	1.333(3)	C(1)—N(1)—O(1)	106.8(2)	N(6)—C(3)—C(8)	128.2(3)
N(2)—C(2)	1.294(3)	C(2)—N(2)—O(1)	105.7(2)	N(6)—C(3)—C(4)	112.7(2)
O(3)—C(12)	1.197(3)	C(2)—N(3)—C(12)	124.2(2)	O(3)—C(12)—N(3)	124.5(3)
N(3)—C(2)	1.363(3)	C(13)—N(4)—C(12)	128.5(2)	O(3)—C(12)—N(4)	121.4(2)
N(3)—C(12)	1.384(3)	C(13)—O(5)—C(14)	118.6(2)	N(3)—C(12)—N(4)	114.1(2)
O(4)—C(13)	1.219(3)	N(6)—N(5)—C(1)	115.1(2)	O(4)—C(13)—O(5)	124.7(2)
N(4)—C(13)	1.359(3)	N(5)—N(6)—C(3)	118.4(2)	O(4)—C(13)—N(4)	124.8(3)
N(4)—C(12)	1.385(3)	N(1)—C(1)—N(5)	128.7(3)	O(5)—C(13)—N(4)	110.3(2)
N(5)—N(6)	1.265(3)	N(1)—C(1)—C(2)	106.0(2)	C(15)—C(14)—O(5)	109.9(3)
N(5)—C(1)	1.376(3)	N(5)—C(1)—C(2)	125.4(2)		
N(6)—C(3)	1.386(3)				
C(1)—C(2)	1.423(4)				

(2.733 Å) due, apparently, to the presence of the strong intramolecular N(3)—H(3N)...O(4) bond (N(3)...O(4), 2.632(3) Å; N(3)H(3N)O(4), 149.3°) in molecule **4c**. The formation of the H-bonded six-membered ring in molecule **4c** leads to weakening of the conjugation between the N(3) atom and the furoxan ring and an insignificant distortion of the planarity of the molecule. The dihedral angle between the plane of the furoxan ring and the H-bonded six-membered ring is 16.4°. The dihedral angle between the furoxan ring and the arylazo substituent is 1.0°.

Analysis of the crystal packing of **4c** demonstrated that there is not only the intramolecular hydrogen bond but also the intermolecular N(4)—H(4N)...O(5´) hydrogen bond (–*x*, 2 – *y*, 1 – *z*) (N(4)...O(5´), 2.880(3) Å; N(4)H(4N)O(5´), 175°) through which the molecules are linked in centrosymmetrical dimers. In addition, the crystal contains dimers linked by stacking interactions between the furoxan ring and the aryl substituent with the shortest C(1)...C(4) distance (1 – *x*, 2 – *y*, –*z*) of 3.397(2) Å.

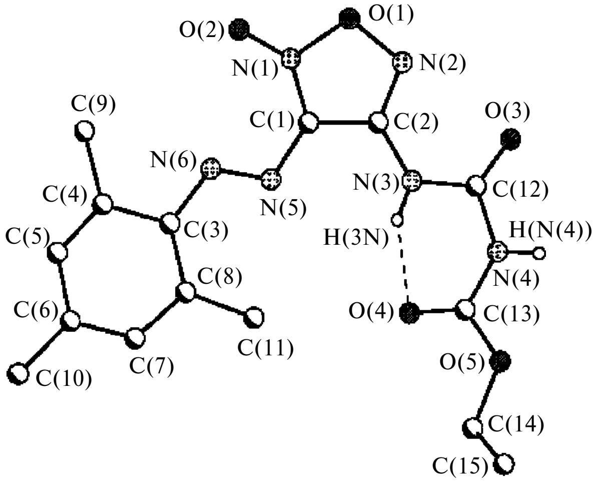


Fig. 1. Overall view of molecule **4c**. The hydrogen atoms, which are not involved in hydrogen bonding, are omitted.

Taking into account that the mechanism of this cascade rearrangement involves the charge transfer from the lone electron pair of the O(3) atom to the antibonding orbital of the N(2)—O(1) bond (see Scheme 3), it was of interest to analyze the character of the shortened N(2)...O(3) contact observed in molecule **4c**.

Studies of intramolecular contacts[14] have demonstrated that the topological theory known as "Atoms in Molecules" (AIM)[15] is the method of choice for analysis of the nature of such interactions. This approach is of interest because it not only allows one to unambiguously reveal the presence of interactions but also to relate the topological characteristics of the electron density at critical points to the energy of the contact.[16]

To study the character of the intramolecular O(3)...N(1) contact, we performed the topological analysis of the electron density distribution (ρ(**r**)) in compound **4c** in which the ethyl group at the O(5) atom is replaced by the methyl group. Quantum-chemical calculations with full geometry optimization in the symmetry point group C_1 were carried out within the framework of the density functional theory (B3LYP/6-31G**) using the Gaussian98W program package.[17]

The calculated geometry of the molecule, including the intramolecular contacts and parameters of the N—H...O hydrogen bond, are in good agreement with the experimental values (see Table 3). It should be noted that the isolated molecule, unlike the molecule in the crystal, is planar (except for the H atoms of the methyl group). Therefore, the rotation of the N—H...O-bonded six-membered ring with respect to the furoxan ring observed in the crystal is caused by the intermolecular N—H...O bond and the stacking interaction present in the crystal rather than by weakening of conjugation.

Analysis of the topological electron density showed that the critical points (3, −1) are located not only on all expected C—C, N—O, and N—N chemical bonds but also in the regions of the N—H...O and O(3)...N(2) contacts. Analysis of the topological characteristics at the critical points (3, −1) demonstrated that all chemical bonds, except for H(3N)...O(4) and O(3)...N(2), correspond to shared interactions (the Laplacian of the electron density $\nabla^2\rho(r)$ at the critical points (3, −1) is negative). For the H(3N)...O(4) and O(3)...N(2) contacts, the Laplacian $\nabla^2\rho(r)$ at the critical points (3, −1) takes positive values (2.20 and 1.03 $e\text{Å}^{-5}$, respectively), which is characteristic of closed-shell interactions.

As can be seen from the section of $-\nabla^2\rho(r)$, the O(3)...N(2) contact can be described within the framework of the peak—hole model[15] and corresponds to the transfer of accumulation of $\rho(\mathbf{r})$ on the valence shell of the O(3) atom (the lone electron pair) to the region of depletion of $\rho(\mathbf{r})$ on the valence shell of the N(2) atom (the antibonding orbital of the N(2)—O(1) bond) (Fig. 2).

In spite of rather low electron densities at the corresponding critical points (0.20 and 0.080 $e\text{Å}^{-3}$) for the H(3N)...O(4) and O(3)...N(2) contacts, the energies of the contacts estimated from the empirical dependence of the energy of the contact on the potential energy density[16] are 7.5 and 2.2 kJ mol^{-1}, respectively.

Hence, the O(3)...N(2) interaction in the starting 3-arylazo-4-(3-ethoxycarbonylureido)furoxans corresponds to the charge transfer, and, apparently, an elongation of this contact in molecule **4c** is in part responsible for more drastic conditions required for this rearrangement.

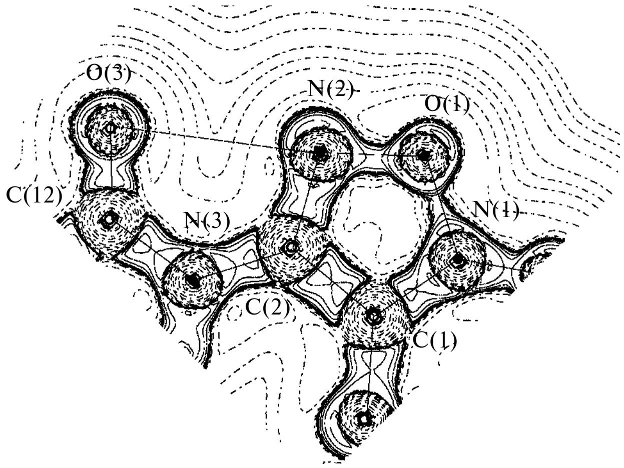


Fig. 2. Sections of the Laplacian of the electron density ($-\nabla^2\rho(r)$) in the region of the contact in molecule **4c**. The maps are countered on a base-2 logarithmic scale. The regions of charge concentration ($-\nabla^2\rho(r) > 0$) and charge depletion are indicated by solid and dashed lines, respectively.

The mass spectra of all the compounds synthesized have molecular ion peaks. The ^{1}H and ^{13}C NMR spectra have all necessary resonances for the hydrogen and carbon atoms. The ^{14}N NMR spectra of the rearrangement products show signals of the nitro groups in the δ region from −23 to −25 and signals for the N(2) atom of the triazole ring. Some ^{14}N NMR spectra have also a broadened signal of the NH_2 group. The properties of triazole **6c** are identical with those described for this compound earlier.[7]

To summarize, we synthesized first representatives of carbamoylaminofuroxans **4** and found conditions for their involvement in cascade rearrangements giving rise to 4-amino-3-nitro-containing derivatives of 1,2,3-triazole **6**. Taking into account the cascade rearrangements of acylaminoazofuroxans, which we have carried out earlier,[5,7] it can be stated that these reactions have a general character.

Experimental

The IR spectra were recorded on a UR-20 spectrometer in KBr pellets. The ^{1}H NMR spectra were measured on a Bruker WM-250 spectrometer (250 MHz). The ^{13}C and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer (75.5 and 21.69 MHz, respectively). The mass spectra were obtained on a Finigan MAT INCOS-50 spectrometer. The melting points were measured on a Boetius PHMK 05 instrument. The TLC analysis was carried out on Silufol UV-254 plates (visualization using a UV lamp).

Synthesis of 3-arylazo-4-(3-ethoxycarbonylureido)furoxans 4a—c (general procedure). Ethoxycarbonyl isocyanate (0.14 g, 0.125 mL, 12 mmol) was added dropwise to a solution of the corresponding 4-amino-3-arylazofuroxan **3a—c** (10 mmol), which was prepared according to a procedure described earlier,[7] in dry ethyl acetate (20 mL). The reaction mixture was kept at ~20 °C for 12 h. Then the ethyl acetate and unconsumed ethoxycarbonyl isocyanate were removed on a rotary evaporator and the residue was recrystallized from ethanol.

Synthesis of 4-amino-2-aryl-3-nitro-2*H*-1,2,3-triazoles 6a—c in the presence of Bu^{t}OK (general procedure). Potassium *tert*-butoxide (0.22 g, 20 mmol) was added to a solution of 3-arylazo-4-(3-ethoxycarbonylureido)furoxan **4a—c** (10 mmol) in dry DMF (5 mL). The reaction mixture was stirred at 100 °C for 3 h. The resulting solution was cooled and poured into a 5% aqueous solution of acetic acid (20 mL). The precipitate of **6a—c** that formed was filtered off and recrystallized from ethanol.

Synthesis of 4-amino-2-aryl-3-nitro-2*H*-1,2,3-triazoles 6a,c under conditions of thermal rearrangement (general procedure). A solution of 3-arylazo-4-(3-ethoxycarbonylureido)furoxan **4a,c** (10 mmol) in DMSO (10 mL) was heated at 110 °C for 3 h. Then DMSO was evaporated and the oily residue was separated on a column (Merck 0.063—0.200 silica gel, chloroform as the eluent).

X-ray diffraction study of compound 4c ($C_{15}H_{18}N_6O_5$) was carried out at 24 °C on an automated four-circle Siemens P3/PC diffractometer (MoKα radiation, graphite monochromator, θ/2θ scanning technique, $2\theta_{max} \leq 56°$). The crystals belong to the monoclinic system, at 24 °C: $a = 7.300(2)$ Å, $b = 9.448(2)$ Å, $c = 13.555(3)$ Å, $\alpha = 99.70(3)°$, $\beta = 96.00(3)°$, $\gamma = 108.37(3)°$, $V = 861.9(3)$ Å^3, $d_{\text{calc}} = 1.396$ g cm^{-3}, $M = 362.35$, $F(000) = 380$, $\mu = 1.08$ cm^{-1}, $Z = 2$, space group $P\bar{1}$. Of a total of 8348 measured reflections, 4177 independent reflections were used in subsequent calculations and refinement. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method based on F^2_{hkl}. The hydrogen atoms were revealed from difference Fourier syntheses and included in the final refinement using the riding model. The final reliability factors were as follows: $R = 0.0.0543$ using 955 reflections with $I > 2\sigma(I)$, $wR_2 = 0.2278$ and GOOF = 0.963 for all reflections. All calculations were carried out on an IBM-PC/AT computer using the SHELXTL PLUS program package.

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