In addition to benzene cycle signals, the ^{13}C NMR spectrum contains one signal of the oxathiadiazole ring with a chemical shift of 160—161 ppm, typical of azomethine carbon signals; this signal differs slightly from the corresponding signals in 5-amino-3-aryl-1,2,4-oxadiazoles (167 ppm[1]).

Experimental

IR spectra were recorded with a Specord spectrophotometer in KBr pellets, the mass-spectra were taken with a Varian MAT CH-6 instrument. ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded with a Bruker AM-300 instrument at working frequencies of 300, 75.5, 21.6, and 30 MHz. The chemical shifts were measured relative to the signals of the DMSO-d_6 solvent: δ 2.5 (^1H) and 39.5 (^{13}C), or relative to nitromethane as the external standard: δ 0.0 (^{14}N, ^{15}N). The melting points were determined on a Boetius table at a heating speed of 4 degrees min^{-1} at the melting point. The course of the reactions was monitored by TLC on Silufol UV-254 plates using chloroform—acetone, 20:1, as the eluent.

Nitrile oxides **1a—d** were obtained according to the procedure in ref. **3**. Bis-trimethylsilylthiodiimide **2** was prepared according to the procedure in ref. **4**.

Interaction of aromatic nitrile oxides with bis-trimethylsilylthiodiimide. General procedure. To a solution of nitrile oxide **1a—d** (1 mmol) in 10 mL of benzene a solution of thiodiimide **2** (1 mmol) in 3 mL of benzene was added dropwise with stirring at 5—10°C. The mixture was stirred for 1.5 h, the temperature gradually rising to ~20°C. The solvent was distilled off, the residue was purified by chromatography on a SiO_2 column (L 40/100 μ), using chloroform—acetone, 20:1, as the eluent. The yields and the properties of the compounds obtained are given in Table 1.

Substituted benzamidoximes (5a—d). A solution of 1,2,3,5-oxathiadiazole **3a—d** (1 mmol) in 10 mL of benzene was kept at ~20°C for 48 h until compounds **3a—d** disappeared. The solution was concentrated *in vacuo*, and the residue was crystallized from EtOH. Yield 96—98 %.

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α-Bromoacetyl derivatives of furazan and furoxan

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Bromination of acetylfurazans and furoxans has been studied. The conditions for the synthesis of bromoacetyl derivatives have been found.

Key words: furazan, furoxan, bromination, bromoacetyl derivatives.

The range of uncondensed derivatives of furazan and their N-oxides (furoxans) with reactive substituents is very limited.

Bromination of alicyclic ketones fused with a furazan or furoxan cycle is known to afford the corresponding α-bromo derivatives.[1] Halogenation of acylfurazans has not been reported. At the same time, α-haloketones are effective synthons for the synthesis of functional derivatives of alkanes and different heterocyclic systems.[2,3]

This study is devoted to the synthesis of bromoacetyl derivatives of furazan (**3**) and furoxan (**4**). With this goal bromination of 3-acetyl-4-*R*-furazans (**1**) and 4-acetyl-

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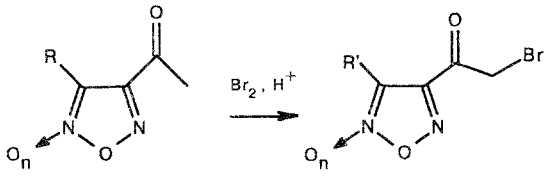
3-*R*-furoxans (**2**) in acidic medium has been studied.



1: n = 0
2: n = 1

R = NH_2(**a**), CH_3(**b**), $COCH_3$(**c**), NO_2(**d**)

3: n = 0
4: n = 1

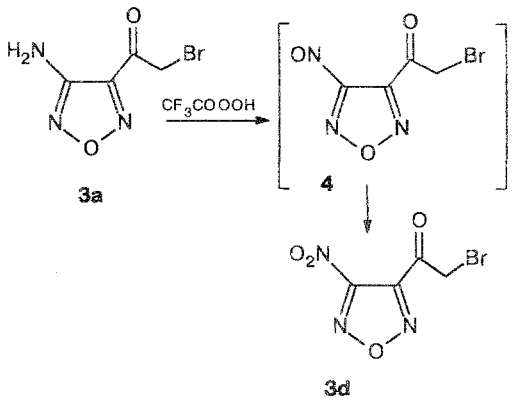
R' = NH_2(**a**), CH_3(**b**), $COCH_2Br$(**c**), NO_2(**d**)

Halogenation of methyl ketones is known[2] to proceed through their enolization, which is facilitated by the electron-donor effect of the second substiuent at the carbonyl group. However, the furazan and furoxan rings exhibit a significant electron-acceptor effect comparable to that of the dinitrophenyl group.[4] In fact, unlike acetophenone, neither **1** nor **2** can be brominated in acetic acid at 0—15 °C; however, the bromo derivatives of the ketones under study can be obtained under appropriately selected conditions. As expected, compounds **1** undergo bromination more readily than the corresponding derivatives **2**, which comprise a more electron-accepting furoxan ring. The ability of the acetyl group to undergo bromination also depends on the character of the substituent R and drops with the increase in its acceptor properties. The results obtained are presented in Table 1.

One can notice that **1a** and **1b** are brominated in acetic acid, whereas **2b** is inert under these conditions. Compound **1d**, which contains a strong electron-accepting substituent, also does not react under these conditions. In the medium of stronger trifluoroacetic acid, **1d** affords the bromoacetyl derivative, although in low yield. If the reaction is carried out in hydrochloric acid, the bromo derivatives can be prepared even from the most deactivated compounds of series **1** and **2**.

It should be noted that both **1c** and **2c** are brominated simultaneously at the both acetyl groups. The deficiency of bromine results in mixtures of the bis(bromoacetyl) derivative with the starting compound; the monobromo derivative is present in the reaction mixture only in trace amounts (TLC).

3-(Bromoacetyl)-4-nitrofurazan (**3d**) was also obtained by oxidation of 3-(bromoacetyl)-4-aminofurazan (**3a**) with trifluoroperacetic acid.



The reaction passes through the intermediate nitroso-derivative, as judged by the appearance and the subsequent disappearance of a blue coloration of the reaction mixture. The conditions used preclude isolation of **4**; special conditions should be chosen[5] to this end.

Experimental

IR spectra were recorded in KBr pellets on a UR-20 spectrometer. Electron impact mass-spectra were obtained on a Varian CH-6 instrument. ^1H, ^{13}C, and ^{14}N NMR spectra (δ; Hz) were recorded on a Bruker AM-300 instrument at working

Table 1. The conditions of synthesis of furazan and furoxan bromoacetyl derivatives

Starting compound	Solvent	Reaction temperature (°C)	Reaction time (h)	Product	Yield (%)
1a	CH_3COOH	20	18	**3a**	62
1a	»	55	1	**3a**	81
1b	»	55	1	**3b**	74
1c	»	20	48	**3c**	45
1d	»	55		No reaction	
2b	»	55		No reaction	
1d	CF_3COOH	20	48	**3d**	27
2b	»	20	24	**4b**	19
1d	conc.HCl	20	28	**3d**	37
2b	»	20	36	**4b**	95
2c	»	20	0.5	**4c**	46

Table 2. Melting points, IR and mass spectra, and elemental analysis data of α-bromoacetylfurazans **3a—d** and **4a,b**

Product	M.p. (°C)	$[M^+]$ (*m/z*)	IR spectrum (cm^{-1})	Found / Calculated (%)		
				C	H	N
3a	162—163	207, 205	3440, 3320, 2990, 2945, 1705, 1620, 1495, 1380, 1330, 1220, 1005, 990	23.32 23.47	1.96 1.90	20.40 20.28
3b	34—35	206, 204	3015, 2915, 1740, 1575, 1475, 1455, 1430, 1410, 1390, 1285, 1220, 1143, 1050, 1020, 995	29.29 29.20	2.46 2.34	13.66 13.73
3c	81—83	314, 312, 310	2995, 2935, 1720, 1600, 1430, 1380, 1300, 1240, 990, 960, 910, 880.	23.10 23.22	1.29 1.21	8.98 9.11
3d	Oil	237, 235	2990, 2950, 1730, 1580, 1455, 1420, 1390, 1350, 1240, 1180, 1040, 1015, 990, 910, 880, 830			
4b	48—49	222, 220	3020, 2940, 1710, 1610, 1530, 1480, 1430, 1370, 1360, 1310, 1225, 1170, 1080, 1050, 1000, 955, 860, 840	27.17 27.27	2.28 2.39	12.68 12.55
4c	113—114	233, 231 $[M—Br—O]^+$	2995, 2935, 1720, 1705, 1585, 1460, 1410, 1360, 1295, 1230, 1125, 1030, 980, 920, 860	21.98 22.07	1.23 1.15	8.54 8.69

Table 3. ^1H and ^{13}C NMR spectra of **3a—d**, **4a,b**

Compound	^1H		^{13}C				
	CH_2	Other signals	C-3	C-4	C=O	CH_2	Other signals
3a	4.83	6.11(NH_2)	142.94	156.99	186.47	33.45	—
3b	4.80	2.65(CH_3)	149.25	151.46	184.21	31.86	9.04
3c	4.87	—	150.81	150.81	183.26	34.56	—
3d	4.50	—	144.41	158.16	179.71	31.04	—
4b	4.83	2.38(CH_3)	110.26	152.17	184.37	29.93	8.35
4c	4.71	4.82(CH_2)	111.64	152.99	180.57	33.51 (at C-3) 183.92 (at C-4)	36.36

frequencies of 300, 75.5, and 21.5 MHz, respectively. The chemical shifts for ^1H and ^{13}C NMR are given relative to tetramethylsilane (internal standard), for ^{14}N NMR relative to CH_3NO_2 (external standard). TLC was carried out on Silufol-254 plates in $CHCl_3$.

Bromination: typical procedure. Br_2 (10 mmol; for **1c** and **2c**, 20 mmol) was added dropwise to a solution or a suspension of compound **1** or **2** (10 mmol) in 20 mL of an acid. The reaction mixture was stirred at the appropriate temperature until completion of the reaction (monitored by TLC) and poured into water. The product was isolated by filtration or extraction with CH_2Cl_2. The experimental results and the characteristics of the compounds thus obtained are given in Tables 1 and 2.

3-Acetyl-4-nitrofurazan (1d). 3-Acetyl-4-aminofurazan (**1a**) (1.02 g, 8 mmol) was added in one portion at 15°C to a mixture of CH_2Cl_2 (20 mL), trifluoroacetic anhydride (7 mL), and hydrogen peroxide (1 mL, 90 % solution), and the reac-

tion mixture was stirred for 3—4 h. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×15 mL). The combined extracts were washed with water and dried with $MgSO_4$. The solvent was removed at reduced pressure, and the residue was distilled in vacuum; 0.75 g (60 %) of **1d** was obtained as a slighly-yellow liquid, b.p. 49—50 °C (3—4 Torr), n_D^{20} 1.461; R_f 0.68. IR, ν (cm^{-1}): 2930, 1720, 1460, 1410, 1370, 1210, 1090, 1050, 1020, 960, 890, 860, 820. ^1H NMR (CCl_4): 2.81 (CH_3). ^{13}C NMR (CCl_4+$CDCl_3$): 28.94 (CH_3), 145.64 (C—Ac), 170.65 (C—NO_2), 185.35 (C=O). ^{14}N NMR (CCl_4+$CDCl_3$): −36.1 (NO_2). MS, *m/z* (I_{rel}, %): 157(56) [M^+], 142(100), 127(14), 97(28), 96(95), 69(53).

3-(α-Bromoacetyl)-4-nitrofurazan (3d) was obtained by oxidation of **3a** according to the procedure described above. The yield was 48 %. The substance is unstable and decomposes on storage.

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Synthesis of 3-substituted 4-imino-4,5-dihydro-1,2,3-triazole 1-oxides and 4-amino-1,2,3-triazole 1-oxides. Crystal and molecular structure of 4-imino-5,5-dimethyl-3-phenyl-4,5-dihydro-1,2,3-triazole 1-oxide

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A new procedure for the synthesis of triazole N-oxides, based on base-induced intramolecular cyclization of 1-(α-cyanoalkyl)-3-aryl(hetaryl)triazen-1-oxides, is proposed. An X-ray study of 4-imino-5,5-dimethyl-3-phenyl-4,5-dihydro-1,2,3-triazole 1-oxide was carried out.

Key words: 1,2,3-triazole N-oxides, synthesis; triazene 1-oxides, bases; 4-imino-5,5-dimethyl-3-phenyl-4,5-dihydro-1,2,3-triazole 1-oxide, X-ray study.

1,2,3-Triazole N-oxides, which possess a number of valuable properties (fluorescent,[1—4] insecticide,[5,6] fungicide[5] properties, etc.), remain difficult to obtain. The known methods for synthesis of 1,2,3-triazole 1-oxides, including oxidation of *vic*-hydrazone oximes[7—11] and 1,2,3-triazoles[12] with Cu(II) salts, N_2O_4, or peracids, are characterized by a narrow field of application, low availability of the starting compounds, and low yields of the target products.

In this work we offer a novel approach to the preparation of heterocyclic compounds of this class. The method which we discovered is based on cyclization of

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