Experimental

GLC-analysis was carried out with a Biokhrom 1M chromatograph on a glass column (58.5×0.25 mm) with a PEG-40M stationary liquid phase and nitrogen as the carrier gas. NMR spectra were recorded with a Bruker AM-300 spectrometer at working frequencies of 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, 21.7 MHz for ^{14}N, and 30.4 MHz for ^{15}N. The reactions of *t*-BuNHMgBr and *t*-BuNHLi with nitro compounds were carried out according to the previously described procedure.[1,2] All reactions were performed in a dry argon atmosphere using absolute solvents. The products were isolated by column chromatography on SiO_2 and recrystallized from MeOH: **4**, mp 86°C; **6**, mp 82°C; **13**, mp 161°C; **14**, mp 91°C; **15**, mp 112°C; **16**, mp 97°C; **5,6,** and **7** are viscous liquids. The structures of **4—8** and **13—16** were established on the basis of NMR spectral data (see Tables 1 and 2) and elemental analysis. Compounds **9—11** and **17** were identified by comparison with known samples.[4—7]

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Syntheses based on nitrile oxides. 3.* Interaction of aromatic nitrile oxides with bis-trimethylsilylthiodiimide

V. A. Ogurtsov, O. A. Rakitin, Yu. A. Strelenko, N. V. Obruchnikova, and L. I. Khmel'nitskii*

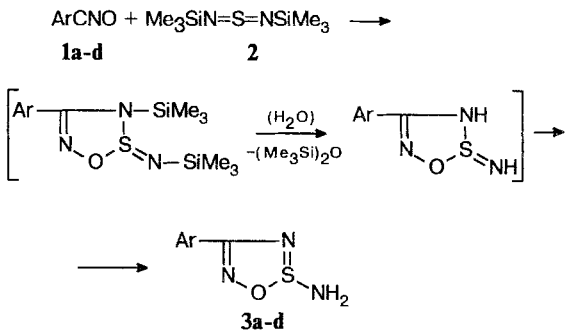
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117334 Moscow, Russian Federation. Fax: +7 (095) 135 5328

Interaction of aromatic nitrile oxides with bis-trimethylsilylthiodiimide results in 2-amino-4-aryl-1,2,3,5-oxathiadiazoles, the first representatives of a new class of heterocyclic compounds.

Key words: nitrile oxides, thiodiimide, oxathiadiazoles, amidooximes.

Earlier[1] we reported that aromatic nitrile oxides interact with bis-trimethylsilylcarbodiimide to give 5-amino-3-aryl-1,2,4-oxadiazoles.

To continue this work we studied the reaction of aromatic nitrile oxides (**1a—d**) with trimethylsilylthiodiimide (**2**). The main products of this reaction are 2-amino-4-aryl-1,2,3,5-oxathiadiazoles (**3a—f**), the formation of which can be explained by a scheme similar to the formation of 5-amino-3-aryl-1,2,4-oxadiazoles upon interaction of aromatic nitrile oxides with bis-trimethylsilylcarbodiimide:[1]



3a-d

Ar = *m*-$O_2NC_6H_4$ (**a**); *p*-$O_2NC_6H_4$ (**b**); *p*-ClC_6H_4 (**c**); *p*-BrC_6H_4 (**d**).

*For Part 2, see ref. 1.

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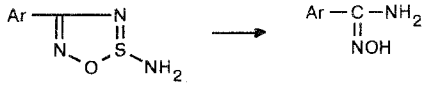
Table 1. Interaction of nitrile oxides **1a—d** with bis-trimethylsilylthiodiimide (**2**)

Starting compound	R	Product	Yield (%)	R_f	m.p. (°C)	Mass-spectrum (*m/z*)	IR (cm^{-1})	Molecular formula	Found / Calculated (%) C	H	N	S	Hal
1a	*m*-NO_2	**3a**	27	0.12	108-109	226	3320 NH_2 3150 1605 C=N	$C_7H_6N_4O_3S$	32.98 33.17	2.64 2.65	24.15 24.78	14.08 14.16	—
		4a	21	0.85	182-183[5]	—	—	—	—	—	—	—	—
		5a	10	0.10	170-172[6]	—	—	—	—	—	—	—	—
1b	*p*-NO_2	**3b**	35	0.13	134-135	226	3310 NH_2 3090 1605 C=N	$C_7H_6N_4O_3S$	33.01 33.17	2.68 2.65	24.25 24.78	14.02 14.16	— —
		4b	18	0.87	203-204[5]	—	—	—	—	—	—	—	—
		5b	2	0.12	158-160[7]	—	—	—	—	—	—	—	—
1c	*p*-Cl	**3c**	34	0.11	87-90	215	3300 NH_2 3100 1570 C=N	$C_7H_6ClN_3OS$	38.89 38.98	2.76 2.78	19.14 19.49	14.97 14.88	16.11 16.47
		4c	23	0.81	142-143[5]	—	—	—	—	—	—	—	—
		5c	3	0.10	128-130[8]	—	—	—	—	—	—	—	—
1d	*p*-Br	**3d**	29	0.10	72-75	260	3310 NH_2 3100 1580 C=N	$C_7H_6ClN_3OS$	32.15 32.31	2.32 2.31	15.98 16.15	12.16 12.31	30.43 30.70
		4d	22	0.82	162-163[5]	—	—	—	—	—	—	—	—
		5d	8	0.09	139-141[9]	—	—	—	—	—	—	—	—

The reaction is complicated by two additional processes leading to the formation of two by-products. Nitrile oxides **1a—d** partially dimerize into the corresponding furoxans (**4a—d**). Furthermore, one can observe the formation of substituted benzamidoximes (**5a—d**), the decomposition products of oxathiadiazoles **3a—d**. It was shown in special experiments that the exposure of oxathiadiazoles **3a—d** in a benzene solution results in their decomposition into amidoximes **5a—d**.



3a-d **5a-d**

Ar = *m*-$O_2NC_6H_4$ (**a**); *p*-$O_2NC_6H_4$ (**b**); *p*-ClC_6H_4 (**c**); *p*-BrC_6H_4 (**d**).

The adducts of nitrile oxides with thiodiimide **2** synthesized by us are the first representatives of 1,2,3,5-oxathiadiazoles, a new class of heterocyclic compounds. The structure of these compounds was confirmed by the elemental analysis and IR, mass-, and NMR spectral data (Tables 1, 2).

The mass-spectra of **3a—d** contain intense peaks of molecular ions. The characteristic bands in the IR-spectra of these compounds are the absorption bands corresponding to the stretching vibrations of the amino group (a doublet near 3300 and 3100 cm^{-1}) as well as the stretching vibrations of the C=N bond near 1600 cm^{-1} that are close to the similar absorption bands for oxadiazoles.[2] To reveal other characteristic vibrations of the 1,2,3,5-oxadiazole ring, further investigations are required.

The existence of an amino group is also proved by the presence in the ^1H NMR spectrum of broadened signals at 7.66—8.16 ppm with integral intensity corresponding to two protons. The ^{15}N NMR spectrum of **3b** revealed an amino group signal with $^1J_{H-^{15}N}$ = 82.3 Hz, which characterizes the NH_2-group.

Table 2. NMR spectra of 1,2,3,5-oxathiadiazoles **3a—d** in DMSO-d_6, δ

Compound	^1H Ar	^1H NH_2	^{13}C Ar	^{13}C C-Ar	^{14}N NO_2
3a*	8.47	8.16	147.90 134.05 133.58 130.58 125.33 121.96	160.23	−8.7
3b**	8.33	8.13	148.34 134.65 128.65 123.81	160.36	−13.4
3c	7.6— 7.9	7.66	134.88 129.48 128.47 127.47	160.89	—
3d	7.6— 7.9	7.96	131.52 129.69 127.61 123.56	160.94	—

* The signals of 3-nitrobenzamidoxime were also observed.
**^{15}N NMR, δ: −272.99 ($^1J_{H-^{15}N}$ = 82.3 Hz).

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

A. B. Sheremetev,* A. S. Kulikov, and L. I. Khmel'nitskii

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

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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