SYNTHESES WITH NITRILE OXIDES.
2.* REACTION OF AROMATIC NITRILE OXIDES WITH BIS(TRIMETHYLSILYLCARBODIIMIDE)

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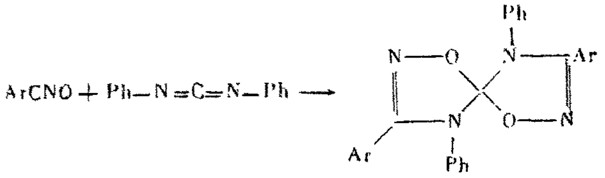
The reaction of aromatic nitrile oxides with bis(trimethylsilylcarbodiimide) gives 5-amino-3-aryl-1,2,4-oxadiazoles.

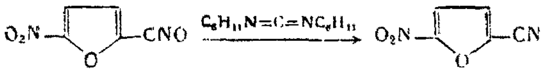
Keywords: *nitrile oxides, oxadiazoles, carbodiimide.*

Nitrile oxides usually undergo facile 1,3-dipolar cycloaddition with compounds containing a C═N bond (see the monograph of Grundmann [2], p. 128). Only two examples of the reaction of nitrile oxides with carbodiimides have been reported. In one case, reaction with diphenylcarbodiimide leads to the addition of two nitrile oxide molecules to give the corresponding spiro compound [3]:

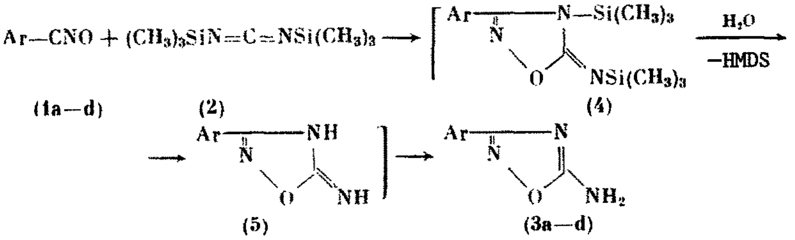


Ar = 2, 4, 6-$Me_3C_6H_2$, 4-$NO_2C_6H_4$.

In the other case, only the corresponding nitrile could be separated from the products of the reaction of 5-nitro-2-furonitrile oxide with dicyclohexylcarbodiimide [4]:



We have studied the reaction of aromatic nitrile oxides (**1a**)-(**1d**) with bis(trimethylsilylcarbodiimide) (**2**). The reaction does not proceed in the absence of catalyst. The use of boron trifluoride etherate leads to the formation of 5-amino-3-aryl-1,2,4-oxadiazoles (**3a**)-(**3d**). Intermediate (**4**) formed by the addition of nitrile oxide **1** to carbodiimide **2** is hydrolyzed in the presence of atmospheric moisture to give imine **5**, which, in turn, isomerizes to give amine **3**.



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

The reaction requires 24-48 h and, thus, the nitrile oxides partially undergo dimerization to give diarylfuroxanes (**6a**)-(**6d**).

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*For previous communication, see [1].

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TABLE 1. Reaction of Nitrile Oxides **1a-1d** with Bis(trimethylsilylcarbodiimide) **2**

Starting compound	Ar	Product	Yield, %	R_f	mp, °C	Ref.
1a	*m*-$O_2NC_6H_4$	**3a**	50	0.15	232–234	[6]
		6a	39	0.78	182–183	[7]
1b	*p*-$O_2NC_6H_4$	**3b**	36	0.19	287–288	[6]
		6b	33	0.81	203–204	[7]
1c	*p*-ClC_6H_4	**3c** *	49	0.13	240–242	
		6c	35	0.77	142–143	[7]
1d	*p*-BrC_6H_4	**3d** *	29	0.12	245–247	
		6d	38	0.74	162–163	[7]

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*Products **3c** and **3d** have not been described previously.

The data on the reaction of the nitrile oxides with bis(trimethylsilylcarbodiimides) are given in Table 1. Products **3c** and **3d** are reported for the first time. Their structures were indicated by elemental analysis, IR and NMR spectroscopy, and mass spectrometry.

EXPERIMENTAL

The IR spectra were taken on a Specord spectrometer for KBr pellets, while the mass spectra were taken on a Varian MAT CH-6 mass spectrometer. The ^1H and ^{13}C NMR spectra were taken on a Bruker AM-300 spectrometer at 300 and 75.5 MHz, respectively, relative to TMS as the internal standard. The melting points were obtained on a Boetius table at a heating rate of 4 deg/min at the melting point.

Nitrile oxides **1a-1d** were obtained according to Grundmann [2, p. 242], while bistrimethylsilylcarbodiimide **2** was obtained according to Stenzel and Sundermeyer [5].

Reaction of Aromatic Nitrile Oxides with Bistrimethylsilylcarbodiimides. General Method. A sample of 1.1 mmole carbodiimide **2** was added dropwise to a solution of 1 mole nitrile oxide **1a-1d** in 10 ml benzene and then, 0.2 mmole $BF_3 \cdot Et_2O$ was added with stirring. The reaction mixture was stirred for 24-48 h at 20-25°C until the starting nitrile oxide completely disappeared. The solvent was distilled off. The residue was subjected to chromatography on a column packed with L40/100 μ silica gel using 20:1 chloroform—acetone as the eluent. The results are given in Table 1.

5-Amino-3-(4-chlorophenyl)-1,2,4-oxadiazole (**3c**) has not been described previously. Found: C, 45.36; H, 3.25; Cl, 19.21; N, 23.01%. Calculated for $C_8H_6ClNO_3$: C, 45.78; H, 3.27; Cl, 19.35; N, 22.89%. IR spectrum for KBr pellet (ν, cm^{-1}): 3327 and 3124 (NH_2), 1666 (NH_2), 1600 (C═N). PMR spectrum in DMSO-d_6 (δ, ppm): 6.18 s (2H, NH_2), 7.51-7.99 m (4H, C_6H_4). ^{13}C NMR spectrum in DMSO-d_6 (δ, ppm): 126.53 (C_i), 128.41 (C_o), 129.06 (C_m), 135.56 (C_p), 166.81 (C−Ph), 172.31 (C−NH_2). Mass spectrum, *m/z*: 183 $(M)^+$.

5-Amino-3-(4-bromophenyl)-1,2,4-oxadiazole (**3d**) has not been described previously. Found: C, 43.83; H, 3.11; Br, 41.53; N, 21.79%. Calculated for $C_8H_6BrNO_3$: C, 43.75; H, 3.12; Br, 41.67; N, 21.88%. IR spectrum for KBr pellet (ν, cm^{-1}): 3336 and 3127 (NH_2), 1666 (NH_2), 1600 (C═N). PMR spectrum in DMSO-d_6 (δ, ppm): 6.18 s (2H, NH_2), 7.51-7.93 m (4H, C_6H_4). ^{13}C NMR spectrum in DMSO-d_6 (δ, ppm): 124.38 (C_p), 126.68 (C_i), 128.64 (C_o), 132.05 (C_m), 166.92 (C—Ph), 172.31 (C—NH_2). Mass spectrum, *m/z*: 191 $(M)^+$.

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