CHEMISTRY OF FURAZANO[3,4-b]PYRAZINE.

# 5.* 1,2,3-TRIAZOLO[4,5-e]FURAZANO[3,4-b]PYRAZINE 6-OXIDES

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New representatives of a little-investigated class of compound — 1,2,3-triazole 2-oxides — were obtained by a nonphotochemical method. Mononitroamines and dinitroamines are produced during their formation as intermediate products.

The construction of planar polycondensed molecules based on the furazano[3,4-b]pyrazine fragment has proved a worthwhile direction of research; compounds with unique energy characteristics were obtained from them [2-5]. In a continuation of research into the chemistry of furazano[3,4-b]pyrazine [1, 5-10] we are reporting on some reactions of 5,6-diaminofurazano[3,4-b]pyrazine (I) [5, 9] leading to high-energy products.

While studying the nitration of the diamine (I) by nitronium fluoroborate or a mixture of trifluoroacetic anhydride and nitric acid, we established that 1,2,3-triazolo[4,5-e]furazano[3,4-b]pyrazine 6-oxide (II) was formed instead of the expected o-di(nitroamine) [5, 10].
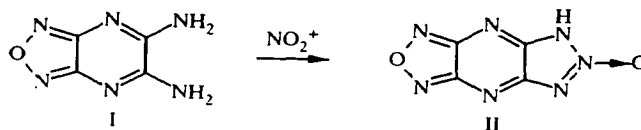

1,2,3-Triazole 1-oxides were obtained a long time ago and have been studied well [11, 12], but the 2-N-oxides are practically unknown. (An exception is the formation of benzotriazole 2-oxide during the photoisomerization of the 1-oxide [13].) We therefore studied the formation of the N-oxide (II), an intermediate in the synthesis of which is the mononitroamine (III), in greater detail. The direct cyclization of the nitroamine (III) to the N-oxide (II) must be caused by dehydration, but the formation of the N-oxide (II) was not observed during investigation of the behavior of the nitroamine (III) under the influence of such dehydrating agents as sulfuric acid or trifluoroacetic anhydride. The nitroamine (III) was decomposed by concentrated sulfuric acid to 5-amino-6-hydroxyfurazano[3,4-b]pyrazine (IV).
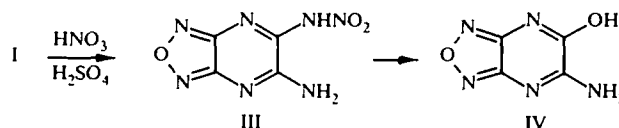

The cyclization of the nitro derivatives (V) to the 1-N-oxides takes place under the conditions of alkaline catalysis and includes nucleophilic attack on the nitrogen atom of the nitro group. The reaction begins with deprotonation of the hydrazine function [11]:

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*For Communication 4, see [1].
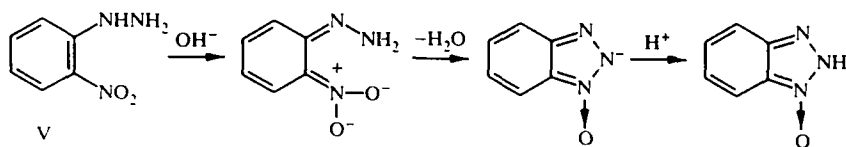
The main structural difference between the nitroamine (III) and the nitrohydrazine (V) is the different arrangement of the amino and nitro groups. It is for this reason that the 2-N-oxide and not the 1-N-oxide is formed during the cyclization of the nitroamine (III). The cyclization of derivatives with amino−nitroamino structural fragments had not been investigated before. In our case the nitroamine (III), unlike the nitrohydrazine (V), did not undergo cyclization under the influence of alkali, and this is probably explained the fact that the nitroamino group, the proton of which is significantly more "acidic," and not the amino group undergoes deprotonation.

Thus, the cyclization of the nitroamine (III) only takes place under the influence of the nitrating mixture. In our opinion the reaction takes place through a stage involving the formation of the dinitroamino derivative, which is in turn converted into the N-oxide. This suggestion is supported by the fact that the nitration of the monomethylamino derivative (VI) also leads to the 2-N-oxide (VII), while the nitration of the dimethyl derivative (VIII) leads to the dinitroamine (IX), which is incapable of cyclization on account of the absence of a mobile hydrogen atom:

I, II R = H; VI, VII R = Me
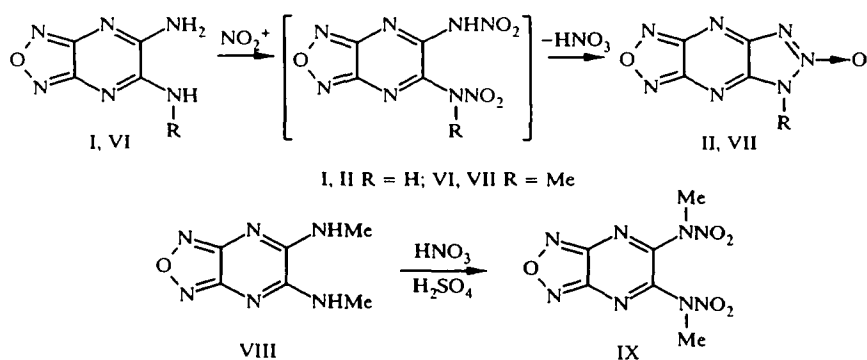
The structure of the obtained 2-N-oxide (II) was confirmed by the data from elemental analysis and IR, mass, and ^{1}H and ^{13}C NMR spectroscopy. In the mass spectrum of this compound there is a molecular peak at 179 (M^+), and elimination of the NO group, characteristic of furazans, with the formation of a fragment with mass 149 is observed. The ^{13}C NMR spectrum only contains two signals at 163.09 and 156.99 ppm. The reason for this is clearly the averaging of the signals for the carbon of the furazan and triazole rings as a result of the migration of a proton:

The PMR spectrum contains one singlet at −12.07 ppm, belonging to the NH proton. The most convincing evidence for the proposed structure is provided by x-ray crystallographic analysis of the methyl derivative of the 2-N-oxide (VII) (Fig. 1). The bond lengths, bond angles, and atomic coordinates in the structure of compound (VII) are given in Tables 1-3. The molecule contains 16 electrons in the π orbitals, i.e., is not aromatic. The stabilization of the planar nonaromatic system (Ia = 53, [7]) is due to the strong electron-accepting characteristics of the five-membered heterocycles condensed with the pyrazine. Due to this the excess π-electron charge is transferred from the π orbitals of the pyrazine ring. It is clear that delocalization of the electron density takes place not along the peripheral contour of the molecule but mainly in the five-membered heterocycles, i.e., there is a tendency for the π electrons to unite into groups of aromatic character, each containing 6 π electrons.

The derivative (VII) was also synthesized by the alkylation of the N-oxide (II) by dimethyl sulfate, and this confirms the proposed structure.

TABLE 1. Bond Lengths in the Molecule of Compound (VII)

Bond	δ, Å	Bond	δ, Å
$O_{(1)}$—$N_{(2)}$	1,221(3)	$C_{(6)}$—$C_{(10)}$	1,427(4)
$N_{(2)}$—$N_{(3)}$	1,316(4)	$N_{(7)}$—$O_{(8)}$	1,389(4)
$N_{(2)}$—$N_{(13)}$	1,392(3)	$O_{(8)}$—$N_{(9)}$	1,395(3)
$N_{(3)}$—$N_{(13)}$	1,380(4)	$N_{(9)}$—$C_{(10)}$	1,314(4)
$C_{(4)}$—$N_{(5)}$	1,303(4)	$C_{(10)}$—$N_{(11)}$	1,378(4)
$C_{(4)}$—$C_{(12)}$	1,466(4)	$N_{(11)}$—$C_{(12)}$	1,301(3)
$N_{(5)}$—$C_{(6)}$	1,375(4)	$C_{(12)}$—$N_{(13)}$	1,359(4)
$C_{(6)}$—$N_{(7)}$	1,316(4)	$C_{(13)}$—$C_{(14)}$	1,452(4)

TABLE 2. Bond Angles in the Molecule of Compound (VII)

| Angle	ω, deg	Angle	ω, deg
$O_{(1)}$—$N_{(2)}$—$N_{(3)}$	125,6(2)	$N_{(7)}$—$O_{(8)}$—$N_{(9)}$	112,8(2)
$O_{(1)}$—$N_{(2)}$—$N_{(13)}$	120,4(2)	$O_{(8)}$—$N_{(9)}$—$C_{(10)}$	103,8(2)
$N_{(3)}$—$N_{(2)}$—$N_{(13)}$	114,0(2)	$C_{(6)}$—$C_{(10)}$—$N_{(9)}$	109,8(2)
$N_{(2)}$—$N_{(3)}$—$C_{(4)}$	105,0(2)	$C_{(6)}$—$C_{(10)}$—$N_{(11)}$	125,1(2)
$N_{(3)}$—$C_{(4)}$—$N_{(5)}$	125,2(3)	$N_{(9)}$—$C_{(10)}$—$N_{(11)}$	125,1(2)
$N_{(3)}$—$C_{(4)}$—$C_{(12)}$	109,3(2)	$C_{(10)}$—$N_{(11)}$—$C_{(12)}$	108,1(2)
$N_{(5)}$—$C_{(4)}$—$C_{(12)}$	125,5(3)	$C_{(4)}$—$C_{(12)}$—$N_{(11)}$	127,2(2)
$C_{(4)}$—$N_{(5)}$—$C_{(6)}$	109,0(2)	$C_{(4)}$—$C_{(12)}$—$N_{(13)}$	104,8(2)
$N_{(5)}$—$C_{(6)}$—$N_{(7)}$	125,1(3)	$N_{(11)}$—$C_{(12)}$—$N_{(13)}$	127,9(2)
$N_{(5)}$—$C_{(6)}$—$C_{(10)}$	125,1(3)	$N_{(2)}$—$N_{(13)}$—$C_{(12)}$	106,8(2)
$N_{(7)}$—$C_{(6)}$—$C_{(10)}$	109,8(3)	$N_{(2)}$—$N_{(13)}$—$C_{(14)}$	120,8(3)
$C_{(6)}$—$N_{(7)}$—$O_{(8)}$	103,8(2)	$C_{(12)}$—$N_{(13)}$—$C_{(14)}$	132,4(3)
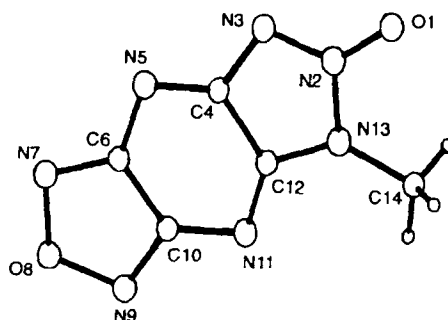
Fig. 1. General appearance of the molecule of compound (VII).

Initially the nitroamine (III) was obtained with a mixture of nitric acid and acetic anhydride as nitrating agent. A safer and more convenient method has now been developed for the nitration of the diamine (I) in a sulfuric — nitric acid mixture at 20°C with a yield of 93%. It is interesting that the N-oxide (II) is formed in the same mixture but at an elevated temperature (70°C). Unfortunately, this method cannot provide a preparative method, due to the difficulty of isolating the 1,2,3-triazolo[4,5-e]furazano[3,4-b]pyrazine 6-oxide (II) on account of its high solubility in water.

EXPERIMENTAL

The IR spectra were recorded in Nujol on a Perkin-Elmer 580B instrument. The PMR spectra were obtained in DMSO-d_6 on a Bruker WH-90/DS spectrometer at 22.63 MHz in DMSO-d_6 solution. The mass spectra were obtained on a VS-50AET instrument at 70 eV. The purity of the products was monitored by TLC on Silufol UV-254 plates and also by HPLC on a Du Pont 850 chromatograph with a column of Zorbax SIL (4.6 × 250 mm). The derivatograms were recorded on AN OD-103 MOM derivatograph (Hungary). The heating rate was 5 deg/min, and the sample weight was 50-80 mg.

TABLE 3. Coordinates of the Nonhydrogen Atoms and Hydrogen Atoms in the Molecule of Compound (VII)

Atom	x	y	z
O$_{(1)}$	0,52635	0,28428	0,43221
N$_{(2)}$	0,59325	0,24325	0,37317
N$_{(3)}$	0,58096	0,37906	0,31091
C$_{(4)}$	0,67385	0,26024	0,25941
N$_{(5)}$	0,69136	0,33106	0,18920
C$_{(6)}$	0,78772	0,16508	0,15428
N$_{(7)}$	0,82918	0,17980	0,08295
O$_{(8)}$	0,92415	-0,02719	0,07425
N$_{(9)}$	0,94233	-0,16847	0,14090
C$_{(10)}$	0,85721	-0,04946	0,18982
N$_{(11)}$	0,83792	-0,12099	0,26434
C$_{(12)}$	0,74579	0,03935	0,29539
N$_{(13)}$	0,69303	0,03845	0,36748
C$_{(14)}$	0,72214	-0,12784	0,43186
H$_{(14)}$	0,77691	-0,05402	0,47501
H$_{(14)}$	0,78495	-0,25410	0,41893
H$_{(14)}$	0,61900	-0,19343	0,44156

TABLE 4. Characteristics of the Synthesized Compounds

Com-pound	Molecular formula	mp, °C	IR spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm	Yield, %
II	C$_4$HN$_7$O$_2$	237...239	955 (furazan) ; 1520, 1620 (C-N); 1640 (N—O)	12,07 (1H, s, NH)	92
III	C$_4$H$_3$N$_7$O$_3$	219...220	1020 (furazan) ; 1310 (NO$_2$); 1575 (C-N); 3150, 3438 (NH, NH$_2$)	6,20 (2H, s, NH$_2$); 7,71 and 8,33 (1H, s, s NH)	93
IV	C$_4$H$_3$N$_5$O$_2$	294...296 (dec.)	1018 (furazan) ; 1630, 1707 (C-N); 3280, 3430 (NH, OH)	7,96and8,40 (2H, s, s, NH$_2$); 12,51 (1H, s, OH)	87
VII	C$_5$H$_3$N$_7$O$_2$	258...259	1030 (furazan); 1610 (C-N); 1640 (N—O)	3,89 (3H, s, CH$_3$)	75
IX	C$_6$H$_6$N$_8$O$_5$	154...155	1033 (furazan); 1270, 1570 (NO$_2$)	3,75 (6H, s, CH$_3$)	79

Elemental analysis for C, H, and N was conducted on a Carlo-Erba instrument.

1,2,3-Triazolo[4,5-e]furazano[3,4-b]pyrazine 6-Oxide (II). To a nitrating mixture prepared from 60 ml of trifluoroacetic anhydride and 25 ml of anhydrous nitric acid we added 15.20 g (0.1 mole) of the diamine (I) [9] in portions over 5 min at −8 to −10°C. After 10 min the cooling bath was removed, and the mass was kept at 20°C for 30 min. The nitrating mass was then cooled to −22°C and quickly filtered. The bright-yellow crystals were dried over potassium hydroxide under vacuum. Mass spectrum (m/z): 179 (M$^+$), 149 (M−NO), 135 (M−N$_2$O), 105 (M−NO−N$_2$O). ^{13}C NMR spectrum: 163.09 and 156.99 ppm (pyrazine). Found, %: C 26.70; H 0.51; N 54.97. C$_4$HN$_7$O$_2$. Calculated, %: C 26.81; H 0.56; N 54.75. The temperature at the beginning of intense decomposition was 224°C.

5-Amino-6-nitroaminofurazano[3,4-b]pyrazine (III). We added 5.0 g (0.033 mole) of the diamine (I) [9] in small portions to a mixture of 30 ml of concentrated sulfuric acid and 15 ml of anhydrous nitric acid with cooling in an ice bath. After stirring for 10 min we removed the ice bath and kept the mixture at 20°C for 1 h. The nitrating mass was then poured onto ice and water (100 g), and the precipitate was filtered off. The product was washed with water (3 × 30 ml); the impure product was recrystallized from aqueous acetone. Found %: C 24.24; H 1.43; N 49.49. C$_4$H$_3$N$_7$O$_3$. Calculated %: C 24.37; H 1.53; N 49.75.

5,6-Di(methylnitroamino)furazano[3,4-b]pyrazine (IX) was obtained similarly from the amine (VIII) [8]. Found %: C 37.72; H 3.27; N 58.72. C$_6$H$_6$N$_8$O$_5$. Calculated %: C 37.89; H 3.16; N 58.95.

5-Amino-6-hydroxyfurazano[3,4-*b*]pyrazine (IV). We added 0.98 g (0.005 mole) of the nitroamine (III) to 5 ml of concentrated sulfuric acid. The mixture was heated at 70°C for 10 min, cooled, and poured onto 50 g of ice. After neutralization of the acid with sodium carbonate the precipitate was filtered off. The product was washed with water (2 × 5 ml) and crystallized from ethylene glycol. Found %: C 31.03; H 1.85; N 45.97. $C_4H_3N_5O_2$. Calculated %: C 31.38; H 1.97; N 45.74.

5-Methylfurazano[3,4-*b*]-1,2,3-triazolo[4,5-*e*]pyrazine 6-Oxide (VII). To a nitrating mixture prepared from 6 ml of anhydrous nitric acid and 14 ml of trifluoroacetic anhydride at 0°C we added 1.66 g (0.01 mole) of 5-amino-6-methyl-aminofurazano[3,4-*b*]pyrazine (VI) [9]. The temperature of the mixture was raised to 10°C, and the mixture was kept for 2 h. The nitration mass was poured onto ice, and the product was filtered off. After washing with water the product was recrystallized from aqueous acetone. Found %: C 31.33; H 1.45; N 51.01. $C_5H_3N_7O_2$. Calculated %: C 31.01; H 1.55; N 50.78.

X-Ray Crystallographic Investigation of the Molecule of (VII). Crystals of compound (VII), grown from aqueous acetone, were monoclinic: $a = 7.727(3)$, $b = 5.601(2)$, $c = 17.350(4)$ Å, $\beta = 96.60(3)°$, $Z = 4$, $d_{calc} = 1.72$ g/cm^3, space group P2$_1$/C. The intensities of 1336 reflections were measured on an automatic Syntex P2$_1$ diffractometer. The structure was interpreted by the direct method and refined by least-squares treatment in anisotropic approximation to $R = 0.045$. The atomic coordinates are given in Table 3.

REFERENCES

1. I. B. Starchenkov and V. G. Andrianov, Khim. Geterotsikl. Soedin., No. 11, 1561 (1997).
2. L. Willer and D. W. Moore, J. Org. Chem., **50**, 5123 (1985).
3. R. L. Willer, US Patent No. 4,503,229; Chem. Abs., **103**, 54099 (1986).
4. R. L. Willer, US Patent No. 4,539,405; Ref. Zh. Khim., 12N224P (1986).
5. I. B. Starchenkov, Thesis for Candidate of Chemical Sciences [in Russian], Riga (1989).
6. I. B. Starchenkov and V. G. Andrianov, Khim. Geterotsikl. Soedin., No. 5, 717 (1996).
7. I. B. Starchenkov, V. G. Andrianov, and A. F. Mishnev, Khim. Geterotsikl. Soedin., No. 2, 250 (1997).
8. V. G. Andrianov, I. B. Starchenkov, and A. F. Mishnev, Khim. Geterotsikl. Soedin., No. 8, 1120 (1997).
9. I. B. Starchenkov and V. G. Andrianov, Khim. Geterotsikl. Soedin., No. 10, 1402 (1997).
10. I. B. Starchenkov, V. G. Andrianov, and A. V. Eremeev, Furazano[3,4-*b*]-1,2,3-triazolo[4,5-*e*]pyrazine 6-Oxide and a Method for its Production [in Russian], USSR Inventor's Certificate No. 294,686 (1988).
11. R. N. Butter, Adv. Heterocycl. Chem., **21**, 323 (1977).
12. T. I. Godovikova, E. L. Ignat'eva, and L. I. Khmel'nitskii, Khim. Geterotsikl. Soedin., No. 2, 147 (1989).
13. M. P. Serve, W. A. Field, P. G. Seybold, and R. N. Steppel, J. Heterocycl. Chem., **12**, 811 (1975).