Synthesis, properties, and structures of 5-nitroalkyl-5*H*-(1,2,3)triazolo[4,5-*c*]furazans

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Methods for the synthesis of the first representatives of 5-nitroalkyl-5*H*-(1,2,3)triazolo[4,5-*c*]furazans have been developed, and some of their properties have been studied.

Key words: amino- and azidofurazans, azofurazans, 5-nitroalkyl-5*H*-(1,2,3)triazolo[4,5-*c*]furazans, diazotization, azo coupling, thermal and oxidative cyclization.

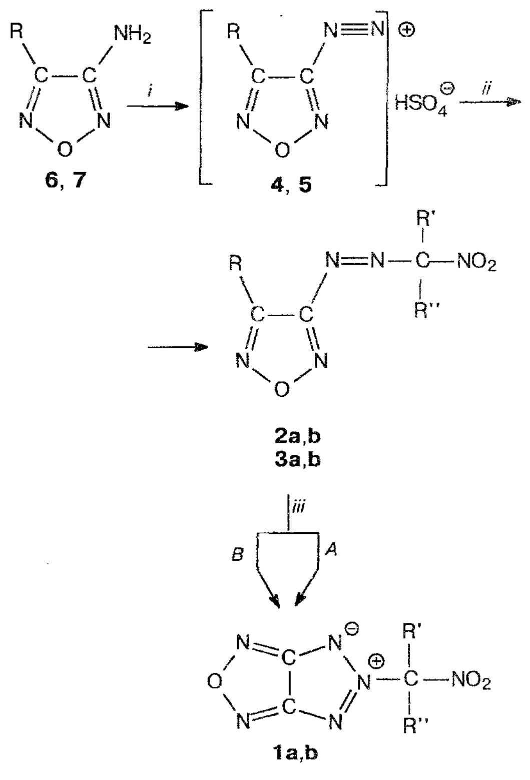
5-Substituted 1,2,3-triazolo[4,5-*c*]furazans are poorly investigated compounds. At this time, only 5-phenyl derivatives have been described.[1,2] In the present work we have considered the synthesis of the first representatives of 5-nitroalkyl-5*H*-(1,2,3)triazolo[4,5-*c*]furazans (**1a,b**) by thermocyclization of 3-azido-4-(nitroalkylazo)furazans (**2a,b**) (method *A*) or by oxidative cyclization of 3-amino-4-(nitroalkylazo)furazans (**3a,b**) by lead tetraacetate (method *B*). Compounds **3a,b** were prepared by azo coupling of the corresponding anions of nitroalkanes with diazonium salts derived from azido- (**4a,b**) or nitrofurazans (**5a,b**) (Scheme 1).

Since aminofurazans are weakly basic compounds, their diazotization was carried out by nitrosylsulfuric acid with addition of acetic acid,[2] and azo coupling with nitroalkane anions was carried out in the presence of 50 % aqueous alcohol. Under these conditions, the yields of 3-azido- and 3-amino-4-(nitroalkylazo)furazans were 46 to 93 %.

3-Azido-4-(2-nitropropylazo)furazan (**2a**) is a yellow oily liquid and 3-azido-4-(5-nitro-1,3-dioxanyl-5-azo)furazan (**2b**) is a yellow crystalline solid. Both compounds gradually decompose during storage to evolve nitrogen (the intensity of the absorption band due to the azide group in the IR spectrum decreases). The decomposition also affords the desired 5-(2-nitropropyl)-5*H*-(1,2,3)triazolo-[4,5-*c*]furazan (**1a**) and 5-(5-nitro-1,3-dioxanyl-5)-5*H*-(1,2,3)triazolo[4,5-*c*]furazan (**1b**). The formation of compounds **1a,b** dramatically accelerates when compounds **2a,b** are heated in an organic solvent (hexane, benzene, xylene, *etc.*). At 80 °C, the reaction is completed over a period of 3 h, and at 120 °C, it is completed over several minutes.

3-Amino-4-(2-nitropropylazo)furazan (**3a**) and 3-amino-4-(5-nitro-1,3-dioxanyl-5-azo)furazan (**3b**) are crystalline solids stable during storage. They are able to

Scheme 1



1a: $R' = R'' = Me$
1b: $R' = Me$; $R'' = CH_2—O—CH_2—O—CH_2$
2,4,6: $R = N_3$;
3,5,7: $R = NH_2$;
2a: $R' = R'' = Me$;
2b: $R', R'' = CH_2—O—CH_2—O—CH_2$

i. $NaNO_2/H_2SO_4$
ii. $R'R''C{=}NO_2$
iii. A. Benzene, boiling
B. Benzene, boiling, $Pb(AcO)_4$

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Table 1. Mass spectra of compounds **1a**, **1b**, and **2b**

Compound	*T*/°C	*m/z* (I_{rel}(%))*
1a	70	198 $[M]^+$ (2), 153 (32), 152 $[M - NO_2]^+$ (100), 113 (95), 97 (14), 96 (38), 94 (49), 82 $[M - 116]^+$ (19), 70 (13), 69 (12), 68 (12), 57 (27), 55 (45), 54 (20), 46 (23), 45 (13), 38 (23), 29 (41), 16 (30), 14 (25) (45), 55 (60), 54 (26), 52 (55), 40 (70), 39 (91), 38 (26), 29 (79), 24 (83)
1b	80	242 $[M]^+$ (9), 196 $[M - NO_2]^+$ (50), 168 (15), 166 (43), 141 (20), 138 (100), 111 (23), 102 (21), 86 (20), 82 $[M - 160]^+$ (37), 80 (50), 74 (25), 73 (20), 70 (32), 66 (20), 60 (16), 57 (45), 56 $[M - 186]^+$ (47), 54 (57), 53 (43), 52 (34), 49 (35), 48 (33), 41 (64), 40 (61), 39 (24), 26 (64)
2b	80	224 (6), 196 $[M - NO_2]^+$ (4), 166 (12), 164 (5), 139 (5), 138 (100), 134 (4), 112 (9), 108 (6), 83 (12), 82 $[M - 160]^+$ (12), 81 (11), 79 (5), 71 (22), 70 (14), 60 (15), 58 (35), 54 (31), 52 (32), 46 (33), 45 (22), 40 (52)

* The peaks of ions with intensities of ≥ 2 %.

undergo oxidative cyclization when heated with lead tetraacetate in benzene to give the corresponding 1,2,3-triazolo[4,5-*c*]furazans **1a** and **1b**.

Triazolo[4,5-*c*]furazans **1a** and **1b** are colorless crystals readily soluble in most organic solvents and insoluble in water. They are resistant to the action of concentrated or dilute acids but completely decompose through the action of concentrated solutions of alkalis (KOH or NaOH). According to the data of differential thermal analysis (DTA), the temperature of the onset of decomposition is 125 °C for compound **1a** and 114 °C for compound **1b**, and intense decomposition of both compounds occurs at 155 °C.

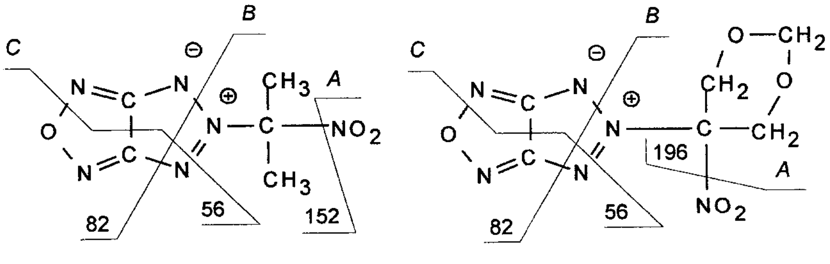
The structures of the compounds obtained were confirmed by elemental analysis and the set of IR, UV, ^{1}H NMR, and mass spectral data (See Experimental and Table 1).

The mass spectrum of compound **1a** exhibits a low-intensity peak corresponding to the molecular ion, *m/z*, 198 $[M^+]$ (2 % of the intensity of the maximal peak) only when the spectrum is recorded at 70 °C. In a spectrum recorded at 80 °C this peak no longer appears, which indicates low stability of this molecular ion. Conversely, the mass spectrum of compound **1b** recorded at 80 °C exhibits a relatively intense molecular ion peak, *m/z*, 242 $[M^+]$ (9 %), which indicates that this ion is rather stable.

The further decomposition of the molecular ions of both compounds occurs similarly, according to three main paths (Scheme 2): (1) the formation of intense $[M-46]^+$ ions through the cleavage of the C—NO_2 bond (path *A*); (2) the formation of an ion with *m/z* 82 due to the cleavage of the N—N and C—N bonds in the triazole ring (path *B*); (3) the formation of an ion with *m/z* 56 through the cleavage of the N—O and C—C bonds in the furazan ring and the N—N bond in the triazole ring (path *C*) leading to the formation of the rather stable nitrosocyane ion (O=N—C≡N). The fragmentation according to path *A* is typical of all of the nitro compounds, and the fragmentation according to path *B* is typical of fused triazoles.[3] Decomposition according to path *C* is specific and involves both rings. It can apparently serve as an analytical marker of the 1,2,3-triazolo[4,5-*c*]furazan system.

The mass spectrum of compound **2b** contains no molecular ion, probably due to its low stability, but the $[M-46]^+$ ion, which indicates decomposition of the molecular ion at the C—NO_2 bond, is recorded. The mass spectrum of this compound is to a large extent similar to that of compound **1b** (as regards the presence of ions with *m/z* 196 (50), 138 (100), 82 (37), *etc.* in the latter), which indicates that the fragment ion of compound **2b** can undergo cyclization to give the fragment ion of product **1b** through an electron impact.

Scheme 2



1a **1b**

Experimental

IR spectra were recorded on a Specord 75 IR spectrophotometer, UV spectra were obtained on a Specord UV-VIS instrument, ^{1}H NMR spectra were run on a Bruker WM-250 spectrometer (250 MHz), and mass spectra were obtained on a Varian MAT-112 mass spectrometer at an ionizing voltage of 70 eV. DTA was carried out using a MOM Q-1500-1500 derivatograph at a heating rate of 2.5 deg min^{-1}. The R_f values are given for Silufol 254 UV TLC plates.

Azofurazans (2a,b; 3a,b). At 0—5 °C, 10 mL of a 1 *N* solution of $NaNO_2$ in concentrated H_2SO_4 was added to a solution of 10 mmol of 3-azido-4-aminofurazan (**6**)^2 or diaminofurazan (**7**) in the minimum volume of concentrated H_2SO_4 at 0—5 °C. The solution was stirred for 15 min at 0—5 °C and diluted with an equal volume of glacial AcOH at 0—5 °C. The resulting solution was cooled to −15 to −10 °C, and a solution of 10 mmol of the sodium salt of 2-nitropropane or 5-nitro-1,3-dioxane in 50% aqueous ethanol cooled to −5 to 0 °C was added to it in one portion. The mixture was stirred for 1 h at 0—10 °C and poured into ice water. Products **2b** and **3a,c** were filtered off, washed with water, and dried. Compound **3b** was recrystallized from benzene, and product **2a** was extracted with CH_2Cl_2 and isolated after evaporation of the solvent.

3-Azido-4-(2-nitropropyl)azofurazan (2a). Yield 46 %, oily yellow liquid, R_f 0.47 (elution with chloroform). Found (%): C, 6.3; H, 2.7; N, 49.7. $C_5H_6N_8O_3$. Calculated (%): C, 26.55; H, 2.65; N, 49.56. IR (in NaCl plate), ν/cm^{-1}: 3025 w, 2970 w, 2910 w, 2275 m, 2150 s (N_3), 1560 s, 1550 s (as, NO_2), 1475 s, 1400 s, 1375 s, 1355 s (s, NO_2), 1290 s, 1230 m, 1210 m, 1175 s, 1040 s, 930 w, 850 s, 805 w, 760 m, 630 w, 630 m, 540 m.

3-Amino-4-(2-nitropropyl)azofurazan (3a). Yield 54 %, m.p. 98—99 °C, R_f 0.22 (elution with chloroform). Found (%): C, 30.7; H, 4.10; N, 41.90. $C_5H_8N_6O_3$. Calculated (%): C, 30.3; H, 4.04; N, 42.42. IR (KBr), ν/cm^{-1}: 3480 s, 3330 s (NH_2), 2950 m, 2930 s, 2855 m, 1620 s, 1550 s (as, NO_2), 1535 s, 1475 m, 1445 m, 1375 m, 1350 s (s NO_2), 1325 m, 1265 w, 1200 m, 1175 w, 1145 m, 1100 w, 1010 m, 930 w, 825 m, 750 m, 660 w, 580 m, 530 m.

3-Azido-4-(5-nitro-1,3-dioxanyl-5-azo)furazan (2b). Yield 53 %, m.p. 95—97 °C. An additional 22 % of the product with a melting point of 93—95 °C was isolated from the acidic mother liquor by extraction with CH_2Cl_2. The overall yield was 75 %. R_f 0.56 (elution with benzene). Found (%): C, 26.5; H, 2.2; N, 41.3. $C_6H_6N_8O_5$. Calculated (%): C, 26.67; H, 2.22; N, 41.48. IR (KBr), ν/cm^{-1}: 3040 w, 2960 w, 2925 w, 2890 w, 2260 w, 2175 m, 2140 m (N_3), 1580 s, 1560 s (as, NO_2), 1525 m, 1470 s, 1450 s, 1415 w, 1395 w, 1375 m (s, NO_2), 1350 w, 1280 s, 1200 m, 1150 s, 1080 m, 1040 s, 1025 s, 960 m, 950 m, 910 m, 860 w, 840 m, 825 m, 780 m, 725 m, 690 w, 640 m, 600 s, 585 m, 550 w, 515 w, 450 m. ^{1}H NMR, δ: 4.65 d (2 H_a), 4.88 d (2 H_e), (4 H, 2 CH_2O); 5.04 (H_a), 5.18 d (H_e), (2 H, OCH_2O).

3-Amino-4-(5-nitro-1,3-dioxanyl-5-azo)furazan (3b). Yield 93 %, m.p. 179—180 °C (from benzene). R_f 0.46 (elution with hexane : ethyl acetate, 1 : 4). Found (%): C, 29.6; H, 3.3; N, 34.2. $C_6H_8N_6O_5$. Calculated (%): C, 29.51; H, 3.28; N, 34.43. IR (KBr), ν/cm^{-1}: 3470 s, 3340 s (NH_2), 3245 m, 3190 m, 2950 w, 2925 w, 2880 m, 2785 w, 1630 s, 1560 s, 1550 s (as, NO_2), 1475 m, 1440 m, 1435 m, 1385 w, 1345 m (s, NO_2), 1295 m, 1250 w, 1190 m, 1145 s, 1060 s, 1040 s, 1025 s, 940 s, 910 s, 860 w, 845 m, 825 w, 750 m, 740 m, 690 w, 650 m, 580 w, 560 m.

5-(2-Nitropropyl)-5*H*-(1,2,3)triazolo-[4,5-*c*]furazan (1a). *A*. A solution of compound **2a** (1.03 g, 4.5 mmol) in 20 mL of benzene was boiled at reflux for 3 h until the starting compound disappeared. The reaction was monitored by TLC (elution with chloroform). The solvent was evaporated and the residue was recrystallized from hexane. Yield 0.88 g (98 %), m.p. 118—119 °C. R_f 0.67 (elution with chloroform). Found (%): C, 30.7; H, 3.0; N, 41.8. $C_5H_6N_6O_3$. Calculated (%): C, 30.3; H, 3.03; N, 42.4. IR (KBr), ν/cm^{-1}: 2960 w, 2900 w, 1615 w, 1570 s, 1555 s (as, NO_2), 1540 w, 1450 m, 1430 m, 1385 m, 1370 m, 1340 s (s, NO_2), 1325 m, 1255 s, 1180 s, 1140 s, 1045 m, 959 w, 925 w, 830 m, 810 m, 645 m, 610 m, 575 m, 560 m. ^{1}H NMR, δ: 2.62 s (6 H, $C(CH_3)_2NO_2$). UV (MeOH), λ_{max}/nm: 253, 313.5.

B. Compound **3a** (1.03 g, 5.1 mmol) in 50 mL of benzene was boiled at reflux in the presence of 3.0 g of lead tetraacetate for 26 h. The solid precipitate was filtered off, the mother liquor was concentrated, and the residue was recrystallized from chloroform. Yield 0.29 g (28 %), m.p. 116—118 °C. The value of the R_f and the IR spectrum were identcal to those of the product prepared by procedure *A*.

5-(5-Nitro-1,3-dioxanyl-5)-5*H*-(1,2,3)triazolo-[4,5-*c*]-furazan (1b) was prepared similarly to compound **1a**. The yield of **1b** prepared from **2b** according to procedure *A* was 95 % and the yield of **1b** prepared from **3b** by procedure *B* was 30 %, m.p. 115—117 °C (from CCl_4). R_f 0.43 (elution with benzene). *Found* (%): C, 29.5; H, 2.5; N, 34.3. $C_6H_6N_6O_5$. Calculated (%): C, 29.75; H, 2.47; N, 34.71. IR (KBr), ν/cm^{-1}: 3145 w, 3025 w, 2960 w, 2935 w, 2900 w, 2875 w, 2855 w, 2780 w, 1590 s, 1575 s (as, NO_2), 1475 s, 1445 s, 1430 m, 1395 m, 1330 s (s, NO_2), 1305 s, 1250 w, 1215 s, 1190 w, 1150 s, 1080 s, 1040 s, 960 w, 915 s, 825 m, 800 s, 780 s, 660 m, 625 w, 580 m, 475 w, 450 w. ^{1}H NMR, δ: 5.02 d (2 H_a), 5.18 d (2 H_e), (4 H, 2 CH_2O); 5.12 (H_a), 5.38 d (H_e), (2 H, OCH_2O). UV (MeOH), λ_{max}/nm: 256.5, 315.5.

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