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SYNTHESIS OF (1,2,3-TRIAZOL-1-YL)FURAZANS. 2*. REACTION OF AZIDOFURAZANS WITH MORPHOLINONITROETHENE

L. V. Batog, V. Yu. Rozhkov, Yu. A. Strelenko, O. V. Lebedev, and L. I. Khmel'nitskii

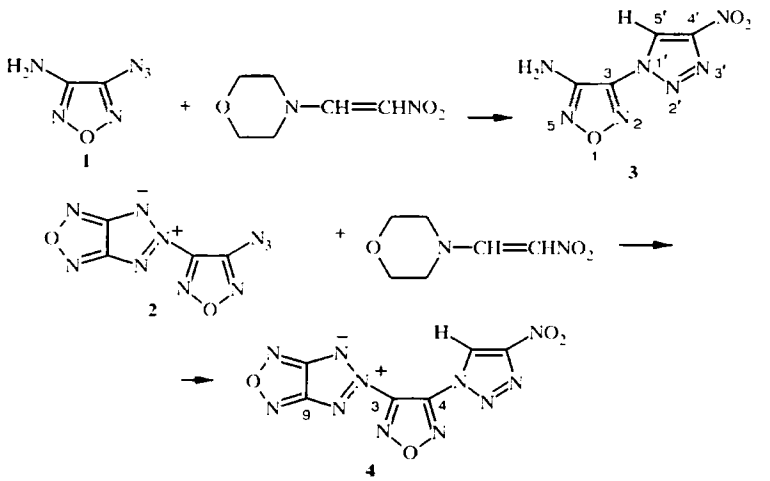
We have studied the 1,3-dipolar cycloaddition of azidofurazans to morpholinonitroethene and prepared 1,2,3-triazoles with furazan ring in position 1 and NO_2 group at position 4.

Keywords: 4-amino-3-azidofurazan, 5-(4-azido-1,2,5-oxadiazolyl)-5H-1,2,3-triazolo[4,5-*c*]-1,2,5-oxadiazole, morpholinonitroethene, 4-R-3-(4-nitro-1,2,3-triazol-1-yl)furazan, 1,3-cycloaddition.

We recently reported [1] the reaction of 4-amino-3-azidofurazan (**1**) and 5-(4-azido-1,2,5-oxadiazolyl)-5H-1,2,3-triazolo[4,5-c]-1,2,5-oxadiazole (**2**) with substituted acetylenes which had resulted in the first preparation of 1,2,3-triazoles with furazan ring at the 1-N atom and with different substituents (AlkOH, Ph, CH_2Cl, COOH, COOR) at position 5.

In this work, with the aim of preparing similar structures containing nitro group in the triazole ring, we have studied the cycloaddition of azidofurazans **1** and **2** to morpholinonitroethene. There are a few reports in the literature [2, 3] of the use of the latter for forming 1,2,3-triazoles.

As a result of the reaction of compounds **1** and **2** with morpholinonitroethene we have prepared the corresponding 1,2,3-triazoles **3** and **4** in high yields. It should also be mentioned that for cycloaddition of azide **2** to occur the reaction was carried out in the presence of orthoformic ester for removal of morpholine from the reaction medium, otherwise decomposition of the starting azide happens.



* For Communication 1 see [1].

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913; e-mail: mnm@carc.ioc.ac.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 406-408, March, 2000. Original article submitted September 15, 1998; revision submitted January 20, 1999.

TABLE 1. ^{15}N NMR Spectroscopic Data for Compound **3***

Nitrogen atom	$N_{(2)}$	$N_{(5)}$	$N_{(1')}$	$N_{(2')}$	NH_2
Chemical shift, δ, ppm	-21.5	-9.8	-145.8	-32.3	-337.0
n	4	3	2	3	1
J, Hz	0.5	2.5	4.2	1.2	88.6

* Signals for the $N_{(3')}$ atom and the nitrogen atom of the NO_2 group were not observed.

In the case of azide **1** the condensation discussed was studied in more detail in various solvents, *viz.* toluene, benzene, ethanol, butanol, carbon tetrachloride, and nitromethane. The reaction with morpholinonitroethene was found to occur quite slowly in refluxing solvent and depends strongly on the nature of the latter. The most suitable is toluene, in which compound **3** was obtained in 87% yield by refluxing the reagents for 70 h. Along with this main product several by-products were also formed (according to TLC) which are, evidently, a result of the instability of the starting compound (they were detected using TLC in control experiments after prolonged, separate refluxing of azide **1** and morpholinonitroethene).

At separation and purification of triazolylfurazan **3** it turned out that this compound is able to form, in the crystalline state, two mutually interconverting forms having different IR spectra (especially in the region of 3200-3500 cm^{-1}) and melting points. We have already reported similar features for 4-amino-3-(4-hydroxymethyl-1,2,3-triazolyl)furazan [1]. As in study [1], the lower-melting form for compound **3** (mp 188-189°C) was arbitrarily assigned the α- and the higher-melting (mp 194-195°C) the β-form. Depending on the nature of the solvent and also other factors (e.g. temperature) both a mixture of these two forms and also each of them separately without contamination by the other can be formed. Hence toluene and methanol permit formation of the β-form and water – the α.

The reason for the existence of two forms for compound **3** is evidently, as also proposed in [1], the formation of different types of hydrogen bond in them.

Reaction of azide **2** with morpholinonitroethene in the presence of orthoformic ester, in contrast to the reaction considered above, occurs quite rapidly. Even after 30 min refluxing of the reagents in benzene, the cycloaddition product **4** was obtained in 71% yield.

The structure of the synthesized triazolylfurazans **3** and **4** was established on the basis of the set of elemental analysis data and IR; ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR and mass spectra. ^{15}N NMR spectra for the compound were obtained using the INEPT pulse sequence [4] (see Table 1).

EXPERIMENTAL

IR spectra were taken using KBr pellets on an UR-20 spectrometer. ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a Bruker AM-300 spectrometer at 300, 75.5, 21.7, and 30.4 MHz respectively. The chemical shifts of signals from ^{14}N and ^{15}N were measured relatively to $MeNO_2$ as external standard and chemical shifts of ^{1}H and ^{13}C signals referred to the solvent. Mass spectra were taken on a Varian MAT CH-6 spectrometer. Monitoring by TLC was carried out on Silufol grade UV-254.

4-Amino-3-azidofurazan (1) and 5-(4-azido-1,2,5-oxadiazolyl)-5H-1,2,3-triazolo[4,5-c]-1,2,5-oxadiazole (2) were synthesized by a known method (see [5] and [1] respectively). Morpholinonitroethene was prepared on the basis of [6, 7].

4-Amino-3-(4-nitro-1,2,3-triazol-1-yl)furazan (3). Solution of morpholinonitroethene (1 g, 6.3 mmol) and azide **1** (0.88 g, 7 mmol) in toluene (30 ml) was refluxed for 70 h. The precipitate was filtered off and the filtrate was evaporated under vacuum. Solution of HCl (0.1 N, 40 ml) was added to the residue and, after 12 h, the acid layer was poured off and the residue washed with water until the water washings were neutral, and then dried

in air. Compound **3** (1.08 g, 87%) was obtained in the α-form. R_f 0.82 (benzene–ethyl acetate, 2: 1); mp 188-189°C (benzene). IR spectrum: 3475, 3430, 3350, 3340 (NH_2), 3155 (C–H), 3090, 1645, 1595, 1560, 1525, 1460, 1430, 1395, 1375, 1325, 1285, 1215, 1195, 1185, 1065, 1050, 1040, 1000, 980, 875, 860, 830; 760, 735 cm^{-1}. After refluxing in MeOH the product was obtained as the β-form with mp 194-195°C. IR spectrum: 3450, 3345 (NH_2), 3155 (CH), 1650, 1595, 1580 1570, 1560, 1535, 1460, 1430, 1395, 1370, 1325, 1280, 1220, 1195, 1060, 1040, 985, 875, 840, 760 cm^{-1}. ^1H NMR spectrum (acetone-d_6): 9.70 (1H, 2, CH); 6.30 ppm (2H, s, NH_2). ^{13}C NMR spectrum (DMSO-d_6): 153.48 ($C_{(4)}$); 151.88 ($C_{(4)}$); 142.67 ($C_{(6)}$); 125.59 ppm ($C_{(5)}$), (J_{C-H} = 212.9 Hz). ^{14}N NMR spectrum (DMSO-d_6): -27.2 ($\Delta\nu_{1/2}$ = 400 Hz) (NO_2). Mass spectrum, *m/z* (I_{rel}, %): 197 (100) $[M]^+$, 152 (9), 149 (15), 140 (17), 119 (14), 111 (98), 84 (10), 69 (68). Found, %: C 24.74; H 1.58; N 49.65. $C_4H_3N_7O_5$. Calculated, %: C 24.37; H 1.53; N 49.74.

5-[4-(4-Nitro-1,2,3-triazol-1-yl)furazan-3-yl]-5H-1,2,3-triazolo[4,5-c]furazan (4). Solution of the azide **2** (1.1 g, 5 mmol) and morpholinonitroethene (0.95 g, 6 mmol) in mixture of benzene and orthoformic ester (30 ml, 1: 1 by volume) was refluxed for 30 min. The reaction mixture was then evaporated to dryness and the solid residue was dissolved in a small amount of benzene and chromatographed on silica gel (40-100 μm) column (3 × 10 cm) with benzene as eluent. Compound **4** (0.8 g, 71%) was obtained; R_f 0.11 (benzene), mp 193-194°C (decomp.) (methanol). IR spectrum: 3145 (CH); 1600, 1590, 1560, 1500, 1440, 1410, 1400, 1380, 1320, 1300, 1280, 1255, 1210, 1180, 1130, 1050, 1040, 990, 950, 900, 870, 850, 825, 790, 760 cm^{-1}. ^1H NMR spectrum (acetone-d_6) 9.85 ppm (CH). ^{13}C NMR spectrum (DMSO-d_6): 166.63 (C_8); 154.42 (C_4); 149.76; 115.93; 128.18 ppm (CH). ^{14}N NMR spectrum (acetone-d_6): -28.89 (NO_2); -101.24; -155.54 ppm. Mass spectrum, *m/z* (I_{rel}, %): 246 (100) $[M-N_2OH]^+$, 216 (35) $[M-N_2OH-NO]^+$. Found, %: C 24.86; H 0.38; N 52.84. $C_6HN_{11}O_4$. Calculated, %: C 24.75; H 0.35; N 52.92.

REFERENCES

1. L. V. Batog, L. S. Konstantinova, V. Yu. Rozhkov, Yu. A. Strelenko, O. V. Lebedev, L. I. Khmel'nitskii, *Khim. Geterotsikl. Soedin.*, No. 1, 100 (2000).
2. D. Pocar, S. Maiorana, and P. Dalla Croce, *Gazz. Chim. Ital.*, **98**, 949 (1968).
3. S. Maiorana, D. Pocar, and P. Dalla Croce, *Tetrahedron Lett.*, **48**, 6043 (1966).
4. E. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, **101**, 760 (1979).
5. O. A. Rakitin, O. A. Zalesova, A. S. Kulikov, N. N. Makhova, T. I. Godovikova, and L. I. Khmel'nitskii, *Izv. Russ. Akad. Nauk, Ser. Khim.*, No. 11 , 1949 (1993).
6. Synthesis of Organic Compounds [Russian translation], Inostr. Lit., Moscow (1953), Vol. 4, p. 596.
7. D. Hurd and L. T. Sherwood, *J. Org. Chem.*, **13**, 471 (1948).