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SYNTHESIS OF 4-R-3-(4-R^1-5-R^2-1,2,3-TRIAZOL-1-YL)FURAZANS. 1. AZIDOFURAZANS IN 1,3-DIPOLAR CYCLOADDITION REACTIONS WITH SUBSTITUTED ACETYLENES

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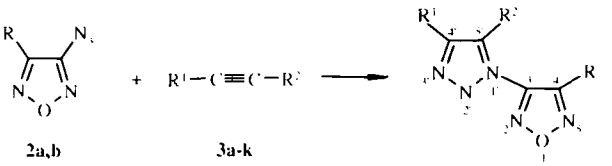
The 1,3-dipolar cycloaddition of azidofurazans to substituted acetylenes has been studied and substituted 3-(1,2,3-triazol-1-yl)furazans have been synthesized.

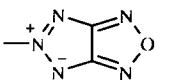
Keywords: 1,3-cycloaddition, 4-amino-3-azido-furazan, 5-(4-azido-1,2,5-oxadiazolyl)-5H-1,2,3-triazolo-[4,4-*c*]-1,2,5-oxadiazole, substituted acetylenes, 4-amino-3-(1,2,3-triazol-1-yl)furazans.

Furazans and 1-substituted 1,2,3-triazoles attract the attention of investigators as being substances distinguished by a broad spectrum of biological activity [1-4]. From this point of view structures of type **1** containing both heterocycles linked by a N–C bond might give rise to undoubted interest, however they have not been reported in the literature.



2a,b **3a-k** **1a-v**

1 a-v R = NH_2; **a** R^1 = CH_2OH, R^2 = H; **b** R^1 = H, R^2 = CH_2OH; **c** R^1 = CMe_2OH, R^2 = H; **d** R^1 = CH_2Cl, R^2 = H; **e** R^1 = H, R^2 = CH_2Cl; **f** R^1 = Ph, R^2 = H; **g** R^1 = H, R^2 = Ph; **h** R^1 = COOH, R^2 = H; **i** R^1 = H, R^2 = COOH; **j** R^1 = COOEt, R^2 = H; **k** R^1 = H, R^2 = COOEt; **l** R^1 = CHMeOH, R^2 = H; **m** R^1 = H, R^2 = CHMeOH; **n** R^1 = R^2 = CH_2OH; **o** R^1 = R^2 = CMeEtOH; **p** R^1 = R^2 = COOH; **q** R^1 = R^2 = COOMe; **r** R^1 = COOMe, R^2 = H; **s** R^1 = R^2 = H; **t-v** R = Z; **t** R^1 = CH_2OH, R^2 = H; **u** R^1 = H, R^2 = CH_2OH; **v** R^1 = R^2 = CH_2OH.
2a R = NH_2; **b** R = Z. **3 a-g** R^1 = H; **a** R^2 = CH_2OH; **b** R^2 = CMe_2OH; **c** R^2 = CH_2Cl; **d** R^2 = Ph; **e** R^2 = COOH; **f** R^2 = COOEt; **g** R^2 = CHMeOH; **h** R^1 = R^2 = CH_2OH; **i** R^1 = R^2 = CMeEtOH; **j** R^1 = R^2 = COOH; **k** R^1 = R^2 = COOMe

Z = 

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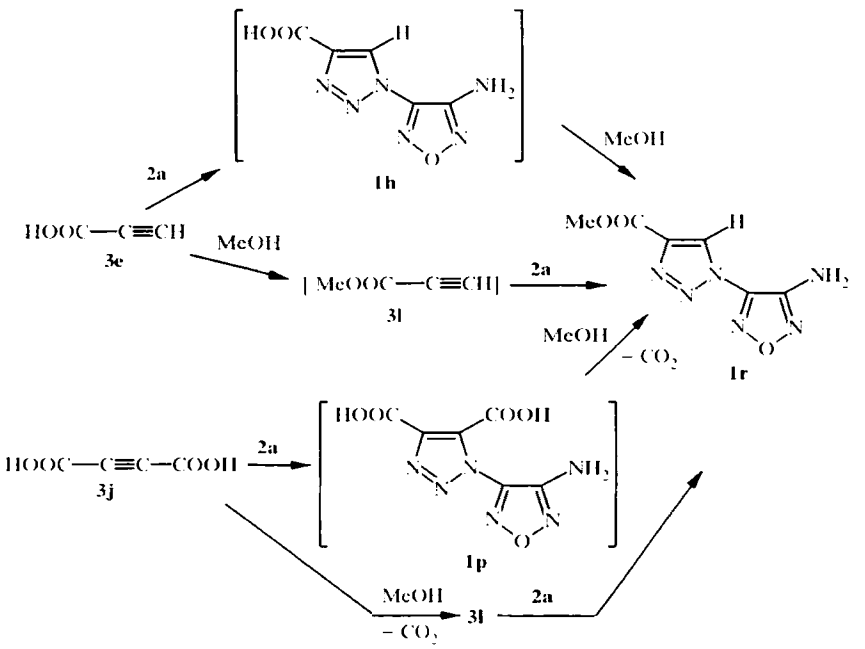
To us it seemed possible to obtain triazolyl-furazans **1** by the known method of synthesis of 1-substituted 1,2,3-triazoles by the reaction of various azides with acetylenes [5]. In this work the 1,3-dipolar cycloaddition of azidofurazans to acetylenes was used for the first time. 4-Amino-3-azidofurazan (**2a**) and 5-(4-azido-1,2,5-oxadiazolyl)-5H-1,2,3-triazolo[4,5-*c*]-1,2,5-oxadiazole (**2b**) were selected as reactants in addition to the mono- and disubstituted acetylenes **3a-k**. The behavior of azide **2a** in the 1,3-dipolar cycloaddition reaction was studied in the greatest detail. Azide **2b** was only reacted with acetylenes **3a** and **3h**. The reaction was carried out with an excess of the dipolarophile **3** by boiling in various organic solvents for 20-100 h. A check on the progress of reactions was carried out using TLC.

The 1,2,3-triazoles (**1a-v**) with the furazan ring substituted at the $N_{(1)}$ nitrogen atom were synthesized for the first time by the reaction indicated (Tables 1-3). The structure of these compounds was established by a combination of results of elemental analysis, data of IR spectra, ^1H, ^{13}C, ^{14}N (**1q**), and ^{15}N (**1b**) NMR, mass spectra, and X-ray structural analysis (**1a,n**)*.

Compound **1r** was obtained unexpectedly on carrying out the reaction of azide **2a** with acetylenecarboxylic acids **3e** or **3j** in MeOH. Its formation under these conditions may be explained by esterification of the carboxyl group in the initial acids **3e** and **3j** or in the initial products of cycloaddition to azide **2a** (**1h** and **1p**). In addition a necessary condition of obtaining ester **1r** from compounds **3j** or **1p** must be the decarboxylation of one of the COOH groups.



Decarboxylation as a byreaction takes place in the reaction of azide **2a** with acetylenes **3e** and **3j** indicated by the formation of the monocarboxylic acid **1h** from acetylenedicarboxylic acid **3j** (expt. 13, Table 3) and 4,5-unsubstituted triazolylfurazan (**1s**) from acetylenecarboxylic acid **3e** (expt. 7, Table 3). Compound **1s** was recorded from the data of the ^1H NMR spectrum together with isomers **1h** and **1i** (see footnote *[2] to Table 2).

The regiodirectivity of the addition of azide **2a** to certain monosubstituted acetylenes was clarified with the aid of ^1H and ^{13}C NMR spectroscopy. It was established that the reaction of this compound with acetylenes **3a,g** occurs regioselectively with a predominance of the 5-isomer, with acetylenes **3e,f** of the 4-isomer. On reaction with acetylene **3b** practically only the 4-isomer **1c** was formed.

* The X-ray structural investigations on compounds **1a** and **1n** will be published in a separate paper.

TABLE 1. Characteristics of the Synthesized 4-R-3-(4-R^1-5-R^2-1,2,3-triazol-1-yl)furazans **1**

Compound	Empirical formula	Found, % Calculated, %			mp, °C (solvent)	R_f (solvent system)
		C	H	N		
1a	$C_5H_5N_9O_2$	33.16 32.50	3.42 3.29	46.32 46.20	146-147* (dry EtOAc) 165-166*[2] (MeOH)	0.22 ($CHCl_3$–Me_2CO–MeOH, 10:2:1)
1b	$C_5H_6N_8O_2$	33.05 32.90	3.37 3.29	46.28 46.20	195-196 (EtOAc)	0.34 ($CHCl_3$–Me_2CO–MeOH, 10:2:1)
1c	$C_5H_{10}N_8O_2$	39.76 40.00	4.75 4.80	39.86 40.00	110-111 (H_2O)	0.11 (PhH–EtOAc, 3:1)
1d	$C_5H_5ClN_8O$*[3]	29.24 29.42	2.39 2.49	41.70 41.94	145-148 (CH_2Cl_2)	0.76 (CH_2Cl_2–EtOAc, 3:1)
1e	$C_5H_5ClN_8O$*[4]	29.26 29.42	2.41 2.49	41.75 41.94	100-104*[5]	0.66 (CH_2Cl_2–EtOAc, 3:1)
1f	$C_{10}H_6N_8O$	52.50 52.62	3.48 3.54	36.51 36.83	231-232 (PhH)	0.63 (PhH–EtOAc, 3:1)
1g	$C_{10}H_6N_8O$*[6]	—	—	—	107-108 (MeOH)	0.46 (PhH–EtOAc, 3:1)
1h	$C_5H_3N_9O_3$	30.66 30.60	2.06 2.04	43.02 42.80	174-175 (MeOH)	0.22 (PhH–MeOH, 11:4)
1j	$C_5H_8N_8O_3$	37.63 37.50	3.65 3.57	37.72 37.50	133-134 (EtOAc)	0.40 (PhH–EtOAc, 2:1)
1m	$C_6H_6N_8O_2$	36.51 36.73	4.08 4.12	42.72 42.85	118-119 (H_2O)	0.67 (PhH–EtOAc, 3:1) 3-fold elution
1n	$C_6H_8N_8O_3$	33.77 33.96	3.71 3.76	39.12 39.50	162-163 (H_2O)	0.25 ($CHCl_3$–Me_2CO–MeOH, 10:2:1)
1o	$C_{12}H_{30}N_8O_4$	48.57 48.63	6.70 6.82	28.06 28.37	159-160 (H_2O)	0.81 (PhH–Me_2CO, 1:1)
1p	$C_6H_3N_9O_3$	30.51 30.20	1.68 1.67	35.08 35.00	161-162 (precipitation from EtOAc by hexane)	0.13 (PhH–MeOH, 11:3)
1q	$C_5H_8N_8O_4$	35.93 35.82	2.87 2.98	32.56 31.34	144-145 (MeOH)	0.50 (PhH–EtOAc, 2:1)
1r	$C_6H_6N_8O_3$	34.04 34.28	2.80 2.86	39.63 40.00	198-199 (EtOAc)	0.42 (PhH–MeOH, 11:3)
1t + 1u	$C_5H_5N_{10}O_3$	*[7]			Oil	0.22; 0.38 (PhH–EtOAc, 3:1)
1v	$C_5H_8N_{10}O_4$	31.27 31.38	1.89 1.98	45.52 45.75	148-149 (PhH)	0.15 (PhH–EtOAc, 3:1)

* mp of α-form.

*[2] mp of β-form.

*[3] Found, %, Cl 17.49. Calculated, %, Cl 17.70.

*[4] Found, %, Cl 17.59. Calculated, %, Cl 17.70.

*[5] Not crystallized.

*[6] Elemental analysis unsuccessful.

*[7] According to ^{13}C NMR data the mixture of compounds **1t,u** contains contamination by byproducts.

In difference to the above azide **2a** reacts with propargyl chloride (**3c**) and with phenylacetylene (**3d**), and azide **2b** reacts with propargyl alcohol (**3a**) forming mixtures of isomers **1d,e**, **1f,g**, and **1t,u** respectively in approximately equimolar amounts.

TABLE 2. Spectral Characteristics of the Synthesized Compounds **1a-v***

Compound	IR spectrum, ν, cm^{-1}	Mass spectrum, m z (I_{rel}, %)	^{13}C NMR spectrum, δ, ppm	^{1}H NMR spectrum, δ, ppm
1	2	3	4	5
1a	α-Form 3480, 3320, 3265, 3155, 3110, 2960, 2900, 1635, 1590, 1460, 1260, 1240, 1220, 1065, 1050, 1020, 1000, 980, 865, 835 β-Form 3420, 3320, 3160, 2930, 2880, 1645, 1595, 1460, 1420, 1360, 1250, 1230, 1075, 1045, 1030, 980, 870, 810	α-Form 182 (50 [M]$^+$), 153 (32 [M-N_2H]$^+$), 137 (85 [M-N_2-OH]$^+$), 111 (50), 106 (100), 97 (100), 95 (46), 84 (60), 82 (70), 61 (8), 60 (30), 59 (8), 58 (18), 57 (50), 56 (30) β-Form 182 (50 [M]$^+$), 153 (35 [M-N_2H]$^+$), 137 (100 [M-N_2-OH]$^+$), 111 (55), 106 (100), 97 (100), 95 (50), 84 (65), 82 (75), 61 (41), 60 (31), 59 (7), 58 (18), 57 (22), 56 (24)	151.05 ($C_{(3)}$); 149.21 ($C_{(5)}$); 142.90 ($C_{(3)}$); 122.96 ($C_{(5)}$); 54.52 (4'-CH_2)	8.56 (1H, s, 5'-H); 6.52 (2H, s, NH_2); 5.80 (1H, s, OH); 4.63 (2H, s, 4'-CH_2)
1b*[2]	3480, 3335, 3260, 3160, 3130, 2930, 2865, 1640, 1585, 1450, 1425, 1350, 1310, 1280, 1230, 1110, 1055, 985, 870	182 (100 [M]$^+$), 154 (23 [M-N_2]$^+$), 153 (29 [M-N_2H]$^+$), 138 (83), 124 (25), 106 (100), 84 (100)	151.77 ($C_{(3)}$); 142.94 ($C_{(5)}$); 141.05 ($C_{(5)}$); 133.09 ($C_{(4)}$); 53.69 (5'-CH_2)	7.95 (1H, s, 4'-H); 6.45 (2H, s, NH_2); 5.56 (1H, t, J = 3.6, OH); 4.90 (2H, d, J = 3.6, 5'-CH_2)
1c	3415, 3340, 3230, 2990, 2950, 2890, 1650, 1600, 1570, 1470, 1440, 1410, 1385, 1300, 1280, 1200, 1170, 1120, 1080, 1040, 995, 930, 910, 865, 770, 740	211 (4), 210 (4 [M]$^+$), 195 (4 [M-CH_3]$^+$), 168 (3 [M-CH_3-OH]$^+$), 167 (24), 137 (31), 125 (49), 109 (82), 98 (35), 83 (86), 55 (100)	156.96 ($C_{(3)}$); 151.01($C_{(5)}$); 142.90 ($C_{(3)}$); 120.77 ($C_{(4)}$); 66.94 (C-OH); 30.35 (CH_3)	8.54 (1H, s, 5'-H); 6.60 (2H, s, NH_2); 5.40 (1H, s, OH); 1.54 (6H, s, 2CH_3)

TABLE 2 (continued)

1	2	3	4	5
1d	3410, 3325, 3270, 3220, 3180, 1650, 1600, 1590, 1280, 1260, 1230, 1215, 1050, 980, 875, 735	200 (60 [M]$^+$), 138 (75), 137 (100), 115 (65), 100 (82), 95 (100), 84 (100)	151.15 ($C_{(3)}$); 144.79 ($C_{(7)}$); 142.87 ($C_{(4')}$); 124.58 ($C_{(5')}$); 35.49 (4'-CH_2)	8.90 (1H, s, 5'-H); 6.63 (2H, s, NH_2); 4.93 (2H, s, 4'-CH_2)
1e	3450, 3410, 3325, 3270, 3225, 3190, 3165, 3000, 2960, 1645, 1630, 1575, 1555, 1400, 1265, 1135, 1100, 1060, 980, 870, 785	200 (100 [M]$^+$), 165 (30[M-CH_2Cl]$^+$), 138 (40), 137 (100 [M-CH_2Cl-N_2]$^+$), 115 (100), 100 (60), 84 (100)	151.81 ($C_{(4)}$); 142.34 ($C_{(3)}$); 136.47 ($C_{(5')}$); 134.79 ($C_{(4')}$); 32.84 (5'-CH_2)	8.17 (1H, s, 4'-H); 6.67 (2H, s, NH_2); 5.09 (2H, s, 5'-CH_2)
1f	3465, 3430, 3325, 3140, 1640, 1590, 1560, 1485, 1460, 1425, 1355, 1330, 1290, 1260, 1240, 1100, 1110, 1080, 1050, 1020, 980, 960, 920, 875, 820, 770, 750	229 (1), 228 (1 [M]$^+$), 200 (2 [M-N_2]$^+$), 170 (56), 152 (5), 143 (28), 128 (20), 116 (74), 44 (100)	151.00 ($C_{(3)}$); 147.36 ($C_{(4')}$); 142.78 ($C_{(7)}$); 129.07 ($C_{(3',5')}$); 128.88 ($C_{(4')}$); 128.68 ($C_{(4',5')}$); 125.68 ($C_{(2',6')}$); 121.16 ($C_{(5')}$)	9.28 (1H, s, 5'-H); 8.00 (2H, d, J = 7.0, 2 o-H_{Ph}); 7.45 (2H, t, J = 7.0, 2 m-H_{Ph}); 7.35 (1H, t, J = 7.0, 1 n-H_{Ph}); 6.65 (2H, s, NH_2)
1g	3460, 3350, 1650, 1640, 1580, 1560, 1490, 1460, 1435, 1410, 1320, 1280, 1250, 1190, 1140, 1095, 1040, 1015, 990, 930, 910, 865, 770, 740, 705		153.67 ($C_{(3)}$); 143.98 ($C_{(7)}$); 140.99 ($C_{(5')}$); 134.32 ($C_{(4')}$); 131.01 ($C_{(4',5')}$); 129.80 ($C_{(2',6')}$); 129.72 ($C_{(3',5')}$); 126.25 ($C_{(4',5')}$)	8.10 (1H, s, 4'-H); 7.50 (5H, m, H_{Ph}); 6.18 (2H, s, NH_2)
1h*[3]	3425, 3300, 3210, 3150, 2950, 2760, 2665, 2580, 1720, 1640, 1590, 1540, 1460, 1420, 1280, 1245, 1185, 1040, 980, 890, 750	196 [M]$^+$, 152 [M-CO_2]$^+$, 111, 93, 84	161.37 (C=O); 151.67 ($C_{(3)}$); 143.22 ($C_{(7)}$); 141.11 ($C_{(5')}$); 129.64 ($C_{(4')}$)	13.50 (1H, br. s, COOH); 9.23 (1H, s, 5'-H); 6.59 (2H, s, NH_2)
1j*[4]	3490, 3335, 3150, 3010, 3000, 2955, 2920, 1745, 1640, 1590, 1475, 1455, 1380, 1355, 1280, 1255, 1190, 1160, 1120, 1040, 1025, 980, 870, 860, 845, 780, 730	224 (35 [M]$^+$), 179 (43), 151 (48), 138 (47), 120 (74), 110 (57), 95 (51), 84 (54), 69 (65), 58 (100)	160.44 (C=O); 152.08 ($C_{(3)}$); 143.75 ($C_{(7)}$); 141.55 ($C_{(5')}$); 129.11 ($C_{(4')}$); 62.21 (4'-CH_2); 14.62 (CH_3)	9.20 (1H, s, 5'-H); 6.27 (2H, s, NH_2); 4.45 (2H, q, J = 7.6; CH_2); 1.40 (3H, t, J = 7.6; CH_3)

TABLE 2 (continued)

1	2	3	4	5
1m*	3475, 3320, 3250, 3220, 3010, 2950, 2780, 2740, 1650, 1590, 1480, 1450, 1390, 1350, 1310, 1290, 1235, 1160, 1130, 1110, 1090, 1070, 1040, 1000, 990, 900, 870, 850, 750, 730	197 (37), 196 (100 $[M]^+$), 181 (2 $[M\text{-}CH_3]^+$), 179 (4 $[M\text{-}CH_3\text{-}OH]^+$), 153 (6), 152 (69), 124 (36), 110 (21), 96 (22), 94 (22)	152.46 ($C_{(1)}$); 145.10; 143.26; 131.95 ($C_{(3)}$); 59.69 (C-OH); 22.65(CH_3)	7.93 (1H, s, 4'-H); 6.52 (2H, s, NH_2); 5.80 (1H, d, J = 5.7, OH); 5.10 (1H, m, CH); 1.43 (3H, d, J = 7.3, CH_3)
1n	3440, 3370, 3310, 3260, 3000, 2950, 2870, 1635, 1575, 1460, 1350, 1285, 1255, 1190, 1140, 1070, 1030, 1000, 970, 870	212 (21 $[M]^+$), 165 (20), 153 (100), 136 (100), 110 (85), 94 (43), 84 (100)	143.05 ($C_{(4)}$); 136.68 ($C_{(3)}$); 133.84 ($C_{(1)}$); 127.67 ($C_{(2)}$); 44.75 (4'-$\underline{CH_2}$); 42.29 (5'-$\underline{CH_2}$)	6.05 (2H, s, NH_2); 5.10 (1H, t, J = 5.4, 5'-$CH_2\underline{OH}$); 4.96 (1H, t, J = 5.4, 4'-$CH_2\underline{OH}$); 4.34 (2H, d, J = 5.4, 5'-CH_2); 4.20 (2H, d, J = 5.4; 4'-CH_2)
1o*	3430, 3340, 3250, 2980, 2950, 2810, 1650, 1580, 1510, 1470, 1440, 1410, 1390, 1350, 1290, 1200, 1170, 1130, 1040, 1005, 930, 865, 810, 740	296 (2 $[M]^+$), 281 (4 $[M\text{-}CH_3]^+$), 267 (20), 249 (10), 222 (11), 192 (47), 124 (45), 123 (93), 55 (100)	153.77; 149.60; 149.50; 145.05; 144.89; 142.79; 72.06 (C-OH); 71.50 (C-OH); 35.84; 34.83; 34.60 ($CH\underline{CH_3}$); 29.06; 28.76; 28.37 (CH_3); 8.39; 8.34; 7.85 ($CH_2\underline{CH_3}$)	6.45 (1H, d, J = 15.3; OH); 6.02 (2H, s, NH_2); 5.62 (1H, d, J = 15.3; OH); 2.27-1.76 (4H, m, $2CH_2$); 1.75 (3H, d, J = 4.2; CH_3); 1.52 (3H, d, J = 4.2; CH_3); 0.97-0.80 (6H, m, $2CH_2\underline{CH_3}$)
1p*	3430, 3325, 3230-2550, 1745, 1650, 1595, 1560, 1470, 1410, 1270, 1240, 1205, 1040, 1000, 895	196 (53 $[M\text{-}CO_2]^+$), 152 (100 $[M\text{-}2CO_2]^+$), 124 (42), 120 (50), 95 (60), 94 (50), 84 (100)	164.43 (C=O);157.52 (C=O); 154.24 ($C_{(1)}$); 144.38 ($C_{(3)}$); 139.84 ($\underline{C}$-C=O); 136.03 ($\underline{C}$-C=O)	5.30 (1H, s, NH_2)
1q*	3440, 3335, 2970, 1760, 1635, 1580, 1460, 1440, 1310, 1260, 1225, 1205, 1170, 1125, 1080, 1040, 1000, 870	268 $[M]^+$, 237 $[M\text{-}OCH_3]^+$, 209 $[M\text{-}OCH_3\text{-}N_2]^+$, 197, 178	160.31 (C=O); 158.60 (C=O); 153.15 ($C_{(1)}$); 143.27 ($C_{(3)}$); 139.94 ($C_{(4)}$); 133.54 ($C_{(2)}$); 54.66 (CH_3); 53.40 (CH_3)	6.28 (2H, s, NH_2); 4.00 (3H, s, CH_3); 3.98 (3H, s, CH_3)
1r	3435, 3325, 3120, 3090, 2965, 1735, 1650, 1600, 1560, 1470, 1440, 1430, 1350, 1300, 1285, 1210, 1170, 1040, 980, 950, 875, 780	210 (46 $[M]^+$), 179 (20); 151 (22);125 (61); 120 (100); 84 (38)	160.6 (C=O); 152.2 ($C_{(1)}$); 143.6 ($C_{(3)}$); 140.9 ($C_{(4)}$); 129.6 ($C_{(2)}$); 52.7 (CH_3)	9.73 (1H, s, 5'-H); 6.95 (2H, s, NH_2); 4.40 (3H, s, CH_3)

TABLE 2 (continued)

1	2	3	4	5
1t + **1u**[*9]	3560, 3400, 3180, 3100, 3040, 2960, 2900, 1610, 1580, 1485, 1475, 1430, 1390, 1370, 1330, 1260, 1250, 1205, 1175, 1135, 1080, 1060, 1020, 980, 950, 890, 850, 820, 780, 760	276 (22 [M]$^+$), 201 (17); 188 (13); 158 (13); 138 (36); 110 (44); 108 (55); 95 (49); 81 (68); 77 (80); 54 (100)	54.97 (CH_2); 53.31 (CH_2)	8.69 (1H, s, 4'(5')-H); 7.98 (1H , s, 5'(4')-H); 5.75 (2H, s, 2 OH); 4.72 (2H, s, CH_2); 4.68 (2H, s, CH_2)
1v	3475, 3335, 2960, 2940, 2890, 1605, 1490, 1470, 1430, 1365, 1300, 1270, 1240, 1220, 1200, 1180, 1135, 1120, 1060, 1040, 1010, 980, 960, 900, 840, 810, 730	307 (1 [MH]$^+$), 289 (1 [M-H_2O]$^+$); 260 (1 [M-H_2O-N_2]$^+$); 247 (3); 188 (1); 164 (2); 136 (9); 93 (29); 84 (50); 55 (100)	165.85; 150.11; 146.13; 144.6, 138.56; 54.10 (CH_2); 52.71 (CH_2)	5.56 (1H, t, J = 4.5, OH); 5.35 (1H, s, OH); 4.75 (2H, d, J = 4.5,CH_2); 4.67 (2H, s, CH_2)

* The ^{1}H and ^{13}C NMR spectra of compounds **1a-f,h,l,m,t-v** were obtained in DMSO-d_6, of compounds **1g,j,k,n,q** in acetone-d_6, and of compound **1r** in a mixture of DMSO-d_6 and acetone-d_6.

*[2] ^{15}N NMR spectrum (DMSO-d_6): -125.8 ($N_{(1')}$); -22.6 ($N_{(2')}$); 22.7 ($N_{(3')}$); -13.4 ($N_{(5)}$); 8.8 ($N_{(2)}$); -337.5 (NH_2).

*[3] ^{1}H NMR spectrum of the mixture of compounds **1h,1i,1s** (DMSO-d_6): 9.23 (1H, s, 5'-H) (**1h**); 8.78 (1H, s, CH) (**1s**); 8.28 (1H, s, 4'-H) (**1i**); 8.05 (1H, s, CH) (**1s**); 6.40 (NH_2) (**1h,1i,1s**).

*[4] ^{1}H NMR spectrum of the mixture of isomers **1j,1k**: 9.20 (1H, s, 5'-H) (**1j**); 8.45 (1H, s, 4'-H) (**1k**); 6.27 (2H, s, NH_2) (**1j**); 6.15 (1H, s, NH_2) (**1k**); 4.5-4.3 (4H, m, $2CH_2$); 1.45-1.28 (6H, m, $2CH_3$).

*[5] ^{1}H NMR spectrum of the mixture of isomers **1l** and **1m**: 8.57 (1H, s, 5'-H); 7.96 (1H, s, 4'-H); 6.58 (2H, s, NH_2) (**1l**); 6.50 (2H, s, NH_2) (**1m**); 5.62 (1H, d, J = 5.7, OH) (**1m**); 5.42 (1H, d, J = 5.7, OH) (**1l**); 5.12 (1H, m, CH=CH_3) (**1m**); 4.98 (1H, m, CH–CH_3) (**1l**); 1.50 (3H, d, J = 6.7, CH_3) (**1l**); 1.46 (3H, d, J = 6.7, CH_3) (**1m**). ^{13}C NMR spectrum of the mixture of isomers **1l** and **1m**: 154.54; 152.12; 151.10; 145.26; 143.41; 143.24; 132.27; 120.98; 62.68 (CH–OH); 60.80 (CH–OH); 23.26 (CH_3); 22.42 (CH_3).

*[6] The ^{1}H and ^{13}C NMR spectra of amine **1o** was a complex picture caused by the presence of two asymmetric carbon atoms in this compound.

*[7] No signal was observed in the ^{1}H NMR spectrum for the protons of the COOH groups.

*[8] ^{15}N NMR spectrum (DMSO-d_6): -152.6 ($N_{(2)}$); -344.0 (NH_2).

*[9] The signals at 125-160 ppm were greater than would correspond to the carbon atoms of the heterocycles of two isomers (**1t,u**), which indicates contamination by byproducts.

TABLE 3. Conditions and Results of the Reaction of Azides **2** with Substituted Acetylenes **3**

Experiment	Acetylenic component	Azide **2***, g	Acetylenic component **3**	Molar ratio **2** : **3**	Solvent (ml)	Reaction products (molar ratio)	Yield, g (%)
1	**3a**	1	17.3 ml	1:12	MeOH (25)	**1a** : **1b** (1:2.6)	3.56 (79)
2	**3a**	2.3	12 ml	1:15	MeOH (20)	**1b** **1a**	1.86 (50) 0.97 (25)
3	**3b**	1	1g	1:1.5	EtOH (30)	**1c**	1.44 (87)
4	**3c**	2.15	24.8 ml	1:20	C_6H_6 (50)	**1d** : **1e** (1:1)	2.38 (70)
5	**3d**	1	1.6 g	1:2	MeOH (50)	**1f** **1g**	0.83 (46) 0.81 (45)
6	**3e**	0.38	1.4 ml	1:7	Ether (25)	**1h***[2]	0.13 (22)
7	**3e**	1	1.1 g	1:2	$CHCl_3$ (30)	**1h** **1h**, **1i**, **1s***[3]	0.93 (60) 0.25
8	**3e**	1.88	4.5 ml	1:5	CH_2Cl_2 (40) MeOH (10)	**1h** **1r**	0.61 (20) 0.21 (6.7)
9	**3f**	2	3.5 ml	1:2	CH_2Cl_2 (60) $CHCl_3$ (60)	**1j** **1j**, **1k***[4]	2.90 (81.7) 0.40 (11.3)
10	**3g**	1	0.83 g	1:1.5	MeOH (30)	**1m** **1l** : **1m** (1:1)*[5]	0.45 (29) 0.25 (16)
11	**3h**	2.8	3.8 g	1:2	EtOH (50)	**1n**	2.65 (57)
12	**3i**	0.53	1 g	1:5	MeOH (25)	**1o**	1.14 (92)
13	**3j**	0.38	1.19 g	1:3	Ether (25)	**1p***[6]	0.22 (30)
14	**3j**	1	2.10 g	1:2	Ether (10)–MeOH (20)	**1p**, **2a** **1r**	0.14 0.17 (5.1)
15	**3k**	0.5	1.5 ml	1:3	$CHCl_3$ (40)	**1q**	0.68 (64)
16	**3h**	1	0.58 g	1:1.5	MeOH (30)	**1v**	1.04 (75)
17	**3a**	1	0.51 g	1:2	MeOH (30)	**1t** : **1u** (1:1)	1.03 (82)

* Azide **2a** was used in experiments 1-15, and **2b** in 16 and 17.

*[2] Much initial azide remains in the reaction mixture after 60 h boiling.

*[3] See footnote *[3] to Table 2.

*[4] See footnote *[4] to Table 2; TLC (eluent PhH–EtOAc, 3:1): R_f 0.40 (**1j**); R_f 0.30 (**1k**).

*[5] See footnote *[5] to Table 2.

*[6] Much initial azide remained in the reaction mixture after extended boiling; compound **1h** was recorded in the reaction products (TLC, IR) together with substance **1p**.

Comparison of the ^{1}H NMR spectra of isomeric triazolylfurazans showed that the signal of the 5-H atom in 4-substituted isomers was found at lower field than the signal of the 4-H atom in 5-substituted isomers. With an increase in the electronegativity of the substituent the position of these signals of both isomers were displaced mainly towards low field (see Table 4). Other 1,2,3-triazoles have also shown the same tendency [6,7].

An interesting feature was noted when isolating and purifying triazolylfurazan **1a**. This compound has two forms in the crystalline state having differences in IR spectra (particularly at 3100-3500 cm^{-1}) and different melting points. We provisionally designated the low-melting form as α (mp 146-147°C) and the high-melting as β (mp 165-166°C). Each form may pass into the other, though the degree of interconversion depends on the nature of the solvent, solution temperature, and the method of isolating the crystals. On evaporation in vacuo to dryness of

TABLE 4. Chemical Shifts of Protons in Positions 4' or 5' (δ, ppm) in 4-Amino-3-(4-R^1-5-R^2-1,2,3-triazol-1-yl)furazans **1**

Compound	R^1/R^2	4'-H	5'-H	Solvent
1b	5'-CH_2OH	7.95		DMSO-d_6
1a	4'-CH_2OH		8.56	DMSO-d_6
1m	5'-CH(OH)Me	7.93		DMSO-d_6
1l	4'-CH(OH)Me		8.55	DMSO-d_6
1c	4'-C(OH)$(Me)_2$		8.44	Acetone-d_6
1e	5'-CH_2Cl	8.17		DMSO-d_6
1d	4'-CH_2Cl		8.90	DMSO-d_6
1g	5'-Ph	8.30		DMSO-d_6
1f	4'-Ph		9.28	DMSO-d_6
1i	5'-COOH	8.28		DMSO-d_6
1h	4'-COOH		9.23	DMSO-d_6
1k	5'-COOEt	8.40		Acetone-d_6
1j	4'-COOEt		9.20	Acetone-d_6
1r	4'-COOMe		9.42	DMSO-d_6, acetone-d_6 (1 : 1)

solutions of the α-form of **1a** in CH_2Cl_2, $MeNO_2$, H_2O, or MeOH, no change was observed in the case of the first two solvents but in the case of the last two complete conversion into the β-form occurred. The α-form was obtained on crystallizing compound **1a** from water or MeOH. One of the reasons for the existence of these forms may be the presence in them of different types of intermolecular and intramolecular hydrogen bonds, such as OH···O, OH···N (NH_2, N=), NH_2···O, or NH_2···N (NH_2, N=).

EXPERIMENTAL

The IR spectra were taken in KBr disks on a UR 20 spectrometer. The NMR spectra were recorded on a Bruker AM 300 spectrometer (^1H 300, ^{13}C 75.5, ^{14}N 21.7, and ^{15}N 30.4 MHz), the chemical shifts of ^{14}N and ^{15}N signals were measured relative to $MeNO_2$ as internal standard, and ^1H and ^{13}C relative to the solvent. Mass spectra were taken on a Varian MAT CH-6 spectrometer. Checks by TLC were carried out on Silufol UV 254 plates.

4-Amino-3-azidofurazan (2a) was obtained by the procedure [8]. The previously described 5-(4-azido-1,2,5-oxadiazolyl)-5H-1,2,3-triazolo[4,5-c]-1,2,5-oxadiazole (**2b**) [9] was synthesized in 70% yield by a method developed by V. E. Eman in the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences (RAN). This consisted of the oxidation of azide **2a** with potassium permanganate in HCl and subsequent thermolysis of the resulting 3,3-diazido-4,4-azofurazan in hexane.

4-R-3-(4-R1-5-R2-1,2,3-triazol-1-yl)furazans (1a-v). Azide **2** was boiled with the substituted acetylene **3** in the appropriate solvent for 20-100 h. The conditions and results of the synthesis of each product **1** are given in Table 3. Variants in the processing of reaction mixtures (A-C) were as follows.

A. When a solid was present it was filtered off (expt. 2,5-8,14) and in expt. 5-8 it was washed with the solvent in which the reaction had been conducted. Compounds **1f** (expt. 5) and **1h** (expt. 6-8) were obtained. The filtrates from expt. 5,7 were evaporated to dryness. Isomer **1g** (expt. 5) and a mixture of substances **1h**, **1i**, and **1s** (expt. 7) were obtained. The filtrates in expt. 6, 14 contained mainly the initial azide according to TLC with contamination by reaction products **1h** (expt. 6) and **1p** and **1r** (expt. 14). In expt. 2, after boiling for 6 h and leaving at room temperature for 12 h, product **1b** was filtered off and washed with hot CH_2Cl_2. The filtrates were boiled for a further 24 h, concentrated to one third of the initial volume, and the mixture of isomers **1a** and **1b** filtered off. After fractional crystallization from nitromethane the α-isomer of **1a** was obtained. In expt. 8 triazolylfurazan **1h** was filtered off initially, but on concentrating the filtrate an additional amount of compound **1h**

and substance **1g** were filtered off sequentially. In expt. 14 product **1r** was filtered off, washed with ether, the filtrate concentrated, ether (5 ml) was added, and additional triazolylfurazan **1r** was filtered off. After several days a mixture of compounds **1p** and **2a** precipitated from the filtrate.

B. The reaction mixture was evaporated to dryness (expt. 4,10,12,15,16). The residue (expt. 12,15,16) was washed as indicated in variant A. Compounds **1o**, **1q**, and **1v** respectively were obtained. Dichloromethane (5 ml) was added to the solid residue of expt. 4, and a mixture of isomers **1d** and **1e** was filtered off. This mixture (2.2 g) was dissolved by boiling in dichloromethane (25 ml) with activated carbon (0.1 g), the sorbent was filtered off, the solvent evaporated in vacuum to the start of crystallization, and compound **1d** (0.98 g; 44%) was filtered off. On concentrating the filtrate a mixture (0.8 g) of isomers **1d** and **1e** was precipitated containing a predominance of the latter. After separating the isomers on plates (21 × 30 cm, silica gel 5/40, eluent EtOAc–CH_2Cl_2, 1:3) compound **1e** (0.32 g, 14%) was obtained. The solid residue in expt. 10 was dissolved in boiling water (20 ml), the solution cooled, and KI (1 g) was added. Isomer **1m** was filtered off on the following day, the mother liquor was evaporated in vacuum to one tenth of the initial volume, and the mixture of isomers **1l** and **1m** was filtered off.

C. The reaction mixture was concentrated until precipitation of a solid (expt. 1,9,11,13) or until separation of a viscous oil (expt. 3,17). The solid was filtered off, and washed as indicated in variant A. A mixture of isomers **1a** and **1b** was obtained in expt. 1, compound **1j** in expt. 9, **1n** in expt. 11, and **1h** in expt. 13. The filtrate in expt. 9 was evaporated to dryness. A mixture of isomers **1j** and **1o** was obtained. According to TLC the filtrate of expt. 13 contained mainly the initial azide. In expt. 3 the oil was treated with H_2O (30 ml) and substance **1c** was filtered off on the following day. In expt. 17 the oil was dissolved in EtOAc (5 ml) and passed through a column of silica gel L 40/100 (eluent C_6H_6–EtOAc, 3:1). A mixture of isomers **1t** + **1u** was obtained in the form of an oil.

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