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SYNTHESIS AND INVESTIGATION OF RING–CHAIN ISOMERISM OF THE DERIVATIVES OF N-AMINO-5-HYDROXY-1,2,3-TRIAZOLE-4-CARBOXYLIC ACID

Yu. A. Rozin, E. A. Vorob'ova, Yu. Yu. Morzherin, and V. A. Bakulev

A series of sodium salts of 4-substituted 1-amino-5-hydroxy-1,2,3-triazoles was obtained by the "diazo transfer" reaction to arylmethylene-protected α-ethoxycarbonyl- and α-(methylcarbamoyl)-acetohydrazides. In DMSO solution the corresponding neutral hydroxytriazoles exist in equilibrium with the isomeric diazo compounds with an open chain. Electron-donating substituents stabilize the cyclic form. A good correlation was obtained between the equilibrium constants and the Hammett σ-constants. During the diazotization of benzaldehyde α-amino-α-cyanoacetylhydrazone the initially formed diazo compound undergoes spontaneous cyclization in solution to hydroxytriazole. Removal of the arylmethylene protection leads to N-unsubstituted sodium salts of 1-amino-5-hydroxytriazoles, but acidification of the latter leads to diazoacetohydrazides with an open chain.

Keywords: diazomalonomonohydrazide, ring–chain isomerism, equilibrium constants, diazo-transfer reaction, Hammett equation.

1,2,3-Triazoles and their benzo analogs have found widespread use in organic synthesis, medicine, and industry [1]. N-Amino-1,2,3-triazoles are of particular interest. Of them, however, 5-H-, 5-alkyl-, and 5-aryl-substituted derivatives are mainly known [2], while only individual representatives of N-amino-5-hydroxy-1,2,3-triazoles (AHT) are known [1, 3]. A general method for the synthesis of AHT was not known before our previous publication [4]. The present paper is devoted to the development of general method for the synthesis of AHT and also investigation of stability of these compounds in relation to the opening of the triazole ring.

One approach to the synthesis of 5-hydroxy-1,2,3-triazoles is method involving the generation of α-diazoacetamides followed by their 1,5-electrocyclization in the presence of bases [5]. Base-catalyzed diazo transfer to amides and amidines with an active α-methylene group by the action of sulfonyl azides followed by electrocyclization has often been regarded as the most effective method for the production of triazoles [6].

We found that if diazo-transfer reaction is applied to O-ethylmalonylhydrazine **1** triazole is not formed on account of a side reaction at the hydrazide group. Subsequently, therefore, hydrazides **1** and **2** were transformed by the action of substituted benzaldehydes into arylmethylene-protected α-ethoxycarbonyl- and α-methylcarbamoylacetohydrazides **3** and **4**, which were brought into the diazo-transfer reaction (Scheme 1). According to data from the ^{1}H NMR spectra, these compounds exist as two conformers (Tables 1 and 2). During their reaction with tosyl azide in ethanol in the presence of sodium ethoxide sodium salts of 5-hydroxytriazoles **5** and **6** are formed smoothly (Tables 3 and 4), as confirmed by the data from IR spectroscopy, i.e., by the absence of an absorption band of the diazo group in the region of 2120-2160 cm^{-1}.

Urals State Technical University, Ekaterinburg, Russia; e-mail: vab@htf.ustu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 323-333, March, 2001. Original article submitted July 23, 1999.

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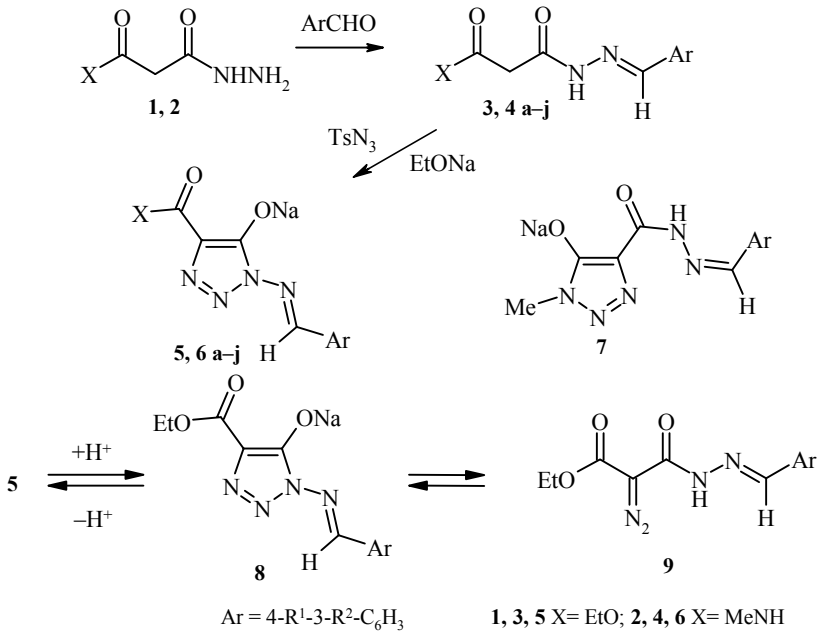
Scheme 1



3–12	a	b	c	d	e	f	g	h	i	j
R^1	H	Cl	F	Me	Me_2N	NO_2	H	MeO	MeO	Br
R^2	H	H	H	H	H	H	NO_2	H	MeO	H

A characteristic feature of the ^{1}H NMR spectra of triazololates **5** and **6** is the shift of the signals from the protons of the azomethine fragment (9.20-9.43 ppm) downfield by 1.0-1.5 ppm compared with their position in the initial hydrazones **3** and **4**.

In the case of the reaction of the carbamoyl derivatives **4** with tosyl azide the formation of the isomeric triazoles **6** and **7** could be expected on account of cyclization of α-diazo compound *via* the nitrogen atom of the amide or hydrazide groups. However, only the last possibility was realized, as indicated by the position of the signals from the protons of the N=CH and CH_3 groups in the ^{1}H NMR spectra, located at 9.25-9.48 and 2.60-2.75 ppm respectively and not at 8.3 and 3.75 ppm as for the isomer **7** [7]. In solutions 5-hydroxy-1,2,3-triazoles are in equilibrium with their chain isomers, α-diazoacetamides (DAA), while in the presence of bases they exist in the form of triazol-5-olates [7-9].

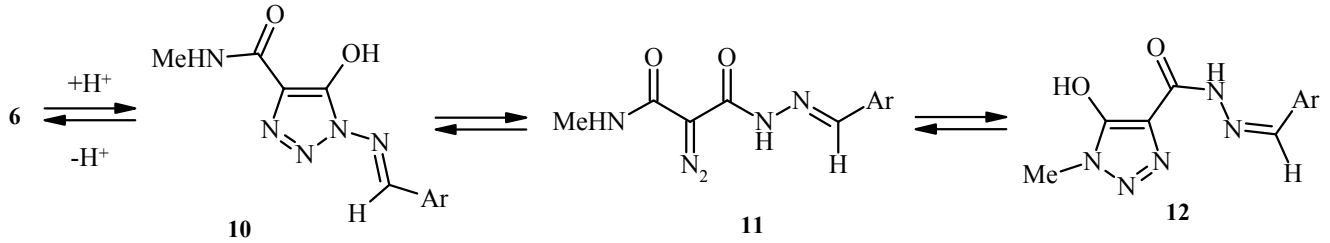
During treatment of aqueous solutions of salts **5** with one equivalent of HCl 5-hydroxytriazoles **8**, which are in equilibrium with the open-chain diazo compounds, are obtained. In the solid state these products largely represent the diazo compounds **9** (Table 5), as shown by the strong absorption band of the diazo group in the IR spectra in the region of 2140-2155 cm^{-1}. On treatment with sodium ethoxide diazo compounds **9** undergo irreversible cyclization to triazolates **5**.

In solutions of the products from acidification of compounds **5** in DMSO an equilibrium **8** $\rightleftharpoons$ **9**, detected by means of the ^{1}H NMR spectra, is observed. The content of triazole **8** in the equilibrium mixture is in the range of 4-80% depending on the substituents, and the thermodynamic stability of the cyclic form increases with increase in the electron-donating activity of substituent. The discovered relationships agree with data on the effect of substituents at position 1 of the triazole ring of 5-hydroxy-1,2,3-triazoles [8]. The calculated equilibrium constants (Table 5) correlate well with the σ-constants of the substituents in the phenyl ring:

$$\lg K_i = -0.867^* \Sigma\sigma_R - 0.613;\ r^2 = 0.959.$$

On acidification of sodium salts of hydroxytriazoles **6** products that are also predominantly diazo compounds (with the exception of hydroxytriazole **10a**, the IR spectrum of which does not contain the absorption band of the diazo group) separate from the aqueous solution. According to the ^{1}H NMR spectra, the solutions of the mentioned compounds in DMSO under the equilibrium conditions contain diazo compound **11** and the two isomeric hydroxytriazoles **10** and **12** (Scheme 2).

Scheme 2



To determine the structure of the products it is possible to use the position of the signals for the protons of the methyl group and the protons of the azomethine fragment, which are shifted downfield by 0.93-0.94 ppm on closure of the triazole ring *via* the nitrogen atom of the carboxamide group and by 0.86-0.99 ppm on closure *via* the nitrogen atom of the hydrazide group. The content of components **10**, **11**, and **12**, calculated from the integral intensities of the indicated peaks, and also the equilibrium constants (the stability constants of triazoles) (Table 6) indicate that the diazo compound predominates. The arylmethyleneamino group stabilizes the triazole ring to a greater degree than the methyl group. Some tendency for the decrease of stability of triazoles with the introduction of electron-withdrawing substituents into the phenyl ring is observed, but no strict Hammett correlation is observed.

In contrast to acetylhydrazones **3** and **4**, in the reaction of α-cyanoacetylhydrazones **13** with tosyl azide in the presence of sodium ethoxide the toluenesulfonamide group is not splitted off but takes part in cycloaddition with the formation of benzylidenehydrazide of 5-amino-1-(*p*-toluenesulfonyl)-1,2,3-triazole-4-carboxylic acid, which undergoes Dimroth rearrangement, giving 4(5)-tosylaminotriazole **14** (Scheme 3). Diazotization of amine **15** by butyl nitrite in acetic acid gives diazohydrazone **16**, which in solutions gradually undergoes cyclization to 5-hydroxytriazole **17**.

Scheme 3

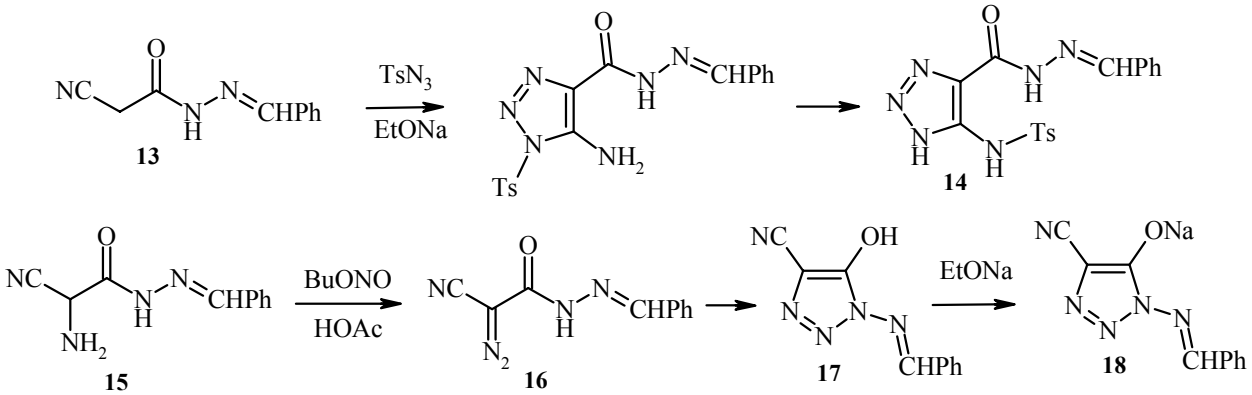


TABLE 1. The Characteristics of Hydrazones **3**

Compound	Empirical formula	Found N, % / Calculated N, %	mp, °C	^{1}H NMR spectrum, δ, ppm (SSCC, *J*, Hz)*,*[4]						Yield, %
				$\underline{CH_3}CH_2$, t, *J* = 7.1	$CH_3\underline{CH_2}$, q, *J* = 7.1	$CH_2(CO–)_2$, s	H_{arom}	N=CH, s+s	NH, s+s	
3a	$C_{12}H_{14}N_2O_3$	11.95 / 11.96	112-113	1.17	4.09	3.34+3.64	7.44-7.70 m	7.97+8.18	11.55	83
3b	$C_{12}H_{13}ClN_2O_3$	11.06 / 10.43	160-163	1.15	4.13	3.65	7.48+7.68 (8.5)*[2]	7.96+8.18	11.61+11.57	83
3c	$C_{12}H_{13}FN_2O_3$	11.26 / 11.11	163-168	1.17	4.10	3.27	7.22+7.51 m+m	7.92+8.2	11.42+11.46	86
3d	$C_{13}H_{16}N_2O_3$	11.38 / 11.28	163-165	1.16	4.10	3.26+3.30	7.30+7.55 (8.4) *[2]	7.80+8.20	11.40+11.44	87
3e	$C_{14}H_{19}N_3O_2$	15.50 / 15.15	117-121	1.17	4.09	2.95	6.70+7.44 (8.4) *[2]	7.83+8.30	11.18	63
3f	$C_{12}H_{13}N_3O_4$	15.32 / 15.05	180-181	1.17	4.11	3.41+3.71	7.89+8.26 (8.9) *[2]	8.8	11.82	84
3g	$C_{12}H_{13}N_3O_4$	15.34 / 15.05	163-165	1.18	4.11	3.41+3.70	7.68-8.55 m	8.09+8.31	11.75	84
3h	$C_{13}H_{16}N_2O_4$	10.30 / 10.60	110-111	1.18	4.09	3.34+3.62	6.98+7.57 (8.8)*[2]	7.92+8.12	11.39+11.44	74
3i	$C_{14}H_{18}N_2O_5$	9.37 / 9.50	145-147	1.14	4.08	3.33+3.61	*[3]	7.88+8.09	11.40+11.41	65

* Two conformers are present.

*[2] 4H, dd.

*[3] 7.32-6.92 (3H, ABC system, J_o = 8.3, J_m = 1.8, H_{arom}).

*[4] Signals of the methyl groups of compounds **3d**: 2.32 (3H, s, MeAr); **3e**: 2.95 (6H, s, Me_2N); **3h**: 3.80 (3H, s, MeO); **3i**: 3.789 + 3.793 + 3.80 (6H, s + s + s, MeO).

TABLE 2. The Characteristics of Hydrazones **4**

Com-pound	Empirical formula	Found N, % / Calculated N, %	mp, °C	^{1}H NMR spectrum, δ, ppm (SSCC, *J*, Hz)						Yield, %
				CH_3N	CH_2	MeN<u>H</u>	H_{arom}	N=CH	C=NNH	
4a	$C_{11}H_{13}N_3O_2$	19.30 / 19.17	206-208	2.61 (4.5)	3.14+3.48	7.88	7.44+7.63	7.96+8.22	11.32+11.22	50
4b	$C_{11}H_{12}ClN_3O_2$	16.31 / 16.56	222-224	2.62+2.66 (4.8)	3.14+3.48	7.94	7.71+7.67 (8.6)*	7.94+8.19	11.51+11.41	80
4d	$C_{12}H_{15}N_2O_2$	17.68 / 18.01	130-133	2.61 (4.7)	3.14+3.49	8.20	7.22+7.52 (8.1)	7.93+8.18	11.28+11.42	54
4f	$C_{11}H_{12}N_4O_4$	20.74 / 20.20	210-215	2.62 (4.8)	3.15+3.50	8.10	7.22+7.49 (8.4)	7.95	11.30	75
4h	$C_{12}H_{15}N_3O_3$	18.29 / 16.86	153-155	2.63 (4.3)	3.09+3.45	7.78	6.84+6.89 (8.7)*^{2}	7.87+8.10	11.15+11.21	73
4j	$C_{11}H_{12}BrN_3O_2$	15.57 / 13.97	180-185	2.60 (4.8)	3.14+3.48	8.13	7.35+7.52 (8.5)	7.89	11.35	54

* 7.71 (2H, d, *J* = 8.6); 7.67 (2H, d, *J* = 8.6); isomers at 7.49 and 7.77 (*J* = 8.6).
*^{2} 6.84 (2H, d, *J* = 8.7); 6.89 (2H, d, *J* = 8.7); isomers at 7.54 and 7.61 (*J* = 8.7).

TABLE 3. The Characteristics of Sodium Salts of 5-Hydroxytriazoles

Com-pound	Empirical formula	Found N, % / Calculated N, %	mp, °C	^{1}H NMR spectrum, δ, ppm (SSCC, *J*, Hz)				Yield, %
				CH_3CH_2, t *J* = 6.9-7.1	CH_3CH_2, q *J* = 6.9-7.1	N=CH, s	H_{arom}	
5a	$C_{12}H_{11}N_4NaO_3$	19.45 / 19.85	225 (decomp.)	1.25	4.16	9.30	7.6-7.9, m	72
5b	$C_{12}H_{10}ClN_4NaO_3$	17.29 / 17.69	>300 (decomp.)	1.26	4.17	9.27	7.52+7.87 (8.5)*	60
5c	$C_{12}H_{10}FN_4NaO_3$	18.13 / 18.66	>300 (decomp.)	1.26	4.16	9.30	7.30+7.88, m	56
5d	$C_{13}H_{13}N_4NaO_3$	18.31 / 18.91	250-255	1.26	4.16	9.26	7.28+7.72 (8.0)*	56
5e	$C_{14}H_{16}N_5NaO_3$	21.08 / 21.53	240-242	1.28	4.18	9.06	6.77+7.50 (8.9)*	66
5f	$C_{12}H_{10}N_5NaO_5$	21.22 / 21.40	>250 (decomp.)	1.24	4.13	9.43	8.06+8.31 (8.8)*	72
5g	$C_{12}H_{10}N_5NaO_5$	21.31 / 21.40	305-311 (decomp.)	1.25	4.15	9.42	*[2]	75
5h	$C_{13}H_{14}N_5NaO_4$	17.60 / 17.94	207-209 (decomp.)	1.24	4.14	9.25	7.45+7.01 (8.6)*	88
5i	$C_{14}H_{15}N_4NaO_5$	16.20 / 16.37	>250 (decomp.)	1.25	4.15	9.22	*[3]	76

* 4H, dd.

*[2] **5g**: 8.65 (1H, m, 2-H); 8.3-8.2 (2H, м, 4,6-H); 7.76 (1H, dd, *J* = 8.0, 5-H).

*[3] **5i**: 7.47 (1H, d, $J_м$ = 1.8, 2-H); 7.32 (1H, dd, J_o=8.5, $J_м$ = 1.8, 6-H); 7.04 (1H, t, J_o = 8.5, 5-H).

*[4] Signals of methyl groups - **5d**: 2.36 (3H, s, MeAr); **5e**: 2.99 (6H, s, Me_2N); **5h**: 3.82 (3H, s, MeO); **5i**: 3.83 (6H, s, $(MeO)_2$).

TABLE 4. The Characteristics of Sodium Salts of 5-Hydroxy-4-methylcarbamoyltriazoles

Com-pound	Empirical formula	Found N, % / Calculated N, %	mp, °C	^{1}H NMR spectrum, δ, ppm (SSCC, *J*, Hz)				Yield, %
				CH_3N*	H_{arom}	NH	N=CH	
6a	$C_{11}H_{10}N_5NaO_2$	26.13 / 26.21	240-245 (decomp.)	2.75 (4.8)	7.83+7.47	7.89 (4.8)	9.33	94
6b	$C_{11}H_9ClN_5NaO_2$	23.08 / 23.22	>300 (decomp.)	2.77 (4.8)	7.53+7.88 (8.6)	7.82 (4.8)	9.31	83
6d	$C_{12}H_{12}N_5NaO_2$	24.42 / 24.90	>250 (decomp.)	2.65 (4.7)	7.21+7.58 (8.1)	7.59 (4.7)	9.32	94
6f	$C_{11}H_9N_6NaO_4$	26.91 / 26.92	>250 (decomp.)	2.62 (4.8)	7.22+7.49 (8.4)	7.51 (4.8)	9.48	95
6h	$C_{12}H_{12}N_5NaO_3$	23.70 / 23.56	>250 (decomp.)	2.75 (5.0)	7.03+7.77 (8.9)	7.94 (5.0)	9.25	86
6j	$C_{11}H_9BrN_5NaO_2$	19.87 / 20.23	>250 (decomp.)	2.60 (4.7)	7.33+7.51 (4.7)	7.53 (4.7)	9.33	93

* Other signals of methyl groups – **6d**: 2.33 (3H, s, CH_3Ph); **6h**: 3.82 (3H, s, CH_3O).

TABLE 5. The Characteristics of the Products from Neutralization of Sodium Salts of AHT **5**

Initial compound	^{1}H NMR spectrum, δ, ppm (DMSO-d_6)			Content of **8**, %	$K_{eq}\cdot10^3$	lg *K*	IR spectrum (KBr), ν_{N_2}, cm^{-1}
	8, N=CH	**9**					
		N=CH	NH				
5a	9.31	8.35	10.81	16.88	212±18	-0.67	2142
5b	9.35	8.36	10.84	14.87	919±16	-0.72	2145
5c	9.36	8.36	10.79	15.27	245±21	-0.61	2140
5d	9.27	8.30	10.73	24.42	288±24	-0.54	2150
5e	9.09	8.15	10.51	80.26	1514±130	0.18	2140
5f	9.48	8.49	11.04	7.00	60±5	-1.25	2150
5g	9.50	8.51	10.98	4.21	39±3	-1.41	2145
5h	9.26	8.28	10.68	36.00	463±40	-0.34	2155
5i	9.22	8.25	10.70	22.94	380±33	-0.42	2142

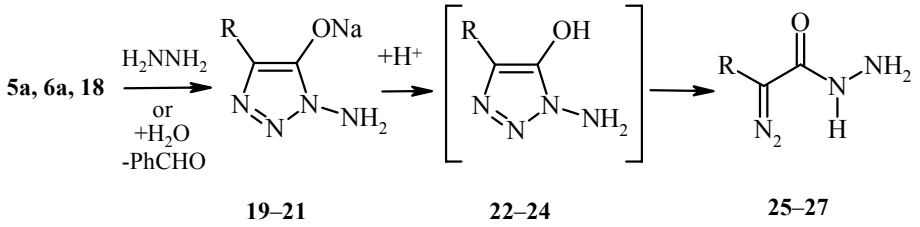
TABLE 6. The Ring–Chain Equilibrium in the Series of Hydroxytriazoles **10** and **12**

Compound	^{1}H NMR spectrum, δ, ppm (DMSO-d$_6$)				Content, %	K_{st}	IR spectrum (KBr), ν_{N_2}, cm^{-1}
	CH_3N	CH_3NH	CONHN	N=CH			
10a	2.81	8.05	—	9.35	11.3	0.14	
11a	2.81	8.05	11.73	8.43	79.9	—	2118
12a	3.75	—	11.73	8.43	8.8	0.11	
10b	2.81	8.40	—	9.36	12	0.16	
11b	2.81	8.40	11.80	8.40	73	—	2130
12b	3.74	—	11.75	8.40	15	0.20	
10d	2.81	8.00	—	9.30	15.3	0.20	
11d	2.81	8.35	12.01	8.49	83.3	—	2140
12d	3.75	—	12.01	8.49	4.2	0.05	
10j	2.81	8.03	—	9.34	13.1	0.17	
11j	2.81	8.03	11.73	8.42	77.1	—	2110
12j	3.74	—	11.73	8.42	9.8	0.13	

The cyclic structure of the compound **17** is confirmed by the absence of the absorption band of the diazo group in the region of 2060-2160 cm^{-1} and by the downfield shift of the peak for the proton of the N=CH group compared with the initial hydrazone. In contrast to hydroxytriazoles **8**, **10**, and **12**, it was not possible to detect the presence of diazo compound **16** in the DMSO solution by means of the ^{1}H NMR spectra. Hydroxytriazole **17** forms sodium salt **18** with sodium ethoxide.

The benzylidene protection in triazolates **5a**, **6a**, and **18** was removed by boiling them in ethanol with one equivalent of hydrazine or by boiling for many hours in water with distillation of benzaldehyde as an azeotrope with water (Scheme 4). The structure of the obtained sodium salts of the derivatives of 1-amino-5-hydroxy-1,2,3-triazole-4-carboxylic acid **19**, **20**, and **21** is confirmed by the absence of the absorption band of the diazo group in the IR spectra and by the magnitude of the chemical shift of the amino group, typical of N-aminotriazoles [2].

Scheme 4



19–21 **22–24** **25–27**

19, 22, 25 R = EtOCO; **20, 23, 26** R = MeNHCO; **21, 24, 27** R = CN

The products obtained during acidification of sodium salts of hydroxytriazoles **19-21** are mostly diazo compounds **25-27**, formed as a result of opening of the triazole ring in the supposed intermediate 5-hydroxytriazoles **22-24**. This is indicated by the presence of a strong absorption band of the diazo group at 2145 cm^{-1} in the IR spectrum and a broad one-proton singlet, corresponding to the proton of the C(O)NH group at 9.95 ppm in the ^{1}H NMR spectra.

Thus, an accessible general method has been developed for the production of N-amino-5-hydroxy-1,2,3-triazoles. A correlation was obtained between their thermodynamic stability and the nature of the substituents.

EXPERIMENTAL

The IR spectra were recorded on an UR-20 instrument in tablets with potassium bromide. The ^{1}H NMR spectra in DMSO-d_6 solution were obtained on a Bruker WM-250 instrument with TMS as internal standard. The AHT $\rightleftarrows$ DAA equilibrium constants were determined in DMSO-d_6 solution at 23±2°C from the integral intensities of the peaks in the ^{1}H NMR spectra measured 24, 48, and 72 h after dissolution. The equilibrium constants were calculated as the ratio of the integral intensities of the signals from the protons of the azomethine (or methyl) groups of hydroxytriazoles **8** (**10** or **12**) and the respective diazo compounds **9** (or **11**). The parameters of the correlation equation for the dependence of the equilibrium constant on the σ-constants of the substituents were obtained by the method of least squares. The Jaffe σ-constants were used [11].

O-Ethylmalonylhydrazine **1** was obtained by the method [12].

Methylcarbamoylacetohydrazide (2). Solution of hydrazide **1** (29.24 g, 0.2 mol) in ethanol (65 ml) was saturated at 10-15°C with gaseous methylamine, produced from methylamine hydrochloride (53.8 g, 0.8 mol) and potassium hydroxide (44.7 g, 0.8 mol), and was left at room temperature overnight. The solvent and the excess of methylamine were removed under vacuum at a temperature not exceeding 50°C. The residue was diluted with equal volume of ethanol and left at 0-5°C for 2-3 h. The precipitate was filtered off, recrystallized from a small amount of ethanol, and dried under vacuum at room temperature. Yield 19.8 g (50%); mp 104-106°C. Found, %: N 31.65. $C_4H_9N_3O_2$. Calculated, %: N 32.04.

Hydrazones of Ethoxycarbonyl- and Methylcarbamoylacetohydrazide (3) and (4). Mixture of equimolar amounts of hydrazide **1** (or **2**) and the respective substituted benzaldehyde was heated in ethanol at 50-60°C for 2-3 h and cooled to 5-10°C. The precipitate was filtered off, washed with ethanol, and recrystallized from ethanol (Tables 1 and 2).

Sodium Salts of 1-Arylmethylideneamino-4-ethoxycarbonyl- and 1-Arylmethylideneamino-4-methylcarbamoyl-5-hydroxy-1,2,3-triazoles (5) and (6). To suspension of hydrazone **3** (or **4**) (0.01 mol) in absolute ethanol (20 ml) under stirring at 5-10°C we added sodium ethoxide (0.01 mol) in ethanol (6 ml) and over 15 min *p*-tosyl azide (1.97 g, 0.01 mol) in ethanol (10 ml). The mixture was stirred at 5-10°C for 3 h and kept for further 24 h at room temperature. The precipitate was filtered off, washed with ethanol, and crystallized from ethanol (Tables 3 and 4).

Acidification of Sodium Salts 5 and 6. Salt **5** (or **6**) was dissolved in a small amount of water, and the solution was acidified at 5-10°C with one equivalent of dilute hydrochloric acid. The precipitate was filtered off, washed with water, and dried under vacuum at room temperature over calcium chloride (Tables 4 and 6).

4(5)-Tosylamino[1,2,3]triazole-5(4)-benzylidenecarbohydrazide (14). The compound was obtained under conditions similar to those described for compounds **5** and **6**. The yield was 81%; mp >290°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 13.67 (1H, br. s, 1-H); 11.80 (1H, br. s, SO_2NH); 8.14 (1H, s, N=CH); 7.87 (2H, m, H_{arom}); 7.75 + 7.30 (4H, d + d, *J* = 8.2, AB system); 7.50 (3m, H_{arom}); 2.32 (3H, s, CH_3). Found, %: N 21.46; S 8.17. $C_{17}H_{16}N_6O_3S$. Calculated, %: N 21.86; S 8.34.

Aminocyanoacetobenzylidenehydrazide (15). The compound was obtained by analogy with compound **3**. Equimolar amounts of α-amino-α-cyanoacetohydrazide [13] and benzaldehyde were stirred for 2 h in ethanol at room temperature. Yield 78%; mp 123-125°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 13.67 (1H, br. s, CONH); 8.37 + 8.06 (1H, s + s, N=CH); 7.8-7.3 (5H, m, H_{arom}); 5.17 + 4.86 (2H, s + s, NH_2). Found, %: N 27.4. $C_{10}H_{10}N_4O$. Calculated, %: N 27.7.

α-Diazo-α-cyanoacetobenzylidenehydrazide (16) and 1-Benzylideneamino-5-hydroxy-1,2,3-triazole-4-carbonitrile (17). To solution of amine **15** (4 g, 0.02 mol) in glacial acetic acid (12 ml) we added dropwise with stirring and cooling (10-15°C) butyl nitrite (3 ml, 2.65 g, 0.025 mol). After stirring at 0-5°C for 1 h the precipitate of **16** was filtered off and washed with acetic acid and then with ether. IR spectrum, ν, cm^{-1}: 2218 (CN), 2148 (N=N), 1658 (CO). Recrystallization of hydrazide **16** from acetonitrile gave triazole **17**.

Yield 2.22 g (52%); mp 164°C (expl.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.31 (1H, s, N=CH); 12.31 (1H, s, NH). IR spectrum, ν, cm^{-1}: 2217 (C≡N), 1705, 1687 sh, 1665 sh (C=O). Found, %: N 33.1. $C_{10}H_7N_5O$. Calculated, %: N 32.8.

Sodium Salt of Hydroxynitrile 17 (18). Suspension of compound **17** in absolute ethanol was treated with one equivalent of sodium ethoxide. The salt was precipitated with ether. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 9.30 (1H, s, N=CH); 7.93 + 7.54 (5H, m + m, H_{arom}). Found, %: N 29.25. $C_{10}H_6N_5NaO$. Calculated, %: N 29.78.

Sodium 1-Amino-4-R-1,2,3-triazol-5-olates (19-21). A. Mixture of salt **5a** (or **6a** or **18**) (10 mmol), 100% hydrazine (0.35 g, 11 mmol), and ethanol (150 ml) was boiled for 15 h. The reaction mass was evaporated under vacuum to 20-30 ml and cooled at 0-5°C for 2 h. The precipitate was filtered off, washed with ethanol, and dried at 50-60°C. Compound **19**: yield 81%; mp >250°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 5.25 (2H, br. s, NH_2); 4.13 (2H, q, *J* = 7.0 Hz, CH_2); 1.23 (3H, t, *J* = 7.0). Found, %: N 28.25. $C_5H_7N_4NaO_3$. Calculated, %: N 28.85. Compound **20**: yield 90%; mp 300-305°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 7.86 (1H, q, *J* = 4.7, CONH); 5.30 (2H, s, NH_2); 2.72 (3H, d, *J* = 4.7, CH_3). Found, %: N 38.70. $C_4H_6N_5NaO_2$. Calculated, %: N 39.10. Compound **21**: yield 50%; mp >250°C. Found, %: N 47.22. $C_3H_2N_5NaO$. Calculated, %: N 47.62.

B. For compound **19**. Solution of salt **5a** (3 g) in distilled water (200 ml) was filtered and boiled with distillation of the azeotropic mixture of benzaldehyde and water. Water was added from time to time, and the process took about 50 h. The reaction mixture was evaporated to dryness. The residue was suspended in the minimum amount of ethanol and cooled to 0-5°C. The precipitate was filtered off and dried. Yield 70%. The product was identical with that obtained in method A.

α-Diazo-α-R-acetohydrazides (25-27). Solution of salt **19** (**20** or **21**) in water was acidified with one equivalent of hydrochloric acid and evaporated to dryness under vacuum. The product was dissolved in boiling ethanol, sodium chloride was filtered off, and the filtrate was evaporated to dryness under vacuum. The precipitate was suspended in ether and filtered off. Compound **25**: yield 55%; mp 157-160°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 9.94 (1H, br. s, NH); 5.5-7.5 (2H, br. s, NH_2); 4.28 + 4.23 (2H, q + q, *J* = 7.2, CH_2); 1.27 (3H, t, *J* = 7.2, CH_3). IR spectrum, ν, cm^{-1}: 2145 (N_2). Found, %: N 33.03. $C_5H_8N_4O_3$. Calculated, %: N 33.25. Compound **26**: yield 65%; mp 200-203°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 7.87 (1H, br. s, NH); 4.25 (2H, br. s, NH_2); 2.75 (3H, d, *J* = 4.0, CH_3). Found, %: N 44.02. $C_4H_7N_5O$. Calculated, %: N 44.57. Compound **27**: yield 50%; mp 150°C (decomp.) IR spectrum, ν, cm^{-1}: 2250 (CN), 2150 (N=N). Found, %: N 55.27. $C_3H_3N_5O$. Calculated, %: N 55.99.

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