B) A 0.2-g sample of anhydrous ferric chloride and 2 g of hydroxymethyl derivative IId were added to fused p-toluenesulfonyl chloride (1.7 g), and the mixture was heated at 90°C until hydrogen chloride evolution ceased (1.5 h). It was then cooled and treated with water, and the aqueous mixture was filtered. The solid material was washed to neutrality with water and dissolved in acetone. The acetone solution was filtered, the solvent was removed from the filtrate by evaporation, and the residue was crystallized to give 1.4 g (42%) of tosyl derivative Vd.

1-Iodomethyl-3-nitro-1,2,4-triazole (VIb). A) From Chloromethyl Derivative IIIb. A mixture of 2 g of IIIb and 2.04 g of potassium iodide in 50 ml of acetone was refluxed for 3 h, after which the solvent was removed by evaporation, and the residue was washed with petroleum ether until it solidified. The solid was crystallized from ethanol.

B) From Tosylate Vb. A mixture of 1.5 g of Vb and 1.46 g of ammonium iodide in 100 ml of acetone was refluxed for 10 h, after which it was filtered, and the solvent was removed by evaporation. The residue was dissolved in ethyl acetate, and the solution was washed with 5% sodium thiosulfate solution and water. The ethyl acetate was removed by evaporation, and the residual oil was triturated with petroleum ether until it solidified. The solid was recrystallized from ethanol.

LITERATURE CITED

1. M. S. Pevzner, T. N. Kulibabina, N. A. Povarova, and L. V. Kilina, Khim. Geterotsikl. Soedin., No. 8, 1132 (1979).
2. C. Ainsworth and R. G. Jones, J. Am. Chem. Soc., 77, 1538 (1955).
3. L. A. Vlasova, E. M. Shemaeva, G. B. Afanas'eva, and I. Ya. Postovskii, Khim.-Farm. Zh., No. 8, 25 (1971).
4. M. S. Pevzner, T. N. Timofeeva, G. M. Frolova, and N. N. Gorbunova, Zh. Org. Khim., 12, 1361 (1976).
5. A. L. Fridman, V. P. Ivshin, and S. S. Novikov, Usp. Khim., 38, 1448 (1969).
6. L. Goodman, J. Am. Chem. Soc., 75, 3019 (1953).
7. A. G. Korepin, R. G. Gafurov, and L. T. Eremenko, Izv. Akad. Nauk SSSR, Ser. Khim., 474 (1974).
8. L. I. Bagal and M. S. Pevzner, Khim. Geterotsikl. Soedin., No. 4, 558 (1970).

HETEROCYCLIC NITRO COMPOUNDS. 26.* REACTION OF 1-SUBSTITUTED 3,5-DINITRO-1,2,4-TRIAZOLES WITH ANIONS OF HETEROCYCLIC NH ACIDS

M. S. Pevzner, T. P. Kofman,
E. N. Kibasova, L. F. Sushchenko,
and T. L. Uspenskaya

UDC 547.792.3.7'779

1-Substituted 3-nitro-5-(N-azolyl)-1,2,4-triazoles mixed with 1-substituted 3-nitro-1,2,4-triazol-5-ones are obtained in the reaction of 1-substituted 3,5-dinitro-1,2,4-triazoles with anions of heterocyclic NH acids (1,2,4-triazole, 1,2,3-triazole, pyrazole, benzotriazole, benzimidazole, and indazole derivatives). 1-Methyl-3-nitro-5-amino-1,2,4-triazole is formed instead of the expected 5-tetrazolyl derivative in the reaction of 1-methyl-3,5-dinitro-1,2,4-triazole with tetrazole in alkaline media.

The use of anions of heterocyclic NH acids in nucleophilic aromatic substitution reactions has been described in the case of the reaction of pyrazole [2, 3], imidazole [2-4], 1,2,3- [5] and 1,2,4-triazoles [2, 6, 7], benzimidazole [2], and benzotriazole [8] with halodinitro- and trinitrobenzenes. Analogous reactions in the heterocyclic series have been

*See [1] for communication 25.

Lensovet Leningrad Technological Institute, Leningrad 198013.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 257-261, February, 1980. Original article submitted January 29, 1979; revision submitted July 16, 1979.

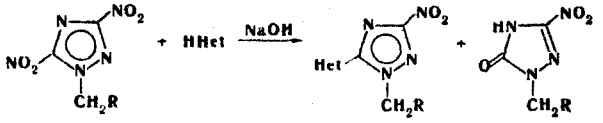
0009-3122/80/1602-0194$07.50

realized for isomeric 1(4)-methyl-3(5)-halo-1,2,4-triazoles [9] (replacement of halogen by 1,2,4-triazole) and 1,4-benzodiazepines [10] (replacement by pyrrole and imidazole).

It seemed of interest to subject 3,5-dinitro-1,2,4-triazole derivatives, in which the nitro group in the 5 position is readily replaced by the action of nucleophilic agents [10-16], to reactions of this sort. This would make it possible to synthesize diverse compounds with an N–C bond between the rings.

In the reaction of 1-substituted 3,5-dinitro-1,2,4-triazoles (I-V) with the anions of azoles the nitro group is replaced by an azole residue to give the corresponding 5-N-hetaryl derivatives of 1,2,4-triazole (VI-XXVIII) (Table 1).

1-Substituted 3-nitro-1,2,4-triazol-5-ones (XXIX-XXXI) were detected in the mixture along with the desired compounds (VI-XXVIII) and were isolated in a number of cases. It was demonstrated by special experiments that triazolones are formed from the starting compounds rather than through reaction of hetaryltriazoles with hydroxide ion.



I-V VI-XXXI

I R = H; II R = CH_2COOCH_3; III R = $COCH_3$; IV R = $-CH=CH_2$; V R = $COOCH_3$; VI R = H, Het = 1,2,4-triazol-1-yl; VII R = H, Het = 3-nitro-1,2,4-triazol-1-yl; VIII R = H, Het = 3-chloro-1,2,4-triazol-1-yl; IX R = H, Het = 3-acetamido-1,2,4-triazol-1-yl; X R = H, Het = 3-nitro-5-methyl-1,2,4-triazol-1-yl; XI R = H, Het = 3,5-dichloro-1,2,4-triazol-1-yl; XII R = H, Het = 4-nitro-1-pyrazolyl; XIII R = H, Het = 3,5-dimethyl-4-nitro-1-pyrazolyl; XIV R = H, Het = 3,5-dicarbomethoxy-4-nitro-1-pyrazolyl; XV R = H, Het = 4-carbomethoxy-1-pyrazolyl; XVIa R = H, Het = 1,2,3-triazol-1-yl; XVIb R = H, Het = 1,2,3-triazol-2-yl; XVII R = H, Het = 5 methyltetrazolyl; XVIII R = H, Het = 1-benzimidazolyl; XIX R = H, Het = 5-nitro-1-indazolyl; XX R = H, Het = benzotriazolyl; XXI R = CH_2COCH_3, Het = 3-bromo-1,2,4-triazol-1-yl; XXII R = CH_2COCH_3, Het = 3-choloro-1,2,4-triazol-1-yl; XXIII R = CH_2COCH_3, Het = 3-nitro-1,2,4-triazol-1-yl; XXIV R = CH_2COCH_3, Het = 3-nitro-5-methyl-1,2,4-triazol-1-yl; XXV R = CH_2COCH_3, Het = 3-nitro-1-pyrazolyl; XXVI R = $COCH_3$, Het = 3-nitro-1,2,4-triazol-1-yl; XXVII R = $CH=CH_2$, Het = 3-nitro-1,2,4-triazol-1-yl; XXVIII R = $COOCH_3$, Het = 3-nitro-1,2,4-triazol-1-yl; XXIX R = H; XXX R = CH_2COCH_3; XXXI R = $COCH_3$.

Absorption bands at 1580-1560 and 1300-1320 cm^{-1}, which correspond to the vibrations of the nitro group in the 3 position of the triazole ring, and a number of bands at 800-1500 cm^{-1}, which are related to various types of vibrations of the heterorings, were observed in the IR spectra of the compounds obtained. Absorption bands of carbonyl groups (1720-1760 cm^{-1}) were noted in the IR spectra of IX, XIV, XV, XXI-XXVI, and XXVIII.

A definite tendency for a decrease in the yields of the two-ring compounds and an increase in the yields of the triazolones is observed as the acidities of the corresponding azoles increase. Thus, the desired compounds are obtained in 60-90% yields in the reaction of I with the salts of weakly acidic azoles (benzimidazole, benzotriazole, indazole, pyrazole, and 1,2,3- and 1,2,4-triazoles with pK_a 6-13). The yields of the desired products decreased as the acidities of the azoles increased: the yields were only 18% (IX) and 6.5% (XVII) when salts of 3,5-dichloro-1,2,4-triazole (pK_a 5.22 [17]) were used. We were unable to carry out substitution reactions with 3-nitro-5-bromo-1,2,4-triazole (pK_a = 3.05 [19]).

These results constitute evidence for a decrease in the nucleophilicities of azole anions in S_NAr reactions as the acidities of the corresponding NH acids increase and are in complete agreement with the data on other reactions of azoles that take place at the ring heteroatom [19-21]. Isomeric compounds involving replacement of the nitro group in the 3 position of starting I-V were not detected. This is not surprising if one takes into account the high selectivity of the 5 position of the sym-triazole ring in the case of attack by nucleophilic reagents [11-16].

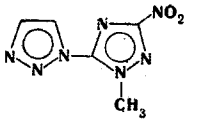
Two isomers that differ with respect to the site of addition of the v-triazole ring to the 5 position of s-triazole were detected in the reactions of triazole I with 1,2,3-triazole and benzotriazole in both cases (XVI and XX); this was proved by means of thin-layer chromatography (TLC) and the PMR spectra. The singlet signal in the PMR spectrum of XVI at 8.30 ppm was assigned to the C_3–H and C_4–H protons of the v-triazole ring attached to the s-

TABLE 1. 1-Substituted 3-Nitro-5-(N-azolyl)-1,2,4-triazoles

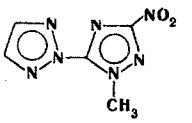
Compound	mp, °C[a] (crystallization solvent)	R_f [b]	PMR spectrum, δ, ppm	Found				Empirical formula	Calc.				Reaction time, h	Calc. %	
				C, %	H, %	N, %	M		C, %	H, %	N, %	M		desired product	triazolone
VI	109	0,26	4,30 (N—CH_3); 8,40 (C_3—H); 9,23 (C_5—H)	31,0	2,9	50,1	188	$C_5H_5N_7O_2$	30,7	2,6	50,2	195	10	53	11
VII	184	0,33	4,27 (N—CH_3); 9,92 (C_5—H)	25,2	1,5	47,0	246	$C_5H_4N_8O_4$	25,0	1,7	46,7	240	6,5	60	30
VIII	159	0,54	4,30 (N—CH_3); 9,30 (C_5—H)	26,4	2,0	42,6	237	$C_5H_4N_7O_2Cl$[c]	26,1	1,8	42,7	229,5	4,5	75	15
IX	200	0,11	4,30 (N—CH_3); 9,15 (C_5—H); 2,20 ($COCH_3$); 7,80 (N—H)	33,7	3,5	44,7	—	$C_7H_8N_8O_3$	33,3	3,2	44,4	252	9,5	42	29
X	204	0,37	4,30 (N—CH_3); 2,97 (C—CH_3)	28,4	2,4	44,7	244	$C_6H_6N_8O_4$	28,4	2,4	44,1	254	3	37	21
XI	149	0,61	4,20 (N—CH_3)	22,9	1,5	36,4	260	$C_5H_3N_7O_2Cl_2$[d]	22,7	1,1	37,0	264	10	18	66
XII	130	0,74	4,30 (N—CH_3); 8,80 (C_3—H); 9,36 (C_5—H)	30,0	2,1	41,2	249	$C_6H_5N_7O_4$	30,1	2,1	40,9	239	8,5	87	10
XIII	109	0,58	4,18 (N—CH_3); 2,60 (C_3—CH_3); 2,82 (C_5—CH_3)	36,1	3,4	37,0	270	$C_8H_9N_7O_4$	36,0	3,4	36,7	267	6	52	24
XIV	154	0,37	4,17 (N—CH_3); 3,49 (C_3—$COOCH_3$); 3,92 (C_5—$COOCH_3$)	34,3	2,8	28,4	348	$C_{10}H_9N_7O_8$	33,9	2,5	28,6	355	10	90	7
XV	244	0,15	4,20 (N—CH_3); 8,30 (C_3—H); 8,60 (C_5—H); 2,08 ($COCH_3$); 10,5 (NH)	38,2	3,8	38,9	261	$C_8H_9N_7O_3$	38,2	3,6	39,0	251	6	39	34
XVI	98	0,30[e] 0,33	4,35 (N—CH_3); 8,30 (c, C_3H and C_4H, isomer b), 8,80 (d); 8,10 (d, J=4 isomer a)	30,6	2,6	50,5	198	$C_5H_5N_7O_2$	30,7	2,6	50,2	195	6	67 (two isomers)	14
XVII	136	0,43	4,25 (N—CH_3); 2,82 (C—CH_3)	28,7	3,1	53,1	215	$C_5H_6N_8O_2$	28,6	2,9	53,4	210	10	6,6	83
XVIII	192	0,20	4,40 (N—CH_3); 8,55 (imidazole C-H), 7,1—8,0 (arom. H)	49,0	3,8	33,9	—	$C_{10}H_8N_6O_2$	49,2	3,3	34,3	244	7	80	18
XIX	208	0,46	4,40 (N—CH_3); 8,60 (C_3—H); 9,0—9,10 (arom. H)	43,3	2,8	30,8	—	$C_{10}H_7N_7O_4$	43,6	2,5	30,6	275	7	43	16
XX	159	0,51[e] 0,57	4,43 4,47 } N—CH_3 (isomers); 7,6—8,5 (arom. H)	44,3	3,0	40,2	241	$C_9H_7N_7O_2$	44,1	2,9	40,0	245	5	80	10
XXI[f]	106	—	4,90 (t, N—CH_2); 3,30 (t, CH_2CO, J=7 Hz); 2,15 ($COCH_3$); 9,25 (C_5—H)	29,1	2,3	29,8	339	$C_8H_7N_7O_3Br$	29,0	2,4	29,6	330	6	67	30
XXII[f]	109	—	4,85 (t, NCH_2); 3,30 (t, CH_2CO, J=6 Hz), 2,15 ($COCH_3$); 9,23 (C_5—H)	33,9	3,1	34,8	294	$C_8H_8N_7O_3Cl$	33,6	2,8	34,5	285,5	6	62	20
XXIII[f]	121	—	4,90 (t, NCH_2); 3,30 (t, CH_2CO, J=6 Hz); 2,15 ($COCH_3$); 9,52 (C_5—H)	32,6	2,7	38,1	291	$C_8H_8N_8O_5$	32,4	2,7	37,8	296	6	67	18
XXIV	161	—	4,75 (t, NCH_2); 3,30 (t, CH_2CO, J=6 Hz; 2,12 ($COCH_3$); 2,80 (C—CH_3)	35,5	3,7	35,8	323	$C_9H_{10}N_8O_5$	35,1	3,2	36,1	310	6	64	30
XXV	135	—	4,90 (t, NCH_2); 3,30 (t, CH_2CO, J=6 Hz); 9,40 (C_3—H); 8,7 (C_5—H)	36,5	3,4	33,1	298	$C_9H_9N_7O_5$	36,7	3,1	33,2	295	3,5	60	30
XXVI	162	—	5,85 (N—CH_2); 2,40 ($COCH_3$); 9,70 (C_5—H)	29,8	2,1	39,9	285	$C_7H_8N_8O_5$	29,8	2,1	39,8	282	5,5	65	Not isolated
XXVII[f]	105	—	6,20 (—CH=); 5,35 (NCH_2); 5,55 and 5,35 (CH_2=C); 9,50 (C_5—H)	31,5	2,3	41,3	270	$C_7H_6N_8O_4$	31,6	2,3	41,2	266	6	49	Not isolated
XXVIII[f]	116	—	5,60 (NCH_2); 3,75 (CH_3); 9,60 (C_5—H)	28,6	2,2	38,1	301	$C_7H_6N_8O_3$	28,2	2,0	37,6	298	6	30	Not isolated

[a]The compounds were crystallized: VI, IX-XV, XVIII-XXI, XXVII, and XXVIII from ethanol, VII from water with acetone, and VIII from water with ethanol. [b]From thin-layer chromatography in acetone—petroleum ether (2:3). [c]Found, %: Cl 15.85. calculated, %: Cl 15.4. [d]Found, %: Cl 26.4. Calculated, %: Cl 26.9. [e]From TLC in hexane—ethyl acetate (20:10:8). [f]Ethyl acetate was used as the solvent; acetone was used in the remaining cases.

triazole ring by the N_2 heteroatom (XVIb), while the doublets at 8.80 and 8.10 ppm with J = 4 Hz were assigned to the same protons in the isomeric compound, in which the v-triazole is connected to the s-triazole by the N_1 heteroatom (XVIa). The ratio of the XVIa and XVIb isomers is ∿1:1, which was estimated from the intensities of the signals. The signals of the



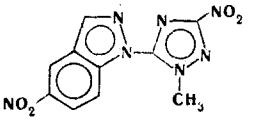
XVI a



XVI b

N-methyl groups of the two isomers do not differ as a consequence of the closeness of their values and the insufficient resolving power of the recording instruments. In the case of the XX isomers the signals of the methyl groups do not coincide (4.43 and 4.47 ppm with an intensity ratio of 2:1); however, it is difficult to assign them specifically.

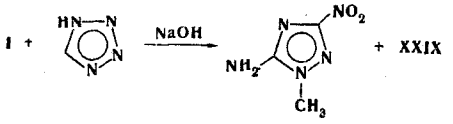
Only isomer XIX was obtained in the reaction of I with 5-nitroindazole. The signal of the C_3—H proton of the indazole ring (8.60 ppm) in the PMR spectra of isomer XIX remains virtually unshifted as compared with the signal in the PMR spectrum of the starting 5-nitroindazole (8.55 ppm [22]). If the reaction had taken place at the N_2 atom of indazole, one should have expected a significant shift of the signal of the C_3—N proton to weak field.



XIX

As to product XVII, which was obtained by the reaction of I with 5-methyltetrazole, the spectral and analytical data, as well as the literature data on the reactivities of tetrazole anions [23], do not make it possible to unambiguously assert whether product XVII contains a bond between the N_1 or N_2 atom of the tetrazole and the triazole ring.

The reaction of I with the salt of unsubstituted tetrazole proceeded in an unusual manner. Instead of the expected substitution product, we isolated 1-methyl-3-nitro-5-amino-1,2,4-triazole (XXXII) in 60% yield, as well as triazolone XXIX:



XXXII

The formation of amine XXXII is possibly due to reaction of triazole I with the products of cleavage of the tetrazole ring formed in the reaction medium by the action on the tetrazole of the nitrous acid that is formed by replacement of the nitro group in I by hydroxide ion.

EXPERIMENTAL

The IR spectra of films of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Perkin—Elmer R-12 spectrometer (60 MHz). Thin-layer chromatography (TLC) was carried out on Silufol UV-254; the chromatograms were developed with UV illumination.

Compounds I-IV were obtained by the methods in [21, 24, 25].

1-(Carbomethoxymethyl)-3,5-dinitro-1,2,4-triazole (V). A 26-g (0.17 mole) sample of methyl bromoacetate was added to a solution of 32.5 g (0.15 mole) of the sodium salt of dinitrotriazole in 100 ml of acetone, and the mixture was heated at 60°C for 40 h. It was then cooled, and the sodium bromide was removed by filtration. The filtrate was evaporated, and the residue was washed with water and crystallized from ethanol to give 14 g (40%) of a product with mp 115-116°C. IR spectrum: 1755 (C=O); 1560, 1315 cm^{-1} (NO_2). Found, %: C 25.8; H 2.2; N 30.2; M 228. $C_5H_5N_5O_6$. Calculated, %: C 26.0; H 2.2; N 30.2; M 231.

Reaction of I-V with Azole Anions. A solution of an equimolar amount of the azole and 0.011 mole of sodium hydroxide in 6 ml of water was added to a solution of 0.012 mole of dinitrotriazole I-V in 25 ml of acetone (or ethyl acetate), and the mixture was heated at 60°C (in the case of acetone) or 70°C (in the case of ethyl acetate) for the time indicated in Table 1 (with monitoring by TLC). At the end of this period, the solvent was removed by evaporation, and the residue was washed with water and crystallized (Table 1). For the isolation of triazolones XXIX-XXXI, the wash waters were acidified to pH 1.0 with 10% sulfuric acid and extracted with ethyl acetate. The solvent was removed by evaporation, and the residue was crystallized from aqueous ethanol.

1-Methyl-3-nitro-5-amino-1,2,4-triazole (XXXII). This compound, with mp 252-253°C (mp 254°C [11]), was obtained in 60% yield by reaction of I with tetrazole. The product was identical to a genuine sample with respect to its spectral characteristics and the results of TLC and a mixed-melting-point determination.

1-Methyl-3-nitro-1,2,4-triazol-5-one (XXIX). This compound had mp 228°C (mp 229°C [11]) and was identical to an authentic sample with respect to its IR and PMR spectra and the results of TLC.

1-3'-Oxobutyl)-3-nitro-1,2,4-triazol-5-one (XXX). This compound had mp 159-160°C. IR spectrum: 1720 (C=O), 1550, 1380 cm^{-1} (NO_2). PMR spectrum (in hexadeuteroacetone): 4.05 (t, NCH_2), 3.01 (t, CH_2CO, J = 6 Hz), and 2.18 ppm (s, CH_3). Found, %: 36.0; H 3.9; N 28.3; M 201. $C_6H_8N_4O_4$. Calculated, %: C 36.0; H 4.0; N 28.0; M 200.

1-(2'-Oxopropyl)-3-nitro-1,2,4-triazol-5-one (XXXI). This compound had mp 192-193°C. IR spectrum: 1730 (C=O); 1560, 1380 cm^{-1} (NO_2). PMR spectrum (in hexadeuteroacetone): 4.88 (s, CH_2) and 2.15 ppm (s, CH_3). Found, %: C 31.9; H 3.1; N 29.9; M 183. $C_5H_6N_4O_4$. Calculated, %: C 32.2; H 3.2; N 30.2; M 186.

LITERATURE CITED

1. M. S. Pevzner, P. A. Ivanov, N. V. Gladkova, O. N. Sushchenko, V. P. Tverdokhlebov, and Z. S. Myasnikova, Khim. Geterotsikl. Soedin., No. 2, 251 (1980).
2. J. F. K. Wilshire, Austral. J. Chem., 19, 1935 (1966).
3. M. A. Khan and B. M. Lynch, J. Heterocycl. Chem., 7, 1237 (1970).
4. M. D. Coburn and P. N. Neumann, J. Heterocycl. Chem., 7, 1391 (1971).
5. P. N. Neumann, J. Heterocycl. Chem., 8, 51 (1971).
6. R. Jaquier, M. L. Roumestant, and R. Viallefont, Bull. Soc. Chim. Fr., 2634 (1967).
7. M. D. Coburn and T. E. Jackson, J. Heterocycl. Chem., 5, 199 (1968).
8. M. D. Coburn, J. Heterocycl. Chem., 10, 743 (1973).
9. M. Aquial, A. Bernardini, and R. Viallefont, J. Heterocycl. Chem., 14, 397 (1977).
10. W. W. Gilman, B. C. Holland, G. R. Walsh, and R. J. Fayer, J. Heterocycl. Chem., 14, 1157 (1977).
11. L. I. Bagal, M. S. Pevzner, and V. Ya. Samarenko, Khim. Geterotsikl. Soedin., No. 2, 269 (1970).
12. L. I. Bagal, M. S. Pevzner, V. Ya. Samarenko, and A. P. Egorov, Khim. Geterotsikl. Soedin. No. 5, 702 (1970).
13. L. I. Bagal, M. S. Pevzner, V. Ya. Samarenko, and A. P. Egorov, Khim. Geterotsikl. Soedin. No. 7, 997 (1970).
14. L. I. Bagal, M. S. Pevzner, V. Ya. Samarenko, and A. P. Egorov, Khim. Geterotsikl. Soedin. No. 12, 1701 (1970).
15. M. S. Pevzner, L. I. Bagal, and V. Ya. Samarenko, Khim. Geterotsikl. Soedin., No. 1, 117 (1972).
16. L. I. Bagal, M. S. Pevzner, and V. Ya. Samarenko, Khim. Geterotsikl. Soedin., No. 4, 568 (1972).
17. W. Freiberg and C. F. Krüger, Chimia, 21, 159 (1967).
18. J. S. Mihina and R. M. Herbst, J. Org. Chem., 15, 1082 (1950).
19. T. P. Kofman, G. A. Zykova, V. I. Manuilova, T. N. Timofeeva, and M. S. Pevzner, Khim. Geterotsikl. Soedin., No. 7, 997 (1974).
20. T. P. Kofman, V. I. Manuilova, M. S. Pevzner, and T. N. Timofeeva, Khim. Geterotsikl. Soedin., No. 5, 705 (1975).
21. T. P. Kofman, T. L. Uspenskaya, N. Yu. Medvedeva, and M. S. Pevzner, Khim. Geterotsikl. Soedin., No. 7, 991 (1976).

22. J. Elguero and A. Fruchier, Bull. Soc. Chim. Fr., 2075 (1966).
23. R. N. Butler, Adv. Heterocycl. Chem., 21, 361 (1977).
24. L. I. Bagal, M. S. Pevzner, N. I. Sheludyakova, and V. I. Kerusov, Khim. Geterotsikl. Soedin., No. 2, 265 (1970).
25. A. A. Stotskii and N. P. Tkacheva, Zh. Org. Khim., 10, 2232 (1974).

SYNTHESIS OF 1-(1,2,4-TRIAZOL-3-YL)-1,2,3-TRIAZOLES

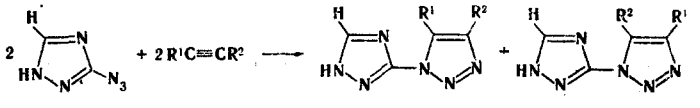
G. I. Tsypin, T. F. Sharamet,
T. A. Kravchenko, and M. S. Pevzner

UDC 547.791'792.07

1-(1,2,4-Triazol-3-yl)-1,2,3-triazoles were obtained by 1,3-dipolar cycloaddition of 3-azido-1,2,4-triazole to acetylene derivatives.

1,3-Dipolar cycloaddition of organic azides to acetylene derivatives usually leads to the formation of substituted 1,2,3-triazoles. Aliphatic and aromatic azides have been investigated extensively as starting reagents in this reaction [1-6].

In the present research we have studied the possibility of subjecting heterocyclic azido compounds, particularly 3-azido-1,2,4-triazole, to this reaction. The reaction of the latter with a number of acetylene derivatives made it possible to obtain the corresponding 1-(1,2,4-triazol-3-yl)-1,2,3-triazoles (I-IV) (Table 1); the participation of monosubstituted acetylenes in the reaction led to the formation of two isomers, viz., Ia and Ib and IIIa,b-IVa,b.



I-V a I-V b

Ia,b $R^1=H$, $R^2=C_6H_5$; II $R^1=R^2=C_6H_5$; III a,b $R^1=H$, $R^2=HOCH_2$; IV a,b $R^1=H$, $R^2=CH_3OOC$; V $R^1=R^2=H$

In most cases we were able to separate the mixtures of isomers into individual compounds. Two-ring product V, which does not contain a substituent, was obtained by alkaline saponification of IVa and subsequent decarboxylation.

The structures of the isolated compounds were determined on the basis of the PMR spectra (Table 2). It is apparent from the spectral data presented in Table 2 that a change in the substituent in the ditriazolyl series has a slight effect on the chemical shift of the proton of the 1,2,4-triazole ring (δ_{CH} ranges from 8.90 to 9.08 ppm) because of the remoteness of this proton from the functional group in the 1,2,3-triazole ring.

The type of isomer (Ia or Ib) among the products of addition of the azide to phenylacetylene was easily established from the signal of the phenyl protons: in conformity with the data in [5-9], it is split in the case of 1,4-substituted 1,2,3-triazole Ia, whereas in the case of 1,5 isomer Ib it is recorded in the form of a singlet. Similar character of the signals of the phenyl groups is also observed in the spectrum of 1-(1,2,4-triazol-3-yl)-4,5-diphenyl-1,2,3-triazole (II).

The assignment of the chemical shifts in the PMR spectra of isomers IIIa,b and IVa,b was made on the basis of the general observation that the singlet of the proton bonded to the ring lies at weaker field in the spectra of 1,4-substituted 1,2,3-triazoles than in the spectrum of the corresponding 1,5 isomer [6]. This, as well as the data in [10], served as a basis for the interpretation of the spectrum of 1-(1,2,4-triazol-3-yl)-1,2,3-triazole (V).

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 262-264, February, 1980. Original article submitted January 31, 1979; revision submitted July 16, 1979.

0009-3122/80/1602-0199$07.50