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Reactions of 3-Azido-1,2,4-triazole with Electrophiles

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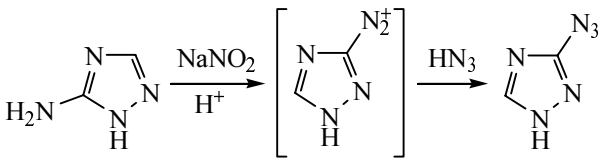
Abstract—Alkylation of 3-azido-1,2,4-triazole with oxiranes, bromoacetone, and methyl vinyl ketone furnished a mixture of N-substituted 3- and 5-azido-1,2,4-triazoles, 3-azido compounds prevailing. The same substrate subjected to heterylation with 3,5-dinitro-1,2,4-triazole derivatives reacted selectively at the N^1 atom, and its bromination afforded 3-azido-5-bromo-1,2,4-triazole. .

In the 1,2,4-triazole series the reactivity of its azido derivatives is almost unknown, even that of the first representative of the series, 3-azido-1,2,4-triazole (**I**), although the synthesis [1, 2], electronic structure, vibration spectra [3], and acid-base properties [4] of 3-azido-5-R-1,2,4-triazoles has been described some time ago.

The azido derivative **I** was first synthesized by nitrozation of 3-hydrazino-1,2,4-triazole [1]. We developed a simpler method of its preparation in a high yield from the more available 5-amino-1,2,4-triazole through diazotization: by replacing the amino group following the procedure similar to that described in [2] for the other 3-azido-5-R-1,2,4-triazoles (Scheme 1).

Scheme 1.

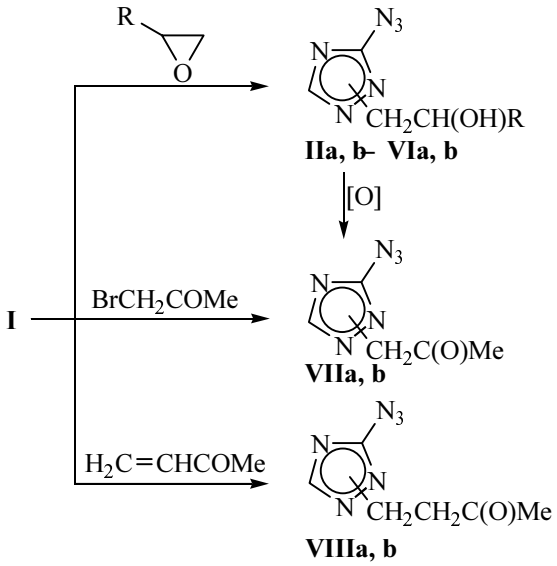


I

Compound **I** is a weak NH-acid (pK_a 9.37, 60% ethanol, ^{1}H NMR [4]; 8.64, water, UV spectroscopy, our data).

In the series of 3-R-1,2,4-triazoles only the reactivity of 3-nitro-1,2,4-triazoles is sufficiently well documented. This compound was studied in reactions of N-alkylation [5–7], N-addition to unsaturated compounds with an activated double bond [7], N-heterylation [8], and halogenation [9]. We attempted to perform analogous reactions for the 3-azido-1,2,4-triazole using electrophiles of various characters: bromine, 3,5-dinitro-1,2,4-triazole derivatives, and also substrates ensuring functional group introduction into its N-alkyl fragment. To the latter group belong oxiranes providing alcohols [**II–VI**, R = H (**II**), CH_3 (**III**), CH_2OH (**IV**), CH_2ONO_2 (**V**), CH_2Cl (**VI**)], and also bromoacetone and methyl vinyl ketone furnishing the corresponding ketones (**VII, VIII**) (Scheme 2).

Scheme 2.



3-Nitro-1,2,4-triazole in such syntheses reacts as a rule at the N^1atom, distal with respect to the substituent in the ring, and does not form appreciable amount of N^2-isomers. The alkylation with a hard electrophile diazomethane forms an exception, when the N^2-isomer (1-methyl-5-nitro-1,2,4-triazole) attains 24% in the mixture of N^1- and N^2-isomers [5]. We found another exception in reaction with the bromoacetone where the content of

TLC and ^{1}H NMR data, and the ratio of 3- (**IIIa,VIIa,VIIIa**) and 5-azido derivatives of 1,2,4-triazole (**IIIb,VIIb,VIIIb**)

Compd. no.	TLC		^{1}H NMR spectrum, δ, ppm				Ratio a:b
	Solvent system	R_f	CH_2	CH	CH_3	$C_{Ht}H$	
IIIa, b	Acetone–hexane, 1:1	0.370.51	4.30 d 4.10 d	3.90 m 3.90 m	1.15 d 1.15 d	8.40 s 7.80 s	12:5
VIIa, b	Hexane–acetone–EtOAc, 14:3:2	0.310.49	5.25 s 5.00 s	–	2.20 s 2.20 s	8.40 s 7.90 s	4:1
VIIIa, b	Hexane–acetone–EtOAc, 14:3:2	0.410.57	4.32 t, 3.10 t 4.10 t, 3.05 t	–	2.10 s 2.10 s	8.22 s 7.70 s	7:1

N^2-isomer, 5-nitro-1-(2-oxopropyl)-1,2,4-triazole, in the reaction products reacted to 5–7% (^{1}H NMR spectroscopy).

N-Alkylation of 3-azido-1,2,4-triazole is not selective (scheme 2). According to the data of ^{1}H NMR and TLC (see table) in all cases formed a mixture of N^1- and N^2-isomers, the former prevailing. At the same time the content of the N^2-isomer is significant, and it grows in the series of alkylating agents methyl vinyl ketone – oxiranes–bromoacetone. The isomers ratio was estimated from the intensity ratio of the signals of the ring protons (C^5H and C^3H) whose positions in the ^{1}H NMR spectrum was essentially different (Δδ 0.5–0.6 ppm). Beside these signals in the spectra appear the triplets of methylene group protons from the substituent attached to the heteroatom of the ring, and the corresponding resonances of the N^1-isomers are located in a weaker field (see table).

The alkylation of 3-azido-1,2,4-triazole with oxiranes, same as in reactions with the other triazoles [10], occurs with regularly increasing pH of the medium caused by the NH-acid consumption. The accumulation of the target reaction product proceeds simultaneously and reaches the maximum yield at pH exceeding the pK_a of the 3-azido-1,2,4-triazole by 2.0–2.5 units. Unlike more acidic substrates (pK_a 3–7) the 3-azido-1,2,4-triazole reacts with epoxides in aqueous ethanol at room temperature at a considerable rate and without bases, but the addition of bases significantly accelerates the reaction (adding 1–10% of the base amount necessary for the total conversion of the NH-acid into a salt). The use of a larger quantity of alkali in these syntheses is not required. Besides the reaction should be stopped in due time: at pH < 10.5–11. The observance of these conditions prevents secondary reactions: alkylation of the alcohol formed with excess epoxy compound and dehydrochlorination or denitration of alcohols **V** and **VI** resulting from reactions of the 3-azido-1,2,4-triazole with epichlorohydrin and nitroglycide respectively.

The alkylation with oxiranes furnished a mixture of secondary alcohols, 2-hydroxyalkyl derivatives **II–VI**. Their structure was proved by oxidation of alcohol **III** with chromium(VI) oxide to propanone **VII** analogous to the ketone obtained by the direct alkylation of 3-azido-1,2,4-triazole with bromoacetone. The structures of alcohols were also confirmed by the ^{1}H NMR spectra. In the spectra of all alcohols obtained the chemical shifts of protons from the CH_2 group attached to the heteroatom had characteristically similar values, both in the spectrum of the *a fortiori* primary alcohol **II** and in the spectra of all other hydroxy derivatives **III–VI**. In the spectra of diols **IV** the nonequivalence of two methylene groups in their structure is well seen.

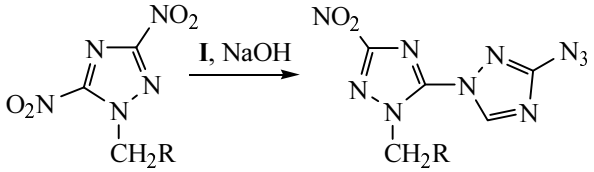
The reactions of the 3-azido-1,2,4-triazole with bromoacetone and methyl vinyl ketone were performed by prolonged keeping of the reagents at room temperature (TLC monitoring). In the first reaction triazole **I** was converted into the anion form by sodium hydroxide, in the second case by triethylamine.

The alkylation products mixtures are as a rule viscous nondistillable oily substances. However since the N^2-isomers are more soluble in ether, we succeeded in most cases in separation in a pure state of the prevailing N^1-isomer. To this end the latter was precipitated from the concentrated ethyl ether solution of the isomer mixture with petroleum ether (compounds **III** and **VIII**) or it was frozen out from the ether solution (compounds **II** and **VII**), or a fractional crystallization was performed (compounds **IV–VI**). The most reach with N^2-isomer propanone **VIII** was an exception for even after 2–3 reprecipitations it still contained an impurity of this isomer.

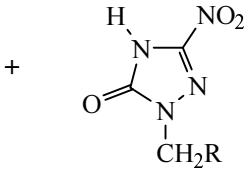
In reactions introducing heterocyclic substituents into the 3-azido-1,2,4-triazole we did not observe any notable nonselectivity like that found in alkylation. In crude

products of reaction with 3,5-dinitro-1,2,4-triazole derivatives (R = H, CH_2COMe) the N^2-isomer was not revealed by ^1H NMR spectroscopy. The reaction mixture contained only the products of the nitro group replacement in the substrate: N-C-bitriazoles **IXa** and **Xa** and the corresponding triazole-5-ones **IXb** and **Xb** (Scheme 3). Therewith under standard conditions the overall yield of the main reaction products was close to quantitative one [equimolar reagents ratio, medium 90% acetone (two-phase system ethyl acetate–water), 60 (80)°C, the reaction mixture stored till complete consumption of the substrate as shown by TLC]. Note that the NH-acidity of the 3-arido-1,2,4-triazole falls in the optimal range for these substitution reactions ensuring both the high yield of N-C-bitriazoles and the lack of considerable heterolysis of the initial and bicyclic butanones **X** under the synthesis conditions; the latter process is fairly common for this type compounds [8].

Scheme 3.



IXa, Xa

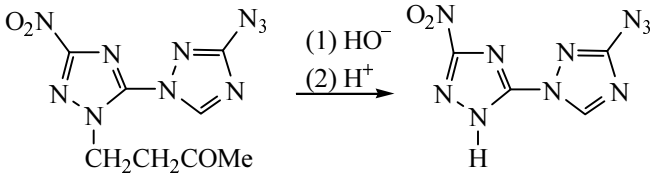


IXb, Xb

R = H (**a**), CH_2COMe (**b**).

Ketone **Xa** undergoes hydrolysis in alkaline medium furnishing a new compound from the bitriazole series, 5-(3-azido-1,2,4-triazol-1-yl)-3-nitro-1,2,4-triazole (**XI**) (Scheme 4).

Scheme 4.

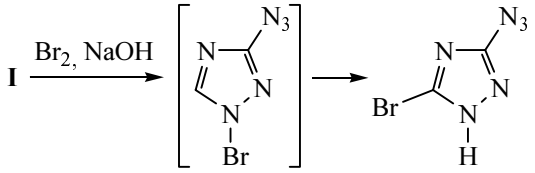


Xa **XI**

Azole **XI** possesses relatively high acidity: As estimated by spectrophotometric procedure, pK_a is 1.75 [11].

The bromination of the 3-azido-1,2,4-triazole with bromine along the procedure formerly used with 3-nitro-1,2,4-triazole [9] gave rise to a bromo derivatives whose ^1H NMR spectrum lacked the signal from the proton C^5H.

Scheme 5.



XII

Evidently here like in the other triazoles reactions with a halogen in an alkaline medium the primary attack is directed on a heteroatom giving an intermediate N-bromo derivative that at heating undergoes thermal intramolecular rearrangement resulting in 3-azido-5-bromo-1,2,4-triazole (**XII**) (Scheme 5).

EXPERIMENTAL

^1H NMR spectra were registered on spectrometer Perkin Elmer R-12 (60 MHz) in acetone-d_6, internal reference HMDS. IR spectra were recorded on spectrophotometer Specord 75IR (from films). Elemental analysis was carried out on CHN-analyzer Hewlett-Packard-185B. Molecular weight was determined by the method of reversed ebullioscopy in acetone. TLC was performed on Silufol UV-254 plates.

NH-Acidity of biazole **XI** was measured by spectrophotometric procedure using a spectrophotometer CF-16 and a pH-meter pH-262 in aqueous buffer media by a standard method [11].

3-Azido-1,2,4-triazole (I). To a solution of 10 g (0.12 mol) of 3-amino-1,2,4-triazole in 124 ml (0.288 mol) of 20% sulfuric acid at a temperature not exceeding 0–3°C was added dropwise a solution of 8.26 g (0.12 mol) of sodium nitrite in 10 ml of water. The reaction mixture was maintained for 30 min at 0°C, to the obtained solution of the diazonium salt was added a small amount of urea, and at a temperature not exceeding 0–2°C was added by portions a solution of 20 g (0.154 mol) of sodium azide in 80 ml of water. The mixture was kept for 30 min at 18–20°C, the precipitated azido compound **I** was filtered off, the filtrate was neutralized with sodium hydrogen carbonate till pH 5–6 and extracted with ethyl acetate

(3×50 ml). The combined extracts were washed with water and dried on calcined magnesium sulfate. The residue after removing the solvent was added to the main product, and it was crystallized from toluene. Yield 80%, mp 121–123°C. IR spectrum, ν, cm^{-1}: 980, 1020, 1090, 1175, 1260, 1340, 1460, 1515, 2140 (N_3). ^1H NMR spectrum, δ, ppm: 8.40.

3(5)-Azido-N-(2-hydroxyalkyl)-1,2,4-triazoles (II–VI). To a solution of 2.9 g (0.026 mol) of azidotriazole **I** in 15 ml of ethanol placed into a graduated flask of 25 ml capacity was added a solution of 0.106 g (0.0026 mol) of sodium hydroxide in 2 ml of water, and 0.046 mol of epoxide. Then ethanol was added to the 25 ml mark. The reaction mixture was kept at room temperature in a stoppered flask measuring intermittently the pH of the solution (pH_{init} 7.8). When the pH reached the value of 10.5–11 (48–72 h) the reaction mixture was diluted with a double volume of water, and the alcohol formed was extracted into ethyl acetate (5×50 ml). The extract was washed with water, dried with calcined magnesium sulfate, the solvent was removed in a vacuum. 3-Azido-1-(2-hydroxyalkyl)-1,2,4-triazoles were separated from 5-azido isomers by freezing out from ether solution (alcohol **II**), reprecipitation from ether solution with petroleum ether (alcohol **III**), or by fractional crystallization (compounds **IV–VI**).

3-Azido-1-(2-hydroxyethyl)-1,2,4-triazole (II). Yield 80%, mp 35–36°C (ether). IR spectrum, ν, cm^{-1}: 870, 950, 1050, 1075, 1130, 1210, 1250, 1280, 1355, 1380, 1435, 1495, 1540 (cycle), 2170 (N_3), 3200–3600 (OH). ^1H NMR spectrum, δ, ppm: 8.40 s (1H, H^5), 5.60 t (1H, OH), 4.30 t (2H, CH_2), 3.97 t (2H, CH_2). Found, %: C 30.88, 31.31; H 3.51, 3.42; N 54.94, 54.32. $[M]^+$ 153. $C_4H_6N_6O$. Calculated, %: C 31.12; H 3.92; N 54.53. *M* 154.13.

3-Azido-1-(2-hydroxypropyl)-1,2,4-triazole (III). Yield 85%, n_D^{20} 1.5253. IR spectrum, ν, cm^{-1}: 860, 950, 1060, 1090, 1150, 1200, 1250, 1280, 1290, 1350, 1390, 1450, 1480, 1530 (cycle), 2170 (N_3), 3200–3600 (OH). ^1H NMR spectrum, δ, ppm: 8.40 s (1H, H^5), 5.00 (1H, OH), 4.30 d (2H, CH_2), 3.90 m (1H, CH), 1.15 d (3H, CH_3). Found, %: C 35.72, 35.47; H 5.15, 5.29; N 49.54, 49.28. $[M]^+$ 164. $C_5H_8N_6O$. Calculated, %: C 35.71; H 4.80; N 49.98. *M* 168.16.

3-Azido-1-(2,3-dihydroxypropyl)-1,2,4-triazole (IV). Yield 75%, mp 77–78°C (MeOH). IR spectrum, ν, cm^{-1}: 870, 940, 960, 980, 1040, 1060, 1090, 1160, 1210, 1250, 1365, 1460, 1540 (cycle), 2170 (N_3), 3200–3600 (OH). ^1H NMR spectrum, δ, ppm: 8.35 s (1H, H^5), 4.90 s (OH), 4.51 d (2H, CH_2), 4.29 m (1H, CH), 3.97 d (2H, CH_2). Found, %: C 32.85, 32.48; H 4.40, 4.10; N 45.55, 45.94. $[M]^+$ 188. $C_5H_8N_6O_2$. Calculated, %: C 32.88; H 4.38; N 45.64. *M* 184.16.

3-Azido-1-(2-hydroxy-3-nitrooxypropyl)-1,2,4-triazole (V). Yield 72%, mp 88–89°C (benzene). IR spectrum, ν, cm^{-1}: 855, 875, 900, 980, 1060, 1070, 1160, 1250, 1310, 1360, 1375, 1425, 1550, 1650 (ONO_2), 2160 (N_3), 3200–3600 (OH). ^1H NMR spectrum, δ, ppm: 8.40 s (1H, H^5), 5.60 s (OH), 4.65 d (2H, CH_2), 4.37 d (2H, CH_2), 4.00 m (1H, CH). Found, %: C 25.97, 25.93; H 3.33, 3.24; N 42.62, 42.77. $[M]^+$ 226. $C_5H_7N_7O_4$. Calculated, %: C 26.21; H 3.08; N 42.79. *M* 229.16.

3-Azido-1-(2-hydroxy-3-chloropropyl)-1,2,4-triazole (VI). Yield 82%, mp 119–120°C (MeOH). IR spectrum, ν, cm^{-1}: 1050, 1105, 1160, 1190, 1250, 1350, 1360, 1460, 1490, 1540, 2160 (N_3), 3400–3600 (OH). ^1H NMR spectrum, δ, ppm: 8.40 s (1H, H^5), 5.60 (OH), 4.35 d (2H, CH_2), 4.00 m (1H, CH), 3.70 d (2H, CH_2). Found, %: C 29.73, 29.85; H 3.19, 3.45; N 41.59, 41.37. $[M]^+$ 198. $C_5H_7ClN_6O$. Calculated, %: C 29.89; H 3.48; N 41.48. *M* 202.61.

3-Azido-1-(3-oxopropyl)-1,2,4-triazole (VII). (a) To a solution of 0.07 mol of alcohol **III** in 190 ml of acetonea was added by portions while stirring at 25–30°C a solution of 7 g (0.07 mol) of CrO_3 in a diluted sulfuric acid [preliminary prepared from 14 ml of water and 6.1 ml (0.11 mol) of concn. H_2SO_4]. The reaction mixture was stirred for 30 min at 25–30°C, then several drops of 2-propanol was added, the precipitate was filtered off and washed with acetone. The combined acetone washings and filtrate were stirred with 10 g of sodium hydrogen carbonate, the precipitate was filtered off, the solvent was removed, the residue was dissolved in ether, the ether solution was washed with water, and dried on calcined magnesium sulfate. The drying agent was filtered off, and petroleum ether was added to the solution in ethyl ether. The arising oily substance was separated, dissolved in a minimum amount of ether, and the solvent was removed in a vacuum. Yield 75%, n_D^{20} 1.5772. IR spectrum, ν, cm^{-1}: 1040, 1070, 1170, 1185, 1230, 1340, 1375, 1435, 1460, 1530, 1725 (C=O), 2140 (N_3). ^1H NMR spectrum, δ, ppm: 8.40 s (1H, H^5), 5.25 s (2H, CH_2), 2.20 s (3H, CH_3). Found, %: C 36.49, 36.23; H 3.55, 3.62; N 51.01, 50.77. $[M]^+$ 170. $C_5H_6N_6O$. Calculated, %: C 36.15; H 3.64; N 50.62. *M* 166.14.

(b) To a solution of 5 g of azole **I** in 20 ml of ethanol was added at room temperature while stirring a solution of 1.84 g of sodium hydroxide in 3 ml of water, and 7 ml of bromoacetone. The reaction mixture was left standing

for 5 days. The solvent then was removed, the residue was dissolved in ether, the solution was washed with water, and dried on calcined magnesium sulfate. The solvent was removed in a vacuum, the oily residue (isomer mixture) was dissolved in a minimum amount of ether, and petroleum ether was added thereto. The precipitated product was separated, and the reprecipitation was repeated 2–3 times, yield 40% (impurity of N^2-isomer, TLC).

3-Azido-1-(3-oxobutyl)-1,2,4-triazole (VIII). To a solution of 0.044 mol of triazole **I** in 15 ml of ethanol was added 1 ml of triethylamine and 4.5 ml (0.054 mol) of methyl vinyl ketone. The reaction mixture was kept for 48 h at room temperature, the solvent was removed, and the residue was crystallized from ether by cooling the concentrated ether solution to –30...–40°C. Yield 65%, mp 34–35°C (ether). IR spectrum, ν, cm^{-1}: 1040, 1070, 1170, 1185, 1230, 1340, 1375, 1435, 1460, 1530, 1725 (C=O), 2140 (N_3). ^1H NMR spectrum, δ, ppm: 8.22 s (1H, H^5), 4.32 t (2H, CH_2), 3.10 t (2H, CH_2), 2.15 s (3H, CH_3). Found, %: C 39.86, 40.18; H 4.59, 4.74; N 46.90, 46.58. $[M]^+$ 177. $C_6H_8N_6O$. Calculated, %: C 40.00; H 4.48; N 46.65. *M* 180.17.

1-R-Methyl-3-nitro-5-(3-azido-1,2,4-triazol-1-yl)-1,2,4-triazoles (IXa, Xa). To a preliminary prepared solution of 0.03 mol of azidotriazole **I** in 5 ml of water containing 0.03 mol of sodium hydroxide was added at room temperature while stirring a solution of 0.025 mol of 1-RCH_2-3,5-dinitro-1,2,4-triazole (R = H, CH_2COMe) [5, 7] in 45 ml of acetone (ethyl acetate). The reaction mixture was heated at reflux till complete consumption of the substarate [TLC monitoring, solvent system: hexane–acetone–ethyl acetate, 5:2:1; R_f of susbtrates: 0.58 (R = Me), 0.56 (R = CH_2COMe)]. The solvent was evaporated, 20 ml of water was added to the residue, the mixture was stirred for 20 min, the insoluble part (bi-triazole) was filtered off, washed with water on the filter, dried, and crystallized. The combined filtrates and wash water were acidified with 10% sulfuric acid to pH 1, extracted with ethyl acetate (3×25 ml), the extract was washed with water, and dried with calcined magnesium sulfate, the solvent was removed, and the residue (the corresponding triazolones **IXb, Xb**) were crystallized. Triazolones **IXb** and **Xb** were identical to compounds we had described before [8].

5-(3-Azido-1,2,4-triazole-1-yl)-1-methyl-3-nitro-1,2,4-triazole (IXa). Yield 75%, mp 125–126°C (EtOH). IR spectrum, ν, cm^{-1}: 850, 900, 980, 1190, 1320, 1340, 1420, 1460, 1530 (bicycle), 1570 (bicycle), 1590 (NO_2), 2160 (N_3). ^1H NMR spectrum, δ, ppm: 9.18 s (1H, H^5), 4.30 (3H, CH_3). Found, %: C 25.73, 25.50; H 1.81, 1.72; N 59.72, 59.81. $[M]^+$ 230. $C_5H_4N_{10}O_2$. Calculated, %: C 25.64; H 1.83; N 59.31. *M* 236.16.

5-(3-Azido-1,2,4-triazol-1-yl)-3-nitro-1,2,4-triazole-1-butan-3-one (Xa). Yield 65%, mp 79–80°C (aqueous EtOH). ^1H NMR spectrum, δ, ppm: 9.13 s (1H, H^5), 4.81 t (2H, CH_2), 3.25 t (2H, CH_2), 2.15 s (3H, CH_3). IR spectrum, ν, cm^{-1}: 1340, 1360, 1425, 1480, 1540 (bicycle), 1600 (bicycle), 1750 (C=O), 2175 (N_3). Found, %: C 32.96, 32.81; H 2.90, 2.99; N 48.45, 48.07. $[M]^+$ 301. $C_8H_8N_{10}O_3$. Calculated, %: C 33.15; H 2.76; N 47.93. *M* 292.22.

5-(3-Azido-1,2,4-triazol-1-yl)-3-nitro-1,2,4-triazole (XI). To a solution of 0.48 g (0.12 mol) of sodium hydroxide in 25 ml of water was added at cooling while stirring 0.04 mol of butanone **Xa**, the reaction mixture was left standing at 18–20°C till it turned homogeneous, the mixture was extracted with ether (25 ml) to remove the formed methyl vinyl ketone, the water layer was acidified with 10% sulfuric acid till pH 1, and extracted with ethyl acetate (3×25 ml). The extract was washed with water, the solvent was removed, and the residue was crystallized. Yield 72%, mp 154–155°C (chloroform). IR spectrum, ν, cm^{-1}: 850, 970, 1050, 1205, 1312, 1335, 1465, 1515, 1532, 1565, 1605, 2155 (N_3). ^1H NMR spectrum, δ, ppm: 9.20 s (H^5). Found, %: C 21.20, 21.55; H 0.78, 0.81; N 62.75, 62.80. $[M]^+$ 226. $C_4H_2N_{10}O_2$. Calculated, %: C 21.63; H 0.91; N 63.10. *M* 222.13.

3-Azido-5-bromo-1,2,4-triazole (XII). A mixture of 1.08 g (0.027 mol) of NaOH in 20 ml of water, 3 g (0.027 mol) of azole **I**, and 1.5 ml of bromine was cautiously heated to boiling and maintained on the boiling water bath for 20 h, then it was cooled, acidified with 20% sulfuric acid till pH 3, and extracted with ether (3×30 ml). The extract was washed with water, dried with calcined magnesium sulfate, the solvent was removed, and the residue was crystallized. Yield 60%, mp 64–65°C (hexane). IR spectrum, ν, cm^{-1}: 995, 1030, 1140, 1235, 1255, 1330, 1425, 1480, 1530, 2145 (N_3). Found, %: C 12.52, 12.87; H 0.72, 0.81; N 44.92, 44.71. $[M]^+$ 198. C_2HBrN_6. Calculated, %: C 12.71; H 0.53; N 44.47. *M* 188.98.

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