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Dedicated to Full Member of the Russian Academy of Sciences V.A. Tartakovskii on the 70th Anniversary of His Birth

Synthesis, Structure, and Alkylation of 4-Nitroamino-1,2,4-triazole*

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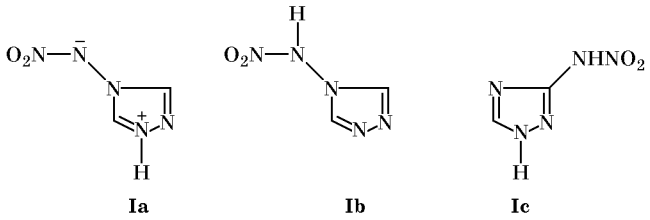
Abstract—Nitration of 4-amino-1,2,4-triazole with nitric acid in acetic anhydride gives the corresponding *N*-nitroamino derivative which has an inner salt structure. Its alkylation with alkyl halides, as well as with oxiranes, occurs only at the endocyclic nitrogen atom, while the exocyclic reaction center is not involved. All the 1-substituted products have the structure of 1-alkyl-1,2,4-triazol-1-io-4-*N*-nitroimides.

N-Nitroamino derivatives of 1,2,4-triazole constitute an interesting but poorly studied class of compounds. Apart from endocyclic nitrogen atoms, their molecules possess an exocyclic reaction center, *N*-nitroamino group. Such multident systems could give rise to a wider variety of properties than those intrinsic to the other 1,2,4-triazole derivatives. The structure of nitroaminotriazoles suggests that their reactions with electrophilic reagents could occur at both exo- and endocyclic nitrogen atoms. According to the data given in [1], such *N*-nitroamines can be regarded as medium-strength NH acids (pK_a 4–5).

Compounds in which the *N*-nitroamino group is attached to the ring heteroatom, in particular 4-nitroamino-1,2,4-triazole, attract specific attention among nitroaminoazoles. The properties and reactivity of 4-nitroamino-1,2,4-triazole were poorly studied: only a few its derivatives were reported [2, 3]. According to Arriau *et al.* [4], this compound is stable toward acids; moreover, it can be protonated. On the other hand, 4-nitroamino-1,2,4-triazole is a very weak base (pK_{BH^+} = –3.24), and the most probable protonation center is the oxygen atom in the nitro group rather than the ring nitrogen atom. Specific structure of heteroaromatic *N*-nitroamines, including 4-nitroamino-1,2,4-triazole, should be noted. Theoretically, such compounds can exist as ylide (**Ia**) and nitroamine form (**Ib**). Most researchers believe [1–6] that the ylide structure is more favorable. The recent X-ray diffraction data [7] confirmed the ylide structure of 4-nitroamino-1,2,4-triazole which exists in crystal in the form of 1,2,4-triazol-1-io-4-*N*-nitroimide (**Ia**). The triazole ring and the nitroimide fragment are almost planar, and the angle between their planes is about 50°. The N–N bond linking these fragments is the longest bond in the molecule and is also the weakest one. The hydrogen atoms are localized on the C^3 and C^5 carbon atoms and N^1:



Ia **Ib** **Ic**

The inner salt structure of this compound in solution follows from the ^{1}H NMR spectrum (Table 1), where the 3-H and 5-H protons give a single singlet. Although such coincidence of the ring proton signals is most probable for more symmetric nitroamine structure **Ib**, the downfield position of the corresponding signal (δ 9.55 ppm) is indicative of the ylide structure. Presumably, this is the result of fast and reversible protonation of the endocyclic N^1 and N^2 atoms. The coincidence of the 3-H and 5-H signals in nearly symmetric structures is typical, e.g., of

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Table 1. IR and ^{1}H NMR spectra of 1,2,4-triazole derivatives **Ia**, **Ic**, **V**–**VII**, and **XII**–**XVI**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm			
		3-H	5-H	CH_2N (*J*, Hz)	other protons
Ia	865, 900, 990, 1025, 1050, 1080, 1180, 1220, 1240, 1285 v.s, 1325 s, 1365 s, 1500, 1525, 1550, 1565, 1580, 3120, 3170	9.55		–	–
Ic	865, 900, 980, 1013, 1070, 1080, 1160, 1240 s, 1260 s, 1305 v.s, 1345 v.s, 1415, 1455 s, 1480, 1555 s, 1600 v.s, 1610, 3300, 3490, 3520	–	8.40	–	–
V	860, 900, 985, 1035, 1088, 1165, 1250, 1295 v.s, 1300 s, 1380, 1390, 1415, 1430, 1480, 1525, 1550, 1570, 2870 s, 2940 v.s, 2975, 3060, 3140	9.40	10.40	4.35 t (9)	1.90 m, 1.25 m, 0.8 d [19H, $(CH_2)_8CH_3$]
VI	860, 900, 985, 1040, 1088, 1165, 1290 v.s, 1300 s, 1380, 1390, 1415, 1430, 1460, 1480, 1530, 1550, 1570, 2865 s, 2940 v.s, 2975, 3060, 3140	9.45	10.45	4.40 t (10)	1.90 m, 1.25 m, 0.9 d [23H, $(CH_2)_{10}CH_3$]
VII	860, 900, 985, 1035, 1088, 1165, 1250, 1290 v.s, 1300 s, 1380, 1390, 1420, 1430, 1480, 1525, 1550, 1570, 2870 s, 2940 v.s, 2975, 3060, 3140	9.45	10.40	4.40 t (10)	1.85 m, 1.25 m, 0.85 m [31H, $(CH_2)_{14}CH_3$]
XII	1000, 1075 s, 1085, 1110, 1130, 1155, 1175, 1205, 1240, 1265, 1320 v.s, 1345 s, 1388, 1412 s, 1515, 1530, 1575, 3100, 3145, 3400, 3420	9.20	10.15	4.45 d (8)	3.83 d (2H, CH_2, *J* = 8 Hz), 5.10 t (1H, OH)[a]
XIII	1015, 1030, 1080 s, 1145, 1205, 1225, 1235, 1280 s, 1305 v.s, 1330 s, 1388, 1400, 1430 s, 1450, 1530, 1545, 1570, 3430	9.05	10.05	4.25 d (8)	4.05 m (1H, CH), 1.15 d (3H, CH_3, *J* = 8 Hz), 5.20 t (1H, OH)[a]
XIV	1020, 1040, 1080 v.s, 1312 v.s, 1380 s, 1426 s, 1465, 1550, 1570, 3080 s, 3140 s, 3350, 3630	–	8.40	4.55 d (9)	4.30 m (1H, CH), 3.65 d (2H, CH_2, *J* = 9 Hz), 5.10 t (1H, OH)[a]
XIVa	1060, 1090 s, 1180, 1205, 1230, 1265 s, 1290 v.s, 1307 s, 1340 s, 1355 s, 1410, 1440, 1450, 1480 s, 1505, 1510, 1540, 1560 s, 1590 v.s, 3400, 3440, 3450, 3520, 3545	9.40	10.40	4.05 d (7)	4.30 m (1H (CH), 3.65 d (2H, CH_2, *J* = 7 Hz), 5.30 t (1H, OH)[a]
XV	1000, 1040, 1080 v.s, 1160, 1285 v.s, 1300 v.s, 1375 v.s, 1420 s, 1480, 1520, 1570, 1640 s, 3440	9.50	10.45	4.85 d (8)	4.40 m (1H, CH), 4.95 d (2H, CH_2, *J* = 8 Hz), 5.80 (1H, OH)[a]
XVI	1025, 1060, 1085, 1180, 1240, 1290 v.s, 1310 v.s, 1380 s, 1420 s, 1475, 1530, 1575, 1645 v.s, 3120	9.20	10.15	4.60 d (8)	4.05 d (2H, CH_2, *J* = 8 Hz)

[a] Exchanges with D_2O.

1,2,4-triazole itself: its signals appear separately only at a very low temperature [8]. It is interesting that in the ^{1}H NMR spectrum of isomeric 3-nitroamino-1,2,4-triazole (**Ic**), in which the nitroamino group is attached to C^3, the 5-H signal is observed in a weaker field ($\Delta\delta$ 1.15 ppm, Table 1).

The predominance of structure **Ia** both in the gas phase and in water was confirmed by the results of PM3 quantum-chemical calculations. It is known [9] that the PM3 procedure provides a good agreement with experimental data for most calculated geometric, thermodynamic, and other physicochemical parameters of azoles. The calculations were performed with the use of MNDO-90 software package [10]. The gas-phase enthalpies of formation ΔH_f of isomeric species **Ia** and **Ib** are 88.17 and 93.92 kcal/mol, respectively, and their dipole moments are 9.32 and 3.93 D. Taking into account nonspecific solvation (in terms of the point dipole approximation [11]), it was found that polar structure **Ia** in water is even more favorable: the calculated ΔH_f values are 66.95 and 83.75 kcal/mol for **Ia** and **Ic**, respectively. It should also be noted that the calculated bond lengths and bond angles in molecule **Ia** are very consistent with the X-ray diffraction data [7]. However, the dihedral angle between the planes of the nitroimide and heterocyclic fragments (as might be expected) approaches 90°; presumably, the smaller angle in the crystalline state is explained by the crystal field effect.

Compounds having a nitroamino group at a nitrogen atom were reported for the first time in [12, 13], and the first heterocyclic ylides were pyridine-1-nitroimides obtained by treatment of 1-aminopyridine nitrates [12, 13] or sulfonylimide nitrates [13] with concentrated nitric acid in the system AcOH–Ac_2O. An analogous procedure was succesffully applied to compounds of the 1,2,4-triazole series. In particular, 1-benzyl-4-phenylsulfonyl-1,2,4-triazolioimides were thus converted into 1-benzyl-1,2,4-triazol-1-io-4-nitroimides [3]. However, the nitration of unsubstituted 4-amino-1,2,4-triazole under the same conditions gave the initial amine nitrate in a poor yield. Only treatment of 4-amino-1,2,4-triazole with alkyl nitrate in alcohol in the presence of a base gave the corresponding nitroimide sodium salt which was then neutralized with hydrochloric acid to obtain free triazolionitroimide **Ia** [2]. Nitronium salts in anhydrous acetonitrile were used more frequently for the nitration of *N*-aminoazoles [2, 5, 14]. Just that procedure was successful in the preparation of dinitroamino derivatives of both monocyclic 1,2,4-triazole and fused heterocycles based thereon [5].

It is seen that the procedures used previously for the nitration of 4-amino-1,2,4-triazole and its analogs require either preliminarily preparation of nitrating agents or very pure and dry solvents for reactions with nitronium salts. Therefore, the primary goal of our study on the properties of 1,2,4-triazol-1-io-4-nitroimide was to improve the procedure for its preparation. For this purpose, it seemed reasonable to apply direct nitration of 4-amino-1,2,4-triazole under mild conditions in the system HNO_3–Ac_2O. Some modification of the conventional procedure for preparation of the nitrating mixture was necessary. Our experiments showed that acceptable results are obtained when initial 4-amino-1,2,4-triazole is preliminarily acylated by dissolving it in acetic anhydride at elevated temperature (50°C) and nitric acid is then added to the cold solution (Scheme 1). In this case, the target product is formed in a satisfactory yield and is sufficiently pure.

Up to now, published data on the chemical properties of nitroimide **Ia** are limited to methylation and benzylation of its sodium salt [2]. Therefore, it was important not to examine the possibility for its alkylation but to extend a series of alkylating agents through the use of more complex electrophiles, such as long-chain alkyl halides and compounds with functional groups capable of undergoing further transformations. Nitroimide **Ia** may be used as starting compound for the synthesis of new and practically important derivatives, e.g., surfactants (which as a rule have a salt-like structure).

As in our previous study of 3-mercapto-1,2,4-triazole derivatives [15], we examined reactions of nitroimide **Ia** with C_{10}-, C_{12}-, and C_{16}-alkyl halides and determined the product structure. The alkylation products described in [2] were characterized only by the data of elemental analysis. Prolonged heating of nitroimide **Ia** with the above halogen derivatives in

Scheme 1.

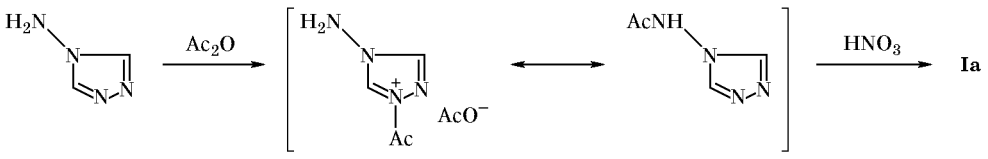


Table 2. Yields, melting points, and elemental analyses of nitroaminotriazole derivatives **V**–**VII** and **XII**–**XVI**

Comp. no.	Yield, %	mp °C (solvent)	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
V	50	112–113 (EtOH)	53.41	8.21	26.11	$C_{12}H_{23}N_5O_2$	53.53	8.55	26.02
VI	55	108–110 (H_2O–DMF)	56.81	9.12	23.85	$C_{14}H_{27}N_5O_2$	56.56	9.09	23.57
VII	50	100–101 (H_2O–DMF)	61.25	10.21	19.61	$C_{18}H_{35}N_5O_2$	61.19	9.90	19.83
XII	62	124–125 (EtOH)	27.77	3.83	40.88	$C_4H_7N_5O_3$	27.74	4.05	40.46
XIII	42	139–140 (EtOH)	32.23	5.27	37.48	$C_5H_9N_5O_3$	32.08	4.81	37.43
XIV	82	135–136 (EtOH)	27.59 27.58	4.00 3.77	31.40	$C_5H_8ClN_5O_3$[a]	27.09	3.61	31.60
XIVa	75	142–143 (EtOH)	26.83 26.86	3.31 3.46	31.79 31.95	$C_5H_8ClN_5O_3$[b]	27.09	3.61	31.60
XV	76	168–169 (MeOH–H_2O)	24.01 23.93	3.12 3.22	33.74 33.82	$C_5H_8N_6O_6$	24.19	3.22	33.87
XVI	16	88–89 (EtOH)	21.79 22.00	3.45 3.65	37.72 37.91	$C_4H_6N_6O_5$	22.00	2.75	37.50

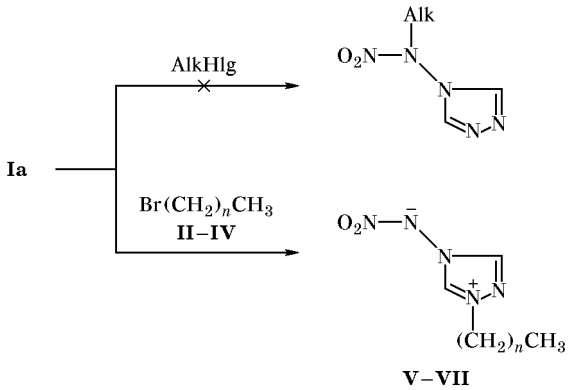
[a] Found Cl: 16.26%; calculated Cl: 16.02%.
[b] Found Cl: 15.85%; calculated Cl: 16.02%.

the presence of a base in strongly polar aprotic media (DMF, DMA) resulted in formation of only monosubstituted products (Table 2) regardless of whether an equimolar or excess amount of alkyl halide was used. In all cases, the reaction product contained unchanged initial triazole **Ia** (more than 40%). The latter can readily be separated, for it remains in the solution after dilution of the reaction mixture with water. Therefore, we succeeded in isolating the target products which contained almost no initial nitroimide **Ia**. After purification, the yield of alkylated triazoles **V**–**VII** was 50–55%. When the reaction was carried out in other aprotic solvents (such as acetone or acetonitrile), the yield of the products was lower but the reaction time considerably increased. As follows from the general principles of alkylation in alkaline media, proton-donor solvents should not be used for this purpose. For example, the yield of 1-benzyl-1,2,4-triazol-1-io-4-nitroimide was only 10% in 24 h when the reaction was performed in boiling ethanol [2].

The structure of the products as N^1-alkylated compounds was proved by the ^{1}H NMR spectra. All products **V**–**VII** are characterized by similar ^{1}H NMR spectra. The 3-H and 5-H protons are nonequivalent: their signals are observed in a very weak field, and the difference in their chemical shifts is ~1 ppm (Table 1). These data suggest unsymmetrical zwitterionic structure of the products, which means that the substitution occurred at the triazole ring. In the case of alkylation at the nitroamino group, the structure is symmetric, and the 5-H and 3-H protons should be equivalent. An analogous spectral pattern was observed previously for 1-benzyl derivatives: the ring protons (5-H and 3-H) appeared at δ 9.85 and 8.71 ppm, respectively [3].

Thus the alkylation of nitroaiminotriazole **I** occurs at the heteroring with high selectivity, and the products have the structure of 1-alkyl-1,2,4-triazol-1-io-4-nitroimides (Scheme 2). Compounds **V**–**VII** are readily soluble in dipolar aprotic solvents, such as DMF, DMSO, and acetone, but insoluble (at room

Scheme 2.



V–**VII**

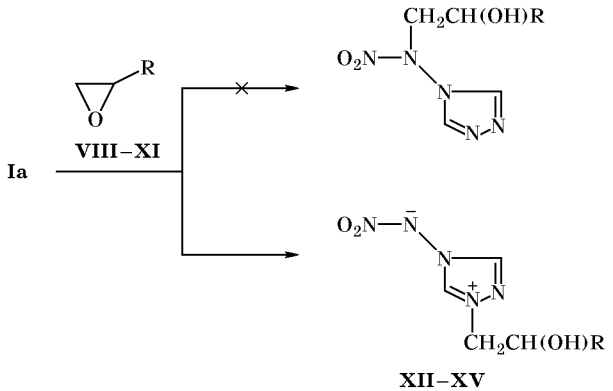
II, **V**, n = 9; **III**, **VI**, n = 11; **IV**, **VII**, n = 15.

temperature) in ether, alcohols, aliphatic hydrocarbons, toluene, and chlorinated hydrocarbons. Despite their salt-like structure, they are almost insoluble in water. On heating, compounds **V**–**VII** are sparingly soluble in alcohols, water, and chloroform. The low solubility of the products is just the factor hampering their study as potential surfactants.

With the goal of obtaining functionally substituted derivatives we thought it reasonable to examine the reaction of 1,2,4-triazol-1-io-4-nitroimide **I** with oxiranes. This reaction in the series of 1,2,4-triazoles was thoroughly studied by us previously [15]. As before, the alkylation with oxiranes was carried out in aqueous–alcoholic media in the presence or in the absence of bases, at room temperature and on heating (50°C). As a result, the corresponding *N*-(2-hydroxyalkyl) derivatives were obtained in satisfactory yields.

According to the analytical and spectral data, the alkylation of triazole **I** occurred exclusively at the endocyclic nitrogen atom to give 1-(2-hydroxyalkyl) ylides **XII**–**XV** (Scheme 3). Unsymmetrically substituted oxiranes were opened according to the Krasuskii rule: the spectral pattern corresponding to the alkyl fragment in **XII**–**XV** is similar to that observed for the other 2-hydroxyalkyl derivatives of triazoles [16]. In the ^{1}H NMR spectra of **XII**–**XIV**, as well as in the spectra of **V**–**VII**, the 3-H and 5-H signals appear as two downfield singlets (Table 1).

Scheme 3.



XII–XV

VIII, **XII**, R = H; **IX**, **XIII**, R = Me; **X**, **XIV**, R = CH_2Cl; **XI**, **XV**, R = CH_2ONO_2.

As a rule, the amount of alkali was 2–5% of that necessary for complete deprotonation of triazole **I**. Initially, the reaction mixture was heterogeneous, and the pH value was 2–2.5, regardless of the amount of base added. Triazole **I** gradually dissolved, and pH slightly decreased. When the reaction mixture became homogeneous, pH appreciably increased due to consumption of the acid reagent for formation of the N-alkylated product (Table 3). Accumulation of the product was accompanied by increase in pH. After a time, the product began to separate from the reaction mixture, and pH then attained a constant value (5–8, depending on the conditions; see Table 3). The reaction was slow at room temperature in the presence of a catalyst, as well as on heating in the absence of a base. Addition of a base and rise in temperature appreciably accelerate the process. Appropriate combination of these factors ensures a fast and sufficiently effective synthesis. For example, the alkylation of triazole **I** with chloromethyloxyirane (**X**) at 50°C (reactant concentrations, M: **I**, 0.92; **X**, 1.84; NaOH, 0.0184) in 5, 9, 14, 22, and 48 h gave, respectively, 15, 35, 51, 79, and 83% of product **XIV**. It should be noted that opening of the oxirane ring was not accompanied by replacement of the chlorine atom.

Table 3. Variation of pH in the alkylation of triazole **I** with oxiranes **VIII** and **X** in 90% ethanol; [**I**] = 0.92 M, [NaOH] = 0.0184 M, [**VIII**] = [**X**] = 1.84 M

Oxirane (**VIII**), 20°C		Chloromethyloxirane (**X**), 50°C	
pH	time, h	pH	time, h
2.20	0	2.45	0
2.10	19[a]	2.12	1.5[a]
2.60	23	2.45	2.0
2.72	24	2.70	2.5
2.85	25[b]	3.63	3.0
4.12	36	4.80	3.5[b]
5.17	45	5.13	4.0
5.45	48	7.40	5.0
5.05	72[c]	7.40	6.0[d]

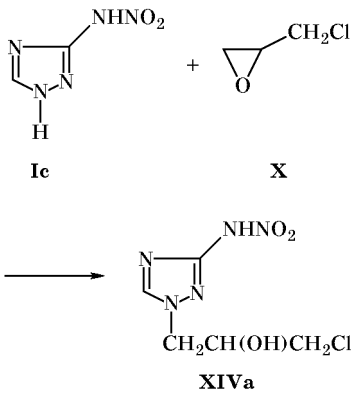
[a] The moment at which the mixture became homogeneous.
[b] Start of product separation.
[c] Yield 62%.
[d] Yield 48%.

Thus the conditions, specific features, and results of alkylation of triazole **Ia** with oxiranes are the same as in the alkylation of other triazole derivatives.

It should be noted that the alkylation with chloromethyloxirane (**X**) of 3-nitroamino-1,2,4-triazole (**Ic**), which is isomeric to **Ia**, gave hydroxy derivative **XIVa** whose ^{1}H NMR spectrum considerably differred from the spectrum of **XIV**. The ring proton signal of **XIVa** appeared in a stronger field, as compared to ylide **XIV** (Table 1). On the whole, the ^{1}H NMR spectrum of **XIVa** resembles those obtained for the other

1,2,4-triazole derivatives synthesized by the same reaction [16]. Compound **XIVa** was thus assigned the structure of 1-(3-chloro-2-hydroxypropyl)-3-nitroamino-1,2,4-triazole (Scheme 4).

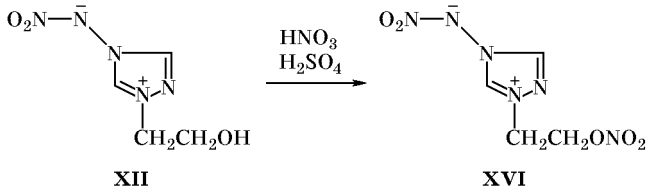
Scheme 4.



The differences in the ^{1}H NMR spectra of isomeric products **XIV** and **XIVa**, as well as in the spectra of the corresponding initial compounds, include mainly the position of the 5-H signal which is located by δ 1.65 ppm more upfield in the spectrum of **XIVa**. Protons of the NCH_2 group are characterized by a smaller upfield shift (δ 0.5 ppm), and signals from the other side-chain protons are almost similar for both compounds. The IR spectra of nitroamino derivatives **Ic** and **XIVa** (Table 1) contain a very strong absorption band at 1555–1600 cm^{-1} due to asymmetric vibrations of the nitro group (presumably, this band overlaps that arising from scissoring NH vibrations, δ_{NH}). No such band is observed in the spectra of zwitterionic nitroamino compounds, but strong bands are present in the region corresponding to symmetric vibrations of the nitro group (1290–1380 cm^{-1}).

Thus, unlike 1,2,4-triazol-1-io-4-nitroimide (**Ia**) and its derivatives **V**–**VII** and **XII**–**XV**, the structure of nitroamine **Ic** and alkylated product **XIVa** involves no charge separation. Presumably, stabilization via proton transfer from the exocyclic nitroamino group to the ring nitrogen atom with formation of zwitterionic structure is typical of only 4-nitroaminotriazoles.

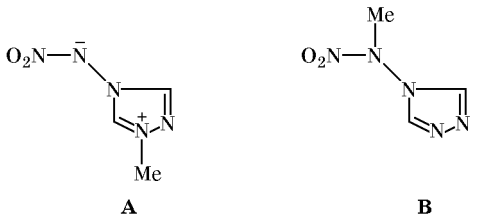
Scheme 5.



The hydroxy group in 1-(2-hydroxyalkyl)-1,2,4-triazol-1-io-4-nitroimides can be converted into other functional groups. For example, the nitration of alcohol **XII** with a mixture of nitric and sulfuric acids afforded the corresponding nitroxy derivative **XVI** (Scheme 5). According to the ^{1}H NMR data (Table 1), treatment of nitroimides with strong acids does not change their ylide structure.

Turning back to the alkylation of nitroaminotriazole **Ia** with alkyl halides and oxiranes, it should be noted that in both reactions the reactive species is likely to be 4-nitroamino-1,2,4-triazole anion, for these processes occur only in the presence of bases. The results of MNDO quantum-chemical calculations showed that the negative charge in the anion derived from **Ia** is delocalized over the oxygen atoms (–0.459, –0.504) and imide (–0.316) and endocyclic nitrogen atoms (–0.215, –0.216). Taking into account statistical factor, attack on an electrophile by the two endocyclic nitrogen atoms is equally probable.

In order to elucidate fine details of the mechanism of alkylation of compound **Ia**, we performed PM3 quantum-chemical calculations of model structures **A** and **B** as possible alkylation products at the heteroring and at the exocyclic nitrogen atom, respectively:



The calculated gas-phase enthalpies of formation ΔH_f of structures **A** and **B** are, respectively, 84.96 and 90.72 kcal/mol, and their dipole moments are 9.10 and 4.78 D. With account taken of nonspecific solvation in terms of the point dipole approximation, more polar isomer **A** appears to be even more stable: the corresponding enthalpies of formation are 39.35 (**A**) and 57.94 kcal/mol (**B**). On the basis of these data, we presume that the alkylation of 1,2,4-triazol-1-io-4-nitroimide (**Ia**) to N^1-substituted derivatives is a thermodynamically controlled process.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Perkin–Elmer R-12 spectrometer (60 MHz) in acetone-d_6 using HMDS as internal reference. The IR spectra were measured on a Specord 75IR instrument from

samples prepared as thin films. The elemental analyses were obtained on a Hewlett–Packard 185B CHN analyzer.

3-Nitroamino-1,2,4-triazole (Ic) was synthesized by direct nitration of 5-amino-1,2,4-triazole with a mixture of nitric and sulfuric acids, following a procedure analogous to that reported in [17]. The stage of synthesis of the corresponding nitrate was omitted. Yield 90–95%, mp 217°C (decomp.) [17].

1,2,4-Triazol-1-io-4-nitroimide (I). 4-Amino-1,2,4-triazole, 16 g (0.19 mol), was added in portions with stirring to 25 ml of acetic anhydride at such a rate that the temperature did not exceed 55–60°C. The resulting solution was cooled to 0°C, and 50 ml of concentrated nitric acid was added dropwise over a period of 3 h, maintaining the temperature at 0°C. The mixture was stirred for 0.5 h at 0°C and was gradually warmed up to room temperature. The mixture was kept for an additional 1 h and was poured into 500 ml of water containing ice. The solution was evaporated on a water bath to a volume of 50–70 ml and diluted with methanol, and the precipitate was filtered off and recrystallized from aqueous methanol. Yield 9–10 g (37–40%), mp 179°C (decomp.) [2].

1-Alkyl-1,2,4-triazol-1-io-4-nitroimides V–VII. Dimethylformamide, 20 ml, was added to a solution of 0.62 g (0.016 mol) of sodium hydroxide in 3 ml of water, and 2 g (0.015 mol) of triazole **I** and 0.015 mol of alkyl bromide **II**–**IV** was added. The mixture was heated for 18–20 h at 80°C, cooled, and poured into 200 ml of water. The precipitate was filtered off and recrystallized from appropriate solvent.

1-(2-Hydroxyalkyl)-1,2,4-triazol-1-io-4-nitroimides XII–XV. Oxirane **VIII**–**XI**, 46–69 mmol, was added to a suspension of 3 g (23 mmol) of nitroimide **Ia** in 15 ml of ethanol, placed in a 25-ml volumetric flask. If necessary, a solution of 0.018–0.046 g (0.45–1.2 mmol) of sodium hydroxide in 2 ml of water was also added, and the volume was adjusted to 25 ml by adding ethanol. The mixture was stirred with a magnetic stirrer at room temperature (in a flask with a ground stopper) or heated at 50°C with stirring (in a flask equipped with a reflux condenser). As a rule, the mixture became homogeneous in 18–21 h at room temperature or in 1–1.5 h on heating in the presence of alkali. By this moment, the pH value attained 2.0–2.2, it then gradually rose, and, later on, the product began to separate from the solution. When the pH was 5–6, the precipitate was filtered off, the filtrate was evaporated under reduced pressure, and the residue was recrystallized from water and combined with the main part of the product. Compounds **XII**–**XV** were purified by recrystallization from aqueous ethanol. The products are soluble in DMF, DMA, and acetone, sparingly soluble in hot alcohols and water, and insoluble in chlorinated hydrocarbons.

1-(3-Chloro-2-hydroxypropyl)-3-nitroamino-1,2,4-triazole (XIVa) was synthesized by alkylation of nitroamine **Ic** with chloromethyloxirane in aqueous ethanol in the presence of sodium hydroxide at room temperature, according to the procedure described above. During the process, the initial compound dissolved in parallel with separation of the product. The product was filtered off and recrystallized.

1-(2-Nitroxyethyl)-1,2,4-triazol-1-io-4-nitroimide (XVI). Compound **XII**, 2 g (0.012 mol), was added in portions to 20 ml of a 1 : 1 mixture of concentrated sulfuric and nitric acid, stirred at 0–5°C. The mixture was stirred for 6 h at that temperature, poured into 100 ml of an ice–water mixture, neutralized with sodium hydrogen carbonate, and repeatedly extracted with ethyl acetate. The extract was dried over calcined magnesium sulfate, the solvent was removed under reduced pressure, and the residue was recrystallized.

REFERENCES

1. Catalan, J., Abbond, J.L., and Elquero, J., *Adv. Heterocycl. Chem.*, 1987, vol. 41, pp. 187–274.
2. Katritzky, A.R. and Mitchell, J.N., *J. Chem. Soc., Perkin. Trans. 1*, 1973, no. 21, pp. 2624–2626.
3. Timpe, H.-J., *Z. Chem.*, 1971, vol. 11, no. 9, pp. 340–341.
4. Arriau, J., Dargelos, A., Epsztajn, I., Katritzky, A.R., Lunt, E., Mitchell, I.W., Rizvi, S.Q.A., and Roch, G., *J. Chem. Soc., Perkin Trans. 1*, 1976, no. 11, pp. 1245–1248.
5. Myasnikov, V.A., Vyaznikov, V.A., Yudin, I.L., Shitov, O.P., and Tartakovskii, V.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, no. 5, p. 1239.
6. Astachov, A.M., Stepanov, R.S., Kruglyakova, L.A., and Kekin, Y.V., Abstracts of Papers, *31st Int. Annual Conf. of ICT (Energetic Materials)*, 2000; *Chem. Abstr.*, 2000, vol. 133, no. 283 735 u.
7. Vasiliev, A.D., Astachov, A.M., Stepanov, R.S., and Kirik, S.D., *Acta Crystallogr., Sec. C*, 1999, vol. 55, no. 5, pp. 830–832.
8. Elguero, J., Marzin, C., Katritzky, A.R., and Linda, P., *The Tautomerism of Heterocycles*, New York: Academic, 1976.
9. Ostrovskii, V.A., Erusalimskii, G.B., and Shcherbinin, M.B., *Zh. Org. Khim.*, 1993, vol. 29, no. 9, pp. 1297–1302.
10. Bliznyuk, A.A. and Voityuk, A.A., *Zh. Strukt. Khim.*, 1986, vol. 27, no. 4, pp. 190–191.

11. Burshtein, K.Ya., *Zh. Strukt. Khim.*, 1987, vol. 28, no. 2, pp. 3–9.
12. Epsztajn, J. and Katritzky, A.R., *Tetrahedron Lett.*, 1969, no. 54, pp. 4739–4742.
13. Epsztajn, J., Lunt, E., and Katritzky, A.R., *Tetrahedron*, 1970, vol. 26, no. 7, pp. 1665–1673.
14. Shvaika, O.P., Korotkikh, N.I., Tereshchenko, G.F., and Kovach, N.A., *Khim. Geterotsikl. Soedin.*, 1976, no. 6, pp. 853–856.
15. Abramzon, A.A., Pevzner, M.S., Kofman, T.P., and Alam, L.V., *Zh. Prikl. Khim.*, 1996, vol. 69, no. 12, pp. 2026–2033.
16. Kofman, T.P., Zykova, G.A., Manuilova, V.I., Timofeeva, T.N., and Pevzner, M.S., *Khim. Geterotsikl. Soedin.*, 1974, no. 7, pp. 997–1002; Kofman, T.P., Vasil'eva, I.V., and Pevzner, M.S., *Khim. Geterotsikl. Soedin.*, 1976, no. 9, pp. 1281–1285; *ibid.*, 1977, no. 10, pp. 1407–1410.
17. Chipen, G.I., Grinshtein, V.Ya., and Preiman, R.P., *Zh. Obshch. Khim.*, 1962, vol. 32, no. 2, pp. 454–459; Chipen, G.I., *Metody polucheniya khimicheskikh reaktivov i preparatov* (Methods of Preparation of Chemical Reagents), Moscow: IREA, 1966, no. 14, pp. 77–78.