Chemistry of Heterocyclic Compounds, Vol. 44, No. 12, 2008

QUANTUM-CHEMICAL INVESTIGATION OF CERTAIN PHYSICOCHEMICAL PROPERTIES OF C-NITRO-1,2,3-TRIAZOLE AND N-ALKYL-4(5)-NITRO-1,2,3-TRIAZOLES

O. A. Ivashkevich[1], Vadim E. Matulis[1], P. N. Gaponik[1], G. T. Sukhanov[2], J. V. Filippova[2], and A. G. Sukhanova[2]

Quantum-chemical calculations have been carried out on molecular electrostatic potentials, proton affinity in the gas phase, gas phase basicity, and pK_{BH+} values in aqueous solution for C-nitro- and N-alkyl-4(5)-nitro-1,2,3-triazoles, and the relative stability of the isomeric N-alkyl-4(5)-nitrotriazoles (alkyl = Me, Et, i-Pr, t-Bu) in the gas phase and in aqueous solution. For all the studied substances in the gas phase the 2H-tautomer and the N(2)-isomers were considerably more stable than the corresponding N(1) compounds, and the 3H-tautomer and N(3)-isomer were the least stable. In aqueous solution 1- and 3-isomers had close values of energies, but in the case of C-nitro-1,2,3-triazole the 1H form became even more stable than the 2H-form. It was established which ring nitrogen atoms of 1,2,3-triazoles are protonated in the gas phase and in solution. The obtained data correlate well with the results of experimental investigations on the alkylation of 1,2,3-triazoles in acidic and basic media and of the experimental investigation on the alkylation of C-nitro-1,2,3-triazoles with diethyl sulfate carried out in the present work.

Keywords: 4(5)-nitro-1,2,3-triazoles, alkylation, quantum-chemical calculations, B3LYP method, basicity.

Nitro-1,2,3-triazoles are characterized by high positive enthalpies of formation, by significant nitrogen content in the molecule, and are of interest as effective components of mixed fuels, pyrotechnics, explosives, and gas-generating compositions, and also as starting materials for the synthesis of biologically active molecules [1]. In this connection the development of new and the improvement of known methods of synthesis of compounds of this series is urgent.

One of the methods of obtaining N-substituted 4-nitro-1,2,3-triazoles is the alkylation of 4(5)-nitro-1,2,3-triazole. The process is complicated by the fact that in the 4(5)-nitro-1,2,3-triazole molecule there are three potential reaction centers for attack by electrophilic reagents, *viz* the nitrogen atoms at positions 1, 2, and 3 of the ring. This predetermines interest in the investigation of processes of alkylation of nitrotriazole, both

---

[1]Research Institute of Physical and Chemical Problems, Belarusian State University, Minsk 220030, Belarus; e-mail: fhp@bsu.by. [2]Institute for Problems of Chemical and Energetic Technologies, Siberian Branch of the Russian Academy of Sciences, Biysk 659322, Russia; e-mail: admin@ipcet.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1816-1828, December, 2008. Original article submitted November 9, 2007.

 0009-3122/08/4412-1472

from the point of view of developing the theory of reactivity of heterocycles and solving the problem of regioselective functionalization of chemical compounds possessing ambident properties, and from the position of developing methodology for the directed synthesis of monosubstituted 4-nitro-1,2,3-triazoles and N,N-disubstituted 4-nitro-1,2,3-triazolium salts.

On alkylating N-unsubstituted C-nitro-1,2,3-triazole the formation of products of N-monosubstitution at all three nitrogen atoms is theoretically possible, as are products of exhaustive alkylation – N,N-dialkylnitrotriazolium salts. It was reported previously [2] that on alkylation in basic media a mixture is formed of 1- and 2-substituted isomers. Data obtained by us recently indicate that a certain amount of N(3)-alkyltriazoles was also present in the products of the alkylation of the sodium salt. The ratio of 1-, 2-, and 3-alkyl-1,2,3-triazoles was 4:8:1. A detailed investigation devoted to the formation of N(3)-alkyl-substituted isomers will be published shortly.

There is no information in the literature on the alkylation of C-nitro-1,2,3-nitrotriazole in neutral or acidic media.

In the case of thermodynamically controlled reactions the ratio of isomers formed on functionalizing the triazole ring at a nitrogen atom must be determined by their relative stability. At the same time there are no data in the literature on the relative stability of the isomeric N-substituted C-nitro-1,3,5-triazoles, but a series of works has been published devoted to a theoretical and experimental investigation of the relative stability of the tautomeric forms of 1,2,3-triazole [3, 4] and a series of C-substituted 1,2,3-triazoles [5-7].

For kinetically controlled reactions the ratio of isomers will be determined by the rates of formation of each isomer and the rates of their interaction with alkylating agent with the formation of a product of exhaustive alkylation. In this case, when predicting the ratio of reaction products information on the distribution of electrostatic potential of the substrate molecules and on the proton affinity of the various ring nitrogen atoms may be used.

The basicity of several 1,2,3-triazoles in the gas phase and in aqueous solution was studied in [6]. However there is no information in the literature on the basicity constants of N-substituted C-nitro-1,2,3-triazoles. In addition there are no data on which nitrogen atom of the triazole ring protonation of molecules in solution occurs.

In the present work quantum-chemical calculations have been carried out on the molecular electrostatic potentials (*MESP*), proton affinity in the gas phase (*PA*), gas phase basicity (*GB*), pK_{BH^+} values in aqueous solution for C-nitro- and N-alkyl-4(5)-nitro-1,2,3-triazoles, and the relative stability of the isomeric N-alkyl-4(5)-nitrotriazoles (alkyl = Me, Et, *i*-Pr, *t*-Bu) in the gas phase and in aqueous solution. Since calculations of the basicity constants of 1,2,3-triazoles in aqueous solution have not been carried out previously, for an assessment of the correctness of the method used in the present work, values of *PA*, *GB*, and pK_{BH^+} were calculated for unsubstituted 1,2,3-triazole, 1-methyl-, 2-methyl-, C-phenyl-, 1-methyl-4-phenyl-, and 2-methyl-4-phenyl-1,2,3-triazoles for which there are corresponding experimental data. This enables a comparison to be made with the results carried out in the present work on the experimental investigation of N-mono- and the exhaustive alkylation of C-nitro-1,2,3-triazoles with diethyl sulfate (DES).

The results of the quantum-chemical calculations of the relative energies of the tautomers of C-nitro-1,2,3-triazole and the isomeric N-alkyl-4(5)-nitro-1,2,3-triazoles are given in Table 1.

The results for the tautomers of C-nitro-1,2,3-triazole are in agreement with those calculated previously in [5-7]. For all the studied compounds, as for the unsubstituted 1,2,3-triazole [3, 4], in the gas phase the 2H-tautomer and 2-alkyl-substituted triazoles were significantly more stable than the corresponding N(1)-compound, but the 3H-tautomer and the N(3)-isomers were less stable. This is in agreement with the data on the fact that, under conditions when interconversions of isomeric N-substituted 1,2,3-triazoles are possible, the N(1)- and N(3)-isomers are converted in nonpolar solvents into the corresponding N(2)-compounds [8, 9].

The 1H-form and the 1-substituted triazoles possess high dipole moments in comparison with the 2H-forms and 2-isomers [3, 6], consequently they must be more strongly stabilized by a polar medium. The calculations carried out indicate that in aqueous solution the 1- and 2-isomers correspond with close energies,

and in the case of C-nitro-1,2,3-triazole the 1H-form becomes somewhat more stable than the 2H-form. The latter is in agreement with the fact that C-nitro-1,2,3-triazole in the crystalline state is found in the 1H-form [6]. If in the process of functionalization of the triazole interconversions of the resulting 1- and 2-isomers are possible, then under the conditions of thermodynamic control the ratio of isomers in the mixture may be regulated effectively by the change in polarity of the solvent.

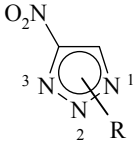
The contour *MESP* pictures of certain 1,2,3-triazoles and triazolate anions are given in Fig. 1, and the calculated values of the basicity constants of the compounds being investigated are given in Table 2. For this, in order to trace the effect of the nitro group on the *MESP* distribution, the analogous contour pictures for the tautomeric forms of unsubstituted 1,2,3-triazole and the corresponding triazolate anion are also given in Fig. 1.

From Fig. 1 it is seen that regions of negative *MESP* values are found near the ring nitrogen atoms, and also the oxygen atoms of the nitro group. On introducing an electron-withdrawing nitro group into the ring the depths of the minima are sharply reduced, which indicates a significant fall in basicity and nucleophilicity of the ring nitrogen atoms and is in agreement with the calculated values of the basicity constants (Table 2).

The *MESP* minima for all the nitrogen atoms of C-nitro-1,2,3-triazolate anion have practically the same depth. This is in agreement with the fact that on alkylation of C-nitro-1,2,3-triazole in basic media a mixture is formed of substitution products at the N(1) and N(2) atoms [2]. The 1,5-isomer is not formed, probably due to steric hindrance.

Regions of negative and positive *MESP* values are found on opposite sides of molecules of N(1)-tautomers and isomers (Fig. 1), in difference to N(2)- and N(3)-compounds, which shows the high polarity of the first and, as a result, their high stabilization compared with other tautomeric forms and isomers (Table 1). The *MESP* values of N(1)-tautomers and isomers have local minima near the N(2) and N(3) atoms. The minimum near the N(2) atom is significantly more shallow. This is in agreement with the results of calculating the basicity constants of triazoles (Table 2), indicating that protonation of the triazole ring proceeds preferably at the N(3) atom.

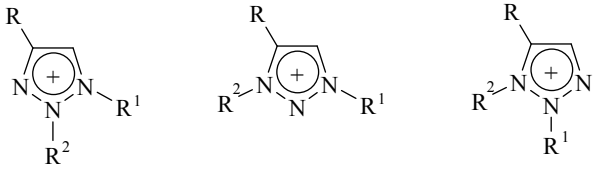
TABLE 1. Calculated Energies of Isolated Molecules at 0 K (ΔE_0) and Gibbs Free Energies ($\Delta G^0_{298,H_2O}$) in Aqueous Solution Relative to the 1H-Form or 1-Alkyl-substituted Compound for Tautomers of C-Nitro-1,2,3-triazole and Isomeric N-Alkyl-4(5)-nitro-1,2,3-triazoles



R and its position on the ring	ΔE_0, kJ/mol	$\Delta G^0_{298,H_2O}$, kJ/mol
H-1	0.0	0.0
H-2	-13.9	4.2
H-3	5.3	24.2
1-Me	0.0	0.0
2-Me	-17.9	-0.4
3-Me	11.5	28.1
1-Et	0.0	0.0
2-Et	-18.6	-0.4
3-Et	17.5	32.7
1-*i*-Pr	0.0	0.0
2-*i*-Pr	-19.7	-1.7
3-*i*-Pr	16.5	33.1
1-*t*-Bu	0.0	0.0
2-*t*-Bu	-18.9	-0.5
3-*t*-Bu	33.5	49.2

On protonation of the triazole ring the following tautomeric forms may be formed.

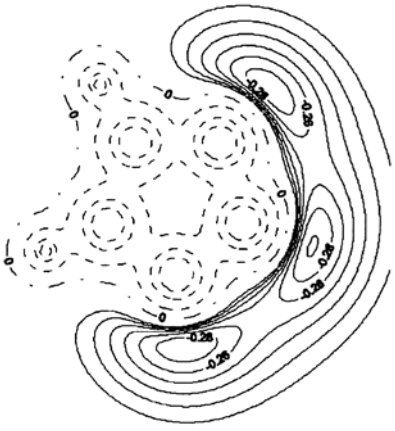
Scheme 1



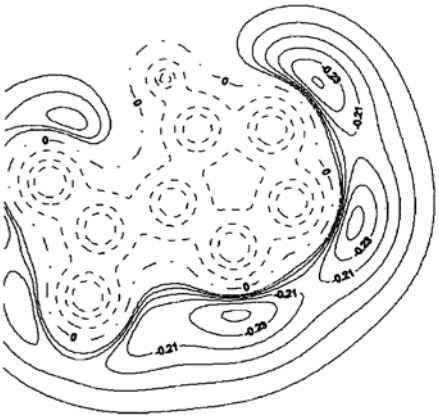
a **b** **c**

R^1 and R^2 = Alk or H

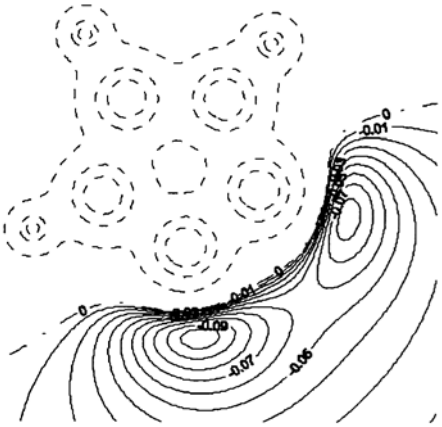
The calculated values given in Table 2 for proton affinity and gas phase basicity are in good agreement with the corresponding experimental data. Calculated and experimental values of pK_{BH+} are also close, with the greatest deviation for 4-nitro-1,2,3-triazole (**1**). In this, as in the case of 5-nitrotetrazole, the calculated value was appreciably less than the experimental [14].



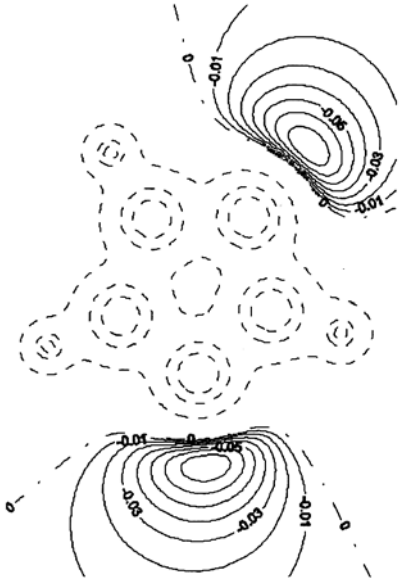
1,2,3-Triazolate anion



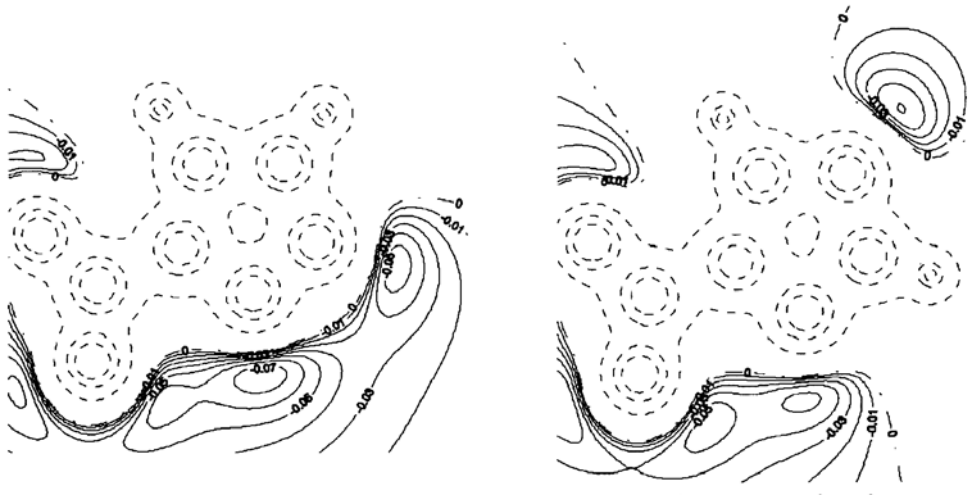
C-Nitro-1,2,3-triazolate anion



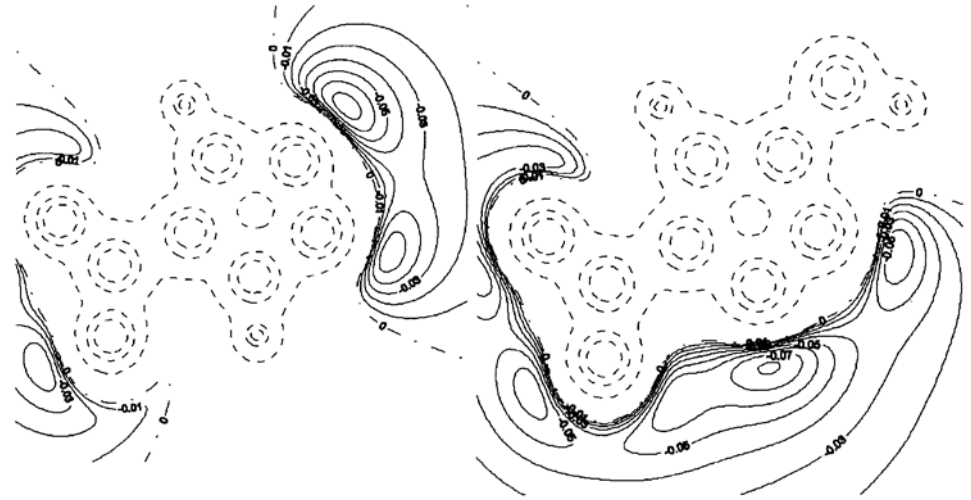
1H-1,2,3-triazole



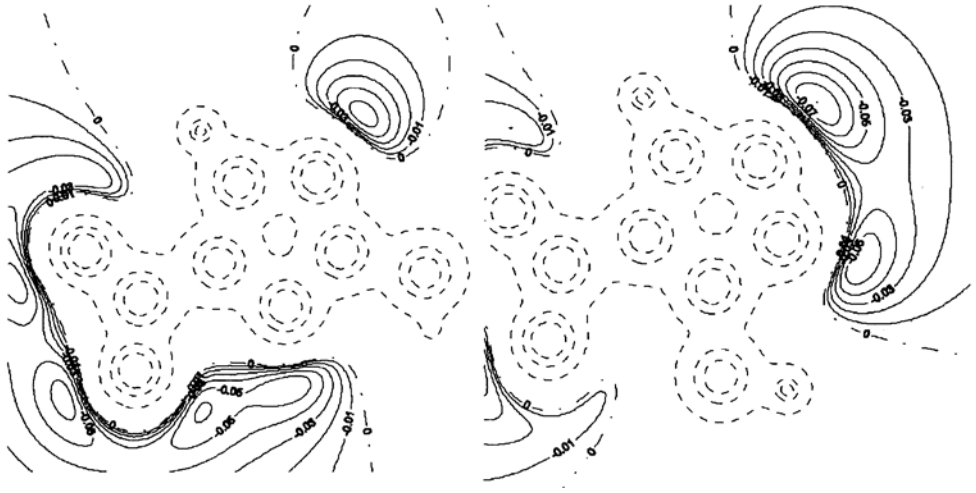
2H-1,2,3-triazole



1H-4-Nitro-1,2,3-triazole 2H-4-Nitro-1,2,3-triazole



1H-5-Nitro-1,2,3-triazole 1-Methyl-4-nitro-1,2,3-triazole



2-Methyl-4-nitro-1,2,3-triazole 1-Methyl-5-nitro-1,2,3-triazole

Fig. 1. Contour *MESP* pictures (a.u.) in the plane of the ring of molecules of 1,2,3-triazoles and the corresponding triazolate anions (positive values are denoted by dotted lines).

The obtained results enable the place of protonation of the triazole ring in the gas phase and in solution to be established with a sufficient degree of reliability. Protonation both in the gas phase and in solution proceeds predominantly with the formation of tautomeric form **b** for the unsubstituted triazole, 1-, C-, 1,4-, and 1,5-substituted triazoles. The basicity of 1-substituted 1,2,3-triazoles is greater than that of the isomeric 2-substituted 1,2,3-triazoles, since on protonation of the latter tautomeric form **b** may not be formed.

The presence of a nitro group on the ring leads to a strong reduction in basicity both in the gas phase and in solution. This is in good agreement with the calculated *MESP* distribution. The calculated value of pK_{BH^+} for 1-methyl-5-nitro-1,2,3-triazole is more than four units greater than for the 1,4-isomer. This is explained by

TABLE 2. Calculated and Experimental Values of *PA*, *GB*, and pK_{BH^+} of 1,2,3-Triazoles

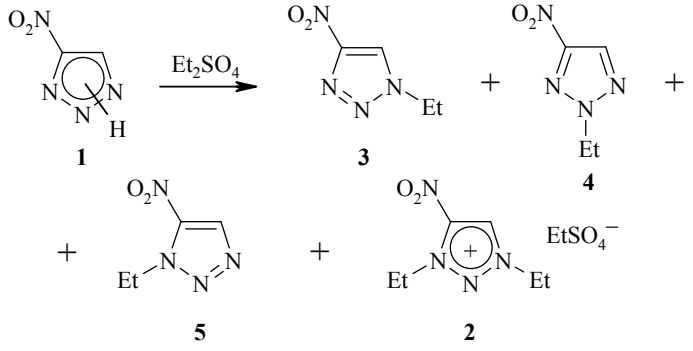
Compound	Protonated form	*PA*, kJ/mol	*GB*, kJ/mol	pK_{BH^+}
1,2,3-Triazole	**a**	827.1	797.5	-4.45
	b	877.0 (879.9 [10])	844.8 (847.4 [10])	1.00 (1.17 [11], -0.16 [12])
1-Methyl-1,2,3-triazole	**a**	872.5	840.1	-3.59
	b	921.4 (915.2 [6])	888.9 (881.6±1.4 [6])	2.39 (1.25 [11])
2-Methyl-1,2,3-triazole	**a**	857.6 (857.4 [6])	825.2 (824.6±0.3 [6])	-3.60 (-3.5±0.1 [6])
C-Phenyl-1,2,3-triazole	**a**	854.9	822.5	-4.71
	b	908.6 (904.8 [6])	876.1 (872.7±1.7 [6])	0.40 (0.4 [13])
	c	869.4	837.0	-4.75
1-Methyl-4-phenyl-1,2,3-triazole	**a**	893.8	861.3	-3.71
	b	947.1 (936.4 [6])	914.6 (903.9±1.9 [6])	1.55 (0.05±0.01 [6])
2-Methyl-4-phenyl-1,2,3-triazole	**a**	878.9	846.5	-3.87 (-3.71±0.02 [6])
	c	891.2 (884.2 [6])	858.7 (853.6±1.5 [6])	-3.92
C-Nitro-1,2,3-triazole	**a**	757.5	725.0	-12.01
	b	804.3	771.8	-9.64 (-6.80 [12])
	c	752.2	719.7	-16.69
1-Methyl-4-nitro-1,2,3-triazole	**a**	800.2	767.7	-11.00
	b	845.7	813.3	-8.60
2-Methyl-4-nitro-1,2,3-triazole	**a**	788.5	756.0	-10.25
	c	784.2	751.8	-14.75
1-Methyl-5-nitro-1,2,3-triazole	**b**	851.8	819.4	-4.21
	c	800.1	767.6	-11.19
1-Ethyl-4-nitro-1,2,3-triazole	**a**	810.8	778.4	-10.93
	b	855.0	822.5	-8.47
2-Ethyl-4-nitro-1,2,3-triazole	**a**	798.8	766.4	-10.05
	c	794.7	762.3	-14.54
1-Isopropyl-4-nitro-1,2,3-triazole	**a**	821.3	788.8	-10.84
	b	863.5	831.0	-8.22
2-Isopropyl-4-nitro-1,2,3-triazole	**a**	808.9	776.5	-10.12
	c	804.6	772.2	-14.24
1-*tert*-Butyl-4-nitro-1,2,3-triazole	**a**	829.9	797.4	-10.98
	b	870.1	837.6	-7.99
2-*tert*-Butyl-4-nitro-1,2,3-triazole	**a**	821.1	788.6	-9.70
	c	816.7	784.2	-14.01

the fact that cationic forms **b** formed in both cases have close Gibbs free energies in aqueous solution, while the initial 1,5-disubstituted triazole is significantly less stable than the corresponding 1,4-isomer (Table 1). The basicity in the gas phase grows regularly with the increase in electron-donating properties of the alkyl substituent, and in this way the basicity in aqueous solution is changed significantly more weakly than in the gas phase.

The results of the calculations explain why alkylation of 1,2,3-triazole in acidic media leads to the selective preparation of substitution products at the N(1) atom [15]. Evidently under these conditions the process proceeds through the intermediate formation of the most stable cation **b**, which is converted after deprotonation into a 1-substituted 1,2,3-triazole.

In the present work the alkylation of C-nitro-1,2,3-triazole with DES has been studied and the obtained data have been compared with the results of quantum-chemical calculations. C-Nitrotriazole **1** dissolves in DES to a limited extent. Nonetheless on increasing the temperature to 80°C complete homogenization of the reaction mass occurs after 2.5 h. Analysis of the mixture indicated that products of N-monoalkylation **3-5** and N,N-dialkylation **2** are formed in the reaction.

Scheme 2



1-Ethyl-4-nitro-1,2,3-triazole [N(1)-isomer], 2-ethyl-4-nitro-1,2,3-triazole [N(2)-isomer], and 1-ethyl-5-nitro-1,2,3-triazole [N(3)-isomer] were identified in the mixture of products of N-monoalkylation. The overall yield of isomer mixture after 10 h reaction amounted to 26%. The predominant N-monoalkylation product was the 3-substituted nitrotriazole **5**. The ratio of N(1)-, N(2)-, and N(3)-isomers, according to the intensities of the singlet signals of C atoms of the nitrotriazole ring in the ^{1}H NMR spectrum, was 1:5:8.

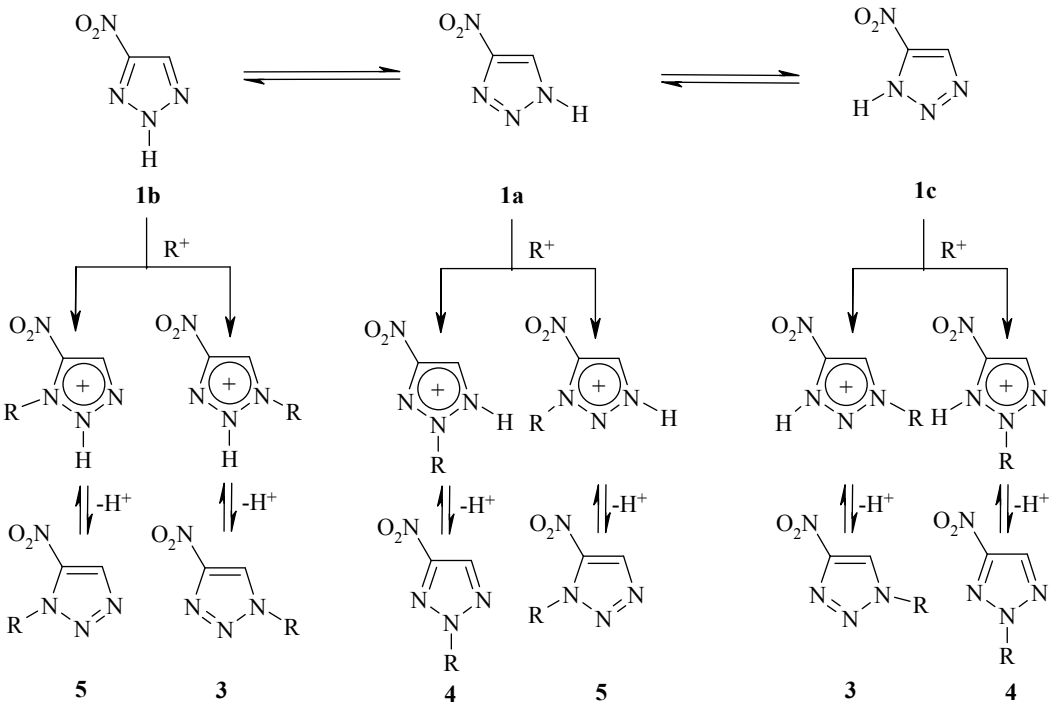
Together with the monoalkylation products a significant quantity of salt **2** was formed, identified as 1,3--diethyl-4-nitro-1,2,3-triazolium perchlorate obtained by an exchange reaction of the ethyl sulfate anion in salt **2** with perchloric acid anion. The yield after 10 h reaction was 41%.

On the basis of the results of the experimental investigation of the alkylation processes of C-nitro-1,2,3-triazole and of the quantum-chemical calculations carried out the following scheme is proposed by us for the interaction of **1** with DES.

The electrophile may attack tautomer **1b** at the two available reaction centers, the N(1) and N(3) atoms. According to the calculations carried out on the basicity constant (Table 2), attack of the 2H-form proceeds predominantly at the N(1) atom with the formation of 1-ethyl-2H-4-nitrotriazolium salt which, by splitting off proton, is converted into 1-ethyl-4-nitro-1,2,3-triazole.

Tautomer **1a** also has two reaction centers, at N(2) and N(3). Attack is effected at the unshared electron pair of electrons of each of these atoms with the formation of protonated compounds 1H-2-ethyl- and 1H-3-ethyl-4-nitro-1,2,3-triazolium salts, which, on splitting off proton, are converted into the corresponding

substitution products at the N(2) (**4**) and N(3) (**5**) atoms. The proportion of compound **5** was significantly greater since the 1H-3-ethyl-4-nitro-1,2,3-triazole cation (form **b,** Scheme 1) is the thermodynamically most favorable.



Analogously 1- and 2-substituted 4-nitro-1,2,3-triazoles **3** and **4** are formed from tautomer **1c**.

Considering that the tautomeric form **1a** was the most stable under the alkylation conditions (polar medium), it will make the main contribution to the formation of the isomeric N-ethyl-4-nitro-1,2,3-triazoles. This causes the predominant content in the mixture of products of N-monoalkylation of nitrotriazole **1** to be the N(2)- (**4**) and N(3)- (**5**) isomers respectively of 36 and 57%.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-500 (500 and 125 MHz respectively) in DMSO-d_6, internal standard DMSO-d_6, IR spectra on a Perkin-Elmer instrument in KBr disks, and UV spectra on a Specord instrument. Melting points were determined on a Boetius hot stage with a PNMK 05 eyepiece.

Preparation of Components and Reactants. N-Ethyl-4(5)-nitro-1,2,3-triazoles, comparison and reference samples in the study of ^{1}H NMR spectra were synthesized by the procedure of [2]. Diethyl sulfate was washed with 3% sodium carbonate solution to remove traces of acid, then with distilled water, dried, and redistilled in vacuum (main substance ≥99.9%, acid calculated as sulfuric ≤0.1%). Triazole **1** was recrystallized from ethyl acetate, mp 164°C.

Interaction of 4-Nitro-1,2,3-triazole with Diethyl Sulfate. A suspension of 4-nitro-1,2,3-triazole in DES with a reactant ratio of **1** : DES = 1 : 0.86 was maintained at 78-80°C with constant stirring for 10 h. At the end, the reaction mass was cooled to 20°C, diluted with water, and extracted with methylene chloride. 1-Ethyl-

4-nitro-, 2-ethyl-4-nitro-, and 1-ethyl-5-nitro-1,2,3-triazoles were identified in the extract by ^{1}H NMR spectroscopy. The organic extract was washed with aqueous Na_2CO_3 solution and with water to neutral pH, dried with $MgSO_4$, and the solvent distilled off under reduced pressure. The yield of N-monoalkylation products was 26%, isomer ratio N(1) : N(2) : N(3) = 1 : 5 : 8.

1-Ethyl-4-nitro-1,2,3-triazole. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.36 (3H, t, *J* = 7.3, CH_3); 4.46 (2H, q, *J* = 7.3, CH_2); 9.29 (1H, s, =CH).

2-Ethyl-4-nitro-1,2,3-triazole. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.47 (3H, t, *J* = 7.3, CH_3); 4.54 (2H, q, *J* = 7.3, CH_2); 8.60 (1H, s, CH).

1-Ethyl-5-nitro-1,2,3-triazole. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.47 (3H, t, *J* = 7.0, CH_3); 4.70 (2H, q, *J* = 7.0, CH_2); 8.64 (1H, s, =CH).

Isolation of 1,3-diethylnitrotriazolium salts was carried out by adding ammonium perchlorate to the residue of the reaction mixture at 75-80°C. The solution was cooled to 20°C, the precipitated solid was filtered off, and 1,3-diethyl-4-nitro-1,2,3-triazolium perchlorate was obtained in 41% yield.

1,3-Diethyl-4-nitro-1,2,3-triazolium Perchlorate. Mp 101-102°C (water). IR spectrum, ν_{NO2}, cm^{-1}: 1318, 1585. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.58 (3H, t, *J* = 7, CH_3); 1.63 (3H, t, *J* = 7, CH_3); 4.76 (2H, q, *J* = 7, CH_2); 4.99 (2H, q, *J* = 7, CH_2); 10.14 (1H, s, =CH). UV spectrum, λ_{max}, nm: 241.

Quantum-chemical calculations were carried out with the aid of the Gaussian-03 set of programs [16] within the framework of DFT theory (B3LYP functional) [17]. The 6-31G* basis set was used to find the geometric parameters. Our investigations show that the geometric characteristics of tetrazole derivatives, calculated in the indicated approximation, are in good agreement with experimental values [18-20].

Total energies (*E*) were calculated using the 6-311+G** basis. The effect of solvent was taken into account within the framework of the COSMO model [21], in which a molecule of dissolved substance is placed in a cavity in the solvent, and the interaction between the molecules leads to a local interaction between the virtual adjoining surfaces of the dissolved molecule and the solvent molecule. The local interactions are determined only by charge densities on the adjoining surfaces. Geometries optimized for isolated molecules were used in the calculations.

It was shown previously, that continuum models permit a correct desciption of the effect of solvent on the relative stability of N-substituted tetrazole derivatives [22] and tautomeric and protonated forms of tetrazole and its derivatives [14, 23, 24]. For unsubstituted 1,2,3-triazoles the values of *PA* and *GB* were calculated starting from the computed total energies (*E*), zero vibrational energies (*ZPVE*), thermal corrections to enthalpy $(H^0_{298} - H^0_0)$ and Gibbs free energies $(G^0_{298} - G^0_0)$ ccording to the formulas.

$$PA = E_0(\mathrm{B}) - E_0(\mathrm{BH^+}) + (H^0_{298} - H^0_0)(\mathrm{B}) + (H^0_{298} - H^0_0)(\mathrm{H^+}) - (H^0_{298} - H^0_0)(\mathrm{BH^+}), \quad (1)$$

$$GB = E_0(\mathrm{B}) - E_0(\mathrm{BH^+}) + (G^0_{298} - G^0_0)(\mathrm{B}) + (G^0_{298} - G^0_0)(\mathrm{H^+}) - (G^0_{298} - G^0_0)(\mathrm{BH^+}), \quad (2)$$

where $E_0 = E + ZPVE$; $(H^0_{298} - H^0_0)$ and $(G^0_{298} - G^0_0)$ for proton is equal to 6.20 and –26.25 kJ/mol, respectively [25]; B is the triazole molecule.

On account of the structural flexibility of the molecules of the other 1,2,3-triazoles considered in the present work, the procedure for calculating thermal corrections for these compounds is complicated, consequently for 1,2,3-triazoles containing substituents we assumed

$$(H^0_{298} - H^0_0)(\mathrm{B}) - (H^0_{298} - H^0_0)(\mathrm{BH^+}) = 0 \text{ and}$$

$$(G^0_{298} - G^0_0)(\mathrm{B}) - (G^0_{298} - G^0_0)(\mathrm{BH^+}) = RT \ln[\frac{\sigma(\mathrm{B})}{\sigma(\mathrm{BH^+})}],$$

where σ is the symmetry number.

This means that the thermal corrections to the enthalpy for the neutral and protonated forms are equal and the change in entropy is caused only by their different symmetry. Allowing for the approximations made, formulas (1) and (2) will take on the form:

$$PA = E_0(\mathrm{B}) - E_0(\mathrm{BH}^+) + (H^0_{298} - H^0_0)(\mathrm{H}^+)\,, \qquad (3)$$

$$GB = E_0(\mathrm{B}) - E_0(\mathrm{BH}^+) + RT\ln[\frac{\sigma(\mathrm{B})}{\sigma(\mathrm{BH}^+)}] + (G^0_{298} - G^0_0)(\mathrm{H}^+) \qquad (4)$$

For unsubstituted 1,2,3-triazole the values of *PA*, *GB*, and p$K_{\mathrm{BH+}}$ calculated according to equations (1) and (2) are very close to the corresponding values calculated according to formulas (3) and (4) (Table 3). The estimated error in superimposing the basis set (*BSSE*) on calculations of *PA* and *GB* for 1,2,3-triazole amounts to 1.6 kJ/mol. Since this value is not too large we have not calculated *BSSE* for the other triazoles and all the data of the present work were obtained without calculating *BSSE*.

TABLE 3. Values of *PA*, *GB*, and p$K_{\mathrm{BH+}}$ for Unsubstituted 1,2,3-Triazole

Parameters	Calculated with equation	
	(1) and (2)	(3) and (4)
PA, kJ/mol	877.0	877.0
GB, kJ/mol	844.8	844.6
p$K_{\mathrm{BH+}}$	1.00	0.97

The Gibbs free energy for the processes of protonation in aqueous solution and the value of p$K_{\mathrm{BH+}}$ were computed starting from the calculated values for the solvation energy:

$$\Delta_{sol}G = G_{sol} - E,$$

where G_{sol} is the energy of a molecule of dissolved substance allowing for electrostatic and nonelectrostatic components of the free energy of solvation; *E* is the total energy of the isolated molecule. The following formula was used:

$$\Delta_r G^0_{298,\mathrm{H_2O}} = GB + \Delta_{sol}G(\mathrm{B}) + \Delta_{sol}G(\mathrm{H}^+) - \Delta_{sol}G(\mathrm{BH}^+)\,,$$

$$pK_{\mathrm{BH}^+} = \frac{\Delta_r G^0_{298,\mathrm{H_2O}}}{2.303 \cdot R \cdot T}\,,$$

where $\Delta_{sol}G(\mathrm{H}^+)$ = -1085.8 kJ/mol; *GB* is the calculated gas-phase basicity.

The work was carried out with the financial support of the Belorussian Republican Fund for Fundamental Investigations, grant No. KhO7SO-010.

REFERENCES

1. V. P. Krivopalov and O. P. Shkurko, *Usp. Khim.*, **74**, 369 (2005).
2. L. I. Vereshchagin, N. I. Kuznetsova, L. P. Kirillova, G. T. Sukhanov, and V. V. Shcherbakov, *Khim. Geterotsikl. Soedin.*, 932 (1986). [*Chem. Heterocycl. Comp.*, **22**, 745 (1986)].

3. V. Jimenez and J. B. Alderete, *Theochem*, **775**, 1 (2006).
4. M. Begtrup, C. J. Nielsen, L. Nygaard, S. Samdal, C. E. Sogren, and G. O. Sorensen, *Acta Chem. Scand.* **A42**, 500 (1988).
5. P. Politzer, M. E. Grice, and J. M. Seminario, *Int. J. Quant. Chem.*, **61**, 389 (1997).
6. J.-L. M. Abbound, C. Foces-Foces, R. Notario, R. E. Trifonov, A. P. Volovodenko, V. A. Ostrovskii, I. Alkorta, and J. Elguero, *Eur. J. Org. Chem.*, 3013 (2001).
7. W. P. Oziminski, J. Cz. Dobrowolski, and A. P. Mazurek, *J. Mol. Struct.*, **651-653**, 697 (2003).
8. L. Birkofer and P. Wegner, *Chem. Ber.*, **100**, 3485 (1967).
9. P. Ykman, G. L'abbe, and G. Smets, *Tetrahedron Lett.*, 5225 (1970).
10. E. P. L. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data*, **27**, 413 (1998).
11. J. Catalan, J.-L. M. Abbound, and J. Elguero, *Adv. Heterocycl. Chem.*, **41**, 187 (1987).
12. R. E. Trifonov, V. A. Ostrovskii, L. I. Vereshchagin, M. B. Shcherbinin, N. P. Shirokova, and A. O. Koren', *Zh. Org. Khim.*, **31**, 928 (1995).
13. R. E. Trifonov, M. B. Shcherbinin, and V. A. Ostrovskii, *Zh. Org. Khim.*, **33**, 1116 (1997).
14. Vad. E. Matulis, Thesis for Candidate of Chemical Sciences, Minsk (2005).
15. O. Koren, *J. Heterocycl. Chem.*, **39**, 1111 (2002).
16. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03*, Revision B.03, Gaussian Inc., Pittsburgh, PA (2003).
17. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
18. P. N. Gaponik, S. V. Voitekhovich, A. S. Lyakhov, Vadim E. Matulis, O. A. Ivashkevich, M. Quesada, and J. Reedijk, *Inorg. Chim. Acta*, **358**, 2549 (2005).
19. P. N. Gaponik, M. M. Degtyarik, A. S. Lyakhov, Vadim E. Matulis, O. A. Ivashkevich, M. Quesada, and J. Reedijk, *Inorg. Chim. Acta*, **358**, 3949 (2005).
20. Vadim E. Matulis, A. S. Lyakhov, P. N. Gaponik, S. A. Voitekhovich, and O. A. Ivashkevich, *J. Mol. Struct.*, **649**, 309 (2003).
21. F. Eckert and A. Klamt, *AIChE J.*, **48**, 369 (2002).
22. O. A. Ivashkevich, P. N. Gaponik, Vit. E. Matulis, and Vad. E. Matulis, *Zh. Obshch. Khim.*, **73**, 296 (2003).
23. M. W. Wong, R. Leung-Toung, and C. Wentrup, *J. Am. Chem. Soc.*, **115**, 2465 (1993).
24. A. P. Mazurek and N. Sadlej-Sosnowska, *Chem. Phys. Lett.*, **330**, 212 (2000).
25. L. V. Gurvich, G. A. Khachkuruzov, V. A. Medvedev, I. V. Veits, G. A. Bergman, V. S. Yungman, N. P. Rtishcheva, L. F. Kuratova, G. N. Yurkov, A. A. Kane, B. F. Yudin, B. I. Brounshtein, V. F. Baibuz, V. A. Kvlividze, E. A. Prozorovskii, and B. A. Vorob'ev, *Thermodynamic Properties of Individual Substances* [in Russian], Akad. Nauk SSSR, Moscow (1962).