ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 11, pp. 1695–1707. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.V. Lipson, T.M. Karnozhitskaya, S.V. Shishkina, O.V. Shishkin, A.V. Turov, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 11, pp. 1717–1728.

Reactions of α-Aminoazoles with (2*E*)-3-Phenylacryloyl Chloride

V. V. Lipson[a], T. M. Karnozhitskaya[a], S. V. Shishkina[b], O. V. Shishkin[b], and A. V. Turov[c]

[a]*Danilevskii Institute of Endocrine Pathology Problems, Ukrainian Academy of Medical Sciences, Kharkov, 61002 Ukraine*
e-mail: lipson@ukr.net
[b]*Research & Development Complex "Institute of Single Crystals", Ukrainian National Academy of Sciences, Kharkov, Ukraine*
[c]*Kiev National University, Kiev, Ukraine*

Received February 26, 2008

Abstract—Reaction of 5-amino-3-methylpyrazole, 3-amino-, 5-amino-3-methylsulfanyl-1,2,4-triazole and 5-amino-1,2,4-triazole-3-thione with 3-phenylacryloyl-chloride under mild conditions is characterized by low selectivity and does not lead to the formation of fused heterocyclic systems but gives mixtures of products of mono- and diacylation of the nucleophilic sites in the molecules of α-aminoazoles. Endocyclic monoacyl derivatives of aminotriazoles in DMF undergo a transacylation at the *exo*-amino- group followed by cyclization into dihydro-1,2,4-triazolo[1,5-*a*]-pyrimidin-5-ones.

DOI: 10.1134/S1070428008110225

Reactions of α-aminoazoles with unsaturated acylating 1,3-bielectrophiles resulted in fused azoloazine systems distinguished by the location of the junction and/or by the position of substituents in the azine ring due to the nonequivalence of the reactive sites in both components of the cyclocondensation. The prevalence of one among the possible paths of the reaction originates from both the nature of the reactants and the reaction conditions. The numerous publications deal with this kind transformations involving substituted acrylic and propiolic acids [1–3], cinnamic acid and derivatives [4–9], aroyl- and arylmethylenepyruvates [9–13], ethoxymethylene- and arylmethyleneethylacetoacetates [3, 14–20], ethoxyalkylidene- and arylmethylenemalonates [3, 13, 21–25], derivatives of Meldrum's acid [26–35], but in contrast scanty data concern the reactions of heterylamines with (2*E*)-3-phenylacryloyl chloride (cinnamoyl chloride) [5, 7].

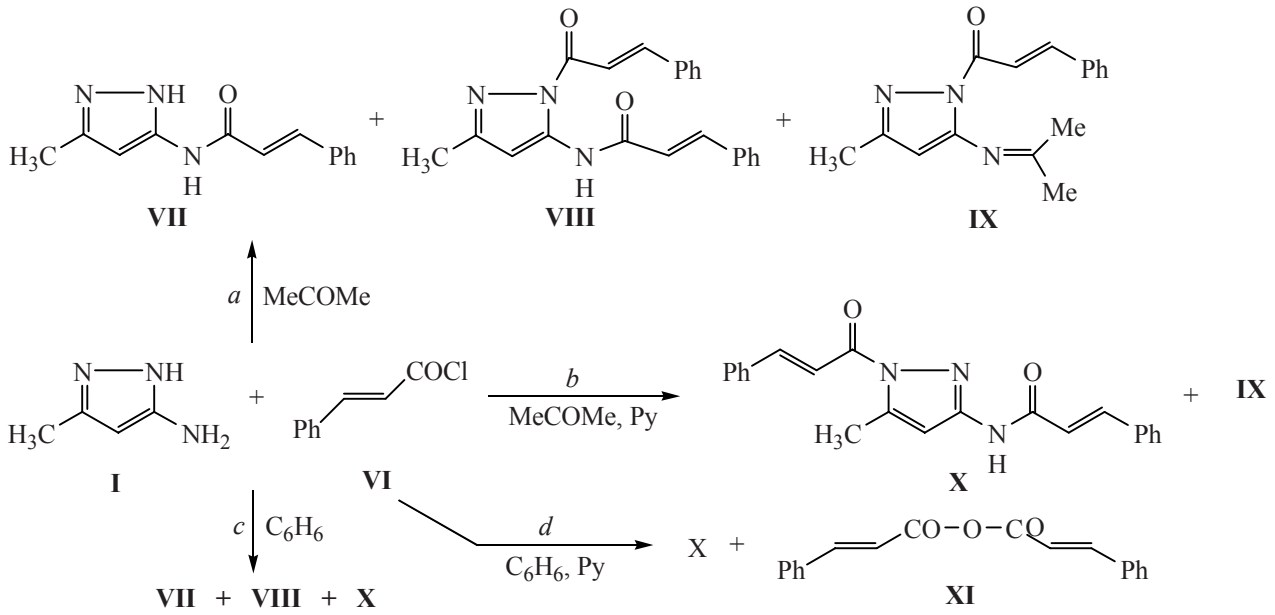
The aim of this work was to elucidate the direction of the reactions of 5-amino-3-methylpyrazole (**I**), 2-aminobenzimidazole (**II**), 3-amino-, 5-amino-3-methylsulfanyl-1,2,4-triazole (**III, IV**), and 5-amino-1,2,4-triazole-3-thione (**V**) with cinnamoyl chloride (**VI**) under various conditions.

The processes involving aminopyrazole **I** and acid chloride **VI** provide multicomponent mixtures without cyclization products and containing prevailingly acylation products at all nitrogen atoms but not at the endocylic carbon in the molecule of amine **I** (Scheme 1). For instance, in the reaction with a 1.5-fold excess of acid chloride **VI** in acetone at 40°C three compounds **VII–IX** were obtained. Into the formation of one among them, azomethine **IX**, also the solvent was involved. The main component of this mixture was pyrazolylcinnamamide **VII**. We failed to convert the latter into pyrazolo[3,4-*b*]-pyridinone or pyrazolo[1,5-*a*]pyrimidinone even at prolonged boiling (2 h) in DMF. At a catalysis with pyridine in acetone a mixture of two compounds **IX** and **X** was obtained in a ratio 1:1. A mixture of three compounds, **VII, VIII**, and **X**, two among them containing two acyl residues each, was obtained at boiling in benzene. Without heating with pyridine catalysis in benzene dicinnamoyl derivative **X** and cinnamic anhydride **XI** were obtained. In no synthesis the fused pyrazolopyridines or pyrazolopyrimidines were detected (Scheme 1).

The identification of structures **VII–X** was performed based on the analysis of mass, IR, ^{1}H spectra and XRD of compound **X**. Anhydride **XI** was identified by comparison of its physicochemical and spectral characteristics with the published data [36].

The comparison of data on the nitrogen content with the mass spectra made it possible to distinguish monoamide **VII** from dicinnamoyl derivatives **VIII** and **X** and azo-

Scheme 1.



methine **IX**. At the electron impact ionization of compounds **VIII** and I**X** their mass spectra lack peaks of the molecular ions. Therefore for these compounds ^{252}Cf plasma-desorption spectra were registered that permitted the establishment of the molecular mass.

In the IR spectra of compounds **VII, VIII**, and **X** the most characteristic are the vibrations of NH 3324–2928, "amide I" 1692–1660, "amide II" 1592–1528 cm^{-1}. However these data are insufficient for establishing the position of substituents in the ring.

^{1}H NMR spectrum of amide **VII** differs from the spectra of all other products of amine **I** acylation for it contains two broadened singlets from the NH group, δ 12.03, 10.51 ppm, and a single *AB* system of signals in the range δ 7.51–6.86 ppm, *J* 15.6 Hz, characteristic of the *trans*-located protons of the cinnamoyl fragment. In the spectrum of compound **VIII** two similar *AB* systems were observed (see EXPERIMENTAL) and one proton of the imino group, δ 10.78 ppm, In the spectrum of azomethine **IX** the resonance of the NH group is absent, one system of proton signals belonging to a cinnamoyl fragment and three singlets of methyl groups were registered. The nuclear Overhauser effect involving the CH_3 group of the pyrazole ring in compounds **VIII** and **IX** was only observed with respect to the H^4 proton of this ring suggesting the lack of substituents at N^2 atom in both structures. The spectrum of diacyl derivative **X** differed from the spectrum of isomer **VIII** mainly by the value δ_{NH}. The more downfield position of this signal in the spectrum of compound **VIII** should be caused by the deshielding effect of the cinnamoyl fragment contiguous to the NH group. In the NOE experiment with compound **X** on the irradiation of the CH_3 group of the pyrazole ring responded the proton H^4 (δ 6.8 ppm) and protons of one of the cinnamoyl substituents. The final choice between structures **VIII** and **X** was done based on XRD analysis on a single crystal of compound **X** (Fig. 1, Table 1, 2) that proved the structure of this compound as (2*E*)-*N*-{5-methyl-1-[(2*E*)-3-phenyl-prop-2-enoyl]-1*H*-pyrazol-3-yl}-3-phenylacryl-amide.

Table 1. Bond lengths (*d*, Å) in the molecule of (2*E*)-*N*-{5-methyl-1-[(2*E*)-3-phenyl-prop-2-enoyl]-1*H*-pyrazol-3-yl}-3-phenylacrylamide

Bond	*d*	Bond	*d*	Bond	*d*
O^1–C^4	1.16(1)	C^{14}–C^{15}	1.47(1)	C^4–C^5	1.49(1)
N^1–C^1	1.33(1)	C^{16}–C^{17}	1.46(1)	C^6–C^7	1.47(1)
N^1–N^2	1.428(9)	C^{17}–C^{18}	1.39(1)	C^7–C^8	1.38(1)
N^3–C^4	1.39(1)	C^{19}–C^{20}	1.35(1)	C^9–C^{10}	1.34(1)
C^1–C^3	1.37(1)	C^{21}–C^{22}	1.34(1)	C^{11}–C^{12}	1.36(1)
C^2–C^3	1.39(1)	O^2–C^{14}	1.23(1)	C^{15}–C^{16}	1.37(1)
C^5–C^6	1.32(1)	N^1–C^{14}	1.40(1)	C^{17}–C^{22}	1.37(1)
C^7–C^{12}	1.33(1)	N^2–C^2	1.31(1)	C^{18}–C^{19}	1.37(1)
C^8–C^9	1.41(1)	N^3–C^2	1.41(1)	C^{20}–C^{21}	1.36(1)
C^{10}–C^{11}	1.39(1)	C^1–C^{13}	1.54(1)		

The pyrazole ring and all nonhydrogen atoms of th substituent at the atom N^1 are located in the same plan within 0.03 Å. Therewith the enone fragment is in the *cis*-conformation, torsion angle $O^2C^{14}C^{15}C^{16}$ is –2(2) deg The planar conformation of this fragment of the molecul is apparently additionally stabilized by the attractive inter action $H^{15}\cdots N^2$ 2.39 Å (the sum of van der Waals radii 2.67 E [37]) and leads to a considerable steric strain a show the shortened intramolecular contacts $H^{15}\cdots C^{22}$ 2.7 (2.87 Å), $H^{15}\cdots H^{22}$ 2.27 (2.34 Å), $H^{16}\cdots H^{18}$ 2.26 (2.34 Å $H^{22}\cdots C^{15}$ 2.81 (2.87 Å), $O^2\cdots C^{13}$ 2.87 (3.00 Å). It i presumable that the steric strain is partially compensate by lengthening of bonds N^1–N^2 1.428(9), N^1–C^{14} 1.40(1), C^{15}–C^{16} 1.37(1) Å compared to their mean values 1.366, 1.347, 1.316 Å respectively [38]. The carbamide group and the atoms C^5, C^6 are located in one plane with an accuracy of 0.01 Å notwithstanding the repulsion between hydrogen atoms [shortened intramolecular contact $H^{3N}\cdots H^5$ 2.07 (2.34 Å)]. Therewith the carbamide group and the pyrazole ring are slightly noncoplanar [torsion angle $C^4N^3C^2C^3$ 19(2) deg] evidently because of the repulsion between the atoms of the pyrazole ring and the carbonyl group [shortened intramolecular contact $O^1\cdots C^{13}$ 2.90 (3.00 Å)]. The enone fragment is in the *s-cis*-conformation [torsion angle $O^1C^4C^5C^6$ –1(2) deg]. The phenyl substituent at the atom C^6 is also somewhat turned with respect to the double bond C^5–C^6 [torsion angle $C^5C^6C^7C^8$ –9(2) deg] because of shortened intramolecular contact $H^8\cdots C^5$ 2.81 (2.87 Å).

The lost selectivity in reactions of amine **I** with the cinnamoyl chloride and the lack of products formed at the reaction site C^4 in the pyrazole ring may be understood taking into consideration the principle of hard and soft acids and bases. Acid chloride **VI** behaved as a hard acid attacking only hard basic sites, *exo*- and *endo*-cyclic nitrogen atoms in the heterylamine.

The acylation of 2-aminobenzimidazole (**II**) with cinnamoyl chloride at 18–20°C in DMF, acetone, and also at short (5–10 min) boiling in benzene provided amide **XII** that at long (2 h) boiling in DMF converted into pyrimido[1,2-*a*]benzimidazol-2-one (**XIII**) in a high yield (Scheme 2). No acylation products **XIV** and **XV** at the endocyclic nitrogen atoms or at two reaction sites in the molecule of amine **II** were detected in any of the above described syntheses in contrast to the processes involving acid chloride **VI** and aminopyrazole **I**.

Physicochemical and spectral characteristics of benzimidazolylcinnamamide **XII** and pyrimidobenzimid-azolone **XIII** are consistent with the previously published in [4, 5] for compounds obtained respectively by melting 2-carbomethoxyaminobenzimidazole with cinnamic acid without solvent or from amine **II** with cinnamoyl chloride in THF. However amide **XII** failed to be converted pyrimido-[1,2-*a*]benzimidazol-2-one (**XIII**) in [5, 7] by heating in diglyme and DMF.

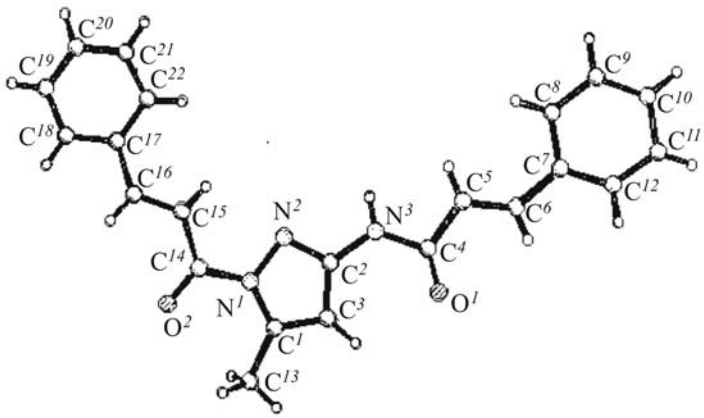


Fig. 1. Structure of the molecule of (2*E*)-*N*-{5-methyl-1-[(2*E*)-3-phenylprop-2-enoyl]-1*H*-pyrazol-3-yl}-3-phenylacrylamide **(X)**

3-Aminotriazole **III** at equimolar ratio with acid chlorideOm **VI** in acetone at heating gave a mixture of three substances: acyl derivative **XVI**, amide **XVII**, and salt **XVIII** (Scheme 3). The prevailing component is the product of acylation at the atom N^1 in the azole ring **XVI**. At the catalysis with pyridine both in acetone and in benzene the electrophilic attack is aimed at endocyclic atoms N^1 and N^2. Depending on the conditions only the yield of compounds **XVI** and **XIX** varied, but the main

Table 2. Bond angles (φ, deg) in the structure of (2*E*)-*N*-{5-methyl-1-[(2*E*)-3-phenyl-prop-2-enoyl]-1*H*-pyrazol-3-yl}-3-phenylacryl-amide (**X**)

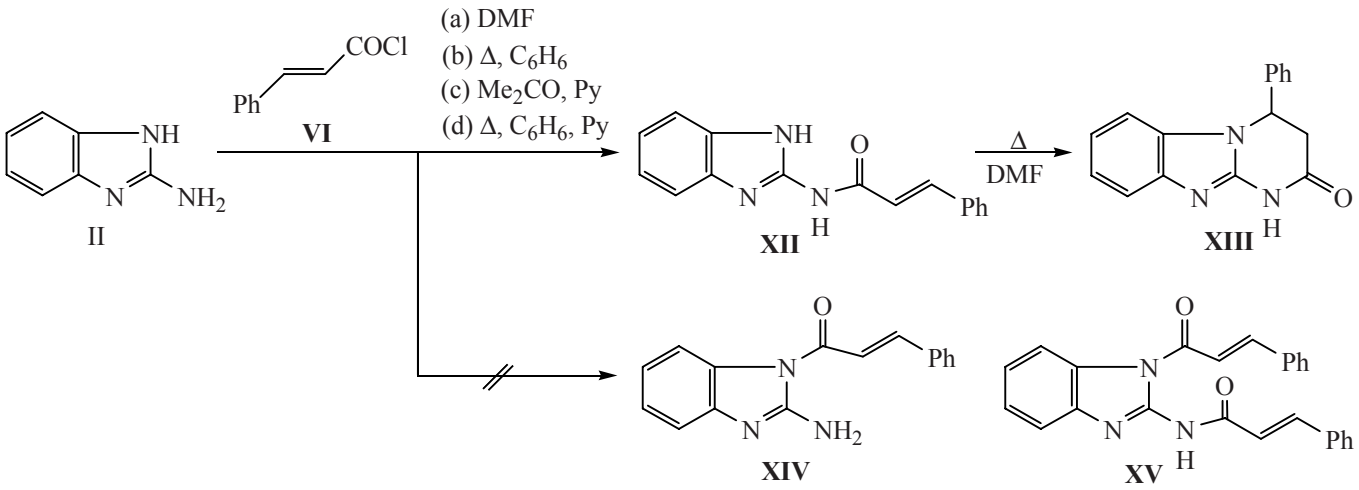
Angle	φ	Angle	φ	Angle	φ
$C^1N^1C^{14}$	129.9(8)	$O^1C^4C^5$	132(1)	$O^2C^{14}C^{15}$	122(1)
$C^1N^1N^2$	112.7(7)	$N^3C^4C^5$	105(1)	$N^1C^{14}C^{15}$	118.7(9)
$C^{14}N^1N^2$	117.4(8)	$C^6C^5C^4$	116(1)	$C^{16}C^{15}C^{14}$	125.0(9)
$C^2N^2N^1$	101.6(7)	$C^5C^6C^7$	130(1)	$C^{15}C^{16}C^{17}$	127.3(9)
$C^4N^3C^2$	124.0(9)	$C^{12}C^7C^8$	117(1)	$C^{22}C^{17}C^{18}$	121.5(9)
$N^1C^1C^3$	105.9(9)	$C^{12}C^7C^6$	121(1)	$C^{22}C^{17}C^{16}$	124(1)
$N^1C^1C^{13}$	125.7(8)	$C^8C^7C^6$	122(1)	$C^{18}C^{17}C^{16}$	115(1)
$C^3C^1C^{13}$	128.3(9)	$C^7C^8C^9$	120(1)	$C^{19}C^{18}C^{17}$	119(1)
$N^2C^2C^3$	114(1)	$C^{10}C^9C^8$	119(1)	$C^{20}C^{19}C^{18}$	120(1)
$N^2C^2N^3$	117.4(8)	$C^9C^{10}C^{11}$	122(1)	$C^{19}C^{20}C^{21}$	120(1)
$C^3C^2N^3$	129(1)	$C^{12}C^{11}C^{10}$	116(1)	$C^{22}C^{21}C^{20}$	123(1)

product always was compound **XVI**. In benzene in the absence of pyridine it was the only acylation product, but in a low yield. In all events at the end of the reaction the mixture contained also the initial aminotriazole **III**.

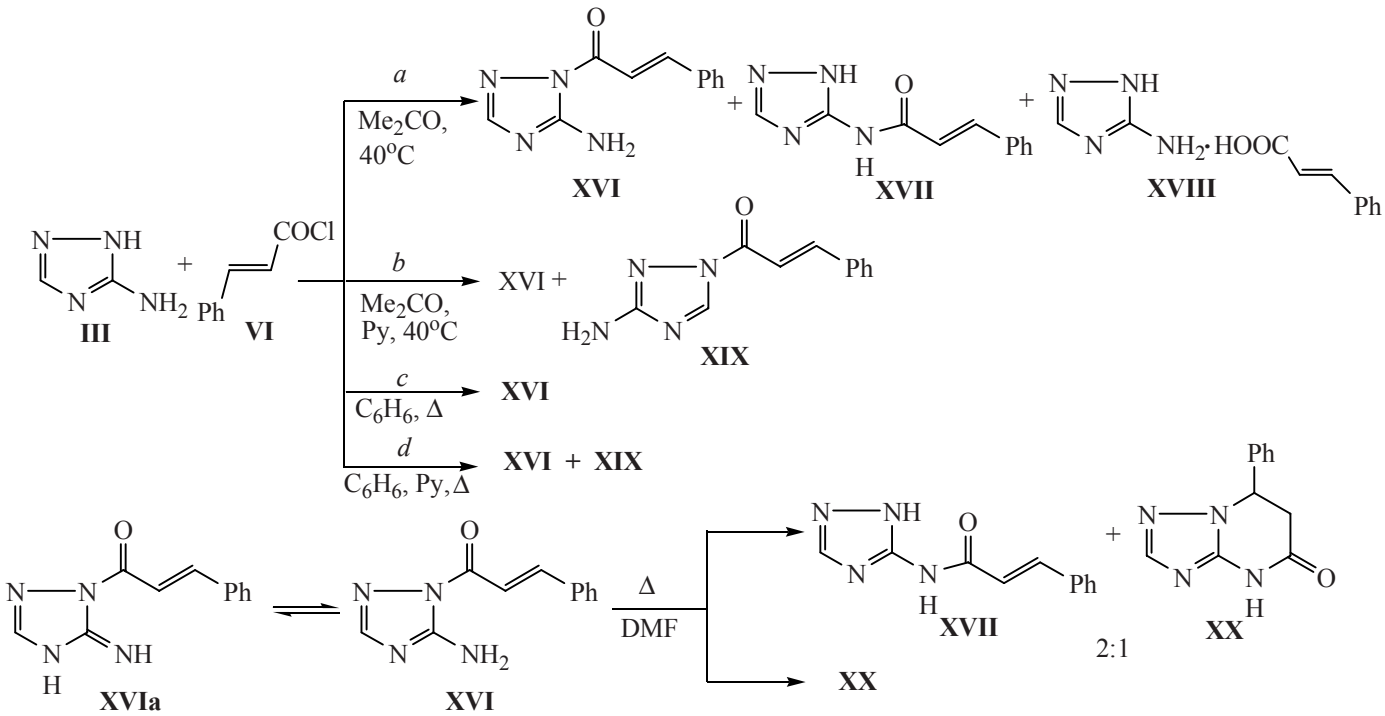
Cinnamoyl derivative **XVI** at boiling in DMF for 1.5 h suffered a transacylation converting into amide **XVII** that in its turn underwent a cyclization into tetrahydrotriazolo[1,5-*a*]-pyrimidin-5-one (**XX**). A complete conversion of compound **XVI** into pyrimidinone **XX** occurred in 5–6 h. The latter by physicochemical and spectral characteristics coincided with the substance obtained by the reaction of amino-triazole with methyl cinnamate whose structure was confirmed by XRD and described in [8].

7-Oxo derivatives and also triazolo[4,3-*a*]-pyrimidinones were not found among the products of transformations of substances **XVI** and **XVII**. The structure of compounds **XVI–XIX** was established by spectral

Scheme 2.



Scheme 3.



methods. The most characteristic feature of the IR spectra of acyl derivatives **XVI, XVII, XIX**, and salt **XVIII** is the absorption band of the carbonyl group at 1684–1704 cm^{-1}. The distinguishing of structures **XVI** and **XIX** was carried out by ^{1}H NMR spectroscopy from the chemical shifts of methine protons of the triazole ring and of amino groups. In keeping with [39] the signal of H^5 proton in the spectrum of N^1-acyl-3-amino-1,2,4-triazoles appeared downfield with respect to that in the N^2-substituted compounds. For the signals of NH_2 protons the opposite trend is valid. Actually, in the spectrum of compound **XVI** the proton signal of H^5 was observed in the region of aromatic protons, δ(NH_2) 7.8, and for substance **XIX** δ(CH) 9.0, δ(NH_2) 6.1 ppm. Besides in the spectrum of compound **XIX** the signal of NH group was absent. The scope of these data suggests the assign-ment to compounds **XVI** and **XIX** of structures 1-[(2*E*)-3-phenylprop-2-enoyl]-1*H*-1,2,4-triazol-5-amine and 1-[(2*E*)-3-phenylprop-2-enoyl]-1*H*-1,2,4-triazol-3-amine respectively.

For the spectrum of amide **XVII** the lack of the resonance of the protons of NH_2 group and the presence of signals from two imino groups as broadened singlets was characteristic. However in event of existence of a tautomeric form **XVIa** it would be difficult to distinguish it from structure **XVII**. Besides in the reactions under consideration the formation of N^4-acyl derivatives also is not excluded. To solve this problem a 2D HMBC spectrum of compound **XVI** was registered. The correlations between the atoms ^{13}C and ^{1}H revealed in this spectrum and serving as a reason for assignment the quaternary carbon atoms are presented in Fig. 2. The signals of the protonated carbon atoms were assigned using HMQC spectra.

For H^3 proton only the interaction with C^5 was observed, no correlation occurred with the carbonyl carbon atom. Consequently, the substituent was located not at N^2 or N^4, but at the atom N^1. The findings obtained unambiguously proved the structure of compound **XVI** as N^1-acyl derivative and permitted choosing among its tautomer forms **XVI** and **XVIa** the first one.

The revealed acylation direction of amine **III** at the reaction sites N^1, N^2, and NH_2, but not N^4, and also the ability of 3-acylamino derivative **XVI** of transacylation is consistent in general with the data previously obtained [40–42] in reactions with acid chlorides of the structure RCOCl (R = Me, Et, Pr, Ph, OMe, OEt) which are not 1,3-bielectrophiles.

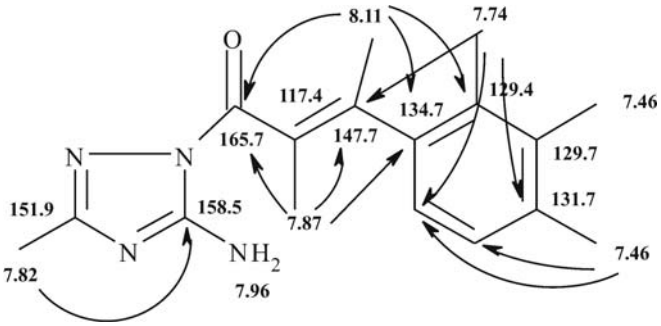


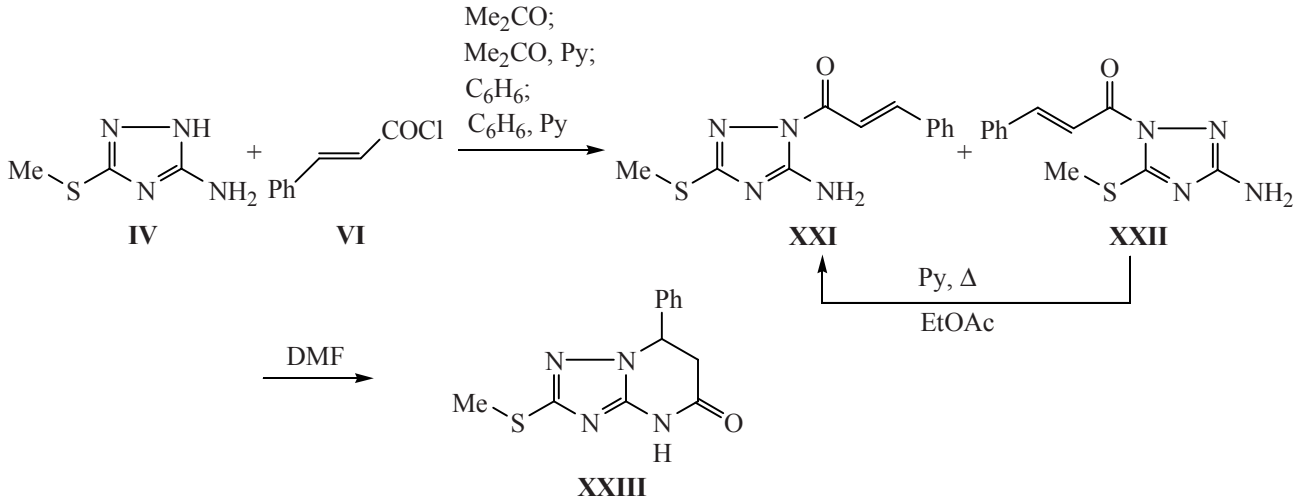
Fig. 2. Assignment of signals in ^{1}H and ^{13}C NMR spectra for 1-[(2*E*)-3-phenylprop-2-enoyl]-1*H*-1,2,4-triazol-5-amine (**XVI**) with indication of the main correlations ^{1}H–^{13}C in the two-dimensional HMBC spectrum.

At a short (30 min) heating of 5-amino-3-methylsulfanyltriazole (**IV**) with acid chloride **VI** in acetone or benzene without catalyst or in the presence of pyridine a mixture formed of the initial amine with products of acylation at the endocylic atoms N^1 and N^2 (Scheme 4). The prevailing product was always compound **XXI**. Cinnamoyl derivative **XXII** in good yield was converted into isomer **XXI** at boiling in a mixture ethyl acetate–pyridine for 2.5 h. Both compounds **XXI** and **XXII** at prolonged (4 h) boiling in DMF formed triazolo[1,5-*a*]-pyrimidin-5-one (**XXIII**). The structure of compounds **XXI** and **XXII** was proved by spectral methods, the composition was confirmed by elemental analysis. The physicochemical and spectral characteristics of triazolopyrimidinone **XXIII** coincide with those described for the condensation product of amine **IV** with methyl cinnamate in [32].

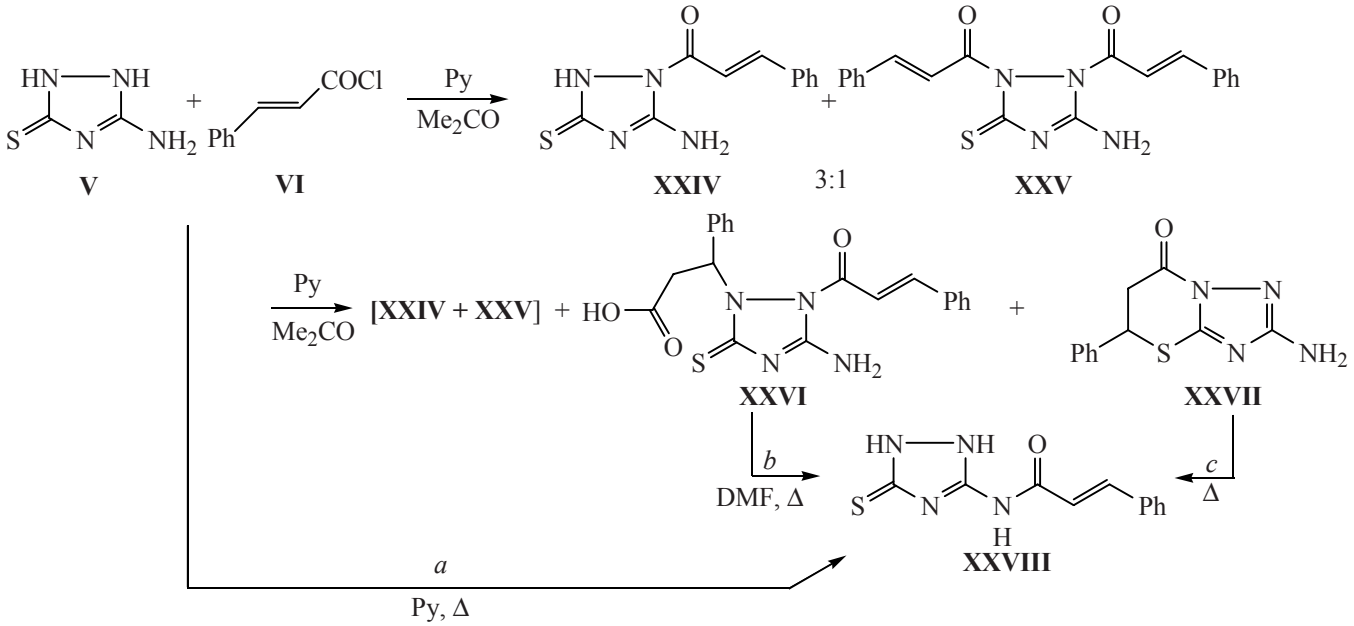
IR spectra of compounds synthesized contain a set of bands characteristic of compounds having in their structure associated groups NH_2, C=O, and CN [43]. The data on nitrogen content in amides **XXI** and **XXII** show that they have in the structure only one acyl residue. This is confirmed also by the ^{1}H NMR spectra. The distinguishing of isomers **XXI** and **XXII** was made based on the comparison of the chemical shifts of the protons of amino -groups. In the spectrum of compound **XXI** the signal of the NH_2 group is shifted downfield by 1.5 ppm compared to the analogous signal in the spectrum of compound **XXII**.

Aminotriazolethione **V** with an equimolar amount of acid chloride **VI** in acetone–pyridine medium within 30 min formed a mixture of mono- **XXIV** and di-cinnamoyl **XXV** derivatives in a ratio 3:1(according to ^{1}H NMR) that we failed to separate (Scheme 5). On prolonging the heating in 3 h two more compounds **XXVI** and **XXVII**

Scheme 4.



Scheme 5.



formed that were isolated as individual substances. The only bicyclic product among these compounds was triazolothiazinone **XXVII**. The structural analog of this compound without the amino group was prepared [44] by the acylation of 1,2,4-triazole-3-thione with acid chloride **VI**.

The product of aminoazole **V** acylation at the amino group **XXVIII** was obtained by boiling the initial reagents in pyridine for 1 h, and also by the thermolysis of compound **XXVI** by its boiling in DMF (1 h) and at the pyrolysis of thiazinone **XXVII** accompanying its melting.

The structure of compounds **XXIV–XXVIII** was established by spectral methods, the composition was confirmed by elemental analysis. In the ^{1}H NMR spectrum of the mixture of compounds **XXIV** and **XXV** appeared all the groups of signals confirming their structures as mono- and dicinnamoyl derivatives of aminotriazolethione: the broadened singlet of NH proton of thione **XXIV**, the signals of three phenyl rings and of three fragments CH=CH giving rise to systems *AB* with J_{trans} ~16 Hz. Therewith the resonance of CH protons of the substituent attached to the atom N^1, both in compound **XXIV** and in diacyl derivative **XXV**, are registered at a large interval of δ values thus permitting the estimation of the mixture composition. The location of the signals of two amino groups, δ 7.79 and 7.86 ppm partially over-

lapped by the signals of aromatic protons was established in the experiment with CD_3OD. Apparently, the downfield signal belongs to the NH_2 group of compound **XXV**.

The comparison of the data on the nitrogen content with the mass spectrum of acid **XXVI** made it possible to regard the peak of *m*/*z* 394 as the molecular ion. Consequently, two molecules of acid chloride **VI** were involved in the acid formation. IR spectrum of compound **XXVI** contains the absorption bands characteristic of associated groups COOH, NH_2. In the ^1H NMR spectrum of this compound alongside the multiplets of the protons of the phenyl rings were registered the *AB* system of the cinnamoyl fragment, J_{trans} 16 Hz, the *ABX* system of the phenylpropionyl residue, and a broadened singlet of the OH proton of the carboxy group, δ 12.34 ppm. The signal of the amino group is overlapped by the signals of aryl protons, and its presence at 7.68 ppm is confirmed by the experiment on deuterium exchange with CD_3OD. Besides in the spectrum of acid **XXVI** only two types of signals from protons capable of exchange are present, groups COOH and NH_2. This result permitted to reject the presence of *a* structure formed by acylation of the reaction site N^1 amd alkylation of the sulfur atom in amine **V**. Otherwise inevitably a proton signal from the NH of the triazole ring should be present. Yet at the alternative position of the phenylpropionyl fragment at the atom N^1 and the cinnamoyl moiety at N^2 the spectrum would contain the same groups of signals as in that of compound **XXVI**. In order to get more precise information on the structure of substance **XXVI** the chemical shifts of ^1H and ^{13}C were established from the correlation spectra HMQC and HMBC (Fig. 3). However for the alternative structure **XXVIa** the chemical shifts should have the same values (Fig. 4). The difference was found only for the carbon atoms of the triazole but the δ values were too close to permit the final choice between the structure. Yet a certain possibility for the establishment of the structure lies in the presence of the HMBC-correlation between the methine proton of the propionyl fragmenta, δ 5.10 ppm,and a carbon atom of the triazole ring, δ 160.4 ppm. From the relaxation characteristics of carbon atoms in this ring it is possible to establish which among them is linked to the NH_2 group or to the sulfur atom. The bond to amino group should result in more efficient relaxation and, respectively, to growing of the signal intensity when the the spectrum is registered with a small relaxation interval. In an experiment of a pulse decoupling without decoupling from protons the signal at

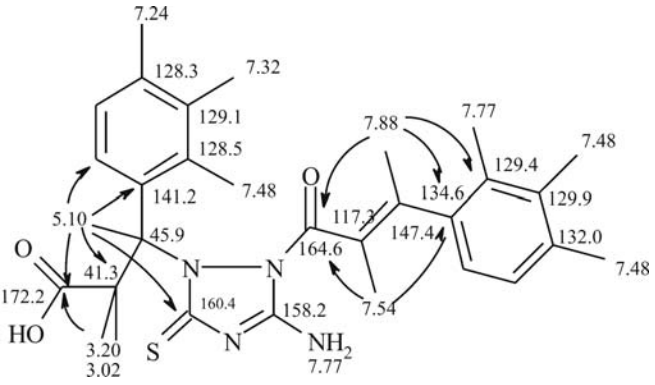


Fig. 3. Assignment of ^1H and ^{13}C NMR signals taking into account HMQC and HMBC correlations for 3-{3-amino-2[(2*E*)-3-phenyl-prop-2-enoyl]-5-thioxo-2,5-dihydro-1*H*-1,2,4-triazol-1-yl}-3-phenyl-propanoic acid (**XXVI**).

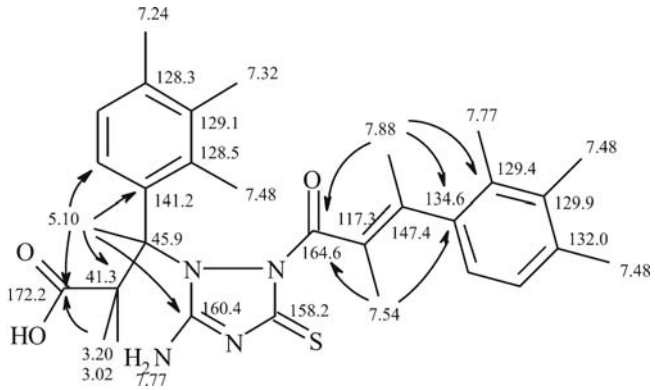


Fig. 4. Assignment of ^1H and ^{13}C NMR signals taking into account HMQC and HMBC correlations for 3-{5-amino-2-[(2*E*)-3-phenyl-prop-2-enoyl]-3-thioxo-2,3-dihydro-1*H*-1,2,4-triazol-1-yl}-3-phenyl-propanoic acid (**XXVIa**).

δ 160.4 ppm appeared as a doublet with *J* 5 Hz, and the signal at δ 158.2 ppm was a singlet, and their intensities related as 0.58:1. Thus the carbon atom signal split by the coupling with the CH proton of the propionyl fragment has lower intensity than the unsplit signal. This fact confirms the structure **XXVI**.

The mass spectrum of compound **XXVII** contains a molecular ion peak, *m*/*z* 246, showing that only one molecule of acid chloride was involved into its formation. The most characteristic absorption bands in the IR spectra originate from vibrations of CO and NH_2 groups at 1724 and 3340–3172 cm^{-1}. In the ^1H NMR spectrum the following groups of signals were observed: a multiplet of phenyl protons, an *ABX* system of azine ring, and a broadened singlet of amino group. The spectrum completely confirmed the structure of compound **XXVII** as a triazolothiazinone.

The comparison of results of the study of reactions between 3-amino-5-methylpyrazole (**I**) and cinnamoyl chloride (**VI**) with the data on the reactions of amino-1,2,4-triazoles **III–V** with the same acylating 1,3-bi-electrophile demonstrated that the significant differentiation of the electronic characteristics of the reaction sites in acid chloride **VI** and on the contrary not so pronounced in the molecules of aminoazoles led to a complete loss of selectivity in reactions between these reagents. Under mild conditions the process is kinetically controlled and ends on the stage of acylation of nucleophilic centers of all the amines under consideration. The cyclization requires more severe conditions (boiling in DMF) that leads in the most cases to a considerable tarring. In cinnamoyl derivatives **XVI**, **XXI**, and **XXII** a migration of the acyl residue was observed leading to the formation of probably more thermodynamically stable products that were able under these conditions to alkylate the endocyclic reaction site of the aminoazole necessary for the building up of the partially hydrogenated pyrimidine ring.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord M-82 from samples pelletized with KBr. ^{1}H NMR spectra were registered on a spectrometer Varian-200 from solutions in DMSO-d_6, internal reference TMS. Experiments on heteronuclear correlations HMBC and HMQC for compounds **XVI** and **XXVI** dissolved in DMSO-d_6 were performed on a spectrometer Varian Mercury 400. Mass spectra of compounds **VIII, IX**, and **XII** were obtained on an instrument MSBC Selmi (Sumy, the Ukraine) (source 10μCi ^{252}Cf) for positive and negative ions at the accelerating voltage ±20 kV. Mass spectra of compounds **VII, X, XXVI**, and **XXVII** were measured on a GC-MS instrument Varian 1200 L with a direct admission of the sample into the ion source, ionization by electron impact, energy 70 eV. Melting points were determined on a Koeffler heating block.

X-ray diffraction analysis of 2(*E*)-*N*-{5-methyl-1-[(2*E*)-3-phenylprop-2-enoyl]-1*H*-pyrazol-3-yl}-3-phenylacrylamide (X). Crystals monoclinic, $C_{22}H_{19}N_3O_2$, at 20°C *a* 20.389(6), *b* 5.335(2), *c* 17.060(5) Å, β 90.14(2) deg, *V* 1856(1) Å^3, M_r 357.40, *Z* 4, space group $P2_1/C$, d_{calc} 1.279 g/cm^3, μ(MoK_α) 0.084 mm^{-1}, *F*(000) 752. parameters of the unit cell and intensity of 8862 reflections (2440 independent, R_{int} 0.139) were measured on a diffractometer Xcalibur-3 (MoK_α radiation, CCD-detector, graphite monochromator, ω-scanning, $2\theta_{max}$ 50°). The structure was solved by the direct method by the software package SHELXTL [38]. The positions of hydrogen atoms were calculated geometrically and refined in the *rider* model with $U_{iso} = nU_{eq}$ (n = 1.5 for the methyl group, n = 1.2 for the other hydrogen atoms). The structure was refined for F^2 by the full-matrix least-mean-squares method in the anisotropic approximation for nonhydrogen atoms till wR_2 0.127 for 2340 reflections [R_1 0.081 for 1106 reflexions with $F > 4\sigma$(F), *S* 0.99].

Reaction of 5-amino-3-methylpyrazole (I) with cinnamoyl -chloride (VI). *a*. To a solution of 5 mmol of amine **I** in 2 ml of acetone at 40°C was added a solution of 7.5 mmol of acid chloride **VI** in 2 ml of acetone, after 30 min the precipitate was filtered off and recrystallized from a mixture acetone–methanol, 1:1. We isolated 0.6 mmol (12%) of **3-methyl-*N*-(1-methylethylidene)-1-[(2*E*)-3-phenylprop-2-enoyl]-1*H*-pyrazol-5-amine (IX)**. mp 290–292°C. IR spectrum, cm^{-1}: 2960 (CH_3), 1684 (CO), 1624 (Ph–C=C), 1516 (C=N). ^{1}H NMR spectrum, δ, ppm: 7.77–7.42 m (5H, C_6H_5), 7.71 d (1H, =CH, J_{AB} 16.4 Hz), 7.64 d (1H, =CH, J_{AB} 16.2 Hz), 7.24 s (1H, C^{4}H), 2.26, 1.46, 1.32 s (3H, CH_3). Mass spectrum: $[M+H]^+$ 268, $[M-H]^+$ 266. Found, %: C 71.87; H 6.33; N 15.53. $C_{16}H_{17}N_3O$. Calculated, %: C 71.91; H 6.37; N 15.57. *M* 267.33.

From the amorphous residue obtained by solvent removal from the acetone filtrate we isolated using methanol 0.5 mmol (10%) of **2(*E*)-*N*-{3-methyl-1-[(2*E*)-3-phenyl-prop-2-enoyl]-1*H*-pyrazol-5-yl}-3-phenylacrylamide (VIII)**. mp 173–174°C. IR spectrum, cm^{-1}: 3264 (NH), 1684 br (CO, CONH), 1624 (Ph–C=C), 1532 (C=N). ^{1}H NMR spectrum, δ, ppm: 12.61 br.s (1H, NH), 8.12–7.48 m (12H, C_6H_5), 7.98 d (1H, =CH, *J* 16.0 Hz), 7.21 d (1H, =CH, J_{AB} 15.8 Hz), 6.87 C (1H, C^{4}H), 2.26 s (3H, CH_3). Mass spectrum: $[M+H]^+$ 358, $[M-H]^+$ 356. Found, %: C 73.98; H 5.28; N 16.29. $C_{22}H_{19}N_3O_2$. Calculated, %: C 73.95; H 5.32; N 16.34. *M* 357.41.

To the methanol filtrate water was added (1:5), and was filtered off 1.25 mmol (25%) of **2(*E*)-*N*-(3-methyl-1*H*-pyrazole-5-yl)-3-phenyl-acryl-amide (VII)** that was crystallized from 2-propanol. mp 238–240°C. IR spectrum, cm^{-1}: 3232–2928 (NH, CH_3), 1660 ("amide I"), 1592 ("amide II"). ^{1}H NMR spectrum, δ, ppm: 12.03 br.s (1H, N^{2}H), 10.51 br.s (1H, NH), 7.56–7.38 m (5H, C_6H_5), 7.51, 6.86 d (1H, =CH, J_{AB} 15.6 Hz), 6.37 s (1H, C^{4}H), 2.19 s (3H, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 227 (43) $[M]^+$, 199 (24), 131 (96), 103 (100). Found, %: C 68.75;

H 5.70; N 18.57. $C_{13}H_{13}N_3O$. Calculated, %: C 68.72; H 5.72; N 18.50. *M* 227.27.

b. To a solution of 5 mmol of amine **I** in 2 ml of acetone at 40°C was added a solution of 7.5 mmol of acid chloride **VI** in 2 ml of acetone and 0.2 ml of pyridine, after 30 min the precipitate was filtered off and recrystallized from methanol. We isolated 1.95 mmol (39%) of diacyl derivative **X**. mp 207–208°C. IR spectrum, cm^{-1}: 3324 (NH), 1692 br. (CO, CONH), 1620 (Ph–C=C), 1528 (C=N). ^1H NMR spectrum, δ, ppm: 10.78 br.s (1H, NH), 7.94 d (1H, =CH, J_{AB} 16.0 Hz), 7.90–7.42 m (12H, C_6H_5), 7.17 d (1H, =CH, J_{AB} 16.0 Hz), 6.80 s (1H, C^4H), 2.26 s (3H, CH_3). Mass spectrum, *m/z* (I_{rel}, %): 357 (25) $[M]^+$, 226 (15), 198 (12), 131(100), 103 (15), 77 (10). Found, %: C 74.04; H 5.38; N 16.32. $C_{22}H_{19}N_3O_2$. Calculated, %: C 73.95; H 5.32; N 16.34. *M* 357.41.

The solvent was removed from the acetone filtrate, 6 ml of a mixture methanol–water, 1:5, was added to the amorphous residue, the mixture was boiled for 2–3 min, the precipitate was filtered off and crystallized from a mixture acetone–methanol, 1:1, to isolate 0.75 mmol (15%) of compound **IX**.

c. To a dispersion of 5 mmol of amine **I** in 2 ml of benzene was added 7.5 mmol of acid chloride **VI** in 2 ml of benzene, the reaction mixture was boiled for 30 min, the amorphous precipitate was filtered off and recrystallized from methanol to obtain 1.35 mmol (27%) of substance **X**. On removal of the solvent from the benzene filtrate the residue was boiled in a methanol–water, 1:5, the precipitate was filtered off and crystallized from 2-propanol to obtain 0.6 mmol (12%) of compoundя **VIII** and on removing a part of solvent from the filtrate a was isolated 1.55 mmol (31%) of amide **VII**.

d. To a mixture of 5 mmol of amine **I** and 0.2 ml of pyridine in 2 ml of benzene was added 7.5 mmol of acid chloride **VI** in 2 ml of benzene, the reaction mixture was boiled for 30 min, the precipitate was filtered off and recrystallized from methanol to obtain 2.4 mmol (48%) of compound **X**. From the benzene filtrate after removing a part of the solvent crystals precipitated of (2*E*)-3-phenylacrylic anhydride **XI**. Yield 0.94 mmol (19%), mp 133°C (134°C [36]).

Reaction of 2-aminobenzimidazole (II) with cinnamoyl- chloride (VI). *a*. To a solution of 1 mmol of aminoazole **II** in 1 ml of DMF was added 1 mmol of acid chloride **VI** in 0.5 ml of DMF, the formed fine precipitate was filtered off and crystallized from methanol to obtain 0.9 mmol (89%) of **(2*E*)-N-1*H*-benzimidazol-2-yl-3-phenylacrylamide (XII),** mp 245–247°C (257–258°C [5]). IR spectrum, cm^{-1}: 3232–2768 (NH), 1688 ("amide I"), 1640, 1480 (C=N), 1616 (Ph–C=C), 1540 ("amide II"). ^1H NMR spectrum, δ, ppm: 8.50 br.s (2H, NH), 7.7–7.0 m (9H, Ar–H), 7.55, 6.50 d (1H, J_{AB} 16.0 Hz). Mass spectrum, *m/z*: $[M + H]^+$ 264, $[M - H]^+$ 262. Found, %: C 73.10; H 6.74; N 16.10. $C_{16}H_{13}N_3O$. Calculated, %: C 73.00; H 6.77; N 15.97. *M* 263.30. Yield of amidea **XII** in acetone 85%.

b. A mixture of 1 mmol of aminoazole **II** and 1 mmol of acid chloride **VI** in 3 ml of benzene was boiled for 10 min, and the precipitate of amide **XII** was filtered off. Yield 0.8 mmol (80%).

c. To a solution of 1 mmol of aminoazole **II** in 3 ml of acetone was added 0.1 ml of pyridine and 1 mmol of acid chloride **VI** in 2 ml of acetone, and the precipitate of amide **XII** was filtered off. Yield 0.6 mmol (57%).

d. A mixture of 1 mmol of aminoazole **II**, 0.1 ml of pyridine, and 1 mmol of acid chloride **VI** in 3 ml of benzene was boiled for 10 min, and the precipitate of amide **XII** was filtered off. Yield 0.55 mmol (55%).

Cyclocondensation of compound XII. The boiling of 1 mmol of amide **XII** in 3 ml of DMF was continued for 4 h, then cooled, 5–7 ml of 2-propanol was added and 0.8 mmol (83%) of **4-phenyl-3,4-dihydropyrimido-[1,2-*a*]benzimidazol-2(1*H*)-one (XIII)** was filtered off**,** mp 289–291°C (289–290 [4], 285–289°C [5, 6]).

Reaction of 3-amino-1,2,4-triazole (III) with cinnamoyl chloride (VI). *a.* To a dispersion of 5 mmol of amine **III** in 5 ml of acetone was slowly added a solution of 5 mmol of acid chloride **VI** in 5 ml of acetone, the mixture was heated at 40°C for 30 min, the formed precipitate was filtered off, boiled with water to remove the unreacted amine, the insoluble precipitate was crystallized from methanol to obtain 2.7 mmol (54%) of **1-[(2*E*)-3-phenylprop-2-enoyl]-1*H*-1,2,4-triazol-5-amine (XVI)**. mp 235–237°C. IR spectrum, cm^{-1}: 3444 (NH_2), 3288–3024 (NH, NH_2), 1700 (CO), 1644 (Ph–C=C), 1628 (C=N). ^1H NMR spectrum, δ ppm: 7.9 d (1H, =CH, J_{AB} 15.8 Hz), 7.8 s (1H, C^5H, Ht), 7.7 br.s (2H, NH_2), 7.6–7.5 m (7H, =CH, C_6H_5). Found, %: C 61.64; H 4.70; N 26.20. $C_{11}H_{10}N_4O$. Calculated, %: C 61.68; H 4.67; N 26.17.

The precipitate separated from the acetone filtrate on cooling was treated with methanol to isolate 0.75 mmol (15%) of insoluble in methanol **3-amino-1,2,4-triazole phenylacrylate (XVIII)**. mp 250–253°C. IR spectrum, cm^{-1}: 3332 (NH_2), 3192–2792 (NH, NH_2), 1704 (COOH), 1660 (Ph–C=C), 1636 (C=N). ^1H NMR

spectrum, δ, ppm: 12.4 br.s (1H, COOH), 10.8 br.s (1H, NH), 9.2 br.s (2H, NH_2), 7.9, 6.7 d (1H, =CH, J_{AB} 16.2 Hz), 7.7–7.4 m (6H, C^5H, Ht, C_6H_5). Found, %: C 56.87; H 5.21; N 24.20. $C_{11}H_{12}N_4O_2$. Calculated, %: C 56.90; H 5.17; N 24.14.

From the filtrate was isolated 0.5 mmol (10%) of **(2*E*)-3-phenyl--N-1*H*-1,2,4-triazole-5-ylacryl-amide (XVII)**. mp 282–284°C. IR spectrum, cm^{-1}: 3240–2800 (NH), 1684 ("amide I"), 1632 (Ph–C=C), 1576 ("amide II"). ^1H NMR spectrum, δ, ppm: 13.4, 11.5 br.s (1H, NH), 7.8–7.4 m (7H, C^5H, Ht, =CH, C_6H_5), 6.9 d (1H, J_{AB} 15.8 Hz). Found, %: C 61.71; H 4.64; N 26.08. $C_{11}H_{10}N_4O$. Calculated, %: C 61.68; H 4.67; N 26.17.

b. To a mixture of 5 mmol of amine **III**, 0.5 ml of pyridine, and 5 ml of acetone was slowly added a solution of 5 mmol of acid chloride **VI** in 5 ml of acetone, the mixture was heated at 40°C for 30 min, the formed precipitate was filtered off, boiled with water to remove the unreacted amine, the insoluble precipitate was crystallized from methanol to obtain 3.5 mmol (70%) of cinnamoyl derivative **XVI**. The acetone filtrate was evaporated, the residue was boiled with water to remove the unreacted amine, the insoluble precipitate was crystallized from methanol to obtain 1 mmol (20%) of **1-[(2*E*)-3-phenylprop-2-enoyl]-1*H*-1,2,4-triazol-3-amine (XIX)**, mp 205–206°C. IR spectrum, cm^{-1}: 3408, 3304–3112 (NH_2), 1696 (CO), 1644 (Ph–C=C), 1624 (C=N). ^1H NMR spectrum, δ, ppm: 9.0 s (1H, C^5H, Ht), 7.9, 7.7 d (1H, =CH, J_{AB} 16.0 Hz), 7.8–7.4 m (5H, C_6H_5), 6.1 br.s (2H, NH_2). Found, %: C 57.43; H 4.38; N 26.12. $C_{11}H_{10}N_4O_2$. Calculated, %: C 57.39; H 4.35; N 26.17.

c. A mixture of 5 mmol of amine **III** and 5 mmol of acid chloride **VI** in 10 ml of benzene was boiled for 30 min, the formed precipitate was filtered off and crystallized from methanol to obtain 0.9 mmol (18%) of compound **XVI**.

d. A mixture of 5 mmol of amine **III**, 5 mmol of acid chloride **VI**, and 0.5 ml of pyridine in 10 ml of benzene was boiled for 30 min, the formed precipitate was filtered off, boiled with water, and recrystallized from methanol to obtain 2.3 mmol (46%) of cinnamoyl -derivative **XVI**, and after removing ~30% of the solvent from the filtrate we isolated 0.7 mmol (12%) of compound **XIX**.

Conversion of compound XVI in 7-phenyl-6,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidin-5-(4*H*)-one (XX). *a*. A solution of 1 mmol of compound **XVI** in 1 ml of DMF was boiled for 1.5 h, cooled, 3 ml of 2-propanol was added, and the solvents were removed at a reduced pressure. The residue was recrystallized from methanol to obtain 0.2 g of a mixture of compounds **XVII** and **XX** in a ratio 2:1 (^1H NMR data).

b. At boiling of 1 mmol of compound **XVI** in DMF for 6 h we obtained 0.64 mmol (64%) of compound **XX**, mp 214–217°C (215–217°C [8]).

Reaction of 5-amino-3-methylsulfanyl-1,2,4-triazole (IV) with cinnamoyl- chloride (VI).

a. To a dispersion of 3 mmol of amine **IV** in 3 ml of acetone was slowly added a solution of 3 mmol of acid chloride **VI** in 3 ml of acetone, the mixture was boiled for 30 min, the formed crystalline precipitate was filtered off and recrystallized from 2-propanol to obtain 1.14 mmol (38%) of **3-(methyl-sulfanyl)-1[(2*E*)-3-phenylprop-2-enoyl]-1*H*-1,2,4-triazol-5-amine (XXI)**. mp 204–206°C. IR spectrum, cm^{-1}: 3428, 3100 (NH_2), 1704 (CO), 1616 (Ph–C=C). ^1H NMR spectrum, δ, ppm: 7.9, 7.6 d (1H, =CH, J_{AB} 16.0 Hz), 7.8–7.4 m (5H, C_6H_5), 7.6 br.s (2H, NH_2), 2.5 s (3H, CH_3). Found, %: C 55.41; H 4.64; N 21.48; S 12.29. $C_{12}H_{12}N_4OS$. Calculated, %: C 55.38; H 4.62; N 21.54; S 12.31.

The residue after removing acetone was boiled with water, the insoluble part was filtered off, and was recrystallized from 2-propanol to isolate 0.7 mmol (24%) of **5-(methylsulfanyl)-1[(2*E*)-3-phenylprop-2-enoyl]-1*H*-1,2,4-triazol-3-amine (XXII).** Amorphous colorless substance, mp 202–204°C. IR spectrum, cm^{-1}: 3424, 3116 (NH_2), 1704 (CO), 1628 (Ph–C=C). ^1H NMR spectrum, δ, ppm: 7.9, 7.6 d (1H, =CH, J_{AB} 15.8 Hz), 7.7–7.5 m (5H, C_6H_5), 6.1 br.s (2H, NH_2), 2.6 C (3H, CH_3). Found, %: C 55.40; H 4.58; N 21.56; S 12.33. $C_{12}H_{12}N_4OS$. Calculated, %: C 55.38; H 4.62; N 21.54; S 12.31.

b. To a mixture of 3 mmol of amine **IV**, 0.2 ml of pyridine in 3 ml of acetone was slowly added a solution of 3 mmol of acid chloride **VI** in 3 ml of acetone, the mixture was boiled for 30 min. We carried out the workup as described above and isolated 1.5 mmol (50%) of compound **XXI** and 0.7 mmol (23%) of amine **XXII**.

c. A mixture of 3 mmol of amine **IV** and 3 mmol of acid chloride **VI** in 5 ml of benzene was boiled for 30 min, the separated precipitate was twice recrystallized from 2-propanol to obtain 0.7 mmol (24%) of compound **XXI**. From the alcoholic filtrates after the removal of ~50% of solvent was isolated 0.5 mmol (16%) of amine **XXII**.

d. To a mixture of 3 mmol of amine **IV**, 0.2 ml of pyridine in 3 ml of benzene slowly added a solution of 3 mmol of acid chloride **VI** in 2 ml of benzene, the mixture was boiled for 30 min, the solvent was decanted from the viscous residue, the latter was twice recrystallized from 2-propanol to obtain 0.5 mmol (16%) of compound **XXI** as yellow crystals. From the alcoholic filtrates 0.3 mmol (10%) of amine **XXII** was isolated.

Conversion of compound XXII into compound XXI. A mixture of 1 mmol of amine **XXII** and 0.25 ml of pyridine in 5 ml of ethylacetate was boiled for 2.5 h; from the cooled solution yellow crystals of compound **XXI** were filtered off. Yield 0.65 mmol (65%). The residue after removing the solvent was recrystallized from 2-propanol to isolate 0.1 mmol (10%) of initial cinnamoyl derivative **XXII**.

2-(Methylsulfanyl)-7-phenyl-6,7-dihydro-1,2,4-triazolo-[1,5-*a*]-pyrimidin-5(4*H*)-one (XXIII). In 2 ml of DMF 2 mmol of the mixture of acyl derivatives **XXI** and **XXII** was boiled for 4 h, then the reaction mixture was cooled, 5–7 ml of 2-propanol was added, and 1.2 mmol (57%) of compound **XXIII** was filtered off, mp 255–256°C (254–256°C [32]). From the filtrate on removal of excess solvent 0.2 mmol (12%) of substance **XXI** was isolated.

Reaction of 5-amino-1,2-dihydro-3*H*-1,2,4-triazole-3-thione (V) with cinnamoyl- chloride (VI). *a*. A mixture of 10 mmol of amine **V**, 0.6 ml of pyridine, and 10 mmol of acid chloride **VI** in 15 ml of acetone was boiled for 30 min, the precipitate was separated and boiled with water, filtered off, recrystallized from methanol to obtain 0.26 g of a mixture of **5-amino-1-[(2*E*)-3-phenylprop-2-enoyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione (XXIV)** and **5-amino-1,2-bis[(2*E*)-3-phenylprop-2-enoyl]-1,2-dihydro-3*H*-1,2,4-triazole-3-thione (XXV)** in a ratio 3:1 (^{1}H NMR data).

Compound **XXIV**. ^{1}H NMR spectrum, δ, ppm: 12.4 br.s (1H, NH), 7.8 br.s (2H, NH_2), 7.58, 6.51 d (1H, =CH, J_{AB} 16.0 Hz), 7.82–7.77, 7.46–7.36 m (C_6H_5).

Compound **XXV**. ^{1}H NMR spectrum, δ, ppm: 7.9 br.s (2H, NH_2), 7.96, 7.70 d (1H, =CH, J_{AB} 16.0 Hz), 7.56, 7.15 d (1H, =CH, J_{AB} 15.8 Hz), 7.8–7.7, 7.5–7.4 m (C_6H_5).

b. A mixture of 10 mmol of amine **V**, 0.6 ml of pyridine, and 10 mmol of acid chloride **VI** in 15 ml of acetone was boiled for 3 h, the precipitate was separated and boiled with water, filtered off, recrystallized from methanol to obtain 0.1 g of a mixture of compounds **XXIV** and **XXV**. From the acetone filtrate after removing ~50% of solvent settled a precipitate that was boiled in succession in water, methanol, and acetone. We isolated 2.9 mmol (29%) of **3-{3-amino-2[(2*E*)-3-phenyl-prop-2-enoyl]-5-thioxo-2,5-dihydro-1*H*-1,2,4-triazol-1-yl}-3-phenylpropanoic acid (XXVI)**, then 2.2 mmol (22%) of **2-amino-5-phenyl-5,6-dihydro-7*H*-[1,2,4]triazolo[5,1-*b*][1,3]thiazin-7-one (XXVII)** as bright yellow crystals.

Compound **XXVI**. mp 245–247°C. IR spectrum, cm^{-1}: 3432, 3272 (NH_2), 1712 (COOH), 1704 (CO), 1624 (Ph–C=C). ^{1}H NMR spectrum, δ, ppm: 12.3 br.s (1H, COOH), 7.68 br.s (2H, NH_2), 5.09 d.d (1H, CH_X, J_{AX} 9.0, J_{BX} 6.0 Hz), 7.8, 7.5 d (1H, =CH, J_{AB} 16.0 Hz), 7.7–7.2 m (10H, C_6H_5), 3.17, 3.02 d.d (2H, CH_{2AB}, J_{AB} –16.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 394 (28), 263 (10), 245 (17), 149 (40), 131 (100), 103 (90), 77 (40). Found, %: C 60.94; H 4.54; N 14.25; S 8.08. $C_{20}H_{18}N_4O_3S$. Calculated, %: C 60.91; H 4.57; N 14.21; S 8.12. *M* 394.40.

Compound **XXVII**. mp 225–227°C. IR spectrum, cm^{-1}: 3340, 3172 (NH_2), 1724 (CO), 1564 (CN). ^{1}H NMR spectrum, δ, ppm: 6.2 br.s (2H, NH_2), 5.30 d.d (1H, CH_X, J_{AX} 3.0, J_{BX} 11.4 Hz), 7.5–7.4 m (5H, C_6H_5), 3.63, 3.22 d.d (2H, CH_{2AB}, J_{AB} –16.8 Hz). Mass spectrum, *m/z* (I_{rel}, %): 246 (34), 131 (80), 103(100), 77 (33). Found, %: C 53.70; H 3.99; N 22.82; S 13.07. $C_{11}H_{10}N_4OS$. Calculated, %: C 53.66; H 4.07; N 22.76; S 13.01. *M* 246.29.

(2*E*)-3-N-(5-Thioxo-2,5-dihydro-1*H*-1,2,4-triazol-3-yl)-3-phenylacrylamide (XXVIII). *a*. A mixture of 2 mmol of amine **V** and 3.3 mmol of acid chloride **VI** in 4 ml of pyridine was boiled for 1 h and poured into water. The formed precipitate was filtered off, washed on the filter with 10% solution of HCl, and recrystallized from a mixture methanol–water, 1:1, yield 0.64 mmol (34%), mp 335–337°C. IR spectrum, cm^{-1}: 3252–3056 (NH), 1672 ("amide I"), 1624 (Ph–C=C), 1564 ("amide II"). ^{1}H NMR spectrum, δ, ppm: 13.9, 12.2, 11.3 br.s (1H, NH), 7.7, 6.7 d (1H, =CH, J_{AB} 15.4 Hz), 7.6–7.4 m (5H, C_6H_5). Found, %: C 53.64; H 4.00; N 22.72; S 13.05. $C_{11}H_{10}N_4OS$. Calculated, %: C 53.66; H 4.07; N 22.76; S 13.01.

b. A solution of 1 mmol of acid **XXVI** in 1 ml of DMF was boiled for 1 h, then 3 ml of 2-propanol was added, and 0.1 mmol (11%) of amide **XXVIII** was filtered off.

c. In a china cup was heated to melting 2 mmol of thiazinone **XXVII**, the melt was cooled, crushed, boiled in a little acetone, filtered while hot from initial thiazinone, from the filtrate 0.4 mmol (20%) of amide **XXVIII** was isolated.

REFERENCES

1. Kost, A.A., *Khim. Geterotsikl. Soedin.,* 1980, p. 1200.
2. Deeb, A., El-Mobayed, M., and Abdel, Hamid, A., *Pol. J. Chem.,* 1992, vol. 66, p. 449.
3. Fissher, G., *Adv. Heterocycl. Chem*., 1993, vol. 57, p. 81.
4. Shazhenov, A.A. and Kadyrov, Ch.Sh., *Khim. Geterotsikl. Soedin.,* 1977, p. 1389.
5. Nawrocka, W., *Pol. J. Chem*., 1995, vol. 69, p. 1158.
6. Nawrocka, W. and Zimecki, M., *Arch. Pharm. Pharm. Med. Chem*., 1998, vol. 331, p. 249.
7. Nawrocka, W., Zimecki, M., Kuznicki, T., and Kowalska, M.W., *Arch. Pharm. Pharm. Med. Chem*., 1999, vol. 33, p. 85.
8. Desenko, S.M., Lipson, V.V., Shishkin, O.V., Komykhov, S.A., Orlov, V.D., Lakin, S.E., Kuznetsov, V.P., and Meier, H., *J. Heterocycl. Chem*., 1999, vol. 36, p. 205.
9. Lipson, V.V., Desenko, S.M., Orlov, V.D., Shishkin, O.V., Shirobokova, M.G., Chernenko, V.N., and Zinov'eva, L.I., *Khim. Geterotsikl. Soedin.,* 2000, p. 1542.
10. Perevalov, S.G., Bur-gart, Ya.V., Saloutin, V.I., and Chupakhin, O.N., *Usp. Khim*., 2001, vol. 70, p. 1039.
11. Krug-lenko, V.P., Gnidets, V.P., Klyuev, N.A. Logachev, E.V., Klykov, M.A., and Povstyanoi, M.V., *Khim. Geterotsikl. Soedin.,* 1985, p. 1402.
12. Yanborisov, T.N., Zhikina, I.A., Yanborisova, O.A. Shurov, S.N., and Andreichikov, Yu.S., *Zh. Org. Khim.,* 1992, vol. 28, p. 2554.
13. Chebanov, V.A., Sakhno, Ya.I., Desenko, S.M., Shishkina, S.V., Musatov, V.I., Shishkin, O.V., and Knyazeva, I.V., *Synthesis*, 2005, p. 2597.
14. Ghassan, M.A. and Sowell, J.W., *J. Heterocycl. Chem*., 1990, vol. 27, p. 1201.
15. Zaki, M.E.A. and Fathalla, O.A., *Egypt. J. Pharm. Sci*., 1997, vol. 38, p. 363.
16. Abdelhamid, A.O., Riad, B.Y., and Aziz, S.I., *Arch. Pharm*., 1987, vol. 320, p. 642.
17. Sadek, K.U., Selim, M.A., Elnagdi, M.H., and Otto, H.H., *Bull. Chem. Soc. Jpn.,* 1993, vol. 66, p. 2927.
18. Sherif, S.M. and Hussein, A.M., *Monatsh. Chem*., 1997, vol. 128, p. 687.
19. Atwal, K.S. and Moreland, S., *Bioorg. Med. Chem. Lett*., 1991, vol. 1, p. 291.
20. Alajarin, R., Jordan, P., Vaquero, J.J. and Alvarez-Builla, J., *Synthesis*, 1995, p. 389.
21. Alajarin, R., Vaquero, J.J., Alvarez-Builla, J., Fau de Casa-Juana, M., Sunkel, C., Priego, J.G., Gomez-Sal, P., and Torres, R., *Bioorg. Med. Chem*., 1994, vol. 2, p. 323.
22. Ram, V.J., Kushwaha, D.S., and Mishra, L., *Indian J. Chem*., 1989, vol. 28B, p. 242.
23. Nagahara, K., Kawano, H., Sasaoka, S., Ukawa, C., Hirama, T., Takada, A., Cottam, H.B., and Robins, R.K. , *J. Heterocycl. Chem*., 1994, vol. 31, p. 239.
24. Hisao, Y., Hideo, K., Shiro, K., and Yoshiaki, O., Japan Patent 59095289, 1984; *Chem. Abstr.,* 1985, vol. 101, 171281a.
25. Quiroga, J., Alvarado, M., Insuasti, B., Moreno, R., Ravina, E., Estevez, I., R.H. and de Almeida, S., *J. Heterocycl. Chem.,* 1999, vol. 36, p. 1311.
26. Lipson, V.V., Karnozhitskaya, T.M, Desenko, S.M., Shishkina, S.V., Shishkin, O.V., and Musatov, V.I., *Zh. Org. Khim.,* 2007, vol. 43, p. 257.
27. Lin-coln, D.G. and Robbins, M.J., US Patent 5061799, 1991; *Chem. Abstr.,* 1992, vol. 116, p. 41475.
28. Quiroga, J., Hormaza, A., Insuasti, B., Saitz, C., Jullian, C., and Canete, A., *J. Heterocycl.Chem.,* 1998, vol. 35, p. 61.
29. Clarke, D., Mares, R.W., and McNab, H., *J. Chem. Soc., Perkin Trans. 1*, 1997, p. 1799.
30. Lipson, V.V., Desenko, S.M., Orlov, V.D., Karnozhitskaya, T.M., and Shirobokova, M.G., *Khim. Geterotsikl. Soedin.,* 1999, p. 664.
31. Lipson, V.V., Orlov, V.D., Desenko, S.M., Shishkina, S.V., Shishkin, O.V., and Shirobokova, M.G., *Khim. Geterotsikl. Soedin.,* 2000, p. 1190.
32. Lipson, V.V., Desenko, S.M., Borodina, V.V., Shirobokova, M.G., Karnozhitskaya, T.M., Musatov, V.I., and Kravchenko, S.V., *Khim. Geterotsikl. Soedin.,* 2005, p. 246.
33. Lipson, V.V., Shirobokova, M.G, and Musatov, V.I., *Zh. Org. Farm. Khim*., 2005, vol. 3, p. 64.
34. Lipson, V.V., Shirobokova, M.G, and Borodina, V.V., *Ukr. Khim. Zh*., 2005, vol. 6, p. 95.
35. Lipson, V.V., Desenko, S.M., Shirobokova, M.G, Shishkin, O.V., and Shishkina, S.V., *Zh. Org. Khim.,* 2006, vol. 42, p. 1040.
36. Samy, Abdel-Baky and Roger, W. Giese, *J. Org. Chem*., 1986, vol. 51, p. 3390.
37. Zefirov, Yu.V., *Kristallografiya* (Crystallography), 1997, vol. 42, p. 936.
38. Burgi, H.-B. and Dunitz, J.D., *Structure Correlation,* New York: Weinheim, 1994, vol. 2, p. 741.
39. Desenko, S.M., Orlov, V.D., Lipson, V.V., Kaganovs'-

kii, A.S., Van-Tue, Z., and Ivkov, S.M., *Dokl. Akad. Nauk USSR, B*, 1990, vol. 7, p. 44.

40. Coburn, M.D., Loughran, E.D., and Smith, L.C., *J. Heterocyclic Chem.,* 1970, vol. 7, p. 1149.
41. Hirata, T., Wood, H.B., and Dricoll, J.S., *J. Chem. Soc., Perkin Trans. 1,* 1973, p. 1209.
42. Fidler, Zh.N., Shibanova, E.F., Makerov, P.V., Kalikhman, I.D., Shulunova, A.M., Sarapulova, G.I., Klyba, L.V., Vitkovskii, V.Yu., Chipanina, N.N., Lopyrev, V.A., and Voronkov, M.G., *Khim. Geterotsikl. Soedin.,* 1980, p. 1414.
43. Bellamy, L.J., *The Infra-Red Spectra of Complex Molecules*, London: Methuen, 1958.
44. Britsun, V.N., Pirozhenko, V.V., and Lozinskii, M.O., *Zh. Org. Khim.,* 2000, 36, 1102.