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Reactions of α-Aminoazoles with Diethyl Benzylidenemalonate

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Abstract—Cyclocondensations of diethyl benzylidenemalonate with 3-amino-5-methylpyrazole, 3,5-diamino-1,2,4-triazole, 3,4,5-triamino-1,2,4-triazole, and 2-amino-benzimidazole in alcohols take a single route and lead to the formation of functionally substituted partially hydrogenated pyrazolo-, triazolo[1,5-*a*]-pyrimidin-5-ones and pyrimido[1,2-*a*]benzimidazol-2-one respectively. From reaction mixtures involving 3-amino-1,2,4-triazole and its 5-methylsulfanyl analog in methanol the intermediate products of heterocyclization were isolated forming as a result of alkylation with the β-carbon of the unsaturated ester the endocyclic nucleophilic sites of aminoazoles. The structure of one among the products obtained, diethyl (3-amino-5-methylsulfanyl-1,2,4-triazol-2-yl)benzylmalonate was proved by X-ray crystallography. In DMF the same reagents yielded mixtures of partially hydrogenated triazolo[1,5-*a*]pyrimidin-5-ones.

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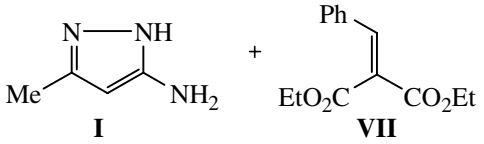
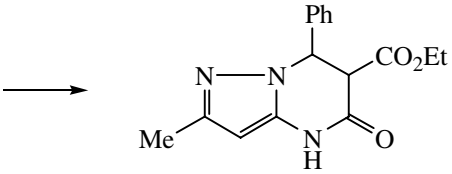
Reactions of α-aminoazoles with esters of unsaturated dicarboxylic acids, diethyl ethoxyethylidenemalonate [1, 2], aryl methylenemalonates [3], and alkyl(aryl) methyleneisopropylidenemalonates [4–10] lead to the formation of fused azoloazine systems distinguished by the place of fusion and/or by the position of substituents in the azine ring originating from nonequivalence of the reaction sites in both components of cyclocondensation. The prevalence of one among the possible reaction pathways depends both on the nature of the reactants and on the reaction conditions.

The goal of the present study was to establish the direction of the reaction under various conditions between 3-amino-5-methylpyrazole (**I**), 2-aminobenzimidazole (**II**), 3-amino- (**III**), 3-amino-5-methylsulfanyl- (**IV**), 3,5-diamino- (**V**), or 3,4,5-triamino-1,2,4-triazole (**VI**) and diethyl benzylidenemalonate (**VII**).

On boiling equimolar amounts of amine **I** with ester **VII** in methanol for 2 h we obtained in low yield 2-methyl-7-phenyl-6-ethoxycarbonyl-6,7-dihydropyrazolo[1,5-*a*]-pyrimidin-5(4*H*)-one (**VIII**). Replacing the solvent by 1-butanol significantly raised the yield, but in DMF even at short exposure the yield decreased due to tarring.

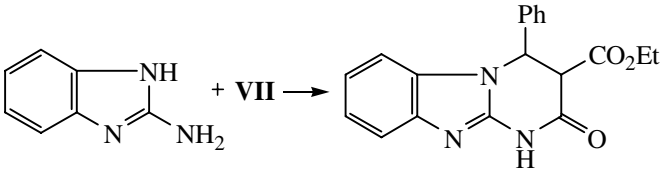


I **VII**

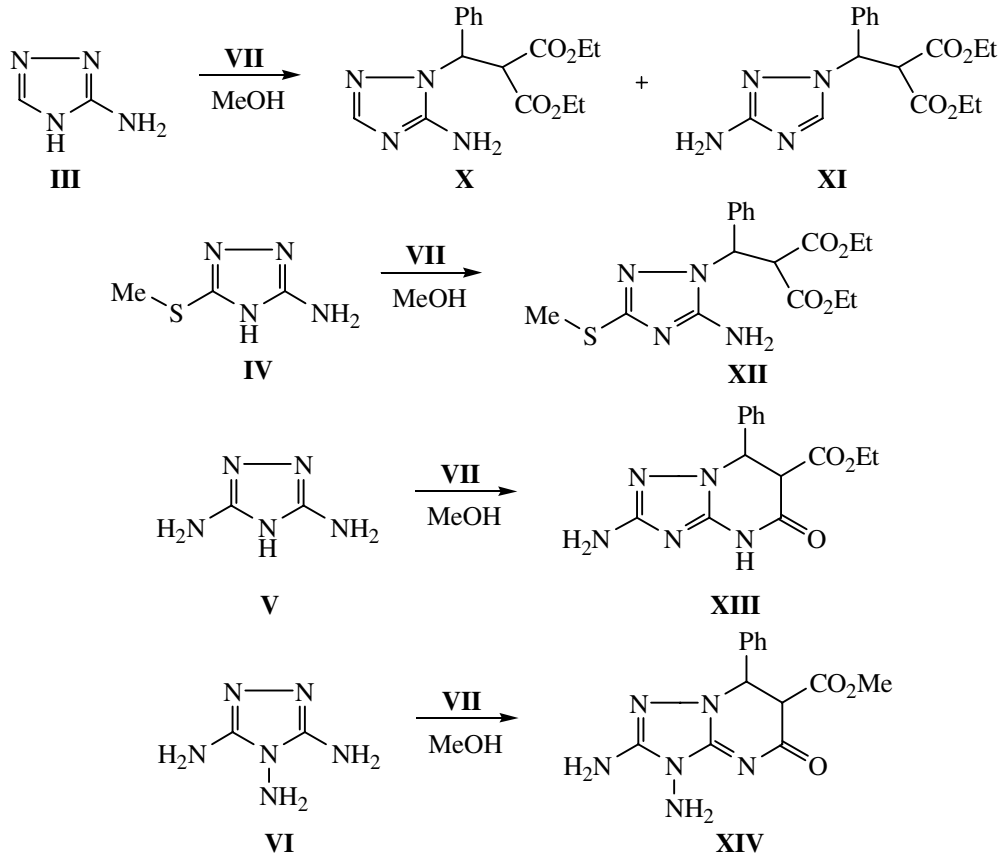


VIII

The reaction of aminoazole **II** with diethyl malonate **VII** both in methanol and in DMF within 5 min gave rise exclusively to 4-phenyl-3-ethoxycarbonyl-3,4-dihydropyrimido[1,2-*a*]benzimidazole-2(1*H*)-one (**IX**) in high yield.

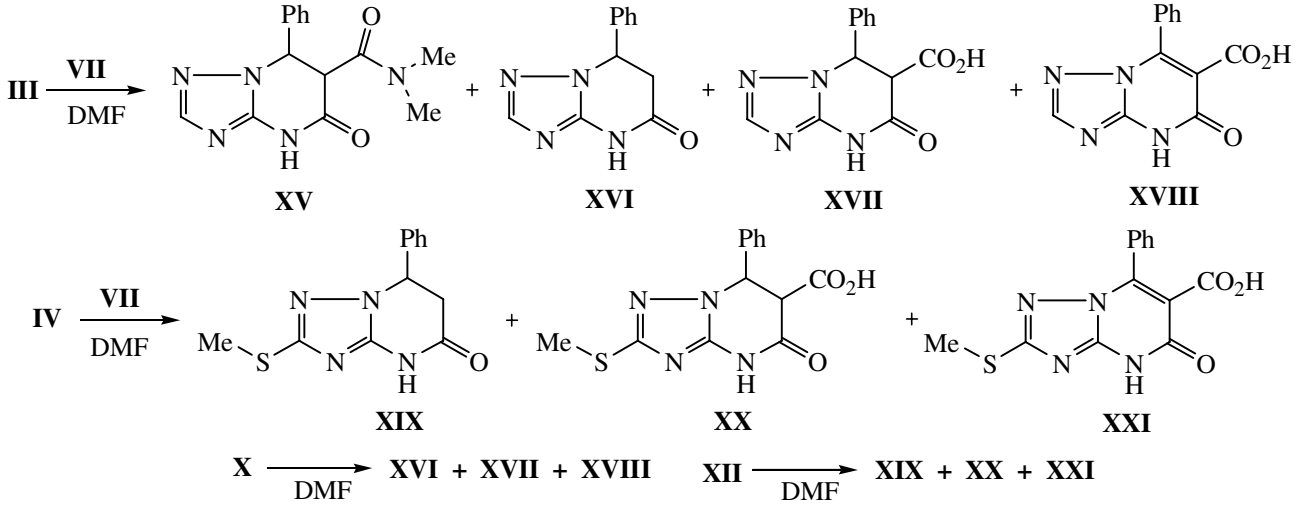


II **IX**



Boiling in methanol ester **VII** with 3-aminotriazoles **III** and **IV** yielded β-adducts **X–XII**, whereas amines **V** and **VI** under the same conditions were converted into partially hydrogenated triazolo[1,5-*a*]pyrimidine derivatives **XIII** and **XIV**.

We succeeded in performing the heterocyclization of aminoazoles **III** and **IV** with ester **VII** by boiling in DMF for 2 h. Therewith in both cases formed mixtures of triazolo[1,5-*a*]-pyrimidin-5-ones **XV–XVIII** and **XIX–XXI**. Triazolopyrimidinones **XV, XVI**, and **XIX** were isolated in individual state. Acids **XVII, XVIII** and **XX, XXI** we failed to separate either by multiple recrystallization or by chromatography. Their ratio in mixtures was estimated from the NMR spectra. Boiling in DMF for 2 h of compound **XI** did not give new substances, and β-adducts **X** and **XII** under these conditions formed



mixtures of triazolopyrimidinones **XVI–XVIII** and **XIX–XXI** respectively. The substances of isomeric structure, triazolo[1,5-*a*]pyrimidin-7-ones or triazolo-[4,3-*a*]-pyrimidin-5-, -7-ones, were not obtained in any of experiments described.

The structure of compounds **VIII–XV, XVII, XVIII, XX**, and **XXI** was established from their spectra. The structure of β-adduct **XII** was proved by X-ray diffraction analysis. Physicochemical and spectral characteristics of triazolo[1,5-*a*]-pyrimidin-5-ones **XVI** and **XIX** are in agreement with those published in [8, 11] for cyclo-condensation products of amines **III** and **IV** with methyl cinnamate. The results of X-ray investigation confirming the structure of compound **XVI** as 7-phenyl-6,7-dihydro--1,2,4-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one were published in [11].

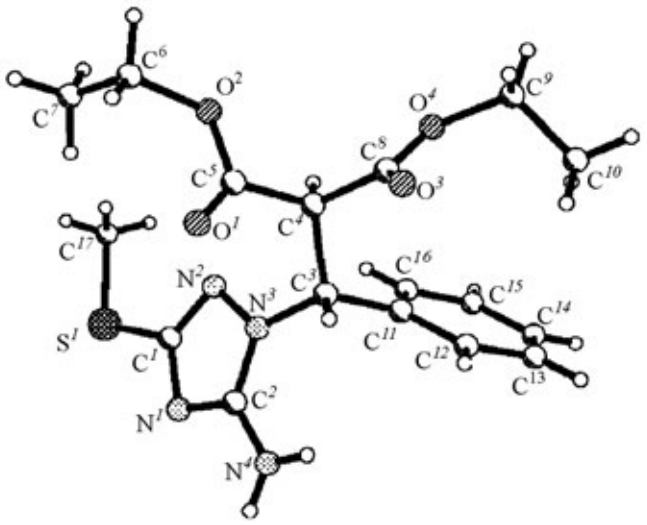
The IR spectra of azolopyrimidinones **VIII, IX, XIII**, and **XIV** and of β-adducts **X–XII** contain strong absorption bands in the region 1760–1716 cm^{-1} characterisic of ester groups. Vibrations of amino groups as two bands in the range 3468–3312 cm^{-1} appeared in the spectra of amino derivatives **XIII** and **XIV** and of adducts **X–XII**. In the spectra of acid mixtures **XVII, XVIII** and **XX, XXI** strong bands were observed in the region of carbonyl vibrations 1720–1660, and also a wide band in the range 3400–2500 cm^{-1} from overlapped vibrations of the associated COOH and NHCO groups. The vibrations of NHCO fragment in the spectra of azolopyrimidinones **VIII, IX**, and **XIII** appear as "amide I" at 1704–1648 and "amide II" at 1596–1584 cm^{-1}. The absorption of two CO groups at 1708 and 1652, and also a band at 3204–2580 cm^{-1} originating from superimposed vibrations of CH_3 groups and associated NH group were observed in the spectrum of compound **XV**.

In the ^1H NMR spectrum of pyrazolo[1,5-*a*]pyrimidin-5(4*H*)-one **VIII** alongside the multiplet of the protons of phenyl ring, signals of CH_3 and CO_2Et groups appeared doublets from protons of the fragment $C^6H–C^7H$ involved in an *AB* system. The presence of singlets of protons C^3H and NH (δ_{NH} 11.05 ppm, characteristic of an imido group [6–9, 11]) permits unambiguous choice of structure **VIII**. The spectrum of pyrimido[1,2-*a*]benzimidazolone **IX** alongside the resonances of aromatic protons and protons of CO_2Et group also contains the *AB* system of methine protons $C^3H–C^4H$ and a singlet of NH group whose downfield position (δ 11.99 ppm) according to [7] evidences formation in the condensation of 2- (**IX**) and not 4-oxo-isomer. The spectra of β-adducts **X–XII** lack imido group signal, but signals of CO_2Et, *AB* system of methine protons, and broadened singlet of NH_2 group are observed. The distinguishing of structures **X** and **XI** was performed based on the chemical shifts of protons C^5H of the triazole ring and of amino groups. The presence of a substituent at N^1 atom is known to effect a downfield shift of methine proton C^5H by 0.6–1.2 ppm [12]. In the spectrum of compound **X** this signal is located in the region of aromatic protons resonances δ 7.52 ppm, and in the spectrum of compound **XI** it is observed at 8.16 ppm. In structure **X** the proton of NH_2 group is capable of forming an intramolecular hydrogen bond with a carbonyl of one of ester groups. Therewith the resonance of NH protons of compound **X** should appear more downfield than in the spectrum of compound **XI** as is actually observed. A similar downfield shift of amino group signal was found also in the spectrum of compound **XII**.

The structure of diethyl (3-amino-5-methylsulfanyl-1,2,4-triazol-2-yl)benzyl-malonate (**XII**) was proved by X-ray crystallography (see the figure, Tables 1 and 2). The sulfanylmethyl substituent is located in the plane of the triazole ring [torsion angle $C^{17}S^1C^1N^2$ –4.2(3)°]. Phenyl group is virtually normal to the heterocycle and turned with respect to $N^3–C^3$ bond [torsion angles $C^2N^3C^3C^{11}$ 77.4(3)°, $N^3C^3C^{11}C^{16}$ 56.4(3)°] resulting in appearance of shortened intramolecular contacts $H^3\cdots H^{12}$ 2.30 Å (sum of van der Waals radii 2.34 Å [13]), and $H^4\cdots C^{16}$ 2.85 Å (2.87 Å). The substituent at C^3 atom exists in a conformation intermediate between *–ac-* and *ap-* with respect to $C^2–N^3$ bond [torsion andgle $C^2N^3C^3C^4$ –158.9(2)°]; it is also turned in such manner that the hydrogen atom is in the *–sc*-conformation with respect to $N^3–C^3$ bond (torsion angele $N^3C^3C^4H^4$ –66°). The ester groups are present in a conformation where the ethyl of the ester group is oriented virtually perpendicular to the C–O bond [torsion angles $C^5O^2C^6C^7$ –98.3(4)°, $C^8O^4C^9C^{10}$ 81.4(3)°]. However the carbonyl groups of these substituents are in different orientation with respect to $C^3–C^4$ bond [torsion angles $C^3C^4C^5O^1$ 29.8(3)°, $C^3C^4C^8O^3$ –66.9(3)°] leading apparently to the shortening of the intramolecular contact $H^{6a}\cdots O^1$ 2.37 Å (sum of van der Waals radii 2.46 Å).

In the crystal of compound **XII** the molecules are bound by weak intermolecular hydrogen bonds $N^4–H^{4Na}\cdots O^{3'}$ (2 – *x*, 1 – *y*, –*z*) H···O 2.32 , N–H···O 158°; $N^4–H^{4Nb}\cdots N^{1'}$ (1 – *x*, 1 – *y*, –*z*) H···N 2.16 Å, N–H···N 164°.

The characteristic feature of the partially hydrogenated azine ring of triazolo[1,5-*a*]-pyrimidinones **XIII–XV** is



1,2,4-triazol-1-yl(phenyl)methyl]-malonate (**XII**).

the resonance of the methine protons in the fragment $C^6H–C^7H$. The imido group singlet (δ_{NH} 11.9–11.6 ppm) was observed in the spectra of compounds **XIII** and **XV**, and the spectrum of compound **XIV** lacked this signal. At the same time in the spectrum of triazolo[1,5-*a*]-pyrimidin-5-one **XIV** signals appeared belonging to two amino groups observed as singlets at δ 6.19, 5.50 ppm with integral intensity corresponding to 2H. The signals disappeared on exchange with deuterium of CD_3OD. Consequently, in reaction with ester **VII** aminoazole **VI** acted not like 1,4-, but as 1,3-binucleophile giving a triazolopyrimidine and not a triazolotriazepine system. Besides the heterocyclization in methanol is accompanied by transesterification of CO_2Et group into CO_2Me; this process also contributed to the appearance of the spectrum of compound **XIV**. The conversion of CO_2Et group into $CONMe_2$ when DMF is involved in the process of triazolo[1,5-*a*]pyrimidin-5-one (**XV**) formation is revealed by the disappearance of the signals from the ethyl substituent and appearance of singlets from two methyl groups. Overall pattern of the spectrum is analogous to the above described for the systems of this type, and it is char-acterized by the presence of a multiplet of a phenyl ring, singlets of C^2H and NH, and doublets of the $C^6H–C^7H$ fragments. In the spectra of acid mixtures **XVII, XVIII** and **XX, XXI** alongside the multiplets of the phenyl rings were observed broadened singlets of NH and COOH groups, and *AB* system of methine protons characteristic of 6,7-dihydro derivatives **XVII** and **XX**. The comparison of integral intensities of C^2H signals in the spectra of compounds **XVII** and **XVIII** and of methylthio groups in the spectra of compounds **XX** and **XXI** makes it possible to estimate the quantitative composition of the mixtures.

Thus the structure of heterocyclization products obtained from aminoazoles **I–VI** with diethyl benzylidene-

Table 1 Bond lengths in the molecule of diethyl [5-amino-3-methylsulfanyl-1,2,4-triazol-1-yl(phenyl)methyl]-malonate (**XII**).

Bond	*d*, Å	Bond	*d*, Å
$S^1–C^{17}$	1.748(3)	$O^4–C^9$	1.466(3)
$S^1–C^1$	1.749(2)	$C^3–C^{11}$	1.508(3)
$N^1–C^2$	1.327(3)	$C^3–C^4$	1.546(3)
$N^1–C^1$	1.356(3)	$C^4–C^5$	1.515(3)
$N^2–C^1$	1.316(3)	$C^4–C^8$	1.525(3)
$N^2–N^3$	1.391(2)	$C^6–C^7$	1.418(5)
$N^3–C^2$	1.346(2)	$C^9–C^{10}$	1.487(5)
$N^3–C^3$	1.465(2)	$C^{11}–C^{16}$	1.372(3)
$N^4–C^2$	1.348(3)	$C^{11}–C^{12}$	1.387(3)
$O^1–C^5$	1.199(3)	$C^{12}–C^{13}$	1.385(4)
$O^2–C^5$	1.325(3)	$C^{13}–C^{14}$	1.359(5)
$O^2–C^6$	1.460(3)	$C^{14}–C^{15}$	1.368(5)
$O^3–C^8$	1.203(2)	$C^{15}–C^{16}$	1.409(5)
$O^4–C^8$	1.320(2)		

Table 2. Bond angles (φ) in the structure of diethyl [5-amino-3-methylsulfanyl-1,2,4-triazol-1-yl(phenyl)methyl]-malonate (**XII**).

Angle	φ, deg	Angle	φ, deg
$C^{17}S^1C^1$	103.16(13)	$C^5C^4C^3$	112.40(16)
$C^2N^1C^1$	102.83(16)	$C^8C^4C^3$	107.18(15)
$C^1N^2N^3$	100.89(16)	$O^1C^5O^2$	125.7(2)
$C^2N^3N^2$	109.86(15)	$O^1C^5C^4$	124.7(2)
$C^2N^3C^3$	127.12(16)	$O^2C^5C^4$	109.53(19)
$N^2N^3C^3$	122.70(14)	$C^7C^6O^2$	109.3(3)
$C^5O^2C^6$	118.2(2)	$O^3C^8O^4$	125.04(18)
$C^8O^4C^9$	117.34(17)	$O^3C^8C^4$	123.55(18)
$N^2C^1N^1$	116.46(18)	$O^4C^8C^4$	111.39(17)
$N^2C^1S^1$	125.43(17)	$O^4C^9C^{10}$	110.4(2)
$N^1C^1S^1$	118.11(14)	$C^{16}C^{11}C^{12}$	119.4(2)
$N^1C^2N^3$	109.95(18)	$C^{16}C^{11}C^3$	120.9(2)
$N^1C^2N^4$	125.15(18)	$C^{12}C^{11}C^3$	119.6(2)
$N^3C^2N^4$	124.89(18)	$C^{13}C^{12}C^{11}$	120.5(3)
$N^3C^3C^{11}$	112.00(16)	$C^{14}C^{13}C^{12}$	119.9(3)
$N^3C^3C^4$	109.87(15)	$C^{13}C^{14}C^{15}$	120.8(3)
$C^{11}C^3C^4$	110.92(15)	$C^{14}C^{15}C^{16}$	119.7(3)
$C^5C^4C^8$	108.93(17)	$C^{11}C^{16}C^{15}$	119.7(3)

malonate (**VII**) shows that this reaction results in formation of azoloazine system of a single type. In all reactions considered the electrophilic attack consists in alkylation of the endocyclic nitrogen and acylation of amino group in the molecule of the heterylamine. Scarce publications contain reliable information on the sequence of stages in such processes proved with firm data on the structure of intermediate products [1, 5]. The regioselectivity of reactions in question and the presence among compounds synthesized of adducts **X–XII** obtained from 3-amino-1,2,4-triazole permit an assumption that also in the case of amines **I, II, V**, and **VI** the first stage of the process involves the alkylation of imino group by δ-carbon of the unsaturated carbonyl compound **VII**. At the same time this reaction is not regioselective for 3-amino-1,2,4-triazole (**III**) since the alkylation occurs at two nucleophilic sites N^1 and N^2. Therewith the cyclization is possible only for N^2-adduct. The lack of pyrazolo-[3,4-*b*]pyridines and triazolo[4,3-*a*]pyrimidines also should be connected with the direction of the electrophilic attack in the alkylation stage. The formation of compounds mixtures in reactions of aminoazoles **III** and **IV** with diethyl benzylidenemalonate in DMF is due to transformations occurring after the closure of the azine ring: pyrolysis of the ester group, decarboxylation, and oxidation.

EXPERIMENTAL

IR spectra were registered on a spectrophotometer Specord M-82 from KBr pellets. ^{1}H NMR spectra were measured on a spectrometer Varian-200 from solutions in DMSO-d_6, internal reference TMS. The composition of the reaction mixtures was controlled and the purity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluent $CHCl_3$–MeOH, 3:1. Melting points were measured on a Koeffler heating block. Diethyl benzylidenemalonate was obtained by procedure [14].

X-ray diffraction analysis of diethyl [5-amino-3-methylsulfanyl-1,2,4-triazol-1-yl-(phenyl)methyl]-malonate (XII). Monoclinic crystals, $C_{17}H_{22}N_4O_4S$, at 20°C *a* 11.756(2), *b* 10.263(4), *c* 16.932(3) Å, β 103.85(1)°, *V* 1983.4(8) Å^3, M_r 378.45, *Z* 4, space group $P2_1/n$, d_{calc} 1.267 g/cm^3, μ(MoK_α) 0.192 mm^{-1}, *F*(000) 800. The parameters of the unit cell and intensities of 10518 reflections (4522 independent, R_{int} 0.024) were measured on a diffractometer Xcalibur-3 (MoK_α radiation, CCD-detector, graphite monochromator, ω-scanning, $2\theta_{max}$ 55°). The structure was solved by the direct method using software package SHELXTL [15]. Hydrogen atoms positions were revealed from the difference synthesis of the electron density and refined in the *rider* model with $U_{iso} = nU_{eq}$ of the nonhydrogen atom linked to this hydrogen (*n* is 1.5 for methyl, 1.2 for other hydrogens). The structure was refined with respect to F^2 by full-matrix least-mean-squares method in the anisotropic approximation for nonhydrogen atoms till wR_2 0.164 for 4468 reflections [R_1 0.053 for 2371 reflections with $F > 4\sigma(F)$, *S* 0.923). Crystallographic data, atomic coordinates, and geometrical parameters of the structure are deposited in Cambridge Structural Database (structure no. CCDC 606004).

2-Methyl-7-phenyl-6-ethoxycarbonyl-6,7-dihydropyrazolo[1,5-*a*]pyrimidin-5(4*H*)-one (VIII). *a*. A mixture of 1 mmol of 3-amino-5-methylpyrazole (**I**) and 1 mmol of diester **VII** in 2 ml of methanol was boiled for 2 h, the solvent was removed in a vacuum, and the residue was crystallized from a mixture ethyl acetate–hexane, 2:1. Yield 0.15 mmol (15%), colorless crystals, mp 150–151°C. IR spectrum, cm^{-1}: 3176–2774 (NH), 1736, 1720 (CO_2Et), 1684 (CO), 1596 (CONH). ^{1}H NMR spectrum, δ, ppm: 11.05 br.s (1H, NH), 7.03–7.35 m (5H, C_6H_5), 5.72 d (1H, C^7H, J_{AB} 4.2 Hz), 5.54 s (1H, C^3H), 4.16–4.05 m (3H, C^6H, CH_2), 2.07 s (3H, CH_3), 1.10 t (3H, CH_3). Found, %: C 64.12; H 5.66; N 14.10. $C_{16}H_{17}N_3O_3$. Calculated, %: C 64.21; H 5.69; N 14.05.

b. A mixture of 1 mmol of 3-amino-5-methylpyrazole (**I**) and 1 mmol of diester **VII** in 2 ml of 1-butanol was boiled for 2 h. The reaction product was isolated as described above. Yield 0.47 mmol (47%).

c. A mixture of 1 mmol of 3-amino-5-methylpyrazole (**I**) and 1 mmol of diester **VII** in 2 ml of DMF was boiled for 10 min. The reaction mixture was poured into water, the reaction products were extracted with chloroform, the extract was dried over Na_2SO_4, the solvent was distilled off in a vacuum, the dark oily residue was dissolved in 2 ml of methanol and subjected to column chromatography on silica gel (Aldrich). Yield 0.05 mmol (5%).

4-Phenyl-3-ethoxycarbonyl-3,4-dihydropyrimido[1,2-*a*]benzimidazol-2(1*H*)-one (IX). *a*. A mixture of 1 mmol of 2-aminobenzimidazole (**II**) and 1 mmol of diester **VII** in 3 ml of methanol (DMF) was boiled for 5 min till white amorphous compound precipitated. From the cooled reaction mixture the precipitate was filtered off. Yield 0.77 mmol (77%) in MeOH, 0.59 mmol (59%) in DMF, mp 238–240°C. IR spectrum, cm^{-1}: 3056–2500 (NH), 1752, 1704 (CO_2Et), 1636 (CO), 1584 (CONH). ^{1}H NMR spectrum, δ, ppm: 11.99 br.s (1H, NH), 6.83–7.45 m ($9H_{arom}$), 6.10 d (1H, C^4H, J_{AB} 4.8 Hz), 4.28 d

(1H, C^{3}H), 4.12 q (2H, CH_2, J 7.2 Hz), 1.65 t (3H, CH_3). Found, %: C 68.10; H 5.10; N 12.50. $C_{19}H_{17}N_3O_3$. Calculated, %: C 68.06; H 5.07; N 12.54.

Diethyl [5-amino-1,2,4-triazol-1-yl(phenyl)-methyl]malonate (X) and diethyl [3-amino-1,2,4-triazol-1-yl(phenyl)methyl]malonate (XI). A mixture of 1 mmol of azole **III** and 1 mmol of diester **VII** in 2 ml of methanol was boiled for 2 h. The reaction mixture was cooled, 1 ml of hexane and 1 ml of ethyl acetate were added, and the mixture was kept in the cold till formation of crystals of compounds **X** and **XI** that were separated by fractional crystallization from a mixture ethyl acetate–hexane, 2:1. We obtained 0.28 mmol (28%) of compound **X** and 0.10 mmol (10%) of compound **XI**.

Compound **X**. mp 159–160°C. IR spectrum, cm^{-1}: 3432, 3336 (NH_2), 1760, 1720 (CO_2Et), 1668 (C=N). ^{1}H NMR spectrum, δ, ppm: 7.28–7.52 m (6H, C_6H_5, C^{5}H), 6.49 br.s (2H, NH_2), 5.90 d (1H, CH, J_{AB} 11.4 Hz), 4.54 d (1H, CH), 4.05 m (2H, CH_2), 3.89 q (2H, CH_2, J 7.2 Hz), 1.06 t (3H, CH_3), 0.84 t (3H, CH_3). Found, %: C 57.85; H 6.06; N 16.90. $C_{16}H_{20}N_4O_4$. Calculated, %: C 57.83; H 6.02; N 16.87.

Compound **XI**. mp 111–113°C. IR spectrum, cm^{-1}: 3388, 3324 (NH_2), 1756, 1728 (CO_2Et), 1648 (C=N). ^{1}H NMR spectrum, δ, ppm: 8.16 s (1H, C^{5}H), 7.29–7.52 m (5H, C_6H_5), 5.86 d (1H, CH, J_{AB} 11.2 Hz), 5.21 br.s (2H, NH_2), 4.58 d (1H, CH), 4.06 q (2H, CH_2, J 7.2 Hz), 3.90 q (2H, CH_2, J 7.1 Hz), 1.08 t (3H, CH_3), 0.89 t (3H, CH_3). Found, %: C 57.80; H 6.01; N 16.92. $C_{16}H_{20}N_4O_4$. Calculated, %: C 57.83; H 6.02; N 16.87.

Diethyl [5-amino-3-methylsulfanyl-1,2,4-triazol-1-yl(phenyl)methyl]malonate (XII). A mixture of 1 mmol of azole **IV** and 1 mmol of diester **VII** in 2 ml of methanol was boiled for 1 h. The reaction mixture was cooled, 1 ml of hexane and 1 ml of ethyl acetate were added, and the mixture was kept in the cold till formation of big colorless crystals. Yield 0.17 mmol (17%), mp 145–147°C. IR spectrum, cm^{-1}: 3424, 3320 (NH_2), 1752, 1724 (CO_2Et), 1656 (C=N). ^{1}H NMR spectrum, δ, ppm: 7.51–7.29 m (5H, C_6H_5), 6.61 br.s (2H, NH_2), 5.74 d (1H, CH, J_{AB} 11.2 Hz), 4.50 d (1H, CH,), 4.07 q (2H, CH_2, J 7.4 Hz), 3.87 q (2H, CH_2, J 7.4 Hz), 1.08 t (3H, CH_3), 0.84 t (3H, CH_3). Found, %: C 54.02; H 5.84; N 14.86; S 8.45. $C_{17}H_{22}N_4O_4S$. Calculated, %: C 53.97; H 5.82; N 14.81; S 8.47.

2-Amino-7-phenyl-6,7-dihydro-6-methoxycarbonyl-1,2,4-triazolo-[1,5-*a*]-pyrimidin-5(4*H*)-one (XIII). A mixture of 1 mmol of azole **V** and 1 mmol of diester **VII** in 2 ml of methanol was boiled for 1.5 h. The reaction mixture was cooled, 2 ml of ethyl acetate was added, and the mixture was kept in the cold till formation of fine colorless crystals. Yield 0.47 mmol (47%), mp 233–235°C. IR spectrum, cm^{-1}: 3464, 3296 (NH_2), 1740, 1720 (CO_2Et), 1640 (CO), 1596 (C=N). ^{1}H NMR spectrum, δ, ppm: 11.60 br.s (1H, NH), 7.16–7.37 m (5H, C_6H_5), 5.23 br.s (2H, NH_2), 5.51 d (1H, C^{7}H, J_{AB} 6.5 Hz), 4.19 d (1H, C^{6}H), 4.10 q (2H, CH_2, J 7.4 Hz), 1.09 t (3H, CH_3). Found, %: C 55.84; H 5.01; N 23.29. $C_{14}H_{15}N_5O_3$. Calculated, %: C 55.81; H 4.98; N 23.26.

2,3-Diamino-6-methoxycarbonyl-7-phenyl-3,5,6,7-tetrahydro-1,2,4-triazolo-[1,5-*a*]-pyrimidin-5-one (XIV). A mixture of 1 mmol of azole **VI** and 1 mmol of diester **VII** in 2 ml of methanol was boiled for 2 h. The reaction mixture was cooled, the amorphous precipitate was filtered off. Yield 0.35 mmol (35%), mp 257–260°C. IR spectrum, cm^{-1} 3432, 3312, 3180 (NH_2), 1736, 1672 (CO_2Et), 1656 (CO), 1576, 1548 (C=N). ^{1}H NMR spectrum, δ, ppm: 7.23–7.36 m (5H, C_6H_5), 6.19 br.s (2H, N$^3NH_2$), 5.50 br.s (2H, C$^2NH_2$), 5.35 d (1H, C^{7}H, J_{AB} 7.2 Hz), 3.74 d (1H, C^{6}H), 3.59 C (3H, CH_3). Found, %: C 51.59; H 4.61; N 27.79. $C_{13}H_{14}N_6O_3$. Calculated, %: C 51.66; H 4.64; N 27.81.

Reaction of 3-amino-1,2,4-triazole (III) with diethylbenzylidenemalonate (VII) in DMF. A mixture of 1 mmol of azole **III** and 1 mmol of diester **VII** in 2 ml of DMF was boiled for 2 h. The reaction mixture was cooled, 5 ml of methanol was added thereto. We obtained 0.1 mmol (10%) of **6-dimethylaminocarbonyl-7-phenyl-6,7-dihydro-1,2,4-triazolo[1,5-*a*]-pyrimidin-5(4*H*)-one** (**XV**), and then 0.17 mmol (17%) of **7-phenyl-6,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one** (**XVI**), and 0.1 g of a mixture of **6-carboxy-7-phenyl-6,7-dihydro-1,2,4-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one** (**XVII**) and **6-carboxy-7-phenyl-1,2,4-triazolo[1,5-*a*]-pyrimidin-5(4*H*)-one** (**XVIII**) in a ratio 1:5 (^{1}H NMR data).

Compound (XV). mp 251–252°C. IR spectrum, cm^{-1}: 3204–2580 (NH, CH_3), 1708 [CON(CH_3)$_2$], 1652 (CONH), 1612, 1544 (C=N). ^{1}H NMR spectrum, δ, ppm: 11.90 br.s (1H, NH), 7.71 s (1H, C^{2}H), 7.26–7.39 m (5H, C_6H_5), 5.71 d (1H, C^{7}H, J_{AB} 7.2 Hz), 4.65 d (1H, C^{6}H), 2.97 s (3H, CH_3), 2.77 s (3H, CH_3). Found, %: C 58.93; H 5.22; N 24.52. $C_{14}H_{15}N_5O_2$. Calculated, %: C 58.95; H 5.26; N 24.56.

Compound (XVI). mp 215–216°C (215–217°C [11]).

Compound (XVII). ^{1}H NMR spectrum, δ, ppm: 13.49 br.s (1H, COOH), 11.95 br.s (1H, NH), 7.74 s (1H,

C^2H), 7.19–7.36 m (5H, C_6H_5), 5.90 d (1H, C^7H, J_{AB} 5.7 Hz), 4.29 d (1H, C^6H).

Compound (XVIII). ^1H NMR spectrum, δ, ppm: 13.62 br.s (1H, COOH), 12.14 br.s (1H, NH), 8.14 s (1H, C^2H), 7.39–7.58 m (5H, C_6H_5).

Reaction of 3-amino-5-methylsulfanyl-1,2,4-triazole (IV) with diethyl- benzylidenemalonate (VII) in DMF. A mixture of 1 mmol of triazole **IV** and 1 mmol of diester **VII** in 2 ml of DMF was boiled for 2h. The reaction mixture was cooled, 3 ml of water was added thereto. We obtained 0.25 mmol (25%) of compound **XIX**, mp 253–254°C (254–256°C [12]), and 0.05 g of a mixture of **6-carboxy-2-methylsulfanyl-7-phenyl-6,7-dihydro-1,2,4-triazolo[1,5-*a*]-pyrimidin-5(4*H*)-one** (**XX**) and **6-carboxy-2-methylsulfanyl-7-phenyl-1,2,4-triazoloO[1,5-*a*]-pyrimidin-5(4*H*)-on** (**XXI**) in a ratio 1:4 (^1H NMR data).

Compound (XX). ^1H NMR spectrum, δ, ppm: 13.44 br.s (1H, COOH), 11.68 br.s (1H, NH), 7.40–7.55 m (5H, C_6H_5), 5.97 d (1H, C^7H, J_{AB} 5.6 Hz), 4.22 d (1H, C^6H), 2.54 C (3H, CH_3).

Compound (XXI). ^1H NMR spectrum, δ, ppm: 14.01 br.s (1H, COOH), 12.14 br.s (1H, NH), 7.07–7.39 m (5H, C_6H_5), 2.64 C (3H, CH_3).

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