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Regioselectivity of Cyclization of 1-(6-Methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-yl)-4-arylthiosemicarbazides by Treating with Methyl Iodide and Dicyclohexylcarbodiimide

R. I. Vas'kevich, P. V. Savitskii, E. B. Rusanov, and V. I. Staninets

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev, 0209 Ukraine
e-mail: vaskevich@ioch.kiev.ua

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Abstract—1-(6-Methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-yl)-4-arylthiosemicarbazides treated with methyl iodide in the presence of sodium acetate in ethanol convert into 6-methyl-3-arylamino[1,2,4]-triazolo[4,3-*b*][1,2,4]triazin-7(1*H*)-ones. In reaction with dicyclohexylcarbodiimide 6-methyl-3-arylamino[1,2,4]triazolo[3,4-*c*][1,2,4]triazin-5(1*H*)-ones were obtained which at heating in alcohol solution in the presence of sodium acetate or at 262–272°C underwent the Dimroth rearrangement to give 3-methyl-7-arylamino[1,2,4]triazolo[5,1-*c*][1,2,4]-triazin-4(8*H*)-ones.

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We studied formerly the cyclization of 1-hetaryl-4-aryl-thiosemicarbazides (Ht = 4,6-dimethylpyrimidin-2-yl, 6-methyl-4-oxo-3,4-dihydropyrimidin-2-yl, 5,6-substituted 4-oxo-3-allylthieno[2,3-*d*]pyrimidin-2-yls and 4-oxo-3,4-dihydrothieno[2,3-*d*]pyrimidin-2-yls, benzothiazol-2-yl) effected by methyl iodide and sodium acetate in ethanol. Thus the fused derivatives of triazolopyrimidine [1], triazolothienopyrimidine [2] were obtained, and in the case of Ht = benzothiazol-2-yl the reaction product was unexpectedly 2,2'-dithiobis[*N*-(3-methylmercapto-4-phenyl-1,2,4-triazol-5-yl) benzenamine] [3].

In extension of the research on the cyclization regioselectivity of the hetaryl-substituted thiosemicarbazides we synthesized a thiosemicarbazide containing as a hetaryl fragment a 6-methyl-5-oxo-2,5-dihydro-1,2,4-triazine ring whose N^2 and N^4 atoms could be involved into the closure of the triazole ring in the reaction with the methyl iodide in the presence of sodium acetate. As show the ^1H NMR spectra of compounds **Ia–Ic** in the triazine ring of the thiosemicarbazides the hydrogen atom is situated at the N^2 atomas indicated by the chemical shift in the region 12.59–12.64 ppm. In the ^{13}C NMR spectrum of compound **Ia** the chemical shift of the atom C^5 is 160.15 ppm, and in the IR spectra of thiosemicarbazides **Ia–Ic** the stretching vibrations of the carbonyl group are observed in the region 1660–1640 cm^{-1} confirming the sp^2-hybridization of the atom N^4.

Taking into consideration the above reasoning, the dependence of the regiochemistry of the fusion of the triazole ring in the thiosemicarbazides **Ia–Ic** on the nature of the electrophilic cyclization agent is a timely question. For its solution we used as the cyclization reagents methyl iodide and dicyclohexylcarbodiimide (DCC) [4]. As we had shown before [1, 2] the cyclization effected by the methyl iodide consisted first in the alkylation with the methyl iodide of the thione sulfur of the thiosemicarbazide with the intermediate formation of thioether which further suffered the intramolecular cyclization forming a triazole ring and eliminating a methylmercaptan. At the use of DCC the reaction begins with its addition to the sulfur atom of the thiosemicarbazide fragment with the formation of the dicyclohexylthiourea and a new carbodiimide, that further can attack one of the nitrogen atoms of the triazine heterocycle. This difference in the action of the cyclization reagents suggests that the cyclization regiochemistry of these processes may be different. Apparently the difference in the experimental conditions also should be taken into account: with the methyl iodide the sodium acetate is used that can produce

a basic medium whereas with DCC the medium is neutral.

It was established that in the reaction of 1-(6-methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-yl)-4-arylthiosemicarbazides **Ia–Ic** with methyl iodide and sodium acetate in ethanol 6-methyl-3-arylamino[1,2,4]triazolo[4,3-*b*][1,2,4]triazin-7(1*H*)-ones **IIa–IIc** were formed (see the scheme).

The structure of triazolotriazine **IIa** was established by XRD analysis. The molecule of compound **IIa** crystallized with two molecules of solvate water (see the figure and the table). The distribution of the bond distances and bond angles in the central bicyclic fragment is common for such systems. The proper bicyclic fragment is virtually planar, the average deviation of atoms from the mean-square plane is 0.017 Å, and the phenyl ring C^{6}–C^{11} is materially coplanar with it (the dihedral angle is 2.5°).

The bonds N^{6}–C^{4} 1.348(3) and N^{6}–C^{6} 1.409(3) Å are somewhat shortened [5] as compared with the standard (1.45 Å) length of the ordinary nitrogen-carbon bond, and the sum of the bond angles at the atom N^{6} is 359.6(16)° indicating the conjugation of the lone electron pairs of the atom N^{6} with the π-systems of the phenyl and the heterocyclic system.

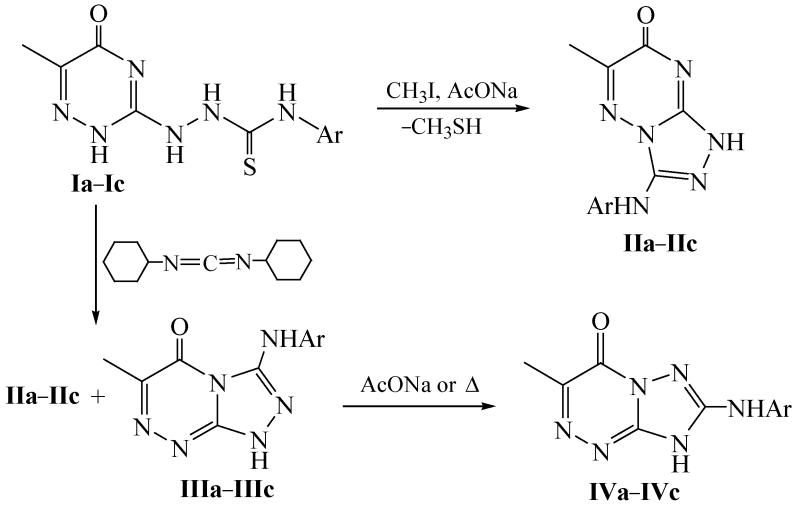
The cyclization of compounds **Ia–Ic** with DCC in toluene takes another route. In this case the yield of triazolotriazines **IIa–IIc** was only 5–12%. To the main reaction products isolated in 63–73% yield we assigned the structure of 6-methyl-3-arylamino[1,2,4]triazolo[3,4-*c*][1,2,4]-triazin-5(1*H*)-ones **IIIa–IIIc** because in their IR spectra the stretching vibrations of the carbonyl group appeared in the region 1700 cm^{-1}, whereas for the triazolotriazines **IIa–IIc** ν(C=O) was 1600 cm^{-1}. In the ^{13}C NMR spectrum of compound **IIa** the chemical shift of C^{7} atom of the triazolotriazine system equals 160.55 ppm, and in the spectrum of compound **IIIa** the chemical shift of the atom C^{5} is observed in the stronger field at 153.02 ppm. This permits a conclusion that the atom N^{4} of triazolotriazine **IIIa** is in the sp^{3}-hybridized state. In the ^{1}H NMR spectra of compounds **III** the singlet of the proton of the NHAr group is located at 8.61–9.25 ppm, and the proton of the triazole ring, in the region 13.53–13.72 ppm. In the spectra of triazolotriazines **II** the singlet of the NHAr group appears at 9.55–10.21 ppm, and the proton of the triazole ring, in the region 13.17–13.29 ppm.

Main geometrical parameters of intermolecular hydrogen bonds in the crystal of compound **IIa** dihydrate

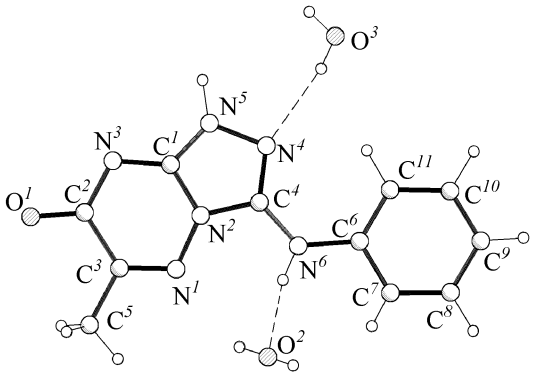
D–H···A[a]	D–H, Å	H···A, Å	D···A, Å	DHA angle, deg
N^{5}–H^{5N}···$N^{3\#1}$	1.00(3)	1.90(3)	2.882(3)	165(2)
N^{6}–H^{6N}···O^{2}	0.89(3)	2.05(3)	2.900(3)	159(2)
O^{2}–H^{1O}···$O^{3\#2}$	0.816(10)	2.148(18)	2.926(4)	160(4)
O^{3}–H^{3O}···N^{4}	0.819(10)	2.17(2)	2.968(3)	165(7)
O^{3}–H^{4O}···$O^{1\#1}$	0.824(10)	1.964(11)	2.786(3)	175(5)

[a] With indices #1 and #2 atoms are marked connected with the initial symmetrical transformations *–x + 1, –y + 1, –z* and *x, y – 1, z*, respectively.

Scheme.



Ar = C_6H_5 (**a**), 4-$CH_3OC_6H_4$ (**b**), 4-$C_2H_5O_2CC_6H_4$ (**c**).



General view of molecule 6-methyl-3-phenylamino[1,2,4]-triazolo-[4,3-*b*][1,2,4]triazin-7(1*H*)-one (**IIa**) dihydrate. The main bond distances and bond angles: N^1–N^2 1.360(3), N^2–C^1 1.356(3), N^3–C^1 1.332(3), N^3–C^2 1.359(3), C^2–C^3 1.494(3), N^1–C^3 1.296(3), N^2–C^4 1.379(3), N^4–C^4 1.308(3), N^4–N^5 1.396(3), N^5–C^1 1.314(3), N^6–C^4 1.348(3) Å; $C^3N^1N^2$ 113.62(19), $C^1N^2N^1$ 124.64(19), $N^3C^1N^2$ 124.1(2), $C^1N^3C^2$ 114.6(2), $N^3C^2C^3$ 119.5(2), $N^1C^3C^2$ 123.3(2), $C^1N^2C^4$ 108.07(19), $N^4C^4N^2$ 110.0(2), $C^4N^4N^5$ 104.42(18), $C^1N^5N^4$ 111.96(19), $N^5C^1N^2$ 105.58(19) deg.

Compounds **IIIa–IIIc** at heating with sodium acetate in ethanol or without solvent at 262–272°C suffered the Dimroth rearrangement with the formation of 3-methyl-7-arylamino[1,2,4]triazolo-[5,1-*c*][1,2,4]triazin-4(8*H*)-ones **IVa–IVc**. Triazolotriazines **IIa–IIc** are less prone to the isomerization, but at melting compound **IIa** the partial formation of triazolotriazine **IVa** was observed in 10–15% yield. Further heating of the sample of compound **IIa** over 315°C led to its decomposition.

In the IR spectra of compounds **IVa–IVc** the stretching vibrations of the carbonyl group are observed in the region 1670–1690 cm^{-1}. In the ^1H NMR spectra of compounds **IV** unlike the spectra of compounds **III** the singlets of the protons of the NHAr group and of the triazole ring are shifted downfield, to 9.61–10.35 and 14.07–14.23 ppm respectively.

Thus the cyclization of compounds **Ia–Ic** proceeded under the action of methyl iodide selectively at the atom N^2 of the triazine ring, and with DCC, unselectively, both at the atom N^4 and the atom N^2. Compounds **IIIa–IIIc** can undergo thermal and catalytic Dimroth rearrangement.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20 in pellets with KBr. ^1H NMR spectra were registered on a spectrometer Varian VXR-300 (300 MHz), ^{13}C NMR spectra of compounds **Ia**, **IIa**, **IIIa**, on a spectrometer Bruker Avance DRX-500 (125.75 MHz) in DMSO-d_6, internal reference TMS.

XRD experiment with a single crystal of compound **IIa** of dimensions 0.14×0.20×0.41 mm was carried out at room temperature on a diffractometer Bruker Smart Apex II (λMoK_α-radiation, graphite monochromator, θ_{max} 26.59 °, spherical segment $-8 \le h \le 8$, $-8 \le k \le 10$, $-13 \le l \le 10$). 5200 reflections were collected, among them 2560 independent (R-factor of averaging 0.0381). Crystals of compound **IIa** [$C_{11}H_{14}N_6O_3 \cdot 2H_2O$, M 278.28] triclinic, space group P-1, a 6.9904(13), b 8.6791(12), c 11.1457(17) Å, α 96.634(8), β 107.721(9), γ 92.126(9)°, V 637.95(18) $Å^3$, Z 2, d_c 1.449, μ 0.110 mm^{-1}, F(000) 292. The structure was solved by the direct method and refined by the lest-mean-squares method in the full-matrix anisotropic approximation applying software SHELXS97 and SHELXL97 [6, 7]. The correction for extinction was done using SADABS program (the ratio of minimal to maximal correction T_{min}/T_{max} 0.755221). Hydrogen atoms were revealed in the difference Fourier synthesis and were refined isotropically. In the refinement 1430 reflections were used with $I > 2\sigma(I)$, 237 refined parameters, 6.03 reflections per a parameter, the weight scheme was used $\omega = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, the ratio of the maximum (average) shift to the error in the final cycle 0.09 (0.004). The final values of the divergence factors $R_1(F)$ 0.0540, $wR_2(F^2)$ 0.1136, GOF 1.067 for the reflections with $I > 2\sigma(I)$. The residual electron density from the difference Fourier series after the final refinement cycle was 0.18 and –0.24 e/ $Å^3$. The complete set of the XRD structural data for compound **IIa** is deposited in the Cambridge Crystallographic Data Center (CCDC 741347).

3-Hydrazino-6-methyl-1,2,4-triazin-5(2H)-one was obtained by procedure [8].

1-(6-Methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-yl)-4-arylthiosemicarbazides Ia–Ic. To a dispersion of 0.71 g (5 mmol) of 3-hydrazino-6-methyl-1,2,4-triazin-5(2H)-one in 30 ml of ethanol was added a solution of 6 mmol of an appropriate isothiocyanate in 20 ml of ethanol. The mixture was boiled for 1.5 h and then cooled. The precipitated crystals of the thiosemicarbazide were filtered off and washed with ethanol and ether.

1-(6-Methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-yl)-4-phenylthiosemicarbazide (Ia). Yield 1.12 g (81%), mp 281–283°C (decomp.). IR spectrum, ν, cm^{-1}: 3320, 3280, 1690, 1660, 1590, 1560, 1510, 1440, 1340, 1280, 1240,

1210, 1160. ^{1}H NMR spectrum, δ, ppm: 2.06 s (3H, CH_3), 7.16 t (1H$_{arom}$, *J* 7.5 Hz), 7.33 t (2H$_{arom}$, *J* 7.5 Hz), 7.53 d (2H$_{arom}$, *J* 7.5 Hz), 9.39 br.s (1H, NH), 9.59 C (1H, NH), 10.02 c (1H, NH), 12.59 c (1H, NH). ^{13}C NMR spectrum, δ, ppm: 15.94, 113.99, 115.81, 128.80, 138.27, 146.59, 148.32, 151.43, 160.15. Found, %: C 47.56; H 4.21; N 30.33; S 11.47. $C_{11}H_{12}N_6OS$. Calculated, %: C 47.81; H 4.38; N 30.41; S 11.60.

1-(6-Methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-yl)-4-(4-methoxyphenyl)thiosemicarbazide (Ib). Yield 1.13 g (74%), mp 189–191°C. IR spectrum, ν, cm^{-1}: 3300, 1640, 1550, 1520, 1430, 1360, 1300, 1240, 1170, 1040. ^{1}H NMR spectrum, δ, ppm: 2.07 s (3H, CH_3), 3.75 s (3H, OCH_3), 6.90 d (2H$_{arom}$, *J* 9.0 Hz), 7.36 d (2H$_{arom}$, *J* 9.0 Hz), 9.36 br.s (1H, NH), 9.51 s (1H, NH), 9.93 s (1H, NH), 12.60 s (1H, NH). Found, %: C 46.94; H 4.58; N 27.31; S 10.38. $C_{12}H_{14}N_6O_2S$. Calculated, %: C 47.05; H 4.61; N 27.43; S 10.47.

1-(6-Methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-yl)-4-(4-carboethoxyphenyl)thiosemicarbazide (Ic). Yield 1.45 g (83%), mp 284–286°C (decomp.). IR spectrum, ν, cm^{-1}: 3320, 3270, 1700, 1660 (C=O), 1610, 1590, 1560, 1460, 1410, 1340, 1310, 1280, 1210, 1190, 1110, 1030. ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, CH_3, *J* 7.2 Hz), 2.07 s (3H, CH_3), 4.31 q (2H, CH_2, *J* 7.2 Hz), 7.80 d (2H$_{arom}$, *J* 8.7 Hz), 7.93 d (2H$_{arom}$, *J* 8.7 Hz), 9.46 br.s (1H, NH), 9.83 s (1H, NH), 10.26 s (1H, NH), 12.64 br.s (1H, NH). Found, %: C 47.99; H 4.57; N 24.05; S 9.13. $C_{14}H_{16}N_6O_3S$. Calculated, %: C 48.27; H 4.63; N 24.12; S 9.20.

6-Methyl-3-arylamino[1,2,4]triazolo[4,3-*b*]-[1,2,4]triazin-7(1*H*)-ones IIa–IIc. A dispersion of 2.5 mmol of an appropriate thiosemicarbazide **Ia–Ic**, 0.25 g (3 mmol) of sodium acetate, and 0.19 ml (3 mmol) of methyl iodide was boiled for 1.5 h in 50 ml of ethanol. The solution was cooled, the precipitated crystals were filtered off and washed on the filter with ethanol and ether.

6-Methyl-3-phenylamino[1,2,4]triazolo-[4,3-*b*]-[1,2,4]triazin-7(1*H*)-one (IIa). Yield 0.44 g (73%), mp 296–297°C (acetone). IR spectrum, ν, cm^{-1}: 1600, 1560, 1500, 1460, 1420, 1300, 1240. ^{1}H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3), 6.99 t (1H$_{arom}$, *J* 7.5 Hz), 7.33 t (2H$_{arom}$, *J* 7.5 Hz), 7.72 d (2H$_{arom}$, *J* 8.1 Hz), 9.74 s (1H, NH), 13.17 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 17.88, 117.44, 121.50, 128.78, 139.40, 141.98, 147.14, 153.26, 160.55. Found, %: C 54.53; H 4.09; N 34.67. $C_{11}H_{10}N_6O$. Calculated, %: C 54.54; H 4.16; N 34.69.

6-Methyl-3-(4-methoxyphenylamino)[1,2,4]-triazolo[4,3-*b*][1,2,4]triazin-7(1*H*)-one (IIb). Yield 0.46 g (67%), mp 230–232°C (acetone). IR spectrum, ν, cm^{-1}: 3270, 3100, 1590, 1550, 1420, 1230, 1170, 1020, 870, 820. ^{1}H NMR spectrum, δ, ppm: 2.29 s (3H, CH_3), 3.73 s (3H, OCH_3), 6.91 d (2H$_{arom}$, *J* 9.0 Hz), 7.62 d (2H$_{arom}$, *J* 9.0 Hz), 9.55 s (1H, NH), 13.21 br.s (1H, NH). Found, %: C 52.87; H 4.35; N 30.76. $C_{12}H_{12}N_6O_2$. Calculated, %: C 52.94; H 4.44; N 30.87.

3-(4-Carboethoxyphenylamino)-6-methyl[1,2,4]-triazolo[4,3-*b*][1,2,4]triazin-7(1*H*)-one (IIc). Yield 0.50 g (63%), mp 302–303°C (acetone). IR spectrum, ν, cm^{-1}: 3320, 1670 (C=O), 1590, 1550, 1430, 1270, 1240, 1080. ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, CH_3, *J* 7.2 Hz), 2.30 s (3H, CH_3), 4.28 q (2H, CH_2, *J* 7.2 Hz), 7.81 d (2H$_{arom}$, *J* 9.0 Hz), 7.92 d (2H$_{arom}$, *J* 9.0 Hz), 10.21 s (1H, NH), 13.29 br.s (1H, NH). Found, %: C 53.45; H 4.39; N 26.67. $C_{14}H_{14}N_6O_3$. Calculated, %: C 53.50; H 4.49; N 26.74.

Reaction of 1-(6-methyl-5-oxo-2,5-dihydro-1,2,4-triazin-3-yl)-4-arylthiosemicarbazides Ia–Ic with DCC. A dispersion of 2.5 mmol of an appropriate thiosemicarbazide **Ia–Ic**, 0.93 g (4.5 mmol) of DCC in 50 ml of toluene was boiled for 1.5 h on an oil bath at 115–120°C. The solution was cooled to 25–30°C, the precipitated crystals of compound **III** were filtered off and washed on the filter with toluene and ether. The filtrate was completely evaporated, 20 ml of ethanol was added, and the mixture was heated till the precipitate dissolved. From the solution by the fractional crystallization were obtained compounds **(IIa)** 7%**, (IIb)** 12%**, (IIc)** 5%.

6-Methyl-3-phenylamino[1,2,4]triazolo-[3,4-*c*]-[1,2,4]triazin-5(1*H*)-one (IIIa). Yield 0.40 g (66%), mp 264–266°C,* 330–332°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 1700, 1630, 1600, 1560, 1500, 1460, 1380, 1350, 1290, 1250. ^{1}H NMR spectrum, δ, ppm: 2.22 s (3H, CH_3), 6.98 t (1H$_{arom}$, *J* 7.5 Hz), 7.34 t (2H$_{arom}$, *J* 7.8 Hz), 7.71 d (2H$_{arom}$, *J* 7.8 Hz), 8.78 s (1H, NH), 13.60 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 15.27, 117.06, 121.28, 128.84, 135.81, 139.47, 144.15, 145.25, 153.02. Found, %: C 54.28; H 4.07; N 34.53. $C_{11}H_{10}N_6O$. Calculated, %: C 54.54; H 4.16; N 34.69.

6-Methyl-3-(4-methoxyphenylamino)[1,2,4]-triazolo[3,4-*c*][1,2,4]triazin-5(1*H*)-one (IIIb). Yield 0.43 g (63%), mp 262–263°C,* 341–343°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 3370, 2860, 1700, 1640, 1600, 1560, 1510, 1430, 1380, 1340, 1290, 1270, 1240, 1190, 1140, 1040. ^{1}H NMR spectrum, δ, ppm:

2.20 s (3H, CH_3), 3.73 s (3H, OCH_3), 6.91 d ($2H_{arom}$, *J* 8.7 Hz), 7.64 d ($2H_{arom}$, *J* 9.0 Hz), 8.61 s (1H, NH), 13.53 s (1H, NH). Found, %: C 52.77; H 4.28; N 30.68. $C_{12}H_{12}N_6O_2$. Calculated, %: C 52.94; H 4.44; N 30.87.

3-(4-Carboethoxyphenylamino)-6-methyl[1,2,4]-triazolo[3,4-*c*][1,2,4]triazin-5(1*H*)-one (IIIc). Yield 0.57 g (73%), mp 271–272°C,[1] 318–320°C (ethanol–DMSO). IR spectrum, ν, cm^{-1}: 1710 (C=O), 1630, 1600, 1560, 1490, 1430, 1380, 1280, 1260, 1180, 1110, 1040. ^1H NMR spectrum, δ, ppm: 1.32 t (3H, CH_3, *J* 7.2 Hz), 2.22 s (3H, CH_3), 4.29 q (2H, CH_2, *J* 7.2 Hz), 7.79 d ($2H_{arom}$, *J* 9.0 Hz), 7.92 d ($2H_{arom}$, *J* 8.7 Hz), 9.25 s (1H, NH), 13.72 c (1H, NH). Found, %: C 53.39; H 4.37; N 26.53. $C_{14}H_{14}N_6O_3$. Calculated, %: C 53.50; H 4.49; N 26.74.

3-Methyl-7-arylamino[1,2,4]triazolo[5,1-*c*]-[1,2,4] triazin-4(8*H*)-ones IVa–IVc. *a*. A dispersion of 2.5 mmol of an appropriate compound **IIIa–IIIc**, 0.25 g (3 mmol) of sodium acetate was boiled for 1.5 h in 50 ml of ethanol. The solution was cooled, the precipitated crystals were filtered off and washed on the filter with ethanol and ether.

b. 1 mmol of an appropriate compound **IIIa–IIIc** was heated for 5 min on a sand bath at 262–272°C. The obtained white crystalline product did not require additional purification.

3-Methyl-7-phenylamino[1,2,4]triazolo-[5,1-*c*]-[1,2,4]triazin-4(8*H*)-one (IVa). Yield 0.56 g (93%) (*a*), 0.60 g (99%) (*b*), mp 331–332°C (ethanol). IR spectrum, ν, cm^{-1}: 1690, 1650, 1620, 1570, 1500, 1460, 1180, 1060. ^1H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3), 6.95 t ($1H_{arom}$, *J* 7.5 Hz), 7.33 t ($2H_{arom}$, *J* 8.1 Hz), 7.69 d ($2H_{arom}$, *J* 8.1 Hz), 9.84 s (1H, NH), 14.13 s (1H, NH). Found, %: C 54.34; H 4.12; N 34.57 $C_{11}H_{10}N_6O$. Calculated, %: C 54.54; H 4.16; N 34.69.

3-Methyl-7-(4-methoxyphenylamino)[1,2,4] triazolo[5,1-*c*][1,2,4]triazin-4(8*H*)-one (IVb*).* Yield 0.58 g (85%) (*a*), 0.68 g (99%) (*b*), mp 343–345°C (ethanol). IR spectrum, ν, cm^{-1}: 3280, 3120, 3010, 1670, 1610, 1570, 1500, 1430, 1390, 1240, 1210, 1170, 1030. ^1H NMR spectrum, δ, ppm: 2.28 s (3H, CH_3), 3.72 s (3H, OCH_3), 6.92 d ($2H_{arom}$, *J* 9.0 Hz), 7.58 d ($2H_{arom}$, *J* 9.0 Hz), 9.61 s (1H, NH), 14.07 s (1H, NH). Found, %: C 52.83; H 4.37; N 30.71. $C_{12}H_{12}N_6O_2$. Calculated, %: C 52.94; H 4.44; N 30.87.

7-*(*4-Carboethoxyphenylamino)-3-methyl[1,2,4]-triazolo[5,1-*c*][1,2,4]triazin-4(8*H*)-one (IVc). Yield 0.64 g (82%) (*a*), 0.76 g (98%) (*b*), mp 320–321°C (ethanol). IR spectrum, ν, cm^{-1}: 1690 (C=O), 1590, 1540, 1420, 1280, 1170, 1100, 1040, 1020. ^1H NMR spectrum, δ, ppm: 1.32 t (3H, CH_3, *J* 7.2 Hz), 2.31 s (3H, CH_3), 4.29 q (2H, CH_2, *J* 7.2 Hz), 7.78 d ($2H_{arom}$, *J* 9.0 Hz), 7.94 d ($2H_{arom}$, *J* 9.0 Hz), 10.35 s (1H, NH), 14.23 s (1H, NH). Found, %: C 53.46; H 4.46; N 26.75. $C_{14}H_{14}N_6O_3$. Calculated, %: C 53.50; H 4.49; N 26.74.

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[1] In this temperature range occurred Dimroth rearrangement with the formation of compounds **IVa–IVc**.