Russian Journal of Organic Chemistry, Vol. 41, No. 1, 2005, pp. 108–113. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 1, 2005, pp. 109–114.

Synthesis and Transformations of 5-Substituted 2-Aryl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]thiazin-7-ones and 2-Aryl-2,3-dihydro-4*H*-[1,3]thiazino[3,2-*a*]benzimidazol-4-ones

V. N. Britsun, A. N. Esipenko, A. N. Chernega, and M. O. Lozinskii

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, ul. Murmanskaya 5, Kiev, 02094 Ukrain

Received July 17, 2003

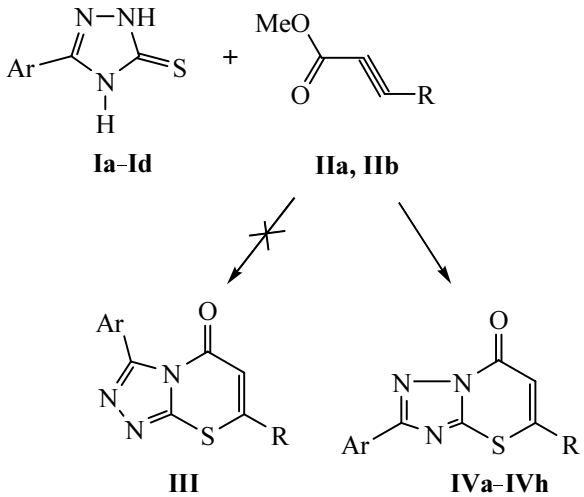
Abstract—3-Aryl-1,2,4-triazole-5-thiones react with dimethyl acetylenedicarboxylate and methyl 3-phenylpropynoate to afford the corresponding 5-substituted 2-aryl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]thiazin-7-ones. Treatment of 2-aryl-2,3-dihydro-4*H*-[1,3]thiazino[3,2-*a*]benzimidazol-4-ones with alkalies leads to formation of 3-(benzimidazol-2-ylsulfanyl)-3-arylpropionic acids, their reaction with methyl *p*-toluenesulfonate yields 1-(3-methyl-2-thioxo-2,3-dihydro-1*N*-benzimidazol-1-yl)-3-phenyl-2-propen-1-one, and oxidation with hydrogen peroxide gives benzimidazole-2-sulfonic acid and 3-aryl-2-propenoic acids.

It is known that reactions of 1,2,4-triazole-5-thione with compounds containing an activated multiple bond, such as propynoic and acetylenedicarboxylic acid esters, diethyl ethoxymethylenemalonate, and 3-aryl-2-propenoyl chlorides, lead to formation of [1,2,4]triazolo[3,2-*b*]-[1,3]thiazine derivatives [1–5]. Here, the acylation of 1,2,4-triazole-5-thione occurs exclusively at the nitrogen atom in position *1*. Heravi *et al*. [6] reported that 3-phenyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (**Ia**) reacts with dimethyl acetylenedicarboxylate (**IIa**) in methanol to give methyl 5-oxo-3-phenyl[1,2,4]triazolo[3,4-*b*][1,3]thiazine-7-carboxylate (**III**) via acylation at the N^4 atom. These data contradict those given in [4], according to which the product has the structure of methyl 7-oxo-2-phenyl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]thiazine-5-carboxylate (**IVa**) (Scheme 1). With the goal of elucidating the structure of the product formed by reaction of 1,2,4-triazole-5-thione (**Ia**) with dimethyl acetylenedicarboxylate (**IIa**) in methanol, we reproduced the procedure described in [6] and isolated a compound whose melting point and ^{1}H NMR spectrum coincided with the data given in [4, 6]. The structure of this compound was unambiguously established by X-ray analysis. We found that the condensation product is methyl 7-oxo-2-phenyl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]-thiazine-5-carboxylate (**IVa**).

The structure of molecule **IVa** is shown in figure. The bicyclic system $S^1N^1N^2N^3C^{1-5}$ is planar: deviations of atoms from the mean-square plane do not exceed 0.027 Å, and the dihedral angle between the six-membered $S^1N^1C^{1-4}$ ring and five-membered $N^1N^2N^3C^4C^5$ ring is as small as 1.6°. The C^6–C^{11} benzene ring and $C^{12}O^2O^3$ ester group lie almost in the fused ring plane: the corresponding dihedral angles are 1.9 and 2.3°. The bond lengths and bond angles in molecule **IVa** have standard values [7] (see figure).

We also examined reactions of 3-aryl-1,2,4-triazole-5-thiones **Ib**–**Id** having various substituents in the ben-

Scheme 1.



Ia, **IVa**, **IVe**, Ar = Ph; **Ib**, **IVb**, **IVf**, Ar = 4-FC_6H_4; **Ic**, **IVc**, **IVg**, Ar = 4-$MeOC_6H_4$; **Id**, **IVd**, **IVh**, Ar = 4-$O_2NC_6H_4$; **IIa**, **IVa**–**IVd**, R = COOMe; **IIb**, **IVe**–**IVh**, R = Ph.

1070-4280/05/4101-0108©2005 Pleiades Publishing, Inc.

zene ring on C^3 with dimethyl acetylenedicarboxylate (**IIa**) and methyl 3-phenylpropynoate (**IIb**). The best yields of compounds **IV** (66–72%) were obtained from 1,2,4-triazole-5-thiones **I** having donor groups in the aryl substituent (Ar = Ph, 4-$CH_3OC_6H_4$); products **IV** with acceptor groups in the aryl substituent (Ar = 4-$NO_2C_6H_4$, 4-FC_6H_4) were formed in slightly lower yields (58–69%).

Triazolo[3,2-*b*][1,3]thiazin-7-one **IVa** was brought into reactions with methyl *p*-toluenesulfonate, hydrogen peroxide, potassium hydroxide, and sulfuric acid (Scheme 2). Compound **IVa** did not change on fusion with an equimolar amount of methyl *p*-toluenesulfonate at 130–150°C (reaction time 1 h), while it decomposed under more severe conditions (170–200°C). Triazolothiazine **IVa** failed to react with hydrogen peroxide in acetic acid at 20°C, whereas raising the temperature to 50–100°C resulted in tarring. Treatment of **IVa** with potassium hydroxide in methanol at 20°C afforded potassium 3-phenyl-1,2,4-triazole-5-thiolate and acetylenedicarboxylic acid which were isolated as 3-phenyl-1,2,4-triazole-5-thione (**Ia**) and dimethyl acetylenedicarboxylate, respectively. When compound **IVa** was heated in boiling methanol in the presence of sulfuric acid, hydrolysis of the ester group occurred, and the product was 7-oxo-2-phenyl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]thiazine-5-carboxylic acid (**V**, yield 72%). This result indicates that triazolo-[3,2-*b*][1,3]thiazin-5-ones **IV** are stable in acid medium under moderate conditions.

It was also interesting to compare the reactivities of 2-aryl-2,3-dihydro-4*H*-[1,3]thiazino[3,2-*a*]benzimidazol-4-ones **VI** synthesized previously [8] and [1,2,4]triazolo-[3,2-*b*][1,3]thiazin-5-ones **IV** (Scheme 3). Treatment of compounds **VIa**–**VIc** with potassium hydroxide in aqueous–alcoholic medium at 20°C, followed by acidification with acetic acid gave 66–71% of 3-aryl-3-(1*H*-benzimidazol-2-ylsulfanyl)propionic acids **VIIa**–**VIIc**. The ^{1}H NMR spectra of **VIIa**–**VIIc** characteristically contained broadened singlets from the COOH and NH protons in the region δ 11.31–11.71 ppm. Thiazino[3,2-*a*]benzimidazol-4-ones **VIa**–**VIc** reacted with 30% hydrogen peroxide in acetic acid at 15°C to give products of decomposition of the 1,3-thiazine ring, benzimidazole-2-sulfonic acid (**VIII**) and 3-aryl-2-propenoic acids **IXa**–**IXc**. Opening of the 1,3-thiazine ring also occurred in an attempt to obtain quaternary salt by fusion of compound **VIa** with methyl *p*-toluenesulfonate; as a result, 1-(3-methyl-2-thioxo-2,3-dihydro-1*H*-benzimidazol-1-yl)-3-phenyl-2-propen-1-one (**XI**) was isolated. Presumably, salt **X** is formed as intermediate, but it is unstable owing to the presence of amide group in the vicinity of the positively charged quaternary nitrogen atom.

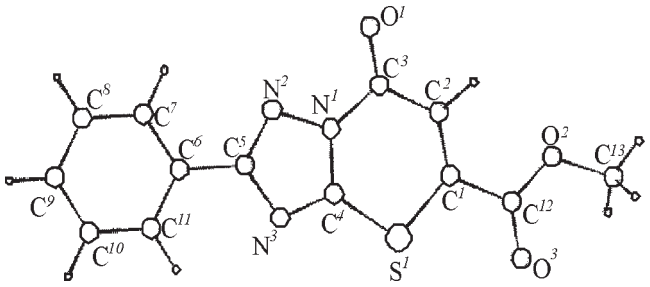
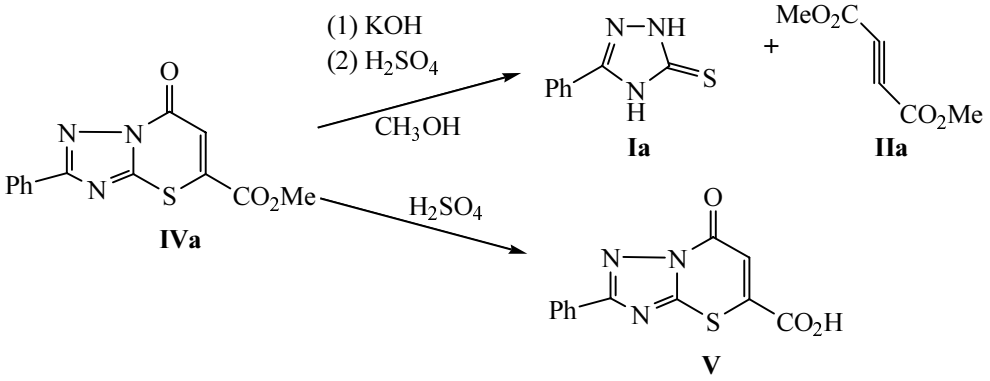
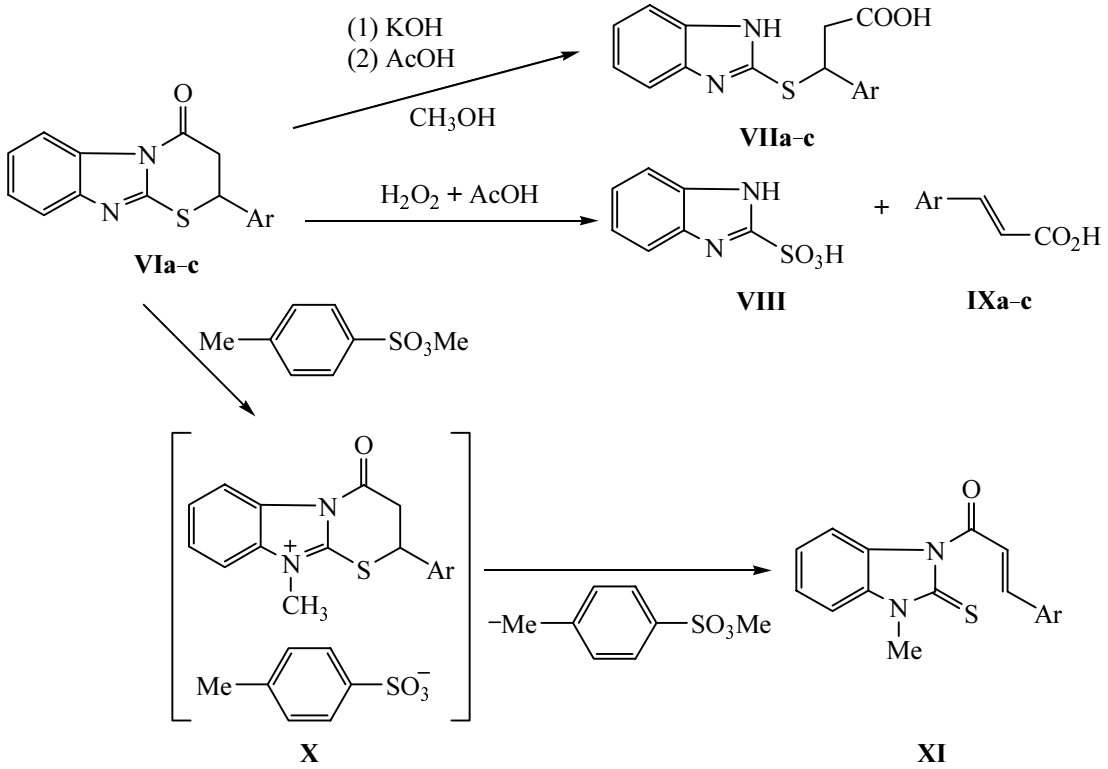


Fig. 1. Structure of the molecule of methyl 7-oxo-2-phenyl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]thiazine-5-carboxylate (**IVa**) according to the X-ray diffraction data (hydrogen atoms are not shown). Principal bond lengths (Å) and bond angles (deg): S^1–C^1 1.742(3), S^1–C^4 1.730(3), C^1–C^2 1.344(4), C^2–C^3 1.444(4), C^3–N^1 1.415(3), N^1–C^4 1.363(3), N^1–N^2 1.372(3), N^2–C^5 1.327(4), N^3–C^4 1.304(4), N^3–C^5 1.379(3), $C^1S^1C^4$ 99.2(1), $N^2N^1C^4$ 108.9(2), $C^3N^1C^4$ 128.4(2), $N^1N^2C^5$ 102.5(2), $C^4N^3C^5$ 103.0(2), $S^1C^1C^2$ 126.7(2), $C^1C^2C^3$ 125.8(3), $N^1C^3C^2$ 115.4(2), $S^1C^4N^1$ 124.4(2), $S^1C^4N^3$ 124.5(2), $N^1C^4N^3$ 111.1(2), $N^2C^5N^3$ 114.6(2).

Scheme 2.



Scheme 3.



VI, **VII**, **IX**, Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 3-$O_2NC_6H_4$ (**c**); **XI**, Ar = Ph.

We can conclude that both fused heterocyclic systems, [1,2,4]triazolo[3,2-*b*][1,3]thiazin-5-ones **IV** and 2-aryl-2,3-dihydro-4*H*-[1,3]thiazino[3,2-*a*]benzimidazol-4-ones **VI** tend to undergo transformations accompanied by opening of the 1,3-thiazine ring. On the other hand, compounds **IV** are more resistant to electrophilic agents, as compared to 2-aryl-2,3-dihydro-4*H*-[1,3]thiazino-[3,2-*a*]benzimidazol-4-ones **VI**. The stability of the former may be rationalized in terms of the reduced nucleophilicity of the nitrogen and sulfur atoms.

The structure of the isolated compounds was confirmed by the ^{1}H NMR spectra and elemental analyses.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz; DMSO-d_6 was used as solvent, and the chemical shifts were measured relative to TMS.

X-Ray diffraction study of a single crystal of compound **IVa** ($0.22\times0.22\times0.35$ mm) was performed at room temperature on an Enraf–Nonius CAD-4 automatic four-circle diffractometer (MoK_α irradiation, $\lambda = 0.71069$ Å, scan rate ratio $2\theta/\omega = 1.2$, θ_{max} 26°, spherical segment $0 \le h \le 8$, $0 \le k \le 18$, $-16 \le l \le 16$). Total of 2901 reflections were acquired, 2554 of which were symmetry independent ($R_{int} = 0.011$). Monoclinic crystals with the following unit cell parameters: $a = 7.260(1)$, $b = 14.881(4)$, $c = 12.116(4)$ Å; $\beta = 98.54(2)°$; $V = 1294.4(7)$ Å^3; $M = 287.3$; $Z = 4$; $d_{calc} = 1.47$ g/cm^3; $\mu = 2.48$ cm^{-1}; $F(000) = 592.6$; space group $P2_1/c$. The structure was solved by the direct method and was refined by the least-squares procedure in full-matrix anisotropic approxima-tion using CRYSTALS software package [9]. In the refinement, 1448 reflections with $I > 3(I)$ were used (181 refined parameters, the number of reflections per parameter was equal to 8.0). All hydrogen atoms were visualized from the difference synthesis of electron density, and they were included into the calculations with fixed positional and thermal parameters. Chebyshev's weight scheme [10] with five parameters (1.53, 1.29, and 1.17) was applied. The final divergence factors were $R = 0.046$ and $R_W = 0.048$, GOF = 1.157. The residual electron density from the Fourier difference series was 0.21 and –0.21 e/ Å^3. The absorption by the crystal was taken into account by the azimuthal scanning technique [11]. The complete set of crystallographic data for

compound **IVa** was deposited to the Cambridge Crystal Structure Database (entry no. CCDC 211 159).

5-Substituted 2-aryl-7*H*-[1,2,4]triazolo[3,2-*b*]-[1,3]thiazin-7-ones IVa–IVh (*general procedure*). Dimethyl acetylenedicarboxylate or methyl 3-phenylpropynoate, 0.012 mol, was added dropwise at 20°C to a solution of 0.01 mol of 3-aryl-1,2,4-triazole-5-thione in 25 ml of methanol, and the mixture was heated for 2 h under reflux. The mixture was cooled, and the precipitate was filtered off, washed with diethyl ether, dried, and recrystallized from acetic acid.

Methyl 7-oxo-2-phenyl-7*H*-[1,2,4]triazolo-[3,2-*b*][1,3]thiazine-5-carboxylate (IVa). Yield 2.01 g (70%), mp 196–198°C; published data: mp 196°C [4], 195–196°C [6]. ^{1}H NMR spectrum, δ, ppm: 3.99 s (3H, $COOCH_3$), 7.55 s (1H, 6-H), 7.57 m (3H, H_{arom}), 8.16 m (2H, H_{arom}). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 54.38 (OCH_3), 122.16 (C^p), 127.74 (C^o), 128.53 (C^i), 128.78 (C^m), 131.19 (C^6), 139.83 (C^7), 152.03 (C^2), 155.02 (C^{8a}), 161.32 (COO), 164.71 (C^5). Found, %: C 54.46; H 3.05; N 14.80. $C_{13}H_9N_3O_3S$. Calculated, %: C 54.35; H 3.16; N 14.63.

Methyl 2-(4-fluorophenyl)-7-oxo-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]thiazine-5-carboxylate (IVb). Yield 2.1 g (69%), mp 207–208°C. ^{1}H NMR spectrum, δ, ppm: 4.00 s (3H, $COOCH_3$), 7.41 m (2H, H_{arom}), 7.54 s (1H, 6-H), 8.23 m (2H, H_{arom}). Found, %: C 51.10; H 2.50; N 13.90. $C_{13}H_8FN_3O_3S$. Calculated, %: C 51.15; H 2.64; N 13.76.

Methyl 2-(4-methoxyphenyl)-7-oxo-7*H*-[1,2,4]-triazolo[3,2-*b*][1,3]thiazine-5-carboxylate (IVc). Yield 2.28 g (72%), mp 247–249°C. ^{1}H NMR spectrum, δ, ppm: 3.84 s (3H, CH_3O), 3.99 (3H, $COOCH_3$), 7.08 d (2H, H_{arom}, J = 9.1 Hz), 7.50 s (1H, 6-H), 8.10 d (2H, H_{arom}, J = 9.1 Hz). Found, %: C 52.86; H 3.41; N 13.52. $C_{14}H_{11}N_3O_4S$. Calculated, %: C 52.99; H 3.49; N 13.24.

Methyl 2-(4-nitrophenyl)-7-oxo-7*H*-[1,2,4]-triazolo[3,2-*b*][1,3]thiazine-5-carboxylate (IVd). Yield 1.93 g (58%), mp 230–232°C. ^{1}H NMR spectrum, δ, ppm: 4.01 (3H, $COOCH_3$), 7.58 s (1H, 6-H), 8.31 d (2H, H_{arom}, J = 8.8 Hz), 8.40 d (2H, H_{arom}, J = 8.8 Hz). Found, %: C 47.16; H 2.62; N 16.94. $C_{13}H_8N_4O_5S$. Calculated, %: C 46.99; H 2.43; N 16.86.

2,5-Diphenyl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]thiazin-7-one (IVe). Yield 2.01 g (66%), mp 218–220°C. ^{1}H NMR spectrum, δ, ppm: 7.29 s (1H, 6-H), 7.44–7.71 m (6H, H_{arom}), 7.86 d (2H, H_{arom}, J = 7.0 Hz), 8.17 d (2H, H_{arom}, J = 3.1 Hz). Found, %: C 66.75; H 3.51; N 13.98. $C_{17}H_{11}N_3OS$. Calculated, %: C 66.87; H 3.63; N 13.76.

2-(4-Fluorophenyl)-5-phenyl-7*H*-[1,2,4]triazolo-[3,2-*b*][1,3]thiazin-7-one (IVf). Yield 2.00 g (62%), mp 213–214°C. ^{1}H NMR spectrum, δ, ppm: 7.30–7.46 m (3H, H_{arom}), 7.57–7.76 m (3H, H_{arom}), 7.89 d (2H, H_{arom}, J = 7.2 Hz), 8.21 m (2H, H_{arom}). Found, %: C 63.11; H 2.92; N 13.19. $C_{17}H_{10}FN_3OS$. Calculated, %: C 63.15; H 3.12; N 13.00.

2-(4-Methoxyphenyl)-5-phenyl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]thiazin-7-one (IVg). Yield 2.28 g (68%), mp 248–250°C. ^{1}H NMR spectrum, δ, ppm: 3.83 s (3H, CH_3O), 7.09 d (2H, H_{arom}, J = 8.6 Hz), 7.24 s (1H, 6-H), 7.53–7.72 m (3H, H_{arom}), 7.82 m (2H, H_{arom}), 8.11 d (2H, H_{arom}, J = 8.6 Hz). Found, %: C 64.40; H 4.04; N 12.39. $C_{18}H_{13}N_3O_2S$. Calculated, %: C 64.46; H 3.91; N 12.53.

2-(4-Nitrophenyl)-5-phenyl-7*H*-[1,2,4]triazolo-[3,2-*b*][1,3]thiazin-7-one (IVh). Yield 1.89 g (54%), mp 244–246°C. ^{1}H NMR spectrum, δ, ppm: 7.37 s (1H, 6-H), 7.64 m (2H, H_{arom}), 7.87 d (2H, H_{arom}, J = 7.2 Hz), 8.16 m (2H, H_{arom}), 8.39 m (3H, H_{arom}). Found, %: C 58.32; H 2.91; N 16.18. $C_{17}H_{10}N_4O_3S$. Calculated, %: C 58.28; H 2.88; N 15.99.

Reaction of methyl 7-oxo-2-phenyl-7*H*-[1,2,4]-triazolo[3,2-*b*][1,3]thiazine-5-carboxylate (IVa) with potassium hydroxide. A solution of 0.019 mol of potassium hydroxide in 9 ml of water was added dropwise at 20°C to a solution of 0.009 mol of compound **IVa** in 20 ml of methanol, and the mixture was left to stand for 48 h. The mixture was diluted with 20 ml of water, 1.5 ml of 95% sulfuric acid was added, and the precipitate of 3-phenyl-1,2,4-triazole-5-thione (**Ia**) was filtered off, dried, and recrystallized from acetic acid. Yield of **Ia** 0.94 g (59%), mp 258–260°C; published data [2]: mp 256°C. Found, %: C 54.08; H 4.06; N 23.81. $C_8H_7N_3S$. Calculated, %: C 54.22; H 3.98; N 23.71. The filtrate was evaporated, 20 ml of methanol was added to the residue, and the mixture was kept for 4 days at 20°C. The mixture was evaporated, the residue was treated with chloroform (2 × 10 ml), the combined extracts were evaporated, and the residue was distilled under reduced pressure (water-jet pump) to isolate 0.5 g of dimethyl acetylenedicarboxylate, bp 100–105°C (20 mm), n_D^{25} = 1.4454; published data [13]: bp 95–98°C (19 mm), n_D^{25} = 1.4450. Found, %: C 50.93; H 4.38. $C_6H_6O_4$. Calculated, %: C 50.71; H 4.26.

7-Oxo-2-phenyl-7*H*-[1,2,4]triazolo[3,2-*b*][1,3]-thiazine-5-carboxylic acid (V). Compound **IVa**, 0.003 mol, was dissolved in 10 ml of methanol, 0.5 ml of 95% sulfuric acid was added dropwise at 20°C, and the mixture was heated for 24 h under reflux. The mixture was cooled and diluted with 10 ml of water, and the precipitate was filtered off. Yield 0.59 g (72%), mp 254–256°C. ^{1}H NMR spectrum, δ, ppm: 7.46 s (1H, 6-H), 7.52–7.70 m (3H, H_{arom}), 8.16 m (2H, H_{arom}), 10.5 br.s (1H, COOH). Found, %: C 52.88; H 2.65; N 15.21. $C_{12}H_7N_3O_3S$. Calculated, %: C 52.74; H 2.58; N 15.38.

3-(1*H*-Benzimidazol-2-ylsulfanyl)-3-arylpropionic acids VIIa–VIIc (*general procedure*). A solution of 0.011 mol of potassium hydroxide in 5 ml of water was added at 20°C to a solution of 0.01 mol of compound **VIa**–**VIc** in 20 ml of ethanol, and the mixture was left to stand for 24 h. The mixture was diluted with 20 ml of water and filtered, 1 ml of acetic acid was added to the filtrate, and the precipitate was filtered off and dried.

3-(1*H*-Benzimidazol-2-ylsulfanyl)-3-phenyl-propionic acid (VIIa). Yield 2.12 g (71%), mp 260–265°C. ^{1}H NMR spectrum, δ, ppm: 3.10–3.25 m (2H, CH_2), 5.34 m (1H, SCH), 7.12 m (4H, H_{arom}), 7.35 m (3H, C_6H_5), 7.48 m (2H, C_6H_5), 11.31 br.s (2H, NH, COOH). Found, %: C 64.30; H 4.58; N 9.52. $C_{16}H_{14}N_2O_2S$. Calculated, %: C 64.41; H 4.73; N 9.39.

3-(1*H*-Benzimidazol-2-ylsulfanyl)-3-(4-methoxy-phenyl)propionic acid (VIIb). Yield 2.49 g (76%), mp 280–285°C. ^{1}H NMR spectrum, δ, ppm: 3.06–3.36 m (2H, CH_2), 3.72 s (3H, CH_3O), 5.27 m (1H, SCH), 6.86 d (2H, H_{arom}, J = 8.2 Hz), 7.11 m (4H, H_{arom}), 7.41 d (2H, H_{arom}, J = 8.2 Hz), 11.66 br.s (2H, NH, COOH). Found, %: C 62.34; H 4.80; N 8.76. $C_{17}H_{16}N_2O_3S$. Calculated, %: C 62.18; H 4.91; N 8.53.

3-(1*H*-Benzimidazol-2-ylsulfanyl)-3-(3-nitro-phenyl)propionic acid (VIIc). Yield 2.26 g (66%), mp 290–295°C. ^{1}H NMR spectrum, δ, ppm: 3.11–3.28 m (2H, CH_2), 5.46 m (1H, SCH), 7.13 m (4H, H_{arom}), 7.69 t (1H, H_{arom}, J = 8.1 Hz), 7.90 d (1H, H_{arom}, J = 8.1 Hz), 8.27 d (1H, H_{arom}, J = 8.1 Hz), 8.46 s (1H, H_{arom}, J = 8.1 Hz), 11.75 br.s (2H, NH, COOH). Found, %: C 56.12; H 3.66; N 12.41. $C_{16}H_{13}N_3O_4S$. Calculated, %: C 55.97; H 3.82; N 12.24.

Reaction of 2-aryl-2,3-dihydro-4*H*-[1,3]thiazino-[3,2-*a*]benzimidazol-4-ones VIa–VIc with hydrogen peroxide. To a solution of 5 mmol of compound **VIa**–**VIc** in 5 ml of acetic acid we added at 15°C 2.5 ml of 30% hydrogen peroxide, and the mixture was left to stand for 24 h. The precipitate of benzimidazole-2-sulfonic acid (**VIII**) was filtered off and dried. Yield 0.51 g (59%), mp 330–335°C; published data [14]: mp 365°C. Found, %: C 42.67; H 2.95; N 14.28; S 16.32. $C_7H_6N_2O_3S$. Calculated, %: C 42.42; H 3.05; N 14.13; S 16.18. The filtrate was evaporated at 20°C, and the residue, compound **IXa**–**IXc**, was dried and recrystallized from ethanol.

3-Phenyl-2-propenoic acid (IXa). Yield 0.44 g (60%), mp 130–132°C; published data [15]: mp 133–134°C. Found, %: C 73.18; H 5.63. $C_9H_8O_2$. Calculated, %: C 72.96; H 5.44.

3-(4-Methoxyphenyl)-2-propenoic acid (IXb). Yield 0.60 g (67%), mp 170–173°C; published data [16]: mp 175–180°C. Found, %: C 67.59; H 5.42. $C_{10}H_{10}O_3$. Calculated, %: C 67.41; H 5.66.

3-(3-Nitrophenyl)-2-propenoic acid (IXc). Yield 0.54 g (56%), mp 199–202°C; published data [17]: mp 202–204°C. Found, %: C 56.09; H 3.51; N 7.38. $C_9H_7NO_4$. Calculated, %: C 55.96; H 3.65; N 7.25.

Reaction 2-aryl-2,3-dihydro-4*H*-[1,3]thiazino-[3,2-*a*]benzimidazol-4-one (VIa) with methyl *p*-toluenesulfonate. A mixture of 0.01 mol of compound **VIa** and 0.011 mol of methyl *p*-toluenesulfonate was heated for 0.5 h at 100°C, cooled, and dissolved in 10 ml of ethanol. A solution of 4 g of $NaHCO_3$ in 30 ml of water was added, and the mixture was extracted with chloroform (2 × 10 ml). The combined extracts were dried over $MgSO_4$ and evaporated, and the crystalline residue, 1-(3-methyl-2-thioxo-2,3-dihydro-1*H*-benzimidazol-1-yl)-3-phenyl-2-propen-1-one (**XI**), was dried and recrystallized from ethanol. Yield 1.88 g (64%), mp 131–133°C. ^{1}H NMR spectrum, δ, ppm: 3.73 s (3H, NCH_3), 7.30–7.43 m (2H, H_{arom}), 7.52 m (4H, H_{arom}), 7.74 m (2H, H_{arom}), 7.81 d (1H, ArC**H**=, J = 12.3 Hz), 7.89 d (1H, H_{arom}, J = 7.1 Hz), 8.09 d (1H, =CHCO, J = 12.3 Hz). Found, %: C 69.07; H 4.91; N 9.35. $C_{17}H_{14}N_2OS$. Calculated, %: C 69.36; H 4.79; N 9.52.

REFERENCES

1. Clayton, J.P., O'Hanlon, P.J., and King, T.G., *J. Chem. Soc., Perkin Trans. 1*, 1980, no. 7, p. 1352.
2. Heindel, N.D. and Reid, J.R., *J. Org. Chem*., 1980, vol. 45, p. 2479.
3. Britsun, V.N., Pirozhenko, V.V., and Lozinskii, M.O., *Russ. J. Org. Chem*., 2001, vol. 37, p. 1056.
4. Upadhyaya, V.P. and Srinivasan, V.R., *Indian J. Chem., Sect. B*, 1978, vol. 16, p. 737.

5. Heravi, M.M., Montazeri, N., Rahimizaden, M., Bakavoli, M., and Ghassemzaden, M., *Monatsh. Chem*., 2001, vol. 132, p. 1225.
6. Heravi, M.M., Beheshtina, Y.Sh., Oskooie, H.A., and Nami, N., *Indian J. Heterocycl. Chem*., 1999, vol. 8, p. 245.
7. Allen, F.H., Kennard, O., Watson, D.G., Brammer, L., Orpen, A.G., and Tailor, R., *J. Chem. Soc. Perkin Trans. 2*, 1987, no. 12, p. S1.
8. Britsun, V.N. and Lozinskii, M.O., *Khim. Geterotsikl. Soedin*., 2003, no. 7, p. 1103.
9. Watkin, D.J., Prout, C.K., Carruthers, J.R., and Betteridge, P.W., *CRYSTALS, Issue 10*, Chemical Crystallography Laboratory, Oxford Univ., 1996.
10. Carruthers, J.R. and Watkin, D.J., *Acta Crystallogr., Sect. A*, 1979, vol. 35, p. 698.
11. North, A.C.T., Phillips, D.C., and Mathews, F.S., *Acta Crystallogr., Sect. A*, 1968, vol. 24, p. 351.
12. Dhaka, K.S., Mohan, J., Chadha, V.K., and Pujari, H.K., *Indian J. Chem*., 1974, vol. 12, p. 485.
13. Huntress, E.H., Lesslie, T.E., and Bornstein, J., *Organic Syntheses*, Noland, W.E., Ed., New York: Wiley, 1963, collect. vol. 4, p. 329. Translated under the title *Sintezy organicheskikh preparatov*, Moscow: Inostrannaya Literatura, 1953, collect. vol. 4, p. 186.
14. Everett, J.G., *J. Chem. Soc*., 1930, p. 2402.
15. *Beilsteins Handbuch der organischen Chemie*, vol. IX, p. 573.
16. *Beilsteins Handbuch der organischen Chemie*, vol. X, p. 298.
17. *Beilsteins Handbuch der organischen Chemie*, vol. IX, p. 605.