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Synthesis of Heterocycles from Arylation Products of Unsaturated Compounds: XIII.* 5-R^1-Benzyl-2-(R^2-2-pyridylimino)thiazolidin-4-ones

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Abstract—Meerwein reactions of arenediazonium bromides with methyl and ethyl acrylates gave 3-aryl-2-bromopropionic acid esters which were subjected to cyclocondensation with *N*-(2-pyridyl)- and *N*-(6-methyl-2-pyridyl)thioureas to obtain 5-R^1-benzyl-2-(R^2-2-pyridylimino)thiazolidin-4-ones. The latter were shown to exist in solution as *E* isomers of the imino form.

The thiazolidine ring is a promising and effective structural fragment for the design of biologically active compounds [2–4]. Methods of synthesis of combinatorial libraries of 4-thiazolidinone derivatives have been developed [5–7]. In the recent time, 5-R-benzylthiazolidine-2,4-diones attract increased interest, and some compounds of this series have already been introduced into medical practice as antidiabetic agents [8–11]. By contrast, 2-imino derivatives of 4-thiazolidinone have been studied to a lesser extent, despite the possibility for introducing an additional pharmacophoric fragment into the 2-position. A probable reason is the limited set of convenient methods for the synthesis of such compounds with various substituents in both the thiazolidine ring and the imino fragment. A general procedure for the synthesis of 2-iminothiazolidin-4-ones is based on cyclocondensation of mono- and disubstituted thioureas with α-halo acids and their esters [2, 12]. However, the application of this procedure is limited due to the fact that the cyclization is selective only when the nitrogen atoms in thioureas are characterized by considerably different nucleophilicities [13] or when other structural factors are favorable (e.g., hydrogen bond formation) [14].

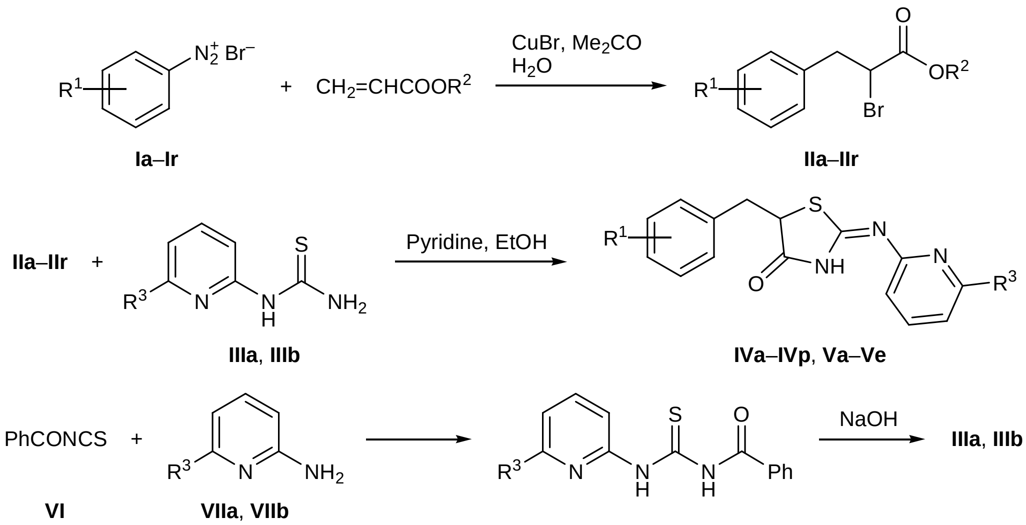
5-Benzyl-2-iminothiazolidin-4-ones can be prepared by reaction of 3-aryl-2-bromopropionic acid esters with thiourea [15, 16]. In the present work we made an attempt to synthesize 5-benzylthiazolidin-4-ones containing a 2-pyridylimino group in position *2*. We found that methyl and ethyl 3-aryl-2-bromopropionates **IIa**–**IIr** react with *N*-(2-pyridyl)thioureas **IIIa** and **IIIb** to give the corresponding 5-R^1-benzyl-2-(R^2-2-pyridylimino)thiazolidin-4-ones **IVa**–**IVp** and **Va**–**Ve** (Scheme 1). The reactions were carried out by heating the reactants for a short time in alcohol in the presence of a base. No elimination of hydrogen bromide from esters **IIa**–**IIr** (with formation of cinnamic acid derivatives) occurred under these conditions. Compounds **IVa**–**IVp** and **Va**–**Ve** were isolated in high yields as colorless crystalline substances which were sparingly soluble in alcohol, dioxane, and DMF. It should be noted that some 2-(2-pyridylimino)thiazolidin-4-ones were found to exhibit antibacterial activity [13].

Esters **IIa**–**IIr** were prepared by reaction of arenediazonium bromides **Ia**–**Ir** with methyl or ethyl acrylate according to Meerwein [17]. The reactions were exothermic, and they were carried out at room temperature or on slight heating. Compounds **IIa**–**IIr** can be distilled under reduced pressure; they were isolated as light yellow liquids or crystalline substances. *N*-(2-Pyridyl)thioureas **IIIa** and **IIIb** were synthesized by the known method [18] from benzoyl isothiocyanate (**VI**) and 2-aminopyridines **VIIa** and **VIIb**.

2-Aryliminothiazolidin-4-ones, which are structurally related to compounds **IVa**–**IVp** and **Va**–**Ve**, are known to exist in solution as mixtures of amino and imino tautomers, and the imino form gives rise to *Z*,*E* isomerism [16, 19–21]. According to the ^{1}H NMR data, thiazolidinones **IVa**–**IVp** and **Va**–**Ve** exist in solution as one isomer of the imino form. This conclu-

* For communication XII, see [1].

Scheme 1.



I, R^1 = 2-Me (**a**), 4-F (**b**), 2-Cl (**c**), 3-CF_3 (**d**), 3-NO_2 (**e**), 2,4-Cl_2 (**f**), 2,5-Cl_2 (**g**), 4-Me-3-Cl (**h**), H (**i**), 3-Me (**j**), 4-Me (**k**), 4-MeO (**l**), 3-Cl (**m**), 4-Cl (**n**), 4-Br (**o**), 4-EtO (**p**), 2,3-Cl_2 (**q**), 3,4-Cl_2 (**r**); **II**, R^2 = Me, R^1 = 2-Me (**a**), 4-F (**b**), 2-Cl (**c**), 3-CF_3 (**d**), 3-NO_2 (**e**), 2,4-Cl_2 (**f**), 2,5-Cl_2 (**g**), 4-Me-3-Cl (**h**); R^2 = Et, R^1 = H (**i**), 3-Me (**j**), 4-Me (**k**), 4-MeO (**l**), 3-Cl (**m**), 4-Cl (**n**), 4-Br (**o**), 4-EtO (**p**), 2,3-Cl_2 (**q**), 3,4-Cl_2 (**r**); **III**, **VII**, R^3 = H (**a**), 6-Me (**b**); **IV**, R^3 = H, R^1 = H (**a**), 2-Me (**b**), 3-Me (**c**), 4-Me (**d**), 4-MeO (**e**), 4-EtO (**f**), 4-F (**g**), 2-Cl (**h**), 3-Cl (**i**), 4-Cl (**j**), 4-Br (**k**), 3-CF_3 (**l**), 3-NO_2 (**m**), 2,3-Cl_2 (**n**), 2,5-Cl_2 (**o**), 3,4-Cl_2 (**p**); **V**, R^3 = Me, R^1 = H (**a**), 3-CF_3 (**b**), 2,4-Cl_2 (**c**), 3,4-Cl_2 (**d**), 3-Cl-4-Me (**e**).

sion is confirmed by comparison of the spectral data of these compounds with those of 2-aryliminothiazolidin-4-ones [16]. Presumably, compounds **IVa**–**IVp** and **Va**–**Ve** are the corresponding *E* isomers, for spatial arrangement of the sulfur atom and nitrogen atom in the pyridine ring (as well as of the methyl group in the pyridine ring of **Va**–**Ve**) in the *Z* isomers is less favorable.

Thus accessible bromoarylation products **IIa**–**IIr** obtained from acrylic acid esters are convenient reagents for the synthesis of 4-thiazolidinone derivatives containing a substituted benzyl group in position *5* and a 2-pyridylimino substituent in position *2*.

EXPERIMENTAL

The ^1H NMR spectra were recorded on Bruker DRX 500 (500 MHz; compounds **IIg**, **Va**, **Vb**), Bruker AM-300 (300 MHz; **IIe**, **IIj**–**IIm**, **IIq**, **IIr**, **IVa**, **IVk**, **IVm**), and Bruker WM-250 instruments (250 MHz; **IVc**–**IVe**, **IVh**) using DMSO-d_6 or DMSO-d_6–CCl_4 (1 : 3) (**IIg**, **Va**, **Vb**) as solvent; the chemical shifts were measured relative to the residual proton signal of the solvent (DMSO, δ 2.50 ppm).

3-Aryl-2-bromopropionic acid esters IIa–IIr (*general procedure***).** A solution of arenediazonium bromide **Ia**–**Ir** (prepared by diazotization of 0.2 mol of the corresponding aromatic amine) was cooled to 0–5°C and added dropwise under stirring to a solution of 0.22 mol of methyl or ethyl acrylate and 3 g of CuBr in 150 ml of acetone. The temperature was maintained in the range from 20 to 40°C so that nitrogen evolved at a rate of 2–3 bubbles per second. When nitrogen no longer evolved, the mixture was diluted with 200 ml of water, and the organic phase was separated and dried over $MgSO_4$. The solvent was evaporated, and the residue was distilled under reduced pressure. Compounds **IIi** and **IIn** were described previously [15, 22].

Methyl 2-bromo-3-(2-methylphenyl)propionate (IIa). Yield 33%, bp 128°C (2 mm), n_D^{20} = 1.5416. Found, %: Br 31.01. $C_{11}H_{13}BrO_2$. Calculated, %: Br 31.08.

Methyl 2-bromo-3-(4-fluorophenyl)propionate (IIb). Yield 40%, bp 113–114°C (2 mm), n_D^{20} = 1.5223. Found, %: C 46.25; H 3.90. $C_{10}H_{10}BrFO_2$. Calculated, %: C 46.00; H 3.86.

Methyl 2-bromo-3-(2-chlorophenyl)propionate (IIc). Yield 47%, bp 128–130°C (2 mm), n_D^{20} = 1.5548. Found, %: Br + Cl 41.50. $C_{10}H_{10}BrClO_2$. Calculated, %: Br + Cl 41.56.

Methyl 2-bromo-3-(3-trifluoromethylphenyl)-propionate (IId). Yield 42%, bp 118–120°C (2 mm), n_D^{20} = 1.4922. Found, %: C 42.34; H 3.08. $C_{11}H_{10}BrF_3O_2$. Calculated, %: C 42.47; H 3.24.

Methyl 2-bromo-3-(3-nitrophenyl)propionate (IIe). Yield 46%, mp 101–102°C (from ethanol) [16]. ^{1}H NMR spectrum, δ, ppm: 3.33 d.d (1H, CH_2, J = 14.0, 8.1 Hz), 3.57 d.d (1H, CH_2, J = 14.0, 6.6 Hz), 3.73 s (3H, OMe), 4.80 t (1H, CH), 7.59 t (1H, H_{arom}), 7.73 d (1H, H_{arom}), 8.11 d (1H, H_{arom}), 8.20 s (1H, H_{arom}).

Methyl 2-bromo-3-(2,4-dichlorophenyl)propionate (IIf). Yield 59%, bp 168–171°C (2 mm), mp 74–75°C (from ethanol). Found, %: Br + Cl 48.20. $C_{10}H_9BrCl_2O_2$. Calculated, %: Br + Cl 48.34.

Methyl 2-bromo-3-(2,5-dichlorophenyl)propionate (IIg). Yield 48%, bp 172–174°C (2 mm), mp 61°C (from ethanol). ^{1}H NMR spectrum, δ, ppm: 3.35 d.d (1H, CH_2, J = 14.4, 8.2 Hz), 3.51 d.d (1H, CH_2, J = 14.4, 7.2 Hz), 3.75 s (3H, OMe), 4.63 t (1H, CH), 7.29 d.d (1H, H_{arom}, ^4J = 2.6, ^3J = 8.6 Hz), 7.36–7.40 m (2H, H_{arom}). Found, %: Br + Cl 48.27. $C_{10}H_9BrCl_2O_2$. Calculated, %: Br + Cl 48.34.

Methyl 2-bromo-3-(3-chloro-4-methylphenyl)-propionate (IIh). Yield 29%, bp 144–146°C (2 mm), n_D^{20} = 1.5521. Found, %: Br+Cl 39.41. $C_{11}H_{12}BrClO_2$. Calculated, %: Br+Cl 39.56.

Ethyl 2-bromo-3-(3-methylphenyl)propionate (IIj). Yield 41%, bp 138°C (2 mm), n_D^{20} = 1.5333 [15]. ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, Me), 2.30 s (3H, Me), 3.14 d.d (1H, CH_2, J = 14.1, 7.8 Hz), 3.35 d.d (1H, CH_2, J = 14.1, 8.7 Hz), 4.13 q (2H, OCH_2), 4.54 t (1H, CH), 6.98–7.20 m (4H, H_{arom}).

Ethyl 2-bromo-3-(4-methylphenyl)propionate (IIk). Yield 37%, bp 149°C (2 mm), n_D^{20} = 1.5343 [15]. ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, Me), 2.30 s (3H, Me), 3.14 d.d (1H, CH_2, J = 13.8, 6.6 Hz), 3.34 d.d (1H, CH_2, J = 13.8, 9.0 Hz), 4.12 d.q (2H, OCH_2), 4.52 t (1H, CH), 7.07 d (2H, H_{arom}, J = 7.8 Hz), 7.11 d (2H, H_{arom}).

Ethyl 2-bromo-3-(4-methoxyphenyl)propionate (IIl). Yield 47%, bp 136–138°C (2 mm), n_D^{20} = 1.5335 [16]. ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, Me), 3.12 d.d (1H, CH_2, J = 13.8, 8.1 Hz), 3.31 d.d (1H, CH_2, J = 13.8, 9.3 Hz), 3.75 s (3H, MeO), 4.12 d.q (2H, OCH_2), 4.51 t (1H, CH), 6.80 d (2H, H_{arom}, J = 9.0 Hz), 7.14 d (2H, H_{arom}).

Ethyl 2-bromo-3-(3-chlorophenyl)propionate (IIm). Yield 43%, bp 141–143°C (2 mm), n_D^{20} = 1.5391. ^{1}H NMR spectrum, δ, ppm: 1.22 t (3H, Me), 3.19 d.d (1H, CH_2, J = 14.1, 7.2 Hz), 3.40 d.d (1H, CH_2, J = 14.1, 8.1 Hz), 4.15 d.q (2H, OCH_2), 4.65 t (1H, CH), 7.18–7.35 m (4H, H_{arom}). Found, %: Br + Cl 39.61. $C_{11}H_{12}BrClO_2$. Calculated, %: Br + Cl 39.56.

Ethyl 2-bromo-3-(4-bromophenyl)propionate (IIo). Yield 53%, bp 162–165°C (2 mm), n_D^{20} = 1.5574. Found, %: Br 47.27. $C_{11}H_{12}Br_2O_2$. Calculated, %: Br 47.56.

Ethyl 2-bromo-3-(4-ethoxyphenyl)propionate (IIp). Yield 45%, bp 151–153°C (2 mm), mp 28–30°C (from ethanol). Found, %: C 51.72; H 5.63. $C_{13}H_{17}BrO_3$. Calculated, %: C 51.84; H 5.69.

Ethyl 2-bromo-3-(2,3-dichlorophenyl)propionate (IIq). Yield 56%, bp 178–180°C (2 mm), n_D^{20} = 1.5542. ^{1}H NMR spectrum, δ, ppm: 1.23 t (3H, Me), 3.40 d.d (1H, CH_2, J = 14.6, 8.1 Hz), 3.57 d.d (1H, CH_2, J = 14.6, 7.8 Hz), 4.17 d.q (2H, OCH_2), 4.65 t (1H, CH), 7.24– 7.35 m (2H, H_{arom}), 7.48 d.d (1H, H_{arom}, ^4J = 1.5, ^3J = 7.5 Hz). Found, %: Br+Cl 46.08. $C_{11}H_{11}BrCl_2O_2$. Calculated, %: Br + Cl 46.26.

Ethyl 2-bromo-3-(3,4-dichlorophenyl)propionate (IIr). Yield 53%, bp 175–177°C (2 mm), n_D^{20} = 1.5530. ^{1}H NMR spectrum, δ, ppm: 1.23 t (3H, Me), 3.17 d.d (1H, CH_2, J = 13.8, 6.9 Hz), 3.39 d.d (1H, CH_2, J = 13.8, 7.2 Hz), 4.16 d.q (2H, OCH_2), 4.68 t (1H, CH), 7.24 d (1H, H_{arom}, J = 8.1 Hz), 7.46 d (1H, H_{arom}, J = 8.1 Hz), 7.51 s (1H, H_{arom}). Found, %: Br + Cl 46.12. $C_{11}H_{11}BrCl_2O_2$. Calculated, %: Br + Cl 46.26.

5-R-Benzyl-2-(2-pyridylimino)thiazolidin-4-ones IVa–IVp (*general procedure*). Ester **II**, 0.01 mol, and pyridine, 1 ml, were added to a solution of 0.01 mol (1.53 g) of *N*-(2-pyridyl)thiourea (**IIIa**) in 10 ml of ethanol. The mixture was heated for 0.5 h under reflux and cooled, and the precipitate was filtered off and recrystallized from DMF–ethanol. Compounds **Va**–**Ve** were synthesized in a similar way using *N*-(6-methyl-2-pyridyl)thiourea (**IIIb**).

5-Benzyl-2-(2-pyridylimino)thiazolidin-4-one (IVa). Yield 73%, mp 217–218°C. ^{1}H NMR spectrum, δ, ppm: 3.00 d.d (1H, CH_2, J = 14.1, 10.2 Hz), 3.43 d.d (1H, CH_2, J = 14.1, 4.0 Hz), 4.54 d.d (1H, CH), 7.10 t (2H, 3-H, 5-H, pyridine), 7.22–7.34 m (5H, H_{arom}), 7.78 t (1H, 4-H, pyridine), 8.34 d (1H, 6-H, pyridine), 11.92 br.s (1H, NH). Found, %: C 63.44; H 4.55; N 15.02. $C_{15}H_{13}N_3OS$. Calculated, %: C 63.58; H 4.62; N 14.83.

5-(2-Methylbenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVb). Yield 70%, mp 222.5–223.5°C. Found, %: C 64.86; H 4.79; N 14.12. $C_{16}H_{15}N_3OS$. Calculated, %: C 64.62; H 5.08; N 14.13.

5-(3-Methylbenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVc). Yield 69%, mp 176–177°C. ^{1}H NMR spectrum, δ, ppm: 2.32 s (1H, Me), 2.88 d.d (1H, CH_2, *J* = 14.5, 10.1 Hz), 3.42 d.d (1H, CH_2, *J* = 14.5, 3.5 Hz), 4.34 d.d (1H, CH), 7.00–7.12 m (4H, H_{arom}), 7.18 t (2H, 3-H, 5-H, pyridine), 7.73 t (1H, 4-H, pyridine), 8.31 d (1H, 6-H, pyridine), 11.90 br.s (1H, NH). Found, %: C 64.88; H 5.01; N 13.95. $C_{16}H_{15}N_3OS$. Calculated, %: C 64.62; H 5.08; N 14.13.

5-(4-Methylbenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVd). Yield 81%, mp 242–243°C. ^{1}H NMR spectrum, δ, ppm: 2.30 s (3H, Me), 2.90 d.d (1H, CH_2, *J* = 14.0, 10.2 Hz), 3.39 d.d (1H, CH_2, *J* = 14.0, 3.8 Hz), 4.32 d.d (1H, CH), 7.05 t (2H, 3-H, 5-H, pyridine), 7.09 d (2H, H_{arom}, *J* = 8.0 Hz), 7.15 d (2H, H_{arom}), 7.73 t (1H, 4-H, pyridine), 8.30 d (1H, 6-H, pyridine), 11.87 br.s (1H, NH). Found, %: C 64.83; H 5.34; N 14.20. $C_{16}H_{15}N_3OS$. Calculated, %: C 64.62; H 5.08; N 14.13.

5-(4-Methoxybenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVe). Yield 77%, mp 208–210°C. ^{1}H NMR spectrum, δ, ppm: 2.89 d.d (1H, CH_2, *J* = 14.3, 10.1 Hz), 3.36 d.d (1H, CH_2, *J* = 14.3, 3.6 Hz), 3.75 s (1H, MeO), 4.31 m (1H, CH), 6.83 d (2H, H_{arom}, *J* = 8.2 Hz), 7.06 t (2H, 3-H, 5-H, pyridine), 7.18 d (2H, H_{arom}), 7.73 t (1H, 4-H, pyridine), 8.31 d (1H, 6-H, pyridine), 11.87 br.s (1H, NH). Found, %: C 61.19; H 5.08; N 13.13. $C_{16}H_{15}N_3O_2S$. Calculated, %: C 61.32; H 4.82; N 13.41.

5-(4-Ethoxybenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVf). Yield 67%, mp 207–208°C. Found, %: C 62.48; H 5.08; N 12.63. $C_{17}H_{17}N_3O_2S$. Calculated, %: C 62.37; H 5.23; N 12.83.

5-(4-Fluorobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVg). Yield 72%, mp 234–235°C. Found, %: C 59.69; H 4.17; N 14.20. $C_{15}H_{12}FN_3OS$. Calculated, %: C 59.79; H 4.01; N 13.94.

5-(2-Chlorobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVh). Yield 65%, mp 217–218°C. ^{1}H NMR spectrum, δ, ppm: 3.03 d.d (1H, CH_2, *J* = 14.5, 10.2 Hz), 3.63 d.d (1H, CH_2, *J* = 14.5, 4.5 Hz), 4.39 m (1H, CH), 7.02–7.14 m (2H, 3-H, 5-H, pyridine), 7.25–7.35 m (2H, H_{arom}), 7.36–7.44 m (2H, H_{arom}), 7.74 t (1H, 4-H, pyridine), 8.31 d (1H, 6-H, pyridine), 12.03 br.s (1H, NH). Found, %: C 56.62; H 4.05; N 13.40. $C_{15}H_{12}ClN_3OS$. Calculated, %: C 56.69; H 3.81; N 13.22.

5-(3-Chlorobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVi). Yield 69%, mp 192–193°C. Found, %: C 56.65; H 3.96; N 13.12. $C_{15}H_{12}ClN_3OS$. Calculated, %: C 56.69; H 3.81; N 13.22.

5-(4-Chlorobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVj). Yield 75%, mp 239–240°C. Found, %: C 56.46; H 3.93; N 13.32. $C_{15}H_{12}ClN_3OS$. Calculated, %: C 56.69; H 3.81; N 13.22.

5-(4-Bromobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVk). Yield 63%, mp 252–253°C. ^{1}H NMR spectrum, δ, ppm: 3.02 d.d (1H, CH_2, *J* = 14.2, 10.1 Hz), 3.38 d.d (1H, CH_2, *J* = 14.2, 4.3 Hz), 4.53 d.d (1H, CH), 7.05–7.11 m (2H, 3-H, 5-H, pyridine), 7.25 d (2H, H_{arom}, *J* = 8.0 Hz), 7.51 d (2H, H_{arom}), 7.79 t (1H, 4-H, pyridine), 8.33 d (1H, 6-H, pyridine), 11.98 br.s (1H, NH). Found, %: C 49.89; H 3.21; N 11.60. $C_{15}H_{12}BrN_3OS$. Calculated, %: C 49.74; H 3.34; N 11.60.

2-(2-Pyridylimino)-5-(3-trifluoromethylbenzyl)-thiazolidin-4-one (IVl). Yield 79%, mp 204–205°C. Found, %: C 54.98; H 3.40; N 11.94. $C_{16}H_{12}F_3N_3OS$. Calculated, %: C 54.70; H 3.44; N 11.96.

5-(3-Nitrobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVm). Yield 75%, mp 231–232°C. ^{1}H NMR spectrum, δ, ppm: 3.26 d.d (1H, CH_2, *J* = 14.1, 9.0 Hz), 3.51 d.d (1H, CH_2, *J* = 14.1, 4.5 Hz), 4.63 d.d (1H, CH), 7.11 t (2H, 3-H, 5-H, pyridine), 7.61 t (1H, 5-H, C_6H_4), 7.72–7.81 m (2H, 4-H, pyridine, and 6-H, C_6H_4), 8.10 d (1H, 4-H, C_6H_4), 8.17 s (1H, 2-H, C_6H_4), 8.33 d (1H, 6-H, pyridine), 12.05 br.s (1H, NH). Found, %: C 54.83; H 3.83; N 16.99. $C_{15}H_{12}N_4O_3S$. Calculated, %: C 54.87; H 3.68; N 17.06.

5-(2,3-Dichlorobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVn). Yield 81%, mp 264–265°C. Found, %: C 51.38; H 2.97; N 12.09. $C_{15}H_{11}Cl_2N_3OS$. Calculated, %: C 51.15; H 3.15; N 11.93.

5-(2,5-Dichlorobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVo). Yield 83%, mp 222–223°C. Found, %: C 51.01; H 3.11; N 12.11. $C_{15}H_{11}Cl_2N_3OS$. Calculated, %: C 51.15; H 3.15; N 11.93.

5-(3,4-Dichlorobenzyl)-2-(2-pyridylimino)thiazolidin-4-one (IVp). Yield 78%, mp 232–233°C. Found, %: C 51.22; H 2.98; N 11.81. $C_{15}H_{11}Cl_2N_3OS$. Calculated, %: C 51.15; H 3.15; N 11.93.

5-Benzyl-2-(6-methyl-2-pyridylimino)thiazolidin-4-one (Va). Yield 75%, mp 236–237°C. ^{1}H NMR spectrum, δ, ppm: 2.44 s (3H, Me), 2.97 d.d (1H, CH_2, *J* = 13.4, 10.4 Hz), 3.45 d.d (1H, CH_2), 4.16 m (1H, CH), 6.83–6.90 m (2H, 3-H, 5-H, pyridine), 7.19–7.23 m (1H, H_{arom}), 7.25–7.30 m (4H, H_{arom}), 7.53–7.59 m (1H, 4-H, pyridine). Found, %: C 64.35; H 5.30; N 14.21. $C_{16}H_{15}N_3OS$. Calculated, %: C 64.62; H 5.08; N 14.13.

2-(6-Methyl-2-pyridylimino)-5-(3-trifluoromethylbenzyl)thiazolidin-4-one (Vb). Yield 72%, mp 242–

243°C. ^{1}H NMR spectrum, δ, ppm: 2.43 s (3H, Me), 3.09 d.d (1H, CH_2, J = 14.0, 9.2 Hz), 3.50 d.d (1H, CH_2, J = 14.0, 3.4 Hz), 4.21 m (1H, CH), 6.84–6.91 m (2H, 3-H, 5-H, pyridine), 7.47–7.54 m (2H, H_{arom}), 7.54–7.59 m (2H, 4-H, pyridine, H_{arom}), 7.60 s (1H, H_{arom}), 11.90 br.s (1H, NH). Found, %: C 56.06; H 3.70; N 11.68. $C_{17}H_{14}F_3N_3OS$. Calculated, %: C 55.88; H 3.86; N 11.50.

5-(2,4-Dichlorobenzyl)-2-(6-methyl-2-pyridylimino)thiazolidin-4-one (Vc). Yield 80%, mp 273–274°C. Found, %: C 52.21; H 3.50; N 11.64. $C_{16}H_{13}Cl_2N_3OS$. Calculated, %: C 52.47; H 3.58; N 11.47.

5-(3,4-Dichlorobenzyl)-2-(6-methyl-2-pyridylimino)thiazolidin-4-one (Vd). Yield 79%, mp 258–259°C. Found, %: C 52.32; H 3.59; N 11.23. $C_{16}H_{13}Cl_2N_3OS$. Calculated, %: C 52.47; H 3.58; N 11.47.

5-(3-Chloro-4-methylbenzyl)-2-(6-methyl-2-pyridylimino)thiazolidin-4-one (Ve). Yield 76%, mp 262–263°C. Found, %: C 59.03; H 4.48; N 12.25. $C_{17}H_{16}ClN_3OS$. Calculated, %: C 59.04; H 4.66; N 12.15.

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