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Cycloacylation of *N*-Phenyl-*N*'-R-Thioureas with 3-Aryl-2-propenoyl Chlorides

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Abstract—Cycloalkylation of *N*-phenyl-*N*'-R-thiourea with 3-aryl-2-propenoyl chlorides in acetone gives as products 6-aryl-3-phenyl-2-(R-imino)-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one and their hydrochlorides. The same reaction carried out in acetone in the presence of K_2CO_3 leads to the formation of 6-aryl-3-phenyl-2-(R-imino)-2,3,5,6-tetrahydro-4H-1,3-thiazin-4-ones, *N*-(3-aryl-2-propenoyl)-*N*-phenylthioureas, 3-aryl-2-propenoylanilides, and phenyl isothiocyanate.

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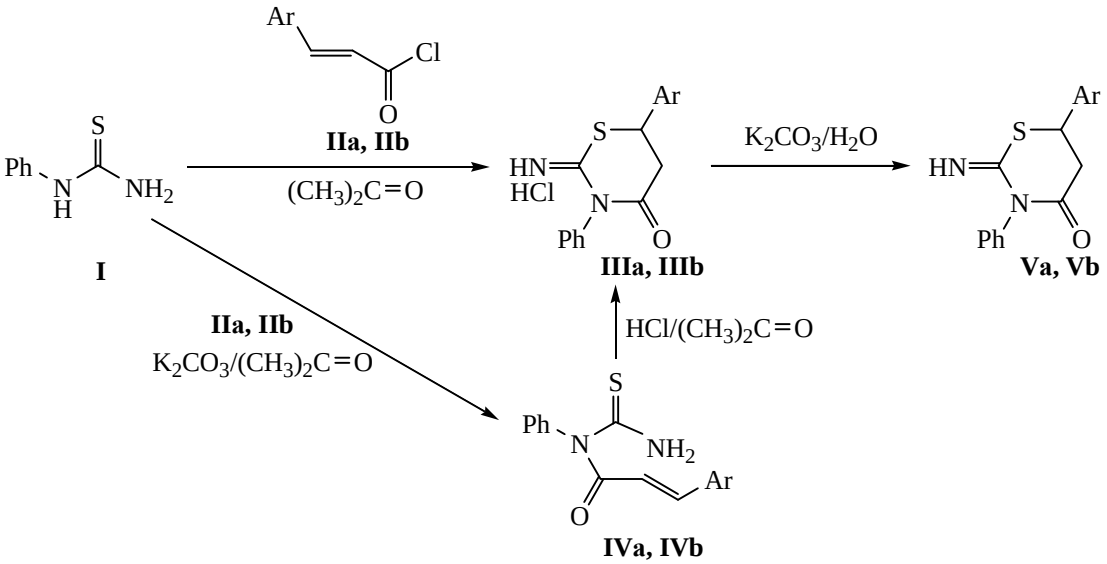
Cycloalkylation of thioamides with compounds containing an activated multiple bond is one of the most available and convenient procedures for preparation of 4*H*-1,3-thiazin-4-one and its derivatives. It should be noted that 4*H*-1,3-thiazin-4-one are endowed with a wide range of physiological activity and can be used as herbicides [1], fungicides [2], helmithicidal [3], antigastritis [4], antipyrotic [5], atitumor [6], and bactericidal [7] agents. Therefore although the first publications on this topic had appeared 50 years ago [8, 9], the synthetic research in this field continued [10, 11] and was still urgent.

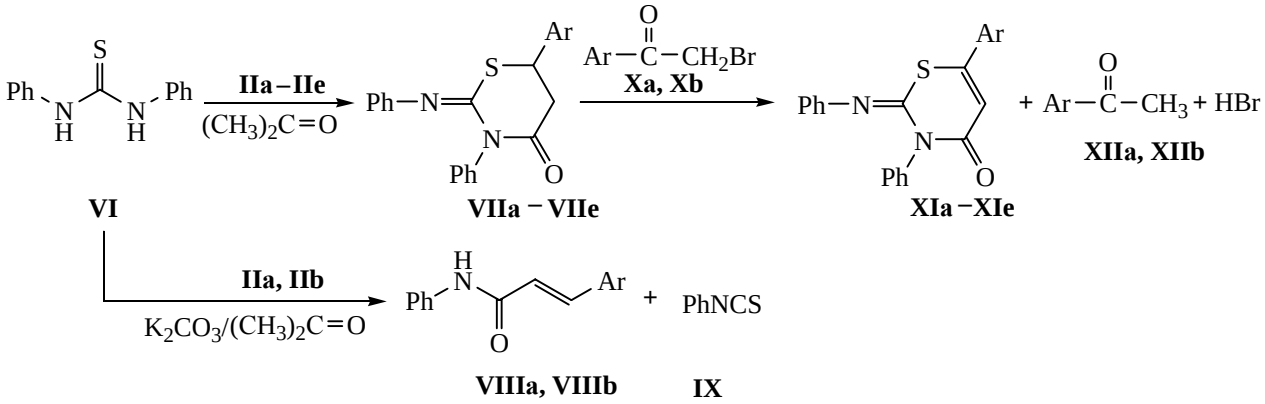
We showed previously that reactions of thioamides containing an active methylene group in the α-position and of cyclic thioureas with 3-aryl-2-propenoyl chlorides constituted a general synthetic procedure for 4*H*-1,3-thiazin-4-one derivatives [12–14]. In continuation of this research we studied the cycloalkylation of *N*-phenyl-*N*'-R-thiourea **I** and **VI** with 3-aryl-2-propenoyl chlorides **IIa–IIe**. This reaction is featured by the possibility to provide both 2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-ones and 1,2,3,5,6-pentahydro-2-thioxo-4*H*-pyrimidin-4-ones; therewith the acylation of an unsymmetrical *N*-phenylthiourea

Scheme 1.



Ar = Ph (**a**), 2-thienyl (**b**).

Scheme 2.



Ar = Ph (**IIa, VIIa, VIIIa, Xa–XIIa**), 2-thienyl (**IIb, VIIb, VIIIb**), *p*-$CH_3OC_6H_4$ (**IIC, VIIC**), *p*-FC_6H_4 (**IId, VIId, XIb**), *m*-$NO_2C_6H_4$ (**IId, VIId**), *p*-ClC_6H_4 (**Xb, XIIb**).

is likely to give two kinds of 4*H*-1,3-thiazin-4-ones and two kinds of 2-thioxo-4*H*-pyrimidin-4-ones.

It was established that the direction of the reaction was governed by the basicity of the medium and by the structure of initial thioures (Schemes 1 and 2).

Acylation products obtained from *N*-phenylthiourea (**I**) and 3-aryl-2-propenoyl chlorides **IIa** and **IIb** in acetone were hydrochlorides **IIIa** and **IIIb**. Condensation of *N*,*N*'-diphenylthiourea (**VI**) with 3-aryl-2-propenoyl chlorides **IIa–IIe** in acetone also occurred selectively resulting in heterocycles **VIIa–VIIe**.

The acylation of *N*-phenylthiourea (**I**) with 3-aryl-2-propenoyl chlorides **IIa** and **IIb** in acetone in the presence of potassium carbonate occurred nonselectively giving compounds of acyclic (**IVa** and **IVb**) and heterocyclic (**Va** and **Vb**) structure, and the products obtained under the same conditions from *N*,*N*'-diphenylthiourea (**VI**) and 3-aryl-2-propenoyl chlorides **IIa** and **IIb** were acylic substances 3-aryl-2-propenoylanilides **VIIIa** and **VIIIb**, and phenyl isothiocyanate (**IX**).

Characteristic signals in the ^{1}H NMR spectra of compounds **IIIa, IIIb, Va, Vb**, and **VIIa–VIIe** are the resonances from the fragment CH_2–CH (three multiplets of *ABX* system in the region 3.15–3.40, 3.49–3.79, 4.94–5.79 ppm). In the ^{1}H NMR spectra of compounds **IIIa** and **IIIb** appear also broadened signals from NH·HCl groups in the region 10.22–11.25 ppm. The IR spectra of compounds **IIIa, IIIb, Va, Vb**, and **VIIa–VIIe** contain characteristic absorption bands of NH, C=O, and C=N groups (at 3300, 1680–1720, and 1570–1610 cm^{-1} respectively).

It is known that in the ^{1}H NMR spectra of thiazinones and pyrimidines the chemical shifts of protons originating from Ar–CH–S and Ar–CH–N fragments have very close values (3.99–4.82 and 4.95–5.25 ppm respectively) [12–15], whereas in the ^{13}C NMR spectra the carbon signals of Ar–<u>C</u>H–S fragment appear upfield (40–45 ppm) with respect to the carbon signal of Ar–<u>C</u>H–N (60–65 ppm). This fact is due to a lesser polarizability of the C–S bond compared to C–N bond [12, 15, 16]. Therefore in order to unambiguously establish the structure of compounds **IIIa, IIIb, Va, Vb**, and **VIIa–VIIe** we measured the ^{13}C NMR spectra of compounds **IIIa, Va,** and **VIIa**. In the ^{13}C NMR spectra of these compounds the signals belonging to C^6 atoms were observed in the range 39.8–39.9 ppm permitting a conclusion that compounds **IIIa, IIIb, Va, Vb**, and **VIIa–VIIe** were 6-aryl-3-phenyl-2-(R-imino)-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-ones. Note that 6-aryl-3-phenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-ones **Va** and **Vb** are isomers of 6-aryl-2-phenylimino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-ones which have been synthesized by intramolecular cyclization of *N*-(3-aryl-2-propenoyl)-*N*'-phenylthioureas in the presence of sodium ethylate [15] or boron trifluoride etherate [17].

Characteristic signals in the ^{1}H NMR spectra of compounds **IVa** and **IVb** are the signals of vicinal protons at the double bond CO–CH=CH (5.90–6.22 and 7.65–7.76 ppm) and the peaks of protons of the NH_2 group (9.75–9.78 and 10.12–10.15 ppm), in the IR spectra, absorption bands of C=O and NH_2 groups (1670–1680 and 3300–3400 cm^{-1} respectrively). The elemental analyses and spectral data of compounds **IVa** and **IVb** suggest that the substances may have both the structures of

N-(3-aryl-2-propenoyl)-*N*-phenylthioureas and of their isomers *N*-(3-aryl-2-propenoyl)-*N*'-phenylthioureas. The latter were however synthesized by reaction of (3-aryl-2-propenoyl) isothiocyanates with anilines and were characterized in [15, 17] Therefore we were able to identify unambiguously compounds **IVa** and **IVb** as *N*-(3-aryl-2-propenoyl)-*N*-phenylthioureas. Inasmuch as *N*-phenylthioureas **IVa** and **IVb** formed alongside 4*H*-1,3-thiazin-4-ones **Va** and **Vb** they were likely to be intermediates in this heterocyclization. It turned out that on heating the acetone solution of *N*-phenylthiourea **IVa** in a hydrochloric acid medium 4*H*-1,3-thiazin-4-one hydrochloride **IIIa** actually formed and was converted into base **Va** by treating with water solution of K_2CO_3. Thus we established the connection between compounds **IIIa, IIIb, IVa, IVb,** and **Va, Vb**.

Formation of 3-aryl-2-propenoylanilides **VIIIa** and **VIIIb**, and phenyl isothiocyanate (**IX**) in the reaction of *N*,*N*'-diphenylthiourea (**VI**) with 3-aryl-2-propenoyl chlorides **IIa** and **IIb** in acetone in the presence of potassium carbonate suggests that the intermediate acyclic product is unstable in the basic medium.

4*H*-1,3-Thiazin-4-ones **VIIa** and **VIIb** did not react with hydrogen peroxide in acetic acid at 25°C, but melting them with phenacyl bromides **Xa** and **Xb** at 160°C resulted in their dehydrogenation with conversion into 6-aryl-3-phenyl-2-phenylimino-2,3-dihydro-4*H*-1,3-thiazin-4-ones **XIa** and **XIb**. It should be noted that phenacyl bromides **Xa** and **Xb** are therewith reduced to acetophenones **XIIa** and **XIIb**. Characteristic peaks in the ^{1}H NMR spectra of compounds **XIa** and **XIb** are singlets from H^5 (7.80–7.81 ppm), and in the IR spectra, absorption band of C=O group (1700–1720 cm^{-1}).

Thus the acylation of *N*-phenyl-*N*'-R-thiourea with 3-aryl-2-propenoyl chlorides is a convenient preparative method of synthesis of 6-aryl-3-phenyl-2-(R-imino)-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-ones whose advantages are the one-step process and the possibility to obtain 4*H*-1,3-thiazin-4-ones with various substituents in the position *6* of the thiazine ring.

EXPERIMENTAL

NMR spectra of compounds in solution in DMSO-d_6 were registered on a spectrometer Varian-300, operating frequencies 300 (^{1}H), 75 MHz (^{13}C), internal reference TMS. IR spectra were recorded on a spectrophotometer UR-20 from KBr pellets.

6-Aryl-3-phenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-ones hydrochlorides IIIa and IIIb. To a solution of 1.52 g (0.01 mol) of *N*-phenylthiourea (**I**) in 15 ml of anhydrous acetone at 20°C was added while stirring a solution of 0.01 mol of 3-aryl-2-propenoyl chloride **IIa** or **IIb** in 10 ml of acetone. The mixture was stirred for 10 min at 20°C and 30 min at 56°C, then it was cooled, reaction product **IIIa** or **IIIb** was filtered off, dried in a drying cabinet at 100°C, and recrystallized from CH_3COOH.

3,6-Diphenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one hydrochloride (**IIIa**). Yield 2.36 g (74%), mp 210–212°C. IR spectrum, cm^{-1}: 1240, 1290, 1380, 1460, 1500, 1540, 1590, 1720, 2700–3000. ^{1}H NMR spectrum, δ, ppm: 3.40 m (1H, H^5), 3.79 m (1H, H^5), 5.47 m (1H, H^6), 7.30–7.71 m (10H, 2Ph), 10.30–11.21 br.s (2H, NH·HCl). ^{13}C NMR spectrum, δ, ppm: 39.9 (C^6), 40.3 (C^5), 127.6, 128.7, 129.1, 129.3, 129.8, 130.0, 134.4, 135.8 (Ar), 156.3 (C^2), 168.2 (C^4). Found, %: C 59.99; H 5.01; N 9.04. $C_{16}H_{15}ClN_2OS$. Calculated, %: C 60.28; H 4.74; N 8.79.

6-(2-Thienyl)-3-phenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one hydrochloride (**IIIb**). Yield 2.24 g (69%), mp 208–210°C. IR spectrum, cm^{-1}: 1160, 1240, 1380, 1490, 1540, 1590, 1720, 2700–3000. ^{1}H NMR spectrum, δ, ppm: 3.62 m (2H, H^5), 5.79 m (1H, H^6), 7.09 d.d (1H, Ar, J_1 5.2, J_2 3.0 Hz), 7.32 m ($3H_{Ar}$), 7.55 m ($4H_{Ar}$), 10.22–11.25 br.s (2H, NH·HCl). Found, %: C 51.97; H 3.77; N 8.35. $C_{14}H_{13}ClN_2OS_2$. Calculated, %: C 51.76; H 4.03; N 8.62.

***N*-(3-Aryl-2-propenoyl)-*N*-phenylthioureas IVa and IVb, and 6-aryl-3-phenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-ones Va and Vb**. To a solution of 1.52 g (0.01 mol) of *N*-phenylthiourea (**I**) in 15 ml of anhydrous acetone, containing 2.07 g (0.15 mol) of powdered dry K_2CO_3, was added at vigorous stirring at 20°C a solution of 0.01 mol of 3-aryl-2-propenoyl chloride **IIa** or **IIb** in 10 ml of acetone. The mixture was stirred for 10 min at 20°C and 30 min at 56°C, then it was cooled, and the precipitate containing potassium hydrocarbonate and chloride and 1,3-thiazin-4-one **Va** or **Vb** was filtered off. The filtrate was evaporated in air, the separated crystals of compounds **IVa** or **IVb** were recrystallized from 2-propanol. The precipitate on the filter was washed with warm (40°C) water (3×20 ml), dried at 100°C, and recrystallized from nitromethane.

N-(3-Phenyl-2-propenoyl)-*N*-phenylthiourea (**IVa**). Yield 0.90 g (32%), mp 141–143°C. IR spectrum, ν, cm^{-1}: 1290, 1330, 1420, 1460, 1500, 1590, 1620, 1680,

3000–3300, 3400. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.22 d (1H, H^2, *J* 14.1), 7.33–7.45 m (10H, 2Ph), 7.65 d (1H, H^3, *J* 14.1), 9.78 s (1H, NH), 10.12 s (1H, NH). Found, %: C 67.78; H 4.72; N 10.11. $C_{16}H_{14}N_2OS$. Calculated, %: C 68.06; H 5.00; N 9.92.

N-[3-(2-Thienyl)-2-propenoyl]-*N*-phenylthiourea (**IVb**). Yield 0.807 g (28%), mp 142–144°C. IR spectrum, cm^{-1}: 1270, 1320, 1410, 1500, 1590, 1670, 3000–3300. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.90 d (1H, H^2, *J* 14.4), 7.04 d.d (1H, Ar, J_1 5.3, J_2 3.0), 7.28–7.57 m (7H, Ar), 7.76 d (1H, H^3, *J* 14.4), 9.75 s (1H, NH), 10.15 s (1H, NH). Found, %: C 58.57; H 3.98; N 9.48. $C_{14}H_{12}N_2OS_2$. Calculated, %: C 58.31; H 4.19; N 9.71.

3,6-Diphenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**Va**). Yield 1.18 g (42%), mp 190–192°C. IR spectrum, cm^{-1}: 1360, 1410, 1460, 1500, 1580, 1695, 3100, 3300. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.18 m (1H, H^5), 3.49 m (1H, H^5), 5.02 m (1H, H^6), 7.15 m (2H, Ar), 7.31–7.50 m (8H, Ar), 8.84 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 39.8 (C^6), 41.6 (C^5), 127.4, 127.6, 128.2, 128.8, 129.0, 129.2, 138.0 (Ar), 155.9 (C^2), 169.3 (C^4). Found, %: C 67.85; H 5.26; N 10.13. $C_{16}H_{14}N_2OS$. Calculated, %: C 68.06; H 5.00; N 9.92.

6-Thienyl-3-phenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**Vb**). Yield 1.12 g (39%), mp 137–140°C. IR spectrum, cm^{-1}: 1280, 1360, 1510, 1570, 1695, 3000, 3100, 3300. ^{1}H NMR spectrum, δ, ppm: 3.39 m (2H, H^5), 5.23 m (1H, H^6), 7.06–7.14 m (4H, Ar), 7.25–7.56 m (4H, Ar), 9.08 br.s (1H, NH). Found, %: C 58.36; H 4.03; N 9.44. $C_{14}H_{12}N_2OS_2$. Calculated, %: C 58.31; H 4.19; N 9.71.

Cyclization of *N*-(3-phenyl-2-propenoyl)-*N*-phenyl-thiourea (IVa) into 3,6-diphenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one hydrochloride (IIIa). Through a solution of 0.282 g (0.001 mol) of *N*-phenylthiourea **IVa** in 3 ml of dry acetone at 50°C was passed for 10 min a flow of dry HCl. The reaction mixture was cooled, and precipitated hydrochloride **IIIa** was filtered off. Yield 0.255 g (80%), mp 208–210°C. The mixed sample of compound **IIIa** thus obtained and that prepared by reaction of *N*-phenylthiourea with 3-phenyl-2-propenoyl chloride in acetone melted without depression of the melting point.

Preparation of base Va from 3,6-diphenyl-2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one hydrochloride (IIIa). A mixture of 0.319 g (0.001 mol) of hydrochloride **Va** with a solution of 0.002 mol of K_2CO_3 in 5 ml of water was stirred for 20 min at 50°C, cooled, and 1,3-thiazin-4-one **Va** was filtered off. Yield 0.243 g (86%), mp188–190°C. The mixed sample of compound **Va** thus obtained and that prepared by reaction of *N*-phenylthiourea with 3-phenyl-2-propenoyl chloride in acetone in the presence of K_2CO_3 melted without depression of the melting point.

6-Aryl-3-phenyl-2-phenylimino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-ones VIIa–VIIe. To a solution of 2.28 g (0.01 mol) of *N*,*N*'-diphenylthiourea (**VI**) in 15 ml of anhydrous acetone at 20°C while stirring was added a solution of 0.01 mol of 3-aryl-2-propenoyl chloride **IIa–IIe** in 10 ml of acetone. The mixture was stirred for 10 min at 20°C and 30 min at 56°C, then it was cooled, the reaction product **VIIa**–**VIIe** was filtered off, dried in a drying cabinet at 100°C, and recrystallized from CH_3COOH.

3,6-Diphenyl-2-phenylimino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**VIIa**). Yield 2.51 g (70%), mp 200–201°C. IR spectrum, cm^{-1}: 1210, 1260, 1350, 1480, 1610, 1685, 3000–3100. ^{1}H NMR spectrum, δ, ppm: 3.20 m (1H, H^5), 3.57 m (1H, H^5), 5.01 m (1H, H^6), 6.66 m (2H $_{Ar}$), 6.98 m (1H, Ar), 7.16–7.55 m (12H$_{Ar}$). ^{13}C NMR spectrum, δ, ppm: 39.8 (C^6), 41.6 (C^5), 120.2, 123.7, 127.5, 128.4, 128.8, 128.9, 129.1, 137.5, 138.8, 147.8 (Ar), 152.4 (C^2), 169.2 (C^4). Found, %: C 73.44; H 4.83; N 8.09. $C_{22}H_{18}N_2OS$. Calculated, %: C 73.72; H 5.06; N 7.82.

6-Thienyl-3-phenyl-2-phenylimino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**VIIb**). Yield 2.37 g (65%), mp 202–204°C. IR spectrum, cm^{-1}: 1210, 1260, 1320, 1340, 1485, 1590, 1680, 3100. ^{1}H NMR spectrum, δ, ppm : 3.45 m (2H, H^5), 5.29 m (1H, H^6), 6.67 m (2H$_{Ar}$), 7.01–7.50 m (11H$_{Ar}$). Found, %: C 66.14; H 4.30; N 7.42. $C_{20}H_{16}N_2OS_2$. Calculated, %: C 65.91; H 4.42; N 7.69.

6-(4-Methoxyphenyl)-3-phenyl-2-phenylimino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**VIIc**). Yield 2.87 g (74%), mp 246–248°C. IR spectrum, cm^{-1}: 1210, 1260, 1330, 1480, 1510, 1595, 1680, 3000. ^{1}H NMR spectrum, δ, ppm: 3.15 m (1H, H^5), 3.55 m (1H, H^5), 3.81 s (3H, CH_3O), 4.94 m (1H, H^6), 6.65 m (2H $_{Ar}$), 6.91 d (2H, ï -C_6H_4, *J* 8.7 Hz), 6.97 m (1H, Ar), 7.24 m (4H$_{Ar}$), 7.34 d (2H, ï -C_6H_4, *J* 8.7 Hz), 7.47 m (3H$_{Ar}$). Found, %: C 70.92; H 5.42; N 6.92. $C_{23}H_{20}N_2O_2S$. Calculated, %: C 71.11; H 5.19; N 7.21.

6-(4-Fluorophenyl)-3-phenyl-2-phenylimino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**VIId**). Yield 2.56 g (68%), mp 213–215°C. IR spectrum, cm^{-1}: 1210, 1230, 1270, 1350, 1510, 1605, 1695, 3100. ^{1}H NMR spectrum, δ, ppm: 3.20 m (1H, H^5), 3.57 m (1H, H^5), 5.04 m (1H,

H^6), 6.68 m ($2H_{Ar}$), 6.98 m ($1H_{Ar}$), 7.10–7.59 m ($11H_{Ar}$). Found, %: C 69.92; H 4.62; N 7.71. $C_{22}H_{17}FN_2OS$. Calculated, %: C 70.19; H 4.55; N 7.44.

6-(3-Nitrophenyl)-3-phenyl-2-phenylimino-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**VIIe**). Yield 2.78 g (69%), mp 176–177°C. IR spectrum, cm^{-1}: 1210, 1270, 1360, 1490, 1550, 1610, 1700, 3100. ^1H NMR spectrum, δ, ppm: 3.37 m (1H, H^5), 3.66 m (1H, H^5), 5.25 m (1H, H^6), 6.70 m ($2H_{Ar}$), 7.00 m ($1H_{Ar}$), 7.21–7.48 m ($7H_{Ar}$), 7.70 m ($1H_{Ar}$), 7.92 d ($1H_{Ar}$, *J* 7.2 Hz), 8.19 d ($1H_{Ar}$, *J* 8.1 Hz), 8.33 s ($1H_{Ar}$). Found, %: C 65.68; H 4.01; N 10.22. $C_{22}H_{17}N_3O_3S$. Calculated, %: C 65.50; H 4.25; N 10.42.

3-Aryl-2-propenoylanilides VIIIa and VIIIb, and phenyl isothiocyanate (IX). To a solution of 4.56 g (0.02 mol) of *N*,*N*'-diphenylthiourea (**VI**) in 25 ml of anhydrous acetone, containing 4.14 g (0.03 mol) of powdered dry K_2CO_3, , was added at vigorous stirring at 20°C a solution of 0.02 mol of 3-aryl-2-propenoyl chloride **IIa** or **IIb** in 10 ml of acetone. The mixture was stirred for 10 min at 20°C and 30 min at 56°C, then it was cooled, and the precipitate containing potassium hydrocarbonate and chloride was filtered off. The filtrate was evaporated in air, the residue was treated with ethyl ether (3×5 ml), the insoluble crystals of compound **VIIIa** or **VIIIb** were dried and recrystallized from 2-propanol.

3-Phenyl-2-propenoylanilide (**VIIIa**). Yield 2.45 g (55%), mp 147–149°C (publ: mp 150–151°C [18]). 3-(2-Thienyl)-2-propenoylanilide (**VIIIb**). Yield 2.29 g (50%), mp 143–145°C. IR spectrum, cm^{-1}: 1170, 1250, 1330, 1440, 1540, 1600, 1670, 3300. ^1H NMR spectrum, δ, ppm: 6.57 d ($1H^2$, *J* 15.1 Hz), 7.11 d.d ($1H_{Ar}$, J_1 5.2, J_2 2.9 Hz), 7.11 m ($2H_{Ar}$), 7.29 m ($3H_{Ar}$), 7.58–7.60 m ($2H_{Ar}$), 7.65 d ($1H^3$, *J* 15.1 Hz). Found, %: C 67.85; H 5.12; N 6.30. $C_{13}H_{11}NOS$. Calculated, %: C 68.10; H 4.84; N 6.11.

The ether extract was evaporated, phenyl isothiocyanate (**IX**) was distilled in a vacuum of a water-jet pump. Yield 1.27 g (47%), bp 110°C (20 mm Hg) {publ.: bp 222°C (762 mm Hg) [19]}.

6-Aryl-3-phenyl-2-phenylimino-2,3-dihydro-4*H*-1,3-thiazin-4-ones XIa and XIb. A mixture of 0.716 g (0.002 mol) 4*H*-1,3-thiazin-4-one **VIIa** or **VIId**, and 0.002 mol of phenacyl bromide **Xa** or **Xb** was maintained for 4 min at 160°C, cooled, treated with ethyl ether (3×3 ml), the separated crystals of compound **XIa** or **XIb** were dried and recrystallized from CH_3COOH. The ether extract was evaporated to isolate acetophenone **XIIa** or **XIIb**.

3,6-Diphenyl-2-phenylimino-2,3-dihydro-4*H*-1,3-thiazin-4-one (**XIa**). Yield 0.235 g (33%), mp 203–205°C. IR spectrum, cm^{-1}: 1270, 1370, 1490, 1580, 1600, 1640, 1700, 3100. ^1H NMR spectrum, δ, ppm: 6.96 m ($2H_{Ar}$), 7.19 m ($1H_{Ar}$), 7.22–7.61 m ($12H_{Ar}$), 7.80 s (1H, H^5). Found, %: C 73.92; H 4.80; N 7.96. $C_{22}H_{16}N_2OS$. Calculated, %: C 74.13; H 4.52; N 7.86.

3-Phenyl-6-(4-fluorophenyl)-2-phenylimino-2,3-dihydro-4*H*-1,3-thiazin-4-one (**XIb**). Yield 0.217 g (29%), mp 205–207°C. IR spectrum, cm^{-1}: 1240, 1280, 1380, 1500, 1600, 1650, 1720, 3050. ^1H NMR spectrum, δ, ppm: 6.94 m ($2H_{Ar}$), 7.16 m (1H, Ar), 7.27–7.38 m ($4H_{Ar}$), 7.41–7.65 m ($7H_{Ar}$), 7.81 s (1H, H^5). Found, %: C 70.39; H 3.85; N 7.72. $C_{22}H_{15}FN_2OS$. Calculated, %: C 70.57; H 4.04; N 7.48.

Acetophenone (**XIIa**), mp 15–17°C (publ: mp 20–20.5°C [20]), yield 0.127 g (53%).

p-Chloroacetophenone (**XIIb**), mp 15–17°C (publ: mp 20°C [21]), yield 0.179 g (58%).

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