# SYNTHESIS OF 2-SUBSTITUTED 5-ARYLIDENETHIAZOLIN-4-ONES FROM α,β-UNSATURATED ACYL ISOTHIOCYANATES

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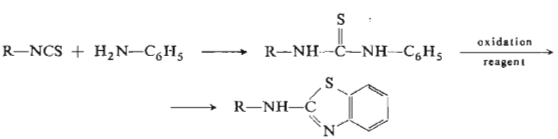
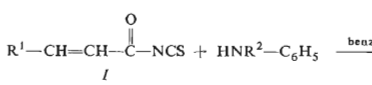
Received February 7th, 1980

α,β-Unsaturated acyl isothiocyanates react with N-methylaniline to give thioureas which, when treated with bromine in chloroform, afford benzothiazoline derivatives. Under the same reaction conditions primary amines, diethylamine, piperidine and morpholine furnish 2-substituted 5-arylidenethiazolin-4-ones. Their structure was corroborated by an independent synthesis and on the basis of spectral (IR, $^1$H-NMR and mass) evidence.

Isothiocyanates react with primary and secondary amines to yield the corresponding thioureas, of which N-aryl-N'-substituted ones were the starting material for preparation of 2-aminobenzo[*d*]thiazoles *via* an oxidation reagent, *cf.*[1].




In isothiocyanate, *trans*-3-phenylpropenoyl isothiocyanate and aniline or N-methylaniline were the model substances.

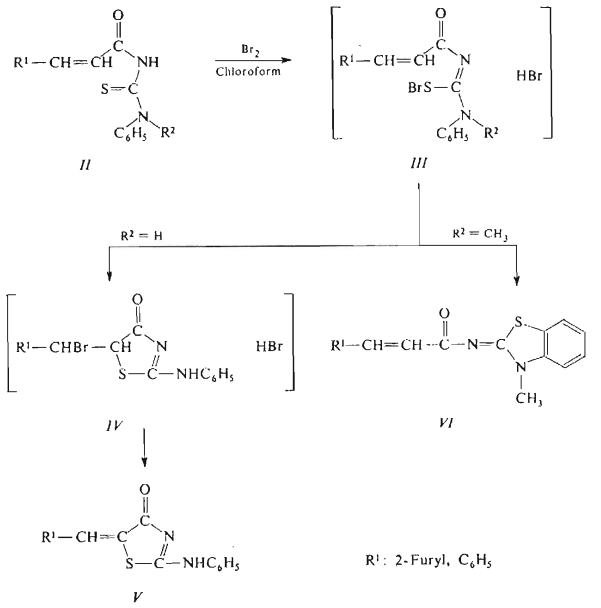



*a*: $R^1$ = 2-Furyl, $R^2$ = H  *b*: $R^1$ = $C_6H_5$, $R^2$ = H
*c*: $R^1$ = 2-Furyl, $R^2$ = $CH_3$  *d*: $R^1$ = $C_6H_5$, $R^2$ = $CH_3$

This study was focussed on the reaction with thioureas prepared from α,β-unsaturated acyl isothiocyanates; thioureas synthesized from *trans*-3-(2-furyl)propenoyl

As found, various products, depending on the structure of the amine residue were formed by treatment of the above-mentioned thioureas in chloroform with bromine as an oxidizing agent. With thioureas *IIa* and *IIb* this reaction occurred unexpectedly at the ethylene double bond to give 2-phenylamino-5-arylidenethiazolin-4-ones. Thioureas *IIc* and *IId* furnished predominantly benzothiazolines *VIa* and *VIb* due to the sufficient activation of the aromatic ring by the methyl group attached to nitrogen. This reaction sequence is illustrated in Scheme 1.

We suggest, analogously with the literature, that thioureas were oxidized with bromine to disulfides[2], which in turn gave with bromine the corresponding sulfenyl bromides *III* (refs[3-5]). The latter can undergo either electrophilic replacement with



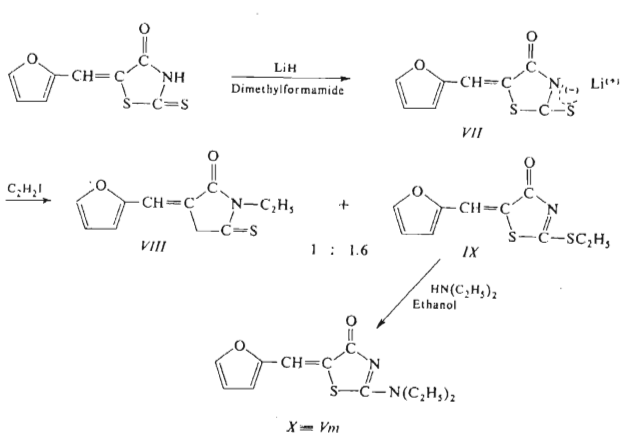

*II* *III* *IV* *V* *VI*

SCHEME 1

aromatic ring[6], or electrophilic addition to double bond[4,5]. Thus thioureas with an N-methylaniline residue (*IIc*, *IId*) afforded the corresponding benzothiazolinium bromides (electrophilic replacement), thioureas with an aniline residue (*IIa*, *IIb*) gave the hydrobromides of 2,5-disubstituted thiazolin-4-ones *IV* (addition). In regard to the fact that β-bromo ketones eliminate very easily HBr (ref.[7]) only hydrobromides of 2-phenylamino-5-arylidenethiazolin-4-ones could be isolated under the given reaction conditions. Crystallization of the respective hydrobromides from alcohol–water yielded the corresponding benzothiazoline derivatives *VIa*, *VIb* and 2-phenylamino-5-arylidenethiazolin-4-ones (*Va*, *Vb*).

This reaction proceeds with other primary and secondary amines as well; it was exploited for preparation of further 14 derivatives of 2-substituted 5-arylidenethiazolin-4-ones *V* (Table I). Their structure was proved by an independent synthesis (Scheme 2). Ethylation of the lithium salt of furfurylidenerhodanine (*VII*) gave a mixture of N-ethyl (*VIII*) and S-ethyl (*IX*) derivatives in a 1 : 1·6 ratio. Treatment of this mixture (compounds *VIII* and *IX*) with diethylamine in ethanol gave 2-diethylamino-5-furfurylidenethiazolin-4-one (*X*) from the S-ethyl derivative, whereas compound *VIII* did not react with diethylamine. Physicochemical constants, spectral data and the elemental analysis confirmed the identity of compounds *X* and *Vm*.

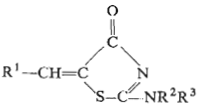
The IR, $^1$H-NMR and mass spectra of the synthesized compounds accorded with the proposed structures (Table II). In contrast to benzothiazoline derivatives *VI* the IR spectra of thiazolines *V* did not contain bending vibrations of *trans*-ethylene




SCHEME 2

TABLE I

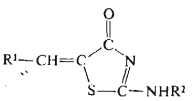
2-Substituted 5-Arylidenethiazolin-4-ones *Va*, *Vb*, *Ve*—*Vs*



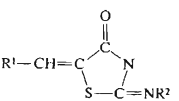
| Compound | $R^1$ $NHR^2R^3$ | Formula (mol.weight) | Calculated/Found | | | Yield, % M.p., °C |
|---|---|---|---|---|---|---|
| | | | % C | % H | % N | |
| *Va* | $C_4H_3O$ $NHC_6H_5$ | $C_{14}H_{10}N_2O_2S$ (270·3) | 62·27 62·40 | 3·73 3·52 | 10·39 10·49 | 74 223—225[a] |
| *Vb* | $C_6H_5$ $NHC_6H_5$ | $C_{16}H_{12}N_2OS$ (280·4) | 68·63 68·70 | 4·32 4·18 | 10·00 9·72 | 69 258—260[a] |
| *Ve* | $C_4H_3O$ $NH_2$ | $C_8H_6N_2O_2S$ (194·2) | 49·53 49·71 | 3·12 3·18 | 14·44 14·61 | 76 248—250[b] |
| *Vf* | $C_6H_5$ $NH_2$ | $C_{10}H_8N_2OS$ (204·3) | 58·87 58·61 | 3·95 4·16 | 13·73 13·66 | 70 198—200[a] |
| *Vg* | $C_4H_3O$ $NHCH_3$ | $C_9H_8N_2O_2S$ (208·2) | 51·96 51·81 | 3·48 3·32 | 13·47 13·59 | 54 210—212[c] |
| *Vh* | $C_6H_5$ $NHCH_3$ | $C_{11}H_{10}N_2OS$ (218·3) | 60·60 60·48 | 4·62 4·78 | 12·85 12·66 | 73 218—220[a] |
| *Vi* | $C_4H_3O$ $NHC_6H_{11}$ | $C_{14}H_{16}N_2O_2S$ (276·4) | 60·92 60·81 | 5·84 5·99 | 10·15 10·36 | 68 221—223[d] |
| *Vj* | $C_6H_5$ $NHC_6H_{11}$ | $C_{16}H_{18}N_2OS$ (286·4) | 67·19 67·12 | 6·34 6·49 | 9·76 9·60 | 80 245—246[a] |
| *Vk* | $C_4H_3O$ $NHCH_2C_6H_5$ | $C_{15}H_{12}N_2O_2S$ (284·2) | 63·48 63·12 | 4·23 4·28 | 9·86 9·70 | 62 226—228[a] |
| *Vl* | $C_6H_5$ $NHCH_2C_6H_5$ | $C_{17}H_{14}N_2OS$ (294·2) | 69·45 69·52 | 4·80 4·78 | 9·53 9·32 | 77 185—187[a] |
| *Vm* | $C_4H_3O$ $N(C_2H_5)_2$ | $C_{12}H_{14}N_2O_2S$ (250·3) | 57·65 57·51 | 5·64 5·81 | 11·20 11·36 | 82 48—50[b] |
| *Vn* | $C_6H_5$ $N(C_2H_5)_2$ | $C_{14}H_{16}N_2OS$ (260·4) | 64·67 64·50 | 6·20 6·42 | 10·77 10·96 | 56 56—58[b] |
| *Vo* | $C_4H_3O$ $N(CH_2)_5$ | $C_{13}H_{14}N_2O_2S$ (262·3) | 59·59 59·58 | 5·38 5·49 | 10·69 10·83 | 80 159—161[b] |
| *Vp* | $C_6H_5$ $N(CH_2)_5$ | $C_{15}H_{16}N_2OS$ (272·4) | 66·24 66·42 | 5·93 6·12 | 10·30 10·08 | 78 209—211[b] |
| *Vr* | $C_4H_3O$ $N(CH_2)_4O$ | $C_{12}H_{12}N_2O_3S$ (264·3) | 54·59 54·42 | 4·58 4·61 | 10·62 10·51 | 80 221—223[a] |
| *Vs* | $C_6H_5$ $N(CH_2)_4O$ | $C_{14}H_{14}N_2O_2S$ (274·4) | 61·37 61·13 | 5·15 5·38 | 10·22 10·14 | 78 203—204[b] |

Crystallized from [a] methanol–water; [b] ethanol–water; [c] chloroform–light petroleum; [d] acetone–water.

C—H bonds $\nu$(CH=CH), nevertheless the presence of $\nu$(C=C) vibration bands at 1 609 – 1 643 $cm^{-1}$ evidenced the maintenance of a double C=C bond. The complexity of carbonyl bands of derivatives *Va*, *Vb*, *Vf*, *Vk* observed either in KBr discs or in chloroform is subject to the possibility of amino-imine tautomerism.



*A*



*B*

The absorption $\nu$(C=O) bands at higher wave numbers are associated with the imino form *B* and those at lower wave numbers with the amino form *A*, ref.[8,9]. The stretching vibrations $\nu$(C=N) appeared at 1 500 – 1 580 $cm^{-1}$. The $^1$H-NMR spectra (ppm, $\delta$ scale) of 2-substituted 5-arylidenethiazolin-4-ones showed the singlet of an olefinic proton at 7·40 – 7·80. Basing upon the method of additive shielding

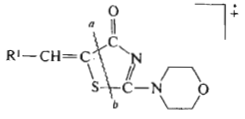
TABLE II

Spectral Data of 2-Substituted 5-Arylidenethiazolin-4-ones *Va*, *Vb*, *Ve*—*Vs*

| Compound | $\nu$(C=N)[a] | $\nu$(C=C)[a] | $\nu$(C=O)[a] | $\delta$(=C—H)[b] |
|---|---|---|---|---|
| *Va* | 1 554 | 1 622 | 1 652, 1 713 | — |
| *Vb* | 1 573 | 1 643 | 1 678, 1 728 | — |
| *Ve* | 1 506 | 1 620 | 1 679 | 7·45 |
| *Vf* | 1 516 | 1 610 | 1 674, 1 694 | — |
| *Vg* | 1 551 | 1 629 | 1 683 | 7·40 |
| *Vh* | 1 577 | 1 630 | 1 694 | 7·66 |
| *Vi* | 1 556 | 1 624 | 1 678 | 7·41 |
| *Vj* | 1 561 | 1 621 | 1 690 | 7·56 |
| *Vk* | 1 549 | 1 609 | 1 679 | 7·43 |
| *Vl* | 1 580 | 1 621 | 1 675, 1 696 | 7·72 |
| *Vm* | 1 560 | 1 621 | 1 679 | 7·51 |
| *Vn* | 1 564 | 1 618 | 1 683 | 7·73 |
| *Vo* | 1 560 | 1 621 | 1 692 | 7·49 |
| *Vp* | 1 565 | 1 614 | 1 682 | 7·77 |
| *Vr* | 1 555 | 1 619 | 1 681 | 7·54 |
| *Vs* | 1 555 | 1 613 | 1 685 | 7·81 |

[a] In $cm^{-1}$; [b] compounds *Va*, *Vb*, *Vf* were not sufficiently soluble for $^1$H-NMR measurement. Chemical shifts in ppm, $\delta$ scale.

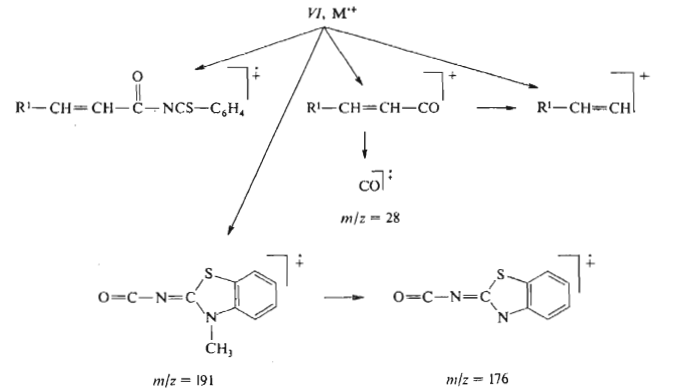
increments[10] they can be assigned the Z-configuration (calculated $\delta$ (Z, =CH) 7·48 ppm; $\delta$ (E, =CH) 6·71 ppm). Two doublets at 6·70 and 7·70 ($J_{AB}$ = 16 Hz) evidence the presence of *trans*-ethylene protons in 2-(α,β-unsaturated acylimino)benzothiazolines *VI*. The structure of cyclic products was also corroborated by means of mass spectra of compounds *Vr*, *Vs*, *VIa* and *VIb*. The *m/z* values of molecular ions were in line with the anticipated molecular weight. Diagnostic feature of the mass spectra of 2-substituted 5-arylidenethiazolin-4-ones is the presence of fragment ions at *m/z* 124 (*Vr*), or 134 (*Vs*), resulting from the *a*, *b* bonds cleavage (Scheme 3).



$R^1$: 2-Furyl (*Vr*), $C_6H_5$ (*Vs*) $M^+$, *m/z* = 264 (*Vr*), 274 (*Vs*)

SCHEME 3

The fragmentation pathway of benzothiazoline molecular ions of derivatives *VIa* and *VIb* is shown in Scheme 4.




$R^1$: 2-Furyl (*VIa*), $C_6H_5$ (*VIb*)

SCHEME 4

## EXPERIMENTAL

*trans*-3-(2-Furyl)propenoyl isothiocyanate (*Ia*) was prepared according to[11], *trans*-3-phenylpropenoyl isothiocyanate (*Ib*) according to[12], N-phenyl-N'-3-phenylpropenoylthiourea (*IIb*) according to[11] and furfurylidenerhodanine according to[13]. The syntheses of N-phenyl-N'-3-(2-furyl)propenoylthiourea (*IIa*), N-methyl-N-phenyl-N'-3-(2-furyl)propenoylthiourea (*IIa*), N-methyl-N-phenyl-N'-3-(2-furyl)propenoylthiourea (*IIc*), N-methyl-N-phenyl-N'-3-phenylpropenoylthiourea (*IId*), 3-(2-furyl)propenoylthiourea (*IIe*), 3-phenylpropenoylthiourea (*IIf*), N-methyl-N'-3-(2-furyl)-propenolylthiourea (*IIg*), N-methyl-N'-3-phenylpropenoylthiourea (*IIh*), N-benzyl-N'-3-(2-furyl)propenoylthiourea (*IIk*) and N-benzyl-N'-3-phenylpropenoylthiourea (*III*) were already described[14,15].

### 3-Methyl-2-(3-substituted Propenoylimino)benzo[*d*]thiazolines *VIa, VIb*

Bromine (1 mmol) was added to a stirred solution of N-methyl-N-phenyl-N'-3-(2-furyl)propenoylthiourea (*IIc*) or N-methyl-N-phenyl-N'-3-phenylpropenoylthiourea (*IId*) (1 mmol) in chloroform (10 ml). The precipitate of benzothiazolinium bromide separated within several minutes was filtered off after 40 min and dried. The respective benzothiazoline was obtained by crystallization from ethanol and water.

3-*Methyl*-2-(3-(2-*furyl*)*propenoylimino*)*benzo*[d]*thiazoline* (VIa). Yield 70%, m.p. 166—168°C. For $C_{15}H_{12}N_2O_2S$ (284·3) calculated: 63·44% C, 4·25% H, 9·86% N; found: 63·58% C, 4·16% H, 10·02% N. IR spectrum ($CHCl_3$, $cm^{-1}$): $\nu_{as}(CH_3)$ 2960, $\nu$(C=O) 1 640, $\nu$(C=C) 1 590, $\nu$(C=N) 1 504, $\nu$(fur) 1 020, $\gamma$(CH=CH) 975. $^1$H-NMR spectrum ($CDCl_3$): 3·78 (s, $CH_3$), 7·63 and 6·71 (dd, — CH=CH—, $J_{AB}$ = 16 Hz), 7·24—7·55 (m, — $C_6H_4$—). Mass spectrum, *m/z* (%): 284 $M^+$, (56); 255 $[M—NCH_3]^+$, (18); 191 [M—2-furyl-CH=CH]$^+$, (24); 176 [M—2-furyl-CH=CH—$CH_3$]$^+$, (6); 149 [M—2-furyl-CH=CH—CON]$^+$, (12); 121 [2-furyl-CH=CH—CO]$^+$, (100); 93 [2-furyl-CH=CH]$^+$, (12); 65 $[C_5H_5]^+$, (83); 39 $[C_3H_3]^+$, (44); 28 $[CO]^+$, (15).

3-*Methyl*-2-(3-*phenylpropenoylimino*)*benzo*[d]*thiazoline* (VIb). Yield 75%, m.p. 160—161°C. For $C_{17}H_{14}N_2OS$ (294·4) calculated: 69·45% C, 4·80% H, 9·53% N; found: 69·56% C, 4·70% H, 9·56% N. IR spectrum, $cm^{-1}$ ($CHCl_3$): $\nu_{as}(CH_3)$ 2950, $\nu$(C=O) 1 643, $\nu$(C=C) 1 592, $\nu$(C=N) 1 510, $\gamma$(CH=CH) 944. $^1$H-NMR spectrum ($CDCl_3$): 3·78 (s, $CH_3$), 6·68 and 7·87 (dd, —CH=CH—, $J_{AB}$ = 16 Hz), 7·33 and 7·60 (mm, $C_6H_5$— and —$C_6H_4$—). Mass spectrum, *m/z* (%): 294 $M^+$, (86); 265 $[M—NCH_3]^+$, (8); 191 [M—$C_6H_5$—CH=CH]$^+$, (48); 176 [M—$C_6H_5$—CH=CH—$CH_3$]$^+$, (16); 131 [$C_6H_5$—CH=CH—CO]$^+$, (100); 103 [$C_6H_5$—CH=CH]$^+$, (100); 77 $[C_6H_5]^+$, (100); 51 $[C_4H_3]^+$, (40); 28 $[CO]^+$, (28).

### 2-Substituted 5-Arylidenethiazolin-4-ones *Va, Vb, Ve—Vs*

Bromine (2 mmol) was added with stirring to a solution of the respective thiourea (2 mmol) in chloroform (25 ml, when using 3-(2-furyl)propenoylthiourea (*IIe*), or 3-phenylpropenoylthiourea (*IIf*) 70 ml) and kept stirred for 1 h. The mixture was worked up by one of the following procedures: *a*) the separated hydrochloride was filtered off with suction, dried with a stream of air and immediately crystallized from the appropriate solvent (Table I — compounds *Vb, Vf, Vk, Vl, Vr, Vs*). *b*) the dark solution was diluted with chloroform (50 ml) and 3 times filtered with charcoal. The oil, obtained by removing the solvent, was warm-dissolved in ethanol–water from which compounds *Va, Vh, Vj, Vm, Vo, Vp* crystallized. *c*) the precipitate or oil, obtained either by method *a*) or *b*) was dissolved in methanol (50 ml), neutralized with 1M-NaOH and diluted with water (50 ml). The product was extracted 3 times with chloroform (25 ml) and the extract was

dried with magnesium sulfate. The half-solid residue, remaining after removal of the solvent, was crystallized (compounds *Ve*, *Vg*, *Vi*, *Vn*).

2-Dimethylamino-5-furfurylidenethiazolin-4-one ($X \equiv Vm$)

Furfurylidenerhodanine (10 mmol) was added during 5 min to a suspension of lithium hydride (10 mmol) in dimethylformamide (40 ml). The mixture was stirred till it became clear, then ethyl iodide (10 mmol) was added and stirred for additional 20 min. The mixture was poured into ice-cold water (150 ml), from which after a 3 h standing a precipitate containing N-ethylfurfurylidenerhodanine (*VIII*) and 2-ethylthio-5-furfurylidenethiazolin-4-one (*IX*) in a 1 : 1·6 ratio separated. It was suction filtered, washed with water (100 ml) and crystallized from acetone–water (the ratio of isomers did not change nor after a repeated recrystallization). Yield 80%, m.p. 104 to 108°C. To the mixture consisting of *VIII* and *IX* (2 mmol) dissolved in boiling ethanol (5 ml) diethylamine (2 mmol) in ethanol (5 ml) was added and left to stand for 14 h. The dark solution was then filtered three times with charcoal, the filtrate diluted with water (35 ml) and the separated precipitate *VIII* filtered off. Addition of water (60 ml) to the filtrate brought the compound $X \equiv Vm$ to crystallize in needles.

N-*Ethylfurfurylidenerhodanine* (VIII). Yield 85%, m.p. 115—116°C (methanol–water). For $C_{10}H_9NO_2S_2$ (239·3) calculated: 50·25% C, 3·79% H, 5·86% N; found: 50·40% C, 3·61% H, 5·77% N. IR spectrum, $cm^{-1}$ ($CHCl_3$): $\nu$(C=C) 1706, $\nu$(C=C) 1611, $\nu$(furan) 1026. $^1$H-NMR ($CDCl_3$): 1·26 (t, $CH_3$, $J = 7$ Hz), 4·16 (q, $-CH_2-$, $J = 7$ Hz, 7·44 (s, =CH—).

2-*Ethylthio-5-furfurylidenethiazolin-4-one* (IX) in mixture with *VIII*. $^1$H-NMR spectrum ($CDCl_3$): 1·44 (t, $CH_3$, $J = 7$ Hz), 3·38 (q, $-CH_2-$, $J = 7$ Hz), 7·56 (s, =CH—).

N-Substituted-N′-(α,β-unsaturated Acyl)thioureas *IIi*, *IIj*,
and N,N-Disubstituted-N′-(α,β-unsaturated Acyl)thioureas *IIm—IIs*

The respective amine (10 mmol) was dropwise added with stirring to a solution of 3-(2-furyl)-propenoyl isothiocyanate (*Ia*, 10 mmol) or 3-phenylpropenoyl isothiocyanate (*Ib*) in cyclohexane (50 ml). After the exothermic reaction was through a precipitate separated; it was filtered off, dried and crystallized from a suitable solvent.

N-*Cyclohexyl*-N′-3-(2-*furyl*)*propenoylthiourea* (IIi). Yield 87%, m.p. 125—127°C (methanol–water). For $C_{14}H_{18}N_2O_2S$ (278·3) calculated: 60·40% C, 6·51% H, 10·06% N; found: 60·18% C, 6·64% H, 10·19% N, IR spectrum, $cm^{-1}$ ($CHCl_3$): $\nu(NH)_{free}$ 3416, $\nu(NH)_{assoc.}$ 3254, $\nu_{as}(CH_2)$ 2935, $\nu_s(CH_2)$ 2861, $\nu$(C=O) 1673, $\nu$(C=C) 1618, $\nu$(NHCS) 1498, $\nu$(furan) 1018, $\gamma$(CH=CH) 969. $^1$H-NMR spectrum ($CDCl_3$): 1·50 and 4·40 (mm, $-CH_2-$ and $-CH-$), 6·44 and 7·53 (dd, $-CH=CH-$, $J_{AB} = 16$ Hz), 9·48 and 10·85 (ss, —NH—).

N-*Cyclohexyl*-N′-3-(*phenylpropenoylthiourea* (IIj). Yield 88%, m.p. 143—144°C (ethanol–water). For $C_{16}H_{20}N_2OS$ (288·4) calculated: 66·73% C, 7·00% H, 9·72% N; found: 66·50% C, 6·91% H, 9·98% N. IR spectrum, $cm^{-1}$ ($CHCl_3$): $\nu(NH)_{free}$ 3419, $\nu(NH)_{assoc.}$ 3230, $\nu_{as}(CH_2)$ 2945), $\nu_s(CH_2)$ 2868, $\nu$(C=O) 1678, $\nu$(C=O) 1627, $\nu$(NHCS) 1535, $\gamma$(CH=CH) 979. $^1$H-NMR, spectrum ($CDCl_3$): 1·50 and 4·30 (mm, $-CH_2-$ and $-CH-$), 6·68 and 7·75 (dd, $-CH=CH-$ $J_{AB} = 16$ Hz), 7·42 (m, $C_6H_5$), 9·76 and 10·86 (ss, —NH—).

N,N-*Diethyl*-N′-3-(2-*furyl*)*propenoylthiourea* (IIm). Yield 82%, m.p. 142—144°C (methanol–water). For $C_{12}H_{16}N_2O_2S$ (252·3) calculated: 57·12% $C_1$ 6·39% H, 11·15% N; found: 57·34% C, 6·10% H, 10·93% N. IR spectrum $cm^{-1}$ ($CHCl_3$): $\nu(NH)_{free}$ 3400, $\nu(NH)_{assoc.}$ 3150, $\nu$(C=O)

1695, ν(C=C) 1633, ν(NHCS) 1544, ν(furan) 1022, γ(CH=CH) 972. $^1$H-NMR ($CDCl_3$): 1·30 (t, $CH_3$, $J$ = 7 Hz), 3·80 (unresolved m, —$CH_2$—), 6·53 and 7·43 (dd, —CH=CH—, $J_{AB}$ = 16 Hz), 8·69 (s —NH—).

N,N-*Diethyl*-N'-3-*phenylpropenoylthiourea* (IIn). Yield 79%, m.p. 109—111°C (ethanol–water). For $C_{14}H_{18}N_2OS$ (262·4) calculated: 64·18% C, 6·93% H, 10·69% N; found: 64·35% C, 7·18% H, 10·48% N. IR spectrum, cm$^{-1}$ ($CHCl_3$): $\nu(NH)_{free}$ 3400, ν(C=O) 1695, ν(C=C) 1635, ν(NHCS) 1523, γ(CH=CH) 980. $^1$H-NMR spectrum ($CDCl_3$): 1·28 (t, $CH_3$, $J$ = 7 Hz), 3·75 (unresolved m, —$CH_2$—), 6·65 and 7·65 (dd, —CH=CH—, $J_{AB}$ = 16 Hz), 7·36 (m, $C_6H_5$—), 9·10 (s, —NH—).

1-(N-3-(2-*Furyl*)*propenoyl*)*thiocarbamoylpiperidine* (IIo). Yield 70%, m.p. 166—167°C (methanol–water). For $C_{13}H_{16}N_2O_2S$ (264·4) calculated: 59·07% C, 6·01% H, 10·59% N; found, 59·10% C, 5·89% H, 10·60% N. IR spectrum, cm$^{-1}$ (KBr): ν(C=O) 1658, ν(C=C) 1623: ν(NHCS) 1563, ν(furan) 1018, γ(CH=CH) 964. $^1$H-NMR spectrum ($CHCl_3$–hexadeuteriodimethyl sulfoxide): 1·68, 3·58 and 4·08 (mmm, —$CH_2$—), 6·55 and 7·40 (dd, —CH=CH—, $J_{AB}$ = 16 Hz), 9·73 (s, —NH—).

1-(N-3-*Phenylpropenoyl*)*thiocarbamoylpiperidine* (IIp). Yield 74%, m.p. 133—134°C (ethanol). For $C_{15}H_{18}N_2OS$ (274·4) calculated: 65·75% C, 6·62U %, 10·22% N; found: 65·56% C, 6·80% H, 10·02% N. IR spectrum, cm$^{-1}$ ($CHCl_3$): $\nu(NH)_{free}$ 3401, $\nu(NH)_{assoc}$ 3160, $\nu_{as}(CH_2)$ 2955, $\nu_s(CH_2)$ 2872, ν(C=O) 1696, ν(C=C) 1634, ν(NHCS) 1541, γ(CH=CH) 981. $^1$H-NMR spectrum ($CDCl_3$): 1·69, 3·63 and 4·09 (mmm, —$CH_2$—), 6·65 and 7·68 (dd, —CH=CH—, $J_{AB}$ = = 16 Hz), 7·36 (m, $C_6H_5$—), 9·25 (s, —NH—).

1-(N-3-(2-*Furyl*)*propenoyl*)*thiocarbamoylmorpholine* (IIr). Yield 69%, m.p. 166—168°C (methanol–water). For $C_{12}H_{14}N_2O_2S$ (264·3) calculated: 54·12% C, 5·23% H, 10·52% N; found: 53·95% C, 5·30% H, 10·11% N. IR spectrum, cm$^{-1}$ (KBr): ν(C=O) 1658, ν(C=C) 1622, ν(NHCS) 1539, ν(furan) 1016, γ(CH=CH) 956. $^1$H-NMR spectrum ($CDCl_3$–hexadeuteriodimethyl sulfoxide): 3·79 (m, —$CH_2$—), 6·46 and 7·43 (dd, —CH=CH—, $J_{AB}$ = 16 Hz), 10·00 (s, —NH—).

1-(N-3-*Phenylpropenoyl*)*thiocarbamoylmorpholine* (IIs). Yield 79%, m.p. 136—138°C (ethanol). For $C_{14}H_{16}N_2O_2S$ (276·3) calculated: 60·93% C, 5·96% H, 10·34% N; found: 60·70% C, 5·84% H, 10·15% N. IR spectrum, cm$^{-1}$ ($CHCl_3$): $\nu(NH)_{free}$ 3402, $\nu(NH)_{assoc}$ 3160, $\nu_{as}(CH_2)$ 2945, $\nu_s(CH_2)$ 2872, ν(C=O) 1703, ν(C=C) 1634, ν(NHCS) 1544, γ(CH=CH) 983. $^1$H-NMR spectrum ($CDCl_3$): 3·78 (m, —$CH_2$—), 6·63 and 7·70 (dd, —CH=CH—, $J_{AB}$ = 16 Hz), 7·41 (m, $C_6H_5$—), 9·21 (s, —NH—).

Spectral Measurements

Infrared spectra of the synthesized compounds were measured with a UR-20 (Zeiss, Jena) spectrometer in the 800—3500 cm$^{-1}$ region, the $^1$H-NMR spectra with a Tesla BS 487 A apparatus operating at 80 MHz tetramethylsilane being the internal reference substance, the mass spectra with an MS 902 S (AEI, Manchester) instrument at 70 eV and 120°C (*VIa*), 105°C (*VIb*), 130°C (*Vr*) and 140°C (*Vs*) ionization chamber temperature.

*Our thanks are due to Dr J. Leško, Laboratory of Mass Spectrometry, Slovak Institute of Technology, Bratislava, for measurement of mass spectra.*

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Translated by Z. Votický.