[3,3]- VERSUS [1,3]-SIGMATROPIC REARRANGEMENT OF *O*-SUBSTITUTED ALLYL *N*-ACYLMONOTHIOCARBAMATES

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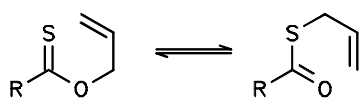
Substituted allylic alcohols (2-buten-1-ol, 1-buten-3-ol, cinnamyl alcohol and 3-methyl-2-buten-1-ol) react with acyl isothiocyanates (4-chlorobenzoyl, 2,6-difluorobenzoyl, 3-phenylpropenoyl, 2-thienocarbonyl, 3-chloro-2-thienocarbonyl and 3-chloro-2-benzo[*b*]thienocarbonyl isothiocyanate) with the formation of highly reactive *O*-substituted allyl *N*-acylmonothiocarbamates, which either spontaneously or by heating in boiling benzene undergo [3,3]-sigmatropic rearrangement to *S*-substituted allyl *N*-acylmonothiocarbamates. The structure of *S*-esters with isomerized allylic group affords the unequivocal evidence of the [3,3]-sigmatropic route of studied rearrangement. Further heating of [3,3]-rearranged *N*-(4-chlorobenzoyl)monothiocarbamates results in the [1,3]-sigmatropic shift of monothiocarbamate group. Using arylalkyl alcohols with the allylic double bond inserted into an aromatic system the obtained *O*-esters either do not undergo any rearrangement (benzyl alcohol) or undergo [1,3]-sigmatropic rearrangement (2- and 3-furylmethanol and 1-(2-furyl)ethanol) to the corresponding *S*-esters. For explanation of this reaction the tandem of [3,3]- and [1,3]-sigmatropic rearrangements is suggested.

The oxygen and sulfur containing 1,5-hexadiene systems of the type *I* (*O*-allyl monothioesters[1–4], monothiocarbamates[5–8], mono-[3] and dithiocarbonates[6,9,10]) are known to undergo a catalyzed or non-catalyzed [3,3]-sigmatropic rearrangement to compounds of the type *II* possessing the carbonyl and *S*-allyl instead of thiocarbonyl and *O*-allyl groups present in *I*. It was found[5,6] that substituents on allylic group, particularly α-methyl, accelerate the reaction $I \rightarrow II$. Reactivity also depends on the nature of group R. *O*-Allyl monothioesters are less reactive than compounds with R bonded via heteroatom, e.g. *O*-allyl *N*,*N*-dialkylmonothiocarbamates. Reactivity of monothiocarbamates



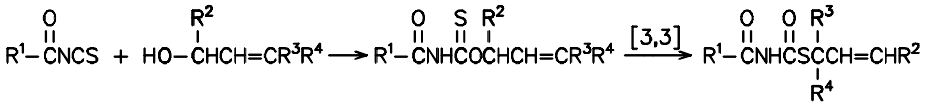
I *II*

is influenced by the nature of substituents on nitrogen atom[8]. *O*-Allyl *N*-phenylmonothiocarbamate rearranges to the corresponding *S*-allyl ester in boiling benzene during 48 h, whereas analogous *N*-benzoyl derivative requires only 9 h. In the present work we have studied the preparation of a series of *O*-substituted allyl *N*-acylmonothiocarbamates (**1** – **20**) from 4-chlorobenzoyl, 2,6-difluorobenzoyl, 3-phenylpropenoyl, 2-thienocarbonyl, 3-chloro-2-thienocarbonyl and 3-chloro-2-benzo-[*b*]thienocarbonyl isothiocyanate and substituted allyl alcohols. Our attention was predominantly focused on the rearrangement of *O*- to *S*-substituted allyl *N*-acylmonothiocarbamates (**21** – **40**, Scheme 1) with the aim to find out whether a [1,3]-sigmatropic rearrangement can be competitive or consequent reaction to the expected [3,3]-sigmatropic rearrangement. The selection of acyl isothiocyanates used in this study is based mainly on the expected higher stability and better yields of corresponding *O*-substituted allyl *N*-acylmonothiocarbamates (**1** – **20**) compared to products which can be obtained from other starting compounds, e.g. acetyl or benzoyl isothiocyanate[8].

It appeared that all of investigated *O*-substituted allyl esters are highly reactive. Whereas unsubstituted *O*-allyl *N*-acylmonothiocarbamates rearrange in boiling benzene during 9 – 30 h (yield 50 – 95%)[8,11], the longest reaction time for *O*-substituted allyl *N*-acylmonothiocarbamates is 3 h (yield 45 – 90%) under the same reaction conditions. According to reactivity in the [3,3]-sigmatropic rearrangement the *O*-substituted allyl esters **1** – **20** can be divided into three groups: (i) stable (**8**, **10**, **11**, **14**, **17**, **19**) which are isolable as pure compounds and undergo [3,3]-sigmatropic rearrangement by heating in boiling benzene; (ii) moderately stable (**1**, **3** – **5**, **20**) which can be isolated only as a mixtures with rearranged products and the [3,3]-sigmatropic rearrangement can be completed in boiling benzene; (iii) unstable (**2**, **6**, **7**, **9**, **12**, **13**, **15**, **16**, **18**) which can not be isolated because the reaction of acyl isothiocyanates with substituted allyl alcohols at room temperature affords dirrectly the products of [3,3]-sigmatropic rearrangement.

The highest reactivity exhibit the *O*-substituted allyl esters having the methyl group in α-position. None of the *O*-(1-buten-3-yl) *N*-acylmonothiocarbamates can be isolated, at least in a mixture with rearranged product, and only *S*-(2-butenyl)esters are obtained already at room temperature. γ-Substitution leads to more stable *O*-esters in the case of methyl group, compared to phenyl group, while compounds with two methyl groups in γ-position of allylic system (**4**, **20**) are less stable then γ-monomethyl derivatives. The acyl group also influences the reactivity of *O*-substituted allyl *N*-acylmonothiocarbamates, but this influence is not well understood. It seems that a bulky groups R^1 having extended conjugated system enabling an effective mesomeric interaction with carbonyl group, increase the stability of corresponding *O*-substituted allyl *N*-acylmonothiocarbamates, e.g. **8**, **10**, **17** and **19**.

The structure of prepared compounds was proved by spectral methods. Except for compounds **35** – **37** and **39** exhibiting in infrared spectra one broad intensive absorption



1 – 20 21 – 40

	R^1	R^2	R^3	R^4
1, 21	4-ClC_6H_4	H	H	CH_3
2, 22	4-ClC_6H_4	CH_3	H	H
3, 23	4-ClC_6H_4	H	H	C_6H_5
4, 24	4-ClC_6H_4	H	CH_3	CH_3
5, 25	2,6-$F_2C_6H_3$	H	H	CH_3
6, 26	2,6-$F_2C_6H_3$	CH_3	H	H
7, 27	2,6-$F_2C_6H_3$	H	H	C_6H_5
8, 28	$C_6H_5CH=CH$	H	H	CH_3
9, 29	$C_6H_5CH=CH$	CH_3	H	H
10, 30	$C_6H_5CH=CH$	H	H	C_6H_5
11, 31	T	H	H	CH_3
12, 32	T	CH_3	H	H
13, 33	T	H	H	C_6H_5
14, 34	CT	H	H	CH_3
15, 35	CT	CH_3	H	H
16, 36	CT	H	H	C_6H_5
17, 37	CBT	H	H	CH_3
18, 38	CBT	CH_3	H	H
19, 39	CBT	H	H	C_6H_5
20, 40	CBT	H	CH_3	CH_3

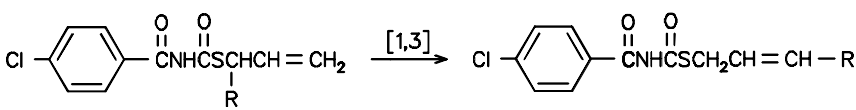
T = 2-thienyl; CT = 3-chloro-2-thienyl;
CBT = 3-chloro-2-benzo[*b*]thienyl

SCHEME 1

band of carbonyl vibrations at 1 650 – 1 690 cm^{-1}, all *S*-substituted allyl esters show two carbonyl absorption bands of CO–NH–CO grouping at 1 650 – 1 715 cm^{-1}, whereas *O*-substituted allyl esters show a single absorption band of ν(C=O) at 1 680 – 1 720 cm^{-1}. Structural evidence provided by NMR spectroscopy can be demonstrated on *N*-(3-phenylpropenoyl)monothiocarbamates **8**, **10**, **28** – **30**. In ^{1}H NMR spectra of compounds **8** and **10**, there are present the signals of OCH_2 protons at 5.**11** and 5.56 ppm, while **29** which is the functional group isomer of **8**, exhibits the SCH_2 signal at 3.93 ppm. In ^{13}C NMR spectra of **8** and **10**, there are present the triplets of OCH_2 group at 73.42 and 71.09 ppm. Corresponding rearranged products show doublets of SCH groups at 41.66 ppm (**28**) and 49.58 ppm (**30**). The triplet of SCH_2 group of **29** is present at 32.21 ppm. As expected, the NMR data (see Experimental) of compounds **21** – **40** are in full agreement with the structure of products formed from starting compounds by [3,3]-sigmatropic rearrangement. Posible [1,3]-sigmatropic rearrangement as a competitive process to the [3,3]-sigmatropic rearrangement can be excluded. Anyway there is described an example of competitive [1,3]-sigmatropic rearrangement of *O*-substituted allyl *N*,*N*-dialkylmonothiocarbamates to *S*-substituted allyl esters by heating to 150 °C, whereas at 130 °C the [3,3]-sigmatropic rearrangement takes place[5]. We have found that the [1,3]-sigmatropic rearrangement can be a consecutive, but not competitive reaction. For instance, heating of [3,3]-rearranged products **21** and **23** with α-substituted allylic group in boiling toluene causes the [1,3]-sigmatropic rearrangement with the formation of compounds **22** and **41** (Scheme 2).

If the reaction is started from *O*-ester **3**, the product **23** is formed in boiling toluene immediately and only after prolonged heating it changes to [1,3]-rearranged product **41** (TLC and ^{1}H NMR). The driving force of observed [1,3]-sigmatropic rearrangement can be ascribed to the conversion of thermodynamically less stable terminal double bond to the more stable internal double bond[7]. In agreement with this explanation is the stability of compound **22** obtained from 4-chlorobenzoyl isothiocyanate and 1-buten-3-ol which does not rearrange by heating in boiling toluene.

In continuation of our study we obtained interesting results by investigation of monothiocarbamates obtained from arylalkyl alcohols in which the allylic double bond is a



21, R = CH_3 **22**, R = CH_3
23, R = C_6H_5 **41**, R = C_6H_5

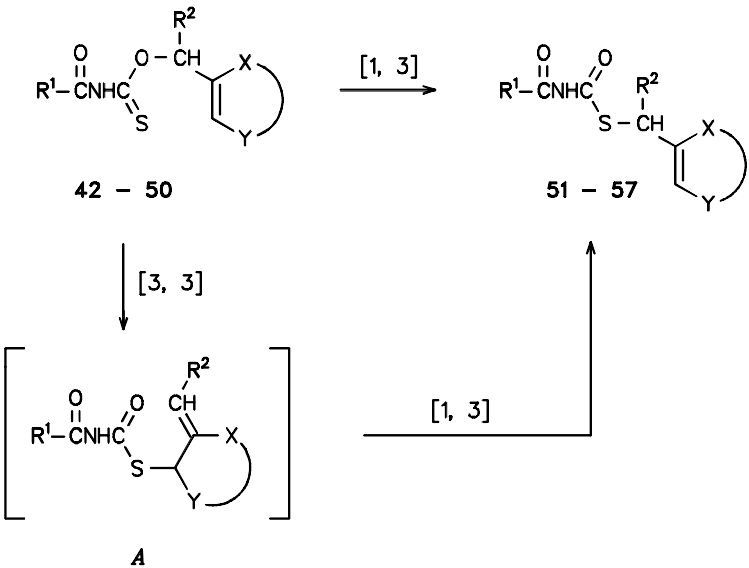
SCHEME 2

part of aromatic system (benzyl alcohol, 2-furylmethanol, 1-(2-furyl)ethanol and 3-furylmethanol) and 4-chlorobenzoyl, 3-phenylpropenoyl and 3-chloro-2-benzo[*b*]thienocarbonyl isothiocyanate (Scheme 3).

O-Benzyl esters **45** and **47** are very stable and even after 20 h of reflux in benzene do not exhibit any tendency to rearrange (TLC and ^{1}H NMR). On the other hand 2-furylmethanol and 1-(2-furyl)ethanol react with acyl isothiocyanates dirrectly with the formation of [1,3]-rearranged products **51**, **52**, **54**, **55** and **56** without the possibility to isolate corresponding *O*-arylalkyl esters **42**, **43**, **46**, **48** and **49**. Products possessing the medium reactivity are obtained from 3-furylmethanol. *O*-(3-Furylmethyl) esters **44** and **50** can be isolated and they undergo the [1,3]-sigmatropic rearrangement to *S*-(3-furylmethyl) esters **53** and **57** by 3 h reflux in benzene. According to above mentioned activation effect of α-methyl group, we expected enhanced reactivity of benzoyloxy group in *O*-[1-(3-nitrophenyl)ethyl] *N*-(4-chlorobenzoyl)monothiocarbamate (**58**). However, heating of compound **58** revealed that it is equally stable and unreactive as compounds **45** and **47**.

Unusually high reactivity of furan derivatives and unreactivity of benzyl esters indicate some specific interaction between furan ring and monothiocarbamate functionality. There might take place a tandem of [3,3]- and [1,3]-sigmatropic rearrangements or dirrect [1,3]-sigmatropic rearrangement of *O*-arylalkyl to *S*-arylalkyl *N*-acylmonothiocarbamates (Scheme 3). In the literature there is only limited information about analogous [1,3]-sigmatropic rearrangements. *O*-Methyl *N*-acylmonothiocarbamates require the BF_3-catalysis[12] whereas *O*-aryl *N*,*N*-diethylmonothiocarbamates undergo [1,3]-sigmatropic rearrangement at 280 – 285 °C in diphenyl ether[13]. It was found that 2-furfuryloxy-4,5-diphenyloxazole affords at 60 °C the isolable [3,3]-rearranged product, similar to intermediate *A* (Scheme 3) which undergoes the [1,3]-sigmatropic shift of hydrogen by heating to 90 °C. The same mechanism of [3,3]-sigmatropic rearrangement followed by [1,3]-sigmatropic shift of amido group is proposed for 2-benzyloxy-4,5-diphenyloxazole, although intermediate is not isolable[14]. All of our attempts to isolate an intermediate of the type *A* during rearrangement of furyl derivatives in benzene and acetonitrile at temperature below 80 °C failed. However, considering the unreactivity of *O*-benzyl *N*-acylmonothiocarbamates and the above mentioned literature data it can be suggested that a tandem of [3,3]- and [1,3]-sigmatropic rearrangements is probably the reason of high reactivity of *O*-(2-furylmethyl), *O*-[1-(2-furyl)ethyl] and *O*-(3-furylmethyl) *N*-acylmonothiocarbamates. We assume that owing to relatively low aromaticity of furan ring, the [3,3]-sigmatropic rearrangement with the formation of species *A* proceeds smoothly. Electron withdrawing effect of carbonyl group enhances the reactivity of sulfur atom and favours its interaction with exocyclic double bond. This interaction probably results in the immediate [1,3]-sigmatropic shift of *N*-acylmonothiocarbamate group and transformation of transiently formed dihydrofuran intermediate *A* onto furan ring in final product. Competitive [1,3]-sigmatropic hydrogen

shift is not observed; no products containing the methyl group can be isolated from the mixture.



	R^1	R^2	X	Y
42, 51	4-ClC_6H_4	H	O	CH=CH
43, 52	4-ClC_6H_4	CH_3	O	CH=CH
44, 53	4-ClC_6H_4	H	CH=CH	O
45	C_6H_5CH=CH	H	CH=CH	CH=CH
46, 54	C_6H_5CH=CH	H	O	CH=CH
47	CBT	H	CH=CH	CH=CH
48, 55	CBT	H	O	CH=CH
49, 56	CBT	CH_3	O	CH=CH
50, 57	CBT	H	CH=CH	O

CBT = 3-chloro-2-benzo[*b*]thienyl

EXPERIMENTAL

The infrared absorption spectra were recorded on an IR-75 (Zeiss, Jena) spectrometer in chloroform (compounds **3**, **5**, **8**, **10**, **11**, **14**, **19**, **21** – **41**, **45**, **50**, **55** – **58**) or in KBr pellets (compounds **44**, **51** – **54**); the wavenumbers are given in cm^{-1}. ^1H and ^{13}C NMR spectra were measured on Tesla BS 487A (80 MHz for ^1H) and Tesla BS 567 (25.15 MHz for ^{13}C) spectrometers in deuteriochloroform (compounds **1**, **3**, **4**, **8**, **11**, **14**, **19** – **29**, **31**, **32**, **34** – **36**, **38** – **41**, **44**, **45**, **47**, **50**, **52**, **56** – **58**) or in hexadeuteriodimethyl sulfoxide (compounds **10**, **30**, **33**, **37**, **51**, **54**, **55**) with tetramethylsilane as an internal standard. Chemical shifts are given in ppm (δ scale), coupling constants *J* in Hz.

2-Buten-1-ol (mixture of isomers), *trans*-cinnamyl alcohol, benzyl alcohol, 2-furylmethanol and 3-furylmethanol (Aldrich), 1-buten-3-ol (Merck), 3-methyl-2-buten-1-ol and 1-(2-furyl)ethanol (Fluka) were used as commercial chemicals. 4-Chlorobenzoyl isothiocyanate[15], 2,6-difluorobenzoyl isothiocyanate[16], 3-phenylpropenoyl isothiocyanate[17], 2-thienocarbonyl isothiocyanate[18], 3-chloro-2-thienocarbonyl isothiocyanate[19], 3-chloro-2-benzo[*b*]thienocarbonyl isothiocyanate[20] and 1-(3-nitrophenyl)ethanol[21] were prepared according to the literature. The reactions were monitored by thin-layer chromatography on Silufol plates (Kavalier, The Czech Republic) using benzene–acetone (7 : 1) as eluent.

O-Substituted Allyl *N*-Acylmonothiocarbamates **1**, **3** – **5**, **8**, **10**, **11**, **14**, **17**, **19**, **20**

Substituted allyl alcohol (18 mmol) was added to acyl isothiocyanate (15 mmol) in dry benzene (20 ml) and the mixture was left asside at room temperature for 1 day (compounds **4**, **11**, **17** and **20**), 2 days (compounds **1**, **3** and **14**), 3 days (compound **10**), 4 days (compounds **5** and **8**) or 5 days (compound **19**). Hexane (80 – 200 ml) was added to turbidity and mixture allowed to stand at 0 °C for 24 h. The precipitate was filtered off and the product crystallized from a suitable solvent. Compounds **1**, **3**, **4**, **5** and **20** were obtained only as mixtures with rearranged products **21**, **23**, **24**, **25** and **40**; the ratio of constituents was determined by ^1H NMR spectroscopy. In these cases the yields of mixtures are given.

O-(2-Buten-1-yl) N-(4-chlorobenzoyl)monothiocarbamate (**1**), in the 1 : 1 mixture with **21**; yield 80%. ^1H NMR spectrum: 1.80 m, 3 H (CH_3); 5.18 m, 2 H (OCH_2); 5.97 m, 2 H (CH=CH); 7.53 d, 2 H and 7.91 d, 2 H, J = 8 (4-ClC_6H_4); 9.40 s, 1 H (NH).

O-Cinnamyl N-(4-chlorobenzoyl)monothiocarbamate (**3**), in the 1 : 1 mixture with **23**; yield 60%. ^1H NMR spectrum: 5.36 m, 2 H (OCH_2); 6.62 m, 2 H (CH=CH); 7.47 m, 5 H (C_6H_5); 7.58 d, 2 H and 7.92 d, 2 H, J = 8 Hz (4-ClC_6H_4); 9.35 s, 1 H (NH).

O-(3-Methyl-2-buten-1-yl) N-(4-chlorobenzoyl)monothiocarbamate (**4**), in the 3 : 1 mixture with **24**; yield 83%. ^1H NMR spectrum: 1.80 m, 6 H (2 × CH_3); 5.18 m, 2 H (OCH_2); 5.57 m, 1 H (=CH); 7.52 d, 2 H and 7.87 d, 2 H, J = 8 (4-ClC_6H_4); 9.39 s, 1 H (NH).

O-(2-Buten-1-yl) N-(2,6-difluorobenzoyl)monothiocarbamate (**5**); in the 1 : 1 mixture with **25**; yield 76%. ^1H NMR spectrum: 1.80 m, 3 H (CH_3); 5.00 m, 2 H (OCH_2); 7.19 m, 2 H and 7.60 m, 1 H (2,6-$F_2C_6H_3$); 9.25 s, 1 H (NH).

O-(2-Buten-1-yl) N-(3-phenylpropenoyl)monothiocarbamate (**8**); yield 80%, m.p. 140 – 142 °C (benzene–hexane). For $C_{14}H_{15}NO_2S$ (260.3) calculated: 64.34% C, 5.79% H, 5.36% N; found: 64.13% C, 5.74% H, 5.25% N. IR spectrum: 1 495 (NHCS), 1 625 and 1 675 (C=C), 1 715 (C=O), 3 380 (N–H). ^1H NMR spectrum: 1.75 m, 3 H (CH_3); 5.01 m, 2 H (OCH_2); 5.90 m, 2 H (CH=CH); 7.09 d, 1 H and 7.86 d, 1 H, J = 16 (CH=CHCO); 7.45 m, 5 H (C_6H_5); 9.25 s, 1 H (NH). ^{13}C NMR spectrum: 17.81 q (CH_3), 73.42 t (OCH_2), 119.52 d and 145.88 d (CH=CHCO), 123.63 d and 133.26 d (CH=$CHCH_3$), 128.37, 128.93, 130.64 and 134.45 (C_6H_5), 163.27 s (C=O), 188.88 s (C=S).

O-Cinnamyl N-(3-phenylpropenoyl)monothiocarbamate (**10**); yield 90%, m.p. 126 – 128 °C (acetone–water). For $C_{19}H_{17}NO_2S$ (323.4) calculated: 70.56% C, 5.30% H, 4.33% N; found: 70.70% C,

5.10% H, 4.61% N. IR spectrum: 1 490 (NHCS), 1 630 and 1 675 (C=C), 1 720 (C=O), 3 385 (N–H). ^{1}H NMR spectrum: 5.56 m, 2 H (OCH_2); 7.20 m, 2 H (CH=CH); 7.60 d, 1 H and 8.08 d, 1 H, J = 16 (CH=CHCO); 7.78 m, 10 H (2 × C_6H_5); 12.08 s, 1 H (NH). ^{13}C NMR spectrum: 71.09 t (OCH_2), 120.73 d and 143.43 d (CH=CHCO), 122.24 d and 133.76 d ($CH=CHCH_2$), 126.29, 127.82, 128.42, 128.75, 130.17, 134.09 and 135.69 (2 × C_6H_5), 162.16 s (C=O), 188.44 s (C=S).

O-(2-Buten-1-yl) N-(2-thienocarbonyl)monothiocarbamate (**11**); yield 53%, m.p. 82 – 84 °C (acetone–hexane). For $C_{10}H_{11}NO_2S_2$ (241.3) calculated: 49.77% C, 4.59% H, 5.80% N; found: 49.90% C, 4.38% H, 5.64% N. IR spectrum: 1 480 (NHCS), 1 675 (C=C), 1 690 (C=O), 3 410 (N–H). ^{1}H NMR spectrum: 1.80 m, 3 H (CH_3); 5.14 m, 2 H (OCH_2); 5.98 m, 2 H (CH=CH); 7.28 m, 1 H, 7.83 m, 1 H and 8.20 m, 1 H (2-thienyl); 11.43 s, 1 H (NH).

O-(2-Buten-1-yl) N-(3-chloro-2-thienocarbonyl)monothiocarbamate (**14**); yield 50%, m.p. 40 – 42 °C (benzene–hexane). For $C_{10}H_{10}ClNO_2S_2$ (275.8) calculated: 43.55% C, 3.65% H, 5.08% N; found: 43.26% C, 3.79% H, 5.21% N. IR spectrum: 1 480 (NHCS), 1 680 (C=O), 3 365 (N–H). ^{1}H NMR spectrum: 1.83 m, 3 H (CH_3); 5.18 m, 2 H (OCH_2); 6.02 m, 2 H (CH=CH); 7.18 d, 1 H and 7.78 d, 1 H, J = 5 (2,3-disubstituted thiophene); 10.10 s, 1 H (NH).

O-(2-Buten-1-yl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**17**); yield 42%, m.p. 97 – 99 °C (benzene–hexane). For $C_{14}H_{12}ClNO_2S_2$ (325.8) calculated: 51.61% C, 3.71% H, 4.30% N; found: 51.42% C, 3.59% H, 4.09% N. IR spectrum: 1 500 (NHCS), 1 690 (C=O), 3 380 (N–H). ^{1}H NMR spectrum: 1.78 m, 3 H (CH_3); 5.10 m, 2 H (OCH_2); 5.93 m, 2 H (CH=CH); 7.56 m, 2 H and 7.79 m, 2 H (2,3-disubstituted benzothiophene); 10.15 s, 1 H (NH).

O-Cinnamyl N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**19**); yield 71%, m.p. 115 – 117 °C (benzene–hexane). For $C_{19}H_{14}ClNO_2S_2$ (387.9) calculated: 58.83% C, 3.46% H, 3.69% N; found: 58.68% C, 3.39% H, 3.47% N. IR spectrum: 1 505 (NHCS), 1 700 (C=O), 3 380 (N–H). ^{1}H NMR spectrum: 5.35 m, 2 H (OCH_2); 6.70 m, 2 H (CH=CH); 7.40 m, 5 H (C_6H_5); 7.55 m, 2 H and 7.90 m, 2 H (2,3-disubstituted benzothiophene); 10.19 s, 1 H (NH).

O-(3-Methyl-2-buten-1-yl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**20**) in the 2 : 1 mixture with **40**. ^{1}H NMR spectrum: 1.83 m, 3 H (CH_3); 5.25 m, 2 H (OCH_2); 5.68 m, 1 H (=CH); 7.68 m, 2 H and 7.98 m, 2 H (2,3-disubstituted benzothiophene); 10.18 s, 1 H (NH).

S-Substituted Allyl *N*-Acylmonothiocarbamates **21** – **41**

A. A solution of the corresponding *O*-allyl ester or its mixture with rearranged product (3 mmol) in benzene (10 ml) was refluxed for 0.5 h (compounds **34** and **37**), 1 h (compound **30**), 1.5 h (compound **31**), 2 h (compounds **21**, **23** and **28**) or 3 h (compounds **24**, **39** and **40**). The solvent was evaporated and the residue crystallized from an appropriate solvent.

B. Substituted allyl alcohol (18 mmol) was added to acyl isothiocyanate (15 mmol) in anhydrous benzene (20 ml) and the mixture was kept at room temperature for 1 day (compounds **22** and **32**), 2 days (compound **36**), 3 days (compounds **33**, **35** and **38**), 4 days (compounds **25** and **26**) or 5 days (compounds **27** and **29**). Hexane (80 – 200 ml) was added to turbidity and mixture allowed to stand at 0 °C for 24 h. The precipitate was filtered off and the product crystallized from a suitable solvent.

C. S-Substituted allyl *N*-(4-chlorobenzoyl)monothiocarbamate **21** or **23** (1 mmol) was refluxed in toluene (8 ml) for 16 h. The mixture was filtered and products **22** or **41** precipitated by addition of light petroleum, dried and crystallized from a suitable solvent.

S-(1-Buten-3-yl) N-(4-chlorobenzoyl)monothiocarbamate (**21**); yield 82%, m.p. 159 – 162 °C (dec., benzene–hexane). For $C_{12}H_{12}ClNO_2S$ (269.8) calculated: 53.42% C, 4.48% H, 5.19% N; found: 53.28% C, 4.56% H, 5.08% N. IR spectrum: 1 650 (C=C), 1 675 and 1 715 (C=O), 3 415 (N–H). ^{1}H NMR spectrum: 1.53 d, 3 H, J = 7 (CH_3); 4.32 m, 1 H (CH); 5.35 m, 2 H ($=CH_2$); 6.09 m, 1 H (=CH); 7.55 d, 2 H and 8.05 d, 2 H, J = 8 (4-ClC_6H_4); 10.17 s, 1 H (NH).

S-(2-Buten-1-yl) N-(4-chlorobenzoyl)monothiocarbamate (**22**); yield 50% (procedure *B*) or 70% (procedure *C*), m.p. 156 – 159 °C (dec., benzene–hexane). For $C_{12}H_{12}ClNO_2S$ (269.8) calculated: 53.42% C, 4.48% H, 5.19% N; found: 53.20% C, 4.62% H, 5.12% N. IR spectrum: 1 635 (C=C), 1 650 and 1 685 (C=O), 3 400 (N–H). ^{1}H NMR spectrum: 1.75 m, 3 H (CH_3); 3.65 m, 2 H (SCH_2); 5.78 m, 2 H (CH=CH); 7.57 d, 2 H and 8.10 d, 2 H, J = 8 (4-ClC_6H_4); 11.30 s, 1 H (NH).

S-(1-Phenyl-2-propen-1-yl) N-(4-chlorobenzoyl)monothiocarbamate (**23**); yield 82%, m.p. 124 – 126 °C (benzene–hexane). For $C_{17}H_{14}ClNO_2S$ (331.8) calculated: 61.54% C, 4.25% H, 4.22% N; found: 61.78% C, 4.09% H, 4.18% N. IR spectrum: 1 643 (C=C), 1 665 and 1 705 (C=O), 3 408 (N–H). ^{1}H NMR spectrum: 5.36 m, 3 H (=CH_2 and CH); 6.18 m, 1 H (=CH); 7.50 m, 5 H (C_6H_5); 7.45 d, 2 H and 7.91 d, 2 H, J = 8 (4-ClC_6H_4); 9.65 s, 1 H (NH).

S-(1-Buten-3-methyl-3-yl) N-(4-chlorobenzoyl)monothiocarbamate (**24**); yield 60%, m.p. 123 – 125 °C (benzene). For $C_{13}H_{14}ClNO_2S$ (283.8) calculated: 55.02% C, 4.97% H, 4.93% N; found: 55.19% C, 5.13% H, 4.88% N. IR spectrum: 1 630 (C=C), 1 660 and 1 695 (C=O), 3 410 (N–H). ^{1}H NMR spectrum: 1.60 s, 6 H (2 × CH_3); 5.15 m, 2 H (=CH_2); 6.15 m, 1 H (=CH); 7.47 d, 2 H and 7.90 d, 2 H, J = 8 (4-ClC_6H_4).

S-(1-Buten-3-yl) N-(2,6-difluorobenzoyl)monothiocarbamate (**25**); yield 76%, m.p. 102 – 104 °C (benzene–hexane). For $C_{12}H_{11}F_2NO_2S$ (271.3) calculated: 53.13% C, 4.09% H, 5.16% N; found: 53.28% C, 3.91% H, 5.02% N. IR spectrum: 1 625 (C=C), 1 670 and 1 715 (C=O), 3 395 (N–H). ^{1}H NMR spectrum: 1.45 d, 3 H, J = 7 (CH_3); 4.26 m, 1 H (CH); 5.28 m (=CH_2); 6.03 m, 1 H (=CH); 7.12 m, 2 H and 7.57 m, 1 H (2,6-$F_2C_6H_3$); 9.28 s, 1 H (NH).

S-(2-Buten-1-yl) N-(2,6-difluorobenzoyl)monothiocarbamate (**26**); yield 83%, m.p. 133 – 135 °C (benzene–hexane). For $C_{12}H_{11}F_2NO_2S$ (271.3) calculated: 53.13% C, 4.09% H, 5.16% N; found: 53.27% C, 4.15% H, 5.31% N. IR spectrum: 1 620 (C=C), 1 660 and 1 715 (C=O), 3 400 (N–H). ^{1}H NMR spectrum: 1.76 m, 3 H (CH_3); 3.60 m, 2 H (SCH_2); 5.68 m, 2 H (CH=CH); 7.13 m, 2 H and 7.62 m, 1 H (2,6-$F_2C_6H_3$); 9.38 s, 1 H (NH).

S-(1-Phenyl-2-propen-1-yl) N-(2,6-difluorobenzoyl)monothiocarbamate (**27**); yield 50%, m.p. 126 – 129 °C (dec., benzene–hexane). For $C_{17}H_{13}F_2NO_2S$ (333.4) calculated: 61.24% C, 3.93% H, 4.20% N; found: 60.96% C, 3.71% H, 4.45% N. IR spectrum: 1 620 (C=C), 1 670 and 1 710 (C=O), 3 400 (N–H). ^{1}H NMR spectrum: 5.40 m, 3 H (=CH_2 and CH); 6.30 m, 1 H (=CH); 7.00 – 7.80 m, 8 H (C_6H_5 and 2,6-$F_2C_6H_3$); 9.26 s, 1 H (NH).

S-(1-Buten-3-yl) N-(3-phenylpropenoyl)monothiocarbamate (**28**); yield 72%, m.p. 119 – 122 °C (dec., benzene–hexane). For $C_{14}H_{15}NO_2S$ (261.3) calculated: 64.34% C, 5.79% H, 5.36% N; found: 64.13% C, 5.74% H, 5.25% N. IR spectrum: 1 625 and 1 655 (C=C), 1 670 and 1 700 (C=O), 3 390 1 H (=CH); 6.90 d, 1 H and 7.90 d, 1 H, J = 16 Hz (CH=CH); 7.47 m, 5 H (C_6H_5); 9.65 s, 1 H (NH). ^{13}C NMR spectrum: 19.52 q (CH_3), 41.66 d (CH), 115.71 t (=CH_2), 118.81 d and 146.02 d (CH=CH), 128.44, 128.93, 130.76 and 134.23 (C_6H_5), 138.45 d (=CH), 164.91 s and 170.45 s (C=O).

S-(2-Buten-1-yl) N-(3-phenylpropenoyl)monothiocarbamate (**29**); yield 80%, m.p. 131 – 133 °C (acetone–water). For $C_{14}H_{15}NO_2S$ (261.3) calculated: 64.34% C, 5.79% H, 5.36% N; found: 64.18% C, 5.90% H, 5.12% N. IR spectrum: 1 620 and 1 660 (C=C), 1 690 and 1 715 (C=O), 3 395 (N–H). ^{1}H NMR spectrum: 2.05 m, 3 H (CH_3); 3.93 m, 2 H (SCH_2); 6.05 m, 2 H (CH=CH); 7.23 d, 2 H and 8.15 d, 2 H, J = 16 (CH=CHCO); 7.95 m, 5 H (C_6H_5); 11.42 s, 1 H (NH). ^{13}C NMR spectrum: 17.69 q (CH_3), 32.21 t (SCH_2), 118.89 d and 145.99 d (CH=CHCO), 125.35 d and 129.90 d (CH=$CHCH_2$), 128.48, 128.97, 130.76 and 134.30 (C_6H_5), 164.95 s and 170.99 s (C=O).

S-(1-Phenyl-2-propen-1-yl) N-(3-phenylpropenoyl)monothiocarbamate (**30**); yield 87%, m.p. 127 – 129 °C (tetrachloromethane). For $C_{19}H_{17}NO_2S$ (323.4) calculated: 70.56% C, 5.30% H, 4.33% N; found: 70.41% C, 5.19% H, 4.03% N. IR spectrum: 1 625 and 1 645 (C=C), 1 670 and 1 710 (C=O), 3 395 (N–H). ^{1}H NMR spectrum: 5.52 m, 3 H (=CH_2 and CH); 6.50 m, 1 H (=CH); 7.10 d, 1 H and 8.01 d, 1 H, J = 16 (CH=CH); 7.63 m, 10 H (2 × C_6H_5); 11.70 s, 1 H (NH).

^{13}C NMR spectrum: 49.58 d (CH), 116.44 t (=CH_2), 119.25 d and 143.57 d (CH=CH), 127.00, 127.79, 127.86, 128.27, 128.76, 130.27, 133.83 and 139.54 (2 × C_6H_5), 137.08 d (=CH), 164.14 s and 167.39 s (C=O).

S-(1-Buten-3-yl) N-(2-thienocarbonyl)monothiocarbamate (**31**); yield 90%, m.p. 96 – 98 °C (benzene–hexane). For $C_{10}H_{11}NO_2S_2$ (241.3) calculated: 49.77% C, 4.59% H, 5.80% N; found: 49.62% C, 4.51% H, 5.50% N. IR spectrum: 1 640 (C=C), 1 665 and 1 695 (C=O), 3 410 (N–H). ^{1}H NMR spectrum: 1.54 d, 3 H, J = 7 (CH_3); 4.38 m, 1 H (CH); 5.30 m, 2 H (=CH_2); 6.12 m, 1 H (=CH); 7.30 m, 1 H, 8.86 m, 1 H and 8.10 m, 1 H (2-thienyl); 10.15 s, 1 H (NH).

S-(2-Buten-1-yl) N-(2-thienocarbonyl)monothiocarbamate (**32**); yield 67%, m.p. 142 – 145 °C (dec., benzene–hexane). For $C_{10}H_{11}NO_2S_2$ (241.3) calculated: 49.77% C, 4.59% H, 5.80% N; found: 49.81% C, 4.43% H, 5.99% N. IR spectrum: 1 630 (C=C), 1 655 and 1 675 (C=O); 3 410 (N–H). ^{1}H NMR spectrum: 1.79 m, 3 H (CH_3); 3.63 m, 2 H (SCH_2); 5.90 m, 2 H (CH=CH); 7.28 m, 1 H, 7.83 m, 1 H and 8.28 m, 1 H (2-thienyl); 11.53 s, 1 H (NH).

S-(1-Phenyl-2-propen-1-yl) N-(2-thienocarbonyl)monothiocarbamate (**33**); yield 52%, m.p. 129 – 131 °C (benzene–hexane). For $C_{15}H_{13}NO_2S_2$ (303.4) calculated: 59.38% C, 4.32% H, 4.62% N; found: 59.56% C, 4.18% H, 4.39% N. IR spectrum: 1 635 (C=C), 1 655 and 1 675 (C=O), 3 405 (N–H). ^{1}H NMR spectrum: 5.37 m, 3 H (=CH_2 and CH); 6.25 m, 1 H (=CH); 7.20 m, 1 H, 7.66 m, 1 H and 8.12 m, 1 H (2-thienyl); 7.42 m, 5 H (C_6H_5); 11.20 s, 1 H (NH).

S-(1-Buten-3-yl) N-(3-chloro-2-thienocarbonyl)monothiocarbamate (**34**); yield 56%, m.p. 55 – 56 °C (tetrachloromethane–hexane). For $C_{10}H_{10}ClNO_2S_2$ (275.8) calculated: 43.55% C, 3.65% H, 5.08% N; found: 43.38% C, 3.50% H, 4.91% N. IR spectrum: 1 670 and 1 685 (C=O), 3 375 (N–H). ^{1}H NMR spectrum: 1.50 d, 3 H, J = 7 (CH_3); 4.38 m, 1 H (CH); 5.30 m, 2 H (=CH_2); 6.05 m, 1 H (=CH); 7.17 d, 1 H and 7.75 d, 1 H, J = 5 (2,3-disubstituted thiophene); 9.50 s, 1 H (NH).

S-(2-Buten-1-yl) N-(3-chloro-2-thienocarbonyl)monothiocarbamate (**35**); yield 60%, m.p. 75 – 77 °C (benzene–hexane). For $C_{10}H_{10}ClNO_2S_2$ (275.8) calculated: 43.55% C, 3.65% H, 5.08% N; found: 43.72% C, 3.44% H, 5.31% N. IR spectrum: 1 650 (C=O), 3 360 (N–H). ^{1}H NMR spectrum: 1.75 m, 3 H (CH_3); 3.69 m, 2 H (SCH_2); 5.75 m, 2 H (CH=CH); 7.17 d, 1 H and 7.78 d, 1 H, J = 5 (2,3-disubstituted thiophene); 9.55 s, 1 H (NH).

S-(1-Phenyl-2-propen-1-yl) N-(3-chloro-2-thienocarbonyl)monothiocarbamate (**36**); yield 61%, m.p. 66 – 69 °C (dec., benzene–hexane). For $C_{15}H_{12}ClNO_2S_2$ (337.8) calculated: 53.33% C, 3.58% H, 4.15% N; found: 53.12% C, 3.43% H, 3.92% N. IR spectrum: 1 680 (C=O), 3 370 (N–H). ^{1}H NMR spectrum: 5.39 m, 3 H (=CH_2 and CH); 6.50 m, 1 H (=CH); 7.10 d, 1 H and 7.70 d, 1 H, J = 5 (2,3-disubstituted thiophene); 10.13 s, 1 H (NH).

S-(1-Buten-3-yl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**37**); yield 60%, m.p. 231 – 234 °C (dec., benzene–hexane). For $C_{14}H_{12}ClNO_2S_2$ (325.8) calculated: 51.61% C, 3.71% H, 4.30% N; found: 51.45% C, 3.52% H, 4.17% N. IR spectrum: 1 670 (C=O), 3 370 (N–H). ^{1}H NMR spectrum: 1.52 d, 3 H, J = 7 (CH_3); 4.37 m, 1 H (CH); 5.28 m, 2 H (=CH_2); 6.01 m, 1 H (=CH); 7.58 m, 2 H and 7.93 m, 2 H (2,3-disubstituted benzothiophene); 9.60 s, 1 H (NH).

S-(2-Buten-1-yl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**38**); yield 45%, m.p. 122 – 124 °C (benzene–hexane). For $C_{14}H_{12}ClNO_2S_2$ (325.8) calculated: 51.61% C, 3.71% H, 4.30% N; found: 51.43% C, 3.63% H, 4.29% N. IR spectrum: 1 670 and 1 690 (C=O), 3 375 (N–H). ^{1}H NMR spectrum: 1.75 m, 3 H (CH_3); 3.93 m, 2 H (SCH_2); 5.78 m, 2 H (CH=CH); 7.58 m, 2 H and 7.95 m, 2 H (2,3-disubstituted benzothiophene); 9.65 s, 1 H (NH).

S-(1-Phenyl-2-propen-1-yl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**39**); yield 60%, m.p. 98 – 100 °C (tetrachloromethane). For $C_{19}H_{16}ClNO_2S_2$ (387.9) calculated: 58.83% C, 3.64% H, 3.61% N; found: 58.69% C, 3.39% H, 3.43% N. IR spectrum: 1 660 (C=O), 3 370 (N–H). ^{1}H NMR spectrum: 5.39 m, 3 H (=CH_2 and CH); 6.30 m, 1 H (=CH); 7.40 m, 7 H and 7.90 m, 2 H (C_6H_5 and 2,3-disubstituted benzothiophene); 9.60 s, 1 H (NH).

S-(1-Butene-3-methyl-3-yl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**40**); yield 50%, m.p. 111 – 113 °C (benzene–acetone). For $C_{15}H_{14}ClNO_2S_2$ (339.9) calculated: 53.00% C, 4.15% H, 4.12% N; found: 53.19% C, 4.07% H, 4.19% N. IR spectrum: 1 665 and 1 690 (C=O), 3 375 (N–H). ^{1}H NMR spectrum: 1.68 s, 6 H (2 × CH_3); 5.30 m, 2 H (=CH_2); 6.30 m, 1 H (=CH); 7.68 m, 2 H and 7.95 m, 2 H (2,3-disubstituted benzothiophene); 9.48 s, 1 H (NH).

S-Cinnamyl N-(4-chlorobenzoyl)monothiocarbamate (**41**); yield 80%, m.p. 146 – 148 °C (benzene–hexane). For $C_{17}H_{14}ClNO_2S$ (331.8) calculated: 61.54% C, 4.25% H, 4.22% N; found: 61.75% C, 4.12% H, 4.41% N. IR spectrum: 1 645 (C=C), 1 670 and 1 710 (C=O), 3 410 (N–H). ^{1}H NMR spectrum: 4.18 m, 2 H (CH_2S); 7.00 m, 2 H (CH=CH); 7.75 m, 5 H (C_6H_5); 7.85 d, 2 H and 8.42 m, 2 H, J = 8 (4-ClC_6H_4); 11.70 s, 1 H (NH).

O-Arylalkyl *N*-Acylmonothiocarbamates **44**, **45**, **47**, **50**

Benzyl alcohol or 3-furylmethanol (6 mmol) was added to a solution of corresponding acyl isothiocyanate (5.57 mmol) in anhydrous benzene (10 ml) and the mixture was kept at room temperature for 3 days. Hexane (100 ml) was added and the mixture allowed to stand at 0 °C for 24 h. The precipitate was filtered off and crystallized from a suitable solvent.

O-(3-Furylmethyl) N-(4-chlorobenzoyl)monothiocarbamate (**44**); yield 86%, m.p. 117 – 119 °C (benzene–light petroleum). For $C_{13}H_{10}ClNO_3S$ (295.7) calculated: 52.80% C, 3.41% H, 4.74% N; found: 52.58% C, 3.38% H, 4.63% N. IR spectrum: 1 520 (NHCS), 1 680 (C=O), 3 390 (N–H). ^{1}H NMR spectrum: 5.53 s, 2 H (OCH_2); 6.53 d, 1 H, J = 2 (furan 4-H); 7.47 m, 4 H and 7.77 d, 2 H, J = 8 (4-ClC_6H_4, furan 2-H and 5-H); 9.11 s, 1 H (NH). ^{13}C NMR spectrum: 66.18 t (OCH_2), 110.45, 118.92, 142.19 and 143.56 (3-furyl), 129.19, 129.26, 131.32 and 139.68 (4-ClC_6H_4), 161.93 s (C=O), 188.54 s (C=S).

O-Benzyl N-(3-phenylpropenoyl)monothiocarbamate (**45**); yield 80%, m.p. 110 – 112 °C (benzene–hexane). For $C_{17}H_{15}NO_2S$ (297.4) calculated: 68.66% C, 5.08% H, 4.71% N; found: 68.51% C, 5.30% H, 4.49% N. IR spectrum: 1 550 (NHCS), 1 635 (C=C), 1 680 (C=O), 3 380 (N–H). ^{1}H NMR spectrum: 5.65 s, 2 H (OCH_2); 7.09 d, 2 H and 7.86 d, 2 H, J = 16 (CH=CH); 7.45 m, 10 H (2 × C_6H_5); 9.38 s, 1 H (NH).

O-Benzyl N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**47**); yield 90%, m.p. 113 – 114 °C (benzene–light petroleum). For $C_{17}H_{12}ClNO_2S_2$ (361.9) calculated: 56.42% C, 3.34% H, 3.87% N; found: 56.21% C, 3.29% H, 3.72% N. IR spectrum: 1 515 (NHCS), 1 700 (C=O), 3 395 (N–H). ^{1}H NMR spectrum: 5.75 s, 2 H (OCH_2); 7.55 m, 7 H and 7.95 m, 2 H (C_6H_5 and 2,3-disubstituted benzothiophene); 10.24 s, 1 H (NH).

O-(3-Furylmethyl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**50**); yield 83%, m.p. 108 °C (benzene–hexane). For $C_{15}H_{10}ClNO_3S_2$ (351.8) calculated: 51.21% C, 2.86% H, 3.98% N; found: 51.14% C, 2.68% H, 3.75% N. IR spectrum: 1 500 (NHCS), 1 685 (C=O), 3 380 (N–H). ^{1}H NMR spectrum: 5.63 s, 2 H (OCH_2); 6.68 d, 1 H, J = 2 (4-H); 7.60 m, 4 H and 7.95 m, 2 H (furan 2-H and 5-H and 2,3-disubstituted benzothiophene); 10.20 s, 1 H (NH).

S-Arylalkyl *N*-Acylmonothiocarbamates **51** – **57**

A solution of corresponding *O*-arylalkyl ester (3 mmol) in benzene (10 ml) was refluxed for 3 h (compounds **53** and **57**). In the case of not isolable *O*-arylalkyl esters, the products were formed already at room temperature by standing of corresponding acyl isothiocyanate (5.57 mmol) with arylalkyl alcohol (6 mmol) in benzene (10 ml) for 2 days (compound **55**), 3 days (compounds **51** and **52**), 4 days (compound **56**). The solvent was evaporated and the residue crystallized from an appropriate solvent.

S-(2-Furylmethyl) N-(4-chlorobenzoyl)monothiocarbamate (**51**); yield 40%, m.p. 141 – 144 °C (dec., benzene–hexane). For $C_{13}H_{10}ClNO_3S$ (295.9) calculated: 52.80% C, 3.41% H, 4.71% N; found: 52.61% C, 3.20% H, 4.51% N. IR spectrum: 1 625 and 1 700 (C=O), 3 450 (N–H). ^{1}H NMR spectrum: 4.18 s, 2 H (SCH_2); 6.35 m, 2 H and 7.55 m, 1 H (2-furyl); 7.65 d, 2 H and 7.95 d, 2 H, J = 8 (4-ClC_6H_4). ^{13}C NMR spectrum: 23.30 t (SCH_2), 111.10, 120.95, 140.58 and 143.20 (2-furyl), 128.42, 130.10, 130.62 and 137.83 (4-ClC_6H_4), 165.37 s and 169.48 s (C=O).

S-[1-(2-Furyl)ethyl] N-(4-chlorobenzoyl)monothiocarbamate (**52**); yield 62%, m.p. 121 – 124 °C (dec., benzene–light petroleum). For $C_{14}H_{12}ClNO_3S$ (309.8) calculated: 54.28% C, 3.90% H, 4.52% N; found: 54.03% C, 3.77% H, 4.63% N. IR spectrum: 1 620 and 1 690 (C=O), 3 430 (N–H). ^{1}H NMR spectrum: 1.75 d, 3 H, J = 7 (CH_3); 4.93 q, 1 H (CH); 6.30 m, 2 H and 7.35 m, 1 H (2-furyl); 7.39 d, 2 H and 7.93 d, 2 H, J = 8 (4-ClC_6H_4). ^{13}C NMR spectrum: 19.45 q (CH_3), 36.69 d (CH), 106.76, 110.45, 142.07 and 154.31 (2-furyl), 129.19, 129.45, 130.12 and 139.94 (4-ClC_6H_4), 164.87 s and 171.93 s (C=O).

S-(3-Furylmethyl) N-(4-chlorobenzoyl)monothiocarbamate (**53**); yield 50%, m.p. 144 – 146 °C (benzene–hexane). For $C_{13}H_{10}ClNO_3S$ (295.7) calculated: 52.80% C, 3.41% H, 4.74% N; found: 52.73% C, 3.25% H, 4.85% N. IR spectrum: 1 620 and 1 690 (C=O), 3 450 (N–H). ^{1}H NMR spectrum: 3.98 s, 2 H (SCH_2); 6.42 m, 1 H and 7.43 m, 2 H (3-furyl); 7.45 d, 2 H and 7.98 d, 2 H, J = 8 (4-ClC_6H_4); 11.36 s, 1 H (NH). ^{13}C NMR spectrum: 24.15 t (SCH_2), 11.60, 121.05, 142.34 and 142.96 (3-furyl), 129.97, 130.65, 139.08 and 140.57 (4-ClC_6H_4), 165.70 s and 170.44 s (C=O).

S-(2-Furylmethyl) N-(3-phenylpropenoyl)monothiocarbamate (**54**); yield 62%, m.p. 144 – 146 °C (methanol–water). For $C_{15}H_{13}NO_3S$ (287.3) calculated: 62.71% C, 4.56% H, 4.87% N; found: 62.43% C, 4.39% H, 4.72% N. IR spectrum: 1 630 (C=C), 1 665 and 1 710 (C=O), 3 400 (N–H). ^{1}H NMR spectrum: 4.22 s, 2 H (SCH_2); 6.33 m, 2 H and 7.39 m, 1 H (2-furyl); 6.85 d, 1 H and 7.85 d, 1 H, J = 16 (CH=CH); 7.45 m, 5 H (C_6H_5); 11.03 s, 1 H (NH).

S-(2-Furylmethyl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**55**); yield 53%, m.p. 151 – 154 °C (dec., benzene–hexane). For $C_{15}H_{10}ClNO_3S_2$ (351.8) calculated: 51.21% C, 2.86% H, 3.98% N; found: 50.89% C, 2.67% H, 3.87% N. IR spectrum: 1 670 and 1 690 (C=O), 3 370 (N–H). ^{1}H NMR spectrum: 4.55 s, 2 H (SCH_2); 6.68 m, 2 H and 7.78 m, 1 H (2-furyl); 7.90 m, 2 H and 8.27 m, 2 H (2,3-disubstituted benzothiophene); 11.70 s, 1 H (NH).

S-[1-(2-Furyl)ethyl] N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**56**); yield 66%, m.p. 122 – 124 °C (benzene–hexane). For $C_{16}H_{12}ClNO_3S_2$ (365.9) calculated: 52.52% C, 3.31% H, 3.83% N; found: 52.38% C, 3.18% H, 3.59% N. IR spectrum: 1 650 and 1 680 (C=O), 3 355 (N–H). ^{1}H NMR spectrum: 1.78 d, 3 H, J = 7 (CH_3); 5.10 q, 1 H, J = 7 (CH); 6.15 m, 2 H and 7.48 m, 1 H (2-furyl); 7.12 m, 2 H and 7.98 m, 2 H (2,3-disubstituted benzothiophene); 9.68 s, 1 H (NH).

S-(3-Furylmethyl) N-(3-chloro-2-benzo[b]thienocarbonyl)monothiocarbamate (**57**); yield 50%, m.p. 137 – 139 °C (benzene–hexane). For $C_{15}H_{10}ClNO_3S_2$ (351.8) calculated: 51.21% C, 2.86% H, 3.98% N; found: 50.98% C, 2.61% H, 3.74% N. IR spectrum: 1 660 and 1 675 (C=O), 3 370 (N–H). ^{1}H NMR spectrum: 4.13 s, 2 H (SCH_2); 6.53 m, 1 H and 7.50 m, 2 H (3-furyl); 7.65 m, 2 H and 7.95 m, 2 H (2,3-disubstituted benzothiophene); 9.70 s, 1 H (NH).

O-[1-(3-Nitrophenyl)ethyl] *N*-(4-Chlorobenzoyl)monothiocarbamate **58**

The product was obtained according to procedure for compounds **44**, **45**, **47** and **49**; the reaction time was 12 days. Yield 60%, m.p. 130 – 131 °C (chloroform–light petroleum). For $C_{16}H_{13}ClN_2O_4S$ (364.8) calculated: 52.68% C, 3.59% H, 3.84% N; found: 52.40% C, 3.43% H, 3.76% N. IR spectrum: 1 630 $(NO_2)_s$, 1 486 (NHCS), 1 540 $(NO_2)_{as}$, 1 725 (C=O), 3 410 (N–H). ^{1}H NMR spectrum: 1.75 d, 3 H, J = 7 (CH_3); 6.60 q, 1 H, J = 7 (CH); 7.53 m, 2 H, 7.82 m, 3 H and 7.53 m, 3 H (4-ClC_6H_4 and 3-$NO_2C_6H_4$); 9.18 s, 1 H (NH).

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