AN ADVANTAGEOUS SYNTHESIS OF S-(2-PROPENYL) N-ACYLMONOTHIOCARBAMATES BY [3,3]-SIGMATROPIC REARRANGEMENT OF O-(2-PROPENYL) N-ACYLMONOTHIOCARBAMATES

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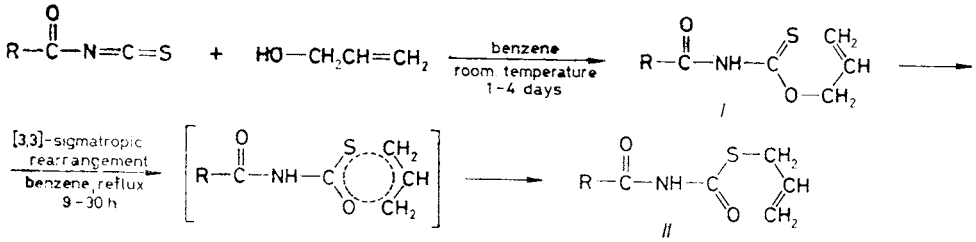
Received September 8th, 1986

Reaction of acetyl, benzoyl, 2-chlorobenzoyl, 3-phenylpropenoyl, 2-naphthoyl, and 3-chloro-2-benzo[*b*]thienocarbonyl isothiocyanate with 2-propen-1-ol afforded the corresponding O-(2-propenyl) N-acylmonothiocarbamates which underwent [3,3]-sigmatropic rearrangement on heating in boiling benzene. The reaction represents a simple method for preparation of S-(2-propenyl) N-acylmonothiocarbamates in yields ranging from 50% to 98%.

[3,3]-Sigmatropic reactions of 1,5-hexadiene derivatives, the so-called Cope rearrangement[1-4], are recently intensively studied because products obtained in this way are often more easily accessible than by other methods. Reactions of this type have been thoroughly reviewed by Lutz[5]. From the synthetic point of view, compounds containing hetero atoms in positions 1 and 3 are of particular interest. Finding suitable conditions for the [3,3]-sigmatropic rearrangement made it possible to change the kind of substitution or to exchange the functional groups as illustrated by reactions of S-(2-propenyl) dithiocarbamates[6] and the corresponding oxa[7], aza[8,9] or thiaza analogues[10]. Only little attention has been paid to compounds containing atoms of oxygen or sulfur in positions 1 and 3 of the 1,5-hexadiene system. O-(2-Propenyl) N,N-dimethylmonothiocarbamates with variously substituted 2-propenyl residues rearrange to the corresponding S-(2-propenyl) esters on heating to 130–140°C (or in some cases spontaneously[11]) without solvent or at room temperature under catalysis with mercuric trifluoroacetate[12]. Recently, a [3,3]-sigmatropic rearrangement of S-methyl-O-(α-pinenyl) dithiocarbonate, induced by heating in dimethyl sulfoxide or on silica gel surface, has been reported[13].

In this paper we focussed our attention on the preparation of S-(2-propenyl) N-acylmonothiocarbamates *II* (Scheme 1) by [3,3]-sigmatropic rearrangement of O-(2-propenyl) N-acylmonothiocarbamates *I*. Compared with other methods, this approach to compounds of the type *II* is much simpler. The desired S-(2-propenyl) esters *II* could be prepared by addition of 2-propene-1-thiol to the corresponding acyl isocyanates; this method has been hitherto used only in the preparation of

analogous S-alkyl esters[14,15]. Compounds of the type *II* were also prepared by treatment of carboxylic acids with alkyl thiocyanates in the presence of tin tetrachloride[16] or by reaction of sodium salts of carboxylic acids with iminothiocarbonic acid derivatives under phase transfer conditions[17]. In our synthesis using the [3,3]-sigmatropic rearrangement we obtained the O-(2-propenyl) esters *I* by addition of 2-propen-1-ol to the corresponding acyl isothiocyanates (Scheme 1) in benzene at



In formulae *I*, *II*: *a*, R = CH_3; *b*, R = C_6H_5; *c*, R = 2-Cl-C_6H_4; *d*, R = $C_6H_5CH{=}CH$; *e*, R = 2-naphthyl; *f*, R = 3-chloro-2-benzo[*b*]thienyl

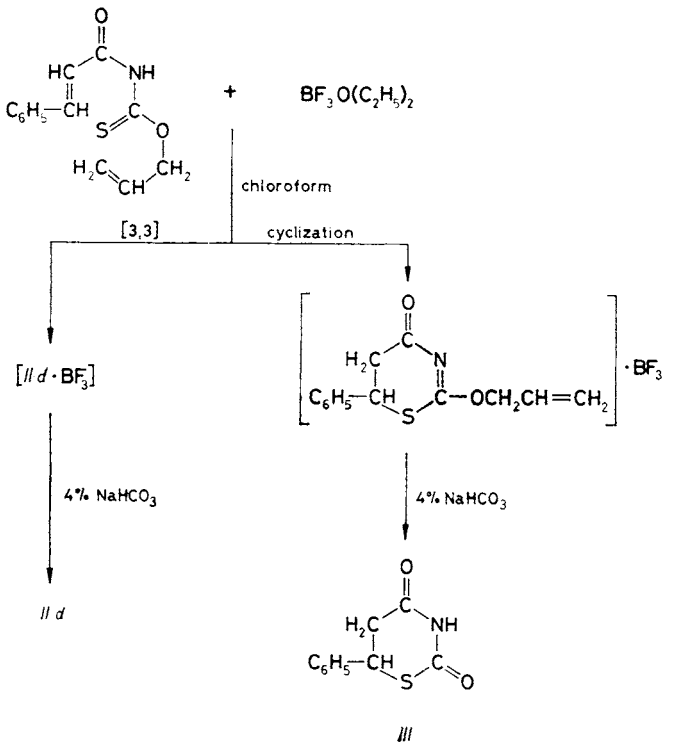
SCHEME 1

room temperature. Whereas compounds *Id* and *If* were stable crystalline products, compounds *Ia*–*Ic* and *Ie* were unstable viscous liquids, decomposing on attempted distillation and isomerizing during several weeks to give *IIa*–*IIc* and *IIe*, respectively. We used therefore these compounds as crude products purified by column chromatography on silica gel. The acetyl derivative *Ia* decomposed on silica gel as well as alumina and, consequently, was isolated only in a low yield. Moreover, silica gel catalyzes the isomerization of *Ia*–*Ic* to *IIa*–*IIc* and therefore the employed crude products contained up to 5% of the rearrangement product (according to ^{1}H NMR spectrum). All the prepared O-(2-propenyl) esters were thermally labile and on heating in boiling benzene underwent [3,3]-sigmatropic rearrangement to the S-(2-propenyl) esters *II* (yields 50–98%) consisting in replacement of the thiocarbonyl functionality by the carbonyl group. The compounds *II* can also be synthesized without isolation of the O-(2-propenyl) esters *I*, directly by heating the corresponding isothiocyanate with 2-propen-1-ol in boiling benzene. However, the reaction at elevated temperature is accompanied by formation of several side-products complicating the isolation and lowering yields of the esters *II* to 5–40% (based on the isothiocyanate). When the reaction was performed at room temperature and then the mixture was refluxed without isolation of the esters *I*, the yields of products *II* were approximately the same as with isolation of the O-(2-propenyl) esters *I*.

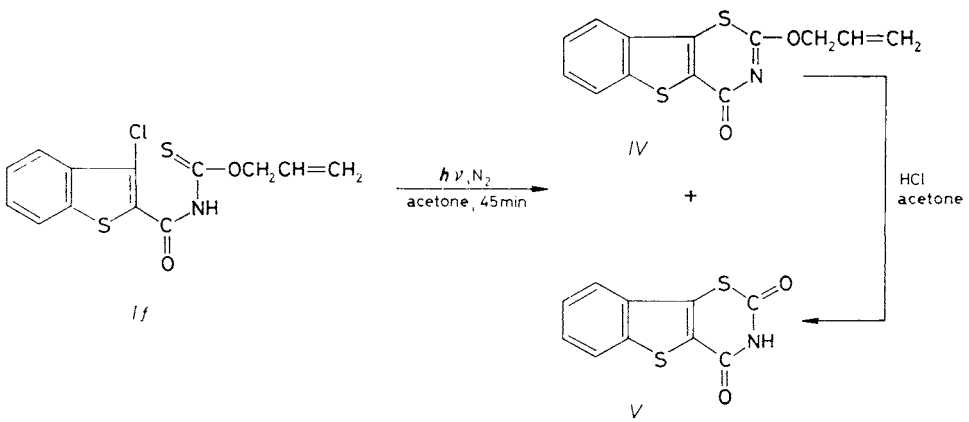
The structure of the prepared compounds was proved by spectral methods. Infrared spectra of S-(2-propenyl) esters *II* exhibit absorption bands due to ν(CONHCO, in-phase) and ν(CONHCO, out-of-phase) at 1 670–1 700 cm^{-1} and 1 682 to 1 735 cm^{-1}, respectively, whereas the starting compounds *I* have ν(C=O) absorption bands in the region 1 667–1 715 cm^{-1}. Unequivocal structural assignment was possible from the NMR spectra. Proton NMR spectra of esters *I* displayed signals of CH_2O protons at δ 4·98–5·12 whereas those of the S-(2-propenyl) esters *II* exhibit CH_2S signals at δ 3·48–3·62. In the ^{13}C NMR spectra of the rearrangement products *II* we observed C=O signals at δ 165·06–172·30 instead of C=S signals at δ 187·46–188·92 for the starting O-(2-propenyl) esters *I*. The marked difference between chemical shifts of the CH_2O (δ 66·59–73·31) and CH_2S (δ 32·55–32·85) carbon atom signals is also in accord with the proposed structure of compounds *I* and *II*.

In the case of the O-(2-propenyl) ester *IId* we studied the effect of solvent polarity and reaction temperature on the rearrangement course. In boiling benzene or ethanol (which have practically the same boiling point) the reaction time was 11 h, in boiling acetone (b.p. 56·3°C) or in benzene at 56°C, 60 h. Comparing the reactivities of the individual derivatives we found a certain effect of the isothiocyanate part on the reactivity. Replacement of the acyl group in the esters *I* by phenyl group resulted in longer reaction time: In boiling benzene, O-(2-propenyl) N-phenylmonothiocarbamate (*Ig*) rearranged to the corresponding S-(2-propenyl) ester *IIg* in 48 h. On the basis of these facts we suppose that the studied [3,3]-sigmatropic rearrangement has a predominantly concerted character, involving partial polarization of the bonds in the transition state. We attempted to catalyze the rearrangement of compound *Ig* by silica gel as described for S-methyl-O-(α-pinenyl) dithiocarbonate[13] but no reaction occurred even after five days. Although the other studied compounds *Ia–If* rearranged on silica gel, the reaction required large amounts of the adsorbent (up to 50 g for 0·1 g of *I*) and was sluggish (20% conversion after 4 days). We have, however, found that rearrangement of the phenyl derivative *Ig* to *IIg* was significantly accelerated by boron trifluoride (reaction time 1·5 h) which is probably bonded to the oxygen atom, facilitating thus fission of the O—CH_2 bond. The reaction rates of the other O-(2-propenyl) esters were not affected by boron trifluoride but the reaction was accompanied by many side-products, probably as a result of complexation of boron trifluoride with the carbonyl oxygen. The ester *Id* represents an exception; its reaction is interesting also because in analogous thioureas[18] and O-alkyl monothiocarbamates[19] boron trifluoride catalyzes the intramolecular addition of sulfur to the C=C bond of the 3-phenylpropenoyl residue under formation of 1,3-thiazine derivatives. Of the two possible reactions ([3,3]-sigmatropic rearrangement to *IId* or intramolecular cyclization (Scheme 2)), the rearrangement to the S-(2-propenyl) ester *IId* is markedly preferred (65%). As the side-product we isolated 6-phenyl-1,3-perhydrothiazine-2,4-dione (*III*; 9·7%) arising

probably by subsequent hydrolysis of the corresponding 2-(2-propenyloxy)thiazine during the work-up of the reaction mixture, similarly as observed for the cyclization of the analogous O-alkyl esters[19]. In connection with our previous studies on photo-



SCHEME 2



SCHEME 3

cyclization reactions of O-alkyl N-(3-chloro-2-benzo[*b*]thienocarbonyl)monothiocarbamates to benzothienothiazine derivatives[20] we also studied the photoreactivity of the O-(2-propenyl) ester *If*. The reaction mixture afforded the expected 2-(2-propenyloxy)benzothienothiazine (*IV*) together with another compound which was assigned the structure *V* according to its mass spectrum (Scheme 3). The formation of the dione *V* can be explained analogously (*vide supra*) by subsequent hydrolysis of derivative *IV* with hydrogen chloride liberated during the reaction. This assumption was confirmed by an independent hydrolysis of the pure compound *IV* with hydrochloric acid in acetone.

EXPERIMENTAL

Infrared absorption spectra were recorded on an IR-75 (Zeiss, Jena) spectrometer in chloroform (*Ia—Ig, IIa—IIg, III*) or in KBr pellets (*IV, V*); the wavenumbers ν are given in cm^{-1}. Proton and ^{13}C NMR spectra were taken on Tesla BS 487A (80 MHz) and Tesla BS 567 instrument (25·15 MHz), respectively, in deuteriochloroform (*Ia—Ig, IIa—IIg, III*) or in hexadeuteriodimethyl sulfoxide (*IV, V*) with tetramethylsilane as internal standard; the chemical shifts δ are given in ppm. The ultraviolet spectrum of *If* was obtained with a Perkin-Elmer 402 spectrometer in ethanol, concentration $0{\cdot}6 \cdot 10^{-4}$ mol l^{-1}; absorption maxima λ_{max} (nm) and molar absorption coefficients $\log \varepsilon$ (m^2 mol^{-1}) are given. Mass spectra were taken on a Jeol JMS-100D spectrometer, ionization energy 70 eV. The reaction course was monitored by thin-layer chromatography (TLC) on Silufol plates (Kavalier, Czechoslovakia). 2-Propen-1-ol and phenyl isothiocyanate (Lachema, Brno) and benzoyl isothiocyanate (Fluka) were commercial products and were distilled prior to use. Acetyl isothiocyanate[21], 3-phenylpropenoyl isothiocyanate[22], 2-chlorobenzoyl isothiocyanate[23], 2-naphthoyl isothiocyanate[24], and 3-chloro-2-isothiocyanatocarbonylbenzo[*b*]thiophene[25] were prepared according to the literature.

O-(2-Propenyl) N-Acylmonothiocarbamates *Ia—If*

2-Propen-1-ol (1·82 g; 2·5 ml; 18 mmol) was added to the acyl isothiocyanate (15 mmol) in anhydrous benzene (20 ml) and the mixture was set aside at room temperature for 4 days (with acetyl isothiocyanate for 1 day). In the preparation of *Id* or *If* the reaction mixture was poured into n-hexane (200 ml) and allowed to stand at 0°C for 24 h. The precipitate was filtered and the product crystallized from a suitable solvent. For compounds *Ia—Ic* and *Ie*, benzene was evaporated and the residue chromatographed on a column of silica gel (250 g; 100/160 μm) in benzene–acetone (7 : 1). The obtained semi-solid products were sufficiently pure (^1H NMR spectra, TLC) for further use.

O-(2-*Propenyl*) N-*acetylmonothiocarbamate* (Ia); yield 14%; IR spectrum: 1 475 (NHCS), 1 629 (C=C), 1 662 (C=O), 3 382 (N—H). ^1H NMR spectrum: 2·36 s, 3 H (CH_3), 5·03 m, 2 H (OCH_2), 5·40 m, 2 H (=CH_2), 5·92 m, 1 H (=CH), 9·60 s, 1 H (NH).

O-(2-*Propenyl*) N-*benzoylmonothiocarbamate* (Ib); yield 62%; IR spectrum: 1 486 (NHCS), 1 631 (C=C), 1 705 (C=O), 3 392 (N—H). ^1H NMR spectrum: 5·10 m, 2 H (OCH_2), 5·45 m, 2 H (=CH_2), 5·98 m, 1 H (=CH), 7·52—7·80 m, 5 H (C_6H_5), 9·25 s, 1 H (NH). ^{13}C NMR spectrum: 66·59 t (OCH_2), 118·99 t (=CH_2), 163·19 s (C=O), 188·87 s (C=S).

O-(2-*Propenyl*) N-(2-*chlorobenzoyl*)*monothiocarbamate* (Ic); yield 75%. IR spectrum: 1 494 (NHCS), 1 630 (C=C), 1 715 (C=O), 3 375 (N—H). ^1H NMR spectrum: 4·98 m, 2 H (OCH_2),

5·36 m, 2 H (=CH_2), 5·85 m, 1 H (=CH), 7·52 m, 2 H and 7·83 m, 2 H (2-Cl—C_6H_4), 9·26 s, 1 H (NH). ^{13}C NMR spectrum: 73·24 t (OCH_2), 119·67 t (=CH_2), 163·20 s (C=O), 187·83 s (C=S).

O-(2-*Propenyl*) N-(3-*phenylpropenoyl*)*monothiocarbamate* (Id); yield 73%, m.p. 103—105°C (methanol–water, at room temperature). For $C_{13}H_{13}NO_2S$ (247·3) calculated: 63·14% C, 5·30% H, 5·66% N; found: 63·28% C, 5·12% H, 5·70% N. IR spectrum: 1 471 (NHCS), 1 621 and 1 672 (C=C), 1 713 (C=O), 3 380 (N—H). ^{1}H NMR spectrum: 5·07 m, 2 H (OCH_2), 5·44 m, 2 H (=CH_2), 5·07 m, 1 H (=CH), 7·00 d, 1 H and 7·80 d, 1 H, J_{AB} = 16 Hz (CH=CH), 7·40 m, 5 H (C_6H_5), 9·20 s, 1 H (NH). ^{13}C NMR spectrum: 73·01 t (OCH_2), 119·82 t (=CH_2), 119·30 d, 146·10 d (CH=CH), 128·41, 129·00, 130·57, 130·79, 134·30 (C_6H_5 and =CH), 163·27 s (C=O), 188·65 s (C=S).

O-(2-*Propenyl*) N-(2-*naphthoyl*)*monothiocarbamate* (Ie); yield 72%. IR spectrum: 1 488 (NHCS), 1 625 (C=C), 1 707 (C=O), 3 400 (N—H). ^{1}H NMR spectrum: 5·09 m, 2 H (OCH_2), 5·47 m, 2 H (=CH_2), 5·98 m, 1 H (=CH), 7·55 m, 2 H, 7·85 m, 5 H (2-naphthyl), 9·35 s, 1 H (NH). ^{13}C NMR spectrum: 73·01 t (OCH_2), 119·45 t (=CH_2), 162·97 s (C=O), 188·92 s (C=S).

O-(2-*Propenyl*) N-(3-*chloro*-2-*benzo*[*b*]*thienocarbonyl*)*monothiocarbamate* (If); yield 85%, m.p. 109—111°C (acetone–water, at room temperature). For $C_{13}H_{10}ClNO_2S_2$ (311·8) calculated: 50·08% C, 3·23% H, 4·49% N; found: 50·41% C, 3·13% H, 4·33% N. UV spectrum: 214 (3·41), 307 (3·13). IR spectrum: 1 487 (NHCS), 1 633 (C=C), 1 671 (C=O), 3 359 (N—H). ^{1}H NMR spectrum: 5·12 m, 2 H (OCH_2), 5·48 m, 2 H (=CH_2), 6·00 m, 1 H (=CH), 7·25 m, 2 H and 7·85 m, 2 H (2,3-disubstituted benzo[*b*]thiophene), 10·16 s, 1 H (NH). ^{13}C NMR spectrum: 73·31 t (OCH_2), 119·67 t (=CH_2), 120·94, 122·81, 123·63, 125·86, 128·41, 130·35, 131·39, 136·62, 138·78 (benzo[*b*]thiophene skeleton and =CH), 155·65 s (C=O), 187·46 s (C=S).

O-(2-Propenyl) N-Phenylmonothiocarbamate (*Ig*)

A mixture of phenyl isothiocyanate (4 g; 30 mmol), 2-propen-1-ol (2·11 g; 2·47 ml, 36 mmol) and anhydrous triethylamine (3·04 g; 4·17 ml; 30 mmol) was allowed to stand at room temperature for 4 days. Chromatography on silica gel (300 g; 100/160 μm) in benzene–acetone (7 : 1) afforded 4·1 g (67%) of *Ig*, m.p. 61—63°C (methanol–water). For $C_{10}H_{11}NOS$ (193·3) calculated: 62·14% C, 5·74% H, 7·25% N; found: 62·23% C, 5·61% H, 7·38% N. IR spectrum: 1 506 (NHCS), 1 640 (C=C), 3 394 (N—H). ^{1}H NMR spectrum: 5·10 m, 2 H (OCH_2), 5·44 m, 2 H (=CH_2), 5·90 m, 1 H (=CH), 7·32 m, 5 H (C_6H_5), 9·20 s, 1 H (NH). ^{13}C NMR spectrum: 72·49 t (OCH_2), 119·01 t (=CH_2), 131·54 d (=CH), 122·14, 125·57, 129·00, 137·14 (C_6H_5), 188·20 s (C=S).

S-(2-Propenyl) N-Acylmonothiocarbamates *IIa—IIf*

A solution of the corresponding O-(2-propenyl) ester (*Ia—If*; 3 mmol) in benzene (10 ml) was refluxed for the time specified (*Ia*: 30 h, *Ib*: 9 h, *Ic*, *Ie*, *If*: 10 h, *Id*: 11 h). The solvent was evaporated and the residue was crystallized from an appropriate solvent.

S-(2-*Propenyl*) N-*acetylmonothiocarbamate* (IIa); yield 50%, m.p. 86—89°C (decomp.) (tetrachloromethane–light petroleum at 0°C). For $C_6H_9NO_2S$ (159·2) calculated: 45·27% C, 5·70% H, 8·80% N; found: 45·43% C, 5·56% H, 8·99% N. IR spectrum: 1 480 (NHCS), 1 638 (C=C), 1 682 and 1 714 (C=O), 3 375 (N—H). ^{1}H NMR spectrum: 2·27 s, 3 H (CH_3), 3·56 m, 2 H (SCH_2), 5·23 m, 2 H (=CH_2), 5·82 m, 1 H (=CH), 9·42 s, 1 H (NH). ^{13}C NMR spectrum: 24·41 q (CH_3), 32·62 t (SCH_2), 118·48 t (=CH_2), 132·66 d (=CH), 169·84 s, 179·73 s (C=O).

S-(2-*Propenyl*) N-*benzoylmonothiocarbamate* (IIb); yield 83%, m.p. 100—103°C (decomp.), (tetrachloromethane). For $C_{11}H_{11}NO_2S$ (221·3) calculated: 59·70% C, 5·01% H, 6·33% N;

found: 59·84% C, 4·87% H, 6·48% N. IR spectrum: 1 455 (NHCS), 1 637 (C=C), 1 656 and 1 682 (C=O), 3 390 (N—H). ^{1}H NMR spectrum: 3·59 m, 2 H (SCH_2), 5·19 m, 2 H (=CH_2), 5·89 m, 1 H (=CH), 7·55 m, 3 H and 8·00 m, 2 H (C_6H_5), 9·91 s, 1 H (NH). ^{13}C NMR spectrum: 32·70 t (SCH_2), 118·33 t (=CH_2), 127·96, 128·78, 131·77, 132·74, 133·33 (C_6H_5 and =CH), 165·88 s, 172·30 s (C=O).

S-(2-*Propenyl*) N-(2-*chlorobenzoyl*)*monothiocarbamate* (IIc); yield 80%, m.p. 66—68°C (tetrachloromethane). For $C_{11}H_{10}ClNO_2S$ (255·7) calculated: 51·67% C, 3·94% H, 5·48% N; found: 51·49% C, 3·82% H, 5·61% N. IR spectrum: 1 464 (NHCS), 1 628 (C=C), 1 657 and 1 690 (C=O), 3 376 (N—H). ^{1}H NMR spectrum: 3·48 m, 2 H (SCH_2), 5·30 m, 2 H (=CH_2), 5·70 m, 1 H (=CH), 7·39 m, 2 H and 7·65 m, 2 H (2-Cl—C_6H_4), 9·76 s, 1 H (NH). ^{13}C NMR spectrum: 32·62 t (SCH_2), 118·48 t (=CH_2), 127·12, 130·12, 130·50, 131·09, 131·76, 132·58, 132·88 (2-Cl—C_6H_4 and =CH), 165·06 s, 170·06 s (C=O).

S-(2-*Propenyl*) N-(3-*phenylpropenoyl*)*monothiocarbamate* (IId); yield 80%, m.p. 140—144°C (decomp.), (tetrachloromethane). For $C_{13}H_{13}NO_2S$ (247·3) calculated: 63·14% C, 5·30% H, 5·66% N; found: 63·31% C, 5·17% H, 5·59% N. IR spectrum: 1 460 (NHCS), 1 621 and 1 652 (C=C), 1 700 and 1 735 (C=O), 3 372 (N—H). ^{1}H NMR spectrum: 3·60 m, 2 H (SCH_2), 5·27 m, 2 H (=CH_2), 5·88 m, 1 H (=CH), 6·83 d, 1 H and 7·82 d, 1 H, J_{AB} = 16 Hz (CH=CH), 7·40 m, 5 H (C_6H_5), 9·60 s, 1 H (NH). ^{13}C NMR spectrum: 32·77 t (SCH_2), 118·23 t (=CH_2), 118·70 d, 146·02 d (CH=CH), 128·41, 128·93, 130·72, 132·81, 134·15 (C_6H_5 and =CH), 164·99 s, 171·03 s (C=O).

S-(2-*Propenyl*) N-(2-*naphthoyl*)*monothiocarbamate* (IIe); yield 80%, m.p. 142—145°C (decomp.), (tetrachloromethane). For $C_{15}H_{13}NO_2S$ (271·3) calculated: 66·41% C, 4·83% H, 5·16% N; found: 66·32% C, 4·90% H, 5·03% N. IR spectrum: 1 520 (NHCS), 1 627 (C=C), 1 653 and 1 687 (C=O), 3 383 (N—H). ^{1}H NMR spectrum: 3·57 m, 2 H (SCH_2), 5·18 m, 2 H (=CH_2), 5·82 m, 1 H (=CH), 7·27 m, 2 H and 7·89 m, 5 H (2-naphthyl), 10·05 s, 1 H (NH). ^{13}C NMR spectrum: 32·55 t (SCH_2), 117·95 t (=CH_2), 124·15, 126·84, 127·66, 128·33, 129·23, 129·53, 132·21, 133·11, 135·27 (2-naphthyl and =CH), 166·55 s, 179·58 s (C=O).

S-(2-*Propenyl*) N-(3-*chloro*-2-*benzo*[*b*]*thienocarbonyl*)*monothiocarbamate* (IIf); yield 98%, m.p. 98—100°C (methanol–water). For $C_{13}H_{10}ClNO_2S_2$ (311·8) calculated: 50·08% C, 3·23% H, 4·49% N; found: 50·21% C, 3·12% H, 4·61% N. IR spectrum: 1 470 (NHCS), 1 625 (C=C),1 658 and 1 682 (C=O), 3 369 (N—H). ^{1}H NMR spectrum: 3·62 m, 2 H (SCH_2), 5·25 m, 2 H (=CH_2), 5·87 m, 1 H (=CH), 7·50 m, 2 H and 7·82 m, 2 H (2,3-disubstituted benzo[*b*]thiophene), 9·27 s, 1 H (NH). ^{13}C NMR spectrum: 32·58 t (SCH_2), 118·55 t (=CH_2), 121·61, 122·88, 123·70, 125·87, 128·55, 130·27, 132·51, 136·62, 138·93 (benzo[*b*]thiophene skeleton and =CH), 158·86 s, 169·02 s (C=O).

S-(2-Propenyl) N-Phenylmonothiocarbamate (*IIg*)

A. The procedure was the same as described for compounds *IIa*—*IIf*; reaction time 48 h, yield 80%.

B. Boron trifluoride etherate (0·94 g; 8 mmol) was added to a solution of the O-(2-propenyl) ester *Ig* (0·77 g; 4 mmol) in chloroform (12 ml). After standing for 1·5 h at room temperature, the reaction mixture was diluted with chloroform (10 ml) and thoroughly washed with a 4% aqueous solution of $NaHCO_3$ (28 ml). The chloroform layer was separated, the aqueous one was extracted with chloroform (10 ml) and the combined chloroform layers were dried over sodium sulfate. After evaporation of the solvent the residue set to crystals, m.p. 65—67°C (tetrachloromethane–light petroleum at 0°C); yield 83%. For $C_{10}H_{11}NOS$ (193·3) calculated: 62·14% C,

5·74% H, 7·25% N; found: 62·30% C, 5·58% H, 7·42% N. IR spectrum: 1 510 (NHCS), 1 633 (C=C), 1 678 (C=O), 3 413 (N—H). ^{1}H NMR spectrum: 3·65 m, 2 H (SCH_2), 5·23 m, 2 H ($=CH_2$), 5·95 m, 1 H (=CH), 7·35 m, 5 H (C_6H_5). ^{13}C NMR spectrum: 33·07 t (SCH_2), 117·81 t ($=CH_2$), 133·71 d (=CH), 120·12, 124·52, 129·08, 137·72 (C_6H_5), 165·51 s (C=O).

Reaction of O-(2-Propenyl) N-(3-Phenylpropenoyl)monothiocarbamate (*Id*) with Boron Trifluoride

Boron trifluoride etherate (2·35 g; 20 mmol) was added to a solution of the O-(2-propenyl) ester *Id* (2·47 g; 10 mmol) in chloroform (12 ml). After standing at room temperature for 1 h, the reaction mixture was diluted with chloroform (60 ml) and washed with 4% aqueous $NaHCO_3$ solution (70 ml). The aqueous layer was extracted with chloroform (50 ml) and the combined chloroform solutions were dried over magnesium sulfate. The solvent was evaporated and the residue chromatographed on a column of silica gel (200 g; 100/250 μm) in benzene–acetone (7 : 1), to give 1·6 g (65%) of compound *IId* and 0·2 g (9·7%) of 6-phenyl-1,3-perhydrothiazine-2,4-dione (*III*), m.p. 154—155°C (tetrachloromethane). For $C_{10}H_9NO_2S$ (207·3) calculated: 57·94% C, 4·38% H, 6·76% N; found: 57·80% C, 4·51% H, 6·59% N. IR spectrum: 1 679 and 1 712 (C=O), 3 407 (N—H). ^{1}H NMR spectrum: 3·16 m, 2 H (CH_2), 4·72 m, 1 H (CH), 7·35 m, 5 H (C_6H_5), 9·00 s, 1 H (NH). ^{13}C NMR spectrum: 40·24 t (CH_2), 42·25 d (CH), 127·21, 128·70, 129·15, 136·62 (C_6H_5), 168·35 s, 178·59 s (C=O).

Photolysis of O-(2-Propenyl) N-(3-Chloro-2-benzo[*b*]thienocarbonyl)-monothiocarbamate (*If*)

A solution of the O-(2-propenyl) ester *If* (1 g; 3·2 mmol) in acetone (250 ml) was irradiated with a TQ 150 mercury lamp (Hanau, Pyrex filter) for 45 min. The lamp was placed in a quartz water-cooled jacket and immersed in the irradiated solution which was stirred with a magnetic stirrer under nitrogen. The precipitated compound *V* (0·15 g) was filtered and the filtrate evaporated. Chromatography of the residue on a silica gel column (100 g; 100/160 μm) in benzene–acetone (7 : 1) yielded 0·45 g (51%) of *IV* and 0·1 g of *V* (together with the portion isolated by filtration 0·25 g; yield 33%). 2-(2-Propenyloxy)-4*H*-benzo[4,5]thieno[2,3-*e*]-1,3-thiazin-4-one (*IV*), m.p. 151—153°C (ethanol–water). For $C_{13}H_9NO_2S$ (275·4) calculated: 56·70% C, 3·29% H, 5·09% N; found: 56·81% C, 3·16% H, 4·91% N. IR spectrum: 1 642 (C=O), 1 555 (C=N). ^{1}H NMR spectrum: 5·11 m, 2 H (OCH_2), 5·32 m, 2 H ($=CH_2$), 6·00 m, 1 H (=CH), 7·62 m, 4 H (2,3-disubstituted benzo[*b*]thiophene). ^{13}C NMR spectrum: 71·52 t (OCH_2), 120·27, 120·42, 122·58, 123·70, 125·49, 129·00, 130·80, 131·24, 135·27, 141·55 (benzo[*b*]thiophene skeleton and $CH=CH_2$), 164·86 s (C=N), 170·81 s (C=O). Mass spectrum *m/z* (relative intensity, %): M^+ 275 (34), $[M - H_2C=CHCH_2OCN]^+$ 192 (100), $[M - 193 - CO]^+$ 164 (15).

4-*H*-Benzo[4,5]thieno[2,3-*e*]-1,3-thiazine-2,4-dione (*V*)

This compound was also prepared by the following procedure. A mixture of benzothienothiazine *IV* (0·1 g; 0·36 mmol), acetone (10 ml), and 4 drops of 35—37% hydrochloric acid was stirred for 2 h at room temperature. After addition of water (40 ml) the precipitate was filtered, dried and crystallized, m.p. 290—293°C (decomp.) (methanol–water); yield 80%. For $C_{10}H_5NO_2S_2$ (235·5) calculated: 51·00% C, 2·41% H, 5·95% N; found: 51·19% C, 2·19% H, 5·89% N. IR spectrum: 1 643 and 1 680 (C=O). ^{1}H NMR spectrum: 7·60—8·50 m (2,3-disubstituted benzo[*b*]-thiophene). Mass spectrum *m/z* (relative intensity, %): M^+ 235 (51), $[M - CHNO]^+$ 192 (100), $[M - 192 - CO]^+$ 164 (15).

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Translated by M. Tichý.