INTRAMOLECULAR CYCLIZATION OF O-ALKYL-N-(3-PHENYL-PROPENOYL)THIOCARBAMATES CATALYZED BY BORON TRIFLUORIDE

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Dedicated to Professor Pavel Kristian on the occasion of his 60th birthday.

2-Alkoxy-6-phenyl-5,6-dihydro-4*H*-1,3-thiazin-4-ones, 6-phenyl-1,3-perhydrothiazine-2,4-dione and S-methyl N-(3-phenylpropenoyl)thiocarbamate are the products of intramolecular rearrangement of O-alkyl N-(3-phenylpropenoyl)thiocarbamates catalyzed by boron trifluoride; their formation depends on the nature of the alkyl group. The rearrangement was shown to proceed intermolecularly by investigating the reaction of O-methyl N-(3-phenylpropenoyl)thiocarbamate to an S-methyl ester by the method of a crossover experiment.

Only few papers concerning the synthesis and reactions of O-alkyl N-substituted thiocarbamates from α,β-unsaturated acyl isothiocyanates have been published[1-5]. O-alkyl N-(1-phenyl-2,3-dimethyl-5-oxo-3-pyrazolin-4-ylcarbonyl)thiocarbamates were obtained from the corresponding acyl isothiocyanate and various primary or secondary alcohols aiming to make use of them as analgesic antipyretics[3]. 1-Phenyl-2,3-dimethyl-3-pyrazolin-5-one (Phenazon) itself and its derivative Aminophenazon were of the most administered antipyretics for a long time. Of reactions described, only the [3,3]-sigmatropic rearrangement of O-(2-propenyl)-N-acylmonothiocarbamates was reported[4]; it constitutes a simple method for preparation of S-(2-propenyl)-N-acylaminothiocarbamates. A photocyclization reaction of O-alkyl N-(3-chloro-2-benzo[*b*]thienocarbonyl)thiocarbamates led to 2-alkoxy-4*H*-benzo[*b*]-thieno[2,3-*c*]-1,3-thiazin-4-ones in high yields[5] (80–90%).

This paper is aimed to examine the possibility to synthesize O-alkyl N-(3-phenylpropenoyl)thiocarbamates and to cyclize them to 2-alkoxy-6-phenyl-5,6-dihydro-4*H*-1,3-thiazin-4-ones. The starting O-alkyl esters *Ia–If* were prepared by addition of primary or secondary alcohols to 3-phenylpropenoyl isothiocyanate in benzene; pure products were obtained in high yields (72–90%) by a simple crystallization from a suitable solvent. We have already reported[6] that boron trifluoride is a good

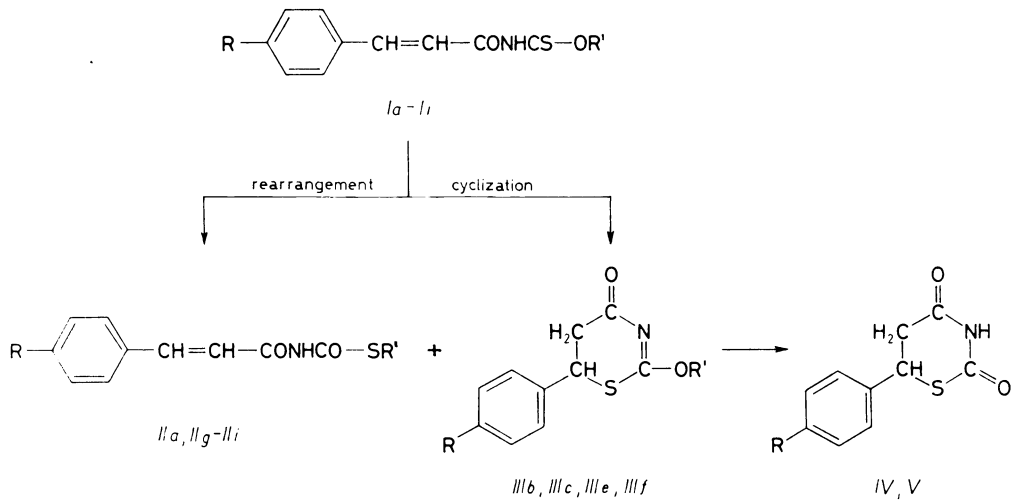
catalyst for cyclization of N-substituted N′-(3-phenylpropenoyl)thioureas to 2,6--disubstituted-5,6-dihydro-4*H*-1,3-thiazin-4-ones and therefore, we expected the formation of 2-alkoxy-6-phenyl-5,6-dihydro-4*H*-1,3-thiazin-4-ones from O-alkyl N-(3-phenylpropenoyl)thiocarbamates *Ia*—*If* on catalysis by this compound. Investigation of this reaction revealed that its course depends on the nature of the O-alkyl group of the ester (Scheme 1, Table I). Contrary to expectation, 6-phenyl-1,3--perhydrothiazin-2,4-dione (*IV*) accompanied by S-methyl N-(3-phenylpropenoyl)-thiocarbamate (*IIa*) or 2-alkoxy-6-phenyl-5,6-dihydro-4*H*-1,3-thiazin-4-one (*IIIb*, *IIIc*, *IIIe*, *IIIf*), separable by chromatography on silica gel, were isolated. Derivative *IV* is a by-product of the reaction; it originates by hydrolysis of 2-alkoxy-1,3-thiazines. The pure dione *IV* was obtained in high yield (78%) provided the alkyl was 2-propyl; with methyl the rearranged S-methyl ester (*IIa*) was isolated, which was also formed when reacting N-phenyl-N′-(3-phenylpropenoyl)thioureas with lithium hydride followed by alkylating the product with methyl iodide in dimethylformamide[7]. From ethyl, propyl, butyl and isobutyl derivatives *Ib*, *Ic*, *Ie*, *If* the corresponding 2-alkoxy-1,3-thiazines *IIIb*, *IIIc*, *IIIe*, *IIIf* were obtained. Compounds *IIIe*, *IIIf* are viscous oils, which were not succeded to crystallize neither to purify by distillation under reduced pressure. Their structures as 2-alkoxy derivatives of thiazine were unequivocally evidenced from their ^{1}H NMR spectral data. In line with this structure is the origination of dione *IV* resulting from hydrolysis with hydrochloric acid in ethanol (Scheme 1); Schulze nd coworkers[8] prepared 2,3-dihydro-6*H*-1,3-thiazin-2--one from 2-alkoxy-6*H*-1,3-thiazines under the same condition. The structures of

TABLE I

Yields of rearrangement products *II*—*V* obtained from O-alkyl N-(3-phenylpropenoyl)monothiocarbamates *IIa*—*IIi* by catalysis with boron trifluoride

Compound	R	R′	Yield, %			
			II	*III*	*IV*	*V*
Ia	H	CH_3	45	—	34	—
Ib	H	C_2H_5	—	73	12	—
Ic	H	C_3H_7	—	68	18	—
Id	H	i-C_3H_7	—	—	78	—
Ie	H	C_4H_9	—	66	10	—
If	H	i-C_4H_9	—	63	11	—
Ig	CH_3	CH_3	17	—	—	35
Ih	H	C^2H_3	28	—	37	—
Ii	CH_3	C^2H_3	12	—	—	34

all products synthesized were corroborated by IR, ^1H and ^{13}C NMR spectral methods.



In formulae *Ia*, *IIa*: R = H ; R' = CH_3 *Ib*, *IIIb*: R = H ; R' = C_2H_5 *Ic*, *IIIc*: R = H ; R' = C_3H_7
Id: R = H ; R' = i-C_3H_7 *Ie*, *IIIe*: R = H ; R' = C_4H_9 *If*, *IIIf*: R = H ; R' = i-C_4H_9
Ig, *IIg*: R = CH_3; R' = CH_3 *Ih*, *IIh*: R = H ; R' = CD_3 *Ii*, *IIi*: R = CH_3; R' = CD_3
IV: R = H *V*: R = CH_3

SCHEME 1

The rearrangement of O-methyl N-(3-phenylpropenoyl)thiocarbamate (*Ia*) to S-methyl N-(3-phenylpropenoyl)thiocarbamate (*IIa*) was investigated in more detail. Crossover experiments were chosen as the most convenient method for determining the reaction mechanism because they enable distinguishing the inter- from intramolecular course especially by using isotopes[9,10]. Therefore, O-metyl N-[3-(4--methylphenyl)propenoyl]thiocarbamate (*Ig*) and O-trideuteriomethyl N-[3-(4--methylphenyl)propenoyl]thiocarbamate (*Ii*) were prepared by treatment of 3-(4--methylphenyl)propenoyl isothiocyanate with methanol and trideuteriomethanol, respectively. Similarly, 3-phenylpropenoyl isothiocyanate gave with trideuteriomethanol O-trideuteriomethyl N-(3-phenylpropenoyl)thiocarbamate (*Ih*). The crossover experiment with compounds *Ia* and *Ii* catalyzed by boron trifluoride under the same conditions as with the respective compounds themselves followed by chromatographic purification on a silica gel-packed column afforded the mixtures of rearrangement products *IIa*, *IIg*, *IIh*, *IIi* and 1,3-thiazin-2,4-diones *IV*, *V* (Scheme 2).

$$Ia + Ii \rightarrow IIa + IIg + IIh + IIi + IV + V$$

SCHEME 2

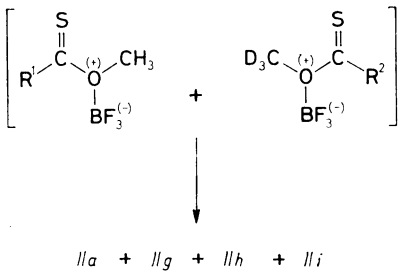
The ^1H or ^{13}C NMR spectra could not be used for evidencing the intra- or the intermolecular reaction course, because the chemical shift values for signals CH=CH and CH_3 are very close and overlapped each other. The crucial solution brought forward the mass spectrometry. The mixture of four compounds, which could not be separated by chromatography was subjected to mass spectral measurement. The evaporation curve showed two peaks at retention times 40 and 87 s, at which the mass spectra were recorded. Comparison of relative abundances of the molecular radical ions of the respective derivatives *IIa* and *IIh* with the analogous *IIg*, *IIi* revealed that the first peak shields the prevalence of *IIa*, *IIh* whilst the second one the preponderance of *IIg*, *IIi*. The ratio of *IIa*, *IIh* to *IIg*, *IIi* was reverse at the single peaks and it could be therefore concluded that the total representation of all four products in the analysed mixture is approximately the same (Table II). It was found that in the mass spectra recorded at 40 and 87 s retention times the ratios *IIa* to *IIh*, and *IIg* to *IIi* are steadily equal what evidences the intermolecular course of the rearrangement under investigation. Other fragment species appearing in the mass spectrum are in a full agreement with the proposed structure.

According to the results of the crossover experiment we feel entitled to propose the intermolecular rearrangement to proceed as follows: due to a strong Lewis acid (boron trifluoride) a complex with oxygen bearing the CH_3 or CD_3 groups was formed (Scheme 3). The alkyloxonium ion being produced can enter the intermolecular alkylation reaction with the second molecule of the appropriate O-ester to give S-methyl esters *IIa*, *IIg* and S-trideuteriomethyl esters *IIh*, *IIi*. The alkylation ability of alkyloxonium ions was already described in some papers, e.g. the S-methylation of thioamides with trimethyloxonium fluoroborate in refs[11,12].

TABLE II

Relationship between the relative intensities of molecular ions of compounds *IIa*, *IIg*, *IIh*, *IIi* and retention time (RT)

RT, s	M^+, m/z (relative intensity, %)			
	IIa	*IIh*	*IIg*	*IIi*
40	221(6)	224(6)	235(4)	238(4)
87	221(4)	224(4)	235(6)	238(6)



IIa + *IIg* + *IIh* + *IIi*

R^1 = $C_6H_5CH{=}CHCONH$; R^2 = 4-$CH_3C_6H_4CH{=}CHCONH$

SCHEME 3

EXPERIMENTAL

3-Phenylpropenoyl isothiocyanate[1], 3-(4-methylphenyl)propenoyl isothiocyanate[13], O-methyl N-(3-phenylpropenoyl)thiocarbamate[2] (*Ia*) and O-ethyl N-(3-phenylpropenoyl)thiocarbamate[1] (*Ib*) were synthesized according to the cited literature.

The infrared spectra (in cm^{-1}) of chloroform solutions were measured with a Specord IR-5 (Zeiss, Jena) spectrophotometer, the ^1H and ^{13}C NMR spectra were recorded with the respective TESLA BS 487 A (80 MHz) and TESLA 567 (25·15 MHz) apparatuses in deuteriochloroform containing tetramethylsilane as an internal reference; the δ values are in ppm. The mass spectrum was taken with a JEOL DX 303/DA 5 000 at an ionization energy 70 eV. The reaction course was monitored by thin-layer chromatography on Silufol (Kavalier, Czechoslovakia) sheets.

O-Alkyl N-(3-(4-Substituted phenyl)propenoyl)thiocarbamates *Ia*—*Ig*

To the solution of 3-phenylpropenoyl isothiocyanate or 3-(4-methylphenylpropenoyl) isothiocyanate (30 mmol) in benzene (20 ml) the appropriate alcohol (35 mmol) was dropwise added. The mixture was left to stand at room temperature for 24 h and the separated precipitate was filtered off and crystallized from a suitable solvent.

O-Methyl N-(3-phenylpropenoyl)thiocarbamate (Ia): Yield 78%, m.p. 132°C (ethanol–water). ^{13}C NMR spectrum: 52·68 q (CH_3O); 119·90 d, 145·35 d (CH=CH); 163·05 s (C=O); 190·29 s (C=S).

O-Ethyl N-(3-phenylpropenoyl)thiocarbamate (Ib): Yield 82%, m.p. 133—134°C (ethanol). IR spectrum: 3 375 (NH), 1 710 and 1 670 (C=O), 1 618 (C=C). ^1H NMR spectrum: 1·43 t, 3 H (CH_3); 4·61 q, 2 H (CH_2O); 7·03 d, 1 H and 7·80 d; 1 H (CH=CH, J_{AB} = 16); 7·41 m, 5 H (C_6H_5); 9·44 s, 1 H (NH). ^{13}C NMR spectrum: 13·81 q (CH_3); 68·31 t, (CH_2O); 120·27 d, 144·98d (CH=CH); 163·12 s (C=O); 189·47 s (C=S).

O-Propyl N-(3-phenylpropenoyl)thiocarbamate (Ic): Yield 72%, m.p. 120·5—121°C (methanol). For $C_{13}H_{15}NO_2S$ (249·3) calculated: 62·64% C, 6·06% H, 5·62% N; found: 62·75% C, 6·18% H, 5·73% N. IR spectrum: 3 380 (NH), 1 715 and 1 672 (C=O), 1 624 (C=C). ^1H NMR spectrum: 1·01 t, 3 H (CH_3); 1·83 m, 2 H (CH_2); 4·50 t, 2 H (CH_2O); 7·01 d, 1 H and 7·80 d, 1 H (CH=

=CH, J_{AB} = 16); 7·45 m, 5 H (C_6H_5); 9·34 s, 1 H (NH). ^{13}C NMR spectrum: 10·38 q, (CH_3); 21·65 t (CH_3); 74·33 t (CH_2O); 119·37 d, 145·95 d (CH=CH); 163·27 s (C=O); 189·32 s (C=S).

O-2-Propyl N-(3-phenylpropenoyl)thiocarbamate (Id): Yield 74%, m.p. 89–90°C (hexane). For $C_{13}H_{15}NO_2S$ (249·3) calculated: 62·64% C, 6·06% H, 5·62% N; found: 62·78% C, 6·21% H, 5·70% N. IR spectrum: 3 372 (NH), 1 713 and 1 672 (C=O), 1 624 (C=C). ^{1}H NMR spectrum: 1·43 d, 6 H ($C(CH_3)_2$); 5·61 m, 1 H (CHO); 7·03 d, 1 H and 7·78 d, 1 H (CH=CH, J_{AB} = 16); 7·43 m, 5 H (C_6H_5); 8·93 s, 1 H (NH). ^{13}C NMR spectrum: 21·35 q (CH_3); 77·42 d (CHO); 119·45 d, 145·73 d (CH=CH); 163·34 s (C=O); 188·28 s (C=S).

O-Butyl N-(3-phenylpropenoyl)thiocarbamate (Ie): Yield 90%, m.p. 104–105°C (methanol–water). For $C_{14}H_{17}NO_2S$ (263·4) calculated: 63·84% C, 6·51% H, 5·32% N; found: 63·96% C, 6·69% H, 5·48% N. IR spectrum: 3 375 (NH), 1 710 and 1 670 (C=O), 1 620 (C=C). ^{1}H NMR spectrum: 0·93 t, 3 H (CH_3); 1·58 m, 4 H (CH_2–CH_2); 4·56 t, 2 H (CH_2O); 6·95 d, 1 H and 7·80 d, 1 H (CH=CH, J_{AB} = 16); 7·33 m, 5 H (C_6H_5); 9·28 s, 1 H (NH). ^{13}C NMR spectrum: 13·66 q (CH_3); 19·19 t and 30·24 t (CH_2CH_2); 73·16 t (CH_2O); 119·37 d, 145·95 d (CH=CH); 163·27 s (C=O); 189·32 s (C=S).

O-Isobutyl N-(3-phenylpropenoyl)thiocarbamate (If): Yield 76%, m.p. 73–74°C (cyclohexane). For $C_{14}H_{17}NO_2S$ (263·4) calculated: 63·84% C, 6·51% H, 5·32% N, found: 63·98% C, 6·57% H, 5·39% N. IR spectrum: 3 388 (NH), 1 712 and 1 673 (C=O), 1 623 (C=C). ^{1}H NMR spectrum: 1·02 d, 6 H ($C(CH_3)_2$); 2·06 m, 1 H (CH); 4·34 d, 2 H (CH_2O); 7·01 d, 1 H and 7·81 d, 1 H (CH=CH, J_{AB} = 16); 7·48 m, 5 H (C_6H_5); 9·42 s, 1 H (NH). ^{13}C NMR spectrum: 19·04 q (CH_3); 27·62 d (CH); 79·36 t (CH_2O); 119·30 d, 145·95 d (CH=CH); 163·13 s (C=O); 189·47 s (C=S).

O-Methyl N-(3-(4-methylphenyl)propenoyl)thiocarbamate (Ig): Yield 89%, m.p. 142–143°C (methanol–water). For $C_{12}H_{13}NO_2S$ (255·3) calculated: 61·25% C, 5·57% H, 5·95% N; found: 61·37% C, 5·64% H, 6·03% N. IR spectrum: 3 396 (NH), 1 704 and 1 618 (C=O), 1 622 (C=C). ^{1}H NMR spectrum: 2·36 s, 3 H (CH_3); 4·15 s, 3 H (CH_3O); 6·90 d, 1 H and 7·88 d, 1 H (CH=CH, J_{AB} = 16); 7·34 m, 4 H (C_6H_4); 9·34 s, 1 H (NH). ^{13}C NMR spectrum: 15·83 q (CH_3); 58·60 q (CH_3O); 118·85 d and 145·28 d (CH=CH); 163·19 s (C=O); 190·37 s (C=S).

O-Trideuteriomethyl N-(3-(4-Substituted phenyl)propenoyl)thiocarbamate (*Ih*, *Ii*)

To the stirred solution of 3-phenylpropenoyl isothiocyanate or 3-(4-methylphenyl)propenoyl isothiocyanate (18 mmol) in benzene (20 ml) tetradeuteriomethanol (20 mmol) was added dropwise. The mixture was heated in water bath set to 90°C for 1·5 h, benzene was removed under diminished pressure and the remaining solid was crystallized from methanol and water.

O-Trideuteriomethyl N-(3-phenylpropenoyl)thiocarbamate (Ih): Yield 74%, m.p. 131–133°C. For $C_{11}H_8{}^2H_3NO_2S$ (224·3) calculated: 58·90% C, 6·29% H, 6·25% N; found: 59·03% C, 6·57% H, 6·36% N. IR spectrum: 3 397 (NH), 1 718 and 1 685 (C=O), 1 631 (C=C). ^{1}H NMR spectrum: 6·96 d, 1 H and 7·83 d, 1 H (CH=CH, J_{AB} = 16); 7·47 m, 5 H (C_6H_5); 9·44 s, 1 H (NH). ^{13}C NMR spectrum: 120·57 d, 144·46 d (CH=CH); 162·90 s (C=O); 190·43 s (C=S).

O-Trideuteriomethyl N-(3-(4-methylphenyl)propenoyl)thiocarbamate (Ii): Yield 86%, m.p. 141–143°C. For $C_{12}H_{10}{}^2H_3NO_2S$ (238·3) calculated: 60·48% C, 6·77% H, 5·88% N; found: 60·61% C, 6·53% H, 5·96% N. IR spectrum: 3 392 (NH), 1 706 and 1 670 (C=O), 1 618 (C=C). ^{1}H NMR spectrum: 2·36 s, 3 H (CH_3); 6·90 d, 1 H and 7·78 d, 1 H (CH=CH, J_{AB} = 16); 7·34 m, 4 H (C_6H_4); 9·28 s, 1 H (NH). ^{13}C NMR spectrum ($CDCl_3$–$(CD_3)_2SO$): 15·83 q (CH_3); 118·78 d, 145·43 d (CH=CH); 163·12 s (C=O); 190·37 s (C=S).

Rearrangement of O-Alkyl N-(3-(4-Substituted phenyl)propenoyl)thiocarbamates *Ia—Ii* with Boron Trifluoride

Boron trifluoride etherate (20 mmol) was added to the solution of the O-alkyl ester *Ia—Ii* (10 mmol) in chloroform (10 ml) and the mixture was allowed to stand at an ambient temperature for 1 h (compounds *(Ia—If)*, or 24 h (compounds *Ig—Ii*). Chloroform (50 ml) was added and the solution was extracted with sodium hydrogencarbonate (4%, 70 ml); the latter was once more extracted with chloroform (40 ml), the combined layers were dried with magnesium sulfate, the solvent was removed and the residue was chromatographed (silica gel, benzene–acetone 19 : 1). The ratio of compounds formed and yields are listed in Table I.

S-Methyl N-(3-phenylpropenoyl)thiocarbamate (IIa): m.p. 137—138°C (heptane). ^{13}C NMR spectrum: 11·76 q (CH_3S); 119·68 and 143·46 d (CH=CH); 164·12 and 169·77 (C=O). Other spectral data are in line with those published[7].

S-Methyl N-(3-(4-methylphenyl)propenoyl)thiocarbamate (IIg): m.p. 217—219°C (tetrachloromethane). For $C_{12}H_{13}NO_2S$ (235·3) calculated: 61·25% C, 5·57% H, 5·95% N; found: 61·48% C, 5·63% H, 5·78% N. IR spectrum: 3 395 (NH), 1 708 and 1 645 (C=O), 1 623 (C=C). ^{1}H NMR spectrum: 2·36 s, 3 H (CH_3); 2·45 s, 3 H (CH_3S); 6·88 d, 1 H and 7·88 d, 1 H (CH=CH, J_{AB} = = 16); 7·49 m, 4 H (C_6H_4); 11·58 s, 1 H (NH). ^{13}C NMR spectrum: 11·76 q (CH_3S); 20·79 q (CH_3); 118·57 d and 143·52 d (CH=CH); 164·26 s and 169·77 s (C=O).

S-Trideuteriomethyl N-(3-phenylpropenoyl)thiocarbamate (IIh): m.p. 129—131°C (tetrachloromethane). For $C_{11}H_8{}^2H_3NO_2S$ (224·3) calculated: 58·90% C, 6·29% H, 6·25% N; found: 59·10% C, 6·41% H, 6·28% N. IR spectrum: 3 387 (NH), 1 698 and 1 656 (C=O), 1 621 (C=C). ^{1}H NMR spectrum: 6·73 d, 1 H and 7·87 d, 1 H (CH=CH, J_{AB} = 16); 7·65 m, 5 H (C_6H_5); 11·62 s, 1 H (NH). ^{13}C NMR spectrum: 119·68 d and 143·46 d (CH=CH); 164·12 s and 169·77 s (C=O).

S-Trideuteriomethyl N-(3-(4-methylphenyl)propenoyl)thiocarbamate (IIi): m.p. 245—247°C (tetrachloromethane). For $C_{12}H_{10}{}^2H_3NO_2S$ (238·3) calculated: 60·48% C, 6·77% H, 5·88% N; found: 60·57% C, 6·62% H, 5·78% N. IR spectrum: 3 381 (NH), 1 703 and 1 661 (C=O), 1 620 (C=C). ^{1}H NMR spectrum: 2·50 s, 3 H (CH_3); 6·88 d, 1 H and 7·78 d, 1 H (CH=CH, J_{AB} = = 16); 7·48 m, 4 H (C_6H_4); 11·57 s, 1 H (NH). ^{13}C NMR spectrum: 20·78 q (CH_3); 118·57 d and 143·52 d (CH=CH); 164·25 s and 169·77 s (C=O).

2-Ethoxy-6-phenyl-5,6-dihydro-4H-1,3-thiazin-4-one (IIIb): m.p. 83—85°C (methanol–water). For $C_{12}H_{13}NO_2S$ (235·3) calculated: 61·25% C, 5·57% H, 5·95% N; found: 61·19% C, 5·63% H, 6·02% N. IR spectrum: 1 690 (C=O), 1 586 (N=C—S). ^{1}H NMR spectrum: 1·35 t, 3 H (CH_3); 2·88 m, 2 H (CH_2); 4·49 q, 2 H (CH_2O); 4·71 m, 1 H (CH); 7·31 m, 5 H (C_6H_5). ^{13}C NMR spectrum: 14·11 q (CH_3); 38·30 t (CH_2); 43·82 d (CH); 66·37 t (CH_2O); 176·33 s (C=N); 178·13 s (C=O).

2-Propoxy-6-phenyl-5,6-dihydro-4H-1,3-thiazin-4-one (IIIc): m.p. 151—152°C (tetrachloromethane–petroleum ether). For $C_{13}H_{15}NO_2S$ (249·3) calculated: 62·64% C, 6·06% H, 5·62% N; found: 62·75% C, 6·18% H, 5·73% N. IR spectrum: 1 693 (C=O), 1 590 (N=C—S). ^{1}H NMR spectrum: 0·95 t, 3 H (CH_3); 1·75 m, 2 H (CH_2–CH_3); 2·88 m, 2 H (CH_2); 4·41 t, 2 H (CH_2O); 4·61 m, 1 H (CH); 7·35 m, 5 H (C_6H_5). ^{13}C NMR spectrum: 10·23 q (CH_3); 21·87 t and 38·73 t (CH_2); 43·82 d (CH); 71·97 t (CH_2O); 176·63 s (C=N); 178·28 s (C=O).

2-Butoxy-6-phenyl-5,6-dihydro-4H-1,3-thiazin-4-one (IIIe): ^{1}H NMR spectrum: 0·95 t, 3 H (CH_3); 1·63 m, 4 H (CH_2–CH_2); 2·94 m, 2 H (CH_2); 4·60 t, 2 H (CH_2O); 4·70 m, 1 H (CH); 7·35 m, 5 H (C_6H_5).

2-Isobutoxy-6-phenyl-5,6-dihydro-4H-1,3-thiazin-4-one (IIIf): ^{1}H NMR spectrum: 0·91 d, 6 H ($CH(CH_3)_2$); 2·03 m, 1 H (CH_3CHCH_3); 2·91 m, 2 H (CH_2); 4·23 d, 2 H (CH_2O); 4·65 m, 1 H (CH); 7·32 m, 5 H (C_6H_5).

6-Phenyl-1,3-perhydrothiazine-2,4-dione (IV): m.p. 154—155°C (tetrachloromethane). Spectral data are presented in the literature[4].

6-(4-Methylphenyl)-1,3-perhydrothiazine-2,4-dione (V): m.p. 162—164°C (methanol–water). For $C_{11}H_{11}NO_2S$ (221·3) calculated: 59·71% C, 5·01% H, 6·33% N; found: 59·87% C, 5·14% H, 6·26% N. IR spectrum: 3 340 (NH), 1 718 and 1 668 (C=O). ^{1}H NMR spectrum: 2·41 s, 3 H (CH_3); 3·23 m, 2 H (CH_2); 5·12 m, 1 H (CH); 7·37 q, 4 H (C_6H_4); 11·76 s, 1 H (NH). ^{13}C NMR spectrum: 20·51 q (CH_3); 39·49 t, (CH_2); 40·81 d, (CH); 168·10 s and 170·86 s (C=O).

Hydrolysis of 1,3-Thiazines *IIIe* and *IIIf*

Hydrochloric acid (26%, 5 mmol) was added to a solution of thiazine *IIIe* or *IIIf* (5 mmol) in ethanol (40 ml). The mixture was allowed to stand at room temperature for 24 h, the solvent was evaporated and the residue was crystallized from tetrachloromethane. Yield of *IV* 78% and 81% from *IIIe* and *IIIf*, respectively.

Crossover Experiment with O-Methyl and O-Trideuteriomethyl Thiocarbamates *Ia* and *Ii*

Boron trifluoride etherate (10 mmol) was added to *Ia* and *Ii* (2·5 mmol each) dissolved in chloroform (10 ml). The mixture was left to stand at an ambient temperature for 24 h, diluted with chloroform (50 ml) and extracted with sodium hydrogencarbonate (4% aqueous solution, 70 ml). The organic layer was separated, dried with magnesium sulfate, the solvent was evaporated and the solid was chromatographed (silica gel, benzene–acetone 19 : 1). Yield of *Ia*, *Ig*, *Ih*, *Ii* 25%, yield of diones *IV*, *V* 35%.

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