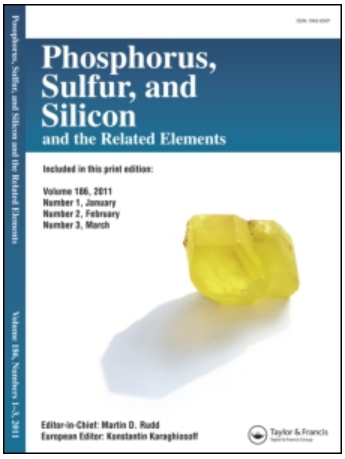

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SYNTHESIS AND THERMAL REARRANGEMENT OF 2-ALKOXYCARBONYL-3-ALKYL-4*H*-BENZO[b][1,4]THIAZINES†

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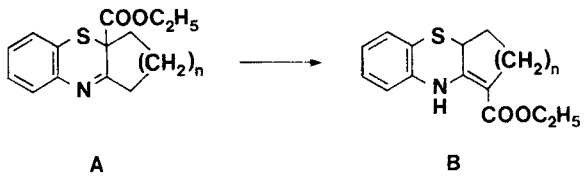
The title compounds **(4b–d)** together with the benzothiazolines **(5b–d)** have been obtained by a reaction between 2,2′-dithiodianiline **(1)** and β-keto esters **(2b–d)**. The reaction between **1** and the β-keto ester **2a** gives 1,4-benzothiazine **3a** in addition to the benzothiazoline **5a**.

It has been established that the 1,4-benzothaizines **4b–d** undergo an acid-catalysed thermal rearrangement involving a [1,3] shift of the sulfur atom, giving rise to the isomeric 1,4-benzothiazines **3b–d**.

Recently we reported[1] that ethoxycarbonyl-1,4-thiazines of type **A** undergo an acid-catalysed thermal rearrangement giving rise to the isomeric 1,4-thiazines **B** and that the size of the aliphatic ring affects the ease with which this process takes place (Scheme I).



A **B**

SCHEME 1

In order to obtain further information on the suggested rearrangement pathway, it seemed useful to study the behaviour of 2-alkoxycarbonyl-3-alkyl-4*H*-benzo[b] [1,4] thiazines on heating. These latter compounds were prepared in a similar manner to the 1,4-benzothiazines of structure **A**, by using acyclic β-keto esters in reactions with 2,2′-dithiodianiline **(1)**.

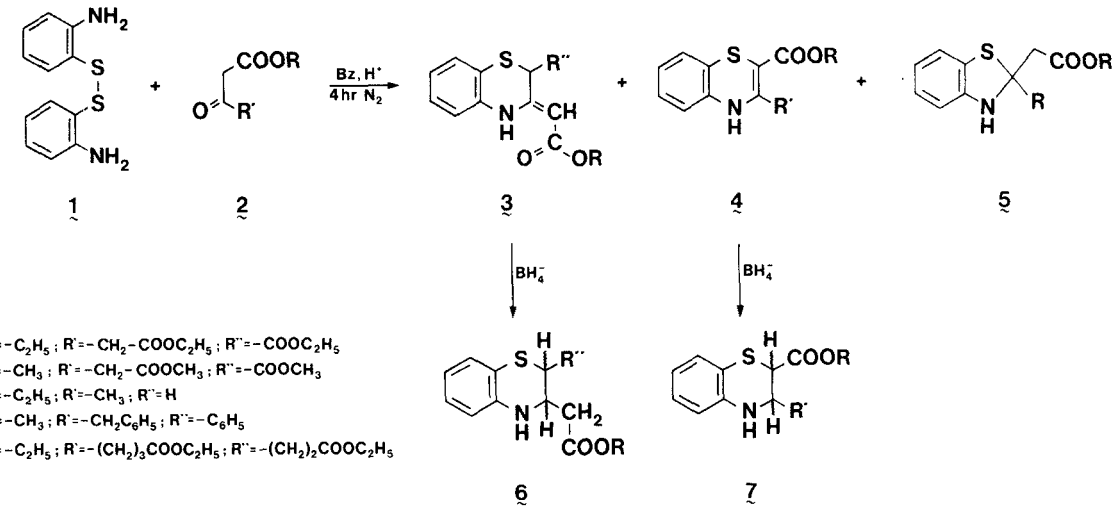
For this investigation we used diethyl or dimethyl 3-oxoglutarate **(2a** or **2a′)**, ethyl acetoacetate **(2b)**, methyl 4-phenylacetoacetate **(2c)**, and diethyl 3-oxoheptanedioate **(2d)**.

Reactions between **1** and the β-keto esters **2a–d** performed for 4 hr in each case under the usual conditions[1-3] yielded 1,4-benzothiazines and benzothiazolines. Furthermore, a difference in the reactivities of the β-keto esters was found; thus, while the reaction with **2c** and with **2d** led in both cases to a mixture of two isomeric 1,4-benzothiazines **(3c, 4c,** and **3d, 4d)**, the reactions with **2a, 2a′**, and **2b** led to a single 1,4-benzothiazine, **3a, 3a′**, and **4b**, respectively (Scheme II). In particular, in the case of diethyl 3-oxoglutarate, **2a**, in addition to the corresponding benzothiazoline **(5a)** the 1,4-benzothiazine **3a** was obtained, the structure of which was shown by the following experimental data: its nmr spectrum showed a broad signal at 10.9 δ (1H, NH) a multiplet at 7.3–6.8 δ (4H, aromatic), a singlet centred at 4.78 δ (1H, vinylic H), a complex signal between 4.3 and 3.99 δ (5H, $-CH_2O-$ + angular H), and 2 triplets, the first centered at 1.3 δ and the second at 1.08 δ (6H, CH_3-); the ir spectrum (Nujol) showed two carbonyl bands, the first at 1725 cm^{-1} attributable to an unconjugated ester carbonyl and the second, at 1660 cm^{-1}, characteristic of the conjugated ester carbonyl; in addition, bands of double bonds and of NH were present at frequencies of 1620 and 3180 cm^{-1}, respectively. The ir and the nmr spectra of the products **3a′–d** proved to be substantially analogous to those of **3a** (Table I and II).

In the case of methyl 4-phenylacetoacetate **2c**, reaction with **1** gave a mixture of the 1,4-benzothiazines **3c** and **4c** and the benzothiazoline **5c** in a molar ratio of 0.5 : 0.5 : 1; the structure of **4c** was shown by the following features of the nmr spectrum: a multiplet between 7.5 and 6.2 δ (9H, aromatic) a broad signal at 5.75 δ (1H, NH), a singlet at 4.3 δ (2H, $-CH_2Ar-$), and a singlet at 3.8 δ (3H, CH_3O-); the ir spectrum (Nujol) showed a band at 1630 cm^{-1} for the conjugated carbonyl and two bands, at 1610 cm^{-1} and 3310 cm^{-1}, attributable to a C=C double bond and to an NH group, respectively. Similar spectrographic characteristics were found for products **4b**

† Part XIII in the series: "A new reaction between bis(*o*-aminophenyl) disulfide and ketones". Part XII: *Phosphorus and Sulfur*, **2**, 123 (1976).

SCHEME II



1 2 3 4 5

*a) R = $-C_2H_5$; R' = $-CH_2-COOC_2H_5$; R'' = $-COOC_2H_5$
*a') R = $-CH_3$; R' = $-CH_2-COOCH_3$; R'' = $-COOCH_3$
**b) R = $-C_2H_5$; R' = $-CH_3$; R'' = H
c) R = $-CH_3$; R' = $-CH_2C_6H_5$; R'' = $-C_6H_5$
d) R = $-C_2H_5$; R' = $-(CH_2)_3COOC_2H_5$; R'' = $-(CH_2)_2COOC_2H_5$

6 7

*In this case the 1,4-benzothiazine of structure 4 is not present.

**In this case the 1,4-benzothiazine of structure 3 is not present.

TABLE I
Analytical data

Compd	Yield %	Mp(solv)[a] or Bp (Torr)	ir, ν_{max}^{nujol} ($\nu_{max}^{CCl_4}$) cm^{-1} N–H	C=O	C=C	uv, λ_{max}^{EtOH} (log ϵ)nm	Formula (Parent peak)
3a	50	78° (A)	3180	1725, 1660 (1665)	1620	336(4.14) 276(4.19) 218(4.18)	$C_{15}H_{17}NO_4S$ (*m/e* 307)
3a'	50	114-116° (A)	3230	1730, 1665(1670)	1610	335(4.28) 277(4.27) 218(4.20)	$C_{13}H_{13}NO_4S$ (*m/e* 279)
3b	20[b]	64-66° (A)	3245	1665(1665)	1610	332(4.30) 276(4.32) 222(4.12)	$C_{12}H_{13}NO_2S$ (*m/e* 235)
4b	50	146-147° (A)	3320	1630(1700)	1610	415(3.32) 335(3.33) 260(4.34) 215(4.22)	$C_{12}H_{13}NO_2S$ (*m/e* 235)
3c	25	110-111° (A)	3200	1650(1665)	1610	337(4.24) 277(4.26) 221(4.30)	$C_{17}H_{15}NO_2S$ (*m/e* 297)
4c	25	133-135° (A)	3310	1630(1700)	1610	415(3.21) 325(3.35) 260(4.33) 205(4.37)	$C_{17}H_{15}NO_2S$ (*m/e* 297)
3d	14	86°(0.25)	3240	1730, 1660(1660)	1615	333(4.07) 273(4.10) 222(4.06)	$C_{17}H_{21}NO_4S$ (*m/e* 335)
4d	36	78-80°	3300	1730, 1660(1700)	1615	415(3.13) 335(3.42) 260(4.24) 216(4.23)	$C_{17}H_{21}NO_4S$ (*m/e* 335)
5a	50	94-96°(0.07)	3350	1730			$C_{15}H_{19}NO_4S$
5a'	50	88-90°(0.07)	3350	1730			$C_{13}H_{15}NO_4S$
5b	50	58°(0.2)	3350	1725			$C_{12}H_{15}NO_2S$
5c	50	84-86°(0.15)	3350	1730			$C_{17}H_{17}NO_2S$
5d	50	74°(0.09)	3345	1730			$C_{17}H_{23}NO_4S$
6a'	73	80°(A)	3365	1720			$C_{13}H_{15}NO_4S$ (*m/e* 281)
6c	75	76-77°(A)	3350	1720			$C_{17}H_{17}NO_2S$ (*m/e* 299)
7b	75	94-98°(0.15)	3380	1730			$C_{12}H_{15}NO_2S$ (*m/e* 237)
7c	75	78-79°(A)	3380	1730			$C_{17}H_{17}NO_2S$ (*m/e* 299)

[a]Solvent of crystallization: A = ethanol.
[b]After 130 hr of reflux in benzene.

TABLE II
Nmr[a] data

Compd	δ, ppm	Assignment
3a	10.9	1, NH
	7.3–6.8	4, aromatic H
	4.78	1, vinylic H
	4.3–3.99	5, $-CH_2O-$ + angular H
	1.3	3, CH_3-
	1.08	3, CH_3-
3a′	10.76	1, NH
	7.3–6.8	4, aromatic H
	4.78	1, vinylic H
	4.1	1, angular H
	3.7	3, CH_3O-
	3.6	3, CH_3O-
3b	10.6	1, NH
	7.2–6.75	4, aromatic H
	4.66	1, vinylic H
	4.14	2, $-CH_2O-$
	3.4	2, $-S-CH_2-$
	1.3	3, CH_3-
4b	7–6.3	4, aromatic H
	6.2–5.8	1, NH
	4.15	2, $-CH_2O-$
	2.28	3, CH_3
	1.3	3, CH_3-
5a	7.1–6.52	4, aromatic H
	5.1	1, NH
	4.1	4, $-CH_2O-$
	3.2	4, $-CH_2CO-$
	1.22	6, CH_3-
5a′	7.08–6.5	4, aromatic H
	5.3	1, NH
	3.64	6, CH_3O-
	3.22	4, $-CH_2-CO-$
5b	7.1–6.5	4, aromatic H
	4.8	1, NH
	4.1	2, $-CH_2O-$
	2.9	2, $-CH_2-CO-$
	1.78	3, CH_3-
	1.22	3, CH_3-CH_2-
5c	7.28	5, aromatic H
	7.1–6.52	4, aromatic H
	4.6–4.3	1, NH
	3.7	3, CH_3O-
	3.4	2, $-CH_2-$Ar
	2.9	2, $-CH_2-CO$
3c	[b]11	1, NH
	7.5–6.8	9, aromatic H
	4.7	1, vinylic H
	4.65	1, angular H
	3.74	3, CH_3O-
4c	[b]7.5–6.2	9, aromatic H
	5.75	1, NH
	4.3	2, $-CH_2-$Ar
	3.8	3, CH_3O
3d	10.64	1, NH
	7.2–6.72	4, aromatic H
	4.66	1, vinylic H
	4.22–3.96	4, $-CH_2O-$
	3.4	1, angular H
	2.4	2, $-CH_2-CO-$
	2.04–1.76	2, $-CH-CH_2-CH_2-CO-$
	1.34–1.12	6, CH_3
4d	7.1	1, NH
	7.24–6.3	4, aromatic H
	4.2–3.94	4, $-CH_2O-$
	2.66–1.6	6, methylene H
	1.4–1.12	6, CH_3-
5d	7–6.42	4, aromatic H
	5.2–4.6	1, NH
	4.2–3.94	4, $-CH_2O-$
	2.9	2, $-CH_2-CO-$
	2.3	2, $-CH_2-CO-$
	2.2–1.6	4, $-CH_2-CH_2CH_2-CO-$
	1.22	6, CH_3-
6a′	7–6.38	4, aromatic H
	4.68	1, NH
	4.4–4.2	1, H_A
	4.06	1, H_B
	3.65	3, CH_3O-
	3.58	3, CH_3O-
	2.8–2.34	2, $-CH_2-CO-$
6c	7.2	5, aromatic H
	7.1–6.38	4, aromatic H
	4.68	1, NH
	4.38	1, H_B
	4.2–3.96	1, H_A
	3.46	3, CH_3O-
	2.6–2.1	2, $-CH_2-CO-$
7b	7.1–6.38	4, aromatic H
	4.14	2, $-CH_2O-$
	4–3.7	3, NH + angular H
	1.4–1.1	6, CH_3-
7c	7.4–6.2	9, aromatic H
	4.1–3.7	3, NH + angular H
	3.58	3, CH_3O-
	2.9–2.5	2, $-CH_2-$Ar

[a]The hydrogen atoms adjacent to the nitrogen and sulfur atoms are indicated as H_A and H_B respectively.
[b]Nmr spectrum recorded on a Varian A-60 spectrometer.

TABLE III
Results of the thermal rearrangement of **4b–d** in toluene containing catalytic amounts of *p* toluenesulfonic acid (20 hr).

Compd	Products of rearrangement	Yield[a] %
4b	**3b**	12
4c	**3c**	72
4d	**3d**	24

[a]Determined by PLC.

and **4d**. By comparing the characteristic absorption bands of the ester carbonyl visible in the ir spectra recorded in Nujol and in CCl_4 solution, the existence of intra- or intermolecular H bonds for the products of structures **3** and **4**, respectively, has been observed; in fact, only the spectra in solution of these last compounds show a consistent high-frequency shift of 40-70 cm^{-1}, while for the first compound it is 10-15 cm^{-1}.[4]

All the 1,4-benzothiazines were found to have the structure of enamino esters, and some of them, **3a'**, **c** and **4b**, **c**, were reduced to the corresponding dihydro derivatives **6a'**, **c** and **7b**, **c** by treatment with $NaBH_4$.

The structures of the benzothiazolines **5a–d** deduced from the spectrographic characteristics and from elemental analyses were also confirmed by comparison with authentic samples prepared by standard methods.[5]

From a study of the reported reactions performed with variable times it was found that the relative yields of the 1,4-benzothiazines **3** and **4** depend on the time of boiling; in particular, in the case of methyl 4-phenylacetoacetate **2c**, where the reaction was continued for 130 hr, only the formation of **3c** and **5c** in equal molar ratios was observed, **4c** being absent. In the case of diethyl 3-oxoglutarate **2a**, only **3a** and **5a** were present in all cases.[6] Furthermore, from toluene solutions of the 1,4-benzothiazines **4b–d** containing catalytic amounts of p-toluenesulphonic acid and boiled for 20 hr the isomeric 1,4-benzothiazines **3b–d** were obtained; the yields of the rearrangement products are given in Table III.

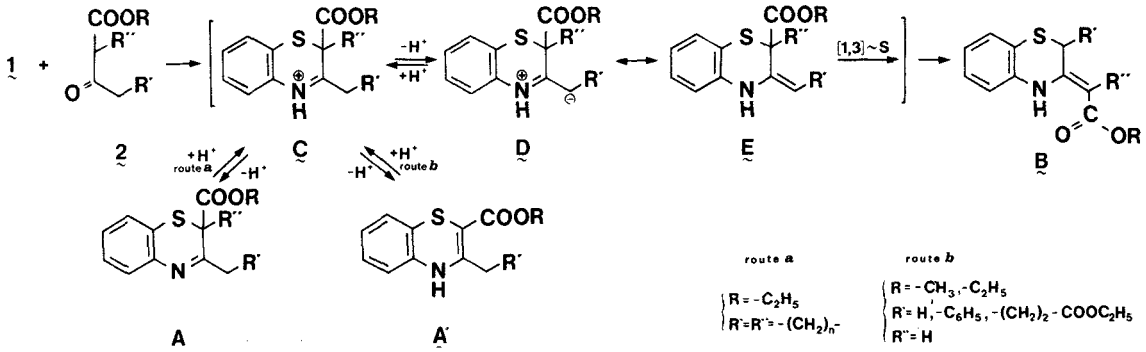
Previously we suggested[1] that the acid-catalysed rearrangement of 5*a*-ethoxycarbonylbenzo[b]cycloalkyl[e][1,4]thiazines **A**, involves a formal sigmatropic[1,3] shift of the sulfur into a structure **E** tautomeric with **A**, the existence of which it had never been possible to observe directly (Scheme III, route *a*). The rearrangement of the 4*H*-1,4-benzothiazines **A'** now observed, which must necessarily take place through a [1,3] shift of the sulfur, as has been demonstrated by the corresponding isomerization products **B** obtained, substantiates the pathway described previously. In fact, it can easily be assumed that protonation of the enamino esters **A'** gives rise to the immonium cation **C** (Scheme III, route *b*), the conjugate base of which is mesomeric with **E**.

In this connection it is useful to point out that treatment of a deuterochloroform solution of the 2-ethoxycarbonyl-3-methyl-4*H*-benzo[b][1,4]thiazine **4b** with $DCl-D_2O$ leads to deuteration of the $-CH_3$ in position 3. This is deduced from the nmr spectrum, which is superimposable on that of the non-deuterated base with the exception of the presence of an additional group of signals between 2.16 δ and 2.26 δ characteristic of a partially deuterated $-CH_3$ group.

On the other hand, the yields of the rearrangement of the 1,4-benzothiazines **4b–d** into the corresponding 1,4-benzothiazines **3b–d** (Table III) are clearly dependent on the $-CH_2-R'$ group in position 3 of the thiazine nucleus. In particular, there is a clear R'-dependent trend of the ease of rearrangement in the following sequence: $-C_6H_5 > -(CH_2)_2-COOEt > H$.

We have suggested that the rearrangement of the 1,4-benzothiazine **A'** → **B** must take place, as already

SCHEME III



reported for **A** → **B**, by means of a preliminary isomerization to **E**.

In our opinion this hypothesis is consistent with the trend observed, since the ease of the formation of the intermediate **E**, which is characterized by the exocyclic enaminic system $-NH-\underset{|}{C}=CHR'$, appears to follow in the same manner the general stability sequence of the enamines.[7]

Another interesting feature of the 1,4-benzothiazines **4** is the observed stability to autoxidation and this fact must be rationalized;[8] in fact, we have reported[3,9] that hydrogen availability at position 2 or 4 of the benzothiazine system is a determining factor in the autoxidation process primarily involving the formation of a highly stabilized radical with enhanced "donor properties" because of the role played by the sulfur atom.[9]

Now, the observed autoxidation stability of compounds **4**, should be ascribed to the decisive role played by the alkoxycarbonyl group, which would confers on the radical "acceptor properties" that can theoretically originate from them an in which intervention on the part of the sulfur atom would be possible.

It is known, in fact, that radicals in the α position to a carbonyl group are of the acceptor type and therefore are not subject to the autoxidation reaction.[10]

EXPERIMENTAL

Melting points and boiling points are uncorrected. Nmr spectra, unless otherwise stated, were obtained on a Varian HA-100 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. All *m/e* values were determined on a Perkin-Elmer model 270 low-resolution mass spectrometer. Ir spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer as nujol mulls or liquid films. UV spectra were recorded on a Cary 15 spectrophotometer.

The indicated yields refer to pure isolated products. Column chromatography was performed on silica gel Merck 70-325 mesh and preparative layer chromatography (PLC) on silica gel Merck PF_{254}. All compounds were analyzed for C, H, N, S and gave analytical results within 0.3% of the theoretical values.

Reaction of 2,2'-dithiodianiline (1) with acyclic β-keto esters (**2a–d**)

0.05 mol of β-keto ester were added under N_2 to a refluxed and stirred solution of 0.05 mol of **1** in benzene (200 ml) containing catalytic amounts of *p*-toluenesulfonic acid. The reaction mixture was refluxed for 4 hr (0.05 mole of H_2O was collected), cooled at room temperature, neutralized (5% K_2CO_3 soln), the organic layer separated, dried (Na_2SO_4), and evaporated. The following compounds were eluted from the residue by column chromatography (light petroleum ether/ethyl acetate, 9:1 as eluent), in the order given:

in the case of **2a** 2-ethoxycarbonyl-3-ethoxycarbonylmethylene-3,4-dihydro-2*H*-benzo[b][1,4]thiazine (**3a**) and 2,2-diethoxycarbonylmethyl-benzothiazoline (**5a**);
in the case of **2a'**: 2-methoxycarbonyl-3-methoxycarbonylmethylene-3,4-dihydro-2*H*-benzo[b][1,4]thiazine (**3a'**) and 2,2-dimethoxycarbonylmethyl-benzothiazoline (**5a'**);
in the case of **2b**: 2-ethoxycarbonylmethyl-2-methyl-benzothiazoline (**5b**) and 2-ethoxycarbonyl-3-methyl-4*H*-benzo[b][1,4]thiazine (**4b**);[11]
in the case of **2c**: 3-ethoxycarbonylmethylene-2-phenyl-3,4-dihydro-2*H*-benzo[b][1,4]thiazine (**3c**), 2-benzyl-2-methoxycarbonylmethyl-benzothiazoline (**5c**) and 3-benzyl-2-methoxycarbonyl-4*H*-benzo[b][1,4]thiazine (**4c**);
in the case of **2d**: 2-(2-ethoxycarbonylethyl)-2-ethoxy-carbonylmethyl-3,4-dihydro-2*H*-benzo[b][1,4]thiazine (**3d**), 2-(3-ethoxycarbonylpropyl)-2-ethoxycarbonyl methyl-benzothiazoline (**5d**) and 2-ethoxycarbonyl-3-(3-ethoxycarbonylpropyl)-4*H*-benzo[b][1,4]thiazine (**4d**) (Scheme I).

Rearrangement of **4b** *to* **3b**, *of* **4c** *to* **3c** *and of* **4d** *to* **3d**

A solution of **4b** or **4c** or **4d** (0.5 g) in toluene (50 ml) containing catalytic amounts of *p*-toluenesulfonic acid was refluxed under N_2 for 20 hr, cooled, neutralized (5% K_2CO_3

TABLE IV
Elemental analysis of the benzothiazines **3** and **4**.

		C%		H%		N%		S%	
Compd	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
3a	$C_{15}H_{17}NO_4S$	58.63	58.80	5.58	5.46	4.56	4.46	10.4	10.28
3a'	$C_{13}H_{13}NO_4S$	55.91	55.65	4.70	4.46	5.02	5.00	11.4	11.65
3b	$C_{12}H_{13}NO_2S$	61.27	61.20	5.57	5.70	5.96	5.85	13.6	13.9
4b	$C_{12}H_{13}NO_2S$	61.27	61.33	5.57	5.71	5.96	5.80	13.6	13.90
3c	$C_{17}H_{15}NO_2S$	68.67	68.97	5.08	5.05	4.71	4.60	10.7	10.42
4c	$C_{17}H_{15}NO_2S$	68.67	68.60	5.08	5.00	4.71	4.66	10.7	10.71
3d	$C_{17}H_{21}NO_4S$	60.88	60.67	6.31	6.25	4.18	4.20	9.6	10.10
4d	$C_{17}H_{21}NO_4S$	60.88	60.90	6.31	6.20	4.18	4.2	9.6	9.45

TABLE V
Elemental analysis of the benzothiazolines **5** and dihydrobenzothiazines **6** and **7**

Compd	Formula	C%		C%		N%		S%	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
5a	$C_{15}H_{19}NO_4S$	58.28	58.58	6.19	5.98	4.53	4.46	10.2	10.10
5a'	$C_{13}H_{15}NO_4S$	55.51	55.71	5.38	5.29	4.98	5.02	11.4	11.6
5b	$C_{12}H_{15}NO_2S$	60.75	61.13	6.37	6.48	5.90	5.14	13.5	13.39
5c	$C_{17}H_{17}NO_2S$	68.21	67.92	5.73	5.71	4.68	4.45	10.7	10.92
5d	$C_{17}H_{23}NO_4S$	60.52	60.36	6.87	7.05	4.15	4.11	9.5	9.7
6a'	$C_{13}H_{15}NO_4S$	55.51	55.42	5.38	5.58	4.98	5.01	11.4	11.6
6c	$C_{17}H_{17}NO_2S$	68.21	68.26	5.73	5.97	4.68	4.38	10.7	10.61
7b	$C_{12}H_{15}NO_2S$	60.75	60.95	6.37	6.55	5.90	5.75	13.5	13.62
7c	$C_{17}H_{17}NO_2S$	68.21	68.04	5.73	5.80	4.68	4.65	10.7	10.6

soln) the organic layer separated dried (Na_2SO_4) and evaporated. PLC of the residue (light petroleum ether/ethyl acetate 9:1 as the solvent) gave **3b** (0.06 g) or **3c** (0.36 g) or **3d** (0.12 g) respectively.

Reaction of 2-mercaptoaniline with keto esters **2a–d**

In agreement with the general standard method for the synthesis of spirobenzothiazolines previously described,[5] equimolar amounts of 2-mercaptoaniline and β-keto esters were refluxed under N_2 for 4 hr in benzene, containing catalytic amounts of *p*-toluenesulfonic acid. The cooled solution was extracted with 10% K_2CO_3 soln, the organic layer separated, dried (Na_2SO_4), and evaporated. PLC of the residue (light petroleum ether/ethyl acetate, 9:1 as the solvent) gave the benzothiazolines **5a–d**.

Reduction of 1,4-benzothiazines of type **3** *and* **4**

$NaBH_4$ (0.03 mole) was added portionwise to a stirred solution of the compound (0.003 mole) in AcOH (50 ml) containing HCl (0.5 g) at 5°. The reaction mixture was kept at room temperature for 30 min neutralized with KOH soln, and extracted with $CHCl_3$.

The organic layer was separated dried (Na_2SO_4), and evaporated; PLC of the residue (light petroleum ether/ethyl acetate 85:15, as the solvent) gave the corresponding dihydro derivative of type **6** or **7**.

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