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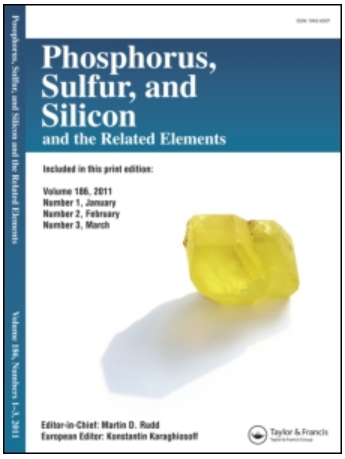

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REACTION BETWEEN 2,2'-DITHIODIANILINE AND ETHYL 2-OXO-1-CYCLOALKANECARBOXYLATES

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REACTION BETWEEN 2,2′-DITHIODIANILINE AND ETHYL 2-OXO-1-CYCLOALKANECARBOXYLATES*

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ABSTRACT

A study has been carried out on the acid-catalysed reaction between 2,2′-dithiodianiline (**1**) and ethyl 2-oxo-1-cycloalkanecarboxylates (**2a–d**). While the 1,4-benzothiazines **3a, b** and benzothiazoles **6a, b** are obtained from the keto esters **2a, b**, mixtures of the 1,4-benzothiazines **3c, d** and **4c, d** and benzothiazolines **5c, d** are obtained from the keto esters **2c, d.**

The formation of the benzothiazines **4** falls within the general pattern previously proposed for reactions between 2,2′-dithiodi(aryl- or alkylamines) and ketones.

The benzothiazines **3** arise from an acid-catalysed rearrangement of the benzothiazines **4**, involving a [1, 3] sulfur migration.

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The acid-catalysed reaction between 2,2′-dithiodi-(aryl- or alkylamines) and ketones (molar ratio 1:1) performed in an inert-gas atmosphere is a practical and convenient method for the preparation of 1,4-thiazines.[1–3]

The simultaneous formation of 2-mercapto-arylamines or -alkylamines provides an important clue to the mechanism of this reaction, and accounts for the isolation, observed in some cases, of thiazolines derived from a competitive reaction of 2-mercapto-amines with particularly reactive ketones.

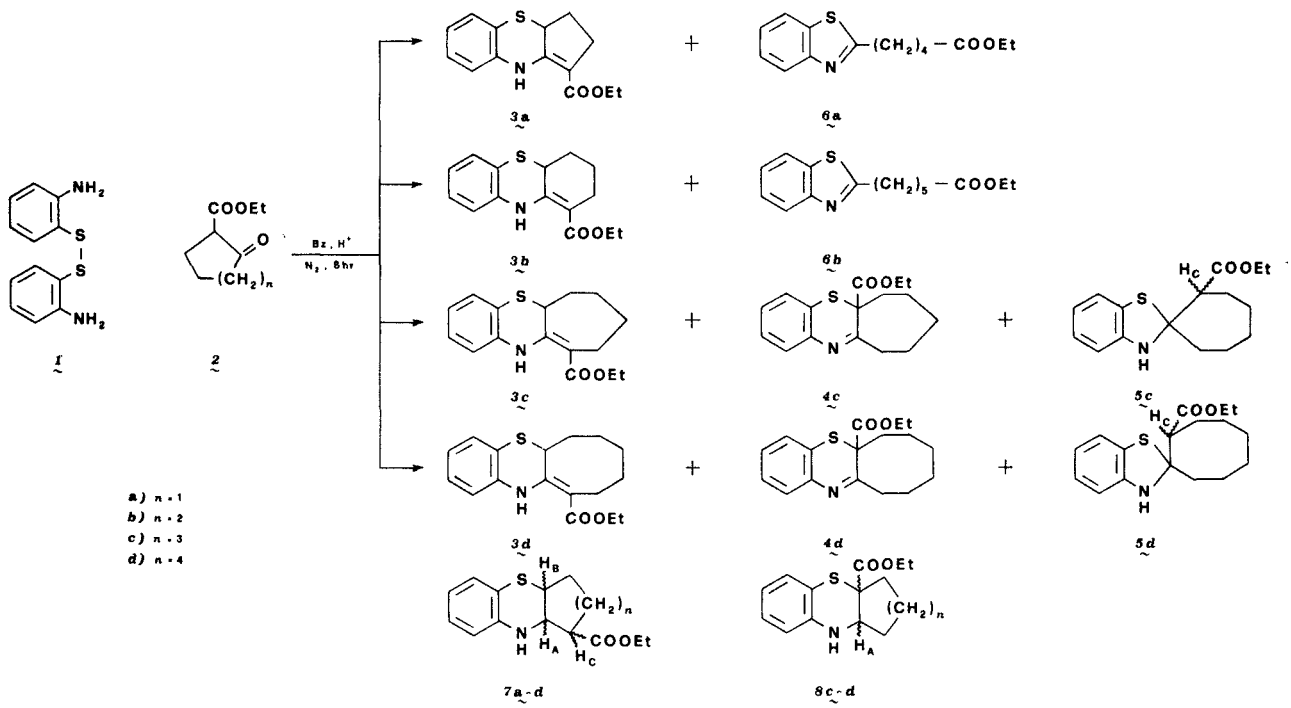
In the present paper we report the results obtained in the reaction of 2,2′-dithiodianiline (**1**) with cyclic β-keto esters (**2a–d**) (Scheme I).

It is apparent that also in this case the reaction gives 1,4-benzothiazines and benzothiazolines or benzothiazoles, the latter derived from a thermal transformation of the benzothiazolines. The different reactivities of the β-keto esters as a function of the size of their rings is also evident.

Thus, while the reaction of **1** with ethyl 2-oxo-1-cyclopentanecarboxylate (**2a**) and ethyl 2-oxo-1-cyclohexanecarboxylate (**2b**) provides, in both cases, a single 1,4-benzothiazine (**3a** or **3b**) and a 2-substituted benzothiazole (**6a** or **6b**), the reaction with ethyl 2-oxo-1-cyclooctanecarboxylate (**2c**) and ethyl 2-oxo-1-cycloheptanecarboxylate (**2d**) carried out under the same conditions provides, in both cases, a mixture of two 1,4-benzothiazines (**3c, 4c** or **3d, 4d**) and a spirobenzothiazoline (**5c** or **5d**).

In the structure of the 1,4-benzothiazines **3a–d** is present an enamino ester moiety; in fact, **3a** has the structure of 1-ethoxycarbonyl-2,3,3*a*,9-tetrahydro-benzo [b] cyclopenta [e] [1, 4] thiazine, as shown by the following evidence: its nmr spectrum exhibits a broad signal at 9.56 δ (1H, NH), a multiplet between 7.6 and 6.8 δ (4H, aromatic H), a complex signal between 4.6 and 4.0 δ (3H, $-CH_2O-$ + angular H), a group of signals between 2.9 and 1.5 δ (4H, $-CH_2-$), and a triplet at 1.35 δ (3H, CH_3-); the ir spectrum shows a carbonyl band at 1670 cm^{-1} and a NH band at 3310 cm^{-1}. The nmr spectra of **3b**, **3c**, and **3d** are substantially identical to that of **3a**, except for the fact that in **3b** the angular proton at C-4*a* appears as a triplet at 3.55 δ and that, in all three compounds, the signal assigned to the NH group appears at lower fields (11–12 δ); their ir spectra show carbonyl and

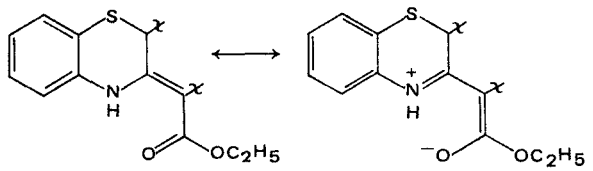
† Part X in the series: "A new reaction between bis(*o*-aminophenyl) disulfide and ketones". Part IX: *Int. J. Sulfur Chem.*, 8, 341 (1973).



SCHEME I

NH bands at lower frequencies than for **3a** (1655–1645 cm^{-1} and 3170–3140 cm^{-1}, respectively) (Tables I and II).

These results can be reasonably taken as a strong evidence for a gradually increasing chelation of the carbonyl group in compounds **3a–d** as a consequence of the relative contributions of the two limiting structures:



It must be observed that our ir and nmr values agree with those reported for some structurally analogous compounds, such as 2-imidazolidylideneacetates[4] and 2-alkyl- or arylaminocyclopentanecarboxylates.[5]

The structures **3a–d** are confirmed by their reduction products **7a–d** whose nmr spectra show, *inter alia,* the presence of a second angular proton on the carbon atom adjacent to the nitrogen atom.

The structure of the 2*H*-1,4-benzothiazines **4c–d** is deduced from their ir and nmr spectra, where the NH signals are absent and, more significantly, from the nmr spectra of the corresponding reduction products **8c, d,** which display signals of an amine proton and a single angular proton on the carbon atom adjacent to the nitrogen atom (Tables I and II).

In previous investigations we have shown[1,3] that the reaction between 2,2′-dithiodi(aryl- or alkylamines) and ketones takes place *via* the initial formation of an enamine intermediate capable of being converted into 1,4-thiazines by cleavage of the disulfide bond consequent upon nucleophilic attack of the β-enamine carbanion.

On the basis of Pennington and Kehret's work,[5] the enamine intermediates involved in the reaction between **1** and **2a–d** should have the structure of enamino esters, from which, according to the mechanism mentioned above, benzothiazines of type **4** should be produced. (Scheme II).

It must be noticed that benzothiazines of type **4** cannot be isolated in the reactions of **1** with keto esters **2a, b,** even when the refluxing time in benzene is reduced, or when solvents of lower boiling point are used, while in the reactions performed with the keto esters **2c, d** their isolation depends on the heating time. In fact, when the reaction mixture is refluxed for 130 hr, the only products that can be isolated are, respectively, the benzothiazine **3c** together with the benzothiazole **6c,** and the benzothiazine **3d** together with the benzothiazole **6d.** Furthermore, the isolated products **4c** or **4d,** by refluxing in toluene containing an acidic catalyst give rise to **3c** or **3d.** These results suggest that the benzothiazines of structures **4** undergo a thermal rearrangement to benzothiazines of structure **3,** and that the size of the aliphatic ring determines the extent of the rearrangement.

This transformation involves, in our opinion, a

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TABLE I

Analytical Data

Compd	Yield %	mp (solv)[a] or bp (Torr)	IR, cm^{-1} N–H	IR, cm^{-1} C=O	IR, cm^{-1} C=C	Formula (Parent peak)
3a	50	52-53° (A)	3310	1670	1615	$C_{14}H_{15}NO_2S$ (*m/e* 261)
3b	48	58-60° (C)	3170	1655	1610	$C_{15}H_{17}NO_2S$ (*m/e* 275)
3c	15	60-61°(B)	3140	1650	1610	$C_{16}H_{19}NO_2S$ (*m/e* 289)
3d	29	101-102° (B)	3140	1645	1610	$C_{17}H_{21}NO_2S$ (*m/e* 303)
4c	37	60-61° (A)		1740	1610 (C=N)	$C_{16}H_{19}NO_2S$ (*m/e* 289)
4d	23	57-59° (A)		1735	1610 (C=N)	$C_{17}H_{21}NO_2S$ (*m/e* 303)
5c	47	52-53° (B)	3340	1720		$C_{16}H_{21}NO_2S$
5d	48	56-57° (B)	3340	1720		$C_{17}H_{23}NO_2S$
6a	50	118° (0.08)		1730		$C_{14}H_{17}NO_2S$
6b	52	150° (0.6)		1730		$C_{15}H_{19}NO_2S$
6c	48	112° (0.2)		1735		$C_{16}H_{21}NO_2S$
6d	48	100° (0.15)		1735		$C_{17}H_{23}NO_2S$
7a	56	106° (0.2)	3375	1720		$C_{14}H_{17}NO_2S$
7b	52	132° (0.09)	3380	1720		$C_{15}H_{19}NO_2S$
7c	50	90° (0.04)	3380	1720		$C_{16}H_{21}NO_2S$
7d	49	132° (0.04)	3380	1720		$C_{17}H_{23}NO_2S$
8c	83	76-77° (B)	3410	1715		$C_{16}H_{21}NO_2S$
8d	79	70-71° (B)	3410	1715		$C_{17}H_{23}NO_2S$

[a] Solvent of crystallization: A = 2-propanol; B = light petroleum ether; C = ethanol.

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previous tautomeric change of **4** into **9**, followed by a formal [1, 3] sigmatropic shift of the sulfur atom. Even though the existence of structures **9** could never be observed directly, it can however be reasonably assumed that **9** were present under the conditions of the rearrangement: in fact, acid catalysis leads to the formation of the imonium cation **10**, whose conjugate base is mesomeric with **9**. (Scheme II). We observed an analogous behaviour in the case of a similar imonium cation, *i.e.* 2,3,4,4*a*-tetrahydro-1 *H*-phenothiazine hydrobromide.[2]

In this connection it may be useful to emphasize that rearrangements involving [1, 3] sulfur migration have been previously observed in dihydro-1,4-thiazines.[6]

The structures of the spirobenzothiazolines **5** and of the benzothiazoles **6** were deduced from their ir and nmr spectra (Tables I and II) and confirmed by comparison with authentic samples prepared as specified in the experimental part. The formation of the benzothiazoles can be ascribed to a β-elimination reaction which the benzothiazolines are known to undergo readily.[7] In this connection, it must be observed that the size of the aliphatic ring has a marked influence also on the stability of the spirobenzothiazolines **5**: in fact, as already stated, the benzothiazoles **6a, b** are obtained directly by the reaction of **1** with **2a, b**, while the reaction of **1** with **2c, d** gives the spirobenzothiazolines **5c, d**, which can be converted into the corresponding benzothiazoles by prolonged heating.

Finally, one should note the stability of the 1,4-benzothiazines **3a-d** and **4c, d** with respect to the autoxidation.

We have demonstrated[3,8] that 2*H*- and 4*H*-1,4-thiazines readily undergo a process of autoxidation when the presence of a hydrogen atom in position 2 or, respectively, 4 allows the formation of a chain-

TABLE II

Nmr Data

Compd	δ, ppm	Assignment
3a	9.55	1, NH
	7.6–6.8	4, aromatic H
	4.6–4.0	3, $-CH_2O-$ + angular H
	2.9–1.5	4, $-CH_2-$
	1.35	3, CH_3-
3b	11.15	1, NH
	7.2–6.6	4, aromatic H
	4.15	2, $-CH_2O-$
	3.55	1, angular H
	2.6–1.3	6, $-CH_2-$
	1.15	3, CH_3-
3c	12.00	1, NH
	7.5–6.7	4, aromatic H
	4.5–4.0	3, $-CH_2O-$ + angular H
	3.3–1.5	8, $-CH_2-$
	1.30	3, CH_3-
3d	11.92	1, NH
	7.5–6.8	4, aromatic H
	4.6–4.0	3, $-CH_2O-$ + angular H
	3.2–1.0	10, $-CH_2-$
	1.32	3, CH_3-
4c	7.7–7.1	4, aromatic H
	4.08	2, $-CH_2O-$
	3.2–2.8	2, allylic H
	2.5–1.5	8, $-CH_2-$
	0.98	3, CH_3-
4d	7.7–7.1	4, aromatic H
	4.18	2, $-CH_2O-$
	3.4–2.6	2, allylic H
	2.5–1.3	10, $-CH_2-$
	1.08	3, CH_3-
5c	7.2–6.5	4, aromatic H
	5.3–4.8	1, NH
	4.4–3.9	2, $-CH_2O-$
	3.6–3.3	1, H_C
	2.6–1.5	10, $-CH_2-$
	1.4–1.0	3, CH_3-
5d	7.4–6.7	4, aromatic H
	5.3–4.8	1, NH
	4.4–3.8	2, $-CH_2O-$
	3.5–3.0	1, H_C
	2.6–1.4	12, $-CH_2-$
	1.4–1.0	3, CH_3-
6a	8.3–7.0	4, aromatic H
	4.20	2, $-CH_2O-$
	3.20	2,
	2.40	2, $-CH_2-CO-$
	2.1–1.5	4, $-CH_2-$
	1.20	3, CH_3-
6b	8.0–7.2	4, aromatic H
	4.08	2, $-CH_2O-$
	3.04	2,
	2.25	2, $-CH_2-CO-$
	2.0–1.3	6, $-CH_2-$
	1.20	3, CH_3-
6c	8.2–7.3	4, aromatic H
	4.18	2, $-CH_2O-$
	3.20	2,
	2.30	2, $-CH_2-CO-$
	2.1–1.4	8, $-CH_2-$
	1.20	3, CH_3-
6d	8.2–7.3	4, aromatic H
	4.18	2, $-CH_2O-$
	3.15	2,
	2.30	2, $-CH_2-CO-$
	2.1–1.3	10, $-CH_2-$
	1.20	3, CH_3-
7a	7.0–6.4	4, aromatic H
	4.65	1, NH
	4.14	2, $-CH_2O-$
	3.9–3.8	1, H_A
	3.4–3.2	1, H_B
	3.0–2.8	1, H_C
	2.4–1.6	4, $-CH_2-$
	1.26	3, CH_3-
7b	7.3–6.6	4, aromatic H
	4.80	1, NH
	4.5–4.1	1, H_A
	4.28	2, $-CH_2O-$
	3.8–3.1	1, H_B
	3.0–2.5	1, H_C
	2.1–1.5	6, $-CH_2-$
	1.30	3, CH_3-
7c	7.2–6.6	4, aromatic H
	4.60	1, NH
	4.5–4.2	1, H_A
	4.25	2, $-CH_2O-$
	3.3–2.8	1, H_B
	2.5–2.0	1, H_C
	2.0–1.5	8, $-CH_2-$
	1.28	3, CH_3-
7d	7.0–6.3	4, aromatic H
	4.42	1, NH
	4.25–4.15	1, H_A
	4.05	2, $-CH_2O-$
	3.1–2.8	1, H_B
	2.7–2.6	1, H_C
	2.6–1.3	10, $-CH_2-$
	1.20	3, CH_3-
8c	7.3–6.6	4, aromatic H
	4.22	2, $-CH_2O-$
	4.00	1, NH
	3.7–3.4	1, H_A
	2.2–1.3	10, $-CH_2-$
	1.12	3, CH_3-
8d	7.0–6.3	4, aromatic H
	4.05	2, $-CH_2O-$
	3.90	1, NH
	3.7–3.5	1, H_A
	2.6–1.3	12, $-CH_2-$
	1.09	3, CH_3-

carrying radical highly stabilized by delocalization of the unpaired electron in the *d*-orbitals of sulfur; the electron-releasing effect of the sulfur atom makes this species an excellent donor radical, capable of reacting with oxygen. The stability of compounds of types **3** and **4** with respect to the autoxidation fits perfectly into this scheme: in fact, the absence of hydrogen atoms in the appropriate positions of the

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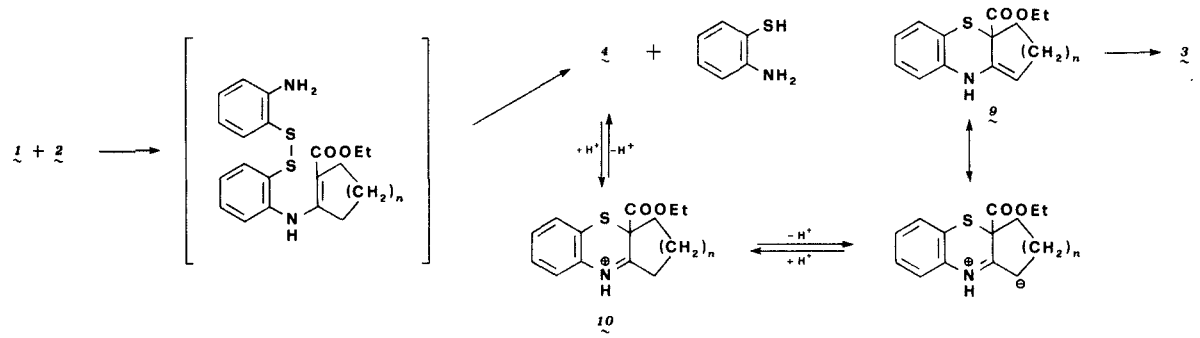

SCHEME II

compounds of structure **4** clearly prevents the formation of a radical capable of starting the autoxidation process, while the presence of the ethoxycarbonyl group in the unsaturated system of compounds with structure **3** would confer acceptor properties to the hybrid radical which could conceivably arise from it, making it incapable of a coupling reaction with oxygen.

Experimental Section

Melting points and boiling points are uncorrected. Nmr spectra were obtained on a Varian HA-100 and Jeol 60 spectrometers in $CDCl_3$ as solvent and TMS as internal standard. All *m/e* values were determined on a Perkin–Elmer mod. 270 low-resolution mass spectrometer. Ir spectra were recorded on a Perkin–Elmer 257 grating spectrophotometer as nujol mulls or liquid films

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 new 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 ethyl 2-oxo-1-cycloalkanecarboxylates (2a–d).

A solution of **2** (0.05 mole) in benzene (30 ml) was added over 30 min to a stirred, refluxing solution of **1** (0.05 mole) in benzene (170 ml) containing catalytic amounts of *p*-toluenesulfonic acid. The reaction mixture was refluxed under N_2 for 8 hr (0.05 mole of H_2O was collected), cooled, 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, 95:5 as eluent), in the order given:

in the case of **2a**:
1-ethoxycarbonyl-2,3,3*a*,9-tetrahydrobenzo [b] cyclopenta [e][1, 4]thiazine (**3a**) and ethyl 5-(2-benzothiazolyl)pentanoate (**6a**);

in the case of **2b**:
1-ethoxycarbonyl-2,4,4*a*,10-tetrahydro-3*H*-phenothiazine (**3b**) and ethyl 6-(2-benzothiazolyl)hexanoate (**6b**);

in the case of **2c**:
10-ethoxycarbonyl-5*a*,6,7,8,9,11-hexahydrobenzo [b] cyclohepta [e] [1, 4] thiazine (**3c**), spiro [benzothiazole-2(3*H*),1′-(2′-ethoxycarbonyl)cycloheptane] (**5c**), and 5*a*-ethoxycarbonyl-5*a*,6,7,8,9,10-hexahydrobenzo [b]cyclohepta [e] [1, 4] thiazine (**4c**);

in the case of **2d**:
11-ethoxycarbonyl-6,7,8,9,10,12-hexahydro-5*aH*-benzo[b]-cycloocta[e][1, 4]thiazine (**3d**), spiro[benzothiazole-2(3*H*),1′-(2′-ethoxycarbonyl)cyclooctane] (**5d**), and 5*a*-ethoxycarbonyl-6,7,8,9,10,11-hexahydro-5*aH*-benzo[b]cycloocta[e][1, 4]-thiazine (**4d**). (Scheme I).

This reaction was repeated for the case of the keto esters **2c, d** under the same conditions except that the refluxing time was extended to 130 hr: working up of the reaction mixtures as described above resulted in the isolation of **3c** (48%) and ethyl 7-(2-benzothiazoly)heptanoate (**6c**) (48%), and, respectively, **3d** (48%) and ethyl 8-(2-benzothiazolyl)-octanoate (**6d**) (48%).

Rearrangement of 4c to 3c and of 4d to 3d

A solution of **4c** or **4d** (0.3 g) in toluene (40 ml) containing catalytic amounts of *p*-toluenesulfonic acid was refluxed under N_2 for 30 hr, cooled, neutralized (5% K_2CO_3 soln), the organic layer separated, dried (Na_2SO_4), and evaporated. PLC of the residue (light petroluem ether/ethyl acetate 9:1 as the solvent) gave **3c** (0.15 g) and **3d** (0.2 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,[9] equimolar amounts of 2-mercaptoaniline and β-keto ester were refluxed under N_2 for 8 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. In the reactions performed with the keto esters **2a, b**, PLC of the residue (light petroleum ether/ethyl acetate, 85:15, as the solvent) gave the benzothiazoles **6a, b**, which were compared with authentic samples prepared by the standard method[10] from 2-mercaptoaniline and diethyl adipate or pimelate respectively. In the reactions performed with the keto esters **2c, d** PLC of the residue (light petroleum ether/ethyl acetate, 95:5, as the solvent) gave the spirobenzothiazolines **5c, d**.

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By refluxing solutions of **5c, d** in xylene containing catalytic amounts of *p*-toluenesulfonic acid for 8 hr and working up as above, the corresponding benzothiazoles **6c, d** were obtained.

Reduction of benzothiazines of type 3

$NaBH_4$ (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 20 min, neutralized with KOH soln, and extracted with $CHCl_3$. The organic layer was separated, dried (Na_2SO_4), and evaporated; purification of the residue by PLC (light petroleum ether/ethyl acetate, 9:1, as the solvent) gave the corresponding dihydro derivative of type **7**.

Reduction of benzothiazines of type 4

This reduction was performed by using a 1:1 mixture of AcOH/EtOH as the solvent (50 ml) with a procedure identical to that described above for compounds of type **3**. By working up the reaction mixture as above the dihydro derivatives of type **8** were obtained.

Elemental Analysis of the Benzothiazines 3 and 4

		C%		H%		N%		S%	
Compd	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
3a	$C_{14}H_{15}NO_2S$	64.34	64.30	5.78	5.79	5.36	5.21	12.27	12.40
3b	$C_{15}H_{17}NO_2S$	65.42	65.55	6.22	6.17	5.09	5.08	11.64	11.90
3c	$C_{16}H_{19}NO_2S$	66.40	66.69	6.62	6.75	4.84	4.85	11.08	11.23
3d	$C_{17}H_{21}NO_2S$	67.29	67.54	6.98	6.73	4.62	4.55	10.57	10.35
4c	$C_{16}H_{19}NO_2S$	66.40	66.64	6.62	6.45	4.84	4.90	11.08	11.09
4d	$C_{17}H_{21}NO_2S$	67.29	67.43	6.98	6.83	4.62	4.55	10.57	10.27

Elemental Analysis of the Benzothiazolines 5 and Benzothiazoles 6

		C%		H%		N%		S%	
Compd	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
5c	$C_{16}H_{21}NO_2S$	65.94	65.70	7.26	7.27	4.81	4.78	11.00	11.15
5d	$C_{17}H_{23}NO_2S$	66.85	67.05	7.59	7.38	4.59	4.58	10.50	10.27
6a	$C_{14}H_{17}NO_2S$	63.85	63.80	6.51	6.40	5.32	5.56	12.18	11.96
6b	$C_{15}H_{19}NO_2S$	64.95	64.70	6.90	6.86	5.05	5.08	11.56	11.37
6c	$C_{16}H_{21}NO_2S$	65.94	65.76	7.26	7.52	4.81	4.71	11.00	11.21
6d	$C_{17}H_{23}NO_2S$	66.85	66.81	7.59	7.48	4.59	4.51	10.50	10.63

Elemental Analysis of the Dihydrobenzothiazines 7 and 8

		C%		H%		N%		S%	
Compd	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
7a	$C_{14}H_{17}NO_2S$	63.85	64.07	6.51	6.55	5.32	5.31	12.18	12.40
7b	$C_{15}H_{19}NO_2S$	64.95	65.20	6.90	7.18	5.05	5.02	11.56	11.36
7c	$C_{16}H_{21}NO_2S$	65.94	66.21	7.26	7.49	4.81	4.69	11.00	10.76
7d	$C_{17}H_{23}NO_2S$	66.85	66.85	7.59	7.86	4.59	4.34	10.50	10.72
8c	$C_{16}H_{21}NO_2S$	65.94	65.94	7.26	7.22	4.81	4.80	11.00	11.14
8d	$C_{17}H_{23}NO_2S$	66.85	67.13	7.59	7.67	4.59	4.81	10.50	10.55

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