5,12-DI(1-ALKYL)THIOQUINANTHRENEDIINIUM BIS-SALTS AND 1-ALKYL-3-ALKYLTHIO-1,4-DIHYDRO-4-THIOOXOQUINOLINES [1]

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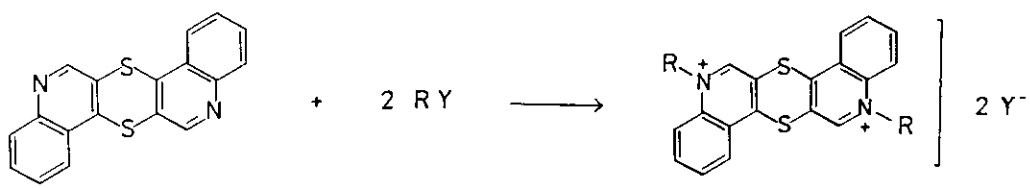
Abstract - The preparation of 5,12-di(1-alkyl)thioquinanthrenediinium bis-salts and their transformation into 1-alkyl-3-alkylthio-1,4-dihydro-4-thiooxoquinolines are described.

5,12-Di(1-alkyl)thioquinanthrenediinium bis-salts (2) obtained from thioquinanthrene i.e. 1,4-dithiino[2,3-c:5,6-c']diquinoline (1) and alkylating agents (3) are of interest for us from two points of view. Firstly, they may be expected to be potentially antibacterial agents taking into consideration the antibacterial activity of several types of 1-alkylpyridinium [2,3] or 1-alkylquinolinium [2,4] salts. Secondly, the quaternization of quinoline derivatives activates the 2- or 4-substituents toward a nucleophilic displacement. [5,6] 4-Quinolinyl-sulfur bonds in salts (2) should be, therefore, much more reactive in the nucleophilic substitution reaction, than those in the molecule of parent dithiin (1).[7]

RESULTS AND DISCUSSION

We attempted to quaternize thioquinanthrene (1) with several alkylating agents:

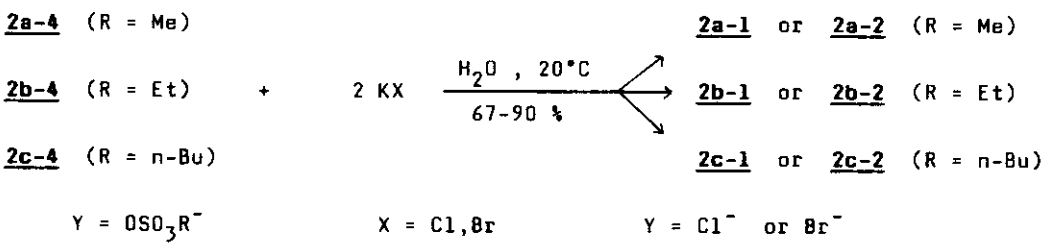


1 3 2

Y = OSO_3R, OTs, I

Good results in the formation of bis-salts (**2**) (Table 1) and a high conversion of thioquinanthrene (**1**) were obtained only with dialkyl sulfates (R = Me, Et, n-Bu) and alkyl tosylates (R = Me, Et) appeared to be less effective, the least effective being alkyl iodides (R = Me,[8] Et,[9] n-Bu, n-Hex). The reactivity of alkylating agents in the quaternization of thioquinanthrene-nitrogen atoms decreased as related to alkyl-groups in the order Me > Et > n-Bu > n-Hex. A similar reactivity was usually observed during the alkylation of heterocyclic tertiary amines with alkylating agents.[10]

Applying a convenient procedure described by W.Schroth and his co-workers [11] for pyrimidinium salts, we were able to achieve an effective exchange of the anion-rests in bis-salts [**2a-4**, **2b-4**, **2c-4** (R = Me, Et, n-Bu)] from alkyl sulfate ions into chloride and bromide ones (Table 2).



^{1}H Nmr spectra confirmed the structure of bis-salts (**2**), because of the occurrence of 1-alkylquinolinium group signals [12] at δ = 4.65-4.70 (N^+Me), δ = 5.12-5.14 (N^+-CH_2) (Table 4) as well as characteristic shifts of the α-quinolinium-type proton signal [12] up to δ = 9.45-9.49 (as compared to those of thioquinanthrene (**1**) δ = 8.90) was observed. All bis-salts (**2**), usually obtained as dihydrates, are deep yellow to orange-coloured solids, readily soluble in water, yielding acidic solutions (e.g. 1 % solution of **2a-1** (R = Me, Y = Cl) exhibited pH value 4.5). Alkalization of water solution of bis-salts (**2**) led to a brick-brown pseudobase-type solid which, if precipitated from concentrated solution or kept at room temperature for several hours, became extremely insoluble in organic solvents and did not undergo re-conversion to the starting bis-salts (**2**) upon acidification. Similar products were obtained by treating the ethanolic solution of bis-salts (**2**) with thiourea. On the other hand, the freshly precipitated pseudo-base solid from diluted aqueous solution underwent solubilization in water and re-conversion to the starting bis-salts upon acidification.

Table 1. 5,12-Dialkylthioquinanthrenediinium bis-salts (**2**) prepared from thioquinanthrene (**1**) and alkylating agents

Run	Alkylating Agent	Conditions of the reaction Temp (°C)[a]	Time (h)	Product	Yield (%)[b]	Formula	Analysis (%) calcd / found[c] C	H	N	S
1.	MeI	50 (Carius tube)	24	**2a-3**	20[b]	non-isolated	———			
2.	MeI	140 (Carius tube)	4	**2a-3**	36[b]	non-isolated	———			
3.	Me_2SO_4	85	2	**2a-4**	100	$C_{22}H_{26}N_2O_{10}S_4$	43.55 / 43.26	4.32 / 4.28	4.62 / 4.36	21.14 / 21.31
4.	MeOTs	85	2	**2a-5**	100	$C_{34}H_{34}N_2O_8S_4$	56.18 / 56.02	4.71 / 4.65	3.85 / 3.80	17.64 / 17.84
5.	EtI	85	48	**2b-3**	2[b]	non-isolated	———			
6.	Et_2SO_4	85	48	**2b-4**	100	$C_{26}H_{34}N_2O_{10}S_4$	47.11 / 46.94	5.17 / 5.06	4.23 / 4.26	19.35 / 19.54
7.	n-BuI	140	24	**2c-3**	20[b]	non-isolated	———			
8.	$(n\text{-}Bu)_2SO_4$	85	72	**2c-4**	50[b]	non-isolated	———			
9.	n-HexI	140	24	**2d-3**	11[b]	non-isolated	———			

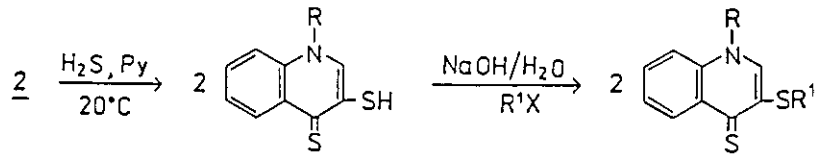
a) Bath-temperature. b) Yield calculated from the content of bis-salt (**2**) in its mixture with (**1**) - see experimental. c) For analytical purposes bis-salts (**2**) were recrystallized from dry methanol or ethanol.

Table 2. 5,12-Dialkylthioquinanthrenediinium bis-salts dihydrates (**2**) x 2 H_2O prepared by exchange of anion-rest

Run	Substrate			Product					**2** [a] Analysis [c]				
		R	Y^-		R	Y^-	Yield (%)	Formula [c]	calcd / found C	H	N	S	Cl or Br
1.	**2a-4**	Me	$MeSO_4^-$	**2a-1** (x 2 H_2O)	Me	Cl^-	74	$C_{20}H_{16}N_2Cl_2S_2$	57.28 57.21	3.84 3.75	6.68 6.70	15.29 15.47	16.90 17.75
2.	**2a-4**	Me	$MeSO_4^-$	**2a-2** (x 2 H_2O)	Me	Br^-	90	$C_{20}H_{16}N_2Br_2S_2$	47.26 47.15	3.17 3.05	5.51 5.42	12.61 12.80	31.44 31.65
3.	**2b-4**	Et	$EtSO_4^-$	**2b-1** (x 2 H_2O)	Et	Cl^-	70	$C_{22}H_{20}N_2Cl_2S_2$	59.05 58.93	4.50 4.40	6.26 6.13	14.33 14.51	15.84 16.02
4.	**2b-4**	Et	$EtSO_4^-$	**2b-2** (x 2 H_2O)	Et	Br^-	83	$C_{22}H_{20}N_2Br_2S_2$	49.27 49.12	3.76 3.66	5.22 5.15	11.96 12.11	29.79 30.00
5.	**2c-4**	n-Bu	$n\text{-}BuSO_4^-$	**2c-1** (x 2 H_2O)	n-Bu	Cl^-	67[b]	$C_{26}H_{28}N_2Cl_2S_2$	62.02 61.90	5.60 5.67	5.56 5.42	12.73 12.91	14.08 14.26
6.	**2c-4**	n-Bu	$n\text{-}BuSO_4^-$	**2c-2** (x 2 H_2O)	n-Bu	Br^-	86[b]	$C_{26}H_{28}N_2Br_2S_2$	52.71 51.59	4.76 4.80	4.73 4.65	10.82 11.01	26.97 27.15

[a] Products lose 2 molecules of water after drying at 110°C under vacuum. [b] Yield calcd from the content of **2c-4** in its mixture with **1** (Table 1, run 8). [c] Analytical purity samples as anhydrous bis-salts (**2**) were obtained after recrystallization of **2** x $2H_2O$ from dry methanol.

Passing hydrogen sulfide through the cold suspension of bis-salts (**2**) in dry pyridine led in each case to the complete consumption of bis-salt substrates and to the formation of 1-alkyl-1,4-dihydro-4-thiooxo-3-quinolinethiols (**4**) (90-100 %), which were transformed to stable final alkylthio products (**5**) in overall yields of 70-85 % calculated from the applied bis-salts (**2**):



4 **5**

Because thioquinanthrene (**1**) or its hydrochloride did not react with hydrogen sulfide in dry pyridine at 0-20°C, the thiones (**4**) or (**5**) could be prepared directly also from the mixture of parent base (**1**) and bis-salts (**2**) i.e. without isolation of pure bis-salt (**2**) (procedure B).

EXPERIMENTAL

All melting points are uncorrected. ^{1}H Nmr spectra were recorded on a Tesla BS 487 C spectrometer at 80 MHz in deuterium oxide or deuteriochloroform solutions. Tlc analysis were performed on aluminium oxide 60 F neutral (type E) using ethyl acetate - chloroform (10:1 v/v) as an eluent.

Thioquinanthrene (**1**) was prepared by sulfurizating quinoline with elemental sulfur and recrystallized from DMF, mp 314-315°C.[13]

5,12-Di(1-alkyl)thioquinanthrenediinium bis-(alkyl sulfate) (**2a-4**, **2b-4**, **2c-4**).

A suspension of 3.18 g (10 mmol) of thioquinanthrene (**1**) in 60 mmol of dialkyl sulfate was heated at 80-85°C while being "magnetically" stirred for 2-96 h. Then 20 ml of dry benzene was added. The mixture was boiled for 5 min, and cooled down to ambient temperature. The solid was filtered off, washed with dry benzene, then dried under vacuum and weighed to give bis-(alkyl sulfate) (**2a-4**, **2b-4**, **2c-4**) or in some cases the mixture of bis-(alkyl sulfate) (**2b-4**, **2c-4**) and parent base (**1**). The reaction parameters and results have been collected in Table 1. The reactions of thioquinanthrene (**1**) with methyl or ethyl tosylates were performed in the same manner.

Determination of the content of bis-(alkyl sulfates) (**2b-4**) or (**2c-4**) in their mixtures with parent base (**1**) could be carried out taking into consideration the fact that thioquinanthrene (**1**) is insoluble in water and very poorly soluble in cold benzene and that bis-salts of type (**2**) are well soluble in water but insoluble in benzene. In order to perform the calculation following observations were used: x) the increase in the weight of solid product obtained as compared with the amounts of the substrate applied - it indicates the amounts of alkylating agent reacted, i.e. the amounts of bis-salt (**2**) formed; xx) the decrease in the weight of solid product after its treatment with water pointing to the amounts of non-converted thioquinanthrene (**1**) as well as the amounts of bis-salt (**2**) dissolved. Both type of data as well as quantitative tlc determination [13] of the content of thioquinanthrene (**1**) in post-reaction solid and determination of the sulfate content after treatment of aqueous solution of bis-salts (**2a-4**, **2b-4**, **2c-4**) with barium chloride led to very close results (± 1.5 %).

Reactions of thioquinanthrene with alkyl iodides

A suspension of 3.18 g (10 mmol) of thioquinanthrene (**1**) in 60 mmol of alkyl iodide was heated and stirred under to conditions presented in the Table 1. Then most of alkyl iodide was removed by vacuum distillation. The residue was then treated with benzene and worked up as in the case of bis-(alkyl sulfates) to give in each case the mixture of base (**1**) and bis-methiodide (**2**). Fresh prepared mixtures of **1** and bis-salts (**2a-3**, **2b-3**, **2d-3**) could be effectively applied for the preparation of quinolinethiones (**5**). Aqueous solutions of bis-iodides on standing at room temperature underwent transformation to water insoluble orange-colored solids.

5,12-Di(n-alkyl)thioquinanthrenediinium bis-chlorides (**2a-1**, **2b-1**, **2c-1**) or bis-bromides (**2a-2**, **2b-2**, **2c-2**).

A solution of bis-(alkyl sulfate) (**2a-4**, **2b-4** or **2c-4**) (1 g) in 4 ml of water was prepared. (In the case of non-complete converted thioquinanthrene, it must be removed by filtrating its suspension with a solution of bis-salt (**2b-4** or **2c-4**) in appropriate amounts of water.) The solution of bis-(alkyl sulfate) was poured into a saturated solution of potassium chloride (4.2 g) or bromide (7.8 g) in 12 ml of water. Immediately, bis-chloride (**2a-1**, **2b-1** or **2c-1**) or bis-bromide

(**2a-2**, **2b-2** or **2c-2**) was precipitated. The mixture was kept at 10°C for 30 min and the solid was filtered off. Bis-chlorides and bis-bromides were usually isolated as di-(or tetra-) hydrate and before analysis they were dehydrated in a vacuum-exsiccator over phosphorus pentoxide.

1-Alkyl-3-alkylthio-1,4-dihydro-4-thiooxoquinolines (**5**)

Procedure A

Dry hydrogen sulfide was passed through a suspension of 5 mmol of bis-salt (**2**) in 80 ml of dry pyridine at 10-20°C until the mixture was clarified (1.5 h). The mixture was next poured into four volumes of 5 % aqueous sodium hydroxide. Then an alkylating agent (20 % molar excess) was added dropwise with stirring (5 - 15 min), and stirring was continued for 15 min. The solid was filtered off, washed with water, dried over calcium chloride in a vacuum exsiccator to give pure thione (**5**) (one spot in tlc). For analytical purposes thiones (**5**) were recrystallized from methanol. The results are presented in the Table 3.

Procedure B

The mixture containing 5 mmoles of bis-salt (**2**) and non-converted thioquinanthrene (**1**) could be used. It was treated with hydrogen sulfide in pyridine suspension as in procedure A. After pouring it into 5 % aqueous sodium hydroxide, the mixture was filtered off to remove non-quaternized thioquinanthrene. The resulting solution of thiolates was then alkylated as in procedure A to give the same yields of thiones (**5**) calculated from the content of bis-salts (**2**) applied.

1-Alkyl-1,4-dihydro-4-thiooxo-3-quinolinethiols (**4**).

The clear pyridine solution of thiols (**4**) obtained according to procedure A was poured into four volumes of water, followed by filtration. The solid obtained was washed with water and dried in vacuum, to give 1-alkyl-1,4-dihydro-4-thiooxo-3-quinolinethiols (**4**). Analytically pure samples were obtained in the cases of compounds (**4a**) (R = Me) and (**4b**) (R = Et): **4a**, 100 %, mp = 264-267°C$_{dec.}$, MS (15 eV) m/z = 207 (100 %, M^+)

4b, 100 %, mp = 225-227°C$_{dec.}$, MS (15 eV) m/z = 221 (100 %, M^+)

Thiols (**4**) could be transformed into their 3-alkylthio derivatives (**5**), as exampli-fied by means of their methylation in 5 % aqueous sodium hydroxide solution with 10 % molar excess of methyl iodide and then treated as described above.

Table 3. 1-Alkyl-3-alkylthio-1,4-dihydro-4-thiooxoquinolines (5)

	Substrate		Alkylating	Results of synthesis and properties of compounds (5)									
	R	Y^-	Agent R^1X		R	R^1	Yield [%]	mp [°C]	Formula	Analysis C	H	N	calcd / found S
2a-1	Me	Cl^-	MeI	**5a-1**	Me	Me	90	260-262	$C_{11}H_{11}NS_2$	59.69	5.00	6.33	28.97
										59.60	4.95	6.40	29.10
2a-2	Me	Br^-	MeI	**5a-1**	Me	Me	90	260-262					
2a-3	Me	I^-	MeI	**5a-1**	Me	Me	90[a)]	260-262					
2a-4	Me	$MeSO_4^-$	MeI	**5a-1**	Me	Me	90	260-262					
	Me	$MeSO_4^-$	EtI	**5a-2**	Me	Et	74	215-216	$C_{12}H_{13}NS_2$	61.24	5.57	5.95	27.24
										61.20	5.51	6.01	27.50
	Me	$MeSO_4^-$	n-BuI	**5a-3**	Me	n-Bu	67	172-174	$C_{14}H_{17}NS_2$	63.83	6.50	5.32	24.34
										63.91	6.44	5.27	24.42
	Me	$MeSO_4^-$	MeEtCHI	**5a-4**	Me	MeEtCH	52	108-110	$C_{14}H_{17}NS_2$	63.83	6.50	5.32	24.34
										63.90	6.41	5.30	24.45
	Me	$MeSO_4^-$	$C_6H_5CH_2Cl$	**5a-5**	Me	$C_6H_5CH_2$	82	219-221	$C_{17}H_{15}NS_2$	68.65	5.08	4.71	21.56
										68.60	5.11	4.82	21.70

Table 3. (continued)

	Substrate		Alkylating	Results of synthesis and properties of compounds (5)								
	R	Y^-	Agent R^1X	R	R^1	Yield [%]	mp [°C]	Formula	Analysis			calcd found
									C	H	N	S
2b-4	Et	$EtSO_4^-$	MeI	**5b-1**	Et	Me	88	196-198	$C_{12}H_{13}NS_2$	61.24	5.57	5.95	27.24
										61.30	5.52	5.99	27.42
	Et	$EtSO_4^-$	EtI	**5b-2**	Et	Et	72	171-174	$C_{13}H_{15}NS_2$	62.61	6.06	5.62	25.71
										62.66	6.01	5.70	25.85
2c-4	n-Bu	$n\text{-}BuSO_4^-$	MeI	**5c-1**	n-Bu	Me	80	141-142	$C_{14}H_{17}NS_2$	63.83	6.50	5.32	24.34
										63.94	6.40	5.25	24.51
2c-3	n-Bu	I^-	MeI	**5c-1**	n-Bu	Me	57[a)]	141-142					
2d-3	$n\text{-}C_6H_{13}$	I^-	MeI	**5d-1**	$n\text{-}C_6H_{13}$	Me	65[a)]	118-120	$C_{16}H_{21}NS_2$	65.93	7.26	4.80	22.00
										66.01	7.20	4.84	22.15

a) Mixture of thioquinanthrene and bis-iodide was used. Yield calculated from the content of bis-iodide (see Table 1, runs 1, 2, 8, 9 and experimental).

Table 4. ^{1}H Nmr data of compounds (**2**, **5**)[a)]

Compound	δ [ppm]
2a-1	4.74(s, 6H, N-CH_3); 8.06-8.69(m, 6H, $H_{arom.}$); 8.71-8.97(m, 2H, H-5); 9.53(s, 2H, H-2)
2a-2	4.65(s, 6H, N-CH_3); 8.03-8.55(m, 6H, $H_{arom.}$); 8.63-8.87(m, 2H, H-5); 9.43(s, 2H, H-2)
2a-4	3.65(s, 6H, O-CH_3); 4.69(s, 6H, N-CH_3); 8.05-8.59(m, 6H, $H_{arom.}$); 8.69-8.89(m, 2H, H-2); 9.45(s, 2H, H-2)
2b-1	1.56-1.97(t, J=7 Hz, 6H, N-CH_2-CH_3); 4.94-5.31(q, J=7 Hz, 4H, N-CH_2-CH_3); 8.03-8.66(m, 6H, $H_{arom.}$); 8.69-8.84(m, 2H, H-5); 9.48(s, 2H, H-2)
2b-2	1.59-1.98(t, J=7 Hz, 6H, N-CH_2-CH_3); 4.91-5.31(q, J=7 Hz, 4H, N-CH_2-CH_3); 7.97-8.66(m, 6H, $H_{arom.}$); 8.72-8.98(m, 2H, H-5); 9.49(s, 2H, H-2)
2b-4	1.22-1.44(t, J=7 Hz, 6H, O-CH_2-CH_3); 1.69-1.97(t, J=7 Hz, 6H, N-CH_2-CH_3); 3.94-4.25(q, J=7 Hz, 4H, O-CH_2-CH_3); 4.97-5.31(q, J=7 Hz, 4H, N-CH_2-CH_3); 7.97-8.69(m, 6H, $H_{arom.}$); 8.78-8.94(m, 2H, H-5); 9.49(s, 2H, H-2)
2c-1	0.85-1.10(t, J=7 Hz, 6H, N-$(CH_2)_3$-CH_3); 1.19-2.18(m, 8H, N-$CH_2(CH_2)_2$-CH_3); 3.95-4.20(t, J=7 Hz, 4H, N-CH_2-CH_2); 7.98-8.60(m, 6H, $H_{arom.}$); 8.71-8.89(m, 2H, H-5); 9.49(s, 2H, H-2)
2c-2	0.84-1.09(t, J=7 Hz, 6H, N-$(CH_2)_3$-CH_3); 1.19-2.19(m, 8H, N-CH_2-$(CH_2)_2CH_3$); 4.00-4.21(t, J=7 Hz, 4H, N-CH_2-CH_2); 7.97-8.71(m, 6H, $H_{arom.}$); 8.81-8.97(m, 2H, H-5); 9.51(s, 2H, H-2)
2c-4	0.47-0.75(t, J=7 Hz, 6H, O-$(CH_2)_3$-CH_3); 0.84-1.09(t, J=7 Hz, 6H, N-$(CH_2)_3$-CH_3); 1.19-2.23(m, 16H, N-CH_2-$(CH_2)_2$-CH_3 ; O-CH_2-$(CH_2)_2$-CH_3); 2.78-3.06(t, J=7 Hz, 4H, O-CH_2-CH_2); 4.00-4.22(t, J=7 Hz, 4H, N-CH_2-CH_2); 7.94-8.50(m, 6H, $H_{arom.}$) 8.69-8.88(m, 2H, H-5); 9.50(s, 2H, H-2)

Table 4. (continued)

Compound	δ [ppm]
5a-1	2.43(s, 3H, S-$\underline{CH}_3$); 3.97(s, 3H, N-$\underline{CH}_3$); 7.27-7.70(m, 4H, $\underline{H}_{arom.}$); 8.90-9.08(m, 1H, $\underline{H}$-5)
5a-2	1.13-1.38(t, J=7.5 Hz, 3H, S-CH_2-$\underline{CH}_3$); 2.67-2.95(q, J=7.5 Hz, 2H, S-$\underline{CH}_2$-CH_3); 3.93(s, 3H, N-$\underline{CH}_3$); 7.22-7.62(m, 4H, $\underline{H}_{arom.}$); 8.93(m, 1H, $\underline{H}$-5)
5a-3	0.75-0.97(t, J=7 Hz, 3H, CH_2-$\underline{CH}_3$); 1.31-1.68(m, 4H, CH_2-($\underline{CH}_2$)$_2$-CH_3); 2.63-2.87(t, J=7 Hz, 2H, S-$\underline{CH}_2$-CH_2); 3.91(s, 3H, N-$\underline{CH}_3$); 7.23-7.68(m, 4H, $\underline{H}_{arom.}$); 8.86-9.02(m, 1H, $\underline{H}$-5)
5a-4	0.81-1.09(t, J=7.5 Hz, 3H, -CH_2-$\underline{CH}_3$); 1.13-1.28(d, J=7.5 Hz, 3H, -CH-$\underline{CH}_3$); 1.34-1.66(m, 2H, -CH-$\underline{CH}_2$-CH_3); 3.31-3.78(m, 1H, S-$\underline{CH}$); 3.91(s, 3H, N-$\underline{CH}_3$); 7.30-7.73(m, 4H, $\underline{H}_{arom.}$); 8.94-9.10(m, 1H, $\underline{H}$-5)
5a-5	3.73(s, 3H, N-$\underline{CH}_3$); 4.15(s, 2H, S-$\underline{CH}_2$); 7.16-7.81(m, 9H, $\underline{H}_{arom.}$); 8.99-9.18(m, 1H, $\underline{H}$-2)
5b-1	1.37-1.70(t, J=7.5 Hz, 3H, N-CH_2-$\underline{CH}_3$); 2.40(s, 3H, S-$\underline{CH}_3$); 4.16-4.50(q, J=7.5 Hz, 2H, N-$\underline{CH}_2$-CH_3); 7.30-7.77(m, 4H, $\underline{H}_{arom.}$); 8.92-9.10(m, 1H, $\underline{H}$-5)
5b-2	1.13-1.38(t, J=7.5 Hz, 3H, S-CH_2-$\underline{CH}_3$); 1.38-1.72(t, J=7.5 Hz, 3H, N-CH_2-$\underline{CH}_3$); 2.75-3.09(q, J=7.5 Hz, 2H, S-CH_2-$\underline{CH}_3$); 4.16-4.53(q, J=7.5 Hz, 2H, N-$\underline{CH}_2$-CH_3); 7.26-7.74(m, 4H, $\underline{H}_{arom.}$); 8.96-9.09(m, 1H, $\underline{H}$-5)
5c-1	0.83-1.10(t, J=7.5 Hz, 3H, CH_2-$\underline{CH}_3$); 1.20-2.05(m, 4H, N-CH_2-($\underline{CH}_2$)$_2$-CH_3); 2.35(s, 3H, S-$\underline{CH}_3$); 4.15-4.40(t, J=7.5 Hz, 2H, N-$\underline{CH}_2$-CH_2); 7.28-7.78(m, 4H, $\underline{H}_{arom.}$); 8.95-9.12(m, 1H, $\underline{H}$-5)

a) ^{1}H Nmr spectra of compounds (**2**) were recorded in deuterium oxide solutions, those of compounds (**5**) in deuteriochloroform.

REFERENCES

1. Presented in part at the 12th Int. Congr. Het. Chem., Jerusalem, 1989. Part XIV in the serie of Azinyl Sulfides.
2. F. S. Yates, "Comprehensive Heterocyclic Chemistry", Vol. 2, p. 513, 515, 519, eds. by A. J. Boulton and A. Mc Killop (A. R. Katritzky and C. W. Rees, general editors), Pergamon Press, Oxford, New York, 1984.
3. G. T. Pisko, O. V. Gudz, I. G. Khaskin, E. A. Shomova and M. N. Korshun Physiol. Akt. Veshchestva (Naukova Dumka, Kiev, USSR), **1986**, 18, 14.
4. J. Pernak, J. Krysiński, L. Michalak and W. Karmiński, Arch. Pharm., **1985**, 318, 410.
5. R. G. Shepherd and J. L. Fedrick, Adv. Heterocycl. Chem., Vol. IV, ed. by A. R. Katritzky, Academic Press, Inc., New York, **1965**, p. 146.
6. G. Illuminati, Adv. Heterocycl. Chem., Vol. IV, ed. by A. R. Katritzky, Academic Press, Inc., New York, **1965**, p. 285.
7. A. Maślankiewicz and K. Pluta, Polish J. Chem., **1980**, 54, 33.
8. (a) A. Edinger, Ber., **1896**, 29, 2456. (b) A. Edinger and H. Lubberger, J. Prakt. Chem., **1896**, 54, 340.
9. L. Szperl and T. W. Jezierski, Rocz. Chemii, **1923**, 3, 177.
10. (a) G. F. Duffin, Adv. Heterocycl. Chem., Vol. III, ed. by A. R. Katritzky, Academic Press, Inc., New York, **1964**, p. 2. (b) J. A. Zoltewicz and L. W. Deady, Adv. Heterocycl. Chem., Vol. XXII, ed. by A. R. Katritzky, Academic Press, Inc., New York, **1978**, p. 71.
11. R. Spitzner, M. Lesiński, M. Richter and W. Schroth, Monatsh. Chem., **1978**, 118, 485.
12. J. Jaroszewska, I. Wawer and J. Oszczapowicz. Org. Magn. Res., **1984**, 22, 323.
13. A. Maślankiewicz, Polish. J. Chem., **1985**, 59, 511.

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