α,ω-Bis(4-substituted-3-quinolinylthio)alkanes from Reactions of Thioquinanthrene with Alkoxides [1]

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The reaction of thioquinanthrene **1** with sodium alkoxides and α,ω-dihaloalkanes leads to the formation of α,ω-bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]alkanes **4**. The yield depends on the nature of α,ω-dihaloalkanes. The effect of α,ω-dihaloalkanes of the following types: XCH_2X (X = Cl,Br,I), $X(CH_2)_2X$ (X = Cl,Br,I), $Br(CH_2)_3Br$ and $Br(CH_2)_6Br$ were studied. The preparation of 4-alkoxy-3'-(ω-bromoalkylthio)-3,4'-diquinolinyl sulfide **3** and their transformation to α,ω-bis(4-alkoxy-3-quinolinylthio)alkanes **6** were studied as well.

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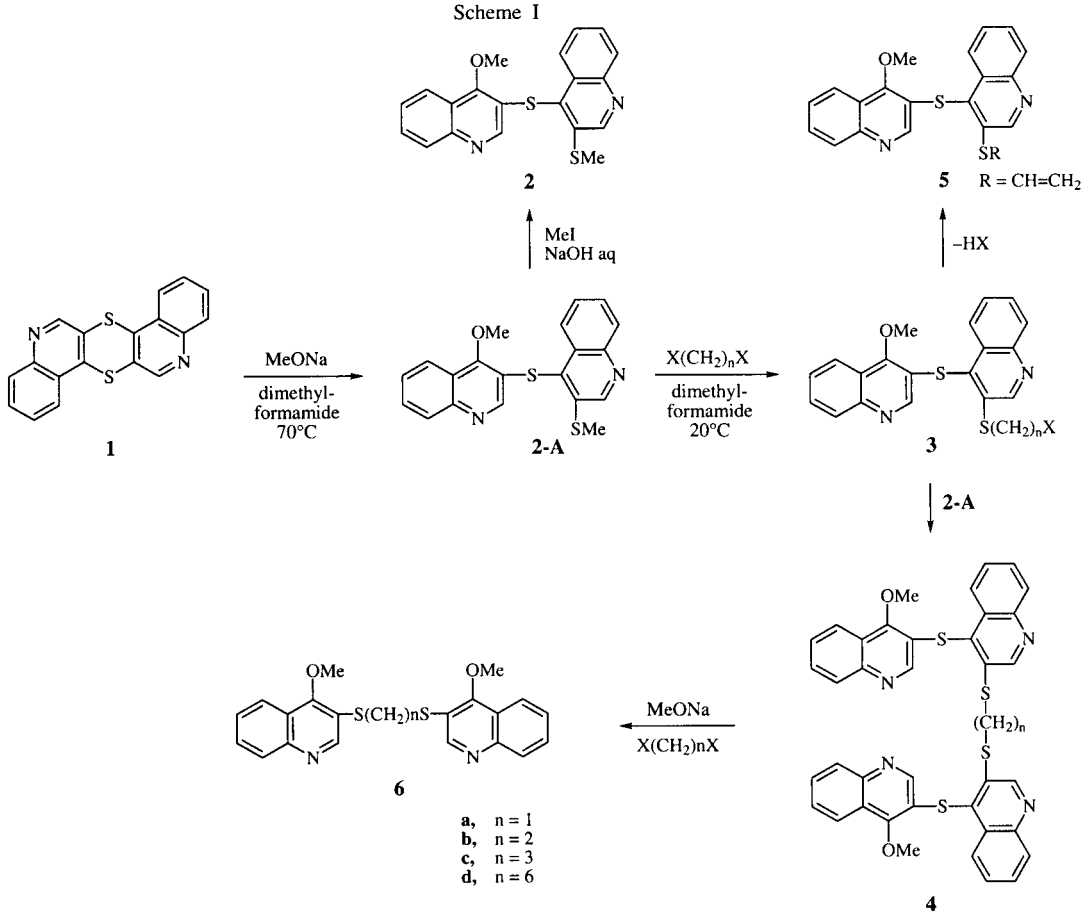
Introduction.

It has been reported that the functionalization of quinoline in the 3 and 4 position can be efficiently carried out by the reactions thioquinanthrene **1** with alkoxides [2-5]. These reactions performed in dimethylformamide or dimethyl sulfoxide solution at 70° run by cleavage of one 4-quinolinyl-sulfur bond in 1,4-dithiin ring of **1** to form sodium 4-(4-alkoxy-3-quinolinylthio)-3-quinolinylthiolates **2-A** as primary products which were alkylated in aqueous solution by alkyl halides to 4-alkoxy-3'-methylthio-3,4'-diquinolinyl sulfides **2** [2]. The 4-quinolinyl-sulfur bond of **2** exhibits greater susceptibility to alkoxides compared to this occuring in the 1,4-dithiin ring of **1**. The cleavage of the 4-quinoline-sulfur bond in sulfides **2** proceeds at 20°, which leads to 4-alkoxy-3-(alkylthio)quinolines after *S*-alkylation [3]. Furthermore, both 4-quinolinyl-sulfur bond cleavage steps and both *S*-alkylation ones have been combined by treatment of **1** with an axcess of alkoxide in dimethyformamide followed by the addition of two moles of an alkylating agent. This process run as a one-pot procedure consists of four steps giving directly 4-alkoxy-3-(alkylthio)quinolines. When α,ω-dibromoalkanes were used as bifunctional alkylating agents along the lines of the one-pot procedure mentioned above, thioquinanthrene **1** may be converted to the oligomers with four 3,4-quinolinediyl units of the type of α,ω-bis[4-(4-

Scheme I



methoxy-3-quinolinylthio)-3-quinolinylthio]alkanes **4** as a result of the *S*-alkylation of sodium 4-(4-alkoxy-3-quinolinylthio)-3-quinolinylthiolates **2-A**. Although the yields for α,ω-dibromoalkane (n = 1 or 3) were only 40% and 38%, respectively, the use of 1,2-dibromomethane gives **4b** in 91% yield [5]. These results prompted us to further study on the different behaviour of α,ω-dihaloalkanes in the above mentioned reaction as a potential method for the construction of polymeric or macrocyclic compounds containing 3,4-quinolinediyl moieties.

In this paper we wish to report the result of our more detailed study on the reaction of **1** with sodium alkoxides and a series of selected α,ω-dihaloalkanes which are used as α,ω-bisalkylating agents.

Results and Discussion.

The reactions of **1** with sodium alkoxides were performed in dimethylformamide solution at 70° and led to the formation of sodium 4-(4-alkoxy-3-quinolinylthio)-3-quinolinylthiolates **2-A**. The later ones were then alkylated directly in dimethylformamide solution at 20° by the addition of α,ω-dihaloalkanes. The reaction mixture was then poured into aqueous sodium hydroxide and the organic products were isolated by extraction and separated by column chromatography. The results obtained for varius α,ω-dihaloalkanes, namely dihalomethane (X = Cl,Br,I), 1,2-dihaloethane (X = CI,Br,I), 1,3-debromopropane and 1,6-dibromohexane used in the present investigation are collected in Table 1.

In the methylene series the reaction of **1** with sodium methoxide and dihalomethane where X = Br or I afforded **4a** as the major reaction product. In these cases a small amount (14-15%) **6a** was successfuly separated by column chromatography. The formation of **6a** suggests that sulfide **4a** probably reacts with sodium methoxide to form **6a** and sodium 4-methoxy-3-quinolinylothiolate. This later one after *S*-alkylation by dihalomethane where X = Br or I gave **6a** (Scheme 1). No reaction was observed when dichloromethane was used as bisalkylating agent. This fact may suggest that dichloromethane is insufficiently strong electrophile to react with sodium salt **2-A**. After the addition of methyl iodide to the reaction mixture sulfide **2** was produced.

In the ethylene series product **4b** was formed in high yield (90%) only for 1,2-dibromoethane. When 1,2-dichloroethane was used as bisalkylating agent the formation of **4b** was not observed. The addition of methyl iodide to the reaction mixture proceeded to sulfide **2**, likewise as for the reaction with dichloromethane. It indicates that 1,2-dichloroethane, is unreactive toward the sodium salt of the type **2-A**. The reaction with 1,2-diiodoethane gave the mixture of two compounds which were separated by column chromatography and identified as sulfide **4b** (55%) and 4-methoxy-3'-vinylthio-3,4'-diquinolinyl sulfide **5** (18%). This later compound probably arise from β-iodoalkyl sulfide of type **3** (n = 2, X = I) as a consequence of hydrogen iodide elimination under the reaction conditions. The formation of product **5** is consistent with the observation that β-haloalkyl sulfides can be dehydrohalogenated giving unsaturated sulfides [6,7].

In the reaction with 1,3-dibromopropane two products were isolated by column chromatography and identified as oligomer **4c** and an unresolved *ca.* 1:1 mixture of the (*E*)-

Table 1

The Results of the Reactions of Thioquinanthrene **1** with Sodium Methoxide and Varius α,ω-Dihaloalkanes

No.	α,ω-Dihaloalkane	Products, Yield (%)
1	$ClCH_2Cl$	**2** (61)
2	$BrCH_2Br$	**4a** (45), **6a** (14)
3	ICH_2I	**4a** (40), **6a** (15)
4	$Cl(CH_2)_2Cl$	**2** (65)
5	$Br(CH_2)_2Br$	**4b** (91)
6	$I(CH_2)_2I$	**4b** (55), **5** (18)
7	$Br(CH_2)_3Br$	**4c** (59), **8b** (20)
8	$Br(CH_2)_6Br$	**4d** (62), **6d** (25)

and (*Z*)-propenyl sulfide **8b** (20%). The formation of the later products can be explained as shown in Scheme 2. The reaction with 1,6-dibromohexane yields products **4d** and **6d**. We assume that the reaction of **1** with sodium alkoxide and dihaloalkanes proceeds through **3**, which is probably an intermediate product and further process, determining the yield, probably depends on the different behavior of **3** under the reaction conditions.

It has been reported in the literature that the relative rates of reaction of the aromatic chloro sulfides with potassium iodide in acetone decreased in the following order [8,9]:

$$ArSCH_2Cl > ArS(CH_2)_3Cl > ArS(CH_2)_4Cl > ArS(CH_2)_5Cl > ArS(CH_2)_2Cl$$

The observed yields of sulfides **4** presented in Table 1 seems to correlate with reactivity of the corresponding ω-haloalkyl sulfides mentioned above.

In order to recognize the behaviour of ω-haloalkyl sulfides **3** under reaction conditions used, we decided to prepare **3** by a modified procedure. In this case the solution of sodium salt **2-A** which was obtained from the reaction of **1** with sodium alkoxide, was added to a dimethylformide solution containing an excess of α,ω-dibromoalkane. Under these conditions the concentration of the **2-A** will always be low and it will favour the formation of the corresponding ω-bromoalkyl sulfides **3**. The obtained results are collected in Table 2.

It can be seen that **2-A** reacts with α,ω-dibromoalkane [$Br(CH_2)_nBr$] where n = 2, 3, 6 giving **3** in good yields. However when **2-A** was reacted with dibromomethane, unexpectedly the oligomer **4a** in 52% yield was obtained. It seems reasonable that the 4-methoxy-3'-(α-bromomethylthio)-3,4'-diquinolinyl sulfide **3a** formed initially may be very reactive and may spontaneously undergo subsequent reaction with **2-A** giving **4a**.

Table 2

The Preparation of 4-Alkoxy-3'-(ω-bromoalkylthio)-3,4'-diquinolinyl Sulfides **3** from Reactions of Thioquinanthrene **1** with Sodium Alkoxides and α,ω-Dibromoalkanes

No	Sodium alkoxide	α,ω-Dibromoalkane	Product, Yield (%)
1	MeONa	$BrCH_2Br$	**4a** (52)
2	MeONa	$Br(CH_2)_2Br$	**3b** (58)
3	MeONa	$Br(CH_2)_3Br$	**3c** (68)
4	EtONa	$Br(CH_2)_3Br$	**3ca** (64)
5	MeONa	$Br(CH_2)_6Br$	**3d** (74)

This fact might suggest that α-bromomethyl sulfide **3a** is probably more reactive than β-bromoethyl **3b** and γ-bromopropyl sulfide **3c**.

We also decided to carry out the reactions of ω-bromoalkylthio diquinolinyl sulfides **3b, 3ca** and **3d** with sodium methoxide. The products obtained and the reaction yields are reported in the Table 3.

Table 3

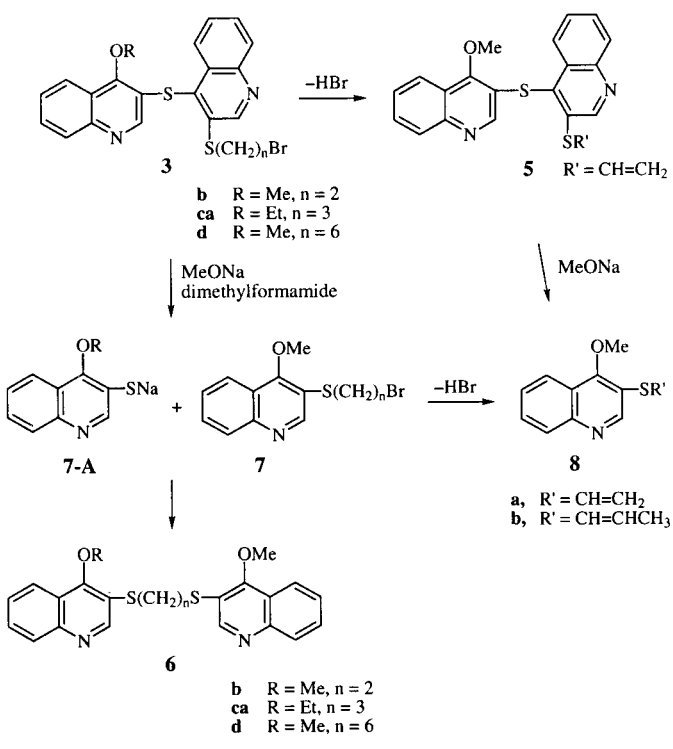
The Results of the Reactions of 4-Alkoxy-3-(ω-bromoalkylthio)-3,4'-diquinolinyl Sulfides **3** with Sodium Methoxide

No.	Substrate	Products, Yield (%)
1	**3b**	**6b** (45), **5** (18), **8a** (9)
2	**3ca**	**6ca** (56), **8b** (16)
3	**3d**	**6d** (67)

The reaction of **3b** with sodium methoxide afforded a mixture of three compounds, which were succesfully separated by column chromatography and identified as sulfide **6b** and vinylic sulfides **5** and **8a**. The reaction of the sulfide **3ca** gave two products which were isolated, *i.e.*, sulfide **6ca**, and an inseparable mixture of the (*E*)- and (*Z*)-propenyl sulfide **8b** in *ca.* 1:1 ratio, determined by ^1H nmr analysis. The observed value of (*E*):(*Z*) isomer ratio seems to suggest that the formation of the propenyl sulfide **8b** can be explained in terms of the rearrangement of the carbocation under the reaction conditions rather than the base-catalyzed isomerization of allyl to propenyl sulfide [10,11,12]. The reaction of sulfide **3d** gave sulfide **6d** as the sole product. The formation of **5** and **8** is consistent with the fact that ω-bromoalkyl sulfides react readily forming unsaturated sulfides [6,7].

The observed reaction products can be accounted for by the reaction pathways outlined in Scheme 2. Reaction of **3** with sodium methoxide proceeds with cleveage of the 4-quinolinyl-sulfur bond and led to 4-methoxy-3-(ω-bromoalkylthio)quinoline **7** and 4-alkoxy-3-quinolnethiolate **7-A** which was alkylated further with **7** giving **6**, as the main reaction product. The elimination of hydrogen bromide from **3** and **7** would produce **5** and **8**, respectively. Cleavage of the 4-quinoline-sulfur bond in sulfide **5** may also proceed to **8**.

Scheme 2



From a synthetic point of view, we were interested in carring out the reaction of **1** with other alkoxides. Compounds **4** were synthesized by the general procedure. The results are presented in Table 4.

Table 4

The Results of Preparation of α,ω-Bis-[4-(4-alkoxy-3-quinolinylthio)-3-quinolinylthio]alkanes **4** from Thioquinanthrene **1** and Sodium Alkoxides and α,ω-Dibromoalkanes

No.	Sodium alkoidde	α,ω.-Dibromoalkane	Product, Yield (%)
1	EtONa	$BrCH_2Br$	**4ab** (61)
2	EtONa	$Br(CH_2)_2Br$	**4bb** (85)
3	$C_6H_5CH_2ONa$	$Br(CH_2)_2Br$	**4bc** (72)
4	$HC{\equiv}CCH_2ONa$	$Br(CH_2)_2Br$	**4bd** (64)

In conclusion, the results described in this paper indicate that the reaction of thioquinanthrene **1** with sodium alkoxides followed by treatment with α,ω-dihaloalkanes leads to α,ω-bis(4-substituted-3-quinolinylthio)alkanes **4** as the main products (40-91%). This process proceeds through 4-alkoxy-3'-(ω-haloakylthio)-3,4'-diquinolinyl sulfides **3** and the yields of this reactions depend on the different behavior of **3** under the reaction conditions.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Boetius melting point apparatus and are uncorrected. The ^1H nmr spectra were recorded on a Bruker MSL 300 spectrometer at 300 MHz in deuteriochloroform. The EI mass spectra were run on a LKB

GC 2091 spectrometer. FAB mass spectra were recorded on Finnigan MAT 95 spectrometer in FAB mode (Cs^+, 13 keV, nba). Thin layer chromatography was performed on silica gel 60 254F plates (Merck) using a mixture of chloroform and ethanol (15:1, v/v) as an eluant. Visualization was accomplished by uv light and iodine.

Thioquinanthrene **1** was obtained by exhaustive sulfurization of quinoline with elemental sulfur [13]. Commercial dihalogenoalkanes were used without further purification.

General Procedure for the Reaction of Thioquinanthrene **1** with Sodium Alkoxide.

A suspension of thioquinanthrene **1** (0.8 g, 2.5 mmoles), sodium alkoxide (7.5 mmoles) and dry dimethylformamide (12 ml) was stiffed at 70° for 30 minutes. The clear solution was then cooled to 20° and α,ω-dihaloalkane (2.5 mmoles) was added dropwise during 30 minutes. The reaction mixture was stirred for 40 minutes and then poured into 50 ml of 10% aqueous sodium hydroxide, and extracted with 3 x 10 ml of chloroform. The combined organic layers were washed with water, dried with anhydrous magnesium sulfate and evaporated *in vacuo*. The residue was separated by column chromatography (silica gel 60, 230-400 mesh, chloroform-ethanol 15:1, v/v) and crystallized from dimethylformamide or ethanol to give the products as shown in Table 1. For the reaction with dichloromethane and 1,2-dichloroethane the reaction mixture was poured into 50 ml of 10% aqueous sodium hydroxide and the methyl iodide (2.5 mmoles) was added dropwise as an alkylating agent. After stirring at 20° during 20 minutes the reaction mixture was extracted with chloroform. The combined extracts were washed with water, dried with anhydrous magnesium sulfate and evaporated *in vacuo*. Purification by column chromatography (silica gel 60, 230-400 mesh, chloroform-ethanol 15:1, v/v) and crystallization from ethanol gives pure 4-methoxy-3'-methylthio-3,4'-diquinolinyl sulfide **2**.

4-Methoxy-3'-methylthio-3,4'-diquinolinyl Sulfide (**2**).

This compound had mp 131-132°, lit [2] mp 131-132°.

Bis-[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]methane (**4a**).

This compound had mp 142-143°, lit [4] mp 142-143°.

1,2-Bis-[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]ethane (**4b**).

This compound had mp 195-196°, lit [4] mp 195-196°.

1,3-Bis-[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]-propane (**4c**).

This compound had mp 134-136° lit [4] mp 133-136°.

1,6-Bis-[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]-hexane (**4d**).

This compound had mp 109-111°; ^1H nmr (deuteriochloroform): δ 1.25-1.58 (m, 8H, 4 x CH_2), 2.99 (t, 4H, J = 7.4 Hz, 2 x CH_2S), 4.17 (s, 6H, 2 x CH_3O), 7.49-8.40 (m, 16H, Ar-H), 8.11 (s, 2H, 2 x H-2), 8.82 (s, 2H, 2 x H-2); ms: FAB (+VE) m/z (relative intensity) 783 (M^+, 100%).

Anal. Calcd. for $C_{44}H_{38}N_4O_2S_4$: C, 67.49; H, 4.89; N, 7.15; S, 16.38. Found: C, 66.12; H, 4.62; N, 7.37; S, 16.25.

Bis-[4-(4-ethoxy-3-quinolinylthio)-3-quinolinylthio]methane (**4ab**).

This compound had mp 143-145°; ^1H nmr (deuteriochloroform): δ 1.45 (t, 6H, J = 7.0 Hz, 2 x CH_3CH_2O), 4.27 (q, 4H, J = 7.0 Hz, 2 x CH_3CH_2O), 4.62 (s, 2H, SCH_2S), 7.42-8.18 (m, 16H, Ar-H), 8.03 (s, 2H, 2 x H-2), 8.96 (s, 2H, 2 x H'-2); ms: FAB (+VE) m/z (relative intensity) 741 (M^++1, 100%).

Anal. Calcd. for $C_{41}H_{32}N_4O_2S_4$: C, 66.47; H, 4.36; N, 7.57; S; 17.28. Found: C, 66.62; H, 4.26; N, 7.37; S, 16.35.

1,2-Bis-[4-(4-ethoxy-3-quinolinylthio)-3-quinolinylthio]ethane (**4bb**).

This compound had mp 157-159°; ^1H nmr (deuteriochloroform): δ 1.52 (t, 6H, J = 7.0 Hz, 2 x CH_3CH_2O), 3.26 (s, 4H, SCH_2CH_2S), 4.40 (q, 4H, J = 7.0 Hz, 2 x CH_3CH_2O), 7.49-8.36 (m, 16H, Ar-H), 8.08 (s, 2H, 2 x H-2), 8.82 (s, 2H, 2 x H'-2); ms: FAB (+VE) m/z (relative intensity) 755 (M^++1, 100%).

Anal. Calcd. for $C_{42}H_{34}NO_2S_4$: C, 66.83; H, 4.54; N, 7.43; S, 16.96. Found: C, 66.68; H, 4.47; N, 7.37; S, 16.75.

1,2-Bis-[4-(4-benzyloxy-3-quinolinylthio)-3-quinolinylthio]-ethane (**4bc**).

This compound had mp 145-146°; ^1H nmr (deuteriochloroform): δ 3.23 (s, 4H, SCH_2CH_2S), 5.35 (s, 4H, 2 x CH_2O), 7.92-8.32 (m, 26H, Ar-H), 8.10 (s, 2H, 2 x H-2), 8.79 (s, 2H, 2 x H'-2); ms: FAB (+VE) m/z (relative intensity) 879 (M^++ 1, 100%).

Anal. Calcd. for $C_{52}H_{38}N_4O_2S_4$: C, 71.06; H, 4.36; N, 6.38; S, 14.56. Found: C, 66.92; H, 4.47; N, 6.28; S, 14.43.

1,2-Bis-[4-(4-propargyloxy-3-quinolinylthio)-3-quinolinylthio]-ethane (**4bd**).

This compound had mp 184-185°; ^1H nmr (deuteriochloroform): δ 2.58 (t, 2H, J = 2.4 Hz, 2 x CC*H*), 3.24 (s, 4H, SCH_2CH_2S), 5.09 (d, 4H, J = 2.4 Hz, 2 x CH_2O), 7.50-8.38 (m, 16H, Ar-H), 8.11 (s, 2H, 2 x H-2), 8.81 (s, 2H, 2 x H'-2); ms: FAB (+VE) m/z (relative intensity) 775 (M^++1, 39%).

Anal. Calcd. for $C_{44}H_{30}N_4O_2S_4$: C, 68.21; H, 3.91; N, 7.24; S, 16.52. Found: C, 68.02; H, 4.02; N, 7.3 7; S, 16.65.

4-Methoxy-3'-(vinylthio)-3,4'-diquinolinyl Sulfide (**5**).

This compound had mp 105-107°; ^1H nmr (deuteriochloroform): δ 4.10 (s, 3H, CH_3O), 5.56 (d, J = 16.5 Hz, 1H, C*H*), 5.58 (d, J = 9.3 Hz, 1H, CH), 6.60 (dd, J = 16.5 Hz, J = 9.3 Hz, 1H, SC*H*), 7.54-8.46 (m, 8H, Ar-H), 8.21 (s, 1H, H-2), 8.89 (s, 1H, H'-2); ms: (EI) (15 eV) m/z (relative intensity) 376 (M^+, 86.6), 345 (M-CH_3O, 12.1), 302 (M-CH_3-SCH=CH_2, 16.8).

Anal. Calcd. for $C_{21}H_{16}N_2OS_2$: C, 67.01; H, 4.29; N, 7.45; S, 17.00. Found: C, 66.72; H, 4.17; N, 7.26; S, 16.84

Bis-(4-methoxy-3-quinolinylthio)methane (**6a**).

This compound had mp 76-78°; ^1H nmr (deuteriochloroform): δ 4.04 (s, 6H, 2 x CH_3O), 4.48 (s, 2H, SCH_2S), 7.47-7.69 (m, 4H, 2 x H-6 and 2 x H-7), 7.98-8.05 (m, 4H, 2 x H-5 and 2 x H-8), 8.82 (s, 2H, 2 x H-2); ms: (EI) (15eV) m/z (relative intensity) 394 (M^+, 40.2), 204 (M-$C_{10}N_8OS$, 95.2), 189 (M-$C_{11}H_{11}NOS$, 100).

Anal. Calcd. for $C_{21}H_{18}N_2O_2S_2$: C, 63.95; H, 4.60; N, 7.11; S, 16.23. Found: C, 64.22; H, 4.87; N, 6.88; S, 15.95.

Synthesis of 4-Alkoxy-3'-(ω-bromoalkylthio)-3,4'-diquinolinyl Sulfide **3**.

A suspension of thioquinanthrene **1** (0.8 g, 2.5 mmoles), sodium alkoxide (7.5 mmoles) and dry dimethylformamide (12 ml) was stirred at 70° for 30 minutes and then cooled to 20°. The clear solution was then added dropwise to a stirred solution of the α,ω-dibromoalkane (10 mmoles) in dimethylformamide (24 ml).

The reaction mixture was stirred for 40 minutes, then was poured into 75 ml of 10% aqueous sodium hydroxide, and extracted with 3 x 10 ml of chloroform. The combined organic layers were washed with water, dried over anhydrous magnesium sulfate and evaporated *in vacuo* to give an oily residue. The crude product was purified by column chromatography (silica gel 60, 230-400 mesh, chloroform-ethanol 15:1, v/v) to give pure 4-alkoxy-3'-(ω-bromoalkylthio)-3,4'-diquinolinyl sulfide **3** as a light yellow oil or in the case reaction with dibromomethane, bis-[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]methane **4a** which was crystallized from dimethylformamide.

4-Methoxy-3'-(2-bromoethylthio)-3,4'-diquinolinyl Sulfide (**3b**).

This compound was obtained as an oil; ^{1}H nmr (deuteriochloroform): δ 3.39-3.61 (m, 4H, SCH_2CH_2Br), 4.17 (s, 3H, CH_3O), 7.52-8.42 (m, 8H, Ar-H), 8.15 (s, 1H, H-2), 8.90 (s, 1H, H'-2); ms: (EI) (15 eV) m/z (relative intensity) 458 (19.8, M+2), 456 (20.9, M$^+$), 377 (35.6, M-Br), 318 (58.6, M-OCH$_3$-CH$_2$CH$_2$Br).

Anal. Calcd. for $C_{21}H_{17}BrN_2OS_2$: C, 55.26; H, 3.76; Br, 17.31; N, 6.14; S, 14.02. Found: C, 55.42; H, 3.89; Br, 17.12; N, 5.97; S, 14.25.

4-Methoxy-3'-(3-bromopropylthio)-3,4'-diquinolinyl Sulfide (**3c**).

This compound was obtained as an oil; ^{1}H nmr (deuteriochloroform): δ 2.14 (m, 2H, J = 7.2 Hz, CH$_2$ CH_2CH$_2$), 3.23 (t, 2H, J = 7.2 Hz, CH_2 CH$_2$CH), 3.43 (t, 2H, J = 7.2 Hz, CH$_2$ CH$_2$CH_2), 4.18 (s, 3H, CH_3O), 7.52-8.41 (m, 8H, Ar-H), 8.13 (s, 1H, H-2), 8.90 (s, 1H, H'-2); ms: (EI) (15 eV) m/z (relative intensity) 472 (94.6, M+2), 470 (87.3, M$^+$), 318 (13.4, M-OCH$_3$-CH$_2$CH$_2$CH$_2$Br).

Anal. Calcd. for $C_{22}H_{19}BrN_2OS_2$: C, 56.17; H, 4.07; Br, 16.79; N, 5.96; S, 13.60. Found: C, 56.32; H, 4.17; Br, 16.98; N, 6.07; S, 13.85.

4-Ethoxy-3'-(3-bromopropylthio)-3,4'-diquinolinyl Sulfide (**3ca**).

This compound was obtained as an oil; ^{1}H nmr (deuteriochloroform): δ 1.54 (t, 3H, J = 7.0 Hz, CH_3CH$_2$O), 2.13 (m, 2H, J = 7.2 Hz, CH$_2$ CH_2CH$_2$), 3.22 (t, 2H, J = 7.2 Hz, CH_2 CH$_2$CH$_2$), 3.46 (t, 2H, J = 7.2 Hz, CH$_2$CH$_2$CH_2), 4.43 (q, 2H, J = 7.0 Hz, CH_2O), 7.48-8.38 (m, 8H, Ar-H), 8.08 (s, 1H, H-2), 8.89 (s, 1H, H'-2); ms: (EI) (15 eV) m/z (relative intensity) 486 (100, M+2), 484 (91.8, M$^+$), 3.18 (12.6, M-OCH$_2$CH$_3$-CH$_2$CH$_2$CH$_2$Br).

Anal. Calcd. for $C_{23}H_{21}BrN_2OS_2$: C, 57.02; H, 4.37; Br, 16.30; N, 5.79; S, 13.21. Found: C, 56.81; H, 4.42; Br, 16.51; N, 5.61; S, 13.05.

4-Methoxy-3'-(6-bromohexylthio)-3,4'-diquinolinyl Sulfide (**3d**).

This compound was obtained as an oil; ^{1}H nmr (deuteriochloroform): δ 1.34-1.77 (m, 8H, 4 x CH_2), 3.06 (t, 2H, J = 7.3 Hz, CCH_2), 3.32 (t, 2H, J = 6.8 Hz, CH_2C), 4.19 (s, 3H, CH_3O), 7.51-8.40 (m, 8H, Ar-H), 8.12 (s, 1H, H-2), 8.85 (s, 1H, H'-2); ms: (EI) (15 eV) m/z (relative intensity) 514 (16.2, M+2), 512 (15.6, M$^+$), 433 (22.4, M-Br), 318 (18.9, M-OCH$_3$-(CH$_2$)$_6$Br).

Anal. Calcd. for $C_{25}H_{25}BrN_2OS_2$: C, 58.59; H, 4.92; Br, 15.41; N, 5.47; S, 12.49. Found: C, 58.82; H, 4.81; Br, 15.64; N, 5.56; S, 12.75.

Reaction of 4-Alkoxy-3'-(ω-bromoalkylthio)-3,4'-diquinolinyl Sulfide **3** with Sodium Methoxide.

A solution of the sulfide **3** (1.5 mmoles) and sodium methoxide (0.16 g, 3 mmoles) in dimethylformamide (10 ml) was stirred at 20° for 2 hours. The reaction mixture was then poured into 25 ml of 10% aqueous sodium hydroxide and extracted with 4 x 10 ml of chloroform. The combined organic layers were washed with water, dried with anhydrous magnesium sulfate and evaporated *in vacuo*. The residue was chromatographed on silica gel 60 (230-400 mesh). Eluation with a mixture of chloroform and ethanol (15: 1, v/v) gave the products as shown in Table 3.

1,2-Bis-(4-methoxy-3-quinolinylthio)ethane (**6b**).

This compound had mp 103-105°; ^{1}H nmr (deuteriochloroform): δ 3.11 (s, 4H, SCH_2 CH_2S), 4.08 (s, 6H, 2 x CH_3O), 7.52-7.76 (m, 4H, 2 x H-6 and 2 x H-7), 8.00-8.18 (m, 4H, 2 x H-5 and 2 x H-8), 8.81 (s, 2H, 2 x H-2); ms: (FAB) (+VE) : m/z (relative intensity) 409 (M$^+$+ 1, 100%).

Anal. Calcd. for $C_{22}H_{20}N_2O_2S_2$: C, 64.69; H, 4.94; N, 6.86; S, 15.67. Found: C, 64.82; H, 4.78; N, 6.71; S, 15.85.

1-(4-Ethoxy-3-quinolinylthio)-3-(4-methoxy-3-quinolinylthio)-propane (**6ca**).

This compound had mp 56-58°; ^{1}H nmr (deuteriochloroform): δ 1.49 (t, 3H, J = 7.0 Hz, CH_3CH$_2$O), 1.85 (m, 2H, J = 7.0 Hz, CH$_2$CH_2CH$_2$), 3.11 (t, 4H, J = 7.0 Hz, CH_2CH$_2$CH_2), 4.10 (s, 3H, CH_3O), 4.36 (q, 2H, J = 7.0 Hz, CH_2O), 7.48-7.72 (m, 4H, 2 x H-6 and 2 x H-7), 8.01-8.13 (m, 4H, 2 x H-5 and 2 x H-8), 8.82 (s, 2H, 2 x H-2); ms: (FAB) (+VE) m/z (relative intensity) 437 (M$^+$+1, 100%).

Anal. Calcd. for $C_{24}H_{24}N_2O_2S_2$: C, 66.04; H, 5.55; N, 7.33; S, 14.66. Found: C, 66.31; H, 5.69; N, 7.17; S, 14.78.

1,6-Bis-(4-methoxy-3-quinolinylthio)hexane (**6d**).

This compound was obtained as an oil; ^{1}H nmr (deuteriochloroform): δ 1.29-1.59 (m, 8H, 4 x CH$_2$), 2.97 (t, 4H, J = 7.2 Hz, 2 x CH_2S), 4.12 (s, 6H, 2 x CH_3O), 7.53-7.70 (m, 4H, 2 x H-6 and 2 x H-7), 8.03-8.11 (m, 4H, 2 x H-5 and 2 x H-8), 8.82 (s, 2H, 2 x H-2); ms: (FAB) (+VE) m/z (relative intensity) 465 (M$^+$+1, 89%).

Anal. Calcd. for $C_{26}H_{28}N_2O_2S_2$: C, 67.22; H, 6.08; N, 6.03; S, 13.78. Found: C, 67.51; H, 6.18; N, 6.17; S, 13.52.

4-Methoxy-3-(vinylthio)quinoline (**8a**).

This compound was obtained as an oil; ^{1}H nmr (deuteriochloroform): δ 4.12 (s, 3H, CH_3O), 5.51 (d, J = 16.8 Hz, 1H, CH), 5.53 (d, J = 9.2 Hz, 1H, CH), 6.62 (dd, J = 16.8 Hz, J = 9.2 Hz, 1H, SC*H*), 7.50-7.74 (m, 2H, H-6 and H-7), 8.04-8.13 (m, 2H, H-5 and H-8), 8.82 (s, 1H, H-2); ms: (EI) (15 eV) m/z (relative intensity) 217 (M$^+$, 100), 204 (M-CH$_3$, 23.6), 160 (M-SCH=CH$_2$, 12.6).

Anal. Calcd. for $C_{12}H_{11}NOS$: C, 66.34; H, 5.11; N, 6.45; S, 14.73. Found: C, 66.62; H, 4.92; N, 6.27; S, 14.45.

4-Methoxy-3-(1-propenylthio)quinoline (**8b**).

This compound was obtained as an oil, an unresolved mixture of'(*E*)- and (*Z*)-isomers in *ca.* 1:1 ratio; ^{1}H nmr (deuteriochloroform): [(*E*)-isomer] δ 1.81 (dd, J = 6.4 Hz, J = 1.2 Hz, 3H, CH_3), 4.11 (s, 3H, CH$_3$O), 5.85-6.03 (m, 1H, C*H*), 6.12 (dq, J = 14.8 Hz, J = 1.2 Hz, 1H, SC*H*), 7.49-7.71 (m, 2H, H-6 and H-7), 8.02-8.12 (m, 2H, H-5 and H-8), 8.77 (s, 1H, H-2), [(*Z*)-isomer] δ 1.89 (dd, J = 6.7 Hz, J = 1.5 Hz, 3H, CH_3), 4.11 (s, 3H, CH_3O), 5.85-6.03 (m, 1H, C*H*), 6.16 (dq, J = 9.2 Hz, J = 1.5 Hz, 1H, SC*H*), 7.49-7.71 (m, 2H, H-6 and H-7), 8.02-8.12 (m, 2H, H-5 and H-8), 8.77 (s, 1H, H-2); ms, (EI) (1.5 eV) m/z (relative intensity) 231 (M$^+$, 100), 216 (M-CH$_3$, 16.8), 190 (M-CH=CHCH$_3$,14.4).

Anal. Calcd. for $C_{13}H_{13}NOS$: C, 67.51; H, 5.67; N, 6.06; S, 13.84. Found: C, 67.72; H, 5.77; N, 6.27; S, 13.53.

REFERENCES AND NOTES

[1] Part **LIV** in the series of Azinyl Sulfides.

[2] S. Boryczka, A. Maślankiewicz, M. Wyszomirski, T. Borowiak and M. Kubicki, *Recl. Trav. Chim. Pays-Bas,* **109**, 509 (1990).

[3] A. Maślankiewicz and S. Boryczka, *Recl. Trav. Chim. Pays-Bas*, **112**, 519 (1993).

[4] A. Maślankiewicz and S.Boryczka, *J. Heterocyclic Chem.,* **30**, 1623 (1993),

[5] S. Boryczka, M. Rudnik and A. Maślankiewicz, *J. Heterocyclic Chem.,* **33**, 1 (1996).

[6] E. Angeletti, F. Montanan, and A. Negrini, *Gazz. Chim. Ital.*, **87**,1115 (1957).

[7] M. Kulka and F. G. Stryk, *Can. J. Chem.*, **35**, 516 (1957).

[8] W. R. Kirner, *J. Am. Chem. Soc.*, **50**,2446 (1928).

[9] F. G. Bordwell and T. Brannen, *J. Am. Chem. Soc.*, **86**,4645 (1964).

[10] J. March, Advanced Organic Chemistry, Wiley & Sons, New York, 1992, p 1054.

[11] D. S. Tarbell, W. E. Lovett, *J. Am. Chem. Soc.*, **78**, 2259 (1956).

[12] C. C. Price, W. H. Snyder, *J. Org. Chem.*, **27**,4639 (1962).

[13] A. Maślankiewicz, *Pol. J. Chem.*, **59**, 511 (1985).