# Reactions of Thioquinanthrene with Alkanethiolates. The Smiles Rearrangement of Diquinolinyl Sulfides‡



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Reactions of thioquinanthrene **1** with alkali metal alkanethiolates in DMSO or DMF at 70° proceeded through a stage of the S→S type of the Smiles rearrangement (3'-quinolinethiolate **2A**→4'-quinolinethiolate **3A**) to give 4,4'-dialkylthio-3,3'-diquinolinyl sulfides **3** as the final products. When these reactions were carried out at 20° two types of the products were isolated: 3',4-dialkylthio-3,4'-diquinolinyl sulfides **2** or sulfides **3** depending on the reaction time (1 hour or 7 days). Under acidic conditions 3'-quinolinethiolate **2A** underwent intramolecular cyclization to dithiin **1**. Reactions of dithiin **1** with sodium alkanethiolates at 20°, realized as a one-pot procedure, led to various 3,4-dialkylthioquinolines **7**. The rearrangement of other 3'-quinolinethiolates **8A** and **11A** (the products of the reactions of dithiin **1** with sodium sulfide and sodium methoxide) needed higher temperature (140°).

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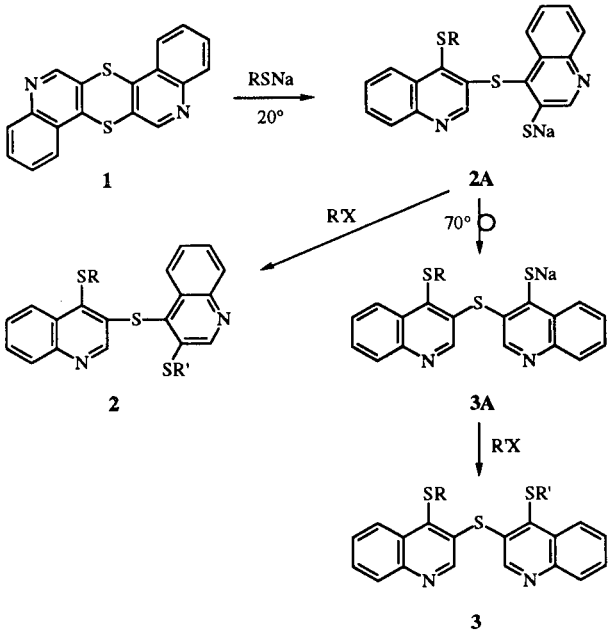
## Introduction.

The 1,4-dithiin ring opening in thioquinanthrene **1** (1,4-dithiino[2,3-*c*:5,6-*c'*]diquinoline) with sodium alkanethiolates or *S*-alkylisothiouronium salts (in the presence of powdered sodium hydroxide) in DMSO or DMF proceeded in two ways depending on the reaction temperature (20° and 70°) to give isomeric dialkylthio-3,4'- and 3,3'-diquinolinyl sulfides **2** and **3** as the final products. The dithiin ring opening reaction ran as a cleavage of the $C_{4\text{-quinolinyl}}$- S bond to form 3'-quinolinethiolate **2A** (disubstituted 3,4'-diquinolinyl sulfide) which underwent at 70° the Smiles rearrangement to 4-quinolinethiolate **3A** (disubstituted 3,3'-diquinolinyl sulfide) [1,2].

The following unusual features of this rearrangement are:

Scheme 1




(a) The unprecedented S→S type of the Smiles rearrangement (the quinolinyl group migrates from one sulfur atom to another). The common type of the Smiles rearrangement found in aryl and hetaryl sulfides is the S→N one. An arenethiolate anion as a nucleophile in the Smiles rearrangement was found only in diaryl ethers (the O→S type) [3-7]. (b) The nucleophilic attack of 3'-quinolinethiolate anion occurs at the position 3 in the quinoline ring (a cleavage of the $C_{3\text{-quinolinyl}}$- S bond), which is not susceptible as a rule for such attack [8]. The more reactive $C_{4\text{-quinolinyl}}$- S bond remains unaffected. The *ab initio* calculations using the 6-31G**/STO -3G* model for all dipyridyl sulfides suggest the possibility of the Smiles rearrangement only for 2,2'-, 2,3'- and 2,4'-dipyridyl sulfides [9] and indeed the rearrangement was observed only for 2,2'- and 2,4'-dipyridyl sulfides [7]. (c) The 1,4-dithiin ring opening in dithiin **1** with other nucleophiles (sodium alkoxides, sodium sulfide and carbanions) in DMSO or DMF at 70° proceeds without the Smiles rearrangement [2,10-14].

In the present paper we report a more detailed study on the reactions of thioquinanthrene **1** with alkali metal alkane- and arenethiolates.

## Results and Discussion.

### 1. The Reactions of Thioquinanthrene **1** with Alkali Metal Alkanethiolates.

The reaction of thioquinanthrene **1** with alkali metal alkanethiolates leading to 3',4-dialkylthio-3,4'-diquinolinyl sulfide **2** and 4,4'-dialkylthio-3,3'-diquinolinyl sulfide **3** is in fact a three stage process: (a) The 1,4-dithiin ring opening in dithiin **1** with the sulfur nucleophile; (b) possibly the Smiles rearrangement of 3'-quinolinethiolate **2A** to 4'-quinolinethiolate **3A**; and (c) alkylation of 3'- and 4'-quinolinethiolates **2A** and **3A** to form sulfides **2** and **3**.

### 1. The 1,4-Dithiin Ring Opening.

Thioquinanthrene **1** is a highly insoluble compound in

Table 1
Reactions of Thioquinanthrene **1** with Nucleophiles

| No. | Nucleophile | Temp/Time, Solvent | Alkyl Halide | Pruduct, Yield (%) |
|---|---|---|---|---|
| 1 | $PhCH_2SM$, M = Li, Na, K | 70°/10 min., DMSO | $PhCH_2Cl$ | **3e** (92-96) |
| 2 | $PhCH_2SH$ + MOH | 70°/10 min., DMSO | $PhCH_2Cl$ | **3e** (88-90) |
| 3 | $PhCH_2SH$ + $K_2CO_3$ | 70°/10 min., DMSO | $PhCH_2Cl$ | **3e** (92) |
| 4 | $PhCH_2SH$ [a] | 70°/60 min., DMSO | — | [b] |
| 5 | PhSNa or HetSNa [c] | 70°/60 min., DMSO | — | [b] |
| 6 | $PhCH_2SNa$ [d] | 70°/10 min., DMSO | $PhCH_2Cl$ | **3e** (93) |
| 7 | *t*-BuSNa | 70°/10 min., DMSO | *t*-BuX | [e] |
| 8 | $PhCH_2SNa$ | 70°/10 min., DMSO | $PhCH_2Cl$ [f] | **3e** (90) |
| 9 | MeSNa | 70°/10 min., DMSO | MeI | $\mathbf{3a_d}$ (90) [g] |
| 10 | EtSNa | 20°/60 min., DMSO | MeI | **2b** (82) |
| 11 | $PhCH_2SNa$ | 20°/60 min., DMSO | MeI | **2c** (94) |
| 12 | $PhCH_2SNa$ | 20°/60 min., DMSO | $PhCH_2Cl$ [f] | **2e** (88) |
| 13 | MeSNa | 20°/7 days, DMSO | MeI | **3a** (82) |
| 14 | EtSNa | 20°/7 days, DMSO | MeI | **3b** (75) |
| 15 | EtSNa | 20°/7 days, DMSO | EtI | **3d** (71) |
| 16 | $PhCH_2SNa$ | 20°/7 days, DMSO | MeI | **3c** (88) |
| 17 | $PhCH_2SNa$ | 20°/7 days, DMSO | $PhCH_2Cl$ | **3e** (88) |
| 18 | $PhCH_2SNa$ | 20°/7 days, DMF | $PhCH_2Cl$ | **3e** (85) |
| 19 | $Na_2S$ [h] | 140°/30 min., DMSO | MeI | **3a** (51), **7a** (9) |
| 20 | MeONa [i] | 140°/30 min., DMSO | MeI | **12** (55) |

[a] Neat or in the presence of triethylamine or tetramethylethylenediamine (5 equivalents). [b] No reaction evidence, thioquinanthrene **1** was isolated in at least 95%. [c] Sodium 2-benzothiazolethiolate or sodium 3-methylthio-4-quinolinethiolate (3 equivalents). [d] Dark reaction. [e] X = Br, I, alkylation was ineffective. [f] Alkylation directly in DMSO. [g] 2,4,9,11-Tetradeuteriothioquinanthrene $\mathbf{1_d}$ was used. [h] 2 Equivalents. [i] 4 Equivalents.

organic solvents. For the 1,4-dithiin ring opening reactions, thioquinanthrene **1** was used as a suspension in DMSO or DMF. The progress of the reaction was followed by observation of a color of the reaction mixture (a change from yellow to deep red) and dissolution of dithiin **1** into solution during the course of the reaction (in the end of this stage the reaction mixture became a transparent solution).

Although sodium alkanethiolates were reported as good nucleophiles for 1,4-dithiin ring opening [1,2] also other alkali metal (lithium and potassium) alkanethiolates gave the final products practically in the same yield (Table 1). No reaction evidence was observed when alkanethiol (phenylmethanethiol) was used alone or with addition of triethylamine or tetramethylethylenediamine in DMSO at 70°. Only when a strong inorganic base (alkali metal hydroxides MOH, M = Li, Na, K or potassium carbonate) was used, the dithiin ring opening was observed. In contrast to alkali metal alkanethiolates, sodium arene- and hetarenethiolates (benzenethiolate, 2-benzothiazolethiolate and 3-methylthio-4-quinolinethiolate) were insufficiently strong nucleophiles to react with thioquinanthrene **1**.

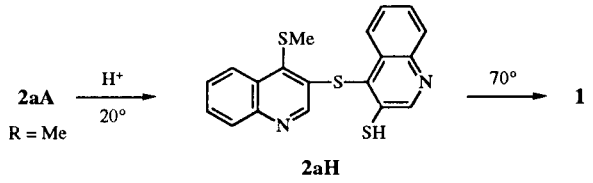
2a. The Smiles Rearangement of 3'-Quinolinethiolates **2A** at 70°.

In the literature only the S→N type of the Smiles rearrangement was described for substituted azinyl sulfides—2- and 4-pyridyl sulfides and 4-(1-oxidoquinolinyl) sulfides [15-34]. Most of these rearrangements proceeded under basic conditions and only a few under acidic conditions [20-22,27,28]. There are some reports [18,20,22] on this rearrangement observed during heating azinyl sulfides alone or in boiling protic solvents. No reports of the photo-Smiles rearrangement of azinyl sulfides were found.

The rearrangement reported herein occurred under basic conditions and was not considered as a photo-stimulated photo-initiated reaction since protection from light did not inhibit the formation of the rearranged product (Table 1). Attempts to carry out the rearrangement under neutral or acidic conditions were unsuccessful. Sodium 3'-quinolinethiolate **2aA** (R = Me, the product of the dithiin ring opening with sodium methanethiolate in DMSO at 20°) neutralized or acidified (with a few drops of sulfuric acid) in DMSO at 20° to form 3'-quinolinethiol **2aH** and next heated at 70° for 30 minutes underwent intramolecular cyclization to form exclusively thioquinanthrene **1** in 97% yield.

This time the 3'-mercapto group, which is a weaker nucleophile than the 3'-thiolate anion, did not attack the position 3 but the position 4 in the quinoline ring. The

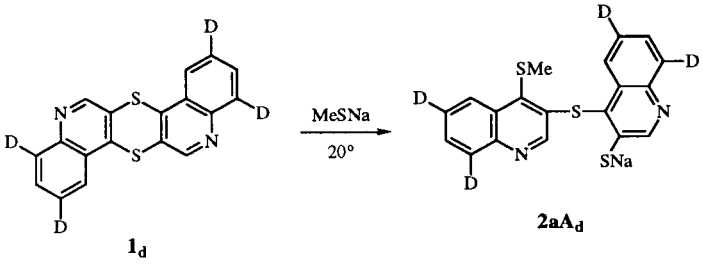
Scheme 2



dithiin ring closure reaction was accompanied by the odor of liberated methanethiol.

The Smiles rearrangement is generally considered to be an intramolecular migration of an aryl group from one nucleophilic center to another. To check if the rearrangement of 3'-quinolinethiolate **2A** to 4'-quinolinethiolate **3A** is an intramolecular process the labeled 3'-quinolinethiolate **2aA$_d$** was synthesized from deuterated thioquinanthrene **1$_d$** at 20°. The 3'-quinolinethiolate **2aA$_d$** obtained was labeled in the positions 6, 6', 8 and 8' in 75% yield.

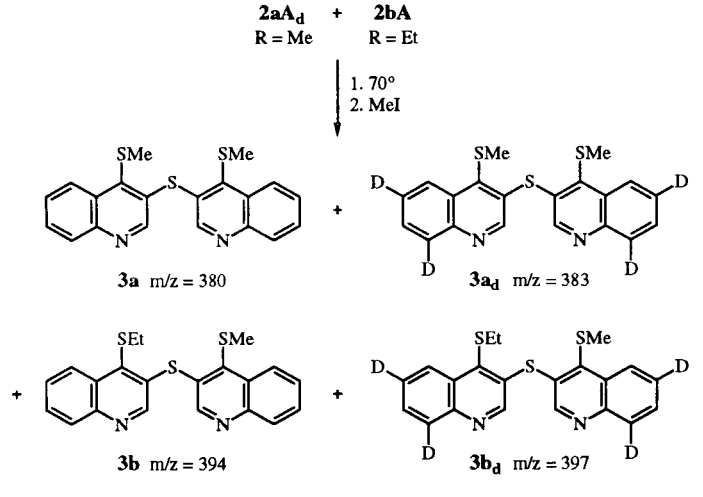
Scheme 3




**1$_d$** **2aA$_d$**

To determine whether the rearrangement is intra- or intermolecular the crossover experiment with 3'-quinolinethiolates **2aA$_d$** and **2bA** (R = Et) in DMSO at 70° was used. After methylation with methyl iodide a mixture of four 4,4'-dialkylthio-3,3'-diquinolinyl sulfides **3a**, **3a$_d$**, **3b** and **3b$_d$** was obtained (analyzed from the mass spectrum).

Scheme 4




The comparison of the peak intensity ratios $i_{380}/i_{383}$ and $i_{397}/i_{394}$ (Table 2) pointed to intermolecular rearrangement but another experiment with 4'-quinolinethiolates **3aA$_d$** and **3bA** (R = Et) in DMSO at 70° questioned the previous result as an evidence for intermolecular process. Surprisingly this time (when the reactants were separately rearranged before the crossover experiment was carried out) the mixture of four sulfides **3a**, **3a$_d$**, **3b** and **3b$_d$** was obtained with similar peak intensity ratios (Table 2). In our opinion the only explanation of two seemingly incoherent results is the suggestion that 4'-quinolinethiolates **3aA$_d$** and **3bA** are in equilibrium with a certain amount of isothioquinanthrene **4**. The ease with which 4'-quinolinethiolates **3A** undergo intramolecular cyclization to dithiin **4** was observed previously [1,2] and was used as the best procedure of the synthesis of compound **4** [1]. A similar effect was observed in the crossover experiment with 3'-quinolinethiolates **2aA$_d$** and **2bA** at 20° (when the Smiles rearrangement did not take place) giving a mixture of sulfides **2a**, **2a$_d$**, **2b** and **2b$_d$** but with lower values of the peak intensity ratios (Table 2). In this case 3'-quinolinethiolates were in equilibrium with thioquinanthrene **1**.

Table 2

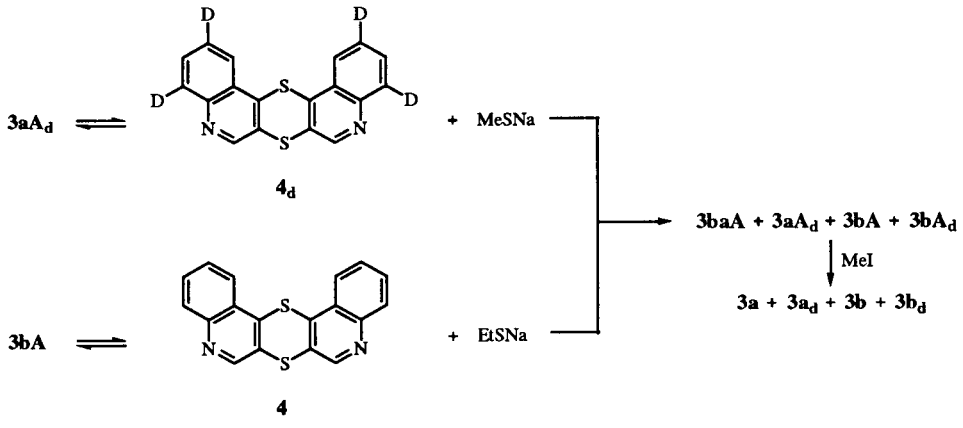
The Peak Intensity Ratio in the Products in Experiment with Labeled Reactants in DMSO

| Reactants | Temp (°) | Products | Peak Intensity Ratio i | |
|---|---|---|---|---|
| | | | $i_{380}/i_{383}$ | $i_{397}/i_{394}$ |
| **2aA$_d$ + 2bA** | 70 | **3a, 3a$_d$, 3b, 3b$_d$** | 2.1 | 0.5 |
| **2aA$_d$ + 2bA** | 20 | **2a, 2a$_d$, 2b, 2b$_d$** | 0.3 | 0.1 |
| **3aA$_d$ + 3bA** | 70 | **3a, 3a$_d$, 3b, 3b$_d$** | 1.9 | 0.3 |
| **3a$_d$ + 3b** | 70 | **3a$_d$, 3b** | 0 | 0 |

The support of this explanation came from another experiment with labeled compounds possessing the 4'-thiolate function blocked what made the equilibrium with dithiin **4** impossible. Heating the mixture of sulfides **3a$_d$** and **3b** in DMSO at 70° did not yield any trace of sulfides **3a** and **3b$_d$** (Table 2). Since the crossover experiment with labeled compounds did not give significant evidence for an intra- or intermolecular process we sought another argument in the rearrangement of 3'-quinolinethiolates **2aA** in the presence of a competitive nucleophile—sodium 3-quinolinethiolate in DMSO at 70°. Isolation of only sulfide **3a** and 3-methylthioquinoline **6** (after methylation) from the reaction mixture and lack of traces of sulfide **5** gave the evidence for intramolecular process. Other evidence came from the observation of the reaction of dithiin **1** with alkali metal alkanethiolates at 70°. If the rearrangement was an intermolecular process alkanethiolate anions as more nucleophilic and less bulky than 3'-quinolinethiolate **2A** would attack position 3 in the quinoline ring to give 3,4-dialkylthioquinoline **7** before the stage of alkylation. No traces of compound **7** were found after pouring the reaction mixture into 15% aqueous sodium hydroxide solution.

On the other hand when the 3'-thiolate function was blocked by *S*-alkylation, as in sulfides **2d** and **2e**, the

Scheme 5

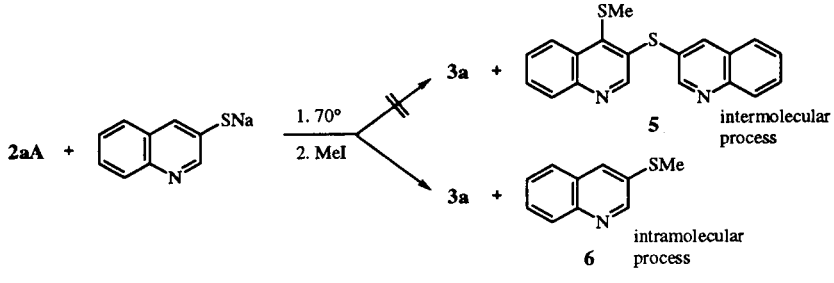



nucleophilic attack of alkanethiolates proceeded at position 4' in the second quinoline ring (the cleavage of the $C_{4'\text{-quinolinyl}}$- S bond) giving 3,4-dialkylthioquinolines **7e** and **7f** in 79 and 81% yield (removed as the neutral compounds by extraction) and 3-quinolinethiolates **7A** which *S*-alkylated gave another isomeric 3,4-dialkylthioquinolines **7b** and **7d** in 74% and 79% yield.

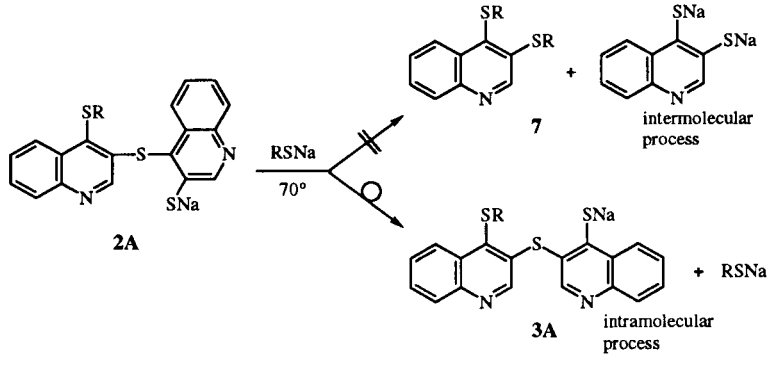
This procedure was simplified (the extraction was omitted) for sulfides **2** (with alkyl groups R and R') which reacted with alkanethiolates RSNa and alkyl halides R'X giving only one 3,4-dialkylthioquinoline **7** in 83-86% yield.

The preparative utility of these reactions prompted us to carry out the reactions of thioquinanthrene **1** with sodium alkanethiolates as a one-pot procedure by the sequentional cleavage of the $C_{4\text{-quinolinyl}}$- S and $C_{4'\text{-quinolinyl}}$- S bonds. This time *S*-alkylation was performed directly in DMSO solution. Since the alkylating agent reacted not only with 3'-quinolinethiolate but also with alkanethiolate anions additional amounts of the nucleophile was necessary. This procedure involves the following steps of the synthesis: (a) The 1,4-dithiin ring opening (the cleavage of the $C_{4}$-

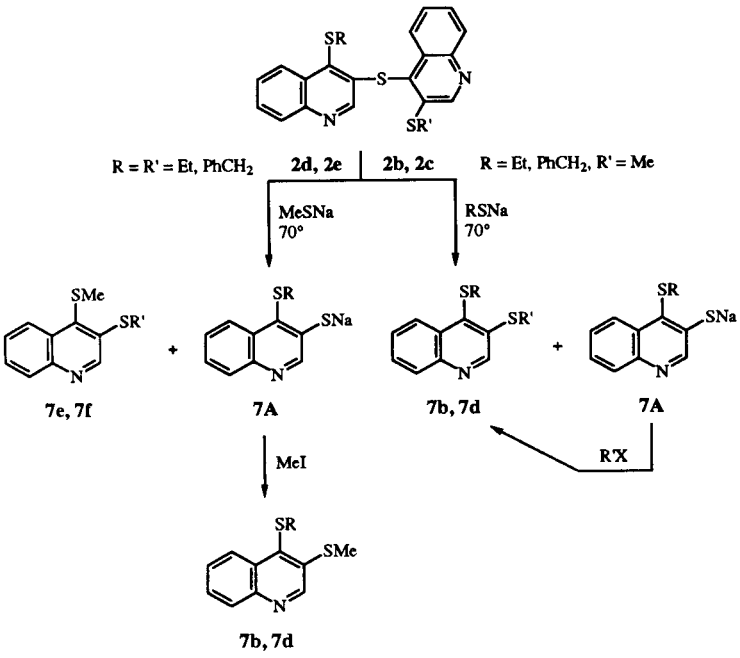
Scheme 6




Scheme 7

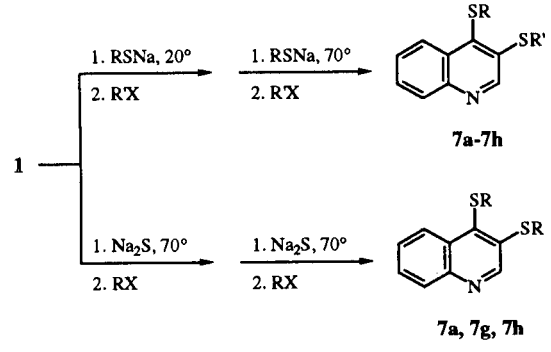


Scheme 8




quinolinyl- S bond) with sodium alkanethiolate (the formation of a transparent deep red solution); (b) the *S*-alkylation with alkyl halide directly in DMSO (the formation of a yellow solution); (c) the cleavage of the $C_{4'\text{-quinolinyl}}$- S bond with another amount of the nucleophile (formation of a deep red solution); and (d) pouring the reaction mixture into aqueous sodium hydroxide solution and *S*-alkylation with alkyl halide. This one-pot procedure gave various 3,4-dialkylthioquinolines **7a-7h** in 74-89% yield. 3,4-Bis(alkylthio)quinolines **7a**, **7g** and **7h** can be obtained in a one-pot procedure using sodium sulfide instead of the odorous sodium alkanethiolates.

Scheme 9




2b. The Smiles Rearangement of 3'-Quinolinethiolates **2A** at 20°.

The rearrangement of 3'-quinolinethiolates **2A** to 4'-quinolinethiolates **3A** proceeded not only at elevated temperature (70°) but to our surprise even at room temperature. When sodium 3'-quinolinethiolates **2aA-2cA** was stored in DMSO solution for a long time (7 days) it underwent progressively the rearrangement to 4'-quinolinethiolates (isolated after alkylation as sulfides **3a-3e** in 71-90% yield, Table 1). To avoid cyclization of 3'- and 4'-quinolinethiolates to dithiins **1** and **4** during such a long time, three equivalents of sodium alkanethiolates were necessary at the beginning of the reaction with thioquinanthrene **1**.

3. Alkylation of 3'- and 4'-Quinolinethiolates **2A** and **3A**.

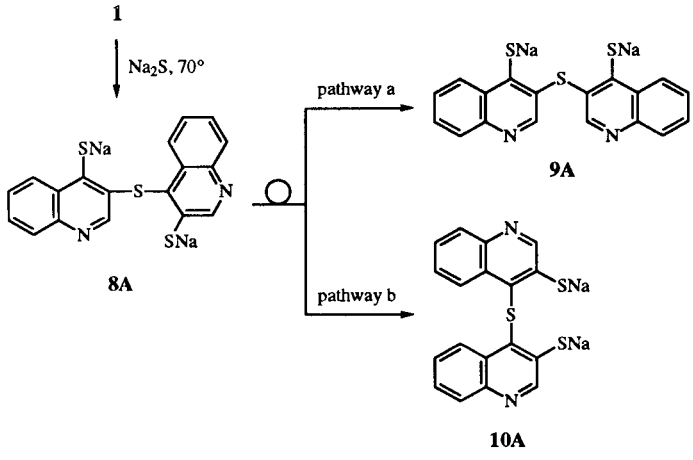
The Smiles rearrangement product—alkali metal 4'-quinolinethiolate **3A** cannot be isolated directly from the reaction medium. The treatment of 4'-quinolinethiolate **3A** with an acid gave not only 4'-quinolinethione but first of all the product of the 1,4-dithiin ring closure reaction—isothioquinanthrene **4** [1]. Even 4'-quinolinethiolate **3A** stored in DMSO solution for a long time (a few months) underwent intramolecular cyclization to dithiin **4** [1]. The best method of identification of the rearrangement products is *S*-alkylation of 4'-quinolinethiolate **3A** to form stable 4,4'-dialkylthio-3,3'-diquinolinyl sulfides **3**. The cooled reaction mixture (usually DMSO solution) was poured to threefold volume of 15% aqueous sodium hydroxide. Possibly unreacted or just formed dithiin or other neutral quinoline derivative was filtered off. The filtrate was stirred with alkyl halide. The progress of alkylation in aqueous DMSO solution was followed by a change of the solution color (from deep yellow to pale-yellow or white) accompanied by precipitation of *S*-alkyl derivatives **3**. The proccess of *S*-alkylation was very efficient and gave sulfide **3** in high yield (for example: benzylation with benzyl chloride 96%, methylation with methyl iodide 91%) [2]. The direct alkylation of 3'- and 4'-quinolinethiolates **2A** and **3A** in the DMSO solution was practically as effective as in the aqueous DMSO solution of sodium hydroxide. Only *t*-butylation with *t*-butyl bromide or iodide was ineffective (no reaction symptoms).

4. Reactions of Thioquinanthrene **1** with Sodium Sulfide and Methoxide.

Whereas alkali metal alkanethiolates or *S*-alkyisothiouronium salts reacted with thioquinanthrene **1** at 70° through the stage of the Smiles rearrangement, sodium sulfide reacted at the same temperature forming quinolinethiolate **8A**, unable to undergo the rearrangement [2], despite two theoretical pathways a and b (to form quinolinethiolates **9A** and **10A**). Moreover, pathway b (but the S→N type) was observed in the reaction of thioquinanthrene **1** with sodium phenylamide at 70°, leading to *N,N*-bis[4-(3-methylthioquinolinyl)]aniline [35].

Considering that the Smiles rearrangement of 3'-quino-

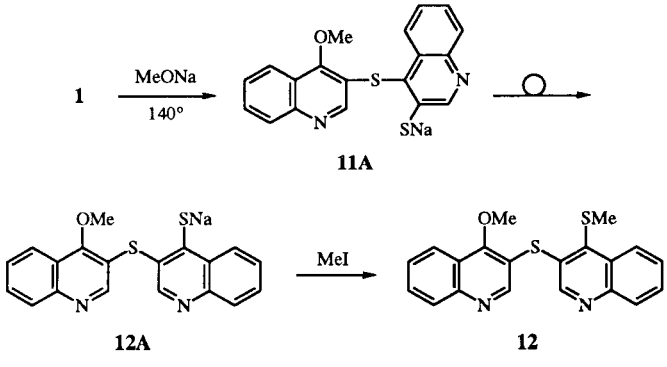
Scheme 10




linethiolate **2A** depended on the reaction conditions (temperature and time) we decided to carry out the reaction of dithiin **1** with sodium sulfide at higher temperature—140° for 30 minutes. After cooling and methylation the main product was the rearranged compound—4,4'-dimethylthio-3,3'-diquinolinyl sulfide **3a** (pathway a) in 51% yield accompanied by small amounts of 3,4-dimethylthioquinoline **7a** (9% yield).

Encouraged by the promising results of the above reaction we carried the reaction of thioquinanthrene **1** with sodium methoxide at 140° for 30 minutes. To our satisfaction we observed the Smiles rearrangement of 3'-quinolinethiolate **11A** to 4'-quinolinethiolate **12A**. After cooling and methylation 4-methoxy-4'-methylthio-3,3'-diquinolinyl sulfide **12** was isolated from the reaction mixture in 55% yield.

Scheme 11




5. Competitive Reaction of Thioquinanathrene **1** and Isothioquinanthrene **4** with Sodium Methanethiolate.

Although the arylthio group is considered as a poor leaving group the 1,4-dithiin ring opening reactions in thioquinanathrene **1** [1,2,10-14] and isothioquinanthrene **4** [1,2] proceeded very smoothly showing the 3'-quinolinylthio and 4'-quinolinylthio groups to be unexpectedly good nucleofuges. It was interesting to determine the relative reactivity of both dithiins and consequently which of both quinolinylthio groups is the better leaving group. To answer this purpose the competitive reaction of both dithiins **1** and **4** with one equivalent of sodium methanethiolate was carried out in DMSO at 20°. The reaction gave two types of products: (a) The resulting precipitate after pouring the reaction mixture into 15% aqueous sodium hydroxide solution containing mainly thioquinanathrene **1** and small amounts of isothioquinanthrene **4** (tlc analysis); (b) the resulting precipitate after methylation of the filtrate with methyl iodide containing a mixture of 4,4'-dimethylthio-3,3'-diquinolinyl sulfide **3a** and 3',4-dimethylthio-3,4'-diquinolinyl sulfide **2a**. The $^1$H nmr analysis of the H-2 and SMe protons signals in the mixture showed the presence of sulfides **3a** and **2a** in a molar ratio 15:1. Hence it was deduced isothioquinanthrene **4** to be 15 times more reactive towards sodium methanethiolate than thioquinanthrene **1**. In our opinion the greater reactivity of isothioquinanthrene **4** is first of all a result of better stabilization of the 4'-quinolinylthiolate anion **3aA** than the 3'-quinolinylthio anion **2aA**. Although both dithiins are practically insoluble and all the reactions started as a suspension of these dithiins in aprotic solvents, however a slightly better solubility of isothioquinanthrene **4** than thioquinanthrene **1** probably also has an influence on the reactivity.

6. Concluding Remarks.

The Smiles rearrangement proceeds as an intramolecular migration of an aryl group from one nucleophilic center to another through the intermediate formation of a Meisenheimer spiro-complex, most often five-membered. The rearrangement is activated by electron-withdrawing substituents and the migration is determined by the relative nucleophilicities of the centers and thermodynamic stabilities of the forming compound [4]. In the discussed rearrangement the nitrogen atom (N') in the second quinoline ring stabilizes the developing charge on the leaving group (*i.e.* the 4'-thiolate anion) by delocalization, thus promoting the rearrangement. The nitrogen atom (N) in the first quinoline ring (in the migrating ring) acts as an electron-withdrawing substituent. The presence of the second substituent situated in the *ortho* position in the migrating ring is considered as a cause of an increase in the rate of rearrangement, attributed to a steric effect regardless of its electron-withdrawing or electron-donating character [24]. The steric effect stabilizes the Morino structure [9], where two aryl rings are perpendicular to each other, facilitating the rearrangement of 3'-quinolinethiolates **2A**, **8A** and **11A**. Although 3'-quinolinethiolates **2A**, **8A** and **11A** were not isolated form the reaction mixture, however their *S*-methyl derivatives **3a** and **11**

Table 3

One-pot Reaction of Thioquinanthrene **1** with Sodium Alkanethiolates or Sodium Sulfide

| No. | RSNa or $Na_2S$ | R'X | Product, Yield (%) |
|---|---|---|---|
| 1 | MeSNa | MeI | **7a** (88) |
| 2 | EtSNa | MeI | **7b** (77) |
| 3 | *t*-BuSNa | MeI | **7c** (89) |
| 4 | $PhCH_2SNa$ | MeI | **7d** (84) |
| 5 | MeSNa | EtI | **7e** (85) |
| 6 | MeSNa | $PhCH_2Cl$ | **7f** (82) |
| 7 | EtSNa | EtI | **7g** (74) |
| 8 | $PhCH_2SNa$ | $PhCH_2Cl$ | **7h** (82) |
| 9 | $Na_2S$ | MeI | **7a** (90) |
| 10 | $Na_2S$ | EtI | **7g** (76) |
| 11 | $Na_2S$ | $PhCH_2Cl$ | **7h** (80) |

were collected. The X-ray examinations of crystals **3a** and **11** revealed that both compounds existed in a skew conformation in the solid state and two quinoline rings were nearly perpendicular to each other (80.9° and 73.8°, respectively) [13,36]. Moreover the X-ray examination showed that the pairs of the *ortho*-situated heteroatoms X...S (X = S, O) and S...S were in very close contacts (less than the sum of their van der Waals' radii). The strong attractive interactions of both pairs of heteroatoms seem to stabilize the conformation of 3'-quinolinethiolates **2A**, **8A** and **11A** and the resulting in spiro-complex. In our opinion the differences in the rate of the rearrangement of 3'-quinolinethiolates **2A**, **8A** and **11A** depend on the steric effects the 4-substituent (SR, SNa and OMe groups) and their different electron-donating character. The inability of 3'-quinolinethiolate **8A** to undergo the Smiles rearrangement through pathway b is a result of the electron-withdrawing character of the nitrogen atom (N) which decreases the nucleophilicity of the 4-thiolate anion by charge delocalization.

## EXPERIMENTAL

Melting points were determined in open capillary tubes on a Boetius melting point apparatus and were uncorrected. The $^1H$ nmr spectra were recorded on a Bruker MSL 300 spectrometer at 300 MHz in deuteriochloroform. Mass spectra were run on a LKB 9000S spectrometer using the electron impact method. Thin layer chromatography was performed on aluminium oxide (type E) and silica gel 60 254F plates (Merck) using methylene chloride and benzene-ethyl acetate (1:1) solutions as eluents.

Thioquinanthrene **1** was obtained by exhaustive sulfuration of quinoline with elemental sulfur [37]. Isothioquinanthrene **4** was obtained from thioquinanthrene **1** *via* ring opening-ring closure reactions [1]. Alkali metal alkanethiolates were commercial (Aldrich Chemical Co. or Merck) or prepared from commercial alkane-, arene- and hetarenethiols and sodium hydride (in anhydrous benzene), sodium ethoxide (in anhydrous ethanol) or lithium and potassium hydroxides (in aqueous ethanol). The solvents were distilled off under reduced pressure (in the last case the solvents were distilled azeotropically in the presence of benzene or toluene) to give the salts as white powder.

2,4,9,11-Tetradeuteriothioquinanthrene $\mathbf{1_d}$.

2,4,9,11-Tetradeuteriothioquinanthrene $\mathbf{1_d}$ was obtained in the following sequence of reactions: (a) Deuteration of the hydrochloride of 1,2,3,4-tetrahydroquinoline with deuterium oxide according to the procedure in references [38,39] followed by dehydrogenation with manganese dioxide [40] gave 6,8-deuterioquinoline. (b) Exhaustive sulfuration of 6,8-deuterioquinoline with elemental sulfur according to the procedure in reference [39] gave 2,4,9,11-tetradeuteriothioquinanthrene $\mathbf{1_d}$, mp 314-315°, lit [39] mp 314-315°; ms: m/z 321 (M + 3, 100), 322 (M + 4, 54.5). Hence, it was deduced that yield of deuteration was 75%.

Reaction of Thioquinanthrene **1** with Alkali Metal Alkanethiolates. General Procedure.

To a suspension of thioquinanthrene **1** (0.32 g, 1 mmole) in 10 ml of dry DMSO or DMF at 20° or 70° alkali metal alkane-, arene- or hetarenethiolate was added (2 or 3 mmoles when reaction at 20° was carried out for 60 minutes or 7 days, respectively, or 1,2 mmoles at 70°). The mixture was stirred from 10 minutes to 7 days (Table 1). The cooled mixture was poured into 30 ml of 15% aqueous sodium hydroxide. Possibly residual dithiin **1** was filtered and the filtrate was stirred with alkyl halide (1.4 mmoles). The solid was collected by filtration, washed with water and air-dried. In two cases alkylation was carried out directly in DMSO solution and then the reaction mixture was poured into sodium hydroxide solution. The crude sulfides **2** and **3** were purified by column chromatography (silica gel 60, chloroform, chloroform-ethanol 20:1).

4-Ethylthio-3'-methylthio-3,4'-diquinolinyl Sulfide **2b**.

This compound had mp 103-104°; $^1H$ nmr (deuteriochloroform): δ 1.38 (t, 3H, $CH_3$, J = 7.4 Hz), 2.62 (s, 3H, $SCH_3$), 3.17 (q, 2H, $SCH_2$, J = 7.4 Hz), 7.51-8.57 (m, $8H_{arom}$), 7.83 (s, 1H, H-2), 8.87 (s, 1H, H-2'); ms: (15 eV) m/z (relative intensity) 394 ($M^+$, 71.2), 347 (M-$CH_3S$, 97.7), 333 (M-$C_2H_5S$, 86.7), 318 (M-$C_2H_5SCH_3$, 100).

*Anal.* Calcd. for $C_{21}H_{18}N_2S_3$: C, 63.92; H, 4.60; N, 7.10; S, 24.38. Found: C, 63.64; H, 4.82; N, 6.92; S, 24.02.

4-Benzylthio-3'-methylthio-3,4'-diquinolinyl Sulfide **2c**.

This compound had mp 159-160°; $^1H$ nmr (deuteriochloroform): δ 2.62 (s, 3H, $SCH_3$), 4.31 (s, 2H, $SCH_2$), 7.23 (s, 5H, $C_6H_5$), 7.51-8.41 (m, $8H_{arom}$), 7.79 (s, 1H, H-2), 8.88 (s, 1H, H-2'); ms: (15 eV) m/z (relative intensity) 456 ($M^+$, 52.8), 409 (M-$CH_3S$, 96.8), 333 (M-$C_6H_5CH_2S$, 53.5), 318 (M-$C_6H_5CH_2SCH_3$, 81.2), 91 ($C_6H_5CH_2^+$, 100).

*Anal.* Calcd. for $C_{26}H_{20}N_2S_3$: C, 68.39; H, 4.41; N, 6.13; S, 21.06. Found: C, 68.12; H, 4.70; N, 6.02; S, 20.82.

4,4'-Dimethylthio-3,3'-diquinolinyl Sulfide **3a**.

This compound had mp 142-143°, lit [2] mp 142-143°.

4,4'-Dimethylthio-3,3'-di(6,8-dideuterioquinolinyl) Sulfide $\mathbf{3a_d}$.

This compound had mp 142-143°, lit [2] mp of undeuterated compound 142-143°; ms: (15 eV) m/z (relative intensity) 383 (M + 3, 50.3), 384 (M + 4, 36.1), 321 (M + 3 -$(CH_3)_2S$, 100).

4-Ethylthio-4'-methylthio-3,3'-diquinolinyl Sulfide **3b**.

This compound had mp 65-66°, lit [2] mp 65-66°.

4-Benzylthio-4'-methylthio-3,3'-diquinolinyl Sulfide **3c**.

This compound had mp 112-113°; $^1$H nmr (deuteriochloroform): δ 2.53 (s, 3H, $SCH_3$), 4.22 (s, 2H, $SCH_2$), 7.01-7.12 (m, 5H, $C_6H_5$), 7.56-8.58 (m, 8H$_{arom}$), 8.46 (s, 1H, H-2), 8.49 (s, 1H, H-2'); ms: (15 eV) m/z (relative intensity) 456 ($M^+$, 39.6), 409 (M-$CH_3S$, 57.3), 333 (M-$C_6H_5CH_2S$, 51.1), 318 (M-$C_6H_5CH_2SCH_3$, 100).

*Anal.* Calcd. for $C_{26}H_{20}N_2S_3$: C, 68.39; H, 4.41; N, 6.13; S, 21.06. Found: C, 68.09; H, 4.62; N, 6.05; S, 20.79.

4,4'-Diethylthio-3,3'-diquinolinyl Sulfide **3d**.

This compound had mp 88-89°, lit [2] mp 88-89°.

4,4'-Dibenzylthio-3,3'-diquinolinyl Sulfide **3e**.

This compound had mp 122-123°, lit [2] mp 122-123°.

Attempted Rearrangement of 3'-Quinolinethiol **3aH** at 70°.

To a suspension of thioquinanthrene **1** (0.32 g, 1 mmole) in 10 ml of dry DMSO at 20° sodium methanethiolate was added (0.14 g, 2 mmoles). The mixture was stirred for 60 minutes to obtain the 3'-quinolinethiol **3aA** solution. The solution was neutralized with a few drops of concentrated sulfuric acid to *p*H = 7. Next the mixture was stirred at 70° for 30 minutes and after cooling poured into 30 ml of 15% aqueous sodium hydroxide. The resulting solid was filtered off, washed with water and air-dried to give thioquinanthrene **1**, 0.31 g (97%), mp 311-312°, lit [41] mp 314-315°. Methylation of the filtrate with methyl iodide did not give any *S*-methyl derivatives. The same results were obtained when the solution was acidified with concentrated sulfuric acid to *p*H = 4 and the resulting mixture was stirred at 70° for 30 minutes.

One-pot Procedure of Reaction of Thioquinanthrene **1** with Alkali Metal Alkanethiolates. General Procedure.

To a suspension of thioquinanthrene **1** (0.32 g, 1 mmole) in 10 ml of dry DMSO at 20° sodium alkanethiolate was added (2 mmoles). The mixture was stirred for 60 minutes. The mixture was stirred with alkyl halide (2.5 mmoles) for 30 minutes. Then another portion of sodium alkanethiolate (3 mmoles) was added and the mixture was stirred at 70° for 30 minutes. The cooled reaction mixture was poured into 30 ml of 15% aqueous sodium hydroxide and stirred with alkyl halide (3 mmoles). The resulting solid was filtered off, washed with water and air-dried. The crude 3,4-dialkylthioquinolines **7a-7h** were purified by column chromatography (silica gel 60, chloroform).

One-pot Procedure of Reaction of Thioquinanthrene **1** with Sodium Sulfide. General Procedure.

To a suspension of thioquinanthrene **1** (0.32 g, 1 mmole) in 10 ml of dry DMSO at 70° sodium sulfide was added (3 mmoles). The mixture was stirred for 30 minutes. Ater cooling, the mixture was stirred with alkyl halide (2.5 mmoles) for 30 minutes. Then another portion of sodium sulfide (3 mmoles) was added and the mixture was stirred at 70° for another 30 minutes. After cooling the solution over sodium sulfide, it was poured into 30 ml of 15% aqueous sodium hydroxide and stirred with alkyl halide (4 mmoles). The resulting solid was filtered off, washed with water and air-dried. The crude 3,4-dialkylthioquinolines **7a**, **7g** and **7h** were purified by column chromatography (silica gel 60, chloroform).

3,4-Dimethylthioquinoline **7a**.

This compound had mp 93-94°, lit [42] mp 93-94°.

3-Methylthio-4-ethylthioquinoline **7b**.

This compound had mp 88-89°, lit [14] mp 75-76°; $^1$H nmr (deuteriochloroform): δ 1.21 (t, 3H, $CH_3$, J = 7.4 Hz), 2.66 (s, 3H, $SCH_3$), 2.96 (q, 2H, $CH_2$, J = 7.4 Hz) 7.56-8.54 (m, 4H$_{arom}$), 8.76 (s, 1H, H-2).

3-Methylthio-4-*t*-butylthioquinoline **7c**.

This compound had mp 105-106°, lit [43] mp 105-106°.

3-Methylthio-4-benzylthioquinoline **7d**.

This compound had mp 106-107°, lit [43] 106-107°.

3-Ethylthio-4-methylthioquinoline **7e**.

This compound had mp 52-53°; $^1$H nmr (deuteriochloroform): δ 1.43 (t, 3H, $CH_3$, J = 7.4 Hz), 2.45 (s, 3H, $SCH_3$), 3.16 (q, 2H, $CH_2$, J = 7.4 Hz), 7.57-8.52 (m, 4H$_{arom}$), 8.80 (s, 1H, H-2); ms: (15 eV) m/z (relative intensity) 235 ($M^+$, 100), 220 (M-$CH_3$, 6.8), 207 (M-$C_2H_4$, 22.6), 206 (M-$C_2H_5$, 28.6).

*Anal.* Calcd. for $C_{12}H_{13}NS_2$: C, 61.24; H, 5.57; N, 5.95; S, 27.25. Found: C, 61.04; H, 5.71; N, 5.62; S, 27.01.

3-Benzylthio-4-methylthioquinoline **7f**.

This compound had mp 71-72°; $^1$H nmr (deuteriochloroform): δ 2.42 (s, 3H, $SCH_3$), 4.34 (s, 2H, $SCH_2$), 7.23-7.42 (m, 5H, $C_6H_5$), 7.58-8.51 (m, 4H$_{arom}$), 8.80 (s, 1H, H-2); ms: (15 eV) m/z (relative intensity) 297 ($M^+$, 87.9), 282 (M-$CH_3$, 2.4), 206 (M-$C_6H_5CH_2$, 8.6), 91 ($C_6H_5CH_2^+$, 100).

*Anal.* Calcd. for $C_{17}H_{15}NS_2$: C, 68.65; H, 5.08; N, 4.71; S, 21.56. Found: C, 68.42; H, 5.25; N, 4.51; S, 21.30.

3,4-Diethylthioquinoline **7g**.

This compound had mp 55-56°; $^1$H nmr (deuteriochloroform): δ 1.19 (t, 3H, 4-$CH_3$, J = 7.4 Hz), 1.41 (t, 3H, 3-$CH_3$, J = 7.4 Hz), 2.96 (q, 2H, 4-$SCH_2$, J = 7.4 Hz) 3.14 (q, 2H, 3-$SCH_2$, J = 7.4 Hz) 7.55-8.53 (m, 4H$_{arom}$), 8.79 (s, 1H, H-2); ms: (15 eV) m/z (relative intensity) 249 ($M^+$, 100), 221 (M-$C_2H_4$, 30.2), 220 (M-$C_2H_5$, 21.6).

*Anal.* Calcd. for $C_{13}H_{15}NS_2$: C, 62.61; H, 6.06; N, 5.62; S, 25.71. Found: C, 62.31; H, 6.29; N, 5.41; S, 25.42.

3,4-Dibenzylthioquinoline **7h**.

This compound had mp 93-94°; $^1$H nmr (deuteriochloroform): δ 4.07 (s, 2H, 4-$SCH_2$), 4.31 (s, 2H, 3-$SCH_2$), 7.06-7.17 (m, 5H, $C_6H_5$), 7.24-7.41 (m, 5H, $C_6H_5$), 7.47-8.37 (m, 4H$_{arom}$), 8.79 (s, 1H, H-2); ms: (15 eV) m/z (relative intensity) 373 ($M^+$, 73.0), 282 (M-$C_6H_5CH_2$, 45.2), 91 ($C_6H_5CH_2^+$, 100).

*Anal.* Calcd. for $C_{23}H_{19}NS_2$: C, 73.96; H, 5.13; N, 3.75; S, 17.17. Found: C, 73.80; H, 5.31; N, 3.61; S, 16.85.

Reactions of 3',4-Dialkylthio-3,4'-diquinolinyl Sulfides **2d** and **2e** with Sodium Methanethiolate.

A solution of sulfide **2d** or **2e** [2] (2 mmoles) in 20 ml of dry DMSO at 70° was stirred with sodium methanethiolate (0.16 g, 2.3 mmoles) for 30 minutes. The mixture was cooled to room temperature, poured into 60 ml of 15% aqueous sodium hydroxide and extracted with chloroform (3 x 20 ml). The combined extracts were washed with with water, dried with anhydrous sodium sulfate and evaporated to give crude products. The products were purified by column chromatography (silica gel 60, chloroform) to give 3,4-dialkylthioquinolines **7e** (79%) or **7f** (81%).

The aqueous layer was stirred with methyl iodide (0.46 g, 3.3 mmoles). The combined extracts were worked-up as described

above to give 3,4-dialkylthioquinolines **7b** (74%) or **7d** (79%).

Reactions of 3',4-Dialkylthio-3,4'-diquinolinyl Sulfides **2b** and **2c** with Sodium Alkanethiolates.

A solution of sulfide **2b** or **2c** (2 mmoles) in 20 ml of dry DMSO at 70° was stirred with sodium alkanethiolate (2.2 mmoles) for 30 minutes. The mixture was cooled to room temperature, poured into 60 ml of 15% aqueous sodium hydroxide and stirred with methyl iodide (0.46 g, 3.3 mmoles). The resulting solid was filtered off, washed with water and air-dried. The crude products were purified by column chromatography (silica gel 60, chloroform) to give 3,4-dialkylthioquinolines **7b** (83%) or **7d** (86%).

The Crossover Experiment with Sodium 3'-Quinolinethiolate **2aA$_d$** and Sodium 3'-Quinolinethiolate **2bA** at 70°.

A solution of sodium 3'-quinolinethiolate **2aA$_d$** in 10 ml of DMSO [1 mmole, obtained from reaction of deuterated thioquinanthrene **1$_d$** (0.32 g, 1 mmole) and sodium methanethiolate (0.14 g, 2 mmoles) at 20° for 60 minutes] was mixed with a solution of sodium 3'-quinolinethiolate **2bA** in 10 ml of DMSO [1 mmole, obtained from reaction of thioquinanthrene **1** (0.32 g, 1 mmole) and sodium ethanethiolate (0.17 g, 2 mmoles) as described above] and stirred at 70° for 30 minutes. The mixture was cooled to room temperature, poured into 60 ml of 15% aqueous sodium hydroxide and stirred with methyl iodide (0.56 g, 4 mmoles). The resulting solid was filtered off, washed with water and air-dried. The $^1$H nmr and ms analyses of the crude products (0.74 g) showed the presence of the mixture of sulfides **3a**, **3a$_d$**, **3b** and **3b$_d$** (Table 2).

The Crossover Experiment with Sodium 3'-Quinolinethiolate **2aA$_d$** and Sodium 3'-Quinolinethiolate **2bA** at 20°.

A solution of sodium 3'-quinolinethiolate **2aA$_d$** in 10 ml of DMSO [1 mmole, obtained from reaction of deuterated thioquinanthrene **1$_d$** (0.32 g, 1 mmole) and sodium methanethiolate (0.14 g, 2 mmoles) at 20° for 60 minutes] was mixed with a solution of sodium 3'-quinolinethiolate **2bA** in 10 ml of DMSO [1 mmole, obtained from reaction of thioquinanthrene **1** (0.32 g, 1 mmole) and sodium ethanethiolate (0.17 g, 2 mmoles) as described above] and stirred at 20° for 30 minutes. The mixture was poured into 60 ml of 15% aqueous sodium hydroxide and stirred with methyl iodide (0.56 g, 4 mmoles). The resulting solid was filtered off, washed with water and air-dried. The $^1$H nmr and ms analyses of the crude products (0.72 g) showed the presence of the mixture of sulfides **2a**, **2a$_d$**, **2b** and **2b$_d$** (Table 2).

The Crossover Experiment with Sodium 4'-Quinolinethiolate **3aA$_d$** and Sodium 4'-Quinolinethiolate **3bA** at 70°.

A solution of sodium 4'-quinolinethiolate **3aA$_d$** in 10 ml of DMSO [1 mmole, obtained from reaction of deuterated thioquinanthrene **1$_d$** (0.32 g, 1 mmole) and sodium methanethiolate (0.14 g, 2 mmoles) at 70° for 10 minutes] was mixed with a solution of sodium 4'-quinolinethiolate **3bA** in 10 ml of DMSO [1 mmole, obtained from reaction of thioquinanthrene **1** (0.32 g, 1 mmole) and sodium ethanethiolate (0.17 g, 2 mmoles) as described above] and stirred at 70° for 30 minutes. The mixture was cooled to room temperature, poured into 60 ml of 15% aqueous sodium hydroxide and stirred with methyl iodide (0.56 g, 4 mmoles). The resulting solid was filtered off, washed with water and air-dried. The $^1$H nmr and ms analyses of the crude products (0.74 g) showed the presence of the mixture of sulfides **3a**, **3a$_d$**, **3b** and **3b$_d$** (Table 2).

Attempted Crossover Experiment with Sulfides **3a$_d$** and **3b** at 70°.

A solution of sulfides **3a$_d$** (0.38 g, 1 mmole) and **3b** (0.39 g, 1 mmole) in 20 ml of DMSO was stirred at 70° for 30 minutes. The mixture was cooled to room temperature, poured into 60 ml of 15% aqueous sodium hydroxide. The resulting solid was filtered off, washed with water and air-dried. The $^1$H nmr and ms analyses of the crude products (0.76 g) showed the presence of the unchanged sulfides **3a$_d$** and **3b** (Table 2).

Rearrangement of Sodium 3'-Quinolinethiolate **2aA** in the Presence of Sodium 3-Quinolinethiolate.

To a solution of sodium 3'-quinolinethiolate **2aA** (1 mmole, obtained from thioquinanthrene **1** and sodium methanethiolate at 20° as described above) in 10 ml of DMSO at 20° sodium 3-quinolinethiolate (0.36 g, 2 mmoles) was added and the mixture was stirred at 70° for 30 minutes. The mixture was cooled down to room temperature, poured into 30 ml of 15% aqueous sodium hydroxide and stirred with methyl iodide (0.46 g, 3.3 mmoles). The resulting solid was filtered off, washed with water and air-dried to give 0.37 g. The $^1$H nmr and tlc analyses of the reaction product showed the presence of two compounds: sulfide **3a** and 3-methylthioquinoline **6** in a molar ratio 1.05:1 ($^1$H nmr). Hence the yields of sulfide **3a** (68%) and 3-methylthioquinoline **6** (31%) were established. There were not observed the H-2 (as a doublet) and H-4 protons signals as it was expected for sulfide **5**. A mass spectrum (EI, 15 eV) of the reaction product was also obtained: m/z (relative intensity) **3a**: 381 ($M^+$+1, 6.3), 380 ($M^+$, 28.9), 334 (M+1-$SCH_3$, 12.0), 380 (M-$SCH_3$, 54.7); **6**: 175 ($M^+$, 100), 160 (M-$CH_3$, 23.1). As the peak intensity ratios of $i_{381/380}$ and $i_{334/333}$ are equal (4.56 and 4.54 respectively), the mass spectrum of sulfide **5** was not observed.

Competitive Reaction of Thioquinanathrene **1** and Isothioquinanthrene **4** with Sodium Methanethiolate.

A suspension of thioquinanthrene **1** (0.32 g, 1 mmole) and isothioquinanthrene **4** in 10 ml of dry DMSO at 20° was stirred for 30 minutes, and then sodium methanethiolate (0.07 g, 1 mmole) was added. The mixture was stirred for 2 hours and poured into 30 ml of 15% aqueous sodium hydroxide. An insoluble solid was filtered off, washed with water and air-dried to give 0.37 g of the mixture of unreacted dithiins. Analysis (tlc) showed the presence of thioquinanthrene **1** (the main compound) and isothioquinanthrene **4** (small amounts). The filtrate was stirred with methyl iodide (0.23 g, 1.6 mmoles). The resulting solid was filtered off, washed with water and air-dried to give 0.25 g of *S*-methyl derivatives. The $^1$H nmr and tlc analysis of the product showed the presence of two compounds: 4,4'-dimethylthio-3,3'-diquinolinyl sulfide **3a** and 3',4-dimethylthio-3,4'-diquinolinyl sulfide **2a**. The observation of the H-2 (8.56 ppm in sulfide **3a** and 7.85/8.88 ppm in sulfide **2a**) and the SMe proton signals (2.56 ppm and 2.62/2.65 ppm, respectively) allowed us to determine the mixture of sulfides **3a** and **2a** in a molar ratio 15:1.

## REFERENCES AND NOTES

‡ Part **XXXIV** in the series of Azinyl Sulfides. Part **XXXIII**: K. Pluta, *Phosphorus Sulfur*, **92**, 149 (1994).

[1] K. Pluta, *Sulfur Letters*, **13**, 9 (1991).

[2] K. Pluta, *J. Heterocyclic Chem.*, **29**, 1599 (1992).

[3] H. J. Shine, Aromatic Rearrangement, Elsevier, Amsterdam, 1967, p 307.

[4] W. E. Truce, E. M. Kreider, and W. W. Brand, *Org. React.*, **18**, 99 (1970).

[5] T. S. Stevens and W. E. Watts, Selected Molecular Rearrangements, Van Nostrand Reinchold Co., London, 1973, p 120.

[6] J. Skarżewski and Z. Skrowaczewska, *Wiad. Chem.*, **28**, 155 (1974).

[7] L. A. Summers, *J. Heterocyclic Chem.*, **24**, 533 (1987).

[8] R. K. Smalley, The Chemistry of Heterocyclic Compounds, Vol **32**, Quinolines. Part **I**, G. Jones, ed, John Wiley and Sons, London, 1977, p 526.

[9] S. J. Dunne, L. A. Summers, and E. I. von Nagy-Felsobuki, *J. Heterocyclic Chem.*, **29**, 851 (1992).

[10] A. Maślankiewicz and K. Pluta, *Monatsh. Chem.*, **114**, 281 (1983).

[11] A. Maślankiewicz and K. Pluta, *Synthesis*, 872 (1982).

[12] A. Jończyk and K. Pluta, *Bull. Chem. Soc. Belg.*, **95**, 1067 (1986).

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

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

[15] Y. Maki, *Yakugaku Zasshi*, **77**, 485 (1957).

[16] Y. Maki, *Yakugaku Zasshi*, **77**, 862 (1957).

[17] T. Takahashi and Y. Maki, *Yakugaku Zasshi*, **78**, 417 (1957).

[18] T. Takahashi and Y. Maki, *Chem. Pharm. Bull.*, **6**, 369 (1958).

[19] Y. Maki, Y. Okada, Y. Yoshida, and K. Obata, *Gifu Yakka Daigaku Kiyo*, **12**, 54 (1962); *Chem. Abstr.*, **59**, 11479b (1962).

[20] O. R. Rodig, R. E. Collier, and R. K. Schlatzer, *J. Org. Chem.*, **29**, 2652 (1964).

[21] O. R. Rodig and R. E. Collier, *J. Med. Chem.*, **9**, 116 (1966).

[22] Y. Maki, K. Yamane, and M. Sato, *Yakugaku Zasshi*, **86**, 50 (1966).

[23] C. O. Okafor, *J. Org. Chem.*, **32**, 2006 (1967).

[24] Y. Maki, M. Suzuki, and T. Masugi, *Chem. Pharm. Bull.*, **16**, 559 (1968).

[25] M. Hamana and S. Kumadaki, *Yakugaku Zasshi*, **88**, 665 (1968).

[26] M. Hamana and S. Kumadaki, *Yakugaku Zasshi*, **88**, 672 (1968).

[27] H. W. Atland, *J. Org. Chem.*, **41**, 3395 (1976).

[28] J. C. Jamoulle, *J. Pharm. Belg.*, **33**, 277 (1978).

[29] R. R. Gupta, N. K. Goswami, S. K. Jain, and K. Kumar, *Ann. Soc. Sci. Bruxelles, Ser. 1*, **94**, 219 (1980); *Chem. Abstr.*, **95**, 97695c (1981).

[30] N. K. Goswami, *Indian J. Chem., Sect. B*, **21B**, 364 (1982); *Chem. Abstr.*, **97**, 182324s (1982).

[31] R. Agrawal, G. K. Oberoi, D. C. Jain, and R. L. Mitai, *Rev. Roum. Chim.*, **32**, 37 (1987).

[32] P. Taneja, V. Khatri, L. Prakash, and R. L. Mital, *Acta Cienc. Indica, Chem.*, **13**, 118 (1987); *Chem. Abstr.*, **109**, 210984u (1988).

[33] A. Sharma and E. Tyagi, *Pharmazie*, **46**, 746 (1991).

[34] K. Bowden and P. R. Williams, *J. Chem. Soc., Perkin Trans. 2*, 216 (1991).

[35] A. Maślankiewicz, K. Pluta, M. Szmielew, and A. Kowalska, *Polish J. Chem.*, **58**, 925 (1984).

[36] A. Maślankiewicz, K. Pluta, T. Glowiak, and S. Boryczka, *J. Cryst. Spectr. Res.*, **21**, 729 (1991).

[37] A. Maślankiewicz, *Polish J. Chem.*, **59**, 511 (1985).

[38] A. Maślankiewicz, Studies on the Reactions of Quinoline with Elemental Sulfur and on the Properties of Thioquinolines Formed in these Reactions, Silesian School of Medicine, Katowice, 1986.

[39] M. Wyszomirski, Structures of 3,4-Diquinolinyl Sulfides and Bis-sulfides Based on the $^{1}H$ and $^{13}C$ NMR Spectroscopy Data, Doctoral Dissertation, University of Wroclaw, Wroclaw, 1992.

[40] E. F. Pratt and T. P. McGovern, *J. Org Chem.*, **29**, 1540 (1964).

[41] I. Baranowska and W. Karmiński, *Polish J. Chem.*, **50**, 785 (1976).

[42] A. Maślankiewicz, *Polish J. Chem.*, **54**, 2069 (1980).

[43] K. Pluta, A. Maślankiewicz, and A. Zięba, *J. Heterocyclic Chem.*, **31**, 447 (1994).