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Reaction of the Thiolsulfonate Group with the Aromatic Nucleus: A New Ring Closure

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The double ring closure of *N,N*-bis[2-(alkyl- or arylsulfonylthio)ethyl]anilines to form 2,3,5,6-tetrahydro[1,4]thiazino[4,3,2-*de*][1,4]benzothiazines, a new ring system, is reported. The effects of various benzene ring substituents upon the ring closure are described.

Thiolsulfonic acid esters react readily with a variety of nucleophilic agents (1) because of the partially-positive character of the divalent sulfur atom. Thus far only one example has been demonstrated of the reaction of a thiolsulfonate group with an aromatic ring carbon atom to form an aryl sulfide. In this respect Brooker and Smiles (2) showed that sodium salts of certain highly ring-sensitive phenols, such as phloroglucinol, underwent thioarylation when treated with aryl thiolsulfonates to give products of type I.

We have now shown that when *N,N*-bis[2-(methylsulfonylthio)ethyl]aniline (IIa) is heated in polar solvents, ring closure occurs through the divalent sulfur atoms of the thiolsulfonate groups to form 2,3,5,6-tetrahydro[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (III) which represents a new ring system. Because of the partially-positive character of the divalent sulfur atom of the thiolsulfonate group, the ring closure presumably proceeded as an electrophilic attack of the sulfur atom upon the aromatic nucleus. This reaction differs from the Brooker-Smiles reaction in that the latter proceeds through a distinct carbanion intermediate (2).

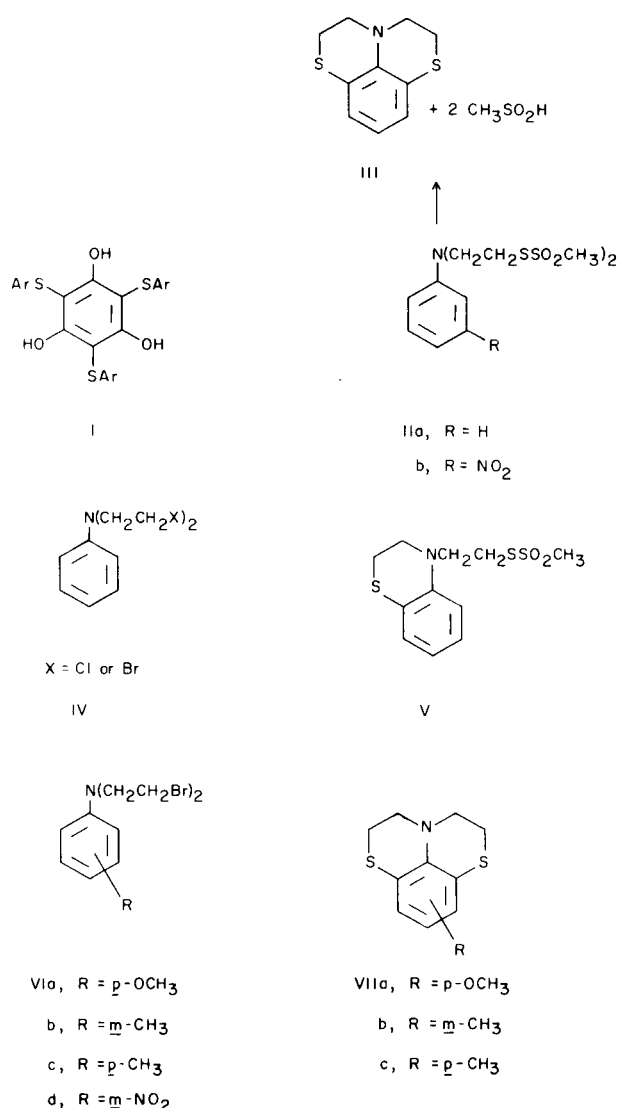
It was found convenient to prepare IIa *in situ* by the treatment of *N,N*-bis(2-chloro- or 2-bromoethyl)aniline (IV) with two moles of potassium methanethiosulfonate in boiling ethanol for a period of 48 hours to obtain the cyclization product (III) in 57 percent yield. A second product, identified by g.l.c. analysis, was methyl methanethiosulfonate, a disproportionation product of the methanesulfinic acid (3) formed in the ring closure condensation. By regulation of the reaction time and by choice of the proper solvents the bithiolsulfonate (IIa) and intermediate V were isolated in 44 and 11 percent yields, respectively. Cyclization of the isolated bithiolsulfonate (IIa) proceeded to give the benzothiazine (III) in 75 percent yield in refluxing ethanol. The reaction was found to occur in other polar solvents, such as nitromethane, glacial acetic acid, and sulfolane but when benzene was used, no product was obtained, and the unreacted bithiolsulfonate was recovered after the solution had

been boiled under reflux for 44 hours. The solvent effect was not surprising since formation of the initial by-product, methanesulfinic acid, requires charge separation.

The infrared spectrum of III showed no evidence for sulfonyl groups but indicated the presence of a 1,2,3-substituted benzene ring. The n.m.r. spectrum (fig. 1) could be separated into four group patterns in the four chemical shift ranges 6.8 to 6.6 p.p.m. (δ scale), 6.5 to 6.2 p.p.m., 3.6 to 3.3 p.p.m. and 3.1 to 2.8 p.p.m. The integrals of these four regions gave a relative proton distribution of 2:1:4:4. The complex pattern in the aromatic region between 6 and 7 p.p.m. is consistent with AB₂ symmetry. The other two patterns showed AA'BB' symmetry where the two A protons have one shift and the B protons another shift ($J_{AB} = J_{A'B'}$ and $J_{AB'} = J_{A'B}$).

In attempts to effect intermolecular condensations between anilines and thiolsulfonates, *N,N*-dimethylaniline and 2,5-dimethoxyaniline were each treated with methyl methanethiosulfonate under the same reaction conditions by which the ring closure proceeds, but no reaction occurred in either case. The failure of the intermolecular reaction to proceed even with the ring-sensitive 2,5-dimethoxyaniline indicates a probable entropy effect in the ring closure condensation.

The presence of electron-donating groups on the aromatic nucleus of the nitrogen mustard (IV) enhances the ring closure. Hence, the reaction of *N,N*-bis(2-bromoethyl)-*p*-anisidine (VIa) and potassium methanethiosulfonate in warm dimethylformamide was complete in 1.5 hours, giving the 2,3,5,6-tetrahydro-9-methoxy[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (VIIa) in 90 percent yield. *N,N*-Bis(2-bromoethyl)-*m*-toluidine (VIb), when treated with potassium methanethiosulfonate for two hours under nitrogen in refluxing ethanol, gave 2,3,5,6-tetrahydro-8-methyl[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (VIIb) in 92 percent yield. Likewise, *N,N*-bis(2-bromoethyl)-*p*-toluidine (VIc) and potassium methanethiosulfonate gave a 98 percent yield of 2,3,5,6-tetrahydro-9-methyl[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (VIIc) in warm dimethylformamide in a three hour period.



The presence of a *m*-nitro group on the ring destroys the nucleophilic character of the *ortho* ring carbons, inhibiting reaction with the thiol sulfonate group. Thus, when *N,N*-bis(2-bromoethyl)-*m*-nitroaniline (VI d) was treated in dimethylformamide with potassium methanethiosulfonate at 90° for 8.5 hours, a 30 percent yield of the bithiol sulfonate (II b) was obtained, and none of the cyclization product could be detected.

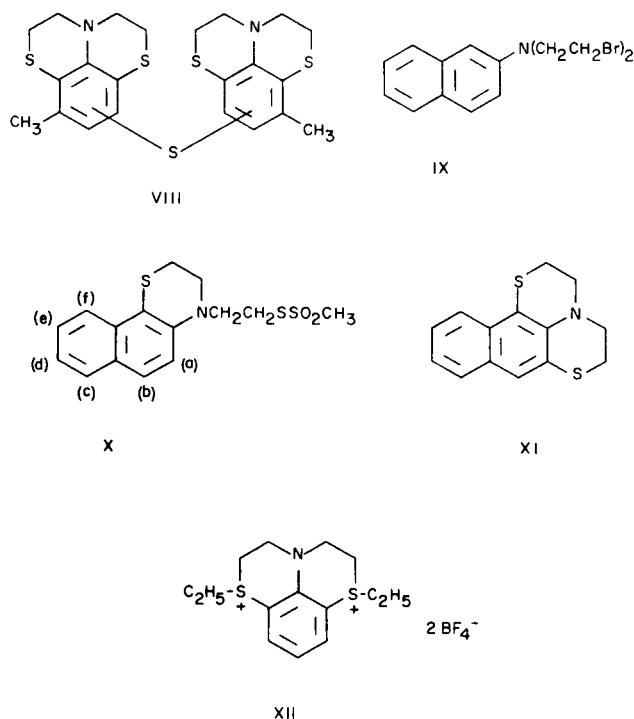
When the reaction of the dibromide (VI b) and potassium methanethiosulfonate was conducted in dimethylformamide at 90°, a by-product, having the empirical formula, C₂₂H₂₄N₂S₅, was obtained in seven percent yield. The structural assignment (VIII) was made on the basis of the n.m.r. and mass spectra. The integration of the n.m.r. spectrum showed the correct proton distribution for structure VIII, and the aromatic protons were represented by a singlet at 6.68 p.p.m. (δ scale), indicating that the bridge sulfur atom occupied the same corresponding

positions on both rings. Whether this position is *meta* or *para* to the nitrogen atom has not been clearly established. The mass spectrum gave a parent peak at mass number 476.

The reaction of *N,N*-bis(2-bromoethyl)-2-naphthylamine (IX) with potassium methanethiosulfonate in refluxing ethanol resulted only in a single ring closure, giving the 2,3-dihydro-4 [2-(methylsulfonylthio)ethyl]naphtho[1,2-*b*][1,4]thiazine (X). When compound X was heated at 90° in dimethylformamide for six hours, 60 percent of X was recovered, and none of the double cyclized product (XI) could be detected.

Evidence for condensation at the α -position was provided by the n.m.r. spectrum. The aromatic proton region of X was analyzed at 100 MHz (Varian model HA-100 NMR spectrometer). Doublets at 7.11 p.p.m. (δ scale) and 7.50 p.p.m. were assigned to H_a and H_b, respectively, on the basis that the two pairs show the same coupling splitting (~9.1 Hz) and intensities characteristic of the AB pattern. The large coupling constant indicates *ortho* placement, ruling out *para* or *meta* orientation. The other four protons in the aromatic region were characterized as being either α - or β -protons by chemical shifts and splitting patterns. The spectrum clearly demonstrated that one ring has two protons located *ortho* to one another, and that the other ring has four protons. Thus the possible 2,3-cyclized product was ruled out.

The weakly basic character of the nitrogen atom in III was demonstrated by the instability of the hydrochloride salt. The hydrochloride was formed and characterized by combustion analysis but was found to decompose to



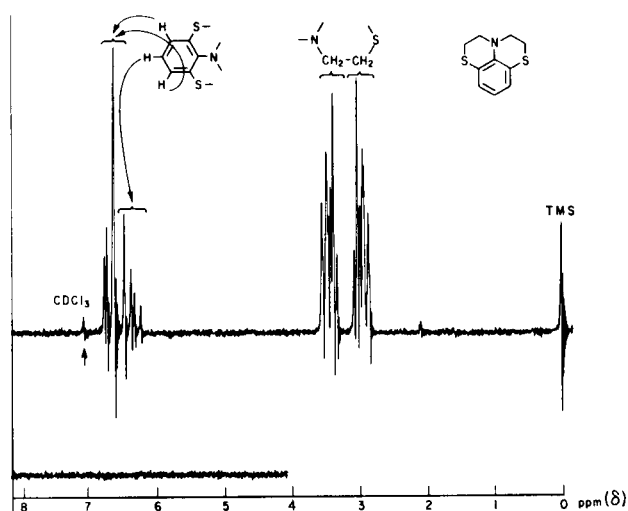


Figure 1

the free amine upon attempted recrystallization from ethanol.

The two sulfur atoms of V are attacked preferentially to the nitrogen atom by an alkylating agent: treatment with 3.5 moles of triethyloxonium tetrafluoroborate in methylene chloride gave the 2,3,5,6-tetrahydro[1,4]thiazino[4,3,2-de][1,4]benzothiazine 1,7-bis(ethyl tetrafluoroborate) (XII).

EXPERIMENTAL

All melting points are uncorrected. NMR spectra were recorded on Varian 60 and Varian HA-100 spectrometers.

2,3,5,6-Tetrahydro[1,4]thiazino[4,3,2-de][1,4]benzothiazine (III). Method A.

A mixture of 200 g. (0.917 mole) of *N,N*-bis(2-chloroethyl)aniline (4,5) and 275 g. (1.83 moles) of potassium methanethiolsulfonate (6) in 5.5 l. of ethanol was heated under reflux with stirring for 48 hours, and the hot reaction mixture was filtered to remove the potassium chloride (114 g., 84%). The filtrate, on cooling, gave a cream colored solid which was collected on a filter and dissolved in methylene chloride. The solution was filtered to remove some insoluble materials, and the solvent was removed by evaporation *in vacuo*, leaving 87.7 g. of tan solid, m.p. 118–121°. A further quantity (33.8 g., m.p. 116–120°) of the crude product was obtained by concentration of the ethanolic filtrate and was combined with the first batch. The crude substance was recrystallized from acetone to give 109.9 g. (57%) of tan platelets, m.p. 120.5–122°. A final recrystallization from methanol gave the pure substance as colorless platelets, m.p. 121.5–123°.

Anal. Calcd. for $C_{10}H_{11}NS_2$: C, 57.38; H, 5.30; N, 6.69; S, 30.63. Found: C, 57.48; H, 5.20; N, 6.59; S, 30.63.

The molecular weight was determined to be 205 compared with the calculated molecular weight of 209.

2,3,5,6-Tetrahydro[1,4]thiazino[4,3,2-de][1,4]benzothiazine (III). Method B.

A mixture of 7.90 g. (0.0258 mole) of *N,N*-bis(2-bromoethyl)aniline (4) and 11.7 g. (0.0516 mole) of potassium *p*-toluenethiolsulfonate (7) in 300 ml. of ethanol was heated under reflux with stirring for 41 hours. The reaction mixture was then filtered to

remove the potassium bromide by-product, and the filtrate was concentrated *in vacuo* to give a yellow solid which was collected on a filter. The crude substance was dried in ether solution over anhydrous magnesium sulfate. Evaporation of the ether gave 4.0 g. (74%) of solid which was recrystallized from methanol to give colorless platelets, m.p. 120–122°.

N,N-Bis[2-(methylsulfonylthio)ethyl]aniline (IIa).

A mixture of 20.0 g. (0.0652 mole) of *N,N*-bis(2-bromoethyl)aniline and 19.6 g. (0.130 mole) of potassium methanethiolsulfonate in 650 ml. of ethanol was heated under reflux with stirring for three hours. After removal of the potassium bromide by-product by filtration, the solvent was removed from the filtrate by evaporation *in vacuo*, leaving the crude solid which was taken up in methylene chloride. The methylene chloride extract was washed with water and then dried over anhydrous magnesium sulfate. The methylene chloride was removed by evaporation *in vacuo*, and the residue was recrystallized from methanol (Norit) to give 10.5 g. (44%) of white crystals, m.p. 122–125°. Three recrystallizations from methanol (Norit) gave the pure substance as colorless prisms, m.p. 130–132.5°.

Anal. Calcd. for $C_{12}H_{19}NO_4S_4$: C, 39.00; H, 5.18; N, 3.79; S, 34.70. Found: C, 39.28; H, 5.13; N, 3.76; S, 34.63.

2,3,5,6-Tetrahydro[1,4]thiazino[4,3,2-de][1,4]benzothiazine (III). Method C.

N,N-Bis[2-(methylsulfonylthio)ethyl]aniline (IIa) (3.0 g., 0.0081 mole) in 100 ml. of ethanol was heated under reflux for 45 hours. Upon cooling, the reaction mixture gave the pure product as 1.3 g. (76%) of colorless platelets, m.p. 120.5–122.5°. The infrared spectrum was identical to that of an authentic sample of 2,3,5,6-tetrahydro[1,4]thiazino[4,3,2-de][1,4]benzothiazine. S-2-(3,4-Dihydro-2*H*-1,4-benzothiazin-4-yl)ethyl Methanethiolsulfonate (V).

A mixture of 10.0 g. (0.0458 mole) of *N,N*-bis(2-chloroethyl)aniline and 13.8 g. (0.0920 mole) of potassium methanethiolsulfonate in 50 ml. of dimethylformamide was heated on a steam bath for nine hours. The hot mixture was poured over ice and the resulting aqueous solution extracted with methylene chloride. The extract was dried over anhydrous magnesium sulfate, and the methylene chloride was removed by evaporation *in vacuo* to give an oil. When the crude substance was chromatographed on an acid-washed activated alumina column, using benzene-isopropanol (3:1) as eluent, a fraction consisting of 1.4 g. (11%) of white solid was obtained. Recrystallization from methanol gave the pure product as colorless needles, m.p. 105–107.5°.

Anal. Calcd. for $C_{11}H_{15}NO_2S_3$: C, 45.65; H, 5.22; N, 4.84; S, 33.23. Found: C, 45.92; H, 5.38; N, 4.55; S, 33.32.

Attempted Reaction of *N,N*-Dimethylaniline and Methyl Methanethiolsulfonate.

N,N-Dimethylaniline (24.2 g., 0.200 mole) was added to a solution of 25.2 g. (0.200 mole) of methyl methanethiolsulfonate (8) in 100 ml. of formula 2B absolute ethanol. A gas-liquid partition chromatograph (9) was taken of this mixture to establish the positions of the peaks of the reactants. The solution was then heated under reflux for 17 hours, after which time a gas-liquid partition chromatograph showed the presence of the two reactants only.

Attempted Reaction of 2,5-Dimethoxyaniline and Methyl Methanethiolsulfonate.

A solution of 2.0 g. (0.0131 mole) of 2,5-dimethoxyaniline and 5.0 g. (0.0397 mole) of methyl methanethiolsulfonate in 20

ml. of dimethylformamide was heated on the steam bath for 15 hours. Gas-liquid partition chromatograms (10), taken at 6, 10 and 15 hours, showed the unreacted starting materials and no products.

2,3,5,6-Tetrahydro-9-methoxy[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (VIIa).

A mixture of 3.0 g. (0.0089 mole) of *N,N*-bis(2-bromoethyl)-*p*-anisidine (4) (VIa) and 2.7 g. (0.018 mole) of potassium methanethiosulfonate in 30 ml. of dimethylformamide was heated on the steam bath for 1.5 hours. The hot reaction mixture was poured on ice to precipitate the crude product as 1.9 g. (89%) of solid, m.p. 83°. Two recrystallizations from ethanol gave the pure product as colorless platelets, m.p. 93–93.5°.

Anal. Calcd. for $C_{11}H_{13}NOS_2$: C, 55.19; H, 5.47; S, 26.79. Found: C, 55.15; H, 5.38; S, 26.51.

2,3,5,6-Tetrahydro-8-methyl[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (VIIb).

A mixture of 10.0 g. (0.0312 mole) of *N,N*-bis(2-bromoethyl)-*m*-toluidine (4) (VIb) and 9.4 g. (0.0625 mole) of potassium methanethiosulfonate in 250 ml. of ethanol was heated under nitrogen at reflux temperature with stirring for two hours. The hot mixture was then filtered to remove the potassium bromide by-product, and the filtrate was concentrated *in vacuo* to give 6.4 g. (92%) of white solid, m.p. 96–99°. Purification was accomplished by two recrystallizations from methanol followed by chromatography on acid-washed activated alumina, using first cyclohexane and benzene as eluents, and then by another recrystallization from ethanol to give colorless crystals, m.p. 102.5–103°.

Anal. Calcd. for $C_{11}H_{13}NS_2$: C, 59.15; H, 5.87; N, 6.27. Found: C, 59.16; H, 5.58; N, 6.26.

2,3,5,6-Tetrahydro-9-methyl[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (VIIc).

A mixture of 32.7 g. (0.102 mole) of *N,N*-bis(2-bromoethyl)-*p*-toluidine (4) (VIc) and 30.6 g. (0.204 mole) of potassium methanethiosulfonate in 350 ml. of dimethylformamide was heated on the steam bath for three hours. The dark, gelatinous reaction mixture was poured over ice and the brown solid collected on a filter. The crude substance was extracted with methylene chloride, and the extract was dried over anhydrous magnesium sulfate and then treated with Norit and filtered. The solvent was removed by evaporation *in vacuo*, leaving a residue of 22.3 g. (98%) of brown oil which crystallized upon cooling. Recrystallization from ethanol gave the pure product as colorless needles, m.p. 98–98.5°.

Anal. Calcd. for $C_{11}H_{13}NS_2$: C, 59.15; H, 5.87; N, 6.27. Found: C, 59.0; H, 5.96; N, 6.14.

8,8'(or 9,9')-Thiobis(2,3,5,6-tetrahydro-10-methyl[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine) (VIII).

A mixture of 51.0 g. (0.159 mole) of *N,N*-bis(2-bromoethyl)-*m*-toluidine (VIb) and 47.7 g. (0.318 mole) of potassium methanethiosulfonate in 400 ml. of dimethylformamide was heated on the steam bath for 2.5 hours. The reaction mixture was then poured over ice, and the yellow, oily solid, which formed, was collected on a filter. The crude substance was dissolved in methylene chloride, and the solution was dried over anhydrous magnesium sulfate, decolorized with Norit, filtered and concentrated to give 9.6 g. of white crystals, which proved to be VIIb and 25.9 g. of brown oil. The oil was chromatographed on an acid-washed, activated alumina column (elution with benzene-cyclohexane 1:1) to give 3.1 g. more VIIb. Further elutions with benzene gave a fraction yielding 2.7 g. (7.2%) of yellow powder. Recrystallization from benzene gave the pure product as powdery, off-white crystals, m.p. 223.5–224.5°.

Anal. Calcd. for $C_{22}H_{24}N_2S_5$: C, 55.42; H, 5.07; N, 5.88; S, 33.62. Found: C, 55.2; H, 4.85; N, 5.89; S, 33.54.

Mass spectrometry showed the parent mass number to be 476.

N,N-Bis(2-bromoethyl)-*m*-nitroaniline (VIId).

N,N-Bis(2-hydroxyethyl)-*m*-nitroaniline (11) (11.7 g., 0.0517 mole) was added portionwise to 41.9 g. (0.155 mole) of phosphorus tribromide in 50 ml. of carbon tetrachloride at 0° at such a rate that the temperature was kept below 10°. After the addition was complete the mixture was allowed to remain at room temperature for 15 hours. The mixture was then heated under reflux for one hour and the solvent removed by distillation under reduced pressure. The orange, oily residue was heated on the steam bath until the evolution of gas ceased. Benzene was then added and the solution poured into ice water. The mixture was treated with sodium bicarbonate and the benzene layer separated. The aqueous layer was extracted with benzene, and the benzene extract was combined with the original benzene layer and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation, leaving 8.0 g. (44%) of brown-yellow solid. Recrystallization from ethanol (Norit) gave the product as yellow crystals, m.p. 131–132.5°.

Anal. Calcd. for $C_{10}H_{12}Br_2N_2O_2$: N, 7.96. Found: N, 7.96.

N,N-Bis[2-(methylsulfonylthio)ethyl]-*m*-nitroaniline (IIb). Attempted Preparation of 2,3,5,6-Tetrahydro-8-nitro[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine.

A mixture of 1.4 g. (0.0040 mole) of *N,N*-bis(2-bromoethyl)-*m*-nitroaniline (VIId) and 1.2 g. (0.0080 mole) of potassium methanethiosulfonate in 150 ml. of dimethylformamide was heated on the steam bath for 8.5 hours. The hot mixture was then poured over ice, and the tan solid that separated was collected on a filter, dissolved in methylene chloride and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation *in vacuo* to give 1.6 g. (97%) of yellow solid. Recrystallization from a mixture of methanol and acetonitrile followed by two recrystallizations from benzene gave the pure product as yellow needles, m.p. 151.5–152°.

Anal. Calcd. for $C_{12}H_{18}N_2O_6S_4$: C, 34.76; H, 4.38; N, 6.76. Found: C, 35.2; H, 4.13; N, 6.48.

2,3-Dihydro-4-[2-(methylsulfonylthio)ethyl]naphtho[1,2-*b*][1,4]thiazine (X).

A mixture of 5.0 g. (0.014 mole) of *N,N*-bis(2-bromoethyl)-2-naphthylamine (12) and 4.2 g. (0.028 mole) of potassium methanethiosulfonate in 150 ml. of ethanol was heated under reflux with stirring for three hours. The hot mixture was then filtered to remove potassium bromide; and, upon cooling, the filtrate yielded 3.8 g. (80%) of crystals, m.p. 129°. Recrystallizations first from petroleum ether (60–70°) and then from ethanol gave the pure product as colorless crystals, m.p. 129–130°.

Anal. Calcd. for $C_{15}H_{17}NO_2S_3$: C, 53.06; H, 5.05; N, 4.13; S, 28.33. Found: C, 52.5; H, 5.18; N, 3.78; S, 28.04.

Attempted Preparation of 2,3,5,6-Tetrahydro[1,4]thiazino[4,3,2-*de*][1,4]naphthothiazine (XI).

A solution of 0.5 g. of 2,3-dihydro-4[2-(methylsulfonylthio)ethyl]naphtho[1,2-*b*][1,4]thiazine (X) in 50 ml. of dimethylformamide was heated on the steam bath for six hours. The hot solution was then poured over ice, and the solid which formed was collected on a filter, and dissolved in methylene chloride. The methylene chloride solution was dried over anhydrous magnesium sulfate. The solvent was evaporated, leaving 0.3 g. of pale yellow solid. Recrystallization from benzene gave pale yellow needles, m.p. 129–129.5°. The n.m.r. spectrum of this substance was identical to that of an authentic sample of X.

2,3,5,6-Tetrahydro[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine Hydrochloride.

An excess of dry hydrogen chloride was passed through a solution of 5.0 g. (0.024 mole) of 2,3,5,6-tetrahydro[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (III) in 100 ml. of methylene chloride. The solvent was then removed by evaporation *in vacuo*, leaving a pink, crystalline residue. The solid was washed with ethyl ether to give 3.5 g. (61%) of the pure product as colorless crystals, m.p. 161–163.5°.

Anal. Calcd. for C₁₀H₁₂ClNS₂: C, 48.86; H, 4.92; N, 5.70. Found: C, 48.73; H, 5.05; N, 5.55.

2,3,5,6-Tetrahydro[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine 1,7-Bis(ethyl tetrafluoroborate) (XII).

To a stirred solution of 15.0 g. (0.0718 mole) of 2,3,5,6-tetrahydro[1,4]thiazino[4,3,2-*de*][1,4]benzothiazine (III) in 500 ml. of methylene chloride was added dropwise a solution of 47.9 g. (0.252 mole) of triethyloxonium tetrafluoroborate in 300 ml. of methylene chloride at such a rate that the reaction mixture gently refluxed. Upon completion of the addition, the mixture was stirred at room temperature for an hour and was then heated under reflux for 20 hours. The reaction mixture was cooled in an ice bath to give white crystals, melting from 200 to 212°. The filtrate was concentrated to give a further quantity of product. Combined yields weighed 21.5 g. (69%). Purification was accomplished by repeated washings with acetone, ether, methylene chloride and ethanol to give white crystals, m.p. 212°.

Anal. Calcd. for C₁₄H₂₁B₂F₈NS₂: C, 38.12; H, 4.80; N, 3.18. Found: C, 38.05; H, 4.75; N, 3.18.

The fact that both sulfur atoms were ethylated, instead of the nitrogen atom and one sulfur atom, was established by the symmetry of the ethylene proton grouping between 3.4 and 4.5 p.p.m. in the n.m.r. spectrum.

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