hol. There remained 1.3 g. of white solid ($III\cdot 3HCl$), m.p. 185–187°.

Anal. Calcd. for $C_{19}H_{24}ClN_3O\cdot 3HCl$: C, 50.12; H, 5.98; N, 9.73. Found: C, 49.92; H, 5.86; N, 9.37.

Compound III was also prepared as a dihydrochloride salt, m.p. 199–201°.

Anal. Calcd. for $C_{19}H_{24}ClN_3O\cdot 2HCl$: C, 54.49; H, 6.26; Cl, 25.40; N, 10.03. Found: C, 54.21; H, 6.30; Cl, 25.80; N, 9.84.

Conversion of β-Form into α-Form.—Compound II (β-form) was heated to 140–150° for a few minutes. The melt was cooled and recrystallized from alcohol giving I (α-form), m.p. 140–142°.

2-(2-Acetamido-5-chloro-α-phenylbenzylideneamino)ethanol (XXI). Method F.—Compound XIX, 3.5 g., was dissolved in a solution of 5 ml. of 4 *N* sodium hydroxide and 50 ml. of ethanol. After 5 min. the solution was diluted with water to yield 1.5 g. of XXI.

Acknowledgment.—We are indebted to Dr. Gordon Ellis and his associates for the microanalyses and to Dr. Charles Hetzel and Mr. Bruce Hofmann for the spectra.

Sulfur Heterocycles from the Ring Closure of Bisarylalkyl Disulfides[1,2]

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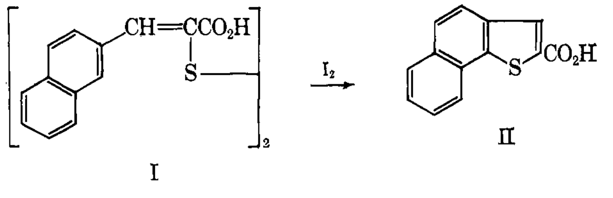
Bis(β-2-naphthylethyl) disulfide (III), bis-β-(3,4-dimethoxyphenyl)ethyl disulfide (VI), and bis(γ-2-naphthylpropyl) disulfide (X) have been synthesized. In the presence of iodine, III undergoes ring closure, giving 2,3-dihydronaphtho[1,2-*b*]thiophene (IV). An excess of iodine converts III or IV into naphtho[1,2-*b*]thiophene (V). On replacing iodine by aluminum bromide, only IV is obtained from III. Both 5,6-dimethoxybenzothiophene (VIII) and 2,3-dihydro-5,6-dimethoxybenzothiophene (VII) are obtained by the action of iodine on VI. Use of the same catalyst leads to the formation of dihydronaphtho[1,2-*b*]thiapyran (XII) from X. The identity of XII has been established by an independent synthesis. Ultraviolet spectral maxima of the products of ring closure are reported.

Disulfides have the ability to function as electrophilic reagents under the influence of acid catalysts. Several instances of their acid-catalyzed addition to olefinic double bonds have been reported[3,4] and a limited number of cases are known in which benzene derivatives undergo substitution reactions with disulfides to give thio ethers.[5,6] Analogous intramolecular interaction between a disulfide sulfur atom and an aromatic moiety in the same molecule leads to the formation of condensed thiophenes.[7,8] To answer the question as to whether or not formation of a thiophene ring, with its accompanying gain in stabilization energy, was a necessary conditions for cyclization, disulfides of the structure $(ArCH_2CH_2S)_2$ were sought in which Ar was the 2-naphthyl or the 3,4-dimethoxyphenyl radical. Results of studies on the cyclization of α,α′-dithiobis-β-arylacrylic acids support earlier evidence[5] of the electrophilic nature of the ring-closure reaction, and these groups are known to be active toward electrophilic attack.



I

II

The ring closure of disulfide I proceeded smoothly, giving II in excellent yield using iodine as the catalyst in dioxane at 50° (see Table I).[7] When the same conditions were employed for the cyclization of bis(β-2-naphthylethyl) disulfide (III), the starting material was recovered. Clearly then, unsaturation in the side chain facilitates the cyclization. Boron trifluoride in benzene also failed to bring about the ring closure of III. However, when the reaction was conducted in refluxing ethylene glycol, using an equimolar quantity of iodine, although more than half of the disulfide remained unchanged, an oil was obtained in 32% yield which was identified as 2,3-dihydronaphthol[1,2-*b*]thiophene (IV).[9] No IV was detected after refluxing III for 12 hr. in ethylene glycol alone.

The same product (IV) was formed when III was treated with aluminum bromide in benzene. Oxidation of IV with hydrogen peroxide gave 2,3-dihydronaphtho[1,2-*b*]thiophene 1,1-dioxide.[10] The ultraviolet spectral maxima of IV are recorded in Table II. A by-product of the reaction employing aluminum bromide was found to be β-2-naphthylethanethiol which, if it were formed also during the cyclization reaction with iodine as the catalyst, would immediately be oxidized to disulfide, thereby increasing the yield of IV.

With excess iodine, III was converted to naphtho[1,2-*b*]thiophene (V) in 60% yield and no disulfide was recovered. V was identified by oxidation to the corresponding sulfone[9] and comparison of the compound and its derivatives with authentic samples. Evidently, initially formed IV was dehydrogenated by iodine to give V, since a sample of IV, treated under similar conditions with an excess of iodine, was converted wholly to V.

Employing iodine in dioxane at 60°, a large proportion of bis-β-(3,4-dimethoxyphenyl)ethyl disulfide (VI) was recovered and less than 5% of an impure product, m.p. 65–75°, was isolated. Here again, the effect of

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[1] This research was supported by the U. S. Army Research Office (Durham) under Contract No. DA-33-008-ORD-1916.

[2] A preliminary communication of a portion of this work: E. Campaigne and B. G. Heaton, *Chem. Ind.* (London), 96 (1962).

[3] B. Holmberg, *Arkiv Kemi Mineral. Geol.*, **13B**, 6 (1939); *Chem. Abstr.*, **34**, 2341 (1940).

[4] D. McCaulay and A. P. Lien, U. S. Patent 2,519,586 (Aug. 22, 1950); *Chem. Abstr.*, **44**, 10,728 (1950).

[5] S. Archer and C. M. Suter, *J. Am. Chem. Soc.*, **74**, 4296 (1952).

[6] H. Behringer and K. Kuchinka, *Angew. Chem.*, **72**, 348 (1960).

[7] E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 39 (1956).

[8] E. Campaigne and W. E. Kreighbaum, *ibid.*, **26**, 1326 (1961).

[9] J. E. Banfield, *et al.*, *J. Chem. Soc.*, 2603 (1956).

[10] W. Davies and Q. N. Porter, *ibid.*, 2609 (1956).

TABLE I

CONDITIONS FOR RING CLOSURE OF DISULFIDES

Disulfide	Ratio,[a] moles	Conditions Solvent	 Temp., °C.	 Time, hr.	% yield	Product
I	6.0	Dioxane	50	36	90	II[b]
III	6.0	Dioxane	50	32	c	
III	1.0	Ethylene glycol	Reflux	0.75	32	IV
III	4.0	Ethylene glycol	Reflux	12	60	V
III	d	Benzene	70	2.5	20	IV
III	e	Benzene	Reflux	10	c	
VI	1.0	Dioxane	60	11	5	VII
VI	2.0	Dioxane	Reflux	12	20	VII[f]
VI	1.0	Ethylene glycol	160–180	0.5	23	VII
X	4.0	Ethylene glycol	Reflux	8	25	XII
X	1.0	Glyme[g]	90	8.5	50	XII[f]

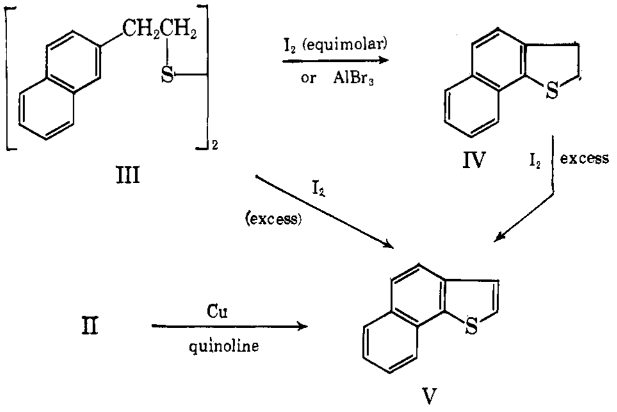
[a] Ratio of iodine–disulfide in reaction. [b] See ref. 7. [c] Starting material recovered. [d] One mole of $AlBr_3$/mole of III in place of I_2. [e] Excess BF_3 in place of I_2. [f] 8% of VIII was also produced. [g] Ethylene glycol dimethyl ether.

TABLE II

ULTRAVIOLET SPECTRAL MAXIMA OF THE PRODUCTS RESULTING FROM DISULFIDE RING CLOSURE

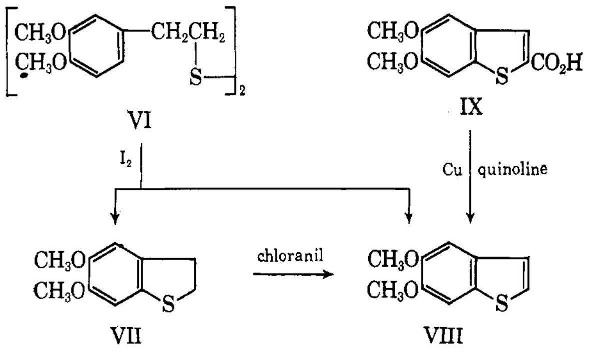
Product	λ_{max}, mμ[a]	log ε
IV	217	4.63
	249	4.35
	314	3.70
	323	3.70
VII	212[b]	4.41
	252	4.03
XII	219	4.66
	244	4.32
	310	3.83
V	255[c]	4.47
	260	4.61
	264	4.61
VIII	237	4.45
	264	3.97
	273	3.95
	295	3.40

[a] Solvent, 95% ethanol (except where shown). A Cary spectrophotometer, Model 14, was used in the range 200–350 mμ. [b] Wave-length range was only 200–300 mμ. [c] Cyclohexane.



the double bond in the side chain of α,α′-dithiobis-β-arylacrylic acids in facilitating ring closure is evident, since 5,6-dimethoxybenzothiophene was formed in 58% yield from α,α′-dithiobis-β-(3,4-dimethoxyphenyl)acrylic acid under similar conditions.[8] Raising the temperature to 100° and increasing the quantity of iodine gave, by column chromatography, *ca.* 20% of impure 2,3-dihydro-5,6-dimethoxybenzothiophene (VII). A major portion of the disulfide was converted into highly colored material which was strongly adsorbed on the alumina of the column.

Reaction at a higher temperature in ethylene glycol for a much shorter reaction time followed by chromatography of the product mixture on alumina, afforded VII (23%), characterized by its ultraviolet spectrum, the formation of a sulfone, and dehydrogenation with chloranil to 5,6-dimethoxybenzothiophene (VIII). VIII was also isolated from the reaction along with VII, in 8% yield, and was undoubtedly obtained as a result of the dehydrogenation by iodine of initially formed VII.



The possibility of obtaining 2,3-dihydrothiapyrans by ring closure of disulfides of the type $(ArCH_2CH_2CH_2S)_2$ was examined using bis(γ-2-naphthylpropyl) disulfide (X). Excess iodine in refluxing ethylene glycol gave a liquid, $C_{13}H_{12}S$, in 25% yield. This product formed a picrate and sulfone and was shown to be dihydronaphtho[1,2-*b*]-4H-thiapyran (XII), arising as expected by cyclization of X at the 1-position, by comparison with a sample prepared from 3-(α-naphthylthio)propanoic acid *via* the thiapyrone XI.[11,12] XI exhibits an unusually low-frequency carbonyl band (1650 cm.$^{-1}$), possibly indicating electronic interaction with the sulfur atom. A much cleaner reaction, giving a 50% yield of XII, together with some unchanged X, was obtained using glycol dimethyl ether as solvent.[13] The experiments involving various conditions used in the ring closure of III, VI, and X are summarized in Table I.

The most striking feature of the ultraviolet spectra of the ring-closed products (Table II) is the presence of an absorption peak in the region 210 to 220 mμ in the spectra of all three partially hydrogenated hetero-

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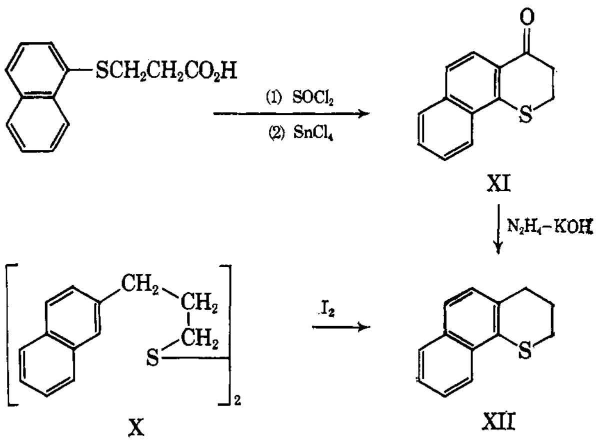
(11) F. Krollpfeiffer and H. Schultze, *Ber.*, **56**, 1819 (1923).

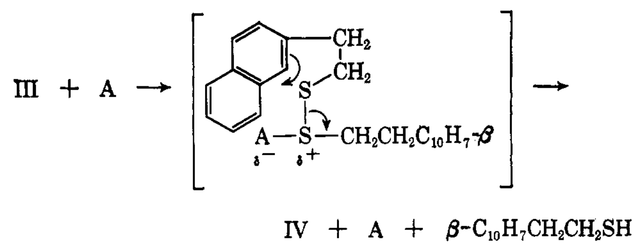
(12) W. E. Truce and G. A. Toren, *J. Am. Chem. Soc.*, **76**, 695 (1954).

(13) E. Campaigne, L. Ergener, and B. G. Heaton, *J. Org. Chem.*, **27**, 4111 (1962).



cycles, IV, VII, and XII, and its absence in the spectra of the aromatic products V and VIII, in which absorption of comparable intensity occurs at longer wave lengths. As expected, the spectral curves obtained for IV and for XII were similar.

Spectral studies[14] indicate that charge-transfer complexes between Lewis acids and disulfides exist in solution, and it is thought that the formation of these complexes may be the initial step in the ring-closure reaction. In the acid-catalyzed formation of thiaxanthone from 2,2′-dithiosalicylic acid and benzene, Archer and Suter[5] provided evidence that protonation of the disulfide bond is the initial step, followed by electrophilic interaction of a sulfur atom with benzene, and the simultaneous cleavage of the disulfide bond, giving thiosalicylic acid as the by-product. Applied to disulfide ring closure of III with a Lewis acid A, the mechanism would be as follows.



The formation of β-(2-naphthyl)ethanethiol in the cyclization of III with aluminum bromide agrees with this scheme. Although there seems to be only one case of the isolation of a sulfenyl iodide,[15] the possible existence of such compounds as intermediates in disulfide ring closures employing iodine cannot be neglected. The presence of a sulfenyl iodide as an intermediate has been postulated in a disulfide cyclization occurring under basic conditions.[16]

Synthesis of Disulfides.—III was obtained from 2-naphthylacetic acid in 52% over-all yield,[17] as outlined in Chart I.

CHART I

SYNTHESIS OF BIS(β-2-NAPHTHYLETHYL) DISULFIDE (III)

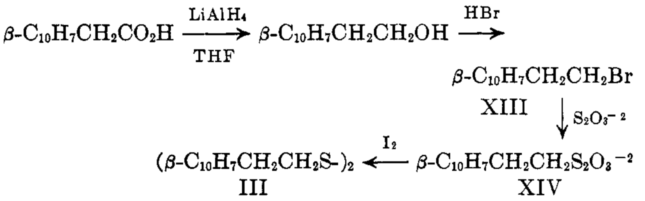
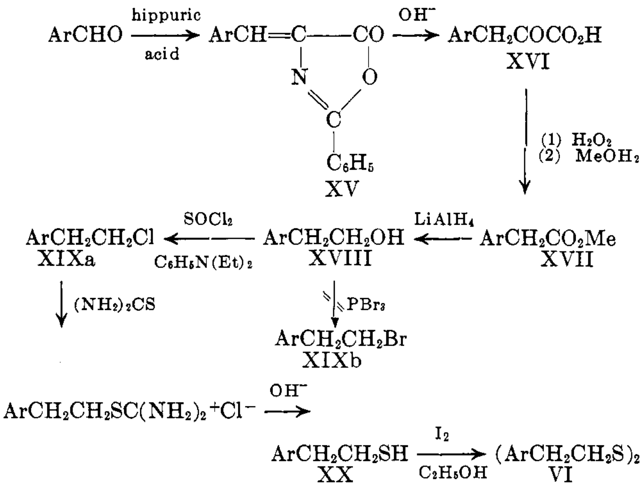


CHART II

SYNTHESIS OF BIS-β-(3,4-DIMETHOXYPHENYL)ETHYL DISULFIDE (VI)



Ar = 3,4-dimethoxyphenyl

The preparation of VI, outlined in Chart II, proceeded *via* the azlactone XV[18] and the ester XVII.[19] Conversion of XVIII to the chloride XIXa was accomplished with thionyl chloride, as described by Barash and Osbond,[20] since treatment with phosphorus tribromide in the manner of Livshits, *et al.*,[21] caused demethylation of one methoxy group. In this connection, Gardner, Horton, and Pincock[22] have observed that in the cleavage of polyalkoxyacetophenones with hydrogen bromide it appears as though a 4-alkoxy group assists the removal of a 3-alkoxy group, but the 4-alkoxy group remains unchanged. The desired disulfide VI was obtained in 22% over-all yield from veratraldehyde.

Bis(γ-2-naphthylpropyl) disulfide (X) was synthesized as outlined in Chart III, *via* 2-bromoethylnaphthalene,[23] in 10% over-all yield.

Experimental[24]

β-(2-Naphthyl)ethanol.—A solvent of 20.0 g. of β-naphthylacetic acid[25] (0.11 mole) in 100 ml. of dry tetrahydrofuran was added dropwise to a slurry of lithium aluminum hydride (6.0 g., 0.16 mole) in 140 ml. of tetrahydrofuran. After completion of the addition, the mixture was heated under reflux for 1 hr. and allowed to cool overnight. After decomposition of excess hydride with ethyl acetate followed by careful addition of 5% hydrochloric acid (100 ml.), filtration gave an ethereal filtrate which was combined with ether washings of the residue and evaporated under reduced pressure. A white solid was obtained which, after washing with water and petroleum ether, crystal-

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(14) H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961).

(15) W. E. Messer, U. S. Patent 2,370,253 (Feb. 27, 1945).

(16) L. Katz and W. Schroeder, *J. Org. Chem.*, **19**, 103 (1954).

(17) H. E. Westlake and G. Dougherty, *J. Am. Chem. Soc.*, **64**, 149 (1942).

(18) W. Kropp and H. Decker, *Ber.*, **42**, 1184 (1909).

(19) H. R. Snyder, J. S. Buck, and W. S. Ide, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 333.

(20) M. Barash and J. M. Osbond, *J. Chem. Soc.*, 2162 (1959).

(21) R. S. Livshits, *et al.*, *Zh. Obshch. Khim.*, **23**, 525 (1953).

(22) P. D. Gardner, W. J. Horton, and R. E. Pincock, *J. Am. Chem. Soc.*, **78**, 2541 (1956).

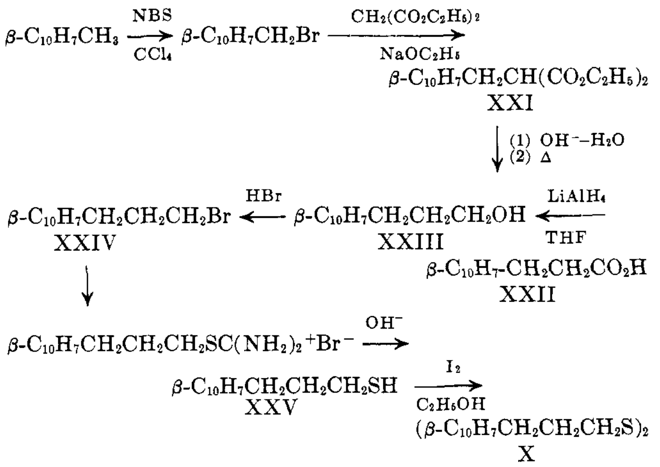
(23) N. B. Chapman and J. F. A. Williams, *J. Chem. Soc.*, 5044 (1952).

(24) All melting points are corrected. Infrared spectra were obtained using a Perkin-Elmer Infracord Model 137 G spectrophotometer. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

(25) F. Mayer and T. Oppenheimer, *Ber.*, **49**, 2137 (1916).

CHART III

SYNTHESIS OF BIS(γ-2-NAPHTHYLPROPYL) DISULFIDE (X)



NBS = N-bromosuccinimide, THF = tetrahydrofuran

lized from petroleum ether (b.p. 30–60°) as small white needles, m.p. 69–70.5° (14.8 g., 80%). The reported[25] m.p. was 67–68°. The α-naphthylurethane was prepared in the usual way and crystallized from hexane–chloroform as feathery crystals, m.p. 153–155°.

Anal. Calcd. for $C_{23}H_{19}NO_2$: C, 80.90; H, 5.61. Found: C, 81.17; H, 5.93.

β-(2-Naphthyl)ethyl Bromide (XIII).—β-(2-Naphthyl)ethanol (13.8 g.) was heated for 4.5 hr. under reflux with 100 ml. of 47% aqueous hydrobromic acid and then allowed to cool overnight. After the addition of 200 ml. of water, extraction with four 50-ml. portions of ether, followed by combination of the extracts and removal of solvent after washing with water gave 17.9 g. (95%) of a solid, m.p. 64.5–66.5°, which depressed the melting point of starting material to 49–53°. The product (12.5 g.) crystallized from chilled petroleum ether as needles, m.p. 64.5–66.5°.[26]

Bis[β-(2-naphthyl)ethyl] Disulfide (III).—To a solution of 11.7 g. of XIII (0.05 mole) in 125 ml. of warm ethanol was added a solution of 12.4 g. of sodium thiosulfate (0.05 mole) in 50 ml. of water. After heating the mixture under reflux for 4 hr., 6.35 g. of iodine (0.05 g.-atom) was added gradually, by drainage from a Soxhlet as described by Viscontini, *et al.*,[27] keeping the reaction mixture refluxing throughout the addition (5.5 hr.). The solid obtained on dilution of the reaction mixture with water was collected by filtration, washed well with water, and dried. Two crystallizations from *n*-hexane, employing Norit for decolorization, gave 6.4 g. (69%) of white needles, m.p. 84–85°.

Anal. Calcd. for $C_{24}H_{22}S_2$: C, 76.96; H, 5.92; S, 17.12. Found: C, 77.23; H, 5.95; S, 16.91.

With sodium nitroprusside solution, III only gave the purple color characteristic of alkyl mercaptans after treatment with warm ethanolic sodium cyanide, thus indicating the presence of the disulfide bond.

2,3-Dihydronaphtho[1,2-*b*]thiophene (IV). A. From Ring Closure of III with Iodine.—Compound III (3.74 g., 0.01 mole) in 300 ml. of ethylene glycol was heated under reflux and 2.7 g. of iodine (0.022 g.-atom) was added portionwise over a period of 30 min., after which the mixture was maintained under reflux for a further 15 min. When cool, the liquid was poured into 800 ml. of water, excess iodine was removed by addition of sodium bisulfite solution, and after cooling to 3°, filtration gave 3.15 g. of an oily brown solid. Chromatography of the product on an alumina column, using *n*-hexane and chloroform (3:1) as the eluting solvent, gave unchanged disulfide, m.p. 80–83° (2.0 g.), and a light brown oil (0.7 g.) which was shown to be essentially pure 2,3-dihydronaphtho[1,2-*b*]thiophene by the formation of a dark red picrate in the form of needles, m.p. 129–131°.

More of the oil (0.5 g.) was obtained by evaporation of ether extracts of the filtrate from above, and this material gave the same picrate, m.p. 128–129°.

B. By Interaction of Aluminum Bromide and III.—Compound III (7.7 g., 0.021 mole), dissolved in 75 ml. of sodium-dried benzene, was treated with 5.5 g. (0.021 mole) of freshly distilled aluminum bromide. The deep brown solution was heated to 70° and maintained between 60 and 70° for 2.5 hr., protected from moisture by a calcium chloride tube. On cooling, the green solution was poured slowly onto excess ice. After several hours, the benzene layer was separated, washed with three 30-ml. portions of 10% sodium hydroxide solution, then water (40 ml.), and dried over anhydrous sodium sulfate. The combined alkaline washings contained only a trace of mercaptan, as indicated by failure to bleach iodine in potassium iodide solution.

Removal of benzene by evaporation under reduced pressure gave a brown oil (7.7 g.) which was dissolved in 30 ml. of ethanol and titrated with a standard solution of iodine in ethanol. Iodine equivalent to 2.7 g. of β-(2-naphthyl)ethanethiol was consumed, and a white solid precipitated. The solid was collected by filtration, washed several times with chilled *n*-hexane, and allowed to dry. The solid (4.4 g., 57%) was purified by treatment with Norit and crystallization from *n*-hexane to give white needles (m.p. 82–83.5°) of starting material.

The filtrate was evaporated to small volume, 50 ml. of water was added, and the mixture was extracted with three 30-ml. portions of *n*-hexane. The combined extracts, after washing with dilute sodium bisulfite solution to remove iodine, were washed with water and dried over sodium sulfate. The yellow oil afforded by removal of the solvent was distilled under reduced pressure and gave 1.5 g. (20%) of IV, an almost colorless distillate, b.p. 150–158° (1.2 mm.).

Anal. Calcd. for $C_{12}H_{10}S$: C, 77.37; H, 5.41; S, 17.21. Found: C, 77.22; H, 5.37; S, 17.34.

Treatment of a small portion of the distillate with an excess of saturated ethanolic picric acid solution gave a picrate which crystallized from ethanol as dark red needles, m.p. 129.5–130°, and did not depress the melting point of the picrate of IV previously prepared. Banfield, *et al.*,[9] report dark red needles, m.p. 132°, for the picrate of IV.

Anal. Calcd. for $C_{18}H_{13}N_3O_7S$: C, 52.05; H, 3.15; N, 10.12; S, 7.72. Found: C, 52.15; H, 3.28; N, 10.11; S, 7.79.

2,3-Dihydronaphtho[1,2-*b*]thiophene 1,1-Dioxide.—A solution of 0.6 g. of IV in 8 ml. of glacial acetic acid containing 3 ml. of 30% hydrogen peroxide was heated to reflux on a steam bath for 90 min. On cooling, the mixture was poured onto ice, and the product was collected by filtration, washed with water, and dried. Recrystallization to constant melting point of the cream-colored solid (0.58 g., m.p. 171.5–176.5°) from methanol afforded 0.28 g. of white needles, m.p. 186.5–188°[10]; $\nu_{\max}^{\text{KBr}}$ 2990 (aliphatic CH), 1274, 1144, and 1121 cm.$^{-1}$ ($-SO_2-$).

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62; S, 14.67. Found: C, 65.89; H, 4.67; S, 14.49.

Attempted Ring Closure of Bis(β-2-naphthylethyl) Disulfide. A. With Iodine in Dioxane.—A solution of 2.0 g. (0.0054 mole.) of III and 8.0 g. of iodine (0.063 g.-atom) in 80 ml. of dioxane was stirred, heated to 50°, and maintained at this temperature for 32 hr. Partial evaporation of the mixture under reduced pressure was followed by the addition of a large volume of water containing sodium bisulfite (*ca.* 10 g.). The solid reaction product was extracted with three 60-ml. portions of ether, the combined extracts were dried ($CaCl_2$) after having been washed with sodium bisulfite solution and then water, and removal of the ether under reduced pressure gave 2.0 g. of a solid residue which, on crystallization from methanol, afforded fine white needles of starting material, m.p. 81.5–83°. Concentration of the crystallization filtrate yielded only more unchanged disulfide.

B. With Boron Trifluoride Etherate in Benzene.—A solution of 7.1 g. (0.019 mole) in III in 600 ml. of dry benzene containing boron trifluoride etherate (40 ml., 47%) was heated under reflux for 10 hr. After work-up as described for the aluminum bromide reaction, removal of solvent afforded 6.6 g. of a solid, which crystallized from hexane as needles, m.p. 84–85.5°, and did not depress the melting point of the starting material.

Naphtho[1,2-*b*]thiophene (V). A. From III and an Excess of Iodine.—Iodine (10.9 g., 0.086 g.-atom) and 4.0 g. of III (0.011 mole) were heated together in 350 ml. of ethylene glycol under reflux for 12 hr. On cooling, the mixture was poured with stirring into 1 l. of water containing 6 g. of sodium bisulfite and the product was extracted with four 150-ml. portions of ether. Washing the combined extracts with water, drying (K_2CO_3), and removal of the solvent gave a dark red-brown oil. Chromatography on an alumina column, using a mixture of *n*-hexane and chloroform in the ratio 4:1, gave 2.24 g. (60%) of a light brown mobile oil, which, on treatment with an excess of saturated eth-

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[26] G. T. Tatevosyan and V. O. Babayan, *Zh. Obshch. Khim.*, **22**, 1421 (1952).

[27] M. Viscontini, *et al.*, *Helv. Chim. Acta*, **37**, 375 (1954).

anolic picric acid solution, gave a picrate which crystallized from ethanol as brown needles, m.p. 142.5–144.5°.

B. From the Decarboxylation of II.—Five grams of II,[7] 1.25 g. of copper–bronze powder, and 37 ml. of quinoline were heated together slowly up to 150°, and the temperature was maintained in the range 150–170° for 1 hr., after which it was raised very slowly, over a period of 2.5 hr., to 205°. On cooling, quinoline was neutralized by the addition of 130 ml. of 10% hydrochloric acid. Steam distillation, followed by acidification of the distillate (40 ml. of concentrated HCl), extraction with three 100-ml. portions of chloroform, combination and drying (K_2CO_3) of the extracts, and removal of solvent gave 2.9 g. of an orange oil which distilled in the range 108–113° (0.2 mm.). Treatment of the distillate with picric acid in ethanol gave a picrate which after two recrystallizations from ethanol gave golden yellow needles, m.p. 146.5–147.5°.[28] A mixture melting point with the brown needles (above) was 142.5–145.5°.

C. From the Action of an Excess of Iodine on 2,3-Dihydro-[1,2-*b*]thiophene.—Compound IV (1.2 g., 0.0065 mole), 3.3 g. (0.026 g.-atom) of iodine, and 100 ml. of redistilled ethylene glycol were heated together under reflux for 12.5 hr. The mixture was allowed to cool, poured into 300 ml. of water, and extracted with four 100-ml. portions of ether. The combined ether extracts were washed in turn with dilute sodium bisulfite solution, sodium bicarbonate solution, then water, dried (K_2CO_3), and the ether was removed to give a dark brown oil. Distillation of the oil under reduced pressure afforded 0.6 g. of a liquid b.p. 110–116° (0.2 mm.). The absorption maxima (255, 260, and 264 mμ) in the ultraviolet spectrum of the distillate were identical with those present in the spectrum of V derived from II by decarboxylation. This oil formed a picrate in golden yellow needles, m.p. 145.5–147°, which did not depress the melting point of the picrate derived from V (above).

Naphtho[1,2-*b*]thiophene 1,1-Dioxide.—The V (2.0 g., obtained from the decarboxylation above) was dissolved in glacial acetic acid (24 ml.), treated with 30% hydrogen peroxide (7.0 ml.), and heated 4 hr. on a steam bath. The cooled solution was poured with stirring onto ice and the product was extracted with five 50-ml. portions of chloroform. After washing the combined extracts with water, drying (K_2CO_3), and removal of the solvent, an orange-yellow solid was obtained (1.15 g.) which, after treatment with Norit and crystallization from methanol gave green-tinged platelets, m.p. 174–175°. Banfield, *et al.*,[9] report m.p. 179° for the sulfone of V, and add that the melting point is variable, depending on the rate of heating; $\nu_{\max}^{\text{KBr}}$ 1131, 1155, and 1287 cm.$^{-1}$ ($-SO_2-$).

Anal. Calcd. for $C_{12}H_8O_2S$: C, 66.65; H, 3.73; S, 14.83. Found: C, 66.20; H, 4.12; S, 14.60.

The same substance, as shown by mixture melting point and congruity of infrared spectra, was obtained by similar oxidation of the oil obtained from the action of excess iodine on III.

β-(3,4-Dimethoxyphenyl)ethanol (XVIII).—Following the method of Kropp and Decker,[18] the azlactone XV, yellow prisms, m.p. 149.5–151°, was obtained in 65% yield. This was converted by the "Organic Syntheses" procedure[19] to methyl homoveratrate (XVII), b.p. 108–109° (0.22 mm.), in 55% yield. A solution of 34.5 g. (0.165 mole) of XVII in 270 ml. of dry ether was added dropwise to a stirred slurry of 10.5 g. (0.36 mole) of lithium aluminum hydride in 250 ml. of dry ether. After the addition was completed, (*ca.* 3 hr.), the mixture was heated and maintained under reflux for 75 min. with continued stirring. Excess hydride was decomposed by the addition of 25 ml. of ethyl acetate. After adding 200 ml. of chilled 2 *N* sulfuric acid to the stirred, cooled reaction mixture, the aqueous layer was separated and extracted with three 90-ml. portions of ether. The combined ethereal solutions were washed twice with dilute sodium bicarbonate solution and dried (Na_2SO_4). After removal of the solvent, the residue was distilled and 24 g. (80%) of XVIII was obtained, b.p. 124–129° (0.4 mm.). The distillate solidified after a few hours and melted at 44.5–46°.[21]

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.09; H, 7.78.

Attempted Formation of β-(3,4-Dimethoxyphenyl)ethyl Bromide.—Compound XVIII (12.2 g., 0.067 mole) was melted, then supercooled with ice–water, and stirred; before solidification could take place, phosphorus tribromide (61 g., 0.23 mole) was added dropwise over a period of 30 min. to the stirred and cooled alcohol. On completion of the addition, the mixture was allowed to warm slowly to room temperature and was then heated on a steam bath for 2 hr., protected from moisture by a calcium chloride tube.

On cooling, the reaction mixture was slowly dripped onto stirred ice and the product was extracted with four 110-ml. portions of ether. After washing the combined extracts with sodium bicarbonate solution, water, and drying (Na_2SO_4), removal of the solvent by evaporation under reduced pressure gave a light brown oil which distilled in the range 116–120° (0.4 mm.), 9.41 g.

Anal. Calcd. for $C_9H_{11}BrO_2$: C, 46.77; H, 4.80; Br, 34.58. Found: C, 46.56; H, 4.89; Br, 33.52.

A narrow and intense absorption band was present in the infrared spectrum (liquid film) at 3620 cm.$^{-1}$ (OH), and a deep green color was obtained on addition of ferric chloride solution to the distillate.

β-(3,4-Dimethoxyphenyl)ethyl Chloride (XIXa).—This compound was obtained from the corresponding alcohol by treatment with thionyl chloride, as described by Barash and Osbond,[20] b.p. 108–115° (0.3 mm.), in 90% yield.

Anal. Calcd. for $C_{10}H_{13}ClO_2$: Cl, 17.67. Found: Cl, 17.82.

β-(3,4-Dimethoxyphenyl)ethylisothiouronium Chloride.—Compound XIXa (8.7 g., 0.042 mole), dissolved in 15 ml. of 95% ethanol was treated with 3.4 g. (0.045 mole) of thiourea. The mixture was heated under reflux for 3 hr., and then the solvent was removed by evaporation under reduced pressure. The viscous residue solidified and was crystallized from a mixture of 0.5 *N* hydrochloric acid and acetone. Material with m.p. 169.5–171.5° (10.4 g.) was obtained in *ca.* 86% yield. Recrystallization gave needles, m.p. 170.5–171.5°.

Anal. Calcd. for $C_{11}H_{17}ClN_2O_2S$: C, 47.73; H, 6.19; S, 11.58. Found: C, 47.59; H, 6.25; S, 11.49.

Bis(β-3,4-dimethoxyphenylethyl) Disulfide (VI).—β-(3,4-Dimethoxyphenyl)ethylisothiouronium chloride (10.4 g.) was heated under reflux for 2 hr. with 10% sodium hydroxide solution (19 ml.). On cooling, the mixture was acidified by the addition of 10% hydrochloric acid (20 ml.) and extracted with three 20-ml. portions of chloroform. After washing the combined extracts with water, the solvent was removed under reduced pressure, leaving a residue of the mercaptan which was dissolved in 20 ml. of 95% ethanol and treated dropwise, under vigorous stirring, with a solution of 4.79 g. of iodine in 100 ml. of ethanol. After 87 ml. of solution had been added, a slight excess of iodine was present and the titration was discontinued. After cooling, the solid product was collected by filtration, washed with dilute sodium bisulfite solution, a large amount of water, and dried under reduced pressure. Crystallization gave 6.36 g. (86%) of white needles from methanol, m.p. 76.5–78°. The over-all yield from veratraldehyde was 2%; $\nu_{\max}^{\text{KBr}}$ 808, 1029, 1138, 1157, 1239, 1263, and 1515 cm.$^{-1}$ (all strong).

Anal. Calcd. for $C_{20}H_{26}O_4S_2$: C, 60.88; H, 6.64; S, 16.25. Found: C, 60.78; H, 6.68; S, 16.01.

Following the technique previously described for the preparation of these derivatives,[29] the N,N-diphenylthiocarbamate of β-(3,4-dimethoxyphenyl)ethanethiol was obtained as white needles, m.p. 107.5–108.5°, from methanol.

Anal. Calcd. for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89; S, 8.15. Found: C, 69.99; H, 6.00; S, 8.18.

2,3-Dihydro-5,6-dimethoxybenzothiophene (VII).—Preliminary attempts to cyclize VI in dioxane were unsuccessful. An equimolar solution of VI and iodine in dioxane was maintained at 60° for 11 hr., but separation of the residues on an alumina column led only to starting material in about 60% recovery. Using a 1 molar excess of iodine with VI in refluxing dioxane for 12 hr. produced about 15% of crystalline product melting at 71–73° after several recrystallizations, and having a molecular weight of 192. It was identified by comparison to the products obtained in ethylene glycol. Compound VI (5.2 g., 0.013 mole), iodine (3.35 g., 0.026 g.-atom), and ethylene glycol (200 ml., redistilled) were heated together and maintained between 160 and 180° for 35 min., after which the dark solution was allowed to cool slowly to room temperature. The reaction mixture was poured slowly into 1.2 l. of water and cooled overnight. The product was extracted with chloroform; the combined extracts were washed with bisulfite solution, then water, and dried (K_2CO_3). Removal of solvent gave a red-brown oil which was subjected to chromatography on a column of alumina (230 g.) using a 2:1 mixture of *n*-hexane and chloroform as the eluting solvent.

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[28] O. Kruber and A. Raeithel. *Ber.*, **86**, 366 (1953).

[29] R. G. Hiskey, *et al.*, *J. Org. Chem.*, **26**, 4756 (1961).

The progress of elution was followed using thin-layer chromatography on silica. The first material to be eluted was 5,6-dimethoxybenzothiophene (VIII), m.p. 101–102°, lit.[7] m.p. 99–100°. The ultraviolet absorption maxima (see Table II) are in good agreement with the recorded maxima for VIII. Furthermore, the infrared spectrum (KBr mull) was identical with that of VIII, obtained by decarboxylation of IX, and no depression in melting point occurred on admixture of the material, m.p. 101°, with authentic VIII.

Further elution yielded solid (0.41 g.), m.p. 72–73.5° after recrystallization from *n*-hexane, closely followed by VII (0.78 g.) which gave flaky needles, m.p. 76–77.5°, on crystallization from *n*-hexane.

Anal. Calcd. for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16; S, 16.34. Found: C, 61.32; H, 6.05; S, 16.17.

Both the solid, m.p. 72°, and VII greatly depressed the melting point of starting material. Comparison of the infrared spectra of the solid (m.p. 72°), VII, and VIII revealed that the solid (m.p. 72°) was VII containing VIII as an impurity. Hence the total crude yield of VII is *ca.* 23% (15% after recrystallization). Neither the solid, m.p. 71–73° (above), nor that with m.p. 72–73.5° showed a melting point depression on admixture with 2,3-dihydro-5,6-dimethoxybenzothiophene.

Continued elution gave a brown oil (0.47 g.) and elution with chloroform alone gave more of the resinous oil; 0.25 g. was obtained from the evaporation of about 1 l. of eluate. Brown and green material was still strongly absorbed on the column after the passage of more than a liter of chloroform.

2,3-Dihydro-5,6-dimethoxybenzothiophene 1,1-Dioxide.—Compound VII (0.33 g.) was oxidized with 1.5 ml. of 30% hydrogen peroxide in 4 ml. of glacial acetic acid in the manner described above, and 0.23 g. of a white solid was obtained, which crystallized from methanol as prisms, m.p. 183.5–184.5°.

Anal. Calcd. for $C_{10}H_{12}O_4S$: C, 52.62; H, 5.30; S, 14.05. Found: C, 52.94; H, 5.50; S, 13.91.

5,6-Dimethoxybenzothiophene (VIII).—A solution of 0.3 g. (0.0015 mole) of VII in 10 ml. of dry xylene was treated with 0.40 g. (0.0016 mole) of chloranil. The addition of chloranil imparted a deep blue-green color to the mixture. The reactants were heated under reflux for 6 hr., and then allowed to cool to room temperature, during which time a solid separated. The solid material was separated by filtration, washed with benzene, and the combined filtrate and washings were evaporated in a stream of nitrogen on the steam bath. The residue was subjected to chromatography on an alumina (40 g.) column using a 2:1 mixture of hexane and chloroform. In this way 0.22 g. (73%) of solid, m.p. 99–101°, was obtained which crystallized from *n*-hexane as clumps of needles, m.p. and m.m.p. 101–102° with authentic VIII, m.p. 100.5–101.5°.[7]

Anal. Calcd. for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19; S, 16.51. Found: C, 62.07; H, 5.04; S, 16.22.

The infrared spectra of the samples (m.p. 101–102°) derived from the cyclization, from the dehydrogenation and from decarboxylation of 5,6-dimethoxybenzothiophene-2-carboxylic acid[7] were virtually identical.

Diethyl 2-Naphthylmethylmalonate (XXI).—To a stirred solution of 40 g. (0.25 mole) of diethyl malonate in 150 ml. of dry ethanol containing dissolved sodium (5.2 g., 0.23 g.-atom) was added dropwise with stirring a solution of 49.3 g. (0.22 mole) of 2-bromomethylnaphthalene (prepared by the method of Chapman and Williams)[23] in 30 ml. of dry benzene over a period of 40 min. The mixture was stirred another 40 min. and then heated under reflux for 90 min. Removal of most of the ethanol followed by the addition of 200 ml. of water, extraction of the product with two 40-ml. portions of chloroform, combination of the water-washed extracts, drying (Na_2SO_4), and removal of the solvent gave a yellow oil which on distillation gave 34.5 g. (52%) of the desired ester, b.p. 160–169° (0.25 mm.), lit.[30] b.p. 170–174° (2 mm.).

3-(β-Naphthyl)propanoic Acid (XXII).—Hydrolysis of XXI with methanolic potassium hydroxide and decarboxylation of the resulting diacid at 180° as described by Mayer and Seiglitz,[31] gave XXII in the form of plates, m.p. 133–136° (16.5 g., 72%). Recrystallization from benzene gave colorless plates, m.p.134–135°.[31]

γ-(2-Naphthyl)propanol (XXIII).—A solution of 15.8 g. (0.079 mole) of XXII in 80 ml. of dry tetrahydrofuran was added dropwise to a stirred suspension of 4.7 g. (0.12 mole) of lithium aluminum hydride in 120 ml. of tetrahydrofuran. After completion of the addition (*ca.* 1 hr.), the mixture was stirred under reflux for 1 hr., and left overnight at room temperature. Decomposition of excess hydride with 15 ml. of ethyl acetate was followed by the addition of 100 ml. of chilled 5% sulfuric acid. Insoluble inorganic material was separated by filtration, washed with tetrahydrofuran, and the combined filtrate and washings were evaporated under reduced pressure. Water (50 ml.) was added and the product was extracted with two 50-ml. portions of ether. The combined extracts were washed with sodium bicarbonate solution, dried (K_2CO_3), and on removal of the solvent, the residue was distilled under reduced pressure giving 13.3 g. (91%) of a viscous oil, b.p. 128–134° (0.2 mm.), which solidified, melting in the range of 36.5–38.5°. This material formed a phenylurethane melting at 95–96°. Searles[32] reported this alcohol to melt at 33° and its phenylurethane to melt at 94°.

γ-(2-Naphthyl)propyl Bromide (XXIV).—A mixture of 13.0 g. of XXIII and 100 ml. of 48% hydrobromic acid was heated under reflux for 5 hr., cooled, poured into 200 ml. of water, and the product was extracted with two 100-ml. portions of ether. After the combined extracts were washed with dilute sodium bicarbonate solution, followed by water, and dried ($MgSO_4$), removal of the solvent gave 16.9 g. (97%) of a solid which, after crystallizing from *n*-hexane, melted at 43.5–44.5°.

Anal. Calcd. for $C_{13}H_{13}Br$: C, 62.67; H, 5.26; Br, 32.07. Found: C, 62.81; H, 5.34; Br, 32.27.

γ-(2-Naphthyl)propylisothiouronium Chloride.—A solution of 16.4 g. (0.066 mole) of XXIV, and 5.0 g. (0.066 mole) of thiourea in 20 ml. of ethanol was heated under reflux for 2.5 hr. The ethanol was removed by evaporation under reduced pressure and 21.4 g. of γ-(2-naphthyl)propylisothiouronium bromide was obtained as a solid, m.p. 164.5–165.5°. Two crystallizations from 0.5 *M* hydrochloric acid gave fine needles, m.p. 173–174°, of the corresponding chloride.

Anal. Calcd. for $C_{14}H_{17}ClN_2S$: C, 59.88; H, 6.10; S, 11.42. Found: C, 59.97; H, 6.15; S, 11.37.

γ-(2-Naphthyl)propanethiol (XXV).—γ-(2-Naphthyl)propylisothiouronium bromide (21.0 g.) was heated for 2 hr. under reflux with an aqueous 5% sodium hydroxide solution. On cooling, the product was extracted with two 40-ml. portions of ether; the combined extracts were washed with water (40 ml.) and dried ($MgSO_4$). Removal of the solvent gave XXV as a red oil (12.8 g.) which was characterized by treatment of a small portion with N,N-diphenylcarbamoyl chloride according to the method of Hiskey, *et al.*[29] γ-(2-Naphthyl)propyl N,N-diphenylthiocarbamate was obtained as fine white needles from methanol, m.p. 102–103°.

Anal. Calcd. for $C_{26}H_{23}NOS$: C, 78.55; H, 5.83; S, 8.07. Found: C, 78.44; H, 5.82; S, 7.92.

Bis(γ-2-naphthylpropyl) Disulfide (X).—A solution of 8.2 g. (0.065 g.-atom) of iodine in 75 ml. of ethanol was added dropwise to a stirred suspension of 12.5 g. (0.062 mole) of XXV in 30 ml. of ethanol. After reduction of the excess of iodine with dilute sodium bisulfite solution, the mixture was cooled; the product was collected by filtration, washed with water, and dried. After treatment with Norit, 8.8 g. (70%) of white needles crystallized from *n*-hexane, m.p. 61.5–63.5°.

Anal. Calcd. for $C_{26}H_{26}S_2$: C, 77.56; H, 6.51; S, 15.93. Found: C, 77.87; H, 6.44; S, 15.72.

3-(α-Naphthylthio)propanoic Acid.—To a solution of 24 g. (0.15 mole) of α-naphthalenethiol (Eastman) and 16.2 g. (0.21 mole) of β-chloropropionic acid in 90 ml. of ethanol was added a solution of sodium (6.9 g., 0.33 g.-atom) in ethanol with stirring. The mixture was heated to reflux, under a constant stream of nitrogen for 16 hr. During this period almost all of the solvent evaporated, and the solution obtained after the addition of sodium bicarbonate solution to the residue was filtered and, on acidification, the crude acid precipitated. After washing several times with water and drying, 23.6 g. (68%) of solid which crystallized from *n*-hexane–benzene as needles, m.p. 88–90°,[11] was obtained.

Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 67.22; H, 5.21; S, 13.80. Found: C, 67.19; H, 5.12; S, 14.00.

Dihydronaphtho[1,2-*b*]-4H-thiapyran-4-one (XI).—3-(α-Naphthylthio)propanoic acid (26.2 g.) dissolved in 50 ml. of anhydrous ether containing 4 drops of pyridine was treated with thionyl chloride (15.7 ml., freshly distilled) and, after 0.5 hr. at room

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(30) R. Huisgen and V. Rietz, *Ber.*, **90**, 2768 (1957).

(31) F. Mayer and A. Sieglitz, *ibid.*, **55**, 1835 (1922).

(32) S. Searles, *J. Am. Chem. Soc.*, **73**, 124 (1951).

temperature, the reactants were heated for 10 min. on a steam bath. The excess of thionyl chloride and ether was removed by evaporation under reduced pressure; final traces of thionyl chloride were removed by adding benzene and evaporating again.

To a solution of the residue in 90 ml. of sodium-dried benzene cooled to 2°, was added a solution of 30 ml. of stannic chloride in 30 ml. of benzene (sodium-dried) in two equal portions, the second portion being added after the reaction mixture had cooled down to 20°. Cooling was maintained during the whole period, and *ca.* 20 min. after the initial addition the reaction mixture was poured over a mixture of ice and concentrated hydrochloric acid. After 12 hr., the benzene layer was separated, combined with a benzene extract (100 ml.) of the aqueous layer, washed with sodium bicarbonate solution, then water, and dried (K_2CO_3). The yellow solid obtained on removal of the benzene crystallized from ethanol as yellow-green prisms, m.p. 108.5–110°[11] (18.9 g., 78%), ν_{max}^{KBr} 1650 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{13}H_{10}OS$: C, 72.86; H, 4.70; S, 14.96. Found: C, 73.32; H, 4.76; S, 14.96.

The compound formed a semicarbazone which crystallized from chloroform–ethanol as fine needles, m.p. 228.5–230°.

Anal. Calcd. for $C_{14}H_{13}N_3OS$: C, 61.97; H, 4.83; S, 11.82. Found: C, 61.40; H, 5.22; S, 11.87.

Dihydronaphtho[1,2-*b*]-4H-thiapyran (XII). A. From Ring Closure of X.—A solution of 5.0 g. (0.012 mole)of X and 12.6 g. (0.10 g.-atom) of iodine in 450 ml. of ethylene glycol was heated under reflux for 8 hr. On cooling, the mixture was poured into 1.3 l. of water and the product was extracted with three 250-ml. portions of ether. The combined extracts were washed with dilute sodium bisulfite solution, followed by water, and dried (K_2CO_3). The dark red oil obtained on removal of the solvent was absorbed onto an alumina column (160 g.) and, on elution with a *n*-hexane–chloroform mixture (4:1), a yellow oil was obtained (1.58 g.) which distilled under reduced pressure giving 1.26 g. (25%) of an almost colorless distillate of XII, b.p. 138–142° (0.2 mm.). Vapor phase chromatography[33] indicated that the distillate was a single compound.

Anal. Calcd. for $C_{13}H_{12}S$: C, 77.95; H, 6.04; S, 16.01. Found: C, 78.25; H, 6.14; S, 15.99.

Compound X (4.44 g., 0.011 mole) and iodine (2.82 g., 0.022 g.-atom) in ethylene glycol dimethyl ether (400 ml.) were heated under reflux (90°) for 8.5 hr. After removing the bulk of the solvent by evaporation under reduced pressure, 250 ml. of water was added and the product was extracted with three 80-ml. portions of ether. After washing the combined extracts with dilute sodium bisulfite solution, then sodium bicarbonate solution, followed by water and drying, removal of the solvent and distillation of the residue under reduced pressure afforded 2.2 g. (50%) of XII as a liquid, b.p. 159–163° (0.4 mm.). The infrared spectrum of the distillate was identical with that of XII above.

The residue (1.45 g.) from the distillation, after chromatography on alumina, gave a white solid, m.p. 60.5–62.5° (0.62 g.) and m.m.p. 60.5–63.5° with starting material, m.p. 61.5–63.5°.

B. By Reduction of XI.—A modification of the Wolff–Kishner reduction used in the naphthiapyrone series was applied with success in the present case.[12] Compound XI (10.0 g.) and hydrazine hydrate (6.4 ml. of 85% aqueous solution) were heated together in diethylene glycol (65 ml., redistilled) under reflux for 1 hr. Water and excess hydrazine were then distilled until the temperature reached 195°, whereupon the solution was cooled to 110° and 8.9 g. of potassium hydroxide was added. The mixture began to boil of its own accord, and heating was resumed. When the temperature again reached 190°, refluxing was continued for 4 hr. On cooling, the liquid was poured into 250 ml. of water and extraction with four 70-ml. portions of ether followed by combination of the extracts, washing with water, drying (K_2CO_3), and removal of the ether gave 7.64 g. (82%) of a yellow oil which distilled under reduced pressure in the range of 132–138° (0.15 mm.).

The infrared spectrum (liquid film) was identical with the spectrum of XII (above). The product formed a picrate and, on oxidation, a sulfone identical with those described below prepared from the product of ring closure of the disulfide X.

Dihydronaphtho[1,2-*b*]-4H-thiapyran Picrate.—Treatment of XII with an excess of a saturated ethanolic solution of picric acid gave a picrate which crystallized from ethanol as dark red needles, m.p. 128.5–130°.

Anal. Calcd. for $C_{19}H_{15}N_3O_7S$: C, 53.14; H, 3.52. Found: C, 53.52; H, 3.29.

Dihydronaphtho[1,2-*b*]-4H-thiapyran 1,1-Dioxide.—A solution of 0.3 g. of XII in 4 ml. of glacial acetic acid was treated with 1.5 ml. of 30% hydrogen peroxide and heated for 2 hr. on a steam bath. The cooled solution was poured onto ice (30 g.) and the product was collected by filtration, washed with water, and crystallized from methanol. Recrystallization yielded 0.15 g. of light yellow plates, m.p. 164.5–166.5°; ν_{max}^{KBr} 1112 (s) and 1277 cm.$^{-1}$ (s).

Anal. Calcd. for $C_{13}H_{12}O_2S$: C, 67.22; H, 5.21; S, 13.80. Found: C, 67.59; H, 4.89; S, 13.74.

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[33] Using an F and M Scientific Corp. Model 500 gas chromatograph.

Organic Disulfides and Related Substances. XI. Bisalkylidene, -alkylene, and -arylene Disulfides Containing 2-Aminoethyl Moieties[1]

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Syntheses and thermal stabilities in solution are reported for a number of bisdisulfides of the general formula RSSR'SSR, where R is a 2-aminoethyl moiety. Syntheses involved reaction of appropriate thiolsulfonates with alicyclic 1,1-dithiols, aromatic and aliphatic 1,2-dithiols, and aliphatic 1,4-dithiols. 1,1-Bisdisulfides are the least stable thermally of the series of bisdisulfides studied; *the cyclohexylidene bisdisulfide is remarkably less stable than its cyclopentylidene counterpart.* Aromatic 1,2-bisdisulfides are less stable than 1,2- and 1,4-aliphatic bisdisulfides; the latter gave 1,2-dithiacyclohexane in good yield upon decomposition. Typical free bases are much less stable than hydrochloride salts and typical amides are more stable.

An earlier paper[2] described syntheses of some unsymmetrical disulfides by reaction of thiosulfonates with thiols according to the previously reported but little used reaction,[3] $RSO_2SR + R'SH \rightarrow RSSR' + RSO_2H$. This paper reports extension of this method to the synthesis of bisdisulfides by reaction of 2-aminoethyl 2-aminoethanethiolsulfonate dihydrochloride (**1**) or 2-acetamidoethyl 2-acetamidoethanethiolsulfonate (**2**) with alicyclic 1,1-dithiols, aliphatic 1,4- and 1,2-di-

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[2] L. Field, T. C. Owen, R. R. Crenshaw, and A. W. Bryan, *J. Am. Chem. Soc.*, **83**, 4414 (1961).

[3] *Cf.* A. Schöberl and A. Wagner, "Methoden der Organischen Chemie" (Houben-Weyl), Vol. 9, E. Müller, Ed., 4th Ed., Georg Thieme Verlag, Stuttgart, 1955, p. 72.