[Contribution No. 689 from the Chemistry Laboratories of Indiana University]

A New Synthesis of Thiophenes and Condensed Thiophenes by Ring Closure of Disulfides[1, 2]

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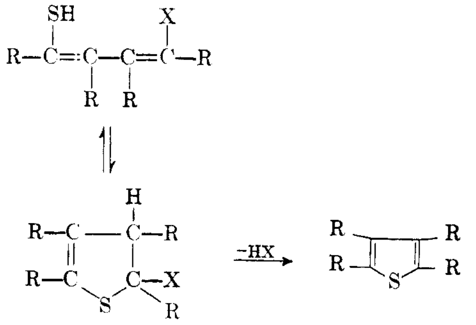
5-Phenyl-2-mercapto-2,4-pentadienoic acid was converted in low yield to 5-phenyl-2-thenoic acid by refluxing with copper chromite in xylene. This conversion was accomplished much more readily, using iodine in organic solvents, and was shown in this case to involve an acid-catalyzed electrophilic attack by disulfide.

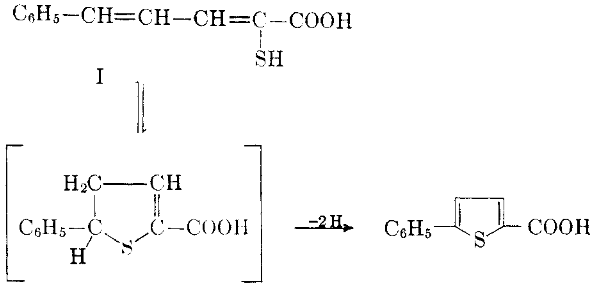
α,α'-Dithiobis(β-arylacrylic) acids were found to undergo similar ring-closures to produce benzothiophene derivatives. In this case ring-closure was promoted by the presence of electron-releasing groups on the aromatic ring. Two new compounds, naphtho[2,1-*b*]thiophene-2-carboxylic acid and naphtho[1,2-*b*]thiophene-2-carboxylic acid, were synthesized by this method, which offers a convenient path to the more complex benzothiophenes and 5-arylthiophenes.

Of all of the unsaturated mercapto-acids studied, only β-2-naphthyl-α-mercaptoacrylic acid was converted to the expected thiophene-2-carboxylic acid by alkaline ferricyanide oxidation. Possible mechanisms for these acidic and alkaline ring closures are briefly discussed.

Ultraviolet spectral maxima for the various thiophenes and thiophene-2-carboxylic acids are reported.

It has previously been suggested[5] that systems which contain the 1-mercapto-1,3-butadiene structure are readily converted to thiophenes because they exist in equilibrium with the 2,3-dihydrothiophene structures, *i.e.*,: Indeed, it was shown that in one such system, where X = H, treatment of a solution of the substance with a dehydrogenating agent, copper chromite, increased the formation of the thiophene product. Furthermore, in another such system, where X = OH, it was found that the conversion to thiophene was promoted by the addition of dehydrating agents to the reaction mixture.[6] In order to investigate this hypothesis further, 5-phenyl-2-mercapto-2,4-pentadienoic acid (I) which contains the desired 1-mercapto-1,3-butadiene system[7] was refluxed in xylene with copper chromite, and after three hours a 10% yield of 5-phenyl-2-thenoic acid (III) was isolated. The conversion of I to III by the mild dehydrogenating agent indicates that there is probably a very small amount of the dihydrothiophene (II) in equilibrium with I in solution. III was identified by its physical properties, derivatives, and absorption spectrum of the decarboxylated product.





I

II

III

Chmelewsky and Friedlander[8] obtained benzothiophene by the alkaline ferricyanide oxidation of *o*-mercaptocinnamic acid. This cyclization was accompanied by decarboxylation, and a sulfenic acid was postulated as an intermediate in the reaction. When solutions of I in dilute sodium hydroxide were treated with potassium ferricyanide, potassium chlorate, sodium hypochlorite, and iodine, III could not be isolated from the amorphous and frequently tarry reaction products. A useful method of isolating even small amounts of III in a rather pure state from large amounts of other oxidation products of I was developed. This method depended on the fact that III was not oxidized by dilute alkaline permanganate at room temperature. Thus a crude mixture containing a little added III could be

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[2] Taken in part from the thesis of Richard E. Cline, presented in partial fulfillment of the requirements for the degree Doctor of Philosophy at Indiana University, June, 1951. A portion of this work was presented before the Organic Division of the American Chemical Society at the 123rd meeting in Los Angeles, 1953.

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[5] Campaigne, *J. Am. Chem. Soc.*, **66**, 684 (1944).

[6] Campaigne and Foye, *J. Org. Chem.*, **17**, 1405 (1952).

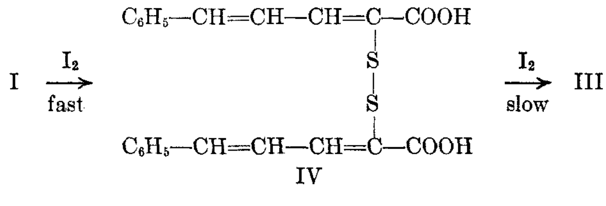
[7] Campaigne and Cline, *J. Org. Chem.*, **21**, 32 (1956).

[8] Chmelewsky and Friedlander, *Ber.*, **46**, 1903 (1913).

stirred with dilute alkaline permanganate, and after removing excess permanganate and manganese dioxide with bisulfite, the solution acidified. III, being the least soluble, precipitated. Other products were benzoic acid and sulfate ion, which were the sole products isolated when I or IV was oxidized with dilute alkaline permanganate.

During the course of the above investigations, in one experiment a large excess of iodine in potassium iodide was added to a solution of I in dilute sodium carbonate, and the mixture was allowed to stand overnight. The following day a precipitate was evident in the mixture, and the solution was acidic. Purification of the precipitate by the permanganate method led to the isolation of 54% of III. Since iodine in alkaline solution did not produce any III, it was apparent that neutral or acidic conditions were necessary. The insolubility of I in aqueous acid led us next to treat I with iodine in ethanol, and after 14 hours at room temperature, III was obtained in 61% yield. Although the reaction of thiols with iodine in ethanol ordinarily leads to disulfides, it had been noted that only tarry products could be obtained when I was treated in this manner for one hour.[7]

By determining the rate of disappearance of iodine from an alcohol solution of I, it was observed that one equivalent of iodine was used up immediately (see Table II) while nearly 18 hours were required to consume a second equivalent of iodine. The obvious inference was that the first equivalent of iodine was consumed in converting I to its disulfide, IV, which then was converted by the second equivalent of iodine to III in a much slower reaction. Accordingly, a sample of IV[7] was treated with iodine in ethanol, and III again was isolated in good yield. A rate study showed that the first equivalent of iodine consumed by the disulfide IV in ethanol required nearly 18 hours, exactly paralleling the consumption of the second equivalent of iodine by I (see Table II). It was therefore certain that IV rather than II was the intermediate in the conversion of I to III by iodine.



Since the disulfide, IV, was only slightly soluble in ethanol, other solvents were investigated. It was found that refluxing IV and iodine in dry benzene led to III in 58% yield, and in another example, glacial acetic acid gave a satisfactory yield of thiophene. However, dioxane proved to be the most generally useful solvent for reaction, and a 68% yield of III was obtained when a solution of IV and iodine in dioxane was kept for 24 hours at room temperature.

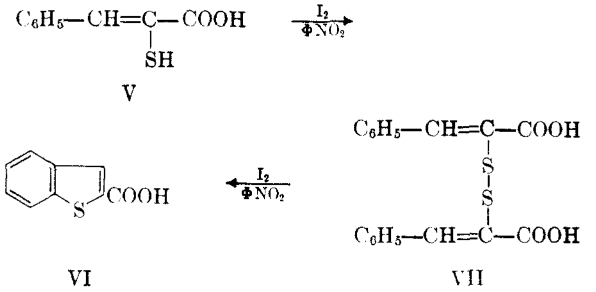
Disulfides have been shown to function as electrophilic reagents under the influence of acid catalysts by Archer and Suter.[9] Lien, McCaulay, and Proell[10] have shown that simple disulfides will attack olefins under strongly acidic conditions, and Holmberg[11] has demonstrated that iodine is an effective catalyst for this reaction. Several experiments were carried out to confirm the hypothesis that ring-closure of IV to III proceeded by an acid-catalyzed reaction. Solution of IV in conc'd sulfuric acid caused charring, and no products were isolated. However, addition of boron trifluoride to a benzene solution of IV caused the formation of a dark red solution, which after 24 hours gave a 40% yield of III. Since there is no oxidizing agent present in this reaction, this yield is actually 80%, according to the equation:

$$\text{IV} \xrightarrow{BF_3} \text{III} + \text{I}.$$

Iodine seemed to be the most effective reagent, since it can function both as a Lewis acid and as an oxidizing agent. The equation is then:

$$\text{IV} + I_2 \xrightarrow{I_2} 2\,\text{III} + 2\,\text{HI}.$$

In view of the fact that the above reaction is apparently an acid-catalyzed electrophilic attack of disulfide, attention was turned to the possibility of effecting similar ring-closures in which the electrophilic attack would occur on an aromatic ring to produce the condensed ring system of benzothiophene. The α-mercaptocinnamic acid system first studied proved difficult. Iodine readily converted V into VII in alcohol, but neither V nor VII produced VI when refluxed with iodine in dioxane for 12 hours. Heating either V or VII with iodine in nitrobenzene at 200° for one or two minutes, however, produced VI in better than 60% yield. The presence of electron-releasing groups on the benzene ring promoted the reaction, since it was found that the disulfide VIII could be converted to 5,6-dimethoxybenzothiophene-2-carboxylic acid (IX) by treatment with iodine in dioxane at 58° for 12 hours. The ring-closure would most likely occur in the less hindered *p*-position, and the correctness of



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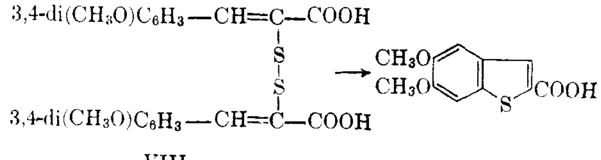
[9] Archer and Suter, *J. Am. Chem. Soc.*, **74,** 4296 (1952).

[10] Lien, McCaulay, and Proell, *Abs. 122nd meeting, Am. Chem. Soc., Sept. 1952,* p. 12-O.

[11] Holmberg, *Arkiv. kemi a. minerol.* **13B,** No. 14, 1 (1939).

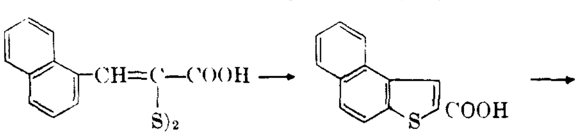
structure IX for this product is indicated by the similarity in properties of this acid and its decarboxylated product to those of 5,6-dimethoxybenzo-



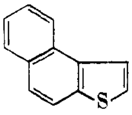
VIII IX

thiophene-2-carboxylic acid and 5,6-dimethoxybenzothiophene which have been prepared unequivocally by Bew and Clemo[12] since this work was completed.

α,α′-Dithiobis(β-1-naphthylacrylic) acid (X) was converted in better than 50% yield to naphtho[2,1-*b*]thiophene-2-carboxylic acid (XI) with iodine in dioxane.

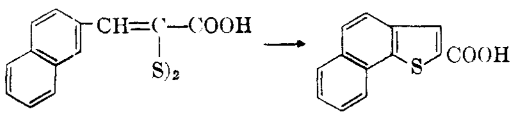


X XI



XII

The structure of XI was confirmed by its conversion to naphtho[2,1-*b*]thiophene (XII), which has recently been described by Tilak[13] and by Carruthers,[14] and by the characteristic ultraviolet spectra. When the isomeric 2-naphthyl derivative, XIII, was treated with iodine in dioxane,



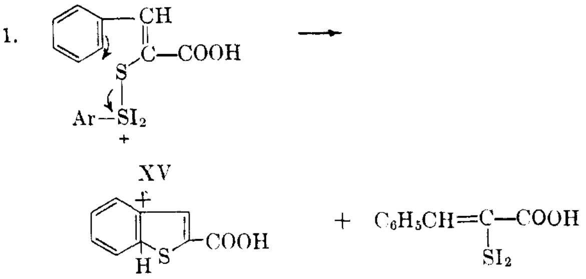
XIII XIV

a naphthothiophene-carboxylic acid was obtained in 90% yield. When decarboxylated, this product gave an oil which was not further identified. The acid was assigned structure XIV, naphtho[1,2-*b*]thiophene-2-carboxylic acid, on the basis of the more likely ring-closure to the 1-position on naphthalene. The improved yield when the ring-closure occurs in the 1-naphthyl position, XIII → XIV, over that when the ring-closure occurs in the 2-position, X → XI, tends to confirm the electrophilic nature of the reaction.

Since Chmelewsky and Friedlander[8] had been able to convert *o*-mercaptocinnamic acid to benzothiophene by ferricyanide oxidation in alkaline solution, all four of the β-aryl-α-mercaptoacrylic acids were subjected to these conditions, but in only one case was any ring-closed product obtained.

β-(2-Naphthyl)-α-mercaptoacrylic acid formed XIV in 40% yield when oxidized at room temperature with potassium ferricyanide in alkaline solution. Although the alkaline ferricyanide ring-closure was effective in only the one most favorable case, other examples of ring-closures of thiols in alkali under oxidizing conditions are known; for example, the well-known oxidation of thiobenzanilide to 2-phenylbenzothiazole by alkaline ferricyanide.[15] More recently[16] iodine in pyridine has been used to effect a similar ring-closure. In these cases, a sulfenium ion stabilized by base (sulfenic acid or sulfenamide) is usually postulated. However, since ferricyanide acts as a monodelectronator, where this reagent is involved the possibility of a free radical mechanism cannot be ruled out. In any event, the different results obtained under acidic and basic conditions in these experiments indicate that different mechanisms are in operation under the different conditions. The acid-catalyzed electrophilic mechanism is illustrated by the following sequence:

1.



XV XVI XVII

2. XVI → VI + H^+
3. XVII + H^+ → V + I_2
4. 2V + $2I_2$ → XV + 2HI.

The ultraviolet absorption data tabulated in Table I were determined principally for purposes of identification. The absorption peaks for 2-phenylthiophene and benzothiophene correspond exactly to those previously reported,[17] [18] and thus confirm the structures of the acids from which they are derived. The absorption spectrum of 5,6-dimethoxybenzothiophene is practically identical to that of benzothiophene, with a bathochromic shift of 8 ± 1 mμ for each peak, indicating the structural relationship. In the same way, the absorption spectrum of naphtho[2,1-*b*]benzothiophene corresponds very closely to that of benzothiophene, except for the peak at 227 mμ, which is shifted toward longer wave lengths.

It should be noted that a dimethoxyphenyl group causes a greater bathochromic effect than a naphthyl group in this series, which agrees with a similar observation in the β-aryl-α-mercaptoacrylic acid series.[7]

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[12] Bew and Clemo, *J. Chem. Soc.*, 1314 (1953).

[13] Tilak, *Proc. Indian Acad. Sci.*, **33A**, 35 (1951).

[14] Carruthers, *J. Chem. Soc.*, 4186 (1953).

[15] Jacobson, *Ber.*, **19**, 1067 (1886).

[16] Katz and Schroeder, *J. Org. Chem.*, **19**, 103 (1954).

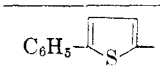
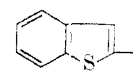
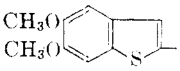
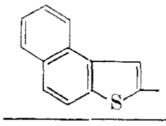
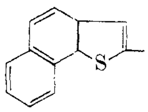
[17] Elpern and Nachod, *J. Am. Chem. Soc.*, **72**, 3379 (1950).

[18] Charlampowicz and Marchlewski, *Bull. intern. acad. polonaise*, **1930A**, 376; *Chem. Abstr.*, **25**, 5097 (1931).

In general, the addition of a carboxyl group to the 2-position of the thiophene ring causes a bathochromic shift of the principle absorption peaks, as would be expected of the increased conjugation. However, in the more complex condensed systems, the magnitude of this shift varies and is unpredictable. The absorption spectra of the various carboxylic acids have similarities which indicate a relationship in structure.

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA AND LOG MOLAR COEFFICIENTS OF THIOPHENE-2-CARBOXYLIC ACIDS AND THIOPHENES

R	R—COOH		R—H	
	$\lambda_{\max}^{m\mu}$	log ϵ	$\lambda_{\max}^{m\mu}$	log ϵ
	310	4.30	282	4.15[a]
	229 276 310	4.26 4.20 3.56	227 256 289 298	4.45[b] 3.75 3.32 3.41
	243 266 301	4.20 3.87 4.22	236 263 297 307	4.43 3.94 3.39 3.48
	236 246 316	4.57 4.50 4.21	243 255 291 302	4.63 4.35 4.01 3.97
	272 301 341 358	4.66 4.08 3.25 3.24		

[a] Elpern and Nachod[17] report $\lambda_{\max}$ 282 mμ, log $\epsilon > 4.0$
[b] Previously reported,[13] $\lambda_{\max}$ 227, 258, 289, 297 mμ.

All of the thiophene derivatives show fluorescence under the ultraviolet lamp. The decarboxylated compounds are bright blue, while the acids were more greenish to reddish, in keeping with the expected bathochromic effect of an additional conjugated group.

Further work on the scope and limitations of this new synthesis of thiophene rings is being carried on.

EXPERIMENTAL

All melting points are corrected. The β-aryl-α-mercaptoacrylic acids and related disulfides used in these experiments were prepared as previously reported.[7]

I. EXPERIMENTS WITH 5-PHENYL-2-MERCAPTO-2,4-PENTADIENOIC ACID (I) AND ITS DISULFIDE (IV)

Iodine oxidation of I. A solution of 2.1 g. (0.01 mole) of I and 5.0 g. (0.019 mole) of iodine in 100 ml. of absolute ethanol was allowed to stand for 14 hours at room temperature, after which it was diluted with 2 l. of water, the excess iodine destroyed with bisulfite, and the precipitate collected. This product was dissolved in 500 ml. of 1% sodium hydroxide containing 4 g. of potassium permanganate, and the mixture was allowed to stand with occasional stirring for one hour. Excess permanganate and manganese dioxide were removed with sodium bisulfite, and the solution acidified with hydrochloric acid. The precipitate weighed 1.25 g. (61%) and melted at 185–187°. Recrystallization from chloroform gave transparent flakes melting sharply at 187–188°, which gave a light blue fluorescence under ultraviolet light. A mixture melting point with the disulfide (IV) (m.p. 184–185°) was depressed to 170–175°.

Anal. Calc'd for $C_{11}H_8O_2S$: S, 15.70; N.E., 214. Found: S, 15.66; N.E., 211.

Steinkopf and Gording[19] report 5-phenyl-2-thenoic acid (III) to melt at 184–185°, and to form a piperidide melting at 103–104°. When the above acid was treated with thionyl chloride, and then added to excess piperidine, a piperidide melting at 102–103° was obtained. In the same way, *5-phenyl-2-thenamide*, melting at 197–198°, was prepared.

Anal. Calc'd for $C_{11}H_9NOS$: N, 6.89. Found: N, 6.84.

2-Phenylthiophene. The above acid was decarboxylated according to the method of Steinkopf and Hanske.[20] A solution of 12 g. (0.037 mole) of mercuric acetate and 3.0 g. (0.015 mole) of 5-phenyl-2-thenoic acid was refluxed for three hours. The solution was diluted with 50 ml. of conc'd hydrochloric acid, and steam-distilled. The cloudy distillate was extracted with ether, with extracts dried and evaporated, and the residue sublimed in a vacuum. White needles were obtained melting at 35–36° and weighing 1.05 g. (44%) which gave a blue-violet positive indophenine test, and a purple color with Ehrlich's reagent (*p*-dimethylaminobenzaldehyde in alcoholic hydrochloric acid). The color tests are described by Kues and Paal,[21] who report 2-phenylthiophene to melt at 40–41°, but more recently its melting point was reported to be 34.0–34.5°.[22] The compound showed a characteristic blue fluorescence under ultraviolet light.

Anal. Calc'd for $C_{10}H_8S$: S, 20.01. Found: S, 19.99.

Copper chromite treatment of I. A solution of 3.0 g. of I in 50 ml. of dry xylene was refluxed with 8 g. of copper chromite powder[23] for 3¹/₄ hours. Acidification of alkaline extracts of the xylene yielded 0.6 g. of white precipitate melting at 178–185°. Recrystallization from ethylene chloride gave 0.3 g. (10%) of transparent needles melting at 187–188°, which did not depress the melting point of III.

Iodine oxidation of the disulfide, IV. A solution of 3.0 g. (0.007 mole) of IV and 3.8 g. (0.015 mole) of iodine in 75 ml. of dioxane was allowed to stand for 24 hours at room temperature. The solution then was diluted with 2 l. of water, decolorized with sodium bisulfite, acidified, and the yellow precipitate was collected. After purification by the permanganate treatment, there was obtained 2.04 g. (68%) of silvery white flakes which melted at 187–188° after one recrystallization, and did not depress the melting point of III.

A similar experiment, in which the reactants were refluxed in dry benzene for three hours, and then allowed to stand overnight, and the products were worked up by alkaline extraction, gave a 58% yield of III.

Boron trifluoride treatment of IV. A solution of 1.0 g. of IV and 6 ml. of 45% boron trifluoride-etherate complex in 100 ml. of dry benzene was refluxed for five hours, and the dark red solution was allowed to stand overnight. After extraction with dilute sulfuric acid to remove excess boron trifluoride, the brown solution was extracted with dilute sodium hydroxide, and the basic solution was acidified with hydrochloric acid. The resulting yellow precipitate was purified by the permanganate treatment, and 0.39 g. (40%) of III, which melted sharply after one recrystallization, was obtained.

Rate of iodine consumption by I *and* IV *in ethanol.* A solu-

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(19) Steinkopf and Gording, *Biochem. Zeitschr.*, **292**, 368 (1937).

(20) Steinkopf and Hanske, *Ann.*, **532**, 246 (1937).

(21) Kues and Paal, *Ber.*, **19**, 3141 (1886).

(22) Voronkov, Brown, Karpenko, and Gol'shtein, *J. Gen. Chem., U.S.S.R.*, **19**, 1356 (1949).

(23) Blatt, *Org. Syntheses*, Coll. Vol. II, 142 (1943).

tion of 0.165 g. (0.8 milliequiv.) of I in 95% ethanol was prepared, and zero time noted upon completion of the operation of rapidly adding from a volumetric pipette 25 ml. of a 0.243 *N* iodine solution in ethanol and diluting with ethanol to a total volume of 200 ml. Concentration at zero time was therefore 0.004 *N* in thiol I, and 0.0304 *N* in iodine. The solution was allowed to stand in the uninsulated volumetric flask at room temperature (23 ± 1°) during the course of the experiment. A standard blank was prepared in the same way, omitting the sulfur compound. At intervals, a 25-ml. aliquot was removed from each of the flasks, quenched in 100 ml. of distilled water, and further quenched at once by the addition of 25 ml. of 0.0216 *N* thiosulfate solution. The titration then was completed with standard thiosulfate and starch indicator. The amount of iodine consumed by the sulfur compound was calculated by difference between the blank and the solution at each time interval. A similar experiment using the disulfide IV was carried out, and the results of these two experiments are presented in Table II.

TABLE II

RATE OF CONSUMPTION OF IODINE BY I AND IV IN ETHANOL. EQUIVALENTS OF IODINE PER EQUIVALENT OF SULFUR COMPOUND

Reaction time, hours	0.05	0.1	0.2	0.5	1.0	2.0	4.0	4.5	10.0	17.5
eq. I_2/eq. I	0.97	1.11		1.13	1.20	1.34	1.51		1.82	1.96
eq. I_2/eq. IV		0.09	0.119	0.184	0.259	0.426		0.506		0.928

II. EXPERIMENTS WITH α-MERCAPTOCINNAMIC ACID (V) AND ITS DERIVATIVES

Benzothiophene-2-carboxylic acid. VI. Iodine (4 g.) was dissolved in 30 ml. of nitrobenzene which was heated to near-boiling, and 0.40 g. of V was added. The mixture was vigorously stirred for one minute, and then was quickly cooled in a water-bath. The product was extracted with dilute sodium hydroxide, and the alkaline solution was decolorized with bisulfite, and acidified with hydrochloric acid. The light brown crystals weighed 0.26 g. (68%) and, after being decolorized with Norit and recrystallized twice from chloroform, afforded white needles melting at 240–241°. In a similar experiment, using 15 g. of iodine and 5 g. (0.014 mole) of α,α'-dithiobicinnamic acid (VII) in 50 ml. of nitrobenzene maintained at 200° for two minutes, 3.0 g. (61%) of the same acid was obtained.

Anal. Calc'd for $C_9H_6O_2S$: S, 17.99. Found: S, 18.18.

Weiszgerber and Kruber[24] report the melting point of VI as 236°, and its amide to melt at 177°. The amide of the above acid was prepared and found to melt at 176–177°.

Anal. Calc'd for C_9H_7NOS: N, 7.91. Found: N, 7.89.

Benzothiophene. A mixture of 2.45 g. (0.014 mole) of VI and 8 g. of mercuric acetate was refluxed in 30 ml. of glacial acetic acid for four hours, after which the mixture was acidified with 10 ml. of conc'd hydrochloric acid and steam-distilled. The distillate was extracted with ether, the extracts dried, and the residues first recrystallized from ethanol and water, and then sublimed under reduced pressure. The yield of white leaflets melting at 31–32° was 0.29 g. (16%). The compound had a naphthalene-like odor, and gave a deep red color in conc'd sulfuric acid, but a negative indophenine test and no color with Ehrlichs reagent. It exhibited a blue fluorescence under ultraviolet light. These properties are characteristic of benzothiophene.[25] The ultraviolet absorption maxima are identical to those previously reported for benzothiophene.[18]

Anal. Calc'd for C_8H_6S: S, 23.80. Found: S, 23.89.

5,6-Dimethoxybenzothiophene-2-carboxylic acid (IX). A solution of 2.0 g. (0.0042 mole) of α,α'-dithiobi(β-veratrylacrylic) acid (VIII) and 2 g. of iodine in 75 ml. of dioxane was maintained at 58° for 12 hours. The solution then was poured into 3 l. of water, decolorized with bisulfite, and the brown precipitate was collected. The crude product was dissolved in dilute sodium hydroxide, treated with Norit, and reprecipitated with dilute acid. The solution was saturated with salt, and the gelatinous precipitate was extracted with ether. The ether extracts were dried and evaporated, leaving light-brown needles which were decolorized in hot toluene with Norit, and recrystallized as silver-white plates melting at 260–261°, and weighing 0.49 g. (25%). No demethylation had occurred, as indicated by a negative ferric chloride test. The acid showed a red fluorescence under ultraviolet light. A similar experiment, using glacial acetic acid as a solvent, gave a 20% yield of the same product.

Anal. Calc'd for $C_{11}H_{10}O_4S$: S, 13.46. Found: S, 13.65.

5,6-Dimethoxybenzothiophene-2-carboxamide. This derivative was found to melt at 214–215°.

Anal. Calc'd for $C_{11}H_{11}NO_3S$: N, 5.91. Found: N, 5.82.

5,6-Dimethoxybenzothiophene. A mixture of 0.77 g. of IX and 0.2 g. of copper-bronze powder was heated in 5 ml. of quinoline at 160–170° for 45 minutes, and then at 200° for a few minutes. The decarboxylated product was worked up in the usual manner, and finally was sublimed under reduced pressure, to give 0.24 g. (38%) of white crystals melting at 99–100°. This product gave a dark green solution in conc'd sulfuric acid, and a deep violet indophenine test, but no color with Ehrlich's reagent even on warming. It exhibited a bright blue fluorescence under ultraviolet light.

Anal. Calc'd for $C_{10}H_{10}O_2S$: C, 61.74; H, 5.19; S, 16.51. Found: C, 61.90; H, 5.25; S, 16.50.

Bew and Clemo[12] report the melting point of IX as 255–257°, and that of 5,6-dimethoxybenzothiophene as 89–91°.

III. EXPERIMENTS WITH THIOLS AND DISULFIDES OF THE β-NAPHTHYLACRYLIC ACID SERIES

Naphtho[1,2-b]thiophene-2-carboxylic acid (XIV). *(a) Iodine oxidation.* A solution of 2.8 g. (0.012 mole) of β-2-naphthyl-α-mercaptoacrylic acid and 6 g. (0.024 mole) of iodine in 150 ml. of dioxane was kept at 50° for 24 hours, after which it was poured into 3 l. of water, and worked up as described above for IX. The resulting acid, after being decolorized several times with Norit, both in alkaline solution and in chloroform, was recrystallized from toluene in white needles melting at 257–258°. The yield of product from the alkaline solution, before recrystallization from organic solvents, was 1.65 g. (60%). In a similar experiment, using 2 g. of the disulfide XIII and 8.0 g. of iodine, maintained at 50° for 36 hours, 1.8 g. (90%) of nearly pure product was obtained from the alkaline solution. One recrystallization from toluene gave silvery-white needles melting at 257–258°, which gave a pink fluorescence under ultraviolet light.

Anal. Calc'd for $C_{13}H_8O_2S$: S, 14.04. Found: S, 14.03.

All attempts to decarboxylate the above acid led to the formation of tarry oils from which no pure products were obtained. Efforts to obtain a picrate from these oils were also unsuccessful. Szmuszkovicz and Modest[26] report naphtho-[1,2-*b*]thiophene to be a yellow oil which forms a picrate melting at 141–142°, an observation which has been confirmed by Carruthers,[14] who reported the compound to melt at 27–28°, and boil at 120°/0.2 mm.

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(24) Weiszgerber and Kruber, *Ber.*, **53**, 1551 (1920).

(25) Bezdrik, Friedlander, and Koenig, *Ber.*, **41**, 227 (1908).

(26) Szmuszkovicz and Modest, *J. Am. Chem. Soc.*, **72**, 571 (1950).

(*b*) *Ferricyanide oxidation.* A solution of 3 g. (0.009 mole) of potassium ferricyanide and 0.5 g. (0.002 mole) of β-2-naphthyl-α-mercaptoacrylic acid in 50 ml. of 1 *N* sodium hydroxide was allowed to stand for 24 hours at room temperature, and then was heated to boiling to dissolve the precipitate which was present. After filtering through a Norit pad to remove some tarry material, the alkaline solution was cooled, and beautiful yellow crystals of a salt of XIV were obtained. On stirring in dilute hydrochloric acid, a white precipitate of XIV, which weighed 0.20 g. (40%) and melted at 257–258° after recrystallizing from chloroform, was obtained. A mixture melting point proved it to be identical with the acid prepared above.

Naphtho[2,1-b]thiophene-2-carboxylic acid (XI). A solution of 2 g. of X and 8 g. of iodine in 100 ml. of dioxane was kept at 45° for 19 hours, and was worked up as previously described. After decolorizing and recrystallizing from hot xylene, silvery-white needles which weighed 1.05 g. (52%) and melted at 277–278° were obtained. This acid exhibited a greenish-blue fluorescence under ultraviolet light.

Anal. Calc'd for $C_{13}H_8O_2S$: S, 14.04. Found: S, 13.84.

Naphtho[2,1-b]thiophene (XII). Decarboxylation of 0.4 g. of the above acid with copper powder and quinoline at 180° for 20 minutes, followed by extraction from acid solution, sublimation, and finally recrystallization from ethanol, gave 0.14 g. (42%) of silvery white plates melting at 113–114° This product formed a dark brown solution in conc'd sulfuric acid, which gave a dark green indophenine test on the addition of isatin. It gave no color with warm Ehrlich's reagent, and a blue fluorescence under ultraviolet light.

Anal. Calc'd for $C_{12}H_8S$: S, 17.39. Found: S, 17.96.

Tilak[13] reported the melting point of naphtho[2,1-*b*]thiophene to be 114–115°, and Carruthers[14] reported m.p. 112–113°, each using different methods of synthesis.

IV. ABSORPTION SPECTRA

The absorption spectra measurements were determined on freshly prepared 95% ethanol solutions using a Beckman Model DU quartz spectrophotometer with a hydrogen discharge tube and 1-cm. quartz cells.

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