

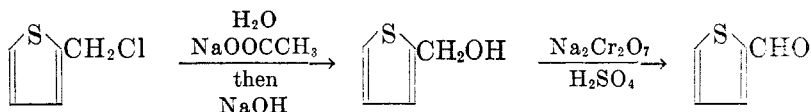
THE PREPARATION OF 2-THIOPHENEALDEHYDE AND SOME OF ITS DERIVATIVES

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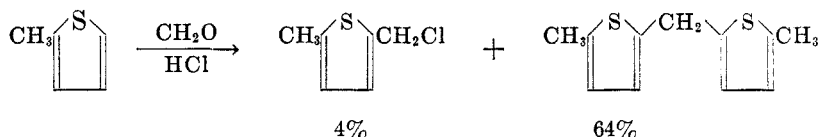
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The various methods which have been used for the preparation of 2-thiophenealdehyde recently have been summarized and a new method involving the use of phosphorus oxychloride and N-methylformanilide has been described in detail (1). We also have studied this method and have found that by using benzene or toluene as a solvent the reaction is more readily controlled and the yields are comparable. Besides this method we have examined an alternate route to 2-thiophenealdehyde starting with 2-thenyl chloride and have studied some of the related 2-chlorothiophene and 2-methylthiophene chemistry.

2-Thenyl chloride was hydrolyzed to 2-thenyl alcohol in 77% yield by boiling with aqueous sodium acetate and then with aqueous sodium hydroxide. Since the first step in this hydrolysis yielded an inseparable mixture of the alcohol and acetate, pure samples of both compounds were prepared in order to compare physical properties. These preparations are included in this paper. Boiling a short while with aqueous sodium hydroxide was sufficient to convert the 2-thenyl acetate to 2-thenyl alcohol. Oxidation of the 2-thenyl alcohol with sodium dichromate and sulfuric acid yielded 65% of 2-thiophenealdehyde. When the hydrolysis and oxidation were conducted successively without isolating the intermediate alcohol, the yield of 2-thiophenealdehyde from 2-thenyl chloride was 62%.



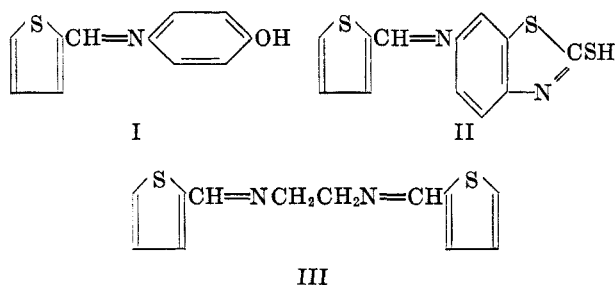
5-Chloro-2-thienyl chloride was hydrolyzed to 5-chloro-2-thienyl alcohol in 64% yield by boiling with aqueous sodium acetate and then with aqueous sodium hydroxide. Under the same conditions 5-methyl-2-thienyl chloride yielded 58% of 5-methyl-2-thienyl alcohol. Since the chloromethylation of 2-methylthiophene yielded only 4% of 5-methyl-2-thienyl chloride and 64% of bis-(5-methyl-2-thienyl)methane, the



5-methyl-2-thienyl chloride was prepared by reducing 5-methyl-2-thiophenealdehyde with iron and acetic acid (2) (56% yield) and then converting the resulting 5-methyl-2-thienyl alcohol to the chloride by means of thionyl chloride

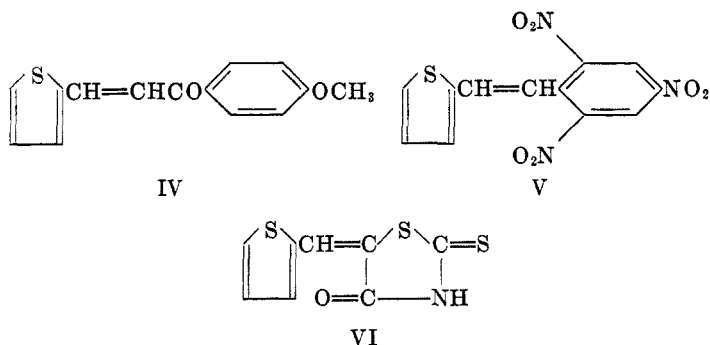
(71% yield). The chloromethylation of 2-methylthiophene has been described (3), but no yields or properties were given.

With *p*-aminophenol, 6-amino-2-mercaptobenzothiazole, and ethylenediamine, 2-thiophenealdehyde gave the corresponding Schiff bases (I, II, and III) in 93–95% yields.

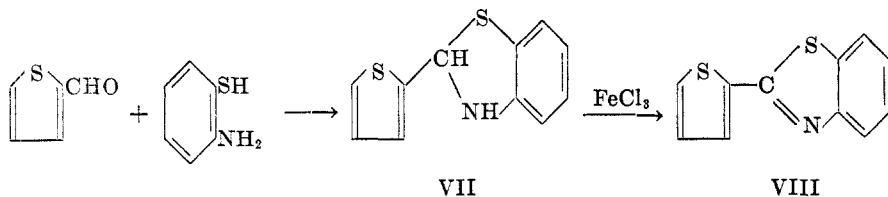


The 2-thenal-*p*-aminophenol was reduced to 2-thenyl-*p*-aminophenol in 11% conversion and 22% yield by means of magnesium and methanol (4).

2-Thiophenealdehyde reacted with malononitrile, acetophenone, *p*-methoxyacetophenone, 2,4,6-trinitrotoluene, and rhodanine to give 80–98% of the corresponding 2-thenal derivatives (IV, V, and VI). 2-Thenalacetophenone has been described previously (5, 6), but no details were given for its preparation and the yield was only 67% (5) in contrast to our yield of 96%.



With *o*-aminothiophenol, 92% of 2-(2'-thienyl)benzothiazoline (VII) was obtained by the method of Lankelma and Sharnoff (7). The corresponding benzothiazole (VIII) was obtained in 74% yield by oxidation with ferric chloride.



EXPERIMENTAL¹

2-Thiophenealdehyde. Most of the 2-thiophenealdehyde used in the condensation reactions was prepared by the method recently described in detail by King and Nord, with the modification that a toluene solvent was used. In a 1.5 molar run 300 cc. of anhydrous toluene was employed and the solution was boiled under reflux for one and one-half hours immediately after mixing. The cooled solution was poured on crushed ice, steam-distilled and the product isolated from the distillate. 2-Thiophenealdehyde (b.p. 85–86°/16 mm., n_D^{25} 1.5884) was isolated in 55% conversion and 67% yield.

5-Methyl-2-thiophenealdehyde and 5-chloro-2-thiophenealdehyde were prepared in the same way using benzene as the solvent in 74% and 75% yields, respectively.

2-Thenyl alcohol from 2-thenyl chloride. A vigorously stirred mixture of 66.3 g. of 2-thenyl chloride (8), 82.0 g. of anhydrous sodium acetate, and a trace of a synthetic non-ionic wetting agent in 500 cc. of water was boiled under reflux for one hour. After the mixture was cooled, 30 g. of sodium hydroxide was added and boiling was continued for fifteen minutes. The organic layer was separated from the cooled mixture and the aqueous layer was extracted three times with benzene. The combined organic layer and extracts were dried over potassium carbonate and distilled to give 44.0 g. (77% yield) of 2-thenyl alcohol, b.p. 97–102°/13 mm., n_D^{25} 1.5612.

With such other hydrolytic agents as sodium hydroxide alone, sodium carbonate, sodium bicarbonate, calcium formate, calcium hydroxide, calcium carbonate, and sodium formate the yield of 2-thenyl alcohol fell to 43–61%.

A higher-boiling fraction, obtained in varying amount in each of these hydrolyses, was found to consist largely of 2-thenyl ether. The pure compound boiled at 120–125°/1 mm., m.p. 38–39°.

Anal. Calc'd for $C_{10}H_{10}OS$: S, 30.5. Found: S, 30.1.

2-Thenyl acetate (9). A mixture of 132.5 g. of 2-thenyl chloride, 82.0 g. of anhydrous sodium acetate, and 1.3 g. of triethylamine was stirred vigorously for three hours while heated to 110–120° by means of an oil-bath. The mixture was cooled and filtered. The residue was treated with water, and the resulting organic layer was separated and combined with the filtrate. The salt solution was extracted twice with benzene. The combined extracts and organic layer were washed successively with dilute hydrochloric acid, aqueous sodium carbonate, and water. After having been dried over sodium sulfate, the solution was distilled to give, besides benzene, 16.6 g. of forerun, b.p. 81–92°/11 mm., and 107.1 g. (69% yield) of 2-thenyl acetate, b.p. 92–97°/11 mm., n_D^{25} 1.5159. The residue was 15.1 g.

The above 107.1 g. of 2-thenyl acetate was boiled for one and one-half hours with 200 g. of acetic anhydride containing 20 g. of anhydrous sodium acetate. The mixture was poured into water, the layers were separated, and the organic portion was washed successively with three portions of water, one of 2% sodium carbonate, and one of water. After it had been dried over calcium chloride, the product was distilled to give 86.9 g. of product, b.p. 94–96°/12 mm., n_D^{25} 1.5142. This was refractionated through a Lecky-Ewell column to give pure 2-thenyl acetate, b.p. 97.3–97.4°/12 mm., n_D^{25} 1.5140.

Anal. Calc'd for $C_7H_8O_2S$: S, 20.5. Found: S, 20.6.

2-Thenyl alcohol from 2-thenyl acetate. A mixture of 49.3 g. of pure 2-thenyl acetate, 40 g. of potassium hydroxide, and 360 g. of 95% ethanol was boiled under reflux for forty-five minutes. After dilution with 1 l. of water, the solution was saturated with sodium chloride. No oil separated. The solution was extracted five times with benzene. The combined extracts were dried over potassium carbonate and fractionated to give 17.6 g. (49% yield) of 2-thenyl alcohol, b.p. 95.2–96.5°/12 mm., n_D^{25} 1.5630. There was a 4.2 g. residue. An analytical sample boiled at 95.7–96.1°/12 mm., n_D^{25} 1.5630.

¹ The carbon-hydrogen and nitrogen analyses are microanalyses performed by the Oakwold Laboratories, Alexandria, Virginia and the Micro-Tech Laboratories, 8000 Lincoln Ave., Skokie, Illinois. The sulfur and chlorine analyses were by Mr. Donald Stoltz, Miss Margaret Magin, and Miss Mary Neal, Monsanto Chemical Company, Dayton 7, Ohio.

Anal. Calc'd for C_6H_6OS : S, 28.1. Found: S, 28.0.

2-Thiophenealdehyde from 2-thenyl alcohol. In a 500 cc., three-necked flask equipped with a stirrer, thermometer, and dropping-funnel and cooled by an ice-salt bath was placed 57.0 g. of 2-thenyl alcohol, 150 cc. of acetone, 83.5 g. of sodium dichromate dihydrate, and 50 cc. of water. While this mixture was stirred at 0–5°, a solution of 55 cc. of conc'd sulfuric acid in 26 cc. of water was added over a four-hour period. After another hour at 0–5°, the mixture was poured on to crushed ice and the resulting suspension distilled with steam. The organic layer was separated from the aqueous portion and the latter was extracted twice with benzene. The combined organic layer and extracts were dried over sodium sulfate and fractionated to give 36.5 g. (65%) of 2-thiophenealdehyde, b.p. 79°/12 mm. [77–78°/12 mm.] n_D^{25} 1.5880.

When benzene was substituted for acetone in the above preparation, the mixture became so viscous it was necessary to dilute it further with water. The yield of 2-thiophenealdehyde fell to 46%. A similar oxidation using chromic acid in aqueous acetic acid yielded 58% of 2-thiophenealdehyde.

2-Thiophenealdehyde from 2-thenyl chloride. In a 2-l., three-necked flask equipped with a stirrer, dropping-funnel, and reflux condenser was placed 132.5 g. of 2-thenyl chloride, 123 g. of sodium acetate, 1 l. of water, and a trace of a non-ionic wetting agent. The vigorously stirred mixture was boiled under reflux for one and one-half hours. After it had been cooled to 40°, 50 g. of sodium hydroxide was added slowly. The mixture was then heated slowly to incipient boiling. It was cooled to 50° and a solution of 110 g. of sodium dichromate in 500 cc. of water was added all at once. While the temperature was held at 40–50°, 200 cc. of 50% sulfuric acid was added over a thirty-minute period. The mixture was heated to boiling and steam-distilled. After the organic layer was separated, the aqueous portion of the distillate was extracted three times with benzene. The combined organic layer and extracts were dried over sodium sulfate and fractionated through a Lecky-Ewell column to give 69.2 g. (62%) of 2-thiophenealdehyde, b.p. 86–87°/17 mm., n_D^{25} 1.5884.

When sodium carbonate was substituted for the sodium acetate and sodium hydroxide in the above experiment, the yield of 2-thiophenealdehyde fell to 48%. Direct oxidation of 2-thenyl chloride with aqueous sodium dichromate gave only 35% of the aldehyde. The yield was increased to 47% when sulfuric acid also was added following the addition of 2-thenyl chloride to the dichromate solution.

5-Chloro-2-thenyl alcohol. A vigorously stirred mixture of 50.1 g. of 5-chloro-2-thenyl chloride, 49.2 g. of anhydrous sodium acetate, a trace of a synthetic non-ionic wetting agent, and 300 cc. of water was boiled under reflux for one hour. The mixture was cooled and 30 g. of sodium hydroxide was added. After boiling for another thirty minutes, the mixture was cooled again. The layers were separated and the aqueous layer was extracted three times with benzene. The combined extracts and organic layer were dried over sodium sulfate and distilled to give 28.3 g. (64% yield) of 5-chloro-2-thenyl alcohol, b.p. 121–126°/15 mm., n_D^{25} 1.5695, and 10.8 g. (26% yield) of 5-chloro-2-thenyl ether, b.p. 205–208°/14 mm., n_D^{25} 1.5907. Pure 5-chloro-2-thenyl alcohol boiled at 116°/12 mm., n_D^{25} 1.5714, d_4^{25} 1.3658. The compound decomposed with the loss of water before a combustion analysis could be performed.

Anal. Calc'd for C_5H_5ClO : M_p, 36.5. Found: M_p, 35.8.

Pure 5-chloro-2-thenyl ether boiled at 147–148°/1.5 mm., n_D^{25} 1.5952, d_4^{25} 1.3896.

Anal. Calc'd for $C_{10}H_9Cl_2OS_2$: Cl, 25.4. Found: Cl, 25.1.

Bis-(5-methyl-2-thenyl)methane. In a 2-l., three-necked flask equipped with a stirrer, thermometer, and dropping-funnel and cooled by an ice-salt bath was placed 294 g. of 2-methylthiophene. While this was stirred at –2° to –7°, there was added over a two-hour and twenty-minute period a solution of 90 g. of paraformaldehyde in 750 cc. of conc'd hydrochloric acid. The mixture was stirred for twenty minutes longer at the same temperature, diluted with 125 cc. of water, and the layers then were separated. The aqueous layer was extracted three times with chloroform and the combined extracts and organic layer were dried over sodium sulfate. Fractionation yielded, in addition to chloroform, 18.7 g. (4%) of 5-methyl-2-thenyl chloride, b.p. 79–83°/10 mm., n_D^{25} 1.5531; 9.0 g. of intermediate, b.p. 83°/10 mm.–122°/1.5 mm., n_D^{25} 1.5583; and 199.1 g. (64%) of bis-(5-methyl-

2-thienyl)methane, b.p. 122°/1.5 mm.-130°/2 mm., n_D^{25} 1.5818. The residue weighed 86.6 g. The product solidified on standing. A sample, after two crystallizations from ethanol, melted at 38.5-39.0°.

Anal. Calc'd for $C_{11}H_{12}S_2$: S, 30.8. Found: S, 30.4.

5-Methyl-2-thenyl alcohol. A vigorously stirred mixture of 33.4 g. of 5-methyl-2-thiophenealdehyde, 165 g. of iron powder, 275 cc. of glacial acetic acid, 280 cc. of water, and 2 g. of nickelous chloride hexahydrate was boiled under reflux for two and one-half hours. The hot mixture was distilled with steam. The distillate, comprising about 1200 cc., was made alkaline with a slight excess of sodium hydroxide and heated to the boiling point with stirring. Upon cooling, it was extracted four times with benzene. The combined benzene extracts were filtered, washed with water, and dried over potassium carbonate. Distillation yielded 18.8 g. (56%) of 5-methyl-2-thenyl alcohol, b.p. 106-111°/13 mm., n_D^{25} 1.5475.

5-Methyl-2-thenyl chloride. To a well-stirred solution of 18.8 g. of 5-methyl-2-thenyl alcohol in 75 cc. of benzene was added over a ten-minute period, with sufficient cooling to keep the temperature below 30°, 30 g. of thionyl chloride. The mixture was stirred fifteen minutes longer at 20-25° and then distilled to give 15.4 g. (71%) of 5-methyl-2-thenyl chloride, b.p. 83-84°/14 mm., n_D^{25} 1.5510.

Anal. Calc'd for C_6H_7ClS : Cl, 24.2. Found: Cl, 24.7.

5-Methyl-2-thenyl alcohol from 5-methyl-2-thenyl chloride. A mixture of 13.3 g. of 5-methyl-2-thenyl chloride, 20 g. of sodium acetate, and 100 cc. of water was stirred under reflux for forty-five minutes. It was then cooled, 5 g. of sodium hydroxide was added, and the stirring under reflux was continued for fifteen minutes. The mixture again was cooled and extracted four times with benzene. The combined extracts were washed with water and dried over potassium carbonate. Distillation yielded 6.8 g. (58%) of 5-methyl-2-thenyl alcohol, b.p. 106-110°/13 mm., n_D^{25} 1.5479. An analytical sample boiled at 105-106°/12 mm., n_D^{25} 1.5471, d_{20}^{25} 1.1409.

Anal. Calc'd for C_6H_8OS : S, 25.0. Found: S, 25.0.

2-Thenal-p-aminophenol. To a solution of 27.5 g. of *p*-aminophenol in 200 cc. of ethanol was added 28.3 g. of 2-thiophenealdehyde. This mixture was boiled under reflux for fifteen minutes with vigorous stirring. The heating was discontinued and the mixture was stirred an additional fifteen minutes. It was then cooled and left in the refrigerator overnight. The tan crystals were separated by filtration, washed twice with 50% ethanol and dried in a vacuum desiccator over potassium hydroxide. The yield was 48.3 g. (94%), m.p. 203-204°. A sample, after three recrystallizations from ethanol, melted at 204-205°.

Anal. Calc'd for $C_{11}H_9NOS$: N, 6.89. Found: N, 7.05.

2-Thenyl-p-aminophenol. In a 2-l., three-necked flask fitted with a stirrer, thermometer, and bulb reflux condenser was placed 30.5 g. of 2-thenal-*p*-aminophenol, 18.0 g. of magnesium turnings, and 750 cc. of methanol which had been dried over magnesium and then distilled. This mixture was stirred vigorously. The reaction was slow at first. When the temperature rose to 32°, the mixture was cooled occasionally by means of an ice-bath. As the reaction became more vigorous with considerable foaming (after twenty minutes), it was necessary to apply the ice-bath continuously to keep the temperature at 30-32°. One hour after the start of the reaction all of the magnesium had dissolved. Then about 500 cc. of methanol was distilled and the residue was poured slowly into 500 cc. of vigorously stirred 5% aqueous sodium hydroxide cooled by an ice-bath. The resulting greenish-brown slurry was diluted with another 250 cc. of 5% sodium hydroxide and filtered. The gelatinous residue was triturated with a further 150 cc. of 5% sodium hydroxide and filtered. After the combined filtrates had been saturated with carbon dioxide, the resulting light tan precipitate was separated by filtration, washed once with water, and dried. It weighed 12.8 g., m.p. 169-185° and was later shown to be recovered 2-thenal-*p*-aminophenol. On cooling the filtrate 3.3 g. (11% conversion, 22% yield) of crude 2-thenyl-*p*-aminophenol was obtained, m.p. 99-102°. An analytical sample was obtained after four recrystallizations from 40-60% methanol, m.p. 107-108°.

Anal. Calc'd for $C_{11}H_{11}NOS$: C, 64.3; H, 5.40.

Found: C, 64.3; H, 5.33.

The crude first precipitate was recrystallized from 95% ethanol, m.p. 194–200°. It was mixed with an authentic sample of 2-thenal-*p*-aminophenol (m.p. 204–205°) and the melting point again determined; m.p. 202–203°. An additional 2.8 g. of 2-thenal-*p*-aminophenol, m.p. 185–190°, was obtained by reworking the original precipitate of magnesium salts, which brought the recovery to 15.6 g. (51%).

2'-Thenal-6-amino-2-mercaptobenzothiazole. A mixture of 1.1 g. of 2-thiophenaldehyde, 1.8 g. of 6-amino-2-mercaptobenzothiazole, and 25 cc. of absolute ethanol was boiled under reflux for one and one-half hours. Another 25 cc. of ethanol was added and the slurry was filtered while hot. The residue was washed twice with ethanol and dried. The crude 2'-thenal-6-amino-2-mercaptobenzothiazole weighed 2.3 g.; m.p. 254–255° (dec.). An additional 0.2 g. which separated from the cooled filtrates brought the yield to 2.5 g. (93%). The entire product was crystallized three times from pyridine, m.p. 255–256° (dec.).

Anal. Calc'd for $C_{12}H_8N_2S_3$: N, 10.14. Found: N, 9.91.

Di-(2-thenal)ethylenediamine. A mixture of 33.6 g. of 2-thiophenaldehyde, 13.1 g. of 69% ethylenediamine, and 100 cc. of benzene was boiled for thirty minutes under a 1-ft. helices-packed column surmounted by a Dean and Stark trap. The theoretical 9.5 cc. of water was collected in twenty minutes. After 60 cc. of benzene had been distilled, the residual solution was cooled and the resulting mush of crystals diluted with 200 cc. of hexane. The crude di-(2-thenal)ethylenediamine was separated by filtration, washed with hexane, and dried over potassium hydroxide in a vacuum desiccator. The main crop weighed 34.4 g., m.p. 88–90°. An additional 1.1 g., m.p. 84–88°, was obtained from the combined cooled filtrates, which brought the total yield to 35.5 g. (95%). A small sample of the first crop was crystallized twice from benzene-hexane, m.p. 90–91°.

Anal. Calc'd for $C_{12}H_{12}N_2S_2$: N, 11.3. Found: N, 11.1.

2-Thenalmalononitrile. A mixture of 11.2 g. of 2-thiophenaldehyde, 6.6 g. of malononitrile, and 100 cc. of absolute ethanol was heated to boiling. After the addition of two drops of piperidine, the heating was continued for an additional five minutes. Upon cooling, the orange crystals were separated by filtration and dried. The yield was 13.4 g., m.p. 97–98°. An additional 2.2 g., m.p. 95–97°, which was obtained by diluting the filtrate with water, raised this yield to 15.6 g. (97%). The first crop was recrystallized twice from 75% ethanol, m.p. 97–98°.

Anal. Calc'd for $C_8H_4N_2S$: S, 20.0. Found: S, 20.0.

2-Thenalacetophenone. To a solution of 13.2 g. of sodium hydroxide in 120 cc. of water and 60 cc. of ethanol held at 12° by means of an ice-bath was added with vigorous stirring 31.2 g. of acetophenone. There was then added 29.0 g. of 2-thiophenaldehyde and the mixture was stirred at 25° for three hours. The resulting oil, after standing in the ice box for two days, crystallized. The yellow crystals were separated by filtration, washed free of alkali with water, washed with 100 cc. of 50% ethanol and dried in a vacuum desiccator over potassium hydroxide. The yield was 53.4 g. (96%), m.p. 52–58°. After four crystallizations from ethanol, an analytical sample melted at 59° [59° (5, 6)].

Anal. Calc'd for $C_{13}H_{10}OS$: C, 72.9; H, 4.70.

Found: C, 72.8; H, 4.74.

2-Thenal-p-methoxyacetophenone was prepared in the same way from 28.0 g. of 2-thiophenaldehyde, 37.5 g. of *p*-methoxyacetophenone, and a solution of 13.2 g. of sodium hydroxide in 120 cc. of water and 60 cc. of ethanol. The crude product weighed 59.6 g. (98% yield), m.p. 104–106°. A sample was recrystallized twice from ethanol, m.p. 106–107°.

Anal. Calc'd for $C_{14}H_{12}O_2S$: C, 68.8; H, 4.95.

Found: C, 68.7; H, 4.94.

1-(2-Thienyl)-2-(2,4,6-trinitrophenyl)ethylene. A mixture of 11.2 g. of 2-thiophenaldehyde, 22.7 g. of 2,4,6-trinitrotoluene, 1 cc. of piperidine, and 100 cc. of xylene was boiled under reflux while the evolved water was collected in a Dean and Stark trap. After fifteen minutes, when 1.9 cc. of water had collected, the solution was cooled. The resulting mass of crystals was diluted with 25 cc. of benzene, cooled and filtered. More product was obtained by diluting the filtrate with hexane and cooling. The precipitates were combined and dissolved in 200 cc. of benzene. The solution was treated with Norit, filtered while hot, diluted

with an equal volume of hexane and cooled. The resulting orange crystals, which were separated by filtration and dried, weighed 21.0 g., m.p. 134–136°. The additional 0.7 g., m.p. 125–131°, which was obtained by diluting the filtrate with hexane brought the total crude yield of the mixed *cis* and *trans* isomers of 1-(2-thienyl)-2-(2,4,6-trinitrophenyl)ethylene to 21.7 g. (68%). A sample of this crude product was crystallized successively from benzene-hexane, benzene, ethanol, and glacial acetic acid; m.p. 132–141°.

Anal. Calc'd for $C_{12}H_7N_3O_6S$: N, 13.08. Found: N, 13.14.

When this experiment was repeated using benzene as the solvent the time required for the production of the theoretical quantity of water was increased to five hours, but the yield rose to 27.2 g. (85%), m.p. 132–142°.

5-(2'-Thenal)-4-keto-2-thiazolinethione. A mixture of 12.3 g. of rhodanine (11), 10.3 g. of 2-thiophenealdehyde, 20 g. of anhydrous sodium acetate, and 100 cc. of glacial acetic acid was boiled under reflux for twenty minutes. Upon cooling, 250 cc. of water was added and the precipitate was separated by filtration, washed with water, and dried *in vacuo* over potassium hydroxide. The orange crystals of 5-(2'-thenal)-4-keto-2-thiazolinethione weighed 16.8 g. (80%), m.p. 227–232°. A sample was crystallized twice from glacial acetic acid, m.p. 232–233°.

Anal. Calc'd for $C_8H_6NOS_3$: S, 42.3. Found: S, 43.2.

2-(2'-Thienyl)benzothiazoline. To a stirred solution of 31.3 g. of *o*-aminothiophenol in 75 cc. of pyridine was added in a thin stream 28.0 g. of 2-thiophenealdehyde. This mixture was stirred at 85–95° for one-half hour, cooled by means of an ice-bath, and acidified with dilute hydrochloric acid. The oil which separated soon solidified. It was separated by filtration, washed with water and dried *in vacuo* over potassium hydroxide and sulfuric acid. The crude yield of 2-(2'-thienyl)benzothiazoline was 50.4 g. (92%), m.p. 73–86°. A sample, after three crystallizations from ethanol in a carbon dioxide atmosphere, was dried *in vacuo* over potassium hydroxide and sulfuric acid, m.p. 95°.

Anal. Calc'd for $C_{11}H_9NS_2$: C, 60.2; H, 4.14.

Found: C, 60.5; H, 3.90.

2-(2'-Thienyl)benzothiazole. To a stirred solution of 31.5 g. of 2-(2'-thienyl)benzothiazoline in 200 cc. of warm ethanol, was added over a one-half hour period a solution of 26 g. of ferric chloride in 50 cc. of ethanol. The mixture was warmed for another half hour, diluted with 100 cc. of water, and cooled. The thick slurry was diluted with another 300-cc. portion of water and filtered. The residue was washed with water and dried *in vacuo* over potassium hydroxide and sulfuric acid. This crude 2-(2'-thienyl)benzothiazole weighed 23.4 g. (74%), m.p. 95–97°. A sample was crystallized twice from ethanol, m.p. 98–99°.

Anal. Calc'd for $C_{11}H_7NS_2$: C, 60.8; H, 3.25.

Found: C, 61.1; H, 3.41.

SUMMARY

A new route to 2-thiophenealdehyde from 2-thenyl chloride has been examined along with some related 2-chlorothiophene and 2-methylthiophene chemistry.

The attempted chloromethylation of 2-methylthiophene yielded 64% of bis-(5-methyl-2-thienyl)methane.

Three Schiff bases were prepared from 2-thiophenealdehyde in 93–95% yields. 2-Thiophenealdehyde reacted with five compounds containing active methyl or methylene groups to give an 80–98% yield of the corresponding 2-thenal derivatives.

With *o*-aminothiophenol, 2-thiophenealdehyde yielded 92% of 2-(2'-thienyl)benzothiazoline. The corresponding benzothiazole was obtained in 74% yield by oxidation with ferric chloride.

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