[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

2-VINYLTHIOPHENES

WILLIAM S. EMERSON AND TRACY M. PATRICK, JR.

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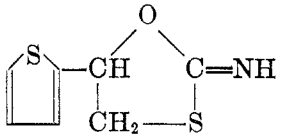
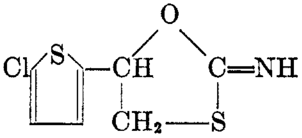
The preparation of 2-vinylthiophene (1) by the reduction of 2-acetothienone and then the dehydration of the resulting carbinol has been examined in detail (2, 3). The highest yield obtained was 54% based on thiophene (2). More recent methods involve the low-temperature condensation of vinyl chloride with 2-thienylmagnesium bromide in the presence of cobaltous chloride to give a 29% yield of 2-vinylthiophene (4) and the dehydration of 2-(2-thienyl)ethanol (from thienylsodium and ethylene oxide) by means of molten potassium hydroxide to give a 38% yield based on 2-chlorothiophene (5). We have studied an alternate route, namely chloroethylation of thiophene with paraldehyde and hydrogen chloride, followed by dehydrochlorination with pyridine. By a careful control of conditions, 2-vinylthiophene has been obtained in 44% conversion and 50% yield. In this same way 5-chloro-2-vinylthiophene has been prepared in 24% conversion and 47% yield and 5-bromo-2-vinylthiophene in 20% conversion and 44% yield from the corresponding halogenated thiophenes.

When an attempt was made to pyrolyze 2-(α-chloroethyl)thiophene over calcium sulfate in order to obtain 2-vinylthiophene, the pyrolysis tube plugged almost immediately. Treatment with alcoholic sodium hydroxide gave mostly 2-(α-ethoxyethyl)thiophene and a little α-(2-thienyl)ethyl ether.

Dibromides have been prepared from all three vinylthiophenes, although that from 2-vinylthiophene decomposed and turned purple on standing in air. While 2-vinylthiophene has been titrated by the Kaufmann method (1), the isolation and properties of the resulting dithiocyanate have not been reported. We have prepared and characterized dithiocyanates from all three vinylthiophenes by treating 2-vinylthiophene and 5-chloro-2-vinylthiophene with thiocyanogen in anhydrous benzene and by treating 5-bromo-2-vinylthiophene with thiocyanogen in glacial acetic acid. When the acetic acid method was applied to the first two compounds mentioned, products were obtained whose empirical formulas corresponded to hypothiocyanous acid addition products of the vinylthiophenes. That from 5-chloro-2-vinylthiophene was examined in detail. It gave negative tests for both the thiocyanate and isothiocyanate groups and evolved ammonia when heated with 25% aqueous sodium hydroxide. After the last test no sulfide ion was found in the solution and acidification and boiling of another hydrolyzed sample caused carbon dioxide to be evolved. Infra-red absorption spectra showed no band at 4.62 microns, which wave length is characteristic for the thiocyano group. A strong band at 6.04 microns can be identified as either a C═N or NH_2 band. A band at 9.14 microns has two possibilities, C—N—C or C—O—

C. By analogy with the behavior of thiocyanoacetone (6) these compounds are probably iminooxathiolanes:





Since these products were obtained either by hydrolysis of the corresponding dithiocyanates or by the addition of hypothiocyanous acid to the vinyl compounds, the oxygen is probably attached to the α-carbon atom. This configuration is favored by the known reactivity of groups in the α-position to thiophene and benzene and by analogy to the mode of addition of hypohalous acids to styrene.

In the preparation of 5-chloro-2-vinylthiophene dithiocyanate a compound believed to be 5-chloro-2-(α-isothiocyano-β-thiocyanoethyl)thiophene also was isolated. It gave a positive test for both the thiocyanate and isothiocyanate groups and the same analysis as the dithiocyanate. Since thenyl thiocyanate readily rearranges to the isothiocyanate (7), it probably is the α-thiocyano group which has rearranged in this case.

5-Chloro-2-vinylthiophene did not add di-*p*-tolyldisulfide in the presence of iodine in anhydrous ether according to the procedure of Holmberg (8). Treatment of 2-vinylthiophene with calcium hypochlorite and carbon dioxide (9) with the object of obtaining the chlorohydrin gave a compound whose analysis and complete inertness to hydrolytic agents suggest it to be β,5-dichloro-2-vinylthiophene. The compound was unsaturated and oxidation with neutral potassium permanganate gave 5-chloro-2-thiophenecarboxylic acid. 5-Chloro-2-vinylthiophene chlorohydrin probably was an intermediate, since in one preparation water was given off during the first part of the distillation. Ring chlorination of thiophene with hypochlorous acid has been observed previously (10).

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EXPERIMENTAL

2-Vinylthiophene. In a 1-liter, three-necked flask were placed 336 g. of thiophene, 176 g. of paraldehyde, and 300 cc. of concentrated hydrochloric acid. While this mixture was stirred and maintained at 10–13° by an ice-salt bath, hydrogen chloride was bubbled in over a thirty-five minute period, at the end of which the solution was saturated. The contents of the flask were poured on ice, the layers were separated, and the organic portion was washed three times with 200-cc. portions of ice-water. This layer was then added with cooling to 316 g. of pyridine containing 2.0 g. of α-nitroso-β-naphthol. After the mixture had stood for one and one-half hours, it was distilled and three fractions were collected at successively lower pressures, the last two over α-nitroso-β-naphthol: I to 70°/175 mm., II to 82°/100 mm., and III to 125°/50 mm. These distillates were combined and poured onto a mixture of ice and 400 cc. of concentrated hydrochloric acid. The layers were separated and the organic portion was washed with very dilute hydrochloric acid and then with very dilute ammonia. After drying over Drierite, the product was filtered and fractionated to give 45.6 g. (13.5% recovery) of thiophene, b.p. 36–47°/150 mm., n_D^{25} 1.5266; 11.8 g. of intermediate, b.p. 47°/150 mm. to 81°/100 mm., n_D^{25} 1.5400; and 191.3 g. (44% conversion, 50% yield) of 2-vinylthiophene, b.p. 65–67°/50 mm. (62–63°/50 mm.) (1, 2), n_D^{25} 1.5710 (n_D^{25} 1.5698) (2). There was a residue of 22.9 g.

In a similar run starting with 84 g. of thiophene, the crude 2-(α-chloroethyl)thiophene was dropped into a tube containing calcium sulfate held at 400–425°. The tube plugged almost immediately. The remainder of the crude 2-(α-chloroethyl)thiophene was added over a one-half-hour period to a solution of 60 g. of sodium hydroxide in 276 cc. of ethanol and 74 cc. of water. After an additional one-half hour at 50–60°, the mixture was poured into 1 liter of water and then extracted three times with benzene. The combined extracts were filtered and distilled to give 61 g. (39%) of 2-(α-ethoxyethyl)thiophene, b.p. 130–150°/170 mm., n_D^{25} 1.5020; 9 g. (7%) of what may be 2-(α-hydroxyethyl)thiophene, b.p. 108–135°/21 mm. (90–103°/14 mm.) (1), n_D^{25} 1.5284 (n_D^{25} 1.5399) (1); and 24 g. (20%) of α-(2-thienyl)ethyl ether, b.p. 135–192°/21 mm., n_D^{25} 1.5505.

An analytical sample of 2-(α-ethoxyethyl)thiophene boiled at 78–79°/16 mm., n_D^{25} 1.4963, d_{25}^{25} 1.021.

Anal.[1] Calc'd for $C_8H_{12}OS$: C, 61.5; H, 7.69.
Found: C, 62.1; H, 7.99.

An analytical sample of α-(2-thienyl)ethyl ether boiled at 150–160°/16 mm. (121–122°/3 mm.) (1), n_D^{25} 1.5754 (n_D^{20} 1.5580) (1), d_{25}^{25} 1.151.

Anal.[1] Calc'd for $C_{12}H_{14}OS_2$: C, 60.5; H, 5.88.
Found: C, 62.0; H, 5.75.

2-Vinylthiophene dibromide was prepared by treating 11 g. of 2-vinylthiophene in 100 cc. of carbon tetrachloride with 5 cc. of bromine in 50 cc. of carbon tetrachloride. The solutions were mixed at ice-bath temperature. Evaporation of the carbon tetrachloride left 21 g. (78%) of 2-vinylthiophene dibromide, a white solid which turned purple on standing in air. An analytical sample was crystallized twice from hexane, m.p. 47–50°. This melting point and all others are corrected.

Anal.[2] Calc'd for $C_6H_6Br_2S$: Br, 59.3. Found: Br, 59.6.

2-Vinylthiophene dithiocyanate. A solution of thiocyanogen in dry benzene was prepared by treating an ice-cold suspension of 194 g. of lead thiocyanate in 300 cc. of benzene with a cold solution of 80 g. of bromine in 300 cc. of benzene. The solid was separated and washed with 150 cc. of benzene. Fifty-five grams of 2-vinylthiophene was added to the filtrate and the solution was allowed to stand all day in the bright sunlight. It was then seeded and placed in an ice-box overnight. The first crop of crystals was separated, and the filtrate was evaporated under reduced pressure at room temperature to a thick syrup. Additional product was filtered from this syrup. The total yield of crude 2-vinylthiophene dithiocyanate was 64 g. (57%). An analytical sample was crystallized four times by dissolving in benzene and precipitating with hexane, m.p. 87°.

Anal.[1] Calc'd for $C_8H_6N_2S_3$: N, 12.4. Found: N, 12.3.

This compound and a number of those following were tested for the presence of the thiocyanate (11) group by boiling a small amount of the solid for three to five minutes with 10% aqueous sodium hydroxide. After cooling, the mixture was acidified with dilute sulfuric acid and a small amount of 1% ferric chloride was added. The appearance of a blood red color constituted a positive test, which was given by vinylthiophene dithiocyanate.

These compounds also were tested for the presence of the isothiocyanate (12) group by shaking a small amount of the solid with aqueous ammoniacal silver nitrate. If necessary the mixture was heated. A black precipitate, which was not obtained with vinylthiophene dithiocyanate, constituted a positive test.

Treatment of 2-vinylthiophene with bromine and potassium thiocyanate in glacial acetic acid, followed by dilution with water, gave an orange solid. Digestion of this material with boiling ethanol extracted a solid, m.p. 140–141° after three crystallizations from ethanol. It is believed to be 5-(2′-thienyl)-2-imino-1,3-oxathiolane.

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[1] Microanalyses performed by the Oakwold Laboratories, Alexandria, Virginia.

[2] Analysis by Mr. Donald Stoltz, Monsanto Chemical Co., Dayton, Ohio.

Anal.[1] Calc'd for $C_7H_7NOS_2$: C, 45.4; H, 3.78; N, 7.57.
Found: C, 45.5; H, 4.02; N, 7.85.

β,5-Dichloro-2-vinylthiophene. In a 2-l., three-necked flask, equipped with a stirrer, thermometer, reflux condenser, dropping-funnel, and gas inlet tube, were placed 55 g. of 2-vinylthiophene, 750 cc. of water, and a trace of Sterox (Monsanto non-ionic synthetic detergent). While this stirred mixture was held at 18–20° by running water, a solution of 82 g. of H.T.H. (a commercial product containing about 70% calcium hypochlorite) in 750 cc. of water was added over a ten-hour period. Carbon dioxide was introduced during the addition. After a twelve-hour period of additional stirring, sodium bisulfite was added, and the mixture was filtered to remove calcium carbonate. A brown oil was separated from the filtrate. The precipitate was washed four times with benzene and each wash was used to extract the filtrate. The combined oil and washings were dried over anhydrous sodium sulfate. Distillation yielded 45 g. (50% based on thiophene or 64% based on H.T.H.) of β,5-dichloro-2-vinylthiophene, b.p. 80°/4–2 mm., n_D^{25} 1.6150. An analytical sample boiled at 116–118°/18 mm., n_D^{25} 1.6169, d_{25}^{25} 1.3885, m.p. 16–18°.

Anal. Calc'd for $C_6H_4Cl_2S$: C, 40.2; H, 2.25; Cl, 39.6.
Found: C[1], 40.7; H[1], 2.55; Cl[3], 39.6.

When 27.3 g. of β,5-dichloro-2-vinylthiophene was boiled for six hours with 18.9 g. of sodium acetate in 75 cc. of water, 24.5 g. (90%) was recovered unchanged, b.p. 64–66°/1.5 mm., n_D^{25} 1.6168. Treatment of 54.6 g. with 15 g. of calcium carbonate suspended in 150 cc. of water for six hours at 120° in an autoclave yielded a 40.5-g. (74%) recovery, b.p. 76–81°/3 mm., n_D^{25} 1.6163–1.6171. Similarly when 40.0 g. was boiled for thirteen hours with 20.5 g. of sodium acetate in 50 cc. of water and 250 cc. of acetone, the recovery was 31.1 g. (77%), b.p. 76–78°/3 mm., n_D^{25} 1.6171–1.6178.

β,5-Dichloro-2-vinylthiophene decolorized a solution of bromine in carbon tetrachloride and the vapors did not fume in moist air. Oxidation with neutral potassium permanganate gave 5-chloro-2-thiophenecarboxylic acid, m.p. 151–152° (146–147°) (13).

5-Chloro-2-vinylthiophene[4] was prepared in the same way as 2-vinylthiophene, starting with 355.5 g. of 2-chlorothiophene, 132 g. of paraldehyde and 225 cc. of concentrated hydrochloric acid. Thirty minutes was required for the saturation with hydrogen chloride and the gas was introduced for another twenty minutes at a maximum temperature of 9°. The distillation from 237 g. of pyridine was conducted to 130°/25 mm. The final distillation yielded 176 g. (50%) of recovered 2-chlorothiophene, b.p. 49–52°/50 mm., n_D^{25} 1.5438; 11.5 g. of intermediate, b.p. 35–73°/20 mm., n_D^{25} 1.5502; and 103.5 g. (24% conversion, 47% yield) of 5-chloro-2-vinylthiophene, b.p. 73–78°/20 mm., n_D^{25} 1.5814. The residual clear, amber resin weighed 55 g. An analytical sample of 5-chloro-2-vinylthiophene boiled at 83.9–84.0°/30 mm., n_D^{25} 1.5820, d_{25}^{25} 1.206.

Anal.[1] Calc'd for C_6H_5ClS: S, 22.2; Cl, 24.5.
Found: S, 22.4; Cl, 24.7.

5-Chloro-2-vinylthiophene dibromide was prepared by adding over a one and one-half-hour period a solution of 48 g. of bromine in 50 cc. of carbon tetrachloride to a solution of 40 g. of 5-chloro-2-vinylthiophene in 300 cc. of carbon tetrachloride held at −5° to −1°. Evaporation of the carbon tetrachloride left 82.7 g. (88%) of 5-chloro-2-vinylthiophene dibromide, m.p. 76°. An analytical sample, after two crystallizations from hexane, showed the same melting point.

Anal.[1] Calc'd for $C_6H_5Br_2ClS$: C, 23.7; H, 1.66.
Found: C, 23.8; H, 1.92.

5-Chloro-2-vinylthiophene dithiocyanate was prepared in the same way as 2-vinylthiophene dithiocyanate starting with 50.6 g. of 5-chloro-2-vinylthiophene and using a thiocyanogen

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[3] Analysis by Miss Mary Neal, Monsanto Chemical Co., Dayton, Ohio.

[4] Since the acceptance of this manuscript an article has appeared by Bachman and Heisey, *J. Am. Chem. Soc.*, **70**, 2378 (1948) describing the properties of these compounds and their preparation by alternative routes.

solution made from 125 g. of lead thiocyanate in 250 cc. of anhydrous benzene and 56 g. of bromine in 300 cc. of anhydrous benzene. The initial precipitate and that obtained by diluting the filtrate with hexane weighed 47.5 g., m.p. 97–98°, and constituted a 52% yield of 5-chloro-2-vinylthiophene dithiocyanate. An analytical sample melted at 99° after two crystallizations from benzene-hexane.

Anal.[1] Calc'd for $C_8H_5ClN_2S_3$: C, 36.9; H, 1.93.
Found: C, 36.8; H, 1.89.

5-Chloro-2-vinylthiophene dithiocyanate gave a positive test for thiocyanate and a negative test for isothiocyanate.

When the original benzene-hexane solution was evaporated to dryness, there remained a crystalline solid which weighed 35.8 g. after washing with ethanol and drying. It was recrystallized from benzene-hexane and then from hexane, m.p. 65°. This compound gave a positive test for both thiocyanate and isothiocyanate and represented a 39% yield of 5-chloro-2-(α-isothiocyano-β-thiocyanoethyl)thiophene.

Anal.[1] Calc'd for $C_8H_5ClN_2S_3$: C, 36.9; H, 1.93; N, 10.74.
Found: C, 37.3; H, 2.10; N, 10.69.

As with 2-vinylthiophene, treatment of 5-chloro-2-vinylthiophene with potassium thiocyanate and bromine in glacial acetic acid yielded 5-chloro-2-vinylthiophene dithiocyanate (18%) and a compound believed to be 5-[5′-chloro-2′-thienyl]-2-imino-1,3-oxathiolane (32%) which melted at 145° after two crystallizations from benzene.

Anal.[1] Calc'd for $C_7H_6ClNOS_2$: C, 38.3; H, 2.76; N, 6.38; S, 29.2.
Found: C, 38.2; H, 2.79; N, 6.80; S, 29.7.

5-[5′-Chloro-2′-thienyl]-2-imino-1,3-oxathiolane gave a negative test for both thiocyanate and isothiocyanate. On boiling with 25% aqueous sodium hydroxide, the compound dissolved, and the evolved vapors turned red litmus paper blue. Subsequent addition of lead acetate gave no black precipitate of lead sulfide. Acidification and boiling of another hydrolysis solution evolved a gas which gave a white precipitate with barium hydroxide.

5-Bromo-2-vinylthiophene.[4] The chloroethylation was conducted in the same manner as for 2-vinylthiophene except that the 88 g. of paraldehyde was dropped over a forty-five-minute period into the mixture of 326 g. of 2-bromothiophene and 150 cc. of concentrated hydrochloric acid during the introduction of the hydrogen chloride. The dehydrochlorination was effected with 158 g. of pyridine and the mixture was distilled to 105°/25 mm. The residue was cooled and washed with water and the organic layer separated and distilled to 100°/15 mm. After the usual washing, fractionation of the combined distillates yielded 96.9 g. of 2-bromothiophene, b.p. 57–73°/30 mm., n_D^{25} 1.5753; 62.4 g. of intermediate, b.p. 73–90°/30 mm., n_D^{25} 1.5908; and 58 g. of 5-bromo-2-vinylthiophene, b.p. 90–103°/30 mm., n_D^{25} 1.6083. Assuming the refractive index of the intermediate to be proportional to the two components present, the intermediate contained 45.5 g. of 2-bromothiophene and 16.9 g. of 5-bromo-2-vinylthiophene. The recovery was, therefore, 142.4 g. (44%) and the conversion 74.9 g. (20%) with a 35% yield. Pure 5-bromo-2-vinylthiophene boiled at 85–87°/16 mm., n_D^{25} 1.6098, d_{25}^{25} 1.5259.

Anal.[1] Calc'd for C_6H_5BrS: C, 38.1; H, 2.67.
Found: C, 38.3; H, 2.99.

5-Bromo-2-vinylthiophene dibromide was prepared from 2.0 g. of 5-bromo-2-vinylthiophene by dissolving the compound in carbon tetrachloirde and adding a slight excess of bromine in carbon tetrachloride. Evaporation of the solution left a quantitative yield of 5-bromo-2-vinylthiophene dibromide, m.p. 80–82°. An analytical sample melted at 83° after two crystallizations from hexane.

Anal.[1] Calc'd for $C_6H_5Br_3S$: C, 20.7; H, 1.44.
Found: C, 21.2; H, 2.05.

5-Bromo-2-vinylthiophene dithiocyanate was prepared by adding a solution of 1.9 g. of 5-bromo-2-vinylthiophene in 5 cc. of glacial acetic acid to a solution of 2.5 g. of potassium thiocyanate in 35 cc. of acetic acid. Then a solution of 1.6 g. of bromine in 10 cc. of acetic acid was added slowly with shaking. After standing for a short time, the mixture was diluted with water, the precipitate separated, and then leached with hot ethanol. When this extract was chilled, 1.3 g. (43%) of 5-bromo-2-vinylthiophene dithiocyanate separated as yellow crystals, m.p. 94–95°. It was recrystallized twice from benzene-hexane, m.p. 96°.

Anal.[1] Calc'd for $C_8H_5BrN_2S_3$: C, 31.5; H, 1.65.
Found: C, 31.8; H, 1.94.

SUMMARY

Thiophene, 2-chlorothiophene, and 2-bromothiophene have been chloroethylated by treatment with paraldehyde and hydrogen chloride followed by dehydrochlorination with pyridine to give, respectively, 2-vinylthiophene, 5-chloro-2-vinylthiophene, and 5-bromo-2-vinylthiophene.

Dibromides and dithiocyanates have been prepared from each of these vinylthiophenes. In the preparation of dithiocyanates from 2-vinylthiophene and 5-chloro-2-vinylthiophene in glacial acetic acid as a solvent, some of the corresponding 5-thienyl (or chlorothienyl)-2-imino-1,3-oxathiolanes appeared as by-products.

Treatment of 2-vinylthiophene with hypochlorous acid gave β,5-dichloro-2-vinylthiophene instead of the expected 2-vinylthiophene chlorohydrin.

DAYTON 7, OHIO.

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