INVESTIGATION IN THE THIOPHTHENE SERIES

COMMUNICATION 2. CYCLIZATION OF SUBSTITUTED (THIENYLTHIO)ACETIC ESTERS AND SOME REACTIONS OF 2-ETHYLTHIOPHTHENE

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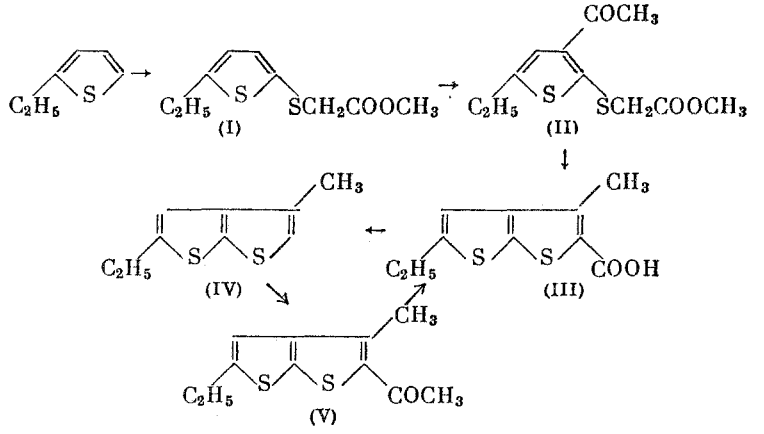
In the preceding communication we showed that by the cyclization of (5-alkyl-3-formyl-2-thienylthio)acetic esters in presence of sodium ethoxide 2-alkylthiophthenes may be prepared with comparative ease in good yield. As will be seen from what follows, this method of cyclization may be extended also to (3-acetyl-5-thienylthio)- and (2-acetyl-5-alkyl-3-thienylthio)-acetic esters, as a result of which 2,4-dialkylthiophthenes and 2,6-dialkylthieno[3,2-b]thiophenes have become accessible. As far as we are aware, there are no data on the synthesis of 2,4-dialkylthiophthenes. Here, it must be mentioned that Friedmann reported that he obtained a 3,4-dialkylthiophthene in about 2% yield by the reaction of octane or octene with sulfur under pressure at 270-280° [1].

By the acetylation of methyl (5-ethyl-2-thienylthio)acetate (I) we obtained an 87% yield of methyl (3-acetyl-5-ethyl-2-thienylthio)acetate (II), by the cyclization of which in alcoholic sodium ethoxide we obtained a 94% yield of 5-ethyl-3-methyl-2-thiophthenecarboxylic acid (III). By the decarboxylation of the latter in presence of copper powder we obtained 2-ethyl-4-methylthiophthene (IV) in about 93% yield. In presence of stannic chloride this last compound was readily acetylated, when, as would be expected, the acetyl group entered into the free α-position. This was confirmed by the fact that the acetylation product (V), on oxidation by Krönke's method [2], gave 5-ethyl-3-methyl-2-thiophthenecarboxylic acid which was found to be identical with the acid (III) obtained in the cyclization of the ester (II).

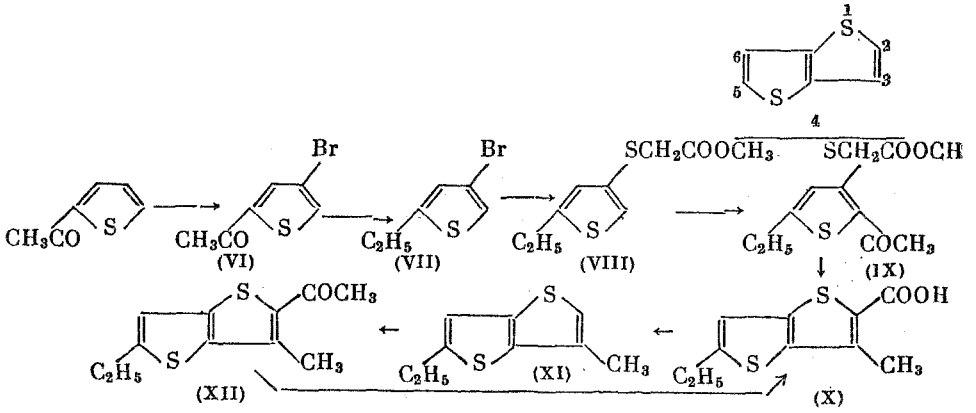
Scheme 1



In view of these results it was of interest to study the possibility of synthesizing alkylated thieno[3,2-b]thiophenes in an analogous way. The known methods of preparing 2-alkylthieno[3,2-b]thiophene itself, are not very effective. Thus, in the cyclization of (3-thienylthio)acetic, 2-(3-thienylthio)propionic, and 2-(3-thienylthio)propionic, and 2-(3-thienylthio)butyric acids in presence of concentrated sulfuric acid Challenger and Holmes [3] obtained, respectively, 13.8% of thieno[3,2-b]thiophene-3-ol, 30% of 2-methylthieno[3,2-b]thiophene-3-ol, and 27% of 2-ethylthieno[3,2-b]thiophene-3-ol, the reduction of which with lithium aluminum hydride gave 80% of thieno[3,2-b]thiophene, 32% of 2-methylthieno[3,2-b]thiophene, and 52% of 2-ethylthieno[3,2-b]thiophene. They synthesized the original 2-(3-thienylthio)alkanoic acids by a very laborious method from 3-thiophenethiol. Tilak and co-workers[4] obtained thieno[3,2-b]thiophene in about 18% yield by the cyclization of 2,2-diethoxyethyl 3-thienyl sulfide in benzene in presence of P_2O_5.

One of us with Vol'kenshtein has developed a comparatively simple method of preparing 4-bromo-2-thienyl methyl ketone [5]. This fact and the work that we had already done on the cyclization of methyl (3-acetyl-5-ethyl-2-thienylthio)acetate enabled us solve the problem of synthesizing 2,6-dialkylthieno[3,2-b]thiophenes. By the reduction of 4-bromo-2-thienyl methyl ketone (VI), prepared in the way indicated [5], we obtained 4-bromo-2-ethylthiophene (VII) in 84% yield. Under the conditions worked out by Gronowitz [6] for the replacement of a halogen atom in the β-position of the thiophene nucleus by an alkylthio group, from (VII) we synthesized methyl (5-ethyl-3-thienylthio)acetate (VIII) in 61.5% yield, and by the acetylation of this we obtained methyl (2-acetyl-5-ethyl-3-thienylthio)acetate (IX) (yield 82%). The cyclization of (IX) in presence of sodium ethoxide gave 5-ethyl-3-methylthieno[3,2-b]thiophene-2-carboxylic acid (X) in 86% yield. The decarboxylation of (X) gave 2-ethyl-6-methylthieno[3,2-b]thiophene (XI) in 84.7% yield, and this on acetylation gave 5-ethyl-3-methylthieno[3,2-b]thiophene-2-yl methyl ketone (XII) in 89.4% yield. By the oxidation of the latter we obtained the acid (X), which confirms that the acetyl group entered the most reactive position (the free α-position) in (XI).

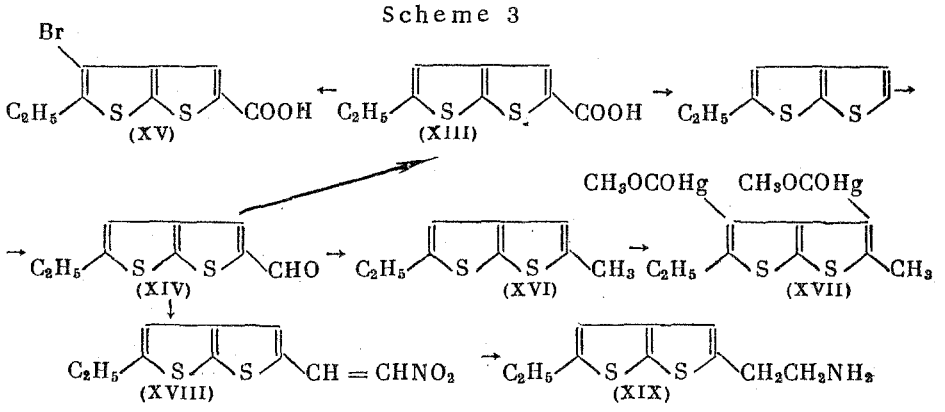
Scheme 2



Hence, 2,4-dialkylthiophthenes and 2,6-dialkylthieno[3,2-b]thiophenes, as also carboxylic acids of the type (III), have now become fairly accessible compounds.

The method that we developed for the preparation of alkylthiophthenes enabled us to undertake an extensive study of the chemistry of thiophthene. We here report the first results of this study. By the action of formylating agents the formyl group can be introduced into the 2-position of thiophthene; thus 5-ethyl-2-thiophthenecarboxaldehyde (XIV) was obtained in 76% yield. Oxidation of the latter gave 5-ethyl-2-thiophthenecarboxylic acid (XIII), identical with the acid obtained in the cyclization of ethyl (5-ethyl-3-formyl-2-thienylthio)acetate (see preceding communication), which shows that formylation occurs in the 2-position of thiophthene. Kizhner reduction of (XIV) gave 2-ethyl-5-methylthiophthene (XVI) in about 70% yield. On attempting to prepare the mono(acetoxymercuri) derivative of 2-ethyl-5-methylthiophthene under conditions analogous to these described by Challenger and Miller [7], we isolated the bisacetoxymercuri derivative (XVII) and unchanged (XVI). An attempt to oxidize 5-ethyl-2-thiophthenecarboxylic acid (XIII) to a sulfone was unsuccessful: part of the acid (XIII) was recovered unchanged. On brominating (XIII) with bromine in glacial acetic acid, we isolated a bromo derivative, probably of structure (XV).

Scheme 3



It is known from the literature [8] that compounds having a 2-aminoethyl group may have the properties of a prophylactic for radiation sickness. In view of this we undertook the synthesis of the appropriate derivative of 2-ethylthiophthene (XIX). By the condensation of 5-ethyl-2-thiophthenecarboxyaldehyde with nitromethane in presence of methylamine hydrochloride by a method described in the literature [9] we obtained 2-ethyl-5-(2-nitrovinyl)thiophthene (XVIII) in 73% yield, and reduction of this with sodium aluminum hydride gave 5-ethyl-2-thiophtheneethylamine. Tests on the hydrochloride of this base showed that it had no protective properties against radiation.

Work on the synthesis of new compounds of the thiophthene series continues.

EXPERIMENTAL

Acetylation of Methyl (5-Ethyl-2-thienylthio)acetate (I). A solution of 108 g of stannic chloride in 80 ml of dry benzene was added over a period of 30 minutes at 0-3° to a mixture of 90 g of (I), 495 ml of dry benzene, and 35 g of acetyl chloride. The mixture was stirred for two hours at room temperature, and hydrochloric acid (45 ml of concentrated HCl + 400 ml of water) was then added. The aqueous layer was separated and extracted with benzene. The combined benzene extracts were washed twice with water and dried over calcium chloride. Benzene was distilled off under somewhat reduced pressure. We obtained 92.8 g (87%) of methyl (3-acetyl-5-ethyl-2-thienylthio)acetate (II); after recrystallization from alcohol it had m.p. 45-45.5°. Found: C 51.07; 51.27; H 5.32; 5.38; S 24.83; 24.53%. $C_{11}H_{14}O_3S_2$. Calculated: C 51.13; H 5.46; S 24.82%.

5-Ethyl-3-methyl-2-thiophthenecarboxylic Acid (III). A solution of 7.7 g of (II) in 30 ml of absolute alcohol was added over a period of ten minutes to an alcoholic solution of sodium ethoxide (prepared from 2.4 g of sodium and 75 ml of absolute alcohol). The mixture was heated for five hours in a water bath, alcohol was driven off, and the residue was dissolved in 200 ml of water acidified to Congo Red with hydrochloric acid. The precipitate formed was filtered off and dried. We obtained 6.4 g (94.3%) of 5-ethyl-3-methyl-2-thiophthenecarboxylic acid (III); after recrystallization from aqueous alcohol it had m.p. 206-207° (decomp.). Found: C 53.34; 53.17; H 4.51; 4.43; S 28.07; 28.15%. $C_{10}H_{10}O_2S_2$. Calculated: C 53.07; H 4.45; S 28.33%.

2-Ethyl-4-methylthiophthene (IV). On decarboxylation of 30 g of the acid (III) in quinoline in presence of copper powder we obtained 22.4 g (93.5%) of 2-ethyl-4-methylthiophthene (IV); b.p. 96-97° (2 mm); n_D^{20} 1.6040. Found: C 59.49; 59.68; H 5.53; 5.54; S 34.87; 35.11%. $C_9H_{10}S_2$. Calculated: C 59.29; H 5.52; S 35.17%.

5-Ethyl-3-methyl-2-thiophthenyl Methyl Ketone (V). 14.3 g of stannic chloride in 20 ml of dry benzene was added over a period of one hour at 1° to a mixture of 10 g of (VI), 105 ml of dry benzene, and 5.1 g of acetyl chloride. The mixture was stirred for three hours at room temperature and then left overnight. We then added dilute hydrochloric acid (10 ml of concentrated HCl + 200 ml of water). The mixture was extracted with benzene, the extract was washed with water, and benzene was distilled off under somewhat reduced pressure. We obtained 12.15 g (98.6%) of 5-ethyl-3-methyl-2-thiophthenyl methyl ketone; after recrystallization from alcohol it had m.p. 50-51°. Found: C 59.13; 59.03; H 5.30; 5.43; S 28.67; 28.58%. $C_{11}H_{12}OS_2$. Calculated: C 58.89; H 5.39; S 28.58%. The oxime, after being recrystallized from alcohol, had m.p. 150-151°. Found: N 5.94; 5.78%. $C_{11}H_{13}ONS_2$. Calculated: N 5.85%.

Oxidation of 5-Ethyl-3-methyl-2-thiophthenyl Methyl Ketone (V). A mixture of 2 g of (V), 10 ml of dry pyridine, and 2.43 g of iodine was heated in a water bath for 40 minutes and left overnight at room temperature; pyridine was then vacuum-distilled off. A solution of 1.9 g of sodium hydroxide in 82 ml of 50% alcohol was added to the residue; the mixture was heated in a water bath for one hour. After extraction with ether [to extract unoxidized (V)] and filtration, the mother solution was acidified to Congo Red with dilute hydrochloric acid. The precipitate formed was crystallized from alcohol. We obtained 0.95 g (46.8%) of 5-ethyl-3-methyl-2-thiophthenecarboxylic acid (III), m.p. 206-207° (decomp.) (in a sealed capillary). Found: C 53.33; 53.27; H 4.39; 4.51; S 28.44; 28.44%. $C_{10}H_{10}O_2S_2$. Calculated: C 53.07; H 4.45; S 28.33%. A mixture with a sample of the acid (III) prepared by the cyclization of methyl (3-acetyl-5-ethyl-2-thienylthio)acetate (II) melted with decomposition in a sealed capillary at 206-207°.

4-Bromo-2-thienyl Methyl Ketone (VI). By the method developed in our laboratory by one of us and Vol'kenshtein [5], from 37.5 g of methyl 2-thienyl ketone we obtained 82.4 g (67%) of 4-bromo-2-thienyl methyl ketone; b.p. 105-107° (4 mm); n_D^{20} 1.6066. The literature [5] gives: b.p. 117-119° (7 mm); n_D^{20} 1.6080.

4-Bromo-2-ethylthiophene (VII). By the Kizhner reduction of 82 g of 4-bromo-2-thienyl methyl ketone we obtained 64.3 g (84.1%) of 4-bromo-2-ethylthiophene; b.p. 88-90° (17 mm); n_D^{20} 1.5611. The literature [5] gives: b.p. 81.5-82.5° (14 mm); n_D^{20} 1.5617.

Methyl (5-Ethyl-3-thienylthio)acetate (VIII). In a stream of nitrogen under conditions excluding the access of moisture a solution of 32 g of 4-bromo-2-ethylthiophene in 70 ml of dry ether was added from a jacketed (cooling to − 70°) dropping funnel to 115 ml of ethereal butyllithium (concentration 0.093 g/ml) at − 70°. The mixture was stirred for five minutes, and 5.5 g of dry sulfur powder was added in small portions. The mixture was then stirred at room temperature for 90 minutes. Dropwise addition was then made of 18.2 g of methyl chloroacetate at − 20°. The contents of the flask were stirred at room temperature for two hours and then treated with 25% ammonium chloride solution at 0-5°. The aqueous layer was separated and extracted with ether; the combined ether extracts were washed twice with water and dried over calcium chloride. After several vacuum distillations we obtained 22.2 g (61.5%) of methyl (5-ethyl-3-thienylthio)acetate (VIII); b.p. 127-130° (2.5 mm); n_D^{20} 1.5522. Found: C 50.27; 50.12; H 5.68; 5.67; S 29.56; 29.48%. $C_9H_{12}O_2S_2$. Calculated: C 50.01; H 5.59; S 29.60%. On treating (VIII) with saturated aqueous ammonia we obtained a 95.7% yield of (5-ethyl-3-thienylthio)acetamide, m.p. 91.5-92.5° after recrystallization from 50% alcohol. Found: C 47.86; 47.72; H 5.58; 5.51; S 31.85; 31.81%. $C_8H_{11}ONS_2$. Calculated: C 47.73; H 5.50; S 31.85%.

Methyl (2-Acetyl-5-ethyl-3-thienylthio)acetate (IX). This was prepared by a method analogous to that described above. From 20 g of methyl (5-ethyl-3-thienylthio)acetate (VIII) we obtained 19.5 g (81.8%) of methyl (2-acetyl-5-ethyl-3-thienylthio)acetate, b.p. 171-173° (2 mm) and m.p. 51.5-52.5° after recrystallization from 50% alcohol. Found: C 51.52; 51.31; H 5.47; 5.40; S 24.87; 24.85%. $C_{11}H_{14}O_3S_2$. Calculated: C 51.31; H 5.46; S 24.82%. A mixture with methyl (3-acetyl-5-ethyl-2-thienylthio)acetate (II) melted at 37-39°.

5-Ethyl-3-methylthieno[3,2-b]thiophene-2-carboxylic Acid (X). This was synthesized by the method described for the experiment on the preparation of (III). From 18.1 g of methyl (2-acetyl-5-ethyl-3-thienylthio)acetate (IX) we obtained 13.65 g (86.2%) of 5-ethyl-3-methylthieno[3,2-b]thiophene-2-carboxylic acid which, after recrystallization from alcohol, had decomp. temp. 219.5-220.5°. Found: C 53.12; 53.40; H 4.81; 4.73; S 28.24; 28.40%. $C_{10}H_{10}O_2S_2$. Calculated: C 53.07; H 4.45; S 28.33%. A mixture with 5-ethyl-3-methyl-2-thiophthenecarboxylic acid (III) melted at 193.5-195.5°.

2-Ethyl-6-methylthieno[3,2-b]thiophene (XI). This was prepared in a yield of 6.1 g (85%) by the decarboxylation of 9 g of 5-ethyl-3-methylthieno[3,2-b]thiophene-2-carboxylic acid; b.p. 87-90° (2 mm); n_D^{20} 1.6052. Found: C 59.19; 59.28; H 5.43; 5.45; S 35.17; 35.21%. $C_9H_{10}S_2$. Calculated: C 59.29; H 5.52; S 35.17%.

5-Ethyl-3-methylthieno[3,2-b]thiophene-2-yl Methyl Ketone (XII). This was prepared as described for the synthesis of the ketone (V). From 4.7 g of 2-ethyl-6-methylthieno[3,2-b]thiophene we obtained 5.15 g (89.4%) of 5-ethyl-3-methylthieno[3,2-b]thiophene-2-yl methyl ketone, m.p. 79-80° after recrystallization from dilute alcohol. Found: C 59.03; 59.24; H 5.32; 5.42; S 28.30; 28.71%. $C_{11}H_{12}OS_2$. Calculated: C 58.89; H 5.39; S 28.58%.

The oxime of this ketone melted at 129-130° after recrystallization from alcohol. Found: N 6.02; 5.88%. $C_{11}H_{15}ONS_2$. Calculated: N 5.85%.

On oxidation of 1.5 g of the ketone (XII) under the conditions described for the experiment on the preparation of the acid (III) we obtained 1.4 g (92.7%) of 5-ethyl-3-methylthieno[3,2-b]thiophene-2-carboxylic acid, m.p. 219.5-220.5°. Found: C 53.22; 53.38; H 4.62; 4.58; S 28.47; 28.41%. $C_{10}H_{10}O_2S_2$. Calculated: C 53.07; H 4.45; S 28.33%. A mixture with the acid (X) obtained by the cyclization of the ester (IX) melted without depression at 219.5-220.5°.

Formylation of 2-Ethylthiophthene. 18.3 g of phosphoryl chloride was added to 17.6 g of N-methylformanilide under conditions that excluded the access of moisture. After 20 minutes 15.1 g of 2-ethylthiophthene was added dropwise with stirring at 20-26°. The mixture was stirred for four hours at 20-30° and allowed to stand overnight; it was stirred further for five hours at room temperature and then treated with ice and water and extracted three times with ether. The combined ether extract was washed with water, with saturated sodium bicarbonate solution, and again with water; it was dried over magnesium sulfate. Ether was distilled off, and the residue was vacuum-distilled. We obtained 13.5 g (76.3%) of 5-ethyl-2-thiophthenecarboxaldehyde (XIV); b.p. 152-154° (5 mm); n_D^{20} 1.6689. Found: C 55.62; 55.62; H 4.28; 4.13; S 32.62; 32.76%. $C_9H_8ONS_2$. Calculated: C 55.07; H 4.10; S 32.66%. After being crystallized from alcohol the oxime of this aldehyde had m.p. 178-179°. Found: N 6.89; 6.99%. $C_9H_9ONS_2$. Calculated: N 6.63%.

Oxidation of 5-ethyl-2-thiophthenecarboxaldehyde. By the oxidation of 5-ethyl-2-thiophthenecarboxaldehyde with silver oxide we obtained 5-ethyl-2-thiophthenecarboxylic acid (XIII) in 82.5% yield; m.p. 213-214° after crystallization from aqueous alcohol. Found: C 51.26; 51.33; H 3.75; 3.77; S 30.38; 30.28%. $C_9H_8O_2S_2$. Calculated: C 50.91; H 3.79; S 30.20%. A mixture with the 5-ethyl-2-thiophthenecarboxylic acid prepared by the cyclization of ethyl (5-ethyl-3-formyl-2-thienylthio)acetate (see preceding communicaton) melted without depression at 213-214°.

2-Ethyl-5-methylthiophthene (XVI). A mixture of 17 g of 5-ethyl-2-thiophthenecarboxaldehyde, 98 ml of ethylene glycol, and 18 g of hydrazine hydrate was heated to 140° and then cooled to 60°; at this temperature 17.4 g of potassium hydroxide was added. The mixture, which contained a crystalline product, was heated for one hour at 190°; it was then cooled to room temperature, poured into 600 ml of water, and extracted three times with ether. The extract was washed with water, with dilute hydrochloric acid, with water, with saturated sodium bicarbonate solution, and again with water; it was dried over calcium chloride. Ether was distilled off, and the residue was vacuum-distilled. We obtained 10.8 g (69.2%) of 2-ethyl-5-methylthiophthene; b.p. 119-120° (5 mm); n_D^{20} 1.60402. Found: C 59.24; 59.20; H 5.49; 5.53; S 35.44; 35.19%. $C_9H_{10}S_2$. Calculated: C 59.29; H 5.52; S 35.17%.

Preparation of the Bisacetoxymercuri Derivative of 2-Ethyl-5-methylthiophthene. A mixture of 1 g of 2-ethyl-5-methylthiophthene in 4 ml of methanol and a solution of 1.9 g of $Hg(OCOCH_3)_2$ in 30 ml of water was prepared in a flask having a ground-in stopper. The mixture was shaken at room temperature in a shaker for 55 hours. The resulting white precipitate was filtered off, washed with alcohol, and dried. The filtrate was extracted twice with ether, and the extract was washed with water and dried over calcium chloride. Ether was distilled off, and we obtained 0.43 g of 2-ethyl-5-methylthiophthene; b.p. 101-103° (2.5 mm); n_D^{20} 1.6029. The precipitate was recrystallized from nitrobenzene; we obtained 1.96 g [93.3% yield on the $Hg(OCOCH_3)_2$ taken] of the bisacetoxymercuri derivative of 2-ethyl-5-methylthiophthene (XVII), m.p. 236-237° (decomp.). Found: C 23.16; 23.04; H 2.11; 1.99%. $C_{13}H_{14}O_4Hg_2S_2$. Calculated: C 22.32; H 2.01%. The mercury content was determined by the method described by Adams and co-workers [10]. Found: Hg 57.07%. Calculated: Hg 57.35%.

2-Ethyl-5-(2-nitrovinyl)thiophthene (XVIII). A mixture of 10.4 g of 5-ethyl-2-thiophthenecarboxaldehyde, 3.24 g of nitromethane, 0.27 g of methylamine hydrochloride, 0.33 g of dry sodium carbonate powder, and 11 ml of absolute alcohol was shaken for five minutes and left at room temperature for four days. The yellowish-red precipitate formed was filtered off and dried. After crystallization from ethyl acetate we obtained 7.05 h (56%) of 2-ethyl-5-(2-nitrovinyl)thiophthene, m.p. 153-154°. Found: C 50.32; 50.33; H 3.92; 3.73; S 26.80; 26.69%. $C_{10}H_9O_2NS_2$. Calculated: C 50.18; H 3.79; S 26.79%.

5-Ethyl-2-thiophtheneethylamine (XIX). In a stream of dry nitrogen under conditions excluding the access of moisture a solution of 4.4 g of 2-ethyl-5-(2-nitrovinyl)thiophene in 70 ml of dry ether and 140 ml of dry benzene was added to a suspension of 1.56 g of lithium aluminum hydride in 150 ml of dry ether (with boiling of the ether). The mixture was stirred for 30 minutes and then cooled to 5°; 2 ml of water and 100 ml of 20% of potassium sodium tartrate solution were added dropwise at 5-10°. The aqueous layer was separated and extracted with three 300 ml portions of ether. The ether extracts were combined, washed with water, and dried over magnesium sulfate. Ether was distilled off, and the residue was vacuum-distilled twice. We obtained 1.81 g (60.3%) of 5-ethyl-2-thiophtheneethylamine; b.p. 147-148° (3 mm); n_D^{20} 1.6091. Found: C 57.09; 56.88; H 6.28; 6.23; S 30.00; 29.87%. $C_{10}H_{13}NS_2$. Calculated: C 56.87; H 6.10; S 30.34%. The picrate of this base, after recrystallization from alcohol, melted at 183-184°. Found: C 43.59; 43.68; H 3.60; 3.72; S 14.73; 14.55%. $C_{16}H_{16}O_7N_4S_2$. Calculated: C 43.63; H 3.66; S 14.54%. The hydrochloride of the base (XIX), after being crystallized from alcohol, melted with decomposition at 250-251°. Found: C 48.52; 48.41; H 5.82; 5.64%. $C_{10}H_{14}NClS_2$. Calculated: C 48.46; H 5.69%.

Bromination of 5-Ethyl-2-thiophthenecarboxylic Acid. A solution of 1.2 g of bromine in 5 ml of glacial acetic acid was added dropwise at room temperature to a solution of 1.6 g of 5-ethyl-2-thiophthenecarboxylic acid (XIII) in 50 ml of glacial acetic acid, and the mixture was stirred at room temperature for five hours and diluted with water. The precipitate formed was filtered off, washed with water, and dried. After five crystallizations from alcohol we obtained 0.8 g (38.1%) of a substance, which was probably 4-bromo-5-ethyl-2-thiophthenecarboxylic acid (XV), m.p. 209-210°. Found: C 37.17; 37.27; H 2.47; 2.52%. $C_9H_7O_2BrS_2$. Calculated: C 37.12; H 2.42%.

SUMMARY

1. An accessible method was developed for the preparation of 2,4-dialkylthiophthenes and 1,6-dialkylthieno[3,2-b] thiophenes.

2. By the cyclization of (3-acetyl-5-ethyl-2-thienylthio)acetic and (2-acetyl-5-ethyl-3-thienylthio)acetic esters good yields were obtained of 5-ethyl-3-methyl-2-thiophthenecarboxylic and 5-ethyl-3-methylthieno[3,2-b]-thiophene-2-carboxylic acids, and by the decarboxylation of these 2-ethyl-4-methylthiophthene and 2-ethyl-6-methylthieno[3,2-b]thiophene, respectively, were obtained.

3. Some transformations of 2-ethylthiophthene were studied.

LITERATURE CITED

1. W. Friedmann, Ber. 49, 1344 (1916).
2. F. Krōhnke, Ber. 66, 604 (1933); L. C. King, J. Amer. Chem. Soc. 66, 894 (1944).
3. F. Challenger and J. L. Holmes, J. Chem. Soc. 1837 (1953).
4. V. V. Chaisas and B. D. Tilak, Current Sci. 22, 184 (1953); Proc. Indian Acad. Sci. 39A, 14 (1954); B. D. Tilak, Tetrahedron, 9, No. 1/2, 76 (1960).
5. Ya. L. Gol'dfarb and Yu. B. Vol'kenshtein, Dokl. AN SSSR 128, 536 (1959).
6. S. Bronowitz, Arkiv kemi 269 (1958).
7. F. Challenger and S. A. Miller, J. Chem. Soc. 1005 (1939).
8. F. Yu. Rachinskii, A. S. Mozzhukhin, N. M. Slavachevskaya, and L. I. Tank, Uspekhi khimii 28, 1488 (1959); E. F. Romantsev and A. V. Savich, Chemical Protection from Ionizing Radiations [in Russian], Gosizdat. med. lit., Moscow (1958).
9. W. Knoevenagel, Ber. 37, 4507 (1904).
10. R. Adams, F. L. Roman, and W. N. Sperry, J. Amer. Chem. Soc. 44, 1781 (1922).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
