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THE SYNTHESIS OF 2,5-DIARYLTHIOPHENES[1]

E. CAMPAIGNE and WILLIAM O. FOYE[2]

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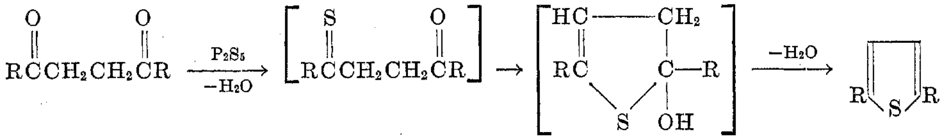
Fusion of the diaroylethanes with phosphorus pentasulfide produces the 2,5-diarylthiophenes. By this method, Kapf and Paal (1) claimed the preparation of 2,5-diphenylthiophene in 60% yield. Holleman (2) also synthesized 2,5-di-*p*-tolylthiophene by this procedure. The reaction is generally unsatisfactory, due to tarry products and unpredictable yields. Since phosphorus pentasulfide acts as a dehydrating agent as well as a sulfurizing agent, it was conceivable that the conversion of 1,4-diketones to thiophenes might procede through the formation of the furan as an intermediate. To test this hypothesis, parallel experiments were carried out, in which acetonylacetone and 2,5-dimethylfuran were treated with phosphorus pentasulfide in an identical manner. Acetonylacetone gave a 70% yield of 2,5-dimethylthiophene, but 2,5-dimethylfuran gave only 13%. In another pair of experiments, 1,2-dibenzoylethane and 2,5-diphenylfuran were used. The former gave 25% of 2,5-diphenylthiophene, but the latter gave none. From these experiments it was concluded that the furan was not an intermediate in the formation of thiophenes from 1,4-diketones, and that therefore the reaction must procede by way of initial thione formation, possibly as follows:



A review of the literature (3) shows that a much superior method of synthesizing thiones involves treatment of the ketone with hydrogen sulfide in the presence of an acid catalyst. It was therefore decided to investigate the possibility of synthesizing some 2,5-diarylthiophenes by treating the appropriate diaroylethanes with hydrogen sulfide. Mitra (4) had used a similar reaction to prepare ethyl 5-ethoxy-2-methyl-3-thenoate from ethyl β-carbethoxylevulinate, but did not report the yield.

Good yields of the required diaroylethanes were obtained by the procedure described by Lutz (5). Fumaryl chloride was condensed with the appropriate benzene derivative, and the resulting *trans*-diaroylethylene or its dibromide (6) was reduced by fresh sodium hydrosulfite in very dilute solution. In the case of 1,2-di-*p*-methoxybenzoylethane, the best yield was obtained by reduction of the

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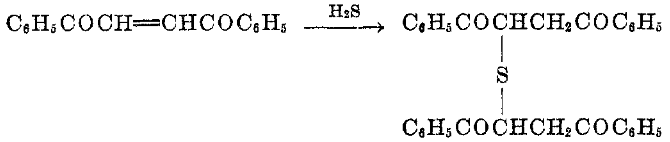
[1] Taken in part from the thesis of William O. Foye, submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy at Indiana University, 1948. Presented before the Organic Division at the 114th Meeting of the American Chemical Society in St. Louis, September, 1948.

[2] Indiana University Fellow in Organic Chemistry, 1947–1948. Present Address: School of Pharmacy, University of Wisconsin, Madison, Wisconsin.

dibromide, but the reverse was true for 1,2-di-*p*-bromobenzoylethane. A comparison of yields and products in the reduction is made in Table I.

A reduction with hydrogen sulfide was considered, due to the resemblance of *trans*-dibenzoylethylene to quinones in its ease of reduction. Furthermore Mitra (7) had obtained some 2,3,5-triphenylthiophene when 1-phenyl-1,2-dibenzoylethylene was treated with hydrogen sulfide and dry hydrogen chloride. It was therefore possible that one might convert the ethylene directly to the desired thiophene by this reaction. However, when *trans*-dibenzoylethylene (I) was treated with hydrogen sulfide in alcohol solution, a compound believed to be bis(1,2-dibenzoyl)ethyl sulfide (II) was formed.



$$C_6H_5COCH{=}CHCOC_6H_5 \xrightarrow{H_2S} \begin{array}{c} C_6H_5CO\overset{}{C}HCH_2COC_6H_5 \\ | \\ S \\ | \\ C_6H_5COCHCH_2COC_6H_5 \end{array}$$

I II

II formed a trioxime, and was readily desulfurized with Raney nickel to 1,2-dibenzoylethane. II was also obtained on heating I in a sealed tube with colorless ammonium sulfide. Treatment of *cis*-dibenzoylethylene with hydrogen sulfide gave no reaction.

A great many experiments were carried out in which the diaroylethanes were treated with hydrogen sulfide and hydrogen chloride, involving various temperatures, solvents, and catalysts. Due to the solubilities of the diketones, the reaction was best carried out in non-polar solvents such as chloroform or benzene, to which was added anhydrous zinc chloride or stannic chloride. This last substance apparently functions as a dehydrating agent rather than an acid catalyst since acetic anhydride also promoted the reaction. Table II shows the results of a set of parallel experiments in which 1.0 g. of di-*p*-bromobenzoylethane in 40 ml. of chloroform was treated with hydrogen sulfide and hydrogen chloride for one hour at room temperature. In the first example, no additional reagent was used, but in the last three, 1.5 g. of acetic anhydride, zinc chloride, or stannic chloride was added. It is obvious that the last two substances greatly promote the reaction. Although stannic chloride appears to give better yields, zinc chloride produced a cleaner product in some cases. Since the unreacted diketones may be recovered and used again, the yields are practically quantitative when zinc chloride or stannic chloride are added to the reaction mixture.

It is curious that when bromine was present on the ethane portion of the diaroylethane molecule, thiophene formation was inhibited completely. None of the dibromides could be converted to the expected 2,5-diaryl-3,4-dibromothiophenes by this reaction.

2,5-Di-*p*-anisylthiophene (III) and 2,5-di-*p*-bromophenylthiophene (IV) were produced for the first time by this reaction. III was readily demethylated to 2,5-di-*p*-hydroxyphenylthiophene, which was in turn acetylated to 2,5-di-*p*-acetoxyphenylthiophene. IV was converted to 2,5-di-*p*-aminophenylthiophene by heating with ammonia and cuprous bromide in a sealed bomb.

The bromination of 2,5-diphenylthiophene was reported by Fromm (8) to yield a tetrabromide melting at 203°. Using Fromm's procedure, it was possible by fractional crystallization to obtain a dibromide (V) and a tribromide (VI).

TABLE I

THE SODIUM HYDROSULFITE REDUCTION OF DIBENZOYLETHYLENES AND THE DIBROMIDES

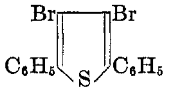
PRODUCT	YIELD FROM ETHYLENE, %	M.P., °C.	YIELD FROM DIBROMIDE, %	M.P., °C.
1,2-Dibenzoylethane	40–70	139–142	50–92	139–142
1,2-Di-*p*-bromobenzoylethane	58–70	180–181	60	172–178
1,2-Di-*p*-methoxybenzoylethane	27	144–149	40–77	150–151

TABLE II

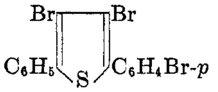
THE EFFECT OF DEHYDRATING AGENTS ON THE FORMATION OF 2,5-DI-*p*-BROMOPHENYLTHIOPHENE

DEHYDRATING AGENT	YIELD, %	M.P., °C.	RECOVERED DIKETONE, %
None	0	—	80
Acetic anhydride	5	183–193	66
Zinc chloride	56	197–198	38
Stannic chloride	73	198–199	17

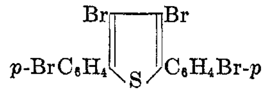
The only product obtained on bromination of IV was a tetrabromide (VII) melting at 209–210°. Since the bromination of the thiophene ring would take place most readily, the structures of the three bromination products are probably as shown.



V

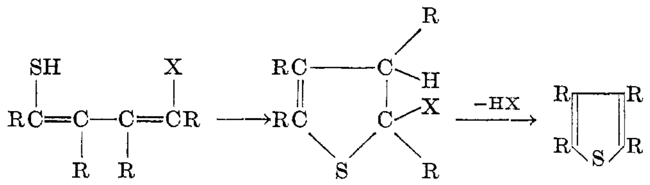


VI



VII

The ready conversion of 1,4-diketones to thiophenes by conditions favorable to the formation of thiones and the enhancement of this reaction by dehydrating agents, conforms to a mechanism previously suggested (9) involving 1-mercapto-1,3-butadienes or structures which can rearrange to this intermediate, *i.e.*:



Many of the recorded thiophene syntheses can be interpreted as occurring by this same mechanism. See, for example, the work of Mitra (7), Chmelewsky and

Friedlander (10), Hansch and Blondon (11), and Moore and Greensfelder (12).

Acknowledgement. The authors wish to express thanks to the Graduate School of Indiana University for a Fellowship, and to Dr. A. L. Wilds, through whose courtesy the microanalysis of the tetrabromide was done. The microanalysis for nitrogen were carried out by Mrs. Betty Jarvis.

EXPERIMENTAL[3]

Preparation of 2,5-dimethylthiophene. When 20 g. (0.175 mole) of acetonylacetone was added dropwise to a boiling mixture of 25.7 g. (0.116 mole) of phosphorus pentasulfide in 50 ml. of dry tetralin in a Claisen flask, crude 2,5-dimethylthiophene rapidly distilled. Refractionation of this product gave 13.5 g. (70%) of colorless product boiling at 134–135°. This is an improvement over the sealed-tube method of Paal (13). When phosphorus pentoxide was substituted for the pentasulfide in this preparation, 2,5-dimethylfuran was obtained in 53% yield of a product boiling at 93–94°, which is also an improvement over the method previously reported (14).

A stirred mixture of 14.9 g. (0.067 mole) of phosphorus pentasulfide in 30 ml. of tetralin was heated to 120°, and 10 g. (0.10 mole) of 2,5-dimethylfuran was added. The mixture was refluxed for 20 minutes, and the resulting dark red solution was filtered while hot and dried over calcium chloride. Refractionation of the first distillation product gave 1.5 g. (13%) of colorless 2,5-dimethylthiophene boiling at 134–135°.

Preparation of 2,5-diphenylthiophene by the phosphorus pentasulfide method. In a 300-ml. flask equipped with a stirrer, funnel, and condenser with a gas trap attached was placed 1.0 g. (0.004 mole) of phosphorus pentasulfide, 1 g. of sand, and 40 ml. of dry tetralin. The mixture was stirred and heated to 150°, and 2.0 g. (0.008 mole) of 1,2-dibenzoylethane in 40 ml. of hot tetralin was added rapidly (approximately five minutes was required). The mixture was then stirred at 150–155° for 15 minutes.

The red solution was filtered while still hot, and was extracted with hot water and warm 5% sodium hydroxide solution. After being dried over calcium chloride, the yellow solution was diluted with an equal volume of petroleum ether (b.p. 63–99°) and passed through a column of activated alumina (Fisher). The resulting solution was distilled under an aspirator vacuum to a very low volume and cooled. The resulting solid was recrystallized from 95% ethanol containing a drop of Perhydrol, and 0.5 g. (25%) of shining yellow platelets of 2,5-diphenylthiophene melting at 149–150° was collected. Reported values for this m.p. range from 150–156° (15).

2,5-Diphenylfuran was prepared by the procedure of Lutz and McGinn (16) for 2,5-diphenyl-3-methylfuran. A solution of 70 ml. of glacial acetic acid and 60 ml. of concentrated hydrochloric acid was heated to boiling, and 36 g. (0.19 mole) of stannous chloride dihydrate was added to the hot solution. Then 10 g. (0.042 mole) of *trans*-dibenzoylethylene (17) was added shortly after, and the mixture was refluxed five minutes, during which time an oil separated. After cooling and diluting with 200 ml. of water, a buff-colored solid precipitated. The product was filtered and washed with water and, after two recrystallizations from methanol, 5.6 g. (61%) of 2,5-diphenylfuran remained which melted at 86–88° (1). Under the same conditions as those of the preceding paragraphs, 1.0 g. (0.0042 mole) of 2,5-diphenylfuran in 15 ml. of tetralin was heated with 1.0 g. (0.0045 mole) of phosphorus pentasulfide in 35 ml. of tetralin. Distillation under reduced pressure of the resulting yellow solution produced a solid which was extracted with alcohol and recrystallized from glacial acetic acid. There was obtained 0.5 g. of orange solid melting at 65–70° which gave a positive test for sulfur. It was not further identified.

1,2-Di-p-bromobenzoylethylene. This compound was prepared by the method of Conant

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[3] All melting points are corrected.

and Lutz (18). Yields of 72–77% of the bright yellow *trans*-compound melting at 182–183° were obtained. If the reaction mixture is warmed much above 40° before the addition of fumaryl chloride, however, a considerable percentage of the *cis* modification results, which lowers the m.p. considerably. For use in the synthesis of the corresponding ethane, the mixture of *cis*- and *trans*-forms presents no disadvantage.

1,2-Di-p-methoxybenzoylethylene. Dry nitrobenzene (200 ml.), 34.7 g. (0.26 mole) of anhydrous aluminum chloride, and 15.3 g. (0.10 mole) of fumaryl chloride were placed in a three-necked flask equipped with a stirrer, a funnel containing 22.5 g. (0.21 mole) of anisole, and a condenser with a gas trap attached. The mixture was stirred at room temperature, and the anisole was admitted at a brisk rate, two minutes being required for the addition. A generous evolution of hydrogen chloride took place, and as soon as the evolution of heat became apparent the flask was cooled by a water-bath (15–18°) for the remainder of the reaction. After the addition was complete, the dark red solution was stirred at 15–18° for six minutes. The oily, red solution was then poured upon 300 g. of cracked ice, containing 10 ml. of hydrochloric acid, and the mixture was stirred vigorously. After it had stood for ten minutes, 300–400 ml. of warm water was added. The bulk of the aqueous layer was removed, and then the organic layer was washed with two more portions of warm water, the first being acidified. The nitrobenzene was then steam-distilled.

After cooling, the water was decanted from the brown, gummy solid remaining in the flask. (Usually, a small quantity of pale yellow crystals of *p*-methoxybenzoylacrylic acid is in suspension.) The brown solid was crystallized by warming in acetone, and after the mixture had cooled, pale orange crystals were collected, washed with acetone, and dried. Isolation of a second crop gave a total yield of 9.1 g. (31%) of 1,2-di-*p*-methoxybenzoylethylene, m.p. 158–160°. Extraction with boiling acetone gives a product melting at 162–164°.[4]

Bromination of the diaroylethylenes. The synthesis of 1,2-di-*p*-methoxybenzoyl-1,2-dibromoethane is new. A mixture of 15 g. (0.05 mole) of di-*p*-methoxybenzoylethylene in 250 ml. of glacial acetic acid was cooled to 15°, and 8.1 g. (0.05 mole) of bromine in 25 ml. of glacial acetic acid was added with stirring. The temperature of the mixture did not rise during the addition. After one hour, during which the mixture was allowed to come to room temperature, stirring was stopped and the pale pink crystals were filtered and washed well with alcohol. The product, melting at 175–176° weighed 16.5 g. (72%).

Anal. Calc'd for $C_{18}H_{16}Br_2O_4$: Br, 35.04. Found: Br, 35.1.

In the same manner, 1,2-dibenzoyl-1,2-dibromoethane was obtained in 77% yield, melting at 178.5–179° (19), and 1,2-di-*p*-bromobenzoyl-1,2-dibromoethane in 85% yield, melting at 209–210° (20).

Reduction of the diaroylethylenes with sodium hydrosulfite. In a representative experiment, 2.4 g. (0.010 mole) of *trans*-dibenzoylethylene, 2.4 g. (0.011 mole) of sodium hydrosulfite, and 250 ml. of 90% ethanol were placed in a flask in that order. The mixture was refluxed for 90 minutes and, after cooling, 200 ml. of water was added. (In the case of the other diketones, glistening needles separated after allowing the solutions to cool to room temperature, without the addition of water.) After the suspension was chilled, 1.8 g. of a pale buff, amorphous solid was collected which melted at 130–138°. Extraction of the solid with 10 ml. of boiling 95% ethanol left a product melting at 139–142° which weighed 1.0–1.7 g. (40–70%). (Similar yields were obtained with the other diketones, and the final extraction was unnecessary.)

Reduction of the diaroyldibromoethanes with sodium hydrosulfite. In a typical experiment, 4.5 g. (0.010 mole) of 1,2-di-*p*-methoxybenzoyl-1,2-dibromoethane, 6.3 g. (0.030 mole) of sodium hydrosulfite, and 250 ml. of 90% ethanol were refluxed for 90 minuts. The reaction mixture, which had become homogeneous, was allowed to cool, and the pale buff needles

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[4] Conant and Lutz, *J. Am. Chem. Soc.*, **45**, 1303 (1923) report an unusually poor yield (7%) of the *para*-methoxy compound, a yellow solid melting at 165°.

formed were collected and washed with water. The yield was 1.2–2.3 g. (40–72%) of 1,2-di-*p*-methoxybenzoylethane which melted at 150–151°.[5]

Bis(1,2-dibenzoyl)ethyl sulfide (II). *trans*-Dibenzoylethylene (10 g., 0.042 mole) was dissolved in 250 ml. of warm 95% ethanol. The solution was allowed to cool until the first evidence of precipitation, and hydrogen sulfide was immediately introduced for a period of 45 minutes at the rate of approximately one mole per hour. White crystals accumulated during the reaction and, after the mixture was chilled, they were filtered and washed with fresh solvent. There was obtained 6 g. (53%) of sulfide which melted at 188–192°.

Anal. Calc'd for $C_{32}H_{26}O_4S$: S, 6.33. Found: S, 6.43.

Trioxime of bis(1,2-dibenzoyl)ethyl sulfide. The pyridine method of Shriner and Fuson (21) was employed, and produced a white solid melting at 195–197°.

Anal. Calc'd for $C_{32}H_{29}N_3O_4S$: N, 7.62. Found: N, 7.69.

Desulfurization of bis(1,2-dibenzoyl)ethyl sulfide. Approximately 18 g. of Raney nickel and 2 g. of the sulfide in 150 ml. of ethanol was refluxed for five hours. The hot solution was filtered, and the clear filtrate was diluted with water to 250 ml. and chilled. A white solid weighing 0.95 g. (56%) which melted at 136–139°, was obtained and, when mixed with 1,2-dibenzoylethane, the melting point was not depressed. It was further characterized by conversion to 2,5-diphenylthiophene, by the method described below.

2,5-Diphenylthiophene. In a 200-ml. two-necked flask fitted with two gas inlet tubes and an outlet tube was placed a filtered solution of 1.0 g. (0.004 mole) of 1,2-dibenzoylethane in 40 ml. of chloroform, and 1.36 g. (0.010 mole) of fused zinc chloride. (The use of stannic chloride gives higher conversions to the crude thiophene, but the product is more difficult to purify.) Dry hydrogen chloride was bubbled into the solution for a minute, and hydrogen sulfide and hydrogen chloride were then admitted simultaneously for 90 minutes at room temperature, with occasional swirling of the flask. The hydrogen sulfide and hydrogen chloride were then admitted at approximate rates of 4 cc. and 1 cc. per second respectively. The faintly red solution was then allowed to remain at room temperature for 24 hours.

After the solution had been decanted from the red oil present, it was progressively evaporated to give two crops of pale yellow crystals and one of yellow amorphous solid. The products were washed with ether. The first two crops melted at 147–150° and weighed 0.45 g. (45% conversion). Recrystallization from 95% ethanol gave shining white crystals of 2,5-diphenylthiophene melting at 150–151°. The third crop was extracted with 95% ethanol to give 0.36 g. (36% recovery) of a mixture of diphenylthiophene and dibenzoylethane melting at 115–120°, useful for further reaction with hydrogen sulfide.

Anal. Calc'd for $C_{16}H_{12}S$: S, 13.56. Found: S, 13.34.

2,5-Di-p-bromophenylthiophene (IV). 1,2-Di-*p*-bromobenzoylethane (1 g., 0.0025 mole) in 40 ml. of chloroform with 1.5 g. (0.006 mole) of stannic chloride was treated for 90 minutes with hydrogen sulfide and hydrogen chloride at 15° in the same manner as in the previous experiment. Progressive evaporation of the resulting blue solution produced three crops of white crystals and a fourth of yellow solid. A gummy residue was discarded. The products were washed with ether, and 0.69 g. (69%) of gleaming white crystals of 2,5-di-*p*-bromophenylthiophene were obtained which melted at 198–199° (no recrystallization was required). Also obtained was 0.21 g. (21%) of unreacted diketone melting at 130–140°.

Anal. Calc'd for $C_{16}H_{10}Br_2S$: Br, 40.55; S, 8.13.
Found: Br, 40.32; S, 8.49.

2,5-Di-p-anisylthiophene (III). 1,2-Di-*p*-methoxybenzoylethane (3 g., 0.01 mole) and 3.4 g. (0.025 mole) of fused zinc chloride in 140 ml. of chloroform were treated for three hours with hydrogen sulfide and hydrogen chloride at 15° in the manner described. After standing for 12 hours, the red solution was decanted from the oil present, and the solvent was evapo-

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[5] This compound was first reported by Borsche, Kettner, Gilles, Kuhn, and Manteuffel, *Ann.*, **526**, 1 (1936) as a by-product in the reaction of anisole with succinoyl chloride, m.p. 108–109°. Winternitz and Mousseron, *Bull. soc. chim. France*, 1087 (1948) report it to be the principle product of this Friedel-Craft reaction, m.p. 154°.

rated. The products were washed with ether, and 1.8 g. (60%) of white 2,5-di-*p*-anisylthiophene, m.p. 215–216°, was obtained, along with 1.1 g. (37%) of recovered diketone melting at 175–180°.

Anal. Calc'd for $C_{18}H_{16}O_2S$: S, 10.82. Found: S, 10.08.

2,5-Di-p-hydroxyphenylthiophene. The procedure given by Kharasch (22) for the demethylation of stilbestrols was used. First, 1 g. (0.0034 mole) of 2,5-di-*p*-anisylthiophene, 25 ml. of ethylene glycol, and 2.5 g. of potassium hydroxide were placed in a steel bomb of 50 ml. capacity. Then the bomb was evacuated to 5 mm. and heated at 215–230° for 18 hours. After cooling, the oily solution was extracted with dilute sodium hydroxide solution, and the extract was acidified with concentrated hydrochloric acid. A gel-like precipitate formed which was digested on a hot water-bath for 30 minutes and was then chilled. A light purple, colloidal solid was filtered, washed with 95% ethanol, and dried over concentrated sulfuric acid. After recrystallization from a 3:2 solution of chloroform and absolute ethanol, a pale purple product was isolated and washed with ether. The yield was 0.14 g. (15%) of 2,5-di-*p*-hydroxyphenylthiophene melting at 266–268°.

Anal. Calc'd for $C_{16}H_{12}O_2S$: OH, 12.68. Found: OH, 12.73.

2,5-Di-p-acetoxyphenylthiophene. The procedure of Shriner (23) for the determination of hydroxyl groups was used, giving simultaneously the preceding analysis and the preparation of the acetoxy derivative. The white, acetylated product from 0.1009 g. of the hydroxy compound was recovered in 86% yield (0.1119 g.) and melted at 173–174°.

Anal. Calc'd for $C_{20}H_{16}O_4S$: S, 9.10. Found: S, 9.24.

2,5-Di-p-aminophenylthiophene. The procedure of Gilman and Jacoby (24) for the preparation of aminodibenzothiophenes was employed. 2,5-Di-*p*-bromophenylthiophene (1 g., 0.0025 mole), 3 g. (0.010 mole) of freshly-prepared cuprous bromide (at room temperature), and 10 ml. of concentrated ammonia were placed in a steel bomb (50 ml. capacity). The bomb was heated at 215–230° for 12 hours. The bomb was opened, the colorless ammonia solution was decanted, and the residual blue solid was exhaustively extracted with boiling benzene. The reddish-blue solution resulting (which had a volume of approximately 150 ml.) was shaken with three 15-ml. portions of 10% hydrochloric acid. The green solid which separated out in the water layer was filtered, washed with water, sucked as dry as possible, and dried on filter paper. The yield was 0.32 g. (48%) of dark green 2,5-di-*p*-aminophenylthiophene which melted at 240–241°.

Anal. Calc'd for $C_{16}H_{14}N_2S$: N, 10.52. Found: N, 10.76.

Bromination of 2,5-diphenylthiophene. The procedure of Fromm (8) was employed in this reaction. 2,5-Diphenylthiophene (0.5 g., 0.002 mole) was dissolved in 50 ml. of chloroform. Approximately 3 ml. of bromine was added, and fumes of hydrogen bromide were evolved after a few minutes. The solution was allowed to remain undisturbed for 24 hours. After removal of the excess bromine with bisulfite and distillation of the solvent, an oil was obtained which was taken up in petroleum ether and chilled. The grey solid obtained was recrystallized from glacial acetic acid and fractionated from ethanol, giving 0.32 g. of grey 2-*p*-bromophenyl-3,4-dibromo-5-phenylthiophene (VI) melting at 150–152°, and 0.08 g. of buff crystals of 2,5-diphenyl-3,4-dibromothiophene (V) which melted at 95–96°.

Anal. Calc'd for (V) $C_{16}H_{10}Br_2S$: C, 48.54; H, 2.55; Br, 40.40.
Found: C, 49.00; H, 2.59; Br, 39.86.

Anal. Calc'd for (VI) $C_{16}H_9Br_3S$: C, 40.50; H, 1.89; Br, 50.50.
Found: C, 39.25; H, 1.84; Br, 49.20.

Bromination of 2,5-di-p-bromophenylthiophene. 2,5-Di-*p*-bromophenylthiophene (0.5 g., 0.0012 mole) was dissolved in 50 ml. of chloroform and treated with 2 ml. of bromine. The solution was allowed to stand at room temperature for two hours, fumes of hydrogen bromide being slowly given off during the reaction. After removal of the excess bromine with aqueous sodium sulfite, the chloroform solution was dried and evaporated to half its volume. On cooling, white platelets separated and were filtered and sucked dry. Complete evaporation produced a second crop of the same material. The yield was 0.68 g. (97%) of 2,5-di-*p*-bromophenyl-3,4-dibromothiophene (VII) which melted at 209–210°.

Anal. Calc'd for $C_{16}H_8Br_4S$: C, 34.81; H, 1.46.
Found: C, 34.73; H, 1.76.

SUMMARY

A new method for the synthesis of 2,5-diarylthiophenes in high yield is described. It involves a standard thione synthesis using diaroylethanes.

A mechanism for this reaction, based upon the formation of a diene-thiol intermediate followed by a polar thiol addition, is postulated.

The reaction of *trans*-dibenzoylethylene with hydrogen sulfide produced bis-(1,2-dibenzoyl)ethyl sulfide which formed a trioxime and was readily reduced to dibenzoylethane.

2,5-Di-*p*-bromophenylthiophene, 2,5-di-*p*-anisylthiophene, 2,5-di-*p*-hydroxyphenylthiophene, 2,5-di-*p*-acetoxyphenylthiophene, and 2,5-di-*p*-aminophenylthiophene are reported for the first time.

Bromination studies indicate that 2,5-diphenylthiophene is readily brominated to 3,4-dibromo-2,5-diphenylthiophene, which can then be further brominated through a tribromide to the same tetrabromide obtained by bromination of 2,5-di-*p*-bromophenylthiophene.

BLOOMINGTON, INDIANA

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