

## 292. Intermediates and Dyes. Part V.\* Derivatives of Thiophanthrene-4 : 9-quinone.

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Derivatives of thiophanthrene-4 : 9-quinone and of  $\beta$ -thiophanthrene-4 : 9-quinone have been examined, with special reference to those compounds with easily replaceable chlorine atoms.

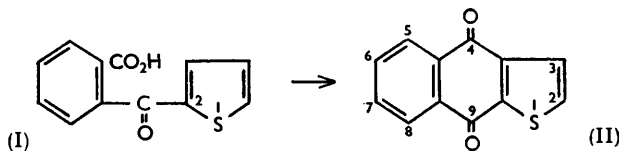
3 : 6-Dichloro-2'-thenoylbenzoic acid, best prepared from 3 : 6-dichlorophthalic anhydride by the Grignard reaction, gave the yellow 5 : 8-dichlorothiophanthrene-4 : 9-quinone, converted into 8-chloro-5-amino- and 5 : 8-diamino-thiophanthrene-4 : 9-quinone, which dye cellulose acetate rayon and Nylon bluish-red and bluish-violet shades, respectively, bluer than the shades given by the anthraquinone analogues.

3 : 6-Dichloro-2-(2 : 5-dimethyl-3-thenoyl)benzoic acid was prepared by the Friedel-Crafts reaction, and was cyclised to the yellow 5 : 8-dichloro-1 : 3-dimethyl- $\beta$ -thiophanthrene-4 : 9-quinone, converted into dyes which are redder than the anthraquinone analogues.

Friedel-Crafts reactions between 3 : 6-dichlorophthalic anhydride and 2- or 3-methylthiophen were also examined; in the latter case, it was established by synthesis that the initial product was 3 : 6-dichloro-2-(3-methyl-2-thenoyl)benzoic acid, with only 5% of the 4-methyl isomer.

Compared with the anthraquinone analogues, there is loss of tinctorial power when a benzene ring is replaced by a thiophen ring.

IN Part IV,\* intermediates and dyes based on benzothiophanthrene-6 : 11-quinone (6 : 11-dihydro-6 : 11-dioxobenzo[*b*]thiophanthrene) were investigated. The present work includes an examination of similar derivatives from thiophanthrene-4 : 9-quinone (II), and a comparison with the anthraquinone analogues.



The parent compound (II) was obtained by cyclisation of 2'-thenoylbenzoic acid (I), which we prepared from phthalic anhydride and thiophen by the Friedel-Crafts reaction, in spite of conflicting claims in the literature. It appears that polymerisation of thiophen predominates at low temperatures. According to Etienne,<sup>2</sup> the carboxylic acid (I) was obtained in 80% yield from 2-thienylmagnesium iodide.

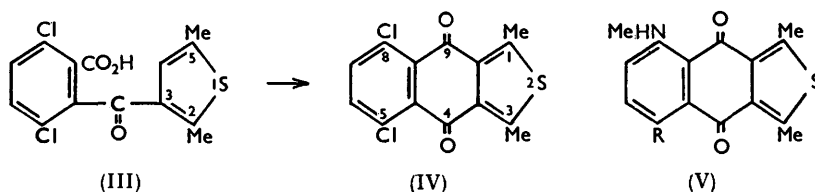
For preparation of 5 : 8-disubstituted derivatives of the quinone (II), containing easily replaceable groups, the use of thiophen-2 : 3-dicarboxylic acid anhydride as intermediate was impracticable owing to the very low yields obtained by oxidising 2-acetyl-3-methylthiophen (cf. other workers<sup>3</sup>).

On applying the above successful Friedel-Crafts reaction for the acid (I) to the interaction of 3 : 6-dichlorophthalic anhydride and thiophen, we obtained only 4% of 3 : 6-dichloro-2'-thenoylbenzoic acid, but Lee and Weinmayr's method<sup>4</sup> afforded an 81.4% yield. Cyclisation to the bright yellow 5 : 8-dichlorothiophanthrene-4 : 9-quinone was best (21.5%) achieved by aluminium chloride in nitrobenzene. To determine the conditions for replacing the chloro-groups in this compound, experiments were carried out with 1 : 4-dichloroanthraquinone. Attempts with methylamine under a variety of conditions gave only poor yields of the 1 : 4-bismethylamino- or 1-chloro-4-methylamino-compound, but fusion with *N*-methyltoluene-*p*-sulphonamide in presence of sodium acetate and copper acetate, followed by hydrolysis, afforded 30% of the monocondensation

\* Part IV, *J.*, 1956, 1429.

product (cf. Ullmann and Bielig<sup>5</sup>). 5 : 8-Dichlorothiophanthrene-4 : 9-quinone similarly yielded 44% of 5 : 8-ditoluene-*p*-sulphonamido- and 40.5% of 8-chloro-5-toluene-*p*-sulphonamido-thiophanthrene-4 : 9-quinone, longer reaction giving 89% of the ditoluene-*p*-sulphonamide. Almost quantitative hydrolysis of the two sulphonamides by 95% sulphuric acid at room temperature afforded the free amines.

The orientation of the amino-chloro-derivative was proved by synthesis of the isomeric 8-amino-5-chloro-analogue. 3-Nitrophthalic anhydride and 2-thienylmagnesium bromide yielded 3- and 6-nitro-2'-2'-thenoylbenzoic acid; cyclisation of both of these acids (with rearrangement of the 3-nitro-compound) yielded solely 5-nitrothiophanthrene-4 : 9-quinone (Weinmayr and Schroeder<sup>1</sup>). However, reduction of 3-nitro-2'-2'-thenoylbenzoic acid by Mitter's method<sup>6</sup> gave 96% of the corresponding amine. Cyclisation by 95% sulphuric acid at 135–140° yielded 8-aminothiophanthrene-4 : 9-quinone, converted into the 8-benzamido-derivative. Subsequent chlorination gave 60% of 8-benzamido-5-chlorothiophanthrene-4 : 9-quinone, hydrolysed by sulphuric acid to 8-amino-5-chlorothiophanthrene-4 : 9-quinone. Unfortunately, when 6-nitro-2'-2'-thenoylbenzoic acid was treated as described, the resulting 5-benzamidothiophanthrene-4 : 9-quinone could not be chlorinated satisfactorily.



5-Amino-8-chlorothiophanthrene-4 : 9-quinone dyes cellulose acetate rayon and Nylon red shades, bluer than those shown by 4-amino-1-chloroanthraquinone; and 5 : 8-diaminothiophanthrene-4 : 9-quinone gives bluish-violet shades, much bluer than those given by 1 : 4-diaminoanthraquinone. Fastness to light and gas fumes is similar to that of the anthraquinone derivatives.

It was of interest to determine if the position of the thiophen ring affected the properties of dyes in the thiophanthrene-4 : 9-quinone series. Only one compound containing the  $\beta$ -thiophanthrene-4 : 9-quinone (naphtho[2,3-*c*]thiophen-4 : 9-quinone) structure has been described, *viz.*, 1 : 3-dimethyl- $\beta$ -thiophanthrene-4 : 9-quinone.<sup>7</sup> We prepared 2 : 5-dimethylthiophen from acetylacetone by a modification of Paal's method.<sup>8</sup> Although the Friedel-Crafts reaction proved unsuitable for preparing 3 : 6-dichloro-2'-2'-thenoylbenzoic acid, derivatives from methylthiophens could be prepared by this method: *e.g.*, 2 : 5-dimethylthiophen and 3 : 6-dichlorophthalic anhydride, best at 40–60°, gave the carboxylic acid (III), which with aluminium chloride in nitrobenzene at 130–140° gave 42.4% of the yellow 5 : 8-dichloro-1 : 3-dimethyl- $\beta$ -thiophanthrene-4 : 9-quinone (IV). Other methods of cyclisation gave lower yields.

On attempting to replace the chlorine atoms of the quinone by the toluene-*p*-sulphonamido-group, decomposition occurred. However, whereas alcoholic methylamine failed

<sup>1</sup> Ernst, *Ber.*, 1886, **19**, 3278; Steinkopf and Butkiewicz, *Annalen*, 1914, **407**, 94; Buu-Hoï, Hoán, and Xuong, *Rec. Trav. chim.*, 1950, **69**, 1083; Lee and Weinmayr, U.S.P. 2,497,334/1950; Weinmayr and Schroeder, *J. Amer. Chem. Soc.*, 1952, **74**, 4353.

<sup>2</sup> Etienne, *Bull. Soc. chim. France*, 1947, 634.

<sup>3</sup> Demuth, *Ber.*, 1885, **18**, 3024; Gerlach, *Annalen*, 1892, **267**, 155; Linstead, Noble, and Wright, *J.*, 1937, 917.

<sup>4</sup> Lee and Weinmayr, U.S.P. 2,513,572—4/1950.

<sup>5</sup> Ullmann and Bielig, *Annalen*, 1911, **381**, 11.

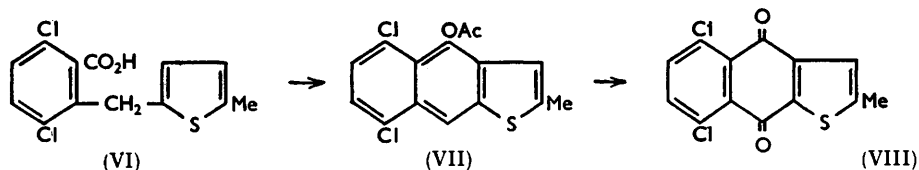
<sup>6</sup> Mitter, *J. Indian Chem. Soc.*, 1930, **7**, 625.

<sup>7</sup> Steinkopf, Barlag, and von Petersdorff, *Annalen*, 1939, **540**, 7; Goncalves and Brown, *J. Org. Chem.*, 1952, **17**, 698.

<sup>8</sup> Paal, *Ber.*, 1885, **18**, 2252.

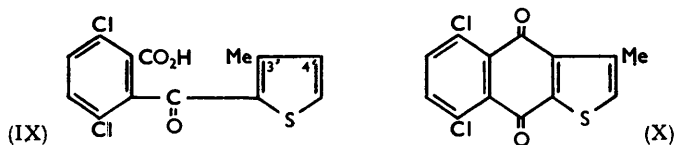
to give dyes from 5 : 8-dichlorothiophanthrene-4 : 9-quinone, it gave with the 1 : 3-dimethyl-quinone (IV), in presence of pyridine and copper acetate at 135—140°, moderate yields of the 5-chloro-8-methylamino- (V; R = Cl) and 5 : 8-bismethylamino-derivative (V; R = NHMe). Refluxing the quinone (IV) in aniline with a trace of copper acetate gave the maroon 5-anilino-8-chloro-1 : 3-dimethyl- $\beta$ -thiophanthrene-4 : 9-quinone. The dyes of the  $\beta$ -thiophanthrene-4 : 9-quinone series do not form alkaline dithionite (hydro-sulphite) vats, unlike the thiophanthrene-4 : 9-quinones. The quinone (V; R = NHMe) dyed cellulose acetate rayon and Nylon violet, compared with the much bluer shades shown by 1 : 4-bismethylaminoanthraquinone; also redder than the anthraquinone analogues were the chloro-derivative (V; R = Cl) and the above anilino-compound, which gave orange and salmon-pink shades, respectively. This hypsochromic effect is in contrast to the bathochromic shift given by derivatives of the normal thiophanthrene-4 : 9-quinones. Replacement of one benzene ring by a thiophen ring in such anthraquinoid dyes, however, leads to loss of colour value.

Slow addition of 2-methylthiophen to 3 : 6-dichlorophthalic anhydride in nitrobenzene at 40—45° gave 57% of 3 : 6-dichloro-2-(5-methyl-2-thenoyl)benzoic acid; direct cyclisation of this proved unsuccessful; prior reduction by zinc dust and aqueous ammonia gave the corresponding thenyl derivative (VI), which with zinc chloride in boiling acetic



anhydride and acetic acid afforded an almost quantitative yield of 4-acetoxy-5 : 8-dichloro-2-methylthiophanthrene (VII), oxidised by potassium dichromate in acetic acid in 82% yield to 5 : 8-dichloro-2-methylthiophanthrene-4 : 9-quinone (VIII). Attempted replacement of chlorine therein by amino, methylamino, or toluene-*p*-sulphonamido, gave only traces of the required products, but refluxing with aniline and copper acetate yielded 36% of the intense greenish-blue dye, 5 : 8-dianilino-2-methylthiophanthrene-4 : 9-quinone.

The conditions favourable for condensation of 2-methylthiophen and 3 : 6-dichlorophthalic anhydride were applied to 3-methylthiophen, and gave unexpectedly 3 : 6-dichloro-2-(3-methyl-2-thenoyl)benzoic acid (IX) and only a small amount of the 4'-methyl isomeride. Heating the acid (IX) with aluminium chloride and sodium chloride at 130—135° gave only 2% of the yellow 5 : 8-dichloro-3-methylthiophanthrene-4 : 9-quinone (X). The acid (IX) was reduced with zinc dust and aqueous ammonia to the thenylbenzoic



acid, which with boiling acetic anhydride, acetic acid, and zinc chloride gave a colourless product slowly soluble in aqueous sodium hydrogen carbonate and unchanged by boiling aqueous sodium hydroxide; such properties indicated that cyclisation had not occurred and that the anhydride of the carboxylic acid had not been formed, and it is considered that the colourless derivative is 2-(5-acetyl-3-methyl-2-thenyl)-3 : 6-dichlorobenzoic acid. The constitution of the carboxylic acid (IX) was confirmed by synthesis.

2-Chloromercuri-3-methylthiophen, obtained by Volhard's method,<sup>9</sup> was converted

<sup>9</sup> Volhard, *Annalen*, 1897, **267**, 180.

into 2-iodo-3-methylthiophen,<sup>10</sup> the Grignard reagent from which with 3 : 6-dichlorophthalic anhydride gave the acid (XI).

The Friedel-Crafts reaction above with 3-methylthiophen gave, as by-product, probably 5% of 3 : 6-dichloro-2-(4-methyl-2-thenoyl)benzoic acid, as indicated by the formation of 2% of the quinone (X) by cyclisation.

#### EXPERIMENTAL

*2-2'-Thenoylbenzoic Acid.*—Phthalic anhydride (29.6 g., 1 mol.), aluminium chloride (58.7 g., 2.2 mols.), and nitrobenzene (100 ml.) were stirred at 55–60° for 1 hr., then cooled to 40°, and thiophen (16.8 g., 1 mol.) was added dropwise during 2 hr. at 40–45°; after a further hr. at 40–45°, and then 1 hr. at 50–55° the mass was added to concentrated hydrochloric acid (13 ml.) in water (1100 ml.) and stirred vigorously for 1 hr. The nitrobenzene layer was separated, the solvent removed with steam, and the acid purified through its aqueous sodium carbonate solution. The acid crystallised from dilute acetic acid in colourless leaflets, m. p. 146–147° (26.8 g., 57.7%) (Found : C, 61.7; H, 3.2; S, 14.2. Calc. for C<sub>12</sub>H<sub>8</sub>O<sub>3</sub>S : C, 62.1; H, 3.5; S, 13.8%).

*3 : 6-Dichlorophthalic Anhydride.*—This was separated from a mixture containing 3 : 4-, 4 : 5-, and 3 : 6-dichloro-derivatives through the calcium salt of the acid, by Villiger's method.<sup>11</sup>

*3 : 6-Dichloro-2-2'-thenoylbenzoic Acid.*—(a) 3 : 6-Dichlorophthalic anhydride (43.4 g., 1 mol.), replacing the phthalic anhydride in the above experiment, gave the carboxylic acid, purified by several precipitations from its aqueous sodium carbonate solution, and by crystallisation from dilute acetic acid in colourless, hexagonal plates, m. p. 146–147° (Found : C, 47.5; H, 1.9; Cl, 23.7; S, 10.8. Calc. for C<sub>13</sub>H<sub>6</sub>O<sub>3</sub>Cl<sub>2</sub>S : C, 47.8; H, 2.0; Cl, 23.6; S, 10.6%).

The *methyl ester*, prepared by the Fischer-Speier method, distilled at 180°/0.9 mm., and had m. p. 63–64° (Found : C, 49.9; H, 2.3; Cl, 22.3; S, 9.8. C<sub>13</sub>H<sub>8</sub>O<sub>3</sub>Cl<sub>2</sub>S requires C, 49.5; H, 2.6; Cl, 22.5; S, 10.2%).

(b) In preparing the following Grignard reagent, and in the condensation, nitrogen was passed continuously. Magnesium turnings (1.5 g., 1.25 mols.), a crystal of iodine, dry ether (60 ml.), and a few drops of 2-bromothiophen were warmed until reaction began, and 2-bromothiophen (total wt., 8.2 g., 1 mol.) in ether (12 ml.) was added during 1 hr., under reflux; after refluxing further for 1 hr. and cooling to 20°, the mixture was run into a stirred solution of 3 : 6-dichlorophthalic anhydride (10.8 g., 1 mol.) in dry benzene (260 ml.) at 50°. The whole was refluxed for 1 hr., then cooled to 20°, water (85 ml.) added gradually, refluxing continued for 1 hr., the mixture cooled to 25°, magnesium oxide (1.7 g.) added, and the whole shaken for 3 hr. at 20–25°. The slightly alkaline aqueous layer was combined with aqueous extracts of the solvent layer, and acidification gave the carboxylic acid, which crystallised from benzene in pale yellow plates, m. p. 142° (12.25 g., 81.4%). This product, although not quite so pure as the sample as prepared above, was used for further experiments.

*5 : 8-Dichlorothiophanthrene-4 : 9-quinone.*—The acid chloride, prepared from the above carboxylic acid by thionyl chloride, was treated in carbon disulphide or nitrobenzene with aluminium chloride (2.2 mols.) at room temperature, but it gave only a trace of quinone; higher temperatures gave a similar result. The use of concentrated sulphuric acid at 165–170° for 5 min. gave 5.2% of quinone, and phosphoric oxide (3 mols.) in nitrobenzene at 130–140° for 30 hr. afforded 17.5%. The best method of cyclisation was to treat the carboxylic acid (4 g.) with aluminium chloride (8 g.) in nitrobenzene (60 ml.) for 24 hr. at room temperature; removal of solvent with steam gave the quinone, which sublimed *in vacuo* at 170° as bright yellow needles, m. p. 225–226° (Found : C, 51.0; H, 1.3; Cl, 24.8; S, 11.3. Calc. for C<sub>12</sub>H<sub>4</sub>O<sub>2</sub>Cl<sub>2</sub>S : C, 50.9; H, 1.4; Cl, 25.1; S, 11.3%). It gives a reddish-orange alkaline dithionite vat.

*Replacement of Chlorine in 1 : 4-Dichloroanthraquinone.*—(a) 1 : 4-Dichloroanthraquinone (2 g.), sodium dithionite (2 g.), and 33% ethanolic methylamine (20 ml.) at 140–150° in a sealed tube for 8 hr. gave a product, which on chromatography in chlorobenzene on alumina yielded 1 : 4-dichloroanthraquinone (1.1 g.) and 1-chloro-4-methylaminoanthraquinone (0.14 g., 7.5%), and a trace only of the bismethylamino-derivative.

(b) Replacing the dithionite by sodium *m*-nitrobenzenesulphonate, and heating at 155–156°

<sup>10</sup> Steinkopf and Hanske, *Annalen*, 1937, 532, 241.

<sup>11</sup> Villiger, *Ber.*, 1909, 42, 3538.

for 8 hr., gave, as above, 1 : 4-dichloro- (0.6 g.), 1-chloro-4-methylamino- (0.16 g., 8.1%), and 1 : 4-bismethylamino-anthraquinone (0.2 g., 10.4%). A similar reaction at 175—180° for 30 hr. gave a similar result, and when pyridine (10 ml.) was added to the mixture (155—165°) the yield of bismethylamino-compound was 0.26 g. (13.5%).

(c) 1 : 4-Dichloroanthraquinone (2 g.), copper acetate (0.2 g.), and 33% ethanolic methylamine (20 ml.) at 150—170° in a sealed tube for 20 hr. afforded unchanged product (0.6 g.), 1-chloro-4-methylamino- (0.2 g., 10%), and 1 : 4-bismethylamino-anthraquinone (0.38 g., 19.8%); similar results were obtained at 180—190°.

(d) *N*-Methyltoluene-*p*-sulphonamide (11 g.) was heated to 170°, and copper acetate (0.1 g.) and sodium acetate (0.25 g.) were added; when the melt became clear (5 min.), 1 : 4-dichloroanthraquinone (1 g.) was added in portions during 15 min. and the melt then kept at 170° for 6 hr. Addition to water, and extraction of the amide from the solid by dilute sodium hydroxide solutions gave an orange-red insoluble solid, which was dried *in vacuo*, then heated in 95% sulphuric acid (10 ml.) at 60—70° (oil-bath) for 1 hr. Dilution with water afforded a solid, which was dried and chromatographed in chlorobenzene on alumina, to give a deep red band of 1-chloro-4-methylamino- (0.3 g., 30%), m. p. 169°, and a trace of 1 : 4-bismethylamino-anthraquinone, m. p. 220°.

(e) 1 : 4-Dichloroanthraquinone (2 g.), toluene-*p*-sulphonamide (3.7 g.), potassium acetate (1.6 g.), and copper acetate (0.1 g.) were refluxed in nitrobenzene (20 ml.) for 4 hr. After removal of nitrobenzene, the residual solid crystallised from acetic acid in orange needles, m. p. 242—243°, of 1 : 4-ditoluene-*p*-sulphonamidoanthraquinone (3.6 g., 90%), hydrolysed almost quantitatively by 95% sulphuric acid on the water-bath in 1 hr. to 1 : 4-diaminoanthraquinone, m. p. 268° (1.6 g.).

8-Chloro-5-toluene-*p*-sulphonamido- and 5 : 8-Ditoluene-*p*-sulphonamido-thiophanthrene-4 : 9-quinone.—5 : 8-Dichlorothiophanthrene-4 : 9-quinone (2 g., 1 mol.), toluene-*p*-sulphonamide (1.9 g., 3 mols.), freshly fused potassium acetate (0.8 g., 2.2 mols), and a trace of copper acetate were refluxed in nitrobenzene (30 ml.) for 4 hr. Nitrobenzene was removed with steam, and the residual reddish-brown solid was crystallised from acetic acid, to yield orange-red plates, m. p. 275—276°, of 5 : 8-ditoluene-*p*-sulphonamidothiophanthrene-4 : 9-quinone (1.7 g., 44%) (Found : C, 56.5; H, 3.8; N, 5.0; S, 17.4.  $C_{26}H_{20}O_6N_2S_3$  requires C, 56.5; H, 3.7; N, 5.1; S, 17.4%). The mother-liquors gave 8-chloro-5-toluene-*p*-sulphonamidothiophanthrene-4 : 9-quinone, which crystallised from dilute acetic acid in brownish-orange needles, m. p. 181—182° (1.2 g., 40.5%) (Found : C, 54.6; H, 2.4; N, 3.3; Cl, 8.5; S, 15.2.  $C_{19}H_{12}O_4NCIS_2$  requires C, 54.6; H, 2.9; N, 3.35; Cl, 8.5; S, 15.3%). Chromatography in benzene on alumina proved an excellent means of separating the above derivatives. A longer time of reaction (12 hr.) in the above experiment gave the ditoluene-*p*-sulphonamide (3.6 g., 89%), and only a trace of monotoluene-*p*-sulphonamido-derivative.

5 : 8-Diaminothiophanthrene-4 : 9-quinone.—A solution of 5 : 8-ditoluene-*p*-sulphonamidothiophanthrene-4 : 9-quinone (2.5 g.) and 95% sulphuric acid (20 ml.) was kept at room temperature for 17 hr.; after 2 hr. on the water-bath the mixture was added to water and the solid collected, dried, and crystallised from chlorobenzene in purple needles with a bronze lustre, m. p. >350°, of 5 : 8-diaminothiophanthrene-4 : 9-quinone (1 g., 97%) (Found : C, 58.8; H, 3.3; N, 11.7; S, 13.0.  $C_{12}H_8O_2N_2S$  requires C, 59.0; H, 3.3; N, 11.5; S, 13.1%). The alkaline dithionite vat was bright yellow.

5-Amino-8-chlorothiophanthrene-4 : 9-quinone.—In similar manner hydrolysis of the corresponding sulphonamide (2 g.) gave 5-amino-8-chlorothiophanthrene-4 : 9-quinone (1.24 g., 98%), which crystallised from benzene in dark red plates with a green lustre, m. p. 227—228° (Found : C, 55.0; H, 2.2; N, 5.3; Cl, 13.4; S, 12.1.  $C_{12}H_6O_2NCIS$  requires C, 54.7; H, 2.3; N, 5.3; Cl, 13.5; S, 12.2%). It gave a golden-yellow alkaline dithionite vat.

6- and 3-Nitro-2-2'-thenoylbenzoic Acid.—Reaction was carried out in nitrogen. Magnesium turnings (3 g., 1.25 mols.), a crystal of iodine, and a few drops of 2-bromothiophen in dry ether (60 ml.) were heated until reaction began, and then 2-bromothiophen (total, 16.3 g., 1 mol.) was added during 1 hr. under reflux. After refluxing for a further hr. and cooling to 20°, the Grignard reagent was added during 10 min. to a suspension of 3-nitrophthalic anhydride (19.3 g., 1 mol.) in dry benzene (300 ml.) at 40°. The mixture was kept at 50—55° for 2 hr., then water (150 ml.) and magnesium oxide (10 g.) were added, and the mixture was refluxed for 1 hr. Acidification of the aqueous layer and aqueous washings of the solvent layer with acetic acid gave 3-nitro-2-2'-thenoylbenzoic acid, which crystallised from dilute acetic acid in colourless

needles, m. p. 215—216° (6.85 g., 25%). The filtrate from the acetic acid acidification was made strongly acid by hydrochloric acid, to give the 6-nitro-isomer, which crystallised from dilute acetic acid in colourless prisms, m. p. 168—169° (4.1 g., 14.75%).

*8-Benzamidothiophanthrene-4 : 9-quinone*.—A boiling solution of ferrous sulphate (25 g.) in water (165 ml.) which was treated with 28% aqueous ammonia (40 ml.) was added during 5 min. to 3-nitro-2-2'-thenoylbenzoic acid (3.5 g.) in 28% aqueous ammonia (35 ml.). The mixture was boiled for 20 min., filtered, and treated while boiling with a hot solution of potash alum (3.5 g.) in water (35 ml.). After filtering, the solution was cooled to give pale yellow needles, m. p. 176—178°, of 3-amino-2-2'-thenoylbenzoic acid (3 g., 96%). This amine (3 g.) was cyclised by 95% sulphuric acid (50 ml.) for 5 min. at 120°, cooled rapidly to 60°, and added to water (500 ml.). The resulting solid was dried and converted by benzoyl chloride in boiling chlorobenzene (4 hr.) into *8-benzamidothiophanthrene-4 : 9-quinone* which crystallised from chlorobenzene in bright orange needles, m. p. 231—232° (1.9 g., 45.2%, based on nitrocarboxylic acid) (Found : C, 68.4; H, 3.2; N, 3.9; S, 9.2.  $C_{12}H_{11}O_3NS$  requires C, 68.5; H, 3.3; N, 4.4; S, 9.6%).

*8-Benzamido- and 8-Amino-5-chlorothiophanthrene-4 : 9-quinone*.—The above 8-benzamido-compound (2 g.) was treated at 100° in nitrobenzene (32 ml.) with sulphuryl chloride (1.5 ml.) for 15 min., with vigorous stirring, then stirred for a further 4 hr. at 100° and at 10° for 1 hr. The light orange crystals were collected, washed with alcohol, and dried. *8-Benzamido-5-chlorothiophanthrene-4 : 9-quinone* crystallised from chlorobenzene in orange, feathery needles, m. p. 225—226° (1.4 g., 63.6%) (Found : C, 62.2; H, 2.7; N, 4.1; S, 9.3.  $C_{13}H_{10}O_3NClS$  requires C, 62.0; H, 2.7; N, 3.8; S, 8.7%). Warming with concentrated sulphuric acid on the water-bath for 1 hr. gave the corresponding *8-amino-derivative*, red plates (from benzene), m. p. 253—254° (Found : C, 55.0; H, 2.4; Cl, 13.4; S, 11.7.  $C_{12}H_8O_3NClS$  requires C, 54.7; H, 2.3; Cl, 13.5; S, 12.2%).

*5-Benzamidothiophanthrene-4 : 9-quinone*.—A solution of 6-nitro-2-2'-thenoylbenzoic acid (2.5 g.) in 95% sulphuric acid was heated at 140—145° for 2 min., cooled to 60°, and added, with stirring, to water (200 ml.). The cyclised product was extracted with hot sodium carbonate solution to remove unchanged carboxylic acid and then was boiled with sodium dithionite (3 g.), sodium hydroxide (2 g.), and water (200 ml.) for 2 hr. Subsequent aeration for 3 hr. gave a flocculent maroon precipitate, which was collected, washed, and dried; chromatography was effected in chlorobenzene on alumina, to give a reddish-blue band, which was separated with chlorobenzene and then treated with benzoyl chloride. After 4 hours' refluxing and concentration, orange needles, m. p. 229—230°, of *5-benzamidothiophanthrene-4 : 9-quinone*, separated (0.75 g., 25%). Chlorination with sulphuryl chloride as above afforded a product containing only 2.7% of chlorine.

*2 : 5-Dimethylthiophen*.—Acetylacetone (129 g.) and phosphorus pentasulphide (250 g.) were mixed intimately and heated carefully until reaction began; sometimes the reaction began spontaneously and vigorously. After reaction had proceeded, with cooling, for 30 min., the mixture was boiled for a few min. and then distilled. The distillate was washed with dilute hydrochloric acid, water, 10% aqueous sodium carbonate, and finally, water. The resulting liquid was distilled and the fraction, b. p. 132—138° (54 g.), collected.

*3 : 6-Dichloro-2-(2 : 5-dimethyl-3-thenoyl)benzoic Acid* (III).—(a) Aluminium chloride (19.6 g., 2.2 mols.) was added during 3 hr. to a mixture of 3 : 6-dichlorophthalic anhydride (14.5 g., 1 mol.), 2 : 5-dimethylthiophen (7.5 g., 1 mol.), and nitrobenzene (45 ml.) at 0—5°. After 20 hours' stirring at room temperature, decomposition with ice and hydrochloric acid, and removal of the nitrobenzene with steam, the tarry residue was extracted with boiling 8% sodium carbonate solution (charcoal); the filtrate from this was acidified with hydrochloric acid; *3 : 6-dichloro-2-(2 : 5-dimethyl-3-thenoyl)benzoic acid* crystallised from dilute acetic acid in colourless needles, m. p. 172—173° (dried at 120°) (2.9 g., 3.2%) (Found : C, 51.0; H, 3.0; Cl, 21.9; S, 9.8.  $C_{14}H_{10}O_3Cl_2S$  requires C, 51.1; H, 2.9; Cl, 21.6; S, 9.7%).

(b) 3 : 6-Dichlorophthalic anhydride (14.5 g., 1 mol.), aluminium chloride (19.6 g., 2.2 mols.), and nitrobenzene (35 ml.) were stirred at 55—60° for 1 hr.; 2 : 5-dimethylthiophen (7.5 g., 1 mol.) was added dropwise during 2 hr. at 40—45°, and the mixture was stirred at 40—45° for a further hr. and then at 55—60° for 2 hr. After being stirred at room temperature for 10 hr., the mixture was decomposed by being stirred with water (700 ml.) and hydrochloric acid (10 ml.) for 1 hr. Purification of the resulting product from aqueous sodium carbonate gave a solid, which crystallised from dilute acetic acid in colourless needles, m. p. and mixed m. p. with above

product, 172—173° (9.7 g., 44.3%). The derived *methyl ester* distilled as a colourless oil, b. p. 180—181°/0.4 mm. (Found : C, 52.1; H, 3.1; Cl, 21.0; S, 9.4.  $C_{15}H_{12}O_3Cl_2S$  requires C, 52.5; H, 3.5; Cl, 20.7; S, 9.35%).

5 : 8-Dichloro-1 : 3-dimethyl- $\beta$ -thiophanthrene-4 : 9-quinone (IV).—(a) 3 : 6-Dichloro-2-(2 : 5-dimethyl-3-thenoyl)benzoic acid (5 g.) and aluminium chloride (10 g.) in nitrobenzene (75 ml.) were stirred at 130—140° for 24 hr. After decomposition, removal of nitrobenzene with steam, and extraction with boiling aqueous sodium carbonate, the insoluble solid was chromatographed in chlorobenzene on alumina, and gave, after crystallisation from the same solvent, the *quinone* in yellow needles, m. p. 262—263° (2 g., 42.4%). The quinone sublimed readily in stout, yellow needles, m. p. 263—264°, at 200°/0.5 mm. (Found : C, 54.1; H, 2.8; Cl, 22.8; S, 9.9.  $C_{14}H_8O_2Cl_2S$  requires C, 54.0; H, 2.6; Cl, 22.8; S, 10.3%). It does not form an alkaline dithionite vat.

(b) 3 : 6-Dichloro-2-(2 : 5-dimethyl-3-thenoyl)benzoic acid (2 g.) was converted by thionyl chloride into its acid chloride, which was then stirred in nitrobenzene (50 ml.) with aluminium chloride (1.8 g., 2.2 mols.) at 120—130° for 6 hr. Subsequent elution, with chlorobenzene, of the yellow band formed on the alumina column gave yellow, feathery needles, 262—263°, of the quinone.

(c) The carboxylic acid (2 g.), in a melt of aluminium chloride (12 g.) and sodium chloride (3 g.) at 120—130° for 6 hr. gave, as above, the quinone (IV), m. p. 262° (0.47 g., 25%).

5-Chloro-8-methylamino- and 5 : 8-Dimethylamino-1 : 3-dimethyl- $\beta$ -thiophanthrene-4 : 9-quinone.—Heating the quinone (IV) (2 g.), 33% ethanolic methylamine (25 ml.), pyridine (10 ml.), and a trace of copper acetate at 135—140° for 8 hr., followed by chromatography in benzene on alumina, gave an orange-red band, quickly eluted; removal of the solvent and crystallisation from light petroleum (b. p. 60—80°) gave orange-red needles, m. p. 197—198°, of 5-chloro-1 : 3-dimethyl-8-methylamino- $\beta$ -thiophanthrene-4 : 9-quinone (V; R = Cl) (0.2 g., 10.4%) (Found : C, 58.7; H, 4.0; N, 4.4; Cl, 12.0; S, 10.4.  $C_{15}H_{12}O_2NCIS$  requires C, 58.9; H, 4.0; N, 4.6; Cl, 11.6; S, 10.5%). After elution of the above orange-red band, a royal-blue band remained on the column and was extracted (Soxhlet) with benzene to give, after crystallisation from light petroleum-benzene, purple needles with a coppery lustre, m. p. 247—248°, of 1 : 3-dimethyl-5 : 8-dimethylamino- $\beta$ -thiophanthrene-4 : 9-quinone (0.54 g., 27.5%) (Found : C, 63.9; H, 5.3; N, 9.1; S, 10.4.  $C_{18}H_{16}O_2N_2S$  requires C, 64.0; H, 5.4; N, 9.3; S, 10.7%). This quinone does not form an alkaline dithionite vat. When the time of the above reaction was 16 hr., no chloro-derivative was obtained, and the diamino-derivative was formed in 36.4% yield.

5-Anilino-8-chloro-1 : 3-dimethyl- $\beta$ -thiophanthrene-4 : 9-quinone.—The quinone (IV) (2 g.) and a trace of copper acetate were refluxed in aniline (100 ml.) for 4 hr. After removal of excess of aniline with steam, the maroon product was collected, washed, and dried. Chromatography of the deep red benzene extract on alumina and several crystallisations from light petroleum (b. p. 100—120°) gave maroon needles, m. p. 185°, of 5-anilino-8-chloro-1 : 3-dimethyl- $\beta$ -thiophanthrene-4 : 9-quinone (1.2 g., 44%) (Found : C, 65.7; H, 3.8; N, 4.2; Cl, 9.5; S, 8.6.  $C_{20}H_{14}O_2NCIS$  requires C, 65.3; H, 3.8; N, 3.8; Cl, 9.6; S, 8.7%). It does not form a vat, and dissolves in cold concentrated sulphuric acid with a brownish-orange colour.

3 : 6-Dichloro-2-(5-methyl-2-thenoyl)benzoic Acid.—3 : 6-Dichlorophthalic anhydride (43.4 g., 1 mol.), aluminium chloride (58.8 g., 2.2 mols.), and nitrobenzene (100 ml.) were stirred at 55—60° for 1 hr., then cooled to 40—45°. 2-Methylthiophen (19.6 g., 1 mol.) was added dropwise during 1½ hr. at 40—45°; heating was continued at 40—45° for 1 hr., then at 50—60° for 4 hr., the colour changing from blood-red to purple. After being stirred overnight at room temperature, the mixture was decomposed, nitrobenzene removed with steam, and the residue extracted with boiling 8% sodium carbonate solution. Acidification of the alkaline extract, followed by crystallisation of the resulting solid from dilute acetic acid, gave colourless prisms, m. p. 160—161°, of 3 : 6-dichloro-2-(5-methyl-2-thenoyl)benzoic acid (36 g., 57.1%) (Found : C, 49.6; H, 2.5; Cl, 22.5; S, 10.2.  $C_{13}H_8O_3Cl_2S$  requires C, 49.5; H, 2.6; Cl, 22.5; S, 10.2%). The *methyl ester* (Fischer-Speier) crystallised from methanol in colourless rhomboids, m. p. 97—98° (Found : C, 50.7; H, 2.8; Cl, 21.9; S, 9.3.  $C_{14}H_{10}O_3Cl_2S$  requires C, 51.1; H, 3.1; Cl, 21.6; S, 9.7%). Attempted cyclisation of the carboxylic acid or its chloride by aluminium chloride in nitrobenzene at 120—130° for 20 hr., by aluminium-sodium chloride at 130° for 8 hr., or by phosphoric oxide in nitrobenzene at 130—140° for 24 hr., gave intractable products.

3 : 6-Dichloro-2-(5-methyl-2-thenoyl)benzoic Acid (VI).—3 : 6-Dichloro-2-(5-methyl-2-thenoyl)benzoic acid (10 g.), 28% aqueous ammonia (500 ml.), copper sulphate (0.25 g.), and zinc dust

(25 g.) were refluxed for 40 hr., and 28% aqueous ammonia (50 ml.) added every 12 hr. The suspension was filtered hot, and the filtrate acidified; on cooling, an oil separated, which became solid after several days. Several crystallisations from dilute acetic acid afforded colourless plates, m. p. 107—108°, of the *thenyl derivative* (V), which were dried at 100° for 24 hr. (4.5 g., 47.4%) (Found: Cl, 23.0; S, 10.2.  $C_{13}H_{10}O_2Cl_2S$  requires Cl, 23.55; S, 10.6%).

4-*Acetoxy-5:8-dichloro-2-methylthiophanthrene* (V).—The above thenyl derivative (2 g.), acetic anhydride (8 ml.), acetic acid (12 ml.), and freshly fused zinc chloride (0.5 g.) were refluxed for 90 min. to give a clear solution; dilution with hot water (20 ml.) afforded a solid which crystallised from acetic acid in feathery, colourless needles, m. p. 191°, of the *acetoxy-compound* (2.1 g., 96%) (Found: C, 55.3; H, 3.1; Cl, 21.6; S, 9.6.  $C_{15}H_{10}O_4Cl_2S$  requires C, 55.4; H, 3.1; Cl, 21.8; S, 9.9%).

5:8-*Dichloro-2-methylthiophanthrene-4:9-quinone* (VIII).—The acetoxy-compound (2 g.) was refluxed in acetic acid (20 ml.) with potassium dichromate (8 g.) for 1 hr., the mixture filtered, and the filtrate concentrated to 8 ml. and added to water (100 ml.). The yellow flocculent precipitate was collected, dried, crystallised three times from acetic acid, and sublimed at 200°/0.5 mm., to give bright yellow needles, m. p. 238°, of 5:8-*dichloro-2-methylthiophanthrene-4:9-quinone* (VIII) (1.5 g., 82%) (Found: C, 52.9; H, 2.0; Cl, 23.8; S, 10.7.  $C_{13}H_6O_2Cl_2S$  requires C, 52.5; H, 2.0; Cl, 23.9; S, 10.8%). It forms a reddish-orange alkaline dithionite vat.

5:8-*Dianilino-2-methylthiophanthrene-4:9-quinone*.—5:8-Dichloro-2-methylthiophanthrene-4:9-quinone (1 g.) was refluxed in aniline (70 ml.) with a little copper acetate for 4 hr., a deep blue solution resulting. Aniline was removed with steam, the dark residue extracted with benzene, and the greenish-blue extract chromatographed on alumina. A faint blue band preceded an intense bluish-green one, and was separated from a dark brown band of impurities by elution with benzene. The bluish-green band gave the *anilino-derivative* in dark blue crystals [from light petroleum (b. p. 60—80°)], m. p. 176—177° (0.5 g., 36%) (Found: N, 7.0.  $C_{25}H_{18}O_2N_2S$  requires N, 6.8%).

3:6-*Dichloro-2-(3-methyl-2-thenyl)benzoic Acid* (IX).—3:6-Dichlorophthalic anhydride (21.7 g., 1 mol.) was treated (Friedel-Crafts) with 3-methylthiophen (9.8 g., 1 mol.), under similar conditions to those recorded for 2-methylthiophen, to yield the *acid* (IX) (20.4 g., 64.8%); five crystallisations from dilute acetic acid gave colourless prisms of constant m. p. 164—165° (Found: C, 49.5; H, 2.4; Cl, 22.6; S, 10.2.  $C_{13}H_8O_2Cl_2S$  requires C, 49.5; H, 2.6; Cl, 22.5; S, 10.2%). The *methyl ester* (Fischer-Speier) crystallised from methanol in colourless rhomboids, m. p. 107—108° (Found: C, 51.1; H, 2.9; Cl, 21.8; S, 9.5.  $C_{14}H_{10}O_2Cl_2S$  requires C, 51.1; H, 3.1; Cl, 21.6; S, 9.7%).

*Cyclisation*. The acid (IX) (4 g.) was added slowly to aluminium chloride (24 g.) and sodium chloride (6 g.) at 130—135°, and kept at this temperature for 10 hr. before being added to ice and water. After extraction with boiling 8% aqueous sodium carbonate, the residue was dried and chromatographed in chlorobenzene on alumina; a yellow band separated from the main diffuse dark brown band, and the former gave a solid which crystallised from acetic acid in brownish-yellow needles, m. p. 272—273° (0.08 g., 2.1%), of, probably, 5:8-*dichloro-3-methylthiophanthrene-4:9-quinone* (X) (Found: C, 53.1; H, 2.5; Cl, 23.1; S, 10.8.  $C_{13}H_6O_2Cl_2S$  requires C, 52.5; H, 2.0; Cl, 23.9; S, 10.8%). Other methods of cyclisation gave no quinone. The alkaline dithionite vat was orange-brown.

3:6-*Dichloro-2-(3-methyl-2-thenyl)benzoic Acid*.—The thenoyl derivative (IX) (10 g.) was reduced by refluxing with zinc dust (25 g.), copper sulphate (0.25 g.), and 28% aqueous ammonia (500 ml.) for 40 hr., 28% aqueous ammonia being added at intervals. The hot mixture was filtered and the filtrate acidified with hydrochloric acid, to give a solid; crystallisation from dilute acid afforded colourless, rod-like needles, m. p. 178—179°, of 3:6-*dichloro-2-(3-methyl-2-thenyl)benzoic acid* (5.5 g., 57.5%) (Found: C, 52.1; H, 3.4; Cl, 23.7; S, 10.4.  $C_{13}H_{10}O_2Cl_2S$  requires C, 51.8; H, 3.3; Cl, 23.55; S, 10.6%).

This compound (2 g.), zinc chloride (0.15 g.), acetic acid (12 ml.), and acetic anhydride (8 ml.) were refluxed for 90 min., the solution becoming blood-red; dilution with water (25 ml.) and cooling gave a red solid, which was extracted with acetic acid (charcoal); the acid was then filtered, diluted with water, and cooled, to give colourless needles, m. p. 241—242°. The needles were soluble in aqueous sodium hydrogen carbonate, indicating that this was not a cyclised product; boiling with aqueous sodium hydroxide gave unchanged material. Analyses supported the view that it was 2-(5-*acetyl-3-methyl-2-thenyl*)-3:6-*dichlorobenzoic acid*



(Found: C, 52.5; H, 3.7; Cl, 21.2; S, 8.9.  $C_{15}H_{12}O_3Cl_2S$  requires C, 52.5; H, 3.5; Cl, 20.7; S, 9.3%). The dark residue from the acetic acid extraction above proved intractable.

*2-Iodo-3-methylthiophen.*—2-Chloromercuri-3-methylthiophen<sup>9</sup> (11.2 g.), iodine (8.6 g.), and potassium iodide (20 g.) in water (150 ml.) were stirred at room temperature for 6 hr. and left overnight. Decolorisation was affected by aqueous sodium hydrogen sulphite, and the mixture distilled with steam, to yield a pale yellow oil; extraction with ether, washing the extract with aqueous sodium hydrogen sulphite and then water, and drying, gave on distillation a pale yellow oil, b. p. 84—86°/11 mm., of 2-iodo-3-methylthiophen.<sup>10</sup>

*Synthesis of 3 : 6-Dichloro-2-(3-methyl-2-thenoyl)benzoic Acid.*—Preparation of the Grignard reagent, and the condensation, were carried out in pure dry nitrogen. Magnesium (0.8 g., 1.25 mols.), a crystal of iodine, and a little 2-iodo-3-methylthiophen in dry ether (60 ml.) were warmed until reaction began, and then 2-iodo-3-methylthiophen (total, 6.0 g., 1 mol.) was added during 30 min. and the mixture refluxed for 1 hr. To a solution of 3 : 6-dichlorophthalic anhydride (5.8 g., 1 mol.) in dry benzene (180 ml.) at 50°, the Grignard solution was pumped in during 3 min., the temperature rising to 55°. After 1 hr. at 55° water (150 ml.) was added and the mixture refluxed for 1 hr. After cooling, magnesium oxide (1.2 g.) was added and the mixture shaken at 25° for 3 hr. The aqueous layer, and aqueous washings of the benzene layer, were acidified; the resulting solid crystallised from dilute acetic acid in colourless plates, m. p. 163° (4.2 g., 50%). No depression in m. p. was observed on admixture with the product obtained from 3-methylthiophen by the Friedel-Crafts reaction. Further, conversion into the methyl ester gave colourless rhomboids, m. p. and mixed m. p. with the methyl ester obtained previously, 107—108°.

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