

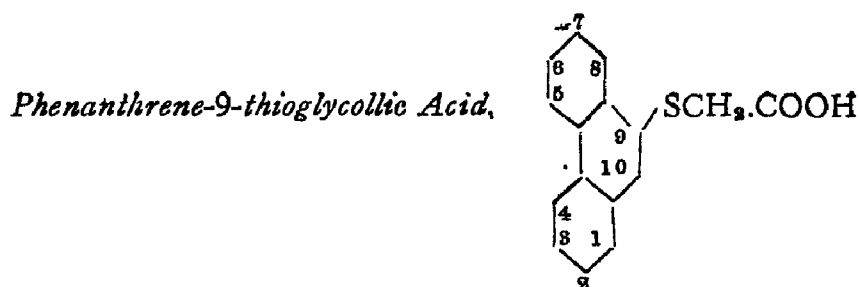
STUDIES IN INDIGOID DYES. PART XI. PHENANTHRATHIOPHENE-INDIGOS

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9-Thiolphenanthrene and some of its derivatives have been synthesised by the author with a view to preparing some interesting dyes from the point of view of colour in relation to chemical constitution. Some of these dyes have already been described in part X of this series. The present communication deals with the preparation of *bis*-9:10-phenanthrathiophene-indigo starting from 9-thiolphenanthrene through 9:10-phenanthra-2'-ketodihydrothiophene. It is a dark chocolate dye and dyes cotton in brown shade and this result is in conformity with the previous findings of the author.

Preparation of some indigoid dyes starting from 9-thiolphenanthrene has been described. 9-Thiolphenanthrene and some of its derivatives have been prepared by the author (*J. Indian Chem. Soc.*, 1941, 18, 469) with a view to preparing some interesting dyes from the point of view of colour in relation to chemical constitution. Some of these dyes have already been described in part X (*ibid.*, 1942, 19, 239). The present communication deals with the preparation of 9:10-phenanthra-2'-ketodihydrothiophene and some indigoid dyes derived from it by oxidation and condensation with *o*-diketones, such as phenanthraquinone, acenaphthaquinone and isatin. *bis*-9:10-Phenanthrathiophene-indigo, described in this paper, is a dark, chocolate dye which dyes cotton in brown shade and this result is in conformity with the findings of the author (*Ber.*, 1934, 67, 1319; 1935, 68, 1447; 1936, 69, 2343). The dyes prepared from acenaphthaquinone and isatin produce as usual bright red shades on cotton. Works on similar dyes prepared from other isomeric phenanthrene sulphonic acids, such as 2 and 3 are in progress.

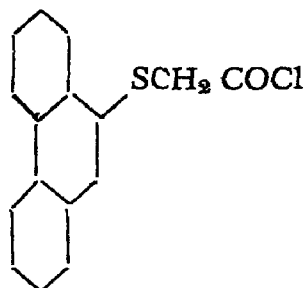
E X P E R I M E N T A L



9-Thiolphenanthrene (10.5 g.) was dissolved in the required quantity of 10% sodium carbonate solution on a water-bath and to the filtered solution was added monochloroacetic acid (5 g.), previously neutralised with sodium carbonate.

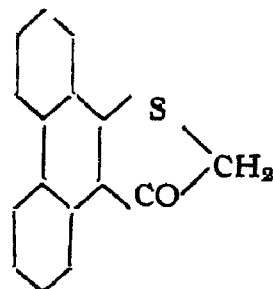
The mixture was heated on a water-bath for half an hour and filtered. The filtrate was then cooled and acidified with hydrochloric acid when the thioglycollic acid separated out as an oil, which after sometime gradually solidified to a white crystalline powder, m.p. 134-35°. (Found : C, 71.23 ; H, 4.6. $C_{16}H_{12}O_2S$ requires C, 71.64 ; H, 4.47 per cent).

Phenanthrene-9-thioglycollic Acid Chloride



The finely powdered, and carefully dried thioglycollic acid (5.36 g.) was suspended in 10 times the quantity of low boiling petroleum ether and then treated with phosphorus pentachloride (4.2 g.). The mixture was then warmed on a water-bath till everything went into a colorless solution. This was cooled in a freezing mixture when the chloride separated out as white crystals which became a sticky mass at ordinary temperature. After the removal of the clear liquid, the mass was subjected to the next operation.

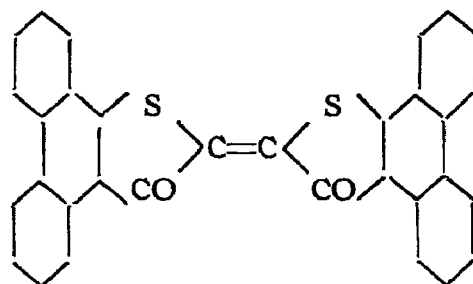
9 : 10-Phenanthra-2'-ketodihydrothiophene,



The above sticky chloride without further purification was dissolved in ten times the quantity of low boiling petroleum ether and then cooled to room temperature and next treated slowly with finely powdered anhydrous aluminium chloride (5 g.). The mixture was boiled on a water-bath till the evolution of hydrochloric acid ceased. Gradually a red substance was produced. This red substance after the removal of petroleum ether by filtration was decomposed by crushed ice, when a yellowish white sticky mass was obtained. This was dissolved in acetic acid and from the solution it was obtained as yellowish white needles, m.p. 173-75°. It becomes reddish on exposure to air. It dissolves in caustic soda easily and the solution soon turns green due to oxidation.

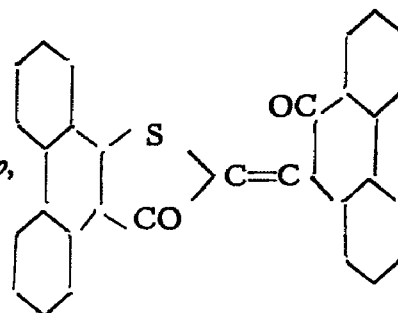
to the *bis*-indigo (Found : C, 76.52 ; H, 4.21. $C_{16}H_{10}OS$ requires C, 76.80 ; H, 4.4 per cent).

bis-9:10-Phenanthrathiophene-indigo,

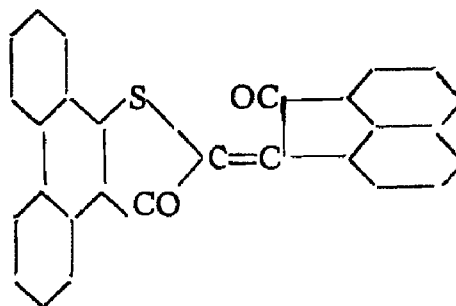


The above oxythiophene (2 g.) was dissolved in 5% dilute caustic soda and an aqueous solution of potassium ferricyanide added until a dark chocolate precipitate was no longer formed. The precipitate was then filtered, and washed with water. It was dissolved in pyridine and from the solution was obtained a chocolate crystalline mass melting above 280° . It dissolves in pyridine, nitrobenzene with a dark brown colour and in concentrated sulphuric acid with a chocolate colour. In alkaline hydrosulphite it dissolves with a yellow colour and dyes cotton in brown shade. (Found : C, 77.17 ; H, 3.37. $C_{32}H_{16}O_2S_2$ requires C, 77.42 ; H, 3.22 per cent).

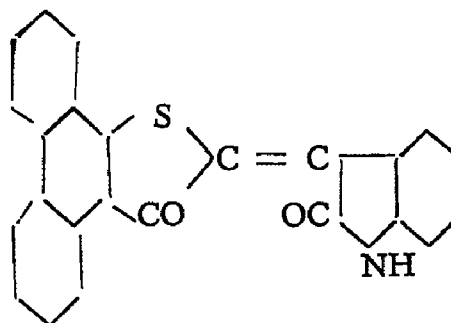
9 : 10-Phenanthrathiophene-9'-phenanthrene-indigo,



This compound was prepared by heating together phenanthraquinone (1.04 g.), dissolved in 30 c.c. of acetic acid and 9 : 10-phenanthra-2'-ketodihydrothiophene (1.25 g.) in 25 c.c. of acetic acid and adding to the hot solution 0.5 c.c. of hydrochloric acid (d 1.19) when immediately a chocolate precipitate separated out. The mixture was boiled for ten minutes and filtered while hot. The residue was next washed with a little acetic acid and alcohol and crystallised from pyridine in chocolate needles melting above 280° . It is fairly soluble in hot pyridine and nitrobenzene and slightly soluble in alcohol and acetic acid. It dissolves in concentrated sulphuric acid with a greenish black colour and in alkaline hydrosulphite with a yellow colour from which it dyes cotton in chocolate-violet shade. (Found : C, 81.51 ; H, 3.81. $C_{30}H_{16}O_2S$ requires C, 81.82 ; H, 3.63 per cent).

9 : 10-*Phenanthrathiophene-2'-acenaphthylene-indigo*,

It was prepared in the same way as the previous compound from 9 : 10-phenanthra-2'-ketodihydrothiophene (1.25 g.) and acenaphthaquinone (0.91 g.) in acetic acid solution with traces of hydrochloric acid, and purified in the same manner. From pyridine it separated out as fine, red needles melting above 280°. It dissolves in concentrated sulphuric acid with a pale green colour and dissolves in hydrosulphite slightly with a yellowish colour and dyes cotton in beautiful scarlet-red shade. (Found: C, 80.81 ; H, 3.45. $C_{28}H_{14}O_2S$ requires C, 81.15 ; H, 3.38 per cent).

9 : 10-*Phenanthrathiophene-3'-indol-indigo*,

It was prepared in the same manner as the previous compounds from 9 : 10-phenanthra-2'-ketodihydrothiophene (1.25 g.) and isatin (0.74 g.) and purified in the same manner. It was crystallised from nitrobenzene in deep red needles melting above 280°. It dissolves in concentrated sulphuric acid with a violet colour and dyes cotton from yellow hydrosulphite vat in red shade. (Found : C, 75.73 ; H, 3.57. $C_{24}H_{13}O_2NS$ requires C, 75.99 ; H, 3.43 per cent).