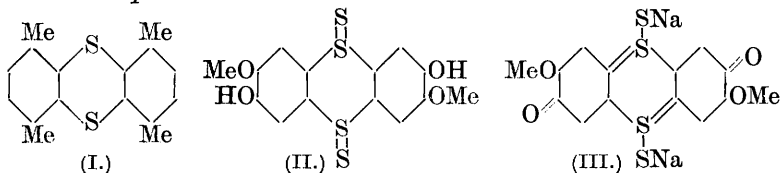


CXLVIII.—*Synthesis in the Thianthren Series.*
Part II.

By MONMOHAN SEN and JÑANENDRA NATH RÂÛ.

THE method described in Part I (J., 1921, 119, 1959) has been applied in the synthesis of other thianthren derivatives. The reaction is apparently a general one, but difficulties are encountered in purifying the product. *Tetramethylthianthren* (I) has been obtained in the crystalline form and characterised by the preparation of its *disulphone*.



From guaiacol, *dimethoxydihydroxythianthren disulphide* (II) was obtained, the crystalline yellow *sodium* salt of which is sparingly soluble in water. The similar disulphide previously isolated (*loc. cit.*) was very unstable. The remarkable stability of the present compound may possibly be due to its acquiring a *p*-quinonoid constitution (III); the sodium salt forms an orange solution in water.

In view of the use of thioaniline in the dye industry, it appeared that diaminothianthren might be a valuable intermediate, and some azo-compounds derived from this base have been prepared.

EXPERIMENTAL.

1 : 4 : 5 : 8-*Tetramethylthianthren* (I).—When dry aluminium-mercury couple (from 0.3 g. of aluminium foil) was added to a mixture of *p*-xylene (6 c.c.) and sulphur monochloride (4 c.c.), the reaction became vigorous in a few minutes and hydrogen chloride was copiously evolved. The mass soon solidified almost completely and carbon disulphide (8 c.c.) was then introduced and the mixture kept at 40° during an hour. The solvent was decanted, the product decomposed with ice, and the colourless precipitate washed successively with yellow ammonium sulphide, aqueous sodium sulphite, and water, dried, and crystallised from boiling nitrobenzene. The crystals were extracted with boiling carbon disulphide, and dissolved in nitrobenzene, the last trace of sulphur being then removed by treatment with copper powder. The filtrate from the copper sulphide deposited the pure substance in colourless needles, m. p. 242° (Found : S, 23.1; C, 70.6; H, 5.8. $C_{16}H_{16}S_2$ requires S, 23.5; C, 70.5; H, 5.8%).

The substance exhibits the normal behaviour of thianthren and dissolves in concentrated sulphuric acid to a green solution which is decolorised on dilution with water, the original compound being precipitated.

The *disulphone* was obtained by repeatedly evaporating the thianthren with an excess of nitric acid (*d* 1.4) on the steam-bath. The product was precipitated with water, washed, and crystallised from glacial acetic acid, separating in needles, which did not melt below 290° (Found : S, 18.7. $C_{16}H_{16}O_4S_2$ requires S, 19.0%).

3 : 7-*Dimethoxy-2 : 6-dihydroxythianthren Disulphide*.—To a solution of 6.2 g. of guaiacol in 10 c.c. of carbon disulphide, 4 c.c. of sulphur monochloride, dissolved in 10 c.c. of the same solvent, were added the amalgam prepared from 0.4 g. of aluminium was quickly introduced. The solution became deep green and a vigorous reaction ensued. After being kept at room temperature

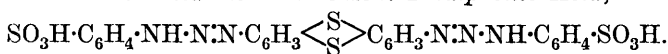
for an hour, the mixture was warmed at 40° for some time, the carbon disulphide evaporated off, and the residue treated with water. The red oil thus obtained was dissolved in alkali. The filtered solution slowly deposited glistening, yellow leaflets. These were filtered off, dissolved in water, and the thianthren derivative precipitated by carbon dioxide. The yellow solid thus obtained crystallised from boiling alcohol in yellow, silky scales, m. p. 202° (Found: S, 33.9. $C_{14}H_{12}O_4S_4$ requires S, 34.4%). The yield was poor.

The substance was easily acetylated by boiling with an excess of acetic anhydride and a few drops of pyridine. The *diacetyl* derivative crystallised from alcohol in needles, m. p. 165° (Found: S, 27.7; C, 47.5; H, 3.6. $C_{18}H_{16}O_6S_4$ requires S, 28.0; C, 47.3; H, 3.5%).

Azo-compound from Diazotised Diaminوثianthren and β-Naphthol.—A solution of 2 g. of diaminوثianthren (*loc. cit.*, p. 1964) in 200 c.c. of water and 1 c.c. of concentrated hydrochloric acid was treated at 0° with 0.44 g. of sodium nitrite and thereafter with an alkaline solution of 0.9 g. of β-naphthol. The solid precipitated on acidification was crystallised from boiling benzene (Found: N, 10.6. $C_{32}H_{20}O_2N_4S_2$ requires N, 10.1%). The deep red dye produced a dull shade on unmordanted cotton.

Tetrazo-compound from Diaminوثianthren and Resorcinol.—Diaminوثianthren hydrochloride (2 g.) was diazotised and then coupled with 0.17 g. of resorcinol in alkaline solution. The dye obtained on acidification could not be crystallised, and therefore it was purified by precipitation from an alkaline solution. The reddish-brown product did not melt below 250° (Found: N, 11.4. $C_{24}H_{16}O_4N_4S_2$ requires N, 11.5%).

Thianthren-2 : 6-bis(diazoaminobenzene-4'-sulphonic Acid,



—A solution of 1.1 g. of sulphanilic acid in water containing sodium hydroxide was diluted to 200 c.c., made faintly acid, and slowly treated with a diazotised solution of 2 g. of diaminوثianthren. The mixture was filtered after a time, and the filtrate made alkaline and then acidified with acetic acid. The reddish-brown dye thus precipitated was dried (Found: N, 12.8. $C_{24}H_{18}O_6N_6S_4$ requires N, 13.6%).

Thianthren derivatives were obtained by the general method in the following cases, but the products could not be isolated free from sulphur: bromobenzene, *p*-chlorophenol, *p*-cresol, quinol dimethyl ether, *p*-tolyl methyl ether, and resorcinol dimethyl ether. The case of bromobenzene is interesting, because, unlike that in

iodobenzene (*loc. cit.*), the halogen atom is not displaced in the reaction.

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COLLEGE OF SCIENCE, CALCUTTA.
THE UNIVERSITY, MANCHESTER.

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