

144. *Stereoisomerism of Disulphoxides and Related Substances. Part IX.
Disulphoxides in the Thianthren Series.*

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THE two disulphoxides of thianthren described by Fries and Vogt (*Ber.*, 1911, **44**, 756) were the only pair of stereoisomeric disulphoxides already known at the time of the publication of Part I of this series (J., 1927, 1798) and their existence had not until then received any satisfactory explanation. The experimental evidence then available did not suggest that such isomerism was a general phenomenon even within the thianthren group, for the oxidation of a dimethylthianthren (Fries and Volk, *Ber.*, 1909, **42**, 1175), a dimethoxythianthren (Fries and Engelbertz, *Annalen*, 1915, **407**, 194), and a mononitrothianthren (Krishna, J., 1923, **123**, 156) had in each case been reported to yield a single dioxide. Indeed, Fries and Engelbertz made a special search for the occurrence of a similar isomerism in the dioxide of dimethoxythianthren. As isomeric dioxides of thianthren had been obtained by the use of two different oxidants (moist chlorine and dilute nitric acid), they applied these two reagents to the dimethoxythianthren, but one and the same dioxide was isolated.

We have therefore made a more extended study of this subject, and now describe a

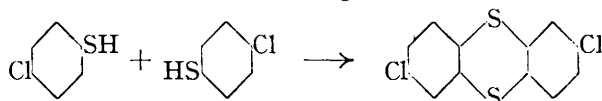
further examination of the formation and properties of the two thianthren dioxides, and of the oxidation of a dimethoxy-, a dimethyl-, and a dichloro-thianthren, in the course of which a pair of stereoisomeric dioxides has been isolated in each case.

The repetition of the preparation of the two dioxides of thianthren showed, as we had expected, that in each case the second isomeride is present in the product. The β -dioxide of m. p. 249° is more than three times as soluble as the α -dioxide of m. p. 284° in glacial acetic acid at 25°. From this we may conclude, by the argument applied to the dithian dioxides (Part I) and justified by an independent stereochemical demonstration in the case of the oxides of trimethylene trisulphide (J., 1929, 15), that the α -dioxide has the *trans*-configuration. The examination of the dipole moments of these dioxides led Bergmann and Tschudnowsky to the same conclusion (*Ber.*, 1932, **65**, 457), for the β -dioxide has a much larger dipole moment than the α -isomeride.

In the oxidation of 2 : 6-dimethoxythianthren the dioxide of m. p. 266—268° described by Fries and Engelbertz was found to be the principal product, but an *isomeride* of m. p. 198—200° was isolated from the mother-liquors.

2 : 6-Dimethylthianthren had been reported as yielding on oxidation a monoxide, m. p. 94°, a dioxide, m. p. 194°, and a disulphone, m. p. 286° (Fries and Volk, *loc. cit.*). We have isolated two dioxides, α -, m. p. 195.5° (202.5° corr.), and β -, m. p. 168.5° (174° corr.), of which the latter is three times as soluble as the former in methyl alcohol and is therefore probably of *cis*-configuration; and a *trioxide*, m. p. 223°, which is reducible to the *monosulphone*, m. p. 171°.

A study has also been made of the oxidation of 2 : 6-dichlorothianthren. This substance was obtained in good yield by the action of sulphuric acid upon *p*-chlorophenylthiol, which appears to leave no doubt as to its configuration :



On the other hand the orientations of the dichlorothianthrens of m. p. 171° (Fries and Vogt, *loc. cit.*) and 147° (Rây, J., 1921, **119**, 1959), both prepared by the condensation of sulphur chloride and chlorobenzene, are still open to question. Our repetition of this reaction, using aluminium chloride as described by the former authors, gave us a very poor yield of a substance from which the complete removal of free sulphur was difficult. The final product was identical with the 2 : 6-dichlorothianthren from *p*-chlorophenylthiol. Fries and Vogt argue that their substance must have the 2 : 7-configuration, as another main product isolated from the reaction was 4 : 4'-dichlorodiphenyl sulphide, which might give rise to a dichlorothianthren of this orientation. But Böeseken and Koning (*Rec. trav. chim.*, 1911, **30**, 116), who studied the same reaction under conditions where no thianthren arose, showed that besides the monosulphide a quantity of 4 : 4'-dichlorodiphenyl disulphide is produced. This disulphide is presumably an intermediate in our preparation of the 2 : 6-dichlorothianthren, and in view of the small yields of the thianthren of m. p. 171° under discussion it must remain doubtful whether the 2 : 7-dichlorothianthren has in fact been isolated.

The separation of the products of oxidising 2 : 6-dichlorothianthren under various conditions was a lengthy process, leading finally to the isolation of a *monoxide*, a *monosulphone*, two stereoisomeric *dioxides*, a *trioxide*, and the *disulphone*.

The polarity of thianthren itself was demonstrated by Bergmann and Tschudnowsky (*loc. cit.*) and must be due to a folded configuration of the molecule (compare Bennett and Glasstone, this vol., p. 128). This should give rise to a number of additional stereoisomerides; from this point of view two monoxides, three dioxides, and two trioxides are to be expected from thianthren or any symmetrically substituted derivative. Notwithstanding careful examination of the products of oxidation of thianthren by Fries and Vogt and of the dimethyl- and dichloro-thianthrens in the present investigation, no indication has been obtained of the separate existence of any of these additional isomerides and it appears probable that they are not sufficiently stable to be distinguished from

those we have isolated. The case is analogous to that of the amines RR'R''N, the configuration of which is shown to be non-planar by their real dipole moments, yet attempts to separate them into enantiomorphous forms have repeatedly been unsuccessful.

EXPERIMENTAL.

Oxidation of Thianthren.—The oxidation by moist chlorine (Fries and Vogt, *loc. cit.*) was repeated. The product, after recrystallisation from acetic acid, formed pointed prismatic needles with straight extinction, m. p. 284°. The mother-liquors from this α -dioxide yielded a small quantity of the β -isomeride, which was identified by m. p. and microscopic examination.

When oxidation was by the method of Krafft and Lyons (*Ber.*, 1896, **29**, 435) using nitric acid (*d* 1.2), the product crystallising directly from the reaction mixture was again the α -isomeride, which was pure after recrystallisation from acetic acid. The acid mother-liquor, on neutralisation, furnished a quantity of the β -isomeride, which separated from absolute alcohol or 50% acetic acid in small monoclinic crystals, m. p. 249°.

The solubilities of these isomerides in glacial acetic acid (100 g.) at 25.0°, stirring being continued for 6 hours, were: α -isomeride, 0.596 g.; β -isomeride, 2.13 g.

Oxidation of 2 : 6-Dimethoxythianthren.—The thianthren (4.5 g.) was boiled with dilute nitric acid (130 c.c., *d* 1.2) until no more nitrous fumes were liberated. Crystals of the α -dioxide described by Fries and Engelbertz separated on cooling, and after recrystallisation from decalin had m. p. 266—268°. The material precipitated from the acid mother-liquor by alkali was crystallised from 50% acetic acid. After some α -dioxide had been separated, a small quantity of the β -dioxide was obtained, m. p. 198—200° (0.5 g. from 3 g. of crude mixed oxides). Oxidation by hydrogen peroxide in acetic acid also yielded mainly the α -isomeride: there was evidence of the presence of a second substance when it was crystallised from butyl alcohol, but the β -dioxide was not isolated from it in a state of purity. The α -dioxide separates from glacial acetic acid in sharply pointed needles with a straight extinction: the β -dioxide from aqueous acetic acid in blunt-ended monoclinic prisms or in clusters of radiating and branched needles, the extinctions being sometimes straight and sometimes oblique at an angle of 20° [Found: (α -dioxide) C, 54.1; H, 4.0; S, 20.7; (β -dioxide) C, 54.3; H, 3.7; S, 20.7. $C_{14}H_{12}O_4S_2$ requires C, 54.5; H, 3.9; S, 20.8%]. Both isomerides crystallise well from *n*-butyl alcohol or decalin, dissolve in concentrated sulphuric acid with a reddish-violet colour, and are reduced readily by zinc dust and dilute hydrochloric acid in acetic acid to the parent thianthren of m. p. 133°.

Oxidation of 2 : 6-Dimethylthianthren.—To a solution of dimethylthianthren (15 g.) in glacial acetic acid (600 c.c.), stirred at 75—80°, hydrogen peroxide (5% in excess of the calculated amount of perhydrol in 350 c.c. of acetic acid) was added (45 mins.). The mixture was kept at 80° for 2 hours, then boiled, and poured into water, and the solution made alkaline with ammonia. The products were collected and fractionally crystallised from methyl alcohol and from ethyl acetate, the final purification of the fractions of higher m. p. being from the former and of those of lower m. p. from the latter solvent. Prolonged fractionation at last gave two dioxides: the α -dioxide, m. p. 195.5° (202.5° corr.), crystallising from methyl alcohol in minute pointed needles with straight extinction (Found: C, 60.8; H, 4.8; S, 23.1. Calc.: C, 60.9; H, 4.4; S, 23.2%), which is evidently the substance (m. p. 194°) described by Fries and Volk (*loc. cit.*); and the β -dioxide, m. p. 168.5° (174° corr.), crystallising from methyl alcohol in blunt-ended needles with an oblique extinction (Found: C, 60.8; H, 4.8; S, 23.1%). Each of these dioxides was reduced by zinc dust in hot glacial acetic acid to the parent thianthren of m. p. 120°.

The solubilities of the two isomerides in ethyl acetate (100 g.) at 18° were identical (1.06 g.). In methyl alcohol (100 g.) at 18° the solubilities were: α -isomeride, 0.55 g.; β -isomeride, 1.66 g. The β -isomeride is moreover the more soluble in water, for the aqueous mother-liquors from the preparation yielded on repeated extraction by chloroform an almost pure specimen of the β -dioxide.

Preparation of the Trioxide and the Monosulphone.—The oxidation of dimethylthianthren described above was repeated, an amount of peroxide calculated to provide 3 g.-atoms of oxygen being used. The product precipitated by aqueous ammonia was recrystallised three times from methyl alcohol. The trioxide so obtained formed small white crystals, m. p. 223° (Found: S, 22.1. $C_{14}H_{12}O_3S_2$ requires S, 22.0%). Reduction with zinc and acetic acid gave the monosulphone, crystallising from glacial acetic acid in minute, doubly refracting polyhedra, m. p. 170—171° (Found: C, 61.3; H, 4.6; S, 23.6. $C_{14}H_{12}O_2S_2$ requires C, 60.9; H, 4.4; S, 23.2%).

This substance resists the action of zinc and acid : its m. p. is depressed by the addition of the β -dioxide of m. p. 168.5°.

Preparation of 2 : 6-Dichlorothianthren.—*p*-Chlorophenylthiol (27 g.) dissolved in sulphuric acid (185 c.c. of concentrated acid with 100 c.c. of 60% oleum) to a green solution which gradually turned purple (18 hrs.). The solution was poured into ice-water, and the brown precipitate collected and washed. The dry solid was extracted with boiling chloroform under reflux, and the solution dried with sodium sulphate and evaporated. The residue was crystallised once from acetic acid and once from benzene (yield, 13 g.). 2 : 6-Dichlorothianthren separates from acetic acid in small colourless needles with an oblique extinction, m. p. 181.5° (186° corr.) (Found : C, 50.3; H, 2.2; Cl, 24.5; S, 22.1. $C_{12}H_6Cl_2S_2$ requires C, 50.5; H, 2.1; Cl, 24.9; S, 22.5%). It dissolves slowly in concentrated sulphuric acid with a violet-blue colour which becomes an intense blue on warming : in this respect it appears to resemble the dichlorothianthrens of Fries and Vogt and of Rây (*loc. cit.*).

The condensation of chlorobenzene and sulphur monochloride in presence of aluminium chloride, described by the former authors, was repeated. The product was boiled with concentrated aqueous sodium hydroxide and kept with acetic acid. The material then extracted by chloroform was distilled under diminished pressure. The fraction, b. p. 240—270°, had m. p. 150—160° after crystallisation from acetic acid and evidently contained free sulphur. It was boiled in glacial acetic acid with metallic mercury to remove this, and then had m. p. 159—168°. This material must either have contained some free sulphur or a second organic substance. Repeated crystallisation from acetic acid and benzene alternately finally raised the m. p. to 180—181° (not depressed by admixture of the 2 : 6-dichlorothianthren from *p*-chlorophenylthiol).

Oxidation of 2 : 6-Dichlorothianthren.—The dichlorothianthren (25 g.) was dissolved in boiling glacial acetic acid (1200 c.c.) and cooled to 80°; a little of the thianthren then crystallised. A solution of hydrogen peroxide (calculated to provide 2 g.-atoms of oxygen) in 300 c.c. of acetic acid was slowly added at 80° (1 hr.), and the mixture kept at this temperature for a further hour and then boiled. The products, separated by dilution and addition of ammonia, were subjected to a tedious process of fractional crystallisation from glacial acetic acid and from a mixture of this solvent with an equal volume of benzene. A difficulty arose from the irregular behaviour of the substances in melting. It was finally found that some of the material tended to melt, resolidify and remelt, but that often when the specimens were slowly heated these changes were not apparent, so that a higher false m. p. might be observed. The difficulty was eliminated by using a preheated bath, and the m. p. data for the isomeric dioxides were obtained in this way. Some control of the elimination of over- or under-oxidised products was also secured by chlorine determinations (Robertson). A pair of stereoisomerides was finally isolated : the α -dioxide, m. p. 301° (313° corr.), crystallises from glacial acetic acid in sharp curved needles with a straight extinction (Found : C, 45.9; H, 2.1; Cl, 22.3; S, 20.2. $C_{12}H_6O_2Cl_2S_2$ requires C, 45.4; H, 1.9; Cl, 22.4; S, 20.2%); the β -dioxide, m. p. 256.5° (267.5° corr.), crystallises from the same solvent in bundles of blunt needles with straight extinction which tend to resemble in arrangement the crystals of phenylglucosazone (Found : C, 45.7; H, 2.0; Cl, 22.3; S, 20.3%). This substance resolidifies above its melting point and then melts at about 300°. Lack of material prevented a detailed examination of this change, which may be essentially a conversion into the α -isomeride.

Both isomerides were readily reduced to the parent thianthren by zinc and acetic acid. Their solubilities in glacial acetic acid (100 c.c.) at 18° were : α -dioxide, 0.07 g.; β -dioxide, 0.37 g.

The oxidation of the dichlorothianthren was repeated, 1 g.-equivalent of peroxide being used. When the products were crystallised from acetic acid, a compound, m. p. 215°, was first isolated, which proved to be the monosulphone (see below). Repeated crystallisation alternately from acetic acid and from toluene then gave the *monoxide*, m. p. 235—237° (decomp.), which separated from both of these solvents in small monoclinic needles with an extinction angle of 20° (Found : C, 47.7; H, 1.8. $C_{12}H_6OCl_2S_2$ requires C, 47.7; H, 2.0%). This substance was readily reduced to the parent thianthren by zinc and acetic acid.

When the dichlorothianthren was oxidised in acetic acid at 75° by addition of hydrogen peroxide in acetic acid as before but in amount calculated for 3 g.-atoms of oxygen, the mixture being heated on the water-bath for $\frac{1}{2}$ hour, the main product crystallised on cooling. The mother-liquors contained lower oxides. The product was washed with hot glacial acetic acid, and crystallised once from acetic acid, forming minute colourless needles, m. p. 281°. By an oversight this substance was not analysed, but it is evidently the trioxide, since it was readily

converted by reduction by zinc and glacial acetic acid into the *monosulphone*, m. p. 215°, identical with that obtained together with the monoxide. The monosulphone crystallises from glacial acetic acid in matted needles with an extinction angle of 10° (Found : C, 45·5; H, 2·0; S, 20·2. $C_{12}H_6O_2Cl_2S_2$ requires C, 45·4; H, 1·9; S, 20·2%) : it resists the action of zinc and acetic acid, and is therefore not a disulphoxide.

The dichlorothianthren was boiled for 1 hour with an excess of chromic anhydride in acetic acid, and the solution diluted. The *disulphone*, m. p. 293° (305° corr.), so produced, crystallised from acetic acid in minute monoclinic plates with an oblique extinction (Found : C, 41·3; H, 1·6; Cl, 20·4. $C_{12}H_6O_4Cl_2S_2$ requires C, 41·3; H, 1·7; Cl, 20·3%). It was not affected by boiling with acetic acid and metallic zinc.

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