

155. *Polymerisation of Thiophen Derivatives. Part VI.**
Some Condensations of Nitrothionaphthen 1 : 1-Dioxides.

By W. DAVIES and Q. N. PORTER.

Although when heated 6-nitrothionaphthen 1 : 1-dioxide does not condense with itself,¹ with thionaphthen 1 : 1-dioxide it forms a mixture of two 10 : 11-dihydro-mononitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxides. Only one mononitro-9-thia-3 : 4-benzofluorene derivative is isolated when thionaphthen 1 : 1-dioxide is heated with its 5-nitro-derivative. 4- and 5-Nitrothionaphthen 1 : 1-dioxide condense with themselves severally, to give the expected dinitro-9-thia-3 : 4-benzofluorene derivatives. Partial reduction of nitro- to amino-groups occurs with 5-nitrothionaphthen 1 : 1-dioxide. All the tetracyclic compounds are apparently derivatives of 9-thia-3 : 4-benzofluorene.

CONDENSATION of certain thionaphthen 1 : 1-dioxides with themselves, to give derivatives of 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (I) has been described by Davies and his co-workers^{1,2} and by Bordwell, McKellin, and Babcock.³ Both groups of workers have indicated that only polymer and sulphur dioxide are produced when 6-nitrothionaphthen 1 : 1-dioxide (III) is heated in solution at 180°. It is now found that when equimolar quantities of this sulphone and thionaphthen 1 : 1-dioxide (II) are heated

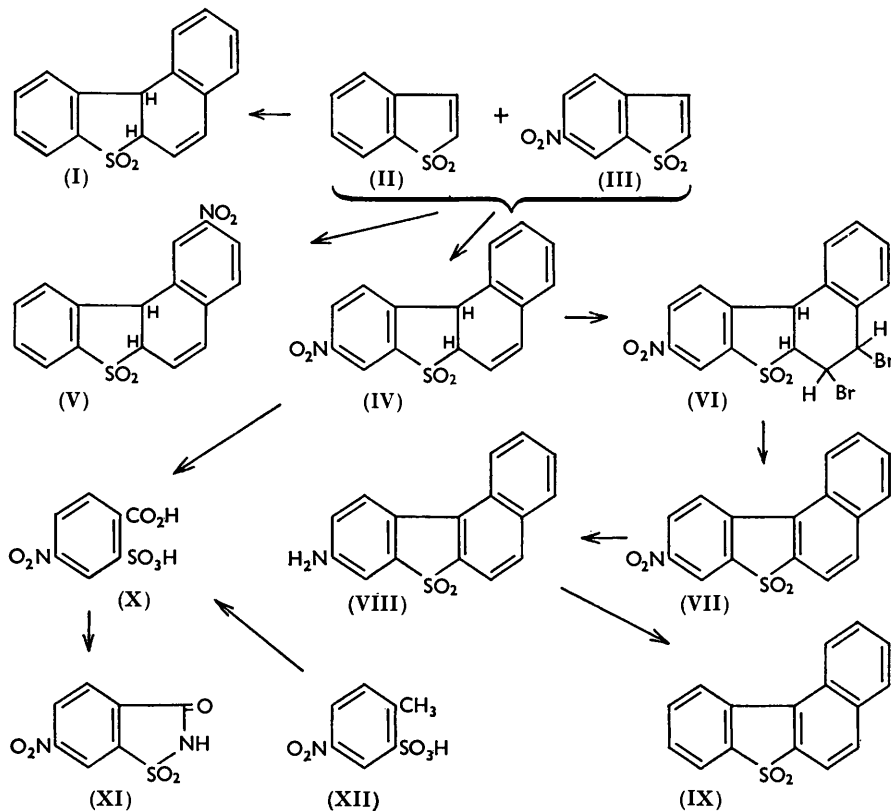
* Part V, *J.*, 1956, 2609.

¹ Davies, James, Middleton, and Porter, *J.*, 1955, 1565.

² Davies, Gamble, and Savige, *J.*, 1952, 4678.

³ Bordwell, McKellin, and Babcock, *J. Amer. Chem. Soc.*, 1951, **73**, 5566.

in solution at 180°, three products are formed, *viz.*, 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (I), and two mononitro-derivatives of it [one, (IV; m. p. 270°) in much higher yield than the other (V; m. p. 311°)]. Addition of bromine to the product (IV) gave a dibromide (VI) which was dehydrobrominated with pyridine to the nitro-sulphone (VII). Reduction of this with stannous chloride in *cyclohexanol* gave an amine



(VIII) which was deaminated to 9-thia-3 : 4-benzofluorene 9 : 9-dioxide (IX). Prolonged oxidation of the nitro-sulphone (IV) gave 4-nitro-2-sulphobenzoic acid (X), which was converted into the imide (XI), identical with a sample synthesised from 4-nitrotoluene-2-sulphonic acid⁴ (XII). These results prove that the nitro-sulphone (IV) is 10 : 11-dihydro-7-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide.

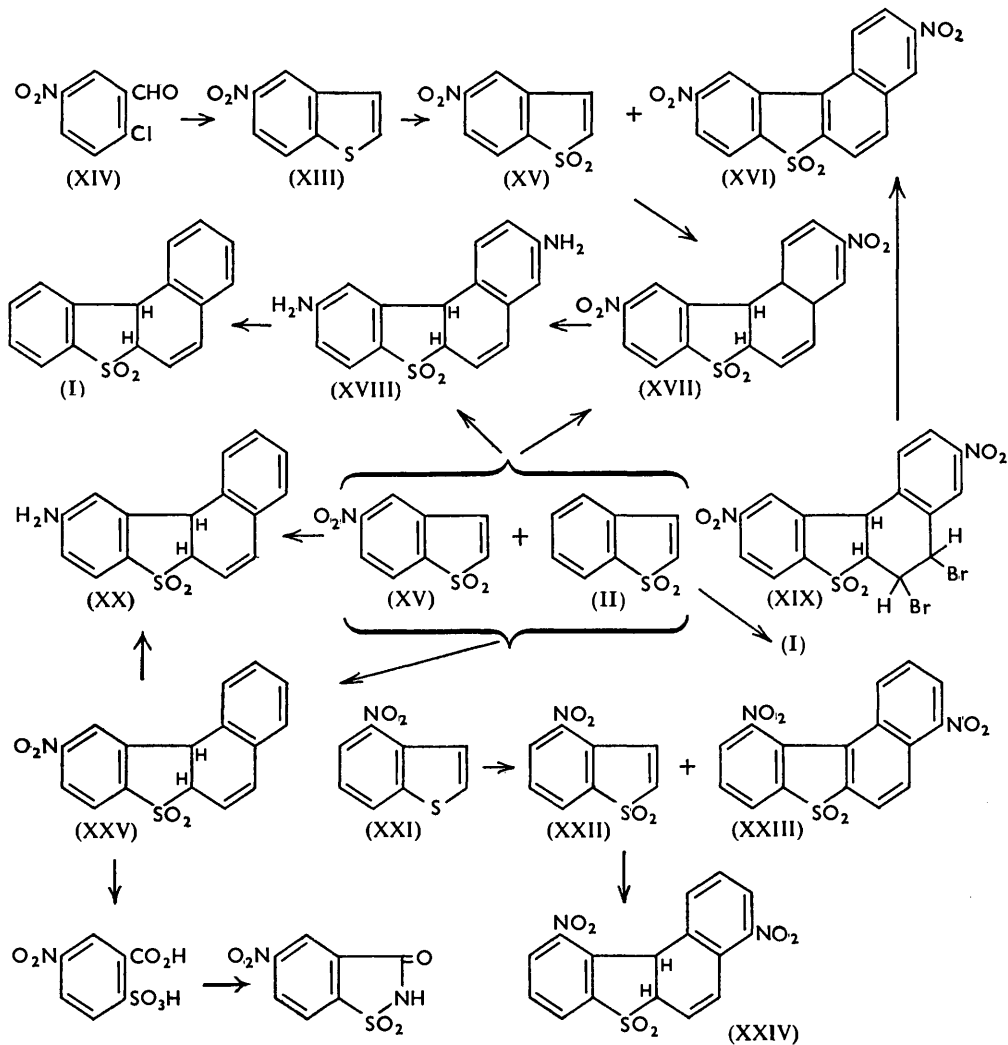
This proof of the structure of the tetracyclic compound (IV), the main product of the interaction of the sulphones (II) and (III), shows that the sulphone (II) reacts as diene towards its nitro-derivative (III). It is to be expected that the introduction of the electrophilic nitro-group in any position in the benzene ring would increase the electron-deficiency and hence the dienophilic properties of the non-aromatic, 2 : 3-double bond in (II).⁵ This view has been used to indicate the probable structure of other derivatives of this series, where complete proof of structure is lacking. Another assumption has been made, namely, that the formation of 9-thia-1 : 2-benzofluorene derivatives is unlikely. Such a derivative has indeed been formed¹ in poor yield by heating thionaphthen 1 : 1-dioxide without solvent at 195—200°, but has not hitherto been detected when the reaction has been carried out in solution, even at 180°. Accordingly the minor product,

⁴ Remsen and Gray, *Amer. Chem. J.*, 1897, **19**, 500.

⁵ Bailey and Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1940.

m. p. 311°, formed by the interaction of the sulphones (II) and (III) in solution at 180° is considered to be 10 : 11-dihydro-3'-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (V).

5-Nitrothionaphthen (XIII) was synthesised from 2-chloro-5-nitrobenzaldehyde (XIV) by a modification of the method of Fries *et al.*⁶ Oxidation with hydrogen peroxide gave the dioxide (XV) as described by Bordwell and Albisetti;⁷ however, a little 6 : 2'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XVI) was also isolated. This may be compared



with the isolation of a small amount of 9-thia-3 : 4-benzofluorene 9 : 9-dioxide (IX) on oxidation of thionaphthen.² When heated in solution at 180° 5-nitrothionaphthen 1 : 1-dioxide evolved sulphur dioxide and 10 : 11-dihydro-6 : 2'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XVII) was formed, the structure of which was proved by reduction to the diamine (XVIII), followed by deamination to 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (I). The dinitro-compound (XVII) was converted into the aromatic oxidation product (XVI) *via* the dibromide (XIX). It is noteworthy that in one experiment heat converted the sulphone (XV) into a substance analysing as an

⁶ Fries, Heering, Hemmecke, and Siebert, *Annalen*, 1937, 527, 83.

⁷ Bordwell and Albisetti, *J. Amer. Chem. Soc.*, 1948, 70, 1955.

amino-10 : 11-dihydro-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide. The conditions for the formation of this compound are apparently critical since the result could not be reproduced.

A mixed condensation of equimolar quantities of 5-nitrothionaphthen 1 : 1-dioxide and thionaphthen 1 : 1-dioxide was also carried out. Only one mononitro-compound was isolated, 10 : 11-dihydro-6-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide. The structure of this was proved by permanganate oxidation to 5-nitro-2-sulphobenzoic acid, identified as before. The self-condensation products (I) and (XVII) of the two dioxides were also isolated. In one experiment 6-amino- and 6 : 2'-diamino-10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide, (XX) and (XVIII), were isolated in low yield as well as the above products. These structures were proved by their formation by reduction of the corresponding nitro-compounds (XXV) and (XVII).

The conditions for the production of these compounds proved difficult to duplicate, most experiments producing little or none of the amino-sulphones. It is found that less than the one mole of sulphur dioxide per mole of 5-nitrothionaphthen 1 : 1-dioxide is evolved when this side reaction occurs, and it may be that the reduction is brought about by sulphur dioxide, the non-aromatic 10 : 11-bond of the molecule acting as hydrogen-donor. The use of aromatic nitro-compounds as dehydrogenating agents for the partly reduced rings produced by Diels-Alder reactions has been reported in a number of cases. Thus Bergmann, Haskelberg, and Bergmann⁸ have shown that, in nitrobenzene, 1-phenyl-butadiene and benzoquinone give the fully aromatic 1 : 5-diphenylantraquinone instead of the expected octahydro-derivative. If such a mechanism is involved in the present case, derivatives of the fully aromatic 9-thia-3 : 4-benzofluorene 9 : 9-dioxide should also be produced; however, possibly owing to the low and variable yields of the reduction products, such compounds have not as yet been isolated.

4-Nitrothionaphthen (XXI) has been synthesised from thionaphthen *via* 3-nitro- and 3 : 4-dinitro-thionaphthen as described by Fries *et al.*^{8,9} Oxidation gave the sulphone (XXI) as well as a little 5 : 1'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XXIII). Self-condensation occurred in the usual way at 180°, to give the dihydro-compound (XXIV). No amine has as yet been isolated from this reaction.

EXPERIMENTAL

Preparation of Nitrothionaphthen 1 : 1-Dioxides.—4-Nitrothionaphthen 1 : 1-dioxide. 3-Nitrothionaphthen was prepared (55%) by nitration of thionaphthen with nitric acid in acetic acid,⁹ then dinitrated with potassium nitrate in sulphuric acid,⁸ and the resultant 3 : 4-dinitrothionaphthen, m. p. 199.5—200° (32%), was reduced and deaminated to 4-nitrothionaphthen, m. p. 84°, with hydrogen sulphide in alcoholic ammonia (94%).

4-Nitrothionaphthen (1.0 g.) in acetic acid (6.0 ml.) and 30% hydrogen peroxide (4 ml.) was heated on the water-bath for 2 hr. The product that separated on cooling was extracted with alcohol, giving 4-nitrothionaphthen 1 : 1-dioxide (XXI), needles (0.8 g.), m. p. 185.5—186° (Found : C, 45.6; H, 2.6. C₈H₅O₄NS requires C, 45.5; H, 2.4%). The portion insoluble in alcohol was crystallised from benzene, giving prisms of 5 : 1'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XXIII) (0.025 g.), m. p. 271—272° (Found : C, 54.0; H, 2.4. C₁₆H₈O₆N₂S requires C, 53.9; H, 2.2%).

5-Nitrothionaphthen 1 : 1-dioxide. 2-Chloro-5-nitrobenzaldehyde was prepared (85%) by nitrating *o*-chlorobenzaldehyde with sodium nitrate in sulphuric acid (cf. Hodgson and Beard¹⁰). The aldehyde was converted into 5-nitrothionaphthen-2-carboxylic acid (33%) in one operation by the method of Fries *et al.*,⁸ successive reaction with sodium disulphide, chloroacetic acid, and sodium hydroxide. The acid, m. p. 238—240°, was decarboxylated to 5-nitrothionaphthen, m. p. 148—149°, with copper bronze in quinoline at 190°.

The dioxide, m. p. 164—165° (Bordwell and Albisetti⁷ report m. p. 166°), was prepared by oxidation with hydrogen peroxide as before (Found : O, 30.5. Calc. for C₈H₅O₄NS : O, 30.3%).

⁸ Bergmann, Haskelberg, and Bergmann, *J. Org. Chem.*, 1942, 7, 303.

⁹ Fries and Hemmecke, *Annalen*, 1929, 470, 1.

¹⁰ Hodgson and Beard, *J.*, 1926, 147.

A small amount of alcohol-insoluble 6 : 2'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XVI), needles (from benzene), m. p. 359—360°, was also formed (Found : C, 54.3; H, 2.4%).

6-Nitrothionaphthen 1 : 1-dioxide. Thionaphthen 1 : 1-dioxide was nitrated with fuming nitric acid, to give this dioxide, m. p. 188° (cf. Challenger and Clapham¹¹).

Self-condensation of Nitrothionaphthen 1 : 1-Dioxides.—(a) 4-Nitrothionaphthen 1 : 1-dioxide (0.25 g.) in *o*-dichlorobenzene (2.0 ml.) was refluxed for 4 hr. The product that separated on cooling was recrystallised from benzene, giving needles of 10 : 11-dihydro-5 : 1'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XXIV) (0.18 g.), m. p. 244—244.5° (Found : C, 53.9; H, 3.2. $C_{16}H_{10}O_4N_2S$ requires C, 53.6; H, 2.8%).

(b) 5-Nitrothionaphthen 1 : 1-dioxide (0.25 g.) in *o*-dichlorobenzene (2.0 ml.) was treated as above. The product was 10 : 11-dihydro-6 : 2'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XVII) (0.16 g.), needles (from benzene), m. p. 236—237° (Found : C, 54.0; H, 3.1%). In one experiment the dioxide (0.1 g.) gave a compound considered to be 2'-amino-6-nitro- or 6-amino-2'-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide, needles (from benzene), m. p. 234—235° (Found : C, 58.3; H, 3.5. $C_{16}H_{12}O_4NS$ requires C, 58.5; H, 3.6%). The m. p. was depressed on admixture with (XVII), and the compound was soluble in dilute hydrochloric acid.

The dioxide (XVII) (0.7 g.) in dry chloroform (30 ml.) was refluxed with bromine (0.6 ml.) for 7 hr. The solvent was removed and the residue, crystallised from cyclohexanol, gave pale yellow prisms of the dibromide (XIX) (0.8 g.), m. p. 320—321° (decomp.) (Found : C, 45.3; H, 2.5. $C_{16}H_{10}O_4N_2SBr_2$ requires C, 45.0; H, 2.3%).

The dibromide (0.3 g.) in pyridine (15 ml.) was refluxed for 6 hr. The product that separated on cooling was recrystallised from benzene, giving prisms of 6 : 2'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XVI), m. p. 359—360°, alone or mixed with the material formed during the oxidation of 5-nitrothionaphthen.

The dioxide (XVII) (0.35 g.) and stannous chloride dihydrate (1.0 g.) in cyclohexanol (15 ml.) containing concentrated hydrochloric acid (2.0 ml.) were refluxed for 1 hr. The complex that separated on cooling was set aside overnight with 40% sodium hydroxide solution (10 ml.). Concentration of a benzene extract of the insoluble material gave 6 : 2'-diamino-10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XVIII) (0.11 g.), m. p. 152—153° (decomp.) (Found : C, 64.3; H, 4.9. $C_{16}H_{14}O_4N_2S$ requires C, 64.3; H, 4.7%).

The diamine (0.07 g.) in dilute hydrochloric acid (3.0 ml.) was treated with sodium nitrite (0.03 g.), and the tetrazo-solution was added to hypophosphorous acid (4.0 ml.) and kept overnight. The mixture was filtered and the brown residue was crystallised from alcohol (charcoal), giving needles of 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide,¹ m. p. and mixed m. p. 181—182°.

Mixed Condensations of Nitrothionaphthen 1 : 1-Dioxides.—(a) 5-Nitrothionaphthen 1 : 1-dioxide (3.0 g.) and thionaphthen 1 : 1-dioxide (2.4 g.) in *o*-dichlorobenzene (36 ml.) were refluxed for 10 hr. The solvent was removed (reduced pressure) and the residue was dissolved in hot benzene (50 ml.). 10 : 11-Dihydro-6 : 2'-dinitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (0.80 g.), m. p. and mixed m. p. 236—237°, separated on cooling. The filtrate was chromatographed on alumina. The first band (colourless, blue fluorescence in ultraviolet light) gave 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (0.82 g.), m. p. and mixed m. p. 181—182°. The second band (pale yellow, non-fluorescent) gave needles of 10 : 11-dihydro-6-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XXV) (1.25 g.), m. p. 212—212.5° (Found : C, 61.65; H, 3.8; S, 10.3. $C_{16}H_{11}O_4NS$ requires C, 61.4; H, 3.5; S, 10.2%).

In one experiment carried out on approximately the above scale, 6-amino-10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XX) (0.07 g.), needles (from benzene), m. p. 248—248.5°, was isolated (third, non-fluorescent band) (Found : C, 67.7; H, 4.5; N, 4.8; S, 11.4. $C_{16}H_{13}O_4NS$ requires C, 67.8; H, 4.6; N, 4.9; S, 11.3%) together with 6 : 2'-diamino-10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (fourth band), m. p. and mixed m. p. 152—153° (0.05 g.). The formation of these amines was erratic, the yields varying from 0 to 5%. The sulphur dioxide evolved was determined by absorption in dilute hydrogen peroxide and titration with standard sodium hydroxide. The yield varied from 0.92 mol. when no amines were formed, to 0.77 mol. where the total yield of amines was 8%.

The dioxide (XXV) (0.3 g.) and stannous chloride dihydrate (0.7 g.) were refluxed with concentrated hydrochloric acid (1.0 ml.) in cyclohexanol (15 ml.) for 1 hr. The complex was

¹¹ Challenger and Clapham, *J.*, 1948, 1615.

decomposed with sodium hydroxide as before, and the product, crystallised from benzene, gave 6-amino-10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide, m. p. and mixed m. p. 247—248°.

The dioxide (XXV) (0.3 g.), potassium hydroxide (0.5 g.), and potassium permanganate (1.0 g.) in water (50 ml.) were refluxed for 20 hr. The solution was filtered from manganese dioxide, decolorised with sulphur dioxide, and concentrated to 10 ml. The salt that separated was dried at 110° and heated with phosphorus pentachloride (0.5 g.) and phosphorus oxychloride (0.5 ml.) for 1 hr. on the water-bath. The cooled mixture was decomposed with ice, and the crude dichloride was treated with aqueous ammonia (*d* 0.880; 15 ml.). The imide recrystallised from hot water as plates, m. p. 228°, undepressed with a sample synthesised from 5-nitro-2-sulphobenzoic acid.¹³

(b) 6-Nitrothionaphthen 1 : 1-dioxide (6.35 g.) and thionaphthen 1 : 1-dioxide (5.0 g.) in *o*-dichlorobenzene (110 ml.) were refluxed for 10 hr. The solvent was removed (reduced pressure) and the residue, in benzene, was chromatographed on alumina. The first band (colourless, blue fluorescence in ultraviolet light) gave 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide, m. p. and mixed m. p. 181—182° (1.3 g.). A second band (pale yellow, no fluorescence) gave pale yellow prisms (from benzene) of 10 : 11-dihydro-7-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (IV), m. p. 269—269.5° (2.7 g.) (Found : C, 61.8; H, 3.8; N, 4.3. C₁₆H₁₁O₄NS requires C, 61.4; H, 3.5; N, 4.4%). The third band (yellow, no fluorescence) gave orange prisms (benzene) of 10 : 11-dihydro-3'-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (V) (0.10 g.), m. p. 310—311° (Found : C, 61.7; H, 3.6%).

The nitro-sulphone (IV) (0.4 g.) and bromine (0.4 ml.) in dry chloroform (30 ml.) were refluxed for 10 hr. The solvent was evaporated and the residue crystallised from benzene, giving prisms of the dibromide (VI) (0.42 g.), m. p. 231—232° (decomp.) (Found : C, 40.7; H, 2.6. C₁₆H₁₁O₄NBr₂S requires C, 40.6; H, 2.3%).

The dibromide (0.35 g.) was refluxed with pyridine (5 ml.) for 4 hr. The product that crystallised on cooling was recrystallised from benzene, giving prisms of 7-nitro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (VII) (0.2 g.), m. p. 282—283° (Found : C, 62.0; H, 3.05. C₁₆H₉O₄NS requires C, 61.7; H, 2.9%).

This nitro-sulphone (0.31 g.) was reduced with stannous chloride dihydrate (0.7 g.) in cyclohexanol and hydrochloric acid as before. 7-Amino-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (VIII), needles (from benzene), had m. p. 266—267° (Found : C, 68.2; H, 4.0. C₁₆H₁₁O₂NS requires C, 68.3; H, 3.9%).

The amine (0.1 g.) was diazotised and treated with hypophosphorous acid as before, giving needles of 9-thia-3 : 4-benzofluorene 9 : 9-dioxide,³ m. p. and mixed m. p. 233—234°.

The dioxide (IV) (0.6 g.) was oxidised as described for the 6-nitro-isomer. The acid was converted into 6-nitrosaccharin (XI), m. p. 208—209°, alone and mixed with a sample prepared from 4-nitrotoluene-2-sulphonic acid (XII).⁴

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¹³ Noyes, *Amer. Chem. J.*, 1886, **8**, 167.