Polymerisation of Thiophen Derivatives. Part IV. The Formation of Some 9-Thia-1 : 2- and 9-Thia-3 : 4-benzofluorene Derivatives.*

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[Reprint Order No. 5949.]

Though the usual products obtained by heating thionaphthen 1 : 1-dioxide (I) are sulphur dioxide and 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (II) (Part I), different conditions cause the formation of some 1 : 2-benzo-9-thiafluorene 9 : 9-dioxide (III). 3-Chloro- and 3- and 5-bromothionaphthen dioxides give good yields of 9-thia-3 : 4-benzofluorene derivatives, of which the structures have been proved. The self-condensation of thionaphthen dioxide derivatives is of wide application, though tars are sometimes the only organic products. New syntheses have been developed for related polycyclic sulphones and sulphoxides.

Bordwell, McKellin, and Babcock (*J. Amer. Chem. Soc.*, 1951, **73**, 5566) showed that thionaphthen 1 : 1-dioxide (I) when heated in solution gives sulphur dioxide and 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (II), convertible by removal of hydrogen into the sulphone (IV) derived from 9-thia-3 : 4-benzofluorene (XVI). This observation was made independently by Davies, Gamble, and Savige (Part I), who moreover found that the tetracyclic sulphone (IV) is formed in small yield during oxidation of thionaphthen to its sulphone. An intermediate adduct of a Diels–Alder type is postulated, and Davies and James (Part II) have isolated such an intermediate in the simpler case of the oxidative conversion of thiophen into thionaphthen dioxide.

The tetracyclic compounds formed in good yield from simple thionaphthen dioxides have so far proved to be 3 : 4- and not 1 : 2-benzo-9-thiafluorene derivatives. Thus, 5-bromothionaphthen 1 : 1-dioxide (XIII) in solution about 180° gives 10 : 11-dihydro-2′ : 6-dibromo-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XIV), whose 1 : 2-dibromide through dehydrobromination gives 2′ : 6-dibromo-9-thia-3 : 4-benzofluorene 9 : 9-dioxide. From this compound lithium aluminium hydride removes both oxygen and both bromine atoms, forming 9-thia-3 : 4-benzofluorene (XVI), a useful reference compound in this series (Part I).

The attempts of Bordwell *et al.* (*loc. cit.*) to extend the self-condensation reaction to thionaphthen dioxides other than (II) were unsuccessful, but in fact 3-halogenothionaphthen dioxides do react at an unusually high temperature. When 3-chlorothionaphthen 1 : 1-dioxide (IX; X = Cl) is heated alone at 280° it gives a 75% yield of 2 : 11-dichloro-10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (X; X = Cl). Dehydrochlorination with pyridine converts this into 2-chloro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (XI; X = Cl), which is also produced by the interaction of (II) and phosphorus pentachloride, which here acts as a chlorinating and dehydrogenating agent (cf. Bert and Annequin, *Compt. rend.*, 1931, **192**, 1107). The " dimerisation " of 3-bromothionaphthen 1 : 1-dioxide also requires a high temperature, and the tetracyclic dihydro-derivative has not been isolated in this case. Instead, the monobromo-compound (XI; X = Br) is obtained which, together with the tetrahydro-derivative (XII; X = Br), is obtained from the dihydro-compound (II) by use of bromine. The reaction chart oversimplifies the course of this halogenation, for which the experimental section should be consulted.

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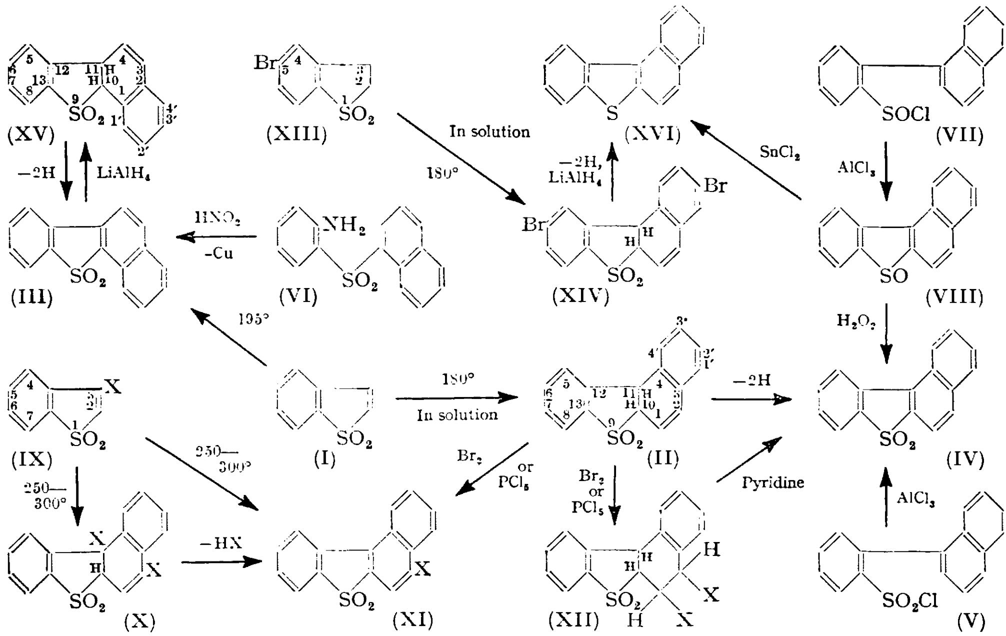
* The papers by Davies, Gamble, and Savige, *J.*, 1952, 4678, and by Davies and James, *J.*, 1954, 15, and *J.*, 1955, 314, are to be regarded as Parts I, II, and III, respectively.

The usual course of the formation of a 3 : 4-benzo-derivative of thiafluorene can be avoided when thionaphthen dioxide (I) is heated at 195° under special conditions. Instead of the tetracyclic dihydro-compound (II), there is formed a small yield of a compound now shown to be 9-thia-1 : 2-benzofluorene 9 : 9-dioxide (III). This structure has been proved by desulphurisation with Raney nickel to 2-phenylnaphthalene, and also by synthesis from *o*-aminophenyl 1-naphthyl sulphone (VI) by a Pschorr type of reaction. Whereas the sulphone (IV) is readily reduced to the sulphide (XVI) by lithium aluminium hydride, the isomer (III) is merely reduced to 10 : 11-dihydro-9-thia-1 : 2-benzofluorene 9 : 9-dioxide (XV). Bromine converts this into the 3 : 4-dibromide which with boiling pyridine gives the original compound (III). Direct dehydrogenation by the use of *N*-bromosuccinimide can be of great value in this series, and instances will be given in a later communication.



It is to be expected that the sulphone group in the 1 : 2-benzo-derivative (III) would, through steric influences, be less easily attacked by certain reagents than that in the isomer (IV). This is true of alkali, but the completely different behaviour of the two compounds towards lithium aluminium hydride may serve as a reliable guide in predicting the 1 : 2- or the 3 : 4-position of the benzo-group in various thiafluorene 9 : 9-dioxide derivatives. Whereas the compounds (IV), (XI; X = Br), and (XIV; after preliminary removal of two hydrogen atoms) are converted into the reference compound (XVI), the sulphone group in the 1 : 2-benzothiafluorene derivative (III) remains intact. This last reaction is up to the present unique in this polycyclic series in that a dihydro-compound is formed; also a crimson colour develops during the reduction and persists until the reagent is destroyed on addition of water. The stereochemical course of reduction of several steroidal ketones by lithium aluminium hydride is thought to be due to the formation of an intermediate organometallic compound (*Ann. Reports*, 1953, **50**, 167), and perhaps the resistance to reduction shown by the sulphone group in the compound (III) is due to hindrance, by the neighbouring 1 : 2-benzo-group, of formation of such an intermediate. It may also be of general significance that Raney nickel removes the sulphone group from the compound (III), giving 2-phenylnaphthalene, because this reagent can be outstanding in overcoming steric effects, as for example in the reduction of the blocked ethylene oxide group in scopolamine (Fodor and Kovacs, *J.*, 1953, 2341). Reagents known to be either responsive or unresponsive to steric effects in certain fields may sometimes make unnecessary the rigid proof of structure which has been provided for all the new compounds reported in this communication.

Among features of general interest in this work is the use of the Pschorr reaction for the cyclisation of aminoaryl sulphones, in which the yields so far have been between 20 and 30%. Dibenzothiophen 1 : 1-dioxide (9-thiafluorene 9 : 9-dioxide) was independently prepared by this method by the present authors and by de Tar and Sagmanli (*J. Amer. Chem. Soc.*, 1950, **72**, 965). It had also been prepared in small yield by an unintentional Pschorr synthesis by Ullmann and Pasdermadjian (*Ber.*, 1901, **34**, 1150). In the present work the tetracyclic compound (III) and an apparently new form of the isomer (IV) [the structure of which was shown by its conversion into the sulphide (XVI)] have been synthesised by the Pschorr cyclisation of the appropriate *o*-aminophenyl naphthyl sulphones. However, though the yield of five-membered rings produced by Pschorr cyclisations at present is often small (see also Hey and Mulley, *J.*, 1952, 2276; de Tar and Sagmanli, *loc. cit.*), this probably homolytic process of making cyclic sulphones is invaluable for determining chemical structure, and the yields should be capable of improvement.

Another useful synthesis is an internal Friedel–Crafts reaction to form cyclic sulphones. Chaix (*Bull. Soc. chim. France*, 1933, **53**, 700) obtained dibenzothiophen 1 : 1-dioxide from diphenyl-2-sulphonyl chloride. This rarely used reaction, which seems to be general and has been used to convert the chloride (V) into the sulphone (IV), is now of potential value as an alternative synthesis of polynuclear thiophen derivatives, which can often be formed by reduction of the corresponding sulphones with lithium aluminium hydride. A related and apparently novel process is the ring-closure, under Friedel–Crafts and related conditions, of diphenyl-2-sulphinyl chloride to form dibenzothiophen 1-oxide, and of *o*-1-naphthylbenzenesulphinyl chloride (VII) to give 9-thia-3 : 4-benzofluorene 9-oxide (VIII). This process has an advantage over that requiring sulphonyl chlorides since the sulphoxides produced are, unlike sulphones, reducible to the sulphides by common reducing agents. Thus the sulphoxide (VIII) is rapidly reduced by stannous chloride, giving an excellent yield of the sulphide (XVI). However, both these Friedel–Crafts cyclisations involve the serious difficulty of previously preparing the acid chlorides with the sulphur-containing groups in the appropriate *ortho*-positions.

There is uncertainty in the literature about the properties or structure of the monochloro- and dichloro-derivatives of thionaphthen. From equimolar quantities of chlorine and thionaphthen Schlesinger and Mowry (*J. Amer. Chem. Soc.*, 1951, **73**, 2614) obtained a liquid monochlorothionaphthen whose dioxide had m. p. 158·5—160°. Hartough and Meisel (" Compounds with Condensed Thiophene Rings," Interscience Publ., New York, 1954, p. 164) refer to the m. p. 167—168·5° for the dioxide of 3-chlorothionaphthen recorded in a Ph.D. dissertation by Lampert. In the present work, 3-chlorothionaphthen 1 : 1-dioxide (IX; X = Cl), m. p. 166—167°, is formed in good yield from phosphorus pentachloride and 3-hydroxythionaphthen 1 : 1-dioxide (IX; X = OH), which was obtained on hydrolysis of 3-diethylaminothionaphthen 1 : 1-dioxide (Bordwell and Albisetti, *J. Amer. Chem. Soc.*, 1948, **70**, 1558), of known structure. Chlorination of thionaphthen with less than a mole of chlorine also gives a monochloro-derivative, the dioxide of which has m. p. 166—167°.

Dichlorination of thionaphthen gives a crystalline dichlorothionaphthen assumed (Komppa, *J. pr. Chem.*, 1929, **122**, 319; Schlesinger and Mowry, *loc. cit.*; Davies, Gamble, and Savige, *loc. cit.*, p. 4681) to be 2 : 3-dichlorothionaphthen (the last authors, through a clerical error, named it 3 : 5-dichlorothionaphthen). There is still no definite proof that the second chlorine atom entered at position 2. However, the dioxide (m. p. 160—161°) of the dichlorothionaphthen is, like that of 2-bromothionaphthen, remarkably stable to heat, and in small quantities can be distilled unchanged at ordinary pressure. All the thionaphthen dioxides of known structure so far investigated which contain a substituent in the benzene ring but have position 2 free are found to be readily decomposed by heat. This tends to support the otherwise very probable 2 : 3-dichloro-structure assigned previously.

The compound represented as 3-hydroxythionaphthen 1 : 1-dioxide (IX; X = OH) has been arbitrarily given the enol form. The dimethyl acetal (m. p. 142·5—143°) of the corresponding ketone is obtained from 3-bromothionaphthen 1 : 1-dioxide (IX ; X = Br) and methanolic potassium hydroxide. This acetal has the expected properties and it has been previously made (m. p. 144°) by Arndt and Martius (*Annalen*, 1932, **499**, 283) by base-catalysed addition of methanol to the non-aromatic double bond in the enol ether (IX ; X = OMe). Hartough and Meisel (*op. cit.*, pp. 157—158) cast doubt on the existence of this acetal : however, its formation by either method presents no theoretical difficulties, though the process is unusual. A close analogy is the conversion, by methanolic alkali, of aliphatic 2-chlorovinyl ketones into 2-keto-acetals [$R\cdot CO\cdot CH{:}CHCl \longrightarrow R\cdot CO\cdot CH_2\cdot CH(OMe)_2$] (Nelles, B.P. 466,890/1937 ; Price and Pappalardo, *J. Amer. Chem. Soc.*, 1950, **72**, 2613).

Generally, thionaphthen dioxides, when heated, evolve sulphur dioxide which, with tars, are the only product so far identified from the dioxides of 3-methyl-, 3-methoxy-, 3-dimethylamino-, 3-piperidino-, and 6-nitro-thionaphthen. 2-Bromo- and 2 : 3-dichlorothionaphthen dioxide were extremely stable to heat. However, an account will shortly be submitted of pure polymerised products from derivatives of thionaphthen substituted in the benzene nucleus. From the point of view of possible carcinogen formation, not only are polycyclic sulphides themselves of interest, but removal of the sulphur atom followed by cyclisation opens up a new route to the synthesis of polycyclic hydrocarbons (Davies, Gamble, James, and Savige, *Chem. and Ind.*, 1952, 804). The type of polymerisation process, detailed in the present communication, is capable of wide extension both to simple thiophen derivatives and to tricyclic (and probably polycyclic) systems in which the benzo-group in benzothiophen is replaced by homocyclic or heterocyclic residues. This and related work is being continued.

EXPERIMENTAL

Preparation of Sulphones of Substituted Thionaphthens.—3-Bromothionaphthen 1 : 1-dioxide, m. p. 183·5—184° (Bordwell and Albisetti, *loc. cit.*), was converted into 3-dimethylamino- and 3-piperidino-thionaphthen 1 : 1-dioxides by their method. These two bases when heated gave tars and sulphur dioxide.

3-Bromothionaphthen 1 : 1-dioxide (0·7 g.) was converted into 3-methoxythionaphthen 1 : 1-dioxide in good yield (m. p. 219—220°) by refluxing it in methanol (10 ml.) containing potassium hydroxide (0·2 g.) for 1 hr. (cf. Bordwell and Albisetti, *ibid.*, p. 1558, who record m. p. 220°). For this reaction commercial methanol had been purified by mixing it with a little hydrochloric acid, distilling it, and redistilling it over potassium hydroxide.

The 2 : 3-dihydro-3 : 3-dimethoxythionaphthen 1 : 1-dioxide (0·43 g. ; m. p. 142·5—143°, from methanol), was obtained when the above process was repeated with commercial methanol (Found : C, 52·7 ; H, 5·1 ; S, 14·3. Calc. for $C_{10}H_{12}O_4S$: C, 52·6 ; H, 5·3 ; S, 14·05%). After 1 hour's heating on the water-bath with 2% hydrochloric acid it gave 3-hydroxythionaphthen 1 : 1-dioxide, m. p. and mixed m. p. 133—133·5° (from benzene).

3-Hydroxythionaphthen 1 : 1-dioxide, which is best made by hydrolysis of 3-diethylaminothionaphthen 1 : 1-dioxide (Bordwell and Albisetti, *loc. cit.*), sintered when strongly heated. If the compound existed in the keto-form, the usual type of self-condensation would not occur.

3-Chlorothionaphthen 1 : 1-dioxide, prisms, m. p. 166—167° (from benzene–light petroleum), was obtained (1·9 g., 83%) by refluxing 3-hydroxythionaphthen 1 : 1-dioxide (2·0 g.) with phosphorus pentachloride (4·0 g.) and phosphorus oxychloride (10 ml.) for 4 hr., and decomposing the cold product with ice. It was also prepared (m. p. and mixed m. p. the same) (Found : Cl, 17·7. Calc. for $C_8H_5O_2SCl$: Cl, 17·7%) by interaction of hydrogen peroxide in glacial acetic acid on the water-bath with 3-chlorothionaphthen made as follows :

Chlorine (2·5 l. ; 0·75 mol.) in carbon tetrachloride (200 ml.) was added drop-wise to a stirred solution of thionaphthen (20 g., 1 mol.) in carbon tetrachloride (100 ml.). Stirring was continued for 8 hr., and the solution then kept overnight and fractionated. After removal of unchanged thionaphthen the fraction (b. p. 140—160°/13 mm. ; 4 g.) was essentially 3-chlorothionaphthen, and the fraction of b. p. 200—220°/13 mm. solidified to needles, m. p. 53—54°, of practically pure 2 : 3-dichlorothionaphthen.

2 : 3-Dichlorothionaphthen 1 : 1-dioxide, made by the action of hydrogen peroxide in the usual way, had m. p. 157—158° (Found : Cl, 30·0. Calc. for $C_8H_4O_2SCl_2$: Cl, 30·2%). It distilled unchanged at 1 atm.

2-Bromothionaphthen 1 : 1-dioxide (Bordwell, Lampert, and McKellin, *J. Amer. Chem. Soc.*, 1949, **71**, 1702) can be distilled unchanged at 1 atm. in small quantities.

6-Nitrothionaphthen 1 : 1-dioxide, made by Challenger and Clapham's method (*J.*, 1948, 1615), readily forms tar and sulphur dioxide when heated.

6-*Amino* 2 : 3-*dihydrothionaphthen* 1 : 1-*dioxide*, pale yellow needles, m. p. 198—198·5° (from benzene), was formed when the above nitro-compound was reduced with tin and hot hydrochloric acid (Found : C, 52·7; H, 5·0. $C_8H_9O_2NS$ requires C, 52·4; H, 4·9%).

6-*Aminothionaphthen* 1 : 1-*dioxide* (Found : C, 53·3; H, 4·0. $C_8H_7O_2NS$ requires C, 53·0; H, 3·9%), yellow needles, m. p. 172·5—173° (from benzene), was formed when the above nitro-compound (3·0 g.) was shaken for 3 hr. with stannous chloride dihydrate (14·0 g.) in concentrated hydrochloric acid (25 ml.), and the solution then kept at room temperature for a further 8 hr. and made alkaline with sodium hydroxide (30%). It yielded 6-*acetamidothionaphthen* 1 : 1-*dioxide*, needles, m. p. 192—192·5° (from benzene), when refluxed with acetic anhydride containing pyridine (Found : N, 6·4. $C_{10}H_9O_3NS$ requires N, 6·3%). This and the parent amine decompose readily on being heated, and no crystalline derivative has been isolated.

Action of Heat on Thionaphthen Dioxide (I).—(*a*) 10 : 11-Dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (II) is obtained in optimum yield (89%) by refluxing thionaphthen dioxide for 6 hr. in four times its wt. of *o*-dichlorobenzene (b. p. 176—180°).

(*b*) The dioxide (2·0 g.) in a Pyrex tube was placed in an oil-bath preheated to 195° ± 5°, and this temperature maintained until the evolution of sulphur dioxide was complete (about 20 min.). A dark yellow-green chloroform extract, partially decolorised with carbon, yielded a dark orange oil whose benzene solution, chromatographed on alumina, developed bands which fluoresced in ultraviolet light. The single yellow band was eluted by benzene, and the crude yellow solid (0·2 g.; m. p. 120—130°), after several crystallisations from methanol and further chromatography on alumina, gave 9-thia-1 : 2-benzofluorene 9 : 9-dioxide (III), colourless needles, m. p. 195·5—196° (from benzene), with a strong blue fluorescence in ultraviolet light [the yellow fluorescence recorded for this substance, m. p. 197° (Davies, Gamble, and Savige, *loc. cit.*), is due to traces of impurity] (Found : C, 72·3; H, 3·8. Calc. for $C_{16}H_{10}O_2S$: C, 72·2; H, 3·8%).

A phenolic oil, soluble in alkali and giving a purple colour with ferric chloride but no crystalline benzoyl derivative, was obtained by fusing the dioxide (III) with excess of potassium hydroxide at 400—420° for 5 min. Desulphurisation occurred when the dioxide (III) (0·1 g.) and activated Raney nickel (3 g.; Mozingo, Wolf, Harris, and Folkers, *J. Amer. Chem. Soc.*, 1943, **65**, 1013) in ethanol (100 ml.) were refluxed for 8 hr.; the organic residue of 2-phenylnaphthalene (from ethanol) had m. p. and mixed m. p. 102—103° (cf. Elks, Haworth, and Hey, *J.*, 1940, 1284).

Lithium aluminium hydride (0·5 g.) reduced the dioxide (III) (0·3 g.) in boiling ether (200 ml.) in 6 hr. to 10 : 11-*dihydro*-9-*thia*-1 : 2-*benzofluorene* 9 : 9-*dioxide* (XV) (0·15 g.), needles, m. p. 157—158° (from ethanol) (Found : C, 71·7; H, 4·5; S, 11·7. $C_{16}H_{12}O_2S$ requires C, 71·7; H, 4·5; S, 11·9%). Unlike the isomeric 3 : 4-benzo-compound (II), it was very resistant to boiling 10% sodium hydroxide solution, 75% being recovered after 5 hr. However, the filtrate on acidification yielded a small amount of an unstable oil, apparently a crude sulphinic acid, for it rapidly lost sulphur dioxide at room temperature, and when freshly isolated gave a red-brown precipitate with ethanolic ferric chloride.

Bromine (0·15 g.) and the dioxide (XV) (0·25 g.) in boiling carbon tetrachloride (10 ml.) (10 hr.) gave 3 : 4-*dibromo*-10 : 11-*dihydro*-9-*thia*-1 : 2-*benzofluorene* 9 : 9-*dioxide*, prisms (from benzene), m. p. 226—226·5° (Found : Br, 37·2. $C_{16}H_{12}O_2SBr_2$ requires Br, 37·4%). When this (0·1 g.) was refluxed with pyridine (2·5 ml.) for 8 hr., it re-formed the unsaturated compound (III), m. p. and mixed m. p. 195—196°.

Action of Phosphorus Pentachloride on 10 : 11-*Dihydro*-9-*thia*-3 : 4-*benzofluorene* 9 : 9-*Dioxide* (II).—Finely powdered phosphorus pentachloride (6·0 g.) and this dioxide (II) (3·0 g.) were heated at 160° for 10 min.; the glass formed on cooling was powdered and stirred with water (50 ml.), and the residual yellow compound dried over phosphoric oxide and extracted with absolute alcohol (4 × 50 ml.). The insoluble portion, twice crystallised from 2-methoxyethanol, gave plates (0·1 g.) of 2-*chloro*-9-*thia*-3 : 4-*benzofluorene* 9 : 9-*dioxide* (XI; X = Cl), m. p. 294—295°, slightly soluble in benzene (Found : C, 64·0; H, 2·95. $C_{16}H_9O_2SCl$ requires C, 63·9; H, 3·0%).

The combined alcoholic filtrates, on cooling, deposited pale yellow needles, m. p. 226—228° (0·5 g.), whose solution in benzene was passed through a short column of alumina. The first 5 c.c. of eluate deposited colourless needles of 9-thia-3 : 4-benzofluorene 9 : 9-dioxide (IV), m. p. and mixed m. p. 234° (though described as pale yellow by Davies *et al.*, *loc. cit.*, p. 4678) (Found : C, 72·1; H, 4·0. Calc. for $C_{16}H_{10}O_2S$: C, 72·2; H, 3·8%).

The alcoholic filtrates, after concentration to 25 ml., gave the main product of the reaction, pale yellow crystals (1·9 g.), m. p. 171—172·5°, which from alcohol (charcoal) yielded colourless prisms of 1 : *2-dichloro-*1 : 2 : 10 : 11*-tetrahydro-*9*-thia-*3 : 4*-benzofluorene* 9 : 9*-dioxide* (XII; X = Cl), m. p. 173·5—174°, showing a strong blue fluorescence in diffused daylight (Found: C, 56·6; H, 3·9; S, 9·2. $C_{16}H_{12}O_2SCl_2$ requires C, 56·6; H, 3·55; S, 9·5%). It was dehydrochlorinated when refluxed with pyridine for 8 hr. or heated alone at 250° for 8 min. The alcoholic solution of the residue was clarified by charcoal. The product in both cases was the sulphone (IV), m. p. and mixed m. p. 234°.

Self-condensation of 3*-Chlorothianaphthen* 1 : 1*-Dioxide* (IX; X = Cl).—The sulphone (1·0 g.) was heated in a Pyrex tube in 1-bromonaphthalene vapour (280°) for 10 min., the cooled melt was extracted with boiling benzene (500 ml.), and the concentrated extract (charcoal) on cooling gave prisms (0·63 g.; 75%) of 2 : 11*-dichloro-*10 : 11*-dihydro-*9*-thia-*3 : 4*-benzofluorene* 9 : 9*-dioxide* (X; X = Cl), m. p. 270—271° (Found: C, 57·4; H, 2·9. $C_{16}H_{10}O_2SCl_2$ requires C, 57·0; H, 3·0%). It (120 mg.) was dehydrochlorinated by refluxing pyridine (10 ml.) (20 hr.), and the pyridine removed under reduced pressure. The benzene extract, clarified with carbon, gave prisms (80 mg.), m. p. 294—295°, of 2-chloro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (Found: Cl, 11·4. $C_{16}H_9O_2SCl$ requires Cl, 11·1%). It was identical (mixed m. p.) with the above product from the interaction of phosphorus pentachloride with the sulphone (II).

In a preliminary experiment pure 3-chlorothionaphthen dioxide, heated in an oil-bath at 260—280° for 30 min., gave, in addition to the above substance, m. p. 270—271°, a small amount of less soluble colourless crystals of unknown constitution, decomp. >300° (Found: C, 49·1; H, 2·8%).

Action of Bromine on 10 : 11*-Dihydro-*9*-thia-*3 : 4*-benzofluorene* 9 : 9*-Dioxide* (II).—Bromine (0·5 ml.) and the dioxide (1·0 g.) were refluxed in carbon tetrachloride (20 ml.) for 6 hr. and the yellow crystals formed after cooling, together with those which separated when the mother-liquor was concentrated to 5 ml., were extracted with ethanol (100 ml.). The small insoluble portion was 2*-bromo-*9*-thia-*3 : 4*-benzofluorene* 9 : 9*-dioxide* (XI; X = Br), which recrystallised from 2-methoxyethanol in needles, m. p. 309—310° (Found: C, 56·0; H, 2·65; S, 9·6. $C_{16}H_9O_2SBr$ requires C, 55·65; H, 2·6; S, 9·3%). The alcoholic extract, when concentrated to 25 ml., gave 1 : 2*-dibromo-*1 : 2 : 10 : 11*-tetrahydro-*9*-thia-*3 : 4*-benzofluorene* 9 : 9*-dioxide* (XII; X = Br), m. p. 185·5—186° (0·85 g.) (Found: C, 45·1; H, 3·0; S, 7·2. $C_{16}H_{12}O_2SBr_2$ requires C, 44·9; H, 2·8; S, 7·5%). On further concentration of the alcoholic filtrate to 5 ml. an additional 0·1 g. thereof was obtained, together with about 5 mg. of colourless needles, m. p. 198—199°, which were separated by hand. This compound could not be obtained when the bromination was repeated. The present work showed that only in this respect was the bromination difficult to repeat, and this is in contrast to the experience of Bordwell, McKellin, and Babcock (*loc. cit.*), whose only product from the reaction was $C_{16}H_{12}O_2SBr_2$, m. p. 175—176°, which may be an impure specimen of our product (XII; X = Br).

The above dibromo-compound, m. p. 186° (0·25 g.), was refluxed with pyridine for 6 hr., and the product obtained after dilution with water gave needles (0·14 g., 90%) (from alcohol), m. p. 234° alone or mixed with the sulphone (IV). This is also formed by heating dibromide (XII; X = Br) alone at 190° for 10 min. It is noteworthy that the aromatic sulphone (IV) is recovered unchanged after 6 hours' refluxing with bromine (2 mols.) in carbon tetrachloride.

Self-condensation of 3*-Bromothionaphthen* 1 : 1*-Dioxide* (IX; X = Br).—This sulphone (0·5 g.) was heated in a Pyrex tube at 290—300° for ½ hr., and the black residue extracted with ethanol (500 ml.). The extract was boiled with charcoal and after concentration and cooling yielded pale yellow needles (0·2 g.), m. p. 309—310° undepressed by admixture with the monobromo-derivative (XI; X = Br) (Found: C, 55·8; H, 2·8%).

5*-Bromothionaphthen* 1 : 1*-Dioxide* (XIII).—5-Bromothionaphthen (100 mg.), prepared by the cyclisation of 4-bromophenylthioacetaldehyde diethyl acetal (cf. Rabindran, Sunthankar, and Tilak, *Proc. Indian Acad. Sci.*, 1952, **36**, *A*, 405), was heated in glacial acetic acid (1·0 ml.) and hydrogen peroxide (0·25 ml.; 30%) for 1 hr. on the water-bath, giving an excellent yield of 5*-bromothionaphthen* 1 : 1*-dioxide*, in colourless needles, m. p. 144—144·5° (from aqueous alcohol) (Found: O, 13·2. $C_8H_5O_2SBr$ requires O, 13·1%). This (50 mg.) was heated under reflux in *o*-dichlorobenzene (1 ml.) until the evolution of sulphur dioxide ceased (3 hr.). The solution was diluted with an excess of light petroleum (b. p. 40—60°), and the precipitate of 2′ : 6*-dibromo-*10 : 11*-dihydro-*9*-thia-*3 : 4*-benzofluorene* 9 : 9*-dioxide* (XIV), formed in good yield, recrystallised from alcohol in prisms, m. p. 228—229° (Found: C, 45·1; H, 2·5. $C_{16}H_{10}O_2SBr_2$ requires C, 45·1; H, 2·35%).

The structure was proved by dehydrogenation and then reduction. The product (XIV) (0·7 g.) was refluxed for 8 hr. with bromine (0·5 ml.) in carbon tetrachloride (50 ml.), and on cooling 1 : 2 : 2′ : 6-*tetrabromo*-1 : 2 : 10 : 11-*tetrahydro*-9-*thia*-3 : 4-*benzofluorene* 9 : 9-*dioxide* separated in good yield and then recrystallised from benzene in prisms, m. p. 239·5—240° (Found : Br, 54·7. $C_{16}H_{10}O_2SBr_4$ requires Br, 54·6%). It was refluxed for 6 hr. with 25 times its wt. of pyridine, and the product, precipitated by water, crystallised from benzene in needles of 2′ : 6-*dibromo*-9-*thia*-3 : 4-*benzofluorene* 9 : 9-*dioxide*, m. p. 354—355° (Found : C, 45·7; H, 2·3. $C_{16}H_8O_2SBr_2$ requires C, 45·3; H, 1·9%). This dibromo-sulphone (30 mg.) was refluxed for 8 hr. with lithium aluminium hydride (75 mg.) in tetrahydrofuran (10 ml.), and excess of hydride decomposed with moist ether; after acidification with dilute hydrochloric acid the non-aqueous layer yielded 9-thia-3 : 4-benzofluorene, m. p. and mixed m. p. 102°.

Preparation of Cyclic Sulphones by the Pschorr Reaction.—(i) *Preparation of the intermediate nitro-sulphones.* α-*Naphthyl* o-*nitrophenyl sulphide*, deep-yellow prisms (from alcohol), m. p. 152—153°, separated (6·8 g., 84%) after 4 hours' refluxing of *o*-chloronitrobenzene (5 g.) and naphthalene-1-thiol (4·7 g.) in a mixture of 40% aqueous sodium hydroxide (10 ml.) and ethanol (10 ml.) (Found : N, 5·05. $C_{16}H_{11}O_2NS$ requires N, 5·0%). This sulphide (6·0 g.) was heated in glacial acetic acid (70 ml.) and hydrogen peroxide (8·0 ml. of 30%) for 1 hr. on the water-bath, and dilution with water gave α-*naphthyl* o-*nitrophenyl sulphone* (6·1 g.), needles (from alcohol), m. p. 128—129° (Found : C, 61·7; H, 3·5; S, 10·0%). The isomeric β-*naphthyl sulphone* (5·8 g.), needles (from alcohol), m. p. 143·5—144°, was similarly obtained from the corresponding sulphide already described (Davies, Gamble, and Savige, *loc. cit.*) (Found : C, 61·3; H, 3·5; O, 20·3. $C_{16}H_{11}O_4NS$ requires C, 61·4; H, 3·5; O, 20·4; S, 10·2%).

o-Nitrophenyl phenyl sulphide, m. p. 79—80°, was made by Roberts and Turner's process (*J.*, 1926, 1208) in the same yield (their m. p. was 79°), though 24% of the *o*-chloronitrobenzene was recovered unchanged by distillation under reduced pressure. The sulphide was converted by hydrogen peroxide, as above, into the *o*-nitro-sulphone, m. p. 146—147° (cf. Ullmann and Pasdermadjian, *Ber.*, 1901, **34**, 1154).

(ii) *Preparation of the amino-sulphones.* To a solution of α-naphthyl *o*-nitrophenyl sulphone (5·0 g.) in ethanol (120 ml.), zinc dust (4·0 g) and concentrated hydrochloric acid (20 ml) were added, and the suspension was refluxed until dissolution was effected, for which further additions of hydrochloric acid were required. The solution was evaporated to dryness on the water-bath and the last traces of free hydrochloric acid were removed by the addition of water and further evaporation. Crystallisation from alcohol gave o-*aminophenyl* α-*naphthyl sulphone*, prisms (3·8 g.), m. p. 177—178° (Found : C, 68·0; H, 4·5. $C_{16}H_{13}O_2NS$ requires C, 67·9; H, 4·6; N, 4·9%). The isomeric β-*naphthyl sulphone*, prisms (3·8 g.), m. p. 136—136·5°, was similarly obtained from β-naphthyl *o*-nitrophenyl sulphone (5·0 g.) (Found : C, 67·8; H, 4·6; N, 5·0%). *o*-Nitrophenyl phenyl sulphone (10 g.) was similarly reduced to the amino-sulphone (8·8 g.), m. p. 120—121° (Ullmann and Pasdermadjian, *loc. cit.*, give m. p. 122°).

(iii) *Cyclisation.* (*a*) *o*-Aminophenyl α-naphthyl sulphone (1·0 g.) in acetic acid (20 ml.) and concentrated hydrochloric acid (20 ml.) was diazotised at 0° with sodium nitrite (1·0 g.) in water (10 ml.), and the solution set aside at room temperature for 15 min. Copper powder (0·5 g.) was added, and the solution shaken for 15 min. The yellow solid formed gave an orange product (m. p. 150—158°, from alcohol), whose benzene solution was chromatographed with alumina. The least adsorbed material, which had a blue-violet fluorescence in ultraviolet light, after removal of the solvent gave the cyclic sulphone (III) (0·3 g.), m. p. and mixed m.p 195·5—196° (from benzene–light petroleum) (Found : C, 72·5; H, 3·9; S, 11·95%).

Decomposing the diazonium solution in boiling 30% sulphuric acid gave some (III) but the material least adsorbed was fluorescent and yielded o-*chlorophenyl* α-*naphthyl sulphone* (0·06 g.), needles, m. p. 182·5—183·5° (from alcohol) (Found : C, 63·7; H, 3·6; S, 10·55. $C_{16}H_{11}O_2SCl$ requires C, 63·5; H, 3·7; S, 10·6%). Another experiment gave a minute amount of halogen-free *substance*, m. p. 154·5—155·5, insoluble in aqueous sodium hydroxide and giving no colour with alcoholic ferric chloride (Found : C, 67·1; H, 3·8; S, 10·8. $C_{16}H_{10}O_3S$ requires C, 67·6; H, 4·2; S, 11·3%).

(*b*) *o*-Aminophenyl β-naphthyl sulphone (1·0 g.) was diazotised and treated as described first for the isomer (VI). Repeated chromatography and crystallisation of the product failed to raise the m. p. above 202·5—203° (Found : C, 72·1; H, 3·7; O, 12·2. Calc. for $C_{16}H_{10}O_2S$: C, 72·2; H, 3·8; O, 12·0%). The compound may be a different form of 9-thia-3 : 4-benzofluorene 9 : 9-dioxide (IV), and a mixture of the two melted at 208°. A hot ethylene glycol solution of this dioxide (IV), when seeded with the crystals of m. p. 202·5—203°, on cooling deposited material of unchanged m. p. (234°). The product from the Pschorr cyclisation was readily reduced with lithium aluminium hydride to give a good yield of 9-thia-3 : 4-benzofluorene (XVI), m. p. and mixed m. p. 103°.

(*c*) *o*-Aminophenyl phenyl sulphone (1·0 g.) was diazotised and the Pschorr process carried out essentially as above, except that excess of nitrous acid was removed by urea, and the solution was shaken for 1 hr. with 2·0 g. of copper. The precipitated solid, after removal of a small amount of *o*-hydroxy-sulphone (m. p. 82—82·5°) by alkali, gave dibenzothiophen 1 : 1-dioxide (0·2 g.), m. p. 228—229°. In a similar experiment, but where the excess of nitrous acid was not removed, o-*chlorophenyl phenyl sulphone*, (0·58 g.), m. p. 105—105·5°, needles (from benzene), was the main product (Found : C, 57·3; H, 3·6; S, 13·0%). $C_{12}H_9O_2SCl$ requires C, 57·0; H, 3·6; S, 12·7%). *o*-Aminophenyl α-naphthyl sulphide readily gave a diazonium solution which gave only tars on attempted cyclisation with copper powder or sulphuric acid.

Preparation of Polycyclic Sulphones by the Friedel–Crafts Reaction.—Cyclisation of diphenyl-2-sulphonyl chloride. Dibenzothiophen 1 : 1-dioxide (0·05 g.), m. p. 229—230° (from ethanol), was obtained when diphenyl-2-sulphonyl chloride (0·1 g.), tetrachloroethane (5 ml.), and aluminium chloride (0·07 g.) were heated on the water-bath for 30 min., the cooled product was diluted with water (30 ml.), and the tetrachlorethane removed in steam. Cyclisation occurred equally when the mixture was kept at room temperature for 24 hr.

Cyclisation of o-α-*naphthylbenzenesulphonyl chloride.* This was obtained when powdered potassium *o*-α-naphthylbenzenesulphonate (4·0 g.) (Davies, Gamble, and Savige, *loc. cit.*) and phosphorus pentachloride (2·5 g.) were heated on the water-bath for 1 hr. o-α-*Naphthylbenzenesulphonyl chloride*, precipitated by ice, crystallised from benzene in prisms (2·9 g., 73%), m. p. 136—136·5° (Found : C, 63·5; H, 3·7. $C_{16}H_{11}O_2SCl$ requires C, 63·5; H, 3·6%). This chloride (1·0 g.) and aluminium chloride (0·5 g.) in tetrachloroethane (40 ml.) were kept at room temperature for 24 hr., and after decomposition by cold water (100 ml.) the tetrachloroethane was removed by steam. The residual 3 : 4-benzothiafluorene 9 : 9-dioxide (IV) crystallised from alcohol in needles (0·6 g., 64%), m. p. and mixed m. p. 233—234°.

Preparation of Polycyclic Sulphoxides by the Friedel–Crafts Reaction.—Cyclisation of diphenyl-2-sulphinyl chloride. Crude diphenyl-2-sulphinic acid (0·6 g.) was obtained when diphenyl-2-sulphonyl chloride (0·8 g.) was slowly added to sodium sulphide (1·2 g.) in water (5 ml.), the mixture heated for 1 hr. on the water-bath, and the cold filtered solution acidified with concentrated hydrochloric acid. The sulphinic acid (9·9 g., 77%) was also prepared from 2-aminodiphenyl (10·0 g.) by the Gattermann process as modified by Jenkins and Hambly (*Austral. J. Chem.*, 1953, **6**, 318).

The sulphinic acid, sparingly soluble in cold water, crystallises from aqueous alcohol or aqueous acetone in colourless prisms which rapidly become light yellow; the m. p. varied between 70° and 126°, and a specimen of m. p. 100—124° was analysed (Found : C, 65·0; H, 4·8. Calc. for $C_{12}H_{10}O_2S$: C, 66·1; H, 4·6%). It responds to the usual tests for a sulphinic acid, and its sodium salt (colourless prisms) is sparingly soluble in excess of sodium hydroxide solution. Moreover, the sulphinic acid (0·6 g.) was reoxidised to pure diphenyl-2-sulphonyl chloride (0·53 g., 76%) when shaken for ½ hr. in carbon tetrachloride (20 ml.) containing excess of chlorine : after evaporation, the sulphonyl chloride was recrystallised from light petroleum (b. p. 100—120°).

A solution of freshly prepared diphenyl-2-sulphinic acid (0·25 g.) in ether (10 ml.) was refluxed for 30 min. with thionyl chloride (0·3 ml.), and the ether removed under reduced pressure. Cyclisation of the crude oily diphenyl-2-sulphinyl chloride was achieved by aluminium chloride (0·2 g.) in tetrachloroethane at 0° in 24 hr. The tetrachloroethane solution yielded dibenzothiophen 5-oxide (0·09 g., 51%), needles m. p. 189·5—190° (Courtot and Pomonis, *Compt. rend.*, 1926, **182**, 893, give m. p. 188—188·5°). It was identified by oxidation with hydrogen peroxide in glacial acetic acid to the dioxide, m. p. 229·5—230°. When the cyclisation was done at room temperature, the yield of the sulphoxide fell to 34%.

Cyclisation of o-α-*naphthylbenzenesulphinyl chloride.* The sulphinic acid (Davies, Gamble, and Savige, *loc. cit.*) (0·75 g.) in ether (25 ml.) was refluxed for 30 min. with thionyl chloride (0·5 ml.). Evaporation gave the oily chloride which was kept with aluminium chloride (0·5 g.) in tetrachloroethane (30 ml.) for 24 hr. at 0°. After steam-distillation the residue was chromatographed in benzene on alumina. The colourless zone with blue fluorescence (ultraviolet) gave colourless prisms, m. p. 147—148° (from benzene–light petroleum), of 9-*thia*-3 : 4-*benzofluorene* 9-*oxide* (VIII) (Found : C, 77·1; H, 4·2. $C_{16}H_{10}OS$ requires C, 76·8; H, 4·0%). In one experiment a compound less strongly adsorbed on the alumina gave a yellow zone with green fluorescence (ultraviolet), and the eluate gave yellow needles (from benzene–light petroleum), m. p. 120·5—121°, in quantity too small for analysis.

The sulphoxide (VIII) (40 mg.) was refluxed with stannous chloride dihydrate (60 mg.) in alcohol (4 ml.) and concentrated hydrochloric acid for 20 min. and then diluted with water. The product from alcohol (m. p. 102—103°; 28 mg., 71%) was identical (mixed m. p.) with the sulphide (XVI). Oxidation of the sulphoxide with hydrogen peroxide in glacial acetic acid gave the sulphone (IV), as shown by identity of m. p.s.

The authors thank Dunlop Rubber Company of Australia Ltd. for a scholarship (to F. C. J.), and N. W. Gamble for assistance. The microanalyses were carried out by Dr. W. Zimmermann and his staff.

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[*Received, December 9th,* 1954.]