669. *Polymerisation of Thiophen Derivatives. Part VII.* The Conversion of Thionaphthen* 1 : 1-*Dioxide into* 1 : 10-*Benzothiaxanthen* 5 : 5-*Dioxide.*

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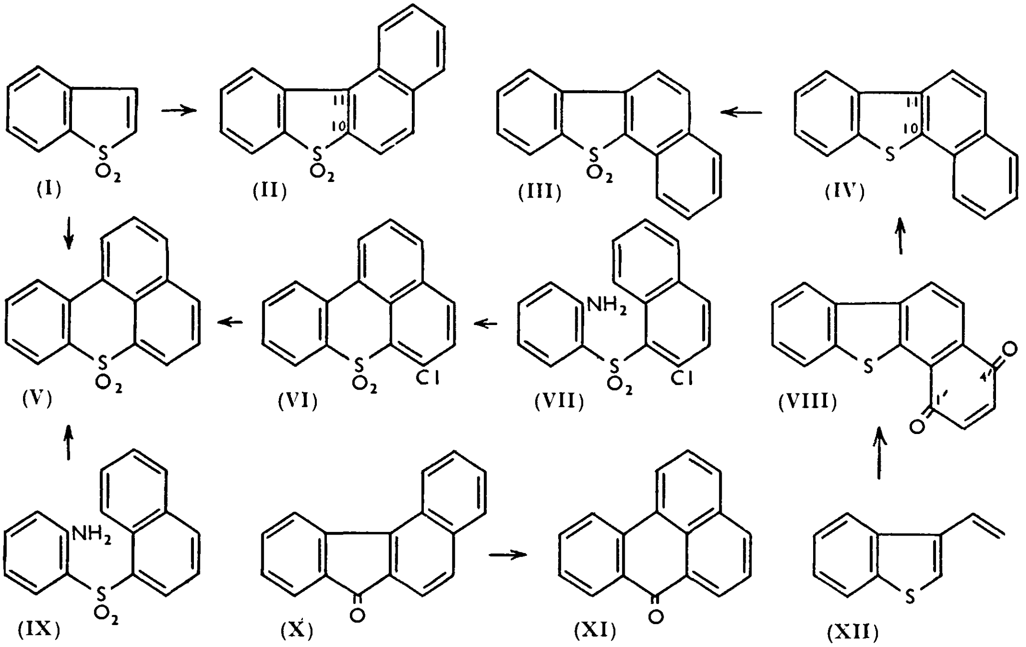
The product, m. p. 195—196°, formed by heating undiluted thionaphthen 1 : 1-dioxide (I) at 195° and claimed [1] as 9-thia-1 : 2-benzofluorene 9 : 9-dioxide (III), is now found to be the isomeric 1 : 10-benzothiaxanthen 5 : 5-dioxide (V).

BY carrying out the decomposition of thionaphthen 1 : 1-dioxide (I) at 195° on a relatively large scale, it is now found that 9-thia-3 : 4-benzofluorene 9 : 9-dioxide (II) can be isolated, as well as the sulphone, m. p. 195—196°, previously obtained.[1] The latter was also made by a Pschorr reaction on *o*-aminophenyl 1-naphthyl sulphone (IX), and the identity of these two compounds [previously regarded as having structure (III)—contrast below] is now confirmed by ultraviolet absorption spectra.



In the course of a new general synthesis of polycyclic thiahydrocarbons which will be described later, the sulphone (III) has been prepared by an unambiguous process and is

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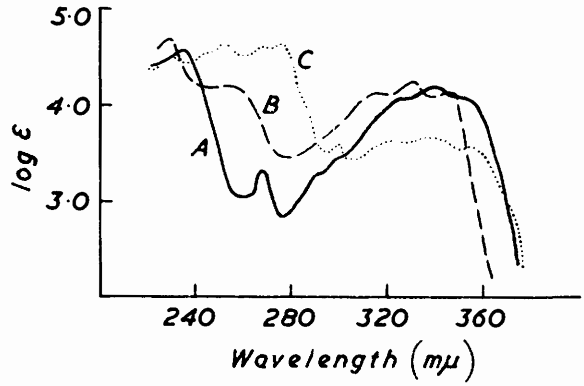
* Part VI, *J.*, 1957, 826.

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

found to have m. p. 236° and not 196°. 3-Vinylthionaphthen (XII) is condensed with benzoquinone and the initial adduct is dehydrogenated by excess of benzoquinone to 1 : 2-benzo-9-thiafluorene-1′ : 4′-quinone (VIII), which is reduced with lithium aluminium hydride to the thiahydrocarbon, m. p. 185—186°. This is the m. p. of 1 : 2-benzo-9-thiafluorene (from coal tar), which was desulphurised to 2-phenylnaphthalene by Kruber and Grigoleit [2] who, however, did not prepare its sulphone. Our synthetic product is readily oxidised with hydrogen peroxide in acetic acid to form 1 : 2-benzo-9-thiafluorene 9 : 9-dioxide (III), m. p. 236°. This is the m. p. of the sulphone from the thiahydrocarbon, m. p. 185—186°, made in a different way [3] and these two compounds (kindly supplied by Professor Badger) are identical (mixed m. p.) with those derived from 3-vinylthionaphthen. The two sulphones, m. p. 196° and 236° respectively, have different solubilities and ultraviolet absorption spectra.

The evidence that the thionaphthen 1 : 1-dioxide pyrolysis product, m. p. 196°, had structure (III) was that of James,[4] who desulphurised it with Raney nickel to a compound accepted as 2-phenylnaphthalene because its m. p. 102—103° was undepressed on admixture with an authentic specimen. This desulphurisation is under investigation, but so far attempts to repeat it have failed.



Ultraviolet absorption of (A) compound (V), *(B) benzanthrene, and (C) compound* (III) *in* 95% *ethanol.*

It therefore seems that in the Pschorr reaction with (IX) cyclisation has occurred in the *peri*-position, and that the product is 1 : 10-benzothiaxanthen 5 : 5-dioxide (V). This was proved by the synthesis of the compound (V) in such a way that only the *peri*-position is available for cyclisation. The Pschorr reaction with *o*-aminophenyl 2-chloro-1-naphthyl sulphone (VII) rapidly gives about a 50% yield of 4-chloro-1 : 10-benzothiaxanthen 5 : 5-dioxide (VI), which has an ultraviolet absorption spectrum similar to that of the dioxide (V). Not only can the chlorine be removed by lithium aluminium hydride to form a small yield of (V), but the reduction can proceed further to form a (slightly impure) thiahydrocarbon which is oxidised in high yield by hydrogen peroxide to give (V), m. p. 196°. The identity of the two products from the sulphones (I) and (VII) is established by the mixed melting points and by identical ultraviolet absorption spectra.

In the cyclisation of *o*-aminophenyl 1-naphthyl sulphone (IX) the yield of pure product is about 33%, and it is apparent that *peri*- and not *ortho*-cyclisation is favoured. The formation of a *peri*-link in the heating of undiluted thionaphthen dioxide (I) is however remarkable, since an 89% yield of 10 · 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (cf. II) is formed in solution at a slightly lower temperature.[1] In the experiments without solvents the self-condensation of thionaphthen 1 : 1-dioxide with the production of the sulphone (II) and sulphur dioxide, essentially follows a normal course, but production of

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[2] Kruber and Grigoleit, *Chem. Ber.*, 1954, **87**, 1895.
[3] Badger and Christie, *J.*, 1956, 3438.
[4] James, Thesis, Melbourne, 1954, p. 115.

the isomer (V) and of 9-thia-3 : 4-benzofluorene is abnormal. It is possible that in the acid environment 9-thia-3 : 4-benzofluorene 9 : 9-dioxide (II) suffers fission and rearranges to (V). A purely formal analogy to this is the conversion [5] of 3 : 4-benzofluorenone (X) into benzanthrone (XI) by aluminium chloride and sodium chloride at 100—150°. However, such rearrangement has not yet been observed with pure 9-thia-3 : 4-benzothiafluorene 9 : 9-dioxide (II) or its 10 : 11-dihydro-derivative.

Reduction of 1 : 10-benzothiaxanthen 5 : 5-dioxide (V) with lithium aluminium hydride gives a crimson solution which on decomposition with water yields a dihydro-derivative. This cannot be 10 : 11-dihydro-9-thia-1 : 2-benzofluorene 9 : 9-dioxide (cf. IV),[1] and this structure should be removed from the literature.[1, 6] The dihydro-derivative of the *peri*-compound (V) forms a dibromo-derivative, which is dehydrobrominated with pyridine to regenerate the sulphone (V). The structure of the dihydro-derivative and the implications of the formation of the crimson colour will be further studied. It is remarkable that very brief exposure of the chloro-compound (VI) to lithium aluminium hydride is sufficient to remove the chlorine, and also the oxygen to a considerable extent.

It is noteworthy that the ultraviolet absorption spectrum [7] of benzanthrene, the hydrocarbon derived from (XI), closely resembles that of (V), which is quite unlike that of genuine (III) (cf. Figure).

o-Aminophenyl 2-chloro-1-naphthyl sulphone (VII) separates from benzene in crystals having the structure $(C_{16}H_{12}O_2NSCl)_2,C_6H_6$. The question of steric effects in naphthalene derivatives connected to an aryl group is worthy of further examination.

EXPERIMENTAL

The ultraviolet absorption spectra were determined in 95% EtOH with a Hilger Uvispek spectrophotometer.

Synthesis of 9-*Thia*-1 : 2-*benzofluorene* 9 : 9-*Dioxide.*—2-3′-Thionaphthenylethanol, b. p. 125—128°/0·2 mm., was prepared (75%) from 3-thionaphthenylmagnesium bromide and ethylene oxide by Cagniant and Cagniant's method.[8]

3-*Vinylthionaphthen.* 2-3′-Thionaphthenylethanol (60 g.) in toluene (60 ml.) was added during 15 min. to molten potassium hydroxide (250 g.) in a distillation flask at 230°/15 mm. The temperature was raised to 260° until distillation ceased. The aqueous layer of the distillate was separated, and the organic layer was concentrated and distilled, giving 3-*vinylthionaphthen*, b. p. 133—134°/25 mm. (35·5 g., 66%) (Found : C, 74·6; H, 4·7. $C_{10}H_8S$ requires C, 75·0; H, 5·0%).

Reaction with benzoquinone. 3-Vinylthionaphthen (1·5 g.) and benzoquinone (4·5 g.) in glacial acetic acid (30 ml.) were heated on the water-bath for 8 hr. The product that separated on cooling was washed with ether, and recrystallised from benzene, giving orange-red needles of 9-*thia*-1 : 2-*benzofluorene* 1′ : 4′-*quinone* (VIII), m. p. 197—198° (2·1 g., 80%) (Found : C, 72·4; H, 3·3. $C_{16}H_8O_2S$ requires C, 72·7; H, 3·0%).

Reduction. The above quinone (1·0 g.) was extracted (Soxhlet) with tetrahydrofuran (50 ml.) containing lithium aluminium hydride (1·0 g.) for 15 hr. The excess of hydride was decomposed with moist ether, and inorganic material dissolved with hydrochloric acid. The organic layer on concentration gave 9-thia-1 : 2-benzofluorene (IV), m. p. 185—186° (0·7 g.), undepressed on admixture with a genuine sample [3] (Found : C, 82·3; H, 4·5. Calc. for $C_{16}H_{10}S$: C, 82·05; H, 4·3%).

Oxidation. The above thiahydrocarbon (0·25 g.) was heated on the water-bath for 1 hr. with 30% hydrogen peroxide (0·75 ml.) and acetic acid (1·5 ml.). The product that separated on cooling was crystallised from ethanol, giving needles of 9-thia-1 : 2-benzofluorene 9 : 9-dioxide [3] (III), m. p. and mixed m. p. 235·5—236° (Found : C, 72·2; H, 3·9. Calc. for $C_{16}H_{10}O_2S$: C, 72·2; H, 3·8%).

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[5] Baddar, *J.*, 1941, 310.

[6] Davies and Porter, *J.*, 1957, 827.

[7] Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," Chapman-Hall, London, 1951, Fig. 436.

[8] Cagniant and Cagniant, *Bull. Soc. chim. France*, 1949, 382.

Action of Heat on Thionaphthen Dioxide (I).—The heating of the dry dioxide (10 g.) at 195° for 25 min. was essentially as previously described.[1] Some water was formed, and the crude dark-green solution in benzene was chromatographed on alumina. The eluate from the first band (yellow, yellow fluorescence in ultraviolet light) gave an oil (5·4 g.), which with hydrogen peroxide gave the sulphone (II), m. p. 234° (0·55 g.), indicating the presence of about 0·5 g. of 9-thia-3 : 4-benzofluorene, which is itself isolated with difficulty. The second band, colourless, but fluorescing pale-blue in ultraviolet light, on arbitary fractionation, gave 0·5 g. of the above sulphone (II), and also crystals (0·4 g.), m. p. 196°. This is identical (mixed m. p.) with the specimen previously prepared,[1] and also with the Pschorr product (mixed m. p. and ultraviolet absorption) from *o*-aminophenyl 1-phenylnaphthalene sulphone (IX). Attempts were made to desulphurise the sulphone, m. p. 196° (from I), by the method previously described. With one specimen of Raney nickel part of the sulphone was recovered, and with a more reactive nickel all the sulphone (0·2 g.) was apparently reduced but the oil (about 0·01 g.) could not be identified. The reduction with Raney nickel of this and allied sulphones is being investigated.

Synthesis of 4-*Chloro*-1 : 10-*benzothiaxanthen* 5 : 5-*Dioxide* (VI).—An aqueous solution (200 ml.) containing sodium 2-aminonaphthalene-1-sulphonate (50 g.) and sodium nitrite (18 g.) was rapidly added to concentrated hydrochloric acid (150 g.) and ice (150 g.), and the process of Dikshit and Tilak[9] then followed, to give a good yield of sodium 2-chloronaphthalene-1-sulphonate and thence (by phosphorus pentachloride) 2-chloronaphthalene-1-sulphonyl chloride. Into a suspension of stannous chloride dihydrate (250 g.) in acetic acid (600 ml.) dry hydrogen chloride was passed until the salt dissolved; 2-chloronaphthalene-1-sulphonyl chloride (30 g.) was then added. After 18 hr. at room temperature, addition of concentrated hydrochloric acid precipitated 2-chloronaphthalene-1-thiol, m. p. 65—65·5°.

2-*Chloro*-1-*naphthyl* o-*nitrophenyl sulphide*, yellow prisms, m. p. 141—142° (from ethanol), was obtained (15 g.) by refluxing 2-chloronaphthalene-1-thiol (10 g.) and *o*-chloronitrobenzene (10 g.) in ethanol (30 ml.) with 30% aqueous sodium hydroxide (30 ml.) for 1 hr. (Found : C, 60·8; H, 3·3; N, 4·2. $C_{16}H_{10}O_2NSCl$ requires C, 60·9; H, 3·2; N, 4·4%).

2-*Chloro*-1-*naphthyl* o-*nitrophenyl sulphone*, very pale-yellow needles, m. p. 145·5—146° (from ethanol), was prepared (9·3 g.) by refluxing for 1 hr. the above sulphide (10 g.) in acetic acid (100 ml.) containing 30% hydrogen peroxide (15 ml.) (Found : C, 55·6; H, 3·0. $C_{16}H_{10}O_4NSCl$ requires C, 55·3; H, 2·9%).

o-*Aminophenyl* 2-*chloro*-1-*naphthyl sulphone* (VII), plates, m. p. 193—194° (from ethanol), was isolated (1·4 g.) by making alkaline a solution of the above nitro-sulphone (2 g.) which had been refluxed for 1 hr. in acetic acid (40 ml.) containing stannous chloride hydrate (15 g.) and concentrated hydrochloric acid (10 ml.) (Found : C, 60·6; H, 4·05. $C_{16}H_{12}O_2NSCl$ requires C, 60·5; H, 3·8%). The crystals from benzene crumble when heated, and the analyses of different samples indicate that benzene of crystallisation is firmly held, about 30% being lost at 60°/20 mm. in 3 hr. However, 11·572 mg. of air-dried crystals [Found : C, 63·8; H, 4·3. $(C_{16}H_{12}O_2NSCl)_2,C_6H_6$ requires C, 64·0; H, 4·2%], from benzene, in a stream of oxygen for 20 min. at 150—160° gave (by difference) 1·312 mg. of volatile material (Found : C, 92·4; H, 7·9. Calc. for C_6H_6 : C, 92·3; H, 7·7%) and 10·260 mg. of a colourless non-volatile residue (Found : C, 60·6; H, 3·8%. Calc. as for the above specimen from ethanol). This result corresponds to 1·04 moles of benzene per two moles of sulphone.

Pschorr Reaction with o-*Aminophenyl* 2-*Chloro*-1-*naphthyl Sulphone*.—This amine (1 g.) in acetic acid (20 ml.) and concentrated hydrochloric acid (20 ml.) was diazotised at 8° with sodium nitrite (0·28 g.) in water (2 ml.). Urea (1 g.) was added after 1 hr. at room temperature, then after 5 min. freshly prepared copper powder (1 g.), a vigorous reaction ensuing. After an hour the mixture was diluted with water, precipitating an additional amount of 4-*chloro*-1 : 10-*benzothiaxanthen* 5 : 5-*dioxide* (VI) (0·45 g.), needles, m. p. 205·5—206° (from ethanol) (Found : C, 63·7; H, 3·05. $C_{16}H_9O_2SCl$ requires C, 63·9; H, 3·0%).

Conversion of 4-*Chloro*-1 : 10-*benzothiaxanthen* 5 : 5-*Dioxide into* 1 : 10-*Benzothiaxanthen* 5 : 5-*Dioxide* (V).—4-Chloro-1 : 10-benzothiaxanthen 5 : 5-dioxide (0·4 g.) in benzene (30 ml.) and ether (100 ml.) was refluxed with lithium aluminium hydride (0·2 g.), and the solution rapidly became crimson. This colour persisted until (45 min.) water was added. The organic solution was washed with dilute sulphuric acid, dried ($MgSO_4$), and yielded an oil which was extracted with light petroleum (30 ml.; b. p. 60—80°). The petroleum-insoluble residue was chromatographed in benzene on alumina, and the blue fluorescent (ultraviolet light) band

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[9] Dikshit and Tilak, *Proc. Indian Acad. Sci.*, 1951, **33**, *A*, 78.

yielded crystals (8 mg.), m. p. 195—196°. This compound is identical (mixed m. p.) with the compound of the same m. p. made by the Pschorr reaction on *o*-aminophenyl 2-naphthyl sulphone.[1] The ultraviolet absorption spectra were identical.

The light petroleum-soluble material was similarly chromatographed and yielded a yellow waxy solid, with blue fluorescence in ultraviolet light, m. p. 50—60°. It (0·08 g.) in benzene (2 ml.) when added to 2 : 4 : 7-trinitrofluorenone (0·1 g.) in hot benzene–alcohol (30 ml.; 1 : 1) gave the slightly impure *addition compound*, black needles with a black smear, m. p. 221—222° (0·14 g.) (from benzene–ethanol) (Found: C, 62·7; H, 2·7; N, 7·0. $C_{29}H_{15}O_7N_3S$ requires C, 63·4; H, 2·75; N, 7·65%). This compound (0·1 g.), in benzene (20 ml.), was decomposed by chromatography through a short column of alumina, and the 1 : 10-*benzo*-5-*thiaxanthen* (0·04 g.), yellow needles, m. p. 79—80° (from ethanol), gave a benzene solution with blue fluorescence in ultraviolet light (Found: C, 81·1; H, 4·3. $C_{16}H_{10}S$ requires C, 82·0; H, 4·3%).

This thiahydrocarbon (0·05 g.) in acetic acid (2 ml.) was refluxed for an hour with excess of hydrogen peroxide, and yielded (0·04 g.) 1 : 10-benzothiaxanthen 5 : 5-dioxide, m. p. 196° (from ethanol). It was identical (mixed m. p. and identical ultraviolet absorption spectra) with the product, m. p. 196°, from the Pschorr reaction (Found: C, 72·1; H, 3·94. Calc. for $C_{16}H_{10}O_2S$: C, 72·2; H, 3·8%).

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