

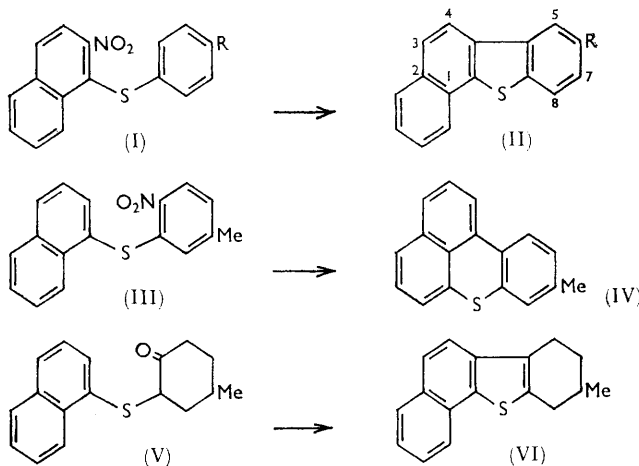
### 322. Methyl Substituted 9-Thia-1,2-benzofluorenes.

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Pschorr cyclisation of 2-amino-1-naphthyl *p*-tolyl sulphide gave 6-methyl-9-thia-1,2-benzofluorene (II; R = Me), and the 8-methyl derivative was similarly obtained from the *o*-tolyl sulphide. The *m*-tolyl sulphide gave a mixture of the 5- and 7-methyl derivatives which were both synthesised by an additional unequivocal route. Their ultraviolet spectra are recorded.

THE present work describes the synthesis of four of the monomethyl-9-thia-1,2-benzofluorenes by the Pschorr cyclisation, a method previously applied by Carruthers and Douglas<sup>1</sup> and by Block<sup>2</sup> to the preparation of substituted 9-thiafluorenes. Preliminary investigations of conditions for the Pschorr cyclisation revealed that the most reliable method is one in which the diazonium salt is prepared by the addition of ethyl nitrite to the amine hydrochloride suspended in glacial acetic acid, and the subsequent cyclisation is catalysed by the addition of copper powder or copper bronze.

Reaction of 1-chloro-2-nitronaphthalene with thiophenol gave a good yield of 2-nitro-1-naphthyl phenyl sulphide (I; R = H) which was reduced by iron powder in aqueous ferrous ammonium sulphate, and the derived amine hydrochloride was diazotised and cyclised by the procedure already described to give 9-thia-1,2-benzofluorene (II; R = H). Starting with *p*-thiocresol and *o*-thiocresol, in a similar series of reactions, no difficulty was experienced in obtaining 6-methyl-9-thia-1,2-benzofluorene (II; R = Me) and 8-methyl-9-thia-1,2-benzofluorene, respectively, there being only one possible cyclisation product in each case. However, with *m*-thiocresol two isomers are possible depending on the direction of cyclisation, and, in fact, a mixture of 5-methyl- and 7-methyl-9-thia-1,2-benzofluorene was obtained. They were finally separated by very careful absorption chromatography on alumina, graded benzene-hexane mixtures being used to elute the two compounds in turn.



In order to identify the position of the substituent in the two isomeric methyl derivatives, it was thought that an unequivocal route to 7-methyl-9-thia-1,2-benzofluorene would be by way of 5-methyl-2-nitrophenyl 1-naphthyl sulphide (III), obtained by condensing naphthalene-1-thiol with 3-chloro-4-nitrotoluene. However, in the cyclisation of the derived diazonium salt a new product was obtained unrelated in its spectra (u.v. and i.r.) to the expected compound. Raney-nickel desulphurisation and subsequent

<sup>1</sup> Carruthers and Douglas, *J.*, 1959, 2813.

<sup>2</sup> Block, *J. Amer. Chem. Soc.*, 1950, **72**, 5641.

dehydrogenation of the desulphurised product gave 1-*p*-tolyl naphthalene, indicating that cyclisation had taken place in the *peri*-position of the naphthalene nucleus to give a six-membered sulphur-containing ring. In view of this, an attempt to prepare the 5-methyl derivative from 3-methyl-2-nitrophenyl 1-naphthyl sulphide was abandoned. Success was achieved by using a method similar to that described by Rabindran and Tilak.<sup>3</sup> 2-Bromo-4-methylcyclohexanone was reacted with naphthalene-1-thiol to give 5-methyl-2-oxocyclohexyl 1-naphthyl sulphide (V) which was cyclised with phosphorus pentoxide to give the tetrahydrothiafluorene (VI). Dehydrogenation with palladium on charcoal gave 7-methyl-9-thia-1,2-benzofluorene. 5-Methyl-9-thia-1,2-benzofluorene was similarly prepared from 2-bromo-6-methylcyclohexanone.

The principal peaks in the ultraviolet absorption spectra of 9-thia-1,2-benzofluorene and four of its monomethyl derivatives are tabulated.

Absorption spectra ( $m\mu$  and  $\log \epsilon$ ) in 95% ethanol.

- 9-Thia-1,2-benzofluorene: 244.5 (4.733), 252.8 (4.764), 266.5 (4.472), 274.5 (4.641), 292 (4.187), 303 (4.243), 318 (infl.) (3.758), 332 (3.404), 337 (infl.) (3.183), 341 (infl.) (3.015), 349 (3.404).  
 5-Methyl-9-thia-1,2-benzofluorene: 245.6 (4.725), 254.5 (4.728), 268 (infl.) (4.514), 276 (4.738), 300 (4.170), 318 (3.825), 334 (3.546), 343 (3.103), 351 (3.834).  
 6-Methyl-9-thia-1,2-benzofluorene: 246 (4.688), 254.5 (4.693), 268 (infl.) (4.287), 277.3 (4.463), 295.5 (4.089), 307 (4.123), 318 (infl.) (3.702), 332 (3.367), 338 (3.173), 341.5 (3.064), 350 (3.316).  
 7-Methyl-9-thia-1,2-benzofluorene: 246.8 (4.695), 255.2 (4.704), 266.8 (4.468), 276.5 (4.633), 294 (4.201), 305 (4.248), 318 (infl.) (3.786), 332 (3.322), 340 (2.993), 349 (3.179).  
 8-Methyl-9-thia-1,2-benzofluorene: 245.4 (4.700), 253.9 (4.716), 265 (infl.) (4.445), 274.5 (4.666), 302 (4.199), 319 (infl.) (3.747), 331 (3.415), 340 (3.072), 349 (3.383).  
 9-Methylbenzo[*b*]naphtho[1,8-*d,e*]thiopyran: 215.5 (4.694), 234 (infl.) (4.615), 243.5 (4.718), 255 (infl.) (4.340), 268 (infl.) (4.235), 278 (infl.) (4.010), 300 (infl.) (3.829), 309 (3.918), 326 (3.801).

#### EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Laboratory of this Department. All m. p.s were determined on a Kofler hot-stage apparatus.

*2-Nitro-1-naphthyl Phenyl Sulphide* (I; R = H).—A solution of 1-chloro-2-nitronaphthalene (4.2 g.) in hot ethanol (25 ml.) was added to thiophenol (2 ml.) dissolved in water (10 ml.) containing sodium carbonate (2.4 g.). The resulting solution was stirred for 1 hr. and poured into cold water (50 ml.). The yellow sulphide (6.2 g.) was filtered off and crystallised from ethanol to give dense yellow crystals (6.1 g.), m. p. 42° (Found: C, 68.6; H, 4.0; N, 4.6.  $C_{16}H_{11}NO_2S$  requires C, 68.3; H, 3.9; N, 4.9%).

*9-Thia-1,2-benzofluorene* (II; R = H).—The above sulphide (5.6 g.) was reduced by refluxing it with a mixture of iron powder (10 g.), ferrous ammonium sulphate (1 g.), and water (100 ml.) during 2 hr. After basification of the solution with dilute sodium hydroxide, the free amine was extracted in ether, and the dried solution was concentrated finally under vacuum. The residue was dissolved in dry benzene (50 ml.), and the resulting solution was saturated with dry hydrogen chloride to give the hydrochloride which was collected and washed with benzene saturated with hydrogen chloride. This pale purple powder (1.7 g.) was suspended in glacial acetic acid (15 ml.) and treated at 15–18° with ethyl nitrite until all the hydrochloride had dissolved. This was cooled to 5–10°, diluted with 50% acetic acid (60 ml.) similarly cooled, and stirred mechanically while precipitated copper (2 g.) was added at such a rate as to avoid excessive frothing. The solution was stirred for a further hour at this temperature and finally at 40° for 2 hr. The solids which separated on cooling were filtered off and extracted with benzene. The filtrate was steam-distilled and the distillate was also extracted with benzene. The combined benzene extracts were dried ( $Na_2SO_4$ ) and concentrated to yield a dark brown solid which was chromatographed in benzene–hexane mixtures on “Woelm” basic alumina. Plates of the *thiafluorene* (0.93 g.), m. p. 187–188°, were obtained following crystallisation from hexane (Found: C, 82.3; H, 4.4. Calc. for  $C_{16}H_{10}S$ : C, 82.0; H, 4.3%). Badger and Christie<sup>4</sup> give m. p. 185° (hexane).

*2-Nitro-1-naphthyl p-Tolyl Sulphide* (I; R = Me).—*p*-Thiocresol (2.3 g.) was treated with

<sup>3</sup> Rabindran and Tilak, *Indian Acad. Sci.*, 1953, **37**, A, 564.

<sup>4</sup> Badger and Christie, *J.*, 1956, 3435.

1-chloro-2-nitronaphthalene (4.3 g.) to give the *sulphide* as yellow needles (5.4 g.) (from alcohol), m. p. 46.5° (Found: C, 69.2; H, 4.7; N, 4.5.  $C_{17}H_{13}NO_2S$  requires C, 69.1; H, 4.4; N, 4.7%).

6-Methyl-9-thia-1,2-benzofluorene (II; R = Me).—The above nitro-sulphide (4.4 g.) was reduced during 3 hr., and the amine was isolated as its hydrochloride (4.4 g.), diazotised, and cyclised to give the *thiafluorene* as plates (0.7 g.) (from hexane), m. p. 166.5° (Found: C, 82.3; H, 4.65.  $C_{17}H_{12}S$  requires C, 82.2; H, 4.9%).

2-Nitro-1-naphthyl *o*-Tolyl Sulphide.—*o*-Thiocresol (2.4 g.) similarly reacted with 1-chloro-2-nitronaphthalene (4.0 g.) to give the *sulphide* (5.7 g.) as fine yellow needles (from ethanol), m. p. 113.5–114° (Found: C, 68.8; H, 4.6; N, 4.5.  $C_{17}H_{13}NO_2S$  requires C, 69.1; H, 4.4; N, 4.7%).

8-Methyl-9-thia-1,2-benzofluorene.—The above nitro-sulphide (4.4 g.) was reduced and the amine hydrochloride (3.7 g.) was diazotised, the product cyclised with copper bronze, and the product chromatographed to give the *thiafluorene* (1.1 g.) as crystals, m. p. 148°, from hexane (Found: C, 82.5; H, 4.8.  $C_{17}H_{12}S$  requires C, 82.2; H, 4.9%).

2-Nitro-1-naphthyl *m*-Tolyl Sulphide.—*m*-Thiocresol (2.8 g.) was treated with 1-chloro-2-nitronaphthalene (4.0 g.) to give the *sulphide* (4.4 g.) as yellow crystals, m. p. 98° (Found: C, 69.25; H, 4.6; N, 4.9.  $C_{17}H_{13}NO_2S$  requires C, 69.1; H, 4.4; N, 4.7%).

5-Methyl-9-thia-1,2-benzofluorene and 7-Methyl-9-thia-1,2-benzofluorene.—The above nitro-sulphide (4.1 g.) was reduced, the amine was diazotised, and the product cyclised to give a mixture of the two isomeric thiafluorenes. The isomers were not separated by preliminary chromatography on alumina (40 g.). The resulting solid (1.22 g.) was carefully chromatographed on "Woelm" basic alumina (200 g.), graded benzene-hexane mixtures being used. Crystallisation of the solid obtained from the first group of fractions gave 5-methyl-9-thia-1,2-benzofluorene (0.42 g.) as white crystals, m. p. 167–168° (Found: C, 82.5; H, 5.1; S, 12.7.  $C_{17}H_{12}S$  requires C, 82.2; H, 4.9; S, 12.9%). The fourth group of fractions yielded 7-methyl-9-thia-1,2-benzofluorene (0.19 g.) as white crystals, m. p. 185–186° (Found: C, 81.8; H, 4.8.  $C_{17}H_{12}S$  requires C, 82.2; H, 4.9%).

5-Methyl-2-nitrophenyl 1-Naphthyl Sulphide (III).—3-Chloro-4-nitrotoluene (3.7 g.) was treated with naphthalene-1-thiol (3 ml.) to give glistening yellow needles of the *sulphide* (6.1 g.) (from ethanol), m. p. 144° (Found: C, 69.3; H, 4.8; N, 4.5.  $C_{17}H_{13}NO_2S$  requires C, 69.1; H, 4.4; N, 4.7%).

9-Methylbenzo[b]naphtho[1,8-d,e]thiopyran (IV).—The above nitro-sulphide (5.63 g.) in aqueous alcohol (50% soln.; 30 ml.) and acetic acid (3 ml.) was reduced with iron powder (6 g.) to the amine, its white hydrochloride (4.88 g.) was diazotised, and the product cyclised to give the *thiopyran* (0.45 g.) (from hexane), m. p. 96.5–97.5°, as amber-coloured crystals (Found: C, 82.1; H, 5.0; S, 12.7.  $C_{17}H_{12}S$  requires C, 82.2; H, 4.9; S, 12.9%). Desulphurisation with Raney nickel followed by dehydrogenation by refluxing with 5% palladium on charcoal gave 1-*p*-tolyl-naphthalene, m. p. 52–53°. Small quantities of other coloured products were not identified.

3-Methyl-2-nitrophenyl 1-Naphthyl Sulphide.—3-Chloro-2-nitrotoluene (1.8 g.) was treated with naphthalene-1-thiol (1.5 g.), and the product purified by chromatography to give the *sulphide* as yellow crystals (0.115 g.), m. p. 117–117.5°, after crystallisation (from ethanol) (Found: C, 69.05; H, 4.6; N, 4.5.  $C_{17}H_{13}NO_2S$  requires C, 69.1; H, 4.4; N, 4.7%).

7-Methyl-9-thia-1,2-benzofluorene.—2-Bromo-4-methylcyclohexanone (10.8 g.) was added during 15 min. to a vigorously stirred solution of naphthalene-1-thiol (8.6 g.) in sodium hydroxide (30% solution; 6.8 ml.) with cooling in ice-water. After being stirred for a further 1½ hr. the thick yellow oil which separated was extracted in ether. The crude 5-methyl-2-oxocyclohexyl 1-naphthyl sulphide (V) (8 g.) was heated at 170–180° for 2 hr. with phosphorus pentoxide (24 g.), and the resulting solid was carefully treated with crushed ice (500 g.). After dilution to 1 l. and neutralisation with sodium hydroxide, the cyclised product was extracted in ether (4 × 100 ml.). The pale brown product (6.92 g.) was purified by chromatography in benzene on alumina to give the *tetrahydrothiafluorene* (VI) (5.3 g.) as white sheaves, m. p. 124–124.5°, after crystallisation from hexane (Found: C, 80.8; H, 6.4.  $C_{17}H_{16}S$  requires C, 80.9; H, 6.4%).

The tetrahydrofluorene (1 g.) was dehydrogenated by refluxing it with 5% palladium on charcoal (0.38 g.) in *p*-cymene (0.83 g.) at 320° (bath temp.) during 10 hr. The product was extracted into benzene and purified by chromatography on alumina. Further crystallisation from hexane gave the *thiafluorene* as sheaves (0.74 g.), m. p. 186° (Found: C, 82.4; H, 4.9; S, 13.0. Calc. for  $C_{17}H_{12}S$ : C, 82.2; H, 4.9; S, 12.9%). The m. p. was not depressed on admixture with the previously described 7-methyl derivative.

*5-Methyl-9-thia-1,2-benzofluorene.*—2-Bromo-6-methylcyclohexanone (10.8 g.) was treated with naphthalene-1-thiol (8.6 g.) to give the crude sulphide (14.3 g.) as an oil. Cyclisation of this material (8.0 g.) with phosphorus pentoxide gave an oil which was purified by chromatography in benzene on alumina. Analysis indicated that some dehydrogenation had taken place simultaneously with cyclisation. Further dehydrogenation with 5% palladium on charcoal in *p*-cymene and purification by chromatography on alumina gave plates of the thiafluorene, m. p. 164° (Found: C, 82.5; H, 4.8; S, 12.7. Calc. for C<sub>17</sub>H<sub>12</sub>S: C, 82.2; H, 4.9; S, 12.9%). The m. p. was not depressed on mixing with crystals obtained by the Pschorr cyclisation described above.

*Absorption Spectra.*—Ultraviolet absorption spectra were obtained on a Shimadzu (model RS 27) spectrophotometer as tabulated.

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