83. *The Synthesis of Two Dinaphthothiophens.*

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Dinaphtho-[1,2-*b*:2′,1′-*d*]- and -[1,2-*b*:2′,3′-*d*]-thiophen have been synthesised. The former was shown to be different from a sulphur compound isolated by Henriques.[1]

TREATING di-(2-hydroxy-1-naphthyl) sulphide (I) withsulphuric acid, Henriques [1] isolated an oxygen-free substance giving analyses for a dinaphthothiophen. Smiles *et al.*[2] found that it was obtained in low yield and only from the unstable form of the sulphide (I). Although structure (II) was claimed, the mechanism of the formation of such a compound is not clear (cf. Hartough and Meisel [3]), and we have therefore undertaken its synthesis.

The first attempt involved reaction of 2,2′-binaphthyl with sulphur in the presence of anhydrous aluminium chloride according to Gilman and Jacoby's method.[4] Some reaction occurred, as hydrogen sulphide was liberated, but no organic sulphur compound could be isolated.

The second attempt was along lines similar to those developed by Armarego and Turner [5] for the synthesis of dibenzothiophens. Tobias [5] acid was converted into potassium 2-iodonaphthalene-1-sulphonate by Cummings and Muir's method.[6] Conversion into the sulphonyl chloride required long heating, probably because of steric hindrance. The chloride gave the ester (III) which with copper bronze at 170—175° produced the biphenyl

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[1] Henriques, *Ber.*, 1894, **27**, 2993.

[2] Smiles, Ross, and Crymble, *J.*, 1912, **101**, 1146.

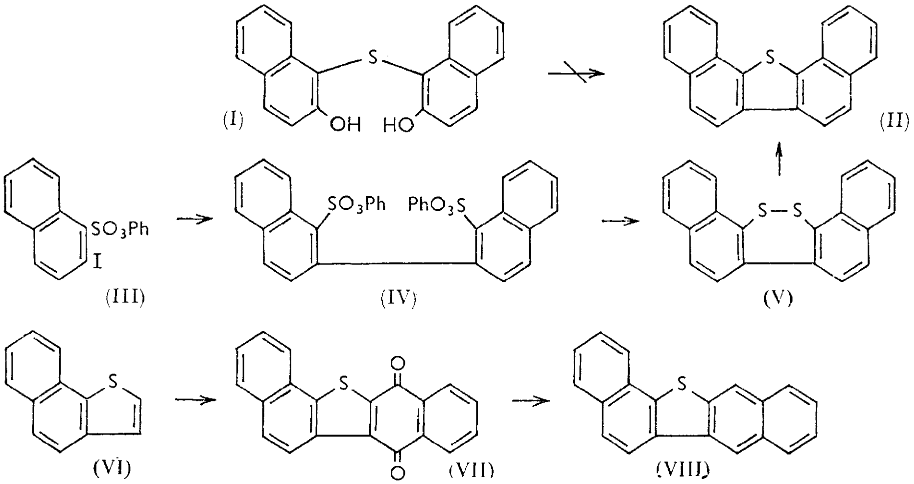
[3] Hartough and Meisel, " Compounds with Condensed Thiophen Rings," Interscience Publ. Inc., New York, 1954, p. 349.

[4] Gilman and Jacoby, *J. Org. Chem.*, 1938, **3**, 108.

[5] Armarego and Turner, *J.*, 1956, 1665; 1957, 13.

[6] Cummings and Muir, *J. Roy. Tech. Coll. (Glasgow)*, 1936, **3**, 562.

derivative (IV) in excellent yield. Hydrolysis of this by sodium butoxide in butan-1-ol required 4 hr. and gave only a 31% yield of the disodium sulphonate (contrast refs. 5 and 7). The resulting salt with phosphorus pentachloride gave the 2,2′-disulphonyl dichloride which, when reduced with hydriodic acid in boiling glacial acetic acid, gave the dinaphthodithiin (V) in 96% yield. This disulphide was converted by copper bronze at 260—280° into dinaphtho[1,2-*b*:2′,1′-*d*]thiophen (II), which differed from the compound described by Henriques.[1]



A priori it was possible that the last step could give the isomer (VIII) though this is unlikely because such skeletal rearrangement was not found in earlier work and because cyclisation to (VIII) would involve ring closure on to a less reactive (β) position of a naphthalene nucleus. Nevertheless the doubt was resolved by synthesis.

The starting material was benzo[*g*]thionaphthen (VI) which was prepared essentially as described by Davies *et al.*[8] Although the overall yield was very poor, this was found to be the best method available. This compound was converted by phthalic anhydride and anhydrous aluminium chloride in nitrobenzene into mixed acids which with polyphosphoric acid at 100° gave the quinone (VII) in 15% overall yield. The quinone was not reduced by zinc dust and ammonia, but Clar's method[9] afforded dinaphtho-[1,2-*b*:2′,3′-*d*]thiophen (VIII) in 11% yield. The structure of this product was confirmed by desulphurisation with Raney nickel to 2,2′-binaphthyl. The compounds (II) and (VIII) gave a depression in a mixed m. p. determination and their ultraviolet spectra were different. This also confirms the structure of compound (II). The nature of the product isolated by Henriques will be investigated further.

EXPERIMENTAL

2-*Iodonaphthalene*-1-*sulphonyl Chloride* (cf. Cummings and Muir [6]).—Sodium 2-iodonaphthalene-1-sulphonate (15 g., 1 mol.; dried at 150° for 2 hr.) was ground with phosphorus pentachloride (8·8 g., 1 mol.), and phosphoryl chloride (5 ml.) added to start the reaction, which was complete on a boiling-water bath in 1 hr. The mixture was poured into water at 0°, and the solid filtered off and dried (KOH). It crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 109—110° (14 g., 93%) (Cummings and Muir gave m. p. 109·5°).

Phenyl 2-*Iodonaphthalene*-1-*sulphonate*.—The preceding chloride (9·0 g., 1 mol.) was heated with phenol (2·6 g., 1·1 mol.) in pyridine (10 ml.) in a boiling-water bath for 1 hr. The solution was poured into cold water, and the *ester* was isolated, dried, and crystallised from methanol

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[7] Armarego and Turner, *J.*, 1956, 3668.

[8] Davies, Banfield, Ennis, Middleton, and Porter, *J.*, 1956, 2603.

[9] Clar, "Aromatische Kohlenwasserstoffe," Springer, Berlin, 1952, p. 107.

as prisms, m. p. 78—79° (8·4 g., 80%) (Found: C, 46·5; H, 3·0. $C_{16}H_{11}O_3IS$ requires C, 46·8; H, 2·7%).

Diphenyl 2,2′-*Binaphthyl*-1,1′-*disulphonate*.—The above phenyl ester (10·4 g.) was heated with copper bronze (10 g.) at 170—175° (temperature of bath not above 220°). When the reaction subsided the mixture was kept in the bath at 210° for 15 min. and then extracted with boiling chlorobenzene. The extract was filtered, concentrated, and cooled. The *ester* that crystallised recrystallised from large volumes of butan-1-ol or acetic acid as rhombs, m. p. 210—211° (6·6 g., 95%) [Found: C, 67·85; H, 4·1; S, 11·5%; *M* (Rast), 651. $C_{32}H_{22}O_6S_2$ requires C, 67·8; H, 3·9; S, 11·3%; *M*, 567].

Disodium 2,2′-*Binaphthyl*-1,1′-*disulphonate*.—The binaphthyl ester (6·6 g., 1 mol.) was treated in boiling butan-1-ol (600 ml.) with a solution from sodium (2·14 g., 8 atom-equiv.) in butan-1-ol (50 ml.). The mixture was boiled under reflux for 4 hr., then concentrated *in vacuo*, poured into water (100 ml.), acidified to pH 2, and extracted with ether. The aqueous solution was neutralised, boiled with charcoal, filtered, concentrated, and cooled. The disodium salt separated as an oil, so the solution was evaporated *in vacuo* at 100°. The sulphonate was extracted from the residue with boiling ethanol and recovered as very hygroscopic plates (1·8 g., 31%) which were stored *in vacuo* after drying at 120° for ¾ hr.

2,2′-*Binaphthyl*-1,1′-*disulphonyl Dichloride*.—The disodium salt (1·4 g., 1 mol.) was heated with an equal weight of phosphorus pentachloride in a boiling-water bath for 1 hr. The *product*, isolated in the usual manner, was dried (KOH) and crystallised from glacial acetic containing 4% of acetic anhydride in prisms; m. p. 236—237° (decomp.) (900 mg., 65%) (Found: C, 53·6; H, 3·0; S, 14·4. $C_{20}H_{12}O_4S_2Cl_2$ requires C, 53·2; H, 2·7; S, 14·2%).

Dinaphtho[1,2-c:2′,1′-e]-[1,2]-*dithiin*.—The preceding chloride (431 mg.) in boiling glacial acetic acid (30 ml.) was treated with 55% w/w hydriodic acid (20 ml.). After a few minutes the dithiin started to separate but the mixture was left overnight at room temperature. It was poured into water and decolorised with sulphur dioxide, and the *dithiin* was filtered off, dried, and crystallised from acetic acid, forming yellow needles, m. p. 195·5—196° (292 mg., 96%) (Found: C, 76·2; H, 3·8. $C_{20}H_{12}S_2$ requires C, 75·9; H, 3·8%). It did not dissolve in alkali and was unaffected by mild oxidants.

Dinaphtho[1,2-b:2′,1′-d]*thiophen*.—The dithiin (200 mg.) was heated with copper bronze (400 mg.) at 260—280°. After 15 min. unchanged disulphide started to sublime. Heating was continued and 30 min. later a white solid sublimed. Sublimation was complete after 1½ hours' heating. The *product* (II) (90 mg., 50%) crystallised from benzene or benzene–light petroleum (b. p. 60—80°) in plates, m. p. 255—256°. With concentrated sulphuric acid it charred and did not give the blue-green solution indicated by Henriques [1] (Henriques gave m. p. 146—147°), $\lambda_{\text{infl.}}$ 254 mμ (log ε 4·6), $\lambda_{\text{max.}}$ 262, 274·5, 284·5 mμ (log ε 4·8, 4·7, 4·7 in 95% EtOH containing 0·1% of $CHCl_3$) [Found: C, 84·5; H, 4·35; S, 11·4%; *M* (Rast), 285. $C_{20}H_{12}S$ requires C, 84·4; H, 4·3; S, 11·3%; *M*, 284], which was homogeneous in chromatography on alumina in benzene–light petroleum.

Dinaphtho[1,2-b:2′,3′-d]*thiophen*-7,12-*quinone* (VII).—Benzo[*g*]thionaphthen (VI) (2·15 g., 1 mol.) and phthalic anhydride (1·73 g., 1 mol.) in nitrobenzene (50 ml., redistilled) were treated with powdered anhydrous aluminium chloride (3·56 g., 2·3 mol.) and kept for 3 days at room temperature, then mixed with 5N-hydrochloric acid (50 ml.) and distilled in steam. The residue was dissolved in saturated sodium carbonate solution, boiled for 5 min. (charcoal), filtered, and acidified. The solid (2·9 g.) that separated was filtered off and dried.

The crude acids were heated with polyphosphoric acid (50 ml.; 82—84% of P_2O_5) in a boiling-water bath with constant shaking for 3 hr., then poured into cold water, and the solid that separated was filtered off. This was then boiled for 5 min. with ammonia (100 ml.; *d* 0·880) and the mixture filtered. The residue was dried and sublimed at 250—300°/0·4 mm. The orange-yellow sublimate of *quinone* crystallised from a large volume of acetic acid in orange needles, m. p. 299—300° (rapid heating) (540 mg., 15%) (Found: C, 76·3; H, 3·3; S, 10·2. $C_{20}H_{10}O_2S$ requires C, 76·4; H, 3·2; S, 10·2%).

Dinaphtho[1,2-b:2′,3′-d]*thiophen* (VIII).—The quinone (VII) (100 mg.) was ground with zinc dust (1·0 g.), sodium chloride (1·0 g.), and anhydrous zinc chloride (5·0 g.) and kept in the air for 5 min. to absorb a small quantity of water, then was placed in a metal-bath at 180°, the temperature being gradually raised to 320°. After 30 sec. at 320° the mixture was allowed to cool to room temperature (longer heating decreased the yield), suspended in excess of 5N-hydrochloric acid (to dissolve the inorganic material) and filtered. After drying, the residue was dissolved in chloroform, and the mixture was filtered, concentrated to a small volume, placed in an alumina column (6″ × ½″; B.D.H. grade), and eluted with benzene–light petroleum (b. p. 40—60°). The proportion of benzene was increased until the band which had a white fluorescence in ultraviolet light was completely removed. The fluorescent eluates were combined, boiled with charcoal, filtered, concentrated to *ca.* 3 ml., and cooled. The *product* crystallised in flakes (10 mg., 11%), m. p. 316—317° [mixed m. p. with (II) was 222—235°], $\lambda_{\text{infl.}}$ 252 mμ (log ε 4·4), $\lambda_{\text{max.}}$ 262, 269·7, 279·8 mμ (log ε 4·7, 4·7, 4·9 in 95% EtOH containing 0·1% of $CHCl_3$). This was sublimed at 250°/0·7 mm., crystallised from ethanol and then benzene, and shown to be chromatographically pure as in the previous case. (Found: C, 84·5; H, 4·8; S, 11·3%). Boiling this product in xylene with an excess of Raney nickel for 5 hr. gave 2,2′-binaphthyl.

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