80. *Isomeric 3-Bromo-derivatives of Dehydro-2-naphthol 1-Sulphide.*

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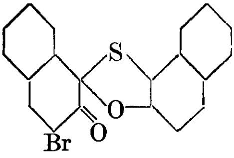
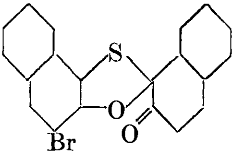
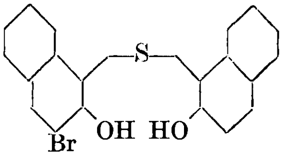
DURING experiments directed to the synthesis of dehydro-2-naphthol 1-sulphide and its substitution products the question arose whether unsymmetrically substituted derivatives exist as two distinct isomerides (*e.g.*, I and II) or whether, owing to instability of the quinolic system and to the possibility of tautomeric interchange, two individuals of the type formulated are incapable of isolation. It is evident that oxidation of an unsymmetrically substituted sulphide (*e.g.*, III) might lead to a mixture of two isomerides of this type (I and II). Preliminary experiments (Stevenson and Smiles, J., 1931, 722) concerning the oxidation of 6-bromo-2-naphthol 1-sulphide indicated that a mixture of dehydro-derivatives was formed; but in this case the evidence was unsatisfactory, since the physical character of the material prevented separation of pure components and the tentative conclusion was based on the formation of a mixture of thioxins by reaction with hydrogen iodide.



(I.)



(II.)



(III.)

Further and more definite evidence has now been obtained by the isolation of two isomerides (I and II) of the type in question. These have been obtained by bromination of dehydro-2-naphthol 1-sulphide and from the oxidation products of 3-bromo-2-naphthol 1-sulphide; their respective structures are evident from the following considerations. With bromine under suitable conditions, dehydro-2-naphthol 1-sulphide yields a deep red *monobromo*-derivative (m. p. 155°). This product must be either (I) or (II), since after reduction to the *iso*-sulphide and conversion of the latter by alkali (Warren and Smiles, J., 1931, 914) it yields a *monobromo-2-naphthol 1-sulphide* (III) which is identical with material synthesised from 3-bromo-2-naphthol and 2-naphthol-1-bromothiol. The latter of these alternatives (II) cannot be admitted, since it implies direct substitution in the 3-position of the 2-naphthol nucleus : on the other hand, the former (I) accords with the usual substitution of β-naphthaquinone by halogens. Confirmation of (I) for this product of direct bromination is given by the fact that, in contrast with the unsubstituted dehydro-derivative, no hydrazone could be obtained from it; this restricted activity generally met with in *o*-substituted quinones has already been recorded for 3-derivatives of dehydronaphthol sulphides (Lesser and Gad, *Ber.*, 1923, **56**, 1802). Moreover, according to the usual course of brominating the β-naphthaquinone nucleus, this substance, being a 3-derivative (I), should yield at the next stage the 3 : 4-dibromodehydrosulphide (IV). It is now shown that the dibromo-compound obtained by further bromination yields with aniline a *monobromoanilino*-derivative and therefore contains bromine in the 4-position (compare Fries and Schimmelschmidt, *Annalen*, 1930, **484**, 247). For these reasons the monobromo-dehydro-sulphide obtained by direct bromination is regarded as the 3-derivative (I).

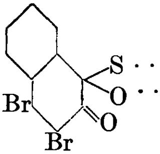
Another distinct isomeride (m. p. 172°) has been isolated by fractionating the oxidation product of the sulphide (III). This *dehydro*-derivative is therefore regarded as the 3′-isomeride (II) and the view is confirmed by the fact that in contrast with (I) it readily yields a *phenylhydrazone*.

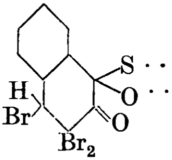
The isolation of these isomeric monobromo-derivatives shows an unexpected stability of the cyclic quinolic system of dehydrosulphides and it may be noted that attempts to effect the direct interconversion of these isomerides have hitherto been unsuccessful.

It has been previously shown (Nolan and Smiles, J., 1912, **101**, 1422) that dehydro-2-naphthol 1-sulphide with excess of bromine in acetic acid yields a tribromo-derivative, from which hydrogen bromide may be removed, leaving a dibromodehydro-sulphide. This is identical with the 3 : 4-derivative, hence it is evident that the tribromo-derivative is (V) and that the distribution previously assigned to halogen in this substance is incorrect.

The restricted activity of the quinolic system observed in the 3 : 3′-dibromo- and 3-bromo-dehydro-sulphides (*e.g.*, I) is not manifest in their reaction with acetyl halides; in fact the substances are suitably characterised by conversion into the corresponding *dinaphthathioxins*, evidently (VI) and (VII), by acetyl iodide.

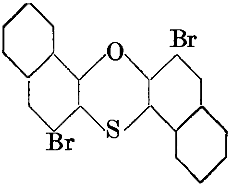
(IV.)

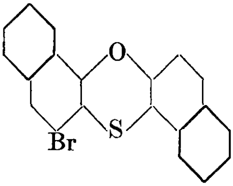




(V.)

(VI.)





(VII.)

EXPERIMENTAL.

3 : 3′-*Dibromo-2-naphthol* 1-*Sulphide*, $(C_{10}H_5Br{\cdot}OH)_2S$.—Sulphur chloride (5 g.) was added to an agitated solution of 3-bromo-2-naphthol (22 g.) in chloroform (100 c.c.). After the reaction had been completed at 100°, the solvent was evaporated and the residue was purified from acetic acid (charcoal). The required *sulphide* (80%) formed needles, m. p. 192° (Found : C, 50·2; H, 2·6; S, 6·7; Br, 33·7. $C_{20}H_{12}O_2Br_2S$ requires C, 50·4; H, 2·5; S, 6·7; Br, 33·6%).

3 : 3′-*Dibromodehydro*-2-*naphthol* 1-*Sulphide*.—A warm solution of the sulphide (15 g.) in aqueous (60 c.c.) sodium hydroxide (3·7 g.)

was added to an excess of water (300 c.c.) and the stirred mixture was immediately treated with a concentrated solution of potassium ferricyanide (2 mols.). The insoluble product, after treatment with hot aqueous sodium chloride, was purified from acetic acid; it formed (55—60% yield) bright red needles, m. p. 205° (Found : C, 50·8; H, 2·2. $C_{20}H_{10}O_2Br_2S$ requires C, 50·6; H, 2·1%). The substance separated from benzene in crystals which retained solvent (Found: C, 53·8; H, 2·6; Br, 31·0; loss on heating, 7·7. $C_{20}H_{10}O_{20}Br_2S,\frac{1}{2}C_6H_6$ requires C, 53·8; H, 2·5; Br, 31·1; loss, 7·6%). This *dehydro*-derivative, like other *o*-substituted quinones of this series, did not yield a phenylhydrazone; it was further characterised by conversion into the following compound.

6 : 13-*Dibromo*-$\alpha\beta\beta'\alpha'$-*dinaphthathioxin* (VI).—A solution of acetyl iodide (1 g.) in acetic anhydride was slowly added to a cooled (0°) and stirred suspension of the dehydro-derivative (1 g.) in the same solvent. After 1 hour (15—20°), the insoluble product was collected (0·9 g.) and washed with sulphurous acid. It separated from *cyclo*hexanone in yellow needles, m. p. 248° (Found : C, 52·0; H, 2·3; Br, 34·9. $C_{20}H_{10}OBr_2S$ requires C, 52·4; H, 2·1; Br, 34·9%).

With boiling acetyl chloride (1 hr.), the dehydro-compound yielded the corresponding ?-*chloro*-6 : 13-*dibromodinaphthathioxin* (compare VI). This formed needles from *cyclo*hexanone, m. p. 264° (Found : C, 48·7; H, 2·0. $C_{20}H_9OClBr_2S$ requires C, 48·7; H, 2·0%).

3-*Bromo*-2-*naphthol* 1-*Sulphide* (III).—3-Bromo-2-naphthol (4·5 g.) was added to carbon tetrachloride containing 2-naphthol-1-bromothiol which had been prepared from 2-naphthol 1-disulphide (3·5 g.) and bromine (J., 1930, 1744). When the solvent had been partly removed by a current of dry air, the product separated (3·3 g.); it crystallised from acetic acid in needles, m. p. 192° (Found : C, 60·3; H, 3·5. $C_{20}H_{13}O_2BrS$ requires C, 60·4; H, 3·2%).

3′-*Bromodehydro*-2-*naphthol* 1-*Sulphide* (II).—3-Bromo-2-naphthol 1-sulphide (III) was oxidised in the usual manner by potassium ferricyanide in alkaline solution. After the crude product had been treated with hot water, it was purified from ethyl acetate and repeatedly from benzene–light petroleum. The substance formed aggregates of orange needles, m. p. 172—173° (Found : C, 61·2; H, 3·1. $C_{20}H_{11}O_2BrS$ requires C, 60·8; H, 2·8%). With phenylhydrazine in hot acetic acid, the *phenylhydrazone* was rapidly formed; orange needles, m. p. 196° (Found : N, 5·7; Br, 16·1. $C_{26}H_{17}ON_2BrS$ requires N, 5·8; Br, 16·5%).

3-*Bromodehydro*-2-*naphthol* 1-*Sulphide* (I).—Chloroform containing bromine (1 mol.) was gradually added to a stirred solution of dehydro-2-naphthol 1-sulphide (1 mol.) in the same solvent. The red oil which remained after removal of the solvent was dissolved in cold pyridine and then liberated therefrom by addition to excess of dilute sulphuric acid. The material then solidified; it crystallised from benzene in dark red prisms, m. p. 155° (Found: C, 60·9; H, 3·1; Br, 20·0. $C_{20}H_{11}O_2BrS$ requires C, 60·8; H, 2·8; Br, 20·3%). The substance was characterised by conversion into 13-*bromo-αββ'α'-dinaphthathioxin* (VII) with acetyl iodide in the usual manner. This formed yellow needles, m. p. 210° (Found: C, 63·5; H, 3·3; Br, 21·6. $C_{20}H_{11}OBrS$ requires C, 63·3; H, 2·9; Br, 21·1%).

Reduction of this dehydro-derivative in alkaline media did not yield a pure product owing to partial removal of bromine; the process was effected as follows. A hot stirred solution of the dehydro-sulphide was treated with small portions of zinc dust until it had become colourless; when the mixture was cooled, the zinc derivative of the *iso*-sulphide separated. The *iso*-sulphide, obtained from this salt in the usual manner, was isolated in the crystalline state; it was not further purified but was converted into the derivative of 2-naphthol 1-sulphide by solution in warm aqueous alkali. From this solution, mineral acids liberated 3-bromo-2-naphthol 1-sulphide (III), which was identified by close comparison with material synthesised from 3-bromo-2-naphthol and 2-naphthol-1-bromothiol as previously described.

3 : 4-*Dibromodehydro-2-naphthol* 1-*sulphide* (IV) was obtained from the 3-monobromo-derivative (I) by reaction with bromine (1 mol.) in chloroform. The product, isolated in the usual manner, crystallised from acetic anhydride in dark red needles, m. p. 204°. These depressed the m. p. of the 3 : 3'-derivative (205°) when mixed with it and were identical with the dibromo-derivative already described (Nolan and Smiles, *loc. cit.*) and obtained by reaction of dehydro-2-naphthol 1-sulphide with excess of bromine. The higher m. p. of this substance previously recorded (*loc. cit.*) has not been attained (Found: C, 50·7; H, 2·2. Calc. for $C_{20}H_{10}O_2Br_2S$: C, 50·6; H, 2·1%).

3-*Bromo*-4-*anilinodehydro*-2-*naphthol* 1-*sulphide* was obtained from the reaction of aniline (5 mols.) with the 3 : 4-dibromo-derivative (1 mol.) in hot acetic acid. It was isolated by addition of water to the mixture and after purification from hot acetone formed a yellow crystalline powder, m. p. 240—241° (Found: N, 2·86; Br, 16·4. $C_{26}H_{16}O_2NBrS$ requires N, 2·9; Br, 16·5%).

In conclusion we wish to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, November 27th,* 1931.]