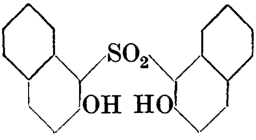
CLXXI.—*Dehydro-2-naphtholsulphone.*

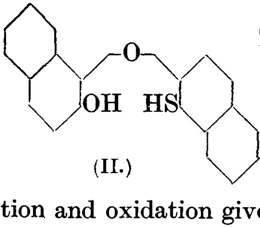
By LEONARD ARTHUR WARREN and SAMUEL SMILES.

HINSBERG has shown (*J. pr. Chem.*, 1914, **90**, 345; 1915, **91**, 307; 1916, **93**, 277) that alkaline ferricyanide removes two hydrogen atoms from 2-naphtholsulphone (I), forming the dehydro-sulphone, and that the latter substance by alkaline reduction yields *iso*-2-naphtholsulphone, two hydrogen atoms being reabsorbed in the process. He regarded these isomerides as having identical structures and as providing a further illustration of the valency isomerism advocated by him to explain the relations between 2-naphthol 1-sulphide and *iso*-2-naphthol sulphide. The last-named substance has been shown (this vol., p. 956) to be the 2-hydroxy-1′-thiol derivative (II) of 1 : 2′-dinaphthyl ether; moreover it evidently is closely related to the *iso*-sulphone, since Hinsberg (*loc. cit.*) has shown that it is formed from an anhydride of this by reduction.

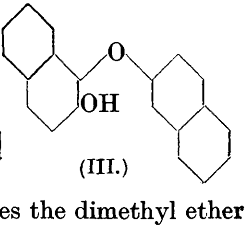
It is thus evident that the structures of *iso*-2-naphtholsulphone and of the dehydro-sulphone need reconsideration; experiments have now been made further to elucidate the nature of these derivatives of 2-naphtholsulphone and their relationship to the corresponding derivatives of 2-naphthol 1-sulphide (I, SO_2 being replaced by S). Of the many important facts bearing on these issues recorded by Hinsberg (*loc. cit.*), it is sufficient to mention the isolation of 2-hydroxy-1 : 2′-dinaphthyl ether (III) from the reduction products of the dehydro-sulphone and the spontaneous formation of this ether and sulphur dioxide from the *iso*-sulphone. These facts appear to indicate the presence in these substances of the 1 : 2′-dinaphthyl ether structure which has been found (this vol., p. 956) in the dehydro- and the *iso*-sulphide. Hinsberg, indeed, discussed the question whether the *iso*-sulphone should be regarded as the sulphinic acid derived from this ether, but rejected the suggestion for the following reasons : (a) both 2-naphthol-1-sulphone (I) and the *iso*-sulphone yield the dehydro-sulphone by oxidation, (b) the *iso*-sulphide by methylation and oxidation gives the dimethyl ether of the *iso*-sulphone, (c) the *iso*-sulphone can be converted into the *iso*-sulphide by reduction of a substance regarded as its anhydride.



(I.)



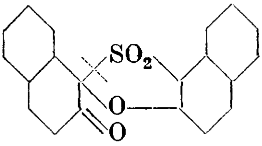
(II.)

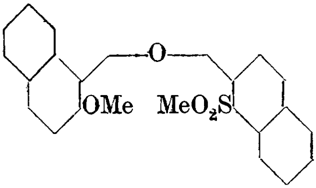


(III.)

Since the *iso*-sulphide is now known to be (II), the relations (b) and (c), if confirmed, entirely lose their effectiveness in refuting the 1 : 2′-oxide structure; on the contrary, they now appear strongly to support this structure for the *iso*-sulphone. The first of the three relations quoted has clearly little value unless the dehydro-sulphone is known or assumed not to contain the 1 : 2′-oxide structure. Important evidence on this question is afforded by reduction of the dehydro-sulphone; with sodium amalgam or with zinc and acetic acid (also Hinsberg, *loc. cit.*) the 2-hydroxy-1 : 2′-dinaphthyl ether (III) is formed, whilst with zinc and hydrochloric acid the *iso*-sulphide (II) is obtained. The dehydro-sulphone therefore contains the 1 : 2′-oxide structure and, since it is formed merely by removal of two hydrogen atoms from 2-naphthol-1-sulphone (I), the structure (IV) must be ascribed to it. As was shown by Hinsberg (*loc. cit.*), the dehydro-sulphone reacts slowly with *p*-nitrophenylhydrazine, fission of the substance occurring with formation of the hydrazone of β-naphthaquinone. This behaviour is analogous to that of dehydro-1-bromo-2-naphthol with aniline (Pummerer and Cherbuliez, *Ber.*, 1919, **52**, 1412), which yields the anilino-derivative of β-naphthaquinone.

(IV.)





(V.)

The chief relations between the members of this group are summarised as follows; the substances are numbered to facilitate reference.

$$\begin{tikzcd}
\text{Dehydro-sulphide (1)} \arrow[r] & \textit{iso}\text{-Sulphide (2)} \arrow[r] & \text{S-Methyl ether of } \textit{iso}\text{-sulphide (3)} \arrow[r] \arrow[d, "H_2O_2"] & \text{Dimethyl ether of } \textit{iso}\text{-sulphide (5)} \arrow[dd, "H_2O_2"] \\
 & & \text{Methyl sulphone (4)} \arrow[d, "Me_2SO_4"] & \\
\text{Dehydro-sulphone (6)} \arrow[r] \arrow[uur] & \textit{iso}\text{-Sulphone (7)} \arrow[r, "Me_2SO_4"'] \arrow[uu] & \text{Dimethyl ether of } \textit{iso}\text{-sulphone (8)} & {}
\end{tikzcd}$$

Previous experiments have shown (this vol., p. 956) that (1), (2), (3), and (4) yield the hydroxydinaphthyl ether (III) with suitable reducing agents; it is now shown that (6) and (7) also yield this substance with sodium amalgam, and (8) gives the methyl ether (III, OH being replaced by OMe). The 1 : 2′-dinaphthyl ether structure has in fact been established for all these with the exception of (5). The important relationships of (3), (4), and (5) to (8) indicated by Hinsberg (*loc. cit.*) have been confirmed, but the substance, m. p. 88°, described by him as the dimethyl ether of the *iso*-sulphone (8) has not been encountered. Moreover the conversion of (6) and (7) into the *iso*-sulphide (II) has been effected by suitable reduction.

The nature of the *iso*-sulphone is clearly revealed by the formation of the mercaptan (II) from it by reduction and by the fact that its *dimethyl* ether has the structure (V), which is assigned to it because reduction yields the methoxydinaphthyl ether (III, OH being replaced by OMe) and the substance is formed by methylation of the methyl sulphone (II, SH being replaced by SO_2Me) (this vol., p. 956) or by oxidation of the dimethyl ether of the *iso*-sulphide (II, OH and SH being replaced by OMe and SMe respectively). Hence the *iso*-sulphone itself is to be regarded as the sulphinic acid corresponding to the thiol (II, SH being replaced by SO_2H), and its formation from the dehydro-sulphone (IV) by reduction as taking place by rupture of the 5-membered ring as indicated, the process being analogous to the formation of the *iso*-sulphide (II) from the dehydro-sulphide (IV, SO_2 being replaced by S) (this vol., p. 956). Moreover, conversion of the *iso*-sulphone and 2-naphthol-1-sulphone into the dehydro-sulphone is thus seen to proceed similarly to the oxidation of *iso*-2-naphthol sulphide and 2-naphthol 1-sulphide to the dehydro-sulphide.

EXPERIMENTAL.

Dehydro-2-naphthol-1-sulphone (IV).—Details of the preparation of this substance were not described by Hinsberg. The following method gave the best results. An aqueous solution (150 c.c.) of potassium ferricyanide (10 g.) was gradually added to a shaken mixture of chloroform (100 c.c.) and water (125 c.c.) which contained 2-naphthol-1-sulphone (5 g.) and sodium hydroxide (1·2 g.). After further agitation (1 hour) the chloroform solution was dried and concentrated. The dehydro-sulphone separated (yield, *ca.* 50%) in the crystalline state and after purification from acetic acid formed bright yellow prisms, m. p. 245° (Found: C, 68·9; H, 3·7. Calc.: C, 68·9; H, 3·4%).

The Dimethyl Ether of the iso-*Sulphone* (V).—The *iso*-sulphone was obtained from the dehydro-sulphone by reduction with sodium sulphide as described by Hinsberg. The chief properties attributed by him to the substance and its solubility in aqueous sodium carbonate were confirmed. A solution of this material in excess of aqueous sodium hydroxide (2*N*) was treated in the usual way with methyl sulphate. The viscous product was further treated with boiling 1% alkali solution. It solidified when cooled and was obtained from acetone–methyl alcohol (charcoal) in prisms, m. p. 144° (Found: C, 69·8; H, 4·9; *M*, 385. $C_{22}H_{18}O_4S$ requires C, 69·8; H, 4·7%; *M*, 378).

The same substance was obtained by the following methods: (a) A suspension of the sodium salt of the methyl sulphone (II, SH being replaced by SO_2Me) derived (this vol., p. 956) from the *iso*-sulphide was treated in warm aqueous sodium hydroxide with methyl sulphate as usual. The semi-solid product was purified by the treatment already described; it then had the same m. p. as the product prepared from the *iso*-sulphone, whether taken alone or mixed with it. (b) A solution of the viscous dimethyl ether of the *iso*-sulphide (II, OH and SH being replaced by OMe and SMe respectively) (1·7 g.) in acetic acid (15 c.c.) containing hydrogen peroxide (2 c.c., 30% sol.) was warmed (1 hour, 100°). When sodium chloride was added to the cooled and diluted liquid, the desired product separated in the crystalline state; this was purified from acetic acid and identified in the usual manner with the products from the two other methods described.

iso-2-*Naphthol Sulphide* (II).—(a) Dehydro-2-naphtholsulphone (IV; 1 g.) was suspended in boiling acetic acid (40 c.c.) containing concentrated hydrochloric acid (5 c.c.). Zinc dust was gradually added until the colour of the solution was discharged. The clear solution was mixed with a little concentrated hydrochloric acid, cooled, and stirred, and water (20 c.c.) slowly added. The crystalline precipitate obtained, after further purification (77% yield), was identified with an authentic sample of *iso*-naphthol sulphide (Found: C, 75·5; H, 4·4. Calc.: C, 75·5; H, 4·4%). This *iso*-sulphide responds to Rheinboldt's test (*Ber.*, 1927, **60**, 184) for aromatic thiols.

(b) Reduction of *iso*-2-naphtholsulphone (II, SH being replaced by SO_2H) was effected by zinc and concentrated hydrochloric acid in boiling alcohol. Addition of water to the cooled liquid gave a crystalline precipitate. This was purified from alcohol and found to be identical with an authentic sample of *iso*-β-naphthol sulphide.

2-*Hydroxy*-1 : 2′-*dinaphthyl Ether* (III).—(a) Zinc dust was added to a hot solution of the dehydro-sulphone (IV; 1 g.) in acetic acid (30 c.c.) until the colour had faded. The cooled solution deposited the hydroxydinaphthyl ether (90% yield), m. p. 197° (Found: C, 83·6; H, 5·2. Calc.: C, 83·9; H, 4·9%), which was further identified by a close comparison of its methyl ether with synthetic material (this vol., p. 956). Reduction of the dehydro-sulphone with sodium amalgam in warm aqueous alcohol gave a poorer yield of the same material. It was isolated from the product of reaction by addition of sulphuric acid after alcohol had been removed by evaporation (charcoal); it was purified from acetic acid and had m. p. 197°.

(b) The *iso*-sulphone (II, SH being replaced by SO_2H) also yielded the hydroxydinaphthyl ether by reduction with these reagents. Reduction with zinc and acetic acid was effected as described in the case of the dehydro-sulphone; the yield was poorer. A solution of the *iso*-sulphone (from 1 g. of dehydro-sulphone) in *N*-sodium hydroxide was stirred and treated with sodium amalgam (35 g.; 5%) for 3 hours. The clear aqueous liquid (charcoal) was rendered acid and set aside. The required substance separated and was purified (m. p. 197°) and identified in the usual manner.

2-Methoxy-1 : 2′-dinaphthyl ether (III, OH being replaced by OMe) was obtained by alkaline methylation of the product of reduction of the dehydro-sulphone with zinc and acetic acid. It was purified from acetic acid and had m. p. 161° (Found: C, 84·0; H, 5·7. Calc.: C, 84·0; H, 5·3%) and was identical with the product obtained by synthesis (this vol., p. 956). The same substance was obtained by reduction of the dimethyl ether of the *iso*-sulphone (V). Sodium amalgam (5%) was gradually added (6 hours) to alcohol (40 c.c.) and water (20 c.c.) which contained this ether in suspension. The alkaline liquid was mixed with acetic acid and boiled (charcoal). When diluted and cooled, the solution yielded the required substance (0·2 g.), which was purified in the usual manner; m. p. 161° (Found: C, 83·7; H, 5·4. Calc.: C, 84·0; H, 5·3%).

In conclusion we wish to thank Dr. A. Cohen for a quantity of the dehydronaphtholsulphone and for information concerning its preparation.

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