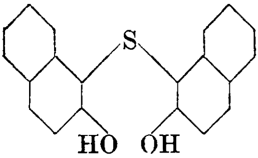
CXVII.—iso-β-*Naphthol Sulphide.*

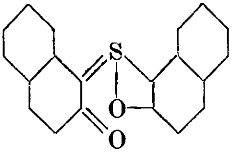
By Leonard Arthur Warren and Samuel Smiles.

When 2-naphthol 1-sulphide (I) is oxidised by alkaline ferricyanide, two hydrogen atoms are removed (J., 1914, **105**, 1750) and the dehydro-sulphide is formed. Reduction of the latter substance yields the *iso*-β-naphthol sulphide by absorption of two hydrogen atoms; these are removed by suitable oxidation, the dehydro-sulphide being regenerated (*loc. cit.*).

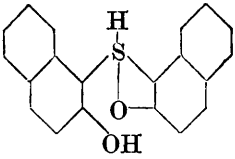
The *iso*-sulphide contains two active hydrogen atoms (J., 1913, **103**, 346) and it yields lead and zinc derivatives which are insoluble in acetic acid (Hinsberg, *J. pr. Chem.*, 1914, **90**, 345) in contrast with 2-naphthol 1-sulphide (I). Lesser and Gad (*Ber.*, 1923, **56**, 970) found that a disulphide is formed from this *iso*-sulphide by oxidation with iodine and they obtained further evidence showing that the *iso*-sulphide is a hydroxy-mercaptan. These authors, assuming the structure (II) proposed by Hinsberg (*J. pr. Chem.*, 1915, **91**, 307) for the dehydro-sulphide, considered that the *iso*-β-naphthol sulphide should be represented by (III), which has the merit of providing a simple explanation of the conversion of the substance into 2-naphthol 1-sulphide (I) by aqueous alkali hydroxide. On the other hand, this formula does not represent the substance



(I.)



(II.)



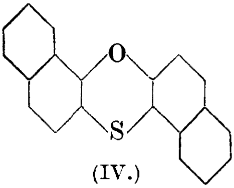
(III.)

as a mercaptan, but assigns to it a dipolar structure derived from dinaphthylsulphonium hydroxide, to which the properties of a mercaptan can hardly be ascribed.

Apart from this criticism of a general nature, there are others which taken together make necessary a revision of the structure (III). For instance, the *iso*-sulphide is unattacked by aqueous acids and no indication of the formation of a sulphonium salt is obtained. If the dipolar structure and the explanation of the action of alkali which it affords were correct, acids as well as alkaline reagents should effect the conversion into 2-naphthol 1-sulphide (I). The zinc derivative of the *iso*-sulphide behaves as if the metal were associated with sulphur. With methyl iodide it gives a methyl ether (Hinsberg, *J. pr. Chem.*, 1916, **93**, 277) which is now shown to be the *S*-methyl derivative, since it is not oxidised by iodine and yields methyl mercaptan on reduction. This behaviour of the salt and its insolubility in acetic acid accord with the character of a zinc mercaptide. The *S*-methyl ether is not attacked by boiling aqueous alkali hydroxide or by boiling concentrated hydrochloric acid. According to the formula of Lesser and Gad (III with SMe in place of SH) 2-naphthol 1-sulphide should be obtained with these reagents, especially easily with the former, since Kehrmann and Duttenhofer (*Ber.*, 1905, **38**, 4198) have shown that dinaphthylmethylsulphonium decomposes rapidly under alkaline conditions, liberating the aromatic sulphide.

The *S*-methyl ether is converted by suitable oxidation into the sulphone : it is difficult to understand how a substance of that type could be formed from the structure in question (III; SH = SMe) without rupture of the molecule.

Finally, αββ'α'-dinaphthathioxin (IV) is obtained by dehydration of the *iso*-sulphide (J., 1913, **103**, 347, 909). Lesser and Gad, anticipating that this "*iso*"-dinaphthathioxin might have the structure later found to be correct (J., 1929, 210), assumed (*Ber.*, 1925, **58**, 2557) that migration of sulphur from the 1- to the 2-position takes place during dehydration and suggested a mechanism which involves the formation of a three-membered ring (V). This explanation appears incomplete; moreover, there is difficulty in admitting that the dipolar structure would survive the attack of concentrated sulphuric acid while hydroxyl is being removed from the naphthalene nucleus. The experiments now described were undertaken as a result of these and other considerations.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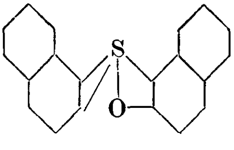
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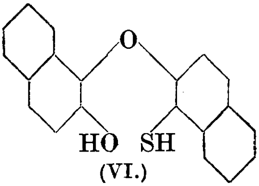
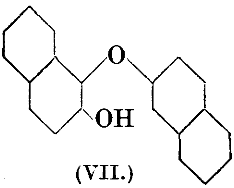

(VI.)

Since it is evidently unsafe to attempt to derive any structure of the *iso*-sulphide from that hitherto ascribed to the dehydro-sulphide (II), the question has been approached independently. The chief characteristics of the *iso*-sulphide are those of a hydroxy-mercaptan (see, *e.g.*, Lesser and Gad, *loc. cit.*). When the substance is dehydrated, αββ′α′-dinaphthathioxin (IV) is formed: during the process, hydroxyl is removed and thiol survives as the thio-group. Interpreted in the simplest manner, this result leads to a structure such as (VI) for the *iso*-sulphide, which would thus appear as a derivative of 1 : 2′-dinaphthyl ether. Experiments have been made to isolate this group by removing sulphur from the substance.

Since the sulphonic group is easily removed from the naphthalene nucleus by alkaline reduction (Friedländer, *Ber.*, 1893, **26**, 3208), the *S*-methyl ether was converted into the *sulphone*. This substance was easily attacked by sodium amalgam, the methanesulphonyl group being eliminated. The sulphur-free residue was identified as 2-hydroxy-1 : 2′-dinaphthyl ether (VII) by comparison of its *methyl* ether with the product synthesised from 1-bromo-2-methoxynaphthalene and potassium 2-naphthoxide in presence of copper.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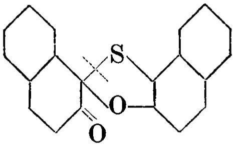
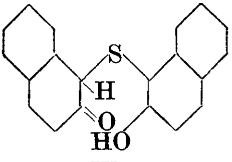

(VIII.)


(IX.)

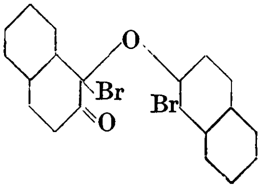
Hydrogen iodide slowly attacked this sulphone, liberating methyl mercaptan, but with this reagent no pure substance was isolated from the sulphur-free products. On the other hand, the *S*-methyl ether, although slowly attacked by sodium amalgam under more intense conditions, was easily attacked by hydrogen iodide, giving good yields of methyl mercaptan and the hydroxydinaphthyl ether

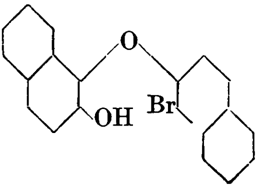
(VII) in question. Moreover, the *iso*-sulphide and the dehydro-sulphide were easily resolved by warm hydrogen iodide into hydrogen sulphide and this ether.

The *iso*-sulphide is therefore to be regarded as the thiol derivative of 2-hydroxy-1 : 2′-dinaphthyl ether, and, since $\alpha\beta\beta'\alpha'$-dinaphthathioxin (IV) is formed on dehydration, the thiol group must be in the 1′-position as indicated by (VI). This structure accords well with all the properties of the *iso*-sulphide hitherto observed and also with the formation of the sulphone and sulphonium derivatives now recorded.

With this information concerning the *iso*-sulphide, the constitution of the dehydro-sulphide may be profitably discussed. This substance is formed from 2-naphthol 1-sulphide (I) or the *iso*-sulphide (VI) by loss of two hydrogen atoms; evidently it contains the 1 : 1′-thio- and the 1 : 2′-oxido-group of the respective generators and should be represented as (VIII), reduction to the *iso*-sulphide taking place by rupture of the five-membered ring as indicated. The formation of the substance from 2-naphthol 1-sulphide may be represented as involving the oxidation of a tautomeric form of the latter (IX); some justification for this view (compare Willstätter and Schuler, *Ber.*, 1928, **61**, 362) is found in the fact that this sulphide and others of its type yield only the monopotassium salts from solutions in more than two molecular proportions of the alkali hydroxide (Lesser and Gad, *Ber.*, 1925, **58**, 2557). The structure (II) assigned by Hinsberg (*loc. cit.*) to this substance was founded on the formation of a monohydrazone and on experiments which indicated the formation of a very unstable perchlorate; but the existence of the latter substance cannot here be accepted as conclusively proving the presence of the sulphonium group, since it is well known that carbonyl in many ketones and quinones is capable of forming additive compounds with acids and salts (Pfeiffer, " Organisch Molekül-Verbindungen," 1927). The properties of the dehydro-sulphide are therefore adequately represented by the *spiro*-structure proposed. Moreover it should be noticed that this structure represents complete analogy with the dehydrophenols investigated by Pummerer (*Ber.*, 1914, **47**, 1472, 2957; 1919, **52**, 1392), who showed, for example, that dehydro-1-bromo-2-naphthol (X), which is obtained by oxid-

(X.)





(XI.)

ation of 1-bromo-2-naphthol, yields on reduction the 1′-bromo-2-hydroxy-1 : 2′-dinaphthyl ether (XI), the quinolic bromine atom being eliminated. The greater stability of the dehydro-sulphide compared with that of other dehydrophenols is well explained by the presence of the five-membered thioxole system.

Finally it must be noticed that the conversion of the *iso*-sulphide into 2-naphthol 1-sulphide by heating or by the action of alkali hydroxide now appears to be an intramolecular change. Further experiments are being made concerning this process and the nature of dehydro-2-naphthol-1-sulphone.

EXPERIMENTAL.

The *iso*-2-naphthol sulphide (VI) used in these experiments was prepared as previously described (J., 1912, **101**, 1423). The characteristic brown nickel derivative, formed by addition of nickel acetate to an alcoholic solution of the mercaptan, is very soluble in benzene.

The S-*Methyl Ether of the* iso-*Sulphide* (VI with SMe in place of SH).—A concentrated solution of zinc acetate (10 g.) in hot water was added to a boiling solution of the *iso*-sulphide (20 g.) in alcohol (100 c.c.). The zinc salt (95%) separated in the crystalline state and was purer and more easily manipulated than the amorphous material prepared from cold solutions. A mixture of this zinc salt (10 g.), methyl iodide (5 c.c.), and ethyl alcohol (100 c.c.) was boiled until the zinc salt had dissolved (*ca.* 1 hour). The solvent was evaporated from the filtered solution and the residue was purified from acetic acid. The product (80—90%) had m. p. 134° (Found : C, 76·1; H, 4·8. Calc. : C, 7·59; H, 4·8%). The substance did not react with iodine in ethereal solution in presence of sodium bicarbonate, and it was recovered unchanged from a boiling (¼ hour) solution in aqueous sodium hydroxide (2*N*) and from a boiling (1½ hours) alcoholic solution containing hydrochloric acid. The formation of a yellow insoluble material when bromine vapour is added to an acetic acid solution may be conveniently used as a test for the presence of the substance.

The *benzoyl* derivative, prepared in cold pyridine, formed plates, m. p. 84—85° (Found : C, 77·2; H, 4·8. $C_{28}H_{20}O_3S$ requires C, 77·1; H, 4·6%).

The *mercuri-iodide* of the *dimethylsulphonium iodide* (VI; SH = SMe_2I,HgI_2) was rapidly formed when acetone containing equimolecular proportions of the *S*-methyl ether and mercuric iodide and a large excess of methyl iodide was boiled. After the mercuric iodide had dissolved, ether was added to the cooled liquid until it became turbid. The required substance separated in pale yellow prisms, m. p. 101° (decomp.); these contained acetone which could not be quantitatively removed without further decomposition of the substance (Found: C, 32·1; H, 2·9; Hg, 20·0. $C_{22}H_{19}O_2I_3SHg,2C_3H_6O$ requires C, 32·1; H, 3·0; Hg, 19·2%).

The dimethyl ether of the *iso*-sulphide (VI; OH and SH = OMe and SMe respectively) was obtained as a clear viscous oil by the action of methyl sulphate on the sodium derivative of the *S*-methyl ether in methyl alcohol. It was characterised as the *methosulphate*, which was formed by heating a mixture of methyl sulphate (1¼ mols.) and the dimethyl ether (1 mol.) at 100° for 1 hour. The required substance was isolated from the product and further purified by addition of ether to a chloroform solution. It formed plates, m. p. 178° (decomp.), which were moderately easily soluble in water (Found: C, 61·4; H, 5·4; S, 13·3. $C_{22}H_{18}O_2S,Me_2SO_4$ requires C, 61·0; H, 5·1; S, 13·6%).

The S-*methylsulphone* (VI; SH = SO_2Me) was obtained by oxidation of the *S*-methyl ether. A product of this process has been described by Hinsberg (*J. pr. Chem.*, 1916, **93**, 277) as the sulphone derived from the monomethyl ether and as having m. p. 218°. The formation of a substance of this m. p. has been confirmed, but analytical data show that it is a mixture of sulphone and sulphoxide in approximately equal proportion (Found: C, 70·7; H, 4·7. Calc. for sulphone: C, 69·2; H, 4·4%. Calc. for sulphoxide: C, 72·4; H, 4·6%). Moreover, it was attacked by zinc and acetic acid, yielding a mixture of lower and indefinite m. p. (185—190°) which was found by the bromine test to contain the *S*-methyl ether. The required sulphone was obtained by renewed oxidation. Acetic acid (20 c.c.) containing the *S*-methyl ether (4 g.) and hydrogen peroxide (8 c.c. of 30%) was heated at 100° for ¼ hour and rapidly cooled. The product (4·1 g.), m. p. 204—209°, was re-oxidised (½ hour) with twice its weight of hydrogen peroxide (30%) in sufficient acetic acid for complete solution at 100°. The material (2·5 g.), which slowly separated from the cooled liquid, crystallised from acetic acid in plates, m. p. 200° (Found: C, 69·2; H, 4·5; *M*, 367. $C_{21}H_{16}O_4S$ requires C, 69·2; H, 4·4%; *M*, 364). The substance was not attacked by zinc dust and acetic acid. The *benzoyl* derivative, prepared in cold pyridine, formed plates, m. p. 149—150° (Found: C, 71·9; H, 4·7. $C_{28}H_{20}O_5S$ requires C, 71·8; H, 4·3%). This substance was also obtained by oxidation of the benzoyl derivative of the *S*-methyl ether.

2-*Hydroxy*-1 : 2′-*dinaphthyl Ether* (VII).—This was obtained by the following methods: (*a*) A mixture of the *S*-methylsulphone (2 g.), aqueous sodium hydroxide (1 mol., 2*N*), ethyl alcohol (10 c.c.), and water (50 c.c.) was treated with sodium amalgam (150 g., 3%)

in the course of 12 hours, sufficient alcohol being added at intervals to redissolve insoluble material. Eventually the alcohol was evaporated and the sparingly soluble sodium salt was collected and decomposed with dilute sulphuric acid. The product (1 g.) crystallised from acetic acid in needles, m. p. 197°.

(*b*) The *S*-methyl ether (1 g.) was gently boiled with purified hydrogen iodide (25 c.c., *d* 1·7) in a long-necked flask. A slow stream of nitrogen passed through the apparatus, and the emergent vapours were washed by aqueous mercuric chloride. When the liberation of methyl mercaptan had ceased, the precipitated mercury derivative was collected (97%) (Found : Hg, 70·6. Calc. for CH_3·S·HgCl : Hg, 70·8%). The cooled contents of the reaction vessel were added to a large bulk of water ; the solid was collected, washed (75%), and purified from acetic acid. It had m. p. 197°.

(*c*) A mixture of the zinc salt of the *iso*-sulphide (1 g.) and hydrogen iodide (10 c.c.) was treated as described in (*b*). Decomposition rapidly took place with liberation of hydrogen sulphide. The product, isolated and treated as described, was purified (36%) from acetic acid and had m. p. 197°.

(*d*) Similar treatment of the dehydro-sulphide (VIII) with hydrogen iodide gave hydrogen sulphide and a product which after purification (45%) had m. p. 197°.

The products from these four sources (*a*, *b*, *c*, and *d*) were identical with one another and with the product formed by reduction of dehydro-2-naphthol-1-sulphone (Hinsberg, *J. pr. Chem.*, 1915, **91**, 307) under suitable conditions (Found : C, 84·0 ; H, 4·8. Calc. for $C_{20}H_{14}O_2$: C, 83·9 ; H, 4·9%). The structure suggested by Hinsberg (*Ber.*, 1915, **48**, 2092) for this substance has been supported by Pummerer (*Ber.*, 1919, **52**, 1414) and is now entirely confirmed by the synthesis of its methyl ether. It yielded a bromo-derivative, m. p. 133—134°, apparently identical with that (XI) isolated by Pummerer and Cherbuliez (*loc. cit.*) from dehydro-1-bromo-2-naphthol ; but no close comparison was made.

2-*Methoxy*-1 : 2′-*dinaphthyl Ether* (VII ; OH = OMe).—(*a*) Potassium 2-naphthoxide was prepared by heating (1 hour, 110—120°) the requisite quantities of 2-naphthol and potassium hydroxide in a current of nitrogen. A mixture of this material (2 mols.) and 1-bromo-2-methoxynaphthalene (1 mol.) containing a little copper acetate was heated (6 hours, 230—240°) in an atmosphere of nitrogen. During the process 2-naphthyl methyl ether sublimed ; a further quantity of this substance was removed from the product by a current of steam in an alkaline medium. The dark-coloured insoluble material was set aside until it had solidified ; then, when dry, it was heated in a vacuum (1—2 mm.). The desired *ether* sublimed, and crystallised from acetone–alcohol in plates, m. p. 161°.

(*b*) The hydroxy-derivative (VII) obtained by the processes of reduction described above was methylated in aqueous alkaline solution with methyl sulphate. The product after purification had m. p. 161° and was identical with that obtained as described in (*a*) (Found : C, 83·7 ; H, 5·4. $C_{21}H_{16}O_2$ requires C, 84·0 ; H, 5·3%).

In conclusion we wish to thank Dr. A. Cohen for the synthesis of 2-methoxy-1 : 2′-dinaphthyl ether and for his help in some of these experiments.

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