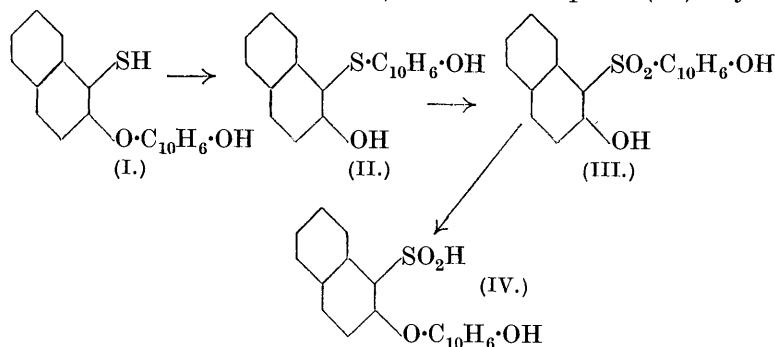


CCC.—*The Rearrangement of 2-Naphthol-1-sulphone.*

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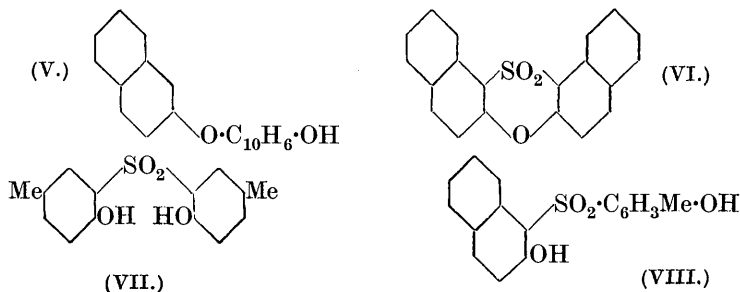
It has been shown (this vol., p. 914) that the conversion of *iso*- β -naphthol sulphide (I) to 2-naphthol 1-sulphide (II) may be regarded as the displacement of oxygen from the positive α -carbon atom by the more negative thiol ion. The accelerating influence of alkali and of picryl chloride on the change and the inactivity of the *iso*-sulphone (IV) or of the *O*-methyl ether of the *iso*-sulphide have been shown to be in accordance with this view. In 2-naphthol-1-sulphone (III) the relative polarities of the hydroxyl oxygen and sulphur are reversed in comparison with these in 2-naphthol 1-sulphide (II), the sulphur by conversion to the sulphone having assumed a positive character. Hence, according to the interpretation given to the conversion of (I) to (II), it is evident that with the sulphone (III) the reverse type of this change should be realisable. Thus the sulphone (III) should be convertible to the sulphinic acid (J., 1930, 1329) or *iso*-sulphone (IV), the positive sulphur of the sulphone being then displaced by the negative ion of the naphthol. It is now shown that this rearrangement may be effected. The conversion (see also Hinsberg, *J. pr. Chem.*, 1916, **93**, 280) is almost complete at 150° in presence of alkali hydroxide, but owing to the ease with which the α -sulphinic acid (*iso*-sulphone) loses sulphur dioxide (compare Hinsberg, *loc. cit.*, p. 284), the dinaphthyl oxide (V) and alkali

sulphite are liberated at this relatively high temperature. Since it has been shown (J., 1930, 1330) that the *iso*-sulphone (IV) may be



converted to the *iso*-sulphide (I) by reduction, it is evident that only the instability of the former prevents the realisation of the complete cycle (I) \rightarrow (IV) \rightarrow (I). Similarly, 6-bromo-2-naphthol-1-sulphone yields sulphite and the *dibromo*-derivative of the hydroxydinaphthyl oxide (V). In fact, from this and other examples drawn from a different type of sulphone now being studied, it appears that the rearrangement may be generally effected if suitable intramolecular conditions are provided.

As might be expected, the dimethyl ether of the sulphone (III) is merely hydrolysed under the conditions stated, 2-methoxy-naphthalene being formed. Moreover, in accordance with the behaviour of the monomethyl ether of the *iso*-sulphide (this vol., p. 920), the *monomethyl ether* of the sulphone does not undergo the rearrangement in presence of alkali; instead, it loses the elements of methyl alcohol, giving high yields of $\alpha\beta\alpha'\beta'$ -dinaphthathioxin dioxide (VI). It is noteworthy that, from the experiments described, the presence of alkali would appear to be necessary to this exceptional behaviour, and that the monomethyl ether of the corresponding sulphide remains unaltered under the conditions effective with the sulphone.



Evidence that the character of the α -carbon atom (this vol., p. 916) has an important influence on the progress of this type of rearrangement is shown by the fact that *p*-cresolsulphone (VII) remains unaltered at 250° under the conditions used in the conversion of 2-naphthol-1-sulphone. Attempts to effect the rearrangement of the former sulphone by increasing the positive character of the α -carbon atom were made in a study of the dinitro-derivative, but this material was profoundly decomposed under the usual conditions. In further experiments evidence was obtained that 2' : 4-dihydroxy-*m*-tolyl-1'-naphthylsulphone (VIII) is converted into a phenol and sulphite at 250° in presence of alkali, but the former product could not be isolated in a pure condition.

EXPERIMENTAL.

2-Naphthol-1-sulphone, prepared by the oxidation of 2-naphthol 1-sulphide, was unaltered by excess of aqueous *N*-alkali hydroxide at 100° (2 hrs.), but when heated with water at 200° for 2 hrs., 1 g. yielded 0.46 g. of 2-naphthol. At this higher temperature (2 hrs.) the sulphone (1 g.) in presence of alkali (*N*-sodium hydroxide, 1 mol.) yielded a mixture of 2-naphthol (0.1 g.) and 2-hydroxy-1 : 2'-dinaphthyl oxide (0.28 g.). Lower temperatures (*e.g.*, 150°) and the presence of 2 mols. of alkali hydroxide are more favourable to the rearrangement. The following data are quoted to show the influence of increasing amounts of alkali; they were obtained by heating the sulphone (2 g.) at 150° for 3 or 12 hrs. in presence of sodium hydroxide. The columns headed "oxide" and "sulphone" respectively show the amounts of these materials isolated from the products; in all cases only small amounts of 2-naphthol were present.

<i>N</i> -NaOH, mols.	Three hours.		Twelve hours.	
	Oxide.	Sulphone.	Oxide.	Sulphone.
2	1.2	none	1.1	none
4	0.65	0.8	1.3	none
8	0.3	1.5	0.8	0.8

The oxide (Found : C, 83.6; H, 5.1. Calc. : C, 83.9; H, 4.9%) was in each case identified by close comparison with an authentic specimen of 2-hydroxy-1 : 2'-dinaphthyl oxide. It is evident that alkali in excess of 2 molecular proportions retards the change. For comparison, it may be added that the dimethyl ether of 2-naphthol-1-sulphone was recovered unchanged after 5 hours at 150° with aqueous *N*-sodium hydroxide (4 mols.), whilst only a small amount of 2-methoxynaphthalene was isolated.

The *monomethyl ether* of 2-naphthol-1-sulphone was obtained in good yield from the corresponding sulphide (2 g.; this vol., p. 918) by treatment in acetic acid (15 c.c.) with "hyperol" (4 g.) at 100°

(1 hr.). The product separated from the cooled liquid. Oxidation was repeated if the presence of sulphoxide in the material could be detected by the production of a green colour with sulphuric acid. From acetic acid, the sulphone formed plates, m. p. 201° (decomp.), sparingly soluble in warm aqueous sodium hydroxide (Found: C, 69.2; H, 4.7. $C_{21}H_{16}O_4S$ requires C, 69.2; H, 4.4%). The *acetyl* derivative had m. p. 211° (decomp.) (Found: C, 68.2; H, 4.4. $C_{23}H_{18}O_5S$ requires C, 68.0; H, 4.4%). The following data are quoted to show the conditions under which $\alpha\beta\alpha'\beta'$ -dinaphthathioxin dioxide (VI) is formed from this substance (2 g.) by reaction with aqueous alkali. The product in question had m. p. 296° and was identical with a sample prepared by the oxidation of the dinaphthathioxin (Nolan and Smiles, J., 1913, **103**, 908). It is note-

Time.	NaOH.	Temp.	Thioxin dioxide.
10 hrs.	Excess of <i>N</i> .	100°	1.7 g.
2 hrs.	1 Mol. of 0.1 <i>N</i> .	200	1.4 g.

worthy that this cyclic sulphone is not formed from the monomethyl ether by boiling acetic anhydride (4 hrs.), by boiling (16 hrs.) alcoholic 10% sulphuric acid or by water at 200° (2 hrs.).

6-Bromo-2-naphthol-1-sulphone.—A suspension of the finely divided sulphide (20 g.) in acetic acid (300 c.c.) containing hydrogen peroxide (25 c.c., 30%) was kept at 100° until the separation of the crystalline *sulphone* was complete (15 g.). This formed prisms, m. p. 227° (decomp.), from acetic acid (Found: C, 47.1; H, 2.5. $C_{20}H_{12}O_4Br_2S$ requires C, 47.2; H, 2.3%). When a mixture of this substance (5 g.) with aqueous *N*-sodium hydroxide (20 c.c., 2 mols.) was kept at 200° (4 hrs.) the conversion to 6 : 6'-*dibromo-2-hydroxy-1 : 2'-dinaphthyl oxide*, $C_{10}H_5Br \cdot O \cdot C_{10}H_5Br \cdot OH$ (compare V) was almost complete (98%). This material had then separated as a fused mass from the aqueous liquid which contained sodium sulphite. After purification from methyl alcohol, the oxide formed needles, m. p. 166° (Found: C, 54.2; H, 3.0; Br, 35.8. $C_{20}H_{12}O_2Br_2$ requires C, 54.1; H, 2.7; Br, 36.0%).

2' : 4-Dihydroxy-m-tolyl-1'-naphthylsulphone (VIII).—A slow current of chlorine was led through a stirred suspension of 2-acetoxynaphthalene 1-disulphide (5 g.) in chloroform (50 c.c.) until the solid had dissolved. After removal of excess of halogen the solution of the chlorothiol was shaken with *p*-cresol (4 g.) until reaction was complete (3 hrs.). The liquid yellow sulphide, remaining after the solvent and excess of cresol had been removed by steam, was treated (100° , 1 hr.) with hydrogen peroxide (10 c.c., 30%) in acetic acid (50 c.c.). After repetition of this treatment, the required *sulphone* (2.5 g.) separated; it formed plates, m. p. 203° , from acetic acid

(Found : C, 64.7; H, 4.4. $C_{17}H_{14}O_4S$ requires C, 64.9; H, 4.4%). The *dibenzoyl* derivative, formed in an aqueous alkaline medium, had m. p. 249—250° (Found : C, 70.9; H, 4.5. $C_{31}H_{22}O_6S$ requires C, 71.2; H, 4.2%). The hydroxy-sulphone remained unchanged after treatment with *N*-sodium hydroxide (2 mols.) at 150° (4 hrs.), but at 250° under similar conditions a liquid phenol and alkali sulphite were formed. Numerous derivatives of this phenolic material were examined but none was obtained in a crystalline state.

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