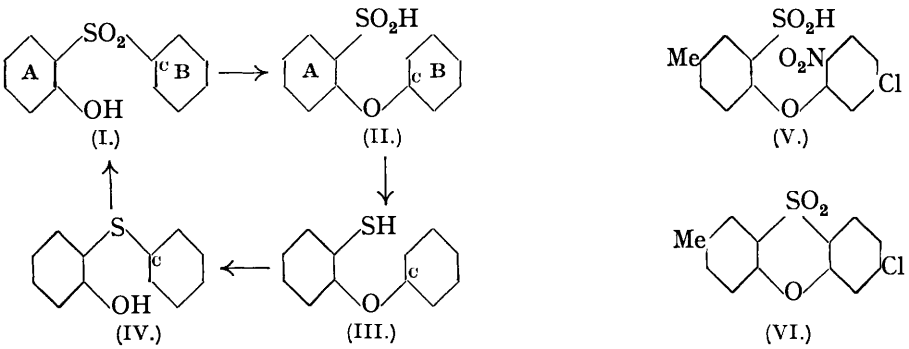
97. *The Rearrangement of Hydroxy-sulphones. Part IV.*

By Bernard A. Kent and Samuel Smiles.

It has been shown (J., 1931, 2207, 3264; 1932, 1040, 1488) that this rearrangement (I ⟶ II) may be regarded as a displacement of sulphonyl from a positive carbon atom of B by oxygen of the *o*-hydroxyl in A. There is no doubt that the close proximity of the oxygen atom and the positive carbon atom is necessary to this intramolecular displacement, but in addition to this fundamental requirement it is evident that the chief conditions controlling the process must be the following: (1) The positive character of c: increase in this should favour the change, not only by lessening the stability of linkage with the positive sulphur of sulphonyl, but also by increasing the demand for the electron supply offered by the oxygen. (2) The character of the medium in which the rearrangement is effected as expressed by the tendency to remove the proton from hydroxyl. (3) The character of the *o*-hydroxyl group as shown by the instability of the electron system of the oxygen or its capacity to act as a donor to meet the demand of the positive carbon atom c. Previous experiments have dealt with the first of these conditions in a qualitative manner and it has been shown that in accord with theory the intensity of the conditions required increases in the following order of substitution in B: *o*-nitro, *p*-nitro, *p*-methanesulphonyl. Further study of the influence of substitution in B and of conditions (2) and (3) needs a more accurate method than that based on comparison of the conditions required to effect rearrangement; a suitable method has now been devised and is based on the facts that sulphones of type (I) containing an *o*- or *p*-nitro-group in B give intensely red solutions in alkaline media, whereas the products of rearrangement, sulphinic acids of type (II), give pale yellow solutions in these media. A colorimetric method is therefore available for comparing the times taken for the completion of the change of various sulphones (I) under standard conditions of temperature and molecular dilution in the same or in different media, the completion of the change being indicated by comparison with solutions of the corresponding sulphinic acids (II) at the same temperature and molecular dilution and in the same solvent. The method cannot be regarded as a very accurate



one and in some cases it fails altogether owing to the formation of subsidiary products during the change. These arise in cases with a strongly positive carbon atom (c) in B,

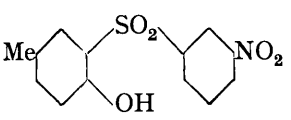
such as the 2 : 4-dinitro-derivative; hydrolysis by the alkaline medium, leading to rupture of the sulphone, may then take place simultaneously with the rearrangement. In other cases the sulphinic acid (II) may generate the thioxin by loss of nitrous acid in the alkaline medium and if this occurs before rearrangement of the sulphone is complete the method evidently becomes inaccurate. Thioxin formation, however, appears to be unusual; the conditions required for it have not been investigated, but generally, as, *e.g.*, in the conversion of (V) into (VI), the process is very slow and only occurs after prolonged heating of the solution. In spite of these limitations the method has proved useful; the following table shows the times in minutes taken to complete the rearrangement of various sulphones in *N*/15-solution at 50° in the stated media. The amounts of the alkaline reagents present in these solutions are expressed relatively to the sulphone present; under A and B are given the substituents present in the aromatic nuclei of the parent 2-hydroxy-sulphone (I).

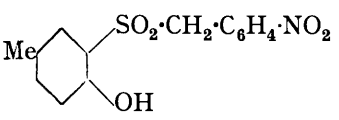
No.	A.	B.	1·25 Mols. NaOH aq.	2·25 Mols. NaOH aq.	1·25 Mols. NaOMe in MeOH.	1·25 Mols. NaOEt in EtOH.	1·25 Mols. NaOPr$^{\beta}$ in Pr$^{\beta}$OH.
1	5-Methyl	2-Nitro	315	240	270	240	180
2	3 : 5-Dimethyl	2-Nitro	93	65	75	61	48
3	5 : 6-Benzo	2-Nitro	5	3¼	3	2½	1
4	5-Hydroxy	2-Nitro	125	28			
5	5-Methoxy	2-Nitro	360				
6	4-Hydroxy	2-Nitro	420	225			
7	5-Methyl	4-Chloro-2-nitro	125				
8	5-Methyl	2 : 4-Dinitro	Rapid rearrangement with hydrolysis				
9	5-Chloro	2-Nitro	Thioxin formed rapidly				
10	5-Hydroxy	2-Carboxy	No rearrangement				
11	5-Methyl	3-Nitro	No rearrangement				

The data referring to the influence of substitution in B confirm those from previous experiments already mentioned. For example, Nos. 1, 7, and 8 form a series with increasing positive character of C; the rearrangement of 8 proceeds very rapidly, but quantitative relationship to 1 and 7 cannot be stated owing to simultaneous hydrolysis. It is important to notice that rearrangement of the corresponding *m*-nitro-sulphone (VII) and of the 2-nitrobenzyl sulphone (VIII), where sulphonyl is attached to feebly positive carbon, could not be realised even under more intense conditions than those effective with the *o*-nitro-compound (1) and the *p*-nitro-compound (J., 1932, 1489). Attention is also directed to the inertness of 10, containing the 2-carboxyl group in B, compared with the activity of 4, in which the carboxyl of 10 is replaced by the 2-nitro-group. Turning to the data illustrating the influence of the medium, it is seen (1, 2, 3, and 6) that within certain limits increase in concentration of aqueous sodium hydroxide facilitates the change and that the influence of the sodium alkoxides is greater than that of aqueous sodium hydroxide (1, 2, 3) and increases in the order: MeONa, EtONa, Pr$^{\beta}$ONa. The order given is that already established for these reagents (Kon and Linstead, J., 1929, 1269) when arranged according to increasing capacity of removing a proton. The effect of varying the substituents in A is also shown in the table and may be interpreted by their influence on the 2-hydroxyl group as an electron source. From this point of view the data relating to 4, 5, and 6 are interesting. When, as in 4, a negative ion is present in the para-position to the 2-oxygen atom, it is to be expected that the latter, owing to the electromeric effect of the ion, should acquire enhanced activity compared with 5 or 1, where the ion is replaced by methoxyl or methyl respectively. No. 6 has the negative ion in the meta-position with respect to the oxygen in question and rearrangement accordingly proceeds less rapidly than in the case of 4. This interpretation is supported by the effect of adding a second molecular proportion of alkali. The usual acceleration produced by this addition is seen in cases 1, 2, and 3 and has already been referred to. In the case of 4 the 2-oxygen atom acquires additional increase in activity owing to further ionisation of the 5-hydroxyl; in fact the second molecular proportion of alkali reduces the time of rearrangement to about one-fourth of that required when one molecule is present. Moreover this enhanced effect of alkali is not shown by the isomeride (6) or by the methoxy-derivative (5). Cases 1, 2, and 3 are also worth attention. Comparison of 1 and 2 shows that in accordance with

theory substitution of an electron repelling methyl at the ortho-position with respect to the 2-hydroxyl increases the activity of the latter, whilst the rapid conversion of 3 accords with the known character of hydroxyl in 2-naphthol.

Evidently, then, these considerations justify the view taken of the part played by the 2-hydroxyl group; moreover it is clear that, if the interpretation given of these results be correct, a sulphone such as (IX), containing aliphatic hydroxyl and c in the favourable 1 : 5 positions with respect to each other, should be more active than the corresponding derivatives of phenols or naphthols. Under usual conditions the conversion of this sulphone (IX) into the sulphinic acid (X) took place so rapidly that measurement of the time required was not possible by the method used. The sulphinic acid was characterised by conversion into the disulphide (XI) by usual methods. To find more satisfactory comparison of the activity of aliphatic and aromatic hydroxyl, attention was turned to the


(VII.)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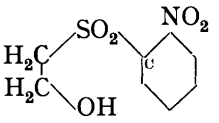
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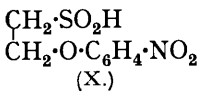
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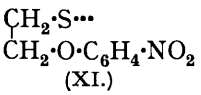
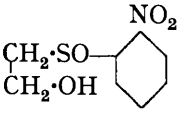
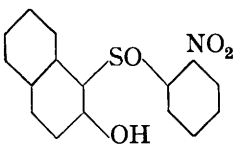

(XI.)


(XII.)

sulphoxides, since previous experience (J., 1933, 1492) had shown that the mononitrosulphoxides corresponding to 1 and 3 of the table (*e.g.*, XIII) do not undergo rearrangement in presence of 2*N*-aqueous alkali, their stability compared with that of the sulphones being ascribed to the more weakly positive character of sulphur in thionyl compared with that in sulphonyl. The sulphoxide (XII), however, with dilute alkali rapidly gave a mixture of the disulphide (XI) and sulphinic acid (X), these being the normal decomposition products of a sulphenic acid (XIV) which is formed from the rearrangement. It is evident, then, that in accord with theory aliphatic hydroxyl is more active in these displacements than aromatic hydroxyl.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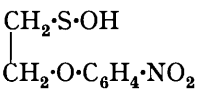
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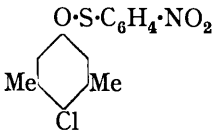
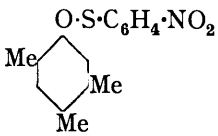

(XV.)


(XVI.)

The sulphide corresponding to (IX) and (XII) was stable in presence of alkali; this is to be expected, since the easy conversion of 2-thiol oxides (III) into 2-hydroxy-sulphides (IV) has already been observed in the aromatic series (J., 1931, 914, 3264; 1932, 1042). Four further examples of this rearrangement (III ⟶ IV) are recorded in the experimental part. The sulphinic acids (II) were converted into disulphides, from which the thiol oxides (III) were generated by reduction; since the use of alkaline media was necessary for this purpose, the thiol oxides were not isolated, but instead the hydroxy-sulphides (IV) were obtained after rearrangement had taken place. This was done with the sulphinic acids obtained by rearrangement of the sulphones 1, 4, 5, and 7 of the table.

The sulphides and sulphones required for these experiments were obtained by known methods; modifications of these which were necessary are described in the experimental part. In attempts to effect nuclear substitution in 2-chloro-*m*-5-xylenol and in ψ-cumenol by reaction with 2-nitrophenyl chlorothiol the sulphenates (XV) and (XVI) were instead obtained. The stability of these substances was remarkably greater than that of less highly substituted derivatives (compare Zincke, *Annalen*, 1912, **391**, 71).

Experimental.

Sulphides and Sulphones.—*4-Chloro-2-nitrophenyl 4-hydroxy*-m-*tolyl sulphide* was obtained by heating 4-chloro-2-nitrophenyl chlorothiol with excess of *p*-cresol (100°, 3 hours). Unattacked *p*-cresol was removed in steam, and the residue triturated with aqueous sodium hydroxide. The required product, liberated from the alkaline solution, crystallised from acetic acid in yellow needles, m. p. 134° (Found : C, 53·0; H, 3·7; N, 4·5; Cl, 12·0; S, 10·7. $C_{13}H_{10}O_3NClS$ requires C, 52·8; H, 3·4; N, 4·7; Cl, 12·0; S, 10·8%). The *acetyl* derivative formed needles, m. p. 86°, from alcohol (Found : C, 53·2; H, 3·8. $C_{15}H_{12}O_4NClS$ requires C, 53·3; H, 3·6%).

4-Chloro-2-nitrophenyl-4'-hydroxy-m-*tolylsulphone* (No. 7). The sulphide (5 g.) was oxidised in acetic acid (50 c.c.) by hydrogen peroxide (30%, 6 c.c.), which was added gradually (90°). When a sample of the product no longer gave a green colour in sulphuric acid, brine was added to the reacting mixture. The precipitated *sulphone* formed plates, m. p. 157°, from acetic acid (Found : C, 47·8; H, 3·2; N, 4·4; Cl, 10·6; S, 9·5. $C_{13}H_{10}O_5NClS$ requires C, 47·6; H, 3·0; N, 4·3; Cl, 10·8; S, 9·8%).

2-Nitro-2' : 5'-dihydroxydiphenylsulphone (No. 4). *p*-Benzoquinone (2·7 g.) was gradually added to a stirred solution (15°) of 2-nitrobenzenesulphinic acid (4·8 g.) in water (100 c.c.). The required *sulphone* slowly separated (6·8 g.); it formed needles, m. p. 214°, from acetic acid (Found : C, 48·8; H, 3·3; N, 4·8; S, 10·8. $C_{12}H_9O_6NS$ requires C, 48·8; H, 3·0; N, 4·7; S, 10·8%).

2-Nitro-2' : 4'-dihydroxydiphenylsulphone (No. 6). The corresponding sulphide (Zincke, *Annalen*, 1912, **391**, 87) was best obtained from the reaction of 2-nitrophenyl chlorothiol with resorcinol in chloroform. It had m. p. 157° and gave an acetyl derivative, m. p. 94° (Zincke records 150—151° and 102—103° respectively). Oxidation of the acetyl derivative of the sulphide (5 g.) was effected in acetic acid (37 c.c.) with hydrogen peroxide (6·2 c.c., 30%) and was complete in about 1 hour (90°). The *acetyl* derivative of the sulphone, obtained by diluting the mixture, and purified from acetic acid, had m. p. 125° (Found : C, 50·8; H, 3·7. $C_{16}H_{13}O_8NS$ requires C, 50·7; H, 3·4%). The required *sulphone* was readily liberated from this by hydrolysis with dilute sulphuric acid in hot alcohol. If formed pale yellow needles, m. p. 132°, from aqueous alcohol (Found : C, 48·7; H, 3·0. $C_{12}H_9O_6N$ requires C, 48·8; H, 3·0%).

2 : 4-Dinitrophenyl 4-hydroxy-m-*tolyl sulphide.* 4-Hydroxy-*m*-tolylthiol (1 mol.), prepared by hydrolysis of the carbonate (Zincke and Arnold, *Ber.*, 1917, **50**, 116) under alkaline conditions, was treated with 2 : 4-dinitrochlorobenzene (1 mol.) and sodium ethoxide (1 mol.) in boiling alcohol. After removal of the solvent the residue was dissolved in excess of warm aqueous sodium hydroxide; when the solution was cooled, the sodium salt of the required sulphide separated. The *sulphide* formed yellow needles, m. p. 123°, from acetic acid (Found : C, 49·9; H, 3·6; N, 9·0. $C_{13}H_{10}O_5N_2S$ requires C, 50·1; H, 3·3; N, 9·1%).

2 : 4-Dinitrophenyl-4'-hydroxy-m-*tolylsulphone* (No. 8) formed by oxidation of the preceding sulphide with hydrogen peroxide in acetic acid, was isolated by the addition of brine and formed pale yellow plates, m. p. 139—140° (Found : C, 46·1; H, 3·0; N, 8·4. $C_{13}H_{10}O_7N_2S$ requires C, 46·1; H, 3·0; N, 8·3%).

3-Nitrophenyl 4-hydroxy-m-*tolyl sulphide* (compare VII). 3-Nitrophenyl disulphide (10 g.), obtained (78% yield) from 3-nitrobenzenesulphonyl chloride by reduction with hydrogen iodide (Ekbom, *Ber.*, 1893, **26**, 338), was converted into the chlorothiol by the usual method. The latter, when warmed in chloroform (20 c.c.) containing *p*-cresol (7 g.), quickly gave the required *sulphide* (14 g.), which was isolated as usual and formed pale yellow needles, m. p. 112° (Found : C, 59·7; H, 4·2; N, 5·6; S, 12·1. $C_{13}H_{11}O_3NS$ requires C, 59·8; H, 4·2; N, 5·4; S, 12·2%). The acetyl derivative formed yellow needles, m. p. 96°, from alcohol.

3-Nitrophenyl-4'-hydroxy-m-*tolylsulphone* (VII), obtained by the usual treatment of the sulphide with hydrogen peroxide in acetic acid, formed pale yellow plates, m. p. 133°, and, in contrast with the 2-nitro- and the 4-nitro-derivative, gave a pale yellow solution in aqueous sodium hydroxide (Found : C, 53·1; H, 3·9; N, 4·9; S, 10·9. $C_{13}H_{11}O_5NS$ requires C, 53·2; H, 3·8; N, 4·8; S, 10·9%). This sulphone was treated with aqueous sodium hydroxide at various dilutions and temperatures, but no evidence of rearrangement was found.

2-Nitro-2'-hydroxy-3' : 5'-dimethyldiphenyl sulphide was obtained by heating (100°) *m*-4-xylenol with 2-nitrophenyl chlorothiol until hydrogen chloride was no longer liberated (3 hours). Isolated in the usual manner, it formed yellow needles, m. p. 123°, from acetic acid (Found : C, 61·0; H, 4·8; N, 5·1. $C_{14}H_{13}O_3NS$ requires C, 61·1; H, 4·7; N, 5·1%). The *acetyl* derivative had m. p. 158° (Found : C, 60·8; H, 4·9. $C_{16}H_{15}O_4NS$ requires C, 60·6; H, 4·7%).

The hydroxy-sulphide was converted by the usual treatment with hydrogen peroxide into

2-*nitro*-2′-*hydroxy*-3′ : 5′-*dimethyldiphenylsulphone* (No. 2), which formed yellow plates, m. p. 178° (Found: C, 54·4; H, 4·0; N, 4·6. $C_{14}H_{13}O_5NS$ requires C, 54·5; H, 4·2; N, 4·5%).

2-*Nitro*-2′-*hydroxy*-5′-*methoxydiphenyl sulphide* was prepared by heating 2-nitrophenyl chlorothiol with 4-methoxyphenol (100°) and was isolated by extracting the cold mass with warm aqueous sodium hydroxide (2*N*). It formed yellow needles, m. p. 135°, from acetic acid (Found: C, 56·2; H, 4·0; N, 5·1; S, 11·7. $C_{13}H_{11}O_4NS$ requires C, 56·3; H, 4·0; N, 5·0; S, 11·5%). Conversion of this sulphide into 2-*nitro*-2′-*hydroxy*-5′-*methoxydiphenylsulphone* (No. 5) was effected by the usual process. This formed plates, m. p. 152°, from alcohol (Found: C, 50·8; H, 3·8; N, 4·4: S, 10·3. $C_{13}H_{11}O_6NS$ requires C, 50·5; H, 3·6; N, 4·5; S, 10·3%).

5′-*Chloro*-2-*nitro*-2′-*hydroxydiphenyl sulphide*, which could not be obtained from 4-chlorophenol by the usual method, was prepared by heating 2-nitrobenzenesulphinic acid (5 g.) with 4-chlorophenol (5 g.) during 2½ hours (100°) under diminished pressure. The resulting mass was extracted with boiling dilute aqueous sodium hydroxide (charcoal); from the solution, dilute sulphuric acid (5°) liberated the required sulphide in an impure state. After purification from acetic acid it had m. p. 159° (Found: C, 51·0; H, 3·0; N, 5·3. $C_{12}H_8O_3NClS$ requires C, 51·1; H, 2·8; N, 5·0%).

Oxidation of this sulphide to 5′-*chloro*-2-*nitro*-2′-*hydroxydiphenylsulphone* (No. 9) was effected as usual. The product formed plates, m. p. 175°, from acetic acid (Found: C, 45·7; H, 2·8; N, 4·6; S, 10·3. $C_{12}H_8O_5NClS$ requires C, 45·9; H, 2·6; N, 4·4; S, 10·2%).

2-*Nitrobenzyl*-4′-*hydroxy*-m-*tolylsulphone* (VIII). Alcohol (50 c.c.) which contained the sodium salt of 4-hydroxy-*m*-tolylthiol (7·8 g.) and 2-nitrobenzyl chloride (9·5 g.) was boiled (15 mins.). The impure sulphide which remained after removal of the solvent and 2-nitrobenzyl chloride was oxidised with excess (4 mols.) of hydrogen peroxide in acetic acid. The *sulphone*, isolated as usual, formed needles, m. p. 139°, from alcohol (Found: C, 54·8; H, 4·2; N, 4·8. $C_{14}H_{13}O_5NS$ requires C, 54·7; H, 4·2; N, 4·6%). The substance was recovered from solutions in 2*N*-sodium hydroxide which had been heated for periods between 2 and 6 hours and at temperatures ranging from 100° to 180°.

2-*Nitrophenyl* β-*hydroxyethyl sulphoxide* (XII). The corresponding sulphide (Bennett and Berry, J., 1927, 1668) was converted into the acetate, which without complete purification was treated (11 g.) with hydrogen peroxide (10 c.c., 30%) in acetic acid (50 c.c.) at 90—100° (1 hour). The *acetyl* derivative of the required sulphoxide, isolated by addition of brine to the mixture, formed yellow needles, m. p. 113°, from aqueous acetic acid (Found: C, 46·4; H, 4·2. $C_{10}H_{11}O_5NS$ requires C, 46·6; H, 4·3%). This substance was hydrolysed by boiling 2*N*-sulphuric acid; the required *hydroxy-sulphoxide* separated from the cooled solution in pale yellow needles, m. p. 157° (Found: C, 44·7; H, 4·1; N, 6·6; S, 14·8. $C_8H_9O_4NS$ requires C, 44·6; H, 4·1; N, 6·5; S, 14·9%).

2-*Nitrophenyl*-β-*hydroxyethylsulphone* (IX) was obtained by oxidising the acetyl derivative of the sulphoxide (XII) (5 g.) in acetic acid (25 c.c.) with hydrogen peroxide (4·5 c.c., 30%) at 100° (1 hour). When the mixture was diluted, the acetate of the sulphone separated as an oil; this was hydrolysed by hot dilute sulphuric acid, yielding the hydroxy-sulphone, which separated from the cooled mixture in needles, m. p. 88° (Found: C, 41·8; H, 4·3; S, 13·8. $C_8H_9O_5NS$ requires C, 41·5; H, 3·9; S, 13·8%).

The preparation of the sulphones No. 1 (Levi, Rains, and Smiles, J., 1931, 3266), No. 3 (*loc. cit.*, p. 3268), and No. 10 (Price and Smiles, J., 1928, 3154) has already been described, together with the products obtained from the rearrangement of Nos. 1 and 3.

Sulphinic Acids and Disulphides.—The sulphinic acids were generally prepared from the relevant hydroxy-sulphones by warming (50—90°) solutions of the latter in aqueous sodium hydroxide (10%) containing one and a half times the theoretical amount of the reagent. The treatment was continued until the red colour had faded to pale yellow; the sulphinic acid was then liberated and usually purified from aqueous acetone.

The disulphides were obtained from the sulphinic acids by warming their solutions in acetic acid containing hydrogen iodide, sulphur dioxide being added during the process. The disulphides usually separated and were purified from acetic acid.

The rearrangement of the thiols (II ⟶ IV) corresponding to these disulphides was generally done by reduction of the latter with glucose in presence of alkali as previously described (J., 1931, 3269) in the case of the disulphide generated from sulphone No. 3 by rearrangement and subsequent reduction in acid solution. A better method is described in the case of the disulphide related to sulphone No. 1.

4-*Chloro*-2-*nitrophenyl* 3-*sulphino*-p-*tolyl ether* (V), from sulphone No. 7, formed needles, m. p. 137° (Found: C, 48·0; H, 3·1. $C_{13}H_{10}O_5NClS$ requires C, 47·6; H, 3·0%). Elimination

of the sulphinic group from this substance was effected by oxidising the sodium salt with the theoretical amount of permanganate in aqueous solution. The impure sulphonate remaining after oxides of manganese and the solvent had been removed was hydrolysed with warm sulphuric acid (60%). During this process *4-chloro-2-nitrophenyl p-tolyl ether* separated as an oil; it was purified from light petroleum and formed plates, m. p. 103°, which were identical with a sample obtained by the method of Le Fèvre, Saunder, and Turner (J., 1927, 1168) from potassium *p*-tolyloxide and 2 : 5-dichloronitrobenzene (Found : C, 59·4; H, 3·9; N, 5·3. $C_{13}H_{10}O_3NCl$ requires C, 59·2; H, 3·8; N, 5·3%).

The sulphinic acid also yielded *di-*(4-p-*chloro*-o-*nitrophenoxy*-m-*tolyl*) *disulphide* (compare V), pale yellow needles, m. p. 133° (Found : C, 52·8; H, 3·3; N, 4·7; S, 10·7; *M*, 589. $C_{26}H_{18}O_6N_2Cl_2S_2$ requires C, 52·9; H, 3·0; N, 4·7; S, 10·8%; *M*, 589). Reduction of this disulphide with glucose and alkali hydroxide gave 4-chloro-2-nitrophenyl 4-hydroxy-*m*-tolyl sulphide, m. p. 134°, identical with the product of synthesis already described.

If during the preparation of the sodium sulphinate heating was continued for a longer period than that required to effect the rearrangement of the sulphone, the solution became turbid and after the lapse of some hours a solid had separated. This substance was *3-chloro-8-methoxyphenothioxin 10-dioxide* (VI), m. p. 173° (Found : C, 55·6; H, 3·2; Cl, 12·7. $C_{13}H_9O_3ClS$ requires C, 55·6; H, 3·2; Cl, 12·7%).

2-Nitro-4'-hydroxy-2'-sulphinodiphenyl ether, from sulphone No. 4, had m. p. 64° (Found : C, 48·7; H, 3·3. $C_{12}H_9O_6NS$ requires C, 48·8; H, 3·1%). It yielded *di-*(5-*hydroxy*-2-p-*nitrophenoxyphenyl*) *disulphide*, m. p. 207° (Found : C, 54·7; H, 3·2; N, 5·3; S, 12·1; *M*, 526. $C_{24}H_{16}O_8N_2S_2$ requires C, 54·9; H, 3·1; N, 5·3; S, 12·2%; *M*, 524), reduction of which with glucose yielded, after concurrent rearrangement, *2-nitro-2' : 5'-dihydroxydiphenyl sulphide*, m. p. 161° (Found : C, 54·9; H, 3·8. $C_{12}H_9O_4NS$ requires C, 54·7; H, 3·4%). The identity of this sulphide was established by oxidation of its acetyl derivative, followed by hydrolysis of the product. The material then obtained, m. p. 212°, was identical with the sulphone No. 4.

2-Nitro-5'-hydroxy-2'-sulphinodiphenyl ether, from sulphone No. 6, had m. p. 107° (decomp.) (Found : C, 48·5; H, 3·3. $C_{12}H_9O_6NS$ requires C, 48·8; H, 3·1%).

2 : 4-Dinitrophenyl 3-sulphino-p-tolyl ether, formed together with sodium dinitrophenoxide from sulphone No. 8 by the usual treatment, had m. p. 117—118° (Found : C, 46·4; H, 3·4. $C_{13}H_{10}O_7N_2S$ requires C, 46·1; H, 3·0%).

2-Nitro-2'-sulphino-4' : 6'-dimethyldiphenyl ether, from sulphone No. 2, had m. p. 129° (Found : C, 54·6; H, 4·5. $C_{14}H_{13}O_5NS$ requires C, 54·7; H, 4·2%), and was converted by the usual method into *di-*(2-o-*nitrophenoxy*-3 : 5-*dimethylphenyl*) *disulphide*, pale yellow needles, m. p. 208° (Found : C, 61·6; H, 4·2; N, 5·4; *M*, 534. $C_{28}H_{24}O_6N_2S_2$ requires C, 61·3; H, 4·3; N, 5·1%; *M*, 548).

2-Nitro-4'-methoxy-2'-sulphinodiphenyl ether, from sulphone No. 5, had m. p. 122—123° (Found : C, 50·3; H, 3·7. $C_{13}H_{11}O_6NS$ requires C, 50·5; H, 3·5%), and yielded after the usual treatment *di-*(2-o-*nitrophenoxy*-5-*methoxyphenyl*) *disulphide*, pale yellow needles, m. p. 114° (Found : C, 56·3; H, 3·9; N, 5·2; S, 11·8; *M*, 560. $C_{26}H_{20}O_8N_2S_2$ requires C, 56·5; H, 3·6; N, 5·0; S, 11·5%; *M*, 552), which on reduction with glucose in alkaline solution was converted into the sulphide from which the sulphone No. 5 had been prepared.

4'-Chloro-2-nitro-2'-sulphinodiphenyl ether, m. p. 117—118° (Found : C, 45·9; H, 2·9. $C_{12}H_8O_5NClS$ requires C, 45·9; H, 2·6%), was slowly formed from sulphone No. 9 together with the thioxin; owing to this circumstance comparison with the activity of other sulphones was not possible. The insoluble thioxin was removed with ether and the sulphinic acid was isolated as usual from the aqueous solution. *Di-*(5-*chloro*-2-o-*nitrophenoxyphenyl*) *disulphide*, readily formed from the sulphinic acid, had m. p. 159° (Found : C, 51·2; H, 2·8; N, 5·2; S, 11·5. $C_{24}H_{14}O_6N_2Cl_2S_2$ requires C, 51·3; H, 2·5; N, 5·0; S, 11·4%).

Reduction of di-(4-*o*-nitrophenoxy-*m*-tolyl) disulphide was effected by glucose as described (J., 1931, 3267), but in this and other cases the following method is to be preferred on account of the greater purity of the product. Alcohol (40 c.c.) containing sodium sulphide (0·2 g.), sodium hydroxide (0·1 g.), and the suspended disulphide (1 g.) was boiled until solution was complete. After dilution and addition of dilute sulphuric acid, 2-nitrophenyl 4-hydroxy-*m*-tolyl sulphide (compare sulphone No. 1) was liberated (90%) in an almost pure condition.

β-o-*Nitrophenoxyethanesulphinic acid* (X) was rapidly formed in a solution of the sulphone (IX) (1 mol.) in aqueous sodium hydroxide (0·5%; 1·25 mols.). The sulphinic acid was liberated in the usual manner and, purified from hot water, formed needles, m. p. 121° (Found : C, 41·7; H, 4·3; N, 6·2; S, 13·7. $C_8H_9O_5NS$ requires C, 41·5; H, 3·9; N, 6·1; S, 13·8%). Under more intense conditions 2-nitrophenol was observed as a subsidiary product. The sul-

phinic acid was also obtained from the rearrangement of the sulphoxide (XII) as subsequently described. When it was reduced with hydriodic and sulphurous acids in warm dilute (50%) acetic acid, *di*-(β-o-*nitrophenoxyethyl*) *disulphide* (XI) was formed, and separated in needles, m. p. 76° (Found: C, 48·4; H, 4·4; S, 16·1; *M*, 382. $C_{16}H_{16}O_6N_2S_2$ requires C, 48·4; H, 4·0; S, 16·1%; *M*, 396). This was also obtained by rearrangement of the sulphoxide (XII), which rapidly proceeded in presence of dilute sodium hydroxide solution. When the reagent (1·25 mols.; 1·5%) was added to the clear warm aqueous solution of the sulphoxide (1 mol.; 3%), the disulphide separated as an oil which quickly solidified. After this had been removed, the sulphinic acid was liberated from the solution in the usual manner and was found to be identical with that obtained by rearrangement of the sulphone.

ψ-Cumenyl 2-*nitrobenzenesulphenate* (XVI). 2-Nitrophenyl chlorothiol (5 g.) and ψ-cumenol (4 g.) were heated (100°) until hydrogen chloride was no longer liberated. Unattacked phenol was removed by steam, and the residue triturated with cold 2*N*-alkali hydroxide. The residue (5 g.) consisted essentially of the *sulphenate*, which separated from propyl alcohol in yellow needles, m. p. 162° (Found: C, 61·9; H, 5·1; N, 5·1. $C_{15}H_{15}O_3NS$ requires C, 62·2; H, 5·2; N, 4·8%). The substance was not attacked by boiling acetic acid and was slowly hydrolysed by boiling 2*N*-sodium hydroxide, yielding 2-nitrophenyl disulphide.

2-*Chloro*-m-5-*xylyl* 2-*nitrobenzenesulphenate* (XV) was prepared by a similar process. It formed yellow needles, m. p. 190°, from propyl alcohol and showed similar chemical behaviour (Found: C, 54·2; H, 4·1; N, 4·8. $C_{14}H_{12}O_3NClS$ requires C, 54·3; H, 3·9; N, 4·5%).

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