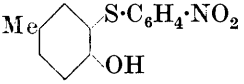
CCCCLII.—*The Rearrangement of Hydroxy-sulphones. Part I.*

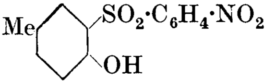
By Arthur A. Levy, Harry C. Rains, and Samuel Smiles.

It has been shown (this vol., p. 2207) that the sodium salt of 2-naphthol-1-sulphone undergoes rearrangement when heated in aqueous solution. The essential feature of the change is the transference of 2-oxy-1-naphthyl from sulphonyl to oxygen; but the sulphinic acid which is then formed, being unstable under the conditions, loses sulphurous anhydride with the result that 2-hydroxy-1 : 2′-dinaphthyl oxide is finally isolated. This rearrangement, which is evidently a reversal of that observed in the conversion (Warren and Smiles, this vol., p. 914) of "*iso*"-2-naphthol sulphide into 2-naphthol 1-sulphide, has been regarded as a displacement of sulphonyl from the positive α-carbon atom of 2-naphthol by the negative phenolic ion (*loc. cit.*). Further experiments have now been made to justify this view by examining the behaviour of other hydroxy-sulphones in which similar intramolecular conditions are provided and it has been found that this type of intramolecular change is of wide occurrence. Two examples drawn from a different class of hydroxy-sulphone are now described.

When the *sulphide* (I), which is formed in the reaction of *p*-cresol with 2-nitrophenylchlorothiol, is oxidised, the *sulphone* (II) is obtained. In this substance, sulphonyl is attached to the strongly positive carbon ortho to that bearing the nitro-group and it is much more easily displaced by the *o*-phenolic ion than in the case of 2-naphthol-1-sulphone. The rearrangement proceeds slowly but smoothly at 15° in presence of one molecular proportion of aqueous alkali hydroxide. This increased activity may be ascribed to the strongly positive character of the *o*-nitro-carbon atom compared with the α-carbon atom of 2-naphthol and perhaps also to the operation of a mechanism which is discussed later. The *sulphinic acid* (III) is then formed; its constitution has been shown by conversion into a *disulphide* (IV) with the usual reagents and also by oxidation, followed by hydrolysis of the sulphonic group, the ether (V) being



(I.)



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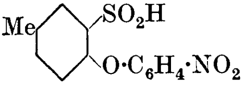
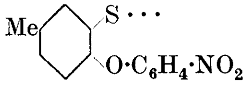
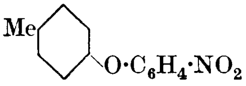


(III.)

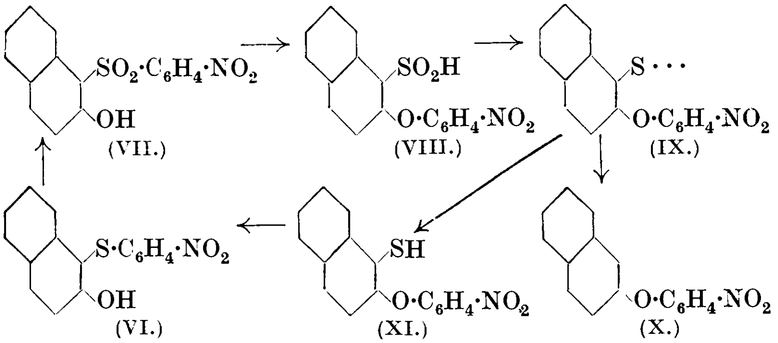
(IV.)





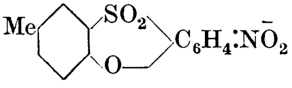
(V.)

isolated. This substance was identical with synthetic material obtained from 2-chloronitrobenzene and potassium *p*-tolyloxide by the method of Le Fèvre, Saunders, and Turner (J., 1927, 1168). Another more interesting case is provided by the *sulphone* (VII), which was obtained by oxidation of the sulphide (VI) generated from 2-naphthol and 2-nitrophenylchlorothiol. Rearrangement of this sulphone proceeds easily under the same conditions as those applied to (II) and the constitution of the *product* (VIII) was demonstrated in a similar manner. Thus the *disulphide* (IX) was obtained by the usual reactions, and the corresponding sulphonic acid, which was not isolated in the pure condition, yielded on hydrolysis the *ether* (X), identical with synthetic material furnished by the reaction of potassium 2-naphthoxide and 2-chloronitrobenzene.

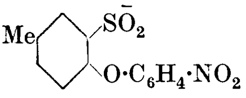


The two disulphides encountered (IV and IX) correspond to thiols (*e.g.*, XI) in which intramolecular conditions are similar to those occurring in "*iso*"-2-naphthol sulphide (this vol., p. 917). Accordingly it is to be expected that in presence of alkali the oxido-group attached to the positive *o*-nitro-carbon atom will be displaced by the more strongly negative thiol ion and that the related sulphide will be formed from the thiol (*e.g.*, VI from XI). Owing to the difficulty attending the selective reduction of the dithio-system in presence of the nitro-group in acid solution, neither of these thiols (*e.g.*, XI) has been isolated; but by using glucose in alkaline media (compare Claasz, *Ber.*, 1912, **45**, 2424) which provide conditions favourable to the expected rearrangement of the thiols formed by reduction, it is shown that the disulphide (IX) yields the sulphide (VI). Thus it is seen that the complete cycle (VI ⟶ VII ⟶ IX ⟶ XI ⟶ VI) has been realised and that the 2-nitrophenyl nucleus may be transferred from oxygen to sulphur or vice versa according to the relative states of these atoms.

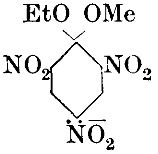
There is little doubt that the remarkable ease with which the rearrangement of these sulphones (II and VII) takes place is primarily due to the strongly positive character of the *o*-nitro-carbon atom, which facilitates attack by the negative phenolic ion, but it is evident that in these cases the change may be further promoted by a mechanism involving the nitro-group. Thus it is suggested that, when attack of the positive *o*-nitro-carbon atom takes place, the ion of the phenol (*e.g.*, II) yields the unstable nitronic ion (XII) and this by transference of the ionic charge to sulphonyl is converted into the ion of the sulphinic acid (XIII). Accordingly it is seen that after the initial attack of the positive carbon atom has taken place the further progress of the change consists essentially in the intramolecular migration of an ionic charge and thus explanation is forthcoming of the ease with which the process is accomplished. Independent facts afford some justification for the view expressed. The colourless sulphones yield with aqueous alkali deeply-coloured solutions of their salts; during the progress of the change this colour fades as conversion into the colourless sulphinate proceeds. The intermediate phase thus indicated by the coloured salts is adequately represented by the nitronic structure (XII) suggested. Moreover it may be noticed that substances of analogous type (XIV) are capable of existence and have been isolated by Meisenheimer (*Annalen*, 1902, **323**, 223) in an investigation of the additive products formed from potassium alkoxides and trinitroanisole or trinitrophenetole.



(XII.)



(XIII.)



(XIV.)

Further information concerning the conditions required for this rearrangement is being sought.

EXPERIMENTAL.

*2-Nitrophenyl 4-Hydroxy-*m*-tolyl Sulphide* (I).—A concentrated solution of *p*-cresol (21 g.) in chloroform was added to a solution of 2-nitrophenylchlorothiol (38 g.) in the same solvent. The mixture was warmed until reaction was complete and then, after the solvent had been removed, the residue was purified from acetic acid. The required *product* (32 g.) formed yellow prisms, m. p. 146—147° (Found: C, 59·8; H, 4·2. $C_{13}H_{11}O_3NS$ requires C, 59·7; H, 4·2%). The *acetyl* derivative, prepared with acetic anhydride in pyridine, had m. p. 106° (Found: C, 59·4; H, 4·6. $C_{15}H_{13}O_4NS$ requires C. 59·4; H, 4·2%).

2-*Nitrophenyl*-4-*hydroxy*-m-*tolylsulphone* (II).—An excess of "hyperol" (11 g.) was gradually added in small portions to a warm solution of the sulphide (10 g.) in acetic acid (100 c.c.), which was constantly agitated. The oxidation was completed at 80—90° (about 1 hr.). The *sulphone* was isolated by cautious addition of water and was purified (8 g.) from aqueous acetic acid; m. p. 140—141° (Found: C, 52·9; H, 4·0. $C_{13}H_{11}O_5NS$ requires C, 53·2; H, 3·7%).

2-*Nitrophenyl* 3-*Sulphino*-p-*tolyl Ether* (III).—Conversion of the sulphone (II) into this sulphinic acid proceeds slowly at 15—18° in presence of alkali hydroxide (1 mol.). The process was more rapid under the following conditions. A solution of sodium hydroxide (0·8 g.; 1·2 mols.) in water (50 c.c.) was added to a suspension of the sulphone (5 g.) in water (150 c.c.). The solution, at first red, was kept at 50—60° ($\frac{3}{4}$ hr.); the colour had then faded to very pale yellow. The *sulphinic acid* was liberated from the cooled solution in almost theoretical amount; after purification from aqueous acetone it formed needles, m. p. 132—133° (Found: C, 53·2; H, 3·9. $C_{13}H_{11}O_5NS$ requires C, 53·2; H, 3·8%). The substance was soluble in aqueous ammonium carbonate and gave a blue solution in sulphuric acid.

4-o-*Nitrophenoxy*-m-*tolyl Disulphide* (IV).—Aqueous hydrogen iodide (0·5 c.c., *d* 1·7) was added to a warm solution of the sulphinic acid (III) (4 g.) in acetic acid (30 c.c.). The separation of the *disulphide* soon began and was completed by addition of a little sulphurous acid at intervals. The product crystallised from acetic acid in very pale yellow needles, m. p. 117° (Found: C, 60·1; H, 4·2; S, 12·4; *M*, 522. $C_{26}H_{20}O_6N_2S_2$ requires C, 60·0; H, 3·8; S, 12·3%; *M*, 520).

2-*Nitrophenyl* p-*Tolyl Ether* (V).—(a) The sulphone (II) was converted (2 g.) into the sodium sulphinate (III) with alkali hydroxide in the usual manner. An aqueous solution of permanganate in slight excess (0·8 g.) of that required for conversion into sulphonate was gradually added to the warm solution of the sodium sulphinate. After removal of the oxides of manganese, the clear solution was evaporated and the solid residue containing the required sulphonate was warmed ($\frac{1}{2}$ hr.) with dilute sulphuric acid (60 c.c.; 60% H_2SO_4). The ether which separated slowly volatilised in steam and was isolated by this means (1·3 g.). After purification from light petroleum the product had m. p. 48° (Found: N, 6·0. Calc.: N, 6·1%). Cook and Hillyer (*Amer. Chem. J.*, 1900, **24**, 525) quote m. p. 49° for this substance. (b) Synthesis of this ether was effected from *p*-cresol (1·75 mols.), concentrated potassium hydroxide (1·33 mols.), and 2-chloronitrobenzene at 160°. The product from (a) was identified with this material (m. p. 48°) by close comparison.

2-*Nitrophenyl* 2-*Hydroxy*-1-*naphthyl Sulphide* (VI) (Zincke and Farr, *Annalen*, 1912, **391**, 86).—This compound was prepared by the reaction of 2-naphthol and 2-nitrophenylchlorothiol in warm chloroform. The acetyl derivative (Zincke and Farr, *loc. cit.*) prepared from it in presence of pyridine was used for the preparation of the following sulphone.

2-*Nitrophenyl*-2-*hydroxy*-1-*naphthylsulphone* (VII).—Hydrogen peroxide (20 c.c.; 30%) was added at intervals to a warm solution (*ca.* 90°) of the acetyl derivative of the sulphide (10 g.) in acetic acid (75 c.c.). Oxidation was completed by continued heating (4 hrs.); the *acetyl* derivative of the sulphone, which separated from the cooled mixture, crystallised from acetic acid (50% yield) in plates, m. p. 152—153° (Found: C, 58·2; H, 3·6; S, 8·5. $C_{18}H_{13}O_6NS$ requires C, 58·2; H, 3·5; S, 8·6%). This material was hydrolysed by a boiling (3 hrs.) solution (10%) of sulphuric acid in alcohol. The required *sulphone* separated (80%) from the cooled liquid and formed plates from acetic acid, m. p. 181° (Found: C, 58·2; H, 3·6; S, 9·8. $C_{16}H_{11}O_5NS$ requires C, 58·3; H, 3·3; S, 9·7%). The substance gave a colourless solution in sulphuric acid. The red sodium salt was precipitated when sodium ethoxide was added to a benzene solution of the sulphone, but the salt rapidly changed to the sulphinate before isolation was possible.

2-*Nitrophenyl* 1-*Sulphino*-2-*naphthyl Ether* (VIII).—The conversion of the sulphone (VII) into this sulphinic acid proceeded slowly (*ca.* 2·5 hrs.) at 15° in dilute aqueous alkaline (1·2 mols. NaOH) solution; at 60—70° the change was more rapid (*ca.* 20 mins.). As in the case of (II) the progress of the change was indicated by the fading of the orange-red colour, the solution finally becoming almost colourless. The *sulphinic acid* was isolated and purified as in the case of (III); it formed needles which gave a blue solution in sulphuric acid and had m. p. 118° (Found: C, 58·2; H, 3·7. $C_{16}H_{11}O_5NS$ requires C, 58·3; H, 3·3%). The substance was further characterised by the corresponding methyl sulphone, which was formed from the sulphinic acid by treatment with a large excess of methyl sulphate in an aqueous alkaline medium. *Methyl* 2-o-*nitrophenoxynaphthalene*-1-*sulphinate*, thus obtained, separated from acetic acid in needles, m. p. 141° (Found: C, 59·2; H, 3·8; S, 9·2. $C_{17}H_{13}O_5NS$ requires C, 59·4; H, 3·8; S, 9·3%). The sulphinic acid is most conveniently prepared by hydrolysis of the acetylsulphone with alcoholic alkali hydroxide.

2-o-*Nitrophenoxy*-1-*naphthyl disulphide* (IX) was obtained from the sulphinic acid by reduction in warm acetic acid with dilute hydrogen iodide under the usual conditions. It separated from benzene in fibrous needles, m. p. 207° (Found : C, 64·6 ; H, 3·7 ; S, 10·7 ; *M*, 601. $C_{32}H_{20}O_6N_2S_2$ requires C, 64·8 ; H, 3·4 ; H, 10·8% ; *M*, 592). Reduction of this disulphide was effected by adding glucose to a warm stirred suspension of the material (2 g.) in alcoholic sodium hydroxide (20%). Addition of glucose was continued from time to time until a clear solution was obtained ; this was diluted with water, cooled, and then acidified with dilute sulphuric acid. The very impure product was first recrystallised from acetic acid and then further purified by means of the sodium salt, which separated from an aqueous solution containing an excess of sodium hydroxide. After being liberated from this sodium salt, the material separated from acetic acid in bright yellow needles, m. p. 182°. The substance (Found : S, 10·8. Calc. : S, 10·8%) was found by close comparison with an authentic sample to be identical with 2-nitrophenyl 2-hydroxy-1-naphthyl sulphide (VI).

2-*Nitrophenyl* 2-*Naphthyl Ether* (X).—(a) The sulphinic acid (VII) in aqueous alkaline solution was oxidised to the sulphonate with the necessary amount of permanganate. The solvent was evaporated, and the residue treated with hot 60% sulphuric acid. The *ether*, rapidly liberated as an oil, was collected in ether ; after removal of the solvent the residual oil solidified when stirred with cold light petroleum. The crystalline material was purified first from this solvent (charcoal) and subsequently from methyl alcohol ; it formed colourless prisms, m. p. 58° (Found : C, 72·3 ; H, 4·1 ; N, 5·3. $C_{16}H_{11}O_3N$ requires C, 72·4 ; H, 4·1 ; N, 5·2%). (b) Reaction between potassium 2-naphthoxide and molten 2-chloronitrobenzene did not give satisfactory results ; the required ether was obtained in small yield from molecular proportions of these reagents in boiling alcohol (13 hrs.). The solvent and unchanged chloronitrobenzene were removed with steam, then, after addition of alkali hydroxide to the liquid, the insoluble darkly coloured oil was collected in ether, dried, and recovered ; it slowly solidified in contact with light petroleum, and was then purified as in (a). The product had m. p. 58° and was identical with that produced by degradation of the sulphinic acid.

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