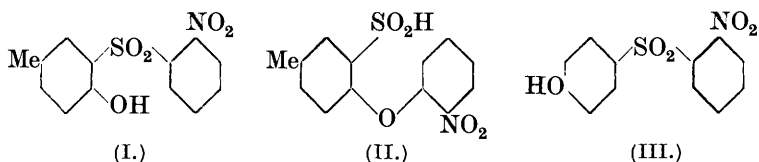


199. *The Rearrangement of Hydroxy-sulphones.*
Part III.

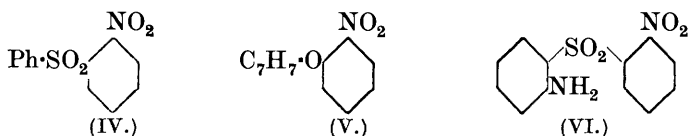
By ALFRED A. LEVI and SAMUEL SMILES.

PREVIOUS communications (J., 1931, 2207, 3264; this vol., p. 1040) on the rearrangement of *o*-hydroxy-sulphones have been mainly concerned with the influence of nitro- or methanesulphonyl groups on the carbon atom from which sulphonyl is displaced. In support of the view (J., 1931, 917) that this change and the retrograde conversion of the thiol oxide into hydroxy-sulphide are intramolecular displacements, and that the provision of conditions which permit contiguity of the atoms concerned, sulphur, oxygen, and carbon of the aromatic nucleus, must be regarded as important, it has now been shown that, whereas the *o*-hydroxy-sulphone (I) smoothly undergoes conversion (J., 1931, 3264) into the sulphinic acid (II) in presence of alkali, the *p*-hydroxy-derivative (III) does not and is

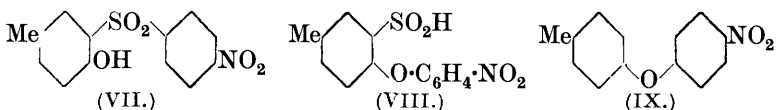
instead merely hydrolysed, yielding *o*-nitrophenol. Moreover, the view adopted implies that these displacements should be realisable intermolecularly, although it may be expected that the conditions then required would be more intense than those sufficient to effect the intramolecular processes. Accordingly it is found that the



benzenesulphonyl group of (IV) may be displaced by reaction with sodium *p*-tolylloxide, the *o*-nitrophenyl *p*-tolyl ether (V) being formed.



2-Nitrodiphenylamine is obtainable from (IV) by reaction with aniline, and this displacement of the benzenesulphonyl by the phenylamino-group indicates the possibility of effecting the intramolecular displacement in *o*-amino-sulphones of the type (VI). The *p*-nitro-derivative (VII) is converted by the usual rearrangement into the *sulphinic acid* (VIII), which has been characterised by the corresponding *disulphide*, and by degradation to *p*-nitrophenyl *p*-tolyl ether (IX), identified by comparison with synthetic material. The chief interest attached to this case lies in a comparison with the corresponding *o*-nitro-sulphone (I). Accurate methods of measuring the speeds of these rearrangements are at present not available, but the conditions required in each case leave no doubt that the rearrangement of (VII) proceeds more slowly and less smoothly



than that of (I). Evidently this result must be attributed to a more weakly positive character of the carbon atom from which sulphonyl is displaced in the *p*-nitro- as compared with that in the *o*-nitro-sulphone. It was suggested (J., 1931, 3266) that the smooth rearrangement of (I) may be assisted by the operation of a mechanism involving a quinonoid nitronic ion, but data then available and others since obtained with a different type of sulphone (this vol., p. 1040) have not permitted any conclusion as to the relative import-

ance of this process in the conversion. In the sulphones (I) and (VII) there appears to be equal opportunity for the establishment and operation of the mechanism; it is therefore concluded that, although the formation of the nitronic ion may assist the progress of the change, the mechanism involved is not of primary importance to it. So far as the migrating group is concerned, the process appears to depend primarily on the positive character of the carbon atom from which sulphonyl is displaced. Further information on this question is being sought.

EXPERIMENTAL.

2-Nitro-4'-hydroxydiphenyl Sulphide.—2-Nitrophenyl chlorothioliol and a slight excess of dry phenol were heated together (100°) until reaction was complete. The remaining phenol was removed by a current of steam, and the cooled residue purified from benzene; m. p. 132° (compare Zincke, *Annalen*, 1912, **391**, 85).

2-Nitro-4'-hydroxydiphenylsulphone (III).—“Hyperol” (6 mols.) was gradually added to a warm, stirred solution (100–100°) of the sulphide (10 g.) in acetic acid (100 c.c.). When a sample of the product no longer gave a blue colour with sulphuric acid, the mixture was diluted with water; the sulphone obtained crystallised from xylene (60% yield) in prisms, m. p. 255–256° (Found: C, 51.6; H, 5.6; S, 11.5. $C_{12}H_9O_5NS$ requires C, 51.6; H, 3.2; S, 11.5%). Like other sulphones of this class, the substance was readily decomposed by exposure to sunlight. This sulphone was recovered unchanged from solutions in 2*N*-aqueous or alcoholic sodium hydroxide after 2 hours, but after treatment (3 hours) with boiling aqueous 2*N*-sodium hydroxide *o*-nitrophenol was isolated from the products in almost theoretical amount.

2-Nitrodiphenylsulphone (IV).—Excellent yields of the requisite sulphide, uncontaminated by the resinous matter observed by Mauthner (*Ber.*, 1906, **39**, 3597), were obtained from sodium phenyl mercaptide and excess of 2-bromonitrobenzene at 100°, the use of copper being unnecessary: after removal of the excess of the halogen derivative by steam, the residue crystallised from alcohol in yellow needles, m. p. 80° (Found: C, 62.5; H, 4.1. Calc.: C, 62.3; H, 3.9%). The sulphide was oxidised (100°) in acetic acid by gradual addition of “hyperol” (4 mols.). The sulphone, isolated in the usual manner, crystallised from alcohol in prisms, m. p. 145° (Found: C, 54.4; H, 3.8; S, 12.1. $C_{12}H_9O_4NS$ requires C, 54.7; H, 3.4; S, 12.2%).

The sulphone was readily attacked by boiling alcoholic sodium hydroxide, yielding *o*-nitrophenol. A solution of the sulphone in aqueous alcohol containing a slight excess of sodium *p*-tolylloxide

was boiled for 6 hours, then made alkaline with sodium hydroxide, and submitted to steam-distillation; *o*-nitrophenyl *p*-tolyl ether, which slowly volatilised, was collected from the distillate in ether and crystallised from light petroleum; m. p. and mixed m. p. 48° (Found: N, 6.3. Calc.: N, 6.1%). A solution of the sulphone in aniline was boiled for 2 hours; 2-nitrodiphenylamine, which slowly volatilised in steam, was removed by ether from the acidified distillate and crystallised from methyl alcohol, forming red plates, m. p. 76° (Found: N, 12.9. Calc.: N, 13.1%). Fischer (*Ber.*, 1891, 24, 3796) gives m. p. 75°.

4-Nitrophenyl 4-Hydroxy-m-tolyl Sulphide (compare VII).—This was obtained by interaction (24 hours, 20°) of *p*-nitrophenyl chlorothioliol and *p*-cresol in dry chloroform. The impure product was isolated by removal of the solvent. If the chlorothioliol used had been prepared from crude di-*p*-nitrodiphenyl disulphide, the product contained di-*p*-nitrodiphenyl sulphide; the latter was conveniently eliminated at this stage by solution of the required *hydroxy-sulphide* in aqueous alkali hydroxide. After liberation from this solution the sulphide crystallised from dilute acetic acid (50%) in yellow needles, m. p. 100° (Found: C, 60.0; H, 4.5; N, 5.2. $C_{13}H_{11}O_3NS$ requires C, 59.8; H, 4.2; N, 5.3%).

4-Nitrophenyl-4'-hydroxy-m-tolylsulphone (VII).—This was prepared ("hyperol," 4 mols.; sulphide, 10 g., in acetic acid, 100 c.c.; 3—4 hours at 90°) and isolated (80% yield) in the same way as the sulphone (III); it crystallised from dilute acetic acid in prisms, m. p. 158° (Found: C, 53.5; H, 3.9; S, 11.2. $C_{13}H_{11}O_5NS$ requires C, 53.2; H, 3.7; S, 10.9%), and gave a colourless solution in sulphuric acid.

4-p-Nitrophenoxytoluene-3-sulphinic Acid (VIII).—The sulphone (VII) was warmed with excess (6 mols.) of 2*N*-aqueous alkali hydroxide at 90°; the *sulphinic acid* (maximum yield, about 70%), isolated in the usual manner, crystallised from aqueous acetone in needles, m. p. 113—114°, which gave a blue solution in sulphuric acid (Found: C, 53.5; H, 3.9. $C_{13}H_{11}O_5NS$ requires C, 53.2; H, 3.7%).

Di-4-p-nitrophenoxydi-m-tolyl Disulphide (compare VIII).—The sulphinic acid was converted by hydrogen iodide and a little sulphurous acid in acetic acid into this *disulphide*, which formed needles, m. p. 182°, from acetic acid (Found: C, 59.7; H, 4.3; S, 12.6; *M*, 516. $C_{26}H_{20}O_6N_2S_2$ requires C, 60.0; H, 3.8; S, 12.3%; *M*, 520).

p-Nitrophenyl p-Tolyl Ether (IX).—The sodium salt of the sulphinic acid (VIII) was oxidised in aqueous solution with the theoretical amount of permanganate required for conversion into sulphonate.

After removal of oxides of manganese the solution was treated with excess of carbon dioxide and evaporated. The residue when warmed with sulphuric acid (60%) rapidly yielded the required ether as an oil (80%). This, removed in ether from the diluted mixture, crystallised from methyl alcohol in prisms, m. p. 66°, which darkened on exposure to light (Found : C, 68.1; H, 4.7; N, 6.3. Calc. : C, 68.1; H, 4.8; N, 6.1%). Cook (*J. Amer. Chem. Soc.*, 1903, **25**, 60) gives m. p. 66°.

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