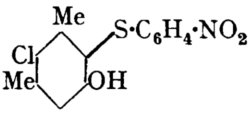
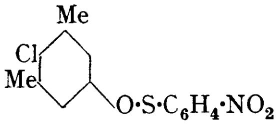
73. o-*Nitrophenylsulphenates of Phenols.*

By Eric K. Learmonth and Samuel Smiles.

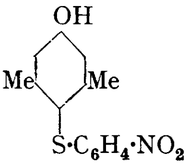
The products obtained from the fusion of 2-nitrophenylchlorothiol with *ψ*-cumenol or 2-chloro-*m*-5-xylenol were provisionally regarded (J., **1934**, 424) as the sulphenates of these phenols (*e.g.*, II). This view has now been found to be incorrect; the substances are evidently hydroxy-sulphides (*e.g.*, I), since they yield acetyl derivatives and are different from the sulphenates which have been obtained from the sodium salts of these phenols and 2-nitrophenylchlorothiol. These and other sulphenates of similar type under suitable conditions are converted by hydrogen chloride into the hydroxy-sulphides (*e.g.*, II ⟶ I). The 2-nitrophenylsulphenate of *m*-5-xylenol yielded a sulphide to which the structure (III) must be assigned, since the corresponding sulphone did not show the characteristic rearrangement of *o*-hydroxy-sulphones in alkaline media. The formation of this *p*-hydroxy-sulphide suggests that the conversion of sulphenates of phenols into hydroxy-sulphides is not a true intramolecular rearrangement. The conclusion is supported by the fact that in molten phenol the sulphenate (II) and hydrogen chloride yielded the sulphide (IV). The 2-nitrophenylsulphenates of the more fully substituted phenols are more stable than that derived from phenol (compare Zincke, *Annalen*, 1912, **391**, 71), but they are destroyed by hydrogen peroxide in acetic acid and are slowly hydrolysed in alkaline media.



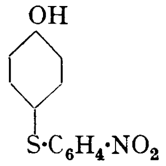
(I.)



(II.)



(III.)



(IV.)

Experimental.

The 2-nitrophenylsulphenates of the phenols were obtained by slowly adding a concentrated solution of the sodium phenoxide in alcohol to a cooled stirred solution of 2-nitrophenylchlorothiol (1 mol.) in ether. The insoluble product was washed with water to remove sodium chloride and the residue was usually purified by addition of water to a cold acetone solution. The yellow crystalline sulphenates obtained in most cases began to decompose at about 120°. They were destroyed by hydrogen peroxide or other oxidising agents in warm acetic acid, the formation of the corresponding sulphonates not being observed; they were hydrolysed with varying ease by warm aqueous sodium hydroxide (2*N*). Their behaviour with hydrogen chloride is described below.

	2-Nitrophenylsulphenate of	M. p.	N, % found.	N, % calc.
1	*m*-4-Xylenol	85°	5·1	5·1
2	*m*-5-Xylenol	74	5·1	5·1
3	2-Chloro-*m*-5-xylenol	118—120	4·4	4·5
4	2 : 6-Dichloro-*m*-5-xylenol	125—127°	4·0	4·1
5	5-Chloro-*p*-2-xylenol	120	4·4	4·5
6	*ψ*-Cumenol	103	4·8	4·8

Conversion of the sulphenates into the hydroxy-sulphides was effected by leading hydrogen chloride into boiling benzene solutions; the process was usually complete in 30 minutes, and sometimes, *e.g.*, in Nos. 1 and 2, required only 10 minutes. After removal of benzene and hydrogen chloride the residue was purified from a suitable solvent. The following sulphides were obtained in this manner. 2-Nitro-2′-hydroxy-3′ : 5′-dimethyldiphenyl sulphide, from No. 1, had m. p. 120° (Found: N, 5·0. Calc.: N, 5·1%) and was identical with the sulphide previously obtained (J., 1934, 422) from *m*-4-xylenol and the chlorothiol at 110°. The *methyl* ether formed pale yellow needles from alcohol, m. p. 79° (Found: N, 4·7. $C_{15}H_{15}O_3NS$ requires N, 4·8%).

2-*Nitro*-4′-*hydroxy*-2′ : 6′-*dimethyldiphenyl sulphide* (III) was obtained (*a*) from No. 2 with hydrogen chloride or (*b*) from the interaction of *m*-5-xylenol and the chlorothiol at 80—100°. It formed yellow needles, m. p. 154°, from benzene (Found: C, 61·0; H, 4·7; N, 5·0. $C_{14}H_{13}O_3NS$ requires C, 61·1; H, 4·7; N, 5·1%). The *acetyl* derivative, pale yellow needles from alcohol, had m. p. 121° (Found: N, 4·4. $C_{16}H_{15}O_4NS$ requires N, 4·4%); and the *methyl* ether, m. p. 130°, formed yellow prisms from alcohol (Found: N, 4·7. $C_{15}H_{15}O_3NS$ requires N, 4·8%). In contrast with the sulphides obtained from Nos. 3 and 6 the sodium salt of this sulphide was readily formed from and soluble in aqueous alkali hydroxide (2*N*).

2-*Nitro*-4′-*hydroxy*-2′ : 6′-*dimethyldiphenylsulphone* was obtained from the sulphide (4 g.) by oxidation (3 hours) in acetic acid (20 c.c., 100°) with hydrogen peroxide (7·3 c.c., 30%); it formed cream-coloured needles, m. p. 218° (decomp.), from acetic acid (Found: C, 54·4; H, 4·3; N, 4·4. $C_{14}H_{13}O_5NS$ requires C, 54·7; H, 4·2; N, 4·5%). This sulphone was recovered from a solution in aqueous alkali hydroxide (2*N*) which had been warmed and kept (2 hours); the contrast of this behaviour with that of analogous *o*-hydroxy-sulphones is evident (compare J., 1934, 422).

3′-Chloro-2-nitro-6′-hydroxy-2′ : 4′-dimethyldiphenyl sulphide (I) was obtained (*a*) from No. 3 with hydrogen chloride in benzene or (*b*) from 2-chloro-*m*-5-xylenol and the chlorothiol as previously described (J., 1934, 424); it formed yellow needles from acetic acid, m. p. 196° (Found: N, 4·5. Calc.: N, 4·5%). The *acetyl* derivative formed pale yellow needles, m. p. 145°, from alcohol (Found: C, 54·4; H, 3·9. $C_{16}H_{14}O_4NClS$ requires C, 54·6; H, 4·0%). The orange sodium salt of this sulphide is sparingly soluble in aqueous alkali hydroxide and is readily hydrolysed; it was obtained by shaking a benzene solution of the sulphide with the alkaline reagent. The *methyl* ether, obtained by boiling (5 hours) a solution of the sodium salt in benzene containing methyl iodide and a little methyl alcohol, formed yellow prisms, m. p. 156°, from acetic acid (Found: C, 55·9; H, 4·2; N, 4·3. $C_{15}H_{14}O_3NClS$ requires C, 55·6; H, 4·3; N, 4·3%).

Conversion of the sulphenate No. 3 into the hydroxy-sulphide (IV) was effected as follows: Hydrogen chloride was led into a solution of the sulphenate (10 g.) in phenol (60 g.). When reaction was complete (80°, 30 mins.) the phenols were removed with steam and the finely powdered residue was shaken with excess of cold aqueous sodium hydroxide (2*N*). A small quantity of the sulphide (I) and its sodium salt remained insoluble; addition of dilute sulphuric acid to the solution yielded the sulphide (IV), which, after purification from benzene, had m. p. 130—131° and was identical with a sample prepared by Zincke's method (*loc. cit.*).

2-Nitro-2′-hydroxy-3′ : 5′ : 6′-trimethyldiphenyl sulphide was obtained (*a*) from No. 6 with hydrogen chloride in benzene or (*b*) from *ψ*-cumenol and 2-nitrophenylchlorothiol at 100—110° as already described (J., 1934, 424) (Found: N, 4·8. Calc.: N, 4·8%). Purified from acetone, it had m. p. 161°. The *acetyl* derivative formed yellow needles, m. p. 135°, from acetic acid (Found: C, 61·7; H, 5·0. $C_{17}H_{17}O_4NS$ requires C, 61·6; H, 5·1%). This hydroxy-sulphide is insoluble in aqueous alkali hydroxide (2*N*) and the formation of a sodium salt was not observed when a benzene solution was shaken with the reagent.

The conversion of the nitrophenylsulphenates into the hydroxy-sulphides serves in most cases as a convenient source of the latter substances, but the method is inapplicable in some cases where the phenol is highly substituted; *e.g.*, the sulphenate No. 4 under the usual treatment yielded the phenol and 2-nitrophenylchlorothiol.

KING'S COLLEGE, LONDON.

[*Received, January* 14*th*, 1936.]