203. *Exchange of Sulphonyl Groups in Thiolsulphonic Esters.*

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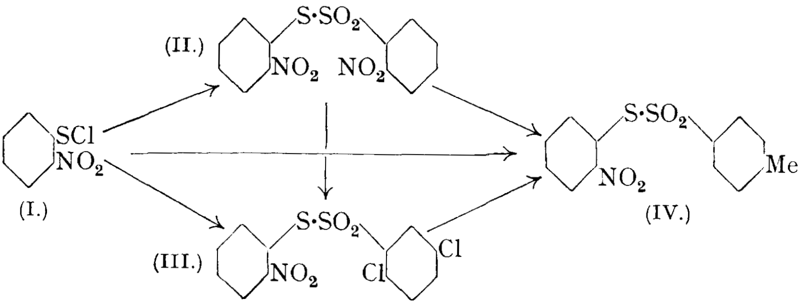
THE exchange of sulphonyl groups in 2 : 4-dinitrodiphenylsulphones by the action of sulphinates (Loudon, this vol., p. 537) is closely paralleled by the interconversion of 2 : 4-dinitrophenyl alkyl ethers (Blanksma, *Centr.*, 1909, I, 1809), which, in turn, is related to the " Umesterung " phenomena exhibited by derivatives of carboxylic acids. It is therefore to be anticipated that sulphonyl exchange will be displayed in such compounds as acyl sulphones, disulphones, and in the so-called disulphoxides which Smiles and his co-workers have shown to be thiolsulphonic esters (J., 1924, **125**, 176; 1925, **127**, 224, 1821).

The following account is concerned chiefly with the behaviour of thiolsulphonic esters towards alkali sulphinates and the test case devised is illustrated in the diagram :



The identity of the products of the sulphonyl exchange (II → III; II → IV; III → IV) with those synthesised from the chlorothiol fully confirmed our expectations; moreover the fundamental similarity of the two preparative routes is obvious and this we have emphasised in condensations with the chlorothiol (I → II; I → III; I → IV) by substituting alkali sulphinates for the silver sulphinates employed by other workers (Zincke and Farr, *Annalen*, 1912, **391**, 67; Smiles, *loc. cit.*). From the point of view of its synthetic value, however, the new process is subject to certain limitations, as is shown in the table, in which the success or failure of various instances of the following reaction is denoted by + or — respectively:

$$R'S{\cdot}SO_2{\cdot}R'' + R'''{\cdot}SO_2Na \longrightarrow R'S{\cdot}SO_2{\cdot}R''' + R''{\cdot}SO_2Na$$

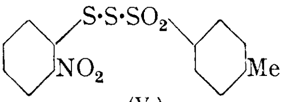
R′ = R″.	R‴.	
Phenyl	*p*-Tolyl	+
p-Tolyl	Phenyl	—
Benzyl	*p*-Tolyl	+
p-Chlorophenyl	,,	+
p-Bromophenyl	,,	+
2 : 5-Dichlorophenyl	,,	+
,,	*m*-Nitrophenyl	+
,,	*o*-Nitrophenyl	—
o-Nitrophenyl	Phenyl	+
,,	*p*-Tolyl	+
,,	*p*-Chlorophenyl	+
,,	*p*-Bromophenyl	+
,,	2 : 5-Dichlorophenyl	+

R′.	R″.	R‴.	
Phenyl	*p*-Tolyl	*p*-Chlorophenyl	—
,,	,,	*p*-Bromophenyl	—
Benzyl	,,	Phenyl	—
o-Nitrophenyl	Phenyl	2 : 5-Dichlorophenyl	—
,,	*p*-Chlorophenyl	*p*-Tolyl	+
,,	,,	*p*-Bromophenyl	+
,,	*p*-Bromophenyl	Phenyl	+
,,	,,	*p*-Chlorophenyl	—
,,	2 : 5-Dichlorophenyl	*p*-Tolyl	+
,,	,,	Phenyl	+
,,	,,	*p*-Chlorophenyl	+

As a first approximation it may be concluded from these results that here, as with 2 : 4-dinitrodiphenylsulphones, facile exchange is only operative when the potential anion is of greater stability than the free sulphinate ion. It is further to be expected that the nature of the group R′S will also exert some influence on the reaction, but no clear evidence of this is available, although, in the sulphone series, it has now been found that no exchange occurs either with benzyl or with *p*-nitrobenzyl sulphones—a result which supports Smiles's conclusion (actually made with reference to the *o*-nitrobenzyl group; Kent and Smiles, J., 1934, 422) that the centres concerned are too feebly charged to engender pronounced sulphonyl mobility.

The action of potassium *p*-toluenethiolsulphonate ($C_7H_7{\cdot}SO_2{\cdot}SK$) on 2-nitro- and on 2 : 4-dinitro-chlorobenzene was examined as a possible source of the thiolsulphonic esters, but only the corresponding *p*-tolylsulphones were isolated. This behaviour recalls Fromm and Erfurt's suggestion (*Ber.*, 1909, **42**, 3822) that the product of a similar action on benzyl chloride consists of an inseparable mixture of *p*-tolylbenzylsulphone and benzyl *p*-toluenethiolsulphonate. Reinvestigation of the point, however, established that the product was simply benzyl *p*-toluenethiolsulphonate, also prepared by the exchange process from benzyl benzylthiolsulphonate.

It was expected that vigorous treatment of *o*-nitrophenyl *p*-toluenethiolsulphonate (IV) by alkali sulphinates would result in production of *o*-nitrophenyl sulphones. This, however, has not been realised, but replacement of the thiolsulphonic group by sulphonyl in the analogous case of *p*-toluenesulphonyl *o*-nitrophenyl disulphide (V) was readily effected ($C_7H_7{\cdot}SO_2{\cdot}S$ replaced by *p*-toluenesulphonyl and by *p*-bromophenylsulphonyl but not by 2 : 5-dichlorophenylsulphonyl).



(V.)

Although, with alkali mercaptides, sodium benzylthiosulphate ($CH_2Ph{\cdot}S{\cdot}SO_3Na$) yields disulphides (Footner and Smiles, J., 1925, **127**, 2887) and sodium anthraquinone-1-sulphonate yields thio-ethers (Emmet Reid, Mackall, and Miller, *J. Amer. Chem. Soc.*, 1921, **43**, 2104), the corresponding replacements do not occur with alkali sulphinates.

EXPERIMENTAL.

Sulphonyl Exchange with Thiolsulphonic Esters.—The general procedure adopted was to warm a homogeneous mixture of the sodium sulphinate (3 mols.) in water with the thiolsulphonic ester (0·5 to 1 g.; 1 mol.) in a suitable solvent (alcohol, acetic acid, or dioxan) for 2 minutes and thereafter to cool and, where necessary, precipitate the product with water. The recrystallised products (alcohol or acetic acid) were identified by m. p. and mixed m. p. with synthetic specimens where these were known (Smiles and colleagues, *loc. cit.*) or alternatively characterised by analysis.

Phenyl p-*toluenethiolsulphonate*, obtained from phenyl benzenethiolsulphonate and sodium *p*-toluenesulphinate, had m. p. 74° (from alcohol) (Found: C, 58·9; H, 4·7. $C_{13}H_{12}O_2S_2$ requires C, 59·1; H, 4·5%).

Benzyl p-*Toluenethiolsulphonate*.—(1) A homogeneous mixture of potassium *p*-toluenethiolsulphonate (2 g.) in water and benzyl chloride (1 c.c.) in alcohol was gently refluxed for 1 hour and the oil precipitated on cooling was washed with water and placed in the ice-chest till it solidified. The product was obtained from alcohol in coarse crystals, m. p. 60° (Fromm and Erfurt, *loc. cit.*, give m. p. 55°).

(2) The same product resulted from treatment of benzyl benzylthiolsulphonate and sodium *p*-toluenesulphinate, in the usual way (Found: C, 60·5; H, 5·0. Calc. for $C_{14}H_{14}O_2S_2$: C, 60·4; H, 5·0%).

p-*Nitrobenzyl* p-*toluenethiolsulphonate*, prepared as in the previous case from *p*-nitrobenzyl bromide, melted at 120° after two crystallisations from acetic acid–alcohol (Found: N, 4·4. $C_{14}H_{13}O_4NS_2$ requires N, 4·3%).

p-*Chlorophenyl* p-*toluenethiolsulphonate*, obtained from *p*-chlorophenyl *p*-chlorobenzenethiolsulphonate, had m. p. 65° (from alcohol) (Found: Cl, 11·7. $C_{13}H_{11}O_2ClS_2$ requires Cl, 11·9%).

p-*Bromophenyl* p-*toluenethiolsulphonate*, by exchange (cf. Table), had m. p. 107° (from alcohol) (Found: Br, 23·6. $C_{13}H_{11}O_2BrS_2$ requires Br, 23·3%).

2 : 5-*Dichlorophenyl* p-*Toluenethiolsulphonate*.—The compound obtained from sodium *p*-toluenesulphinate and 2 : 5-dichlorophenyl 2 : 5-dichlorobenzenethiolsulphonate crystallised in two forms, which were separated by fractional extraction of the crude product with hot alcohol. The more soluble form, on slow heating, melted sharply at 86—87° and on continued heating resolidified, finally re-melting at the m. p. of the second form, *viz.*, 103° (Found: Cl, 21·2. $C_{13}H_{10}O_2Cl_2S_2$ requires Cl, 21·3%).

o-*Nitrophenyl benzenethiolsulphonate* was obtained (1) by sulphonyl exchange (cf. table) and (2) by interaction of *o*-nitrophenylsulphenyl chloride and sodium benzenesulphinate. In the latter process the sulphenyl chloride (5 g.), dissolved in ether (30 c.c.), was warmed with the dried powdered sulphinate (5 g.) in suspension for 15 minutes. After filtration the ether was evaporated, and the residue crystallised from alcohol; m. p. 87° (Found: N, 4·6. $C_{12}H_9O_4NS_2$ requires N, 4·7%).

o-*Nitrophenyl* p-*bromobenzenethiolsulphonate*, from *o*-nitrophenyl *o*-nitrobenzenethiolsulphonate, had m. p. 137° (from alcohol) (Found: N, 3·8. $C_{12}H_8O_4NBrS_2$ requires N, 3·7%).

2 : 5-Dichlorophenyl 3-nitrobenzenethiolsulphonate, from 2 : 5-dichlorophenyl 2 : 5-dichlorobenzenethiolsulphonate and sodium *m*-nitrobenzenesulphinate, had m. p. 116° after two crystallisations from alcohol (Found: N, 3·8. $C_{12}H_7O_4NCl_2S_2$ requires N, 3·8%).

Replacement of Thiolsulphonic Group.—When a dioxan solution of *p*-toluenesulphonyl *o*-nitrophenyl disulphide (V, m. p. 139°) was treated in the usual way with sodium *p*-toluenesulphinate, the product was identified as *o*-nitrophenyl *p*-toluenethiolsulphonate (m. p. and mixed m. p. 97—98°). Similarly, sodium *p*-bromobenzenesulphinate yielded *o*-nitrophenyl *p*-bromobenzenethiolsulphonate (m. p. 131°; mixed m. p. 132—133°; depressed by admixture with V to below 120°). Sodium 2 : 5-dichlorobenzenesulphinate, on the other hand, effected no replacement even when the reaction time was extended to 30 minutes (product had m. p. and mixed m. p. with V 138°).

o-Nitrophenyl *p*-toluenethiolsulphonate was refluxed for 45 minutes with sodium *p*-toluenesulphinate in ethylene glycol (neither reagent is separately affected by this treatment). The solution on cooling deposited a semi-solid mass, which crystallised from alcohol (charcoal) in colourless needles, m. p. 46°, unaffected by admixture with di-*p*-tolyl disulphide. In a second experiment, with the heating curtailed to 30 minutes, *p*-tolyl *p*-toluenethiolsulphonate was isolated (m. p. 74°; mixed m. p. 76°).

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