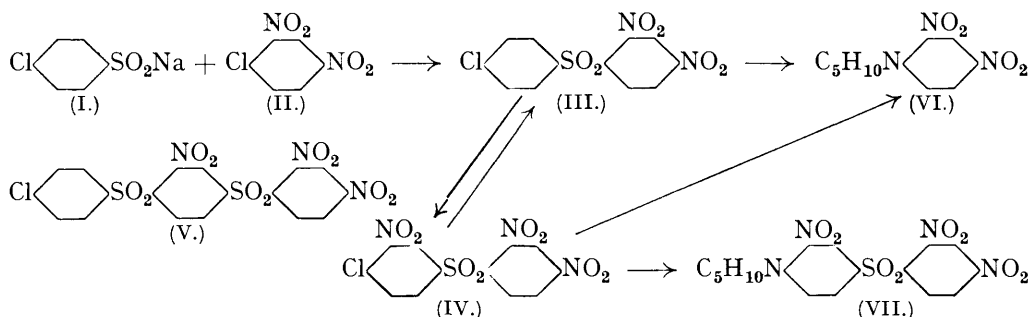


124. 2 : 4-Dinitrodiphenylsulphones.

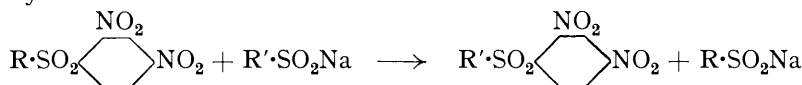
By JAMES D. LOUDON.

A STUDY of the properties of 2 : 4-dinitrodiphenylsulphones has revealed some interesting examples of their reactivity, of which the following is a preliminary account. Their preparation has been effected by extension of Ullmann and Pasdermadjian's original procedure (*Ber.*, 1901, **34**, 1150), *e.g.*, condensation of (I) and (II), or by the modification in which (II) is replaced by 2 : 4-dinitrophenyl-*p*-toluenesulphonate. The facility with which the reaction proceeds suggested the possibility of forming polysulphones, *e.g.*, (V) by nitration of (III), followed by condensation with a second molecule of (I).



The mononitration of (III) proceeded smoothly and the product was submitted to the piperidine test for reactive halogen, following the procedure of Le Fèvre and Turner (*J.*, 1927, 1113). The difficulty of obtaining a homogeneous product, together with the ultimate isolation of (VI), showed that under these conditions (excess of piperidine) rapid scission of the sulphone linkage occurs. This was further demonstrated by the smooth conversion of other 2 : 4-dinitrodiphenylsulphone derivatives (*e.g.*, III) into (VI), the reaction being analogous to the slower replacement of the phenylsulphonyl group in *o*-nitrodiphenylsulphone by aniline (Levi and Smiles, *J.*, 1932, 1488). That piperidine, however, exerts a preferential attack on the halogen of (IV) is shown by the isolation of (VII) from the reaction conducted in dioxan with the theoretical amount of base.

The mobility of the arylsulphonyl group in these compounds also frustrated the attempt to prepare (V) by interaction of (I) and (IV), the sole result being regeneration of (III), apparently by exchange of arylsulphonyl anions. The following table summarises the results obtained in other cases, the sign + denoting completion, and - failure of the reaction in which, with the exceptions noted, three molecular proportions of sulphinate were employed.



R.	R'.		R.	R'.	
Ethyl	Methyl *	+	Phenyl	Ethyl	+
Methyl	Ethyl	+	Phenyl	2 : 5-Dichlorophenyl	-
Ethyl	<i>p</i> -Tolyl *	+	<i>p</i> -Chlorophenyl	Phenyl	+
<i>p</i> -Tolyl	Ethyl	+	<i>p</i> -Chloro- <i>m</i> -nitrophenyl	<i>p</i> -Chlorophenyl	+
<i>p</i> -Tolyl	Phenyl †	+	<i>p</i> -Bromo- <i>m</i> -nitrophenyl	<i>p</i> -Bromophenyl	+
Phenyl	<i>p</i> -Tolyl	+	<i>m</i> -Nitrophenyl	<i>p</i> -Tolyl	+
Phenyl	Methyl	+	<i>p</i> -Chloro- <i>m</i> -nitrophenyl	<i>m</i> -Nitrophenyl	-

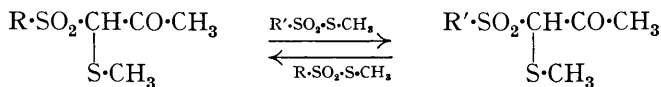
* Large excess.

† 12 Molecules.

The table includes only those examples in which the nature of the isolated substance was clearly established by melting point and mixed melting point observations. In several other cases (*e.g.*, R = phenyl, R' = *p*-chlorophenyl) the product was obviously a mixture (qualitative halogen test), which resisted fractionation from acetic acid.

The results recorded suffice to indicate in a qualitative manner that the reaction is

influenced (*a*) by the concentration of free sulphinate ion and (*b*) by the relative stabilities of the competing anions (actual and potential). They offer some points of contrast to the work of Gibson (J., 1931, 2637; 1932, 1819, *et seq.*), who has recently demonstrated sulphonyl mobility in the following case, and records failure of the exchange process (1)



when purely aromatic thiolsulphonic esters (*e.g.*, Ph·SO₂·SPh as distinct from Ph·SO₂·S·CH₃) are employed and (2) where replacement of arylsulphonyl by alkylsulphonyl is attempted. With sulphones of the present series these limitations do not apply, for, on the one hand, both types of disulphoxide in presence of carbonate produced a facile exchange and, on the other, the effected replacement of arylsulphonyl by sodium alkylsulphinates was less readily reversed.

Experiments are in progress on the exchange of the sulphone group when attached to other cationoid centres, such as in thiolsulphonic esters.

EXPERIMENTAL.

Preparation of 2 : 4-Dinitrodiphenylsulphones.—2 : 4-Dinitrochlorobenzene (or 2 : 4-dinitrophenyl *p*-toluenesulphonate) and the requisite sodium sulphinate in molecular proportion were heated in aqueous alcoholic solution for 10–20 minutes. After cooling, the solid was collected, washed with alcohol and water, and crystallised from acetic acid. The compounds, phenyl (159–160°), *p*-tolyl (187°), *o*-tolyl (154°), *p*-chlorophenyl (168°), *p*-bromophenyl (190°), methyl (187°), and ethyl (157°) -2 : 4-dinitrodiphenylsulphones, had the uncorrected melting points indicated, the values being in close agreement with those recorded for the same substances formed by oxidation of the corresponding sulphides (*J. Amer. Chem. Soc.*, 1932, 54, 1985; 1933, 55, 4956). 2 : 4 : 3'-Trinitrodiphenylsulphone had m. p. 196–197° (Found : N, 11.8. C₁₂H₇O₈N₃S requires N, 11.9%), and 2' : 5'-dichloro-2 : 4-dinitrodiphenylsulphone, m. p. 178° (Found : N, 7.5. C₁₂H₆O₈N₂Cl₂S requires N, 7.4%).

4'-Chloro-2 : 4 : 3'-Trinitrodiphenylsulphone.—A solution of potassium nitrate (1.01 g.) in 20 c.c. of concentrated sulphuric acid was added to 4'-chloro-2 : 4-dinitrodiphenylsulphone (3.42 g.) in 60 c.c. of concentrated sulphuric acid. The crystals formed on standing were recrystallised from acetic acid and had m. p. 203° (Found : N, 10.9. C₁₂H₆O₈N₃ClS requires N, 11.1%).

4'-Bromo-2 : 4 : 3'-trinitrodiphenylsulphone.—The product of the nitration of 4'-bromo-2 : 4-dinitrodiphenylsulphone, conducted as above, had m. p. 210° after several crystallisations from acetic acid (Found : N, 9.9. C₁₂H₆O₈N₃BrS requires N, 10.0%).

Action of Piperidine.—The reaction (0.2 g. of sulphone and 2 c.c. of piperidine) was rapid even in the cold. After being warmed for a few minutes, the solution was cooled and treated with dilute acid; the precipitated oil rapidly became solid except in the cases of 4'-chloro (and bromo)-2 : 4 : 3'-trinitrodiphenylsulphones, where partial solidification occurred only after several weeks. After crystallisation from alcohol the product in each case was identified as 2 : 4-dinitropiperidinobenzene, m. p. and mixed m. p. 92°.

2 : 4 : 3'-Trinitro-4'-piperidinodiphenylsulphone.—4'-Chloro-2 : 4 : 3'-trinitrodiphenylsulphone (0.5 g.; 1 mol.) in 5 c.c. of dioxan was treated with piperidine (0.22 g.; 2 mols.) in 2 c.c. of dioxan, and the resulting orange solution kept for 12 hours. The crystalline deposit was identified as piperidine hydrochloride (m. p. and mixed m. p. 236°). The oil formed by addition of water to the filtrate was extracted with concentrated hydrochloric acid. The extract on dilution with water yielded a solid which crystallised from acetone-alcohol in yellow plates, m. p. 190–191° (Found : N, 13.0. C₁₇H₁₆O₈N₄S requires N, 12.8%). The same piperidine derivative was formed from the corresponding bromotrinitrodiphenylsulphone.

Sulphonyl Exchange.—The following example is typical of the procedure employed. Dinitrodiphenylsulphone (0.5 g.), dissolved in 6 c.c. of warm dioxan, was treated with a hot solution of sodium *p*-toluenesulphinate (0.9 g.) in 2 c.c. of water. The homogeneous mixture was heated for a few minutes and cooled (prolonged or more drastic treatment leads to complications which are under investigation). The solid which separated was washed with alcohol and then with water; it melted crude at 179–181°; crystallised from acetic acid, it had m. p. 187–188°, unaffected by admixture with 2 : 4-dinitrophenyl-*p*-tolylsulphone (m. p. 187°).

Action of Disulphoxides.—*p*-Tolyl *p*-toluenethiolsulphonate (0.3 g.) and 2 : 4-dinitrodiphenylsulphone (0.3 g.), dissolved in hot dioxan, were treated with a small amount of sodium carbonate and a few drops of water. The product, isolated as above, yielded 2 : 4-dinitrophenyl-*p*-tolylsulphone (m. p. and mixed m. p. 185—186°).

Methyl *p*-toluenethiolsulphonate gave the same result, but in the absence of alkali carbonate no reaction occurred in either case.

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