CCCLXXVI.—*The Interaction of Nitroamines with Sulphonyl Chlorides.*

By FRANK BELL.

MOST amines react with an equivalent amount of an aryl sulphonyl chloride in pyridine solution to give a quantitative yield of pure sulphonamido-derivative, but in two cases recently examined the product has been a mixed one. Both *o*-nitroaniline with *m*-nitrobenzenesulphonyl chloride and 1 : 8-dinitro-β-naphthylamine with *p*-toluenesulphonyl chloride yield a mixture of *mono*- and *di-sulphonamido*-derivatives. The constitution of the disulphonamido-compound is proved by preparation from the monosulphonamido-derivative by interaction with a further molecule of the sulphonyl chloride and also by hydrolysis to the original amine. The *p*-toluenesulphonyl derivatives of aniline, β-naphthylamine, and *p*-aminodiphenyl show little tendency to interact with a further molecule of *p*-toluenesulphonyl chloride, although that of *p*-nitroaniline will do so, even if somewhat less readily than that of *o*-nitroaniline. The conclusion can be drawn that, although nitroamines react somewhat sluggishly with sulphonyl chlorides, the monosulphonamido-derivatives are easily converted into the disulphonamido-derivatives. It is suggested that the sluggishness of the primary reaction indicates some combination between nitro- and amino-groups and that the increased reactivity of the monosulphonamido-derivative is caused by the greater tendency towards ionisation of the amino hydrogen owing to the presence of the positive (electron-absorbing) nitro-group.

The replacement of the hydrogen of the monosulphonamido-group by another sulphonyl radical enormously decreases the ease of substitution within the molecule. For instance, *di*-m-*nitrobenzenesulphon*-o′-*nitroanilide* could be recovered unchanged after solution in fuming nitric acid, whereas m-*nitrobenzenesulphon*-o′-*nitroanilide* was immediately converted into the o′p′-*dinitro*-derivative under the same conditions. Hence, arranging the groups in order of orienting influence, we have the series

$$NH_2 > NH{\cdot}SO_2 > NMe{\cdot}SO_2 > N(SO_2)_2$$

and, very approximately, the group $NH \cdot SO_2$ is comparable in influence with the hydroxyl group and $N(SO_2)_2$ is comparable with the $O \cdot SO_2$ group.

If benzenesulphonamides are energetically nitrated, a nitro-group always enters the benzenesulphonyl part of the molecule. Although Reverdin and Crépieux (*Ber.*, 1901, **34**, 3000) state that *p*-toluenesulphon-*p*′-nitroanilide on solution in fuming nitric acid yields *p*-toluenesulphon-*o*′*p*′-dinitroanilide, it is now shown that their product is *m*-nitro-*p*-toluenesulphon-*o*′*p*′-dinitroanilide.

EXPERIMENTAL.

Di-m-*nitrobenzenesulphon*-o′-*nitroanilide*.—(a) *m*-Nitrobenzenesulphonyl chloride (1 mol.) was added to *o*-nitroaniline in pyridine, the solution, after standing over-night, was poured into water, and the precipitate (m. p. *ca.* 155°) fractionally crystallised from benzene; it separated into pale yellow needles, m. p. 165°, of the slightly more soluble m-*nitrobenzenesulphon*-o′-*nitroanilide* (Found: C, 44·4; H, 2·9. $C_{12}H_9O_6N_3S$ requires C, 44·6; H, 2·8%) and almost colourless prisms, m. p. 179°, of *di*-m-*nitrobenzenesulphon*-o′-*nitroanilide* (Found: C, 42·4; H, 2·7. $C_{18}H_{12}O_{10}N_4S_2$ requires C, 42·3; H, 2·4%).

(b) By interaction of *o*-nitroaniline with *m*-nitrobenzenesulphonyl chloride (2 mols.) in pyridine solution.

The constitution was proved by hydrolysis as follows. 5 G. of the well-powdered material were left in contact with sulphuric acid (15 c.c.) for 4 hours, the suspension was poured into water, and the liquid filtered from unchanged substance and neutralised with ammonia. The resulting precipitate was identified as *o*-nitroaniline.

Di-p-*toluenesulphon*-o′-*nitroanilide* was obtained in quantitative yield by the interaction of *p*-toluenesulphon-*o*′-nitroanilide with *p*-toluenesulphonyl chloride in pyridine solution. It crystallised from acetic acid in large prisms, m. p. 191° (Found: C, 53·9; H, 4·2. $C_{20}H_{18}O_6N_2S_2$ requires C, 53·9; H, 4·0%), and was readily hydrolysed by solution in concentrated sulphuric acid to give *o*-nitroaniline.

m-*Nitrobenzenesulphon*-p′-*nitroanilide*, prepared by the interaction of *p*-nitroaniline and *m*-nitrobenzenesulphonyl chloride in pyridine, crystallised from acetic acid in prisms, m. p. 180° (Found: C, 44·8; H, 3·0. $C_{12}H_9O_6N_3S$ requires C, 44·6; H, 2·8%).

Di-p-*toluenesulphon*-p′-*nitroanilide*, prepared by the interaction of *p*-toluenesulphon-*p*′-nitroanilide and *p*-toluenesulphonyl chloride, crystallised from acetic acid in plates, m. p. 219° (Found: C, 53·8; H, 4·1. $C_{21}H_{18}O_6N_2S_2$ requires C, 53·9; H, 4·0%).

Di-p-*toluenesulphon*-1 : 8-*dinitro*-β-*naphthalide*.—(a) *p*-Toluenesulphonyl chloride (1 mol.) was added to 1 : 8-dinitro-β-naphthylamine, after a week the solution was poured into water, and the precipitate separated by crystallisation from acetic acid into unchanged base, p-*toluenesulphon*-1 : 8-*dinitro*-β-*naphthalide*, yellow needles, m. p. 221° (Found: C, 53·1; H, 3·5. $C_{17}H_{13}O_6N_3S$ requires C, 52·8; H, 3·4%), and a very difficultly soluble, white, amorphous powder, m. p. 258° (decomp.), which was the slightly impure *di*-p-*toluenesulphonamido*-derivative (Found: C, 52·7; H, 3·4. $C_{24}H_{19}O_8N_3S_2$ requires C, 53·3; H, 3·5%).

(b) By the interaction of *p*-toluenesulphon-1 : 8-dinitro-β-naphthalide with *p*-toluenesulphonyl chloride in pyridine solution.

The constitution was readily proved by hydrolysis. 1 G. was suspended in sulphuric acid (3 c.c.) and when dissolution had taken place (about 3 hours) the solution was poured into water; pure 1 : 8-dinitro-β-naphthylamine was then precipitated.

m-*Nitrobenzenesulphon*-o′p′-*dinitroanilide*.—(a) *m*-Nitrobenzenesulphon-*p*′-nitroanilide (2 g.) was added to nitric acid (10 c.c., *d* 1·5). The clear solution rapidly deposited needles of the *dinitro*-compound (2·4 g.), m. p. 210°, which could be recrystallised from acetic acid (Found: C, 39·4; H, 2·4. $C_{12}H_8O_8N_4S$ requires C, 39·2; H, 2·2%).

(b) *m*-Nitrobenzenesulphon-*o*′-nitroanilide, treated as in (a), furnished an identical result.

p-*Toluenesulphon*-o′p′-*dinitroanilide*.—(a) *p*-Toluenesulphon-*p*′-nitroanilide (2·5 g.) and nitric acid (*d* 1·42; 10 c.c.) were warmed on a water-bath for several hours. The product after repeated crystallisation from acetic acid furnished p-*toluenesulphon*-o′p′-*dinitroanilide* in needles, m. p. 161° (Found: C, 46·3; H, 3·2. $C_{13}H_{11}O_6N_3S$ requires C, 46·3; H, 3·3%).

(b) *p*-Toluenesulphon-*o*′-nitroanilide, treated as under (a), gave the same product.

This compound (1 g.) readily dissolved in nitric acid (*d* 1·5; 2·5 c.c.). The solution was diluted with acetic acid, and the precipitated nitro-compound recrystallised from acetone; it then gave *m*-nitro-*p*-toluenesulphon-*o*′*p*′-dinitroanilide in long needles, m. p. 220°.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, October 24th*, 1929.]