116. *Reactions of 4-Nitro-2-naphthylamine. Part II. Mono- and Di-nitration of 4-Nitro-p-toluenesulphon-2-naphthalide and Preparation of 4 : 6-Dinitro-1-naphthol.*

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4-Nitro-2-naphthylamine readily forms a mono- and a di-sulphonamido-derivative with *p*-toluenesulphonyl chloride. 4-*Nitro*-p-*toluenesulphon-2-naphthalide* is mononitrated in the 1-position and dinitrated in the 1 : 6-positions. Combined hydrolysis and deamination of 1 : 4 : 6-*trinitro*-p-*toluenesulphon-2-naphthalide via* the diazo-oxide forms 4 : 6-*dinitro*-1-*naphthol.*

Nitration of *p*-toluenesulphon-β-naphthalide gives first the 1-nitro-derivative and then the 1 : 6-dinitro-derivative (cf. Morgan and Micklethwait, J., 1912, **101**, 148; Bell, J., 1929, 2784), whereas nitration of the *p*-toluenesulphonyl derivatives of 5-nitro- and 8-nitro-β-naphthylamines takes place in the 1-position, the products being fairly resistant to further nitration (cf. Bell, *loc. cit.*). Since 4-nitro-2-naphthylamine has now been rendered accessible (Hodgson and Birtwell, J., 1944, 75; Hodgson and Hathway, Part I, J., 1944, 385), it appeared of interest to ascertain how its *p*-toluenesulphonyl derivative would be nitrated. The mononitration product, 1 : 4-*dinitro*-p-*toluenesulphon*-2-*naphthalide*, is readily isolated, and dinitration also readily occurs to form 1 : 4 : 6-*trinitro*-p-*toluenesulphon*-2-*naphthalide*. In this respect the nitro-group in position 4 does not exert the retarding influence to further nitration which the nitro-groups in positions 5 and 8 were found to do.

The constitution of the 1 : 4-dinitro-*p*-toluenesulphon-2-naphthalide follows from its conversion by combined hydrolysis and deamination into 1 : 4-dinitronaphthalene (Veselý and Dvořák, *Bull. Soc. chim.*, 1923, **33**, 326). That the dinitrated product has the constitution 1 : 4 : 6-trinitro-*p*-toluenesulphon-2-naphthalide follows from its diazotisation, and decomposition of the diazonium sulphate by steam, to give a new dinitronaphthol (cf. Hodgson and Birtwell, J., 1943, 468) which differs from both 4 : 5- and 4 : 8-dinitro-1-naphthol and must therefore be 4 : 6-*dinitro*-1-*naphthol*, since nitration of 1 : 4-dinitro-*p*-toluenesulphon-2-naphthalide in position 7 would be contrary to all experience of substitution in naphthalene derivatives (cf. Robinson and Thompson, J., 1932, 2015, on the transmission of effects between the 2- and the 6-position; Bell, J., 1932, 2732; Veselý and Jakeš, *Bull. Soc. chim.*, 1923, **33**, 955). 4-Nitroaceto-2-naphthalide resisted nitration in glacial acetic acid solution with fuming nitric acid (*d* 1·52) at — 5° and with concentrated nitric acid (*d* 1·42) at 90°, in marked contrast to the ease of substitution shown by the *p*-toluenesulphonyl derivative; this behaviour recalls the analogous experience of Bell (J., 1928, 2779), who found that 5 : 4′-dinitro-2-acetamidodiphenyl could be recovered unchanged after solution in fuming nitric acid, whereas 4′-nitro-2-*p*-toluenesulphonamidodiphenyl under gentle conditions of nitration yielded the 3 : 5 : 4′-trinitro-derivative.

Bell (J., 1929, 2787) records that *o*- and *p*-nitroaniline and 1 : 8-dinitro-2-naphthylamine readily give disulphonamido-derivatives with *p*-toluenesulphonyl chloride, whereas the mono-*p*-toluenesulphonyl derivatives of aniline and β-naphthylamine show little tendency to react with a further molecule of this reagent. It is now found that 4-nitro-2-naphthylamine not only reacts with two equivalents of *p*-toluenesulphonyl chloride, but that even with one equivalent a certain amount of the disulphonamido-derivative is obtained. The facile reactions of 4-nitro-2-naphthylamine compared with those of β-naphthylamine recall the abnormal behaviour of 4-nitro-2-naphthol compared with that of β-naphthol (Morgan and Evens, J., 1919, **115**, 1126).

Experimental.

4-*Nitro*-p-*toluenesulphon*-2-*naphthalide*.—An intimate mixture of 4-nitro-2-naphthylamine (3·8 g.) and *p*-toluenesulphonyl chloride (4 g.) was stirred for 3 hours with boiling water, maintained slightly alkaline by additions of sodium carbonate. The solid was collected and treated with hot aqueous sodium hydroxide (5%) to extract 4-*nitro*-p-*toluenesulphon*-2-*naphthalide* (5 g.), which was reprecipitated by acidification and crystallised from chloroform, forming pale orange parallelepipeds, m. p. 145° (Found : S, 9·2. $C_{17}H_{14}O_4N_2S$ requires S, 9·4%). The insoluble residue from the alkali extraction was 4-*nitrodi*-p-*toluenesulphon*-2-*naphthalide*. When the above procedure was repeated with double the amount of *p*-toluenesulphonyl chloride (9 g.), the buff crystalline residue of the ditoluenesulphonyl product separated from glacial acetic acid in pale straw-coloured, almost colourless, rhombs (9·0 g.), m. p. 215° (Found : S, 12·7. $C_{24}H_{20}O_6N_2S_2$ requires S, 12·9%).

Mononitration of 4-*Nitro*-p-*toluenesulphon*-2-*naphthalide*.—Nitric acid (0·5 c.c., *d* 1·42) was stirred cautiously into a solution of the naphthalide (2·6 g.) in glacial acetic acid (10 c.c.) at 46°; the temperature rose to 70° and 1 : 4-*dinitro*-p-*toluenesulphon*-2-*naphthalide* separated, on cooling, in small yellow crystals. These were washed with glacial acetic acid, methyl alcohol, and ligroin and recrystallised from glacial acetic acid, forming clusters of pure lemon rhombs, m. p. 150° (Found : N, 10·8. $C_{17}H_{13}O_6N_3S$ requires N, 10·9%).

1 : 4-*Dinitronaphthalene*.—Dissolution of 1 : 4-dinitro-*p*-toluenesulphon-2-naphthalide (2 g.) in sulphuric acid (10 c.c., *d* 1·84) by stirring below 10° brought about hydrolysis to the amine, and subsequent addition of sodium nitrite (0·4 g.) in sulphuric acid (6 c.c., *d* 1·84) followed by stirring of the mixture gradually into glacial acetic acid (30 c.c.) below 20°, with continued stirring for 30 minutes, secured complete diazotisation. The solution of the diazonium salt was added to a stirred suspension of red cuprous oxide (1·5 g.) in methyl alcohol (50 c.c.) and, when decomposition had ceased, the mixture was poured into ice-water (300 g.). The precipitated 1 : 4-dinitronaphthalene was washed with water and extracted in hot ethyl alcohol, from which it crystallised (charcoal) in long yellow needles (1·3 g.), m. p. 134° (m. p.'s between 129° and 133·5° are given in the literature) (Found : N, 12·9. Calc. : N, 12·8%). In acetone solution it gave no colour with aqueous sodium hydroxide or with alcoholic potash, unlike the 1 : 3-isomeride, which gives magenta and blood-red colours respectively.

Dinitration of 4-*Nitro*-p-*toluenesulphon*-2-*naphthalide*.—Nitric acid (0·6 c.c., *d* 1·5) was stirred cautiously into a solution of the naphthalide (2·0 g.) in glacial acetic acid (20 c.c.) at 60°, and the temperature gradually raised to 80°;

nitration then occurred. The 1 : 4 : 6-*trinitro*-p-*toluenesulphon*-2-*naphthalide* (1·7 g.) formed separated on cooling; after being washed with glacial acetic acid, methyl alcohol, and ligroin, it crystallised from glacial acetic acid in a mass of yellow needles resembling shot silk, m. p. 194° (Found : N, 12·9. $C_{17}H_{12}O_8N_4S$ requires N, 13·0%).

4 : 6-*Dinitro*-1-*naphthol*.—1 : 4 : 6-Trinitro-*p*-toluenesulphon-2-naphthalide (1·5 g.) was dissolved in sulphuric acid (15 c.c., *d* 1·84) below 10°, sodium nitrite (0·3 g.) in sulphuric acid (5 c.c.) added, and the mixture stirred dropwise into glacial acetic acid (60 c.c.) below 20°, agitation being continued for 20 minutes. After addition of ice (300 g.), steam was passed through the mixture, and the hot liquid filtered, cooled, and extracted with chloroform to remove the 4 : 6-*dinitro*-1-*naphthol*. This was extracted from the chloroform by 5% aqueous sodium hydroxide, precipitated by acidification, and crystallised from methyl alcohol (charcoal), forming fine yellow needles, m. p. 240° (depressed by 4 : 5- and 4 : 8-dinitro-1-naphthol) (Found : N, 11·7. $C_{10}H_6O_5N_2$ requires N, 11·9%).

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