CCCLXXV.—*The Nitration of β-Naphthylamine.*

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NITRATION of β-naphthylamine in sulphuric acid solution furnishes a mixture of the 5- and the 8-mononitro-derivative (Friedländer and Szymanski, *Ber.*, 1892, **25**, 2078), nitration of aceto-β-naphthalide gives first a mixture of 1-, 6-, and 8-mononitro-derivatives and then a mixture of 1 : 5- and 1 : 8-dinitro-derivatives (Jacobson, *Ber.*, 1881, **14**, 805; Veselý and Jakes, *Bull Soc. chim.*, 1923, **33**, 942), and nitration of *p*-toluenesulphon-β-naphthalide gives first the 1-nitro-derivative and then most probably the 1 : 6-dinitro-derivative (Morgan and Micklethwait, J., 1912, **101**, 148).

Two interesting points emerge from these results, namely, the marked difference in orienting influence of the *p*-toluenesulphonamido- and the acetamido-group and the failure of either of these groups to direct a substituent into the 3-position. The difference in orienting influence of the two groups has been discussed previously (J., 1928, 2771), but in all those examples the *p*-toluenesulphonamido-group was sufficiently powerful to introduce two substituents in the *o*-positions to it, the behaviour being identical with that of the hydroxyl group.

The nitration of β-naphthol is a complex action and has been worked out only as far as the 1 : 6-dinitro-derivative (Wallach and Wichelhaus, *Ber.*, 1870, **3**, 846; Schmidt, *Ber.*, 1900, **33**, 3246); the less powerfully orienting methoxy- and ethoxy-derivatives, however, can be converted into the 1 : 6 : 8-trinitro-compounds (Staedel, *Annalen*, 1883, **217**, 171).

It appeared of interest, therefore, to examine the nitration of several *p*-toluenesulphon-β-naphthalides to see if in any circumstances groups could be introduced into both the 1- and the 3-position.

Morgan and Micklethwait's results with *p*-toluenesulphon-β-naphthalide were confirmed. A uniform dinitro-derivative was produced which showed no tendency towards further nitration. Its constitution as the 1 : 6-dinitro-derivative was confirmed by hydrolysis and acetylation, the product being identical with that obtained by the nitration of 6-nitroaceto-β-naphthalide. No difficulty was encountered in the isolation of 1 : 6-*dinitroaceto*-β-*naphthalide*, a compound which had been overlooked by previous workers, from the products of nitration of aceto-β-naphthalide. Similar results were obtained with the *p*-toluenesulphonyl derivatives of 5-nitro- and 8-nitro-β-naphthylamines. Nitration occurred in the 1-position and the products were fairly resistant to further

nitration. In order to use more powerful conditions of nitration, m-*nitrobenzenesulphon*-β-*naphthalide* was prepared and converted into the 1 : 6-*dinitro*-derivative, which could be easily nitrated to give a trinitro-compound. This, however, proved to be the 1 : 6 : 8-*trinitro*-derivative, for it was identical with the trinitro-compound obtained by the vigorous nitration of m-*nitrobenzenesulphon*-8-*nitro*-β-*naphthalide*. Therefore, even the toluenesulphonamido-group is unable to direct a group into the 3-position of β-naphthylamine.

EXPERIMENTAL.

Nitration of p-*Toluenesulphon*-β-*naphthalide*.—To this compound (20 g.) in acetic acid (200 c.c.), nitric acid (*d* 1·5; 15 c.c.) in acetic acid (15 c.c.) was added. The liquid filled with crystals of the 1 : 6-dinitro-derivative, m. p. 204° after recrystallisation from pyridine. It was readily converted, by solution in cold sulphuric acid (4 parts), into the corresponding base, which was precipitated by pouring the solution on ice and formed a bright yellow powder, m. p. 245° after recrystallisation from pyridine. The base (10 g.) was warmed for ½ hour with acetic anhydride (100 c.c.) containing sulphuric acid (1 c.c.), the cooled solution poured into water, and the precipitate collected and dried. Fractional crystallisation from acetone separated it into a more soluble *diacetyl* derivative, which formed long needles, m. p. 185° (Found: C, 52·8, 53·2; H, 3·7, 3·5. $C_{14}H_{11}O_6N_3$ requires C, 53·0; H, 3·5%), and a less soluble product, m. p. 230° after recrystallisation from pyridine, acetic acid, acetone, or benzene. This product had the properties of a *monoacetyl* derivative, for it could be hydrolysed by alcoholic hydrochloric acid, 1 : 6-dinitro-β-naphthylamine being regenerated, and it could be acetylated by boiling acetic anhydride to give the diacetyl derivative (above). No explanation could be found for the anomalous combustion result (Found: C, 53·2; H, 3·5. $C_{12}H_9O_5N_3$ requires C, 55·1; H, 3·4%).

Dinitration of Aceto-β-*naphthalide*.—The compound was mononitrated by the method of Veselý and Jakes (*loc. cit.*). 4 G. of the more soluble material (a mixture of 6- and 8-nitroaceto-β-naphthalides) were added slowly to nitric acid (*d* 1·5; 10 c.c.). After ½ hour the mixture was diluted with acetic acid (10 c.c.) and the liquid was filtered from the precipitated 1 : 8-dinitroaceto-β-naphthalide and diluted with water. The solid then precipitated had, after recrystallisation from pyridine, m. p. 230°, alone or mixed with 1 : 6-dinitroaceto-β-naphthalide (above) (Found: C, 52·6, 52·8; H, 3·4, 3·3%).

Nitration of p-*Toluenesulphon*-5-*nitro*-β-*naphthalide*.—This *compound* was prepared by the interaction of 5-nitro-β-naphthylamine

(Friedländer and Szymanski, *loc. cit.*) and *p*-toluenesulphonyl chloride in dry pyridine, and crystallised from acetic acid in stellate masses, m. p. 158° (Found: C, 59·9; H, 4·2. $C_{17}H_{14}O_4N_2S$ requires C, 59·6; H, 4·1%). To 4 g., dissolved in acetic acid (40 c.c.), nitric acid (*d* 1·5; 4 c.c.) in acetic acid (4 c.c.) was added. On cooling, the liquid filled with crystals of p-*toluenesulphon*-1 : 5-*dinitro*-β-*naphthalide*, m. p. 182° after recrystallisation from acetic acid (Found: C, 53·0; H, 3·4. $C_{17}H_{13}O_6N_3S$ requires C, 52·8; H, 3·4%). The constitution of this compound was proved by hydrolysis. 2 G. were dissolved in sulphuric acid (6 c.c.) and the solution was poured into water. The precipitated 1 : 5-dinitro-β-naphthylamine, after recrystallisation from alcoholic pyridine, formed needles, m. p. 191° (Veselý and Jakes, *loc. cit.*).

Nitration of *p*-toluenesulphon-8-nitro-β-naphthalide by the same method gave p-*toluenesulphon*-1 : 8-*dinitro*-β-*naphthalide*, m. p. 221° (decomp.) (Found: C, 53·1; H, 3·5. $C_{17}H_{13}O_6N_3S$ requires C, 52·8; H, 3·4%), identified by hydrolysis to 1 : 8-dinitro-β-naphthylamine. p-*Toluenesulphon*-8-*nitro*-β-*naphthalide*, prepared from 8-nitro-β-naphthylamine, crystallised from acetic acid in needles, m. p. 139° (Found: C, 59·8; H, 4·0. $C_{17}H_{14}O_4N_2S$ requires C, 59·6; H, 4·1%).

m-*Nitrobenzenesulphon*-β-*naphthalide*, prepared by the interaction of *m*-nitrobenzenesulphonyl chloride and β-naphthylamine, crystallised from acetic acid in long needles, m. p. 167—169° (Found: C, 58·5; H, 4·0. $C_{16}H_{12}O_4N_2S$ requires C, 58·5; H, 3·7%). Nitrated in the usual way, this compound gave m-*nitrobenzenesulphon*-1 : 6-*dinitro*-β-*naphthalide*, which formed small needles, m. p. 252° (decomp.) after recrystallisation from acetic acid (Found: C, 46·0; H, 2·5. $C_{16}H_{10}O_8N_4S$ requires C, 45·9; H, 2·4%). This dinitro-derivative dissolved only very slowly in sulphuric acid to furnish 1 : 6-dinitro-β-naphthylamine, m. p. 246° (above).

Nitration of m-*Nitrobenzenesulphon*-1 : 6-*dinitro*-β-*naphthalide*.—3 G. were added slowly to nitric acid (*d* 1·5; 12 c.c.) and after ½ hour the solution was diluted with acetic acid (12 c.c.). The precipitated m-*nitrobenzenesulphon*-1 : 6 : 8-*trinitro*-β-*naphthalide* crystallised from acetic acid in almost colourless needles, m. p. 227° (Found: C, 41·2; H, 1·7. $C_{16}H_9O_{10}N_5S$ requires C, 41·4; H, 1·9%), and from pyridine in golden prisms, m. p. 212° (Found: C, 50·9; H, 3·0. $C_{16}H_9O_{10}N_5S, 2C_5H_5N$ requires C, 50·3; H, 3·1%). Hydrolysis with sulphuric acid gave 1 : 6 : 8-trinitro-β-naphthylamine, m. p. 300° (decomp.) after crystallisation from pyridine (van der Kam, *Rec. trav. chim.*, 1926, **45**, 564).

m-*Nitrobenzenesulphon*-8-*nitro*-β-*naphthalide*, prepared by the interaction of 8-nitro-β-naphthylamine and *m*-nitrobenzenesulphonyl

chloride in pyridine solution, crystallised from acetic acid in needles, m. p. 196° (Found : C, 51·3; H, 3·1. $C_{16}H_{11}O_6N_3S$ requires C, 51·5; H, 3·0%). This compound (3 g.) was added to nitric acid (*d* 1·5; 8 c.c.), and the resulting solution diluted with acetic acid. The precipitate was identical with the above-described *m*-nitrobenzenesulphon-1 : 6 : 8-trinitro-β-naphthalide.

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