155. *The Influence of the 5-Nitro-group on the Halogenation and Nitration of 5-Nitro-1-naphthylamine and of Some Related Naphthalides.*

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The 5-nitro-group favours halogenation and mercuration of 5-nitro-1-naphthylamine and some related naphthalides at the 2-position, and nitration at the 4-position.

5-NITRO-1-NAPHTHYLAMINE is readily monobrominated and monomercurated in the 2-position, but direct iodination in the presence of yellow mercuric oxide is unsatisfactory and the reaction of chlorine is very rapid and complicated. 5-Nitroaceto-1-naphthalide, however, was chlorinated simultaneously in the 2- and the 4-position and monochlorination was not detected. The restraining kationoid field effect of the 5-nitro-group thus promoted halogenation and mercuration at the 2-position. 5-Nitroaceto-1-naphthalide, however, was nitrated initially at the 4-position, and 5-nitro-*p*-toluenesulphon-1-naphthalide simultaneously at the 2- and the 4-position, even with nitric acid in amount sufficient for mononitration only (see Hodgson and Walker, J., 1934, 180, for the analogous nitration of *p*-toluenesulphon-1-naphthalide). That nitration favours 4-

rather than 2-substitution has analogy with the nitration of 1-nitronaphthalene itself, which occurs predominantly in the 8-position (Hodgson, *J. Soc. Dyers and Col.*, 1936, **52**, 369).

EXPERIMENTAL.

Chlorination of 5-*Nitroaceto*-1-*naphthalide*.—5-Nitro-1-naphthylamine (10 g.) was acetylated by boiling it for 10 mins. in a mixture of acetic anhydride (7 c.c.) and glacial acetic acid (100 c.c.), and the filtered solution was treated with chlorine on the boiling water-bath until crystals of 2 : 4-*dichloro*-5-*nitroaceto*-1-*naphthalide* began to separate (*ca.* 30 mins.). After cooling, the product (8 g.) was collected and washed with and crystallised from glacial acetic acid; it formed colourless needles, m. p. 235·5° (Found : N, 9·4. $C_{12}H_8O_3N_2Cl_2$ requires N, 9·4%). Hydrolysis with boiling 50% sulphuric acid (80 c.c.) and ethyl alcohol (100 c.c.) gave 2 : 4-*dichloro*-5-*nitro*-1-*naphthylamine* (5·6 g.), which crystallised from aqueous ethyl alcohol in bright orange needles, m. p. 116·5° (Found : N, 11·1. $C_{10}H_6O_2N_2Cl_2$ requires N, 10·9%).

2 : 4-*Dichloro*-5-*nitronaphthalene*.—A solution of the above amine (2 g.) in glacial acetic acid (15 c.c.) was stirred into nitrosylsulphuric acid (0·8 g. of sodium nitrite and 10 c.c. of sulphuric acid, *d* 1·84) below 20° (cf. Hodgson and Walker, J, 1933, 1620). After 15 mins., the diazo-solution was stirred into a suspension of cuprous oxide (1 g.) in ethyl alcohol (50 c.c.), the temperature being finally raised to 70°. When the cooled solution was poured into water (500 c.c.), 2 : 4-*dichloro*-5-*nitronaphthalene* (1·7 g.) separated as a brown solid which, twice crystallised from 80% aqueous acetone, formed almost colourless parallelepipeds, m. p. 116·5° (Found : Cl, 29·1. $C_{10}H_5O_2NCl_2$ requires Cl, 29·3%).

2-*Chloro*-5-*nitronaphthalene*, obtained by diazotisation of 5-nitro-2-naphthylamine in nitrosylsulphuric–glacial acetic acid (cf. Hodgson and Walker, *loc. cit.*) and subsequent treatment with cuprous chloride in concentrated hydrochloric acid, crystallised from aqueous acetone (charcoal) in colourless needles, m. p. 100·5° (Found : N, 6·9. $C_{10}H_6O_2NCl$ requires N, 6·7%).

Bromination of 5-*Nitro*-1-*naphthylamine*.—2-*Bromo*-5-*nitro*-1-*naphthylamine* was prepared by the gradual addition at 50° of 7 c.c. of a solution of bromine (1 c.c.) in dry chloroform (9 c.c.) to a well-stirred solution of 5-nitro-1-naphthylamine (3 g.) in dry chloroform. The precipitated hydrobromide was converted into the amine by grinding with 5% aqueous ammonia. It is necessary to use slightly less than the calculated amount of bromine for monobromination, otherwise dibromination takes place to some extent. 2-Bromo-5-nitro-1-naphthylamine crystallised from ethyl alcohol in bright orange-red, felted needles, m. p. 121·5° (Found: N, 10·65. $C_{10}H_7O_2N_2Br$ requires N, 10·5%). 2-*Bromo*-5-*nitroaceto*-1-*naphthalide* crystallised from aqueous acetic acid in cream needles, m. p. 139° (Found: N, 9·0. $C_{12}H_9O_3N_2Br$ requires N, 9·0%).

2-*Bromo*-5-*nitronaphthalene* was obtained by submitting 2-bromo-5-nitro-1-naphthylamine to the diazotisation–deamination procedure described above. From the extract of the solid product by boiling acetone, 2-bromo-5-nitronaphthalene separated on cooling; it crystallised from 90% acetone–10% ethyl alcohol (charcoal) in almost colourless needles or plates, m. p. and mixed m. p. with an authentic specimen prepared from 5-nitro-2-naphthylamine, 95·5° (Found : N, 5·6. $C_{10}H_6O_2NBr$ requires N, 5·5%). The mixed m. p. with 1-bromo-8-nitronaphthalene was 55—60°.

2 : 4-*Dibromo*-5-*nitro*-1-*naphthylamine*.—5-Nitro-1-naphthylamine (3 g.) was brominated as described above, 8 c.c. of the bromine solution being used. The hydrobromide which separated was collected and basified, and the product dried, dissolved in dry chloroform (15 c.c.), and stirred with 8 c.c. of the bromine solution, giving another precipitate of hydrobromide, which was washed with chloroform and converted into 2 : 4-*dibromo*-5-*nitro*-1-*naphthylamine* (3·2 g.); this crystallised from aqueous acetone in orange plates, m. p. 159·5° (Found : Br, 45·9. $C_{10}H_6O_2N_2Br_2$ requires Br, 45·9%).

2 : 4-*Dibromo*-5-*nitroaceto*-1-*naphthalide* crystallised from aqueous acetic acid in white needles, m. p. 230·5° (decomp.) (Found : N, 7·4. $C_{12}H_8O_3N_2Br_2$ requires N, 7·2%).

Mercuration of 5-*Nitro*-1-*naphthylamine*.—Hot solutions of 5-nitro-1-naphthylamine (8 g.) in glacial acetic acid (60 c.c.) and of mercuric acetate (14 g.) in glacial acetic acid (30 c.c.) were mixed and, after the reaction abated, heated for 3 hours on the water-bath; after cooling, the 5-*nitro*-1-*naphthylamine*-2-*mercuriacetate* was washed with and crystallised from glacial acetic acid, forming light brown needles or plates, m. p. above 400° (Found : Hg, 44·6. $C_{12}H_{10}O_4N_2Hg$ requires Hg, 44·9%).

2-*Iodo*-5-*nitro*-1-*naphthylamine*.—The above mercuriacetate (5 g.) was made into a paste with water, stirred into a solution of iodine (2·9 g.) in boiling aqueous potassium iodide, and heated on the water-bath for 1 hour. The solid obtained was washed successively with water, dilute aqueous sodium thiosulphate, and water (yield, 3·3 g.) and crystallised twice from glacial acetic acid, giving deep red needles, m. p. 121·5—122·5° (Found : N, 9·0. $C_{10}H_7O_2N_2I$ requires N, 8·9%).

2-*Iodo*-5-*nitroaceto*-1-*naphthalide*, obtained by heating the above amine (3·9 g.) with acetic anhydride (8 c.c.) and glacial acetic acid (100 c.c.) for 2 hours on the water-bath, was precipitated (3·1 g.) with water and crystallised twice from aqueous acetic acid, giving almost colourless needles, m. p. 169·5° (Found: I, 34·8. $C_{12}H_9O_3N_2I$ requires I, 35·5%).

2-*Iodo*-5-*nitronaphthalene*.—A diazotised solution of 2-iodo-5-nitro-1-naphthylamine (3 g.) (Hodgson and Walker's procedure, *loc. cit.*) was run into absolute ethyl alcohol (125 c.c.) and heated on the water-bath for 1 hour; the alcohol was then removed, and excess of water added to precipitate the 2-iodo-5-nitronaphthalene. This was boiled with alcohol (charcoal) (125 c.c.), reprecipitated by water, and crystallised from ether and aqueous alcohol, giving almost colourless plates or needles having a very pale purple tint, m. p. 91·5° (Chudözilov, *Chem. Listy*, 1925, **191**, 187, gives m. p. 89—90°) (Found : I, 42·0. Calc. : I, 42·3%). Yield, 1·3 g.

1 : 2-*Di-iodo*-5-*nitronaphthalene* was prepared from 2-iodo-5-nitro-1-naphthylamine (2·5 g.), a diazotised solution of which, after treatment with urea, was stirred into saturated aqueous potassium iodide (40 c.c.) at 15°. After an hour, the mixture was diluted with water, and the precipitate (3·2 g.) crystallised once from 90% formic acid and twice from pyridine, forming small, deep brown plates, m. p. 132·5° (Found : I, 59·5. $C_{10}H_5O_2NI_2$ requires I, 59·7%).

Nitration of 5-*Nitroaceto*-1-*naphthalide*.—The nitration is described in D.R.-P. 145,191 as giving 4 : 5-dinitroaceto-1-naphthalide. This constitution has now been confirmed by hydrolysis of the product to 4 : 5-dinitro-1-naphthylamine, diazotisation, and deamination by cuprous oxide–ethyl alcohol to give 1 : 8-dinitronaphthalene, m. p. and mixed m. p. with an authentic sample 168·5°; mixed m. p. with authentic 1 : 6-dinitronaphthalene (m. p. 163·5°), 123·5°.

5-*Nitro*-p-*toluenesulphon*-1-*naphthalide*.—5-Nitro-1-naphthylamine (7 g.) was refluxed for 1 hour with *p*-toluenesulphonyl chloride (10 g.) in pyridine (30 c.c.), and the mixture poured into dilute hydrochloric acid (1 : 1). The precipitated 5-*nitro*-p-*toluenesulphon*-1-*naphthalide* (11 g.), crystallised three times from dilute alcohol (charcoal), formed pale cream plates, m. p. 171° (Found : N, 8·4. $C_{17}H_{14}O_4N_2S$ requires N, 8·5%).

2 : 4 : 5-*Trinitro*-p-*toluenesulphon*-1-*naphthalide* was prepared by nitrating the above compound (3 g.) in glacial acetic acid (25 c.c.) with 2 c.c. of a solution of nitric acid (4·25 c.c., *d* 1·5) in glacial acetic acid (5·75 c.c.), and heating the mixture on the water-bath for 5 mins. On cooling, the compound separated in cream needles (2·5 g.), m. p. 206° (decomp.) after recrystallisation from glacial acetic acid (Found : N, 12·9. $C_{13}H_{14}O_8N_4S$ requires N, 12·9%).

2 : 4 : 5-*Trinitro*-1-*naphthylamine*, obtained by hydrolysis of the above naphthalide (2·5 g.) with sulphuric acid (8 c.c., *d* 1·84) at 50—60°, the orange-brown solution being poured on ice, crystallised from aqueous pyridine in golden-yellow plates, m. p. 310° (Rindl, J., 1913, **103**, 1915, gives m. p. 305°, and Talen, *Rec. Trav. chim.*, 1928, **47**, 355, gives m. p. 310°) (Found : N, 20·5. Calc. : N, 20·2%).

The authors thank I.C.I. (Dyestuffs) Ltd. for gifts of chemicals.

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[*Received, July* 11*th*, 1942.]