103. *The Influence of the 6-Nitro-group on the Halogenation, Nitration, Mercuration, and Diazo-coupling of 6-Nitro-1-naphthylamine and of Some Related Naphthalides.*

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The 6-nitro-group favours halogenation, nitration, mercuration, and diazo-coupling at the 4-position in 6-nitro-1-naphthylamine and related naphthalides.

In many of the reactions of 6-nitro-1-naphthylamine, *e.g.*, bromination, nitration, mercuration, and diazo-coupling, the 4-position is found to be so much more reactive than the 2-position, that monosubstitution by electrophilic (kationoid) reagents occurs in that position exclusively. These results are in accord with the deductions of Robinson and Thompson (J., 1932, 2015; cf. also Bell, *ibid.*, p. 2732) which indicate that electronic effects (in this case inhibiting effects) are readily transmitted from the 6- to the 2- rather than to the 4-position, whereas the nitration of 1-nitro-*p*-toluenesulphon-2-naphthalide in the 6-position is an example of an activating effect. In this respect, therefore, 6-nitro- differs from the isomeric 5-nitro-1-naphthylamine, whose reactivity in the 2-position towards some electrophilic reagents other than nitric acid is probably due to the inhibiting effect on the 4-position of the kationoid nitro-group in the 5-position (Hodgson and Turner, J., 1942, 723).

The nitration of 5-nitroaceto-1-naphthalide in the 4-position must be regarded as anomalous and analogous to the predominant 8-nitration of nitronaphthalene itself (Hodgson, *J. Soc. Dyers Col.*, 1936, **52**, 369), whereas the nitration of 6-nitroaceto-1-naphthalide gives a mixture of 2 : 6- and 4 : 6-dinitroaceto-1-naphthalides in the ratio of *ca.* 1 : 5, determined as described on p. 393.

Like the 5-nitro-isomeride, 6-nitroaceto-1-naphthalide is chlorinated simultaneously in the 2- and the 4-position, monochlorination not being detectable, but 6-nitro-1-naphthylamine, unlike its 5-isomeride, is monobrominated exclusively in the 4-position. The authenticity of 4-*bromo*-6-*nitro*-1-*naphthylamine* was established by its conversion into 1 : 4-*dibromo*-6-*nitronaphthalene*, which in turn was oriented by its difference from the only possible alternative, 1 : 2-*dibromo*-6-*nitronaphthalene*, prepared from 1-*bromo*-6-*nitro*-p-*toluenesulphon*-2-*naphthalide* by hydrolysis, diazotisation of the amine produced, and introduction of bromine by the Sandmeyer reaction. The 1-bromo-compound was prepared by nitration of 1-bromo-*p*-toluenesulphon-2-naphthalide, made according to Consden and Kenyon (J., 1935, 1595), and that the nitro-group entered the 6-position was confirmed by hydrolysis to the amine and deamination to form 1-*bromo*-6-*nitronaphthalene*.

4-*Bromo*-6-*nitro*-1-*naphthylamine* was deaminated to give 8-*bromo*-2-*nitronaphthalene*, which was different from the monobromonitronaphthalene prepared but not identified by Braun, Hahn, and Seemann (*Ber.*, 1922, **55**, 1697) by monobromination of 2-nitronaphthalene, but now identified as 5-bromo-2-nitronaphthalene, since it is identical with the product obtained by replacement of the amino-group in 6-nitro-1-naphthylamine by bromine (Sandmeyer reaction).

Like its 5-nitro-isomeride (Hodgson and Turner, *loc. cit.*), 6-*nitro*-p-*toluenesulphon*-1-*naphthalide* is nitrated simultaneously at the 2- and the 4-position, even with nitric acid in amount insufficient for mononitration, and the 2 : 4 : 6-*trinitro*-compound is hydrolysed to 2 : 4 : 6-*trinitro*-1-*naphthylamine*.

The 4-mercuration of 6-nitro-1-naphthylamine was established by conversion of the 6-*nitro*-1-*naphthylamine*-4-*mercuriacetate* into 1-*bromo*-4-*iodo*-6-*nitronaphthalene*, which was different from an authentic specimen of the 2-*iodo*-analogue prepared from 1-*bromo*-6-*nitro*-p-*toluenesulphon*-2-*naphthalide* by hydrolysis and replacement of the amino-group by iodine.

Finally, diazotised *p*-toluidine coupled with 6-nitro-1-naphthylamine in the 4-position, as shown by the formation of a stable hydrochloride and by ready diazotisation of the amino-group and subsequent coupling of the diazonium compound with resorcinol, an ease of reactivity unknown in *o*-aminoazo-compounds.

Experimental

All m. p.'s are corrected.

6-Nitro-1-naphthylamine was prepared according to Hodgson and Turner (this vol., p. 318). Its *picrate* crystallised from ethyl alcohol in pale yellow prisms, m. p. 197° (Found : N, 17·1. $C_{10}H_8O_2N_2,C_6H_3O_7N_3$ requires N, 16·8%).

Acylation of 6-*Nitro*-1-*naphthylamine.*—6-*Nitroformo*-1-*naphthalide*, from the amine and formic acid, crystallised from methyl alcohol (charcoal) in cream needles, m. p. 193° (Found : N, 12·65. $C_{11}H_8O_3N_2$ requires N, 12·95%).

6-*Nitro*-p-*toluenesulphon*-1-*naphthalide* was obtained by grinding the nitro-amine (1·5 g.) with *p*-toluenesulphonyl chloride (2·0 g.), and heating the mixture on the water-bath for 1½ hrs. with acetone (7 c.c.) and water (30 c.c.), sodium carbonate being added as required. The solid was filtered off, washed with water, extracted with hot 4% aqueous sodium hydroxide (175 c.c.), and the filtered extract treated with carbon dioxide to give the naphthalide (2·15 g.), which crystallised from ethyl alcohol in slender, colourless needles, m. p. 205·5° (Found : N, 8·6. $C_{17}H_{14}O_4N_2S$ requires N, 8·55%). The insoluble residue from the extraction was 6-*nitrodi*-p-*toluenesulphon*-1-*naphthalide*, which crystallised from acetone in colourless prisms, m. p. 204·5—205·5° (sinters at 192°) (Found : N, 5·8. $C_{24}H_{20}O_6N_2S_2$ requires N, 5·65%).

6-*Nitronaphthyl*-1-*maleamic acid.* A solution of 6-nitro-1-naphthylamine (1·0 g.) and maleic anhydride (0·6 g.) in chloroform (15 c.c.) was boiled for ½ min., a trace of tar removed, and the filtrate allowed to cool; the resulting yellow 6-*nitronaphthyl*-1-*maleamic acid* (0·7 g.) crystallised from ethyl acetate–ethylene dichloride (equal vols.) in cream microneedles, m. p. 181° (Found : N, 9·6. $C_{14}H_{10}O_5N_2$ requires N, 9·8%), readily soluble in alkalis and reprecipitated by acids.

Replacement of the Amino-group by Halogen.—1-*Chloro*-6-*nitronaphthalene.* A solution of 6-nitro-1-naphthylamine (1·0 g.) in glacial acetic acid (10 c.c.) was stirred below 20° into one of sodium nitrite (0·6 g.) in sulphuric acid (5 c.c., *d* 1·84), the mixture kept for 15 mins., and then poured into a cold solution of cuprous chloride (3 g.) in hydrochloric acid (30 c.c., *d* 1·16); after an hour, the mixture was diluted with water, the precipitate filtered off, dried, and extracted

with acetone, and the decolorised (charcoal) extract evaporated to 5 c.c., and treated with ice. The crystalline precipitate of 1-*chloro*-6-*nitronaphthalene*, recrystallised from aqueous methyl alcohol and then from aqueous ethyl alcohol, formed cream needles, m. p. 118—120° (Found: N, 6·8. $C_{10}H_6O_2NCl$ requires N, 6·7%).

1-*Bromo*-6-*nitronaphthalene* was obtained when 6-nitro-1-naphthylamine (1·0 g.) was ground with a mixture of hydrobromic acid (5 c.c., 60%), ice and water (40 g.), the resulting hydrobromide being diazotised by addition of sodium nitrite (0·7 g. in 5 c.c. of water) below 10°. The filtered solution of the diazonium salt was added to a solution of cuprous bromide (5 g.) in hydrobromic acid (60 c.c., 20%) at 60°; nitrogen was evolved during ½ hr., and the precipitate of 1-bromo-6-nitronaphthalene was then removed and crystallised first from acetone and then from aqueous acetone (charcoal), being obtained in very pale yellow (almost colourless) needles, m. p. 130·5—131° (Found: N, 5·75. $C_{10}H_6O_2NBr$ requires N, 5·55%).

1-*Iodo*-6-*nitronaphthalene* was formed when a solution of the nitroamine (1·0 g.) in hydrochloric acid (4 c.c., *d* 1·16) and water (25 c.c.) was diazotised (1·0 g.) at 0—5° with sodium nitrite (0·7 g. in 5 c.c. of water), and the solution of the diazonium salt filtered and treated with one of potassium iodide (5 g.) in the minimum quantity of water. After ½ hr. the black precipitate was removed and refluxed with ethyl alcohol (35 c.c.) and charcoal; the liquid was filtered hot, and on cooling, 1-iodo-6-nitronaphthalene was deposited in colourless needles, which were recrystallised from ethyl alcohol–acetone (9 : 1); m. p. 73° (Found: I, 42·1. $C_{10}H_6O_2NI$ requires I, 42·3%).

Chlorination of 6-*Nitroaceto*-1-*naphthalide.* A solution of 6-nitro-1-naphthylamine (3·0 g.) in glacial acetic acid (25 c.c.) was boiled with acetic anhydride (4 c.c.) for 10 mins., and the filtered solution treated with chlorine at 90° under reflux for ¾ hr. After being evaporated to 20 c.c., the cooled solution deposited (scratching), 2 : 4-*dichloro*-6-*nitroaceto*-1-*naphthalide*, which crystallised from glacial acetic acid in short, cream needles, m. p. 243° (Found: N, 9·6. $C_{12}H_8O_3N_2Cl_2$ requires N, 9·4%). This (1·1 g.) was heated under reflux with sulphuric acid (10 c.c., 50%) and ethyl alcohol (10 c.c.) for 1 hour; the red solution, from which the amine sulphate had already begun to crystallise, was cooled, diluted with water, and the red 2 : 4-*dichloro*-6-*nitro*-1-*naphthylamine* (0·85 g.) was twice crystallised from ethyl alcohol containing 20% of acetone, being obtained in orange-red, felted needles, m. p. 177—178° (Found: N, 11·0. $C_{10}H_6O_2N_2Cl_2$ requires N, 10·9%).

Monobromination of 6-*Nitro*-1-*naphthylamine.*—A solution of the amine (3·0 g.) in dry chloroform (70 c.c.) was vigorously stirred at −5° during the addition of a solution of bromine (0·75 c.c.) in dry chloroform (12·5 c.c.) during 10 mins.; after a further 30 mins.' stirring at −5°, the red-tinted precipitate of 4-bromo-6-nitro-1-naphthylamine hydrobromide (4·0 g.) was filtered off, washed with chloroform and dry ether, dried, and gradually hydrolysed by trituration with very dilute aqueous ammonia. The *base* was washed with water and dried in a vacuum; it crystallised from aqueous ethyl alcohol in red needles, m. p. 123—124° (Found: N, 10·8. $C_{10}H_7O_2N_2Br$ requires N, 10·5%).

1-*Bromo*-7-*nitronaphthalene.*—The foregoing base (2·55 g.), dissolved in glacial acetic acid (35 c.c.), was diazotised by addition below 20° to a solution of sodium nitrite (1·0 g.) in sulphuric acid (20 c.c., *d* 1·84), and added to a well-stirred suspension of finely divided yellow cuprous oxide (4·0 g.) in ethyl alcohol (70 c.c.) (cf. Hodgson and Turner, J., 1942, 748). This mixture was poured into water (600 c.c.) and kept for 2 days for the precipitate to become tangible; this was removed, extracted with acetone, the extract refluxed with norit, filtered, and allowed to crystallise by gradual addition of ice. When twice recrystallised from 90% alcohol containing 5% of acetone, 1-*bromo*-7-*nitronaphthalene* was obtained in cream needles, m. p. 104—105° (Found: N, 5·7. $C_{10}H_6O_2NBr$ requires N, 5·5%).

1 : 4-*Dibromo*-6-*nitronaphthalene.*—4-Bromo-6-nitro-1-naphthylamine (3·1 g.), dissolved in glacial acetic acid (35 c.c.), was diazotised as above, and the solution of the diazonium salt added to a cold solution of cuprous bromide (8·0 g.) in hydrobromic acid (80 c.c., 30%), and left overnight to complete decomposition. On dilution with water, the crude product was precipitated, removed, and extracted with acetone, the extract being decolorised (norit) and allowed to crystallise; 1 : 4-*dibromo*-6-*nitronaphthalene* (1·65 g.) was obtained in cream needles, m. p. 110° (Found: Br, 48·1. $C_{10}H_5O_2NBr_2$ requires Br, 48·4%).

6-*Nitronaphthalene*-1-*azo*-β-*naphthol* was formed when a solution of 6-nitro-1-naphthylamine (1·5 g.) in glacial acetic acid (20 c.c.) was diazotised by addition to a mixture of sodium nitrite (0·8 g.) in sulphuric acid (15 c.c., *d* 1·84) below 20°; after 20 mins. the solution of the diazonium compound was diluted by ice (100 g.), added to one of β-naphthol (1·2 g.) in 20% aqueous sodium hydroxide (165 c.c.) and water (90 c.c.) below 10°, the mixture heated on the water-bath for 15 mins., and the azo-compound (yield, almost theoretical) removed, and crystallised first from hot acetone and then from glacial acetic acid, forming deep red needles, m. p. 220° (Found: N, 12·2. $C_{20}H_{13}O_3N_3$ requires N, 12·2%).

Nitration of 1-*Bromo*-p-*toluenesulphon*-2-*naphthalide*: *Preparation of* 1 : 2-*Dibromo*-6-*nitronaphthalene.*—The naphthalide (5 g.), prepared according to Consden and Kenyon (J., 1935, 1595), was dissolved in glacial acetic acid (25 c.c.), treated at 30—40° with a solution of nitric acid (0·45 c.c., *d* 1·5) in glacial acetic acid (4·5 c.c.), then heated carefully on the water-bath at 50—60° for 15 mins. until crystals of 1-*bromo*-6-*nitro*-p-*toluenesulphon*-2-*naphthalide* appeared; the mixture was then cooled (with scratching) below 10°, and the crystals (2·1 g.) filtered off and washed with glacial acetic acid; they crystallised from acetone in cream prisms, m. p. 197—198° (Found: N, 6·75. $C_{17}H_{13}O_4N_2BrS$ requires N, 6·65%). This compound (3·0 g.) was hydrolysed to the free amine by dissolution in sulphuric acid (8 c.c., *d* 1·84) at 40°, and the solution cooled below 20°; sodium nitrite (0·8 g.) in sulphuric acid (5 c.c., *d* 1·84) was added, and the mixture diazotised by running it into glacial acetic acid (20 c.c.) below 20°. After 15 mins., the diazonium solution was added to one of cuprous bromide (7·5 g.) in hydrobromic acid (60 c.c., 25%), kept overnight, diluted with water (200 c.c.), and filtered; the precipitate was boiled with acetone, the extract cooled, and the resulting crystals of 1 : 2-*dibromo*-6-*nitronaphthalene* recrystallised from methyl alcohol–acetone (1 : 1), forming cream needles, m. p. 175° (Found: Br, 48·1. $C_{10}H_5O_2NBr_2$ requires Br, 48·4%).

Orientation of 1-*Bromo*-6-*nitro*-p-*toluenesulphon*-2-*naphthalide.*—The substance (3 g.) was hydrolysed and diazotised as above, and the solution of the diazonium salt run into a suspension of red cuprous oxide (8·0 g.) in methyl alcohol (40 c.c.); a vigorous evolution of nitrogen occurred, and the temperature rose to 60°. After dilution with water, the precipitate was refluxed with acetone (50 c.c.) for ½ hr., the extract decolorised (charcoal), filtered, evaporated to 8 c.c., and cooled, and the precipitated 1-bromo-6-nitronaphthalene recrystallised from methyl alcohol containing 30% of acetone; it formed long, pale yellow needles, m. p. 129·5° (Found: N, 5·7%), mixed m. p. with authentic sample (see above) 130°; mixed m. p. 105—116° with 1-bromo-3-nitronaphthalene (m. p. 131·5—132·5°) prepared from 3-nitro-1-naphthylamine (cf. Veselý and Chudozilov, *Chem. Listy*, 1925, **19**, 260, who give m. p. 128—129° for 1-bromo-3-nitronaphthalene).

2 : 4-*Dibromo*-6-*nitro*-1-*naphthylamine.*—6-Nitro-1-naphthylamine (0·7 g.) was monobrominated as above (bromine, 0·18 c.c.; chloroform, 11·6 c.c.), the 4-bromo-6-nitro-1-naphthylamine removed, washed, dried, redissolved in chloroform (50 c.c.), and brominated a second time exactly as before. The precipitated 2 : 4-dibromo-6-nitro-1-naphthylamine hydrobromide was removed, basified, and the free *base* crystallised from acetone, forming red, felted needles, m. p. 195° (Found: N, 8·4. $C_{10}H_6O_2N_2Br_2$ requires N, 8·1%).

Nitration of 6-*Nitroaceto*-1-*naphthalide.*—The finely divided substance (3·3 g.) was added gradually (15 mins.) to well-stirred nitric acid (25 c.c., *d* 1·5) below 5°, the stirring continued for 5 mins., the mixture poured on ice, and a small sample, which proved to be a mixture, crystallised from glacial acetic acid; m. p. 183·5° (darkens at 170·5°) (Found: N, 14·8. Calc. for a dinitroacetonaphthalide: N, 15·3%). The remainder of the precipitate (2·0 g.) was refluxed for

¾ hr. with a mixture of ethyl alcohol (20 c.c.) and 50% aqueous sulphuric acid (20 c.c.); the red solid (1·6 g.) deposited on cooling was filtered off, washed with aqueous ethyl alcohol, dried, and, after three crystallisations from ethyl alcohol containing 40% of acetone, obtained in scarlet prisms of 4 : 6-*dinitro*-1-*naphthylamine*, m. p. 178° (Found : N, 17·95. $C_{10}H_7O_4N_3$ requires N, 18·0%). Another sample of the crude red hydrolysed product (1·8 g.) was dissolved in glacial acetic acid (30 c.c.) and diazotised by addition below 20° to a solution of sodium nitrite (0·65 g.) in sulphuric acid (10 c.c., *d* 1·84); the diazo-solution was added to a suspension of cuprous oxide (3·0 g.) in methyl alcohol (35 c.c.), nitrogen being evolved and the temperature rising to 56°. When the evolution of nitrogen had ceased, a further quantity of cuprous oxide (3·0 g.) was added, the mixture stirred for 5 mins., poured into iced water (400 c.c.), and the precipitate filtered off, washed, dried, and refluxed for 1 hour with ethylene dichloride (50 c.c.). The filtered extract was evaporated to 5 c.c. (charcoal), filtered, diluted with ligroin, and the yellow precipitate (0·5 g.) crystallised three times from 90% acetic acid; pale orange needles (0·1 g.) of a mixture of 1 : 7- and 2 : 6-dinitronaphthalenes (m. p. 136—174°) were obtained (Found : N, 12·9. Calc. : N, 12·8%). This mixture was sublimed at 200—220°/10—15 mm., and the orange solid obtained was fractionally sublimed at 10—15 mm. as follows : (i) for 2 hrs., at 180°, giving a pale orange-yellow solid; (ii) at 200°, all but a few mg. of the solid being obtained as a bright orange-yellow compound. The residual few mg. were sublimed separately (iii) as stout orange needles of 2 : 6-dinitronaphthalene, m. p. 278°, mixed m. p. with an authentic specimen kindly supplied by Prof. W. P. Wynne, 278—279° (Chatt and Wynne, this vol., p. 35, give m. p. 279°). Sublimate (i) was resublimed at 165—170°/10—15 mm., and the first crop (ia) of very pale orange-yellow needles had m. p. 144—147·5°; the remainder (*ca.* 5%), collected at 175°, proved to be 2 : 6-dinitronaphthalene. Crop (ia) was resublimed as follows : the first crop collected during 5 mins. at 175° was rejected, and the main crop (*ca.* 70%) was collected at 160° during 2 hours as creamy-white needles of 1 : 7-dinitronaphthalene, m. p. 148—149°, raised to 156° by repeated sublimations (Veselý and Dvorák, *Bull. Soc. chim.*, 1923, **33**, 319, give m. p. 156°).

Further Nitration of 6-*Nitroaceto*-1-*naphthalide*.—The naphthalide (5·1 g.) was stirred into nitric acid (35 c.c., *d* 1·5) below 3°, the stirring continued for 5 mins., the mixture poured on ice (400 g.) and kept for 1 hour, and the precipitate (5·6 g.) filtered off, washed, and dried in a vacuum. It was hydrolysed by 2 hours' refluxing on the water-bath with ethyl alcohol (55 c.c.) and 50% sulphuric acid (55 c.c.); on cooling, a deep red solid (4·1 g.) consisting mainly of 4 : 6-dinitro-1-naphthylamine separated; the mother-liquors on dilution with ice gave an orange-yellow solid (0·37 g.), which crystallised from aqueous acetone in deep yellow needles of 2 : 6-*dinitro*-1-*naphthylamine*, m. p. 226·5—228·5° (Found : N, 17·35. $C_{10}H_7O_4N_3$ requires N, 18·0%). The crude 4 : 6-dinitro-compound was crystallised four times from ethyl alcohol containing 10% of acetone and deaminated, but the product was a mixture of 2 : 6- with 1 : 7-dinitronaphthalene as the chief constituent, from which the former was obtained by recrystallisation of the vacuum-sublimed product three times from 90% pyridine, once from glacial acetic acid, and finally from 90% pyridine; it crystallised in creamy-white needles, m. p. 274—275°, mixed m. p. with an authentic sample 277°.

Nitration of 6-*Nitro*-p-*toluenesulphon*-1-*naphthalide*.—This naphthalide (2·5 g.) was dissolved in glacial acetic acid (25 c.c.), and treated at 60° with 7·5 c.c. of a solution of nitric acid (1 c.c., *d* 1·5, in 9 c.c. of glacial acetic acid); the mixture was heated at 90° for 5 mins. and then allowed to cool, whereupon 2 : 4 : 6-*trinitro*-p-*toluenesulphon*-1-*naphthalide* set to a mass of fine cream needles (1·65 g.), which were filtered off, and washed with glacial acetic acid, methyl alcohol, and light petroleum; it crystallised from glacial acetic acid in cream needles, m. p. 172·5° (Found : N, 13·1. $C_{17}H_{12}O_8N_4S$ requires N, 12·9%). 2 : 4 : 6-*Trinitro*-1-*naphthylamine* was formed when the above naphthalide (1·25 g.) was stirred into cold sulphuric acid (5 c.c., *d* 1·84), the mixture heated at 40° for 5 mins., and poured on ice; the orange-red amine which separated (0·72 g.) crystallised from pyridine in deep yellow, felted needles, m. p. 301—304° (decomp. begins at *ca.* 280°) (Found : N, 20·1. $C_{10}H_6O_6N_4$ requires N, 20·15%).

Mercuration of 6-*Nitro*-1-*naphthylamine*.—The amine (5·0 g.), dissolved in boiling glacial acetic acid (30 c.c.), was added to a hot solution of mercuric acetate (8·6 g.) in glacial acetic acid (15 c.c.), and the mixture boiled for 5 mins., cooled, and filtered; the precipitate (8·5 g.) of 6-*nitro*-1-*naphthylamine*-4-*mercuriacetate* crystallised from glacial acetic acid (charcoal) in silvery-white prisms, m. p. above 400° (Found : Hg, 44·1. $C_{12}H_{10}O_4N_2Hg$ requires Hg, 44·9%).

4-*Iodo*-6-*nitro*-1-*naphthylamine* was obtained when the above mercuriacetate (2·5 g.), made into a paste with 20% aqueous potassium iodide (20 c.c.), was heated on the water-bath during addition of a solution of iodine (1·45 g.) in 20% aqueous potassium iodide (20 c.c.); after a further ½ hr.'s heating, the mixture was cooled, the crude 4-iodo-6-nitro-1-naphthylamine (0·75 g.) filtered off, washed with water and dilute sodium thiosulphate, and crystallised from aqueous alcohol containing 15% of acetone (charcoal), forming bright red needles, m. p. 175° (Found : N, 9·1; I, 40·0. $C_{10}H_7O_2N_2I$ requires N, 8·9; I, 40·4%).

The above amine (2·1 g.), dissolved in glacial acetic acid (10 c.c.), was diazotised by addition with stirring below 20° to a solution of sodium nitrite (0·7 g.) in sulphuric acid (3 c.c., *d* 1·84), and the cold diazo-solution added to one of cuprous bromide (3·0 g.) in 20% hydrobromic acid (60 c.c.); after an hour, the mixture was poured on ice, the crude 1-*bromo*-4-*iodo*-6-*nitronaphthalene* filtered off, dried in a vacuum, extracted with acetone (charcoal), and the extract concentrated; the resulting dull fawn-coloured solid was sublimed at 180—190°/10—15 mm., and the scaly yellow sublimate crystallised from acetone, forming lemon-yellow needles, m. p. 130·5—131·5° (Found : N, 3·8. $C_{10}H_5O_2NBrI$ requires N, 3·7%).

Synthesis of 1-*Bromo*-2-*iodo*-6-*nitronaphthalene*.—1-Bromo-6-nitro-*p*-toluenesulphon-2-naphthalide (3·0 g.) was hydrolysed and diazotised as previously described, excess of nitrous acid removed by urea, and the solution added to one of potassium iodide (30 g.) in water (50 c.c.); the temperature rose to 40°, and was taken to 50° to complete the reaction. Ice was then added, free iodine removed by dilute sodium thiosulphate, and the 1-*bromo*-2-*iodo*-6-*nitronaphthalene* (1·6 g.) filtered off, washed, and dried in a vacuum; it crystallised first from acetone and then from aqueous acetic acid (charcoal) in clusters of yellow needles, m. p. 193—194° (Found : N, 3·85. $C_{10}H_5O_2NBrI$ requires N, 3·7%).

Coupling of Diazotised p-*Toluidine with* 6-*Nitro*-1-*naphthylamine*.—*p*-Toluidine (1·71 g.) was heated with hydrochloric acid (6·5 c.c., *d* 1·16) and sufficient water to dissolve the hydrochloride when the mixture was hot. The cooled solution was diazotised by addition of sodium nitrite (1·2 g.) dissolved in a little water, excess of nitrous acid removed by urea, and the diazo-solution stirred gradually at −5° into a solution of 6-nitro-1-naphthylamine (3·0 g.) in ethyl alcohol (160 c.c.), the stirring being continued for ½ hr.; the mixture was then heated to 20°, and a slight excess of saturated aqueous sodium acetate added. The crude 6-*nitro*-4-p-*tolueneazo*-1-*naphthylamine* (3·05 g.) was filtered off, washed with water, dried at 50°, and crystallised from toluene, forming deep maroon boat-shaped crystals; from benzene it afforded very deep maroon clusters of micro-needles, m. p. 242·5° (Found : N, 18·2. $C_{17}H_{14}O_2N_4$ requires N, 18·3%). The *acetyl* derivative crystallised from glacial acetic acid (charcoal) in felted orange needles, m. p. 300—301° (Found : N, 16·3. $C_{19}H_{16}O_3N_4$ requires N, 16·1%).

6-*Nitro*-4-p-*tolueneazonaphthalene*-1-*azoresorcinol*.—The above aminoazo-compound (1·5 g.) was dissolved in glacial acetic acid (50 c.c.), hydrochloric acid (2·0 c.c., *d* 1·16) added at 8°, and then, gradually, solid sodium nitrite (0·5 g.). After 0·2 g. had been added, the temperature rose rapidly to 12° and was maintained there during the addition. The clear orange-red solution of the diazo-compound was stirred for ½ hr. and then added at 10° to a solution of resorcinol (0·7 g.) in 20% aqueous sodium hydroxide (225 c.c.), mixed with ice (200 g.). Coupling ensued and the mixture was kept for 2 hrs., then heated to 50°, and the dye (1·23 g.) removed, washed, and dried in a vacuum; it was obtained as a deep violet-black solid with a greenish-gold reflex, which was purified by repeated dissolution in hot cellosolve (20 c.c., charcoal)

and precipitation by light petroleum (100 c.c.) until no ash was left after ignition on platinum foil; m. p. >400° (Found: N, 16·8. Calc. for $C_{23}H_{17}O_4N_5$: N, 16·4%); the dye gave a deep blue colour with concentrated sulphuric acid in contrast to the behaviour of the previous monoazo-dye, which afforded an orange-pink colour.

Note.—Deaminations by Hodgson and Turner's cuprous oxide–alcohol method (J., 1942, 748) are best carried out with methyl alcohol (rather than with ethyl alcohol), the yields being improved and the formation of troublesome ester avoided.

The authors thank I.C.I. (Dyestuffs) Ltd. for several micro-analyses and for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, April 12th*, 1943.

NOTE.

Preparation of the Œstrogen β-Bromo-β-phenyl-αα-di-(p-ethoxyphenyl)ethylene. By WADIE TADROS and A. SCHÖNBERG.

THIS œstrogen, the remarkably prolonged action of which when given orally has been reported by Robson, Schönberg, and Tadros (*Nature*, 1942, **150**, 22; the name of the last author was inadvertently omitted in this publication) was prepared as follows: To the Grignard reagent prepared from magnesium (14 g.), benzyl chloride (85 g.), and ether (400 c.c.), 4 : 4′-diethoxybenzophenone (95 g.) was added, and after 2 hours' strirring, the solution was left overnight and then decomposed with cold aqueous ammonium chloride. Benzene–ether extracted *di-(p-ethoxyphenyl)benzylcarbinol*, which separated from petroleum (b. p. 100—110° or 100—150°) in colourless crystals, m. p. 124°, in almost theoretical yield (Found: C, 80·0; H, 7·0. $C_{24}H_{26}O_3$ requires C, 79·5; H, 7·2%). *β-Phenyl-αα-di-(p-ethoxyphenyl)ethylene*, obtained in almost theoretical yield by the vacuum distillation of the carbinol (50 g.) in presence of 1 drop of 20% sulphuric acid (the distillation was effective only when the substance, which turned violet on heating, became almost colourless), separated from alcohol in colourless crystals, m. p. 74° (Found: C, 83·6; H, 6·6. $C_{24}H_{24}O_2$ requires C, 83·7; H, 7·0%). *β-Bromo-β-phenyl-αα-di-(p-ethoxyphenyl)ethylene* was prepared by adding a solution of bromine (37 g.) in glacial acetic acid (50 c.c.) to a solution of the ethylenic compound (80 g.) in the same solvent (200 c.c.) and refluxing the mixture for 45 minutes. The bromo-compound, which separated on cooling, was recrystallised from glacial acetic acid, methyl alcohol, or alcohol, forming almost colourless or very pale yellow crystals, m. p. 97—98°. Yield, about 90% (Found: C, 67·9; H, 5·5; Br, 18·5. $C_{24}H_{23}O_2Br$ requires C, 68·1; H, 5·5; Br, 18·9%).—FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, April 16th*, 1943.]