388. *7-Nitro-1-naphthylamine. Part I. Its Preparation, Halogenation, and Diazo-coupling; and* 1 : 2 : 4 : *7-Tetrahalogenonaphthalenes.*

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7-Nitro-1-naphthylamine is best prepared by rearrangement of 1 : 2 : 3 : 4-tetrahydro-7-nitro-1-oxonaphthalene oxime acetate.[1] Diazo-coupling, chlorination, and bromination of the amine or its *N*-acetyl derivative are described. 1 : 2 : 4 : 7-Tetrachloro- and 1 : 2 : 4 : 7-tetrabromo-naphthalene have been prepared. The former is identical with the 1 : 2 : 7 : *x*-tetrachloronaphthalene described by Turner and Wynne.[2] Guareschi's tetrabromonaphthalene [3] is now unequivocally orientated as 1 : 2 : 4 : 6-tetrabromonaphthalene.

7-NITRO-1-NAPHTHYLAMINE was first prepared by Vesely and Dvorak [4] by partial reduction of 1 : 7-dinitronaphthalene (cf. Barltrop and MacPhee [5]) : the product was impure and the yield very low. Subsequently Schroeter [1] obtained it by re-arrangement of 1 : 2 : 3 : 4-tetrahydro-7-nitro-1-oxonaphthalene oxime acetate in hot acetic acid saturated with hydrochloric acid (the so-called Wolff aromatisation, see below). We have re-investigated both methods and find the latter much superior.

1 : 7-Dinitronaphthalene was reduced by Hodgson and Turner's method,[6] this being better than that of Vesely and Dvorak.[4] Although we obtained a 42% yield of 7-nitro-1-naphthylamine in this reaction, the overall yield from β-naphthylamine was only *ca.* 1%.

A mixture of 1 : 2 : 3 : 4-tetrahydro-7- and -5-nitro-1-oxonaphthalene, in which the former greatly predominates, is obtained by nitration of 1 : 2 : 3 : 4-tetrahydro-1-oxonaphthalene. Von Braun's method of nitration [7] is much better than that of Vesely and Stursa,[8] the latter being difficult to control and the yield only half that for the alternative method. A variety of techniques was employed in an endeavour to improve the conversion of the ketoxime into 7-nitro-1-naphthylamine, but none proved better than the original one of Schroeter, and our yield of amine could not be raised above 45%. The first paper [1a] claimed a 51% yield, and the patent [1b] 67%, but these yields were based on the product isolated as hydrochloride, which was almost certainly impure, and yields were not given for the pure amine. We investigated the effect of using a more polar medium and of acylating the oxime with more strongly electron-attracting groups. The oxime trifluoroacetate showed no appreciable difference in behaviour from the oxime acetate, and rearranged unsatisfactorily in trifluoroacetic acid. Failure also attended attempts to rearrange the oxime *p*-nitrobenzoate and to use Beringer and Ugelow's technique [9] with the acetate. The oxime itself could be rearranged in polyphosphoric acid but the yield was only 10% (cf. Horning and his co-workers [10]).

Whilst we made no attempt to investigate the rearrangement in detail there are points worth notice. The conversion of the oximes of unsaturated cyclic ketones into

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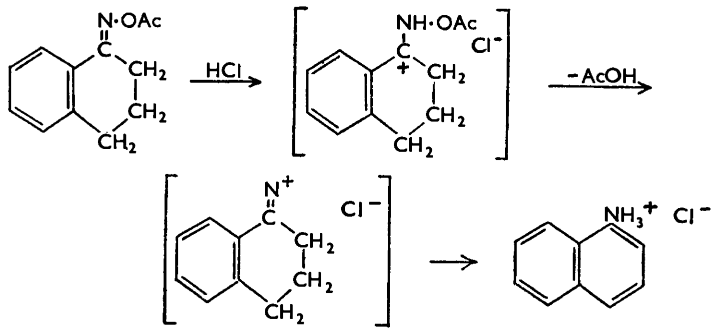
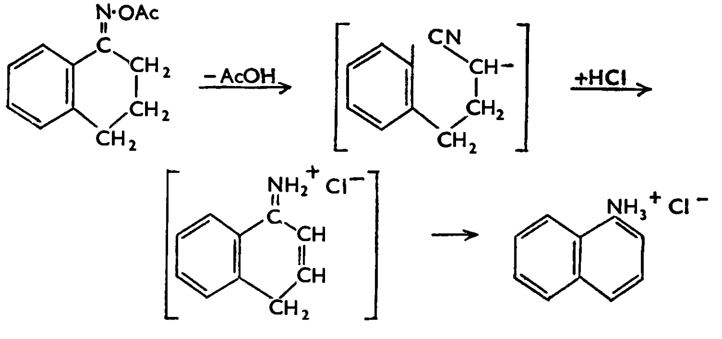
[1] Schroeter, (*a*) *Ber.*, 1930, **63**, 1308; (*b*) G.P. 563,627/1932.
[2] Turner and Wynne, *J.*, 1941, 243.
[3] Guareschi, *Gazzetta*, 1886, **16**, 146.
[4] Vesely and Dvorak, *Bull. Soc. chim. France.*, 1923, **33**, 319.
[5] Barltrop and MacPhee, *J.*, 1952, 638.
[6] Hodgson and Turner, *J.*, 1943, 318.
[7] von Braun, *Annalen*, 1926, **451**, 1.
[8] Vesely and Stursa, *Coll. Czech. Comm.*, 1933, **5**, 174.
[9] Beringer and Ugelow, *J. Amer. Chem. Soc.*, 1953, **75**, 2635.
[10] Horning, Stromberg, and Lloyd, *ibid.*, 1952, **74**, 5153.

aromatic amines by acidic reagents is often referred to as the Wolff aromatisation. Like those of many other named organic reactions [11, 12, 13] its title is historically inaccurate (the first example was described by Semmler [14] and there were several others reported before Wolff's); it is also confusing, there being also the "Wolff rearrangement" of diazoketones. If it must be named at all, this reaction should be called the Semmler aromatisation. There have been several investigations of the reaction [1, 10] but none can be regarded as really thorough: aspects such as the configuration of the oxime or its acylated derivatives, the effect of substituent groups in the nucleus (or nuclei for naphthalene derivatives), and the nature of the by-products (which may often be considerable) have been largely ignored. The reaction is closely related to the Beckmann rearrangement, which often (*e.g.*, with 1 : 2 : 3 : 4-tetrahydro-5 : 8-dimethyl-1-oxonaphthalene oxime acetate [1]) occurs as an alternative, and the same compound can undergo either when the nature of the acylating group is altered (*e.g.*, the toluene-*p*-sulphonyl derivative of 1 : 2 : 3 : 4-tetrahydro-1-oxonaphthalene oxime undergoes the Beckmann change in warm alcohol but the acetate is aromatised in acid [1]). Hence the annexed mechanism (A) seems reasonable. An alternative (B) (based on a suggestion by Dr. O. Brady) receives support from the work of Thorpe and Atkinson.[16] There is need for further investigation since the reaction is of value in obtaining difficultly accessible aromatic amines, *e.g.*, from phenanthrene,[1] quinoline,[17] and thiophen.[18]

(A)



(B)



Chlorination of *N*-acetyl-7-nitro-1-naphthylamine in hot acetic acid yielded successively 1-acetamido-4-chloro- and 1-acetamido-2 : 4-dichloro-7-nitronaphthalene; continued reaction (cf. Bell [19]) introduced no more chlorine, in contrast to the behaviour of *N*-acylated-β-naphthylamines or their substituted derivatives, where addition as well as

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[11] Bunnett, *Chem. Eng. News*, 1954, **32**, 4019.
[12] Ward, *Chem. and Ind.*, 1955, 68.
[13] Brooker, *ibid.*, p. 1261.
[14] Semmler, *Ber.*, 1892, **25**, 3352.
[15] Wolff, Gabler, and Heyl, *Annalen*, 1902, **322**, 5.
[16] Thorpe and Atkinson, *J.*, 1906, **89**, 1906; 1907, **91**, 1687.
[17] Johnson, Worock, and Buell, *J. Amer. Chem. Soc.*, 1949, **71**, 1901.
[18] Cheney and Pienning, *ibid.*, 1945, **67**, 729.
[19] Bell, *J.*, 1953, 3035.

substitution can occur. The monochloro-derivative was orientated by deamination to the known 1-chloro-6-nitronaphthalene, and the dichloro-compound by its conversion into 4-chloro-1-diazo-7-nitro-2-naphthol and by deamination of its reduction product (2 : 4-dichloro-1 : 7-naphthylenediamine) to the known 1 : 3-dichloronaphthalene. The dichloro-diamine was tetrazotised by Hodgson and Turner's method [20] and a subsequent Sandmeyer reaction gave 1 : 2 : 4 : 7-tetrachloronaphthalene, first reported by Claus and Miekle [21] who left little doubt as to its orientation. Turner and Wynne [2] obtained 1 : 2 : 7 : *x*-tetrachloronaphthalene (m. p. 144°) by treating 1 : 2 : 7-trichloronaphthalene-*x*-sulphonyl chloride with phosphorus pentachloride: our compound proved identical with this, thus orientating the latter and the chloride from which it was derived. Further, the 1 : 4 : 7 : *x*-tetrachloronaphthalene (m. p. 109°) also described by Turner and Wynne [2] was not identical with our compound.

Bromination of the *N*-acetyl derivative in boiling acetic acid afforded similar results, monohalogenation being exclusively at the 4-position and further substitution at the 2-position; the brominated compounds were orientated by methods similar to those used for the chloro-analogues.

7-Nitro-1-naphthylamine in cold chloroform gave the 2 : 4-dibromo-derivative, even with only 1 mol. of bromine. Use of the bromine–dioxan complex in dioxan also led to dibromination, though this method (Kosolapoff [22]) causes only monobromination of aniline and its derivatives. This emphasises again the greater reactivity of naphthalene compounds and indicates that Kosolapoff's method is of limited application. 1 : 2 : 4 : 7-Tetrabromonaphthalene (m. p. 164°) was obtained by a Sandmeyer reaction from tetrazotised 2 : 4-dibromo-1 : 7-naphthylenediamine. It differs from the tetrabromonaphthalene (m. p. 119—120°) which had been considered to be a 1 : 2 : 4 : 6- or 1 : 2 : 4 : 7-tetrasubstituted compound [3, 23, 24] and so it must be the former.

Reaction of 7-nitro-1-naphthylamine with diazotised *p*-nitroaniline in aqueous alcohol yielded 7-nitro-4-*p*-nitrophenylazo-1-naphthylamine only, the orientation following from its easy acetylation, failure to form a triazole on oxidation, and the ready diazotisation and subsequent coupling with β-naphthol. Coupling in the 2-position may have occurred to a minor extent but we made no special attempt to detect it by chromatography (cf. Turner [25] who investigated the diazo-coupling of α-naphthylamine and its derivatives); it is rendered unlikely anyway by the exclusive 4-substitution found with the more strongly electrophilic agents.

EXPERIMENTAL

Rearrangement of 1 : 2 : 3 : 4-*Tetrahydro*-7-*nitro*-1-*oxonaphthalene Oxime Acetate and Related Derivatives.*—(a) *Schroeter's method.*[1] Our oxime had m. p. 167—169° (Schroeter gives 150°). The yield of 7-nitro-1-naphthylamine (m. p. 110—120°) was 38—45%; recrystallised from ethanol, the amine had m. p. 132—133° (Schroeter gives m. p. 133—134°).

(b) *The oxime phenylcarbamate.* To the oxime (2·5 g.) in dry ether (50 c.c.) phenyl *iso*cyanate (1·5 g.) was added; after 10 min. on the water-bath the mixture was cooled, the precipitate collected, washed with ether (3·6 g., 91%; m. p. 196—199°), and suspended in ethanol (30 c.c.), and hydrogen chloride was passed in for 2 hr. at 90°. On cooling, 7-nitro-1-naphthylamine was deposited (yield after basification 22%).

(c) *Rearrangement of the oxime with polyphosphoric acid.* The oxime (1 g.) was dispersed in tetraphosphoric acid (20 g.) and heated at 95° for 20 min., then for a further 10 min. at 105°. Pouring the mixture into warm water (100 c.c.) gave a grey solid which was basified at 0° with aqueous ammonia. The product was dissolved in benzene and chromatographed on alumina with benzene–ethyl acetate (4 : 1; v/v) as eluant, yielding 7-nitro-1-naphthylamine (10%). Heating the reaction mixture at 180° for 5 min. yielded a black solid from which no amine could be obtained (cf. Horning [10]).

Reduction of 1 : 7-*Dinitronaphthalene.*—The procedure followed was similar to that of Hodgson and Turner [6] for 1 : 6-dinitronaphthalene. The yield of 7-nitro-1-naphthylamine was

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[20] Hodgson and Turner, *J.*, 1943, 68.
[21] Claus and Mielke, *Ber.*, 1885, **19**, 1182
[22] Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3596.
[23] Korczynski, *Roczniki Chem.*, 1929, **9**, 731.
[24] Zalkind and Stetsuvo, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 94.
[25] Turner, *J.*, 1949, 2282.

42% based on dinitronaphthalene converted and in addition was obtained *ca.* 5% of 1 : 7-naphthylenediamine.

Derivatives of 7-*Nitro*-1-*naphthylamine.*—The hydrochloride was unstable on exposure to air. N-*Formyl*-, m. p. 218° (Found : C, 60·9; H, 4·1. $C_{11}H_8O_3N_2$ requires C, 60·0; H, 3·7%), *N*-acetyl-, m. p. 213° (Vesely and Dvorak[4] give 206—207°), and N-*toluene*-p-*sulphonyl*-7-*nitro*-1-*naphthylamine*, m. p. 202° (Found : N, 7·9; S, 9·2. $C_{17}H_{14}O_4N_2S$ requires N, 8·2; S, 9·4%), and 7-*nitro*-1-4′-*nitrobenzylideneaminonaphthalene*, m. p. 210° (Found : C, 63·5; H, 3·9. $C_{17}H_{11}O_4N_3$ requires C, 63·5; H, 3·45%), were prepared.

Chlorination of N-*Acetyl*-7-*nitro*-1-*naphthylamine.*—(a) *Monochlorination.* A stream of dry chlorine was slowly passed into a solution of the amide (1 g.) in acetic acid (25 c.c.) at *ca* 50° until 1 mol. was absorbed. Next morning the precipitated 1-*acetamido*-4-*chloro*-7-*nitronaphthalene* was collected, washed with acetic acid (yield, 0·5 g., 43%), and crystallised from acetic acid (charcoal); it had m. p. 256° (Found : Cl, 13·5. $C_{12}H_9O_5N_2Cl$ requires Cl, 13·4%). Pouring the original filtrate on ice-water and crystallisation from acetic acid gave a further 0·1 g. (total yield *ca.* 50%). The acetyl compound (0·8 g.) was refluxed for 6 hr. with ethanol (10 c.c.) and aqueous sulphuric acid (50% w/v; 10 c.c.), the hot solution filtered, and, on cooling, the precipitated amine sulphate collected. Basification at 0° with aqueous ammonia gave 4-*chloro*-7-*nitro*-1-*naphthylamine* (0·60 g., 90%) (red needles) from ethanol, m. p. 206° (Found : C, 53·8; H, 3·3. $C_{10}H_7O_2N_2Cl$ requires C, 53·9; H, 3·1%). This was deaminated by the method[26a] of Hodgson and Turner giving 1-chloro-6-nitronaphthalene (0·15 g., 37%), m. p. 126°, from ethanol (charcoal) and mixed m. p. with an authentic specimen 125° (Hodgson and Turner[26b] give m. p. 118—120°). The diazo-solution from this experiment did not give a diazo-oxide when poured into aqueous sodium acetate.

(b) *Dichlorination.* The above procedure for chlorination and isolation was repeated with acetyl compound (3 g.) in acetic acid (15 c.c.), chlorine being passed in for 1 hr. at 100°. The original precipitate had m. p. 223—225° (1·72 g., 44%); crystallised as above, 1-*acetamido*-2 : 4-*dichloro*-7-*nitronaphthalene* had m. p. 237° (Found : C, 47·9; H, 3·2. $C_{12}H_8O_3N_2Cl_2$ requires C, 48·2; H, 2·7%). The filtrate yielded a product, m. p. 153—163° (2·2 g.) (crystallised from acetic acid it had m. p. 192—193°) (Found : Cl, 24·9%. $C_{12}H_8O_3N_2Cl_2$ requires Cl, 23·2%). When the acetyl compound (1 g.) was used in acetic acid (25 c.c.) at 50°, continuing till 2 mols. of chlorine were absorbed, a 52% yield of dichloro-compound was precipitated and a further 12% obtained almost pure from the filtrate.

Hydrolysis of the dichloro-compound (1·5 g.) in ethanol–sulphuric acid as above for 8 hr. gave a red slurry; after cooling the solids were removed, and basified with aqueous ammonia at 0°, giving 2 : 4-*dichloro*-7-*nitro*-1-*naphthylamine* (1·25 g., 97%), m. p. 222°; recrystallised from ethanol (charcoal) this had m. p. 228° (Found : Cl, 27·6. $C_{10}H_6O_2N_2Cl_2$ requires Cl, 27·6%).

Diazotising this amine by Hodgson and Turner's method[20] and adding the diazo-solution to aqueous sodium acetate gave 4-*chloro*-1-*diazo*-7-*nitro*-2-*naphthol* (in quantitative yield), m. p. 175° (decomp.) (before or after crystallisation from dioxan) (Found : C, 48·1; H, 1·6. $C_{10}H_4O_3N_3Cl$ requires C, 48·1; H, 1·6%).

The dichloro-amine was converted into 2 : 4-*dichloro*-1 : 7-*naphthylenediamine* by refluxing it (1·0 g.) with water (20 c.c.) containing iron dust (2·5 g.) and ferrous ammonium sulphate (0·2 g.) in carbon dioxide for 10 hr. The solids separating on cooling were collected, washed with water, and extracted with hot ethanol (50 c.c.), the extract was diluted with water (100 c.c.), and the solids were collected, washed with water, and dried *in vacuo* (yield 0·73 g., 84%); crystallisation from ethanol gave white needles, m. p. 135—136° (Found : Cl, 30·9. $C_{10}H_8N_2Cl_2$ requires Cl, 31·3%). This was diazotised by dissolving it (0·75 g.) in acetic acid (12 c.c.), adding sulphuric acid (*d* 1·84; 2 c.c.), then pouring the whole into sodium nitrite (0·6 g.) in sulphuric acid (*d* 1·84; 4 c.c.) below 20°. After 30 min. the mixture was added rapidly to methanol (15 c.c.) containing cuprous oxide (1·75 g.), so as to keep the mixture at the b. p. After 15 min. the mixture was poured into water (100 c.c.), and the solids were collected, washed with water, and extracted with boiling ethanol (30 c.c.). After refluxing with charcoal, the extract was filtered, and concentration to 15 c.c. gave crude 1 : 3-dichloronaphthalene, purified by sublimation, yielding material (0·05 g., 8%), m. p. 58°, which on crystallisation from ethanol (charcoal) had m. p. 61° (Weissberger[27] gives m. p. 61—62°).

(c) 1 : 2 : 4 : 7-*Tetrachloronaphthalene.* The dichloro-diamine (0·56 g.) was tetrazotised as above and the diazo-solution added with stirring to one of cuprous chloride (0·6 g.) in hydrochloride acid (*d* 1·2; 6 c.c.) at 60°. After 30 min. the whole was poured into water (25 c.c.),

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[26] Hodgson and Turner, *J.*, 1943, (*a*) 862; (*b*) 391.

[27] Weissberger, *Trans. Faraday Soc.*, 1934, **30**, 884

and the solids were washed with water and dried, giving material (0·57 g.), m. p. 115°. Extraction with hot ethanol (35 c.c.; charcoal) gave a product, m. p. 138—140° (0·17 g., *ca.* 26%); crystallised from ethanol this had m. p. 143—144° alone or mixed with Turner and Wynne's specimen (Found: Cl, 53·8. $C_{10}H_4Cl_4$ requires Cl, 53·4%).

Dibromination and Attempted Monobromination of 7-*Nitro*-1-*naphthylamine*.—To a solution of the amine (10 g.) in dry chloroform (200 c.c.) was added dropwise at room temperature, during 15 min., a solution of bromine (18·5 g., 4·4 mols.) in chloroform (6 c.c.). Solid hydrobromide separated at once but the mixture was kept overnight before the precipitate was separated, washed with chloroform, and air-dried. The hydrobromide (which hydrolysed in air) was basified with aqueous ammonia, yielding 2 : 4-*dibromo*-7-*nitro*-1-*naphthylamine* (16·5 g., 90%), m. p. 225—227°, forming crimson needles, m. p. 237°, from ethanol (Found: Br, 45·9; N, 8·1. $C_{10}H_6O_2N_2Br_2$ requires Br, 46·2%; N, 8·1%). Using only 1 mol. of bromine gave the same product, plus unchanged starting material, readily separable by cold dilute hydrochloric acid (5% w/v).

Bromination by Kosolapoff's method[22] was carried out by mixing the amine (0·5 g.) in dioxan (1 c.c.) with potassium hydroxide (0·15 g.) in water (0·5 c.c.), and then adding bromine (0·43 g.) in dioxan (4·6 g.) during 1 hr. at 3—4°. Next morning 0·4N-aqueous potassium hydroxide (2·5 c.c.) was added and the red product collected, washed with water, and dried (0·36 g.; m. p. 213—215°). The crude product (0·1 g.) was chromatographed in benzene, with benzene–ethyl acetate (9 : 1; v/v) as eluant. In this way 2 : 4-dibromo-7-nitro-1-naphthylamine (0·070 g.) and 7-nitro-1-naphthylamine (0·010 g.) were obtained, no monobromo-amine being detected.

The dibromo-amine was converted into 4-*bromo*-1-*diazo*-7-*nitro*-2-*naphthol* by dissolving it (0·6 g.) in hot acetic acid (12 c.c.), cooling to 15°, adding it to a solution of sodium nitrite (0·2 g.) in sulphuric acid (*d* 1·84; 1 c.c.) below 20°, keeping the solution for 30 min. and then adding it to sodium acetate (5 g.) in water (50 c.c.). The precipitated product was collected, dried *in vacuo* in the dark; crystallised from aqueous dioxan it had m. p. 156·5° (Found: Br, 27·45. $C_{10}H_4O_3N_3Br$ requires Br, 27·2%).

The dibromo-amine was reduced to 2 : 4-*dibromo*-1 : 7-*naphthylenediamine* by a method similar to that adopted for the corresponding dichloro-compound. The yield was 51% of almost pure product, which from aqueous ethanol (1 : 1; v/v) formed white needles, m. p. 122° (decomp.) (Found: Br, 47·0; C, 40·7; H, 3·3. $C_{10}H_8N_2Br_2$ requires Br, 50·7; C, 37·9; H, 2·55%). 1 : 3-Dibromonaphthalene was obtained from this diamine in the same way as for the corresponding dichloro-compound. The crude product was purified by sublimation, giving a 7% yield of product, m. p. 63° (from ethanol) (Meldola[28] gives m. p. 64°) (Found: Br, 54·8. Calc. for $C_{10}H_6Br_2$: Br, 55·9%).

Mono- and Di-bromination of N-*Acetyl*-7-*nitronaphthylamine*.—To a solution of the acetyl compound (2 g.) in acetic acid (10 c.c.) containing anhydrous sodium acetate (0·75 g.) was added, during 45 min. under reflux, bromine (1·05 mol.) in acetic acid (13·4 c.c.). Heating was continued for a further 30 min. on the water-bath, the mixture cooled with stirring, and the precipitate of 1-*acetamido*-4-*bromo*-7-*nitronaphthalene* washed with acetic acid and water; after drying, it gave 2·25 g. (84%) of product, m. p. 258—261°, which on crystallisation from acetic acid had m. p. 265° (Found: Br, 25·9. $C_{12}H_9O_3N_2Br$ requires Br, 25·8%). This (2·0 g.) was refluxed with aqueous sulphuric acid (50% w/v; 10 c.c.) and ethanol (10 c.c.) for 3 hr., the considerable residue removed by filtering the hot solution, and the amine sulphate deposited on cooling collected. The original residue was again refluxed with the hydrolysing mixture (50 c.c.) for 5 hr., and the combined amine sulphates were basified at 0° with aqueous ammonia, yielding 4-*bromo*-7-*nitro*-1-*naphthylamine* (1·60 g., 92%), which, crystallised from light petroleum (b. p. 100—120°), had m. p. 197° (Found: Br, 30·1. $C_{10}H_7O_2N_2Br$ requires Br, 30·0%). Deamination as for the corresponding chloro-compound yielded 1-bromo-6-nitronaphthalene (18%), m. p. and mixed m. p. 129° (from ethanol) (Hodgson and Turner[26] give m. p. 131°).

1 : 2 : 4 : 7-*Tetrabromonaphthalene*.—2 : 4-Dibromo-1 : 7-naphthylenediamine (0·8 g.) was tetrazotised as for the corresponding chloro-compound and the diazo-solution added to one of cuprous bromide (0·9 g.) in hydrobromic acid (6 c.c.; 50% w/v) at 20°, left overnight, and then poured on ice-water (200 c.c.). The dried collected solids were extracted with ethanol portionwise (total 45 c.c.), and the extract was refluxed with charcoal and filtered. On cooling it deposited crude 1 : 2 : 4 : 7-*tetrabromonaphthalene*, m. p. 147—150° (0·22 g., 20%); recrystallised from ethanol it had m. p. 165° (Found: C, 27·7; H, 0·8; Br, 69·5. $C_{10}H_4Br_4$ requires C, 27·1; H, 0·9; Br, 72·1%).

[28] Meldola, *Ber.*, 1879, **12**, 1961.

Coupling with 7-*Nitro*-1-*naphthylamine*.—A solution of *p*-nitrobenzenediazonium hydrogen sulphate (0·65 g.) in water (15 c.c.) was added slowly during 30 min., with stirring, to one of the amine (0·5 g.) in ethanol (15 c.c.) containing sodium acetate (0·36 g.) sufficient to neutralise all the mineral acid, the temperature being kept at 0°. After a further 30 minutes' stirring, the precipitate was collected and washed with cold ethanol (10 c.c.) and hot water (20 c.c.). The yield of 7-*nitro*-4-p-*nitrophenylazo*-1-*naphthylamine* (m. p. 264—270°) was 0·78 g. (88%), which from nitrobenzene (charcoal) formed purple-black needles with a greenish-golden reflux, m. p. 297° (Found: C, 56·7; H, 3·44. $C_{16}H_{11}O_4N_5$ requires C, 56·7; H, 3·3%). This could not be oxidised to a triazole with chromium trioxide in boiling acetic acid. It was, however, acetylated by refluxing it (0·15 g.) in acetic acid (10 c.c.), acetic anhydride (2 c.c.), and sodium acetate (1 g.) for 2 hr. On cooling, 1-*acetamido*-7-*nitro*-4-p-*nitrophenylazonaphthalene* was deposited (0·125 g., 75%), having m. p. 329—330° (decomp.) unchanged by extraction with boiling acetic acid (10 c.c.) (Found: C, 57·0; H, 3·5. $C_{18}H_{13}O_5N_5$ requires C, 57·0; H, 3·4%). 7-*Nitro*-4-(p-*nitrophenylazo*-1-*naphthylazo*)-2-*naphthol* was prepared by adding sodium nitrite (0·14 g.) to a solution of the original azo-compound (0·4 g.) in acetic acid (15 c.c.) containing hydrochloric acid (*d* 1·2; 0·5 c.c.) below 12°, stirring the whole for 30 min., and adding it slowly to a solution of β-naphthol (0·25 g.) in aqueous sodium hydroxide (20% w/w; 60 c.c.) containing crushed ice (50 g.) After 1 hour's stirring the mixture was heated to 50°, and the product collected and washed with water (0·48 g., 82%; m. p. 215—220°). From nitrobenzene (charcoal) it formed violet-black needles with a greenish-golden reflex, having m. p. 292° (decomp.) (Found: C, 57·2; H, 3·15; N, 20·9. $C_{26}H_{16}O_5N_6$ requires C, 63·5; H, 3·3; N, 17·1%).

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