971. 2 : 3-*Derivatives of Naphthalene. Part III.*[1] *The Electrophilic Substitution Reactions of* 3-*Nitro*-2-*naphthylamine and* N-*Acylated Derivatives.*

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Diazo-coupling, chlorination, bromination, and nitration of 3-nitro-2-naphthylamine, and several of its *N*-acyl derivatives, have been studied. Nitro-groups can be introduced at the 1-, 5-, 6-, or 8-position.

Some general features of electrophilic substitution of naphthalene derivatives, in contrast to those of benzene derivatives, are discussed.

Diazo-naphthol formation by a variety of 1-substituted 3-nitro-2-naphthylamines and 1 : 3 : *x*-trinitro-2-naphthylamines always occurs by nucleophilic displacement of a group at the 1-position, forming a 1 : 2-diazonaphthol. This confirms the apparent impossibility of forming a 2 : 3-diazonaphthol structure.

1 : 6 : 7-Trinitronaphthalene has been synthesised and found to be identical with the mononitration product of 2 : 3-dinitronaphthalene.

Continuing our investigation of electrophilic substitution of nitronaphthylamines we now present semiquantitative data for 3-nitro-2-naphthylamine, which are summarised in Table 1.

Present interest in aromatic electrophilic substitution largely centres on the efforts to place the simplest possible cases on a quantitative theoretical base, namely, benzene

[1] Part II, Ward and Coulson, *J.*, 1954, 4545.

derivatives [2] and unsubstituted polycyclic aromatic hydrocarbons.[3] Naphthalene derivatives present more complex problems since there is a wider variety of possible substitutions and the modifying effects of substituents are more subtle, wherein lies the value of studies in this field.

Our tentative general analysis [4] of the effects of substituents in the 1- or 2-position of naphthalene compounds on other ring positions, as compared with a similar analysis for

TABLE 1. *Position of substitution (with, in parentheses, yields †) of* 3-*nitro*-2-*naphthylamine and its acyl derivatives.*

Reaction	Conditions	Amine	Acyl $CH_3{\cdot}CO$	Acyl p-$C_6H_4Me{\cdot}SO_2$	Acyl m-$NO_2{\cdot}C_6H_4{\cdot}SO_2$	Acyl o-$C_6H_4(CO)$
Diazo-coupling	Aq. EtOH	1 (95%)	—	—	—	—
Chlorination	AcOH, 50°	—	1 (80%)	—	—	—
Bromination	$CHCl_3$, room temp.	1 (100%), 1 : 6 (88%)	—	—	—	—
	AcOH, b. p.	—	1 (95%)	—	—	—
Nitration	A	—	—	1 (84%)	1 (53%)	—
Nitration	B	—	1, 6, 8 (75%), (15 : 2 : 3)	—	—	—
Nitration	C	—	1 : 5, 1 : 8 (85%) (19 : 16)	—	1 : 6 (55%) *	5, 8 (70%) (39 : 35)

A, nitric acid (d 1·5)–acetic acid at 80°. B, nitric acid (d 1·5)–acetic acid–boron trifluoride at 80°. C, nitric acid (d 1·5) at −5°. * At 20°.

† Yields refer to isolated products, when necessary after hydrolysis, and usually after chromatography.

benzene compounds, is given in Table 2. The relative strengths are given in terms of each effect separately and are not intended to show any particular relationship between effects. Where no strength is indicated it is assumed that the effect is negligible. The steric effect (S) is represented as equivalent at all positions " *ortho* " to the substituent, although it is likely from a consideration of the geometry of the naphthalene system [5] that in finer detail the effects are in the order 8 > 2, and 1 > 3 for 1- and 2-substituents respectively.

TABLE 2. *Relative strengths of the various reactivity-determining factors due to a single substituent* X *in the benzene or naphthalene nucleus.*

	1-$C_{10}H_7X$				2-$C_{10}H_7X$				C_6H_5X		
Posn.	I	T	S	Posn.	I	T	S	Posn.	I	T	S
2	++	++	+	1	++	++	+	*o*	++	+	+
3	+	δ+		3	++	+	+	*m*	+	δ+	
4	+	++		4	+			*p*	+	+	
5	δ+	+		5	δ+						
6	δ+			6	δ+	+					
7	δ+	+		7	δ+						
8	+		+	8	δ+	+					

I = inductive; T = tautomeric; S = steric. ++ Very strong; + strong; δ+ weak.

To apply to naphthalene a treatment similar to that given by H. C. Brown [3] to benzene derivatives, further physical data are required similar to those reported by Price and by Bryson [4] and, for our work, further substituent constants for other acylated amino-groups.

It is not possible to discuss fully the effect of acylation on the directing influence

[2] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913, and references therein.

[3] Dewar, Mole, and Warford, *J.*, 1956, 3581 and references therein.

[4] Cf. Roberts, Clement, and Drysdale, *J. Amer. Chem. Soc.*, 1951, **73**, 2181; Taft in Newman's " Steric Effects in Organic Chemistry," John Wiley & Sons, New York, 1956, Chap. XIII; Jaffe, *Chem. Rev.*, 1953, **53**, 191; Price and Michel, *J. Amer. Chem. Soc.*, 1952, **74**, 3652; Price, Mertz, and Wilson, *ibid.*, 1954, **76**, 1531; Bryson, *Trans. Faraday Soc.*, 1949, **45**, 257; 1950, **46**, 528; Dewar in Cook's " Progress in Organic Chemistry," Butterworths, London, 1953, Vol. II, pp. 1—28.

[5] Abrahams, Robertson, and White, *Acta Cryst.*, 1949, **2**, 233.

of the amino-group in aromatic electrophilic substitution until more experimental facts and theoretical treatments are available. *E.g.*, the phthalimido-group has previously been considered to be a simple *o*/*p*-directing group [6,7] but the data for naphthalene compounds [8] suggest that it exerts a deactivating influence comparable to that of a halogen atom. Nevertheless certain valid comments can already be made.

Our results for 2-naphthylamines illustrate the selectivity of the weaker electrophilic reagents (*e.g.*, polarised halogen molecules), which give a single monosubstitution product, in contrast to the more powerful nitrating agents which give mixed products (cf. H. C. Brown [2]). This however is not so obvious as with 2- or 4-substitution in a 1-naphthylamine derivative, presumably because in a 2-naphthylamine derivative the 1-position is normally by far the most activated, whereas the 2- and the 4-position in the 1-substituted compound may not differ greatly in reactivity—for a 1-naphthylamine (+*T*) derivative it can no longer be accepted that the 4-position is always the most activated (cf. Ingold; [6b] Ward and Coulson; [9] Hardy and Ward [8] for the nitration of 7-nitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine; Hodgson and Turner [10] for the monobromination of 5-nitro-1-naphthylamine).

The reactivities of 8- and 3-nitro-2-naphthylamine and their *N*-acyl derivatives in electrophilic substitution are similar: both amines are considerably less reactive than β-naphthylamine itself and slightly less reactive than 4-nitro-2-naphthylamine (*e.g.*, the *N*-toluene-*p*-sulphonyl derivative of the latter can be dinitrated [11]). For 3-nitro-2-naphthylamine this can be attributed to weakening of the activating influence of the 2-amino-group by the adjacent 3-nitro-group.

The dinitration of *N*-acetyl-3-nitro-2-naphthylamine by fuming nitric acid requires to be considered in the light of possible salt formation at the amido-group (cf. Ward and Coulson [9]). Since we find that *N*-acetyl-1 : 3-dinitro-2-naphthylamine is not further nitrated under these conditions, nitration must occur at the 5- and 8-positions before the 1-position is attacked. This indicates that salt formation does occur and that substitution takes place at the less deactivated α-positions in the other nucleus (this is analogous to the formation of the 1 : 6 : 7-trinitronaphthalene on mononitration of 2 : 3-dinitronaphthalene [12] and to the nitration of *N*-phthaloyl-3-nitro-2-naphthylamine reported above). This salt formation must be substantially complete since, if any neutral form were present, nitration would take place through this form and in a different manner from that found. Further, one must tentatively postulate that introduction of a second nitro-group so reduces the basicity of the acetamido-group that some of the neutral form is present which is nitrated further at the 1-position (cf. also Dewar [13]).

As regards the orientation of our products we need only comment on the three trinitronaphthylamines. All these yielded diazo-naphthols, confirming the presence of a nitro-group in the 1-position. 1 : 3 : 5- and 1 : 3 : 8-Trinitro-2-naphthylamines were identical with the amines arising from the nitration of *N*-acetyl-3 : 5- and -3 : 8-dinitro-2-naphthylamine respectively. The third trinitro-amine must be 1 : 3 : *x*-trinitro-2-naphthylamine, where $x = 4$, 6 or 7. Position 4 can reasonably be excluded and it is almost certain that $x = 6$ by analogy with the electrophilic substitution of 2-naphthylamine derivatives.

We have assumed above that in diazo-naphthol formation for 1-substituted 3-nitro-2-naphthylamines and 1 : 3 : *x*-trinitro-2-naphthylamines only the group in the 1-position is replaced and that the alternative formation of a 2 : 3-diazonaphthol is impossible. This is supported by the fact that neither 3-amino-2-naphthol nor its 7-sulphonic acid appears

[6] Ingold, "Structure and Mechanism in Organic Chemistry," Bell & Sons, London, 1953, pp. (*a*) 239—240, (*b*) 264—266.
[7] Brady, Quick, and Welling, *J.*, 1925, 2264.
[8] Hodgson and Crook, *J.*, 1936, 1844; Hardy and Ward, *J.*, 1957, 2634.
[9] Ward and Coulson, *J.*, 1954, 4541.
[10] Hodgson and Turner, *J.*, 1942, 723.
[11] Hodgson and Hathaway, *J.*, 1945, 453.
[12] Ward and Coulson, unpublished work.
[13] Dewar, *J.*, 1949, 463.

to form a diazo-naphthol [14] and that diazotised 3-nitro-2-naphthylamine does not form one even under the most favourable conditions. The fact that a 2 : 3-diazonaphthol structure cannot be formed seems to be another consequence of the weak interaction between 2- and 3-positions in naphthalene compounds.

1 : 6 : 7-Trinitronaphthalene was prepared by a diazo-decomposition from either 3 : 5- or 3 : 8-dinitro-2-naphthylamine and was identical with the mononitration product of 2 : 3-dinitronaphthalene,[12] thus orientating the latter.

We have re-investigated the nitration of *N*-acetyl-3-chloro-1-naphthylamine and find it to be much more complex than originally described.[15] The only satisfactory product we obtained was an *N*-acetyl-chlorodinitronaphthylamine which we did not orientate. Further, our authentic 2-chloro-3-nitronaphthalene, prepared by diazo-decomposition from 3-nitro-2-naphthylamine, was not identical with that previously described.[15,16]

Experimental

N.B. 1 : 3-Dinitro-2-naphthylamine has an irritant action on the skin, especially round the mouth, nose, and eyes; the effects persist for some minutes with disturbance of the senses of taste and smell.

Ultraviolet absorption spectra of 3-nitro-2-naphthylamine and related compounds were recorded as described by Hardy and Ward [8] for EtOH media. Maxima (mμ) and, in parentheses, log *E* were:

3-Nitro-2-naphthylamine, 234 (4·56), 260 (4·25), 330 (3·79), 470 (3·29) (the maximum at 470 mμ is noteworthy in comparison with spectra of other nitronaphthylamines).

1 : 3-Dinitro-2-naphthylamine, 229 (4·55), 255 sh (4·53), 268 sh (4·41), 330 (3·95), 453 (3·66).

3 : 5-Dinitro-2-naphthylamine, 224 (4·30), 252 sh (4·43), 268 sh (4·35), 319 (3·84), 471 (3·47).

3 : 8-Dinitro-2-naphthylamine, 228 (4·27), 258 (4·49), 316 sh (3·89), 370 sh (3·33), 480 (3·63).

N-*Acyl Derivatives of* 3-*Nitro*-2-*naphthylamine*.—(*a*) The amine (1 g.) and phthalic anhydride (1·2 g.) were refluxed in acetic acid (10 c.c.) for 1 hr., water (70 c.c.) was added, and the mixture re-boiled; on cooling, 3-*nitro*-N-*phthaloyl*-2-*naphthylamine* separated (1·57 g., 93%); it formed red needles, m. p. 239—240°, from acetic acid (Found: C, 67·6; H, 3·2. $C_{18}H_{10}O_4N_2$ requires C, 67·9; H, 3·2%).

(*b*) The amine (1 g.) was intimately ground with toluene-*p*-sulphonyl chloride (5 g., 5 mols.), and the mixture stirred into cold water and slowly brought to the b. p., solid sodium carbonate being stirred in from time to time to keep the liquid alkaline. After 1 hour's boiling the mixture was cooled and neutralised (litmus) with hydrochloric acid, and the solids were collected and repeatedly extracted with warm (5% w/v) aqueous potassium hydroxide. This extract on acidification yielded 3-*nitro*-N-*toluene*-p-*sulphonyl*-2-*naphthylamine* (0·8 g., 44%), orange needles (from ethanol), m. p. 187—189° (Found: S, 9·2. $C_{17}H_{14}O_4N_2S$ requires S, 9·4%). From the alkali-insoluble residue 3-nitro-2-naphthylamine (0·5 g., 50%) was recovered by extraction with boiling 10% w/v hydrochloric acid.

(*c*) The reactants as in (*b*) were heated in pyridine (20 c.c.) on the steam-bath for 2 hr., the mixture was poured into 10% w/v hydrochloric acid (300 c.c.), and the solid was collected and worked up as before, giving almost identical yields. This experiment with 10 mols. of toluene-*p*-sulphonyl chloride gave amine (60%) and 3-*nitro*-NN-*ditoluene*-p-*sulphonyl*-2-*naphthylamine* (30%), the monoamide apparently being absent. The diamide had m. p. 230—234° (from acetic acid) (Found: S, 13·0. $C_{24}H_{20}O_6N_2S_2$ requires S, 12·9%).

(*d*) The amine (1 g.) and *m*-nitrobenzenesulphonyl chloride (2 g., *ca.* 2 mols.) were heated together on the steam-bath for 2 hr. Unchanged amine was extracted from the powdered product by warm 10% w/v hydrochloric acid (500 c.c.), and the residue triturated with warm 10% w/v aqueous sodium hydroxide (2 × 100 c.c.), then with warm water (2 × 100 c.c.). Acidification of this extract gave 3-*nitro*-N-m-*nitrobenzenesulphonyl*-2-*naphthylamine* [from acetic acid (charcoal)], m. p. 212° (0·28 g., 22%) (Found: C, 51·4; H, 3·2. $C_{16}H_{11}O_6N_3S$ requires C, 51·5; H, 3·0%). From the original acid extract unchanged amine (*ca.* 10%) was

[14] Goldstein and Gardiol, *Helv. Chim. Acta*, 1937, **20**, 516; Cassela, B.P. 28,107/1897.
[15] Hodgson and Elliott, *J.*, 1936, 1151.
[16] Hodgson and Hathaway, *J.*, 1945, 841; cf. Ufimtsev and Manachkina, *Doklady Akad. Nauk. S.S.S.R.*, 1953, **92**, 581.

recovered but crystallisation from acetic acid of the residues from the alkali extract only yielded material which appeared to be mixed mono- and di-amide. Yields were variable, and even lower if the reaction was carried out in pyridine.

Diazotisation and Diazo-reactions of 3-*Nitro*-2-*naphthylamine*.—(a) *Diazotisation in aqueous medium*. The amine (1 g.) was stirred into hot 10% w/v aqueous sulphuric acid (7·5 c.c.), the mixture cooled to 0°, crushed ice (2 g.) added and then sodium nitrite (0·6 g.) in the minimum amount of water rapidly with vigorous stirring.

(b) *Diazotisation in sulphuric–acetic acid*. The amine (1 g.) was dissolved in sulphuric acid (*d* 1·84, 4 c.c.) and to this was added a solution of sodium nitrite (0·4 g.) in sulphuric acid (*d* 1·84, 2·5 c.c.). This mixture was then stirred into acetic acid (13 c.c.) below 30°.

(c) 2-*Chloro*-3-*nitronaphthalene*. The diazo-solution prepared as in (b) was added to a solution of cuprous chloride (2 g.) in hydrochloric acid (*d* 1·2; 10 c.c.) and after 24 hr. the solids were collected, washed with water, dried, and refluxed with ethanol (50 c.c.; charcoal) for 30 min. The filtered extract, on concentration to 10 c.c., yielded 2-chloro-3-nitronaphthalene (0·72 g., 65%), m. p. 71—72° [from light petroleum (b. p. 100—120°)] (Found: Cl, 17·5; N, 7·0. Calc. for $C_{10}H_6O_2NCl$: Cl, 17·1; N, 6·7%). The m. p. was unchanged by steam-distilling the product or further recrystallisation from light petroleum (cf. Hodgson and Elliott [15] who give m. p. 94·5°).

(d) 2 : 3-*Dinitronaphthalene*. The diazo-solution prepared as in (a) was poured on chalk (1·2 g.) and ice (2 g.) with a little silicone antifoam and stirred vigorously. The mixture was then *immediately* added to a mixture prepared by adding a solution of crystalline copper sulphate (6·5 g.) in water (25 c.c.) to one of crystalline sodium sulphite (6·5 g.) in water (50 c.c.) and just before the reaction adding sodium nitrite (13 g.), dissolved in water (25 c.c.). The whole was stirred for 1 hr., the solid collected, washed with water, and dried, and the product obtained by extraction with boiling ethanol (charcoal) [yield 70%; m. p. 172—174° (Ward and Coulson [1] give m. p. 172—174°)].

Azo-coupling to 3-*Nitro*-2-*naphthylamine*.—*p*-Nitroaniline (0·74 g.) in hot 25% w/w aqueous sulphuric acid (3 g.) was poured into ice-water (5 g.), further ice (3 g.) added, and the whole treated rapidly with sodium nitrite (0·6 g.) in water (2 c.c.). Excess of nitrous acid was removed with sulphamic acid, and the filtered diazo-solution added, with stirring, to the amine (1 g.) in ethanol (220 c.c.), containing sodium acetate (1·4 g.). After 1 hr. the precipitated 3-*nitro*-1-p-*nitrophenylazo*-2-*naphthylamine* was collected and washed with ethanol (30 c.c.) and much hot water (yield 1·7 g., 95%). Recrystallised from hot nitrobenzene the dye had m. p. 240° (Found: C, 56·8; H, 3·5. $C_{16}H_{11}O_4N_5$ requires C, 56·7; H, 3·3%).

To a solution of the dye (0·25 g.) in boiling acetic acid was added dropwise one of chromium trioxide (0·25 g.) in water (0·5 c.c.). The mixture was then cooled and diluted with water, and the solid collected and washed with hot water, yielding 3′-*nitro*-2-p-*nitrophenylnaphtho*(1′ : 2′-4 : 5)*triazole* (60%), m. p. 244—246° (from acetic acid) (Found: N, 20·7. $C_{16}H_9O_4N_5$ requires N, 20·9%).

Chlorination of N-*Acetyl*-3-*nitro*-2-*naphthylamine* (By A. Hardy).—The procedure for monochlorination was as used by Hardy and Ward.[17] Almost pure N-*acetyl*-1-*chloro*-3-*nitro*-2-*naphthylamine* was precipitated. This was collected, washed with acetic acid, and dried (0·89 g., 77%); crystallised from acetic acid it had m. p. 241° (Found: C, 54·8; H, 3·4. $C_{12}H_9O_3N_2Cl$ requires C, 54·5; H, 3·4%). Further amounts of less pure material were obtained by pouring the reaction liquors on ice. After hydrolysis of both products the combined yield of 1-*chloro*-3-*nitro*-2-*naphthylamine* was *ca.* 90%; from acetic acid this formed red needles, m. p. 135° (Found: C, 53·5; H, 3·1; Cl, 15·7. $C_{10}H_7O_2N_2Cl$ requires C, 54·0; H, 3·3; Cl, 15·9%). Chromatography of this amine on alumina in benzene gave one band only and no other products were detected on elution.

Diazotisation and subsequent deamination by the methods of Hodgson and Turner [18] gave 1-chloro-3-nitronaphthalene (65%), m. p. 130°, identified with a specimen prepared by a Sandmeyer reaction from 3-nitro-1-naphthylamine (Hodgson and Birtwell [19] give m. p. 129·5°).

Pouring the diazonium solution into water containing sodium acetate instantly precipitated in almost quantitative yield 2-*diazo*-3-*nitro*-1-*naphthol*, m. p. 187° (decomp.) (from benzene) (Found: C, 55·8; H, 2·4; N, 19·7. $C_{10}H_5O_3N$ requires C, 55·8; H, 2·3; N, 19·5%).

[17] Hardy and Ward, *J.*, 1956, 1979.
[18] Hodgson and Turner, *J.*, (*a*) 1942, 748; (*b*) 1943, 68.
[19] Hodgson and Birtwell, *J.*, 1944, 75.

When chlorination was continued for 1 hr. at 100° subsequent hydrolysis, followed by chromatography, revealed only the monochloroamine.

Bromination of 3-*Nitro*-2-*naphthylamine*.—(*a*) The amine (1 g.) in chloroform (20 c.c.) was treated with bromine (1 g., *ca.* 1·1 mol.) in chloroform (5 c.c.). After 10 hr. the precipitated hydrobromide was collected, air-dried, and on basification with aqueous ammonia yielded 1-*bromo*-3-*nitro*-2-*naphthylamine*. Chromatography of this on alumina in benzene yielded a single band and elution gave red needles, m. p. 133—134° (Found: C, 44·7; H, 2·6. $C_{10}H_7O_2N_2Br$ requires C, 45·0; H, 2·6%). Further bromo-amine was obtained by concentration of the original filtrate, making the total yield quantitative.

The bromo-amine was diazotised by the method of Hodgson and Turner,[18b] and pouring the diazo-solution into water gave an almost quantitative yield of 2-diazo-3-nitro-1-naphthol.

(*b*) The above monobromo-amine (1 g.) in chloroform (25 c.c.) was treated with bromine (2·3 g., 3 mol.) in chloroform (12 c.c.). The precipitated 1 : 6-*dibromo*-3-*nitro*-2-*naphthylamine* was collected and from benzene gave deep red needles, m. p. 186° (Found: Br, 46·3. $C_{10}H_6O_2N_2Br_2$ requires Br, 46·2%). Further dibromo-amine was obtained by concentration of the original filtrate (total yield, 88%). Direct dibromination of the 3-nitro-2-naphthylamine was less satisfactory.

Diazotisation of the dibromoamine by the Hodgson–Walker method [20] and subsequent Sandmeyer reaction yielded 1 : 2 : 6-*tribromo*-3-*nitronaphthalene* (85%), m. p. 181° (from 1 : 1 ethanol–acetone) (Found: C, 29·5; H, 1·05. $C_{10}H_4O_2NBr_3$ requires C, 29·3; H, 1·0%). This was converted into 3 : 4 : 7-*tribromo*-2-*naphthylamine* by refluxing the crude product (1 g.) with 90% hydrazine hydrate (0·5 g.) and 10% palladised charcoal (0·5 g.) in ethanol (60 c.c.) for 30 min. (cf. Dewar and Mole [21]), the amine being obtained by concentration of the cooled filtered mixture. This gave white needles (0·42 g., 46%), m. p. 167° (Found: C, 31·1; H, 1·6; Br, 63·2. $C_{10}H_6NBr_3$ requires C, 31·6; H, 1·6; Br, 63·1%). This amine was diazotised by Hodgon and Walker's method [19] and deaminated by Hodgson and Turner's method,[18a] yielding impure 1 : 2 : 6-tribromonaphthalene, m. p. 104—106° (56%). Purification of this by crystallisation and chromatography gave the pure compound, m. p. 117°, identical with a specimen prepared by a Sandmeyer reaction from 1 : 6-dibromo-2-naphthylamine (Claus and Philipson [22] give m. p. 118°).

Bromination of N-*Acetyl*-3-*nitro*-2-*naphthylamine*.—Treating the amide in acetic acid at room temperature for 24 hr. with bromine (1 mol.) gave crude *N*-acetyl-1-bromo-3-nitro-2-naphthylamine, identified by hydrolysis to the amine (*ca.* 95%). Refluxing the amide with 2 mols. of bromine in acetic acid for 24 hr. gave mainly the monobromo-amide with a little 1 : 6-dibromo-2-naphthylamine (arising by hydrolysis followed by bromination). N-*Acetyl*-1 : 6-*dibromo*-3-*nitro*-2-*naphthylamine*, prepared by treating a solution of the amine in warm acetic anhydride with a drop of sulphuric acid (*d* 1·84), had m. p. 251° (decomp.) (from acetic acid) (Found: Br, 41·0. $C_{12}H_8O_3N_2Br_2$ requires Br, 41·2%).

Nitration of 3-*Nitro*-N-*toluene*-p-*sulphonyl*-2-*naphthylamine*.—A suspension of the amide (1 g.) in acetic acid (3 c.c.) was treated with a mixture of nitric acid (*d* 1·5; 0·3 c.c., *ca.* 2·3 mols.) and acetic acid (2 c.c.), a crystal of sodium nitrite added, and the temperature raised slowly to 80°. After 15 min. at 70—80° the mixture was cooled to 0° for 30 min., and the solid collected and washed with acetic acid (1 c.c.), then with ether (2 × 3 c.c.), yielding material (84%), m. p. 210° (decomp.). 1 : 3-*Dinitro*-N-*toluene*-p-*sulphonyl*-2-*naphthylamine*, m. p. 228° (decomp.), crystallised from acetone (Found: C, 52·5; H, 3·4; S, 8·1. $C_{17}H_{13}O_6N_3S$ requires C, 52·7; H, 3·4; S, 8·3%). Repeating this experiment with 6 mols. of nitric acid and leaving the reaction mixture for 24 hr. at room temperature gave similar results. The amide was hydrolysed by dissolution in sulphuric acid (*d* 1·84) at 30° and pouring on ice, giving a quantitative yield of 1 : 3-*dinitro*-2-*naphthylamine*, orange red needles [from light petroleum (b. p. 100—120°)], m. p. 158—159° (Found: C, 51·5; H, 2·9. $C_{10}H_7O_4N_3$ requires C, 51·5; H, 3·0%).

N-*Acetyl*-1 : 3-*dinitro*-2-*naphthylamine* was prepared by treating the amine in acetic anhydride with a drop of sulphuric acid (*d* 1·84) and purified by extraction with cold 2N-aqueous sodium hydroxide. Subsequent acidification and crystallisation from aqueous acetic acid gave the amide, m. p. 240° (Found: C, 52·8; H, 3·2. $C_{12}H_9O_5N_3$ requires C, 52·4; H, 3·3%).

[20] Hodgson and Walker, *J.*, 1933, 1620.
[21] Dewar and Mole, *J.*, 1956, 2556.
[22] Claus and Philipson, *J. prakt. Chem.*, 1891, **43**, 47.

The 1 : 3-dinitro-2-naphthylamine was diazotised by Hodgson and Turner's method.[18b] Pouring the diazonium solution into water gave a quantitative yield of 2-diazo-3-nitro-1-naphthol. Attempts to convert this into 3-nitro-1-naphthol by the methods of Hodgson and Turner,[23] or Hodgson and Birtwell,[24] failed, the former yielding largely unchanged starting material.

Nitration of 3-*Nitro*-N-*phthaloyl*-2-*naphthylamine*.—The amide (2 g.) was stirred gradually into nitric acid (*d* 1·5; 7 c.c.) during 10 min. below −5°. After 30 min. more the mixture was poured on ice (50 g.), and the solid collected and washed well with water (the yield calc. for mononitration was quantitative) (Found: N, 11·5. Calc. for $C_{10}H_7O_4N_3$: N, 11·6%). The crude phthalimide was hydrolysed by refluxing with aqueous-ethanolic hydrazine hydrate (cf. Hardy and Ward [8]), the dried crude product so obtained was extracted with warm 9 : 1 v/v benzene–ethyl acetate, and the mixed amines were separated by chromatography.[25] 3 : 8-*Dinitro*-2-*naphthylamine* had m. p. 239—241° (Found: C, 51·3; H, 3·0. $C_{10}H_7O_4N_3$ requires C, 51·5; H, 3·0%) and 3 : 5-*dinitro*-2-*naphthylamine* m. p. 228—230° (Found: C, 51·1; H, 3·0%).

N-*Acetyl*-3 : 5-, m. p. 249° (Found: C, 52·4; H, 3·9. $C_{12}H_9O_5N_3$ requires C, 52·4; H, 3·3), and -3 : 8-*dinitro*-2-*naphthylamine*, m. p. 204° (Found: C, 52·2; H, 3·5%), were prepared.

The amines were diazotised and deaminated as by Hodgson and Turner,[18] 3 : 5-dinitro-2-naphthylamine giving 1 : 7-dinitronaphthalene (21%), and 3 : 8-dinitro-2-naphthylamine giving 1 : 6-dinitronaphthalene (38%), identical with authentic specimens.

1 : 6 : 7-*Trinitronaphthalene*.—This was prepared directly from the mixed 3 : 5- and 3 : 8-dinitro-2-naphthylamines.[8,9] The crude dry product from 0·2 g. was extracted by boiling chloroform (charcoal), and the filtered extract concentrated to 10 c.c. to afford 1 : 6 : 7-*trinitronaphthalene* (0·07 g., 31%), m. p. 196—199° (Found: C, 45·6; H, 2·0; N, 15·7. $C_{10}H_5O_6N_3$ requires C, 45·6; H, 1·9; N, 16·0%).

Nitration of N-*Acetyl*-3-*nitro*-2-*naphthylamine*.—(*a*) The amide (1 g.), suspended in acetic acid (10 c.c.), was treated with a mixture of nitric acid (*d* 1·5; 0·5 g., 1·8 mols.), boron trifluoride–acetic acid complex (40% w/w; 4 g.), and acetic acid (15 c.c.). A crystal of sodium nitrite was added, and the temperature raised to 75° during 20 min. and then kept at 60—65° for 5 min. The mixture was added to ice-water (500 g.), and the solid collected, washed with water, and dried at 50° in a vacuum (yield 1 g., 85%) (Found: N, 15·1. $C_{12}H_9O_5N_3$ requires N, 15·3%). The product was hydrolysed for 2 hr. with a refluxing mixture of ethanol (12 c.c.) and aqueous sulphuric (1 : 1 v/v; 8 c.c.). Pouring the whole on ice and basification gave an almost quantitative yield of mixed dinitronaphthylamines (Found: C, 51·7; H, 2·8; N, 17·9. Calc. for $C_{10}H_7O_4N_3$: C, 51·5; H, 3·0; N, 18·0%). Chromatography of the mixture [25] yielded pure 1 : 3-dinitro-2-naphthylamine, 3 : 8-dinitro-2-naphthylamine, and 3 : 6-*dinitro*-2-*naphthylamine*, m. p. 239—240° (Found: C, 50·9; H, 3·1%).

3 : 6-Dinitro-2-naphthylamine, by diazotisation and deamination,[18] gave 2 : 7-dinitronaphthalene (53%), identical with an authentic specimen.

(*b*) The amide (1 g.) was added gradually to nitric acid (*d* 1·5; 6 c.c.) below −5°, and kept at −5° to −10° for 90 min. with stirring. The mixture was poured into ice-water (50 g.), and the solid collected, washed with water, and dried *in vacuo* at 55° (yield 1 g., 72%). After hydrolysis (as above) and pouring into ice-water a quantitative yield of mixed trinitronaphthylamines was obtained. Chromatography [25] afforded 1 : 3 : 8-*trinitro*-2-*naphthylamine*, m. p. 268—270° (decomp.) (Found: C, 42·8; H, 2·1; N, 19·9. $C_{10}H_6O_6N_4$ requires C, 43·2; H, 2·2; N, 20·2%) and 1 : 3 : 5-*trinitro*-2-*naphthylamine* (after rechromatography, m. p. 181—183°) (Found: C, 43·0; H, 2·2; N, 19·8%).

Diazo-naphthols were obtained from these amines by diazotisation [18a] and pouring of the diazonium solutions into water. 1-*Diazo*-3 : 5-*dinitro*-2-*naphthol* had m. p. 128—130° (decomp.) (from aqueous ethanol) (Found: C, 46·2; H, 1·5; N, 22·0. $C_{10}H_4O_5N_4$ requires C, 46·2; H, 1·5; N, 21·5%). 1-*Diazo*-3 : 8-*dinitro*-2-*naphthol* had m. p. 220° (decomp.) (from acetone) (Found: 46·2; H, 1·5; N, 21·7%).

Nitration of 3-*Nitro*-N-m-*nitrobenzenesulphonyl*-2-*naphthylamine*.—(*a*) The amide (1 g.) in acetic acid (15 c.c.) at 50° was treated (dropwise) with nitric acid (*d* 1·5; 1 c.c., *ca.* 7 mols.), and the temperature raised to 80° and kept thereat for 15 min. The mixture was then set aside for 1 hr., and the solid collected and washed with acetic acid (1·5 c.c.) and then ether (3 × 8 c.c.) (yield 0·7 g., 62%). The product was hydrolysed by dissolution in sulphuric acid (*d* 1·84;

[23] Hodgson and Turner, *J.*, 1944, 8.
[24] Hodgson and Birtwell, *J.*, 1943, 86.
[25] Ward and Wells, *J.*, 1957, 2836.

40 c.c.) at 50°, storage overnight, and pouring on ice. Purification by chromatography gave pure **1** : 3-dinitro-2-naphthylamine.

(*b*) The amide (1 g.) was added slowly with stirring to nitric acid (*d* 1·5; 2 c.c.) at 20° and the solution set aside for 1 hr. Acetic acid (3·5 c.c.) was added and after 40 hr. the solid was collected, washed with acetic acid (3 c.c.), then ether (6 c.c.), and dried *in vacuo* at 20° (0·72 g., 60%) (Found: C, 40·8; H, 1·92; N, 14·1. $C_{16}H_9O_{10}N_5S$ requires C, 41·5; H, 1·96; N, 15·5%). Further material was obtained by pouring the original filtrate on ice. After hydrolysis, as above, both products afforded a red amine which was further purified by chromatography (single band only), giving **1** : **3** : 6-*trinitro-2-naphthylamine*, m. p. 140—142° (Found: C, 42·1; H, 2·2. $C_{10}H_6O_6N_4$ requires C, 43·2; H, 2·2%).

Further Nitration of N-*Acetyl-dinitro-2-naphthylamines*.—(*a*) The procedure was as employed for the dinitration of *N*-acetyl-3-nitro-2-naphthylamine, the yields (calc. for mononitration) were almost quantitative. *N*-Acetyl-**3** : 5-dinitro-2-naphthylamine gave [after hydrolysis, purification by chromatography, and crystallisation from light petroleum (b. p. 100—120°)] **1** : **3** : 5-trinitro-2-naphthylamine, and *N*-acetyl-**3** : 8-dinitro-2-naphthylamine similarly gave **1** : **3** : 8-trinitro-2-naphthylamine, these being identical with the amines obtained by dinitration of *N*-acetyl-3-nitro-2-naphthylamine. *N*-Acetyl-**1** : 3-dinitro-2-naphthylamine was recovered unchanged.

(*b*) *N*-Acetyl-**3** : 5- and -**3** : 8-dinitro-2-naphthylamine were recovered unchanged when treated by the procedure employed for mononitrating *N*-acetyl-3-nitro-2-naphthylamine.

Nitration of N-*Acetyl-3-chloro-1-naphthylamine* (with A. HARDY).—The amide (0·1 g.) was added to nitric acid (*d* 1·42) during 5 min., then heated on the steam-bath for 15 min. After cooling, the solution was poured into water, and the solid collected, washed with water, and dried (0·083 g.). This was chromatographed in benzene on alumina, elution being with benzene–ethyl acetate. Four bands were obtained but the main yellow one gave white needles of an N-*acetyl-chlorodinitronaphthylamine* (0·055 g.), m. p. 275° (from acetic acid) (Hodgson and Elliott [15] give the m. p. of their supposed *N*-acetyl-**2** : 3-dinitro-**1**-naphthylamine as 275·5°) (Found: C, 46·8; H, 2·9; Cl, 11·4. $C_{12}H_8O_5N_3Cl$ requires C, 46·6; H, 2·9; Cl, 11·4%).

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