511. *7-Nitro-1-naphthylamine. Part II.*[1] *The Nitration of* N-*Acyl Derivatives and Decompositions of Diazotised* 2 : 4 : x-*Trinitro-1-naphthylamines.*

By A. Hardy and E. R. Ward.

Nitration of three *N*-acyl-7-nitro-1-naphthylamines has been studied, the predominant mononitration of the toluene-*p*-sulphonyl derivative in the 2-position being noteworthy. Decompositions of diazotised 2 : 4 : 7-trinitro-1-naphthylamine, compared with those of other diazotised 2 : 4 : *x*-trinitro-1-naphthylamines, indicate the decisive influence of internuclear effects on their reactivity. 1 : 4 : 6-Trinitronaphthalene has been prepared and is further nitrated to 1 : 3 : 5 : 8-tetranitronaphthalene only.

In halogenation or diazo-coupling of 7-nitro-1-naphthylamine or its *N*-acetyl derivative monosubstitution was restricted to the 4-position, and further substitution, when it occurred, was at the 2-position. Nitration of *N*-acyl derivatives is much more complex. Whereas the *N*-acetyl derivative is mononitrated at both the 2- and the 4-position, with the latter clearly the more activated, the *N*-toluene-*p*-sulphonyl derivative reacts predominantly at the 2-position.

In previous studies of the nitration, in acetic acid above room temperature, of *N*-toluene-*p*-sulphonyl derivatives from 5-, 6-, and 8-nitro-1-naphthylamines[2,3] only simultaneous dinitration at the 2- and the 4-position was recorded. With 7-nitro-1-naphthylamine we find that the products depend on whether the reaction is conducted in solution or suspension, on the temperature, and on the amount of nitrating acid. Our extended studies were only made possible by chromatography. Thus, in suspension at 20—30°, with more than sufficient nitric acid to cause dinitration, 2 : 7-dinitro- and 2 : 4 : 7-trinitro-1-naphthylamine were obtained (after hydrolysis) the latter predominating. At 85° the trinitro-amine, with a trace of 2 : 7-dinitro-1-naphthylamine, was obtained. In

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[1] Part I, Hardy, Ward, and Day, *J.*, 1956, 1979.

[2] Hodgson and Turner, *J.*, 1942, 723; 1943, 791.

[3] Ward and Day, *J.*, 1951, 782.

neither case was 4 : 7-dinitro-1-naphthylamine detected, even by chromatography. But by nitration in solution at 20° with only enough acid to effect mononitration, a mixture of 2 : 7- and 4 : 7-dinitro-1-naphthylamine was obtained, the former predominating. It appears therefore that the 2-position is the more activated, but it is difficult to see why some 4 : 7-dinitro-1-naphthylamine is not *always* found with the 2 : 7-isomer.

Investigation of the nitration of 7-nitro-*N*-phthaloyl-1-naphthylamine was limited by difficulty in hydrolysing the product, the yield of hydrolysed amines being equivalent to only about a third of the starting material; the identity of the polynitronaphthylamines isolated suggests that some nitration products may have been destroyed. Thus 2 : 7- and 4 : 7-dinitro-1-naphthylamine were obtained (demonstrating mononitration at both the 2- and the 4-position) but no 2 : 4 : 7-trinitro-1-naphthylamine although a new trinitro-1-naphthylamine was formed. The relative proportion of isomers isolated in these circumstances can be of little significance. Electrophilic substitution at positions other than 2 or 4 has never been observed with the related 5-, 6-, or 8-nitro-1-naphthylamine (although the nitration of their *N*-phthaloyl derivatives has not been studied).

4 : 7-Dinitro-1-naphthylamine was oriented by diazotisation and deamination to 1 : 6-dinitronaphthalene but deamination of 2 : 7-dinitro-1-naphthylamine by Hodgson and Turner's[4] or Hodgson and Birtwell's method[5] gave unidentifiable products. The 2 : 7-dinitro-amine was oriented by the fact that its diazonium salt readily gave a diazo-oxide, also by conversion of the diazonium compound into 1-bromo-2 : 7-dinitronaphthalene, followed by dehalogenation of this to 2 : 7-dinitronaphthalene by Smith's method.[6] A similar dehalogenation carried out on the corresponding 1-chloro-2 : 7-dinitronaphthalene gave only unchanged starting material. 2 : 4 : 7-Trinitro-1-naphthylamine was oriented by reason of the fact that after diazotisation it readily gave a diazo-oxide (confirming 2-nitration) and could not be further brominated (showing that the 4-position was already occupied), whilst 2 : 7- and 4 : 7-dinitro-1-naphthylamine were readily monobrominated under analogous conditions.

The new trinitro-1-naphthylamine is unlikely to contain adjacent nitro-groups in one nucleus. Since the diazotised amine does not give a diazo-oxide there cannot be a nitro-group at position 2 (or at 3 : 4 since 3 : 4-dinitro-1-naphthylamine very readily gives a 1 : 4-diazo-oxide[7]), and the most likely structure appears to be 4 : 5 : 7-trinitro-1-naphthylamine.

Attempts to deaminate diazotised 2 : 4 : 7-trinitro-1-naphthylamine by the methods cited above[4, 5] failed. The only product from the Sandmeyer reaction that could be identified by chromatography was 1-diazo-4 : 7-dinitro-2-naphthol, although small amounts of products containing appreciable amounts of halogen were also isolated (almost certainly arising by Sandmeyer decompositions of the diazo-oxide). The results are analogous to those obtained, in similar circumstances,[3, 7] with other 2 : 4 : x-trinitro-1-naphthylamines ($x = 3, 5, 6,$ or 8). We conclude that with all these diazotised trinitronaphthylamines the tendency to form a diazo-oxide, even in the concentrated acid medium of a Sandmeyer decomposition, is so strong that normal reaction either does not occur at all or does so only to a minor extent. This behaviour can be contrasted with that of diazotised 2 : 4-dinitro-1-naphthylamine, which under analogous conditions gives excellent yields of 1 : 3-dinitronaphthalene by deamination[8] and of 1-chloro-2 : 4-dinitronaphthalene by Sandmeyer decomposition.[9] The introduction of a 3-, 5-, 6-, 7-, or 8-nitro-group into 2 : 4-dinitro-1-naphthylamine might perhaps be expected to exert little effect on the reactivity of the diazonium salt since at the 3-position it is *meta* to the diazo-group and in the other

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[4] Hodgson and Turner, *J.*, 1942, 748.

[5] Hodgson and Birtwell, *J.*, 1944, 112.

[6] Smith, *J. Amer. Chem. Soc.*, 1949, **71**, 2885.

[7] Ward, Pierce, and Wells, unpublished work; Ward, Thesis, London, 1946; Coulson, Thesis, London, 1955; Staedel, *Ber.*, 1881, **14**, 898; *Annalen*, 1883, **217**, 153, 173, 174; Hodgson and Hathway, *J.*, 1944, 651.

[8] Hodgson and Birtwell, *J.*, 1943, 433.

[9] Hodgson and Ward, *J.*, 1948, 2017.

compounds it is not in the same nucleus as the diazo-group. In any case it should increase the positivity of the 1-carbon atom and facilitate diazo-decompositions. It is clear however that the introduction of this third nitro-group exerts a decisive effect on the reactivity of the diazonium salts and it appears that the positivity of the 1-carbon atom is increased sufficiently to render it more prone to nucleophilic attack by water molecules (despite the acidic medium), forming a diazo-oxide rather than undergoing the alternative " normal " diazo-decomposition. The effect of the third nitro-group might well be interpreted as an overall effect on the molecule (somewhat analogous to the displacement of a nitro-group from 1 : 3 : 5-trinitrobenzene by nucleophilic reagents), complications due to steric factors in 2 : 3 : 4- or 2 : 4 : 8-trinitro-1-naphthylamine and the quinonoid or non-quinonoid disposition of the third nitro-group to the (1-)diazo-group being borne in mind. Whatever may be the explanation internuclear effects arising from the substitution of a further nitro-group at position 5, 6, 7, or 8 are of definite significance and this is probably one of the best available demonstrations of electronic interaction between groups in different nuclei in a naphthalene molecule, such interactions usually being regarded as weak when compared to effects transmitted within one nucleus (cf. Bunnett and Zahler [10]). Interaction of polynitronaphthalenes with aqueous-methanolic sodium hydrogen sulphide,[11] which can lead to nucleophilic displacement of nitro-groups, also indicated internuclear activation whereas such effects were not apparent in reactions between polynitronaphthalenes and sodium nitrophenyl sulphides,[12] displacement of nitro-groups in the latter reaction requiring at least two nitro-groups in any nucleus to be in 1 : 2-, 2 : 3-, or 1 : 4-positions.

By a Sandmeyer reaction from diazotised 2 : 4 : 5-trinitro-1-naphthylamine Ward and Day [3] obtained a substance designated as crude 1-chloro-2 : 4 : 5-trinitronaphthalene and dehalogenated it in an attempt to prepare 1 : 3 : 5-trinitronaphthalene but the product differed from that described by Dimroth and Ruck.[13] This result is not surprising if considered in terms of the diazo-decompositions discussed above and the Sandmeyer product was probably largely material arising from the diazo-oxide rather than the expected trinitrochloro-compound. Authentic 1 : 3 : 5-trinitronaphthalene has now been prepared by diazo-decomposition from 3 : 5-dinitro-1-naphthylamine and its identity with Dimroth and Ruck's compound established by infrared spectra.

The new 1 : 4 : 6-trinitronaphthalene was obtained from diazotised 4 : 7-dinitro-1-naphthylamine by the method of Hodgson, Mahadevan and Ward,[14] but a similar decomposition of diazotised 2 : 7-dinitro-1-naphthylamine failed to yield 1 : 2 : 7-trinitronaphthalene. In other investigations [15] we failed to obtain 1 : 2 : 4-trinitronaphthalene from 2 : 4- or 3 : 4-dinitro-1-naphthylamine, 1 : 2 : 5-trinitronaphthalene from 2 : 5-dinitro-1-naphthylamine, or 1 : 2 : 8-trinitronaphthalene from 1 : 8-dinitro-2-naphthylamine: in each case diazo-oxide formation in the aqueous decomposition medium intervenes to prevent replacement of the diazonium by the nitro-group.

1 : 4 : 6-Trinitronaphthalene is further nitrated in sulphuric acid to 1 : 3 : 5 : 8-tetranitronaphthalene only, as expected from the simplest considerations but also in agreement with calculations by the theoretical treatment of Sixma,[16] as applied to nitrations of other polynitronaphthalenes.

EXPERIMENTAL

Ultraviolet Absorption Spectrum of 7-*Nitro*-1-*naphthylamine*.—The spectrum was recorded by means of a Unicam SP 500 photoelectric spectrophotometer, the concentration of amine being 0·010 g. of amine per l. of absolute ethanol or *cyclo*hexane. Maxima and, in parentheses,

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[10] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.
[11] Hodgson and Ward, *J.*, 1949, 1187; Ward, Coulson, and Hawkins, *J.*, 1954, 2974.
[12] Hodgson and Ward, *J.*, 1948, 2017; cf. Coulson, ref. 7.
[13] Dimroth and Ruck, *Annalen*, 1926, **446**, 123.
[14] Hodgson, Mahadevan, and Ward, *J.*, 1947, 1392.
[15] Ward, Hawkins, Pierce, and Wells, unpublished work.
[16] Sixma, *Rec. Trav. chim.*, 1954, **73**, 235.

log *E*, were: in EtOH, 2240 (4·47), 2860 (4·28), 3400 sh (3·42), 4380 (3·62): in *cyclo*hexane, 2210 (4·52), 2780 (4·38), 3080 (3·51), 3320 sh (3·34), 4020 (3·64).

*7-Nitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine.*—A mixture of the amine (10 g.) and toluene-*p*-sulphonyl chloride (15 g.) was added slowly, with stirring, to pyridine (30 c.c.). After being heated on the water-bath for 30 min. the mixture was poured into 10% w/v hydrochloric acid (500 c.c.), and the solids were collected, washed with water, and dissolved in warm 2% aqueous sodium hydroxide (500 c.c.). The extract was filtered and acidified by hydrochloric acid, and the solids (17·5 g., 95%) were washed with water; the *product*, crystallised from methanol, had m. p. 208—209° (Found: N, 7·9; S, 9·2. $C_{17}H_{14}O_4N_2S$ requires N, 8·2; S, 9·4%).

*7-Nitro-*N*-phthaloyl-1-naphthylamine.*—The amine (5 g.) and phthalic anhydride (5 g.) were fused together for 5 min. and after cooling extracted with boiling acetic acid (150 c.c.). The extract was refluxed with charcoal, filtered hot, and by concentration to small volume gave 7-nitro-*N*-phthaloyl-1-naphthylamine (6·8 g., 90%), m. p. 252° (from acetic acid) (Found: C, 66·2; H, 3·3. Calc. for $C_{18}H_{10}O_4N_2$: C, 67·9; H, 3·2%).

Nitration of N*-Acetyl-7-nitro-1-naphthylamine.*—The acetyl compound (10 g.) was stirred into nitric acid (*d* 1·5; 10 c.c.) during 40 min. at 12—15°, then set aside for 1 hr., poured on ice and the yellow precipitate of mixed *N*-acetyl-2 : 7- and -4 : 7-dinitro-1-naphthylamine collected (10·8 g., 90%). The mixed amides (5 g.) were refluxed with 0·025N-sodium methoxide in methanol (250 c.c.) for 90 min. and filtered hot, affording 4 : 7-dinitro-1-naphthylamine, which when washed with methanol had m. p. 283° (2·0 g., 47% calc. on amides). The filtrate was poured on ice, yielding impure 2 : 7-dinitro-1-naphthylamine, m. p. 200—214° (2·0 g., 47%) (combined yield on hydrolysis, *ca.* 94%). Alternatively hydrolysis by refluxing ethanol and aqueous sulphuric acid (50% w/v) gives almost a quantitative yield of dinitronaphthylamines. From this mixture (A), 4 : 7-dinitro-1-naphthylamine (40%) is separated by refluxing with methanol (55 c.c./g.), the hot solution being filtered and poured on ice; this yields impure 2 : 7-dinitro-1-naphthylamine (43%).

The pure dinitronaphthylamines were prepared by chromatography of the products from the original hydrolysis in benzene on alumina, with (4 : 1, v/v) benzene–ethanol for elution. Each contained traces of the other, as shown by the formation of two bands on the columns. 2 : *7-Dinitro-1-naphthylamine* was obtained as yellow needles, m. p. 252° (Found: N, 18·1. $C_{10}H_7O_4N_3$ requires N, 18·1%), and 4 : *7-dinitro-1-naphthylamine* as red needles, m. p. 288° (Found: C, 51·3; H, 3·15. $C_{10}H_7O_4N_3$ requires C, 51·5; H, 3·03%).

Spectrographic analysis of the mixture (A) (By J. G. HAWKINS). The measurements were as described[17] earlier for a similar mixture. The spectra of pure 2 : 7- and 4 : 7-dinitro-1-naphthylamine were compared with that of the mixture (A) and, after allowance for differences in the thickness of the films, the amounts were judged to represent 35 ± 10% of 2 : 7-, and 65 ± 10% of 4 : 7-dinitro-1-naphthylamine. All absorption peaks in the mixture were accounted for and further comparison with known spectra failed to show the presence of 7-nitro-1-naphthylamine.

Diazotisation and Diazo-decompositions of 2 : 7- *and* 4 : *7-Dinitro-1-naphthylamines.*—Both amines were readily diazotised by Hodgson and Turner's method.[18] The diazonium salt from 4 : 7-dinitro-1-naphthylamine was deaminated, giving 1 : 6-dinitronaphthalene (43%), but the salt from 2 : 7-dinitro-1-naphthylamine gave no identifiable products. However the latter when poured into water containing sodium acetate, afforded *1-diazo-7-nitro-2-naphthol* (from dioxan; charcoal), m. p. 160—162° (decomp.) (Found: C, 55·6; H, 3·0. $C_{10}H_5O_3N_3$ requires C, 55·8; H, 2·3%). *1-Chloro-*2 : *7-dinitronaphthalene* (50%), m. p. 132—133° (Found: Cl, 13·8. $C_{10}H_5O_4N_2Cl$ requires Cl, 14·0%), *1-bromo-*2 : *7-dinitronaphthalene* (50%), m. p. 137—138° (Found: Br, 26·8. $C_{10}H_5O_4N_2Br$ requires Br, 26·9%), and *1-bromo-*4 : *7-dinitronaphthalene* (40%), m. p. 148° (Found: Br, 27·5%), were prepared by adding the diazonium solutions to solutions of the appropriate cuprous halide (1 g./g. of amine) in the concentrated halogen acid (10 c.c./g.), storage overnight, pouring on ice, extraction of the dried product with hot ethanol, and crystallisation of material from the extract from light petroleum (b. p. 100—120°).

Dehalogenation of 1-bromo-2 : 7-dinitronaphthalene by Smith's method[6] gave 2 : 7-dinitronaphthalene (40%) but the chloro-analogue yielded only unchanged starting material.

*Nitration of 7-Nitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine.*—(a) *Nitration in suspension at* 20—30°. The amide (1 g.) in acetic acid (2 c.c.) was treated with 1 : 1 v/v nitric acid (*d* 1·5)–acetic acid (0·55 c.c.; 10% excess for dinitration) during 15 min. at 20—30°. After storage

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[17] Ward, Coulson, and Hawkins, *J.*, 1954, 918.

[18] Hodgson and Turner, *J.*, 1943, 86.

overnight the solids were collected, washed with ether, and dried (0·80 g., 63% calc. as trinitroamide). A portion (0·2 g.) was chromatographed in benzene on alumina; elution with benzene-ethanol (3 : 1) gave 3 bands which successively yielded a resin (0·005 g.), 2 : 7-*dinitro*-N-*toluene*-p-*sulphonyl*-1-*naphthylamine* (0·075 g.), m. p. 195—200° (Found: C, 52·2; H, 3·5; S, 7·5. $C_{17}H_{13}O_6N_3S$ requires C, 52·6; H, 3·4; S, 8·3%), and water-soluble orange-yellow needles (0·120 g.), m. p. 283° (decomp.), probably the aluminium derivative of 2 : 4 : 7-trinitro-1-naphthol (m. p. unchanged on crystallisation from aqueous ethanol) (Found: C, 42·5; H, 2·4; Al, 3·1. Calc. for $C_{30}H_{12}O_{21}N_9Al$: C, 41·7; H, 1·4; Al, 3·1%). The dinitroamide was identified by hydrolysis to the dinitro-amine.

The original nitration product (0·60 g.) was hydrolysed by sulphuric acid (*d* 1·84; 1 c.c.) at 40° for 5 min. (yield 0·34 g.). This product was chromatographed in benzene on alumina, elution being by benzene–ethyl acetate (4 : 1) and then benzene–ethanol (7 : 3). This yielded both pure 2 : 7-dinitro-1-naphthylamine and 2 : 4 : 7-trinitro-1-naphthylamine (recovery 85%), the latter predominating.

(b) *Nitration in suspension at* 85°. The amide (10·0 g.) in acetic acid (16 c.c.) with a crystal of sodium nitrite was nitrated at 65° by the addition during 20 min. of nitric acid (*d* 1·5; 2·7 c.c.) in acetic acid (2·7 c.c.). The mixture was then heated at 85° for 5 min. and cooled in ice for 30 min. and the solids were collected and washed with ether, yielding 2 : 4 : 7-*trinitro*-N-*toluene*-p-*sulphonyl*-1-*naphthylamine*, m. p. 199—200° (60—75%) (from aqueous acetic acid; charcoal) (Found: C, 47·6; H, 3·05; S, 7·8. $C_{17}H_{12}O_8N_4S$ requires C, 47·2; H, 2·8; S, 7·4%). Hydrolysis as above gave 2 : 4 : 7-*trinitro*-1-*naphthylamine*, m. p. 251—253° (from ethanol) (Found: C, 43·5; H, 2·45. $C_{10}H_6O_6N_4$ requires C, 43·1; H, 2·2%). Chromatography of the hydrolysed nitration product as above gave a tiny amount of 2 : 7-dinitro-1-naphthylamine in addition to the trinitronaphthylamine.

(c) *Nitration in solution at* 20°. The amide (2 g.) in acetic acid (100 c.c.) was treated with nitric acid (*d* 1·5; 0·25 c.c., 1·02 mol.) in acetic acid (10 c.c.), added dropwise during 10 min. at 20°. After 24 hr. the solution was evaporated in a vacuum to 5 c.c., and the solids were collected and washed with acetic acid. A further amount was obtained by pouring the original filtrate into ice-water (combined yield, 92% for mononitration). After hydrolysis the mixed dinitronaphthylamines (1·20 g., 88% overall yield) were extracted portionwise with hot 9 : 1 v/v benzene–ethyl acetate (800 c.c. in all). The extract was filtered to remove an insoluble brown residue (0·3 g.; m. p. >300°) and chromatographed on alumina, elution being with 4 : 1 v/v benzene–ethyl acetate, which gave two bands. The first, yellow band yielded pure 2 : 7-dinitro-1-naphthylamine (0·47 g., 35%) and the second, orange band yielded pure 4 : 7-dinitro-1-naphthylamine (0·25 g., 19%).

Attempts to prepare the *N*-toluene-*p*-sulphonyl derivatives of 2 : 7- and 4 : 7-dinitro-1-naphthylamine by the usual methods failed.

Nitration of 7-*Nitro*-N-*phthaloyl*-1-*naphthylamine*.—The phthalimide (2·3 g.) was added during 30 min. to nitric acid (*d* 1·5; 10 c.c.) below 5°, kept for a further hour at this temperature, then poured on ice, and the product (2·5 g., 98% for mononitration) collected (Found: C, 58·1; H, 3·3. Calc. for a dinitronaphthylphthalimide: C, 59·5; H, 2·5%).

The product (2·3 g.) was hydrolysed by aqueous ammonia (*d* 0·88; 5 c.c.) for 1 hr. at 120°. The black product was washed with water, dried (1·6 g.), then extracted portionwise with 9 : 1 v/v benzene–ethyl acetate (300 c.c. total), and the cooled extract chromatographed on alumina. Elution by the original solvent and then by 3 : 1 v/v benzene–ethyl acetate produced four bands on the column which yielded successively 2 : 7-dinitro-1-naphthylamine (0·050 g.; m. p. 248°), some tar, 4 : 7-dinitro-1-naphthylamine (0·215 g.; m. p. 288°), and a red 7 : x : x-*trinitro*-1-*naphthylamine* (0·225 g.), m. p. 265 (decomp.) (Found: C, 43·1; H, 2·5. $C_{10}H_6O_6N_4$ requires C, 43·2; H, 2·2%) (total yield calc. as dinitronaphthylamines, *ca.* 33%). Similar products, but in lower yield (*ca.* 18%), were obtained by refluxing the nitration product (2·5 g.) with ethanol (15 c.c.) and hydrazine hydrate (90—95% w/w; 1 c.c.) for 2 hr.

The trinitronaphthylamine was diazotised by Hodgson and Turner's method;[18] the diazonium solution coupled readily with alkaline β-naphthol, but did not give a diazo-oxide on addition to ice-water. Attempted deamination by Hodgson and Turner's method[4] yielded a tiny amount of material which was not 1 : 6 : 7-trinitronaphthalene (Coulson[7]) but may have been impure 1 : 3 : 8-trinitronaphthalene.

Diazotisation and Diazo-decompositions of 2 : 4 : 7-*Trinitro*-1-*naphthylamine*.—The amine was diazotised by Hodgson and Turner's method employing a solution in sulphuric acid obtained by hydrolysis of the *N*-toluene-*p*-sulphonyl derivative. Addition of the diazo-solution to water gave an almost quantitative yield of 1-*diazo*-4 : 7-*dinitro*-2-*naphthol*, m. p. 158° (decomp) (from dioxan) (Found : C, 46·8; H, 1·8. $C_{10}H_4O_5N_4$ requires C, 46·2; H, 1·5%). The diazo-oxide (1·0 g.) was refluxed with ethanol (30 c.c.) and freshly prepared copper powder (0·3 g.) till the liquid no longer coupled with alcoholic alkaline resorcinol (*ca.* 3 hr.). Charcoal (0·4 g.) was added and after another hour's refluxing the mixture was filtered hot and, on cooling, deposited 4 : 7-*dinitro*-2-*naphthol*; this was washed with water, dried (0·2 g., 22%), and crystallised from aqueous alcohol as greenish-yellow needles, m. p. 215—217° (Found : C, 51·3; H, 2·9. $C_{10}H_6O_5N_2$ requires C, 51·3; H, 2·6%); 4 : 7-*dinitro*-2-*naphthyl acetate* had m. p. 155—156° (Found : C, 52·0; H, 2·9. $C_{12}H_8O_6N_2$ requires C, 52·2; H, 2·9%).

Attempts to produce 1 : 3 : 6-trinitronaphthalene by deamination using Hodgson and Turner's[4] or Hodgson and Birtwell's method[5] gave complex mixtures from which only 4 : 7-dinitro-2-naphthol could be isolated, even by chromatography. In Sandmeyer reactions the only identifiable material was 1-diazo-4 : 7-dinitro-2-naphthol.

Bromination of 2 : 7- *and* 4 : 7-*Dinitro*-1-*naphthylamines and Attempted Bromination of* 2 : 4 : 7-*Trinitro*-1-*naphthylamine*.—The amine (0·1 g.) was dissolved in pyridine (7 c.c.) and to this was added a 1 : 10 w/v solution of bromine (2 mols) in pyridine (1·5 c.c.). After 2 days the precipitate of almost pure bromodinitronaphthylamine was collected, washed with ether, and crystallised from hot ethanol; 4-*bromo*-2 : 7-*dinitro*-1-*naphthylamine* had m. p. 272° (Found : C, 38·0; H, 1·9; Br, 26·7. $C_{10}H_6O_4N_3Br$ requires C, 38·5; H, 1·9; Br, 25·6%); 2-bromo-4 : 7-dinitro-1-naphthylamine had m. p. 278° (Found : C, 39·0; H, 1·7; Br, 25·1%). Further amounts of products were obtained by pouring the original filtrates into dilute hydrochloric acid (combined yields *ca.* 70%). The trinitroamine was recovered unchanged.

1 : 2 : 4-*Tribromo*-7-*nitronaphthalene* was obtained by diazotising 2 : 4-dibromo-7-nitro-1-naphthylamine by Hodgson and Walker's method[19] and a subsequent Sandmeyer reaction (cf. the behaviour of diazotised 2 : 4 : 7-trinitro-1-naphthylamine) in 50% yield; crystallised from ethanol it had m. p. 183° (Found : C, 29·3; H, 0·98; Br, 56·8. $C_{10}H_4O_2NBr_3$ requires C, 29·3; H, 0·98; Br, 58·5%).

1 : 4 : 6-*Trinitronaphthalene and Attempted Preparation of* 1 : 2 : 7-*Trinitronaphthalene*.—4 : 7-Dinitro-1-naphthylamine (1·5 g.) was dissolved in sulphuric acid (*d* 1·84; 1·5 c.c.) and added to a solution of sodium nitrite (0·6 g.) in sulphuric acid (*d* 1·84; 3·0 c.c.). The mixture was added to acetic acid (9 c.c.) below 20° and after 30 min. ice-cold dry ether was added (20 c.c. quickly, then 80 c.c. slowly), precipitating an oil which started to solidify. The top layer was decanted from the pasty mass, and dry ethanol (10 c.c.) stirred in; after a further 15 min. the solid diazonium sulphate (2·4 g.) was collected. This was made into a slurry with water (20 c.c.) and added to the freshly prepared decomposition medium with vigorous stirring, the latter having been prepared by mixing solutions of copper sulphate crystals (10 g.) in water (100 c.c.) and of crystalline sodium sulphite (10 g.) in water (100 c.c.) and then just before use adding sodium nitrite (30 g.). After 15 min. the product was collected, washed with water, dried, and extracted with hot alcohol (100 c.c.); the extract was refluxed with charcoal, filtered, and concentrated, to give crude 1 : 4 : 6-*trinitronaphthalene* (0·3 g., *ca.* 40%; m. p. 97°); recrystallised from alcohol (charcoal) it formed almost white needles, m. p. 113—114° (Found : N, 16·3. $C_{10}H_5O_6N_3$ requires N, 16·0%). In a similar experiment 2 : 7-dinitro-1-naphthylamine failed to yield a solid diazonium sulphate, but the oily precipitate (cf. Ward and Coulson[20]) was decomposed as above, yielding a complex product from which no trinitronaphthalene could be isolated even by chromatography.

Further Nitration of 1 : 4 : 6-*Trinitronaphthalene* (By J. G. HAWKINS).—To the trinitronaphthalene (1·0 g.) suspended in sulphuric acid (*d* 1·84; 5 c.c.) was added, during 5 min., nitric acid (*d* 1·5; 2·5 c.c., 15 mols.) and the temperature then raised to 80°, kept there for 3 min., then between 70—75° for 1 hr. After 30 min. at 0° the solids were collected, and washed with ice-cold aqueous sulphuric acid (1 : 1 v/v; 4 × 1 c.c.), and then with water (yield 0·67 g., 60%; m. p. 191—193°), identified as slightly impure 1 : 3 : 5 : 8-tetranitronaphthalene by mixed m. p. and infrared spectra. Pouring the original filtrate on ice-water gave a small amount of low-melting material.

1 : 3 : 5-Trinitronaphthalene was prepared (by T. M. COULSON) in *ca.* 60% yield from diazotised 3 : 5-dinitro-1-naphthylamine by a procedure similar to that used by Ward and

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[19] Hodgson and Walker, *J.*, 1933, 1620.

Coulson [20] to make 1 : 2 : 3 : 4-tetrahydro-6 : 7-dinitronaphthalene. After crystallisation from ethanol it had m. p. 119—121° (Found: C, 46·1; H, 2·0. Calc. for $C_{10}H_5O_6N_3$: C, 45·6; H, 1·9%) (Dimroth and Ruck [13] give 119·5°) alone or mixed with 1 : 3 : 5-trinitronaphthalene prepared from 1 : 5-dinitronaphthalene; [13, 21] infrared spectra of the molecular complexes with β-naphthol were also identical.

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Leicester College of Technology and Commerce,
Leicester.

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[20] Ward and Coulson, *J.*, 1954, 4545.

[21] Day, Thesis, London, 1952.