170. *The Preparation and Reactions of* 2 : 4 : 8-*Trinitro*-1-*naphthylamine.*

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2 : 4 : 8-Trinitro-1-naphthylamine is obtained by nitration of 8-nitro-1-toluene-*p*-sulphonamidonaphthalene in acetic acid, followed by hydrolysis in sulphuric acid. Its reactions show the effect of steric hindrance from the 2- and the 8-nitro-group. Nitration of 1-bromo- and 1-chloro-8-nitronaphthalenes affords mixtures of halogenotrinitronaphthalenes which have been dehalogenated to the corresponding trinitronaphthalenes. A new route to 7-nitro-1-naphthylamine has been investigated. Improved hydrolyses of mononitrated α- and β-naphthylphthalimide are reported.

2 : 4 : 8-Trinitro-1-naphthylamine is readily prepared by the dinitration of 8-nitro-1-toluene-*p*-sulphonamidonaphthalene in acetic acid, followed by hydrolysis in sulphuric acid.

Nitration with one equivalent or less of nitric acid still affords the trinitro-compound together with unchanged starting material. The simultaneous dinitration in the 2- and the 4-position is analogous to the dinitrations experienced with the corresponding naphthalides from 1-naphthylamine itself or from 3-, 5-, or 6-nitro-1-naphthylamine (Hodgson and Walker, *J.*, 1934, 180; Hodgson and Turner, *ibid.*, 1942, 723; 1943, 391; Hodgson and Hathway, *J.*, 1944, 561), the nitro-groups entering at the expected 2- and 4-quinonoid positions (Veselý and Jakeš, *Bull. Soc. chim.*, 1923, **33**, 955; Hodgson and Hathway, *J. Soc. Dyers and Col.*, 1945, **61**, 283). The constitution of the trinitronaphthylamine follows from its oxidation to 3-nitrophthalic acid and the ready formation of a diazo-oxide from its diazonium salt showing the adjacence of the nitro- to the amino-group.

The presence of nitro-groups in the 2- and 8-positions, relative to the 1-amino-group, might be expected to lead to a certain amount of steric hindrance in the reactivity of the amino-group, although the reactions of 8-nitro-1-naphthylamine or of 2 : 4-dinitro-1-naphthylamine would not suggest such interference by the 2- or 8-nitro-group alone (cf. Mills and Elliott, *J.*, 1928, 1291; Hunter and Chaplin, *J.*, 1938, 375, 1034). Such diminished activity of the amino-group is now found in attempts to prepare derivatives of the trinitronaphthylamine, in its diazotisation, and in reactions of its diazonium salt. This diminished activity cannot be entirely accounted for by the influence of the 2- and the 4-nitro-group on the basicity of the amino-group [the 8-nitro-group being in a non-quinonoid position will have no effect other than possibly to reinforce the $-I$ effect of the second nucleus (cf. Hodgson and Elliott, *J. Soc. Dyers and Col.*, 1938, **54**, 264)] since it is not shown in the comparable 2 : 4-dinitro-1-naphthylamine which is readily diazotised by Hodgson and Walker's method, and the diazonium salt gives exceptionally good yields in subsequent deamination and Sandmeyer reactions (Hodgson and Walker, *J.*, 1933, 1620; Hodgson and Birtwell, *J.*, 1943, 433).

Thus no reaction could be obtained between 2 : 4 : 8-trinitro-1-naphthylamine and the following reagents: picric acid, 1-chloro-2 : 4-dinitrobenzene, 2 : 3 : 4-trinitrotoluene, 1 : 4-dinitronaphthalene, and *p*-nitrobenzaldehyde. An acetyl compound was obtained with some difficulty. Diazotisation by Hodgson and Turner's method (*J.*, 1943, 86) was only complete after 12 hours, and in subsequent Sandmeyer reactions the yields of 1-bromo- and 1-chloro-2 : 4 : 8-trinitronaphthalenes were very low, their formation being accompanied by large amounts of resinous material containing azo-compounds, the halogeno-compounds being separated from the latter only with great difficulty. Various attempts to prepare 1-iodo-2 : 4 : 8-trinitronaphthalene failed completely. 1-Chloro-2 : 4 : 8-trinitronaphthalene has previously been obtained in an impure form by fractional crystallisation from a mixture with 1-chloro-2 : 4 : 5-trinitronaphthalene, which is the main product of nitration of 1-chloro-2 : 4-dinitronaphthalene (Rindl, *J.*, 1913, 1911; Talen, *Rec. Trav. chim.*, 1928, **47**, 346).

1-Diazo-4 : 8-dinitro-2-naphthol was instantly formed when the diazo-solution prepared as above was poured on ice; it also tends to be formed as a by-product in the Sandmeyer reactions, and its decomposition might account for some of the resinous by-products formed therein. The diazo-naphthol is a comparatively stable compound, and attempts to introduce halogen in place of the diazo-group by Sandmeyer reaction gave largely unchanged material. It could however be deaminated to 4 : 8-dinitro-2-naphthol by being refluxed with a mixture of aluminium and copper powder in ethanol (cf. Hodgson and Turner, *J.*, 1944, 8). Decomposition by copper powder alone was much faster but yields of the deaminated product were lower.

Deamination of 2 : 4 : 8-trinitro-1-naphthylamine should afford 1 : 3 : 5-trinitronaphthalene, a compound previously reported only as a minor product in the nitration of 1 : 5-dinitronaphthalene, and whose existence is not absolutely proven. However, diazotisation of the trinitronaphthylamine and deamination by cuprous oxide alone or with cuprous oxide–methanol afforded as main product 4 : 8-dinitro-2-naphthol. Similar failures to replace the diazonium group by hydrogen have been experienced with 2 : 4 : 6-trinitro-1-naphthylamine (Ward, Ph.D. Thesis, London University, 1948) and with 1 : 4 : 6-trinitro-2-naphthylamine, which afforded only 4 : 6-dinitro-1-naphthol (Hodgson and Hathway, *J.*, 1945, 453).

Against this Hodgson and Hathway (*J.*, 1944, 561) obtained 1 : 2 : 3-trinitronaphthalene by deamination of 2 : 3 : 4-trinitro-1-naphthylamine. Staedel's claims (*Ber.*, 1881, **14**, 898; *Annalen*, 1883, **217**, 153, 173, 174) to have deaminated both 2 : 4 : 5-trinitro-1-naphthylamine and 1 : 6 : 8-trinitro-2-naphthylamine cannot be accepted. He claims to have diazotised 1 : 6 : 8-trinitro-2-naphthylamine in concentrated nitric acid and then decomposed the diazonium salt by pouring it into hot alcohol (*sic*), getting two products (neither in sufficient quantity for analysis), one of which was supposed to be 1 : 3 : 8-trinitronaphthalene. No experimental details of the preparation or deamination of the other trinitronaphthylamine are reported.

Since we desired to examine the properties of an authentic specimen of 1 : 3 : 5-trinitronaphthalene in detail we attempted its preparation by dehalogenation of 1-halogeno-2 : 4 : 8-trinitronaphthalenes using Smith's method (*J. Amer. Chem. Soc.*, 1949, **71**, 2855). It was obvious from the Sandmeyer reactions reported above that we could not obtain the halogeno-compound in any quantity from 2 : 4 : 8-trinitro-1-naphthylamine and we therefore investigated their preparation by dinitration of 1-halogeno-8-nitronaphthalenes (Rindl's method, *loc. cit.*, for preparing 1-chloro-2 : 4 : 8-trinitronaphthalene is unsatisfactory). 1-Chloro- and 1-bromo-8-nitronaphthalenes were readily dinitrated in sulphuric acid but the products were mixtures since on dehalogenation they afforded mixtures of trinitronaphthalenes. On nitrating the dehalogenated product of the dinitration of 1-bromo-8-nitronaphthalene both 1 : 4 : 5 : 8- and 1 : 3 : 5 : 8-tetranitronaphthalene were obtained pure, together with a very small amount of a third product. The production of 1 : 4 : 5 : 8-tetranitronaphthalene demonstrates that the original trinitronaphthalenes must have contained the 1 : 4 : 5-compound (arising from the dehalogenation of 1-bromo-4 : 5 : 8 trinitronaphthalene), and the amount of 1 : 3 : 5 : 8-tetranitronaphthalene produced indicated the presence of a trinitronaphthalene other than the 1 : 4 : 5-isomer. This was therefore probably 1 : 3 : 5-trinitronaphthalene although the 2 : 5 : 8(1 : 4 : 6)-isomer, arising from 1-bromo-2 : 5 : 8-trinitronaphthalene, is not completely excluded. We were unable to separate the mixtures of trinitronaphthalenes nor could we obtain pure 1 : 3 : 5-trinitronaphthalene by treating the mixture in organic solvents with compounds with which it has been reported to form molecular compounds.

We had therefore no alternative but to dehalogenate crude 1-chloro-2 : 4 : 8-trinitronaphthalene (from the Sandmeyer reaction reported above) and from this we obtained a trinitronaphthalene, m. p. 151—152°. This melting point is much higher than that previously reported for 1 : 3 : 5-trinitronaphthalene (Dimroth and Ruck, *Annalen*, 1925, **446**, 123, give 120°). Nevertheless the amount obtained was so small that we are now pursuing alternative routes to its preparation, starting from 1 : 7-dinitronaphthalene.

We have investigated a new route to the rare 7-nitro-1-naphthylamine. Nitration of 1-aceto-4-bromo-8-nitronaphthalide yields a mononitration product which can reasonably be regarded as 1-aceto-4-bromo-2 : 8-dinitronaphthalide. Hydrolysis of this naphthalide followed by deamination to 1-bromo-3 : 5-dinitronaphthalene and subsequent reduction of this by stannous chloride should yield the required product. Unfortunately attempts to hydrolyse the 1-aceto-4-bromo-2 : 8-dinitronaphthalide failed and we have temporarily discontinued the investigation.

An improved procedure for obtaining 8-nitro-1-naphthylamine from the nitration products of α-naphthylphthalimide, by Hodgson and Ratcliffe's method (*J.*, 1949, 1314), is reported and this method has also been applied to the hydrolysis of the similar products from the β-naphthylphthalimide. Hydrolyses of the former mixture with aqueous ethanolic sulphuric acid or with aqueous ethanolic sodium hydroxide failed to give the desired product. Hydrolysis with aqueous ethanolic hydrochloric acid (Hey and Lawton, *J.*, 1940, 281; Hodgson and Dean, *J.*, 1950, 820) gave much lower yields of mixed nitro-amines after long reaction periods.

Experimental.

(Analyses are by Drs. Weiler and Strauss, Oxford.)

α- and β-Naphthylphthalimides were nitrated by Hodgson and Crook's method (*J.*, 1936, 1844).

Improved Preparation of 8-*Nitro*-1-*naphthylamine.*—Hydrazine sulphate (450 g.) and sodium hydroxide (280 g.) were dissolved in water (850 c.c.), ethanol (2800 c.c.) was added to the cooled solution, and the precipitated sodium sulphate filtered off. The mixed nitronaphthylphthalimides (560 g.) were then refluxed with this solution for 45 minutes, giving a clear, red liquid, which, after cooling, was acidified with aqueous sulphuric acid (50% w/v) at 0° and filtered, and the residue extracted repeatedly with cold 2N-sulphuric acid (in all *ca.* 5 l.). The combined extracts were basified at 0° with ammonia solution (*d* 0·88). The crude 8-nitro-1-naphthylamine (175 g.; 53%, calculated on the total theoretical yield of nitro-amines) had m. p. 90—95° (cf. Hodgson and Ratcliffe, *J.*, 1949, 1314, who obtained a 36% yield of similar purity).

Improved Hydrolysis of the Mixture of 5- *and* 8-*Nitro*-2-*naphthylphthalimide.*—The mixed nitronaphthylphthalimides (560 g.) were hydrolysed as above for 1 hour, and the residue obtained by pouring the product into water was extracted by boiling hydrochloric acid (10% w/v). The extracts on basification afforded *ca.* 270—300 g. of mixed nitro-amines (80—90%) (cf. Hodgson and Dean, *loc. cit.*, who record a yield of 56%).

8-*Nitro*-1-*naphthylphthalimide.*—8-Nitro-1-naphthylamine (2 g.) was fused with phthalic anhydride (2 g.) until frothing ceased (10 minutes). The cooled melt was extracted with boiling acetic acid (50 c.c.) and filtered, and the *phthalimide* obtained by concentration of the extract. Recrystallisation from the same solvent gave needles, m. p. 239·5° (Found: N, 8·6. $C_{18}H_{10}O_4N_2$ requires N, 8·8%).

8-*Nitro*-1-*toluene*-p-*sulphonamidonaphthalene.*—8-Nitro-1-naphthylamine (45 g.) was ground with

toluene-*p*-sulphonyl chloride (135 g.), and pyridine (110 c.c.) added; there was an immediate evolution of heat and considerable frothing. The reaction was completed by heating the solution on the water-bath for 1 hour. The cooled solution was poured into hydrochloric acid (10% w/v; 2 l.) with vigorous stirring. The precipitate was filtered off, washed with dilute hydrochloric acid and then water, and extracted with warm aqueous sodium hydroxide (3% w/v; 1500 c.c.). The extract was filtered and the naphthalide reprecipitated with hydrochloric acid. The yield was almost quantitative (m. p. 152—155°). Recrystallised twice from alcohol the 8-*nitro*-1-*toluene*-p-*sulphonamidonaphthalene* had m. p. 162—166° (Found : S, 9·5. $C_{17}H_{14}O_4N_2S$ requires S, 9·4%). No ditoluene-*p*-sulphonamide was obtained when the reaction was continued for longer periods, a very large excess of toluene-*p*-sulphonyl chloride being used, or when the reaction was carried out in aqueous medium (cf. Hodgson and Ward, *J.*, 1947, 327).

1-*Chloro*-8-*nitronaphthalene.*—8-Nitro-1-naphthylamine (10 g.) was dissolved in boiling glacial acetic acid (50 c.c.), and the solution cooled to 15° and added to sodium nitrite (4·5 g.) dissolved in sulphuric acid (25 c.c.; *d* 1·84) below 30°. After 10 minutes the mixture was poured with vigorous stirring into a solution of cuprous chloride (20 g.) in hydrochloric acid (80 c.c.; *d* 1·2) and left overnight. The product was obtained by pouring the reaction mixture on ice, separated, washed with water, and extracted with boiling ethanol (200 c.c.; charcoal). On concentration to about 50 c.c. the chloro-compound (6·5 g., 60%), m. p. 95—97°, was obtained (Ullmann and Consonno, *Ber.*, 1902, **35**, 2802, give 94—95°). The yield was almost the same when the amine was diazotised in aqueous hydrochloric acid.

1-*Bromo*-8-*nitronaphthalene.*—This was obtained by a similar procedure, cuprous bromide (20 g.) and hydrobromic acid (80 c.c. 48%) being used to decompose the salt. The bromo-compound (6·5 g.; *ca.* 50%) had m. p. 95—98° after recrystallisation from ethanol (Meldola and Streatfeild, *J.*, 1893, **63**, 1057, give 99—100°). A similar yield was obtained by diazotisation in hydrobromic acid.

Nitration of 8-*Nitro*-1-*toluene*-p-*sulphonamidonaphthalene.*—The naphthalide (40 g.) was suspended in glacial acetic acid (80 c.c.) at 65° and a solution of nitric acid (12 c.c.; *d* 1·5) in glacial acetic acid (48 c.c.) added slowly (after the addition of a crystal of sodium nitrite), the temperature being maintained below 80°. The reaction was complete almost immediately and, after cooling in ice, the product was filtered off, and washed with small amounts of glacial acetic acid and then several times with ether. It was dried *in vacuo* (29·7 g., 58%) and on recrystallisation twice from glacial acetic acid the 2 : 4 : 8-*trinitro*-1-*toluene*-p-*sulphonamidonaphthalene* was obtained as cream needles, m. p. 215° (decomp.) (Found : S, 7·2. $C_{17}H_{12}O_8N_4S$ requires S, 7·4%). This compound was hydrolysed by dissolution in twice its weight of sulphuric acid (*d* 1·84), warming it to 40° for 5 minutes, and pouring it on ice. The yield was quantitative. Recrystallised twice from alcohol the 2 : 4 : 8-*trinitro*-1-*naphthylamine* formed orange-yellow needles, m. p. 189—190° (Found : N, 19·8. $C_{10}H_6O_6N_4$ requires N, 20·2%). The trinitro-naphthylamine was recovered unchanged after being refluxed with acetic acid–acetic anhydride–fused sodium acetate for 12 hours. 1-*Aceto*-2 : 4 : 8-*trinitronaphthalide* was however obtained by the following procedure. The amine (0·5 g.) was warmed with acetic anhydride (1 c.c.) and sulphuric acid (1 drop) for 2 minutes, water (3 c.c.) was added dropwise with cooling, and the solution warmed gently and then cooled. The product was recrystallised twice from hot acetic acid, giving creamy plates, m. p. 207° (Found : N, 17·7. $C_{12}H_8O_7N_4$ requires N, 17·5%).

Diazotisation of 2 : 4 : 8-*Trinitro*-1-*naphthylamine.*—The toluene-*p*-sulphonyl derivative (30 g.) was dissolved in sulphuric acid (30 c.c.), hydrolysed by being warmed, and then added to a solution of sodium nitrite (10 g.) in sulphuric acid (50 c.c.) below 20°. The mixture was slowly added, with stirring, to acetic acid (160 c.c.) below 30°. When this solution (12 c.c.) was treated with ice-cold, dry ether (50 c.c.) at 0° and left for a day in the ice-bath it gave a small yield of the solid diazonium sulphate admixed with sodium sulphate (1 g. in all).

1-*Diazo*-4 : 8-*dinitro*-2-*naphthol.*—The above diazonium solution (40 c.c.) (from 5 g. of naphthalide) was poured on crushed ice (200 g.) and the precipitate filtered off, washed with water, and dried *in vacuo* in the absence of light. The 1-*diazo*-4 : 8-*dinitro*-2-*naphthol* (2·7 g.; *ca.* 90%) crystallised from aqueous dioxan (1 : 1) in golden-yellow needles, m. p. 152—155° (decomp.) (Found : N, 21·0. $C_{10}H_4O_5N_4$ requires N, 21·5%).

4 : 8-*Dinitro*-2-*naphthol.*—The diazo-naphthol (2·5 g.) was refluxed with ethanol (75 c.c.), aluminium powder (0·5 g.), and copper powder (0·2 g.) until the liquid no longer coupled with alkaline alcoholic resorcinol (*ca.* 5 hours), charcoal (1 g.) was added and refluxing continued for a further hour. The mixture was filtered, and concentration afforded 4 : 8-*dinitro*-2-*naphthol* (1 g., 45%), which crystallised from sulphuric acid (*d* 1·84) in greenish-yellow needles, m. p. 262—263° (decomp.) (Found : N, 11·8. $C_{10}H_6O_5N_2$ requires N, 11·95%). When copper powder (0·7 g.) was used alone, reaction was complete in 3 hours but the yield was then only 36%; substitution of ethanol by methanol in these reactions produced similar results (cf. Hodgson and Turner, *J.*, 1944, 8). 4 : 8-*Dinitro*-2-*naphthyl acetate* was formed when the dinitronaphthol (0·5 g.) was warmed with glacial acetic acid (1 c.c.) and acetic anhydride (1 c.c.) for 10 minutes. The ester was precipitated by addition of water (5 c.c.) and recrystallised twice from acetic acid, giving plates, m. p. 146° (Found : N, 10·25. $C_{12}H_8O_6N_2$ requires N, 10·2%).

Sandmeyer Reactions with 2 : 4 : 8-*Trinitro*-1-*naphthylamine.*—The toluene-*p*-sulphonyl derivative (3·9 g.; equivalent to 2·5 g. of amine) was diazotised as above and decomposed as follows :

(*a*) With cuprous chloride (8 g.) and hydrochloric acid (40 c.c.; *d* 1·2) at 20° overnight. The mixture was poured on ice, giving a dark brown powder, which was separated, washed with water, and extracted with boiling methanol (100 c.c.; charcoal). The filtered extract on concentration gave crude 1-chloro-2 : 4 : 8-trinitronaphthalene (0·4 g.; m. p. 130—140°), which formed yellow needles, m. p. 152·5—155·5°, from aqueous dioxan (1 : 1) (Rindl, *loc. cit.*, gives 118—126°; Talen, *loc. cit.*, gives 120°) (Found : Cl, 12·4. $C_{10}H_4O_6N_3Cl$ requires Cl, 11·9%). A small amount of dark-red product (m.p. >400°) (probably an azo-compound) was insoluble in the aqueous dioxan (Found : N, 8·7%).

(*b*) With cuprous bromide (12 g.) and hydrobromic acid (50 c.c.; 48%); the procedure was as in (*a*). The ethanol extract afforded dark brown, crude 1-*bromo*-2 : 4 : 8-*trinitronaphthalene* (1·3 g.; m. p. 90—95°) which could not be satisfactorily purified by recrystallisation from organic solvents. Dark brown needles, m. p. 95—115°, were obtained from aqueous dioxan (1 : 1) (Found: Br, 20·15. $C_{10}H_4O_6N_3Br$ requires Br, 23·3%). Again a small amount of dark-red azo(?)-compound (m. p. 326°) was obtained as a by-product.

Attempted Deamination of 2 : 4 : 8-*Trinitro*-1-*naphthylamine.*—Deamination of the diazonium solution described above with cuprous oxide alone or with cuprous oxide–methanol afforded small yields of brown products (m. p. 180—195°), which on crystallisation from warm concentrated sulphuric acid gave pure 4 : 8-dinitro-2-naphthol. The free amine was diazotised similarly and gave the same product. The sulphuric acid residues when poured on ice gave tiny amounts of a golden-yellow substance which had m. p. 117—119° when crystallised from alcohol (Found: N, 14·1%).

Nitration of 1-*Chloro- and* 1-*Bromo*-8-*nitronaphthalenes.*—The halogenonitronaphthalene (15 g.) was suspended in sulphuric acid (100 c.c.; *d* 1·84) and treated at 20° with a mixture of nitric acid (7 c.c.; *d* 1·5) (*ca.* 30% excess for dinitration) and sulphuric acid (28 c.c.; *d* 1·84) for 15 minutes, the temperature being kept below 40°. The mixture was then cooled in ice for 20 minutes, and the precipitate filtered off, washed with water, and dried.

The crude 1-*chloro*-compound (m. p. 180—210°; 11·0 g.) was recrystallised from hot ethanol; the straw-coloured product had m. p. 250—255° [Found: Cl, 12·3. $C_{10}H_4(NO_2)_3Cl$ requires Cl, 11·9%]. The residual liquors from the nitration were poured on ice and yielded a yellow product (0·8 g.), m. p. 60—90°.

The bromonitronaphthalene gave a cream *trinitro*-compound (m. p. 160—162° after shrinking at 152°) (14 g.), which, after crystallisation from hot ethanol, melted sharply at 168—169° (shrinking from 152°) Found: Br, 23·6. $C_{10}H_4O_6N_3Br$ requires Br, 23·3%). The residual filtrate gave a product (4 g.; m. p. 120°) which was more soluble in ethanol than the first.

Dehalogenation of Halogenotrinitronaphthalenes.—The general procedure was that used by Smith (*loc. cit.*) (cf. Rindl, *loc. cit.*) for preparing 1 : 3-dinitronaphthalene from 1-chloro-2 : 4-dinitronaphthalene.

(*a*) The bromotrinitronaphthalene (10 g.) from the nitration of 1-bromo-8-nitronaphthalene, after removal of the copper bronze and excess of benzoic acid, was extracted with ethanol (50 c.c.). On cooling the extract deposited a yellow-orange substance (4 g.) which on recrystallisation from ethanol had m. p. 108—109° (2 g.) (Found: C, 46·4; H, 1·85. Calc. for $C_{10}H_5O_6N_3$: C, 45·6%; H, 1·9%).

This was very soluble in dioxan, ether, benzene, toluene, and chloroform; it was not sublimed by being heated to 180° at 15 mm. It gave the following colour reactions, suggestive of a trinitronaphthalene: cherry red with a cold aqueous ethanol solution of sodium sulphite, red becoming brown with sodium hydroxide in aqueous acetone, and pale red on being heated with aqueous sodium hydroxide. When it (0·2 g.) was dissolved in the minimum quantity of chloroform and a saturated solution of β-naphthol added there was no precipitate, and concentration only afforded mixed crystals of the two reactants, there being no evidence of the formation of a molecular compound (cf. Dimroth and Ruck, *loc. cit.*). No molecular compounds could be obtained with α-naphthylamine, β-naphthylamine or diphenylamine (cf. Sudborough and Karvé, *J. Indian Inst. Sci.*, 1921—1922, **4**, 43). The "trinitronaphthalene" (2 g.) was added to a mixture of nitric acid (8 c.c.; *d* 1·5) and sulphuric acid (10 c.c.; *d* 1·84) with stirring at 20°, and the mixture cautiously warmed to 80—90° until frothing ceased (about 10 minutes), then on a water-bath for 30 minutes. After cooling to 0° the solid which separated was removed, repeatedly washed with water, and then repeatedly extracted with boiling acetone (150 c.c. in all); the residue (0·23 g.) had m. p. 375° (decomp.) and was identical with an authentic specimen of 1 : 4 : 5 : 8-tetranitronaphthalene. The acetone extracts on concentration (to 20 c.c.) deposited a white product (0·07 g.), m. p. 280° (decomp.), consisting mainly of needles with bifurcate ends with smaller amounts of cubic crystals. The residual acetone solution on evaporation to dryness affording almost pure 1 : 3 : 5 : 8-tetranitronaphthalene (0·5 g.), identical with an authentic specimen. 0·23 g. of 1 : 4 : 5 : 8-tetranitronaphthalene would be produced from about 0·8 g. of 1 : 4 : 5-trinitronaphthalene which at the same time would yield only about 0·1 g. of 1 : 3 : 5 : 8-tetranitronaphthalene (Ward and Day, unpublished work).

(*b*) The chlorotrinitronaphthalene (10 g.) from the nitration of 1-chloro-8-nitronaphthalene in a similar manner gave an orange-yellow product (0·6 g.; m. p. 108—125°) with properties similar to those of the substance reported above.

(*c*) Crude 1-chloro-2 : 4 : 8-trinitronaphthalene (5 g.), from the Sandmeyer reaction described above, gave a yellow-orange product (0·4 g.; m. p. 141—146°). Recrystallised from aqueous dioxan (1 : 1) it had m. p. 151—152° (Found: N, 15·5. Calc. for $C_{10}H_5O_6N_3$: N, 16·0%). The mixed melting point with the starting material was 119—130° and with 1 : 4 : 5-trinitronaphthalene was 116—125° (1 : 4 : 5-trinitronaphthalene has m. p. 149°). The Lassaigne test showed the absence of chlorine.

Preparation and Attempted Hydrolysis of 1-*Aceto*-4-*bromo*-2 : 8-*dinitronaphthalide.*—1-Aceto-8-nitronaphthalide was easily prepared by dissolving 8-nitro-1-naphthylamine (5 g.) in warm glacial acetic acid, adding acetic anhydride (5 c.c.), and refluxing for 10 minutes. This was converted directly into its 4-bromo-derivative by adding more glacial acetic acid (10 c.c.) followed by a solution of bromine (1·5 c.c.) in acetic acid (15 c.c.), added dropwise. The solution was refluxed for 1 hour and charcoal added after 45 minutes. The hot solution was filtered and concentrated giving 1-aceto-4-bromo-8-nitronaphthalide which when recrystallised from alcohol had m. p. 197—201° (Hodgson and Crook, *J.*, 1936, 1338, give 202°), depressed by 1-aceto-2 : 4-dibromo-8-nitronaphthalide.

The naphthalide was nitrated by adding it slowly to nitric acid (5 c.c.; *d* 1·5) at 0°, the temperature being kept at 5—10° until it became steady (30 minutes). The mixture was poured into ice-water

(250 g.), and the product separated, washed with water, and dried *in vacuo* (yield 1·7 g., 98%). Recrystallised from aqueous acetic acid (60% v/v) the 1-*aceto*-4-*bromo*-2 : 8-*dinitronaphthalide* formed micro-crystals, m. p. 208—211° (Found : Br, 22·5. $C_{12}H_8O_5N_3Br$ requires Br, 22·6%). When heated under reflux for periods of up to 10 hours with aqueous ethanolic hydrochloric acid or aqueous ethanolic sulphuric acid (60% w/v) the dinitronaphthalide was largely recovered unchanged.

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