2 : 3-*Derivatives of Naphthalene. Part I. The Nitration of* N-*Acetyl-3-nitro-1-naphthylamine.*

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N-Acetyl-3-nitro-1-naphthylamine with fuming nitric acid yields a mixture of 3 : 5- and 3 : 8-dinitro-derivatives, and not the 2 : 3-dinitro-amide as claimed by Hodgson and Turner (*J.*, 1943, 635). Their " 2 : 3-dinitronaphthalene " and " 3-nitro-2-naphthylamine " were therefore mixtures of 1 : 6- and 1 : 7-dinitronaphthalene, and of 5- and 8-nitro-2-naphthylamine respectively. Data reported for this " 3-nitro-2-naphthylamine " are consequently invalid. The interpretation of the new results, and of those of Sihlbom (*Acta Chem. Scand.*, 1954, in the press), who used boron trifluoride as catalyst in the nitration, is discussed.

Reduction of 1 : 3-dinitronaphthalene by catalytic transfer hydrogenation yields a mixture of 3-nitro-1- and 4-nitro-2-naphthylamine.

3-NITRO-2-NAPHTHYLAMINE was first claimed to have been prepared by Hodgson and Turner (*J.*, 1943, 635) by partial reduction of 2 : 3-dinitronaphthalene. The latter was made by the nitration of *N*-acetyl-3-nitro-1-naphthylamine in fuming nitric acid below 0°, giving the 2 : 3-dinitro-compound, which was then hydrolysed, diazotised, and deaminated. Physical properties of the amine were subsequently investigated [Hodgson and Hathway, *J.*, 1945, 841; *Trans. Faraday Soc.*, 1947, **43**, 643 (ultra-violet spectrum); Bryson, *ibid.*, 1949, **45**, 257 (pK_a); Hathway and Flett, *ibid.*, p. 818 (infra-red spectrum)].

However, the m. p. (159°) of the 2 : 3-dinitronaphthalene obtained by Hodgson and Turner could not be raised to that (170·5—171°) given by Chudožilov (*Coll. Czech. Chem. Comm.*, 1929, **1**, 302) for the specimen he prepared by dehydrogenation of 1 : 2 : 3 : 4-tetrahydro-6 : 7-dinitronaphthalene.

Nitration of *N*-acetyl-3-nitro-1-naphthylamine under the conditions used by Hodgson and Turner has now been shown to yield a mixture of *N*-acetyl-3 : 5- and 3 : 8-dinitro-1-naphthylamine. The free amines obtained by hydrolysis can be separated by extraction with ligroin. The proportions of the two amines were shown to be 35(±5) : 65(±5) by infra-red spectrographic analysis. The two amines were orientated by diazotisation and deamination to the known 1 : 7- and 1 : 6-dinitronaphthalene respectively; identification of the deamination products by mixed m. p. determinations was confirmed by comparison of their infra-red spectra with those of authentic specimens (Whiffen, Hawkins, and Ward, unpublished work). A wide variety of reaction conditions was then tried in vain attempts to prepare *N*-acetyl-2 : 3-dinitro-1-naphthylamine: *e.g.*, on attempted nitrations with diacetylorthonitric acid in acetic acid, and with acetyl nitrate in acetic anhydride, at room temperature and at 60°, the only basic product isolated after hydrolysis was 3-nitro-1-naphthylamine; such reaction as did occur appeared to be oxidation rather than nitration. The significance of this resistance of *N*-acetyl-3-nitro-1-naphthylamine to nitration is discussed below.

These results imply (cf. Ward and Coulson, *Chem. and Ind.*, 1953, **542**, where a preliminary account was given) that Hodgson and Turner's " 2 : 3-dinitronaphthalene " was a variable mixture of 1 : 6- and 1 : 7-dinitronaphthalene, and that the " 3-nitro-2-naphthylamine " obtained by partial reduction was a variable mixture of 5- and 8-nitro-2-naphthylamine. A detailed critical examination of all of the reported properties of the supposed " 3-nitro-2-naphthylamine " accords with this conclusion. The physical measurements made on the supposed " 3-nitro-2-naphthylamine " are therefore invalid, and authentic results will be published in forthcoming papers.

Sihlbom (*Acta Chem. Scand.*, 1954, in the press; and personal communication) has also been unable to repeat Hodgson and Turner's work but reports that nitration of *N*-acetyl-3-nitro-1-naphthylamine in acetic acid with fuming nitric acid in the presence of boron trifluoride gave in good yield a mixture of *N*-acetyl-2 : 3- and -3 : 4-dinitro-1-naphthylamine (ratio *ca.* 1 : 7). Examination of the infra-red spectra of 2 : 3- and 3 : 4-dinitro-1-naphthylamine obtained by Sihlbom, and of 3 : 5- and 3 : 8-dinitro-1-naphthylamine obtained by us, showed the absence, in each of these specimens, of any significant amounts of the others; furthermore 2 : 3- and 3 : 4-dinitro-1-naphthylamine were absent from our crude nitration product after hydrolysis (Whiffen, Hawkins, and Ward, unpublished work).

Further, *N*-acetyl-2 : 3-dinitro-1-naphthylamine, as obtained by Sihlbom, was not identical with the original specimen of " 2 : 3-dinitro-1-acetnaphthalide " prepared by Hodgson and Elliott (*J.*, 1936, 1151) by nitration of *N*-acetyl-3-chloro-1-naphthylamine. The latter nitration is now under reinvestigation.

In attempting to interpret these results on the nitration of *N*-acetyl-3-nitro-1-naphthylamine both the relative difficulty of reaction and the positions of substitution must be accounted for. The 1-acetamido-group is theoretically expected to activate the 2- and, more strongly, the 4-position (cf. Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953, pp. 264—266), this hypothesis having been demonstrated experimentally for *N*-acetyl-1-naphthylamine itself and for its other nitro-derivatives. The 3-nitro-group is expected to deactivate the 4-position strongly, and the 2-position only weakly, owing to the presumed lower order of the 2 : 3- as compared to the 3 : 4-bond. On these grounds, Hodgson and Turner's expectation (*loc. cit.*) that *N*-acetyl-3-nitro-1-naphthylamine would be nitrated only, or mainly, in the 2-position is reasonable, even if steric factors are also considered (Ingold, *op. cit.*, pp. 267—278).

Since *m*-nitroacetanilide is nitrated with acetyl nitrate (giving mainly 3 : 4-dinitroacetanilide; Pictet and Rhotinsky, *Ber.*, 1907, **40**, 1165), and *N*-acetyl-8-nitro-1-naphthylamine is nitrated with diacetylorthonitric acid (giving *only* the 4 : 8-dinitro-derivative; Hodgson and Crook, *J.*, 1936, 1138), *N*-acetyl-3-nitro-1-naphthylamine might be expected to be nitrated under similar mild conditions. In fact, nitration occurs only when the electrophilic reagent is much more reactive. Although 1 : 3-derivatives of naphthalene often show unusual properties (cf. Ward, Coulson, and Hawkins, *J.*, 1954, 5252), our explanation in this case is that, while the 4-position is too weakly activated for substitution under mild conditions, reaction at the 2-position is prevented by steric hindrance. Under the conditions used by Sihlbom (*loc. cit.*) the electrophilic activity of the reagent is increased, presumably by formation of a nitronium complex (Booth and Martin, " Boron Trifluoride and its Derivatives," Wiley and Sons, New York, 1949, p. 196) and nitration then occurs. In Sihlbom's experiments the boron trifluoride may co-ordinate at either the 1-acetamido-group or the 3-nitro-group, in both cases producing a strongly deactivated complex. It must be concluded that if such complex formation does occur it cannot go to completion, otherwise either no reaction would occur at all, or substitution would be entirely in the nitrogen-carrying nucleus. It seems to us, therefore, that Sihlbom's results point again to considerable steric hindrance at the 2-position which outweighs the stronger activation there, accounting for the predominance of *N*-acetyl-3 : 4-dinitro-1-naphthylamine in the product.

Our results suggest that in fuming nitric acid salt formation occurs at the acetamido-group, with consequent deactivation of the substituted nucleus. Further substitution would then occur at the reactive α-positions (5 and 8) of the unsubstituted nucleus, numerous cases being known where naphthalene derivatives strongly deactivated in one nucleus undergo further substitution in this manner. One might also cite here the nitration of *N*-acetyl-2-naphthylamine in fuming nitric acid to the 1 : 5- and 1 : 8-dinitro-derivatives (Veselý and Jakeš, *Bull. Soc. chim.*, 1923, **33**, 942), which Dean (Thesis, London, 1952) suggested was rational on the basis of salt formation. Nevertheless we are not entirely satisfied with this explanation since one would not expect ready salt formation with *N*-acetyl-3-nitro-1-naphthylamine and if it occurred it would not necessarily be complete. In these circumstances reaction might have proceeded entirely through the neutral form with substitution confined to the same nucleus or alternatively some substitution would have been expected at the 2- and the 4-position (Ingold, *op. cit.*, pp. 241—243). We are now studying *N*-acetyl-3- and 4-nitro-2-naphthylamine.

Whilst all other methods of reducing 1 : 3-dinitronaphthalene yield a mixture of 3-nitro-1- and 4-nitro-2-naphthylamine, it was claimed by Veselý and Rein (*Arhiv Kem.*, 1927, **1**, 55) that reduction by hydrogen–platinum black yielded the former only. We have found reduction by catalytic transfer hydrogenation (Linstead, Braude, Mitchell, Wooldridge, and Jackman, *Nature*, 1952, **169**, 100) to give a mixture of the nitronaphthylamines.

A modification of Hodgson and Birtwell's method (*J.*, 1944, 75) for separating 3-nitro-1- and 4-nitro-2-naphthylamine by selective acetylation, which is more convenient for obtaining *N*-acetyl-3-nitro-1-naphthylamine in quantity, is described. Attempts to separate these two nitronaphthylamines by chromatography from benzene on alumina failed (cf. Dean, *loc. cit.*, who reported failure with both alumina and silica).

EXPERIMENTAL

M. p.s are corrected.

Reduction of 1 : 3-*Dinitronaphthalene by Catalytic Transfer Hydrogenation.*—1 : 3-Dinitronaphthalene (2·5 g.) was refluxed vigorously with *cyclo*hexene (9 c.c.), ethanol (25 c.c.), and 10% palladised charcoal (0·25 g.) for 24 hr. The hot solution was then filtered and evaporated to dryness. The residue was extracted thrice with boiling hydrochloric acid (10% w/v; 100 c.c. total), and the combined extracts were cooled and basified. The product, a mixture of 3-nitro-1- and 4-nitro-2-naphthylamine (1·3 g., 60%), had m. p. 117·5° and therefore contained *ca.* 14% of 4-nitro-2-naphthylamine (cf. Hodgson and Hathway, *J.*, 1944, 385). 1 : 3-Dinitronaphthalene (0·45 g., 20%) was recovered from the acid-insoluble residue. Reduction occurred only when all the reactants were very carefully purified.

Preparation of N-*Acetyl*-3-*nitro*-1-*naphthylamine from the Mixed Nitronaphthylamines.*—Mixed 3-nitro-1- and 4-nitro-2-naphthylamine, containing *ca.* 16% of the latter, dissolved in acetic acid (5 c.c. per g.), was boiled with a slight excess of acetic anhydride for 30 min. The mixture was cooled and set aside, and the precipitated *N*-acetyl-3-nitro-1-naphthylamine collected, washed with acetic acid and then ether, and dried in the air (yield, *ca.* 80% of total in mixture). The mother-liquor was heated to boiling, and water added, cautiously at first to destroy excess of acetic anhydride, and then more rapidly to initiate crystallisation. The mixture was then cooled; a product containing *ca.* 80% of *N*-acetyl-4-nitro-2-naphthylamine separated (yield, *ca.* 20% of total starting material; hence total recovery, *ca.* 86%).

Ditoluene-p-*sulphonyl Derivatives of* 3-*Nitro*-1- *and* 4-*Nitro*-2-*naphthylamine*.—The amine (1 g.) was ground with toluene-*p*-sulphonyl chloride (10 g., *ca.* 10 mols.), and slowly heated in water (100 c.c.) to boiling, with periodic additions of sodium carbonate to keep the liquid alkaline. After 2 hours' boiling the mixture was cooled and filtered, and the procedure repeated on the residue. The final product was washed with water, dried, and recrystallised from hot acetic acid (charcoal). N-*Ditoluene*-p-*sulphonyl*-3-*nitro*-1-*naphthylamine* (59%) had m. p. 264—266° (Found: S, 12·9. $C_{24}H_{20}O_6N_2S_2$ requires S, 12·9%). *N*-Ditoluene-*p*-sulphonyl-4-nitro-2-naphthylamine (64%) had m. p. 220—221° (Hodgson and Hathway, *J.*, 1945, 455, give m. p. 215°). The reaction is much less effective in pyridine (cf. Hodgson and Ward, *J.*, 1947, 327).

Nitration of N-*Acetyl*-3-*nitro*-1-*naphthylamine*.—The naphthalide (15 g.) was added gradually to nitric acid (90 c.c.; *d* 1·5) with vigorous stirring; stirring was continued for a further 90 min. at −10° to −6°. The mixture was poured on ice-water (450 g.) with stirring, and the residue collected, washed with water, and dried at 60° (yield, 14·2 g., 80%).

The mixed amides were refluxed for 2 hr. with aqueous sulphuric acid (50% v/v; 9 pts.) and ethanol (105 c.c., 7 pts. by vol.). After cooling, the mixture was stirred into ice-water (450 g.) and basified at 0° with aqueous ammonia, and the precipitate collected, washed with water, and dried at 60° (11·7 g., 98%). This mixture (A) of amines (8·5 g.) was dissolved in dry benzene (2·1) and dry hydrogen chloride passed in until no further precipitation occurred. The precipitate was collected, exposed to the air until free from benzene, and basified with aqueous ammonia. The mixed amines were filtered off, washed with water, and dried (7·4 g., 87%). The product was extracted with boiling ligroin (5 × 1 l.). Concentration of the ligroin solution, followed by crystallisation of the product from hot aqueous pyridine (1 : 1 v/v) and then from acetone–water (2 : 1 v/v), yielded 3 : 8-*dinitro*-1-*naphthylamine* (2·24 g.), m. p. 176°, which, on recrystallisation from aqueous pyridine (1 : 1 v/v), gave orange crystals, m. p. 179·5—180·5° (Found: C, 51·5; H, 3·1. $C_{10}H_7O_4N_3$ requires C, 51·5; H, 3·0%). The ligroin-insoluble residue was dissolved in boiling ethanol (400 c.c.) and filtered, and the filtrate diluted with an equal volume of water and allowed to crystallise, yielding 3 : 5-*dinitro*-1-*naphthylamine* (2·47 g.), m. p. 215—217°. Recrystallisation from hot aqueous ethanol (1 : 2 v/v) gave deep red needles, m. p. 225—226° (Found: C, 51·9; H, 3·2%). From the mother-liquors was recovered a further amount of mixed amines (1·64 g.), giving a total recovery of 6·35 g. (*ca.* 85%) from the mixed hydrochlorides.

(By J. G. HAWKINS.) *Spectrographic analysis of the mixture* (A). The measurements were made on a Grubb-Parsons infra-red spectrometer fitted with a rock-salt prism and an automatic pen recorder. The spectra were obtained with a Nujol mull between rock-salt plates in the region 7·5—15 μ.

The spectra of pure 3 : 5- and pure 3 : 8-dinitro-1-naphthylamine were first compared with that of the mixture (A), and an approximate estimate made of the relative proportion of the two isomers in the latter. In order to facilitate the estimation, the spectrum of the mixture was bracketed with thicker and thinner films of the same sample. To a first approximation, after due allowance for differences in the thickness of the films, the amounts were judged to be 40% of 3 : 5- and 60% of 3 : 8-dinitro-1-naphthylamine. The solubility of these amines in the usual infra-red solvents was too low to allow of their quantitative determination in a 0·1-mm. cell in the conventional manner. An artificial mixture (B) containing 40·6% of 3 : 5- and 59·4% of 3 : 8-dinitro-1-naphthylamine was therefore prepared by grinding the weighed amounts of the pure specimens together in a Nujol mull. The resulting spectrum contained two absorption maxima (at 1138 and 877 cm.$^{-1}$) which were not present in the reference spectra or in the spectrum of the original mixture (A), but disappeared on crystallisation of the mixture (B) from benzene [mixture (C)]. Comparison of the spectra of mixtures (B) and (C) with that of mixture (A) revealed that there was 35 (±5)% of 3 : 5- and 65 (±5)% of 3 : 8-dinitro-1-naphthylamine in the mixture (A).

Further comparison of all of the above spectra with those of the appropriate compounds [this work was undertaken as part of a general investigation of the infra-red spectra of polynitronaphthalenes and polynitronaphthylamines (Whiffen, Hawkins, and Ward, unpublished work)] failed to show in any of them the presence of 3-nitro-1-naphthylamine (which would be obtained by hydrolysis of the starting compound), of 2 : 3- or 3 : 4-dinitro-1-naphthylamine, or of the amine obtained by the dinitration and subsequent hydrolysis of *N*-toluene-*p*-sulphonyl-3-nitro-1-naphthylamine (cf. Hodgson and Hathway, *J.*, 1944, 561).

Derivatives of 3 : 5- *and* 3 : 8-*Dinitro*-1-*naphthylamine*.—N-*Acetyl*-3 : 5-*dinitro*-1-*naphthylamine*, m. p. 260—262° (decomp.) (Found : C, 52·5; H, 3·5. $C_{12}H_9O_5N_3$ requires C, 52·4; H, 3·3%), and its 3 : 8-*dinitro*-isomer, m. p. 206—207° (Found : C, 52·5; H, 3·5%), were prepared by refluxing the amine in acetic acid containing a trace of pyridine, with a slight excess of acetic anhydride for 30 min. The products obtained by adding water to incipient crystallisation under reflux and then cooling were recrystallised from hot aqueous acetic acid. 3 : 5-*Dinitro*-N-p-*nitrobenzylidene*-1-*naphthylamine*, m. p. 309—310° (Found : C, 55·8; H, 2·9. $C_{17}H_{10}O_6N_4$ requires C, 55·8; H, 2·75%), and the 3 : 8-*dinitro*-isomer, m. p. 263·5—264·5° (Found : C, 55·8; H, 2·9%), were prepared by mixing saturated solutions of the reactants in cold acetic acid, and refluxing them for 1 hr. After cooling, the products were separated and recrystallised from warm acetic acid. 1-(3 : 5-*Dinitronaphthylazo*)-2-*naphthol* was prepared by diazotising the amine by the inverted Hodgson–Walker method (Hodgson and Turner, *J.*, 1943, 86), and adding the diazonium solution to 2-naphthol in aqueous sodium hydroxide. After recrystallisation from hot nitrobenzene, it had m. p. 315° (decomp.) (Found : C, 61·9; H, 3·1. $C_{20}H_{12}O_5N_4$ requires C, 61·9; H, 3·1%).

Orientation of the Dinitronaphthylamines.—The amines were diazotised by Hodgson and Turner's method (*loc. cit.*), and deaminated by adding the diazonium solution to ethanol containing cuprous oxide (Hodgson and Turner, *J.*, 1942, 748). 3 : 5-Dinitro-1-naphthylamine gave 1 : 7-dinitronaphthalene (43%), m. p. 157—158° (Veselý and Dvořák, *Bull. Soc. chim.*, 1923, 33, 319, and Veselý and Jakeš, *ibid.*, p. 952, give m. p. 156°), identified by mixed m. p. (153—156·5°) with an authentic specimen. 3 : 8-Dinitro-1-naphthylamine gave 1 : 6-dinitronaphthalene (50%), m. p. 164—165° (Hodgson and Turner, *J.*, 1943, 86, give m. p. 166·5°), identified by mixed m. p. (165—166°). The identities of the dinitronaphthalenes were confirmed by their infra-red spectra.

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