

956. Nitration of the *N*-Acyl-nitronaphthylamines.

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The nitration of some *N*-acyl derivatives of all fourteen mononitronaphthylamines has been studied under a variety of conditions. Comparisons of their reactivity and mode of substitution with those of the parent naphthylamines have permitted the formulation of some general conclusions regarding substituent effects. Anomalous orientations observed for nitration of *N*-acetyl derivatives in strongly acidic media are rationalised in terms of protonation of the amide-oxygen atom of the acetyl group.

A STUDY of the nitration of some of the *N*-acyl derivatives of all the nitronaphthylamines is here presented. From the position and extent of reaction and the distribution of isomers a clear picture emerges of the effect of the acylated amino-group and the influence of the nitro-group at various positions. The latter is particularly interesting and depends upon the fact that orientation in these compounds is controlled by the amido-substituent. The nitro-group alone, as in the nitronaphthalenes,¹ permits reaction to occur detectably only in the α -positions of the unsubstituted ring, thus somewhat limiting the information that can be derived.

The mildest nitrating condition employed in these studies has been nitric acid in acetic acid solution. This reagent is effective only for the more reactive substrates, the sulphonyl derivatives and the parent *N*-acetylnaphthylamines. On addition of boron trifluoride, however, *N*-acetyl-dinitro-compounds are obtained. In fuming nitric acid (which in favourable cases leads to the formation of trinitronaphthylamine derivatives), there are abnormal results ascribed to protonation.

The mononitration of the *N*-acetyl derivatives has proved the most informative of these investigations. The α -derivatives react in the 2- and the 4-position; the β -derivatives at positions 1, 6, and 8, the ratios in which the products are formed depending on the position of the nitro-group. The more reactive *N*-arylsulphonyl derivatives have proved extremely difficult to mononitrate: the significance of the composition of the resulting product is thus difficult to interpret; study of these derivatives has, however, been of value in the synthesis of otherwise inaccessible compounds. The *N*-phthaloyl derivatives have similarly provided new isomers, but they could not be studied quantitatively owing to the lack of a satisfactory method of hydrolysis.

In previous studies of these nitrations the usual procedure has been to permit the product to crystallise from the reaction medium, thus obtaining fairly pure material immediately. While this is useful in preparative work it was necessary for the present

¹ Ward, Johnson, and Day, *J.*, 1959, 487.

investigation to examine the whole reaction product. In order that the final isomer distribution shall be significant, yields at all stages should be high and the by-products that are carried through to the final stage efficiently separated from the nitro-amines.

TABLE 1.

Nitration of *N*-acetyl derivatives in acetic acid.

Expt. no.	Position of		Reagent & temp.	Yields (%)			Posn. of substn., refs., notes
	NHAc	NO ₂		I	II	III	
1	1	—	A, 0°	87	96	76	2; 4*
2	1	—	B, 70	82	95	76	2; 4
3	1	3	B, 70	86	—	61*	2; 4 (a)
4	1	5	B, 70	79	91	66	2; 4
5	1	8	B, 80	30	—	18	2; 4
6	2	—	A	81	—	—	1; 6; 8 (b)
7	2	—	B, 70	63	84	47	1; 6; 8
8	2	3	B, 70	83	100	75	1; 6; 8 (c)
9	2	4	B, 70	81	83	54	1; 6

Reagents: A, HNO₃ (*d* 1.5) in acetic acid. B, HNO₃ (*d* 1.5) and BF₃ in acetic acid. C, HNO₃ (*d* 1.5) alone.

Yields: I, Crude nitration product. II, Crude hydrolysis product. III, Purified and separated hydrolysis product. I and II are yields referring to the particular operation. III is a combined overall yield in relation to starting material. Separation and purification by chromatography of the hydrolysis product was generally the step of highest yield.

References: (a) Cf. Sihlbom, *Acta Chem. Scand.*, 1954, **8**, 1709. (b) Saunders and Hamilton, *J. Amer. Chem. Soc.*, 1932, **54**, 636; Hartman and Smith, *Org. Synth.*, Coll. Vol. II, p. 438. (c) Ward, Coulson, and Wells, *J.*, 1957, 4816.

* Similar yields reported by Hodgson and Walker (*J.*, 1933, 1205) using nitric acid (*d* 1.4) in acetic acid and in acetic anhydride.

TABLE 2.

Nitration of *N*-acetyl derivatives in nitric acid.

Expt. no.	Position of		Reagent & temp.	Yields (%)			Posn. of substn., refs., notes
	NHAc	NO ₂		I	II	III	
10	1	—	C, 0°	74	93	—	2,4; 4,5; & 4,8*
11	1	2	C	—	—	—	4,8
12	1	3	C, 0	80	98	87	5; 8 ^d
13	1	4	C, 0	87	90	67	2; 5; 8†
14	1	5	C, 0	97	93	74	2; 4‡
15	1	6	C, 0	88	99	80	2; 4
16	1	7	C, 0	97	90	62	2; 4*
17	1	8	C, 0	92.5	—	—	2; 4¶
18	2	—	C	—	—	—	1,5; 1,8
19	2	1	C, 0	90	—	—	6,8
20	2	1	C	—	—	—	5; 8 ^f
21	2	3	C, 0	72	100	65	1,5; 1,8 ^e
22	2	4	C, 0	81	62	29	1,5; 1,8
23	2	5	C, 0	—	—	—	1 ^f
24	2	6	C, 0	—	—	—	1 ^g
25	2	7	C, 0	95	—	—	1 ^h
26	2	8	C, 0	—	—	—	1 ^f

References: (c) See Table 1. (d) Ward, Coulson, and Hawkins, *J.*, 1957, 4541. (e) Hardy and Ward, *J.*, 1957, 2634. (f) Vesely and Jakes, *Bull. Soc. chim. France*, 1923, **33**, 942. (g) Bell, *J.*, 1929, 2784. Hodgson and Ward, *J.*, 1947, 1060.

* Hodgson and Walker (*J.*, 1933, 1205) report 2- and 4-nitration at 10° by HNO₃ (*d* 1.4). † Lellman (*Ber.*, 1884, **17**, 114) reports 2-nitration only. ‡ By Mr. H. Pierce. ¶ Hodgson and Crook (*J.*, 1936, 1338) report 4-nitration only.

Discussion.—The principal results are summarised in Tables 1—6. In the nitration of acetanilide *p* : *o* ratios of great variety are observed depending on the nitration conditions.² Thus the ratio falls from 8 : 1 in mixed acid through various values of >1 : 1 for aqueous nitric acid to 0.9 : 1 for nitric acid in acetic anhydride. The ratio for positions 4 and 2 of *N*-acetyl-1-naphthylamine is, by comparison, remarkably constant. In addition

² Hodgson and Crook, *J.*, 1936, 1844.

TABLE 3.

Nitration of *N*-arylsulphonyl derivatives.

Expt. no.	Position of		X *	Reagent & temp.†	Yields I (%)	Posn. of substn., refs., notes
	NHX	NO ₂				
27	1	—	T	A, 20°	100	4; 2,4
28	1	—	T	2A, 20	85	2,4
29	1	—	M	B, 0	—	2,4,5 ⁱ
30	1	3	T	A, 0	83	2; 4
31	1	3	T	2A, 0	—	2,4 ^j
32	1	5	T	A, 0	—	2; 2,4 [‡]
33	1	5	T	2A, 0	65	2,4 [‡]
34	1	6	T	A, 0	95	2; 4; 2,4
35	1	6	T	2A, 90	53	2,4 ^k
36	1	7	T	A, 0	92	2; 4 ^e
37	1	7	T	2A, 0	67	2; 2,4 ^e
38	1	8	T	2A, 80	58	2,4 ⁱ
39	2	—	T	A, 0	—	1 ^m
40	2	—	T	2A, 0	—	1,6 ^p
41	2	—	M	B, 0	—	1,6; 1,8; 1,6,8
42	2	1	T	A, 60	90	6
43	2	3	T, M	2A, 80	84	1 ^c
44	2	3	M	B, 0	90	1,6 ^c
45	2	4	T	A, 70	—	1 ⁿ
46	2	4	T	2A, 80	—	1,6 ⁿ
47	2	5	T	A, Warm	—	1 ^o
48	2	6	T	A	—	1 ^o
49	2	6	M	B	—	1,8 ^o
50	2	7	T	5A, 70	50	1 ^{h, o}
51	2	7	M	B, 35	—	1,5 ^o ; 1,5(?)
52	2	8	T	A	—	1 ^o
53	2	8	M	B	—	1,6 ^o

References: (c) See Table 1. (e, g, h) See Table 2. (i) Conden and Kenyon, *J.*, 1935, 1591. (j) Hodgson and Hathaway, *J.*, 1945, 841. (k) Hodgson and Turner, *J.*, 1943, 391. (l) Ward and Day, *J.*, 1951, 782. (m) Morgan and Micklethwait, *J.*, 1912, 101, 1438. (n) Hodgson and Hathaway, *J.*, 1945, 453. (o) Hodgson and Dean, *J.*, 1950, 818.

* T = Toluene-*p*-sulphonyl, M = *m*-nitrobenzenesulphonyl derivative. † 2A, 5A, etc., refer to the number of mol. of nitric acid employed. ‡ By Mr. H. Pierce.

TABLE 4.

Nitration of *N*-phthaloyl derivatives.

Expt. no.	Position of		Yields (%)			Posn. of substn., refs., notes
	NPh	NO ₂	I	II	III	
54	1	—	—	—	—	4; 5; 8 (1 : 6 : 12) *
55	1	—	86	62	35	4; 5; 4,8 (1 : 1) *
56	1	3	60	—	—	Dinitrated *
57	1	4	91	70	—	5; 8 *
58	1	7	90	—	—	2; 4; 4,5 (1 : 4 : 4) *
59	2	—	80—90	—	—	5; 8 ⁱ
60	2	1	90	77	57	6,8 *
61	2	3	100	—	—	5; 8 ^c (1 : 1)
62	2	4	100	90	59	5; 8 (1 : 1)
63	2	6	—	—	—	1; x; y (9 : 2 : 1) †

References: (c) See Table 1. (l) See Table 3. (x) Ref. 2.

* Nitration conducted for several hours. † By Mr. J. G. Hawkins.

to the values given in Table 5, Hodgson and Walker³ report that nitration in acetic anhydride gives the ratio 2.5 : 1. This constancy is a strong argument that the same nitrating species (the nitronium ion) is concerned in all these reactions. Small variations, in so far as they are real, can be attributed to changes in solvent and temperature. The lower ratio for the reaction catalysed by boron trifluoride would then be due to the decreased selectivity of the reagent at the higher temperature. In support of this the ratio of the logarithm (1.28 : 1) of the isomer ratios is essentially equal to the inverse ratio of the absolute temperatures (1.26 : 1).

³ Hodgson and Walker, *J.*, 1933, 1205.

TABLE 5.
4-Nitration/2-nitration of *N*-acetyl-1-naphthylamines.

Expt. no.	Position of		Conditions *		
	NHAc	NO ₂	A	B	C †
1, 2	1	—	2.9 ± 0.05	2.3 ± 0.05	2.7
3	1	3	—	ca. 4	—
4, 14	1	5	—	1.2 ± 0.02	2.6 ± 0.1
15	1	6	—	—	2.0 ± 0.15
16	1	7	—	—	1.7
5, 17	1	8	—	ca. 30	ca. 18.5

* See Experimental section for estimation of accuracy. † For HNO₃ (*d* 1.4) at 10° by thermal analysis (ref. 3).

TABLE 6.
Proportions of nitration at positions 1, 6, and 8 of *N*-acetyl-2-naphthylamines.

Expt. no.	Position of		Conditions	Proportions		
	NHAc	NO ₂		1	6	8
6	2	—	A	51	4	5
7	2	—	B	ca. 9	1	—
8	2	3	B	15	2	3
9	2	4	B	ca. 17.5	1	—

The high *p* : *o* ratios for acetanilide have been variously explained in terms of specific *para*-activation^{4,5} or of specific *ortho*-deactivation,^{4,5} or as a direct consequence of the mode of operation of +*M*, -*I* substituents.^{6,*} These considerations should apply equally to *N*-acetyl-1-naphthylamine; in addition the greater reactivity of the α - than of the β -position should lead to an even higher proportion of 4- : 2-nitration. That these proportions are in fact smaller, except for nitration in acetic anhydride, indicates considerable steric effect due to the *peri*-hydrogen atom.

Table 5 indicates that, while 5, 6, and 7-nitro-groups have relatively little effect upon the 4- : 2-nitration ratio, an 8-nitro-group greatly reduces the amount of 2-nitration. This is an unusual steric effect. The nitro-group is not here affecting the reaction centre directly but by "buttressing" the effect of the acylated amino-group. This feature has been reported by Brown and McGary⁷ for 2,3,5-tri- and 2,3,5,6-tetra-methylbenzene and will be more important for the naphthalenes owing to the close proximity of the *peri*-position. We have drawn attention above to the steric hindrance to nitration at the 4-position, so that the slightly increased ratio of 4- : 2-nitration of *N*-acetyl-5-nitro-1-naphthylamine is surprising when compared with the ratios for the 6- and the 7-nitro-isomer; an explanation of this has been presented⁸ in terms of dipolar activation by the nitro-group.

The isomer ratios for the nitro-2-naphthylamines generally could not be determined with precision comparable to those mentioned above. It is of preparative interest that nitration of *N*-acetyl-2-naphthylamine in acetic acid is best carried out by the procedure of Hartman and Smith⁹ but with only a 10% excess of nitric acid;¹⁰ this affords a ~80%

* Unusually low *p* : *o*-ratios for nitrations in acetyl nitrate have been explained by Norman and Radda (*Proc. Chem. Soc.*, 1960, 423) in terms of reaction of the nitrating agent with the substituent before substitution and by Bordwell and Garbisch (*J. Amer. Chem. Soc.*, 1960, **82**, 3588) in terms of some reagent other than the nitronium ion.

⁴ Ingold, *Ann. Reports*, 1926, **23**, 140.

⁵ Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1951, pp. 256—267.

⁶ Dewar, *J.*, 1949, 463; Roberts and Streitweiser, *J. Amer. Chem. Soc.*, 1952, **74**, 4723; R. D. Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 4077.

⁷ H. C. Brown and McGary, *J. Amer. Chem. Soc.*, 1955, **77**, 2310.

⁸ Wells and Ward, *Chem. and Ind.*, 1958, 1172.

⁹ Hartman and Smith, *Org. Synth.*, Coll. Vol. II, p. 438.

¹⁰ Ward and Hawkins, unpublished work.

yield of mixed *N*-acetyl-nitro-2-naphthylamines, which, on hydrolysis, yield 1-, 6-, and 8-nitro-2-naphthylamine in approximate ratios 9·8 : 1 : 1·25.¹⁰ We have repeatedly obtained this result, in contrast to Saunders and Hamilton,¹¹ further, the material remaining in the nitration mixture after removal of the precipitated mixed products appears to be entirely *N*-acetyl-1-nitro-2-naphthylamine.

The results in Table 6 accord well with the predicted substituent effect of the 2-acetamido-group in that the 1-position is the most reactive although 6- and 8-activation is quite marked.

In nitric acid solution most of the homonuclear-substituted derivatives show a tendency to nitration at positions 5 and 8, *i.e.*, in the unsubstituted ring (sometimes accompanied by reaction in the substituted ring). This type of behaviour is well known for naphthalene compounds and is normally associated with the presence of a deactivating substituent. That it occurs only in strongly acidic conditions points to protonation as the cause.¹² The acetamido-group could take up a proton at either the nitrogen or the acetyl-oxygen atom. In the former case a substituent resembling the strongly deactivating NH_3^+ group would be produced. This seems unlikely because, first the *N*-protonated derivatives should be less reactive than the dinitronaphthalenes which cannot be nitrated under these conditions, and, secondly, both α - and β -naphthylammonium salts undergo more 5- than 8-nitration,¹³ unlike the "abnormal" acetyl reactions where the reverse is often true. As will be seen for the *N*-phthaloyl derivatives and as is known¹⁴ for the methyl-naphthalenes, a deactivating substituent is not essential for reaction at position 5 or 8. A very weakly activating or deactivating substituent, such as would be produced by protonation of oxygen, will be able only to give direction to a choice among the available α -positions. Whether reaction occurs through the protonated amide or not will depend upon a number of factors. The unprotonated form being considerably more reactive must be in extremely low concentration, otherwise reaction would proceed almost entirely through this form. This is another argument against *N*-protonation, which would cause much more deactivation so that a trace of unprotonated derivative would provide for all the reaction. This condition being fulfilled, the protonated derivative must still be sufficiently reactive to be nitrated. It can be seen from Table 2 that a nitro-group in the second ring prevents the "abnormal" reaction by making the compound too unreactive. *N*-Acetyl-1-naphthylamine and its 4-nitro-derivative show behaviour consistent with the above analysis in that both normal and "abnormal" reactions are observed.

The 6,8-dinitration of *N*-acetyl-1-nitro-2-naphthylamine is unexpected. *N*-Acetyl-6- and -8-nitro-2-naphthylamine are only mononitrated under these conditions, yielding products at least one of which must be intermediate in the formation of the 1,6,8-trinitro-compound. In mixed acid the 1,5- and 1,8-dinitro-compounds are obtained, in conformity with the general behaviour of the other homonitro-isomers and *N*-acetyl-2-naphthylamine itself.

In contrast to the apparently stronger electron-withdrawing power of the arylsulphonyl group,¹⁵ the *N*-toluene-*p*-sulphonyl derivatives are more easily nitrated than the *N*-acetyl derivatives. All the 1-naphthylamine derivatives having positions 2 and 4 vacant can be dinitrated in hot acetic acid. To avoid nitration of the arylsulphonyl group, *N*-*m*-nitrobenzenesulphonyl derivatives were nitrated in nitric acid. Under these more vigorous conditions the 2-naphthylamine derivatives are also dinitrated. The comparable reactivities of the 2- and the 4-position and of the mononitration products of the 1-naphthylamine derivatives lead in general to a mixed product. For the 2-naphthylamine derivatives, on the other hand, the differences are sufficient for mononitration to be confined to the 1-position. Contrasting with the *N*-acetyl derivatives, the sulphonyl derivatives

¹¹ Saunders and Hamilton, *J. Amer. Chem. Soc.*, 1932, **54**, 636.

¹² Ward and Coulson, *J.*, 1954, 4541; Ward, Coulson, and Wells, *J.*, 1957, 4816.

¹³ Hodgson and Davey, *J.*, 1939, 348; Finelli, U.S.P., 2,790,831, *Chem. Abs.*, 1957, **51**, 14,815.

¹⁴ Wells and Alcorn, unpublished work.

¹⁵ Cf. Hammett's σ -values, Jaffé, *Chem. Rev.*, 1953, **53**, 191.

have further reactivities in the order $6 > 8$. 1,8-Dinitration is observed for the 6-nitro-derivatives only. Steric hindrance presumably prevents reaction of the 5-nitro-derivative at the 6-position and would be expected to affect the 7-nitro-isomer similarly. It has been suggested therefore that the dinitration of this latter compound occurs in the 1,5-positions.

While the *N*-phthaloyl derivative of aniline undergoes nitration in the *ortho*- and *para*-positions, the corresponding derivative of *p*-toluidine reacts at the *ortho*-position to the methyl group.¹⁶ The substituent is thus at best very weakly activating or, more probably, weakly deactivating, being *o/p*-directing by virtue of a +*M*-effect. The result of this appears in Table 4 where it can be seen that reaction in the 5- and the 8-position (unsubstituted ring) competes favourably with that at positions appearing from the studies of the other derivatives to be normally activated by the acylated amino-group. In view of the unsatisfactory nature of the hydrolysis and subsequent separation of the nitration products, the ratio of isomers given has little significance. Noteworthy, however, is that 8-substitution is not unfavourable despite the bulk of the acyl group. Reactions of the 7-nitro-derivative at positions 2 and 4, and of the 6-nitro-derivative at position 1 accord with the suggested +*M*-effect of the substituent, since in these cases a nitro-group in the second ring will deactivate positions 5 and 8.

Viewed overall, the nitrations of the various naphthylamine derivatives are in good agreement with the analysis of the effect of substituents on electrophilic substitution in naphthalene, as set out by Ward, Coulson, and Wells.¹² Only in the presence of a strongly activating *o/p*-directing group does reaction take place in the β -positions of the naphthalene system. In other cases the preference for α -reaction has control and the substituent affects only the choice between available α -positions. The nitro-group does not appear to exert a very specific effect, except on positions adjacent to it and remote from the activating group: in accordance with its predominant inductive effect¹⁷ overall deactivation appears to be the best description of its influence. There is, in addition, however, evidence that the position *peri* to the nitro-group is not unfavourable, as observed in the nitronaphthalenes.

EXPERIMENTAL

The derivatives used in these studies were prepared by established procedures and purified by crystallisation. M. p.s are corrected.

New *N*-phthaloyl derivatives are tabulated ($C_{18}H_{10}O_4N_2$ requires C, 67.9; H, 3.2; N, 8.8%).

Nitro-*N*-phthaloylnaphthylamines.

N	Position of		M. p.	Found (%)		
		NO ₂		C	H	N
1		5	230°	67.4	3.0	8.9
2		4	263	68.2	3.6	—
2		6 *	305	65.8	3.4	8.0

* Prepared by Mr. J. G. Hawkins.

Nitration: General Procedures.—(A) The *N*-acetyl derivative (1.0 g.) in glacial acetic acid (20 c.c.) was treated with nitric acid (*d* 1.5; *ca.* 1 c.c. excess) and left at the reaction temperature for *ca.* 30 min. Addition of ice (*ca.* 200 g.) produced a fine precipitate which was collected, washed with water, and dried at *ca.* 50° *in vacuo*.

(B) The *N*-acetyl derivative (1.0 g.) in acetic acid (50 c.c.) was treated with a mixture of nitric acid (*d* 1.5; 0.24 g.) and a 40% solution (2 c.c.) of boron trifluoride-acetic acid complex in acetic acid (2.4 c.c.). After *ca.* 15 min. at the reaction temperature, ice (*ca.* 500 g.) was added, yielding the product as a precipitate that was worked up as in (A).

(C) The *N*-acetyl derivative (1.0 g.) was dissolved by small additions to ice-cold nitric acid (*d* 1.5; 10 c.c.). After *ca.* 30 min. the brown solution was poured on ice (*ca.* 200 g.), to yield the product as a precipitate. The arylsulphonyl and phthaloyl derivatives were nitrated analogously.

¹⁶ Brady, Quick, and Welling, *J.*, 1925, **127**, 2264.

¹⁷ Wepster, *Rev. Trav. chim.*, 1956, **75**, 1473.

Hydrolysis: General Procedures.—The nitrated *N*-acetyl derivatives (0.5 g.) were hydrolysed by 2 hours' refluxing in 10 c.c. each of 50% v/v aqueous sulphuric acid and ethanol; then an excess of cold dilute ammonia solution was added. The precipitated amines were collected, washed, and dried at *ca.* 50° *in vacuo*.

The nitrated arylsulphonyl derivatives (0.5 g.) were dissolved in sulphuric acid (*d* 1.84; 10 c.c.) and kept at *ca.* 40° for 4 hr., the solution was poured on ice (*ca.* 200 g.). The product was collected, washed, and dried at *ca.* 50° *in vacuo*.

Of the methods described for hydrolysis of the *N*-phthaloyl derivatives, *e.g.*, 2*N*-aqueous sodium hydroxide,¹⁶ ammonia at 120–130°,² ethanolic mineral acid,¹⁸ and ethanolic hydrazine,¹⁹ only the last was generally successful and even then, in many cases, gave poor yields of impure product.

The crude hydrolysis product (0.5 g.) was chromatographed in benzene on alumina (a column of 2.6 × 30 cm.; 50 cm. for 2- and 4-nitro-1-naphthylamine, and for separation of 1- from 6- and 8-nitro-2-naphthylamine; the last pair and other pairs of mononitronaphthylamines were never completely separated). The various by-products that had been carried through to this final stage were adsorbed at the top of the column and did not interfere with recovery of purified nitro-amines.

Nitronaphthylamines and their acetyl derivatives.

Position of		Amine				Acetyl derivative			
NH ₂	NO ₂	M. p.	Found (%)		Notes	M. p.	Found (%)		Note
			C	H			C	H	
1	2,5	243°				242°			
1	2,6	318	51.5	3.0	<i>a, b</i>	270	52.5	3.85	<i>g</i>
1	2,8	166							
1	4,6	250	51.5	2.9	<i>b, c</i>	256	50.4	4.4	<i>g</i>
2	1,4	161	51.0	3.0	<i>b</i>	—	—	—	
2	4,6	204	52.7	4.0	<i>b</i>	—	—	—	
2	4,8	268	52.2	3.4	<i>b</i>	—	—	—	
2	1,4,5	203	—	—	<i>d, e</i>	239	45.2	2.7	<i>h</i>
2	1,4,8	171	43.2	2.25	<i>e, f</i>	215	44.9	2.6	<i>i</i>

^a Hodgson and Turner (*J.*, 1943, 391) give m. p. 228.5°. ^b C₁₀H₇N₂O₄ requires C, 51.5; H, 3.0%. ^c *Idem, loc. cit.*, give m. p. 178°. ^d Found: N, 20.0%. ^e C₁₀H₆N₄O₆ requires C, 43.2; H, 2.25; N, 20.2%. ^f Found: N, 19.8%. ^g C₁₂H₉N₃O₅ requires C, 52.4; H, 3.3%. ^h C₁₂H₈N₄O₇ requires C, 45.0; H, 2.5%; N, 17.5%. ⁱ Found: N, 17.5%.

To assess the accuracy of the separation 3:1 mixtures of any intermediate mixed fraction were added to the weights of pure isomer obtained. This gave two extreme values for the isomer ratio which were averaged and the extremes indicated in the form of a possible deviation. This procedure was only applied where nitration, hydrolysis, and separation yields were high.

Characteristics of New or Improved Compounds.—See annexed Tables.

Orientation of New Products.—On deamination by Hodgson and Turner's method,²⁰ 2,6-dinitro-1-, 4,6-dinitro-1-, 1,4-dinitro-2-, and 4,8-dinitro-2-naphthylamine gave, respectively, 2,6-, 1,7-, 1,4-, and 1,5-dinitronaphthalene, identified by mixed m. p. 1,4,5-Trinitro-2-naphthylamine was obtained from both 1,4- and 4,5-dinitro-2-naphthylamine, and the 1,4,8-isomer from the 1,4- and the 4,8-isomer. The structures of 2,8-dinitro-1- and 4,6-dinitro-2-naphthylamine, while not proved owing to an insufficiency of material, follow by analogy; the latter was shown by mixed m. p. determinations to differ from the 1,4-, 4,5-, and 4,8-isomer.

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¹⁸ Hodgson and Dean, *J.*, 1950, 820.

¹⁹ Hodgson and Ratcliffe, *J.*, 1949, 1314; Ward and Day, *J.*, 1951, 782.

²⁰ Hodgson and Turner, *J.*, 1942, 748; 1943, 68.