101. *Polynitronaphthalenes. Part II.*[1] *A Quantitative Study of the Nitration of* 1- *and* 2-*Nitronaphthalene and of* 1 : 5-*Dinitronaphthalene.*

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Methods are described for the application of column and paper chromatography, and complex formation, to the detection, separation, and estimation of products arising from the nitration of 1- and 2-nitronaphthalene and of 1 : 5-dinitronaphthalene. The influence of nitration medium, temperature, and added catalyst has been studied in appropriate cases. Significant differences have been found between sulphuric and aqueous nitric acids as media, and these are discussed in relation to current theories of aromatic nitration, particularly the dipolar influences of the nitro-group (the *D*-effect of Ward and Wells[2]).

1 : 3 : 5 : 7-Tetranitronaphthalene is identified for the first time as a nitration product of 1 : 5-dinitronaphthalene. Improved and convenient preparative methods for 1 : 3 : 5- and 1 : 4 : 5-trinitronaphthalene, and for 1 : 3 : 5 : 8-, 1 : 3 : 5 : 7-, and 1 : 4 : 5 : 8-tetranitronaphthalene are described. The last can be prepared directly from 1-nitronaphthalene and is thus made readily available for the first time.

Since the nitration of naphthalene has been studied for over a hundred years it is rather surprising that all the polynitronaphthalenes that can thereby be formed have not yet been identified and that reasonably accurate determinations of the proportions of isomers formed have only been made in the case of mononitration. The completion of the present investigation leaves only the products arising from 1 : 7-dinitronaphthalene (*via* 2-nitronaphthalene) to be precisely identified and estimated, although preliminary studies of this have been made.[3, 4] The present work is essentially a continuation of that of Hodgson and Ward[1] and will be completed by a quantitative study of the nitration of all ten dinitronaphthalenes. The results of the present investigation are summarised in Table 1.

In a previous communication[5] we have pointed out that the proportions of 1 : 5- and 1 : 8-dinitronaphthalene arising from the nitration of 1-nitronaphthalene in sulphuric acid have never been accurately determined and that indeed this ratio might not be 2 : 1, as it has always been assumed to be. However, we have now avoided the complications due to concurrent formation of trinitronaphthalenes (cf. Ward and Hawkins[6]) and shown that for nitrations at 0°, to a very high degree of accuracy, the ratio can be taken as exactly 2 : 1.

No satisfactory explanation has ever been given why the 8-position should be so much favoured over the alternative 5-position in this nitration, when one would have expected on steric grounds that the reverse would apply. Wells and Ward[2] (cf. Hammond *et al.*[7]) have discussed this in relation to the general problem of dipole influences in aromatic substitution, and concluded that it can be satisfactorily explained in terms of the favourable orientation of the substituent dipole to the incoming positively charged nitronium ion, thus reducing the deactivating influence of the α-nitro-group at the 8-position. They have suggested that such dipolar influences be considered as a specific reactivity-determining influence, the *D*-effect. For nitrations in aqueous nitric acid the definite increase in 5-substitution could be ascribed to the fact that an increase in reagent size (the effective

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[1] Part I, Hodgson and Ward, *J.*, 1946, 533.
[2] Wells and Ward, *Chem. and Ind.*, 1958, 1172.
[3] Day, Thesis, London, 1952.
[4] Ward and Hawkins, unpublished work.
[5] Ward, *Chem. and Ind.*, 1956, 195.
[6] Ward and Hawkins, *J.*, 1954, 2975.
[7] Hammond, Modic and Hedges, *J. Amer. Chem. Soc.*, 1953, **75**, 1388.

agent in this medium probably being the hydrated nitronium ion $H_2NO_3^+$, cf. Halberstadt, Hughes, and Ingold[8]) may bring about greater steric hindrance at the 8-position.

Unfortunately, the situation is complicated by the claim of Bachman *et al.*[9,10] (cf. Ward[5]) that nitration of naphthalene by the boron trifluoride–nitrogen tetroxide complex in nitroethane at 80° produces a mixture of 1 : 5- and 1 : 8-dinitronaphthalene in a ratio of *ca.* 1·5 : 1 (cf. our nitration in sulphuric acid containing boron trifluoride). The claim being accepted at its face value, it is a remarkable result and one can only tentatively suggest that it might be explained in terms of a much increased reagent size greatly reducing reactivity at the usually favoured 8-position.

TABLE 1. *Nitration of* 1- *and* 2-*nitronaphthalene,* 1 : 5-*dinitronaphthalene, and* 1 : 3 : 5- *and* 1 : 4 : 5-*trinitronaphthalene.*

Nitro-compound	Nitration conditions	HNO_3 (mole)	Yield (%)	Product composition * (%)	Analysis
1	A1, 0°	1	98·1	1 : 5, 33·5; 1 : 8, 66·5 *†	C
1	A2, 0°	0·7	98·3	1 : 5, 33·3; 1 : 8, 66·7 *†	C
1	A3, −40°	0·85	—	1 : 5, 32·4; 1 : 8, 67·6 †‡	C
1	B1	X	93·7	1 : 5, 37·2; 1 : 8, 56·5; T, 6·3	C
			93·3	1 : 5, 38·6; 1 : 8, 54·7; T, 6·1	C
2	A1, −5°	0·5	99·6	1 : 6, 41 ± 1; 1 : 7, 59 ± 1	C
1 : 5	A4, 30°	1·5	93·5	1 : 4 : 5, 94; 1 : 3 : 5, 6	C, S, P
1 : 5	B1	X	52	1 : 4 : 5, 34; 1 : 3 : 5, 47; 1 : 3 : 5 : 7, 19	M
1 : 5	B2	X	38	1 : 4 : 5, 48; 1 : 3 : 5, 49; 1 : 3 : 5 : 7, 3	M, P
1 : 5	B3	X	71	1 : 4 : 5, 92; 1 : 3 : 5, 8	M
1 : 5	A4, 80°	14	51	1 : 4 : 5 : 8, 53; 1 : 3 : 5 : 8, 47	SL, P
1 : 3 : 5	A4, 80°	25	60	1 : 3 : 5 : 8	
1 : 3 : 5	B3	X	42	1 : 3 : 5 : 7	P
1 : 4 : 5	A4, 90°	14	37	1 : 4 : 5 : 8, 67; 1 : 3 : 5 : 8, 33	SL
1 : 4 : 5	B3	X	51	1 : 3 : 5 : 8	

The initial compound and nitration products are described by the position of the nitro-groups in the naphthalene nucleus.

Nitration conditions. A1, sulphuric acid (*d* 1·84)–nitric acid (*d* 1·42). A2, sulphuric acid (*d* 1·84)–nitric acid (*d* 1·5)–boron trifluoride–acetic acid. A3, sulphuric acid (*d* 1·84)–nitric acid (*d* 1·42)–acetic anhydride. A4, sulphuric acid (*d* 1·84)–nitric acid (*d* 1·5). B1, 70% w/w aqueous nitric acid (reflux). B2, 85% w/w aqueous nitric acid (reflux). B3, 92·5% w/w aqueous nitric acid (reflux). X = Excess.

Yield. For the mononitronaphthalenes this represents the proportion of the nitration product (including unchanged reactant) recovered by chromatography. For the remainder this represents the yield of polynitronaphthalenes isolated from the nitration product in relation to the original reactant and the degree of nitration achieved.

* Calculated on the isolated polynitronaphthalenes.

† Accurate to ±0·2%, losses on chromatography being assumed to be due to oxidation products only.

‡ Mean of two determinations, within 0·2% of each other.

T, Trinitronaphthalenes. C, Column chromatography. P, Paper chromatography. S, Infrared spectroscopy. M, Molecular complex formation. SL, Solvent separation.

The composition of the product is accurately given for the first time for the nitration of 2-nitronaphthalene and again it is suggested that the preferential substitution at the 8-position can be explained by the *D*-effect, weakened in this case by the less favourable position of the β-nitro-group, but counterbalanced to some extent by the decrease in steric hindrance at the 8-position. Thus the *D*-effect can only operate at an *ortho*-position in benzene, but in naphthalene it can operate in several ways, two of which we have already illustrated, and another of the original Hammond type manifested by the formation of 1 : 2 : 4 : 6- and 1 : 2 : 6 : 8-tetranitronaphthalenes in the dinitration of 2 : 6-dinitronaphthalene.[11]

The nitration of 1 : 5-dinitronaphthalene both in sulphuric acid and in aqueous nitric

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[8] Halberstadt, Hughes, and Ingold, *J.* 1950, 2441.

[9] Bachman, Feuer, Bleustein, and Vogt, *J. Amer. Chem. Soc.*, 1955, **77**, 6188.

[10] Bachman and Vogt, *J. Amer. Chem. Soc.*, 1958, **80**, 2381.

[11] Chatt and Wynne, *J.*, 1943, 32.

acid medium has been studied by various workers. Qualitatively this work [12-15] demonstrated the formation of 1 : 4 : 5-trinitro- and of 1 : 3 : 5 : 8- and 1 : 4 : 5 : 8-tetranitronaphthalene in sulphuric acid, and that of 1 : 3 : 5- and 1 : 4 : 5-trinitronaphthalene in nitric acid medium; Pascal's claim [16] to have obtained 1 : 3 : 5-trinitronaphthalene in sulphuric acid is considered unreliable. Detailed examination of the published work [3] showed that of Dimroth and Ruck [15] to be apparently the most reliable. A comprehensive reinvestigation was clearly indicated.

Qualitatively, we have shown that 1 : 3 : 5-trinitronaphthalene is a minor product of nitration in sulphuric acid, and have identified 1 : 3 : 5 : 7-tetranitronaphthalene as a nitration product in aqueous nitric acid (it could not be detected even by paper chromatography for nitration in sulphuric acid). We have made reasonably accurate determinations of the composition of the nitration products, this being important for interpretative purposes. We have also devised more satisfactory preparative methods for the various nitration products. 1 : 4 : 5 : 8-Tetranitronaphthalene can now be made directly from 1-nitronaphthalene instead of through 1 : 5-dinitronaphthalene (involving separation from 1 : 8-dinitronaphthalene). 1 : 3 : 5 : 7-Tetranitronaphthalene was previously only available by nitration of the difficultly accessible 2 : 6-dinitronaphthalene. 1 : 3 : 5-Trinitronaphthalene is made more accessible by decomposition of its complex with 2-naphthol on alumina.

Our nitration results for 1 : 5-dinitronaphthalene can be given a satisfactory explanation. The operation of the *D*-effect favours the formation of 1 : 4 : 5-trinitronaphthalene as against the alternative 1 : 3 : 5-isomer for mononitration in sulphuric acid, whereas in aqueous nitric acid increase in reagent size increases the relative amount of 1 : 3 : 5-isomer, the latter being complicated by the fact that the stronger aqueous nitric acid will contain an increased amount of the nitronium ion. In the further nitration of 1 : 4 : 5-trinitronaphthalene a possible complicating effect is the presence of the adjacent nitro-groups at the 4- and the 5-position. These must sterically interfere with one another and consequently be forced out of the plane of the rings. This may therefore aid substitution in the superficially deactivated 8-position but again the issue seems to turn on the favouring *D*-effect from the 1-nitro-group giving predominant substitution at the 8- rather than the 7-position. The formation of 1 : 3 : 5 : 8-tetranitronaphthalene in the nitration of 1 : 4 : 5-trinitronaphthalene in aqueous nitric acid can be accounted for by increase in reagent size. The nitrations of 1 : 3 : 5-trinitronaphthalene are not complicated by steric factors and are straightforward in terms of the above ideas. It must be borne in mind that nitration in aqueous nitric acid is complicated by attendant oxidation and renders the results less susceptible to precise interpretation.

EXPERIMENTAL

Column Chromatography: General Technique and Separation of Synthetic Mixtures.—An alumina column was prepared by using 1 : 1 benzene–light petroleum (b. p. 40—60°) as solvent medium, and the mixed polynitronaphthalenes were applied to this in solution in benzene, elution also being by benzene. The eluate was collected in small fractions (varied according to the nature of the separation as determined by a preliminary trial); each fraction was concentrated to small volume and evaporated to dryness. The progress of the separation was largely followed from the weights and m. p.s of the eluted products rather than by the appearance of the column during elution. In all cases a slight pink or yellow band appeared at the top of the column; dinitronaphthalenes may give pale yellow bands but trinitro- and tetranitronaphthalenes tend to give a red or intense red colour to the whole column. These colours appeared to be due to decomposition brought about both by the alumina and by the photosensitivity of the nitro-compounds when on the column. Although they may aid in following

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[12] de Aguiar, *Ber.*, 1872, **5**, 370, 897.
[13] Beilstein and Kuhlberg, *Annalen*, 1873, **169**, 81.
[14] Will, *Ber.*, 1895, **28**, 367.
[15] Dimroth and Ruck, *Annalen*, 1926, **446**, 123.
[16] Pascal, *Bull. Soc. chim.* (*France*), 1920, **27**, 388.

the separation, it is best to reduce the exposure of the column to light to a minimum, and furthermore it was not found that irradiation by ultraviolet light was of any assistance in detecting the bands. The decomposition that occurs on the column is negligible with mono- or di-nitronaphthalenes but may become appreciable with some trinitronaphthalenes and is excessive, producing quantities of coloured intractable tars, from tetranitronaphthalenes. Other absorbents such as neutralised alumina, magnesium oxide, or silica gave less colour or decomposition but were not satisfactory for separative purposes. In the chromatography of actual nitration products it appears that the by-products are usually much more strongly adsorbed on the column and tend to remain at the top of it until, following the elution of the actual nitro-compounds, powerful eluting solvents (*e.g.*, ethyl acetate) are applied to remove them. The method appears to be capable of separating favourable mixtures with an accuracy as high as ±0·2%.

(a) 1 : 8- *and* 1 : 5-*Dinitronaphthalene*. A mixture of 1 : 5- (0·299 g.) and 1 : 8-dinitronaphthalene (0·301 g.), dissolved in benzene (100 c.c.), was poured on alumina (35 × 3 cm.). The first 11 fractions (× 100 c.c.) contained only 1 : 5-dinitronaphthalene, the next was free from nitro-compounds, and subsequent elution was by ethyl acetate, the 1 : 8-dinitronaphthalene being completely eluted in fractions 14—19. Recovery of the 1 : 5-isomer was 0·298 g. and that of the 1 : 8-isomer 0·301 g., the overall recovery being 99·8%.

(b) 1 : 6- *and* 1 : 7-*Dinitronaphthalene*. 1 : 6- (0·196 g.) and 1 : 7-Dinitronaphthalene (0·201 g.) were used on alumina (40 × 2·5 cm.). A yellow band appeared on the column and later split into two: by the time the lower, yellow band (corresponding to the 1 : 7-isomer, the 1 : 6-isomer giving no colour) had been eluted the other was about halfway down the column; 50 c.c. fractions were taken, the first ten were solvent only, the next four gave pure 1 : 6-isomer (0·144 g.), the next four gave mixed isomers (0·179 g.), and the next six pure 1 : 7-isomer (0·082 g.). The mixed isomers were dissolved in 1 : 1 benzene–light petroleum and rechromatographed. The 6th and 7th fractions gave pure 1 : 6-isomer, the next three gave mixed isomers, and the next ten gave pure 1 : 7-isomer. This procedure was repeated again with the mixed isomers and these decreased to *ca.* 0·003 g. (*ca.* 1% of original mixture). Recovery of the 1 : 6-isomer was 0·190 g. (97%) and of the 1 : 7-isomer 0·203 g. (100%).

(c) 1 : 3 : 8- *and* 1 : 4 : 5-*Trinitronaphthalene*. A 1 : 1 mixture (0·60 g.) on alumina (40 × 4 cm.) was used. The 1 : 4 : 5-isomer was quantitatively recovered from the first ten fractions (× 100 c.c.) and the 1 : 3 : 8-isomer (98·2%) in the next five. The red coloration of the column and tar found in the final fractions appeared to be due to decomposition of the 1 : 3 : 8-isomer.

Paper Chromatography: General Technique and Accuracy of Method (*With* L. A. TELESZ).—The paper chromatography was largely carried out by the method due to Franc and Latinák.[17] Strips of Whatman No. 4 paper, of sufficient width to accommodate five separations at 1·5 in. apart, and with the machine direction running vertically, were impregnated with petroleum distillate (Shell distillate: boiling range 190—275°) by dipping them first in the pure solvent, and then in a 9 : 1 mixture of benzene–petroleum distillate, and allowing the benzene to evaporate off.

The polynitronaphthalene mixtures were applied to the paper in acetic acid–pyridine or acetone (0·25—0·5% w/v solutions, depending on the composition of, and the number of components in, the mixture). The chromatogram was developed by downward displacement, elution being with ethanol–water–acetic acid (20 : 14 : 1 by vol.) for *ca.* 8 hr., during which the front traversed a distance of *ca.* 25 cm. The temperature was kept at 21° ± 1° throughout.

After the chromatogram had been dried, the individual nitronaphthalenes were faintly visible as brown, red, or yellow spots, and clearly visible as black or blue fluorescent spots under ultraviolet light.

The size of an individual spot in a mixture appeared to have no correlation with the proportion of that substance in the mixture, and the method was therefore used mainly as a qualitative procedure. However, in 1 : 3 : 5- and 1 : 4 : 5-trinitronaphthalene mixtures referred to later, the amount of each isomer present appeared to be approximately equal to the area of the spot. A semi-quantitative result was obtained in this case by comparing the areas and intensities of the spots with those from a standard 1 : 1 mixture of 1 : 3 : 5- and 1 : 4 : 5-trinitronaphthalene and with spots of the individual isomers of known concentration.

Mononitration of α-Nitronaphthalene.—(*a*) The nitro-compound (4·0 g.) was nitrated as described by Ward and Hawkins,[6] care being taken to avoid all dinitration. The yield was

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[17] Franc and Latinák, *Chem. Listy*, 1955, **49**, 872.

5·04 g. (100% for mononitration). In the subsequent chromatography (1·049 g.; alumina column, 40 × 3·5 cm.) 100 c.c. fractions were collected; pure 1 : 5-dinitronaphthalene (0·323 g.) appeared in fractions 4—9, fractions 10 and 11 gave 0·042 g. of mixed isomers, and the remainder was pure 1 : 8-isomer, no trinitronaphthalenes being found. After rechromatography of the mixed isomers the overall recovery was 98·1%. Brown and yellow bands remained at the top of the column after the nitro-compounds had been eluted.

(*b*) The nitro-compound (2·00 g.) in sulphuric acid (*d* 1·84; 16 c.c.) was slowly treated at 0° by a mixture of nitric acid (*d* 1·5; 0·5 g., 0·68 mol.) and boron trifluoride–acetic acid complex in acetic acid (40% boron trifluoride; 15 c.c.). The nitration product was isolated as above (2·29 g.); 1·018 g. of this were chromatographed, 75 c.c. fractions being collected. Pure 1-nitronaphthalene was found in fractions 8—11, fractions 12—14 were a mixture of 1-nitronaphthalene and 1 : 5-dinitronaphthalene (separated by rechromatography), and fractions 15—24 gave pure 1 : 5-dinitronaphthalene; the 1 : 8-isomer was subsequently eluted by ethyl acetate (3 × 75 c.c.), and nothing more was obtained by further elution. The 1-nitronaphthalene gave a clear yellow band on the column and its elution was easy to follow.

(*c*) A suspension of 1-nitronaphthalene (2·00 g.) in acetic anhydride (12 c.c.) was treated at −50° to −40° with a 4 : 1 v/v mixture (3·1 c.c.) of sulphuric acid (*d* 1·84) and nitric acid (*d* 1·42) during 10 min., and after a further 10 min. the mixture poured on ice. The nitration product (2·23 g.) was separated as in (*b*).

(*d*) The 1-nitronaphthalene (2·00 g.) was warmed with nitric acid (*d* 1·42; 5 c.c.) until solution occurred and then refluxed a further 10 min. Chromatography of the nitration product gave pure 1 : 5- and 1 : 8-isomers together with intermediate fractions which appeared to be mainly 1 : 4 : 5-trinitronaphthalene. 1 : 3 : 8-Trinitronaphthalene was probably not present to any significant extent since there was no deep red colour on the column.

Mononitration of 2-*Nitronaphthalene*.—The nitration was carried out as in (*a*) above but at −10° to −5°. Chromatography gave first most of the unchanged 2-nitronaphthalene, then a small amount of this mixed with 1 : 6-dinitronaphthalene, then successively about equal amounts of pure 1 : 6-isomer, mixed 1 : 6- and 1 : 7-isomers, and pure 1 : 7-isomer. The mixtures were separated by rechromatography.

Trinitration of 1-*Nitronaphthalene and Preparation of* 1 : 4 : 5 : 8-*Tetranitronaphthalene*.—1-Nitronaphthalene (25 g.) in sulphuric acid (*d* 1·84; 115 c.c.) was treated with a 4 : 1 v/v mixture (45 c.c.) of sulphuric acid (*d* 1·84) and nitric acid (*d* 1·42). The temperature was allowed to rise to 30° and then nitric acid (*d* 1·5; 160 c.c.) was added, the temperature being kept below 75°. The mixture was kept at 75—90° till frothing ceased, and then heating was continued on the water-bath for 2 hr. After being kept at −5° for 30 min. the solids were collected, and washed with small portions of sulphuric acid, then thoroughly with water. The yield was 23 g. (52% as tetranitronaphthalenes). The product (11 g.) was boiled with acetone (100 c.c.), and the residual 1 : 4 : 5 : 8-tetranitronaphthalene collected (1·8 g.; 8·5% overall yield). The latter began to decompose and sublime at *ca.* 280°, finally exploding at *ca.* 360°. The acetone mother-liquor was concentrated to 30 c.c. and then treated with 2-naphthol (4 g.) whereupon its complex with 1 : 3 : 6 : 8-tetranitronaphthalene separated (7 g.). This was decomposed by boiling methanol to give almost pure 1 : 3 : 6 : 8-tetranitronaphthalene (m. p. 195°). Further concentration of the residual solvent gave material (6 g.) which could not be purified. In another attempt to develop a method for isolating the 1 : 3 : 5 : 8-tetranitronaphthalene, a synthetic mixture (1 : 1 : 4) of 1 : 3 : 5 : 8-, 1 : 4 : 5 : 8-, and 1 : 3 : 5 : 8-tetranitronaphthalene was first extracted with acetone (16 c.c./g.). This gave almost quantitative recovery of the 1 : 4 : 5 : 8-isomer but treatment of the mother-liquors with 2-naphthylamine gave a complex from which no pure isomer could be obtained on decomposition by hydrochloric acid.

Mononitration of 1 : 5-*Dinitronaphthalene in Sulphuric Acid and the Preparation of* 1 : 4 : 5-*Trinitronaphthalene*.—To a vigorously stirred suspension of 1 : 5-dinitronaphthalene (10 g.) in sulphuric acid (*d* 1·84; 50 c.c.) was added dropwise, during 15 min., nitric acid (*d* 1·5; 2·9 c.c.), the temperature not being allowed to rise above 30°. After being stirred for 3 hr. more, the mixture was poured on crushed ice, and the solids were collected, thoroughly washed, and dried *in vacuo* at 60° (11·9 g.). Pure 1 : 4 : 5-trinitronaphthalene (m. p. 147—149°) was obtained by dissolving this product in hot benzene (10 c.c./g.) and collecting the solids after storage overnight (8·5 g. from 10 g.; *ca.* 80% overall yield). A portion of the filtrate (containing 0·33 g. of solute) was examined by chromatography on alumina (20 × 2·5 cm.). A deep red band was immediately formed at the head of the column and then rapidly moved down until the whole column was of uniform colour. The eluted product, however, was pale yellow. No nitro-compounds were eluted until the red band had reached the bottom of the column and all the subsequent fractions contained mainly 1 : 3 : 5-trinitronaphthalene, the later fractions being contaminated with a little 1 : 4 : 5-isomer; the m. p.s ranged from 101° to 119°, the latter being that of pure 1 : 3 : 5-trinitronaphthalene (Ward, Hardy, and Coulson[18] give m. p. 119—121°). The weights and m. p.s of the various fractions indicated a ratio of 19 : 1 for 1 : 4 : 5- to 1 : 3 : 5-trinitronaphthalene in the original nitration product, this being confirmed by infrared spectroscopy or paper chromatography, which indicated limits of ±2%.

Dinitration of 1 : 5-*Dinitronaphthalene in Sulphuric Acid, and the Preparation of* 1 : 3 : 5 : 8-*Tetranitronaphthalene*.—A suspension of 1 : 5-dinitronaphthalene (10 g.) in sulphuric acid (*d* 1·84; 25 c.c.) was treated dropwise, with vigorous stirring, with nitric acid (*d* 1·5; 27 c.c.). When addition was complete the temperature was allowed to rise to 80° whereat there was considerable frothing. After 1 hr. at 80° the mixture was cooled and poured on ice, washed thoroughly with water, and dried *in vacuo* (yield 7·6 g.; 51% as tetranitronaphthalenes). This product (0·65 g.) was extracted with hot benzene (3 × 20 c.c.), affording a residue (0·24 g.) of pure 1 : 4 : 5 : 8-tetranitronaphthalene. The mother-liquors were chromatographed on a cellulose column (35 × 1·5 cm.), fractional elution being by benzene. The initial fractions (100 c.c.) contained some 1 : 4 : 5 : 8-tetranitronaphthalene (total weight 0·342 g.) which was separated from the 1 : 3 : 5 : 8-isomer by acetone or benzene extraction. The next 150 c.c. gave reddish material; from benzene this gave almost pure 1 : 3 : 5 : 8-tetranitronaphthalene, m. p. 186—192° (total 0·308 g.). Paper chromatography of solids obtained by evaporation of the original mother-liquor did not show the presence of 1 : 3 : 5 : 7-tetranitronaphthalene.

To prepare 1 : 3 : 5 : 8-tetranitronaphthalene, the nitration mixture was cooled to −5° for 30 min., and the solids were collected and washed with small amounts of ice-cold 50% w/v aqueous sulphuric acid, and then thoroughly with water. After drying *in vacuo* the solids were extracted with hot benzene or acetone (2 × 7 c.c./g.), the 1 : 4 : 5 : 8-isomer removed, and further amounts of this removed by concentration; further concentration then yielded almost pure 1 : 3 : 5 : 8-tetranitronaphthalene, m. p. 191—196°, raised by recrystallisation from hot fuming nitric acid to 194° (Will[14] gives 194—195°) (overall yield *ca.* 20%).

Nitration of 1 : 5-*Dinitronaphthalene in Aqueous Nitric Acid, and Preparation of* 1 : 3 : 5-*Trinitronaphthalene and* 1 : 3 : 5 : 7-*Tetranitronaphthalene*.—(a) *In* 70% *w/w aqueous nitric acid.* The nitro-compound (20 g.) was refluxed with the acid for 20 hr., solution being complete after 6 hr. The mixture was poured on ice, and the solid collected, thoroughly washed with water, and dried *in vacuo* (15 g.). This was extracted by boiling benzene (100 c.c.), the extract cooled, and the precipitated 1 : 3 : 5 : 7-tetranitronaphthalene collected (1·5 g., m. p. 260°). To the filtrate was added 2-naphthol (9 g.) in benzene (20 c.c.), the whole warmed and stored overnight, and the red solids collected, washed with benzene, and dried (10·2 g.). The mother-liquor was evaporated to dryness; the red product on recrystallisation from benzene (charcoal) gave pure 1 : 4 : 5-trinitronaphthalene (4·2 g.). The 2-naphthol complexes were partially separated by crystallisation from chloroform (35 c.c.); the residue was mainly that from 1 : 3 : 5 : 7-tetranitronaphthalene, and the 1 : 3 : 5-trinitronaphthalene complex was obtained from the mother-liquors. These complexes were decomposed by repeatedly boiling them with methanol until the colour disappeared. Alternatively, the 1 : 3 : 5-complex was much more satisfactorily decomposed by chromatography in benzene on alumina. The 2-naphthol forms a bright red band at the top of the column, the 1 : 3 : 5-trinitronaphthalene giving a pale red colour to the column (recovery *ca.* 85%). A similar experiment was carried out in 85% w/w aqueous nitric acid.

(b) *In* 92·5% *w/w nitric acid.* The nitro-compound (20 g.) was intimately mixed with water (10 c.c.) and then treated with nitric acid (*d* 1·5, 100 c.c.), whereupon it immediately dissolved. The solution was refluxed for 12 hr. and poured on ice, and the solid collected, thoroughly washed with water, and dried (20·5 g.). This (15 g.) was dissolved in hot benzene, and overnight almost pure 1 : 4 : 5-trinitronaphthalene was deposited, further small amounts being obtained by concentration of the filtrate (total 12·5 g.). The mother-liquor was mixed with a solution of 2-naphthol (3 g.) in benzene (50 c.c.), the mixture warmed, and the complex subsequently separated, further amounts being obtained by concentration. After decomposition on alumina the yield of 1 : 3 : 5-trinitronaphthalene was 1·04 g. The losses almost certainly represent oxidation products formed during nitration.

[18] Ward, Hardy, and Coulson, *J.*, 1957, 2634.

Mononitration of 1 : 3 : 5- *and* 1 : 4 : 5-*Trinitronaphthalene in* 92·5% *w/w aqueous Nitric Acid.*—The nitration procedure for the individual trinitronaphthalenes was as described in the previous experiment.

Formation of Molecular Complexes between Polynitronaphthalenes and 2-*Naphthol.*—The nitro-compound (1 g.) was dissolved in the minimum amount of hot chloroform and treated with a saturated solution of 2-naphthol (1 g.) in chloroform, and the solids were collected and washed with chloroform. The *complex* from 1 : 3 : 6 : 8-tetranitronaphthalene was pale orange, m. p. 205°, stable in chloroform, benzene, acetic acid, or acetone, but decomposed by hot methanol with difficulty (Found: N, 12·8. $C_{20}H_{12}O_9N_4$ requires N, 12·8%). That from 1 : 3 : 5 : 8-tetranitronaphthalene was salmon-pink, m. p. 168°, with similar properties (Found: N, 12·8%). The scarlet *complex* from 1 : 3 : 5 : 7-tetranitronaphthalene had m. p. 197°, decomposed with difficulty by hot methanol but more readily by hot acetone (Found: N, 12·8%). Complexes were not given by 1-nitronaphthalene, 1 : 2-, 1 : 3-, 1 : 4-, and 1 : 5-dinitronaphthalene, or 1 : 4 : 5-, 1 : 3 : 6-, or 1 : 3 : 8-trinitronaphthalene.

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