## 127. *Synthesis of* 8 : 8′-*Dinitro*-1 : 1′-*dinaphthyl and Related Compounds.*

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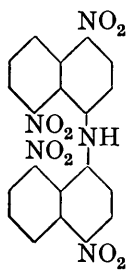
From a study of the reactivities of various iodonitronaphthalenes with copper-bronze, Cumming and Howie (J., 1931, 3176) concluded that dinaphthyl formation only occurred when both the nitro-group and the iodine atom were in the same nucleus. Salkind also (*Ber.*, 1931, **64**, 289) claimed that the influence of a nitro-group in producing high reactivity in a halogen atom did not extend from one ring to the other of the naphthalene nucleus. The present investigation, however, has established that 8 : 8′-*dinitro*-1 : 1′-*dinaphthyl*

is formed in a 43·5% yield when 1-*iodo*-8-*nitronaphthalene* is boiled with copper-bronze in nitrobenzene solution, a result which indicates considerable activation of the iodine in the 1-position by the *peri* (8)-nitro-group with respect to anionoid reagents. The intensity of activation, however, is less than in the case of 1-iodo-2-nitronaphthalene, which, under similar (though not identical) conditions affords a 70% yield of the corresponding dinaphthyl (Cumming and Howie, *loc. cit.*).

Two general methods are now described for the preparation of 8 : 8′-dinitro-1 : 1′-dinaphthyl and related substances: (1) The treatment of 8-nitro-1-naphthalenediazonium sulphate or derivatives with a neutral suspension of cuprous hydroxide, and (2) the action of copper-bronze on 1-iodo-8-nitronaphthalene or its derivatives. By these means 4 : 4′-*dibromo*-8 : 8′-*dinitro*-1 : 1′-*dinaphthyl* was readily formed from 4-bromo-1-iodo-8-nitronaphthalene, but in attempts to prepare 4 : 8 : 4′ : 8′-*tetranitro*-1 : 1′-*dinaphthyl* by the decomposition of 4 : 8-dinitro-1-naphthalenediazonium sulphate with cuprous hydroxide the reaction took an entirely different course and 4 : 8 : 4′ : 8′-*tetranitro*-1 : 1′-*dinaphthylamine* (I) resulted. Such a decomposition of diazonium salts appears to be new and could hardly have been anticipated. This tetranitrated diphenylamine appears to be a $\psi$-acid, since, like 2 : 2′ : 4 : 4′ : 6 : 6′-hexanitrodiphenylamine (aurantia), it readily dissolves in aqueous alkaline hydroxides to give highly coloured solutions, indicating salt formation.



(I.)

4 : 8 : 4′ : 8′-Tetranitro-1 : 1′-dinaphthyl was readily formed from 1-*iodo*-4 : 8-*dinitronaphthalene* by the copper-bronze procedure.

The melting point of 1-iodo-8-nitronaphthalene (80°) is much lower than that of the chloro- (94°) and the bromo- (99—100°) analogue, and may indicate chelation between the iodine atom and the nitro-group. Such chelation could readily occur, since the *peri*-positions are nearer together than the ortho-positions (Mills and Elliott, J., 1928, 1291).

8-Nitro-1-naphthylamine was found to be readily diazotisable either in glacial acetic acid solution by means of nitrosylsulphuric acid (Hodgson and Walker, J., 1933, 1620) or by the ordinary procedure in dilute sulphuric acid, thereby differing from the 2- and 4-isomerides, which require the former method. This fact, taken in conjunction with the reduced activity of the iodine in the *peri*-position in 1-iodo-8-nitronaphthalene compared with that in the 2-nitro-isomeride, would suggest a direct effect (— *D*) of the nitro-group through space, rather than a relayed inductive effect (— *I*) *via* the carbon atoms of the nucleus.

## Experimental.

1-*Iodo*-8-*nitronaphthalene*.—8-Nitro-1-naphthylamine (9·4 g., 0·05 mol.), dissolved in glacial acetic acid (100 c.c.), was added to a solution of sodium nitrite (3·8 g.) in concentrated sulphuric acid (40 c.c.) at 10—15°. The mixture was vigorously stirred for 10 minutes and then added to an ice-cold solution of potassium iodide (10 g.) in water (40 c.c.). The light brown 1-*iodo*-8-*nitronaphthalene* thereby precipitated was recrystallised from ligroin (b. p. 80—100°) and then from alcohol or glacial acetic acid, and obtained in large, pale yellow needles, m. p. 80° (Found: I, 42·2. $C_{10}H_6O_2NI$ requires I, 42·5%). The brown impurity in the crude product could not be removed except by crystallisation from ligroin.

1-*Iodo*-4 : 8-*dinitronaphthalene*.—(a) Finely powdered 1-iodo-8-nitronaphthalene (3 g.) was added gradually to a mixture of nitric acid (15 c.c., *d* 1·4) and fuming nitric acid (5 c.c., *d* 1·5) at 0—10°. After 2 hours' stirring at 15°, the 1-*iodo*-4 : 8-*dinitronaphthalene* (3·2 g.) was precipitated by the addition of water; it crystallised from glacial acetic acid in pale yellow needles, m. p. 146° (Found: I, 36·8. $C_{10}H_5O_4N_2I$ requires I, 36·9%). Iodine was evolved when the nitration was attempted with nitric acid (*d* 1·5) alone.

(b) 4 : 8-Dinitro-1-naphthylamine (2 g.) was precipitated from its solution in boiling glacial acetic acid (20 c.c.) by rapid cooling, and the resulting suspension diazotised by adding it to a solution of sodium nitrite (1·0 g.) in concentrated sulphuric acid (10 c.c.). After 10 minutes' stirring, the diazo-solution was poured into one of potassium iodide (2·0 g.) in water (20 c.c.) initially at 15°. The resulting light brown precipitate was recrystallised first from ligroin and then from glacial acetic acid; m. p. and mixed m. p. with product from (a) 146° (Found: I, 36·6%).

8 : 8′-*Dinitro*-1 : 1′-*dinaphthyl*.—(a) 8-Nitro-1-naphthylamine (18 g.) was boiled with concentrated sulphuric acid (30 c.c.) and water (80 c.c.) until dissolution occurred; the fine suspension of the sulphate which resulted on rapid cooling to 0° was diazotised by the addition, below the surface, of a solution of sodium nitrite (7·0 g.) in water (14 c.c.). An aqueous suspension of cuprous hydroxide was prepared by the addition of 20% aqueous sodium hydroxide to a solution of cuprous chloride (30·0 g.) in concentrated hydrochloric acid (120 c.c.) until the mixture was faintly alkaline, the precipitate being washed by decantation until no alkaline reaction was given. The above diazo-solution was then added at 15—20° with stirring, the mixture heated on the water-bath for 15 minutes, and the solid collected and repeatedly extracted with dilute aqueous ammonia to remove copper compounds. The dried material was boiled under reflux with just sufficient nitrobenzene to effect solution; 8 : 8′-*dinitro*-1 : 1′-*dinaphthyl* separated from the filtered solution in well-defined brown prisms (5·4 g.; 32·8% yield), which were recrystallised from the same solvent and, after being washed with methyl alcohol, obtained in pale lemon-yellow prisms, m. p. 295° (Found : N, 8·1. $C_{20}H_{12}O_4N_2$ requires N, 8·1%). The product was liable to contain an azo-compound, since an intense violet-red coloration was obtained on warming with concentrated sulphuric acid. This impurity, however, could be removed by recrystallisation from nitrobenzene until the product afforded only a dull green colour with concentrated sulphuric acid.

(b) Copper-bronze (1·5 g.) and 1-iodo-8-nitronaphthalene (4 g.) were refluxed in nitrobenzene (20 c.c.) for 1¼ hours; the hot filtered solution deposited almost pure 8 : 8′-dinitro-1 : 1′-dinaphthyl (1 g.; 43·5% yield) on cooling, m. p. and mixed m. p. with the product from (a) 295° (Found : N, 8·2%). The dinaphthyl was insoluble in boiling methyl or ethyl alcohol, very slightly soluble in boiling glacial acetic acid (*ca.* 1 g. in 300 c.c.), but more soluble in boiling tetrahydronaphthalene, aniline, nitrobenzene and cellusolve (*ca.* 1 g. in 100 c.c.).

4 : 8 : 4′ : 8′ :-*Tetranitro*-1 : 1′-*dinaphthyl*.—1-Iodo-4 : 8-dinitronaphthalene (4 g.) was refluxed for 30 minutes with copper-bronze (2 g.) in nitrobenzene (30 c.c.). The cooled filtered solution deposited light brown crystals (0·9 g.; 36% yield) of 4 : 8 : 4′ : 8′-*tetranitro*-1 : 1′-*dinaphthyl*, which separated from nitrobenzene in very pale yellow prisms, m. p. 260° (bath initially at 250°). The pale yellow liquid obtained at 260° became dark on further heating, resolidified, and melted again at 270—280° (Found : N, 13·2. $C_{20}H_{10}O_5N_4$ requires N, 12·9%). Slow heating gave m. p. 260° with darkening and evolution of gas. Warm concentrated sulphuric acid was coloured port-wine red by this substance.

4 : 4′-*Dibromo*-8 : 8′-*dinitro*-1 : 1′-*dinaphthyl*.—(a) 4-Bromo-8-nitro-1-naphthylamine (5 g.) was dissolved in boiling glacial acetic acid (50 c.c.), mixed ice-cold with concentrated sulphuric acid (30 c.c.) and water (100 c.c.), sodium nitrite (3 g.), dissolved in water (10 c.c.), added with stirring at 0—5°, and the diazo-solution mixed with a neutral suspension of cuprous hydroxide prepared as described above from cuprous chloride (7·5 g.). The resulting 4 : 4′-*dibromo*-8 : 8′-*dinitro*-1 : 1′-*dinaphthyl* crystallised from nitrobenzene in yellow prisms, m. p. 294° (decomp.) (Found : Br, 32·0. $C_{20}H_{10}O_4N_2Br_2$ requires Br, 31·9%).

(b) 4-Bromo-1-iodo-8-nitronaphthalene (2·5 g.) and copper-bronze (1·0 g.) were refluxed in nitrobenzene for 1 hour; 4 : 4′-dibromo-8 : 8′-dinitro-1 : 1′-dinaphthyl (0·5 g.; 29% yield) crystallised from the cooled filtered solution and formed pale yellow prisms, m. p. and mixed m. p. with product from (a) 294° (decomp.), on recrystallisation from nitrobenzene (Found : Br, 31·8%).

*Attempted Preparation of* 2 : 4 : 2′ : 4′-*Tetrabromo*-8 : 8′-*dinitro*-1 : 1′-*dinaphthyl*.—2 : 4-Dibromo-1-iodo-8-nitronaphthalene (5 g.) was refluxed with copper-bronze (20 g.) in nitrobenzene (20 c.c.) for 30 minutes. The solution obtained was unworkable owing to the large amount of colloidal matter present.

4 : 8 : 4′ : 8′-*Tetranitro*-1 : 1′-*dinaphthylamine*.—4 : 8-Dinitro-1-naphthylamine (4·6 g.) was diazotised as above, and the diazo-solution treated with an aqueous suspension of cuprous hydroxide prepared from cuprous chloride (7·5 g.). The *product* (1·3 g.; 29% yield) crystallised from nitrobenzene in colourless plates, m. p. 244° (Found : N, 15·5. $C_{20}H_{11}O_8N_5$ requires N, 15·6%), which were readily soluble in aqueous sodium hydroxide to give a yellow colour in dilute and a red colour in more concentrated solutions, and precipitated therefrom unchanged by dilute hydrochloric acid; no acetyl derivative could be obtained.

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