

141. *The Preparation and Chromoisomerism of 4 : 5-Dinitro-1-naphthylamine, and Some Perimidines and Perinones from 4-Chloro- and 4-Bromo-1 : 8-naphthylenediamine.*

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The preparation of 4 : 5-dinitro-1-naphthylamine and its chromoisomerism are described; 4-chloro- and 4-bromo-1 : 8-dinitronaphthalene have been prepared from this amine, and a number of perimidines and perinones have been made from the corresponding 4-chloro- and 4-bromo-1 : 8-naphthylenediamines. The *p*-nitrobenzeneazo-derivative of 6 (or 7)-chloro-2-methylperimidine gives remarkable differences of colour in various solvents.

ALTHOUGH the preparation of 4 : 5-dinitroaceto-1-naphthalide and 4 : 5-dinitro-1-naphthylamine has been claimed in D.R.-P. 145191, the details given are inadequate. It has now been found that 4 : 5-dinitroaceto-1-naphthalide is readily obtained in over 95% yield by nitration of 5-nitroaceto-1-naphthalide and is easily hydrolysed to 4 : 5-dinitro-1-naphthylamine. This amine exhibits pronounced chromoisomerism since it crystallises in yellow needles from glacial acetic acid and in red needles from amyl alcohol.

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The preparations of 4-chloro- and 4-bromo-1 : 8-dinitronaphthalene in yields of 88 and 98%, respectively, from 4 : 5-dinitro-1-naphthylamine were made by Hodgson and Walker's diazotisation procedure (J., 1933, 1620), followed by the appropriate Sandmeyer reaction. These compounds have been previously prepared by the dinitration of 1-chloronaphthalene (Atterberg, *Ber.*, 1876, 9, 928; cf. also Ekstrand, *J. pr. Chem.*, 1888, 38, 171, who dinitrated 5-chloro-1-naphthoic acid), and by the dinitration of 1-bromonaphthalene (Merz and Weith, *Ber.*, 1882, 15, 2710; cf. also the dinitration of 5-bromo-1-nitronaphthalene by Ullmann and Consonno, *Ber.*, 1902, 35, 2805). Repeated recrystallisation, however, failed to raise the m. p.'s of our products to those previously recorded, but our methods of preparation are unequivocal. Moreover, the 4 : 5-dinitro-1-naphthylamine used in our experiments, when deaminated by Hodgson and Turner's procedure (J., 1942, 748), gave an almost quantitative yield of 1 : 8-dinitronaphthalene, thereby establishing its constitution and purity.

Reduction of 4-chloro- and 4-bromo-1 : 8-dinitronaphthalene by Hodgson and Marsden's iron procedure (J., 1944, 316) gave quantitative yields of the 4-chloro- and 4-bromo-1 : 8-naphthylenediamines when isolated as *sulphates*. For subsequent work, the diamines were extracted from the reduction mixtures of the 4-chloro- and 4-bromo-1 : 8-dinitronaphthalenes by ether or benzene, and the extract dried before reactions with toluene-*p*-sulphonyl chloride, formic acid, and acetic, phthalic, or naphthalic anhydrides, perimidine (or perinone) formation taking place with great ease (cf. Sachs *et al.*, *Annalen*, 1909, 365, 53—166).

The *p*-nitrobenzenemonoazo-derivative of 6(or 7)-chloro-2-methylperimidine exhibited remarkable colours when dissolved in the concentrated mineral acids, sulphuric (green), hydrochloric (blue-green), and nitric (yellow), all turning to scarlet on dilution; and also when dissolved in acetic acid, benzene, or toluene (crimson), and in acetone and nitrobenzene (violet). The red colours probably represent the azo-form, and the violet colours the tendency to an indamine structure, whereas the colours with mineral acids indicate salt formation.

EXPERIMENTAL.

Preparation of 4-Chloro- and 4-Bromo-1 : 8-dinitronaphthalenes.—4 : 5-Dinitroaceto-1-naphthalide was obtained when finely divided 5-nitroaceto-1-naphthalide (12.3 g.) was dissolved below 0° in sulphuric acid (60 c.c., *d* 1.84), and the solution treated dropwise below 0° with one of nitric acid (3.6 c.c., *d* 1.42) and sulphuric acid (3.6 c.c., *d* 1.84). Stirring was continued for 2 hours after the addition was completed, and the mixture was then poured on ice (1 l.), the precipitate of 4 : 5-dinitroaceto-1-naphthalide (14.0 g.) removed, washed with water, dried at 100°, and dissolved in boiling glacial acetic acid from which it crystallised on cooling in lemon prisms with pointed ends, m. p. 244° (D.R.-P. 145,191 records felted yellow needles, m. p. 244°) (Found : N, 15.2. Calc. : N, 15.2%). 4 : 5-Dinitro-1-naphthylamine was obtained from the above naphthalide (14.0 g.), by refluxing it for 1 hour with a mixture of sulphuric acid (90 c.c., *d* 1.84), ethyl alcohol (180 c.c.), and water (90 c.c.), the resulting solution being filtered, diluted with ice (700 g.), and neutralised with aqueous ammonia; the yellow precipitate of the amine (11.2 g.) was removed, washed, and dried at 100°, and then crystallised from glacial acetic acid in yellowish needles, m. p. 236° (D.R.-P. 145,191 gives brownish-orange leaflets, m. p. 236°, from acetic acid) (Found : N, 18.2. Calc. : N, 18.0%), and long red needles, m. p. 236°, from amyl alcohol (Found : N, 18.1%).

4 : 5-Dinitro-1-naphthol was formed when 4 : 5-dinitroaceto-1-naphthalide (2 g.) was boiled under reflux for 30 minutes with a solution of potassium hydroxide (1 g.) in ethyl alcohol (20 c.c.), the mixture acidified with dilute mineral acid, and the resulting precipitate purified by dissolution in 5% aqueous potassium hydroxide, and reprecipitated by acid (0.5 g.); it finally crystallised in brownish needles from ethyl alcohol, m. p. 208° (decomp.) [Ullmann and Consonno, *loc. cit.*, give m. p. 208° (decomp.)] (Found : N, 11.9. Calc. : N, 11.9%).

4-Chloro-1 : 8-dinitronaphthalene was obtained when a solution of 4 : 5-dinitro-1-naphthylamine (10 g.) in glacial acetic acid (150 c.c.) was diazotised by addition to a mixture of sodium nitrite (3.0 g.) and sulphuric acid (20 c.c., *d* 1.84) below 20° with stirring continued for 30 minutes, and the chilled solution stirred into one of cuprous chloride (12 g.) in hydrochloric acid (40 c.c., *d* 1.18) at 0° and kept overnight. The chloro-compound (9.8 g.) was precipitated from the mixture by pouring it on ice (800 g.), removed, washed, digested with 5% aqueous sodium hydroxide to remove any 4 : 5-dinitro-1-naphthol, and crystallised first from aqueous acetic acid and then from amyl alcohol, forming long golden needles with a metallic lustre, m. p. 173° (Atterberg, *loc. cit.*, gives m. p. 180°) (Found : N, 11.2. Calc. : N, 11.1%).

4-Bromo-1 : 8-dinitronaphthalene was obtained in precisely analogous manner, but by means of cuprous bromide (12 g.) in hydrobromic acid (30 c.c., *d* 1.7); it crystallised from amyl alcohol (charcoal) in golden prismatic needles (12.5 g.) having a metallic lustre, m. p. 167° (Ullmann and Consonno, *loc. cit.*, give yellow crystals, m. p. 170°) (Found : N, 9.5. Calc. : N, 9.4%).

Some Perinones and Perimidines from 4-Chloro- and 4-Bromo-naphthylenediamines.—The *sulphates* of 4-chloro- and 4-bromo-1 : 8-naphthylenediamines. 4-Chloro- or 4-bromo-1 : 8-dinitronaphthalene (1 g.) was refluxed with a mixture of iron powder (2 g.), ferrous ammonium sulphate (0.5 g.), and water (50 c.c.) for 1 hour; ethyl alcohol (25 c.c.) was then added, the mixture again boiled, and filtered hot into dilute iced sulphuric acid, and the corresponding *sulphate* was precipitated in small platelets. These were removed, washed successively with dilute sulphuric acid, water, and ether, and dried in a vacuum over sulphuric acid (Found : H₂SO₄, 33.9. C₁₀H₆N₂Cl.H₂SO₄ requires H₂SO₄, 33.7%. Found : H₂SO₄, 29.5. C₁₀H₆N₂Br.H₂SO₄ requires H₂SO₄, 29.2%).

These *sulphates*, which are colourless (pure white in bulk) when freshly prepared, rapidly become grey with manipulation. In consequence, the free diamines were not isolated in the subsequent experiments, but were used in a solution, prepared by reduction as above, the chilled mixture being rendered alkaline with ammonia, extracted with 50 c.c. of ether or benzene, and the extract filtered and dried (sodium sulphate).

4-Chloro-*NN'*-bistoluene-*p*-sulphonyl-1 : 8-naphthylenediamine was obtained when a dry benzene solution of 4-chloro-1 : 8-naphthylenediamine, toluene-*p*-sulphonyl chloride (1.7 g.), and anhydrous sodium carbonate (2 g.) was boiled under reflux for 1 hour, the mixture filtered, and the benzene removed by evaporation; the residue of the diamine crystallised from glacial acetic acid in rosettes of colourless, oval plates, m. p. 220° (decomp.) (Found : N, 5.6. C₂₄H₂₁O₄N₂ClS₂ requires N, 5.6%). The *bromo*-analogue, similarly prepared, crystallised from glacial acetic acid in rosettes of colourless plates, m. p. 225° (decomp.) (Found : N, 5.0. C₂₄H₂₁O₄N₂BrS₂ requires N, 5.1%).

6(or 7)-Chloro-10-*phthaloperinone* was formed when phthalic anhydride (0.5 g.) was added to a dry ethereal solution of 4-chloro-1 : 8-naphthylenediamine (from 1 g. of dinitro-compound), the ether removed, the residue transferred to a large boiling-tube and heated at 210° for 2—3 hours; the perinone sublimed in scarlet needles, m. p. 212° (Found : N,

9-3. $C_{18}H_9ON_2Cl$ requires N, 9.2%), which gave a violet colour with concentrated sulphuric acid; it also crystallised from benzene in red needles, m. p. 212°.

6(*or* 7)-*Bromo-10-phthaloperinone*, prepared as above, sublimed in small vermilion needles having a metallic lustre, and crystallised from benzene in red needles, m. p. 214° (Found: N, 8.1. $C_{18}H_9ON_2Br$ requires N, 8.0%), which gave a violet colour with concentrated sulphuric acid.

6(*or* 7)-*Chloro-10-naphthaloperinone*, prepared by addition of naphthalic anhydride (0.6 g.) to a dry ethereal solution of 4-chloro-1:8-naphthylenediamine, followed by removal of the ether and heating the residue at 220°, sublimed in long, salmon-pink needles, which crystallised from nitrobenzene in pink needles, m. p. 276° (Found: N, 7.9. $C_{22}H_{11}ON_2Cl$ requires N, 7.9%), and gave a blue-green colour with concentrated sulphuric acid.

6(*or* 7)-*Bromo-10-naphthaloperinone*, similarly prepared, sublimed in feathery, flesh-coloured needles, which crystallised from nitrobenzene in pale pink needles, m. p. 286° (Found: N, 7.0. $C_{22}H_{11}ON_2Br$ requires N, 7.0%), and gave a faint green colour with concentrated sulphuric acid.

6(*or* 7)-*Chloroperimidine*, prepared by addition of formic acid (3 c.c., 90%) to an ethereal solution of 4-chloro-1:8-naphthylenediamine (from 1 g. of the dinitro-compound), and, after removal of the ether, refluxing the formic acid solution for 15 minutes, was isolated by pouring the solution on ice, with subsequent addition of ammonia until just alkaline; the green precipitate of the perimidine crystallised from hot water in olive platelets, m. p. 200° (Found: N, 13.8. $C_{11}H_7N_2Cl$ requires N, 13.8%). The *bromo*-analogue, similarly obtained, crystallised from aqueous alcohol in olive-green platelets, m. p. 220° (Found: N, 11.3. $C_{11}H_7N_2Br$ requires N, 11.3%).

6(*or* 7)-*Chloro-2-methylperimidine* was formed by use of acetic anhydride (5 c.c.) instead of formic acid, the other conditions being as above; the green perimidine crystallised from aqueous alcohol in long, green parallelepipeds, m. p. 127° (Found: N, 12.6. $C_{12}H_9N_2Cl$ requires N, 12.8%). The *p*-nitrobenzenemonoazo-derivative was prepared (0.15 g.) by addition of an aqueous solution of *p*-nitrobenzenediazonium chloride (from 0.14 g. of *p*-nitroaniline) to an alcoholic solution of the perimidine (0.22 g.) below -5° in the presence of excess of sodium acetate, and crystallised from benzene in shining purple plates, m. p. 125° (Found: N, 19.0. $C_{18}H_{12}O_2N_3Cl$ requires N, 19.1%), solutions of which exhibited the remarkable differences in colour already described.

6(*or* 7)-*Bromo-2-methylperimidine* crystallised from aqueous alcohol in dark green needles, m. p. 130° (Found: N, 10.8. $C_{12}H_9N_2Br$ requires N, 10.7%).

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