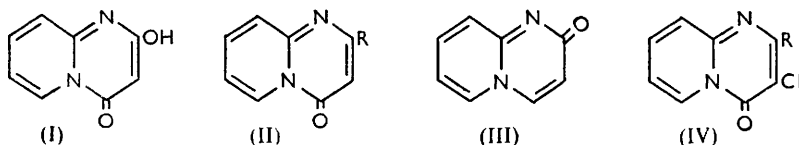


#### 44. Polyazanaphthalenes. Part VI.\* Some Derivatives of 4 : 10-Dihydro-4-oxo-1 : 10-diazanaphthalene.

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Some derivatives of 4 : 10-dihydro-4-oxo-1 : 10-diazanaphthalene, with substituents in the 2- and the 3-position, have been prepared from the 2-hydroxy-4-oxo-compound (malonyl- $\alpha$ -aminopyridine).

SNYDER and ROBISON<sup>1</sup> obtained a monochloro-compound by treatment of 4 : 10-dihydro-2-hydroxy-4-oxo-1 : 10-diazanaphthalene<sup>2</sup> (I) (or a tautomer) with phosphorus oxychloride; they assigned the structure (II; R = Cl) to this product on both spectroscopic and chemical grounds. We have improved the yield of this product and shown that, as expected, it reacts readily with nucleophilic reagents, *e.g.*, hydrazine, ammonia, and sodium methoxide, affording the hydrazino-, amino-, and methoxy-compounds (II; R = NH·NH<sub>2</sub>, NH<sub>2</sub>, and OMe), respectively. Some confirmation of the structure (II; R = Cl) for the monochloro-compound was obtained by oxidation of the hydrazino-compound with copper sulphate<sup>3</sup> which gave a product, albeit in very poor yield, with properties corresponding to those of the 4-oxo-compound<sup>4</sup> (II; R = H) rather than to those of the 2-oxo-compound<sup>5</sup> (III).



By treatment of the starting material (I) with a mixture of phosphorus oxychloride and pentachloride, Snyder and Robison<sup>1</sup> obtained a second monochloro-compound (IV; R = OH) and a dichloro-compound (IV; R = Cl). We have improved the preparation of the dichloro-compound and shown that, again in agreement with expectation, only one of the two chlorine atoms is reactive towards nucleophilic reagents, treatment with ammonia, aniline, and phenol yielding the 2-amino-, 2-anilino-, and 2-phenoxy-compounds (IV; R = NH<sub>2</sub>, NHPh, and OPh) respectively. Deamination of the amino-compound with nitrous acid afforded a monochloro-compound (IV; R = OH), identical with Snyder and Robison's second monochloro-compound.

In an attempt to obtain 4-arylamino-derivatives, the compound (I) was heated with aniline and with *p*-chloroaniline, in the presence of their hydrochlorides;<sup>6</sup> under the reaction conditions, however, the bicyclic structure was broken down, the only isolated products being malonanilide and the *p*-chloromalonanilide, respectively.

#### EXPERIMENTAL

2-Chloro-4 : 10-dihydro-4-oxo-1 : 10-diazanaphthalene (II; R = Cl).—4 : 10-Dihydro-2-hydroxy-4-oxo-1 : 10-diazanaphthalene (malonyl- $\alpha$ -aminopyridine)<sup>2</sup> (4 g.) was refluxed with phosphorus oxychloride (60 ml.) for 5 hr. Excess of oxychloride was removed under reduced pressure and the residue treated with 10% sodium hydrogen carbonate solution. The solid product was dried and sublimed at 160°/10<sup>-3</sup> mm., affording the monochloro-compound (3 g., 67%), m. p. 159° (Found: C, 53.7; H, 2.9; N, 15.6. Calc. for C<sub>8</sub>H<sub>6</sub>ON<sub>2</sub>Cl: C, 53.2; H, 2.8; N, 15.5%) (lit.,<sup>1</sup> m. p. 155—156°).

\* Part V, preceding paper.

<sup>1</sup> Snyder and Robison, *J. Amer. Chem. Soc.*, 1952, **74**, 4910.

<sup>2</sup> Tschitschibabin, *Ber.*, 1924, **57**, 1168.

<sup>3</sup> Cf. Baumgarten and Su, *J. Amer. Chem. Soc.*, 1952, **74**, 3828.

<sup>4</sup> Adams and Pachter, *ibid.*, p. 5491.

<sup>5</sup> *Idem, ibid.*, p. 4906.

<sup>6</sup> Curd, Raison, and Rose, *J.*, 1947, 899.

*2-Hydrazino-4 : 10-dihydro-4-oxo-1 : 10-diazanaphthalene* (II; R = NH·NH<sub>2</sub>).—The monochloro-compound (2 g.) was heated under reflux on a water-bath for 2 hr. with hydrazine hydrate (4 g.) in dioxan (50 ml.). After cooling, the solid was collected and washed with water; recrystallisation from water gave the *hydrazino-compound* (1.75 g., 90%) as needles, m. p. 245° (Found: C, 54.6; H, 4.2. C<sub>8</sub>H<sub>8</sub>ON<sub>4</sub> requires C, 54.6; H, 4.6%).

*4 : 10-Dihydro-4-oxo-1 : 10-diazanaphthalene* (II; R = H).—The hydrazino-compound (1 g.), in water (40 ml.) containing acetic acid (10 ml.), was heated to boiling and treated slowly with 15% copper sulphate solution. After 30 minutes' refluxing, the solution was evaporated under reduced pressure and the residue sublimed at 140°/10<sup>-3</sup> mm., affording the 4-oxo-compound (50 mg., 6%), m. p. 129° (lit.,<sup>4</sup> m. p. 127°, lit.<sup>5</sup> for the 2-oxo-compound, 248°) (Found: C, 65.4; H, 4.3; N, 18.9. Calc. for C<sub>8</sub>H<sub>6</sub>ON<sub>2</sub>: C, 65.8; H, 4.1; N, 19.2%).

*2-Amino-4 : 10-dihydro-4-oxo-1 : 10-diazanaphthalene* (II; R = NH<sub>2</sub>).—The monochloro-compound (1 g.) was heated at 170° for 16 hr. with saturated ethanolic ammonia (10 ml.). The cooled mixture was filtered and the solid product washed with water until chloride-free. Sublimation at 160°/10<sup>-4</sup> mm. gave the *amino-compound* (350 mg., 39%), m. p. 257° (Found: C, 60.1; H, 4.3; N, 26.0. C<sub>8</sub>H<sub>7</sub>ON<sub>3</sub> requires C, 59.7; H, 4.4; N, 26.1%); the *picrate* crystallised from ethanol in needles, m. p. 222° (Found: C, 42.3; H, 2.3; N, 21.7. C<sub>14</sub>H<sub>10</sub>O<sub>8</sub>N<sub>8</sub> requires C, 43.1; H, 2.6; N, 21.6%).

*4 : 10-Dihydro-2-methoxy-4-oxo-1 : 10-diazanaphthalene* (II; R = OMe).—The monochloro-compound (540 mg.) was refluxed for 4 hr. with sodium methoxide (from sodium, 80 mg., and methanol, 25 ml.). The product was evaporated to dryness under reduced pressure and the residue extracted with benzene. Evaporation of the extract afforded the *methoxy-compound* (475 mg., 90%), which crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 146° (Found: C, 61.2; H, 4.5; N, 15.4. C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>N<sub>2</sub> requires C, 61.4; H, 4.6; N, 15.9%).

*2 : 3-Dichloro-4 : 10-dihydro-4-oxo-1 : 10-diazanaphthalene* (IV; R = Cl).—The compound (I) (10 g.) was refluxed for 5 hr. with phosphorus pentachloride (30 g.) and phosphorus oxychloride (120 g.). Excess of oxychloride was removed under reduced pressure and the residue cooled and treated with 10% sodium hydrogen carbonate solution. The yellow solid was filtered off and sublimed at 170°/10<sup>-4</sup> mm.; the dichloro-compound (11.8 g., 89%) crystallised from ethanol in yellow needles, m. p. 230° (lit.,<sup>1</sup> m. p. 226—226.5°) (Found: C, 45.0; H, 1.7; N, 13.5; Cl, 32.6. Calc. for C<sub>8</sub>H<sub>4</sub>ON<sub>2</sub>Cl<sub>2</sub>: C, 44.7; H, 1.9; N, 13.0; Cl, 33.0%).

*2-Amino-3-chloro-4 : 10-dihydro-4-oxo-1 : 10-diazanaphthalene* (IV; R = NH<sub>2</sub>).—The dichloro-compound (2 g.) was heated at 170° for 16 hr. with saturated ethanolic ammonia (10 ml.). After cooling, the crystals were collected, washed with water until chloride-free, and dried at 100°; the *amino-chloro-compound* (1.7 g., 93%) crystallised from ethanol in needles, m. p. 254° (Found: C, 48.9; H, 3.2; N, 21.6; Cl, 18.1. C<sub>8</sub>H<sub>6</sub>ON<sub>3</sub>Cl requires C, 49.15; H, 3.1; N, 21.5; Cl, 18.1%).

When ammonia was passed for 6 hr. through a boiling solution of the dichloro-compound (1 g.) in phenol (10 g.), the only isolated products were the amino-chloro-compound (390 mg., 43%), m. p. 254°, and the phenoxy-compound (see below) (290 mg., 23%), m. p. 148°.

*3-Chloro-4 : 10-dihydro-2-hydroxy-4-oxo-1 : 10-diazanaphthalene* (IV; R = OH).—The amino-chloro-compound (1 g.), in water (20 ml.) containing sulphuric acid (7 g.), was treated dropwise, at 0°, with sodium nitrite (6 g.) in water (15 ml.). After 1 hr., the monochloro-compound separated as a cream-coloured solid (930 mg., 93%) which, sublimed at 170°/10<sup>-4</sup> mm., had m. p. 310° (lit.,<sup>1</sup> decomp. 290°) (Found: C, 48.7; H, 2.4. Calc. for C<sub>8</sub>H<sub>5</sub>O<sub>2</sub>N<sub>2</sub>Cl: C, 48.9; H, 2.55%).

*2-Anilino-3-chloro-4 : 10-dihydro-1 : 10-diazanaphthalene* (IV; R = NHPh).—The dichloro-compound (500 mg.) was heated at 100° for 5 hr. with aniline (500 mg.) in 50% acetic acid (10 ml.). On cooling, the *anilino-compound* (450 mg., 71%) separated in needles and was recrystallised from ethanol or from aqueous dioxan, forming leaflets, m. p. 195° (Found: C, 62.3; H, 3.6; N, 15.3; Cl, 13.5. C<sub>14</sub>H<sub>10</sub>ON<sub>3</sub>Cl requires C, 61.9; H, 3.7; N, 15.5; Cl, 13.05%).

*3-Chloro-4 : 10-dihydro-4-oxo-2-phenoxy-1 : 10-diazanaphthalene* (IV; R = OPh).—The dichloro-compound (200 mg.) was refluxed with phenol (5 g.) for 4 hr. The product was cooled to about 80° and added to excess of 10% sodium hydroxide solution. After cooling, the precipitated *phenoxy-compound* (225 mg., 89%) was collected, washed with water, and recrystallised from ethanol, forming needles, m. p. 148° (Found: C, 61.6; H, 3.2; N, 10.7. C<sub>14</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>Cl requires C, 61.7; H, 3.3; N, 10.3%).

*Action of Arylamines on Malonyl- $\alpha$ -aminopyridine* (I).—(a) This compound <sup>2</sup> (1.6 g.) was

refluxed for 12 hr. with aniline (4.6 g.) and aniline hydrochloride (1.3 g.). The cooled product was triturated with ethanol (10 ml.) and washed with ethanol and water until chloride-free; recrystallisation of the product from ethanol afforded malonanilide in needles, m. p. and mixed m. p. 227°.

(b) Malonylaminopyridine (1.6 g.) was heated at 190° for 12 hr. with *p*-chloroaniline (6.4 g.) and its hydrochloride (1.6 g.). Working up as before gave *p*-chloromalonanilide (1.75 g., 55%), needles (from ethanol), m. p. 259 (lit.,<sup>7</sup> m. p. 259°) (Found: C, 56.1; H, 3.9; N, 9.1; Cl, 21.8. Calc. for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 55.8; H, 3.7; N, 8.7; Cl, 22.0%).

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<sup>7</sup> Pauw, *Rec. Trav. chim.*, 1936, **55**, 215.

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