325. *Chemiluminescent Organic Compounds. Part IX.*
5-Amino-ββ-naphthalaz-1 : 4-dione.

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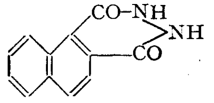
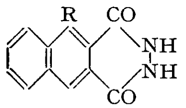
5-Amino-ββ-naphthalaz-1 : 4-dione has been synthesised from 3-hydroxy-2-naphthoic acid, and its chemiluminescence found to be weaker than that of 5-aminophthalaz-1 : 4-dione (luminol). Replacements taking place during diazotisation of 4-nitro-3-amino-2-naphthoic acid and the effect of Sandmeyer reagents on its diazonium salts under various conditions led to the formation of several new derivatives of 2-naphthoic acid.

It was shown by Garwood and one of us (*J.*, 1939, 836) that αβ-naphthalaz-1 : 4-dione (I) and ββ-naphthalaz-1 : 4-dione (II; R = H) emitted a more intense chemiluminescence than did phthalaz-1 : 4-dione when treated with hydrogen peroxide under the conditions of Drew and Pearman (*J.*, 1937, 586).

The preparation of *5-amino-ββ-naphthalaz-1 : 4-dione* (II; R = NH_2) was undertaken in order that its chemiluminescence might be compared with that of luminol, and thus to determine whether the addition of a second benzene ring enhanced the chemiluminescence of 5-substituted phthalaz-1 : 4-diones.

(I.)





(II.)

When 3-acetamido-2-naphthoic acid, prepared from 3-hydroxy-2-naphthoic acid by amination and acetylation (B.P. 330,941; Allen and Bell, *Org. Synth.*, Vol. 22, p. 19), was nitrated in glacial acetic acid solution, it gave a mononitro-compound, which after removal of the acetyl group and reduction with zinc dust and acetic acid, readily condensed with phenanthraquinone to give a *benzphenanthrazinecarboxylic acid*; hence the nitro-group must be in the 4-position. This orientation was confirmed by acidifying a solution of the *4-nitro-3-amino-2-naphthoic acid* in hot dilute sodium hydroxide, to yield 4-nitro-3-hydroxy-2-naphthoic acid.

The preparation of 4-nitro-3-cyano-2-naphthoic acid from the foregoing amine proved troublesome owing to the great readiness with which the nitro-group was replaced during diazotisation and the Sandmeyer reaction. The required nitrile was however obtained in the form of its copper and nickel complexes by diazotising the amine by the method of Hodgson and Walker (*J.*, 1933, 1620), and immediately adding the diazo-suspension obtained to a solution of potassium cuprocyanide or nickelocyanide (Korczynski and Fandrich, *Compt. rend.*, 1926, **183**, 421) in a sufficiently large excess of potassium cyanide to neutralise all the sulphuric acid. Attempts to obtain the nitrile free from metal failed. The complexes could be decomposed only by boiling strong nitric acid, which not only removed the metal but also hydrolysed the cyano-group giving *4-nitronaphthalene-2 : 3-dicarboxylic acid.* The dicarboxylic acid was converted into its *anhydride* and thence into *1-nitronaphthalene-2 : 3-dicarboxyimide.* The imide was reduced with hydrogen and Adams's catalyst to the *1-amino-imide*, which on treatment with hydrazine yielded the required 5-amino-ββ-naphthalaz-1 : 4-dione (II; R = NH_2). When this compound was treated with hydrogen peroxide under the conditions of Drew and Pearman (*loc. cit.*), it emitted a fairly strong luminescence which was at first deep blue, but rapidly became almost white. The luminescence was considerably weaker than that of luminol under similar conditions. Other substituted ββ-naphthalaz-1 : 4-diones may be found to be more weakly chemiluminescent than the corresponding substituted phthalaz-1 : 4-diones.

The reaction of the diazo-suspension (Hodgson and Walker, *loc. cit.*) of 4-nitro-3-amino-2-naphthoic acid with potassium cuprocyanide, or potassium cyanide and copper bronze, in the presence of free sulphuric acid yielded a product, m. p. 270° (decomp.), which on decarboxylation gave α-nitronaphthalene and was undoubtedly 4-*nitro*-2-*naphthoic acid.* Addition of the diazo-suspension (Hodgson and Walker, *loc. cit.*) to potassium nickelocyanide, prepared from nickel chloride (Korczynski and Fandrich, *loc. cit.*), or to aqueous nickel chloride, in both cases in the presence of free sulphuric acid, resulted in the replacement of the nitro-group by chlorine and the elimination of the amino-group, giving a chloro-2-naphthoic acid, m. p. 241°. A mixture of this acid and 3-chloro-2-naphthoic acid (Strohbach, *Ber.*, 1901, **34**, 4160; m. p. 216·5°) melted at *ca.* 190°. Hence the chloro-acid must be the previously unreported 4-*chloro*-2-*naphthoic acid.* It is assumed that the elimination of the diazo-group during the formation of 4-nitro- and 4-chloro-2-naphthoic acids is effected by the reducing action of the cuprous (*cf.* Hodgson *et al.*, *J.*, 1941, 772; 1942, 744; 1947, 173) or nickel ions taking precedence over their more usual catalytic behaviour.

The nitro-group was not attacked during the reaction of the diazo-suspension with cuprous chloride and concentrated hydrochloric acid, which yielded 3-*chloro*-4-*nitro*-2-*naphthoic acid.* However, when the amine was diazotised in a mixture of glacial acetic acid and concentrated hydrochloric acid both the nitro- and the amino-group were replaced by chlorine, giving 3 : 4-*dichloro*-2-*naphthoic acid.*

Replacement of the nitro-group by hydroxyl readily took place during diazotisation in dilute sulphuric acid with the precipitation of *naphthalene*-3-*diazo*-4-*oxide*-2-*carboxylic acid,* a stable yellow compound, which was also formed by diazotisation using the conditions described by Hodgson and Mahadevan (*J.*, 1947, 325) for the preparation of solid diazonium sulphates from *o*-nitro-amines which readily form diazo-oxides under other conditions.

EXPERIMENTAL.

(M. p.s are uncorrected.)

3-Amino-2-naphthoic acid, prepared from the hydroxy-acid by fusion with zinc oxide and ammonium chloride (B.P. 330, 941) or by the method of Allen and Bell (*loc. cit.*), was acetylated giving 3-acetamido-2-naphthoic acid, m. p. 241—243°.

4-*Nitro*-3-*acetamido*-2-*naphthoic Acid.*—Concentrated nitric acid (5·2 g., 0·055 mole) in glacial acetic acid (10 c.c.) was stirred into a solution of 3-acetamido-2-naphthoic acid (11·45 g., 0·05 mole) in glacial acetic acid (90 c.c.), acetic anhydride (8 c.c.), and concentrated sulphuric acid (1·5 c.c.) at 65—70°. The mixture was cooled and allowed to stand overnight. The orange coloured product was collected and crystallised from aqueous ethanol, giving the 4-*nitro-acid* as orange-yellow needles (11·2 g., 82%), m. p. 213° (decomp.) (Found : C, 57·2; H, 4·0; N, 10·55. $C_{13}H_{10}O_5N_2$ requires C, 56·95; H, 3·7; N, 10·2%).

4-*Nitro*-3-*amino*-2-*naphthoic Acid.*—The above acetyl derivative (19·8 g.) was hydrolysed with 15% methanolic potash (550 c.c.). The *amino-acid* crystallised from dilute acetic acid (charcoal) and then dilute ethanol in small orange-brown needles (12·5 g.), m. p. 240° (decomp.) (Found: C, 57·15; H, 3·8; N, 12·45. $C_{11}H_8O_4N_2$ requires C, 56·9; H, 3·45; N, 12·05%). It was insoluble in concentrated hydrochloric acid and in cold dilute sodium hydroxide solution, but dissolved in the latter on heating to form a deep-red solution which on acidification gave a precipitate of 4-nitro-3-hydroxy-2-naphthoic acid, m. p. and mixed m. p. with an authentic specimen, 239—240° (decomp.). 4-*Nitro*-3-*benzamido*-2-*naphthoic acid* formed yellow needles from acetic acid and, after sublimation *in vacuo*, had m. p. 267° (Found : N, 8·65. $C_{18}H_{12}O_5N_2$ requires N, 8·35%). The *phenanthrazine* derivative of 3 : 4-diamo-2-naphthoic acid prepared by reduction of 4-nitro-3-amino-2-naphthoic acid in acetic acid solution with zinc dust, followed by the addition of phenanthraquinone, separated in small yellow crystals, m. p. 321—322° (decomp.), from a large volume of acetic acid (Found : N, 7·5. $C_{25}H_{14}O_2N_2$ requires N, 7·5%).

Reactions of 4-*Nitro*-3-*diazo*-2-*naphthoic Acid Sulphate.*—4-Nitro-3-amino-2-naphthoic acid was diazotised by the method of Hodgson and Walker (*loc. cit.*). A solution of the nitro-amine (0·58 g., 0·0025 mole) in boiling glacial acetic acid (10—12 c.c.) was rapidly cooled to 15°, and the fine suspension thus obtained was stirred into a solution of sodium nitrite (0·22 g., 0·003 mole) in concentrated sulphuric acid (2·7 c.c.) and glacial acetic acid (2—3 c.c.) at $<$ 15°. Towards the end of the diazotisation varying amounts of a yellow solid separated. This diazo-suspension was used immediately in the following replacement reactions.

(*a*) The diazo-suspension was added with stirring to a solution of copper sulphate (0·66 g.) and potassium cyanide (0·75 g.) in water (5 c.c.) at 10—20°. After 1 hour the mixture was heated on a water-bath until effervescence ceased. Dilution with water precipitated a brown solid which, after crystallisation from aqueous ethanol (charcoal) and then acetic acid (90%), formed pale yellow needles of 4-*nitro*-2-*naphthoic acid* (0·27 g.), m. p. 270° (decomp.) (Found : C, 60·8; H, 3·6; N, 6·4. $C_{11}H_7O_4N$ requires C, 60·85; H, 3·25; N, 6·45%). Decarboxylation of this nitro-acid in quinoline in the presence of copper bronze yielded α-nitronaphthalene, m. p. and mixed m. p. 58—59°.

(*b*) Addition of copper bronze (0·6 g.) to the mixture obtained by adding the diazo-suspension to a solution of potassium cyanide (1·0 g.) in water (5 c.c.) at 10—20° also yielded 4-nitro-2-naphthoic acid. The mixture was heated on a water-bath to complete the reaction. The brown solid which separated was worked up as in (*a*) giving pale yellow needles, m. p. and mixed m. p. with a specimen obtained by method (*a*), 270° (decomp.).

(*c*) The diazo-suspension was added with stirring to a solution of nickel chloride (0·6 g.) and potassium cyanide (0·9 g.) in water (5 c.c.) (Korczynski and Fandrich, *loc. cit.*) at 5—10°. The reaction was completed on the water-bath. When the mixture cooled, impure 4-*chloro*-2-*naphthoic acid* separated as a reddish-brown solid which was crystallised from ethanol (charcoal), then dilute acetic acid, and finally benzene in slender cream-coloured needles (0·17 g.), m. p. 241° (mixed m. p. with a specimen of 3-chloro-2-naphthoic acid, 189—193°) (Found : C, 63·9, 64·2; H, 3·4, 3·35; Cl, 17·3. $C_{11}H_7O_2Cl$ requires C, 63·95; H, 3·4; Cl, 17·15%). Addition of the diazo-suspension to a solution of nickel chloride (3·0 g.) in water (20 c.c.) at 5—10°, followed by heating on the water-bath, also yielded crude 4-chloro-2-naphthoic acid which was worked up similarly; m. p. and mixed m. p. with a specimen prepared as above, 241°.

(*d*) 3-*Chloro*-4-*nitro*-2-*naphthoic acid* was prepared by adding the diazo-suspension to a solution of cuprous chloride (2·0 g.) in concentrated hydrochloric acid (10 c.c.) at 10—15°. After being kept overnight the mixture was poured into water (50 c.c.). The yellow precipitate was crystallised from aqueous ethanol (charcoal) and then acetic acid; glittering yellow needles, m. p. 239—240° (decomp.) (Found : N, 5·8 Cl, 14·25. $C_{11}H_6O_4NCl$ requires N, 5·55; Cl, 14·1%).

(*e*) *Naphthalene*-3-*diazo*-4-*oxide*-2-*carboxylic acid*. (i) Ether (30 c.c.) was slowly added to the thick yellow suspension produced by keeping the diazo-suspension for 20 minutes. The yellow solid was collected and washed with glacial acetic acid–ether and then with ether. It had m. p. 130° (decomp.). Purification as in (ii) gave the *diazo-oxide* as dark yellow needles, m. p. and mixed m. p. with a specimen prepared by method (ii), 186° (decomp.). (ii) The diazo-oxide was also formed when the suspension produced by pouring a solution of 4-nitro-3-amino-2-naphthoic acid (0·58 g.) in concentrated sulphuric acid (*d* 1·84; 5 c.c.) on ice (15 g.) was diazotised with sodium nitrite (0·2 g.) in water (2 c.c.) at 5—10°. The amine dissolved to give a dark brown solution which immediately began to deposit a yellow solid. After 1—2 hours the solid was collected. It had m. p. *ca.* 165° (decomp.) and crystallised from aqueous ethanol in orange-brown needles (0·40 g.), m. p. 183—186° (decomp.). Crystallisation from ethyl acetate gave the pure diazo-oxide as dark yellow needles, m. p. 186° (decomp.) (Found : C, 61·7, 61·9; H, 3·1, 3·3; N, 13·4. $C_{11}H_6O_3N_2$ requires C, 61·7; H, 2·8; N, 13·1%).

(*f*) 4-*Nitronaphthalene*-2 : 3-*dicarboxylic acid*. (i) The diazo-suspension (prepared from 2·32 g. of the amine) was rapidly stirred into a solution of copper sulphate (5·0 g.) and potassium cyanide (24·0 g.) in water (60 c.c.), the temperature being kept below 15° by the addition of ice. After 30 minutes the mixture was heated on a water-bath for 1 hour. When cold, the buff-coloured copper complex was collected and heated under reflux with 56% nitric acid (50 c.c.) for 45 minutes. The complex dissolved to give a green solution from which yellow needles separated on cooling. These needles still contained a little copper which was removed by heating under reflux with 56% nitric acid (30 c.c.) for 10 minutes. Crystallisation from water (charcoal) yielded 4-*nitronaphthalene*-2 : 3-*dicarboxylic acid* which melted at 210° with gas evolution, solidified, and remelted at 229—230° (gas evolution). It recrystallised from water in long colourless blades, m. p. 233—234° (gas evolution); yield, 0·96 g. (37%) (Found : C, 54·95; H, 2·7; N, 5·7. $C_{12}H_7O_6N$ requires C, 55·2; H, 2·7; N, 5·35%). The *anhydride*, prepared by heating the acid under reflux with excess of acetic anhydride, had m. p. 237—238° (gas evolution) (Found : C, 58·8; H, 2·3. $C_{12}H_5O_5N$ requires C, 59·25; H, 2·05%). (ii) The preparation (using 1·16 g. of the amine) was carried out as in (i), except that an aqueous solution of nickel sulphate (2·8 g.) and potassium cyanide (12·0 g.) was used in place of the cuprocyanide solution. The buff-coloured nickel complex was decomposed as in (i). Crystallisation gave the dicarboxylic acid, m. p. and mixed m. p. with a specimen prepared by method (i), 231—232° (gas evolution).

3 : 4-*Dichloro*-2-*naphthoic Acid*.—Finely powdered sodium nitrite (0·2 g.) was added with stirring to a suspension of 4-nitro-3-amino-2-naphthoic acid (0·58 g.) in glacial acetic acid (12 c.c.) and concentrated hydrochloric acid (6 c.c.) at 10°. After a few minutes the solution was added to an aqueous solution of copper sulphate (0·66 g.) and potassium cyanide (0·75 g.) at 10—15°. The mixture was heated on the water-bath and cooled, and the product collected. Crystallisation from aqueous ethanol (charcoal), glacial acetic acid, and finally benzene yielded 3 : 4-*dichloro*-2-*naphthoic acid* in slender cream-coloured needles, m. p. 233·5° (decomp.) (Found : C, 55·1; H, 2·8; Cl, 29·5. $C_{11}H_6O_2Cl_2$ requires C, 54·8; H, 2·5; Cl, 29·4%).

1-*Nitronaphthalene*-2 : 3-*dicarboxyimide*.—(*a*) An intimate, finely powdered mixture of the above anhydride (1·9 g.) and urea (0·6 g.) was heated with stirring to 180° and allowed to cool. The *imide* crystallised from absolute ethanol (charcoal) and glacial acetic acid in pale yellow rhombs (1·25 g., 66%), m. p. 270—271° (gas evolution) (Found : C, 59·3; H, 2·5. $C_{12}H_6O_4N_2$ requires C, 59·5; H, 2·5%). (*b*) An intimate, finely powdered mixture of 4-nitronaphthalene-2 : 3-dicarboxylic acid (0·85 g.) and ammonium carbonate (0·85 g.) was fused at 270—280° for 10 minutes. The brown product was worked up as in (i), giving small rhombs (0·4 g.), m. p. 267—268° which did not depress a specimen made by method (*a*).

1-*Aminonaphthalene*-2 : 3-*dicarboxyimide*.—A solution of the foregoing nitro-imide (0·8 g.) in ethyl acetate (100 c.c.) was shaken with Adams's catalyst (40 mg.) in hydrogen for 2 hours. A further quantity of catalyst (20 mg.) was added and the shaking continued for 1 hour. The solvent was removed, the bright-yellow residue taken up in glacial acetic acid and filtered, and the filtrate treated with charcoal and concentrated. The orange-yellow needles, m. p. 299—302° (decomp.), which separated were crystallised from absolute ethanol giving the pure *amine* in felted yellow needles, m. p. 302—303° (decomp.) (Found : C, 67·4; H, 3·4. $C_{12}H_8O_2N_2$ requires C, 67·9; H, 3·8%). Solutions of the amine were greenish-yellow in colour and had a strong greenish-blue fluorescence.

5-*Amino*-ββ-*naphthalaz*-1 : 4-*dione*.—The foregoing imide (0·2 g.) was heated under reflux with hydrazine hydrate (90%; 1·5 c.c.) and water (5 c.c.). The imide dissolved to a yellow solution which was filtered and acidified. The almost white precipitate of the *dione* was collected, dissolved in warm dilute ammonia, treated with charcoal, and filtered, and the filtrate acidified. Reprecipitation from dilute ammonia yielded the pure dione as a cream-coloured powder, m. p. 342—344° (decomp.) (Found : C, 60·6; H, 4·6. $C_{12}H_9O_2N_3,\frac{1}{2}H_2O$ requires C, 61·0; H, 4·25%). The dione was practically insoluble in organic solvents; it formed a sodium salt soluble in hot water but sparingly soluble in cold water.

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