149. *The Diazotisation of 1-Amino-2-hydroxy-4-cyanonaphthalene and the Preparation of 4-Cyano-2-naphthol.*

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The attempted diazotisation of 1-amino-2-hydroxy-4-cyanonaphthalene by dilution of its solution in nitrosylsulphuric acid with water gave mainly 4-cyano-1 : 2-naphthaquinone, and dilution with glacial acetic acid afforded a mixture of this quinone and 4-cyanonaphthalene-1 : 2-diazo-oxide. Solid sodium nitrite added to a glacial acetic acid solution of the above amine produced a 90% yield of 4-cyanonaphthalene-1 : 2-diazo-oxide. Boiling ethyl alcohol rapidly reduced this diazo-oxide to 4-cyano-2-naphthol.

Bradley and Robinson (J., 1934, 1484) reported that 1-amino-2-hydroxy-4-cyanonaphthalene was not diazotised when a concentrated solution of sodium nitrite was added gradually to one of the base in concentrated sulphuric acid at — 10° to — 5°. Instead, they obtained an orange-yellow solid on dilution with water which could not be coupled with resorcinol in alkaline solution. Further, the base was recovered unchanged after being stirred with an acidified solution of copper sulphate and sodium nitrite in contrast to the ready diazotisation of 1-amino-2-naphthol-4-sulphonic acid (D.R.-P., 171,024; Friedländer, vol. 8, p. 640).

The authors have now established that excess of nitrosylsulphuric acid converts 1-amino-2-hydroxy-4-cyanonaphthalene in the presence of water into 4-cyano-1 : 2-naphthaquinone in *ca.* 89% yield. Bradley and Robinson's orange-yellow solid was then found to be this quinone in an impure state, and its identity was established by condensation with *o*-phenylenediamine to form 3-cyano-1 : 2-benzphenazine. When, however, the theoretical amount of nitrosylsulphuric acid necessary for diazotisation was used, the resulting product contained some *4-cyanonaphthalene-1 : 2-diazo-oxide* mixed with the above quinone. In Bradley and Robinson's experiment, therefore, the excess of nitrous acid (or perhaps the nitrosylsulphuric acid itself) had behaved as

an oxidising agent; those authors readily obtained 4-cyano-1 : 2-naphthaquinone from the 1-amino-2-hydroxy-4-cyanonaphthalene by ice-cold oxidation with chromium trioxide in concentrated sulphuric acid.

We have found that the nitrosylsulphuric–glacial acetic acid procedure (Hodgson and Walker, J., 1933, 1620) materially increased the amount of diazo-oxide in the above mixture, and thereby diminished the oxidation which had predominated in the presence of water. As expected from this result, it was found that complete diazotisation was effected by the addition of solid sodium nitrite to a solution of 1-amino-2-hydroxy-4-cyanonaphthalene in glacial acetic acid only, and at room temperature. The yield of 4-cyanonaphthalene-1 : 2-diazo-oxide was 90% (cf. Hodgson and Foster, J., 1942, 30, for similar diazotisations of arylazo-β-naphthylamines).

The above gradual variation in the action of nitrous acid on a readily oxidisable *o*-aminonaphthol, *viz.*, in concentrated sulphuric acid (no action), aqueous sulphuric acid (almost complete oxidation), sulphuric–glacial acetic acid (oxidation with some diazotisation), and glacial acetic acid (almost complete diazotisation), is of interest, especially as it seems to run parallel with the gradual decrease of ionisation of the nitrous acid in the sequence of media.

4-Cyanonaphthalene-1 : 2-diazo-oxide was easily reduced by boiling alcohol to 4-cyano-2-naphthol, but admixed with some azo-by-product formed by a slight amount of coupling of the diazo-oxide with the cyanonaphthol. This impurity was removed as an insoluble barium lake by addition of barium chloride to the solution of the reaction mixture in aqueous alkaline hydroxide.

Experimental.

1-Amino-2-hydroxy-4-cyanonaphthalene.—This was prepared according to Bradley and Robinson (*loc. cit.*), and the crude hydrochloride was employed without further purification in the experiments now described. When sodium cyanide was used instead of potassium cyanide, slightly lower yields were obtained.

4-Cyano-1 : 2-naphthaquinone.—1-Amino-2-hydroxy-4-cyanonaphthalene (1·8 g.), obtained from the hydrochloride by treatment with sodium acetate solution, was dissolved below 10° in sulphuric acid (10 c.c., *d* 1·84) and stirred below 10° into a solution of sodium nitrite (1·75 g., 2·5 equivs.) in sulphuric acid (15 c.c., *d* 1·84). After an hour's stirring, the mixture was poured on ice, whereupon a copious evolution of gas occurred; the yellow-brown precipitate of 4-cyano-1 : 2-naphthaquinone was collected, washed, and dried; m. p. 170°; yield, 1·6 g. (89%). It separated from water in red-brown crystals, m. p. 175°, and from benzene in orange prisms, m. p. 175—176° (Bradley and Robinson, *loc. cit.*, give m. p. 175—176°) (Found : N, 7·8. Calc. for $C_{11}H_5O_2N$: N, 7·7%). Hot glacial acetic acid solutions of the above compound and *o*-phenylenediamine, when admixed, gave an immediate precipitate of 3-cyano-1: 2-benzphenazine, which recrystallised from glacial acetic acid in yellow needles, m. p. 247° (Bradley and Robinson give m. p. 247°) (Found : N, 16·6. Calc.: N, 16·5%).

4-Cyanonaphthalene-1 : 2-diazo-oxide.—Powdered 1-amino-2-hydroxy-4-cyanonaphthalene hydrochloride (13·2 g.) was added portionwise to a solution of anhydrous sodium acetate (6 g.) in glacial acetic acid (60 c.c.) at about 40°. The mixture was then cooled to room temperature, powdered sodium nitrite (5·0 g.) added, and the whole stirred for 30 minutes at about 30°, this temperature being maintained by external cooling. When the reaction was completed, the mixture was externally cooled by ice, so that as much as possible of the 4-cyanonaphthalene-1 : 2-diazo-oxide crystallised out (together with some sodium acetate and chloride). The brown precipitate was then removed, washed successively with a little glacial acetic acid and with cold water, its colour then changing to a brighter yellow; yield, 7·0 g.; m. p. 144° (decomp.). The mother-liquors, when diluted with ice and water, afforded a further 3·0 g., m. p. 138°; total yield, 10 g. (85%). *4-Cyanonaphthalene-1 : 2-diazo-oxide* crystallised from water in bright yellow needles, m. p. 147·5° (slow decomp.) (Found : N, 21·7. $C_{11}H_5ON_3$ requires N, 21·5%). It coupled readily with alkaline phenols and naphthols, evolved nitrogen when treated with alcohol and zinc dust, and decomposed on exposure to sunlight. *2-Hydroxy-4-cyano-1-naphthaleneazo-β-naphthol* was obtained in 90% yield when the above diazo-oxide (0·4 g.) was added to a solution of β-naphthol (0·4 g.) in alcohol (10 c.c.) at 0° into which 20% aqueous sodium hydroxide (2 c.c.) was subsequently stirred. The deep purple solution when acidified with dilute acid gave the azo-compound, which crystallised from toluene or cellosolve in dark brown or black needles with a green reflex, m. p. 250° (decomp.) (Found : N, 12·65. $C_{21}H_{13}O_2N_3$ requires N, 12·4%).

4-Cyano-2-naphthol.—The above diazo-oxide (6·9 g., 0·035 g.-mol.) was heated under reflux with ethyl alcohol (175 c.c.) for 2 hours, after which the alcohol was recovered by distillation, and the residue extracted cold with 2% aqueous sodium hydroxide (70 c.c.), the filtered extract being diluted with water to 150 c.c., and stirred with an aqueous solution of hydrated barium chloride (4·2 g.). The filtered solution, when acidified at this stage, gave a clean, though tarry product, and it was consequently diluted to 500—600 c.c., then heated to boiling (with norit), neutralised with hydrochloric acid, and filtered; on cooling, *4-cyano-2-naphthol* crystallised in cream-coloured needles (1·7 g.), m. p. 125—136°. Repetition of the extraction of the above residue afforded a further 1·0 g., m. p. 123—127°, and the evaporation of the mother-liquor of a third extraction produced 0·3 g.; total yield, 3·0 g. (57%). 4-Cyano-2-naphthol crystallised from benzene and aqueous 30% methyl alcohol in colourless parallelepipeds, m. p. 138° (Found : N, 8·4. $C_{11}H_7ON$ requires N, 8·3%). Its *acetate*, prepared by refluxing it for 30 minutes with acetic anhydride, crystallised from 30% aqueous methyl alcohol (charcoal) in colourless parallelepipeds, m. p. 84° (Found : N, 6·7. $C_{13}H_9O_2N$ requires N, 6·6%).

4-Cyano-2-methoxynaphthalene, prepared by treating the naphthol with methyl sulphate in 10% aqueous sodium hydroxide, crystallised from methyl alcohol in colourless needles, m. p. 103° (Found : N, 7·2. $C_{12}H_9ON$ requires N, 7·1%). *1-Benzeneazo-4-cyano-2-hydroxynaphthalene*, prepared by coupling diazotised aniline with alkaline 4-cyano-2-naphthol, crystallised from glacial acetic acid in small needles, m. p. 206° (Found : N, 15·4. $C_{17}H_{11}ON_3$ requires N, 15·3%).

The authors thank Imperial Chemical Industries Ltd., Dyestuffs Division, for various gifts.

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