CXV—*The Cyanine Dyes. Part II. The Synthesis of o-Aminocinnamylidenequinaldine Methiodide.*

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It has been generally recognised that in the formation of *isocyanines* by the action of alkalis on mixtures of a quinoline with a quinaldine alkyl iodide, a dominant part is played by the highly reactive ψ -bases to which the action of alkalis on a quinoline alkyl iodide is known to give rise.

Two views are held with respect to the constitution of these ψ -bases. In addition to the cyclic carbinol formula (I) suggested by Decker (*Ber.*, 1892, **25**, 3326), an open-chain alkylamino-

aldehyde formula (II) was proposed by Roser (*Annalen*, 1892, **272**, 221; 1894, **282**, 363), and was supported with additional experimental evidence by Gadamer (*Arch. Pharm.*, 1905, **243**, 12; 1908, **246**, 89) and Kaufmann and Strübin (*Ber.*, 1911, **44**, 680).

It was pointed out by W. König (*J. pr. Chem.*, 1912, [ii], **86**, 166) that the possibility that the quinolinium ψ -bases were to be represented by the second of these formulæ made it necessary to take into account a corresponding constitution for the *isocyanines*. Accordingly, in place of the formula (III) which he had originally proposed (*J. pr. Chem.*, 1906, [ii], **73**, 100) for this class of dyes, he now suggested the open-chain formula (IV), and gave reasons for preferring it to the formulæ which had previously been put forward.

With a view to obtain evidence which would bear on the constitution of the *isocyanines*, we undertook the synthesis of a com-

pound of a type almost identical with that represented by formula IV. This substance was *o*-aminocinnamylidenequinaldine methiodide (V), the structural formula of which only differs from König's butadiene formula for dimethylisocyanine iodide in that it contains an amino-group in place of a methylamino-group attached to the benzene nucleus in the ortho-position with respect to the butadiene chain.

Meanwhile, the facts described in a preceding paper (Mills and Wishart, this vol., 579) were discovered. These showed definitely that the isocyanines do not possess an open-chain formula, and the chief object of these experiments was thus attained in another way; we think, however, that the synthesis and properties of *o*-aminocinnamylidenequinaldine methiodide, which in certain respects bears a distinct relationship to the dyes of the cyanine class, may still be of sufficient interest to be recorded.

The synthesis was effected in the following manner. *o*-Nitrocinnamaldehyde was heated with quinaldine and zinc chloride, when condensation took place, with the formation of *o*-nitrocinnamylidenequinaldine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CH} \cdot \text{CH}:\text{CH} \cdot \text{C}_9\text{H}_6\text{N}$. This was reduced with iron and acetic acid to the corresponding amino-compound, which forms deep reddish-brown mono-acid salts and di-acid salts, which are pale yellow and characterised by their sparing solubility.

To prepare the quaternary methiodide of this base, the amino-group was first protected by acylation. The acylamino-compound was then converted into its methiodide by heating with methyl iodide, and finally the acyl group was eliminated. Various acyl derivatives having been examined, the *formyl* compound was found to give the best results, and its *methiodide*, on hydrolysis with dilute hydrochloric acid, gave *o*-aminocinnamylidenequinaldine methiodide (V).

It proved to be a compound which forms deep reddish-brown solutions and crystallises in small, oblique-ended needles showing a dark olive-green metallic reflex; the crystals are strongly pleochroic, but almost opaque. Its strongly coloured aqueous solutions are at once turned pale yellow by the addition of mineral acids, evidently on account of the formation of di-acid salts. It

dyes wool, and especially silk, a beautiful rich reddish-brown, but the colour is surprisingly fugitive in daylight. Its absorption spectrum in the visible region, unlike the spectra of the *isocyanines*, which are characterised by a distinctive pair of bands, shows only general absorption in the violet and blue, which in more concentrated solutions extends as far as the orange. It has also no appreciable sensitising action on a gelatino-bromide photographic plate. Apart, therefore, from its instability towards light and its partial decolorisation by acids, it shows little analogy in properties to the *isocyanines*. At the same time, the fact should not be overlooked that, on account of the presence of the two ethylenic linkings in the butadiene chain, a compound of this structure should be capable of existence in four geometrically isomeric forms, only one of which is closely related in configuration to cyanine dyes, namely, those of the at present unknown $\alpha\alpha$ -class (VI), the properties of which can, however, to some extent be inferred from those of the analogous compounds of the benzothiazole series prepared by Hofmann (*Ber.*, 1888, **21**, 2262).

EXPERIMENTAL.

o-Nitrocinnamaldehyde.—We first prepared this substance by the method described by Diehl and Einhorn (*Ber.*, 1885, **18**, 2336), but as the process proved troublesome to carry out, we sought for some method of nitrating cinnamaldehyde by which the *o*-nitro-derivative could be more easily obtained. Experiments on nitration in the presence of acetic anhydride showed that the process could be conducted so that *o*-nitrocinnamaldehyde was the sole crystalline product.

A solution of 25 grams of nitric acid (D 1.50) in 50 grams of glacial acetic acid was dropped slowly, with frequent shaking, into an ice-cold solution of 50 grams of cinnamaldehyde in 200 c.c. of acetic anhydride. The solution was allowed to remain for two days at the ordinary temperature; dilute hydrochloric acid was then added and the mixture well shaken. Considerable heat was developed, and, on cooling, *o*-nitrocinnamaldehyde crystallised in almost colourless needles. By recrystallising once from alcohol, the compound was obtained pure in very pale yellow needles melting

at 127°. This method thus gives a very simple means of preparing *o*-nitrocinnamaldehyde, and although the yield is only 36 per cent. of the weight of cinnamaldehyde taken, it could probably be improved by further investigation of the process.

o-Nitrocinnamylidenequinaldine.—A mixture of *o*-nitrocinnamaldehyde (10 grams), quinaldine (8.1 grams), and zinc chloride (2 grams) was heated on the water-bath for five hours. The resulting crystalline mass was dissolved in hot acetone, and the solution, on cooling, deposited the pure condensation product in yellow rhombs melting at 149°. The compound dissolves readily in hot acetone or chloroform, sparingly in alcohol, benzene, or ether (Found: N=9.28. $C_{19}H_{14}O_2N_2$ requires N=9.27 per cent.).

p-Nitrocinnamylidenequinaldine.—*p*-Nitrocinnamaldehyde (10 grams) and quinaldine (8.1 grams) were heated together on the boiling-water bath for ten hours. The product was dissolved in alcohol, the solution poured into water, and the yellow solid was collected and crystallised from acetone. Pure *p*-nitrocinnamylidenequinaldine was thus obtained in yellow needles melting at 185.5° (Found: N=9.25. $C_{19}H_{14}O_2N_2$ requires N=9.27 per cent.).

o-Aminocinnamylidenequinaldine,

—An examination of the action of various reducing agents on *o*-nitrocinnamylidenequinaldine showed that the reduction could be carried out most conveniently by means of iron and acetic acid. The nitro-compound (10 grams) was dissolved in warm glacial acetic acid, the solution diluted with water, and excess of iron added. The mixture, which rapidly became a deep reddish-brown, was kept at 60° for two hours, and the excess of iron was then removed. On adding concentrated hydrochloric acid, the sparingly soluble yellow *dihydrochloride* of the new base was precipitated. It was collected, washed with concentrated hydrochloric acid, and decomposed with ammonia. On crystallising the base thus formed from aqueous alcohol, it was obtained in yellow needles melting at 135.5°. It is very readily soluble in alcohol or chloroform, moderately so in acetone, ether, or benzene, and practically insoluble in water (Found: C=83.3; H=5.9; N=10.2. $C_{19}H_{16}N_2$ requires C=83.8; H=5.9; N=10.3 per cent.).

o-Formylaminocinnamylidenequinaldine,

—*o*-Aminocinnamylidenequinaldine was heated with excess of 90 per cent. formic acid under reflux on the sand-bath for three hours. After cooling, the mixture was diluted with water, rendered alkaline with ammonia, and the precipitated formyl derivative was

collected and crystallised from alcohol. It formed pale yellow needles melting at 185.5° . This compound is readily soluble in hot alcohol or chloroform, fairly so in acetone, and sparingly so in ether or benzene (Found: $N=9.4$. $C_{20}H_{16}ON_2$ requires $N=9.3$ per cent.).

o-Formylaminocinnamylidenequinaldine Methiodide.—Formylaminocinnamylidenequinaldine (2 grams) was heated with methyl iodide (6 grams) in a sealed tube at 100° for three hours. The red mass obtained in this way crystallised from alcohol in dark red needles, which melted at 218° . The substance is soluble in hot water or alcohol, sparingly so in acetone or chloroform, and insoluble in ether or benzene (Found: $I=28.7$. $C_{21}H_{19}ON_2I$ requires $I=28.7$ per cent.).

o-Acetylaminocinnamylidenequinaldine,

—The amino-compound (10 grams) was heated for one hour on the water-bath with acetic anhydride (30 grams). The excess of acetic anhydride was then decomposed by heating with water, and the acetyl derivative precipitated by the addition of ammonia. It was collected and crystallised from aqueous alcohol, from which it separates in pale yellow needles melting at 179° . It is soluble in chloroform and dissolves very readily in alcohol. It is almost insoluble in ether, acetone, water, or benzene (Found: $N=9.1$. $C_{21}H_{18}ON_2$ requires $N=8.9$ per cent.).

Acetylaminocinnamylidenequinaldine Methiodide.—The acetyl derivative (2 grams) was heated with methyl iodide (4 grams) in a sealed tube at 100° for three hours. The bright red contents of the tube were crystallised from water, and then recrystallised from alcohol. The methiodide obtained in this way consisted of bright red needles melting at $216-217^{\circ}$ (Found: $I=27.75$. $C_{22}H_{21}ON_2I$ requires $I=27.85$ per cent.).

It is soluble in water, alcohol, or acetone, sparingly so in chloroform, and insoluble in ether or benzene.

Carboxymethylaminocinnamylidenequinaldine,

—A solution of *o*-aminocinnamylidenequinaldine (2.5 grams) in dry chloroform was heated with methyl chloroformate (1 gram) under reflux for four hours. Water was added, and then ammonia until the red colour of the hydrochloride disappeared. The chloroform layer was separated, the chloroform evaporated, and the residue crystallised from alcohol. The compound formed lustrous, yellow plates melting at 175.5° (Found: $N=8.5$. $C_{21}H_{18}O_2N_2$ requires $N=8.5$ per cent.).

This compound is readily soluble in hot alcohol or chloroform,

sparingly so in acetone, ether, or benzene, and practically insoluble in water.

o-Aminocinnamylidenequinaldine Methiodide (V).—This substance was obtained by the hydrolysis of its acyl derivatives, the reaction being most easily carried out with the formyl compound. Formylaminocinnamylidenequinaldine methiodide is readily hydrolysed by dissolving in hot water, adding a little concentrated hydrochloric acid, and boiling for twenty minutes. To ensure getting the iodide uncontaminated with chloride, potassium iodide was added to the mixture, and the greater part of the acid was then neutralised with ammonia, when a dark reddish-brown precipitate of the iodide was obtained. This was recrystallised from methyl alcohol to which a little aqueous potassium iodide had been added. The salt forms needles with a very dark olive-green lustre melting at 194.5° . It is very readily soluble in methyl alcohol, less so in ethyl alcohol or water, and sparingly so in acetone or chloroform. For analysis it was dried in a vacuum at 70° (Found: C=57.5; H=4.6; N=6.53; I=30.4, 30.8. $C_{20}H_{19}N_2I$ requires C=58.0; H=4.6; N=6.76; I=30.7 per cent.).

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