

### 381. Cyanine Dyes from 2 : 3-Dihydro- $\beta$ -quinindene.

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Symmetrical *carbocyanines* (IVa; IVb) have been prepared from 2 : 3-dihydro- $\beta$ -quinindene alkiodides. Unsymmetrical *carbocyanines* (V—Xb) have also been obtained where the second nucleus is derived from trimethylindolenine, quinaldine, 6-methylquinaldine, lepidine, 2-methylbenzoxazole, and 2-methylbenzthiazole.

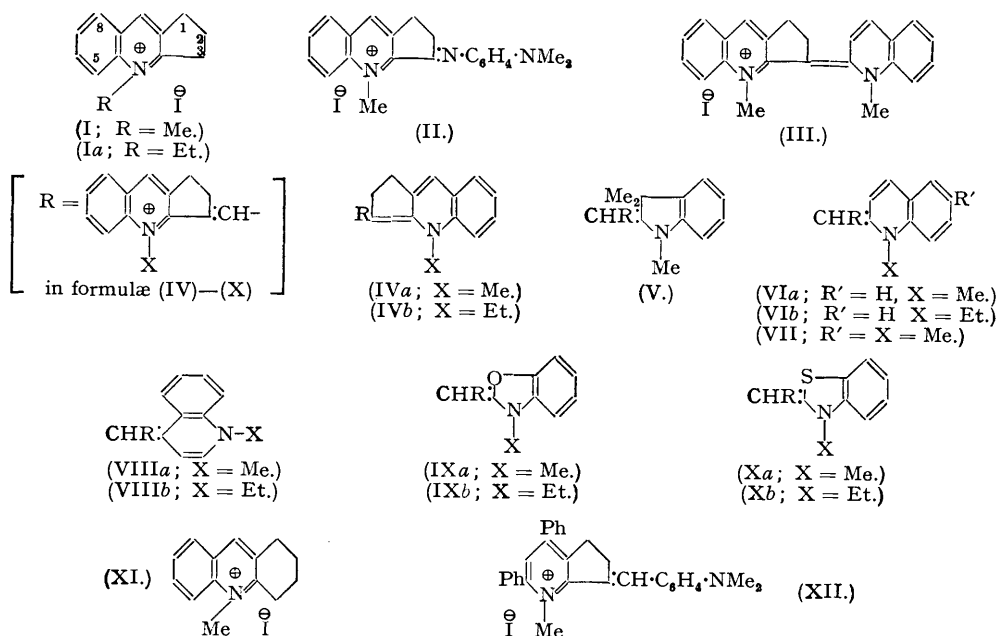
Incidental observations recorded include the conversion of dihydro- $\beta$ -quinindene methiodide into a *dimethylamino-anil* (II) and a  *$\psi$ -cyanine* (III), and the preparation of the *p-dimethylamino-benzylidene* derivative (XII) from 2 : 4-diphenyldihydropyridene methiodide.

THE preparation of cyanine dyes from bases with reactive homocyclic methylene groups, or from their quaternary salts, does not appear to have received much attention hitherto. The possibility of obtaining such compounds was nevertheless foreshadowed in an earlier publication (Petrow, *J.*, 1945, 18), and has now been realised by their synthesis from 2 : 3-dihydro- $\beta$ -quinindene.

Earlier attempts to condense dihydro- $\beta$ -quinindene methiodide (I) with *p*-nitrosodimethylaniline in the presence of piperidine were not successful, only black amorphous precipitates being obtained (Petrow, *loc. cit.*). We now find the reaction follows the expected pattern when carried out under carefully controlled conditions giving the 3-*p-dimethylamino-anil* (II) of dihydro- $\beta$ -quinindene methiodide in excellent yield. This compound is not very stable, however, being decomposed by acids and alkalis, and even on heating in alcoholic solution. Similar instability was encountered in the preparation of a  *$\psi$ -cyanine* from dihydro- $\beta$ -quinindene. Although condensation of (I) with 2-iodoquinoline methiodide and alkali in alcoholic solution (see Hamer, *J.*, 1928, 206) gave [2-(1-methylquinoline)][3-(4-methyldihydro- $\beta$ -quinindene)]cyanine iodide (III) in moderate yield, yet its purification was handicapped by its partial decomposition on crystallisation, and satisfactory analytical figures for it could not be obtained.

Carbocyanines of the dihydro- $\beta$ -quinindene series, in contrast, were both stable and well-defined compounds. *Bis*-[4-methyl-3-(dihydro- $\beta$ -quinindene)]methincyanine iodide (IVa), contaminated with a persistent impurity probably of the neocyanine type, was obtained when (I) was heated with ethyl orthoformate in pyridine-acetic anhydride, but was obtained analytically pure from a reaction mixture containing sodium formate and ethyl orthoformate in boiling acetic

anhydride-pyridine. Essentially the same conditions were employed for converting *dihydro-β-quinindene ethiodide* (Ia) into the *carbocyanine* (IVb) except that the addition of the sodium formate proved unnecessary.



Condensation of (I) with diphenylformamidine by the method of Piggott and Rodd (B.P. 344,409) gave *3-anilinomethylenedihydro-β-quinindene methiodide*, but this intermediate proved unsuitable for the preparation of unsymmetrical carbocyanines. These were ultimately prepared by the reverse procedure, *i.e.*, the condensation of the quinindene alkiodide with the quaternary salt of the appropriate anilino-vinyl compound in boiling acetic anhydride-pyridine. The *carbocyanines* (V–Xb) were obtained in this way from (I; Ia) and the anilino-vinyl salts prepared from trimethylindolenine, quinaldine, 6-methylquinaldine, lepidine, 2-methylbenzoxazole, and 2-methylbenzthiazole. (I) failed to react with *3-methyl-2-β-anilino-vinylbenzimidazole methiodide*.

Attempts to repeat some of the above preparations using tetrahydroacridine methiodide (XI) in place of (I) were not successful; (XI) failed to react with ethyl orthoformate under a variety of experimental conditions. Although it gave a deep green coloration when heated with chloroform and alkali in alcoholic solution, yet attempts to isolate a crystalline dye from the product were not successful. The methiodide (XI) also failed to react with diphenylformamidine on prolonged heating at 125°, and with *2-acetanilidovinylbenzoxazole methiodide* in pyridine-acetic anhydride. Vigorous reaction occurred when (XI) was treated with *p*-nitrosodimethylaniline and piperidine in alcoholic solution, but only black amorphous solids were isolated from the intensely purple products. This result would appear to indicate that steric considerations and not a low reactivity of the 1-methylene grouping are responsible for the failure to convert tetrahydroacridine methiodide (XI) into compounds of the cyanine type.

Preliminary experiments on the preparation of cyanine dyes from 2:4-diphenyl-dihydropyridine methiodide gave discouraging results, only the corresponding 7-*p*-dimethylaminobenzylidene derivative (XII) being obtained. These failures are doubtless due to the lowered reactivity of the 7-methylene grouping owing to the effect of the 2- and 4-phenyl residues on the ring nitrogen. As attempts to prepare the ethiodide of the parent base were likewise unsuccessful, further experiments in this direction were abandoned.

The photographic properties of the above dyes, kindly determined by Messrs. Kodak Ltd. through the courtesy of Dr. F. M. Hamer, M.A., D.Sc., F.R.I.C., will be reported elsewhere.

## EXPERIMENTAL.

(M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.)

2 : 3-Dihydro- $\beta$ -quinindene ethiodide (Ia), light yellow plates from ethyl alcohol, m. p. 206—207° (Found : N, 4.1; I, 39.0.  $C_{14}H_{16}NI$  requires N, 4.3; I, 39.1%), was prepared by heating the components for 4 hours on the water-bath.

2- $\beta$ -Anilino-vinylquinoline ethiodide formed yellowish-brown platelets from spirit, m. p. 277—278° (Found : N, 7.0; I, 31.8. Calc. for  $C_{19}H_{18}N_2I$  : N, 7.0; I, 31.6%) (cf. Piggott and Rodd, *loc. cit.*).

4- $\beta$ -Anilino-vinylquinoline methiodide, red silky needles from spirit, m. p. 259—260° (Found : N, 7.4; I, 32.3. Calc. for  $C_{18}H_{17}N_2I$  : N, 7.4; I, 32.8%), was obtained (62%) by fusing lepidine methiodide (3 g.) with diphenylformamide (2 g.) at 160—165° for one hour, followed by trituration of the melt with dilute hydrochloric acid (cf. Piggott and Rodd, *loc. cit.*).

6-Methyl-2- $\beta$ -anilino-vinylquinoline methiodide, yellowish needles from spirit, m. p. 270° (decomp.) (Found : N, 6.2; I, 32.1.  $C_{19}H_{19}N_2I$  requires N, 6.9; I, 31.6%), was obtained (60%) by heating an intimate mixture of *p*-toluquinoline methiodide (6 g.) and diphenylformamide (4 g.) at 160° for 15 minutes.

3-Methyl-2- $\beta$ -anilino-vinylbenzimidazole methiodide, light yellow needles from absolute alcohol, m. p. 273° (Found : N, 10.8. I, 32.4.  $C_{17}H_{18}N_3I$  requires N, 10.8; I, 32.5%), was obtained (27%) by heating 2 : 3-dimethylbenzimidazole (2.7 g.) and diphenylformamide (2 g.) at 130—135° for 3 hours.

3- $\beta$ -Anilino-methylendihydro- $\beta$ -quinindene methiodide, dark red prisms from absolute alcohol, m. p. 252° (decomp.) (Found : N, 6.3; I, 30.5.  $C_{20}H_{19}N_2I$  requires N, 6.8; I, 30.7%), was obtained (33%) by heating dihydro- $\beta$ -quinindene methiodide with diphenylformamide at 111—115° for 2 hours.

2- $\beta$ -Acetanilidovinylbenzoxazole methiodide, bright yellow needles from ethyl acetate-alcohol, m. p. 238—239° (Found : C, 51.2; H, 4.0; N, 6.9; I, 29.2.  $C_{18}H_{17}O_2N_2I$  requires C, 51.4; H, 4.0; N, 6.7; I, 30.2%), was obtained (60%) by heating 2-methylbenzoxazole methiodide (11 g.), diphenylformamide (8 g.), and acetic anhydride (50 ml.) under reflux for 30 minutes, and setting the product aside overnight.

2- $\beta$ -Acetanilidovinylbenzthiazole methiodide, brownish-black prisms from absolute alcohol, m. p. 226° (Found : S, 7.9.  $C_{18}H_{17}ON_2IS$  requires S, 7.4%), was prepared as for the oxygen analogue above.

3-*p*-Dimethylaminoanil of Dihydro- $\beta$ -quinindene Methiodide (II).—Dihydro- $\beta$ -quinindene methiodide (I) (1.6 g.) in hot absolute alcohol (50 ml.) was treated with *p*-nitrosodimethylaniline (900 mg.) in hot absolute alcohol (25 ml.), followed by immediate addition of piperidine (0.5 ml.). After 10 minutes' heating the dye was collected and crystallised from methyl alcohol, from which it separated (48%) in dark green needles, m. p. 212° (Found : N, 9.3; I, 28.4.  $C_{21}H_{22}N_3I$  requires N, 9.5; I, 28.7%).

[2-(1 : 3 : 3-Trimethylindolenine)][3-(4-methyldihydro- $\beta$ -quinindene)]dimethincyanine (V), brown microcrystals (90%) from spirit, m. p. 264—265° (Found : N, 5.8; I, 25.8.  $C_{22}H_{27}N_2I$  requires N, 5.6; I, 25.7%), was obtained when an intimate mixture of (I) (2.1 g.), 3 : 3-dimethyl-2- $\beta$ -acetanilidovinylindolenine methiodide (2.1 g.), and potassium acetate (2 g.) was added to acetic anhydride (50 ml.) and pyridine (5 ml.), the mixture heated under reflux for 1 hour, and the dye precipitated with water (400 ml.).

[2-(1-Methylquinoline)][3-(4-methyldihydro- $\beta$ -quinindene)]cyanine Iodide (III).—Dihydro- $\beta$ -quinindene methiodide (1.5 g.) and 2-iodoquinoline methiodide (2 g.) in absolute alcohol (100 ml.) were treated with potassium hydroxide (700 mg.) under reflux. After 30 minutes the product was poured into water (400 ml.). After standing overnight the dye was collected and purified from aqueous alcohol, giving dark violet prisms (45%), m. p. 242—243° (decomp.) (Found : I, 25.2.  $C_{23}H_{21}N_2I_2C_2H_5OH$  requires I, 25.5%).

Bis-[4-methyl-3-(dihydro- $\beta$ -quinindene)]methincyanine Iodide (IVa).—Dihydro- $\beta$ -quinindene methiodide (2 g.), sodium formate (1 g.), ethyl orthoformate (2 g.), acetic anhydride (20 ml.), and pyridine (5 ml.) were heated under reflux for 15 minutes. After standing overnight at room temperature, the dye was collected and crystallised from pyridine, giving bronze platelets (20%), m. p. 268° (decomp.) (Found : N, 5.3; I, 25.2.  $C_{27}H_{28}N_2I$  requires N, 5.6; I, 25.2%).

Bis-[4-ethyl-3-(dihydro- $\beta$ -quinindene)]methincyanine iodide (IVb), copper plates from pyridine, m. p. 270° (decomp.) (Found : N, 5.4; I, 23.8.  $C_{29}H_{29}N_2I$  requires N, 5.3; I, 23.9%), was obtained (30%) by heating dihydro- $\beta$ -quinindene ethiodide (2.2 g.) and ethyl orthoformate (2.3 g.) in pyridine (20 ml.) and acetic anhydride (5 ml.) for 1 hour.

[2-(1-Methylquinoline)][3-(4-methyldihydro- $\beta$ -quinindene)]dimethincyanine iodide (VIa), lustrous violet plates (30%) from pyridine, m. p. 272—273° (Found : C, 62.4; H, 4.9; N, 5.8.  $C_{25}H_{23}N_2I$  requires C, 62.7; H, 4.9; N, 5.9%), was prepared by heating dihydro- $\beta$ -quinindene methiodide (1.4 g.), 2- $\beta$ -anilino-vinylquinoline methiodide (1.4 g.), sodium acetate (2 g.), acetic anhydride (50 ml.), and pyridine (5 ml.) under reflux for 1 hour, followed by precipitation with water (500 ml.).

[2-(1-Ethylquinoline)][3-(4-ethyldihydro- $\beta$ -quinindene)]dimethincyanine iodide (VIb), dark green, lustrous plates (52%) from pyridine, m. p. 284—285° (decomp.) (Found : N, 5.6; I, 25.3.  $C_{27}H_{27}N_2I$  requires N, 5.5; I, 25.1%), was prepared by heating (Ia) (1.3 g.), 2- $\beta$ -anilino-vinylquinoline ethiodide (1.6 g.), sodium acetate (2 g.), and acetic anhydride (30 ml.) under reflux for 1 hour, followed by precipitation of the dye with water (400 ml.).

[2-(1 : 6-Dimethylquinoline)][3-(4-methyldihydro- $\beta$ -quinindene)]dimethincyanine iodide (VII), prepared as for (VIa) but using 2- $\beta$ -anilino-vinyl-6-methylquinoline methiodide, formed violet plates (25%) from pyridine, m. p. 269—270° (decomp.) (Found : N, 6.0; I, 25.5.  $C_{26}H_{25}N_2I$  requires N, 5.7; I, 25.8%).

[4-(1-Methylquinoline)][3-(4-methyldihydro- $\beta$ -quinindene)]dimethincyanine iodide (VIIIa), lustrous green platelets from pyridine, m. p. 264—265° (Found : N, 6.1; I, 26.1.  $C_{25}H_{23}N_2I$  requires N, 5.9; I, 26.5%), was obtained (60%) by adding an intimate mixture of (I) (1.5 g.), 4- $\beta$ -anilino-vinylquinoline methiodide (2 g.), and potassium acetate (1.5 g.) to acetic anhydride (50 ml.) and pyridine (5 ml.), and after heating for 1 hour, precipitating the dye with water (500 ml.).

[4-(1-Ethylquinoline)][3-(4-ethyldihydro- $\beta$ -quinindene)]dimethincyanine iodide (VIIIb), obtained (80%) as for (VIIIa), formed green, silky needles from spirit, m. p. 277—278° (decomp.) (Found : N, 5.4; I, 25.2.  $C_{27}H_{27}N_2I$  requires N, 5.5; I, 25.1%).

[2-(3-Methylbenzoxazole)][3-(4-methyldihydro- $\beta$ -quinindene)]dimethincyanine iodide (IXa), dark violet

prisms from pyridine, m. p. 267—268° (Found : N, 5.9; I, 27.0.  $C_{23}H_{21}ON_2I$  requires N, 6.0; I, 27.1%), was obtained (60%) by heating (I) (1.6 g.), 2- $\beta$ -acetanilidovinylbenzoxazole methiodide (2.1 g.), sodium acetate (2.5 g.), and acetic anhydride (40 ml.) for 1 hour, followed by precipitation of the dye with water (500 ml.).

[2-(3-Ethylbenzoxazole)][3-(4-ethyl-dihydro- $\beta$ -quinindene)]dimethincyanine iodide (IXb) formed dark violet prisms (63%) from pyridine, m. p. 274—275° (decomp.) (Found : N, 5.8; I, 25.2.  $C_{25}H_{25}ON_2I$  requires N, 5.7; I, 25.6%).

[2-(3-Methylbenzthiazole)][3-(4-methyl-dihydro- $\beta$ -quinindene)]dimethincyanine iodide (Xa) formed dark green plates (60%) from pyridine, m. p. 271° (Found : N, 5.7; I, 25.6.  $C_{23}H_{21}N_2IS$  requires N, 5.8; I, 26.2%).

[2-(3-Ethylbenzthiazole)][3-(4-ethyl-dihydro- $\beta$ -quinindene)]dimethincyanine iodide (Xb) formed lustrous green prisms (60%) from pyridine, m. p. 279° (Found : N, 5.2; I, 24.5.  $C_{25}H_{25}N_2IS$  requires N, 5.5; I, 24.8%).

3-*p*-Dimethylaminobenzylidene-2 : 3-dihydro- $\beta$ -quinindene ethiodide, blue needles from absolute alcohol, m. p. 221—222° (decomp.) (Found : N, 6.3; I, 27.8.  $C_{23}H_{25}N_2I$  requires N, 6.1; I, 27.9%), was obtained (85%) by adding an intimate mixture of (Ia) (1 g.) and *p*-dimethylaminobenzaldehyde (500 mg.) to boiling acetic anhydride (15 ml.) and, after a further 4 minutes' heating, allowing the solution to cool and collecting the dye.

The 7-*p*-dimethylaminobenzylidene derivative of 2 : 4-diphenyldihydropyridene methiodide (XII), red silky needles from absolute alcohol, m. p. 184—185° (decomp.) (Found : N, 4.8; I, 22.9.  $C_{30}H_{29}N_2I$  requires N, 5.2; I, 23.3%), was obtained (30%) when 4 : 6-diphenyl-2 : 3-trimethylene-pyridine methiodide (1.0 g.), *p*-dimethylaminobenzaldehyde (400 mg.), piperidine (0.5 ml.), and absolute alcohol (25 ml.) were heated under reflux for 15 hours, alcohol (15 ml.) removed by distillation, and the residue allowed to crystallise.

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