Cyanine Dyes derived from 1 : 6-*Dioxojulolidine.*

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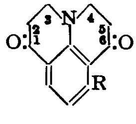
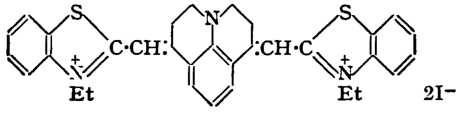
7-Methyl-1 : 6-dioxojulolidine condenses with 2-methylbenzothiazole ethiodide to give the cyanine iodide (III), but the corresponding derivative could not be obtained from 1 : 6-dioxojuloline. The latter readily condenses with *p*-dimethylaminobenzaldehyde and *p*-nitrosodimethylaniline to give *mero*cyanines of type (IV). Other derivatives are briefly described.

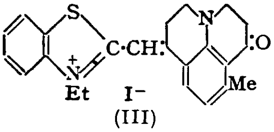
We have attempted to condense both carbonyl groups in 1 : 6-dioxojulolidine (I; R = H) with the reactive methyl groups of 2-methylbenzothiazole ethiodide, quinaldine ethiodide, and lepidine ethiodide, since this condensation would produce a very interesting type of cyanine dye [for example, (II)] in which any two of the three nitrogen atoms could accept the positive charges. These attempts, using either (I; R = H) or its 7-methyl homologue (I; R = Me), failed to produce crystalline products of the desired type, although the intense colour of the reaction mixture indicated some condensation. The condensation of (I; R = Me) with 2-methylbenzothiazole ethiodide in boiling pyridine did however produce [2-(3-ethylbenzothiazole)][1-(7-methyl-6-oxojulolidine)]methincyanine iodide (III),

(I)

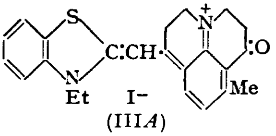




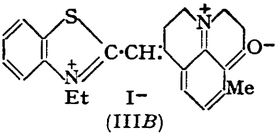
(II)



(III)



(IIIA)



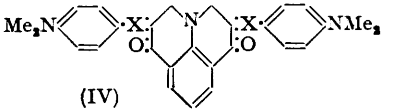
(IIIB)

brownish-red needles giving a reddish-purple solution in methanol. The reason why (I; R = Me) condenses with one but not two equivalents of the ethiodide whilst (I; R = H) gives no satisfactory condensation is obscure. Hyperconjugation between a nuclear methyl group and a ·CO·CH$_2$· system may increase the activity of the ketone by causing increased enolisation (Cardwell and Kilner, *J.*, 1951, 2430); this increased activity in (I; R = Me) might be transmitted to either carbonyl group, and the structure (III) has been adopted solely because no steric hindrance occurs at the 1-keto-group. The compound (III) is a true cyanine dye in that the form (III*A*) will contribute to the salt, with, however, additional contribution by the *mero*cyanine form (III*B*). The compound (III) has certain structural resemblances to cyanine dyes containing the pyrrocoline nucleus (Holliman and Schickerling, *J.*, 1951, 914).

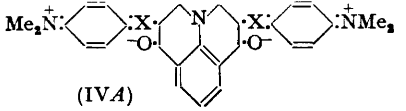
An entirely different type of *mero*cyanine has been obtained by the condensation of (I; R = H) with *p*-dimethylaminobenzaldehyde to give [2 : 5-(1 : 6-dioxojulolidine)][bis-4-(dimethylaminobenzene)]bismonomethin*mero*cyanine (IV; X = CH), orange needles giving a yellow solution in dioxan, and with *p*-nitrosodimethylaniline to give [2 : 5-(1 : 6-dioxojulolidine)][di-4-(dimethylaminobenzene)]dimonoazamethin*mero*cyanine (IV; X = N), bluish-purple needles giving a purple solution in acetone. Each of these compounds will receive contributions from the forms (IV), (IV*A*), and (IV*B*).

Tests carried out by Imperial Chemical Industries Limited, Dyestuffs Division, show that the dye (III) has a moderate sensitising action over the range 460—610 mμ, but that the *mero*cyanines (IV; X = CH) and (IV; X = N) have none (cf. p. 401).

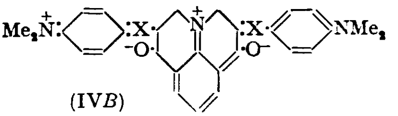
The acid hydrolysis of the *mero*cyanine (IV; X = N) was performed in order to prepare 1 : 2 : 5 : 6-tetraoxojulolidine (V). The brown highly crystalline product, having the composition of (V), was insoluble in all organic solvents except boiling nitrobenzene, would not condense with *o*-phenylenediamine, and dissolved in aqueous sodium hydroxide to form an intensely purple solution. These properties strongly indicate that the tetraketone (V) undergoes dienolisation to 2 : 5-dihydroxy-1 : 6-dioxo*iso*juline (VI), which in turn undergoes intermolecular hydrogen bonding; this suggestion is supported by the infra-red spectrum of the crystals, which shows strong sharp bands at 3·05 and 6·01 μ, the former corresponding to a hydrogen-bonded hydroxyl group and the latter to the carbonyl group.



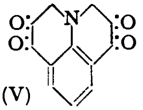
(IV)



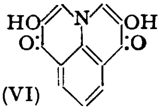
(IV*A*)



(IV*B*)

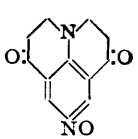


(V)

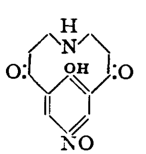


(VI)

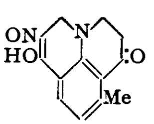
The action of nitrous acid on the system (I) may be briefly recorded. We have attempted to convert (I; R = H) into the 8-nitroso-derivative (VII), in the hope that the action of hot aqueous alkalis would then give the *meta*-bridged derivative (VIII). The compound (I; R = H) resisted nitrosation, but the 7-methyl derivative gave a crystalline mustard-coloured mononitroso-compound, m. p. 156°, soluble in organic solvents. This product, when treated with aqueous sodium hydroxide, or even when subjected to excessive heating during recrystallisation, was converted into a dark brown solid, m. p. 158°, of the same composition, but insoluble in all the usual solvents. There is at present no evidence for the structure of these two products. In view, however, of the known activation of one



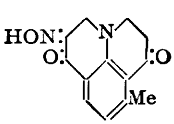
(VII)



(VIII)



(IX)



(X)

ketone group in the dioxo-base (I; R = Me) by the 7-methyl group, it is possible that the initial crystalline derivative is 1-hydroxy-7-methyl-2-nitroso-6-oxojuloline (IX), and that the action of alkali gives the hydroxyimino-compound (X), possibly followed by a Beckmann rearrangement to a seven-membered cyclic acid amide. The remarkable stability of 1 : 6-bishydroxyiminojulolidine has already been described (Braunholtz and Mann, *J.*, 1952, 3046).

EXPERIMENTAL

Certain m. p.s, denoted by (E. T.), were determined in evacuated sealed tubes.

When solutions of the diketone (I; R = H) and 2-methylbenzothiazole ethiodide (1 or 2 mols.) in pyridine, piperidine, or methanolic triethylamine were boiled under reflux for 10—20 hr., evaporation of the intensely red solution gave the unchanged compounds with traces of a deep red gum. Similar results were obtained when the ethiodides of quinaldine and lepidine were employed.

[2-(3-*Ethylbenzothiazole*)][1-(7-*methyl*-6-*oxojulolidine*)]*methincyanine Iodide* (III).—A solution of the base (I; R = Me) (220 mg.) and 2-methylbenzothiazole ethiodide (310 mg., 1 mol.) in pyridine (5 c.c.) was boiled under reflux for 10 hr. A red solid separated on cooling, and a second crop was obtained by concentration. The combined crops were washed with much hot water and ethanol, and then crystallised from methanol, giving the brownish-red monohydrated *iodide* (III), m. p. 288° (decomp.) (Found: C, 53·4; H, 4·75; N, 5·3. $C_{23}H_{23}ON_2IS,H_2O$ requires C, 53·2; H, 4·8; N, 5·3%). The use of the ethiodide (2 mols.) and 15 hours' heating increased the yield from 11% to 17%.

No dye could be isolated when the pyridine in the above experiment was replaced by methanol containing piperidine or 10% aqueous sodium hydroxide, or when the quaternary salt was replaced by quinaldine ethiodide, lepidine ethiodide, or Fischer's base hydriodide.

[2 : 5 - (1 : 6 - *Dioxojulolidine*)][*bis* - 4 - (*dimethylaminobenzene*)]*dimonomethin*mero*cyanine* (IV; X = CH).—A solution of the base (I; R = H) (1 g.) and *p*-dimethylaminobenzaldehyde (1·5 g., 2 mols.) in ethanol (25 c.c.) containing 10% aqueous sodium hydroxide (0·5 c.c.) was boiled under reflux for 15 min., an orange solid separating from the yellow solution. After cooling, the solid was collected and crystallised from dioxan, giving the mero*cyanine* (IV; X = CH), bright orange needles, m. p. 247—248° (1·2 g., 52%) (Found: C, 77·7; H, 6·4; N, 8·85. $C_{30}H_{29}O_2N_3$ requires C, 77·7; H, 6·3; N, 9·05%).

*The Dimonoazamethin*mero*cyanine* (IV; X = N).—A solution of *p*-nitrosodimethylaniline hydrochloride (10 g., 2·2 mols.) in water (50 c.c.) at 60° was slowly added with stirring to one of the diketone (I; R = H) (5 g.) in a mixture of ethanol (50 c.c.) and 10% aqueous sodium hydroxide (50 c.c.), also at 60°, the initial reddish colour of the diketone solution rapidly becoming almost black, with separation of dark purple crystals. The latter, collected from the cold mixture and recrystallised from much acetone, afforded the mero*cyanine* (IV; X = N), blue-purple crystals, m. p. 277° (decomp.) (E.T.) (7 g., 61%) (Found: C, 72·1; H, 5·9; N, 15·2. $C_{28}H_{27}O_2N_5$ requires C, 72·2; H, 5·85; N, 15·05%).

1 : 2 : 5 : 6-*Tetra-oxojulolidine* (V or VI).—A solution of the dye (IV; R = N) (0·5 g.) in concentrated hydrochloric acid (20 c.c.) was boiled under reflux for 30 min., the initial deep red colour changing to pale yellow-brown and brown crystals separating. The crystals, being insoluble, were purified by washing with much dilute hydrochloric acid, water, and acetone, and thus afforded the *compound* (V or VI), m. p. *ca.* 440° (with sublimation) (0·15 g., 60%) (Found: C, 63·1; H, 3·4; N, 5·9. $C_{12}H_7O_4N$ requires C, 62·9; H, 3·1; N, 6·1%). Many attempts under a variety of conditions to condense this compound with *o*-phenylenediamine failed.

Action of Nitrous Acid on the Diketone (I; R = Me).—An aqueous solution of sodium nitrite in slight excess was slowly added with stirring to one of the diketone (I; R = Me) in dilute hydrochloric acid at 5°. Dilution with water then precipitated a voluminous greenish-yellow solid, which, when cautiously and rapidly recrystallised from ethanol, gave the mustard-coloured *mononitroso*-derivative [possibly (IX)], m. p. 156° (decomp.) (E.T.) (Found: C, 64·0; H, 5·3; N, 11·3. $C_{13}H_{12}O_3N_2$ requires C, 63·9; H, 5·0; N, 11·5%).

Contact with aqueous sodium hydroxide, or boiling in ethanolic solution, converted this compound into a dark brown insoluble solid, m. p. 158° (decomp.) (E.T.) (Found: C, 64·0; H, 4·8; N, 11·35%).

We are greatly indebted to Imperial Chemical Industries Limited, Dyestuffs Division, for the following report on the sensitising action of the dyes (III), (IV; X = CH), and (IV; X = N).

" The compounds were examined in solution and in a chlorobromide photographic emulsion. The properties of the solutions were :

Compound	Solvent	Concn.	Absorption max. (mμ)	Half-width (mμ)	Mol. extinction coefficient
(III)	Methanol	5×10^{-6}	523	60	$12{\cdot}2 \times 10^{4}$
(IV; X = CH)...	2-Ethoxyethanol	$1{\cdot}25 \times 10^{-5}$	409	44	$4{\cdot}4 \times 10^{4}$
(IV; X = N) ...	,,	2×10^{-5}	582	139	$1{\cdot}3 \times 10^{4}$

In the emulsion, (III) showed moderate sensitisation at 460—610 mμ with maximum at 545 mμ, but (IV; X = CH) and (IV; X = N) showed no sensitisation."

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