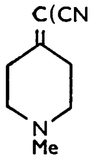
610. *The Condensation Products of Malononitrile and Certain Cyclic Keto-amines.*

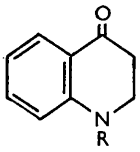
By P. I. Ittyerah and Frederick G. Mann.

Malononitrile condenses with 1-substituted 1 : 2 : 3 : 4-tetrahydro-4-oxoquinolines to give bright red derivatives of the *mero*cyanine type. 1 : 6-Dioxojulolidine and certain substituted derivatives may similarly condense with one or two equivalents of the nitrile to give deep red and purple products respectively. The properties, structures, and photographic sensitisation of these products are briefly discussed.

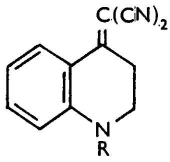
It has been shown by McElvain and Lyle [1] that 1-methyl-4-piperidone condenses with malononitrile to give (1-methyl-4-piperidylidene)malononitrile (I), which was isolated solely as the pale yellow hydrochloride since the base polymerised immediately upon liberation. In contrast to this, we find that 1 : 2 : 3 : 4-tetrahydro-1-methyl-4-oxoquinoline [2] (II; R = Me) condenses with malononitrile to give the intensely red 4-dicyanomethylene-1 : 2 : 3 : 4-tetrahydro-1-methylquinoline (III; R = Me): the 1-phenyl ketone [3]



(I)



(II)



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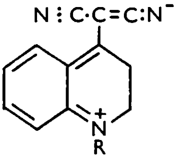
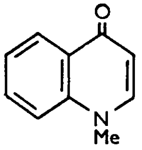


(IIIA)



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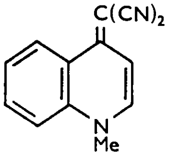

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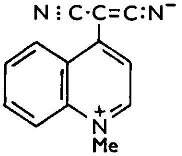

(VA)

(II; R = Ph) similarly gives the deep red product (III; R = Ph). There is little doubt that the colour of these condensation products (III) is due to the fact that they are structurally of the *mero*cyanine type, *i.e.*, that they exist mainly as the polar form (IIIA), in which the *o*-quinonoid ring and resonance involving the two nitrile groups determine the colour. Further, possibly because of this salt-like character, they possess considerable stability, unlike the piperidone derivative (I): for example, an ethanolic solution of the compound (III; R = Me), when treated dropwise with concentrated hydrochloric acid, deposited the unchanged solute; the colour of the ethanolic solution was unaffected by dilution with ethanolic hydrogen chloride, and the solution, when then evaporated at room temperature, again afforded the unchanged solute.

We have failed to condense malononitrile with 1 : 4-dihydro-1-methyl-4-oxoquinoline (echinopsine) (IV); this was not unexpected, as this compound, unlike the tetrahydroquinoline (II; R = Me), shows no normal ketonic properties and does not react with methyl iodide in boiling methanol.[2] Catalytic dehydrogenation of the compound (III; R = Me) furnished however the desired product (V), which has been previously prepared by the action of malononitrile and sodium ethoxide on the methiodide of quinoline and of 4-chloroquinoline.[4] The yellow colour of the compound (V), in marked contrast to the red colour of (III; R = Me), indicates that the benzenoid polar form (VA) makes a greater

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[1] McElvain and Lyle, *J. Amer. Chem. Soc.*, 1950, **72**, 384.

[2] Allison, Braunholtz, and Mann, *J.*, 1954, 403.

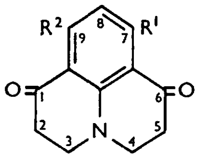
[3] R. C. Cookson and Mann, *J.*, 1949, 67.

[4] Leonard and Foster, *J. Amer. Chem. Soc.*, 1952, **74**, 2110.

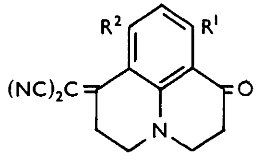
contribution than the *o*-quinonoid form to its structure. *N*-Methylacridone also failed to condense with malononitrile, undoubtedly for analogous structural reasons.

The interaction of malononitrile and various 1 : 6-dioxojulolidines is of particular interest. 1 : 6-Dioxojulolidine [5] (VI; $R^1 = R^2 = H$) reacted with the nitrile (2·4 equivalents) to give a mixture of the deep red 1-dicyanomethylene derivative (VII; $R^1 = R^2 = H$), and the deep purple 1 : 6-bisdicyanomethylene derivative (VIII; $R^1 = R^2 = H$). In these two derivatives the charge separation is undoubtedly similar to that shown in the form (IIIA), and systematically they are therefore also *mero*cyanines. 7-Methyl-1 : 6-dioxojulolidine [6] (VI; $R^1 = Me$, $R^2 = H$) however gave only the red 1-dicyanomethylene derivative (VII; $R^1 = Me$; $R^2 = H$) and 7 : 9-dimethyl-1 : 6-dioxojulolidine (VI; $R^1 = R^2 = Me$) did not react with malononitrile.

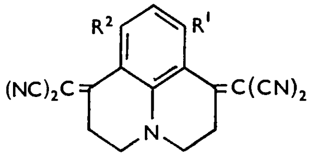
These results can be correlated with those of Braunholtz and Mann,[7] who showed that 1 : 6-dioxojulolidine did not condense with 2-methylbenzothiazole ethiodide even under " forcing " conditions, and 7-methyl-1 : 6-dioxojulolidine reacted with only one keto-group under these conditions to give the cyanine iodide (IX). They argued that activation of the keto-groups in 1 : 6-dioxojulolidine by the 7-methyl group was necessary for the condensation, but that, although this methyl group would activate both keto-groups, it would afford considerable steric hindrance to the 6-keto-group and that the cyanine iodide therefore probably had the structure (IX). Our results with malononitrile show clearly that the 7-methyl group does obstruct the reaction of the 6-keto-group with certain reagents, and that methyl groups in the 7- and the 9-position similarly obstruct both keto-groups. Further evidence for this obstruction is now provided by our failure to condense 7 : 9-dimethyl-1 : 6-dioxojulolidine (VI; $R^1 = R^2 = Me$) with the ethiodide under the " forcing " conditions employed by Braunholtz and Mann.[7] There is very little doubt therefore that the structure (IX) has been correctly assigned to the cyanine iodide (see also p. 3182).



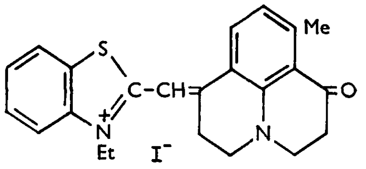
(VI)



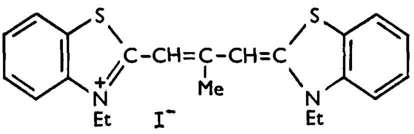
(VII)



(VIII)



(IX)



(X)

This steric hindrance obviously cannot be exerted by substituents in the 8-position. Consequently we find that both 8-chloro- and 8-phenyl-1 : 6-dioxojulolidine [6] give deep red 1-dicyanomethylene derivatives and dark purple 1 : 6-bisdicyanomethylene derivatives.

The light-absorption and sensitising properties of many of the above compounds have been investigated by Imperial Chemical Industries Limited, Dyestuffs Division. In a chloro-bromide emulsion they are all feeble sensitisers. Their most interesting property is that in all cases the sensitising maximum occurs at a lower wavelength than the absorption maximum : the possible significance of this property is discussed more fully in the detailed report (p. 3183).

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[5] Mann and Smith, *J.*, 1951, 1898.
[6] Braunholtz and Mann, *J.*, 1953, 1817.
[7] *Idem, J.*, 1955, 398.

EXPERIMENTAL

The preparation of the compounds (II; R = Me)[2], (II; R = Ph)[3], (IV)[2], 1 : 6-dioxojulolidine [5, 6] and certain of its substituted derivatives [6] has been described in earlier papers.

7 : 9-*Dimethyl*-1 : 6-*dioxojulolidine* (VI; $R^1 = R^2 =$ Me).—(*a*) A mixture of 3 : 5-dimethylaniline (12·1 g.), vinyl cyanide (13·2 g., 2·5 mols.), acetic acid (12 g.), and freshly prepared cuprous chloride (1·2 g.) was boiled under reflux for 4 hr., and the cold brown mobile liquid then added cautiously to aqueous ammonia (100 c.c.; *d* 0·88). The pale brown precipitate, when washed with water and recrystallised from ethanol, afforded NN-*bis*-2-*cyanoethyl*-3 : 5-*dimethylaniline*, colourless crystals, m. p. 130° (Found: C, 74·2; H, 7·3; N, 18·6. $C_{14}H_{17}N_3$ requires C, 74·0; H, 7·5; N, 18·5%) (18 g., 79%). In the absence of cuprous chloride the yield fell to 23%.

Two derivatives were prepared for characterisation. (i) Addition of a slight excess of aqueous sodium nitrite to a solution of this compound in hydrochloric acid at 0° gave a reddish-brown solution, which when basified deposited NN-*bis*-2-*cyanoethyl*-3 : 5-*dimethyl*-4-*nitrosoaniline*, green plates, m. p. 190°, after crystallisation from ethanol (Found: C, 65·6; H, 5·9; N, 22·1. $C_{14}H_{16}ON_4$ requires C, 65·6; H, 6·25; N, 21·9%). (ii) A solution of the dinitrile (3 g.) and potassium hydroxide (4 g.) in water (20 c.c.) and ethanol (10 c.c.) was boiled under reflux for 4 hr. The clear cold solution, when acidified with concentrated hydrochloric acid, slowly deposited the crystalline NN-*bis*-2-*carboxyethyl*-3 : 5-*dimethylaniline hydrochloride*, m. p. 203° (decomp.) (Found: C, 55·5; H, 6·6; N, 4·8. $C_{14}H_{19}O_4N,HCl$ requires C, 55·8; H, 6·6; N, 4·6%).

(*b*) A mixture of the dinitrile (10 g.), powdered anhydrous aluminium chloride (36 g.), *o*-dichlorobenzene (40 c.c.), and concentrated hydrochloric acid (1·5 c.c.) was heated at 150—160° (bath-temp.) for 4 hr., with stirring until the mixture became too viscous. The mixture was treated with ice-water, and the solvent removed with steam. The aqueous residue, on cooling, deposited the crude crystalline 7 : 9-*dimethyl*-1 : 6-*dioxojulolidine* (VI; $R^1 = R^2 =$ Me), which, when washed with water and recrystallised from ethanol, formed yellow needles, m. p. 168—169° (Found: C, 72·9; H, 6·4; N, 6·3. $C_{14}H_{15}O_2N$ requires C, 73·3; H, 6·55; N, 6·1%) (8 g., 80%). The use of chlorobenzene as a solvent in this reaction gave a 30% yield of the diketone.

The following derivatives were prepared. (i) The *bisphenylhydrazone*, prepared in ethanol containing acetic acid, separated in pale yellow crystals, m. p. 230° (decomp.), almost insoluble in all the usual solvents (Found: C, 76·3; H, 6·5; N, 17·25. $C_{26}H_{27}N_5$ requires C, 76·2; H, 6·6; N, 17·1%). (ii) The *bis*-2 : 4-*dinitrophenylhydrazone* formed deep red crystals which when heated decomposed over a wide range (Found: N, 21·3. $C_{26}H_{23}O_8N_9$ requires N, 21·4%). (iii) A solution of the diketone (0·5 g.) in aqueous ethanol (25 c.c.; 66% water) containing hydroxylamine hydrochloride (0·4 g., 2·5 mols.) and anhydrous sodium carbonate (1 g.) was boiled under reflux for 3 hr., and when cooled deposited the *monoxime*, pale yellow needles, m. p. 166° (decomp.) after crystallisation from ethanol (Found: C, 69·3; H, 7·0; N, 11·6. $C_{14}H_{16}O_2N_2$ requires C, 68·85; H, 6·6; N, 11·5%). When the amount of hydrochloride and carbonate was doubled in this experiment, the *dioxime* separated during the boiling, and afforded pale yellow crystals, m. p. 230° after crystallisation from ethanol (Found: N, 16·1. $C_{14}H_{17}O_2N_3$ requires N, 16·2%); a small yield of the more soluble monoxime could still be isolated from the mother-liquor.

Condensation of Ketones with Malononitrile.—In all cases this condensation was effected by boiling a solution of the ketone, the nitrile, anhydrous ammonium acetate, and acetic acid in benzene under reflux in an apparatus by which the water formed in the reaction was automatically separated by azeotropic distillation.[8, 1]

4-*Dicyanomethylene*-1 : 2 : 3 : 4-*tetrahydro*-1-*methylquinoline* (III; R = Me). A mixture of the ketone (II; R = Me) (1·6 g.), the nitrile (1 g., 1·5 mols.), acetic acid (1·5 g.), ammonium acetate (0·5 g.) and benzene (15 c.c.) was boiled in the above apparatus for 1 hr., the colour of the solution changing from yellow to deep red. Benzene and acetic acid were removed by distillation and the red oily residue, which solidified on cooling, when washed with water and recrystallised from methanol furnished the *compound* (III; R = Me), bright intensely red crystals, m. p. 128° (softens at 120°) (Found: C, 74·8; H, 5·4; N, 20·0. $C_{13}H_{11}N_3$ requires C, 74·6; H, 5·3; N, 20·1%) (1 g., 50%).

Use of the ketone (II; R = Ph) with boiling for 3 hr. gave the *compound* (III; R = Ph), deep red crystals, m. p. 115°, after crystallisation from ethanol (Found: C, 79·55; H, 5·0;

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[8] Dean and Stark, *Ind. Eng. Chem.*, 1920, **12**, 486; Cope, Hofmann, Wyckoff, and Hardenbergh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.

N, 15·7. $C_{18}H_{13}N_3$ requires C, 79·7; H, 4·8; N, 15·5%) : yield, 74%. These two compounds give bright red and deep red ethanolic solutions respectively.

4-*Dicyanomethylene*-1 : 4-*dihydro*-1-*methylquinoline* (V).—A mixture of the compound (III; R = Me) (0·7 g.), 10% palladised charcoal (0·1 g.), and ethylene glycol (20 c.c.) was gently boiled under reflux for 1 hr., the initial red colour changing to yellow. The filtered solution deposited the above *compound* (V), golden-yellow crystals (0·5 g.), m. p. 289—290° (softening from 281°) after crystallisation from ethylene glycol, and unaffected by sublimation at 250°/0·1 mm. (Found : C, 75·4; H, 4·55; N, 20·3. Calc. for $C_{13}H_9N_3$: C, 75·4; H, 4·35; N, 20·3%) (lit.,[4] m. p. 291·5—292·5°).

Derivatives of 1 : 6-*Dioxojulolidine*.—(1) A mixture of the diketone (VI; $R^1 = R^2 = H$) (2 g.), the nitrile (1·6 g., 2·4 mols.), ammonium acetate (0·5 g.), acetic acid (1·6 g.), and benzene (15 c.c.), when boiled as previously described for 1 hr. and cooled, deposited a mixture of red and purple crystals. These were collected, and concentration of the filtrate gave a further crop, mainly the red crystals. Fractional crystallisation from acetic acid gave the more soluble 1-*dicyanomethylene*-6-*oxojulolidine* (VII; $R^1 = R^2 = H$) (0·5 g.), deep red crystals, m. p. 178—180° (slight softening at 170°) (Found : C, 72·1; H, 4·3; N, 16·8. $C_{15}H_{11}ON_3$ requires C, 72·3; H, 4·4; N, 16·9%), and the less soluble 1 : 6-*bisdicyanomethylene julolidine* (VIII; $R^1 = R^2 = H$) (1 g.), deep purple crystals, m. p. 205° (softening at 195°) (Found : C, 72·75; H, 3·8; N, 23·35. $C_{18}H_{11}N_5$ requires C, 72·7; H, 3·7; N, 23·6%). Repetition of this experiment with the nitrile (3 mols.), heated for 2 hr., gave almost solely the product (VIII; $R^1 = R^2 = H$) (1·7 g.). These two compounds give red and purple solutions respectively in ethanol.

(2) Repetition of experiment (1), using 7-methyl-1 : 6-dioxojulolidine (VI; R^1 = Me, R^2 = H), gave on concentration a red oil which solidified when stirred with water, and after repeated crystallisation from methanol gave 1-*dicyanomethylene*-7-*methyl*-6-*oxojulolidine* (VII; R^1 = Me, R^2 = H), deep red crystals, m. p. 180—182° (softens at 165°) (Found : C, 72·7; H, 5·1; N, 16·1. $C_{16}H_{13}ON_3$ requires C, 73·0; H, 4·9; N, 16·0%).

(3) Repetition of experiment (1), with 8-chloro-1 : 6-dioxojulolidine and the nitrile (3 mols.), gave a mixture which, similarly recrystallised from acetic acid, furnished 8-*chloro*-1-*dicyanomethylene*-6-*oxojulolidine* (as VII), deep red crystals, m. p. 198° (Found : C, 63·3; H, 3·5; N, 15·0. $C_{15}H_{10}ON_3Cl$ requires C, 63·5; H, 3·5; N, 14·8%), and 8-*chloro*-1 : 6-*bisdicyanomethylenejulolidine* (as VIII), brownish-purple crystals, m. p. 210—211° (Found : C, 65·2; H, 2·95; N, 21·1. $C_{18}H_{10}N_5Cl$ requires C, 65·15; H, 3·0; N, 21·3%). When the period of heating was extended from 1 to 4 hr., the latter compound formed the major product.

(4) The use of 1 : 6-dioxo-8-phenyljulolidine and the nitrile (3·2 mols.) furnished a mixture which on repeated crystallisation from acetic acid gave 1-*dicyanomethylene*-6-*oxo*-8-*phenyljulolidine* (as VII), deep red crystals, m. p. 205° (Found : C, 77·9; H, 4·8. $C_{21}H_{15}ON_3$ requires C, 77·5; H, 4·6%. Low values for nitrogen were always obtained), and 1 : 6-*bisdicyanomethylene*-8-*phenyljulolidine* (as VIII), deep purple crystals, m. p. 233° (Found : C, 77·4; H, 4·9; N, 18·7. $C_{24}H_{15}N_5$ requires C, 77·2; H, 4·0; N, 18·8%). The analysis of this compound gave low values for carbon unless it was burnt at an unusually high temperature, which almost certainly caused the high hydrogen value.

N-Methylacridone and 7 : 9-dimethyl-1 : 6-dioxojulolidine gave no condensation products under the above conditions, even with considerably extended periods of heating.

Note on the Cyanine Iodide (IX).—Braunholtz and Mann obtained this monohydrated salt, m. p. 288° (decomp.), by interaction of 7-methyl-1 : 6-dioxojulolidine (VI; R^1 = Me, R^2 = H) and 2-methylbenzothiazole ethiodide in boiling pyridine. Brooker and White[9] have shown however that the ethiodide alone in boiling pyridine gives rise to the cyanine iodide (X), m. p. 286—287° (decomp.), the crystalline appearance, m. p. and carbon, hydrogen, and nitrogen contents of which all approximate closely to those of the cyanine iodide (IX). The identity of Braunholtz and Mann's compound has now been placed beyond doubt by further analysis [Found : S, 6·1. Calc. for the monohydrated iodide (IX): S, 6·15. Calc. for the iodide (X): S, 12·7%], and by the fact that a mixture of the iodide (IX) and an authentic sample of (X) had m. p. 267—268° (decomp.).

Photographic Properties.—We are greatly indebted to Imperial Chemical Industries Limited, Dyestuffs Division, for the following report on certain of the above compounds.

" The tabulated values were obtained for the absorption and the sensitising maxima. The absorption maxima were determined in 2-ethoxyethanol solutions (1 in 100,000, w/v), and the

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[9] Brooker and White, *J. Amer. Chem. Soc.*, 1935, **57**, 547.

sensitisation maxima in chloro-bromide emulsions. All these compounds proved to be feeble sensitisers, and gave fog at higher concentration.

" The most noteworthy feature of these results is the uniformly negative shift which occurs from the sensitising maximum to the absorption maximum. Similar negative shifts have been observed in certain sensitisers capable of second-order (or " J-band ") sensitisation,[10] and are usually attributed to a dimeric (or more highly associated) state of the dyestuff : with increasing concentrations of sensitiser in the emulsion, one observes first-order sensitisation (small positive shift), then dimeric sensitisation (small negative shift), and finally second-order sensitisation (large positive shift). The sensitising maximum in such cases has also been shown to coincide with the absorption maximum of the dyed silver halide. The compounds listed in the Table have compact molecules which should be capable of aggregation, particularly as they cannot show the geometric isomerism of which many cyanine dyes are theoretically capable. It is possible that their ' dimeric ' state is readily achieved on silver halide, but that concentrations sufficiently high to give second-order sensitisation have not been reached, because of the rapidly increasing and intolerable fog levels."

Compound	Absorption max. λ (mμ)	Absorption max. $10^{-4}\varepsilon$	Sensitisation max. (mμ)	Sensitisation extends to (mμ)
(III; R = Me)	472	1·03	445	490
(III; R = Ph)	461	0·98	445	480
(VII; R^1 = Me, R^2 = H)	469	1·2	465	525
(VIII; R^1 = R^2 = H)	512	0·99	470	510
(VIII; R^1 = R^2 = H, 8-Cl)	523	1·5	470	520
(VIII; R^1 = R^2 = H, 8-Ph)	529	0·7	470	520

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, March 24th*, 1956.]

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[10] " Fundamental Mechanisms of Photographic Sensitivity," Bristol Symposium, Butterworth, London, 1951, pp. 168—172.