S 25. *Cyanine Dyes from 2 : 2'-Dimethyl-4 : 4'-dipyridyl.*

By A. B. Lal and V. Petrow.

2 : 2'-*Dimethyl*-4 : 4'-*dipyridyl alkiodides* (I*a* and I*b*) have been converted into the p-*dimethylamino-anils* (II*a* and II*b*), the p-*dimethylaminostyryl* derivatives (III*a* and III*b*), the *methincyanine* (IV), and into the symmetrical and unsymmetrical *trimethincyanines* (V, VII—XI). Dyes (XII*d* and XII*e*) have also been obtained from the diquaternary *salts* of the base.

The mechanism of formation of cyanine dyes is discussed.

The conversion of pyridine derivatives into compounds related to the cyanine dyes was first achieved by Kaufmann and Vallette (*Ber.*, 1912, **45**, 1736), who prepared the 2-*p*-dimethylamino-anil derivatives from 2-methylpyridine methiodide. This work was followed by the preparation of 2-*p*-dimethylaminostyrylpyridine methiodide by Mills and Pope (*J.*, 1922, **121**, 946), and of the symmetrical trimethincyanines from 2- and 4-picoline alkiodides by Rosenhauer and Barlet (*Ber.*, 1929, **62**, 2724). The corresponding methincyanines were prepared some years later by Hamer and Kelly (*J.*, 1931, 777; see also Brooker *et al.*, *J. Amer. Chem. Soc.*, 1935, **57**, 2488). The preparation of cyanine dyes from 2 : 2'-dimethyl-4 : 4'-dipyridyl, however, has not hitherto been recorded and forms the subject of the present communication.

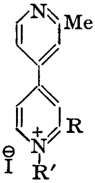
2 : 2'-Dimethyl-4 : 4'-dipyridyl reacted with methyl iodide with explosive violence, giving large amounts of tar together with some of the *dimethiodide* (XII*a*), best prepared by reaction of the components in alcoholic solution under reflux. The *monomethiodide* (I*a*) was obtained when the base was heated with methyl iodide in benzene solution under reflux, small quantities of dimethiodide also formed being easily removed by virtue of its very low solubility in alcohol. The *mono-* (I*b*) and *di-ethiodides* (XII*b*) were obtained similarly.

The 2-p-*dimethylaminoanils* (II*a* and II*b*) from 2-formyl-2'-methyl-4 : 4'-dipyridyl 1-alkiodides, and the 2-p-*dimethylaminostyryl*-2'-*methyl*-4 : 4'-*dipyridyl* 1-*alkiodides* (III*a* and III*b*) were prepared from (I*a* and I*b*) by standard methods. The methiodide (III*a*) was converted into the corresponding *methochloride* for examination as an antibacterial and trypanocidal agent, but this was found to lack outstanding activity. The *methincyanine* (IV) was obtained in very low yield by condensation of 2 : 2'-dimethyl-4 : 4'-dipyridyl 1-methiodide (I*a*) with 2-iodoquinoline methiodide in the presence of triethylamine. The reaction failed to occur with potassium hydroxide as the condensing agent.

Symmetrical trimethincyanines could not be obtained by heating (I*a* and I*b*) with ethyl orthoformate in pyridine and/or acetic anhydride solution under reflux. *Bis*-[2-(1 : 2'-*dimethyl*-

[In formulæ (II)—(XI), R and R′ refer to substituents in (I) and R″ to substituents in additional systems.]

(I.)

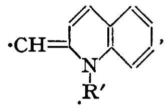


(I*a*; R = R′ = Me.) (I*b*; R = Me, R′ = Et.)

[II; R = CH:N·C_6H_4·NMe_2; (*a*) R′ = Me. (*b*) R′ = Et.]

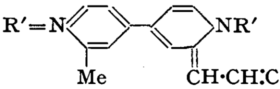
[III; R = CH:CH·C_6H_4·NMe_2; (*a*) R′ = Me. (*b*) R′ = Et.]

(IV.) R =



, R′ = Me

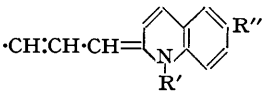
(V.) R′=



(*a*; R′ = Me.) (*b*; R′ = Et.)

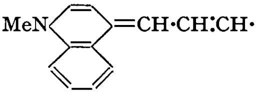
[VI; R = •CH:CH•NHPh; (*a*) R′ = Me. (*b*) R′ = Et.]

(VII.) R =



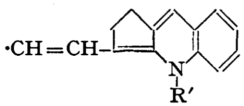
(*a*; R′ = Me, R″ = H.) (*b*; R′ = Et, R″ = H.) (*c*; R′ = R″ = Me.)

(VIII.) R=



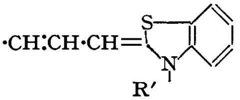
, R′ = Me

(IX.) R=



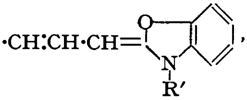
, R′ = Me

(X.) R=



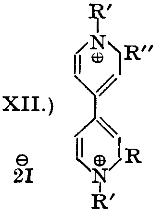
(*a*; R′ = Me.) (*b*; R′ = Et.)

(XI.) R=



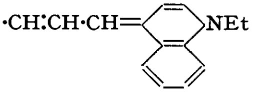
, R′ = Me

(XII.)

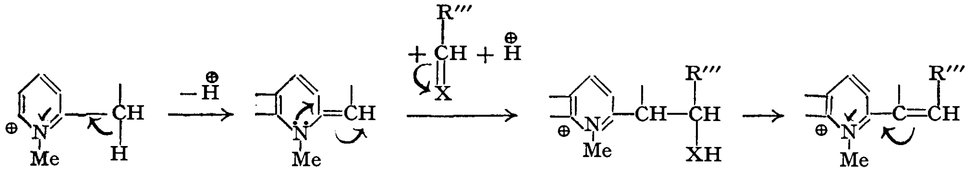


(*a*; R = R′ = R″ = Me.) (*b*; R = R″ = Me, R′ = Et.)
(*c*; R = R″ = •CH:CH•NHPh, R′ = Et.)
(*d*; R = •CH:CH•$C_6H_4NMe_2$, R′ = R″ = Me.)

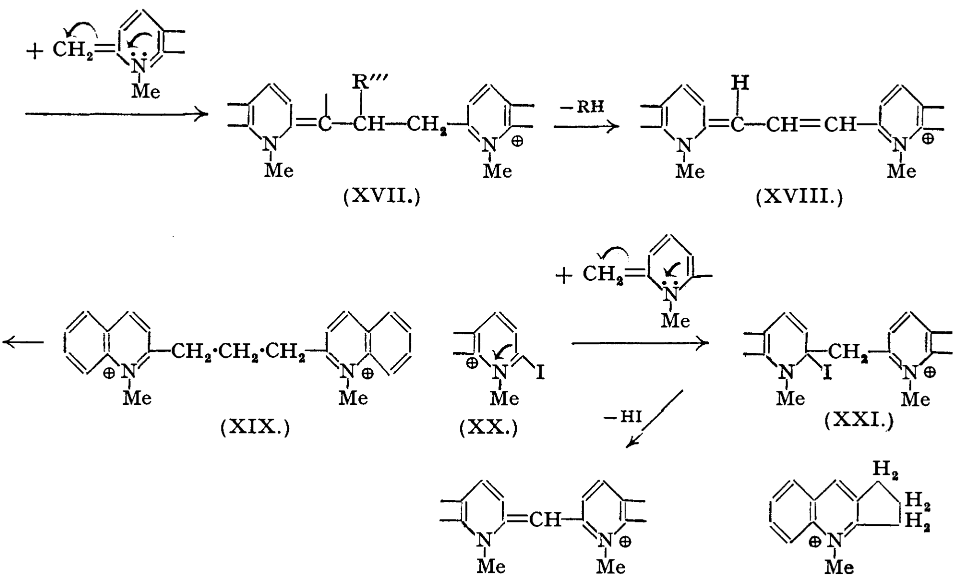
(*e*; R = R″ =



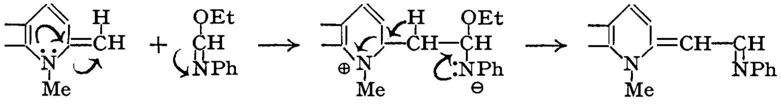
R′ = Et.)



(XIII.) (XIV.) (XV.) (XVI.)



(XVII.) (XVIII.) (XIX.) (XX.) (XXI.) (XXII.) (XXIII.)



(XXIV.) (XXV.) (XXVI.)

4 : 4′-*dipyridyl*)]*trimethincyanine iodide* (V*a*) was ultimately obtained by rapidly heating a warm alcoholic solution of (I*a*) with chloroform and potassium hydroxide under reflux. The corresponding *ethiodide* (V*b*) was prepared in the same way.

Condensation of (I*a*) with diphenylformamidine at 150° (cf. Piggott and Rodd, B.P. 344,409) gave 2′-*methyl*-2-β-*anilinovinyl*-4 : 4′-*dipyridyl* 1-*methiodide* (VI*a*). The *ethiodide* (VI*b*) and the 2 : 2′-*di*-(β-*anilinovinyl*)-4 : 4′-*dipyridyl diethiodide* (XII*c*) were obtained in the same way. These compounds proved to be necessary intermediates for the synthesis of unsymmetrical trimethincyanines as 2-anilinovinylquinoline methiodide failed to react with (I*a*) under the usual conditions. [2-(1-*Methylquinoline*)][2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine iodide* (VII*a*) was therefore prepared by condensation of (VI*a*) with quinaldine methiodide in acetic anhydride–pyridine solution in the presence of potassium acetate. The *trimethincyanines* (VII*c*, VIII, IX, VII*b*) were likewise prepared from (VI*a*) and 2 : 6-dimethylquinoline methiodide, lepidine methiodide, dihydro-β-quinindene methiodide, and (VI*b*), and quinaldine ethiodide. Condensation of (VI*a*) with 2-methylbenzthiazole methiodide, the foregoing experimental conditions being used, could not be effected, and [2-(3-*methylbenzthiazole*)][2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine iodide* (X*a*) was finally obtained by heating these components in pyridine solution. The corresponding *ethiodide* (X*b*) was obtained in the same way. 2-Methylbenzoxazole methiodide failed to react with (VI*a*) under a variety of experimental conditions, [2-(3-*methylbenzoxazole*)][2-(1 : 2-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine iodide* (XI) only being formed when 2-β-acetanilidovinylbenzoxazole methiodide was fused with (I*a*) and potassium acetate. Experiments to prepare the corresponding ethiodide were not successful.

Attempts to condense 2 : 2′-dimethyl-4 : 4′-dipyridyl dimethiodide (XII*a*) with 1 mol. of *p*-dimethylaminobenzaldehyde were not successful owing to the very low solubility of the diquaternary salt in alcohol and in other polar solvents. 2-p-*Dimethylaminostyryl*-2′-*methyl*-4 : 4′-*dipyridyl dimethiodide* (XII*d*) was therefore prepared by heating (III*a*) with methyl iodide. In contrast to the facile reaction between (III*a*) and methyl iodide or methyl sulphate, (III*b*) failed to react with ethyl iodide under a variety of experimental conditions.

The sensitising properties and absorption spectra of the above dyes were kindly determined by Messrs. Kodak Ltd. through the courtesy of Dr. F. M. Hamer. The trimethincyanines were poor sensitisers with the exception of (X*b*). The anils (II*a* and II*b*) behaved normally, showing desensitising properties usually associated with compounds of their type. The styryl dyes (III*a*), (III*b*), and (XII*d*), however, showed strong desensitising properties, a behaviour no doubt associated with their dipyridyl structure (cf. Mills and Pope, *loc. cit.*).

Mills and Raper (*J.*, 1925, **127**, 2466) interpreted the formation of *p*-dimethylaminostyrylquinoline methiodide from quinaldine methiodide and *p*-dimethylaminobenzaldehyde in the presence of piperidine as taking place by initial formation of the methylene base, followed by reaction of the latter with the aldehydic component to give an intermediate having the chain =C=CH–. This view needs revision following recent results (Petrow, *J.*, 1945, 18; Lal and Petrow, *J.*, 1948, 1895) that dihydro-β-quinindene methiodide (XXIII) also takes part in cyanine-dye formation in the normal manner, although in this case formation of the " allene " chain is precluded on structural grounds. The mode of formation of trimethincyanines from quinaldine methiodide by the formaldehyde method has been studied by Hamer (*J.*, 1923, **123**, 246), who succeeded in isolating (XIX) under mild conditions of reaction, the latter passing into the trimethincyanine (XVIII) on treatment with alkali (and quinoline methiodide, the function of which in increasing the yield is unknown).

Quinaldine methiodide [partial formula (XIII)] may be converted into a trimethincyanine by means of diphenylformamidine (Piggott and Rodd, B.P. 344,409/1929), ethyl*iso*formanilide (Knott, *J.*, 1946, 120), ethyl orthoformate (König, *Ber.*, 1922, **55**, 3293; Hamer, *J.*, 1925, **127**, 211), or formaldehyde (Meister, Lucius, and Brüning, G.P. 172,118/1905). There seems little doubt that reaction is preceded by removal of a proton from (XIII) by the basic catalyst present (see below) with formation of the " methylene base " (XIV). Its condensation with diphenylformamidine ($R''' = NHPh$, $X = {:}NPh$) then gives (XV), which passes by loss of aniline into 2-β-anilinovinylquinoline methiodide (XVI; $R''' = NHPh$). Ethyl*iso*formanilide ($R''' = OEt$; $X = {:}NPh$) likewise gives an intermediate of type (XV), which by loss of alcohol again gives 2-β-anilinovinylquinoline methiodide (XVI; $R''' = NHPh$). Ethyl orthoformate, on the other hand, first undergoes association with the proton made available by the change (XIII) → (XIV) to give the complex $[(EtO)_2CH{:}\underset{\textstyle\ddot{}\,H}{\ddot{O}}{:}Et]^{\oplus}$. The latter passes into the cation $(EtO)_2\overset{\oplus}{C}H$, and hence by reaction with (XIV) and loss of ethyl alcohol into 2-β-ethoxyvinylquinoline methiodide (XVI; $R''' = OEt$). Higher vinylene homologues of the latter are mentioned by Kodak Ltd. in B.P. 556,266/1940. Formaldehyde ($R''' = H$; $X = O$) likewise gives (XV; $R''' = H$, $X = O$) and hence 2-vinylquinoline methiodide (XVI; $R''' = H$) by loss of water, although in this case the possibility that (XIX) is formed as an intermediate cannot be ruled out (Ogata, *Proc. Imp. Acad. Tokyo*, 1927, **3**, 334). Condensation of (XVI; $R''' = NHPh$, OEt, or H) with a further molecule of (XIII), reacting as the " methylene base ", then occurs by an essentially similar series of changes giving (XVII) and hence the trimethincyanine (XVIII).

The formation of methincyanine from 2-iodoquinoline methiodide and quinoline methiodide in the presence of basic catalysts can be explained along similar lines to those indicated in (XX) → (XXII).

The conversion of methylene bases into dianilo-derivatives (Hamer, Rathbone, and Winton, *J.*, 1947, 1434) by reaction with ethyl*iso*formanilide follows the same pattern. Reaction of the methylene base (XXIV) with one molecule of ethyl*iso*formanilide gives (XXV) which, in the absence of a proton only available when the quaternary salt is employed [see reaction sequence (XIII) → (XVI)], loses ethyl alcohol, giving (XXVI) which can then react with a further molecule of the anilide. Hamer's failure (private communication) to isolate dianilo-derivatives from quaternary salts thus appears to receive a satisfactory explanation.

Catalysts such as piperidine, potassium hydroxide, or potassium acetate in acetic anhydride, in general necessary for cyanine formation, thus function by removing incipiently ionised hydrogen from (XIII), etc., and the reaction mechanism falls into line with current views on the Claisen, Knoevenagel, and Perkin reactions. As styryl formation, for example, often requires only acetic anhydride as a condensing agent, it appears that this compound, too, can function as a " base ", a view already expressed by Luder and Zuffanti (" Electronic Theory of Acids and Bases ", Wiley and Sons, Inc., 1946, p. 93).

EXPERIMENTAL.

(M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford. Absorption maxima were measured in methyl-alcoholic solution.)

2 : *2'-Dimethyl-*4 : *4'-dipyridyl monomethiodide* (I*a*), light yellow, feathery needles (ethyl alcohol), m. p. >300° (Found : N, 8·8; I, 38·9. $C_{13}H_{15}N_2I$ requires N, 8·6; I, 38·9%), was prepared by heating

2 : 2′-dimethyl-4 : 4′-dipyridyl (2 g.) and methyl iodide (1·5 g.) in benzene (30 ml.) under reflux for 6 hours. The *monoethiodide* (I*b*), yellow prisms from alcohol–ethyl acetate, m. p. 162—163° (Found : N, 8·3; I, 37·5. $C_{14}H_{17}N_2I$ requires N, 8·2; I, 37·4%), was obtained (66%) similarly. The *dimethiodide* (XII*a*), lustrous orange-yellow plates from aqueous alcohol, m. p. >318° (Found : N, 5·6; I, 53·4. $C_{14}H_{18}N_2I_2$ requires N, 5·9; I, 54·2%), was prepared by heating 2 : 2′-dimethyl-4 : 4′-dipyridyl (1·8 g.) and methyl iodide (2·8 g.) in ethyl alcohol (10 ml.) under reflux for 4 hours; and a similar reaction afforded the *diethiodide* (XII*b*), orange prisms from spirit, m. p. 271—273° (decomp.) (Found : N, 5·3; I, 50·9. $C_{16}H_{22}N_2I_2$ requires N, 5·6; I, 51·2%).

2-p-*Dimethylaminoanil from* 2-*Formyl*-2′-*methyl*-4 : 4′-*dipyridyl* 1-*Methiodide* (II*a*).—*p*-Nitrosodimethylaniline (400 mg.) in warm alcohol (15 ml.) was treated with (I*a*) (800 mg.) in warm alcohol (25 ml.), followed by piperidine (1 ml.). The mixture was quickly concentrated and allowed to stand overnight; the *dye* was deposited as a crystalline solid (50%), which was collected, washed with spirit, and crystallised from alcohol, forming bronze plates, m. p. 222—223° (Found : N, 11·9; I, 27·5. $C_{21}H_{23}N_4I$ requires N, 12·2; I, 27·7%). The absorption maximum was at 5260 A. The dye desensitised badly both a bromide and a chloride plate.

2-p-*Dimethylaminoanil from* 2-*Formyl*-2′-*methyl*-4 : 4′-*dipyridyl* 1-*Ethiodide* (II*b*).—*p*-Nitrosodimethylaniline (450 mg.) in warm alcohol (5 ml.) was treated with (I*b*) (800 mg.) in alcohol (10 ml.), followed by piperidine (0·5 ml.). The mixture was concentrated, cooled, and ether added; the *dye* which separated (65%) crystallised from aqueous alcohol, forming dark green prisms, m. p. 208—209° (Found : N, 12·1; I, 26·5. $C_{22}H_{25}N_4I$ requires N, 11·9; 26·9%). Absorption maximum at 5250 A. This behaved photographically as (II*a*).

2-p-*Dimethylaminostyryl*-2′-*methyl*-4 : 4′-*dipyridyl* 1-*methiodide* (III*a*), lustrous orange-red platelets from spirit, m. p. 236—237° (decomp.) (Found : N, 9·3; I, 28·0. $C_{22}H_{24}N_3I$ requires N, 9·2; I, 27·8%), was prepared (55%) by heating a mixture of (I*a*) (300 mg.) and *p*-dimethylaminobenzaldehyde (150 mg.) in alcohol (12 ml.) containing piperidine (0·5 ml.) for 2 hours under reflux. Absorption maximum at 4950 A. The dye desensitised a gelatinobromide photographic emulsion.

2-p-*Dimethylaminostyryl*-2′-*methyl*-4 : 4′-*dipyridyl* 1-*methochloride*, deep brown microcrystals from ether–alcohol, m. p. 228—229° (Found : N, 10·4; Cl, 8·6, 8·7. $C_{22}H_{24}N_3Cl, C_2H_5{\cdot}OH$ requires N, 10·2; Cl, 8·6%), was obtained by heating (III*a*) (1·5 g.) and freshly precipitated silver chloride (1 g.) in alcohol (50 ml.) under reflux for 2 hours.

2-p-*Dimethylaminostyryl*-2′-*methyl*-4 : 4′-*dipyridyl* 1-*ethiodide* (III*b*), dark red prisms with a steel-blue reflex from spirit, m. p. 256—257° (Found : N, 8·6; I, 26·7. $C_{23}H_{26}N_3I$ requires N, 8·9; I, 27·0%), was obtained (55%) as described for (III*a*). Absorption maximum at 4970 A. Photographic behaviour was as for (III*a*).

[2-(1-*Methylquinoline*] [2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*methincyanine iodide* (IV), separating from alcohol in dark red rosettes having a bronze lustre, m. p. 233—234° (Found : N, 8·6; I, 27·1. $C_{23}H_{22}N_3I$ requires N, 9·0; I, 27·2%), was obtained (5—7%) by heating (I*a*) and 2-iodoquinoline under reflux in alcohol in the presence of triethylamine for 50 minutes, and then pouring the red solution into water. Absorption maximum at 5030 A. Some desensitisation of both chloride and bromide emulsion was produced.

Bis-[2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine Iodide* (V*a*).—Chloroform (2 g.) was added to (I*a*) (1·6 g.) in warm alcohol (40 ml.), followed by potassium hydroxide (3 g.) in alcohol (20 ml.), and the mixture vigorously heated under reflux for 5—6 minutes. The dark green solution was poured into cold water (300 ml.) containing potassium iodide (2 g.). After standing overnight, the *dye* was collected and crystallised from alcohol, giving dark brown prisms with a bronze reflex (40%), m. p. 260—261° (decomp.) (Found : N, 10·2; I, 23·6. $C_{27}H_{27}N_4I$ requires N, 10·5; I, 23·8%). Absorption maximum at 6060 A. The dye sensitised a gelatinobromide emulsion very weakly from 5600 to 7200 A., depressed blue speed, and produced slight fog.

Bis-[2-(2′-*methyl*-1-*ethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine Iodide* (V*b*).—Chloroform (600 mg.) was added to (I*b*) (1·7 g.) in warm alcohol (30 ml.), followed by potassium hydroxide (1·2 g.) in alcohol (20 ml.), and the whole vigorously heated under reflux for 5 minutes. The mixture was cooled, filtered, and ether added, whereupon the *dye* (16%) separated out. It was crystallised from ethyl acetate–alcohol and obtained in brilliant coppery plates, m. p. 211—212° (Found : N, 9·6; I, 22·1. $C_{29}H_{31}N_4I$ requires N, 10·0; I, 22·6%). Absorption maximum at 6110 A. The dye desensitised a bromide emulsion slightly and fogged.

2-*Anilinovinyl*-2′-*methyl*-4 : 4′-*dipyridyl* 1-*methiodide* (VI*a*), red needles with a blue reflex from spirit, m. p. 235—236° (Found : N, 9·4; I, 29·1. $C_{20}H_{20}N_3I$ requires N, 9·8; I, 29·6%), was obtained (60%) by fusing (I*a*) and diphenylformamidine at 150—155° for 45 minutes.

2-*Anilinovinyl*-2′-*methyl*-4 : 4′-*dipyridyl* 1-*ethiodide* (VI*b*), orange prisms from ethyl acetate–alcohol, m. p. 224—225° (Found : N, 9·3; I, 29·2. $C_{21}H_{22}N_3I$ requires N, 9·5; I, 28·9%), was prepared in the same way as (VI*a*).

2 : 2′-*Dianilinovinyl*-4 : 4′-*dipyridyl diethiodide* (XII*c*), deep brown microcrystals from spirit, m. p. 304° (decomp.) (Found : I, 33·9, 34·1. $C_{30}H_{32}N_4I_2,C_2H_5OH$ requires I, 33·9%), was prepared as for the monoethiodide analogue (VI*b*).

[2-(1-*Methylquinoline*)][2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine Iodide* (VII*a*).—A mixture of quinaldine methiodide (700 mg.), (VI*a*) (1·1 g.), and potassium acetate was added to acetic anhydride–pyridine (20 ml. of 4 : 1), and the whole heated under reflux for 15 minutes. The blue solution was poured into water (300 ml.), and the *dye* (64%) separated. It was collected, washed with water, and crystallised from alcohol, separating in dark green microcrystals, m. p. 253—254° (Found : N, 7·9; I, 23·2. $C_{25}H_{24}N_3I$ requires N, 7·8; I, 23·6%). Absorption maximum at 6000 A. The dye produced very weak sensitisation.

[2-(1-*Ethylquinoline*)][2-(2′-*methyl*-1-*ethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine iodide* (VII*b*), lustrous coppery plates from alcohol, m. p. 252—253° (Found : N, 8·3; I, 24·7. $C_{27}H_{28}N_3I$ requires N, 8·1; I, 24·4%), was prepared (75%) as for (VII*a*). Absorption maximum at 6030 A. A gelatinobromide emulsion showed very weak sensitisation extending to 7100 A., accompanied by slight fogging action.

[2-(1 : 6-*Dimethylquinoline*)][2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine iodide* (VII*c*), dark blue microcrystals from alcohol, m. p. 278—279° (decomp.) (Found : N, 8·1; I, 24·6. $C_{26}H_{26}N_3I$ requires N, 8·3; I, 25·1%), was obtained (50%) in the same way as (VII*a*). Absorption maximum at 6060 A. The dye sensitised a chloride emulsion weakly from 5500 to 6900 A. with the maximum at 6350 A. It decreased the blue sensitivity.

[4-(1-*Methylquinoline*)][2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine iodide* (VIII), dark green microcrystals from alcohol, m. p. 239—240° (Found : N, 8·7; I, 25·8. $C_{25}H_{24}N_3I$ requires N, 8·5; I, 25·6%), was prepared (25%) as for (VII*a*). Absorption maximum at 7010 A. When tested in a bromide emulsion, the dye caused weak sensitisation from 6700 to 7900 A., with a sharp peak at 7500 A. It decreased the blue speed and fogged slightly.

[3-(4-*Methyl*-1 : 2-*dihydro*-β-*quinindene*)][2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*dimethincyanine iodide* (IX), dark microcrystals from alcohol, m. p. 272—273° (decomp.) (Found : N, 7·8; I, 24·1. $C_{27}H_{26}N_3I$ requires N, 8·1; I, 24·3%), was obtained (31%) in a similar manner to (VII*a*).

[2-(3-*Methylbenzthiazole*)][2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine Iodide* (X*a*).—2-Methylbenzthiazole methiodide (350 mg.) and (VI*a*) (500 mg.) were intimately mixed and heated under reflux in pyridine (3 ml.) solution for 30 minutes at 140—145°. The *dye* separated on cooling as a crystalline solid (50%). It was purified from alcohol, forming red platelets with a bronze lustre, m. p. 268—270° (Found : N, 8·2; I, 25·4. $C_{23}H_{22}N_3SI$ requires N, 8·4; I, 25·5%). Absorption maximum at 5800 A. On being tested in a bromide emulsion the dye showed very weak sensitisation extending to 6100 A. It decreased the blue sensitivity.

[2-(3-*Ethylbenzthiazole*)][2-(2′-*methyl*-1-*ethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine iodide* (X*b*), brilliant steel-blue needles from alcohol, m. p. 263—264° (decomp.) (Found : N, 7·5; I, 23·6. $C_{25}H_{26}N_3SI$ requires N, 8·0; I, 24·1%), was obtained (25%) in the same way as (X*a*). Absorption maximum at 5550 A. When tested in a bromide emulsion, the dye gave good sensitisation extending to 6500 A., and slight stain.

[2-(3-*Methylbenzoxazole*)][2-(1 : 2′-*dimethyl*-4 : 4′-*dipyridyl*)]*trimethincyanine Iodide* (XI).—2-β-Acetanilidovinylbenzoxazole methiodide (2·1 g.), (I*a*) (1·6 g.), and potassium acetate (700 mg.) were intimately mixed and heated in a paraffin-bath for 4—5 minutes at 160—165°. The mixture fused and turned dark red. On cooling, it solidified and was crystallised from spirit, giving lustrous green microcrystals of the *dye* (33%), m. p. 262—263° (decomp.) (Found : N, 8·2; I, 25·9. $C_{23}H_{22}ON_3I$ requires N, 8·7; I, 26·3%). Absorption maximum at 5250 A. The dye desensitised slightly.

2-p-*Dimethylaminostyryl*-2′-*methyl*-4 : 4′-*dipyridyl Dimethiodide* (XII*d*).—Methyl iodide (200 mg.) and (III*a*) (500 mg.) were heated in a sealed tube at 100° for 6 hours. The product was extracted repeatedly with warm spirit and then crystallised from a large volume of spirit, from which it separated in dark red platelets, m. p. 270—272° (decomp.) (Found : N, 6·3; I, 38·5. $C_{23}H_{27}N_3I_2,1\frac{1}{2}C_2H_5\cdot OH$ requires N, 6·3; I, 38·0%). Absorption maximum at 5320 A. It desensitised a bromide emulsion completely.

2-p-*Dimethylaminostyryl*-2′-*methyl*-4 : 4′-*dipyridyl* 1-*methiodide* 1′-*methosulphate*, dark red plates from spirit, m. p. 235—236° (decomp.) (Found : S, 6·2. $C_{24}H_{30}O_4N_3SI$ requires S, 5·5%), was obtained (60%) by heating (III*a*) (600 mg.) with methyl sulphate (200 mg.) in nitrobenzene (15 ml.) at 170° for 5—6 minutes. Absorption maximum at 5310 A. The dye desensitised a bromide emulsion so strongly that the wedge spectrogram showed nothing.

2 : 2′-*Bis*-[4-*trimethin*-(1-*ethylquinoline*)]-4 : 4′-*dipyridyl Diethiodide* (XII*e*).—Lepidine ethiodide (1·2 g.), (XII*c*) (1·7 g.), and potassium acetate (1 g.) were mixed thoroughly and added to a hot mixture of acetic anhydride–pyridine (24 ml. of 5 : 1) and heated under reflux for 10 minutes. When the deep blue solution was poured into water (400 ml.), the *dye* separated (45%) as a black powder. It was collected, washed, and crystallised from methyl alcohol, giving bronze platelets, m. p. >310° (Found : N, 5·8, 6·3; I, 26·6, 27·0. $C_{42}H_{44}N_4I_2,3MeOH$ requires N, 6·0; I, 26·6%). Absorption maximum at 7010 A. The dye desensitised a bromide emulsion slightly.

The authors thank the Government of Bihar, India, for a State Scholarship awarded to one of them (A. B. L.). Their best thanks are also due to Dr. F. M. Hamer, D.Sc., Sc.D., F.R.I.C., and Messrs. Kodak Ltd. for assistance with the photographic aspects of the work.

QUEEN MARY COLLEGE (UNIVERSITY OF LONDON), E.1. [*Received, July* 17*th*, 1948.]