

419. *Cyanine Dyes containing an isoQuinoline Nucleus.*

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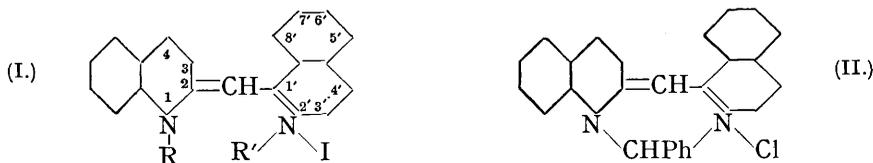
HOOGWERFF and VAN DORP wrote that the only essential difference between quinoline and isoquinoline is that, under the influence of potassium hydroxide, quaternary iodides of the former give cyanine dyes with quaternary iodides of lepidine and of quinaldine, whereas those of the latter do not (*Rec. trav. chim.*, 1886, **5**, 305). In comparatively recent years, additional types of cyanines containing a quinoline nucleus have been discovered, but the corresponding cyanines containing an isoquinoline nucleus are here described for the first time. The successful method is different from that attempted by Hoogwerff and van Dorp, and consists in an extension of the ψ -cyanine condensation.

The first ψ -cyanine was isolated and identified by Fischer and Scheibe, who condensed 2-iodoquinoline methiodide with quinaldine methiodide (*J. pr. Chem.*, 1919, **100**, 86). It was shown by one of us that the condensation is a general one between 2-iodoquinoline alkiodide and a heterocyclic ammonium salt containing a reactive methyl group (Hamer, J., 1928, 206; cf. *idem*, J., 1929, 2598; 1930, 995), and subsequently the method was extended, in that the 2-iodoquinoline alkiodide was replaced by an alkiodide of 2-iodopyridine or of 2-iodo- β -naphthaquinoline (Hamer and Kelly, J., 1931, 777).

In the present work, new intermediates, 1-iodoisoquinoline alkiodides, are condensed with heterocyclic ammonium salts containing a reactive methyl group, for synthesising cyanine dyes of various new types.

The method of preparation of 1-iodoisoquinoline alkiodides is analogous to that used for the 2-iodoquinoline compounds. Thus by that modification of Decker's original method (*J. pr. Chem.*, 1893, **47**, 28) which proved suitable in the quinoline series (Hamer and Kelly, *loc. cit.*), a quaternary salt of isoquinoline was converted into 2-alkyl-1-isoquinolone. From 2-methyl- and 2-ethyl-1-isoquinolone was prepared 1-chloroisoquinoline, which has a considerably lower melting point than that which Gabriel and Colman ascribed to the same base, as prepared by a different method (*Ber.*, 1900, **33**, 980). Just as alkyl iodides convert 2-chloroquinoline into 2-iodoquinoline alkiodide (Roser, *Annalen*, 1894, **282**, 373; cf. Hamer, J., 1928, 206), so similarly 1-iodoisoquinoline methiodide and ethiodide may be prepared from 1-chloroisoquinoline. The action of *n*-propyl iodide and of ethyl bromide on 1-chloroisoquinoline gave 1-iodoisoquinoline *n*-propiodide and 1-bromoisoquinoline ethobromide, respectively, though analogous compounds were not obtained from 2-chloroquinoline. The reactivity of 1-iodoisoquinoline alkiodides is illustrated by the very great loss which occurs in attempts to recrystallise them from water or from alcohol. They react with ammonia and with aniline to give, respectively, 1-amino- and 1-anilinoisoquinoline alkiodides.

Just as quinaldine alkyl salts condense with 2-iodoquinoline alkiodide to give ψ -cyanines (better called 2 : 2'-cyanines), so also do they condense with 1-iodo*iso*quinoline alkiodides, under the influence of alkali, to give dyes (I) of a new type. It is not proposed to introduce a special name for these compounds, since their description as 2 : 1'-cyanines, together with the numbering of the alkyl groups, makes evident the presence of the *iso*quinoline nucleus. The method of numbering is indicated, and dashes are appended to the numerals of the

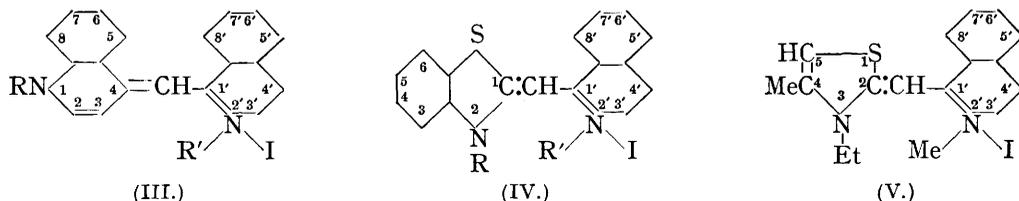


*iso*quinoline nucleus. Five 2 : 1'-cyanines have been prepared, including one containing a β -naphthaquinoline instead of a quinoline nucleus; the yields of recrystallised product varied from 23—70%. The colours of alcoholic solutions of the 2 : 1'-cyanines are visually indistinguishable from those of the corresponding ψ -cyanines.

Besides the foregoing method of preparation, 2 : 1'-cyanines may also, in certain cases, and in spite of the statement to the contrary, be obtained by condensation of a quaternary salt of quinaldine with one of *iso*quinoline. Thus by the action of alkali on an alcoholic solution of the ethiodides of quinaldine and *iso*quinoline, was obtained the same 2 : 1'-cyanine as had already been prepared from quinaldine ethiodide and 1-iodo*iso*quinoline ethiodide. Our colleague, Dr. L. G. S. Brooker, independently, and indeed previously, came to the same conclusion. This was the very instance in which Hoogewerff and van Dorp obtained a negative result (*loc. cit.*), but of course the colour of the 2 : 1'-cyanine is very different from the *isocyanine* colour which they, perhaps, expected. The method is definitely inferior to our new method, since the yield of recrystallised product was only 9%. Moreover it is apparently not a general reaction, for in attempts to condense the methiodides of quinaldine and *iso*quinoline, no 2 : 1'-cyanine was isolated: the dye, which resulted in 12% yield after recrystallisation, was identified with the *isocyanine* obtained by condensing together two molecules of quinaldine methiodide.

*iso*Quinoline-red (II) is, according to the formula of Vongerichten and Homann (*Ber.*, 1912, 45, 3446; cf. Scheibe, *Ber.*, 1921, 54, 786), a 2 : 1'-cyanine of a special kind. The colour of its solution, although similar to those of our simple 2 : 1'-cyanines, differs markedly from them in being fluorescent.

Just as lepidine alkyl salts condense with 2-iodoquinoline alkiodides to give *isocyanines* (Hamer, J., 1928, 206) (better called 2 : 4'- or 4 : 2'-cyanines), so also they condense with 1-iodo*iso*quinoline alkiodides to give 4 : 1'-cyanines (III). After recrystallisation, a dye of



this type was obtained in 56% yield. Although its colour was like that of a typical *isocyanine*, the absorption band was very broad and could not be resolved into two bands, whereas the spectra of the *isocyanines* are definitely double-banded.

Corresponding to the thia- ψ -cyanines (better called thia-2'-cyanines) which are obtained by condensing 1-methylbenzthiazole quaternary salts with 2-iodoquinoline alkiodides (Hamer, *loc. cit.*), thia-1'-cyanines (IV) are now obtained, from 1-methylbenzthiazole quaternary salts and 1-iodo*iso*quinoline alkiodides. Four dyes of this type were prepared, including examples containing a 1-methyl- α - or a 2-methyl- β -naphthathiazole nucleus instead of a 1-methylbenzthiazole nucleus; the yields of recrystallised product varied from

40—52%. The thia-1'-cyanines give orange to pink solutions and the absorption occurs somewhat nearer to the region of long wave-length than with the corresponding thia-2'-cyanines. In certain cases there are indications that the broad absorption band might be resolvable into two bands, but this is very indefinite.

Similarly, corresponding to the seleno- ψ -cyanines (or seleno-2'-cyanines) (I. G. Farbenind. A.-G., B.P. 386,791/1932), a seleno-1'-cyanine has now been prepared from 1-methylbenzselenzazole ethiodide and 1-iodoisoquinoline methiodide. We have already recorded how little the absorption band of a cyanine dye shifts on replacement of a sulphur by a selenium atom (Fisher and Hamer, J., 1933, 189), and in the present case the absorption of the seleno-1'-cyanine is practically identical with that of a simple thia-1'-cyanine; the maximum is nearer to the red than that of the corresponding seleno-2'-cyanine.

By condensing 2 : 4-dimethylthiazole ethiodide with 1-iodoisoquinoline methiodide, the thiazolo-1'-cyanine (V) was prepared, and it corresponds to the thiazolo-2'-cyanines prepared by use of 2-iodoquinoline alkiodides (Kodak Ltd., B.P. 408,570/1932). We pointed out in the carbocyanine series how little colour change is caused by replacing benzthiazole by thiazole nuclei (J., 1930, 2502), and similarly here the thiazolo-1'-cyanine shows the same colour in alcoholic solution as do the simple thia-1'-cyanines. Comparing the ψ -cyanines with the 2 : 1'-cyanines, the isocyanines with the 4 : 1'-cyanines, the thia- ψ -cyanines with the thia-1'-cyanines, and the seleno- ψ -cyanines with the seleno-1'-cyanines, it is seen that, for both members of a pair, the length of the carbon chain which joins the nitrogen atoms is the same. It is perhaps not surprising, therefore, that the colours of both members should be so similar. However, as regards photographic sensitising action, the analogy is by no means so complete: thus, although the new groups of cyanines containing an isoquinoline nucleus do comprise dyes possessing colour-sensitising properties, their action is, in general, definitely weaker than that of the corresponding compounds which contain a quinoline in place of the isoquinoline nucleus.

All the absorption spectra were photographed in methyl-alcoholic solution and we are indebted to Dr. A. Batley and to Mr. R. H. Bomback for doing this work.

EXPERIMENTAL.

2-Methyl-1-isoquinolone.—Pure isoquinoline (50 g.; 1 mol.) was warmed on the water-bath with methyl *p*-toluenesulphonate (72 g.; 1 mol.): vigorous reaction occurred and a white crystalline compound was formed; heating was continued for one hour. The isoquinoline metho-*p*-toluenesulphonate was then dissolved in warm water (200 c.c.) and slowly added to an ice-cooled mixture of finely powdered potassium ferricyanide (280 g.; 2.2 mols.) and potassium hydroxide solution (87 g., 4 mols., in 200 c.c. of water), which had been covered with benzene (2 l.). The temperature being kept below 35°, more potassium hydroxide powder (800 g.) was then added. Finally the mixture was heated on the water-bath, and the benzene extract filtered hot. The solid was further extracted with hot benzene (2 l., 1 l., 1 l.) and the combined extracts were dried over anhydrous sodium sulphate. After distillation of the solvent, the residue was submitted to vacuum distillation. A small fraction (2.8 g.), b. p. up to 182°/20—30 mm., was kept separate and then the chief fraction, b. p. 182—207°/20—30 mm., was collected, a tarry residue being rejected. Inoculation of the main fraction gave a 62% yield (38.5 g.) of 2-methyl-1-isoquinolone, m. p. 35°, b. p. 197°/20—30 mm. After recrystallisation from petrol (40 c.c. per g.) the m. p. was 38°, with previous softening. Decker (*J. pr. Chem.*, 1893, 47, 28) gives m. p. 38—40°.

2-Ethyl-1-isoquinolone (and similarly 2-methyl-1-isoquinolone) was prepared by Bamberger and Frew from 2-ethyl-1-isoquinolone-3-carboxylic acid, as a liquid, b. p. 310—311°/721 mm., 240°/120 mm. (*Ber.*, 1894, 27, 198). In the present work, however, the method is exactly analogous to that employed for the corresponding 2-methyl compound. A 55% yield was obtained; the product was a yellow oil, b. p. 195—197°/10—20 mm.

1-Chloroisoquinoline.—A mixture of 2-methyl-1-isoquinolone (30 g.; 1 mol.), phosphorus pentachloride (46 g.; 1.2 mols.), and phosphorus oxychloride (50 c.c.), heated under reflux in an oil-bath at 150—160° for 28 hours and frequently shaken, became completely liquid. The excess of oxychloride was distilled off and the residue was poured on ice and made alkaline with sodium hydroxide. The liberated base was extracted in benzene, dried (anhydrous sodium sulphate), recovered, and distilled in a vacuum; b. p. 158—165°/20—30 mm. Analysis indicated the

presence of about 20% of unchanged 2-methyl-1-isoquinolone. As this is non-volatile in steam, and the chloro-compound is volatile, separation was effected by steam-distillation. The non-volatile residue was extracted in benzene, dried, and after removal of the solvent, distilled in a vacuum, yielding 13% of the original quinolone as a crystalline solid. The distillate from the steam-distillation was similarly extracted, and the base distilled in a vacuum. Calculated from the original weight of quinolone, the yield of 1-chloroisoquinoline was 66% (20.3 g.), b. p. 160—165°/20—30 mm.; there was a little higher-boiling residue (Found : Cl, 21.8. Calc. for $C_9H_8NCl:Cl$, 21.7%). When cooled, it solidified to colourless crystals, m. p. 23—24°, with softening from 19°, b. p. 277—278°/759 mm. Gabriel and Colman prepared 1-chloroisoquinoline from 1-hydroxyisoquinoline and record m. p. 37—38°, b. p. 274—275°/768 mm. (*Ber.*, 1900, **33**, 980).

The preparation of 1-chloroisoquinoline from 2-ethyl-1-isoquinolone is conducted similarly.

1-Iodoisoquinoline Methiodide.—1-Chloroisoquinoline (5.7 g.; 1 mol.) and methyl iodide (5.2 c.c.; 2.4 mols.) were heated in a sealed tube at 100° for 2 days. The solid contents were ground with acetone (20 c.c. \times 3) and the residual yellow substance was further purified by extraction with ether. The yield of undissolved 1-iodoisoquinoline methiodide (10.5 g.) was 76%.

In preparing this compound in an open vessel, there is no advantage in boiling for more than 2 hours. Although the yield is not so good, being only 61% after acetone treatment, the method is more convenient for large-scale work. The salt as prepared by either of these methods was considered satisfactory for use, though its iodine content was somewhat high (Found : I, 64.4, 65.3% for the two preparations). Its purification could be effected by suspending it (2 g.) in acetone (10 c.c.) and passing in sulphur dioxide; the solid was filtered off, washed with acetone, and recrystallised from water (50 c.c. per g.; 0.83 g. obtained). The pale yellow crystals were dried in a vacuum until of constant weight and analysed by the method of Carius. The temperature of drying was 80—100°. These methods of drying and analysis were used throughout this work, except where otherwise stated (Found : I, 64.1. $C_{10}H_9NI_2$ requires I, 63.9%). M. p. 228° (decomp.).

1-Iodoisoquinoline ethiodide was similarly prepared (sealed tube) and purified (yield, 77%). When the preparation was carried out in an open vessel, the optimum result, a 72% yield after grinding with acetone, was obtained by boiling for 16 hours (Found : I, 62.4%). Treatment as in the case of the methiodide, with sulphur dioxide, followed by recrystallisation from water (20 c.c. per g.) effected a purification, but reduced the weight to one-eighth, since great loss occurred on recrystallisation (Found : I, 62.1. $C_{11}H_{11}NI_2$ requires I, 61.8%). M. p. 188—189° (decomp.).

1-Aminoisoquinoline Ethiodide.—On treatment of 1-iodoisoquinoline ethiodide (2 g.) with cold aqueous ammonia (*d* 0.880; 2 c.c.), vigorous reaction occurred, with evolution of heat. After being heated under reflux for 10 minutes, all the original solid had dissolved, but when the pinkish solution was cooled, a white substance crystallised. Its iodine content was high (Found : I, 57.3%), but after two recrystallisations from methyl alcohol (10 c.c. per g.), the value approximated to the theoretical, and the yield was 31% (Found : I, 42.55. $C_{11}H_{13}N_2I$ requires I, 42.3%). M. p. 194°.

1-Anilinoisoquinoline Ethiodide.—A suspension of 1-iodoisoquinoline ethiodide (5 g.; 1 mol.) in absolute alcohol (50 c.c.) was treated with aniline (2.2 c.c.; 2 mols.), and the mixture was boiled, with mechanical stirring, for 5 minutes. The original solid dissolved and pale yellow crystals separated on cooling. After washing with ether, the yield was 87% (4.0 g.). Recrystallisation from methyl alcohol (10 c.c.) gave a 57% yield of pale yellow solid (Found : I, 33.9. $C_{17}H_{17}N_2I$ requires I, 33.75%). M. p. 192—193°, with previous softening.

1-Bromoisoquinoline ethobromide was obtained from 1-chloroisoquinoline and ethyl bromide, by the sealed tube method. After ether extraction, the yield of almost colourless residue was 28% (Found : Br, 50.1. $C_{11}H_{11}NBr_2$ requires Br, 50.4%). It is hygroscopic; m. p. 128° with softening from 118°.

1-Iodoisoquinoline n-propiodide was prepared from 1-chloroisoquinoline and *n*-propyl iodide by the sealed tube method. After washing with ether, the brown sticky residue changed to a yellow solid on treatment with acetone, and was finally purified by extraction with ether in a Soxhlet apparatus. The yield of residue was 40% (Found : I, 60.4. $C_{12}H_{13}NI_2$ requires I, 59.7%). M. p. 116—117° (decomp.).

1 : 2'-Dimethyl-2 : 1'-cyanine Iodide (I).—Quinaldine methiodide (1.8 g.; 1 mol.) and 1-iodoisoquinoline methiodide (2.5 g.; 1 mol.) were stirred mechanically with boiling absolute alcohol (30 c.c.) A solution of sodium (0.32 g.; 2.2 atoms) in absolute alcohol (20 c.c.) was added, and boiling and stirring were continued for 20 minutes. During this time the original

solids dissolved, a red colour developed, and dye crystallised on cooling. It was filtered off and washed with ether, and the yield was 79%. After recrystallisation from methyl alcohol (45 c.c.), the yield (1.58 g.) was 57% (Found: I, 30.1. $C_{21}H_{19}N_2I$ requires I, 29.8%). M. p. 234° (decomp.). By using triethylamine instead of sodium, as recommended by Kodak Ltd. (B.P. 408,571/1932), the yield of recrystallised product was 70%. The chief absorption band has its maximum at λ 515 μ and there is a secondary band at 485 μ .

An unsuccessful attempt was made to prepare this dye by the interaction of the methiodides of quinaldine and isoquinoline: quinaldine methiodide (4.74 g.; 1 mol.) and isoquinoline methiodide (9 g.; 2 mols.), dissolved in boiling absolute alcohol (125 c.c.), were treated with a solution of sodium (0.46 g.; 2 atoms) in absolute alcohol (50 c.c.); the mixture was boiled and stirred for 15 minutes, and acetic acid then added (2.5 c.c.). Dye separated as a tar, and more was obtained by decanting the liquid and concentrating it in a vacuum. The tar did not harden when washed with ether, but solid was obtained by treatment with hot acetone (50 c.c.), followed by cooling in a freezing mixture. It was filtered off and ground with ice-water and finally with ether. The crude dye (0.34 g.; 23% yield) was boiled out with four successive amounts of methyl alcohol (60 c.c. in all), but as all four gave identical products, they were combined, the total yield being 12% (0.18 g.). The colour of an alcoholic solution was red, whereas that of 1 : 2'-dimethyl-2 : 1'-cyanine iodide is orange. The red colour is the same as that of 1 : 1' : 2-trimethylisocyanine iodide, the isocyanine obtained when two molecules of quinaldine methiodide condense. The present compound was identical with this isocyanine in m. p. 273° (decomp.), mixed m. p., absorption spectrum, and photographic action (Found: I, 28.5. Calc. for $C_{22}H_{21}N_2I$: I, 28.8%).

2'-Methyl-1-ethyl-2 : 1'-cyanine iodide was prepared from quinaldine ethiodide and 1-iodoisoquinoline methiodide, triethylamine being used as condensing agent. After recrystallisation from methyl alcohol (25 c.c. per g.), the yield was 60%. The dye was dried for analysis in a vacuum at 60—80° (Found: I, 29.0. $C_{22}H_{21}N_2I$ requires I, 28.8%). M. p. 250° (decomp.). The chief absorption maximum lies at λ 520 μ and a secondary one at 480 μ .

1 : 2'-Diethyl-2 : 1'-cyanine iodide was prepared from quinaldine ethiodide and 1-iodoisoquinoline ethiodide, sodium dissolved in alcohol being used as condensing agent. After recrystallisation from methyl alcohol (40 c.c. per g.), the yield was 55%. The dye was again recrystallised before analysis (Found: I, 27.9. $C_{23}H_{23}N_2I$ requires I, 27.95%). M. p. 258° (decomp.). The principal absorption band has its crest at λ 525 μ and the secondary one at 480 μ .

The dye was also prepared by the interaction of quinaldine ethiodide (5 g.; 1 mol.) and isoquinoline ethiodide (9.53 g.; 2 mols.) by the method which failed in the case of 1 : 2'-dimethyl-2 : 1'-cyanine iodide. In the present instance, the desired product crystallised on cooling, and a small further crop was obtained by concentrating the filtrate in a vacuum. After extraction with ether (Soxhlet), the undissolved dye (1.19 g.; 16% yield) was recrystallised from methyl alcohol (40 c.c.), the yield then being 9% (0.72 g.), and again from methyl alcohol (30 c.c.), the yield being 6% (0.45 g.) (Found: I, 27.9%). This dye had the same m. p. and mixed m. p. as the sample prepared from quinaldine ethiodide and 1-iodoisoquinoline ethiodide; moreover their absorption spectra were identical, as also were their effects on a photographic plate.

6 : 2'-Dimethyl-1-ethyl-2 : 1'-cyanine iodide was prepared from *p*-toluquinaldine ethiodide and 1-iodoisoquinoline methiodide, by means of triethylamine. After recrystallisation from methyl alcohol (25 c.c. per g.), the yield was 42%. The dye was again recrystallised before analysis (Found: I, 27.9. $C_{23}H_{23}N_2I$ requires I, 27.95%). M. p. 234° (decomp.). The absorption maxima are at λ 525 μ and 490 μ , the former band being the stronger. This and the three preceding dyes are all very similar in appearance: dull red crystals with a greenish reflex.

2'-Methyl-1-ethyl-5 : 6-benz-2 : 1'-cyanine iodide was prepared from β -naphthaquinaldine ethiodide and 1-iodoisoquinoline methiodide, by means of sodium. As the crude product appeared to contain unchanged salts, it was well washed with water before ether extraction. After recrystallisation from methyl alcohol (75 c.c. per g.), the yield was 23% (Found: I, 25.9. $C_{26}H_{23}N_2I$ requires I, 25.9%). M. p. 250° (decomp.). The chief absorption maximum lies at λ 525 μ and there is another ill-defined maximum at 500 μ .

2'-Methyl-1-ethyl-4 : 1'-cyanine iodide (III).—This was prepared from lepidine ethiodide and 1-iodoisoquinoline methiodide, by means of triethylamine. After washing with water and with ether, the yield was 63%. The dye was recrystallised from a mixture of methyl alcohol and ethyl acetate (5 c.c. and 20 c.c., respectively, per g.), the yield being 56%. The recrystallisation was repeated before analysis (Found: I, 28.9. $C_{22}H_{21}N_2I$ requires I, 28.8%). M. p. 210° (decomp.). A solution of the olive-green crystals has a very broad absorption band with a maximum at about λ 550 μ .

2 : 2'-Diethylthia-1'-cyanine Iodide (IV).—This was prepared from 1-methylbenzthiazole ethiodide (1.86 g.) and 1-iodoisoquinoline ethiodide (2.5 g.) in boiling absolute alcoholic solution (100 c.c.), by the action of sodium (0.31 g.) dissolved in absolute alcohol (20 c.c.). The yield was 57% after washing with water and ether, and 41% (1.15 g.) after recrystallisation from methyl alcohol (30 c.c. per g.). The dye was again recrystallised before analysis (Found : I, 27.7. $C_{21}H_{21}N_2IS$ requires I, 27.6%). M. p. 246° (decomp.). This, like the following dye forms red crystals with a green reflex. The very broad absorption band has its maximum at about λ 500 $\mu\mu$.

2-Ethyl-2'-n-propylthia-1'-cyanine iodide was similarly prepared from 1-methylbenzthiazole ethiodide and 1-iodoisoquinoline *n*-propiodide. After recrystallising from methyl alcohol (22 c.c. per g.), the yield was 40% (Found : I, 26.8. $C_{22}H_{23}N_2IS$ requires I, 26.8%). M. p. 237° (decomp.). The broad absorption band has its chief crest at λ 505 $\mu\mu$ and a weaker one at λ 480 $\mu\mu$.

2'-Methyl-2-ethyl-3 : 4-benzthia-1'-cyanine iodide was prepared from 2-methyl- β -naphthathiazole ethiodide and 1-iodoisoquinoline methiodide, by means of triethylamine. After recrystallisation from methyl alcohol (60 c.c. per g.) the yield was 44% (Found : I, 25.95%). It was again recrystallised (Found : I, 25.8. $C_{24}H_{21}N_2IS$ requires I, 25.6%). The dark red powder had m. p. 235° (decomp.). This and the following dye show a broad absorption band with a maximum at about λ 510 $\mu\mu$.

2'-Methyl-2-ethyl-5 : 6-benzthia-1'-cyanine iodide was prepared from 1-methyl- α -naphthathiazole ethiodide and 1-iodoisoquinoline methiodide, by means of sodium, being obtained in 52% yield after recrystallisation from methyl alcohol (50 c.c. per g.) (Found : I, 26.2%). The recrystallisation was repeated (Found : I, 25.7. $C_{24}H_{21}N_2IS$ requires I, 25.6%). The dark greenish crystalline powder melted at 233° (decomp.).

2'-Methyl-2-ethylseleno-1'-cyanine iodide was prepared from 1-methylbenzselenzazole ethiodide (2.22 g.) and 1-iodoisoquinoline methiodide (2.5 g.) in boiling absolute alcohol, by means of triethylamine. The yield of washed dye was 71%, and it was 61% after recrystallisation from methyl alcohol (28 c.c. per g.). The method of analysis, after drying in a vacuum at 60–80°, was that described by Hamer (*Analyst*, 1933, 58, 26) (Found : I, 25.9. $C_{20}H_{19}N_2ISe$ requires I, 25.7%). The crystals are dull red with a green reflex and have m. p. 238° (decomp.). The broad absorption band has its maximum at λ 500 $\mu\mu$.

4 : 2'-Dimethyl-3-ethylthiazolo-1'-cyanine Iodide (V).—This was prepared from 2 : 4-dimethylthiazole ethiodide (1.70 g.) and 1-iodoisoquinoline methiodide (2.5 g.) in boiling absolute alcohol (30 c.c.), by means of triethylamine (1.8 c.c.) in absolute alcohol (20 c.c.). The yield of washed solid was 72%, and after recrystallisation from methyl alcohol (16 c.c. per g.), it was 56% (Found : I, 31.1. $C_{17}H_{19}N_2IS$ requires I, 30.8%). M. p. 235° (decomp.) for the dark reddish crystals. The very broad absorption band has its crest at about λ 500 $\mu\mu$.