215. *Preparation of 4'-Cyanines.*

By Frances M. Hamer.

In the 2 : 4'-cyanine condensation, by changing the molecular proportions of quinaldine ethiodide, quinoline ethiodide, and caustic alkali from the classic 1 : 2 : 1·2 to 1 : 3 : 3, the yield has been raised from 37 to 76—82%. Potassium carbonate is applicable to this condensation, but when the same dye is prepared from lepidine ethiodide and 2-iodoquinoline ethiodide, caustic alkali produces a 60% yield, whereas potassium carbonate or triethylamine produces 76%. Although 1-methylbenzthiazole alkiodide, on condensing with quinoline alkiodide, gave only 7—13% yields of thia-4'-cyanine, it is now condensed with 4-cyanoquinoline alkiodide to give 30—37% yields: the improvement is due partly to replacement of a hydrogen atom by the more reactive cyano-group and partly to replacement of the *iso*cyanine condensation, where 2 hydrogen atoms must be eliminated as well as 1 mol. of acid, by a condensation which proceeds simply by removal of 2 mols. of acid. 4-Cyanoquinoline methiodide has been condensed with compounds having a cyclic methylene group. 2-Cyanoquinoline methiodide may be used in preparing thia-2'-cyanine, but the yield is low because the greater reactivity of the 4- as compared with the 2-position is opposing the condensation. When 4-chloroquinoline is heated with ethyl iodide, it does not simply give its ethiodide, as recorded in the literature, but a mixture of that with 4-iodoquinoline ethiodide. This is condensed with quinaldine ethiodide, to give *iso*cyanine. Pure 4-chloro- and 4-iodo-quinoline methiodide and ethiodide were prepared.

Two of the earliest observations concerning cyanine dyes are (1) that lepidine ethiodide and quinoline ethiodide react in alcohol, under the influence of alkali, to give 4 : 4'-cyanine (Hoogewerff and van Dorp, *Rec. Trav. chim.*, 1883, **2**, 28, 41, 317; 1884, **3**, 337), (2) that quinaldine ethiodide and quinoline ethiodide react to give 2 : 4'-cyanine, or *iso*cyanine (*idem, ibid.*, 1883, **2**, 317; 1884, **3**, 337; Spalteholz, *Ber.*, 1883, **16**, 1847). From the non-formation of 2 : 4'-cyanine in the first condensation, and of 2 : 2'-cyanine in the second, it may be deduced that the 4-position is more reactive than the 2-position of the quinolinium nucleus.

The course of these earliest processes for preparing cyanines is not obvious, in so far as two hydrogen atoms are eliminated, in addition to the one mol. of acid which is taken up by alkali:

$$C_9H_7N,C_2H_5I + C_{10}H_9N,C_2H_5I = C_{23}H_{23}N_2I + H_2 + HI$$

The original observers pointed out that it is advantageous to use twice the calculated amount of quinolinium salt (Spalteholz, *loc. cit.*; Hoogewerff and van Dorp, *Rec. Trav. chim.*, 1883, **2**, 317) and this received confirmation from the comparative experiments of Miethe and Book (*Ber.*, 1904, **37**, 2008). It became standard practice to take about one mol. of quinaldinium salt, two of quinolinium salt, and 1—2 mols. of alkali (G.P. 167,159; 167,770/1903; Kaufmann and Vonderwahl, *Ber.*, 1912, **45**, 1404; Mills and Pope, *Phot. J.*, 1920, **60**, 183; Barbier, *Bull. Soc. chim.*, 1920, **27**, 427; Hamer, J., 1921, **119**, 1432; 1930, 995). Vongerichten and Höfchen showed that more than two mols. of alkali are harmful (*Ber.*, 1908, **41**, 3054).

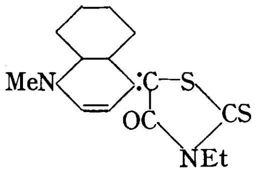
In the present work, the preparation of a typical 2 : 4′-cyanine by this classic method resulted in a 37% yield. Potassium carbonate has an advantage, as condensing agent, over the original caustic alkali, in that an excess of it is innocuous (Kodak Ltd. and Beilenson, B.P. 435,542/1933); in the present instance, its use in 20% excess gave only a 25% yield, whereas a large excess gave a 47% yield. When Braunholtz and Mills prepared thia-4′-cyanine from 1-methylbenzthiazole ethiodide, quinoline ethiodide, and caustic alkali in alcohol, they used these reagents in the molecular proportions of 1 : 1 : 1·2, and obtained only 9—13% yields of crude product (J., 1922, **121**, 2004), but Keyes and Brooker, by taking the proportions 1 : 3 : 3, obtained a yield of recrystallised dye as high as 63% (*J. Amer. Chem. Soc.*, 1937, **59**, 74). It is now found that in the 2 : 4′-cyanine condensation, as in the thia-4′-cyanine condensation, the classic proportions are not the best, since the yield rises to 82% when the molecular proportions of quinaldine ethiodide, quinoline ethiodide, and caustic alkali are 1 : 3 : 3.

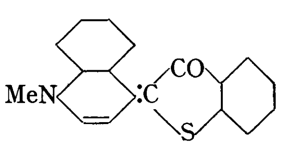
Coupling with the quinolinium nucleus can be made to occur in the 2- instead of the 4-position if the hydrogen atom in the 2-position be replaced by the more active iodine atom. Thus lepidine ethiodide and quinaldine ethiodide, respectively, condense with 2-iodoquinoline ethiodide to give the 2 : 4′- and 2 : 2′-cyanines (Hamer, J., 1928, 206). The original 45% yield of 2 : 4′-cyanine (Hamer, *loc. cit.*), obtained by use of caustic alkali as condensing agent, has now been increased to 60%. By use of triethylamine, as recommended by Brooker and Keyes for 2′-cyanine condensations (*J. Amer. Chem. Soc.*, 1935, **57**, 2488), or of potassium carbonate, as recommended by Kodak Ltd. and Beilenson (*loc. cit.*), it has, however, been increased to 75—77%. Unlike the *iso*cyanine condensation, the 2′-cyanine condensation is straightforward, equimolecular quantities of the quaternary salts reacting to give 1 mol. of dye, with elimination of 2 mols. of acid.

The use of 4-cyanoquinoline alkiodide, in place of quinoline alkiodide or 2-iodoquinoline alkiodide, has now been studied. 4-Cyanoquinoline methiodide was prepared by Kaufmann's method, through 4-cyano-1-methyl-1 : 4-dihydroquinoline (*Ber.*, 1909, **42**, 3776), and was converted into 4-cyanoquinoline by Kaufmann and Widmer's method (*Ber.*, 1911, **44**, 2058; cf. Kaufmann and Vallette, *Ber.*, 1913, **46**, 49), and that into 4-*cyanoquinoline ethiodide*. Although Kaufmann and Vonderwahl observed that the quinaldine *iso*-base did not condense with 4-cyanoquinoline methiodide (*Ber.*, 1912, **45**, 1404), three thia-4′-cyanines, in 30—37% yields, have now been prepared by condensing 4-cyanoquinoline methiodide or ethiodide with 1-methylbenzthiazole alkiodide. A selena-4′-cyanine was prepared in 35% yield. This improvement upon the 7—13% yields of Braunholtz and Mills (*loc. cit.*), obtained by using 4-cyanoquinoline alkiodide instead of quinoline alkiodide, is probably due partly to the greater reactivity of the cyano-group as compared with hydrogen, and partly to replacing their condensation of the *iso*cyanine type by one of the more straightforward type.

4-Cyanoquinoline methiodide can also be condensed with heterocyclic compounds, containing a methylene group in the ring, to give dyes of a type described by Kendall (B.P. 426,718/1933) and by Kodak Ltd. (B.P. 450,958/1934). Thus with 3-ethylrhodanine and 2-ketodihydrothionaphthen, respectively, (I) and (II) were produced.

(I.)





(II.)

By the action of caustic alkali on an alcoholic solution of quinaldine methiodide and 2-cyanoquinoline methiodide, Mills and Pope obtained 2′-cyano-1 : 1′-dimethyl-4′-cyanine iodide (*Phot. J.*, 1920, **60**, 183), *i.e.*, the hydrogen atom in the 4-position was, under their conditions, more reactive than the cyano-group in the 2-position. The preparation of

2-*cyanoquinoline methiodide* has now been accomplished by following directions supplied by Miss M. C. Biggs. By reaction of 2-cyanoquinoline methiodide, 1-methylbenzthiazole methiodide, and potassium carbonate in alcohol, in the molecular proportions 1 : 1 : 1·2, some thia-2′-cyanine was obtained, but the yield of recrystallised product was only 10%. It is not surprising that the yield of thia-2′-cyanine from 2-cyanoquinoline alkiodide is less than the yield of thia-4′-cyanine from 4-cyanoquinoline alkiodide, because in the former case the greater reactivity of the 4- as compared with that of the 2-position is opposing the reaction, whereas in the latter case it is helping it.

In their historic contribution to the constitution of the *iso*cyanines, Kaufmann and Vonderwahl recorded the formation of ethyl-red by the action of alkali on an alcoholic solution of quinaldine ethiodide and 4-chloroquinoline ethiodide (*Ber.*, 1912, **45**, 1404). They stated that 4-chloroquinoline ethiodide resulted on boiling 4-chloroquinoline with ethyl iodide, but the reaction is actually not so simple as that. When 4-chloroquinoline is boiled under reflux with methyl iodide, there is obtained 4-*chloroquinoline methiodide*, but when the base is boiled with ethyl iodide the product is a mixture of the ethiodides of 4-chloroquinoline and 4-iodoquinoline, from which the more soluble 4-chloroquinoline ethiodide could not be isolated. 4-*Chloroquinoline ethiodide* was prepared by bringing about reaction at a low temperature, as in Sprague and Brooker's preparation of 4-chloropyridine alkiodide (*J. Amer. Chem. Soc.*, 1937, **59**, 2697), which method can also be applied to the preparation of 4-chloroquinoline methiodide. When 4-chloroquinoline is heated in a sealed tube with two molecular proportions of methyl or ethyl iodide, it yields 4-iodoquinoline methiodide (Brydówna, *Rocz. Chem.*, 1932, **12**, 39) and 4-*iodoquinoline ethiodide*, respectively; this is like the behaviour of 2-chloroquinoline (Roser, *Annalen*, 1894, **282**, 373; Hamer, J., 1928, 206). The successful preparation of 4-iodoquinoline alkiodide is interesting in view of Sprague and Brooker's failure to prepare 4-iodopyridine alkiodide from 4-chloropyridine (*loc. cit.*). Attempts to prepare 2-chloroquinoline methiodide and ethiodide, by reaction of base and alkyl iodide at a low temperature, were unsuccessful. By condensing 4-iodoquinoline ethiodide with quinaldine ethiodide, ethyl-red was produced, the yield with triethylamine as condensing agent being 67%.

The absorption spectra of the dyes were photographed in methyl-alcoholic solution, for which work I am indebted to Dr. E. P. Davey.

EXPERIMENTAL.

4-Cyano-1-methyl-1 : 4-dihydroquinoline was obtained in 81—94% yields by the method of Kaufmann (*Ber.*, 1918, **51**, 116), the only modification being that quinoline metho-*p*-toluenesulphonate was used instead of its methomethylsulphate.

4-Cyanoquinoline methiodide was obtained in 75% yield by Kaufmann's method (*loc. cit.*). On repeated grinding with acetone, the yield dropped to 66%, and on subsequent recrystallisation from methyl alcohol (14 c.c. per g.) to 57%. The salt was dried in a vacuum at 60—80° and analysed by the method of Carius, which methods of drying and analysis were used throughout this work, except where otherwise stated (Found : I, 42·7. Calc. for $C_{11}H_9N_2I$: I, 42·9%). M. p. 225° (decomp.). Kaufmann and Widmer give m. p. 216° (decomp.) (*Ber.*, 1911, **44**, 2058). By heating 4-cyanoquinoline (1 mol.), obtained as described below, with methyl iodide (1·2 mols.) in a sealed tube at 100° for 2 days, the methiodide was re-obtained, the yield, after washing with ether, being 92%. After recrystallisation from methyl alcohol, the yield was 69% (Found : I, 42·95. Calc. for $C_{11}H_9N_2I$: I, 42·9%).

4-*Cyanoquinoline ethiodide*, in 93% yield after washing with ether, is obtained by heating 4-cyanoquinoline with ethyl iodide. After grinding three times with acetone (2·5 c.c. per g. × 3), the yield dropped to 88%, and on recrystallisation from methyl alcohol (5 c.c. per g.) to 79% (Found : I, 41·15. $C_{12}H_{11}N_2I$ requires I, 40·9%). The orange crystals melted at 200°, with some decomposition before melting and much afterwards.

4-Cyanoquinoline was prepared from its methiodide by Kaufmann and Widmer's method (*Ber.*, 1911, **44**, 2058) of heating in a vacuum. To remove some unchanged methiodide (6% yield), the crude base was taken up in ether and was thus obtained in 93% yield. After recrystallisation from methyl alcohol (4 c.c. per g.), the yield was 80% and the m. p. 101°, with previous softening, whereas Kaufmann and Widmer record m. p. 95° (*loc. cit.*) (Found for material dried in a vacuum desiccator : N, 18·4. Calc. for $C_{10}H_6N_2$: N, 18·2%).

2-Cyanoquinoline.—In applying Kaufmann and Dändliker's method (*Ber.*, 1913, **46**, 2924), their yield of 55—70% was not approached. Thus phosphorus pentachloride (20 g.; 1·25 mols.) was gradually added to a boiling solution of 1-benzoyl-2-cyano-1 : 2-dihydroquinoline (20 g.; 1 mol.) in dry chloroform (100 c.c.); the solution was then boiled for 2 hours, cooled, treated with water and sodium carbonate, and steam-distilled. The distillate was extracted with chloroform and the crude base (32—42% yield) was recrystallised from methyl alcohol (6 c.c. per g.), the yield being 24—29%; m. p. 95°, as recorded by Kaufmann and Dändliker. Sometimes, as they noted, a yellow substance crystallised during the boiling, but this did not seem to be due to inadequate drying of the chloroform, since this was in all cases dried over phosphoric oxide and redistilled just prior to use.

2-Cyanoquinoline Methiodide.—The attempted preparation by heating 2-cyanoquinoline with methyl iodide gave a negative result. 2-Cyanoquinoline (4·09 g.; 1 mol.) was heated with methyl sulphate (2·6 c.c.; 1 mol.) on a boiling water-bath for 2 hours. The product was ground three times with absolute ether (12·5 c.c. × 3) and dried in a vacuum desiccator; the yield was 89% (6·61 g.). This methomethylsulphate was stirred into boiling absolute alcohol (66 c.c.) and quickly treated with a hot solution of potassium iodide (6·6 g.) in water (7 c.c.). A red solution was formed. It was quickly cooled, and the red solid which crystallised was filtered off and dried (9·15 g. obtained). To remove inorganic matter, it was ground with cold water (4·5 c.c.) and further washed with water (2·2 c.c.) on the filter. The yield was 67% (5·29 g.) (Found for material dried in a vacuum desiccator: I, 43·1. $C_{11}H_9N_2I$ requires I, 42·9%). After recrystallisation from absolute alcohol (50 c.c. per g.), the yield fell to 40% (Found: I, 42·9%). When heated, darkening began below 100° and there was violent decomposition at about 177°.

4-Chloroquinoline.—2-Aminoquinoline (Hamer, J., 1924, 1348) was converted into 4-chloroquinoline by Wenzel's method (*Monatsh.*, 1894, **15**, 453). The product (yield, 83%) had b. p. 145—150°/22 mm., m. p. 25—26°, whereas Skraup gives m. p. 34° (*Monatsh.*, 1889, **10**, 730) and Wenzel gives m. p. 29—30° (Found: Cl, 21·5. Calc. for C_9H_6NCl: Cl, 21·7%).

4-Chloroquinoline Methiodide.—Methyl iodide (3 c.c.; 4 mols.) was cooled and added to 4-chloroquinoline (2 g.; 1 mol.), also cooled. The resultant solution was kept in the ice-chest for 4 days, its colour becoming orange and yellow crystals separating. After filtration and washing with ether, the yield of pure product was 62% (2·31 g.) (Found: Cl + I, 53·4. $C_{10}H_9NClI$ requires Cl + I, 53·2%). After recrystallisation from absolute alcohol (20 c.c. per g.), the yield dropped to 52% (Found: Cl + I, 53·2%). The yellow crystals became orange at about 60°; decomp. 208°. The pure *salt* was obtained in 74% yield by heating the same proportions of 4-chloroquinoline and methyl iodide under reflux for 24 hours, and washing the resultant solid with ether (Found: Cl + I, 53·0%). Methyl alcohol (16 c.c. per g.) is a worse solvent for the recrystallisation than is ethyl alcohol, for with its use the yield fell to 50% (Found: Cl + I, 53·1%).

4-Iodoquinoline Methiodide.—4-Chloroquinoline (2 g.; 1 mol.) and methyl iodide (1·7 c.c.; 2·2 mols.) were heated in a sealed tube at 100° for 2 days. The yield of ether-washed product was 84% (4·07 g.). This was boiled out with methyl alcohol (60 c.c.), with the object of removing 4-chloroquinoline methiodide (0·33 g. obtained. Found: Cl + I, 52·7. Calc. for $C_{10}H_9NClI$: Cl + I, 53·2%). The undissolved residue was recrystallised from methyl alcohol (300 c.c.); the yield was 45% (2·2 g.) (Found: I, 64·4. Calc. for $C_{10}H_9NI_2$: I, 63·9%). M. p. 259° (decomp.), with previous blackening. Brydówna gives m. p. 234—237° (decomp.) (*Rocz. Chem.*, 1932, **12**, 89).

4-Chloroquinoline Ethiodide.—4-Chloroquinoline (2 g.; 1 mol.) and ethyl iodide (4 c.c.; 4 mols.) were cooled separately in ice, then mixed, and the mixture was kept in the ice-chest for 7 weeks. The crystals, which had begun to appear after 1 week, were filtered off and washed with ether; the yield of pure *salt* was 28% (1·08 g.) (Found: Cl + I, 51·0. $C_{11}H_{11}NClI$ requires Cl + I, 50·8%). On recrystallisation from methyl alcohol (12 c.c.), the yield fell to 17% (Found: Cl + I, 50·9). When heated, the yellow salt began to turn orange at about 70°; m. p. 191° (decomp.). When the reagents were heated together under reflux, the product consisted of a mixture of 4-chloroquinoline ethiodide and 4-iodoquinoline ethiodide, from which only the latter, being the less soluble, could be separated in a state of purity by fractional crystallisation.

4-Iodoquinoline Ethiodide.—4-Chloroquinoline (5 g.; 1 mol.) and ethyl iodide (5·4 c.c.; 2·2 mols.) were heated together in a sealed tube at 100° for 2 days. The yield of ether-washed product was 84% (10·49 g.) (Found for material dried in a vacuum at 80—100°: I, 60·8%). After recrystallisation from methyl alcohol (25 c.c. per g.), the yield fell to 58% (Found: I, 62·1. $C_{11}H_{11}NI_2$ requires I, 61·8%). On heating, the yellow colour deepened from about 150° and violent decomposition occurred at about 234°. The mixture of 4-chloroquinoline ethiodide and 4-iodoquinoline ethiodide which was obtained by heating the reactants under reflux could be converted into pure 4-iodoquinoline ethiodide by further heating with ethyl iodide in a sealed tube.

1 : 1′-*Diethyl*-2 : 4′-*cyanine Iodide* [(1-*Ethyl*-2-*quinoline*)(1-*ethyl*-4-*quinoline*)*methincyanine Iodide*].—To a boiling solution of 1 mol. of quinaldine ethiodide (2·5 g.) and 2 mols. of quinoline ethiodide (4·76 g.) in absolute alcohol (60 c.c.) was added a solution of 1·2 atoms of sodium (0·23 g.) in absolute alcohol (10 c.c.), *i.e.*, the classic proportions. After boiling, with mechanical stirring, for 15 minutes, the mixture was cooled. The dye was filtered off and washed, successively, with alcohol and water (2·45 g. obtained). It was recrystallised from methyl alcohol (10 c.c. per g.); the yield was 37% (1·42 g.). When the amount of quinoline ethiodide was increased to 3 mols. (7·15 g.) and that of sodium to 3 atoms (0·58 g.), the washed dye (3·75 g.) gave on recrystallisation a 76% yield (2·87 g.). When 3 mols. of potassium hydroxide were used instead of 3 atoms of sodium, the washed product (4·18 g.) gave on recrystallisation an 82% yield (3·13 g.). By boiling and stirring 1 mol. of quinaldine ethiodide (2·5 g.), 2 mols. of quinoline ethiodide (4·76 g.), 0·6 mol. of anhydrous potassium carbonate (180-mesh, 0·69 g.), and absolute alcohol (70 c.c.) for 15 minutes, and recrystallising the washed dye (2·00 g.), the yield was 25% (0·96 g.); with 2·4 mols. of potassium carbonate, recrystallisation of the washed dye (2·77 g.) gave a 47% yield (1·79 g.).

A mixture of 1 mol. of 2-iodoquinoline ethiodide (3·44 g.), 1 mol. of lepidine ethiodide (2·5 g.), and absolute alcohol (40 c.c.) was heated to boiling, a solution of 2·2 atoms of sodium (0·42 g.), dissolved in absolute alcohol (30 c.c.), was added, and the mixture was boiled and stirred for 15 minutes. The crude dye was washed with alcohol and with water (2·78 g. obtained) and the yield after recrystallisation was 60% (2·26 g.), instead of the 45 % previously obtained (Hamer, J. 1928, 206). By use of a 10% excess of potassium carbonate (1·1 mols.; 1·27 g.) instead of a 10% excess of sodium, the washed dye (1·98 g.) gave on recrystallisation a 38% yield (1·43 g.), but with twice that quantity of carbonate the washed dye (2·84 g.) gave on recrystallisation a 75% yield (2·70 g.). With a 10% excess of triethylamine (2·2 mols.; 2·5 c.c.), the washed dye (3·40 g.) gave on recrystallisation a 77% yield (2·94 g.).

By boiling together 1 mol. of quinaldine ethiodide (1·50 g.), 1 mol. of 4-iodoquinoline ethiodide (2·05 g.), 2 mols. of triethylamine (1·4 c.c.), and absolute alcohol (10 c.c.) for 15 minutes and recrystallising the washed dye (2·06 g.) thus obtained, the yield was 67% (1·53 g.) (Found, after drying in a vacuum at 80—100° : I, 28·2. Calc. for $C_{23}H_{23}N_2I$: I, 27·9%). Its photographic action was identical with that of samples prepared by the other methods.

1′-*Methyl*-2-*ethylthia*-4′-*cyanine Iodide* [(1-*Methyl*-4-*quinoline*)(2-*ethyl*-1-*benzthiazole*)*methincyanine Iodide*].—4-Cyanoquinoline methiodide (2 g.; 1 mol.) and 1-methylbenzthiazole ethiodide (2·06 g.; 1 mol.) were boiled with absolute alcohol (40 c.c.), treated with a solution of potassium hydroxide (0·83 g.; 2·2 mols.) in absolute alcohol (10 c.c.), and boiled and stirred for 15 minutes. The *product* was filtered off and washed, first with water and then with ether (yield, 42%). It was recrystallised from methyl alcohol (120 c.c. per g.); the yield was then 35% (1·06 g.) (Found : I, 28·5. $C_{20}H_{19}N_2IS$ requires I, 28·45%). The dull red crystals melted at 275° (decomp.), with shrinking from 245°. The methyl-alcoholic solution has two absorption bands, at λ 4800 A. and 5000 A., respectively. This preparation, and the next but one, were carried out by Dr. N. I. Fisher.

2 : 1′-*Diethylthia*-4′-*cyanine Iodide* [(1-*Ethyl*-4-*quinoline*)(2-*ethyl*-1-*benzthiazole*)*methincyanine Iodide*].—In the reaction of 1-methylbenzthiazole ethiodide (1 mol.) with 4-cyanoquinoline ethiodide (1 mol.), potassium carbonate was used as condensing agent, in 120% excess, *i.e.*, 2·2 mols. instead of 1 mol., and the yield of recrystallised dye was 37% (Found, after drying in a vacuum at 80—100° : I, 27·7. Calc. for $C_{21}H_{21}N_2IS$: I, 27·6%).

5-*Chloro*-1′-*methyl*-2-*ethylthia*-4′-*cyanine Iodide* [(1-*Methyl*-4-*quinoline*)(5-*chloro*-2-*ethyl*-1-*benzthiazole*)*methincyanine Iodide*].—Similarly, from 4-cyanoquinoline methiodide and 5-chloro-1-methylbenzthiazole ethiodide, a *dye* was prepared (44% yield) and, after two recrystallisations from methyl alcohol (200 c.c. per g.), was obtained in 30% yield (Found, after drying in a vacuum at 80—100° : Cl + I, 33·75. $C_{20}H_{18}N_2ClIS$ requires Cl + I, 33·8%). The scarlet crystals had m. p. 292° (decomp.). The absorption band has its maximum at λ 5000 A.

1′-*Methyl*-2-*ethylselena*-4′-*cyanine Iodide* [(1-*Methyl*-4-*quinoline*)(2-*ethyl*-1-*benzselenazole*)-*methincyanine Iodide*].—4-Cyanoquinoline methiodide (2 g.; 1 mol.), 1-methylbenzselenazole ethiodide (2·38 g.; 1 mol.), and potassium carbonate (180-mesh; 1·12 g.; 1·2 mols.) were boiled together in absolute alcohol (20 c.c.) for 15 minutes, and the *product* washed successively with water and ether (yield, 45%). After recrystallisation from methyl alcohol (200 c.c. per g.), the yield was 35% (1·15 g.) (Found, after a second recrystallisation: I, 25·5. $C_{20}H_{19}N_2ISe$ requires I, 25·7%). Dull red crystals with a green reflex were formed, m. p. about 285° (decomp.). The absorption is double banded, the maxima lying at 4800 and 5100 A.

2 : 1′-*Dimethylthia-2′-cyanine Iodide* [(1-*Methyl-2-quinoline*)(2-*methyl-1-benzthiazole*)*methincyanine Iodide*].—2-Cyanoquinoline methiodide (1·48 g.; 1 mol.), 1-methylbenzthiazole methiodide (1·46 g.; 1 mol.), anhydrous potassium carbonate (180-mesh; 1·52 g.; 2·2 mols.), and absolute alcohol (20 c.c.) were boiled and stirred together for 15 minutes. The solid was filtered off and washed with alcohol and then water (0·97 g. obtained). It was boiled out with methyl alcohol (20 c.c. × 4) and from the last two extracts there separated a 10% yield (0·22 g.) of red dye. It gave a yellow spirit solution [whereas the first extract yielded a dye (0·16 g.) which gave a pinker solution, and the second extract gave a mixture (0·09 g.)]. The absorption of this less soluble product was weaker than that of a sample of dye which was prepared for comparison from 2-iodoquinoline methiodide and 1-methylbenzthiazole methiodide (Hamer, J., 1928, 206), but the maxima were the same. As the two were alike in sensitising action, their identity was regarded as established.

5 : 4′-(1′-*Methyl*-1′ : 4′-*dihydroquinolylidene*)-3-*ethylrhodanine* (I).—4-Cyanoquinoline methiodide (2·76 g.; 1 mol.), 3-ethylrhodanine (1·5 g.; 1 mol.), and anhydrous potassium carbonate (180-mesh; 6·45 g.; 5 mols.) were ground together, treated with boiling absolute alcohol (15 c.c.), and the mixture boiled and stirred for 2 minutes. The *product* was filtered off when cold, washed with absolute alcohol, and ground with water. The iodine-free, red crystals (0·97 g.; 34% yield) were recrystallised from pyridine (30 c.c.); m. p. 269°. The yield was 16% (0·45 g.) (Found: S, 21·4. $C_{15}H_{14}ON_2S_2$ requires S, 21·2%). The absorption maximum lies at λ 5200 A.

1 : 4′-(1′-*Methyl*-1′ : 4′-*dihydroquinolylidene*)-2-*keto*-1 : 2-*dihydrothionaphthen* (II).—4-Cyanoquinoline methiodide (1·98 g.; 1 mol.), 2-ketodihydrothionaphthen (1 g.; 1 mol.), anhydrous potassium carbonate (180-mesh; 1·84 g.; 2 mols.), and absolute alcohol (30 c.c.) were boiled together, with mechanical stirring, for 20 minutes. After cooling, the dye was filtered off, washed with water, and dried. The crude product (0·76 g.; 39% yield) was boiled under reflux with pyridine (10 c.c.) for 10 minutes. The solution was filtered hot and the *dye*, which crystallised on cooling, was filtered off and washed with ether. The yield (0·44 g.) was 23% (Found: S, 10·9. $C_{18}H_{13}ONS$ requires S, 11·0%). The olive-green crystals had m. p. 207—208°. The absorption maximum lies at λ 5400 A.

KODAK LTD., WEALDSTONE, MIDDLESEX.

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