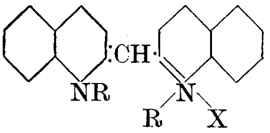
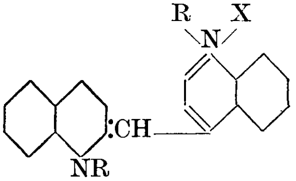
XXXI.—*The ψ-Cyanine Condensation.*

By Frances Mary Hamer.

It has been recorded by Kaufmann that a red dye is very slowly formed by the action of potassium hydroxide on an alcoholic solution of 2-iodoquinoline ethiodide and quinaldine ethiodide (*Ber.*, 1912, **45**, 1417). By a modification of his method, Fischer and Scheibe succeeded in isolating the corresponding methiodide, to which, from the manner of synthesis, they assigned the constitution of a 2 : 2′-cyanine (I) (*J. pr. Chem.*, 1919, **100**, 86). They proposed the name "*ψ-iso*cyanine" for dyes of this type, but the term "ψ-cyanine," as used by Mills and Odams (J., 1924, **125**, 1913), is preferable. Fischer and Scheibe attributed the low yield of ψ-cyanine obtained by Kaufmann to decomposition of the 2-iodoquinoline alkyliodide by alcohol; they state that this decomposition is diminished by a suitable selection of the solvent, and that by dissolving the alkyliodides in dilute hydrochloric acid and adding potassium hydroxide, a 40% yield of pure ψ-cyanine is obtainable. Exact details are not, however, given, and attempts to reproduce this yield proved unsuccessful.

(I.)





(II.)

It is indeed true, as previously noted by Roser (*Annalen*, 1894, **282**, 373), that 2-iodoquinoline methiodide is unstable. But it is now found that acid, far from the power attributed to it, has the effect of increasing this instability, so that its use as solvent is clearly undesirable. In the earlier of the present preparations, the method consisted in adding a slight excess of potassium hydroxide to a boiling aqueous solution of the alkyliodides, and the maximum yield of pure product so obtained was about 20% of that theoretically possible. By using absolute alcohol as solvent, the yields are approximately doubled. If rectified spirit is used, there is a tendency to the formation of impurities of the carbocyanine type.

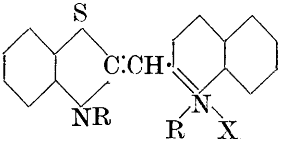
Hitherto only two ψ-cyanines have been prepared (Fischer, *J. pr. Chem.*, 1918, **98**, 204; Fischer and Scheibe, *loc. cit.*), and it is curious, in view of the importance of other cyanine dyes as photographic sensitisers, that no examination of their photographic properties has been recorded. Eight ψ-cyanines are now described, of which seven are new, and Mr. O. F. Bloch has examined their absorption spectra in alcoholic solution and has studied their photographic action, both by bathing plates in solutions of the dyes and also by adding the latter to the emulsion before coating. He has found that the ψ-cyanines exert a sensitising action in the bluish-green region of the spectrum, and that certain of them are of practical value.

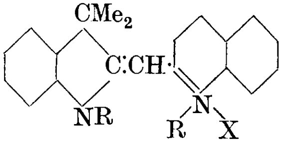
The ψ-cyanine reaction may be applied to the preparation of other cyanine dyes. Thus by condensation of lepidine alkyliodide with

2-iodoquinoline alkyliodide, an *iso*cyanine is produced, and this new method of synthesis confirms the now well-established formula (II) for *iso*cyanine.

To one of the reaction products which Mills and Braunholtz obtained by heating quinaldine ethonitrate with di-*o*-formylethylaminodiphenyl disulphide in pyridine solution they assigned formula (III) (J., 1923, **123**, 2804). This structure is now confirmed by the synthesis of this and three new thio-ψ-cyanines by condensation of 1-methylbenzthiazole alkyliodide with 2-iodoquinoline alkyliodide.

(III.)





(IV.)

The method has been further extended to the synthesis of two dyes of a new type, for which the name indo-ψ-cyanine is proposed : for this preparation, 2-iodoquinoline alkyliodide is condensed with a substituted indolenine quaternary salt containing a reactive 2-methyl group. The formula (IV) is written as though the acid radical were attached to what is presumably the more basic part of the molecule (compare Mills and Wishart, J., 1920, **117**, 579).

The nomenclature of the ψ-cyanines requires consideration. Mills and Pope originated the system of affixing dashes to the numerals in the quinoline, as opposed to the quinaldine, nucleus of *iso*cyanine (*Phot. J.*, 1920, **44**, 183). According to the structure of *iso*cyanine (II) as established by Mills and Wishart (*loc. cit.*), this results in attaching dashes to the numerals in the nucleus which bears the acid radical, so that in the case of the thio-ψ-cyanines and indo-ψ-cyanines the dashes should follow the numerals in the quinoline nucleus; this system has apparently been adopted by Mills and Braunholtz (*loc. cit.*), although it is not specifically stated. With the ψ-cyanines themselves, however, the two nuclei are identical, and it is not possible to differentiate between them, so that alternative formulæ must be given. It is moreover found that the ψ-cyanine prepared from quinaldine methiodide and 2-iodoquinoline ethiodide has the same optical and photographic properties, etc., as that prepared from quinaldine ethiodide and 2-iodoquinoline methiodide; similarly, with the ψ-cyanines prepared from *p*-toluquinaldine methiodide and 2-iodoquinoline methiodide and from quinaldine methiodide and 2-iodo-6-methylquinoline methiodide the photographic properties are identical. Thus virtual tautomerism apparently occurs here, as in the case of the thiocyanines (Mills and Braunholtz, J., 1922, **121**, 1489).

EXPERIMENTAL.

2-Iodoquinoline Methiodide.—Roser prepared the iodide by heating 2-chloroquinoline and methyl iodide in a sealed tube (*loc. cit.*); but since methyl chloride is evolved, a considerable pressure develops, so that even with small-scale preparations loss through bursting of the tube is liable to occur: moreover, the product is contaminated by periodide. A higher yield of almost pure product is obtainable by prolonged heating in an open vessel: chloroquinoline (10 g.) and methyl iodide (15 c.c.) were heated in a water-bath, in a flask fitted with a reflux condenser and protected from the light, for 10 days. The product was extracted with ether in order to remove unchanged base and was thus obtained in 92% yield (Found: I, 63·3%) and, for the condensations, this salt was used without further purification. A specimen was rapidly recrystallised from water, dried in the steam-oven, and analysed by the method of Carius (Found: I, 64·1. Calc. for $C_{10}H_9NI_2$: I, 63·9%). It melted at 211—212°, as recorded by Roser. To test the influence of dilute acid on its stability, the crude iodide (1 g.) was added to boiling water (50 c.c.) and the solution was boiled for 5 minutes, filtered, and cooled; the iodide then crystallised (0·61 g.). A similar experiment was carried out, 5% hydrogen chloride solution (50 c.c.) being used, but this on cooling deposited only a black product (0·05 g.). It is therefore clear that dilute acid decreases the stability of 2-iodoquinoline methiodide.

2-Iodoquinoline Ethiodide.—On heating 2-chloroquinoline with ethyl iodide in a sealed tube by Roser's method, the yields are 35% and 49%, respectively, of that theoretically possible, according as heating is continued for 2 or for 4 days. But when a solution of the base (10 g.) in ethyl iodide (15 c.c.) is boiled under reflux for 10 days, the yield is 81%. After recrystallisation from water, the salt has m. p. 205° (decomp.), whereas Roser gives m. p. 220° (Found: I, 61·9. Calc. for $C_{11}H_{11}NI_2$: I, 61·8%).

1 : 6-*Dimethyl-2-quinolone.*—This was prepared by oxidising a solution of 6-methylquinoline methiodide by means of alkaline potassium ferricyanide at 0—7°. After extraction with chloroform and recrystallisation from benzene, a 70% yield resulted, but the compound melted at 82—84° with previous softening, whereas Fischer records the m. p. as 90° (*Ber.*, 1899, **32**, 1297). The quinolone was therefore distilled in a vacuum, by which, however, the m. p. was unaltered; b. p. 205°/15 mm. (Found: C, 76·3; H, 6·5; N, 8·0. Calc. for $C_{11}H_{11}ON$: C, 76·3; H, 6·4; N, 8·1%).

2-*Chloro-6-methylquinoline.*—This was prepared from 1 : 6-dimethyl-2-quinolone by a method analogous to that used by Perkin and Robinson for preparing 2-chloroquinoline (J., 1913, **103**, 1973).

The base cannot be purified by steam distillation, as recommended by Fischer (*loc. cit.*), first because it is only slightly volatile with steam and, further, because it solidifies in the condenser and remains unmelted at 100°. It was therefore extracted with benzene and after removal of the solvent the residue was recrystallised from spirit and then from petrol. As the melting point was still below that recorded by Fischer, the base was purified by crystallisation of its picrate, but even after this it melted at 111—112°, whereas Fischer gives m. p. 116°. It was dried in a vacuum desiccator before analysis (Found : Cl, 20·1. Calc. for $C_{10}H_8NCl$: Cl, 20·0%).

2-*Iodo*-6-*methylquinoline methiodide* was best obtained by heating 2-chloro-6-methylquinoline (3 g.) and methyl iodide (3 c.c.) for 2 days in a sealed tube at 100°. After ether extraction, the residue (87% yield) was recrystallised from water; the yield was then 52% and m. p. about 225° (decomp.) (Found : I, 61·75. $C_{11}H_{11}NI_2$ requires I, 61·8%).

1 : 1'-*Dimethyl*-ψ-*cyanine Iodide.*—This dye has been prepared by Fischer and Scheibe (*loc. cit.*). By the present method, crude 2-iodoquinoline methiodide (4 g.; 1 mol.) was added to boiling water (200 c.c.), and the solution filtered from periodide. Quinaldine methiodide (2·9 g.; 1 mol.) was added to the filtrate and the boiling solution was treated with an aqueous solution (30 c.c.) of potassium hydroxide (1·2 g.; more than 2 mols.). The dye separated (30% yield) and was recrystallised from rectified spirit; the yield was 21% of the theoretical. In another preparation, 2-iodoquinoline methiodide (12 g.) and quinaldine methiodide (8·6 g.) were boiled with absolute alcohol (600 c.c.) and an absolute alcoholic solution (60 c.c.) of potassium hydroxide (4·0 g.) was added; after ½ hour's boiling, all undissolved solid had disappeared. The product (52% yield) was obtained in 39% yield on recrystallisation. From spirit, the iodide separates as compact pleochroic green and purple crystals, and from methyl alcohol as small, red crystals. Its m. p. (not previously recorded) is at 245—246° (decomp.). It was dried under reduced pressure at 100—120° and analysed by the method of Carius, which method of drying and analysis were used throughout this work, except where otherwise stated (Found : I, 29·6. Calc. for $C_{21}H_{19}N_2I$: I, 29·8%). On bathing a plate in its solution, fairly strong extra sensitivity, extending to λ 6000 Å., is produced, with a maximum at λ 5600, but in the emulsion the sensitising action is less powerful.

1 (or 1')-*Methyl*-1' (or 1)-*ethyl*-ψ-*cyanine Iodide.*—This was prepared by the action of potassium hydroxide on an aqueous solution of 2-iodoquinoline methiodide and quinaldine ethiodide and, after recrystallisation from rectified spirit, was obtained in

13% yield, but by carrying out the preparation in alcoholic solution the yield was 33% (Found: I, 28·7. $C_{22}H_{21}N_2I$ requires I, 28·8%). Alternatively, 2-iodoquinoline ethiodide and quinaldine methiodide were condensed in absolute-alcoholic solution: the yield of recrystallised product was 28% (Found: I, 28·8%). By each method, the product was in the form of small, bronze crystals with a green lustre and both specimens and their mixture, when heated simultaneously, melted at 261—262° (decomp.). Their actions on photographic plates on bathing are identical. The first specimen, when added to an emulsion, behaves as a powerful sensitiser, giving a crest at λ 5800 which falls sharply to zero at λ 6000; there is a slight gap between the ordinary and the extra sensitivity, with its minimum at λ 5300. With bathed plates, the maximum is at λ 5750 and the gap is less, so that the rise to the crest is more gradual and the crest appears less marked.

1 : 1′ : 6 (or 1 : 1′ : 6′)-*Trimethyl-ψ-cyanine Iodide*.—By the first method, the interactants were 2-iodoquinoline methiodide and *p*-toluquinaldine methiodide, which were condensed in aqueous solution. On recrystallising the crude product (21% yield) from rectified spirit, fine, purple crystals were obtained, m. p. at about 220° (decomp.) (Found: I, 28·9. $C_{22}H_{21}N_2I$ requires I, 28·8%). On bathing, the dye confers on a plate a fairly uniform sensitisation, with a slight depression at λ 5300 and a maximum at λ 5500, decreasing gradually to zero at λ 6200, but when the compound is used in the emulsion, the extra sensitivity is less. By the second method of preparation, 2-iodo-6-methylquinoline methiodide and quinaldine methiodide were condensed in absolute alcoholic solution, and a 33% yield of recrystallised product resulted (Found: I, 28·8%). The crystals were redder than those obtained previously and melted at about 183° (decomp.), the exact m. p. depending upon the rate of rise of temperature. The extra sensitivity conferred upon a plate on bathing was identical with that given by the dye prepared by the other method.

1 : 6 : 1′ : 6′-*Tetramethyl-ψ-cyanine Iodide*.—The compound prepared by condensation of 2-iodo-6-methylquinoline methiodide and 2 : 6-dimethylquinoline methiodide, in absolute alcoholic solution, was obtained after recrystallisation from spirit in 23% yield. It forms small, dark crystals with a green reflex, m. p. about 250° (decomp.) (Found: I, 27·8. $C_{23}H_{23}N_2I$ requires I, 27·9%). On bathing a plate in its solution, there results a practically uniform band with a very slight minimum at λ 5300 and a maximum at λ 5500, from which the sensitivity gradually decreases to zero at λ 6300; in the emulsion, the sensitivity is extremely feeble, with a decrease in the blue sensitivity. The absorption curves of this and

the preceding ψ-cyanines, in spirit solution, are all very similar. They are characterised by two bands, with maxima at λ 4900 and λ 5220, respectively, and the latter of these is the stronger.

1 : 1′-*Diethyl-ψ-cyanine Iodide.*—By the action of potassium hydroxide on an aqueous solution of 2-iodoquinoline ethiodide and quinaldine ethiodide, followed by recrystallisation of the crude dye from methyl alcohol, there resulted an 18% yield, as small, bluish-red crystals, m. p. 277° (decomp.) (Found : I, 28·1. $C_{23}H_{23}N_2I$ requires I, 27·9%). By carrying out the condensation in dry spirit, the yield was 36% (Found : I, 28·0%). The sensitivity curve of a bathed plate shows a gap with its minimum at λ 5300; it then rises to a strong maximum at λ 5700 and falls sharply to zero at λ 6000. In the emulsion, the sensitisation is somewhat less powerful. There is a strong absorption maximum at λ 5250 and a weaker one at λ 4900.

6 (or 6′)-*Methyl*-1 : 1′-*diethyl-ψ-cyanine Iodide.*—2-Iodoquinoline ethiodide and 2 : 6-dimethylquinoline ethiodide, condensed in absolute alcoholic solution, gave a 31% yield of the ψ-cyanine, after recrystallisation from methyl alcohol. It forms red needles, m. p. 258° (decomp.) (Found : I, 27·0. $C_{24}H_{25}N_2I$ requires I, 27·1%). With a bathed plate, there is a sensitivity maximum at λ 5800, falling off steeply towards the red. The gap between this crest and the band of ordinary sensitivity has its lowest point at λ 5300. The chief absorption band shows a maximum at λ 5300 and the weaker band a maximum at λ 4950.

1 : 1′-*Diethyl*-5 : 6 (or 5′ : 6′)-*benz-ψ-cyanine Iodide.*—The condensation of β-naphthaquinaldine ethiodide with 2-iodoquinoline ethiodide is best effected in aqueous solution, giving, after recrystallisation from spirit, a 26% yield of dye, as minute dark green crystals, m. p. 273° (decomp.) (Found : I, 25·2. $C_{27}H_{25}N_2I$ requires I, 25·2%). A plate bathed in its solution is deeply stained; the extra sensitivity is less strong than the blue sensitivity, there is a gap with its minimum at λ 5300 and a maximum at λ 5750, the sensitisation extending to λ 6100 for moderate exposures. In the emulsion, both the ordinary and the extra sensitivity are less and the maximum lies at λ 5850. The absorption maxima are at λ 5000 and λ 5380, the latter being the stronger.

1 : 1′-*Dimethyl*-5 : 6 (or 5′ : 6′)-*benz-ψ-cyanine Iodide.*—β-Naphthaquinaldine methiodide was condensed with 2-iodoquinoline methiodide in aqueous solution, and the product was washed with boiling water in order to remove unchanged β-naphthaquinaldine methiodide and was then recrystallised from methyl alcohol: a dark, crystalline powder was obtained in 15% yield, m. p. about 266° (decomp.) (Found : I, 26·5. $C_{25}H_{21}N_2I$ requires I, 26·65%).

The sensitising action of a bathed plate extends to λ 6300 for moderate exposures and the maximum lies at λ 5700. The absorption is like that of the preceding compound.

1 : 1′-*Dimethyl*iso*cyanine Iodide*.—The *iso*cyanine was obtained by the action of potassium hydroxide (0·8 g.), dissolved in absolute alcohol (10 c.c.), on a boiling mixture of absolute alcohol (100 c.c.), lepidine methiodide (2 g.; 1 mol.), and 2-iodoquinoline methiodide (2·8 g.; 1 mol.), and the yield after recrystallisation was 34% of that theoretically possible (Found: I, 29·9. Calc. for $C_{21}H_{19}N_2I$: I, 29·8%). The dye was identical in appearance with 1 : 1′-dimethyl*iso*cyanine iodide prepared in the usual way from quinoline methiodide and quinaldine methiodide. Both specimens, and their mixture, possessed the same m. p., and solutions of both showed an identical absorption and imparted the same extra sensitivity to a plate on bathing.

1 : 1′-*Diethyl*iso*cyanine Iodide*.—Condensation of lepidine ethiodide with 2-iodoquinoline ethiodide was carried out similarly and the recrystallised dye was obtained in 45% yield; the yield was only half as great when the condensation was effected in aqueous solution (Found: I, 27·9. Calc. for $C_{23}H_{23}N_2I$: I, 27·9%). The dye was identical in appearance, absorption, and sensitising action on a plate on bathing, with a specimen of 1 : 1′-diethyl*iso*cyanine iodide prepared from quinoline ethiodide and quinaldine ethiodide, and the m. p.'s and mixed m. p. were also the same.

1′ : 2-*Diethylthio-ψ-cyanine Iodide*.—The compound is obtained, in 31% yield, by adding potassium hydroxide (0·7 g.; more than 2 mols.), dissolved in absolute alcohol (10 c.c.), to a hot mixture of absolute alcohol (100 c.c.), 2-iodoquinoline ethiodide (2 g.; 1 mol.), and 1-methylbenzthiazole ethiodide (1·5 g.; 1 mol.), boiling for ½ hour, and recrystallising the product from spirit; it separates as scarlet needles, m. p. 285° (decomp.), as recorded by Mills and Braunholtz (*loc. cit.*) (Found: I, 27·3. Calc. for $C_{21}H_{21}N_2IS$: I, 27·6%). With a bathed plate, the sensitising band is almost uniform, with a maximum at λ 5300 and a very slight depression at λ 5000, the sensitisation extending to λ 5600; in the emulsion, the extra sensitivity is distinctly weaker than the blue sensitivity and the depression is more marked.

1′ : 2-*Dimethylthio-ψ-cyanine Iodide*.—This dye, prepared from 2-iodoquinoline methiodide and 1-methylbenzthiazole methiodide was obtained, after recrystallisation from rectified spirit, in 38% yield; the red crystals show m. p. about 272—276° (decomp.) (Found: I, 29·5. $C_{19}H_{17}N_2IS$ requires I, 29·4%). A plate bathed in its solution shows a uniform sensitisation band extending to λ 5300, falling to a minimum at λ 5700, rising again to a maximum at λ 6000, and decreasing to zero at λ 6400; but in the emulsion there is practically no extra sensitivity.

1′-*Methyl*-2-*ethylthio*-ψ-*cyanine Iodide*.—The compound was prepared from 2-iodoquinoline methiodide and 1-methylbenzthiazole ethiodide and, after recrystallisation from spirit, resulted in 45% yield. It forms small scarlet crystals, m. p. about 266° (decomp.) (Found : I, 28·5. $C_{20}H_{19}N_2IS$ requires I, 28·5%). When the dye is added to the emulsion, there is a strong sensitising band with its maximum at λ 5300 and a weaker one with its crest at λ 5800.

2-*Methyl*-1′-*ethylthio*-ψ-*cyanine Iodide*.—This dye was similarly prepared from 2-iodoquinoline ethiodide and 1-methylbenzthiazole methiodide. It crystallises from spirit, in 36% yield, as red needles, m. p. about 261—264° (decomp.) (Found : I, 28·7. $C_{20}H_{19}N_2IS$ requires I, 28·45%). The sensitivity of a bathed plate is extended to λ 5350 as a uniform band, which then decreases, but rises to a small crest at λ 5900. With addition of the dye to the emulsion there is a distinct gap between the ordinary and the extra sensitivity, so that a maximum becomes visible at λ 5300; the curve then falls off steeply to a minimum at λ 5600, but rises again to a small crest at λ 5800. The absorptions of this and the three preceding thio-ψ-cyanines are very similar : in each case there is a strong absorption band with its maximum at λ 4850 and a very feeble maximum at λ 4600.

1 : 3 : 3 : 1′-*Tetramethylindo*-ψ-*cyanine Iodide*.—2-Iodoquinoline methiodide (2 g.; 1 mol.), 2 : 3 : 3-trimethylindolenine methiodide (1·5 g.; 1 mol.), and absolute alcohol (10 c.c.) were treated with potassium hydroxide (0·7 g.; more than 2 mols.) dissolved in absolute alcohol (10 c.c.), and the mixture was boiled for 2 hours. The alcohol was evaporated off, water added, and the precipitated solid extracted with ether. The undissolved residue was recrystallised from methyl alcohol; the dye was then obtained, in 26% yield, as brick-red, lustrous crystals, m. p. 247° (decomp.) (Found : I, 28·8. $C_{22}H_{23}N_2I$ requires I, 28·7%). Whether the compound is added to the emulsion before coating or whether a plate is bathed in its solution, there is an extremely feeble extension of the sensitivity to λ 5800, accompanied by a decrease in the ordinary sensitivity. The broad absorption curve shows a maximum at λ 4700.

3 : 3-*Dimethyl*-1 : 1′-*diethylindo*-ψ-*cyanine Iodide*.—This was similarly prepared from 2-iodoquinoline ethiodide and 2 : 3 : 3-trimethylindolenine ethiodide. After removal of the alcohol from the reaction mixture, the residue was ground with benzene and water, the solid purified by extraction with ether, and the undissolved residue recrystallised from water : a 22% yield resulted, in the form of brown crystals with a green lustre, m. p. about 222° (decomp.)

(Found : I, 26·8. $C_{24}H_{27}N_2I$ requires I, 27·0%). By bathing a plate in a solution of the dye, or by adding the latter to the emulsion, a feeble sensitisation is imparted, extending to λ 5800, and there is a weak maximum at λ 5250. The symmetrical absorption curve has a maximum at λ 4800.

RESEARCH LABORATORY, ILFORD LIMITED,
ILFORD, E.

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