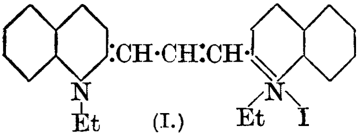
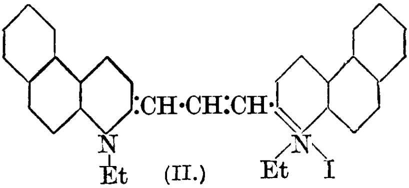
# CXXIII.—*Attempts to prepare Cyanine Dyes from Quaternary Salts of 2-Methylacenaphthpyridine and of 5-Methylacridine.*

By Frances Mary Hamer.

With any class of dye, there is a tendency for increase in molecular weight to be accompanied by a shift of the absorption bands towards the red end of the spectrum. Where the dyes are photographic sensitisers, there is a corresponding shift of the maxima of extra-sensitisation. Dyes which sensitise further into the red should therefore be obtainable by replacing the nuclei of known sensitisers by heavier nuclei. An example of the shift which occurs with increase in molecular weight is afforded by comparison of pinacyanol (I), for which the maximum of the chief sensitising band lies at λ 6375 Å., with the carbocyanine (II), which has its sensitising maximum at λ 6900 Å. (Mees and Gutekunst, *J. Ind. Eng. Chem.*, 1922, **14**, 1060). So also, the cyanine dyes recently prepared from quaternary salts of methyl-α- and -β-naphthathiazoles show absorption further towards the red than the corresponding dyes prepared from salts of methylbenzthiazole, the shift being greater with the thiocarbocyanines, where two benzthiazole nuclei are replaced by two naphthathiazole nuclei, than with the thio-ψ-cyanines, where there is only one such replacement (Hamer, J., 1929, 2598). In this connexion it seemed of interest to prepare quaternary salts of 2-methylacenaphthpyridine (III) and of 5-methylacridine (IV) in order to see whether such salts would give rise to cyanine dyes and, if so, to examine the photographic properties of the latter.



(I.)



(II.)

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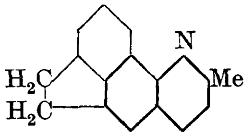
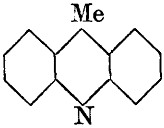
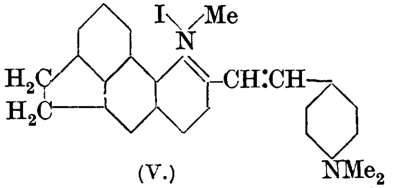




(IV.)

2-Methylacenaphthpyridine has been prepared from 3-amino-acenaphthene. Sachs and Mosebach's original method for reducing 3-nitroacenaphthene (*Ber.*, 1911, **44**, 3855), used also by Stewart (J., 1925, **127**, 1331), has been said by Fleischer and Schranz to give only a 20% yield, the chief product being the sodium salt of *N*-acenaphthyl-3-sulphaminic acid (*Ber.*, 1922, **55**, 3253); their observation that this salt remains in solution was not confirmed. Their method of preparation (see also Morgan and Stanley, *J. Soc. Chem. Ind.*, 1924, **43**, 343T) was adopted, with very slight modification. The preparation, from 3-aminoacenaphthene, by the action of paraldehyde and hydrochloric acid, of 2-methylacenaphthpyridine has been described by Nair and Simonsen (J., 1926, 3140). But as they proceed, without removal of the tar which accompanies the condensation product, to treat the reaction mixture with alkali, modification was required. Comparative experiments showed the large excess of paraldehyde and of hydrochloric acid to be unnecessary, as also is the protracted time of heating.

The *methiodide* of 2-methylacenaphthpyridine was prepared, but similar conditions gave only a trace of the corresponding ethiodide. The methiodide condenses with *p*-dimethylaminobenzaldehyde and with *p*-nitrosodimethylaniline: as in analogous cases (Hamer, J., 1924, **125**, 1348; 1929, 2598), the former product (V) is a sensitiser and the latter (VI) a desensitiser. 2-Methylacenaphthpyridine methiodide reacts with quinoline methiodide or ethiodide to give an iso*cyanine* (VII) and with 2-iodoquinoline methiodide or ethiodide to give a *ψ-cyanine* (VIII), the latter condensation proceeding better in aqueous solution than in the more generally applicable alcoholic solution (compare Hamer, J., 1928, 206). Comparison of the absorption bands of these new cyanines, in alcoholic solution, with those of the parent dyes reveals a shift of 150 Å. towards the red. Mr. O. F. Bloch found the compounds to be photographic sensitisers, but of no outstanding merit. It is remarkable, in view of its reactivity, that 2-methylacenaphthpyridine methiodide does not yield



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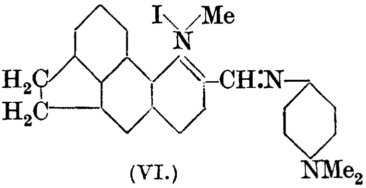
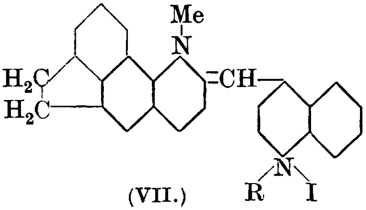
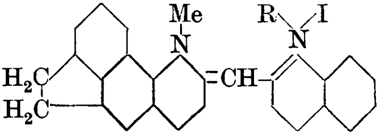


(VI.)



(VII.)



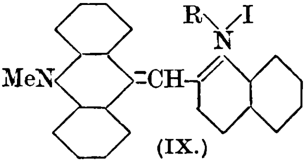
(VIII.)

a carbocyanine by the ethyl orthoformate and pyridine method (Hamer, J., 1927, 2796); the use of acetic anhydride as solvent is no more successful.

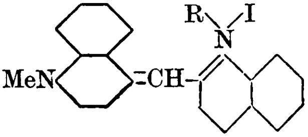
5-Methylacridine has previously been prepared from diphenylamine by the action of acetonitrile or acetic acid (Bernthsen, *Annalen*, 1878, **192**, 29; Fischer and Rudolph, *Ber.*, 1882, **15**, 1500; Besthorn and Fischer, *Ber.*, 1883, **16**, 68; Bernthsen and Bender, *ibid.*, p. 1802; Fischer, *ibid.*, p. 1820; Bernthsen, *Annalen*, 1884, **224**, 1). In the present work, however, it was prepared from acetyldiphenylamine, by heating it with zinc chloride in a sealed tube; it was conveniently isolated as its tartrate, by Koenigs' method (*Ber.*, 1899, **32**, 3599).

5-Methylacridine methiodide has been prepared by Bernthsen (*Annalen*, 1884, **224**, 1), by Decker (*Ber.*, 1905, **38**, 2493), by Freund and Bode (*Ber.*, 1909, **42**, 1746), and by Kaufmann and Albertini (*Ber.*, 1911, **44**, 2052). Except for the statement of the last-named authors, that the dust of the methiodide attacks the breathing organs, there is no reference to the strong sternutatory action which is the most striking characteristic of this salt.

Now the reactivity of the methyl group in 5-methylacridine itself is manifested by its condensation with (*a*) chloral (Bernthsen and Muhlert, *Ber.*, 1887, **20**, 1541), (*b*) benzaldehyde and its *m*- and *p*-nitro-derivatives (Friedländer, *Ber.*, 1905, **38**, 2840; Porai-Koschitz, *Z. Farb. Text.-ind.*, 1907, **6**, 291), (*c*) *p*-nitrosodimethylaniline (Kaufmann and Vallette, *Ber.*, 1912, **45**, 1736), and (*d*) formaldehyde (Koenigs, *loc. cit.*; Homberger and Jensen, *J. Amer. Chem. Soc.*, 1926, **48**, 800). Since the quaternary salts of a base containing a reactive methyl group are, in general, more reactive than is the base itself (Mills and Smith, J., 1922, **121**, 2724), it was both surprising and interesting to obtain a series of negative results in the case of 5-methylacridine methiodide. For instance, it did not react (*a*) with ethyl orthoformate in the presence of pyridine to give a carbocyanine, (*b*) with quinoline methiodide in aqueous-alcoholic solution, under the influence of sodium hydroxide, to give an *iso*cyanine, (*c*) with *p*-dimethylaminobenzaldehyde, in absolute alcoholic solution and in the presence of piperidine, or (*d*) with *p*-nitrosodimethylaniline, under similar conditions. (*e*) An attempt to effect condensation between it and 2-iodoquinoline methiodide by the normal procedure, absolute alcohol being used as solvent and potassium hydroxide as condensing agent (Hamer, J., 1928, 206), also gave a negative result. But when water was employed as the solvent medium, condensation between 5-methylacridine methiodide and 2-iodoquinoline methiodide or ethiodide took place. Although these new dyes (IX) may be regarded as derived from the simple *iso*cyanine (X), their absorption spectra are of a different character, showing one broad band, with an ill-defined maximum, whereas the latter has two well-marked, relatively narrow bands. The maximum of this broad band is in approximately the same position as that of the chief band of the parent *iso*cyanine, instead of showing the expected shift towards the red. Both the new dyes are entirely devoid of sensitising properties.



(IX.)



(X.)

## EXPERIMENTAL.

3-*Aminoacenaphthene.*—A mixture of 3-nitroacenaphthene (40 g.) with spirit (400 c.c.) and water (200 c.c.) was boiled in a flask (3 l. capacity). It was removed from the water-bath for the addition of sodium hydrosulphite (100 g.) in three portions, reaction occurring at each addition. After 15 minutes' boiling, the spirit was distilled off and the residue treated with water (500 c.c.) and boiled. When cold, the solid was filtered off, ground to a paste with water, and hydrolysed by heating on the water-bath with concentrated hydrochloric acid (300 c.c.) and water (1200 c.c.). The violent bumping, which occurs on boiling, does not take place on the water-bath, and the isolation of the solid before hydrolysis has the advantage of avoiding the copious evolution of sulphur dioxide, caused by addition of the acid to the reaction mixture, both these being points whereby the earlier method has been modified. The liquid was filtered hot, to remove a little black matter, and the filtrate was made alkaline with ammonia. The yield of base, after washing with water and drying, was 63—64%, and, after recrystallisation from petrol, 49—53%. M. p. 107°.

2-*Methylacenaphthpyridine.*—3-Aminoacenaphthene (40 g.; 1 mol.) was treated with hydrochloric acid ($d$ 1·19; 40 c.c.) and paraldehyde (26 c.c.; 2·5 mols.). The flask was cooled with water in order to abate the violence of the reaction, which occurs without the application of external heat. Finally it was heated on the water-bath for ½-hour and water (1 l.) was added. When cold, the mixture was filtered from tar, and the filtrate and washings were treated with excess of ammonia. The aqueous liquid was poured off from the semi-solid base and the latter was twice extracted with hot 10% sulphuric acid (80 + 40 c.c.), the extract being filtered hot. The yellow sulphate, which slowly crystallised from the filtrate, was collected, washed with acetone (31·9 g. obtained), dissolved in hot water, and treated with ammonia. The crude base (20·3 g.) was obtained in 39% yield and after recrystallisation from spirit the yield (15·2 g.) was 29%. M. p. 131°, as recorded by Nair and Simonsen (*loc. cit.*).

2-*Methylacenaphthpyridine Methiodide.*—2-Methylacenaphthpyridine (10 g.) and methyl iodide (10 c.c.) were heated in a sealed tube at 100° for 2 days. The product was extracted with ether; the undissolved residue (12·8 g.; 78% yield) separated from spirit in orange crystals (62% yield), m. p. about 212°. A specimen was dried in a vacuum desiccator before analysis, the method of Carius being used in this, and in all subsequent halogen determinations, except where otherwise stated (Found: I, 35·0. $C_{17}H_{16}NI$ requires I, 35·2%).

2-p-*Dimethylaminostyrylacenaphthpyridine Methiodide* (V).—2-Methylacenaphthpyridine methiodide (3 g.; 1 mol.) and *p*-dimethylaminobenzaldehyde (1·24 g.; 1 mol.), dissolved in hot 99% spirit (300 c.c.), were treated with piperidine (0·5 c.c.) and the mixture was boiled for 5 hours. The solid was filtered off when cold, and the filtrate concentrated to ⅓ volume in order to obtain a second crop (total yield, 2·9 g.). The product was twice boiled out with methyl alcohol (2 × 50 c.c.), and the undissolved residue recrystallised from spirit (750 c.c.). The *methiodide* (V) (24% yield) was again recrystallised and was dried for analysis in a vacuum at 100—120° (Found: I, 25·5. $C_{26}H_{25}N_2I$ requires I, 25·8%). The green crystals melt at 224° (decomp.). The spirit solution has a wide absorption band with its maximum at about λ 5200 Å. A plate bathed in this solution acquires a feeble extra sensitivity, extending to λ 7100 Å., but the dye is less effective when added to the emulsion.

p-*Dimethylaminoanil of Acenaphthpyridine-2-aldehyde Methiodide* (VI).—2-Methylacenaphthpyridine methiodide (3 g.; 1 mol.) and *p*-nitrosodimethylaniline (1·25 g.; 1 mol.) were boiled in absolute alcoholic solution (50 c.c.), with addition of piperidine (2 drops), for 6 hours. The product (3·2 g.; 78% yield) was recrystallised from methyl alcohol (1500 c.c.; 2·05 g. obtained; 50% yield). After a second recrystallisation the olive-green crystals, m. p. 195° (decomp.), were dried for analysis in a vacuum at 60—80° (Found: I, 25·4. $C_{25}H_{24}N_3I$ requires I, 25·7%). The *compound* desensitises photographic plates more powerfully than does safranine, but is of no practical use because its desensitising action is destroyed by the sulphite and carbonate of the developer.

iso*Cyanine* (VII) *from* 2-*Methylacenaphthpyridine Methiodide and Quinoline Methiodide.*—2-Methylacenaphthpyridine methiodide

(6 g.; 1 mol.) and quinoline methiodide (9·0 g.; 2 mols.) were boiled with absolute alcohol (300 c.c.) and the mixture was treated with sodium (0·46 g.; 1·2 mols.), dissolved in absolute alcohol (30 c.c.), and then boiled for 15 minutes. The solid (5·5 g.), which separated on cooling, was twice boiled out with methyl alcohol (50 + 100 c.c.), and the undissolved residue was recrystallised from methyl alcohol. The small green crystals (1·17 g.; 14% yield) obtained from this third fraction were again recrystallised from methyl alcohol (200 c.c.; 0·83 g. obtained; 10% yield). The iso*cyanine* was dried in a vacuum at 60—80° (Found: C, 64·2; H, 5·0; I, 25·1. $C_{27}H_{23}N_2I$ requires C, 64·5; H, 4·6; I, 25·3%). When it is heated, a change occurs between 160° and 170° and, if heating is rapid, the dye even melts; if slowly heated, melting with decomposition occurs between 220° and 240°, the exact point depending upon the rate of rise of temperature. The chief absorption band of the spirit solution has its maximum at λ 5750 Å., and there is another maximum at λ 5400 Å. A plate bathed in the solution shows a very uniform band of extra sensitisation, extending to λ 6800 Å. for moderate exposures and with maxima at λ 6100 Å. and λ 5400 Å.

iso*Cyanine from 2-Methylacenaphthpyridine Methiodide and Quinoline Ethiodide.*—Similarly, 2-methylacenaphthpyridine methiodide (6 g.) was condensed with quinoline ethiodide (9·47 g.) and the resultant dye (4·85 g.) was extracted with ether. The undissolved residue (4·5 g.) was boiled with insufficient methyl alcohol (50 c.c.) to dissolve it; the residue was recrystallised from methyl alcohol (200 c.c.), giving green crystals, m. p. about 217° (decomp.), in 16% yield (1·39 g.). They were dried for analysis in a vacuum at 100—110° (Found: I, 24·7. $C_{28}H_{25}N_2I$ requires I, 24·6%). The chief absorption band of the spirit solution lies at λ 5850 Å. and the secondary one at λ 5400 Å. The sensitising action conferred on a plate bathed in a solution of the dye extends to λ 6600 Å., and is not quite so uniform as that of the preceding compound, showing a distinct gap at λ 5000 Å. One maximum, at λ 6050 Å., is more strongly marked than the other, which is at λ 5500 Å.

*ψ-Cyanine* (VIII) *from 2-Methylacenaphthpyridine Methiodide and 2-Iodoquinoline Methiodide.*—Crude 2-iodoquinoline methiodide (8 g.; 1 mol.) was added to boiling water (500 c.c.), and a little undissolved periodide filtered off. 2-Methylacenaphthpyridine methiodide (7·27 g.; 1 mol.) was added, followed by an aqueous solution (40 c.c.) of potassium hydroxide (3·0 g.; 2·4 mols.), and boiling was continued for 5 minutes. The resultant solid was purified by boiling out with water and the residue (3·8 g.) was extracted with ether in a Soxhlet apparatus. The undissolved residue (3·6 g.) was recrystallised from methyl alcohol (750 c.c.; 2·1 g. obtained; 21% yield). After a second recrystallisation from methyl alcohol (400 c.c. for 1·9 g., giving 1·2 g.; 13% yield), the *ψ-cyanine* was dried in a vacuum at 60—80° (Found: I, 24·9. $C_{27}H_{23}N_2I$ requires I, 25·3%). The compact bronze crystals melt at 236° (decomp.). With a spirit solution, the chief absorption band has its crest at λ 5400 Å.: the second band, which is almost as strong, has its crest at λ 5100 Å. On bathing plates, a band of extra sensitisation is conferred, extending to λ 6400 Å. for moderate exposures, and with its maximum at λ 5700 Å.

*ψ-Cyanine from 2-Methylacenaphthpyridine Methiodide and 2-Iodoquinoline Ethiodide.*—From 2-iodoquinoline ethiodide (4 g.) and 2-methylacenaphthpyridine methiodide (3·51 g.), the *ψ-cyanine*, similarly precipitated by the action of potassium hydroxide, was at first obtained in the form of a tar, which improved during boiling and hardened when cold. It was extracted with hot water and the residue (2·44 g.) was extracted with ether in a Soxhlet apparatus. That residue (2·33 g.) was recrystallised from methyl alcohol (200 c.c.; 1·32 g. obtained; 26% yield). It was dried for analysis in a vacuum at 100—110° (Found: I, 24·4. $C_{28}H_{25}N_2I$ requires I, 24·6%). The dye forms small brownish-red crystals, m. p. 201° (decomp.). The principal absorption band is at λ 5450 Å. and there is another at 5100 Å. It exerts a powerful sensitising action on plates bathed in its solution; the action extends to λ 6400 Å. for moderate exposures and shows maxima at λ 5700 Å. and 5100 Å.

*Acetyldiphenylamine.*—Diphenylamine has been acetylated by means of acetyl chloride (Meister, *Ber.*, 1872, **5**, 283; Merz and Weith, *Ber.*, 1873, **6**, 1511) and by acetic anhydride (Claus, *Ber.*, 1881, **14**, 2365). In a modification of the latter method, diphenylamine (30 g.), acetic anhydride (60 c.c.), and fused sodium acetate (30 g.) were heated together on the water-bath for 1½ hours and the product was treated with water and ammonia. After recrystallisation from very dilute spirit, the base was obtained in 80% yield. It melted at 84—85° with previous softening, but lost solvent of crystallisation on drying on the water-bath and in a vacuum desiccator; the anhydrous substance melted at 101—102°. Meister, and Merz and Weith, give m. p. 99·5°, Claus gives m. p. 103°, and Wallach (*Annalen*, 1882, **214**, 234) gives m. p. 101—102°.

5-*Methylacridine.*—A mixture of acetyldiphenylamine (5 g.) with five times its weight of powdered zinc chloride was heated in a sealed tube at 220—240° for 6½ hours. The dark mass was extracted with hot 50% sulphuric acid and the extract was treated with water and excess of ammonia to precipitate the base. This was extracted with benzene and, after removal of the solvent, the residue was dissolved in hot spirit and treated, as by Koenigs (*loc. cit.*), with a hot solution of tartaric acid (5 g.) in spirit (50 c.c.). The tartrate (6·9 g.) was suspended in cold water and treated with excess of sodium carbonate solution and the base was extracted with ether, the extract being dried with potassium hydroxide. The residue (74% yield) after removal of the solvent was recrystallised from dilute spirit and dried on the water-bath and in a vacuum desiccator (46% yield). M. p. 117—118° as found by Koenigs (*loc. cit.*); Decker's observation (*loc. cit.*) as to the low m. p. before removal of solvent of crystallisation was confirmed.

5-*Methylacridine Methiodide.*—5-Methylacridine (3·7 g.) and methyl iodide (3·7 c.c.) were heated for 2 days in a sealed tube at 100°. The product was extracted with ether, and the undissolved residue (5·9 g.; 92% yield) recrystallised from water (about 300 c.c.; 4·1 g. obtained; 64% yield). It was dried in the steam-oven before analysis; a solution in dilute sulphuric acid was treated with silver nitrate (Found: I, 37·8. Calc. for $C_{15}H_{14}NI$: I, 37·9%). Melting with decomposition occurred at about 263°. Bernthsen (*Annalen*, 1884, **224**, 1) gives m. p. 185° (decomp.), Freund and Bode (*loc. cit.*) give m. p. 273—275°, and Kaufmann and Albertini (*loc. cit.*) give m. p. 235—245°, with decomposition from 200°.

1 : 1′-*Dimethyl*-2 : 3(or 2′ : 3′)-*benz*iso*cyanine Iodide* (IX; R = Me).—5-Methylacridine methiodide (1 g.; 1 mol.) and 2-iodoquinoline methiodide (1·2 g.; 1 mol.) were added to boiling water (60 c.c.), potassium hydroxide (0·4 g.; more than 2 mols.) dissolved in water (10 c.c.) was added, and the mixture was boiled for 5 minutes. The blue tar produced, which solidified on cooling, was filtered off and extracted with ether. The undissolved residue (0·84 g.; 59% yield) was recrystallised from methyl alcohol (40 c.c.), the *iodide* (IX) being thus obtained in 25% yield (0·36 g.). It was dried in a vacuum at 100—110° before analysis (Found: I, 26·8. $C_{25}H_{21}N_2I$ requires I, 26·65%). It forms long crystals with a bronze lustre. M. p. about 250—265°, but the exact point is quite indefinite, since decomposition begins at about 230°. Its spirit solution has a broad absorption band extending from λ 4700 Å. to 6200 Å., and with a maximum at about 5500 Å.

1(or 1′)-*Methyl*-1′(or 1)-*ethyl*-2 : 3(or 2′ : 3′)-*benz*iso*cyanine iodide* was similarly prepared from 5-methylacridine methiodide (3 g.) and 2-iodoquinoline ethiodide (3·68 g.). After ether extraction, the undissolved residue (3·05 g.) was dissolved in hot chloroform (800 c.c.). The solution was concentrated and from it, on cooling, the dye was obtained in crystalline form (2·0 g.). It was recrystallised from methyl alcohol (40 c.c.) and was thus obtained in 29% yield (1·25 g.). It was again recrystallised from methyl alcohol and was dried for analysis in a vacuum at 100—110° (Found: I, 25·8. $C_{26}H_{23}N_2I$ requires I, 25·9%). It forms lustrous dark green crystals, which soften at 150—160° but do not melt until about 232°; if they are put into a bath at 160°, however, melting occurs at once. The absorption of the spirit solution is very like that of the preceding dye.

British Photographic Plates and Papers, Ltd.,
Ilford, E.
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