7. *Some Unsymmetrical Pentamethincyanine Dyes and their Tetramethin Intermediates.*

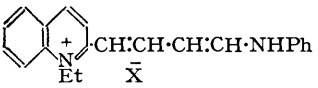
By Frances M. Hamer.

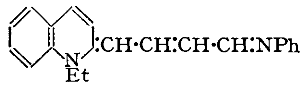
Crude iodides, obtained by condensing quaternary, heterocyclic ammonium salts, having a reactive methyl group, with β-anilinoacraldehyde anil hydrochloride, were converted into bases, and those into *perchlorates*: such anilinobutadienyl compounds were prepared in the 2- and 4-linked quinoline, benzthiazole, substituted indolenine, and benzselenazole series. Corresponding *iodides* (five new) of the 2- and 4-linked quinoline, benzthiazole, 6 : 7-benzbenzthiazole, benzselenazole, benzoxazole, and Δ^2-thiazoline series were prepared by condensing the ammonium salt with β-ethoxyacraldehyde diethyl acetal, then heating with aniline. Nine of the anilino-compounds were acetylated. Such acetanilido-compounds were used for preparing unsymmetrical *pentamethincyanines* containing a thiazoline nucleus and a 2- or 4-linked quinoline, benzthiazole, or benzoxazole nucleus, and one containing a 2-linked and a 4-linked quinoline nucleus. Absorption maxima of methyl-alcoholic solutions are recorded.

Having synthesised neocyanines with dissimilar nuclei (Hamer, Rathbone, and Winton, *J.*, 1948, **1872**), we desired to compare their absorption maxima with those of the corresponding parent dyes, both tri- and penta-methincyanines; also to compare the absorption maxima of certain new anilomethyl intermediate dyes (*loc. cit.*) with the tetramethin dyes which are intermediates in the preparation of pentamethincyanines. As regards unsymmetrical pentamethincyanines and their tetramethin intermediates, we came to certain gaps in the scientific literature. Although such preparations have been covered by patents, the obtaining of pure specimens is not so easy as might appear, and the present account is given in order to bridge the gaps.

The condensation of quaternary, heterocyclic ammonium salts, having a reactive methyl group, with β-anilinoacraldehyde anil hydrochloride, in the presence of acetic anhydride, to give pentamethincyanines or tetramethin intermediates, according to conditions (I.C.I. Ltd., Piggott, and Rodd, B.P. 355,693/1930), was claimed to proceed better in an alkaline medium (I.G. Farbenind. A.-G., B.P. 434,234/1933). But although, for instance, a quinaldinium salt, by boiling with an equimolecular amount of the anil hydrochloride in pyridine, appears to give a quantitative yield of tetramethin intermediate (I; $X = I$), in practice it was not possible to isolate a pure specimen by fractional crystallisation. When such a salt is treated with alkali, presumably HX is eliminated, yielding the base (II) (Kodak Ltd., B.P. 561,172/1940), and the corresponding base of the benzthiazole series has actually been isolated and recrystallised (Brooker, White, Keyes, Smyth, and Oesper, *J. Amer. Chem. Soc.*, 1941, **63**, 3192). In the present work, the base of the 2-quinoline series was freed from impurities by extraction with light petroleum, after which the extract was acidified and the *ethoperchlorate* (I; $X = ClO_4$) was precipitated. A similar procedure was adopted to give the corresponding *lepidinium* salt. *Tetramethin* intermediates of the benzthiazole series (III; $Y = S$) and of the indolenine series (IV) were similarly prepared, but to obtain the *intermediate* in the benzselenazole series (III; $Y = Se$) the extraction with light petroleum was best omitted.

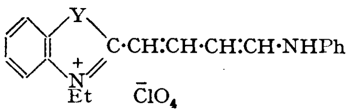
(I.)

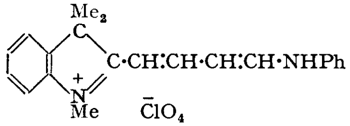




(II.)

(III.)

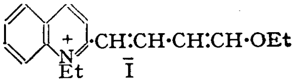


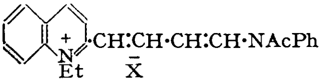


(IV.)

Sprague found that if a quaternary heterocyclic ammonium salt, having a reactive methyl group, is heated with β-ethoxyacraldehyde diethyl acetal in the presence of acetic acid, another type of tetramethin intermediate resulted, *e.g.*, (V), starting from quinaldine ethiodide (Kodak Ltd., B.P. 556,266/1940). In the present work no attempt was made to isolate (V) in a state of purity but the crude product was condensed with aniline, as is suggested (*loc. cit.*), to give the

(V.)



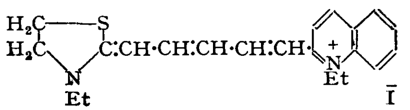


(VI.)

ethiodide (I; X = I); and similarly with the crude ethoxy-compound derived from lepidine ethiodide. (I; X = I) had previously been reached by treating the acetanilido-compound (VI; X = I) with aniline (Brooker *et al.*, *loc. cit.*). Both the ethiodide and the *ethoperchlorate* in the 2-quinoline series (I; X = I or ClO_4) were acetylated to give (VI; X = I or ClO_4), and so also in the 4-quinoline series. The acetal method was also applied in the benzthiazole, 6 : 7-benzbenzthiazole, and benzselenazole series, and proved especially valuable for preparing the *tetramethin* intermediates of the benzoxazole and Δ^2-thiazoline series, as these could not be reached by the anil method; all five of these ethiodides were acetylated.

The absorption curves of methyl-alcoholic solutions were plotted, but to obtain consistent data for the maxima of anilino-compounds such as (I), it proved desirable to use acidified solutions, since there is in solution an equilibrium between the salt (I) and the base (II). In two instances the maxima did show approximately the agreement that should be expected with values recorded for the corresponding ethiodides (B.P. 434,234), but with (I) itself the discrepancy was 105 A., and in the 4-quinoline series (ethoperchlorate compared with methiodide) it was 140 A. To obtain absorption data for bases, such as (II), basified methyl-alcoholic solutions of the perchlorates were used. There were bathochromic shifts on passing from the absorption maximum of base to that of salt, the eight values varying from 295 to 715 A. The shifts on passing from anilino-salts, such as (I), to the corresponding acetanilido-salts, such as (VI), were hypsochromic (cf. Brooker *et al.*, *loc. cit.*), the seven values varying from 435 to 1295 A. The absorption measurements revealed that acetanilido-salts of the benzoxazole, 6 : 7-benzbenzthiazole, and thiazoline series rapidly hydrolyse to the anilino-salts. With the benzoxazole salt it was possible, by avoiding delay, to record the position of the maximum of the acetanilido-compound in methyl-alcoholic solution but in the thiazoline series hydrolysis was too rapid. That maximum, as also that in the benzbenzthiazole series, was determined in acetic acid solution; the maxima of the corresponding anilino-compounds in acetic acid solution, as determined for comparison, proved to be the same as for the acidified methyl-alcoholic solutions. The acetanilido-salts deteriorated on keeping, giving off acetic acid, so that for dye preparations it was desirable to use freshly prepared samples.

The desired unsymmetrical pentamethincyanines were prepared by condensing a quaternary salt, having a reactive methyl group, with a tetramethin intermediate, having an acetanilido-group, in the presence of triethylamine in ice-cold alcohol (cf. Brooker, B.PP. 436,941; 436,017/1933). Thus (VII) was prepared from quinaldine ethiodide and the acetanilido-compound of the Δ^2-thiazoline series, whilst an *isomeride*, having a 4-quinoline, instead of a 2-quinoline nucleus, was similarly prepared by use of lepidine ethiodide. The same acetanilido-compound with 2-methylbenzthiazole ethiodide gave a *pentamethincyanine* with one Δ^2-thiazoline and one benzthiazole nucleus but, even under the mild reaction conditions, this was accompanied by a by-product, the pentamethincyanine with two benzthiazole nuclei. The same acetanilido-compound gave little sign of reaction with 2-methylbenzoxazole ethiodide: (VIII) was, however, prepared by the alternative route of condensing the acetanilido-compound of the benzoxazole series with 2-methyl-Δ^2-thiazoline ethiodide; by using the anilino- instead of the acetanilido-compound of the benzoxazole series, only a negative result was obtained. (IX) was prepared by condensing the acetanilido-compound of the 4-quinoline series with quinaldine ethiodide.



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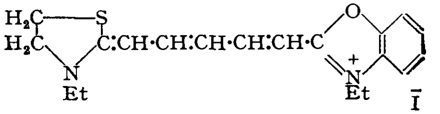

(VIII.)

(IX.)

Both the pentamethincyanines and tetramethin intermediates comprise photographic sensitisers. The photographic tests were carried out on gelatino-bromide plates unless otherwise stated.

EXPERIMENTAL.

2-(4′-*Anilinobuta*-1′ : 3′-*dienyl)quinoline Ethoperchlorate* (I; X = ClO_4).—Quinaldine etho-*p*-toluenesulphonate (6·61 g.; 1 mol.), β-anilinoacraldehyde anil hydrochloride (5·48 g.; 1·1 mols.), and pyridine

(20 c.c.) were boiled together for 3 minutes. The reaction mixture was treated hot with a solution of potassium iodide (12·79 g.; 4 mols.) in water (20 c.c.) and the dye iodide was filtered off and washed (8·28 g.; 100% yield). It was ground and shaken with acetone (80 c.c.) and a solution of sodium hydroxide (9·3 g.; 12 mols.) in water (55 c.c.). After separation of dye by-product, the acetone extract was added to ice-cold water (345 c.c.). After standing in the cold, the liquid was decanted from the deposited tar, which was further washed, dried in a vacuum desiccator, and thrice extracted with light petroleum (b. p. 80—100°; 3 × 500 c.c.). The extracts of base were treated with acetic acid (30 c.c.) and cooled. The solvent was decanted off, the tar taken up in acetic acid (40 c.c.), and the solution treated hot with one of sodium perchlorate (5 g.) in water (30 c.c.). The dye *perchlorate* (3·85 g.; 50% yield), after recrystallisation from methyl alcohol (515 c.c.), was obtained in 26% yield. A specimen was dried to constant weight 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: Cl, 8·8. $C_{21}H_{21}O_4N_2Cl$ requires Cl, 8·85%). The dull purple crystals shrank from about 220°, m. p. at about 246° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4980 A., and of one containing sulphuric acid at 5275 A., whereas the value recorded for the ethiodide is 5380 A. (B.P. 434,234/1933). The dye depressed the normal speed of a photographic plate to light of short wave-length; weak sensitisation extended to 6400 A., the very flat curve having its maximum at 5600 A.

2-(4′-*Anilinobuta*-1′ : 3′-*dienyl*)*quinoline Ethiodide* (I; X = I).—Quinaldine ethiodide (11·96 g.; 1 mol.), β-ethoxyacraldehyde diethyl acetal (15 c.c.; 2 mols.), and acetic acid (20 c.c.) were heated and stirred together on the steam-bath for 10 minutes (cf. B.P. 556,266/1940). The cooled reaction mixture was treated with absolute ether (100 c.c.), and the solid filtered off and washed thrice with ether (3 × 20 c.c.). It was heated on the steam-bath with aniline (3·8 c.c.; 1 mol.) for 2 minutes, and the anilino-compound was heated with acetone (10 c.c.), filtered off after cooling, and washed with acetone (12 c.c.) (11·70 g. obtained). After recrystallisation from methyl alcohol (585 c.c.), the yield was 36% (Found: I, 29·35. Calc. for $C_{21}H_{21}N_2I$: I, 29·65%). The steel-blue crystals had m. p. 234° (decomp.). Brooker, White, Keyes, Smyth, and Oesper (*loc. cit.*) prepared it from the acetanilido-compound with aniline in alcohol and give m. p. 238—240° (decomp.).

2-(4′-*Acetanilidobuta*-1′ : 3′-*dienyl*)*quinoline Ethoperchlorate* (VI; X = ClO_4).—2-(4′-Anilinobuta-1′ : 3′-dienyl)quinoline ethoperchlorate (1·37 g.) was boiled with acetic anhydride (18 c.c.) for 2 minutes. The substance which crystallised represented a 71% yield (Found: Cl, 7·9. $C_{23}H_{23}O_5N_2Cl$ requires Cl, 8·0%). The brick-red crystals began to darken at about 180° and melted at about 240° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4270 A. The *dye* weakly sensitised to 5900 A., whilst depressing the speed of the plate to blue light.

2-(4′-*Acetanilidobuta*-1′ : 3′-*dienyl*)*quinoline Ethiodide* (VI; X = I).—2-(4′-Anilinobuta-1′ : 3′-dienyl)-quinoline ethiodide (1 mol.) was similarly boiled with acetic anhydride (10 c.c. per g.), and the mixture poured into a warm solution of potassium iodide (4 mols.) in water (8 times vol. of acetic acid). The yield was 82% both before and after recrystallisation from acetic acid (14 c.c. per g.), suggesting the presence of solvent of recrystallisation. A sample dried to constant weight in a vacuum at 60—80° (Found: I, 24·65%) lost weight on drying at 100—110° (Found: I, 27·25. Calc. for $C_{23}H_{23}ON_2I$: I, 27·0%). The steel-blue crystals had m. p. *ca.* 226° (decomp.), whereas Brooker *et al.* (*loc. cit.*) record m. p. 231—234° (decomp.).

4-(4′-*Anilinobuta*-1′ : 3′-*dienyl*)*quinoline Ethoperchlorate.*—Lepidine (1·43 g.; 1 mol.) and ethyl toluene-*p*-sulphonate (2·00 g.; 1 mol.) were heated together at 155—160° for 3 hours, β-anilinoacraldehyde anil hydrochloride (1·1 mols.) and pyridine (10 c.c.) were added, and the mixture was boiled for ten minutes. The reaction mixture was treated hot with a solution of potassium iodide (4 mols.) in water (10 c.c.), and the crude, washed ethiodide resulted in 59% yield (2·53 g.). It was treated with acetone (50 c.c.) and an aqueous solution of sodium hydroxide (12 mols.) and the filtered acetone extract was added to cold water. The washed, dried tar was extracted four times with light petroleum (b. p. 80—100°; 4 × 400 c.c.). The extracts were acidified with acetic acid (40 c.c.) and the tars taken up in acetic acid (40 c.c.) and treated hot with a solution of sodium perchlorate (2·53 g.) in water (30 c.c.). The dye *perchlorate* (0·95 g.; 40% yield) was boiled out with, and recrystallised from, methyl alcohol (5 c.c., 55 c.c.) and thus obtained in 9% of the yield theoretically possible, as calculated from the crude ethiodide (Found: Cl, 8·8. $C_{21}H_{21}O_4N_2Cl$ requires Cl, 8·85%). The bluish-green crystals had m. p. about 223° (decomp.) with previous softening. The absorption maximum of a methyl-alcoholic solution containing ammonia was at 5355 A., and of one containing sulphuric acid at 5660 A., but the value given for the corresponding methiodide (B.P. 434,234) is 5800 A. Photographic sensitisation was to 6500 A. with decrease of the sensitivity to blue light.

4-(4′-*Anilinobuta*-1′ : 3′-*dienyl*)*quinoline Ethiodide.*—Lepidine ethiodide (11·96 g.; 1 mol.), β-ethoxy-acraldehyde diethyl acetal (2 mols.), and acetic acid (20 c.c.) were heated together on the steam-bath for 10 minutes. Absolute ether (100 c.c.) precipitated a tar, which was thrice washed with ether (3 × 20 c.c.). It was further heated with aniline (1 mol.) for 2 minutes and the resultant solid was heated with acetone (10 c.c.). After cooling, it was filtered off and washed with acetone (10 c.c.). This *ethiodide* (6·73 g.), after recrystallisation from methyl alcohol (330 c.c.), was obtained in 21% yield (3·63 g.) (Found: I, 29·75. $C_{21}H_{21}N_2I$ requires I, 29·65%). The green crystals had an indefinite m. p. at about 245° (decomp.).

4-(4′-*Acetanilidobuta*-1′ : 3′-*dienyl*)*quinoline Ethoperchlorate.*—4-(4′-Anilinobuta-1′ : 3′-dienyl)-quinoline ethoperchlorate was boiled with acetic anhydride (10 c.c. per g.) for 2 minutes. The filtered solution was precipitated with absolute ether (10 vols.) and the *product* (98% yield) recrystallised from acetic acid (12 c.c. per g), giving an 86% yield (Found: Cl, 8·2. $C_{23}H_{23}O_5N_2Cl$ requires Cl, 8·0%). The yellowish-brown substance melted at about 230° (decomp.), with darkening from 190°. It showed photographic desensitisation. The absorption maximum of a methyl-alcoholic solution was at 4365 A.

4-(4′-*Acetanilidobuta*-1′ : 3′-*dienyl*)*quinoline Ethiodide.*—4-(4′-Anilinobuta-1′ : 3′-dienyl)quinoline ethiodide was similarly acetylated, and the reaction mixture treated with a solution of potassium iodide (87% yield). After recrystallisation from acetic acid (10 c.c. per g.), the yield was 71% (Found, after drying in a vacuum at 100—110° : I, 26·6. $C_{23}H_{23}ON_2I$ requires I, 27·0%). The orange *compound* had m. p. at about 178° (decomp.).

2-(4'-*Anilinobuta*-1' : 3'-*dienyl*)*benzthiazole Ethoperchlorate* (III; Y = S).—2-Methylbenzthiazole etho-*p*-toluenesulphonate, β-anilinoactaldehyde anil hydrochloride, and pyridine were boiled together for 3 minutes, then treated hot with an aqueous solution of potassium iodide, giving a 93% yield of crude, washed ethiodide. Previously it was described as obtained from 2-methylbenzthiazole ethiodide, with the anil, and piperidine in alcohol (I.G. Farbenind. A.-G., B.P. 434,234/1933). For its conversion into base (cf. Kodak Ltd., B.P. 561,172/1940; Brooker *et al.*, *loc. cit.*), the crude ethiodide (4·02 g.; 1 mol.) was suspended in acetone (40 c.c.) and shaken with a solution of sodium hydroxide (15 mols.) in water (33 c.c.). The filtered mixture was separated, the dye by-product washed with acetone (5 c.c.), and the acetone extract again filtered and added to ice-cold water (167 c.c.). The base, precipitated in 62% yield (1·76 g.), was extracted thrice with light petroleum (b. p. 80—100°; 100 c.c., 2 × 50 c.c.), and the united extracts were treated with acetic acid (10 c.c.). The deposited tar was dissolved in acetic acid (20 c.c.) and treated hot with a solution of sodium perchlorate (1·76 g.) in water (20 c.c.). The dye *perchlorate* (0·51 g.) was boiled out with, and recrystallised from, methyl alcohol (5 c.c., 30 c.c.), being obtained in 15% yield (Found : Cl, 8·75. $C_{19}H_{19}O_4N_2ClS$ requires Cl, 8·7%). The light maroon crystals shrank from about 185° and melted at about 225° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4510 A., and of one containing sulphuric acid at 5120 A. The value given for the ethiodide (B.P. 434,234) is 5150 A. The dye slightly depressed photographic sensitivity to blue light, whilst sensitising the plate to 6100 A., the very flat curve having its maximum at 5600 A.

2-(4'-*Anilinobuta*-1' : 3'-*dienyl*)*benzthiazole Ethiodide*.—2-Methylbenzthiazole ethiodide (4·07 g.; 1 mol.), β-ethoxyacraldehyde diethyl acetal (2 mols.), and acetic acid (7 c.c.) were heated together for 10 minutes at 100°, as in B.P. 556,266. After cooling, the solid was filtered off, washed with ether and with acetone, and heated for 2 minutes at 100° with aniline (2 mols.). The product was heated with acetone (10 c.c.), cooled, filtered off, and washed thrice with acetone (3 × 5 c.c.) (82% yield). After recrystallisation from methyl alcohol (60 c.c. per g.), the yield was 61% (Found, after drying in a vacuum at 80—100° : I, 29·05. Calc. for $C_{19}H_{19}N_2IS$: I, 29·25%). The purplish crystals had m. p. about 220° (decomp.), with previous darkening. Brooker *et al.* (*loc. cit.*), who prepared it by the action of aniline on the acetanilido-compound, quoted m. p. 250—252° (decomp.).

2-(4'-*Acetanilidobuta*-1' : 3'-*dienyl*)*benzthiazole Ethiodide*.—This was prepared (89% yield) by boiling the anilino-compound for 2 minutes with acetic anhydride (10 c.c. per g.). After recrystallisation from acetic acid (8 c.c. per g.), the yield was 84% (Found, after drying in a vacuum at 80—100° : I, 26·35. Calc. for $C_{21}H_{21}ON_2IS$: I, 26·65%). The light brown crystals melted at 231° (decomp.), with darkening from about 170°. Brooker *et al.* carried out the acetylation with acetic anhydride in pyridine and gave m. p. 233—234° (decomp.) (*loc. cit.*). The absorption maximum was at 4310 A. The compound sensitised a gelatino-chloride plate very weakly to 5200 A., with the maximum at 5000 A.

2-(4'-*Anilinobuta*-1' : 3'-*dienyl*)-6 : 7-*benzbenzthiazole Ethiodide*.—2-Methyl-6 : 7-benzbenzthiazole ethiodide (14·20 g.; 1 mol.), β-ethoxyacraldehyde diethyl acetal (2 mols.), and acetic acid (20 c.c.) were heated together at 100° for 10 minutes. Absolute ether (120 c.c.) precipitated a tar, which was thrice washed with ether (3 × 20 c.c.), then heated at 100° with aniline (2 mols.) for 2 minutes. The product was heated with acetone (100 c.c.), filtered off, and further washed with acetone (50 c.c.) (80% yield). It was boiled out with methyl alcohol (2 × 370 c.c.) and the product which crystallised (38% yield) was again recrystallised from methyl alcohol (80 c.c. per g.) with charcoal treatment (0·2 g. per g.), and gave a 23% yield (Found, after drying in a vacuum at 80—100° : I, 26·0. $C_{23}H_{21}N_2IS$ requires I, 26·2%). The dark blue crystals had m. p. 215—220° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 4750 A.; one containing sulphuric acid, as also an acetic acid solution, had the maximum at 5300 A. The *dye* sensitised weakly at 6200 A., with the maximum at 5750 A.

2-(4'-*Acetanilidobuta*-1' : 3'-*dienyl*)-6 : 7-*benzbenzthiazole Ethiodide*.—The foregoing ethiodide was boiled with acetic anhydride (10 c.c. per g.) and the crystalline *salt* (95% yield) recrystallised from acetic acid (13 c.c. per g.), giving an 81% yield (Found, after drying in a vacuum at 80—100° : I, 24·25. $C_{25}H_{23}ON_2IS$ requires I, 24·1%). The greenish-yellow solid had no definite m. p.; decomposition began at about 140°, becoming violent at a point between 185° and 220°. The absorption maximum of an acetic acid solution was at 4395 A. The salt decreased the blue sensitivity of a gelatino-chloride plate, whilst conferring extremely weak sensitivity from 4800 to 5400 A., with the maximum at 5000 A.

2-(4'-*Anilinobuta*-1' : 3'-*dienyl*)-3 : 3-*dimethylindolenine Methoperchlorate* (IV).—2 : 3 : 3-Trimethylindolenine methiodide (3·01 g.; 1 mol.), β-anilinoacraldehyde anil hydrochloride (1 mol.), and pyridine (10 c.c.) were boiled together under reflux for 10 minutes and the solution was treated hot with one of potassium iodide (2 mols.) in water (100 c.c.). After cooling, the liquid was decanted off, and the residual tar washed with water. It was dissolved in acetone (40 c.c.) and stirred for 30 minutes with a solution of sodium hydroxide (12 mols.) in water (40 c.c.). The filtered acetone layer was added to a cold solution of ammonium chloride. The dried, crude base (2·27 g.) was twice extracted with light petroleum (b. p. 80—100°; 200 c.c., 100 c.c.). The extracts were treated with acetic acid (10 c.c.), and the resultant tar dissolved in acetic acid (20 c.c.) and treated hot with an aqueous solution of sodium perchlorate (3 g. in 20 c.c.). The washed perchlorate (1·83 g.) was thrice boiled out with ethyl acetate (3 × 20 c.c.) and the residue was recrystallised from absolute alcohol (40 c.c.), giving an 8% yield (Found : Cl, 8·75. $C_{21}H_{23}O_4N_2Cl$ requires Cl, 8·8%). The purple solid began to darken at about 180°, to shrink at about 210°, and had m. p. 223° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 4385 A., and one containing sulphuric acid at 5090 A. The *dye* sensitised to 6100 A., with the maximum at 5800 A., but decreased the normal blue sensitivity.

2-(4'-*Anilinobuta*-1' : 3'-*dienyl*)*benzselenazole Ethoperchlorate* (III; Y = Se).—2-Methylbenzselenazole ethiodide (3·52 g.), β-anilinoacraldehyde anil hydrochloride, and pyridine were similarly heated together, and the reaction mixture treated with potassium iodide solution. The crude ethiodide (3·96 g.) was treated with acetone (40 c.c.) and sodium hydroxide solution. In this case the filtered acetone extract was added to cold water (300 c.c.) containing acetic acid (10 c.c.) and sodium perchlorate (4 g.). The resultant tar, after being washed and dried (2·81 g.), was boiled out with, and recrystallised from, methyl alcohol (10 c.c., 65 c.c.), giving an 11% yield, calculated from the original reactants (Found : Cl, 8·0. $C_{19}H_{19}O_4N_2ClSe$ requires Cl, 7·8%). The purplish *compound* had m. p. 218° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 4505 A., and one containing sulphuric acid at 5220 A. The value given for the ethiodide (B.P. 434,234) is 5250 A. Sensitisation was to 6300 A. with the maximum at 5600 A, and the normal blue sensitivity was decreased.

2-(4'-*Anilinobuta*-1' : 3'-*dienyl*)*benzselenazole Ethiodide*.—2-Methylbenzselenazole ethiodide (14·09 g.; 1 mol.), β-ethoxyacraldehyde diethyl acetal (2 mols.), and acetic acid (20 c.c.) were stirred together at 100° for 10 minutes, as in B.P. 556,266. After cooling, the solid was filtered off, washed twice with ether and twice with acetone (2 × 5 c.c.), and further heated with aniline (2 mols.) for 2 minutes. The product was heated with acetone (20 c.c.), cooled, filtered off, and washed five times with acetone (5 × 10 c.c.) (80% yield). It was twice recrystallised from methyl alcohol (73 c.c. per g.), giving a 53% yield (Found : I, 26·2. $C_{19}H_{19}N_2ISe$ requires I, 26·35%). The dark reddish bronze *compound* had m. p. about 220° (decomp.).

2-(4'-*Acetanilidobuta*-1' : 3'-*dienyl*)*benzselenazole Ethiodide*.—The preceding anilino-compound was boiled with acetic anhydride (10 c.c. per g.) for 2 minutes. The washed salt (88% yield) was recrystallised from acetic acid (47 c.c. per g.), and gave a 78% yield (Found : I, 24·55. $C_{21}H_{21}ON_2ISe$ requires I, 24·25%). The light chestnut-brown powder had m. p. 240° (decomp.) with previous darkening. The absorption maximum was at 4420 A. The *salt* sensitised weakly to 5800 A., and decreased the normal blue sensitivity of the plate.

2-(4'-*Anilinobuta*-1' : 3'-*dienyl*)*benzoxazole Ethiodide*.—2-Methylbenzoxazole ethiodide (11·56 g.; 1 mol.), β-ethoxyacraldehyde diethyl acetal (2 mols.), and acetic acid (20 c.c.) were heated and stirred together on the steam-bath for 10 minutes. The cooled liquid was treated with absolute ether (100 c.c.) and the resultant tar washed thrice with ether (3 × 20 c.c.). Instead of attempting to induce its crystallisation (Kodak Ltd., B.P. 556,266/1940; Brooker and Sprague, *J. Amer. Chem. Soc.*, 1945, **67**, 1869) it was heated with aniline (1 mol.) on the steam-bath for 2 minutes. The resultant product was boiled with acetone (60 c.c.), cooled, filtered off, and further washed with acetone (60 c.c., 2 × 20 c.c.) (7·31 g. obtained). After recrystallisation from absolute alcohol (70 c.c. per g.), the yield was 34% (Found : I, 30·2. $C_{19}H_{19}ON_2I$ requires I, 30·35%). The red crystals had m. p. at about 160°, with previous softening. The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4220 A., and of one containing sulphuric acid at 4785 A. The *substance* was inert towards a gelatino-chloride photographic plate.

2-(4'-*Acetanilidobuta*-1' : 3'-*dienyl*)*benzoxazole Ethiodide*.—The above anilino-compound was boiled with acetic anhydride (10 c.c. per g.) for 2 minutes. The washed crystalline product (61% yield) was recrystallised from acetic acid (7 c.c. per g.), giving a 43% yield (Found : I, 27·35. $C_{21}H_{21}O_2N_2I$ requires I, 27·6%). The orange crystals had m. p. about 210° (decomp.), with darkening from 195°. The absorption maximum of a freshly prepared methyl-alcoholic solution was at 4350 A. The *substance* was inert towards a gelatino-chloride photographic plate.

2-(4'-*Anilinobuta*-1' : 3'-*dienyl*)-Δ^2-*thiazoline Ethiodide*.—2-Methyl-Δ^2-thiazoline ethiodide (5·14 g.) was heated with β-ethoxyacraldehyde diethyl acetal in acetic acid and the product was precipitated with ether and heated with aniline. After treatment with acetone (15 c.c.), the *product* (5·00 g.) was boiled out with, and recrystallised from, methyl alcohol (13 c.c., 75 c.c.), being obtained in 36% yield. After a second recrystallisation from methyl alcohol (20 c.c. per g.), the yield was 27% (Found : I, 33·1. $C_{15}H_{19}N_2IS$ requires I, 32·85%). The orange crystals had m. p. 209° (decomp.). A methyl-alcoholic solution containing ammonia had its absorption maximum at 4200 A.; one containing sulphuric acid, as also an acetic acid solution, had its absorption maximum at 4600 A. The substance sensitised a gelatino-chloride plate from 4200 to 5400 A. with the maximum at 5000 A.

2-(4'-*Acetanilidobuta*-1' : 3'-*dienyl*)-Δ^2-*thiazoline Ethiodide*.—The anilino-compound was boiled with acetic anhydride (20 c.c. per g.) and the *acetanilido*-compound crystallised on cooling in 86% yield (Found : I, 29·8. $C_{17}H_{21}ON_2IS$ requires I, 29·65%). The yellow crystals had m. p. about 226—229° (decomp.), with darkening from 190°. The absorption maximum of an acetic acid solution was at 4100 A. whereas one in methyl alcohol had presumably hydrolysed, since it had the maximum at 4600 A. with an inflexion to the curve at 4200 A. The compound sensitised very weakly to about 5000 A.

[2-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)]*pentamethincyanine Iodide* (VII).—The last ethiodide (1·71 g.; 1 mol.) and quinaldine ethiodide (1·2 g.; 1mol.) were ground together, treated with triethylamine (1·1 c.c.; 2 mols.) in ice-cold alcohol (20 c.c.), and kept in ice for 2 days, with occasional stirring. The crude *dye* was washed with alcohol, ground thrice with water (3 × 20 c.c.) (1·38 g. left), and twice recrystallised from absolute alcohol (30 c.c. per g.), being obtained in 39% yield (Found : I, 27·6. $C_{21}H_{25}N_2IS$ requires I, 27·35%). The blue crystals turned green at about 100°, shrank from 130° with gradual melting, and decomposed violently at about 215°. The absorption maximum was at 6245 A. The dye sensitised weakly from 5600 to 7100 A., with the maximum at 6600 A.

[4-(1-*Ethylquinoline*)][2-(3-*ethyl*-Δ^2-*thiazoline*)]*pentamethincyanine Iodide*.—This was similarly prepared by use of lepidine ethiodide (1·20 g.) in place of quinaldine ethiodide (4 mols. of NEt_3 used). The alcohol-washed *dye* (1·28 g.), recrystallised from methyl alcohol (14 c.c.), was obtained in 51% yield (Found : I, 27·35. $C_{21}H_{25}N_2IS$ requires I, 27·35%). The green crystals had m. p. 207° (decomp.). The absorption maximum was at 6705 A. The substance sensitised from 5700 to 7600 A., with the maximum at 7000 A.

Attempts to effect this condensation by heating with pyridine, or with sodium acetate in acetic anhydride, were unsuccessful.

[2-(3-*Ethyl*-Δ^2-*thiazoline*)][2-(3-*ethylbenzthiazole*)]*pentamethincyanine Iodide*.—2-(4'-Acetanilidobuta-1' : 3'-dienyl)-Δ^2-thiazoline ethiodide (3·42 g.; 1 mol.) and 2-methylbenzthiazole ethiodide (1 mol.) were allowed to react with triethylamine (1·2 mols.) in ice-cold absolute alcohol (20 c.c.) for only 3½ hours, in the hope that deposition of the desired dye would precede that of the by-product. The solid was filtered off, washed with alcohol, and ground with water (3·06 g. left). It was boiled out five times with methyl alcohol (5 × 20 c.c.) and the first three extracts gave a 50% yield (1·88 g.), whilst the last two gave thiadicarbocyanine by-product (0·15 g.). A second fractionation from methyl alcohol (2 × 20 c.c.) removed no more by-product and the yield dropped to 38%. The *dye* was finally recrystallised from methyl alcohol (45 c.c. per g.) with addition of charcoal (0·1 g. per g.) and obtained in 24% yield (Found : I, 26·8. $C_{19}H_{23}N_2IS_2$ requires I, 27·0%). The blue crystals showed decomp. from 165° to 185°. The absorption maximum was at 6005 A. Extra photographic sensitivity extending from 5400 to 7300 A. was conferred, with the maximum at 6300 A. and a weaker one at 6950 A.

[2-(3-*Ethyl-*Δ^2*-thiazoline*)][2-(3-*ethylbenzoxazole*)]*pentamethincyanine Iodide* (VIII).—2-(4′-Acetanilidobuta-1′ : 3′-dienyl)benzoxazole ethiodide (2·30 g. ; 1 mol.) and 2-methyl-Δ^2-thiazoline ethiodide (1 mol.) were mixed with triethylamine (1·2 mols.) in ice-cold absolute alcohol (15 c.c.). After four days in ice, the product was filtered off, washed with alcohol, ground with water (30 c.c.), and extracted with hot acetone (8 c.c.). The residue (9% yield) was recrystallised from absolute alcohol (150 c.c. per g.), and then again with charcoal treatment (0·1 g. and 300 c.c. alcohol, per g.) ; the yield was 4% (Found : I, 27·9. $C_{19}H_{23}ON_2IS$ requires I, 27·95%). The dark blue *compound* had m. p. 220° (decomp.). The absorption maximum was at 5615 A. Sensitisation extended to 6500 A. with the maximum at 5900 A.

[2-(1-*Ethylquinoline*)][4-(1-*ethylquinoline*)]*pentamethincyanine Iodide* (IX).—4-(4′-Acetanilidobuta-1′ : 3′-dienyl)quinoline ethiodide (2·35 g. ; 1 mol.), quinaldine ethiodide (1 mol.), and triethylamine (2 mols.) in ice-cold alcohol (25 c.c.) reacted together for 13 days. The dye was then filtered off, washed with alcohol, and ground with water (50 c.c.) and thrice with acetone (3 × 15 c.c.). The residue (74% yield) was twice boiled out with methyl alcohol (2 × 10 c.c.) and this second residue recrystallised from it (300 c.c.) with charcoal treatment (0·2 g. per g.) (36% yield). A second such recrystallisation (140 c.c. per g.), with charcoal, gave a 21% yield of dye containing only a trace of 2 : 2′-dicarbocyanine, the presence of which in the crude product had been revealed by absorption measurements (Found, after drying in a vacuum first at 80—100° and then at 100—110° : I, 24·75. $C_{27}H_{27}N_2I$ requires I, 25·05%). The greenish-gold crystals had no definite m. p. Shrinking began at about 100° and melting might, or might not, occur at about 130° (decomp. at about 240°). The absorption maximum was at 7605 A. The *dye* sensitised from 6800 to 8500 A., with maxima at 7600 and 8200 A.

I am indebted to Mrs. B. Inman for the absorption data and to Dr. B. H. Carroll and Mr. J. Morgan for sensitising tests.

KODAK LTD., WEALDSTONE, HARROW, MIDDLESEX. [*Received, March* 12*th*, 1948.]