613. *Some Trinuclear Cyanine Dyes. Part V.* Attempted Synthesis of Dyes Isomeric with Those of the Neocyanine Type.*

By Frances M. Hamer.

Four trinuclear trimethincyanines were synthesised by condensing a *meso*-methyltrimethincyanine with a heterocyclic aldehyde or with an anil. Two of them were also obtained by action of sodium ethoxide on a 2-methylbenzothiazolium salt and a 2-vinylbenzoxazolium salt having a heterocyclic substituent on the β-position of the vinyl group. Other *meso*-substituted trimethincyanines were prepared by the known method involving 2-substituted benzoxazolium salts. Absorption data are recorded; in three series a sequence unusual for cyanines is noted. A trinuclear trimethincyanine resisted quaternary salt formation.

A. HETEROCYCLIC ALDEHYDES

For synthesis of trinuclear cyanines, heterocyclic aldehydes were required. According to the original method, the addition compound of quinaldine and chloral had been hydrolysed to β-2-quinolylacrylic acid, which was oxidised by alkaline permanganate to 2-formylquinoline (von Miller and Spady, *Ber.*, 1885, **18**, 3402; 1886, **19**, 130; cf. Cooper and Cohen, *J.*, 1932, 723). Lepidine and chloral similarly gave an addition compound (von Miller and Spady, *loc. cit.*), which had been hydrolysed to β-4-quinolylacrylic acid (Koenigs and Müller, *Ber.*, 1904, **37**, 1337) and then similarly oxidised (Chem. Fabr. auf Aktien, B.P. 240,051/1925). Subsequently 4-formylquinoline was prepared by oxidising

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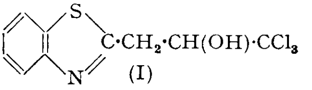
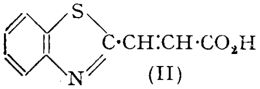
* Part IV, *J.*, 1951, 294.

lepidine with selenium dioxide (Kwartler and Lindwall, *J. Amer. Chem. Soc.*, 1937, **59**, 524), and this method was applied to the preparation of 2-formylbenzothiazole (Borsche and Doeller, *Annalen*, 1938, **537**, 53). The yields of 4-formylquinoline obtained by direct oxidation could not be repeated, a better overall yield resulting by the three-stage method starting from chloral (Clemo and Hoggarth, *J.*, 1939, 1241) ; later it was explained that freshly prepared selenium dioxide is essential for satisfactory yields of 2- and 4-formylquinoline (Kaplan, *J. Amer. Chem. Soc.*, 1941, **63**, 2654).

In the present work, condensation of 2-methylbenzothiazole and 2-methylbenzoselenazole, respectively, with chloral, by the method used for quinaldine and lepidine (*loc. cit.*), yielded (I) and its selenium analogue. Although increased yields had been obtained by addition of pyridine in the preparation of analogous compounds from quinaldine (Alberts and Bachmann, *J. Amer. Chem. Soc.*, 1935, **57**, 1284) and from lepidine (Clemo and Hoggarth, *loc. cit.*), this addition proved disadvantageous with 2-methylbenzothiazole and -benzoselenazole. (I) was hydrolysed to (II), and the selenium analogue of (II) was also prepared. Similar preparations of (I) and (II) have recently been reported (Ettel, Weichet, and Chyba, *Coll. Czech. Chem. Comm.*, 1950, **15**, 528).



(I)



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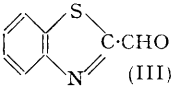


(III)

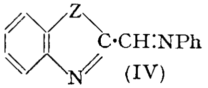
For oxidation of (II) to 2-formylbenzothiazole, the low temperature and high dilution prescribed for 4-formylquinoline (Clemo and Hoggarth, *loc. cit.*) were unsuccessful, and it had indeed been recorded that such conditions tend to the formation of dihydroxy-acids (Fittig, *Ber.*, 1888, **21**, 919). By use of hot concentrated aqueous solutions, 2-formylbenzothiazole (III) and 2-formylbenzoselenazole were prepared. Unfortunately the yields at each stage of the three-stage synthesis (52%, 61 %, and 38% for the former, and 53%, 69%, and 48% for the latter) were below those (80%, 80%, and 58%) recorded in the synthesis of 4-formylquinoline (Clemo and Hoggarth, *loc. cit.*).

According to the equation :

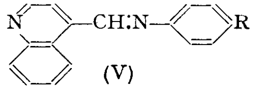
$$3R\cdot CH{:}CH\cdot CO_2K + 4KMnO_4 + 2H_2O = 3R\cdot CHO + 3H\cdot CO\cdot CO_2K + 4MnO_2 + 4KOH$$

three mols. of substituted acrylic acid should require four of potassium permanganate for oxidation to the aldehyde, but in fact about a 50% excess of permanganate had been used in making 2- (Cooper and Cohen, *loc. cit.*) and 4-formylquinoline (Chem. Fabr. auf Aktien, *loc. cit.*; Clemo and Hoggarth, *loc. cit.*). Comparative experiments now carried out on the oxidation of β-2-benzothiazolyl-, β-2-benzoselenazolyl-, and β-2-quinolyl-acrylic acid revealed that the maximum yield was not attained until for every 3 mols. of acid there had been added, not 4, but 7½—9 mols. of permanganate. This 100% excess is presumably used in oxidation of the accompanying glyoxylic acid, compared with which the heterocyclic aldehydes must be relatively stable. However, the latter were accompanied by small amounts of the corresponding 2-carboxylic acids, of which benzoselenazole-2-carboxylic acid was new.

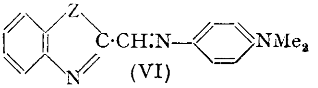
There were prepared three new anils, namely (IV; Z = S, Se, or CH:CH), and the known (V; R = H) (Work, *J.*, 1942, 429), also (VI; Z = S or Se) and the known (VI; Z = CH:CH) (Cooper and Cohen, *J.*, 1932, 723) and (V; R = NMe_2) (Ramsay, Baldwin, and Tipson, *J. Amer. Chem. Soc.*, 1947, **69**, 67). Although only two of these four *p*-dimethylaminoanils had been previously described, the quaternary salts of all of them were known, namely, the ethiodide of (VI; Z = S) (Hamer, *Phot. J.*, 1929, **69**, 409), the ethobromide of (VI; Z = Se) (Fisher and Hamer, *J.*, 1937, 907), and the ethiodides of (VI; Z = CH:CH) (Kaufmann and Vallette, *Ber.*, 1912, **45**, 1736) and of (V; R = NMe_2) (Hamer, *loc. cit.*) ; they had been characterised as photographic desensitisers (Hamer, *loc. cit.*;



(IV)



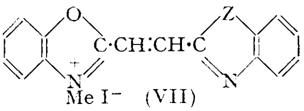
(V)



(VI)

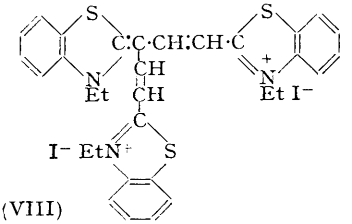
J., 1924, **125**, 1348; Bloch and Hamer, *Phot. J.*, 1930, **70**, 374; Fisher and Hamer, *loc. cit.*). Because of this desensitising action of the quaternary salts, it was surprising to find considerable photographic sensitisation produced by two of the bases, namely by (VI; Z = S or Se), whilst (VI; Z = CH:CH) also had some sensitising power; the fourth base (V; R = NMe_2) did not sensitise. Whereas their four quaternary salts gave purple solutions, with maxima (*locc. cit.*) varying bathochromically on passing along the series benzoselenazolium, benzothiazolium, 2-quinolinium, 4-quinolinium, solutions of the four bases were yellow, being readily decolorised by acid, and the maxima are in the sequence 2-quinoline, 4-quinoline, benzothiazole, benzoselenazole, as shown in the Table (p. 3201).

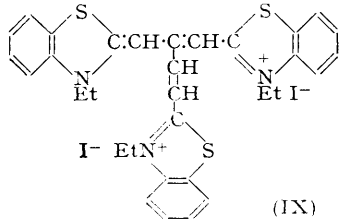
The compounds (VII; Z = S, Se, or CH:CH) were prepared by condensing the appropriate anils (IV; Z = S, Se, or CH:CH) with 2-methylbenzoxazole methiodide in ethanol. Yet attempts to condense either (III) or 2-formylquinoline with a 2-methylbenzoxazolium salt were unsuccessful: this was surprising in view of the reactivity of 2-formylquinoline with primary amines (Huang-Hsinmin and Mann, *J.*, 1949, 2903). The salts (VII) were unstable. No effect on a chlorobromide emulsion was detected. When they were arranged in order of increasing $\lambda_{max.}$, the sequence of nuclei linked to the 2-benzoxazolium nucleus was again 2-quinoline, benzothiazole, benzoselenazole, as recorded in the Table.

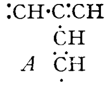

(VII)

B. TRINUCLEAR DYES

Trinuclear dyes of the neocyanine type have been proved to have an unbranched pentamethin chain, with the three nuclei symmetrically arranged, as in (VIII) (where only one of the resonating structures is formulated), whence they may be regarded as both γ-substituted pentamethin- and α-substituted trimethin-cyanines (Hamer, Rathbone, and Winton, *J.*, 1947, 1434; Kendall and Majer, *J.*, 1948, 690). According to a formula proposed by Brooker (B.P. 408,273/1931; cf. Brooker, Hamer, and Mees, *Phot. J.*, 1933, **57**, 258), they had been postulated, not as α-, but as β-substituted trimethincyanines, such as (IX). The synthesis of such unknown salts, which would be isomeric with neocyanines, now seemed of interest. Thus, 2-formylbenzothiazole might be used for synthesising (IX), and similarly, the 2- or the 4-aldehyde of the quinoline series, or the unknown 2-formylbenzoselenazole, seemed possible as starting points for other neocyanine isomers. These would all be characterised by having the chain (*A*) in one canonical form but it is to be noted that the number of structures contributing to the hybrid would be smaller than in the neocyanines themselves. The problem of preparing the required heterocyclic aldehydes has been dealt with in section *A*.


(VIII)

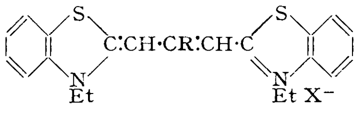

(IX)


A

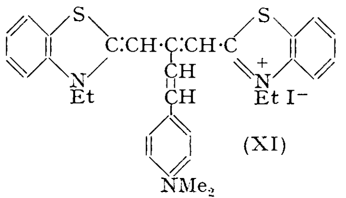
$$\begin{array}{c}:CH\cdot C:CH\cdot\\ \dot{C}H\\ \dot{C}H\\ \cdot\end{array}$$

When considering these heterocyclic aldehydes for synthesis of neocyanines, two facts may be noted. On the one hand, the reactivity of 2-formylquinoline towards primary amines has been demonstrated (Huang-Hsinmin and Mann, *loc. cit.*). Quaternary salts of the heterocyclic aldehydes have not been described, though some such compounds were liberated by the action of acid on their *p*-dimethylaminoanils, and forthwith condensed with heterocyclic hydrazines (Fuchs and Grauaug, *Ber.*, 1928, **61**, 57). On the other hand, the reactivity of the β-methyl group of (X; R = Me, X = I) was discovered by Ogata, who condensed the ethiodide with benzaldehyde, *p*-dimethylaminobenzaldehyde (to give XI), and furfuraldehyde (*Bull. Chem. Soc. Japan*, 1936, **11**, 262). Although trinuclear cyanines, *e.g.*, (XII), had subsequently been made, by condensing a dye such as (X; R = Me) with a heterocyclic quaternary ammonium salt, having, *e.g.*, a reactive alkylthio-group

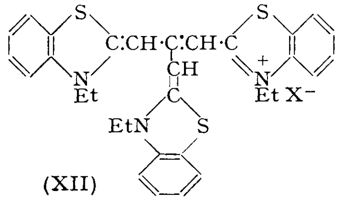
(Brooker, White, and Eastman Kodak Co., U.S.P. 2,282,115/1942), such dyes differ fundamentally from those of the neocyanine type in having only one anion, whereas the neocyanines have two.



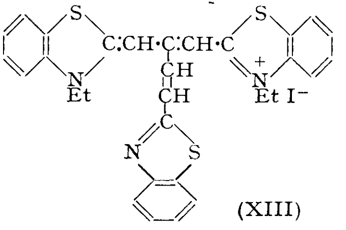
(X)



(XI)



(XII)

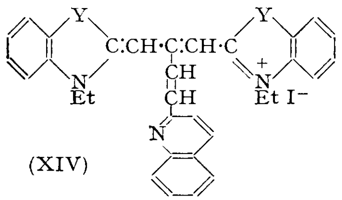


(XIII)

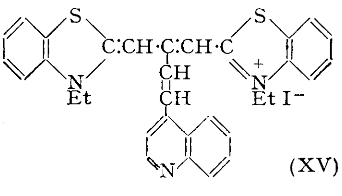
With the present aldehydes, unlike those used by Ogata (*loc. cit.*), condensation could not be effected with piperidine in alcohol, but the ethochloride (X; R = Me, X = Cl) condensed with (III) in pyridine. The product was isolated as iodide and most of the red impurity removed from the bluer dye (XIII) by means of aqueous pyridine. When the selenium analogue of (X; R = Me, X = Cl) was heated with 2-formyl-benzoselenazole or -benzothiazole in pyridine, the only product isolated was the dye iodide (Brooker, White, and Eastman Kodak Co., U.S.P. 2,058,406/1936) corresponding to the unchanged dye reactant. Similarly an attempt to condense (X; R = Me, X = Cl) with 2-formylquinoline in pyridine led to a red dye iodide and after recrystallisation there was a 52% recovery of (X; R = Me, X = I).

In spite of this negative result with 2-formylquinoline, the desired dye (XIV; Y = S) and its analogue (XIV; Y = Se) were prepared by condensing (X; R = Me, X = Cl) and its selenium analogue, respectively, not with the aldehyde, but with the anil (IV;] Z = CH:CH). Similarly, from (X; R = Me, X = Cl), by use of (V; R = H), there was synthesised (XV). Yet an attempt to obtain an improved yield of (XIII) by condensing (X; R = Me, X = Cl) with the anil (IV; Z = S) instead of with (III), was unsuccessful and the only dye isolated was (X; R = Me, X = I).

Dr. L. G. S. Brooker had previously prepared both (XIII) and (XIV; Y = S) and failed to make quaternary salts of such compounds (personal communication).



(XIV)



(XV)

None of the four new trinuclear dyes showed appreciable sensitisation; all depressed the original sensitivity of the plate and this was particularly marked with (XIII) and (XV).

The absorption curves of methanolic solutions (stabilised with alkali) of the new trinuclear trimethincyanines were plotted; acidified solutions gave less intense absorption and were unstable. It has been recorded that the absorption maxima of the unsubstituted trimethincyanine (X; R = H), of its *meso*-methyl derivative (X; R = Me), and of its *meso*-phenyl derivative (X; R = Ph) lie, respectively, at 5575, 5430, and 5600 Å (Brooker and White, *J. Amer. Chem. Soc.*, 1935, **57**, 2480). When the *meso*-substitutent is the much larger β-2-quinolylvinyl group, the absorption maximum, 5600 Å, is the same as for the *meso*-phenyl compound; those of the analogues with a *meso*-β-4-quinolylvinyl group and a *meso*-β-2-benzothiazolylvinyl group are shown in the Table. In the corresponding benzoselenazole series, the unsubstituted trimethincyanine has its absorption maximum at 5700 Å (Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703), the *meso*-methyl derivative at 5560 Å, and that with a *meso*-β-2-quinolylvinyl group at 5700 Å. From the close correspondence of the absorption maxima of (X; R = H), (X; R = Ph), and (XII), Bruylants, van Dormael, and Nys concluded that the *meso*-substitutent lies outside the plane of the conjugated resonating system (*Bull. Acad. Belg., Cl. Sci.*, 1948, **34**, 703; cf. van Dormael, *Bull. Soc. chim. Belg.*, 1949, **58**, 167). Since the absorption maxima of the four new *meso*-dyes lie so close to those of the corresponding unsubstituted trimethincyanines, it appears that here also the *meso*-substituent does not contribute to the charge resonance system.

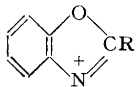
The trinuclear cyanines (XIV; Y = S), (XV), and (XIII), when tabulated according to the nature of the *meso*-substituent, fall into the same new sequence as the anils and the salts (VII). This is not a normal sequence for cyanines but in another series, where S or Se replaced CH⁚CH, the absorption maximum of styrene (Braude and Timmons, *J.*, 1950, 2000) was found to lie at a shorter wave-length than that of methyl phenyl sulphide or ethyl phenyl selenide (Bowden and Braude, *J.*, 1952, 1068).

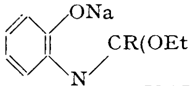
Absorption maxima (Å).

Heterocyclic group	Trinuclear dyes	Anils (IV and V)	Benzoxazole derivatives (VII)
2-Quinolyl	5600 (XIV; Y = S)	4180	3680
4-Quinolyl	5610 (XV)	4320	—
2-Benzothiazolyl	5630 (XIV)	4380	3850
2-Benzoselenazolyl	—	4400	3880

A second synthesis of the β-substituted trimethincyanines, (XIII) and (XIV; Y = S), was based on that remarkable method, by which a β-substituted trimethincyanine (XVI; Y = S or Se) is prepared by breaking down, by means of sodium ethoxide, a benzoxazolium salt (XVII) having the desired substituent in the 2-position, and condensing the product with a 2-methylbenzo-thiazolium or -selenazolium salt (I.G. Farbenind. A.-G., B.P. 439,359; cf. B.P. 439,807/1933). The validity of the method was confirmed by preparing (X; R = Me, X = I) from 2-methylbenzoxazole methiodide, 2-methylbenzothiazole ethiodide, and sodium dissolved in alcohol, and identifying it with a standard sample. In certain particulars it was found desirable to deviate from the procedure of the patent : for instance, since the acetal formulated as intermediate (XVIII) (*loc. cit.*) requires three molecules of sodium ethoxide for its formation from (XVII), three atomic proportions of sodium were used, instead of two. The modified method was applied to the preparation of (X; R = $C_{11}H_{23}$ or $C_{15}H_{31}$, X = I), the latter of which is given in the patent, to the 5 : 5′- and 6 : 6′-dichloro-derivatives of (X; R = $C_{11}H_{23}$, X = I), to the 5 : 5′-, 6 : 6′-, and 7 : 7′-dichloro-derivatives of (X; R = $C_{15}H_{31}$, X = I), and to the 4 : 5 : 4′ : 5′-tetramethoxy-derivative of (X; R = $C_{15}H_{31}$, X = I). The 6 : 7 : 6′-7′-dibenzo-derivatives of (X; R = $C_{15}H_{31}$ or $C_{11}H_{23}$) were also prepared by this method, as was the selenium analogue of (X; R = $C_{15}H_{31}$) which is recorded in the patent. That the method is applicable to the introduction of substituents other than alkyl groups was exemplified in the patent and was now demonstrated by the preparation of (XI) from 2-methylbenzothiazole ethiodide and (XVII; R = CH⁚CH·C_6H_4·NMe_2, R″ = Et, X = SO_3·C_6H_4Me).


(XVI)


(XVII)


(XVIII)

The compounds (XIII) and (XIV; Y = S) were prepared by this method depending on suitable salts (XVII), which were, specifically, (VII; Z = S or CH⁚CH).

Heating (VII; Z = S), 2-methylbenzthiazole ethiodide, and sodium ethoxide in alcohol gave a purple dye iodide. The same treatment with aqueous pyridine, which in the other method had been successful in removing the red component from (XIII), was applied here, and again successfully, although the proportion of desired dye to by-product was here far less. The present sample was identified with (XIII). From (VII; Z = CH⁚CH) and

2-methylbenzothiazole ethiodide, (XIV; Y = S) was similarly obtained, and similarly purified, but again in low yield.

The final stage of the synthesis was not accomplished, namely, the preparation of a diethiodide. These experiments were carried out with (XIV; Y = S) but it was recovered unchanged after being heated with ethyl iodide and decomposed when heated, at a higher temperature, with ethyl toluene-*p*-sulphonate.

EXPERIMENTAL

Unless otherwise stated, samples for analysis were previously heated in a vacuum.

2-(3 : 3 : 3-*Trichloro-2-hydroxypropyl)benzothiazole* (I).—Chloral (38·94 g., 1 mol.) and 2-methylbenzothiazole (33·7 c.c., 1 mol.) were heated together on a steam-bath for 8 hours. The glassy product was crystallised from light petroleum (b. p. 60—80°; 3500 c.c.), giving a 52% yield. Recrystallisation from benzene (3·5 c.c. per g.) reduced the yield to 42%. The white crystals had m. p. 125° (Found: Cl, 35·8; S, 11·0. Calc. for $C_{10}H_8ONCl_3S$: Cl, 35·9; S, 10·8%). Ettel, Weichet, and Chyba reported a 31% yield and m. p. 126—127° (*Coll. Czech. Chem. Comm.*, 1950, **15**, 528).

2-(3 : 3 : 3-*Trichloro-2-hydroxypropyl)benzoselenazole.*—Chloral (38·38 g., 1 mol.) and 2-methylbenzoselenazole (1 mol.) were heated together as above. The powdered product was extracted with light petroleum (b. p. 60—80°; 3000 c.c.). The filtrate from the first crop of crystals was made up to the original volume for a second extraction and this was repeated twice more, giving a 53% yield of *propyl* derivative and a black residue. Recrystallisation from alcohol and water (3 c.c. and 1·5 c.c., respectively, per g.) reduced the yield to 47%. Nitrogen was determined by Dumas's method, and chlorine by the modified Carius method (Hamer, *Analyst*, 1933, **58**, 26) (Found: N, 4·2; Cl, 30·8. $C_{10}H_8ONCl_3Se$ requires N, 4·1; Cl, 30·95%). The buff crystals had m. p. 122° with previous softening.

2-(3 : 3 : 3-*Trichloro-2-hydroxypropyl)quinoline.*—Instead of using the method of von Miller and Spady (*Ber.*, 1885, **18**, 3402; 1886, **19**, 130), who do not quote a yield, that used by Clemo and Hoggarth for the 4-quinoline isomer (*J.*, 1939, 1241) was modified. Quinaldine (39 c.c., 1 mol.), chloral (1 mol.), and anhydrous pyridine (100 c.c.) were heated together on a water-bath for 3 hours and the solution was poured into water (500 c.c.). The product was recrystallised from ethanol (300 c.c.) and well washed; it (72%) had m. p. 146—147°, whereas von Miller and Spady recorded 144—145°.

4-(3 : 3 : 3-*Trichloro-2-hydroxypropyl)quinoline.*—Freshly distilled lepidine (41 c.c., 1 mol.), freshly prepared chloral (1 mol.), and anhydrous pyridine (100 c.c.) were heated together on a boiling water-bath for 5 hours and the dark liquid was poured into water (500 c.c.). The resultant solid, recrystallised from ethanol (450 c.c.), gave a 62% yield of almost colourless crystals, m. p. 176—177°. When heating was for only 2 hours, the yield was 43%. Clemo and Hoggarth (*loc. cit.*) prescribed 2 hours' heating at 85—90° and recorded an 80% yield and m. p. 178°.

β-2-*Benzothiazolylacrylic Acid* (II).—2-(3 : 3 : 3-Trichloro-2-hydroxypropyl)benzothiazole (22·0 g., 1 mol.) was added, during 5 minutes, to an initially boiling solution of potassium hydroxide (18·3 g., 4·4 mols.) in ethanol (375 c.c.), with vigorous mixing. The heat of reaction kept up ebullition. After the addition, the mixture was boiled and stirred for 10 minutes. After cooling, the potassium salts were filtered off, washed thrice with alcohol, and dried. They were dissolved in boiling water (210 c.c.) and the acid was precipitated with acetic acid. After cooling, it was filtered off and well washed with water (yield, 61%) (Found: C, 58·5; H, 3·55. Calc. for $C_{10}H_7O_2NS$: C, 58·5; H, 3·45%). The almost colourless solid had m. p. 215° (decomp.). Ettel, Weichet, and Chyba (*loc. cit.*) gave m. p. 218—219° but not a yield.

Alternatively, 2-(3 : 3 : 3-trichloro-2-hydroxypropyl)benzothiazole (14·8 g., 1 mol.) was added, in one lot, to a hot solution of sodium (4 atoms) in ethanol (250 c.c.) and, when the reaction had abated, boiling and stirring were applied for 10 minutes. The sodium salts were filtered off hot, washed with ethanol, and dissolved in hot water (200 c.c.), and the acid was precipitated by acetic acid in 55% yield. The filtrates from three such preparations were heated, acidified with acetic acid, and added to four volumes of hot water; the acid obtained on cooling was purified through its potassium salt, bringing the yield to 71%.

β-2-*Benzoselenazolylacrylic Acid.*—2-(3 : 3 : 3-Trichloro-2-hydroxypropyl)benzoselenazole (17·2 g., 1 mol.), as in the second method above, gave the *acid* in 48% yield. A sample was purified through its potassium salt, the yield of washed acid being 43% [Found: N (Dumas), N, 5·35. $C_{10}H_7O_2NSe$ requires N, 5·55%]. The almost colourless crystals had m. p. 260°

(decomp.), with previous shrinking. The original filtrates from three such preparations were acidified with acetic acid and added to four volumes of hot water. The product was boiled with potassium carbonate (2 mols. per mol.) in water (300 c.c.), with addition of charcoal (1 g.), and the solution filtered hot. Precipitation with acetic acid gave a 21% yield of the acid, bringing the total to 69%.

β-2-*Quinolylacrylic Acid.*—After 2-(3 : 3 : 3-trichloro-2-hydroxypropyl)quinoline had been boiled with potassium carbonate solution for 3—4 hours, as described by von Miller and Spady (*loc. cit.*), who do not give a yield, addition of excess of hydrochloric acid was necessary, rather than the careful neutralisation they recommend, the yield being 43%. The following procedure was better.

2-(3 : 3 : 3-Trichloro-2-hydroxypropyl)quinoline (55 g., 1 mol.) was gradually added to an initially boiling solution of potassium hydroxide (5·2 mols.) in ethanol (255 c.c.), during 25 minutes, with vigorous mixing. Boiling and stirring were applied for a further 40 minutes. After cooling, the potassium salts were filtered off, washed thrice with ethanol, and dried. They were dissolved in boiling water (165 c.c.), and the acid was precipitated hot with acetic acid. After cooling, it was filtered off and washed with water (yield, 58%). It was nearly colourless and had m. p. 192—194° (decomp.), with previous darkening, whereas the recorded m. p. (*loc. cit.*) was 190—195°. On recrystallisation from methanol (20 c.c. per g.), the yield dropped to 38% but the m. p. was not changed (Found : C, 72·5; H, 4·75. Calc. for $C_{12}H_9O_2N$: C, 72·35; H, 4·55%).

β-4-*Quinolylacrylic Acid.*—4-(3 : 3 : 3-Trichloro-2-hydroxypropyl)quinoline (55·5 g.) was similarly hydrolysed. Clemo and Hoggarth, on a larger scale (65 g.), took 2 hours for the addition, which was followed by an hour's further heating (*J.*, 1939, 1241). Although they found the solid, which they filtered off on cooling, to be only potassium chloride, in the present work it comprised also the bulk of the desired acid, in the form of its potassium salt. Instead, therefore, of their procedure of filtering at this stage, the reaction mixture was added to hot water (1300 c.c.), and the acid precipitated with acetic acid. After cooling, it was filtered off and well washed with water [yield, 76%; cf. Clemo and Hoggarth, 80% of purified acid, m. p. 270° (slight decomp.)]. The m. p. was 260° (decomp.) and was unaltered by recrystallisation from acetic acid (20 c.c. per g.), whereby the yield of colourless crystals dropped to 59% (Found : C, 72·1; H, 4·6. Calc. for $C_{12}H_9O_2N$: C, 72·35; H, 4·55%).

2-*Formylbenzothiazole* (III).—A solution of β-2-benzothiazolylacrylic acid (2·05 g., 3 mols.) and anhydrous potassium carbonate (6 mols.) in water (10 c.c.), together with chloroform (100 c.c.), was heated on a steam-bath, with vigorous stirring. A solution of potassium permanganate (3·96 g., 7½ mols.) in water (75 c.c.) was dropped in during 8½ minutes, and boiling and stirring were continued for 2 minutes more. The manganese dioxide was filtered off hot and the layers were separated. The precipitate was washed with the hot aqueous layer and with chloroform (30 c.c.), and this was repeated. The chloroform extracts were dried (Na_2SO_4) and evaporated in a vacuum. The residual aldehyde (53% yield), recrystallised from light petroleum (b. p. 60—80°; 10 c.c. per g.), in 38% yield, had m. p. 73°, with previous softening, whereas Borsche and Doeller give m. p. 65° (*Annalen*, 1938, **537**, 53) (Found, after drying in a vacuum-desiccator : S, 19·65. Calc. for C_8H_5ONS : S, 19·65%). Similar experiments with 5, 6, 6½, 7, and 8 mols. of permanganate (in 50 c.c., 60—80 c.c. of water) gave crude yields of, respectively, 30, 49, 48, 51, and 47%, although the calculated amount is only 4 mols.

On evaporation of the original aqueous filtrate to crystallisation, potassium benzothiazole-2-carboxylate (average 0·55 g.) was obtained (cf. Hofmann, *Ber.*, 1887, **20**, 2251). After two recrystallisations from water (10 c.c. per g.; about 50% loss each time), the pale buff plates, which remained unmelted at 270°, were analysed (Found, after drying in a vacuum-desiccator : C, 44·7; H, 1·95; N, 6·45; S, 15·0. Calc. for $C_8H_4O_2NSK$: C, 44·2; H, 1·85; N, 6·45; S, 14·75%. Determinations of C and H were by Drs. Weiler and Strauss).

Benzothiazole-2-carboxylic acid has been described and its ready breakdown to benzothiazole noted (Hofmann, *loc. cit.*; Reissert, *Ber.*, 1904, **37**, 3708).

2-*Formylbenzoselenazole.*—A solution of β-2-benzoselenazolylacrylic acid (2·52 g., 3 mols.) and anhydrous potassium carbonate (6 mols.) in hot water, together with chloroform, was treated with aqueous potassium permanganate (7½ mols.) as in the preceding preparation. The *aldehyde* from six such runs (48% yield) was recrystallised from light petroleum (b. p. 60—80°; 10 c.c. per g.), and obtained in 41% yield [Found, after drying in a vacuum-desiccator : N (Dumas), 6·95. C_8H_5ONSe requires N, 6·65%]. The buff crystals had m. p. 72°. Similar experiments with 4, 5, 6, 6½, 7, 8, 9, and 10 mols. of permanganate (in 40—100 c.c. of water) gave crude yields of, respectively, 22, 28, 34, 40, 42, 46, 49, and 35%.

Potassium Benzoselenazole-2-*carboxylate*.—The original aqueous layer from six experiments as above with 7½ mols. of permanganate was concentrated until crystallisation began. The washed *potassium* salt (3·36 g.) was twice recrystallised from water (3 c.c. per g.; 1·82 g. obtained) [Found: N (Dumas), 5·45. $C_8H_4O_2NKSe$ requires N, 5·3%]. The pale beige crystals remained unmelted at 270°.

Benzoselenazole-2-*carboxylic Acid*.—The twice recrystallised potassium salt (2 g.) was added to hot water (40 c.c.), the boiling solution treated with excess of hydrochloric acid, and the precipitated *acid* filtered off and washed (1·27 g.) (Found, after drying in a vacuum-desiccator: C, 42·85; H, 2·4; N, 6·45. $C_8H_5O_2NSe$ requires C, 42·4; H, 2·25; N, 6·2%. C and H determinations were by Drs. Weiler and Strauss). The cream-coloured product had m. p. about 120° (decomp.), depending on the rate of heating.

2-*Formylquinoline*.—A solution of β-2-quinolylacrylic acid (1·99 g., 3 mols.) and anhydrous potassium carbonate (6 mols.) in hot water, together with chloroform, was treated with aqueous potassium permanganate (7½ mols.) as in preceding instances. The aldehyde (80% yield), recrystallised from light petroleum (b. p. 60—80°; 6 c.c. per g.) (54% yield), was buff and had m. p. 69°, whereas 70—71° is recorded (von Miller and Spady, *Ber.*, 1885, **18**, 3402; 1886, **19**, 130). This preparation was satisfactorily carried out on a scale thrice as great. Similar small-scale experiments with 6, 8, 8½, and 10 mols. of permanganate gave crude yields of, respectively, 71, 80, 76, and 71%. On concentration of the original aqueous layer, less potassium salt crystallised than with the corresponding benzothiazole and benzoselenazole compounds.

4-*Formylquinoline*.—In a similar experiment with β-4-quinolylacrylic acid (4·98 g.), addition of permanganate took ½ hour and subsequent boiling and stirring were for 2 minutes. After recrystallisation of the product (2·25 g.) from light petroleum, b. p. 40—60°, the yield dropped to 33% (1·29 g.), m. p. 52°. The colourless crystals were strongly sternutatory. Cooling with ice during the oxidation did not give a better yield and, as the manganese dioxide was not coagulated, filtration was excessively slow. It did not seem practicable to apply to an aqueous solution prolonged cooling with a freezing mixture, as recommended by Clemo and Hoggarth, who, however, recorded a 58% yield (*J.*, 1939, 1241).

2-*Anilomethylbenzothiazole* (IV; Z = S).—Mixing 2-formylbenzthiazole (0·82 g., 1 mol.) and aniline (1·1 mols.) caused evolution of heat. After 30 minutes at 115—120°, the melt solidified on cooling. The product was dissolved in hot methanol (20 c.c.). The nearly colourless *base* (62%), m. p. 102°, crystallised (Found: C, 70·25; H, 4·25; N, 12·05. $C_{14}H_{10}N_2S$ requires C, 70·5; H, 4·25; N, 11·75%). For microanalyses of this and the following eleven compounds, I am indebted to Mr. F. H. Oliver of the Imperial College.

2-*Anilomethylbenzoselenazole* (IV; Z = Se).—A mixture of 2-formylbenzoselenazole (1·05 g., 1 mol.) and aniline (1·1 mols.) was heated at 98—101° for 5 minutes and the product dissolved in hot methanol (35 c.c.). The buff *anil* had m. p. 119° (Found: C, 58·7; H, 3·6; N, 9·85. $C_{14}H_{10}N_2Se$ requires C, 58·9; H, 3·55; N, 9·8%).

Aniloquinaldine (IV; Z = CH:CH).—2-Formylquinoline (0·78 g., 1 mol.) and aniline (1·1 mols.) were heated at 98—104° for 5 minutes. Each reaction mixture, of ten such, was treated with hot ethanol (2 c.c.), and the tubes were further washed with hot ethanol (½ c.c × 10). From the united filtrates the base crystallised in 67% yield. The filtrate and washings were treated hot with an equal volume of water, and a second crop (2·03 g.) crystallised on cooling. Its recrystallisation from light petroleum gave a 16% yield, making the total 83%. The *base* had m. p. 73—74°, with previous softening, and the m. p. of a sample was unchanged by recrystallisation from light petroleum (b. p. 60—80°; 8 c.c. per g.), whilst the yield dropped to 51% (Found: C, 82·35; H, 5·15; N, 12·0. $C_{16}H_{12}N_2$ requires C, 82·7; H, 5·2; N, 12·05%).

Anilolepidine (V; R = H).—A mixture of 4-formylquinoline (0·78 g., 1 mol.) and aniline (1·1 mols.) was heated according to Work's method (*J.*, 1942, 429). After being dried overnight in a vacuum-desiccator, the product was dissolved in warm ether (10 c.c.) and the solution treated with light petroleum (b. p. 40—60°; 10 c.c.). The crystals, m. p. 84°, were obtained in 76% yield; Work obtained a 79% yield (m. p. 85°).

2-p-*Dimethylaminoanilomethylbenzothiazole* (VI; Z = S).—On mixing of 2-formylbenzothiazole (0·41 g., 1 mol.) and *NN*-dimethyl-*p*-phenylenediamine (1 mol.), a yellow colour developed. After 5 minutes' heating at 115—120°, the solid was recrystallised from methanol (110c.c.), giving orange crystals (71%), m. p. 176° with previous shrinking, of *anil* (Found: C, 68·4; H, 5·55. $C_{16}H_{15}N_3S$ requires C, 68·3; H, 5·4%). The orange colour of an alcoholic solution was unchanged by addition of acetic acid but discharged by sulphuric acid and, after a short time, could not be restored by ammonia; with neither acid was there a purple colour resembling that of the ethiodide. A methanolic solution containing ammonia had an absorption maximum at 4380 Å. This and the absorption curves of the following six compounds were obtained with a Hilger spectrograph. The dye strongly sensitised an iodobromide emulsion, sensitivity extending to 6100 Å, with the maximum at 5300 Å.

p-*Dimethylaminoanilomethylbenzoselenazole* (VI; Z = Se).—A mixture of 2-formylbenzoselenazole (0·52 g., 1 mol.) and *NN*-dimethyl-*p*-phenylenediamine (1 mol.) was similarly heated; recrystallisation of the product from benzene (7 c.c.), gave a 64% yield of the orange *base*, m. p. 186° (Found: C, 58·7; H, 4·3. $C_{16}H_{15}N_3Se$ requires C, 58·5; H, 4·6%). A methanolic solution containing ammonia had an absorption maximum at 4400 Å. Like the preceding base, this also was a strong sensitiser, with the same range and maximum.

p-*Dimethylaminoaniloquinaldine* (VI; Z = CH:CH).—Prepared as were the preceding two bases but from 2-formylquinoline (0·39 g.), the product separated from methanol (25 c.c.) as yellow crystals (64%), m. p. 145° (Found: C, 78·35; H, 6·25. Calc. for $C_{18}H_{17}N_3$: C, 78·5; H, 6·25%). Cooper and Cohen, who do not give a yield, recorded m. p. 148—150° (*J.*, 1932, 723). The yellow alcoholic solution on treatment with drops of dilute sulphuric acid gave an evanescent purple colour but excess of acid caused decolorisation. A methanolic solution containing ammonia had an absorption maximum at 4180 Å. The compound did not sensitise an iodobromide emulsion but somewhat decreased the original sensitivity; it sensitised a chlorobromide emulsion weakly, from 5200 to 5700 Å.

p-*Dimethylaminoanilolepidine* (V; R = NMe_2).—Similarly prepared from 4-formylquinoline (0·39 g.), the product crystallised from methanol (30 c.c.) in glistening red crystals (72%), m. p. 155° (Found: C, 78·9; H, 6·2%). A 94% yield and m. p. 156·2—157·2°, have been recorded (Ramsey, Baldwin, and Tipson, *J. Amer. Chem. Soc.*, 1947, **69**, 67). This base, in a methanolic solution containing ammonia, had a maximum at 4320 Å. It did not sensitise a chlorobromide emulsion.

2-(2-2′-*Benzothiazolylvinyl*)*benzoxazole Methiodide* (VII; Z = S).—A mixture of 2-methylbenzoxazole methiodide (0·14 g., 1 mol.), 2-anilomethylbenzothiazole (1 mol.), and acetic anhydride (0·1 c.c.) was heated at 83—88° for 15 minutes; crystallisation began at the end of 3 minutes. To remove acetanilide, the product was extracted with hot water (3 × 5 c.c.), and the residue heated with acetone (0·5 c.c.). After cooling, the *iodide* was filtered off and well washed with acetone (yield, 14%) (Found: C, 48·5; H, 3·3. $C_{17}H_{13}ON_2IS$ requires C, 48·55; H, 3·15%). The absorption maximum of a methanolic solution was at 3850 Å. The crystals were bright orange and had m. p. 202° (decomp.). Recrystallisation from acetic anhydride (100 c.c. per g.) did not raise the m. p., whilst reducing the yield to 3%, and attempted recrystallisation from methanol resulted in decomposition.

A better method was to heat 2-methylbenzoxazole methiodide (1·38 g., 1 mol.), 2-anilomethylbenzothiazole (1 mol.), and ethanol (11 c.c.) at 78—83° for 6 minutes: after 3 minutes, the solids had dissolved and the product began to crystallise. After cooling, the crystals were filtered off and washed thrice with alcohol, thrice with water, then again with alcohol, and were isolated in 29% yield. Addition of anhydrous sodium acetate to the reactants led to a negative result.

Attempted preparations from 2-formylbenzothiazole were unsuccessful.

2-(2-2′-*Benzoselenazolylvinyl*)*benzoxazole Methiodide* (VII; Z = Se).—A mixture of 2-methyl benzoxazole methiodide (1·38 g., 1 mol.), 2-anilomethylbenzoselenazole (1 mol.), and ethanol (11 c.c.) was heated and stirred by hand at 78—83° for 6 minutes. After cooling, the crystals were filtered off and washed, leaving a 34% yield. The absorption maximum of a methanolic solution was at 3880 Å. Recrystallisation of the bright reddish-orange *salt* from acetic anhydride (130 c.c. per g.) caused the yield to drop to 3%, whilst the m. p. rose from 195° (decomp.) to 197° (decomp.) (Found: C, 43·7; H, 3·1. $C_{17}H_{13}ON_2ISe$ requires C, 43·65; H, 2·8%). None of the desired product was obtained when sodium acetate was included with the reactants.

The preparation was also successful from 2-methylbenzoxazole methiodide and 2-anilomethylbenzoselenazole in acetic anhydride, but unsuccessful when 2-formylbenzoselenazole was used in this way instead of its anil.

2-(2-2′-*Quinolylvinyl*)*benzoxazole Methiodide* (VII; Z = CH:CH).—2-Methylbenzoxazole methiodide (1·38 g., 1 mol.) and aniloquinaldine (1 mol.) in ethanol (11 c.c.) were stirred together and heated at 79—83° for 1 minute. After cooling, the deep yellow crystals were filtered off and washed (yield, 45%). Recrystallisation from acetic anhydride (145 c.c. per g.) reduced the yield to 8% but the m. p., 193° (decomp.), was unaltered. The absorption maximum of a methanolic solution was at 3680 Å, with secondary maxima at 2810 and 2920 Å. The absorption band was no longer shown by a solution which had been left overnight (Found, for the washed specimen: C, 54·75; H, 3·8; N, 7·25. $C_{19}H_{15}ON_2I$ requires C, 55·05; H, 3·65; N, 6·75%). Attempted recrystallisation from ethanol (110 c.c. per g.) resulted in a total loss. An attempted preparation by heating together 2-methylbenzoxazole methiodide, 2-formylquinoline, sodium acetate, and ethanol for 45 minutes (Kendall, B.P. 495,197/1937, Ex. 16) was unsuccessful, as would be expected from the instability of the salt.

Bis-2-(3-*ethylbenzthiazole*)-β-*methyltrimethincyanine Iodide* (X; R = Me, X = I).—To a mixture of 2-methylbenzoxazole methiodide (1·38 g., 1 mol.) and 2-methylbenzothiazole ethiodide (2 mols.) in boiling ethanol (7·5 c.c.) was added a solution of sodium (3 atoms) in hot ethanol (10 c.c.), and boiling was continued for only 2 minutes, which was much less than the times in B.P. 439,359. The preliminary heating, there described, of the benzoxazolium salt with sodium ethoxide, before addition of the benzothiazolium salt, proved harmful and was omitted. After cooling, the dye was filtered off, washed and extracted with hot methanol (10 c.c.), and the residue (41%) was recrystallised from methanol (200 c.c. per g.), giving a 34% yield (Found: I, 24·95. Calc. for $C_{22}H_{23}N_2IS_2$: I, 25·05%). The dye had the same absorption and sensitising curves, m. p. and mixed m. p., as had a specimen prepared by use of ethyl orthoacetate (Hamer, *J.*, 1928, 3160).

2-*Undecylbenzoxazole and its Methomethylsulphate*.—This base had been prepared by use of dodecanoamide (Bywater, Coleman, Kamm, and Merritt, *J. Amer. Chem. Soc.*, 1945, **67**, 905). In the present work dodecanoic acid (18·3 g., 1 mol.) and *o*-aminophenol (1 mol.) were heated together at 200—220° for 12 hours. To remove unchanged acid, the mixture was ground with 4% sodium hydroxide solution (3 × 200 c.c.). In the presence of another such quantity, the base was then extracted with benzene. After drying of the extract and removal of the solvent, vacuum-distillation, after removal of a forerun, gave a 62% yield of material, b. p. 225—245°/35—50 mm., which solidified. To convert it into its methomethylsulphate, the base (0·68 g., 1 mol.) was heated at 100—110° for 2 hours with neutral methyl sulphate (1·25 mols.).

Bis-2-(3-*ethylbenzthiazole*)-β-*undecyltrimethincyanine Iodide* (X; R = $C_{11}H_{23}$, X = I).—To the above gummy salt were added 2-methylbenzothiazole ethiodide (2 mols.) and ethanol (5 c.c.), and the mixture was boiled. After addition of a hot solution of sodium (3 atoms) in ethanol (5 c.c.), boiling was continued for 2 minutes. The yield of washed *product*, after crystallisation from ethanol (15 c.c.), amounted to 53%. To obtain an analytically pure specimen, three recrystallisations were used, the first and third from ethanol (25 c.c. per g.) and the second from methanol (7 c.c. per g.) (40% yield) (Found: I, 19·95. $C_{32}H_{43}N_2IS_2$ requires I, 19·65%). The green crystals decomposed at about 120°. A methanolic solution had its absorption maximum at 5500 Å. The sensitising maximum was at 5900 Å, with a secondary one at 5200 Å, and sensitisation extended to 6300 Å; the sensitising action of this and the following dyes was in gelatino-bromide emulsions.

2-*Pentadecylbenzoxazole and its Methomethylsulphate*.—The base was originally prepared by heating the reactants together under reduced pressure (Fierz-David and Kuster, *Helv. Chim. Acta*, 1939, **22**, 82) but the vacuum appears unnecessary (I.G. Farbenind. A.-G., B.P. 439,359/1933). In the present work *o*-aminophenol (10 g., 1 mol.) and palmitic acid (1 mol.) were heated together at 205—220° for 12 hours, in a flask with a short air-condenser, which allowed water vapour to escape. The molten product was poured out and the brown cake ground thrice with sodium hydroxide solution, extracted with benzene, dried, and finally distilled, resulting in material (70%) of b. p. 275°/30—35 mm., m. p. 43·5°, compared with m. p. 45·5° recorded by Fierz-David and Kuster (*loc. cit.*). On 6 hours' heating, the yield was 63% and on 3 hours' heating was only 39%. To convert the base into its *methomethylsulphate*, it (4 g.; 1 mol.) was heated for 2 hours at 100—110° with neutral methyl sulphate (1·2 mols.). The syrupy product was inoculated whilst hot and stirred during cooling. After grinding with absolute ether (40 c.c.), there resulted an 83% yield of almost pure salt (Found: S, 7·4%), which was used for dye preparations. For analysis, the product was twice ground with dry acetone (9 c.c., 25 c.c.), and washed with it (25 c.c.), giving a 48% yield (Found, after drying in a vacuum-desiccator: S, 7·35. $C_{24}H_{41}O_5NS$ requires S, 7·05%). The white salt, which no longer appeared hygroscopic, had an indefinite m. p., softening from about 85° but only becoming clear at about 142°.

Bis-2-(3-*ethylbenzthiazole*)-β-*pentadecyltrimethincyanine Iodide* (X; R = $C_{15}H_{31}$, X = I).—A mixture of 2-pentadecylbenzoxazole methomethylsulphate (1·14 g., 1 mol.) and 2-methylbenzothiazole ethiodide (2 mols.) in boiling ethanol (5 c.c.) was treated with sodium (3 atoms) in ethanol (5 c.c.) and boiled for 2 minutes. The washed product was dissolved in hot alcohol (10 c.c.) and treated with a hot solution of its own weight of potassium iodide, dissolved in water (10 c.c.). The tar hardened on cooling and was ground with water (46% yield); it crystallised from ethyl acetate (30 c.c.), giving a 32% yield. After recrystallisation from ethyl acetate

(95 c.c. per g.), the yield was 26% (Found, after drying in a vacuum-desiccator: I, 17·9. $C_{36}H_{51}N_2I$ requires I, 18·05%). The green *iodide* began to shrink at 80—90°, melted at 124° to a viscous liquid, which became more mobile about 185°, and decomposed at about 210°. The absorption maximum of a methanolic solution was at 5450 Å, and the sensitising maximum at 5800 Å. This is example 5 of B.P. 439,359, but none of its properties is described there.

Bis-2-(5-*chloro*-3-*ethylbenzothiazole*)-β-*undecyltrimethincyanine Iodide*.—2-Undecylbenzoxazole (2·73 g.) and methyl sulphate were heated together at 100—120° for 2 hours. To the crude salt were added 5-chloro-2-methylbenzothiazole ethiodide and ethanol (20 c.c.), and the mixture was boiled. Undissolved solids were present until a solution of sodium in alcohol was added. Boiling and stirring were for 4 minutes. Crystallisation of the washed *product* from ethanol (140 c.c.) gave a 25% yield, and recrystallisation from methanol (70 c.c. per g.) a 19% yield. The crystals consisted of a less stable red and a more stable green form. After another recrystallisation from methanol, the yield was 16% (Found: 2Cl + I, 27·9. $C_{32}H_{41}N_2Cl_2IS_2$ requires 2Cl + I, 27·65%). Shrinking and darkening, with loss of crystalline form, took place at about 95°. Melting began at about 185° and frothing about 205°, but these temperatures depended on the rate of heating. A methanolic solution had its absorption maximum at 5550 Å. Sensitising was weak, with the maximum at 5995 Å.

Bis-2-(6-*chloro*-3-*ethylbenzothiazole*)-β-*undecyltrimethincyanine Iodide*.—In a preparation carried out similarly but with 6-chloro-2-methylbenzothiazole ethiodide, the washed product was boiled with, and recrystallised from, ethanol (30 c.c., 940 c.c.), giving a 25% yield. After a second recrystallisation from methanol (150 c.c. per g.), the yield was 21% (Found: 2Cl + I, 27·85. $C_{32}H_{41}N_2Cl_2IS_2$ requires 2Cl + I, 27·65%). The bluish-green *iodide* darkened from about 170°; the m. p. was at about 202° (decomp.) but depended on the rate of heating. A methanolic solution had the same absorption maximum as the preceding dye. Sensitivity extended to 6400 Å, with the maximum at 6000 Å.

Bis-2-(5-*chloro*-3-*ethylbenzothiazole*)-β-*pentadecyltrimethincyanine Iodide*.—To a hot mixture of 2-pentadecylbenzoxazole methomethylsulphate (2·28 g.) and 5-chloro-2-methylbenzothiazole ethiodide in ethanol (10 c.c.) was added sodium dissolved in ethanol, and boiling was continued for 2 minutes. After being washed, the product was recrystallised from ethanol (30 c.c.), leaving a residue, and giving a 24% yield. After a second recrystallisation from ethanol (20 c.c. per g.), the yield of *salt* was 20% (Found, after drying in a vacuum at 50—60°: 2Cl + I, 24·85. $C_{36}H_{49}N_2Cl_2IS_2,\frac{1}{2}C_2H_5OH$ requires 2Cl + I, 24·9%. Drying in a vacuum-desiccator caused less loss of weight, whilst at 60—80° melting occurred). The green crystals began to shrink at about 88° but with no definite m. p.; violent decomp. occurred at about 200°. The absorption maximum of a methanolic solution was at 5500 Å. The dye sensitised weakly from 5200 to 6100 Å, with the maximum at 5800 Å.

Bis-2-(6-*chloro*-3-*ethylbenzothiazole*)-β-*pentadecyltrimethincyanine Iodide*.—In a similar preparation but with 6-chloro-2-methylbenzothiazole ethiodide, the *dye* crystallised from the purple solution. After washing and two recrystallisations from methanol (250 c.c. per g.) the yield was 17% (Found: 2Cl + I, 25·6. $C_{36}H_{49}N_2Cl_2IS_2$ requires 2Cl + I, 25·65%). The dark green crystals showed sudden shrinking at about 177° and violent decomp. at about 213°. The absorption maximum of a methanolic solution was at 5550 Å. Sensitisation was weak, with the maximum at 5900 Å.

Bis-2-(7-*chloro*-3-*ethylbenzothiazole*)-β-*pentadecyltrimethincyanine Iodide*.—In a similar preparation with 7-chloro-2-methylbenzothiazole ethiodide, the crude washed dye was recrystallised from ethanol (10 c.c.) and obtained in 20% yield. This was boiled with ethanol (11 c.c. per g.), and the product (14%) from the extract was again recrystallised from ethanol (30 c.c. per g.), giving an 8% yield (Found: 2Cl + I, 25·7. $C_{36}H_{49}N_2Cl_2IS_2$ requires 2Cl + I, 25·65%). The *dye* crystallised in a more soluble bronze and green and less soluble blue form. It had no definite m. p. Shrinking occurred from 170° with gradual melting (decomp.) between 180° and 192°. A methanolic solution had its absorption maximum at 5500 Å. There was poor sensitising from 5100 to 6100 Å, with the maximum at 5800 Å.

Bis-2-(3-*ethyl*-5 : 6-*dimethoxybenzothiazole*)-β-*pentadecyltrimethincyanine Iodide*.—In a similar preparation with 5 : 6-dimethoxy-2-methylbenzothiazole ethiodide, the hot reaction mixture was added to ten times its volume of water, containing potassium iodide. The washed *dye* was boiled with ethanol (60 c.c.), from which it crystallised in 24% yield. After two further crystallisations from ethanol (15 c.c. per g.), the yield was 13% (Found: I, 15·7. $C_{40}H_{59}O_4N_2IS_2$ requires I, 15·45%). The dark green crystals showed some decomp. by 120° and were molten by 140° but without a definite m. p.; on more rapid heating, melting and decomposition to a green tar occurred at about 130°. A methanolic solution had its absorption maximum at 5800 Å. Moderate sensitisation extended to 6800 Å with maxima at 5400 and 6200 Å.

Bis-2-[3-*ethylnaphtho*(2′ : 1′-4 : 5)*thiazole*]-β-*pentadecyltrimethincyanine Iodide*.—In a preparation similar but with 2-methylnaphtho(2′ : 1′-4 : 5)thiazole ethiodide, the washed *product* was recrystallised from methanol (100 c.c.), giving a 39% yield. After a second such recrystallisation (65 c.c. per g.), it was 27% and, after further recrystallisation from ethanol (20 c.c. per g.), was 18% (Found, after drying in a vacuum-desiccator: I, 15·8. $C_{44}H_{55}N_2IS_2$ requires I, 15·8%). The dark green crystals melted gradually from 190° but there was no definite m. p.; at about 216° violent decomposition occurred. The absorption maximum of a methanolic solution lay at 5800 Å. Sensitisation was weak, with the maximum at 6100 Å.

Bis-2-[3-*ethylnaphtho*(2′ : 1′-4 : 5)*thiazole*]-β-*undecyltrimethincyanine Iodide*.—To the salt prepared from 2-undecylbenzoxazole (2·73 g.) and methyl sulphate were added 2-methylnaphtho-(2′ : 1′-4 : 5)thiazole ethiodide and ethanol, and the hot mixture was treated with sodium dissolved in alcohol and boiled for 4 minutes. The washed product was boiled with ethanol (2 × 100 c.c.), and the crystals (0·85 g.) from the second extract seemed satisfactory. Those from the first (2·31 g.) were further boiled with ethanol (10 c.c., 2 × 25 c.c., 100 c.c.); the final of these products (0·75 g.) was boiled again with ethanol (2 × 20 c.c.), and the undissolved residue was added to the crystals from the second original extract. Their recrystallisation from ethanol (150 c.c.) gave a 15% yield (Found: I, 16·95. $C_{40}H_{47}N_2IS_2$ requires I, 17·0%). The green *dye* became brown at about 215° and had m. p. about 221° (decomp.). Its methanolic solution had its absorption maximum at 5800 Å. Weak sensitising extended to about 6500 Å with a maximum at 6200 Å.

Attempts similarly to prepare isomers of this dye and the preceding one, by use of 2-methylnaphtho(1′ : 2′-4 : 5)thiazole ethiodide, gave only 2% yields of recrystallised products.

Bis-2-(3-*ethylbenzoselenazole*)-β-*pentadecyltrimethincyanine Iodide*.—The washed dye, obtained by boiling an alcoholic mixture of 2-pentadecylbenzoxazole methomethylsulphate (4·55 g.) and 2-methylbenzoselenazole ethiodide with sodium dissolved in alcohol, was recrystallised from ethanol (80 c.c.), giving a 16% yield and a residue. A second recrystallisation (20 c.c. per g.) gave a 13% yield and no residue, and a third gave 11% (Found: after drying in a vacuum-desiccator: I, 16·1. $C_{36}H_{51}N_2ISe_2$ requires I, 15·95%). The green *dye* had no definite m. p.; it began to shrink at about 85°, was semi-molten below 100°, and frothed at about 150°. The absorption maximum of a methanolic solution was at 5600 Å. Weak sensitisation was from 5200 to 6300 Å, with the maximum at 5900 Å. This is example 6 of B.P. 439,359, where no properties are described.

2-p-*Dimethylaminostyrylbenzoxazole Ethotoluene*-p-*sulphonate* (XVII; $R = CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2$, $R'' = Et$, $X = SO_3{\cdot}C_6H_4Me$).—A mixture of 2-methylbenzoxazole ethotoluene-*p*-sulphonate (6·66 g., 1 mol.), *p*-dimethylaminobenzaldehyde (1 mol.), and triethylamine (0·1 mol.) in ethanol (10 c.c.) was boiled for 7 hours. The washed *dye* was boiled with benzene (20 c.c., then 2 × 10 c.c.), and the residue (38% yield) recrystallised from ethanol (10 c.c. per g.) (yield, 31%) (Found: S, 7·05. $C_{26}H_{28}O_4N_2S$ requires S, 6·9%). The vermilion crystals had m. p. 234° (decomp.), with shrinking from 228°. Their methanolic solution had its absorption maximum at 4970 Å. The dye sensitised a gelatino-chloride plate to 5800 Å, with a maximum at 5300 Å.

Bis-2-(3-*ethylbenzothiazole*)-β-p-*dimethylaminostyryltrimethincyanine Iodide* (XI).—To a hot mixture of 2-*p*-dimethylaminostyrylbenzoxazole ethotoluene-*p*-sulphonate (4·65 g., 1 mol.) and 2-methylbenzothiazole ethiodide (2 mols.) in ethanol (23 c.c.) was added a hot solution of sodium (3 atoms) in ethanol (23 c.c.), and boiling with stirring was continued for 10 minutes. The reaction mixture was filtered hot, residual solid being washed twice with hot ethanol before rejection. When the filtrate and washings were cooled, dye crystallised (1·64 g.). The filtrate from it was treated hot with a solution of potassium iodide (5 g.) in water (50 c.c.); after cooling, the dye iodide was filtered off and washed (0·84 g. obtained). The earlier crop of dye was dissolved in hot alcohol (20 c.c. per g.) and treated with a hot solution of potassium iodide (2 g. per g.) in water (20 c.c. per g. of dye), and the mixture boiled for 2 minutes; whilst hot, the dye iodide was filtered off and washed (0·74 g.), the total yield (1·58 g.) now amounting to 25%. On a second treatment with aqueous potassium iodide, with hot filtration, the yield dropped to 11% and, on recrystallisation from methanol (110 c.c. per g.), to 7% (Found: I, 20·25. Calc. for $C_{31}H_{32}N_3IS_2$: I, 19·9%). This sample, one prepared as below, and their mixture melted at 244° (decomp.), whereas Ogata gives 252° (decomp.) (*Bull. Chem. Soc. Japan*, 1936, **11**, 262).

Bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine bromide (2 g., 1 mol.), *p*-dimethylaminobenzaldehyde (1·25 mols.), ethanol (12 c.c.), and piperidine (3 mols.) were boiled together for 25 minutes, which is Ogata's method, except that he used the less soluble iodide. The solution was treated hot with one of potassium iodide (4 mols.) in water (24 c.c.). The washed product was boiled with methanol (25 c.c.), and the residue (1·11 g.) recrystallised from methanol (125 c.c.) (yield, 27%; 19% after a second such recrystallisation) (Found : I, 19·85%). The methanolic solution had its absorption maximum at 5565 Å. Sensitisation was from 5200 to 6400 Å, with the maximum at 5900 Å.

Bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine Chloride (X; R = Me, X = Cl).—Bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine bromide (10 g., 1 mol.), dissolved in *m*-cresol (25 c.c.), was heated on the water-bath and stirred with freshly prepared silver chloride (3 mols.) for 1 hour, the lumps being broken up at intervals (Brooker and Eastman Kodak Co., U.S.P. 2,245,249—50/1941). The silver halide was filtered off hot and washed thrice with hot methanol. The cooled filtrate and washings were treated with ether (500 c.c.), and the dye chloride was filtered off and washed with ether. On recrystallisation of the crude product (10·09 g.) from methanol (5 c.c. per g.), the yield was 80%; when the filtrate was treated hot with its own volume of water containing potassium bromide, the yield of recovered dye bromide was 13%. A second recrystallisation of the *chloride* from methanol (10 c.c. per g.) gave a 64% yield of navy-blue crystals, with 9% recovery of dye bromide. Recrystallisation of a sample from acetic anhydride (10 c.c. per g.) brought the yield down to 48% (Found: Cl, 8·25. $C_{22}H_{23}N_2ClS_2$ requires Cl, 8·55%). The purple crystals had m. p. 224° (decomp.).

Bis-2-(3-ethylbenzoselenazole)-β-methyltrimethincyanine chloride was similarly prepared from bis-2-(3-ethylbenzoselenazole)-β-methyltrimethincyanine bromide (5 g.). The crude dye chloride (4·90 g.) was boiled with acetone (25 c.c.), and the residue (4·12 g., 90%) was recrystallised from methanol (20 c.c. per g.), giving a 61% yield of dark blue crystals. For analysis a sample was recrystallised from acetic anhydride (16 c.c. per g.), giving purple crystals, no definite m. p. but violent decomp. at about 245°. The absorption maximum of a methanolic solution was at 5560 Å (Found : N, 5·45; Cl, 6·9. $C_{22}H_{23}N_2ClSe_2$ requires N, 5·5; Cl, 6·95%). This and the preceding analysis were by Mr. F. H. Oliver, of the Imperial College. The corresponding iodide is known (Brooker, White, and Eastman Kodak Co., U.S.P. 2,058,406/1936) but no properties are described.

Bis-2-(3-ethylbenzothiazole)-β-(2-2′-benzothiazolylvinyl)trimethincyanine Iodine (XIII).—A mixture of bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine chloride (0·41 g., 1 mol.) and 2-formylbenzothiazole (1·5 mols.) in pyridine (3 c.c.) was heated for 5 minutes at 125—130°. The solution was treated hot with one of potassium iodide (2 mols.) in water (3 c.c.). From the cooled solution, tar separated and later solidified. It was filtered off and washed with aqueous pyridine and then with ether. To free this crude dye (0·46 g.) from pink impurity, it was dissolved in hot pyridine (20 c.c.) and treated with potassium iodide (0·92 g.) in hot water (20 c.c.). The purified, washed product (0·17 g.) was recrystallised from acetic anhydride (5 c.c.) (yield, 0·07 g., 11%). After a second recrystallisation from acetic anhydride (60 c.c. per g.), the yield was 5%. The dark green crystals had no definite m. p.; shrinking began at about 190° and the substance frothed at about 218° (Found : C, 54·7; H, 4·45. $C_{30}H_{26}N_3IS_3$ requires C, 55·3; H, 4·05%). A methanolic solution containing ammonia had its absorption maximum at 5630 Å. With one containing sulphuric acid, the absorption was in the same place but less intense.

When 2-anilomethylbenzothiazole (1·5 mols.) was used in place of 2-formylbenzothiazole, the crude washed dye iodide (0·47 g.) was not made bluer by dissolution in pyridine and treatment with potassium iodide solution, though the yield was reduced (to 0·22 g.). Recrystallisation from methanol (150 c.c. per g.) gave an 18% yield (0·09 g.) of crystals, having the same colour and solubility (Hamer, *J.*, 1928, 3160) as bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine iodide. Concentration of the filtrate gave a second crop (0·04 g.), containing some of the blue dye, and addition of ether to the filtrate from this gave a precipitate (0·02 g.), containing more of the bluer dye but still contaminated by the pink one. The first crop (0·09 g.), on recrystallisation from methanol, with addition of charcoal (0·02 g.) gave a 10% yield of the characteristic coppery crystals of bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine iodide, identified by appearance, colour of solution, m. p., and mixed m. p.

To carry out a preparation by the other method, a cold mixture of 2-(2-2′-benzthiazolylvinyl)benzoxazole methiodide (1·05 g., 1 mol.), 2-methylbenzothiazole ethiodide (2 mols.), and ethanol (5 c.c.) was treated with a hot solution of sodium (3 atoms) in ethanol (5 c.c.). The mixture was stirred and boiled for 1 minute and the purple solution treated hot with potassium iodide (4 mols.) in water (20 c.c.). The precipitated tar hardened on cooling and was filtered off and well washed with water (1·37 g. left). It was dissolved in hot acetic anhydride (2 c.c.) and reprecipitated with ether (40 c.c.). The ether-washed tar was dissolved in hot methanol (4 + 1 c.c.), then precipitated with potassium iodide solution as before, and the solid filtered off and washed with water (0·52 g. obtained). Most of the red dye was removed by boiling the mixture with pyridine (25 c.c.), treating the solution with potassium iodide (1·04 g.) in hot water (25 c.c.), boiling it, and setting it aside to crystallise. The washed crystals (1½% yield) gave a blue alcoholic solution with only a tinge of pink, and this tinge disappeared on recrystallisation of the product from methyl alcohol (2 c.c.; yield ½%). These dark green crystals, the other sample, and their mixture showed gradual decomposition from below 200° and all frothed up together. The absorption maximum of a methanolic solution containing ammonia was the same as that of the other sample.

In test-tube experiments, no blue colour developed when bis-2-(3-ethylbenzoselenazole)-β-methyltrimethincyanine chloride was heated in pyridine with 2-anilomethylbenzoselenazole, but with 2-formylbenzoselenazole there was a transient blue colour. In an attempted condensation, the dye chloride (0·51 g., 1 mol.), 2-formylbenzoselenazole (1·5 mols.), and pyridine (3 c.c.) were heated together at 125—130° for 5 minutes and the solution was treated hot with potassium iodide (2 mols.) in water (3 c.c.). The washed dye was boiled with acetone (5 c.c., 2 × 10 c.c.), giving 42% recovery of dye iodide (0·25 g.), which was similar in colour to the original dye chloride. After recrystallisation from methanol (50 c.c.), the yield was 15%. In contact with the solution the crystals were brassy, but they were dark purple when dry; they decomposed violently at about 278° (Found: C, 44·05; H, 4·1. Calc. for $C_{22}H_{23}N_2ISe_2$: C, 43·95; H, 3·85%). The analysis and the colour in solution identified it as [bis-2-(3-ethylbenzoselenazole)]-β-methyltrimethincyanine iodide (Brooker, White, and Eastman Kodak Co., U.S.P. 2,058,406/1936).

In a similar experiment with 2-formylbenzothiazole, an 8% yield of recrystallised dye iodide was isolated, but not the more soluble blue dye, which appeared to be formed.

Bis-2-(3-*ethylbenzothiazole*)-β-(2-2′-*quinolylvinyl*)*trimethincyanine Iodide* (XIV; Y = S).—A mixture of bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine chloride (0·41 g., 1 mol.), aniloquinaldine (1·5 mols.), and pyridine (6 c.c.) was heated at 125—130° for 3 minutes, becoming blue. The solution was treated hot with potassium iodide (2 mols.) in water (6 c.c.). After cooling, the dye *iodide* was filtered off and washed with aqueous pyridine and then with ether. To remove pink contaminant, the crude dye (0·46 g.) was boiled with pyridine (15 c.c.) and treated with potassium iodide (0·92 g.), in hot water (15 c.c.). After cooling, the crystals were filtered off and washed (0·31 g. obtained). After recrystallisation from ethanol (125 c.c. per g.) and then from acetic anhydride (80 c.c. per g.) the yield was 27%. The dark green crystals had m. p. 216° (decomp.), with previous shrinking (Found: C, 59·75; H, 4·2. $C_{32}H_{28}N_3IS_2$ requires C, 59·5; H, 4·35%). A methanolic solution containing ammonia showed its maximum absorption at 5600 Å. In one containing sulphuric acid, this absorption band was less intense and there was a secondary band with its maximum at 6000 Å.

In a similar experiment in which 2-formylquinoline (1·5 mols.) took the place of aniloquinaldine, the colour of an alcoholic solution of the washed dye iodide (74%, 0·37 g.) was pink instead of blue. After recrystallisation from the amount of methanol (150 c.c. per g.) prescribed for bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine iodide (Hamer, *J.*, 1928, 3160), the yield was 52%. From the characteristic crystals, colour of the solution, m. p., and mixed m. p., the dye iodide was identified with that named.

According to the other method, a hot solution of sodium (3 atoms) in ethanol (5 c.c.) was added to a cold mixture of 2-(2-2′-quinolylvinyl)benzoxazole methiodide (1·04 g., 1 mol.), 2-methylbenzothiazole ethiodide (2 mols.), and ethanol (5 c.c.). The mixture was boiled and stirred for 1 minute and the purple solution treated with potassium iodide (4 mols.) in hot water (20 c.c.). The product (1·51 g.) was purified by precipitating it from hot acetic anhydride (2 c.c.) with ether (40 c.c.). The ether-washed tar was dissolved in hot methanol (4 + 1 c.c.) and precipitated with potassium iodide as before (0·55 g. obtained). Although this product contained far more red impurity than that prepared by the other method, a similar purification proved satisfactory. Thus it was boiled with pyridine (20 c.c.), treated with a hot solution of potassium iodide (1·1 g.) in water (20 c.c.), boiled, cooled, and left overnight. After the crystals had been filtered off and washed with aqueous pyridine and with water, they (0·02 g.) gave an alcoholic solution identical in colour with that of the material prepared by the other method. When the filtrate was treated with more potassium iodide (2·2 g.) in water (80 c.c.), some rather pinker dye (0·33 g.) was recovered. Another treatment of this in hot pyridine (5 c.c.) with potassium iodide (0·66 g.) in water (5 c.c.) gave a further yield (0·01 g.) of blue dye (total

2%). After recrystallisation from the same proportion of ethanol as used in the other method, similar green crystals were obtained, in 1% yield. They had the same m. p. and mixed m. p., and the absorption maximum (methanol containing ammonia) was the same.

In an attempt to prepare its ethiodide, the pure dye (0·29 g., 1 mol.) was heated at 100° with ethyl iodide (8 mols.) for 24 hours. After washing with ether, there was an 80% recovery (m. p., mixed m. p., and colour of solution). A sample heated with ethyl toluene-*p*-sulphonate (10 mols.) at 160—165° for 30 minutes appeared to decompose.

Bis-2-(3-ethylbenzoselenazole)-β-(2-2′-quinolylvinyl)trimethincyanine Iodide (XIV; Y = Se).—A mixture of bis-2-(3-ethylbenzoselenazole)-β-methyltrimethincyanine chloride (0·51 g., 1 mol.), aniloquinaldine (1·5 mols.), and pyridine (6 c.c.) was heated as in the preceding preparation and treated with potassium iodide. The washed crude dye (0·54 g.), dissolved in hot pyridine (12 c.c.), was treated with potassium iodide (0·54 g.) in hot water. The washed *product* (0·35 g.) was boiled with, and recrystallised twice from, methanol (yield, 6%) and then from acetic anhydride (40 c.c. per g.) (yield, 3%). The dark crystals frothed at about 227° (Found: C, 52·0; H, 4·5. $C_{32}H_{28}N_3ISe_2$ requires C, 51·9; H, 3·8%). A methanolic solution containing ammonia had its absorption maximum at 5700 Å. One containing sulphuric acid showed a weak maximum at 5640 and an inflexion at 6250 Å, and faded during exposure to light.

Bis-2-(3-ethylbenzothiazole)-β-(2-4′-quinolylvinyl)trimethincyanine Iodide (XV).—A mixture of bis-2-(3-ethylbenzothiazole)-β-methyltrimethincyanine chloride (0·41 g., 1 mol.), anilolepidine, and pyridine (3 c.c.) was heated as in other instances, and the solution treated hot with one of potassium iodide (2 mols.) in water (3 c.c.). The washed dye (0·48 g.) from two such preparations was boiled with pyridine (25 c.c.), treated with potassium iodide (1·44 g.) in hot water (25 c.c.), and the mixture boiled. The *dye* which crystallised on cooling was filtered off, washed, and dried (0·24 g. obtained). After recrystallisation from acetic anhydride (25 c.c.), the yield was 7% (0·09 g.). The dark purple crystals decomposed at about 241° (Found: C, 59·85; H, 4·2. $C_{32}H_{28}N_3IS_2$ requires C, 59·5; H, 4·35%). A methanolic solution containing ammonia had its absorption maximum at 5610 Å. One containing sulphuric acid showed less intense absorption, with the maximum at 5580 and inflexions at 6200 and 6500 Å: this solution became colourless overnight.

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Imperial College of Science and Technology,
South Kensington, London, S.W. 7.

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