160. *Symmetrical Dicarbocyanines having a Methyl Group as Substituent on the Chain.*

By Frances M. Hamer and Russell J. Rathbone.

The synthesis of *β-bromo-α-methylacraldehyde diethyl acetal* is described. Unlike the dimethyl acetal, it yielded β-anilino-α-methylacraldehyde anil hydrochloride with aniline and hydrochloric acid. With appropriate quaternary salts the anil gave γ-methyldicarbocyanines. β-Methyldicarbocyanines were obtained by means of β-ethoxycrotonaldehyde diethyl acetal. The extension of a known preparation of an oxadicarbocyanine to a γ-methyl- but not to a γ-ethyl-oxadicarbocyanine was effected. Absorption maxima and photographic sensitising action of the dyes are recorded.

The photographic sensitising action of symmetrical dicarbocyanines carrying one or more alkyl groups as substituents on the chain forms the subject of a patent (I.G. Farbenind. A.-G., B.P. 394,537/1931); according to the six examples given, a γ-methyl group was introduced by use of β-ethoxy-α-methylacraldehyde acetal, βγ-dimethyl groups by use of β-ethoxy-αβ-dimethylacraldehyde acetal, and αα′-dimethyl groups by use of a quaternary salt having an ethyl instead of a reactive methyl group. There is no indication of any method of preparing the two acetals, which had not been described in the literature. The patent as originally published also contained two examples of dicarbocyanines having a β-methyl group and prepared by use of β-ethoxycrotonaldehyde acetal in pyridine; dyes monoalkylated in the β-position were, however, specifically excluded from the amended specification and these two examples deleted, apparently because an earlier patent (Kendall, B.P. 390,808/1931) had claimed the preparation of such compounds by use of a β-alkylpropargyl acetal. More recently, a new method for preparing β-alkyldicarbocyanines has been described in the patent literature (Kendall, Wood, and Majer, B.P. 553,144/1941).

More detailed is the paper of Sitnik and Steingardt, who prepared one αα′-dimethyl- and three γ-methylthiadicarbocyanines, and whose work includes the synthesis of the intermediate giving rise to the γ-methyl substituted chain (*J. Appl. Chem. Russ.*, 1936, **9**, 1842). In the present paper we first consider the synthesis of this intermediate. Instead of following previous authors in proceeding in one step from *iso*butyraldehyde to α-bromo*iso*butyraldehyde dimethyl acetal (Zeisel and Daniek, *Monatsh.*, 1909, **30**, 727; Sitnik and Steingardt, *loc. cit.*), we isolated *iso*butyraldehyde diethyl acetal and subsequently brominated it to give *α-bromoisobutyraldehyde diethyl acetal*, $CMe_2Br{\cdot}CH(OEt)_2$. Instead of removing hydrobromic acid by heating with potassium hydroxide (Zeisel and Daniek, *loc. cit.*; Sitnik and Steingardt, *loc. cit.*), in the case of the diethyl acetal we used a solution of sodium ethoxide. Bromination of the resulting α-methylacraldehyde diethyl acetal, $CH_2{:}CMe{\cdot}CH(OEt)_2$, gave *αβ-dibromoisobutyraldehyde diethyl acetal*, $CH_2Br{\cdot}CMeBr{\cdot}CH(OEt)_2$ (cf. Sitnik and Steingardt, *loc. cit.*). We used sodium ethoxide for the second elimination of hydrobromic acid, as did Sitnik

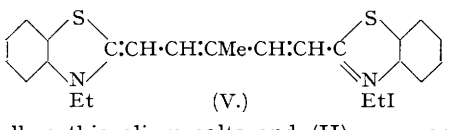
and Steingardt with the dimethyl acetal, and we isolated β-*bromo-α-methylacraldehyde diethyl acetal*, $CHBr{:}CMe{\cdot}CH(OEt)_2$.

By treating the filtrate from the reaction mixture with one mol. of aniline hydrobromide, together with hydrobromic acid, Sitnik and Steingardt obtained their intermediate, which, from its physical and chemical properties, they designated as α-methyl-β-anilinoacraldehyde dimethyl acetal hydrobromide (I) (*loc. cit.*). This conclusion is surprising, since β-ethoxyacraldehyde diethyl acetal, $EtO{\cdot}CH{:}CH{\cdot}CH(OEt)_2$, under substantially similar conditions condenses with 2 mols. of aniline to give (III), the group $-CH(OEt)_2$ having become $-CH{:}NPh$ (Reitzenstein and Bönitsch, *J. prakt. Chem.*, 1912, **86**, 1). With two mols. of aniline, our acetal gave the expected β-*anilino-α-methylacraldehyde anil hydrochloride* (II). With 1 mol. of aniline hydrochloride under various conditions, we still obtained (II) in poorer yield, instead of the hydrochloride corresponding with (I), so that we did not endorse Sitnik and Steingardt's conclusion.

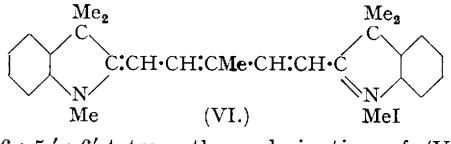
$HBr,PhNH{\cdot}CH{:}CMe{\cdot}CH(OMe)_2$ (I.) $HCl,PhNH{\cdot}CH{:}CMe{\cdot}CH{:}NPh$ (II.) $HCl,PhNH{\cdot}CH{:}CH{\cdot}CH{:}NPh$ (III.) $(EtO)MeC{:}CH{\cdot}CH(OEt)_2$ (IV.)

The starting point in the synthesis of β-anilinoacraldehyde anil hydrochloride (III) is acraldehyde and, to prepare our second intermediate, we aimed at carrying out a similar synthesis starting from crotonaldehyde, $Me{\cdot}CH{:}CH{\cdot}CHO$. At the first stage, αβ-dibromobutyraldehyde, $Me{\cdot}CHBr{\cdot}CHBr{\cdot}CHO$, is unstable (Viguier, *Compt. rend.*, 1909, **149**, 403); after the bromination, therefore, we treated the solution with alcoholic hydrochloric acid, but bromine determinations indicated that only a 90% conversion into the second stage, ααγ-triethoxy-β-bromobutane, $EtO{\cdot}CHMe{\cdot}CHBr{\cdot}CH(OEt)_2$, had been attained. Treatment of this with sodium ethoxide gave a 95% conversion into β-ethoxycrotonaldehyde diethyl acetal (IV); this has previously been prepared from propargyl aldehyde (Viguier, *Ann. Chim.*, 1913, [8], **28**, 433). This acetal did not undergo smooth conversion into the desired methyl derivative of (III), but we were able to use the acetal itself for preparing β-methyl-substituted dicarbocyanines.

In the first series, various heterocyclic quaternary ammonium salts, having a reactive methyl group, were condensed with (II) to give γ-methyldicarbocyanines. Thus from 2-methylbenzthiazole ethiodide we prepared the γ-methylthiadicarbocyanine (V) (I.G. Farbenind. A.-G., B.P. 394,537/1931; Sitnik and Steingardt, *loc. cit.*), and this was also obtained by use of β-bromo-α-methylacraldehyde diethyl acetal. By reaction of substituted

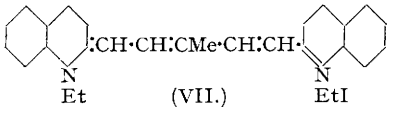


(V.)



(VI.)

2-methylbenzthiazolium salts and (II) we prepared the 5 : 6 : 5′ : 6′-tetramethoxy-derivative of (V) (I.G. Farbenind. A.-G., *loc. cit.*), the 6 : 7 : 6′ : 7′-*dibenz-derivative*, and the corresponding 5 : 5′-*dichlorothiadicarbocyanine chloride*. The γ-*methylselenadicarbocyanine chloride* (cf. I.G. Farbenind. A.-G., *loc. cit.*), the γ-*methylindodicarbocyanine* (VI), the γ-*methyl*-2 : 2′-*dicarbocyanine* (VII), and the γ-*methyl*-4 : 4′-*dicarbocyanine* (VIII) were also prepared. The yields are of the same order as those obtainable by use of the unsubstituted intermediate (III).



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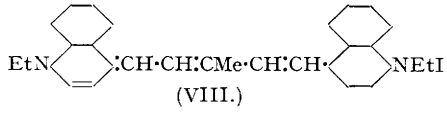
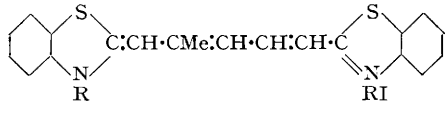


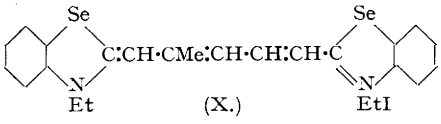
(VIII.)

In the second series, heterocyclic quaternary ammonium salts, having a reactive methyl group, were condensed with the acetal (IV) to give β-methyldicarbocyanines. Thus (IV) with 2-methylbenzthiazole ethiodide and methiodide, respectively, gave the β-*methylthiadicarbocyanine* (IX; R = Et) and its *dimethyl analogue*

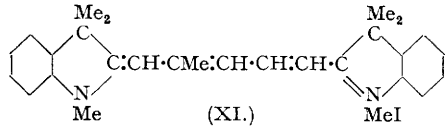


(IX.)

(IX; R = Me). From substituted 2-methylbenzthiazolium salts and (IV), we obtained the 5 : 6 : 5′ : 6′-*tetramethoxy-derivative* of (IX; R = Et), the 4 : 5 : 4′ : 5′-*dibenz-derivative*, the 5 : 5′-*dichlorothiadicarbocyanine* p-*toluenesulphonate*, and the 6 : 7 : 6′ : 7′-*dibenzthiadicarbocyanine bromide*. The β-*methylselenadicarbocyanine* (X) and the β-*methylindodicarbocyanine* (XI) were also prepared.



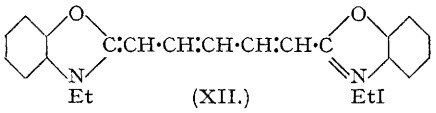
(X.)



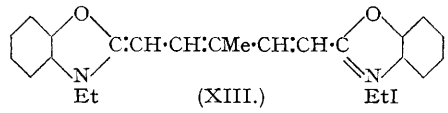
(XI.)

In preparing the oxadicarbocyanine (XII), having an unsubstituted chain (Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703), (III) was condensed with 2-methylbenzoxazole etho-*p*-toluenesulphonate in the

presence of potassium acetate and acetic anhydride. We also prepared it by the interaction of 2-β-acetanilidovinylbenzoxazole ethiodide, malonic acid, and triethylamine (Ogata, *Bull. Inst. Phys. Chem. Res., Japan*, 1937, **16**, 631), and conclude this to be a better method for oxadicarbocyanines, specifically. When we prepared



(XII.)



(XIII.)

(XIII) similarly, by use of methylmalonic acid, our yield was only 3%, against the 36% claimed (*idem., Proc. Imp. Acad. Japan*, 1937, **13**, 325). The method is said to be applicable to ethylmalonic acid also (*idem, ibid.*) but we failed to isolate the γ-ethyl dye.

We compared the absorption maxima in methyl-alcoholic solution of eight dicarbocyanines having a β-methyl substituent, nine having a γ-methyl substituent, and one having αγ-dimethyl substituents, with the parent dyes having an unsubstituted chain. The β-methyldicarbocyanine always had its absorption maximum further into the red, by amounts varying from 30—190 A., than the unsubstituted dye. In six cases, where the γ-methyl dicarbocyanine was also available for comparison, the β-methyl compound absorbed further into the red than did the γ-methyl compound. The one αα′-dimethyldicarbocyanine had a more bathochromic absorption than the α-methyl-, γ-methyl-, or unsubstituted dicarbocyanine. As regards the γ-methyl dyes, no generalisation could be made except for the αα-dimethyl compound; the figures are shown in the accompanying table.

Some of these chain-substituted dicarbocyanines are powerful photographic sensitisers, but it cannot be said that they are better, generally, than the parent dyes with an unsubstituted chain.

Experimental.

iso*Butyraldehyde Diethyl Acetal.*—*iso*Butyraldehyde (144 g., 1 mol.), ethyl orthoformate (296 g., 1 mol.), ethyl alcohol (400 c.c.), and ammonium chloride (4 g.) were heated together under reflux on the steam bath for 15 minutes and the product fractionally distilled. The fraction (179 g.) of b. p. 134—138° amounted to a 61% yield. Oeconomides prepared it from *iso*butyraldehyde and hydrochloric acid, followed by sodium ethoxide, and gives b. p. 134—136° (*Bull. Soc. chim.*, 1881, [2], **35**, 500).

α-*Bromo*iso*butyraldehyde Diethyl Acetal.*—*iso*Butyraldehyde diethyl acetal (73 g., 1 mol.) was dissolved in chloroform (200 c.c.) and, after addition of calcium carbonate (50 g., 1 mol.) was stirred mechanically whilst bromine was added, at such a rate that the heat of reaction kept the mixture gently boiling, until a permanent yellow colour was produced (28 c.c., 2·2 atoms). After cooling, it was treated with water (200 c.c.) and filtered; the chloroform layer was washed with water and dried over potassium carbonate. After removal of the solvent, the residual oil was vacuum distilled, being obtained in 48% yield (53·7 g.); b. p. 89°/18 mm. A sample was analysed by Carius' method, used throughout this work (Found: Br, 35·4. $C_8H_{17}O_2Br$ requires Br, 35·6%).

α-*Methylacraldehyde Diethyl Acetal.*—α-Bromo*iso*butyraldehyde diethyl acetal (120 g., 1 mol.) was added to a solution of sodium (36·8 g.; 2 atoms) in alcohol (460 c.c.) and the mixture boiled under reflux for 48 hours. It was treated with water (400 c.c.) and the oil separated. The aqueous layer was extracted once with ether and the oil added to this extract which was dried with sodium sulphate. After removal of solvent, the residue was distilled, being obtained in 85% yield (64 g.); b. p. 143—148°.

αβ-*Dibromo*iso*butyraldehyde Diethyl Acetal.*—A solution of α-methylacraldehyde diethyl acetal (64 g., 1 mol.) in chloroform (220 c.c.) was stirred mechanically with ice cooling and bromine dropped in until a permanent yellow colour was produced (15·9 c.c., 1·5 atoms). The solution was washed with water and dried over potassium carbonate. After removal of the solvent, the residue was distilled under reduced pressure, and gave a 52% yield (70 g.) of colourless liquid, b. p. 137°/35 mm. (Found: Br, 52·5. $C_8H_{16}O_2Br_2$ requires Br, 52·6%).

β-*Bromo*-α-*methylacraldehyde Diethyl Acetal.*—αβ-Dibromo*iso*butyraldehyde diethyl acetal (35 g., 1 mol.) was added to a solution of sodium (3·18 g., 1·2 atoms) in alcohol (60 c.c.) and the solution was boiled under reflux for 3 hours. After cooling, the sodium bromide was filtered off and washed with alcohol. The alcohol was distilled off from the filtrate and the residue was taken up in ether and this extract dried over sodium sulphate. From it a 61% yield (18·2 g.) of colourless liquid was obtained, b. p. 115°/25 mm. (Found: Br, 35·7. $C_8H_{15}O_2Br$ requires Br, 35·8%).

β-*Anilino*-α-*methylacraldehyde Anil Hydrochloride* (II).—The filtered reaction mixture from the preceding preparation was treated with aniline (22 c.c.; 2 mols.), heated on the steam bath for 1 minute, and then treated with concentrated hydrochloric acid (45 c.c.; 3 mols.). Vigorous reaction occurred and a yellow solid separated. Ice-water (470 c.c.) was added and the solid separated, washed with water and ether and dried, being obtained in 63% yield (20 g.). Before analysis, a sample was extracted with ether in a Soxhlet apparatus. It was dried to constant weight at 60—80° in a vacuum; this method of drying was employed throughout this work except where otherwise stated (Found: Cl, 13·2; N, 10·1. $C_{16}H_{17}N_2Cl$ requires Cl, 13·1; N, 10·3%). It had m. p. 232° (decomp.) and an absorption maximum at 3730 A.

Treatment of β-bromo-α-methylacraldehyde diethyl acetal (whether isolated or in the form of reaction mixture from the previous preparation) with aniline hydrochloride (1 mol.) and excess of hydrochloric acid, in either spirit or aqueous solution, with or without heating, gave the same anil hydrochloride but in poorer yield.

αα*γ-Triethoxy-β-bromobutane.*—After drying over sodium sulphate and distilling, crotonaldehyde (73·2 g.; 1 mol.), b. p. 101—108°, was dissolved in absolute ether (185 c.c.) and to the solution, cooled in a freezing mixture, bromine was added until a permanent yellow colour was produced (56 c.c. required; 2·2 atoms). A 1% solution of hydrochloric acid in absolute alcohol (900 c.c.) was added to the ethereal solution of crotonaldehyde dibromide and the liquid boiled for 46 hours and then poured into water (4000 c.c.). It was extracted with chloroform (3 × 100 c.c.), the extract freed from acid by shaking for 5 minutes with 1% sodium hydroxide solution (1000 c.c.) and then dried over sodium sulphate. The solvent was removed and the residue vacuum distilled (141 g. obtained) and then fractionally distilled under a vacuum. A forerun (11 g.) having a low bromine content (Found: Br, 23·5%) was discarded; three higher-boiling fractions, which approximated to one another in bromine content, were combined and amounted to a 42% yield (118·3 g.), b. p. 105—120°/20—25 mm. Assuming the impurity to be crotonaldehyde dibromide, the conversion is 90% (Found: Br, 33·7. Calc. for $C_{10}H_{21}O_3Br$: Br, 29·7%; calc. for $C_4H_6OBr_2$: Br, 69·5%).

β-*Ethoxycrotonaldehyde Diethyl Acetal.*—αα*γ*-Triethoxy-β-bromobutane (196 g.; 1 mol.) was treated with a solution of sodium (50 g.; 3 atoms) in absolute alcohol (570 c.c.) and the mixture was heated on the steam bath for 96 hours.

After removal of the alcohol under reduced pressure, the residue was treated with water (2500 c.c.) and extracted with chloroform. The extract was dried over sodium sulphate, the solvent removed and the oil fractionally distilled under a vacuum. Viguier (*Ann. Chim.*, 1913, [8], **28**, 433) describes the acetal as having b. p. 82—86°/15 mm., 190—195° at atmospheric pressure, but the first of our three fractions had b. p. 96—106°/8—9 mm., this representing a 28% yield (38·0 g.) and an 86% conversion (Found: Br, 4·3. Calc. for $C_{10}H_{20}O_3$: Br, 0·0%. Calc. for $C_{10}H_{21}O_3Br$: Br, 29·7%); the second, b. p. 106—116°/8—9 mm., represented a 34% yield (46·2 g.) and a 95% conversion (Found: Br, 1·5%), assuming the bromine-containing impurity to be the preceding compound. These two fractions were colourless; the third (3·2 g.), b. p. 116—144°/11 mm., was yellow and was rejected (Found: Br, 5·7%).

The preparations of this acetal and of the preceding compound were carried out by Miss E. M. Wilson.

Dicarbocyanine halide.	Absorption for unsubstituted chain.	Absorption for β-methyl substituent.	Bathochromic shift caused by β-methyl.	Absorption for γ-methyl substituent.	Bathochromic shift caused by γ-methyl.
3 : 3′-diEt-thia-	6500 A.	6610 A.	110 A.	6500 A.	0
3 : 3′-diMe-thia-	6500	6610	110	—	—
3 : 3′-diEt-5 : 6 : 5′ : 6′-tetra-MeO-thia-	6850	6950	100	6750	−100 A.
3 : 3′-diEt-4 : 5 : 4′ : 5′-dibenzthia-	6910	6940	30	—	—
3 : 3′-diEt-6 : 7 : 6′ : 7′-dibenzthia-	6870	6940	70	6840	− 30
3 : 3′-diEt-5 : 5′-diCl-thia-	6600	6660	60	6630	30
3 : 3′-diEt-selena-	6600	6700	100	6550	− 50
1 : 3 : 3 : 1′ : 3′ : 3′-hexaMe-indo-	6350	6540	190	6360	10
1 : 1′-diEt-2 : 2′-	7080	—	—	7050	− 30
1 : 1′-diEt-4 : 4′-	8100	—	—	8180	80
1 : 1′-diEt-oxa-	5800	—	—	5750	− 50

Bis-2-(3-*ethylbenzthiazole*)-γ-*methylpentamethincyanine Iodide* (V).—2-Methylbenzthiazole ethiodide (3·05 g., 2 mols.) and β-anilino-α-methylacraldehyde anil hydrochloride (1·36 g., 1 mol.) were heated with ethyl alcohol (20 c.c.), a solution of sodium (0·23 g., 2 atoms) in ethyl alcohol (5 c.c.) added and the mixture boiled and stirred for 3 minutes. The dye was separated when cold, washed with water and extracted with ether in a Soxhlet apparatus. The residue (2·05 g.) was boiled out with methyl alcohol (10 c.c.) and recrystallised (1·2 g., 45%) from methyl alcohol (325 c.c.) (Found: I, 23·9. Calc. for $C_{24}H_{25}N_2IS_2$: I, 23·85%). It was also prepared from 2-methylbenzthiazole ethiodide (1·53 g.; 2 mols.), β-bromo-α-methylacraldehyde diethyl acetal (1·12 g., 2 mols.), and pyridine (15 c.c.), by boiling them together for 2 minutes and precipitating with ether. The crude dye was washed with hot water, and then with acetone and ether and on recrystallisation from methyl alcohol gave a 26% yield (0·34 g.). It formed dark green crystals with a gold reflex; m. p. 261—263° (decomp.). The absorption maximum of a methyl-alcoholic solution is at 6400 A. This dye is described as having been prepared by use of β-ethoxy-α-methylacraldehyde acetal in pyridine and as having its absorption maximum at 6500 A. and its sensitising maximum at 6950 A. (I.G. Farbenind. A.-G., B.P. 394,537/1931). Sitnik and Steingardt, who prepared it in the same way, obtained a 46% yield and quote m. p. 250° (*J. Appl. Chem. Russ.*, 1936, **9**, 1842).

Bis-2-(5-*chloro*-3-*ethylbenzthiazole*)-γ-*methylpentamethincyanine Chloride*.—This was similarly prepared from 5-chloro-2-methylbenzthiazole (7·68 g., 2 mols.) and β-anilino-α-methylacraldehyde anil hydrochloride (2·73 g., 1 mol.) in alcohol (30 c.c.), the mixture being boiled and stirred for 7 minutes after addition of a solution of sodium (0·51 g., 2·2 atoms) in alcohol (10 c.c.), and then poured into a hot solution of ammonium chloride (5·3 g., 10 mols.) in water (20 c.c.). The dye was filtered off when cold and washed with water and with ether (3·98 g. obtained). It was recrystallised from methyl alcohol (1850 c.c.) and obtained in 34% yield (1·71 g.) (Found: Cl, 20·8. $C_{24}H_{23}N_2Cl_3S_2$ requires Cl, 20·9%). The bluish-grey crystals had m. p. 263° (decomp.). The absorption maximum is at 6630 A. Sensitising is from 6660—7150 A., with the maximum at 6900 A.

Bis-2-(5 : 6-*dimethoxy*-3-*ethylbenzthiazole*)-γ-*methylpentamethincyanine Iodide*.—This was similarly prepared from 5 : 6-dimethoxy-2-methylbenzthiazole ethiodide. The crude dye (1·8 g., 55% yield) was contaminated with purple impurity, from which it was freed by stirring with hot water (100 c.c.), washing several times with water, and then washing with successive quantities of acetone until the filtrates had lost the reddish colour. The residue was recrystallised from methyl alcohol (650 c.c.) and a 34% yield (1·1 g.) of brilliant green crystals obtained (Found: I, 19·35. Calc. for $C_{28}H_{33}O_4N_2IS_2$: I, 19·45%). M. p. 233—235° (decomp.). The absorption maximum of its methyl-alcoholic solution is at 6750 A. It is described as having been prepared by use of β-ethoxy-α-methylacraldehyde acetal in pyridine (I. G. Farbenind. A.-G., B.P. 394,537/1931).

Bis-2-(3-*ethyl*-6 : 7-*benzbenzthiazole*)-γ-*methylpentamethincyanine Iodide*.—This was similarly prepared from 2-methyl-6 : 7-benzbenzthiazole ethiodide. After washing with water and with ether, the crude dye (1·7 g., 54% yield) was boiled out five times with methanol (total 100 c.c.) in order to remove purple impurity. The residue was then recrystallised from methanol (1300 c.c.) and was obtained in 45% yield (Found: I, 20·2. $C_{32}H_{29}N_2IS_2$ requires I, 20·1%). The greenish gold crystals had m. p. 270° (decomp.). The absorption maximum is at 6840 A. It sensitises from 5500—7900, with maximum at 7000 A.

Bis-2-(3-*ethylbenzselenazole*)-γ-*methylpentamethincyanine Chloride*.—2-Methylbenzselenazole (3·92 g., 2 mols.) was heated for 3 hours at 100° with ethyl sulphate (2·6 c.c., 2 mols.), which had been made neutral and anhydrous by treatment with sodium bicarbonate and sodium sulphate. The product was dissolved in hot alcohol and treated with the anil hydrochloride; after adding sodium in alcohol, the mixture was boiled and stirred and poured into hot ammonium chloride solution. The crude dye was filtered off, washed with water and ether (3·78 g. obtained), and recrystallised from methyl alcohol (25 c.c.). A 43% yield (2·50 g.) of green crystals with a golden reflex was obtained (Found: N, 5·35. $C_{24}H_{25}N_2ClSe_2$ requires N, 5·25%); m. p. 214° (decomp.). The absorption maximum of a methanolic solution is at 6550 A. The sensitising maximum is at 7000 and sensitisation extends from 6200—7400 A. The corresponding iodide has been described (I.G. Farbenind. A.-G., B.P. 394,537/1931).

Bis-2-(1 : 3 : 3-*trimethylindolenine*)-γ-*methylpentamethincyanine Iodide* (VI).—2 : 3 : 3-Trimethylindolenine methiodide (6·02 g., 2 mols.), β-anilino-α-methylacraldehyde anil hydrochloride (2·73 g., 1 mol.), anhydrous sodium acetate (7·22 g., 8·8 mols.) and acetic anhydride (40 c.c.) were boiled together, with stirring, for 2 minutes. The solution was poured into a solution of potassium iodide (6·4 g., 4 mols.) in water (30 c.c.). The resultant green tar solidified on cooling and after separation was washed with water and ether (4·49 g. obtained). It was recrystallised by taking up in hot methanol (70 c.c.) and adding hot water (70 c.c.). The yield of dark greenish-blue crystals was 68% (3·54 g.) (Found, after drying to constant weight in a vacuum at 100—110°: I, 24·15. $C_{28}H_{33}N_2I$ requires I, 24·2%). It had m. p. 250—252° (decomp.). The absorption maximum is at 6370 A. and the dye shows no sensitising action.

Bis-2-(1-*ethylquinoline*)-γ-*methylpentamethincyanine Iodide* (VII).—Quinaldine etho-*p*-toluenesulphonate (3·43 g.), β-anilino-α-methylacraldehyde anil hydrochloride, anhydrous sodium acetate and acetic anhydride were boiled together

for 5 minutes and the solution poured into hot aqueous potassium iodide. The crystalline dye was separated when cold, washed with water and ether (1·12 g. obtained), and recrystallised from methanol (400 c.c.), being obtained in 38% yield (Found : I, 24·45. $C_{28}H_{29}N_2I$ requires I, 24·4%). The green crystals had m. p. 260—261° (decomp.). The principal absorption maximum is at 7050 with a secondary one at 6500 A. The principal sensitising maximum is at 7500 with a weaker one at 6850 A.

Bis-4-(1-*ethylquinoline*)-*γ*-*methylpentamethincyanine Iodide* (VIII) —Lepidine (2·86 g., 2 mols.) and ethyl *p*-toluenesulphonate (4·00 g., 2 mols.) were heated together at 145—155° for 3 hours. The product was dissolved in acetic anhydride (70 c.c.) and boiled with the anil hydrochloride and sodium acetate for one minute; the reaction mixture was poured into hot aqueous potassium iodide. After cooling, some ammonia was added to cause separation of the dye, which was filtered off and washed with water and ether (0·6 g. obtained). It was recrystallised from methanol (85 c.c. per g.) and obtained in 3% yield (Found : I, 24·4. $C_{28}H_{29}N_2I$ requires I, 24·4%). The greenish golden crystals had m. p. 240—241° (decomp.). The absorption maximum is at 8180 A., with an inflexion in the curve at 7300 A. Sensitising is from 7000—9200 with the maximum at 8700 A.

Bis-2-(3-*ethylbenzthiazole*)-*β*-*methylpentamethincyanine Iodide* (IX; R = Et).—2-Methylbenzthiazole etho-*p*-toluenesulphonate (1·75 g., 2 mols.), *β*-ethoxycrotonaldehyde diethyl acetal (1 c.c., 2 mols.), anhydrous sodium acetate (1·64 g., 8 mols.) and acetic anhydride (40 c.c.) were mixed together and kept at 0°, with occasional stirring, for 5 days, when the mixture was added to water (300 c.c.). After some hours the product was filtered off, dissolved in hot spirit and treated with a hot solution of potassium iodide (1·7 g., 4 mols.) in water (20 c.c.). After recrystallising the crude dye (0·4 g.) from methanol (200 c.c. per g.) the yield was 27% (0·35 g.). In another preparation 2-methylbenzthiazole ethiodide (1·53 g., 2 mols.), *β*-ethoxycrotonaldehyde diethyl acetal (1 c.c., 2 mols.), and triethylamine (0·35 c.c., 1 mol.) in absolute alcohol (25 c.c.) were boiled and stirred together for 4 minutes. After cooling, the dye was separated, washed with water (0·54 g. obtained), and recrystallised from methanol. The yield of green crystals, m. p. 206—207° (decomp.), was 32% (0·43 g.) (Found : I, 23·9. $C_{24}H_{25}N_2IS_2$ requires I, 23·8%). The absorption maximum is at 6610 A. The sensitising action of the dye extends from 5000—7500 with a maximum at 7000 A.

The preparations of this dye were carried out by Miss E. M. Wilson.

Bis-2-(3-*methylbenzthiazole*)-*β*-*methylpentamethincyanine Iodide* (IX; R = Me).—This was similarly prepared from 2-methylbenzthiazole methiodide, *β*-ethoxycrotonaldehyde diethyl acetal, and triethylamine in alcohol. The washed dye (17% yield) was recrystallised from methanol (750 c.c. per g.) and the yield was 12% (Found : I, 25·05. $C_{22}H_{21}N_2IS_2$ requires I, 25·15%). The greyish blue crystals had m. p. 215° (decomp.). The absorption maximum is at 6610 A. It shows photographic sensitising action from 6000—7500 A. with a maximum at 7000 (cf. Kendall, Wood, and Majer, B.P. 553,144/1941).

Bis-2-(5-*chloro*-3-*ethylbenzthiazole*)-*β*-*methylpentamethincyanine* p-*Toluenesulphonate*.—This was prepared by interaction of 5-chloro-2-methylbenzthiazole etho-*p*-toluenesulphonate, *β*-ethoxycrotonaldehyde diethyl acetal, anhydrous sodium acetate, and acetic anhydride at 0° during 5 days. The reaction mixture was poured into water and after some hours the dye was separated, and washed with water and ether (72% yield). It was recrystallised from methanol (165 c.c. per g.) and obtained in 58% yield. In a similar experiment, pyridine took the place of the sodium acetate and acetic anhydride but, under these conditions, the yield of recrystallised dye was only 15% (Found : Cl, 10·9. $C_{31}H_{30}O_3N_2Cl_2S_3$ requires Cl, 11·0%). The blue-green crystals had m. p. 231° (decomp.). The absorption maximum is at 6660 A. It sensitises from 6000—7500 with a maximum at 7000 A.

Bis-2-(5 : 6-*dimethoxy*-3-*ethylbenzthiazole*)-*β*-*methylpentamethincyanine Iodide*.—5 : 6-Dimethoxy-2-methylbenzthiazole ethiodide (3·65 g., 2 mols.), *β*-ethoxycrotonaldehyde diethyl acetal (2 c.c., 2 mols.), triethylamine (7 c.c., 1 mol.) and ethyl alcohol (50 c.c.) were boiled and stirred together for 5 minutes. The crude dye was washed successively with water, acetone and ether (0·25 g. obtained). It was recrystallised from methanol (100 c.c.) and the yield was 4% (0·15 g.) (Found : I, 19·55. $C_{28}H_{33}O_4N_2IS_2$ requires I, 19·5%). The dull green crystals had m. p. 207° (decomp.). The absorption maximum is at 6950 A., with an inflexion at 6400. The dye sensitises from 6000—7700 with a maximum at 7250 A.

Bis-2-(3-*ethyl*-4 : 5-*benzbenzthiazole*)-*β*-*methylpentamethincyanine Iodide*.—This was similarly prepared by use of 2-methyl-4 : 5-benzbenzthiazole ethiodide. The washed crude dye was recrystallised from methanol (575 c.c. per g.) (3% yield) (Found : I, 20·15. $C_{32}H_{29}N_2IS_2$ requires I, 20·1%). The green crystals had m. p. 224° (decomp.). The absorption maximum is at 6940 A. The dye sensitised to 6500 A. with the maximum at 6100 and there was only a trace of sensitising at 7300 A.

Bis-2-(3-*ethyl*-6 : 7-*benzbenzthiazole*)-*β*-*methylpentamethincyanine Bromide*.—This dye was prepared by interaction of 2-methyl-6 : 7-benzbenzthiazole etho-*p*-toluenesulphonate, *β*-ethoxycrotonaldehyde diethyl acetal, and sodium acetate in acetic anhydride, followed by treatment with water; the rather sticky product was dissolved in hot spirit and the *bromide* precipitated by means of aqueous ammonium bromide. In one case the condensation was carried out at 0° during 4 days, in another at the boiling temperature for 2 minutes. The combined products were recrystallised from methanol and obtained in 7% yield (Found : Br, 13·1. $C_{32}H_{29}N_2BrS_2$ requires Br, 13·2%). The dark green crystals had m. p. 197° (decomp.). The absorption maximum is at 6940 A. The dye sensitises from 6800—7600 with a maximum at 7250 A.

Bis-2-(3-*ethylbenzselenazole*)-*β*-*methylpentamethincyanine Iodide* (X).—After heating a mixture of 2-methylbenzselenazole and ethyl sulphate at 100° for 3 hours, the product was dissolved in acetic anhydride, and anhydrous sodium acetate was added. The mixture was cooled to 0° and treated with *β*-ethoxycrotonaldehyde diethyl acetal. After 4 days at 0° with occasional stirring, the mixture was heated to 100° and treated with hot potassium iodide solution. The precipitated dye was filtered off when cold and washed with water (20% yield). It was recrystallised from methanol (600 c.c. per g.) and obtained in only 4% yield, apparently unstable in solution (Found : I, 20·15. $C_{24}H_{25}N_2ISe_2$ requires I, 20·25%). The greenish gold crystals had m. p. 190° (decomp.). The absorption maximum is at 6700 A. It sensitises from 5800—7600 with a maximum at 7200 A.

Bis-2-(1 : 3 : 3-*trimethylindolenine*)-*β*-*methylpentamethincyanine Iodide* (XI).—2 : 3 : 3-Trimethylindolenine methiodide (3 g., 2 mols.), *β*-ethoxycrotonaldehyde diethyl acetal (2 c.c., 2 mols.), and pyridine (40 c.c.) were boiled together under reflux for 15 minutes. The dye was precipitated with ether (34% yield). The crude product was dissolved in hot ethanol (11 c.c. per g.) and the filtered solution treated with hot water (17 c.c. per g.). The yield of dark purple crystals was 14%. For analysis a sample was dried to constant weight in a vacuum at 90° (Found : I, 24·2. $C_{28}H_{33}N_2I$ requires I, 24·2%). The dark purple crystals had m. p. 133° (decomp.). The absorption maximum is at 6540 A. The dye does not confer extra sensitivity.

Bis-2-(3-*ethylbenzthiazole*)-*aa'*-*dimethylpentamethincyanine Iodide*.—2-Ethylbenzthiazole ethiodide (3·19 g., 2 mols.), *β*-ethoxyacraldehyde diethyl acetal (1·74 g., 2 mols.) and pyridine (15 c.c.) were boiled together under reflux for 5 minutes. Some solid crystallised on cooling and more was precipitated by addition of ether. It was separated, washed with hot water, then with acetone and ether (1·15 g. obtained). On recrystallisation from methanol (375 c.c. per g.), it was obtained in 38% yield (Found : I, 23·3. Calc. for $C_{25}H_{27}N_2IS_2$: I, 23·2%). The dark green crystals had m. p. 241° (decomp.). Sitnik and Steingardt (*J. Appl. Chem. Russ.*, 1936, **9**, 1842) obtained a 15% yield, but did not record any analysis or m. p. The absorption maximum is at 6650 A. The dye is a sensitiser, its action extending to 7700 with a maximum at 7100 A.

Bis-(3-ethylbenzoxazole)pentamethincyanine Iodide (XII).—A mixture of 2-methylbenzoxazole etho-*p*-toluenesulphonate (5 g., 2 mols.), β-anilinoacraldehyde anil hydrochloride (1·94 g., 1 mol.), anhydrous potassium acetate (3·0 g., 4 mols.) and acetic anhydride (20 c.c.) was put into a glycerol bath at 60° and stirred mechanically. The temperature was raised to 130° during 9—10 minutes and kept at 130—132° for ½ minute. The reaction mixture was then poured into a cold solution of potassium iodide (10 g., 8 mols.) in water (200 c.c.). Next day the aqueous part was separated and the tar washed thrice with water and once with ether. After treatment with a cold mixture of methanol (1 c.c.) and ethyl acetate (19 c.c.), solid dye was separated and was washed thrice with ethyl acetate (total 6 c.c.) (0·20 g. obtained). After recrystallisation from methanol (8 c.c.), it was obtained in 3% yield (0·12 g.) (Found, after drying in a vacuum at 100—110° : I, 26·2. Calc. for $C_{23}H_{23}O_2N_2I$: I, 26·1%). The steely crystals had m. p. 232° (decomp.).

2-β-Acetanilidovinylbenzoxazole ethiodide (4·34 g., 2 mols.), malonic acid (0·62 g., 1·2 mols.) and triethylamine (3 c.c., 4 mols.) were heated together in an oil-bath at 80—90° for 20 minutes. The melt was stirred up with hot water which was decanted off when cold and this treatment was repeated. The residue was dissolved in hot acetone (15 c.c.) and dye crystallised on cooling (0·41 g. obtained). On recrystallisation from methanol (25 c.c. per g.) the yield was 15% (0·29 g.). Ogata (*Bull. Inst. Phys. Chem. Res., Japan*, 1937, **16**, 631) quotes a 17% yield.

Bis-(3-ethylbenzoxazole)-γ-methylpentamethincyanine Iodide (XIII).—2-β-Acetanilidovinylbenzoxazole ethiodide (17·36 g., 2 mols.) and methylmalonic acid (2·40 g., 1·2 mols.) were ground together and treated with triethylamine (12 c.c., 4·4 mols.). The mixture was heated with mechanical stirring for 45 mins. in an oil bath at 80—90°. The resultant tar was washed twice with hot water and the residue was then heated with acetone (15 c.c.). Crystals were deposited on cooling and were filtered off, washed with acetone (0·55 g. obtained) and recrystallised from methanol (30 c.c. per g.). The yield, after two crystallisations, was 2% (Found : I, 25·55. Calc. for $C_{24}H_{25}O_2N_2I$: I, 25·35%). The steel-blue crystals had m. p. 242° (decomp.). A methanolic solution had its absorption maximum at 5750 A. The photographic sensitising action extended to 6400 A. and was at its maximum at 6150 A. Ogata (*Proc. Imp. Acad. Japan*, 1937, **13**, 325) records m. p. 217°, absorption maximum 5900 A. in alcohol, and sensitising maximum 6100 A.

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