260. 5-*Chloro- and* 5-*Bromo*-1-*methylbenzthiazole and Cyanine Dyes prepared from them.*

By Bernard Beilenson and Frances M. Hamer.

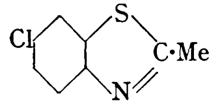
König, Seidel, and Stühmer (*Ber.*, 1928, **61**, 2065) prepared 5-chloro-1-methylbenzthiazole (I), m. p. 81°, by two methods, one of which consisted in oxidising 4-chlorothioacetanilide with alkaline potassium ferricyanide; 5-bromo-1-methylbenzthiazole was prepared in an analogous manner, but no m. p. was recorded, although its methiodide and methoperchlorate were described.

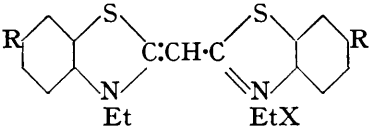
Naiman and Bogert (*J. Amer. Chem. Soc.*, 1935, **57**, 1660), in studying the action of bromine on 1-methylbenzthiazole in acetic acid, describe the formation of an unstable addition product which, when the reaction mixture is heated, is converted into yellow crystals, decomposing between 190 and 220° : analytical data indicate the formula

C_8H_6NSBr and, from analogy, it is concluded that the substance is 5-bromo-1-methylbenzthiazole, but no reference is made to König's preparation.

We doubted the correctness of that conclusion, because of the unlikelihood that the 5-bromo-compound would decompose so much above the m. p. of 5-chloro-1-methylbenzthiazole, which we had already prepared, m. p. 82—83°, by König's method, our 4-chlorothioacetanilide being obtained from 4-chloroacetanilide by an application of Hofmann's method (*Ber.*, 1878, **11**, 339), instead of by those described in the literature (Sachs and Loevy, *Ber.*, 1904, **37**, 874; Worrall, *J. Amer. Chem. Soc.*, 1924, **46**, 2834). On repeating Naiman and Bogert's work, our suspicion was confirmed when we found their yellow crystals to be so unstable that they became oily on treatment with cold water : 5-chloro-1-methylbenzthiazole is stable under such conditions. Although their analytical values would agree with those required for 1-methylbenzthiazole hydrobromide, yet that also is precluded, since it is a white salt, readily soluble in water. In repeating König's preparation of 5-bromo-1-methylbenzthiazole, 4-bromoacetanilide was obtained in 95% yield by the method of Remmers (*Ber.*, 1874, **7**, 346) and converted by the Hofmann method (*loc. cit.*) into 4-bromothioacetanilide, which had originally been prepared by another process (Worrall, *J. Amer. Chem. Soc.*, 1918, **40**, 415). From it, a 49% yield of 5-bromo-1-methylbenzthiazole was obtained, and it melted at 86—87°, *i.e.*, only 4° higher than the corresponding 5-chloro-compound; König's yield was 25%.

(I.)





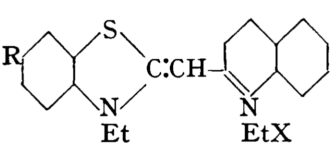
(II.)

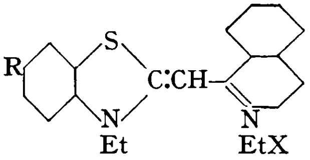
The *ethiodides* of 5-chloro- and 5-bromo-1-methylbenzthiazole were used for making cyanine dyes. It was found that a number of these chloro- and bromo-substituted dyes are less soluble in methyl alcohol than are the unsubstituted dyes; for convenience, other quaternary salts, which gave more soluble dyes, were used in some cases.

A 5 : *5'-dichloro-thiacyanine* (II) was prepared from 5-chloro-1-methylbenzthiazole ethochloride by the method used for preparing unsubstituted thiacyanines (Fisher and Hamer, J., 1930, 2502). The 5 : *5'-dibromo-thiacyanine* was prepared from the appropriate ethiodide, and its purification included treatment with sulphur dioxide, as in purifying oxacyanines (*idem*, J., 1934, 962).

The method for the preparation of thia-ψ-cyanines (Hamer, J., 1928, 206), applied to the preparation of the 5-chlorothia-2'-cyanine (III, R = Cl), gave, with sodium ethoxide as condensing agent, a 38% yield of recrystallised product. It has, however, been found that for effecting the ψ-cyanine condensation, finely-divided, anhydrous potassium carbonate is greatly superior to the stronger alkalis (Kodak Ltd. and Beilenson, B.P. 435,542/1933). Thus in the present instance, use of potassium carbonate raised the yield to 66%, and resulted in a 60% yield of the corresponding *5-bromo-thia-2'-cyanine*. Use of potassium carbonate gave 52 and 56% yields, respectively, of the *5-chloro-* and *5-bromo-thia-1'-cyanines* (IV), whilst the original yields of thia-1'-cyanines, obtained by means of other condensing agents, varied from 40 to 52% (Fisher and Hamer, J., 1934, 1905).

(III.)

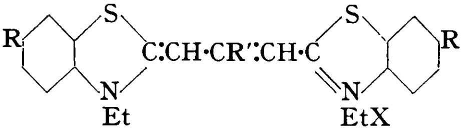




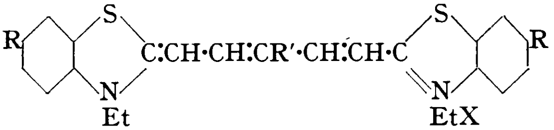
(IV.)

In preparing the 5 : *5'-dichloro-* and *-dibromo-thiacarbocyanines* (V; R' = H) by use of ethyl orthoformate and pyridine, the yields were only 46 and 36%, as compared with an 82% yield for the parent substance (Hamer, J., 1927, 2796); König described the 5 : 5'-dichloro-2 : 2'-dimethylthiacarbocyanine (*loc. cit.*), but the cyanines dealt with here are all

2 : 2'-diethyl-compounds. The 5 : 5'-*dihalogeno*-8-*methylthiacarbocyanines* (V; R = Hal., R' = Me) were prepared by use of ethyl orthoacetate and pyridine (cf. Hamer, J., 1928, 3160), and the corresponding -8-*ethyl*-compounds were prepared by means of methyl orthopropionate and pyridine. Brooker and White (*J. Amer. Chem. Soc.*, 1935, **57**, 2480), in thus preparing the parent 8-ethylthiacarbocyanine, noted the fact that dye formation proceeds more readily with the etho-*p*-toluenesulphonate of 1-methylbenzthiazole than with its ethiodide; similarly, from the etho-*p*-toluenesulphonate of 2-methyl-β-naphthathiazole they were successful in obtaining a 27% yield of the 8-methyldibenzthiacarbocyanine (*ibid.*, p. 547), whereas the ethiodide had given a negative result (Hamer, J., 1929, 2598). The same phenomenon occurs with 5-chloro-1-methylbenzthiazole, for whereas its etho-*p*-toluenesulphonate gave a 23% yield of the 8-ethylthiacarbocyanine, the corresponding ethiodide gave a negative result. It is surprising that the use of acetic anhydride, which is not usually so good a medium as pyridine for condensations of this kind, resulted in a 3% yield being obtained from the ethiodide; the yield from the etho-*p*-toluenesulphonate dropped to 8%. By making use of ethyl orthobenzoate, which was kindly given us by Dr. L. G. S. Brooker, the 5 : 5'-*dihalogeno*-8-*phenylthiacarbocyanines* (V; R = Hal., R' = Ph) were prepared from the etho-*p*-toluenesulphonates of the appropriate bases; whereas the yield from 5-chloro-1-methylbenzthiazole etho-*p*-toluenesulphonate was 43%, that from the corresponding ethiodide was only 2%.

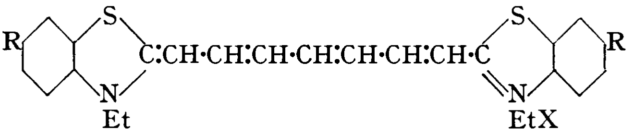


(V.)



(VI.)

The 5 : 5'-*dihalogeno-thiadicarbocyanines* (VI; R' = H) were prepared by the action of sodium ethoxide on a 5-halogeno-1-methylbenzthiazole quaternary salt and β-anilinoacraldehyde anil hydrochloride in alcohol, whilst by making use of the α-chloro- or α-bromo-β-anilinoacraldehyde anil salts (Beattie, Heilbron, and Irving, J., 1932, 260), the corresponding 5 : 5' : 9-*trihalogeno-thiadicarbocyanines* (VI; R = R' = Hal.) were obtained. By use of glutaconaldehyde dianilide hydrochloride, 5 : 5'-*dihalogeno-thiatricarbocyanines* (VII) were prepared (cf. Fisher and Hamer, J., 1933, 189).



(VII.)

Dr. E. P. Davey kindly made wedge spectrograms showing the absorption of methyl-alcoholic solutions of these new cyanines, and also, after their addition to silver halide emulsions, tested them for photographic sensitising properties.

In comparing the absorption and sensitising action of compounds of the cyanine type, it is immaterial whether or not they have the same anion, provided, of course, that the anion is colourless. In the 5-halogeno- or 5 : 5'-dihalogeno-series, it is particularly interesting to compare the absorption maximum of each substituted compound with that of the corresponding unsubstituted parent compound. For instance, introduction of one halogen atom, whether chlorine or bromine, into the thia-2'-cyanine or thia-1'-cyanine molecule does not affect the absorption. When introduced into the molecule of the simple thiacarbocyanine, even two halogen atoms have no effect, but with all the other kinds of dyes studied, seven types in all, the effect of introducing the two halogen atoms is to shift the absorption maximum 50—100 A. towards the region of longer wave-length. It appears from these results that the shift of the absorption maximum is about the same, whether the molecular weight is increased by chlorine or by bromine atoms.

It is known that in simple symmetrical cyanine dyes derived from 1-methylbenzthiazole ethiodide, the absorption maximum is shifted towards the red by replacing the two benzthiazole by two naphthathiazole nuclei : the values noted for eight replacements of this kind vary between 310 and 410 A. (Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703). The present observation that the introduction of two bromine atoms, 2 × 79·92, has so much less effect than that of two C_4H_4 groups, 2 × 52·03, makes it clear that the influence of weight alone is unimportant as compared with that of other factors, such as introducing the conjugated system ·CH:CH·CH:CH·. In the 5 : 5'-dihalogenothiacarbocyanines, the absorption maximum does not move progressively towards the red as the weight of the group on the central carbon atom is increased; these compounds being arranged in order of increasing wave-length of absorption maximum, the 8-substituents fall in the order methyl, ethyl, hydrogen, phenyl, which is the same as that observed by Brooker and White (*J. Amer. Chem. Soc.*, 1935, **57**, 2480) for the corresponding series of 8-substituted parent dyes.

Upon the sensitising maxima also, the introduction of a single halogen atom into the molecule has no effect, whilst two halogen atoms shift the maximum towards the red by an amount varying from 0 to 200 A. Analogously, Moudgill (J., 1922, **121**, 1509) has recorded that the 6 : 6'- and 5 : 5'(or 7 : 7')-dibromo-derivatives of pinacyanol have their sensitising maxima shifted towards the red as compared with that of pinacyanol. He found that the sensitising action of these dibromo-derivatives was weaker than that of pinacyanol; with the 5-halogeno- and 5 : 5'-dihalogeno-compounds now described it is similarly true that, in a number of instances, the sensitising action is weaker than that of the corresponding unsubstituted compounds.

EXPERIMENTAL.

4-*Chlorothioacetanilide*.—4-Chloroacetanilide (28 g.; 1 mol.) in dry xylene (100 c.c.) was heated on the steam-bath and treated with phosphorus pentasulphide (18·5 g.; 0·5 mol.), with hand-stirring. After 30 minutes' heating, the xylene layer was decanted off and the residue further extracted with hot xylene (2 × 100 c.c.). Crystals separated on cooling, and concentration of the mother-liquor made the yield 54%. After drying in a vacuum at 60—80° (the method used except where otherwise stated), the product was analysed by the method of Carius (employed throughout this work) (Found : Cl, 19·1. Calc. for C_8H_8NSCl : Cl, 19·1%); m. p. 142°.

5-*Chloro*-1-*methylbenzthiazole* (I).—4-Chlorothioacetanilide was oxidised by alkaline potassium ferricyanide as described by König, but the reaction mixture was not extracted with ether before steam-distillation. The base, obtained in 28% yield, melted at 82—83° (Found, after drying in a vacuum desiccator : Cl, 19·05. Calc. for C_8H_6NSCl : Cl, 19·3%).

The methiodide was described by König as melting at 222°, but no analysis was given. It was prepared by heating the base with 20% excess of methyl iodide in a sealed tube at 100° for 2 days, in a yield of 94% and, after recrystallising from methyl alcohol (13 c.c. per g.), 79% (Found : Cl + I, 50·2. Calc. for C_9H_9NSClI : Cl + I, 49·9%); m. p. 258—260° (decomp.).

The *ethiodide* was similarly prepared [yields, 71% crude, 59% after recrystallisation from methyl alcohol (7 c.c. per g.)] (Found : Cl + I, 48·2. $C_{10}H_{11}NSClI$ requires Cl + I, 47·8%); m. p. 239° (decomp.), with darkening from 220°.

4-Bromothioacetanilide was obtained from 4-bromoacetanilide, by the same method as was used for 4-chlorothioacetanilide, in 67% yield (Found : Br, 34·8. Calc. for C_8H_8NSBr : Br, 34·7%); m. p. 152°.

5-*Bromo*-1-*methylbenzthiazole*.—4-Bromothioacetanilide (86·3 g.; 1 mol.), dissolved in sodium hydroxide solution (2*N*, 1125 c.c.; 6 mols.), and filtered from some suspended matter, was gradually added to an ice-cooled solution of potassium ferricyanide (248 g.; 2 mols.) in water (1125 c.c.). The oil which separated was washed with water and steam-distilled, and the yield of almost colourless solid was 49% (41·5 g.) (Found, after drying in a vacuum desiccator : Br, 35·1. Calc. for C_8H_6NSBr : Br, 35·05%); m. p. 86—87°.

The base and ethyl bromide were heated together at 100° for 24 hours. Ether extracted 79% of unchanged base, and the yield of undissolved *ethobromide* was 18%. After recrystallisation from absolute alcohol and ether (3 c.c. of each per g.), the yield was 16% (Found : Br, 47·55. $C_{10}H_{11}NSBr_2$ requires Br, 47·4%); m. p. 197°, with previous darkening.

The *etho*-p-*toluenesulphonate*, prepared by heating the base and ethyl *p*-toluenesulphonate (1 mol. of each) together at 140—145° for 3 hours, and washed with hot benzene and cold acetone, was obtained as a hygroscopic salt in 72% yield (Found : Br, 18·6. $C_{17}H_{18}O_3NS_2Br$ requires Br, 18·7%).

The *ethiodide* was quantitatively obtained from the etho-*p*-toluenesulphonate by treatment with potassium iodide in aqueous solution. It was also obtained by heating the base and ethyl iodide in a sealed tube, the yields being 81% after washing with ether and 67% after recrystallisation from methyl alcohol (4 c.c. per g.) (Found : Br + I, 54·0. $C_{10}H_{11}NSBrI$ requires Br + I, 53·9%) ; m. p. 214° (decomp.).

5 : *5'-Dichloro-2 : 2'-diethylthiacyanine Chloride* (II ; R = Cl, X = Cl).—5-Chloro-1-methylbenzthiazole ethochloride was obtained in almost quantitative yield from the ethiodide by the general method already noted (Fisher and Hamer, J., 1930, 2502). The ethochloride (6·65 g. ; 2 mols.), acetic anhydride (105 c.c.), and amyl nitrite (2·6 c.c. ; 1·5 mols.) were heated on the water-bath, as in preparing the unsubstituted dye (*loc. cit.*), but the time of heating was only 1·5 minutes and the reaction mixture was quickly cooled with ice. The yield of crude product was 70% (4·19 g.) ; after recrystallisation from methyl alcohol (60 c.c. per g.), it was 58% (3·47 g.) (Found, after a second recrystallisation : Cl, 23·6. $C_{19}H_{17}N_2S_2Cl_3$ requires Cl, 24·0%). The yellow compound melted at 288° (decomp.).

5 : *5'-Dibromo-2 : 2'-diethylthiacyanine Iodide* (II ; R = Br, X = I).—5-Bromo-1-methylbenzthiazole ethiodide (4·8 g. ; 2 mols.) was boiled with acetic anhydride (50 c.c.). On adding amyl nitrite (1·4 c.c. ; 1·5 mols.), complete solution of the salt occurred, with frothing and darkening. When cold, the dark solid was filtered off and, after being washed with ether, was suspended in acetone and treated, ice-cold, with sulphur dioxide. It was filtered off and washed with acetone (yield 69% ; 2·67 g.) and purified by boiling out with pyridine (300 c.c.). The yield of very insoluble, greenish-yellow residue was 62% (2·4 g.) (Found : Br + I, 46·3. $C_{19}H_{17}N_2S_2Br_2I$ requires 2Br + I, 46·0%) ; m. p. 286° (decomp.). This and the preceding dye have their maximum absorption at λ4300 A. and their maximum sensitising action towards a silver chloride emulsion at λ4500 A.

5-Chloro-2 : 1'-diethylthia-2'-cyanine Iodide (III ; R = Cl, X = I).—By boiling 5-chloro-1-methylbenzthiazole ethiodide (2 g. ; 1 mol.) and 2-iodoquinoline ethiodide (2·42 g. ; 1 mol.) in absolute alcohol (100 c.c.) for 30 minutes, with a solution of sodium (0·30 g. ; 2·2 atoms) in absolute alcohol (10 c.c.), the yield of ether-washed dye was 50% and, after recrystallisation from methyl alcohol (200 c.c. per g.), 38% (1·10 g.). By use of anhydrous potassium carbonate (180-mesh ; 1·2 mols.) instead of sodium, the yield after water-washing was 86%, and after recrystallisation, 66% (Found : Cl + I, 33·0. $C_{21}H_{20}N_2SClI$ requires Cl + I, 32·8%) ; m. p. 287° (decomp.). The colour of the pale orange needles deepened before melting occurred.

5-Bromo-2 : 1'-diethylthia-2'-cyanine Iodide (III ; R = Br, X = I).—From 5-bromo-1-methylbenzthiazole etho-*p*-toluenesulphonate and 2-iodoquinoline ethiodide with potassium carbonate in alcohol, the dye was obtained in 68% yield. Recrystallisation from methyl alcohol (145 c.c. per g.) gave a 60% yield (Found : Br + I, 38·95. $C_{21}H_{20}N_2SBrI$ requires Br + I, 38·8%). The orange needles melted at 278—279° (decomp.). Both this and the preceding dye have an absorption maximum at λ4850 A. and sensitise a gelatino-bromide emulsion, giving a maximum at λ5250 A.

5-Chloro-2 : 2'-diethylthia-1'-cyanine Iodide (IV ; R = Cl, X = I).—From 5-chloro-1-methylbenzthiazole ethiodide, 1-iodo*iso*quinoline ethiodide, and potassium carbonate in absolute alcohol, the dye was obtained in 61% yield after ether extraction. After recrystallisation from methyl alcohol (60 c.c. per g.), the yield was 52% (Found, after drying at 80—100° : Cl + I, 32·5. $C_{21}H_{20}N_2SClI$ requires Cl + I, 32·8%). The dye forms bright red crystals with a green reflex ; m. p. 250° (decomp.).

5-Bromo-2 : 2'-diethylthia-1'-cyanine Iodide (IV ; R = Br, X = I).—From 5-bromo-1-methylbenzthiazole etho-*p*-toluenesulphonate, 1-iodo*iso*quinoline ethiodide, and potassium carbonate in absolute alcohol, the water- and ether-washed dye was obtained in 78% yield. Recrystallisation from methyl alcohol (70 c.c. per g.) resulted in a 56% yield of small, dull red crystals with a green reflex (Found : Br + I, 38·75. $C_{21}H_{20}N_2SBrI$ requires Br + I, 38·4%) ; m. p. 253° (decomp.). This and the preceding dye each show a broad absorption band, with its crest at about 5000 A. They are extremely weak sensitisers.

5 : *5'-Dichloro-2 : 2'-diethylthiacarbocyanine iodide* (V ; R = Cl, R' = H, X = I) was prepared from 5-chloro-1-methylbenzthiazole ethiodide and ethyl orthoformate in pyridine by the standard method (Hamer, J., 1927, 2796). After washing with water and with ether, the yield of dye was 56% ; after recrystallisation from methyl alcohol (900 c.c. per g.), it was 46% (Found : Cl + I, 34·9. $C_{21}H_{19}N_2S_2Cl_2I$ requires 2Cl + I, 35·3%). The steel-blue crystals melt at 292° (decomp.).

5 : *5′-Dibromo-2 : 2′-diethylthiacarbocyanine Bromide* (V; R = Br, R′ = H, X = Br).—The hot reaction mixture from 5-bromo-1-methylbenzthiazole etho-*p*-toluenesulphonate, ethyl orthoformate, and pyridine was treated with excess of 25% aqueous potassium bromide (10 mols. per mol. of dye). The water-washed dye bromide resulted in 57% yield and was recrystallised from methyl alcohol (295 c.c. per g.), the yield of steel-blue crystals then being 36% (Found : Br, 39·5. $C_{21}H_{19}N_2S_2Br_3$ requires Br, 39·8%) ; m. p. 283° (decomp.). This dye, like the corresponding dichloro-compound, has its absorption maximum at λ5600 A., and each sensitising maximum lies at λ6000 A.

5 : *5′-Dichloro-8-methyl-2 : 2′-diethylthiacarbocyanine Iodide* (V; R = Cl, R′ = Me, X = I).—The yield of product from 5-chloro-1-methylbenzthiazole ethiodide, ethyl orthoformate, and pyridine was 43% after washing with ether. After recrystallisation from methyl alcohol (765 c.c. per g.), the yield of dull purple crystals was 20% (Found : Cl + I, 34·1. $C_{22}H_{21}N_2S_2Cl_2I$ requires 2Cl + I, 34·4%) ; m. p. 303° (decomp.).

5 : *5′-Dibromo-8-methyl-2 : 2′-diethylthiacarbocyanine Bromide* (V; R = Br, R′ = Me, X = Br).—The reaction product from 5-bromo-1-methylbenzthiazole etho-*p*-toluenesulphonate, ethyl orthoacetate, and pyridine was treated hot with excess of aqueous potassium bromide. The dye, after washing with water and ether, was obtained in 68% yield and, after recrystallisation from methyl alcohol (1335 c.c. per g.), in 41% yield (Found : Br, 38·65. $C_{22}H_{21}N_2S_2Br_3$ requires Br, 38·9%). The dull purple powder melted at 280° (decomp.). This and the preceding dye show their maximum absorption at 5500 A.

5 : *5′-Dichloro-2 : 2′ : 8-triethylthiacarbocyanine Iodide* (V; R = Cl, R′ = Et, X = I).—5-Chloro-1-methylbenzthiazole etho-*p*-toluenesulphonate was prepared by heating the base and ester at 145—160° for 3 hours. By heating it with methyl orthopropionate and pyridine and treating the reaction mixture with aqueous potassium iodide solution, the yield of dye iodide was 38%. Recrystallisation from methyl alcohol (225 c.c. per g.) gave a 23% yield of minute steel-blue crystals (Found, for material dried in a vacuum at 80—100° : Cl + I, 33·5. $C_{23}H_{23}N_2S_2Cl_2I$ requires 2Cl + I, 33·6%) ; m. p. *ca.* 258° (decomp.).

5 : *5′-Dibromo-2 : 2′ : 8-triethylthiacarbocyanine Iodide* (V; R = Br, R′ = Et, X = I).—Obtained by treating the reaction mixture from 5-bromo-1-methylbenzthiazole etho-*p*-toluenesulphonate, methyl orthopropionate, and pyridine with excess of aqueous potassium bromide, the washed dye resulted in 77% yield. Recrystallisation from methyl alcohol (165 c.c. per g.) gave a 55% yield (Found : Br, 38·0. $C_{23}H_{23}N_2S_2Br_3$ requires Br, 38·0%). The bluish-violet platelets melted at 273° (decomp.). This and the corresponding dichloro-compound have their maximum absorption at λ6000 A.

5 : *5′-Dichloro-8-phenyl-2 : 2′-diethylthiacarbocyanine Iodide* (V; R = Cl, R′ = Ph, X = I).—On treating the reaction mixture from 5-chloro-1-methylbenzthiazole etho-*p*-toluenesulphonate, ethyl orthobenzoate, and pyridine with excess of aqueous potassium iodide solution, the yield of dye, after washing with water and ether, was 67%. Recrystallisation from methyl alcohol (360 c.c. per g.) gave a 43% yield of greenish crystals (Found : Cl + I, 30·8. $C_{27}H_{23}N_2S_2Cl_2I$ requires 2Cl + I, 31·05%) ; m. p. 270° (decomp.).

5 : *5′-Dibromo-8-phenyl-2 : 2′-diethylthiacarbocyanine Iodide* (V; R = Br, R′ = Ph, X = I).—Similarly from 5-bromo-1-methylbenzthiazole etho-*p*-toluenesulphonate the yield of washed dye iodide was 100% and, after recrystallisation from methyl alcohol (700 c.c. per g.), 50% (Found : Br + I, 39·65. $C_{27}H_{23}N_2S_2Br_2I$ requires 2Br + I, 39·5%). The small dull green crystals melted at 280° (decomp.). For this and the preceding compound, the absorption maximum lies at λ5650 A. and the sensitising maximum at λ6050 A.

5 : *5′-Dichloro-2 : 2′-diethylthiadicarbocyanine Iodide* (VI; R = Cl, R′ = H, X = I).—5-Chloro-1-methylbenzthiazole ethiodide (1·97 g.; 2 mols.) and β-anilinoacraldehyde anil hydrochloride (0·75 g.; 1 mol.) were boiled together in absolute alcohol (20 c.c.), treated with a solution of sodium (0·14 g.; 2 atoms) in absolute alcohol (10 c.c.), and further boiled for 3 minutes. The product was filtered off when cold, ground with water, and extracted with ether. On recrystallising the undissolved residue (1·17 g.; 69% yield) from methyl alcohol (555 c.c. per g.), the yield of olive-green crystals was 52% (0·88 g.) (Found : Cl + I, 32·7. $C_{23}H_{21}N_2S_2Cl_2I$ requires 2Cl + I, 32·9%) ; m. p. 278° (decomp.). The absorption maximum lies at λ6600 A., and the sensitising maximum at λ7100 A.

5 : 5′ : *9-Trichloro-2 : 2′-diethylthiadicarbocyanine Iodide* (VI; R = R′ = Cl, X = I).—A similar preparation with α-chloro-β-anilinoacraldehyde anil hydrochloride, instead of the unsubstituted anil, gave an 86% yield of product and, after recrystallisation from methyl alcohol (1000 c.c. per g.), 51% (Found : Cl + I, 37·6. $C_{23}H_{20}N_2S_2Cl_3I$ requires 3Cl + I, 37·5%). The minute green crystals melted at 267° (decomp.).

5 : 5′-*Dibromo*-2 : 2′-*diethylthiadicarbocyanine* p-*Toluenesulphonate* (VI; R = Br, R′ = H, X=p-$C_6H_4Me{\cdot}SO_3$).—Similarly, from 5-bromo-1-methylbenzthiazole etho-p-toluenesulphonate, β-anilinoacraldehyde anil hydrochloride, and sodium in alcohol, a dye was obtained in theoretical yield. After recrystallisation from methyl alcohol (140 c.c. per g.), the yield was 52% (Found : Br, 22·35. $C_{30}H_{28}O_3N_2S_3Br_2$ requires Br, 22·2%). The green crystals had a golden lustre; m. p. 230° (decomp.). The absorption maximum is at λ6600 A., and the sensitising maximum at λ7050 A.

5 : 5′ : 9-*Tribromo*-2 : 2′-*diethylthiadicarbocyanine Bromide* (VI; R = R′ = Br, X = Br).—The dye similarly prepared by use of α-bromo-β-anilinoacraldehyde anil hydrobromide, instead of the unsubstituted anil, was converted into bromide by treating its alcoholic solution with aqueous ammonium bromide. The yield was 60%, and recrystallisation from methyl alcohol (380 c.c. per g.) gave a 42% yield of small green crystals (Found : Br, 45·4. $C_{23}H_{20}N_2S_2Br_4$ requires Br, 45·2%); m. p. 228° (decomp.). Like the corresponding trichloro-compound, this substance has its absorption maximum at λ6500 A., and its sensitising maximum at λ7000 A.

5 : 5′-*Dichloro*-2 : 2′-*diethylthiatricarbocyanine Iodide* (VII; R = Cl, X = I).—5-Chloro-1-methylbenzthiazole ethiodide (3 g.) was treated with glutaconaldehyde dianilide hydrochloride and sodium dissolved in alcohol, as in preparing the unsubstituted tricarbocyanine (Fisher and Hamer, J., **1933**, 189). The product was washed with water and with ether (42% yield) and was boiled out with methyl alcohol (2 × 30 c.c.). The bright green, very insoluble, residue constituted a 36% yield (Found: Cl + I, 31·2. $C_{25}H_{23}N_2S_2Cl_2I,\frac{1}{2}CH_3{\cdot}OH$ requires 2Cl + I, 31·4%); m. p. 227° (decomp.). The absorption maximum is at λ7650 A., and the sensitising maximum at λ8150 A.

5 : 5′-*Dibromo*-2 : 2′-*diethylthiatricarbocyanine* p-*Toluenesulphonate* (VII; R = Br, X = p-$C_6H_4Me{\cdot}SO_3$).—5-Bromo-1-methylbenzthiazole etho-p-toluenesulphonate, when similarly treated, gave a 76% yield of alcohol-washed tricarbocyanine. After recrystallising from methyl alcohol (315 c.c. per g.), the dye resulted in 42% yield as bright green crystals (Found : Br, 21·4. $C_{32}H_{30}O_3N_2S_3Br_2$ requires Br, 21·4%); m. p. *ca.* 184° (decomp.). The absorption maximum is at λ7700 A., and the sensitising maximum at λ8200 A.

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