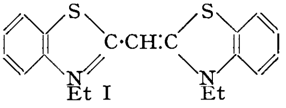
319. *The Reactivity of the Alkylthio-group in Nitrogen Ring Compounds. Part I. A General Method for the Preparation of Symmetrical and Unsymmetrical Thiacyanines.*

By J. D. Kendall and H. G. Suggate.

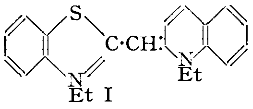
The preparation is described of symmetrical and unsymmetrical monomethin thiacyanines by the reaction, in the presence of basic reagents, of 2-alkylthiothiazolium alkyl salts with quaternary heterocyclic ammonium salts containing a reactive methyl group.

The first symmetrical thiacyanine, 3 : 3′-diethylthiacyanine iodide (I), was isolated by Mills (*J.*, 1922, **121**, 458) from the products of the action of ammonia on an aqueous solution of benzthiazole ethiodide and 2-methylbenzthiazole ethiodide, and its constitution established by synthesis from *o*-aminothiophenol and diethyl malonate. Subsequently, Mills and Braunholtz (*J.*, 1923, 2804) showed that thiacyanines could also be obtained in low yield, in admixture with thiacarbocyanines, by interaction of 2 : 2′-di-(*N*-formyl-*N*-ethylamino)diphenyl disulphide and a 2-methylbenzthiazolium alkyl salt in pyridine. By the action of amyl nitrite and acetic anhydride on a 2-methylbenzthiazolium alkyl salt, selectively a chloride, Fisher and Hamer (*J.*, 1930, 2502) prepared a number of symmetrical thiacyanines, free from the thiacarbocyanines always formed simultaneously by other methods. Their general method, however, was of limited scope and failed with the alkyl salts of simple thiazoles and 2-methyl-β-naphthothiazole.

Using the well-known *pseudo*cyanine and *iso*cyanine condensations, a number of unsymmetrical thiacyanines were also prepared by Mills and Braunholtz (*loc. cit.*), Hamer (*J.*, 1928, 206), Hamer and Kelly (*J.*, 1931, 777), Fisher and Hamer (*J.*, 1934, 1905). These thiacyanines, *e.g.*, 3 : 1′-diethylthia*pseudo*cyanine iodide (II) and 3 : 1′-diethylthia*iso*cyanine iodide (III), contained as second heterocyclic nucleus a pyridine or substituted pyridine ring.



(I.)



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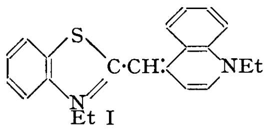
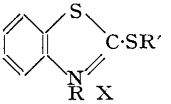


(III.)

Attempts by the present authors to obtain symmetrical and unsymmetrical thiacyanines by replacing, with 2-iodothiazolium alkiodides, the 2-iodoquinoline alkiodides used in the *pseudo*cyanine condensation, were unsuccessful. Although both 2-chloro-4-methylthiazole and 2-chlorobenzthiazole react readily on heating with alkyl iodides to give what are apparently 2-iodothiazolium alkiodides, these salts have low solubility in all solvents and, unlike 2-iodoquinoline alkiodides, do not form cyanine dyes with quaternary heterocyclic ammonium salts containing a reactive methyl group. By interaction, however, in the presence of a basic reagent, of the readily accessible 2-alkylthiothiazolium alkyl salts (IV) with heterocyclic ammonium salts containing a reactive methyl group, both symmetrical and unsymmetrical thiacyanines (VI) are readily prepared. This method was discovered independently by I. G. Farbenindustrie A.G. (B.P. 423,492) and one of the present authors (Kendall, B.P. 424,559). I. G. Farbenindustrie, however, did not envisage the use of an alkyl salt of 2-alkylthiobenzthiazole, but of a 2-thio-3-alkyl-2 : 3-dihydrobenzthiazole alkyl salt which they regarded as a sulphonium compound (V). We prefer to regard as quaternary heterocyclic ammonium salts the compounds (IV) and (V), which are identical, prepared by either process, when $R = R'$.

Unlike 2-alkoxybenzthiazole and 2-keto-3-alkyl-2 : 3-dihydrobenzthiazoles which do not form stable salts with alkyl iodides, 2-alkylthiobenzthiazoles and 2-thio-3-alkyl-2 : 3-dihydrobenzthiazoles form, with methyl and ethyl iodide, salts which can be readily isolated. Contrary to the result obtained by Beilenson and Hamer (*J.*, 1939, 143) who recorded no group interchange, Sexton (*J.*, 1939, 470) states that the reaction of ethyl iodide with 2-methylthiobenzthiazole gives 2-ethylthiobenzthiazole methiodide and not 2-methylthiobenzthiazole ethiodide as expected. Experiments carried out in this laboratory, and discussed in another communication, indicate that a mixture of quaternary salts is formed. The salts obtained by interaction of 2-alkylthiobenzthiazoles and alkyl toluene-*p*-sulphonates also appear in certain cases to undergo anomalous quaternisations. The addition of an alkyl iodide to a thione produces one compound only.

The alkyl salts of 2-alkylthiobenzthiazoles are readily converted into thiones by heat, or by a solvent containing a basic reagent (Kendall, B.P. 475,647). Crystallisation from alcoholic solvents likewise effects decomposition, which can be detected by the odour of alkanethiol in the solvent. Because of the ease with which they are formed, the thiones are found as the principal by-products when 2-alkylthiothiazolium alkyl salts are used in cyanine dye condensations; they can be removed easily from the crude dyes by washing with hot benzene in which the dyes are insoluble.



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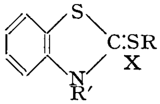

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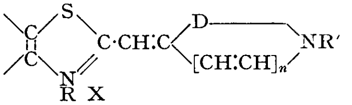

(VI : R and R′ = alkyl, $n = 0$ or 1, and D is remainder of a heterocyclic ring.)

The tendency to thione formation can be reduced, and the yields of thiacyanines increased, by the use of the " fusion process " (Kendall, B.P. 438,420), in which an alkyl toluene-*p*-sulphonate, a heterocyclic base with a reactive methyl group, and a 2-alkylthiobenzthiazole are heated together to at least 120°. Under these conditions partial formation of dye occurs during the fusion, and the condensation can be completed by dissolution in a solvent which may be a base, *e.g.*, pyridine, or which contains a basic reagent, *e.g.*, ethanol to which sodium ethoxide, sodium acetate, or an alkylamine is added. For the preparation of unsymmetrical thiacyanines with two different alkyl groups attached to the nitrogen of the two heterocyclic rings, it is essential in the " fusion process " to use a thione with the required alkyl group attached to the nitrogen. The dye toluene-*p*-sulphonates can be converted into less soluble halide salts by addition of a solution of the former to an aqueous alkali halide solution containing a considerable excess of the halide. In a number of cases in which only a slight excess of the halide was used the resulting dye still contained unchanged toluenesulphonate. By the use of the " fusion process " excellent yields were obtained of many symmetrical and unsymmetrical thiacyanines in a high state of purity. If excess of a 2-alkylthiothiazolium alkyl toluene-*p*-sulphonate is used in the dye condensation, yields approaching theoretical, calculated on the weight of heterocyclic base containing the reactive methyl group, can be obtained.

The thiacyanines obtained by this reaction are photographic sensitizers, which extend the range of colour sensitivity of silver chloride emulsions, with the exception of the thia-2′-quinocyanine (II) and thia-4′-quinocyanine (III) which also sensitise silver iodobromide emulsions.

A few thiacyanines, prepared by our process, have been described by Beilenson and Hamer (*loc. cit.*).

EXPERIMENTAL.

2-*Iodo*-4-*methylthiazole Ethiodide*.—2-Chloro-4-methylthiazole (30 g.) and ethyl iodide (40 c.c.) were heated under reflux on a water-bath for 48 hours. The dark-brown crystals which separated were filtered off and washed well with ethanol and ether; they (16·9 g.) were almost insoluble in the usual solvents and were purified by boiling out with acetone, and then had m. p. 171° (decomp.) (Found : I, 66·1. $C_6H_9NI_2S$ requires I, 66·7%).

2-*Iodobenzthiazole Methiodide*.—This salt, prepared similarly from 2-chlorobenzthiazole (B.P. 310,815) (10 g.) and methyl iodide (10 c.c.), was obtained as brown crystals (16 g.), m. p. 203° (decomp.), by boiling out with acetone (Found : I, 63·3. $C_8H_7NI_2S$ requires I, 63·0%). 2-*Iodobenzthiazole ethiodide*, similarly prepared (1·3 g. from 8 g. of each reagent) and purified by boiling out with acetone, had m. p. 188° (decomp.) (Found : I, 60·7. $C_9H_9NI_2S$ requires I, 60·9%).

2-*Methoxybenzthiazole*.—A solution of sodium (5 g.) in methanol (100 c.c.) was added to a solution of 2-chlorobenzthiazole (33·8 g.) in methanol (100 c.c.), and the mixture boiled for 2 hours. Excess of alcohol was distilled off, the residue diluted with water (500 c.c.), and the precipitated oil separated and dried (K_2CO_3). On distillation (b. p. 135—137°/16 mm.) the product was obtained as a colourless oil (25 g.) which solidified on cooling. Recrystallisation from ethanol (2 c.c. per g.) gave colourless rhombs, m. p. 34° (Found : S, 19·6. Calc. for C_8H_7ONS : S, 19·4%).

3 : 4-*Dimethyl*-1 : 2-*dihydrothiazole*-2-*thione*.—Monochloroacetone (10·4 c.c.) was added gradually with cooling to a suspension of ammonium methyldithiocarbamate (18 g.) in ethanol (36 c.c.). Addition of water precipitated a solid which after several crystallisations from a 50% ethanol–water mixture (1 g. in 10 c.c.) was obtained as pale yellow crystals (4·4 g.), m. p. 119° (Found : S, 44·1. $C_5H_7NS_2$ requires S, 44·1%).

3-*Phenyl*-4-*methyl*-1 : 2-*dihydrothiazole*-2-*thione*.—Ammonium phenyldithiocarbamate (93 g.) was suspended in ethanol (250 c.c.), and monochloroacetone (47 c.c.) added in portions with cooling. The mixture, from which ammonium chloride had separated, was boiled for 30 minutes and diluted with water (500 c.c.), and the crystalline precipitate collected and recrystallised from ethanol (1 g. in 10 c.c.). It was obtained as pale buff crystals (63 g.), m. p. 148—149° (Found : S, 31·1. $C_{10}H_9NS_2$ requires S, 30·9%).

2-*Methylthiobenzthiazole*.—Commercial 2-mercaptobenzthiazole (400 g.) was dissolved in 10% sodium hydroxide solution (1 l.). The solution was filtered, and methyl sulphate (230 c.c.) added with stirring (1 hour), the temperature being kept at about 40° by cooling. The precipitated oil was extracted with ether and dried (K_2CO_3), and the solvent removed. Distillation of the residue gave the product as an almost colourless oil (326 g.) which solidified on cooling; b. p. 174—175°/22 mm., m. p. 46° (Found : S, 35·2. Calc. for $C_8H_7NS_2$: S, 35·4%). If the methyl sulphate was added too rapidly, or in excess, the yield of 2-methylthiobenzthiazole was lowered, appreciable quantities of 1-methyl-2 : 3-dihydrobenzthiazole-2-thione being obtained as a by-product.

2-*Ethylthiobenzthiazole*.—2-Mercaptobenzthiazole (200 g.) was boiled under reflux with ethanol (500 c.c.) and 20% sodium hydroxide solution (300 c.c.). Ethyl bromide (100 c.c.) was then added gradually (1 hour) and the mixture heated for a further hour. After the solution had cooled, the precipitated oil was removed, dissolved in ether, washed with water, and dried (K_2CO_3). Distillation gave a pale yellow oil (170 g.), b. p. 178°/18 mm., m. p. 26° (Found : S, 33·0. Calc. for $C_9H_9NS_2$: S, 32·9%).

2-*Mercapto*-β-*naphthothiazole*.—Carbon disulphide (87 c.c.) and ammonia solution (*d* 0·920; 180 c.c.) were mixed at 0°, and α-naphthylamine (176 g.) in ethanol (350 c.c.) added dropwise with stirring, the temperature being kept below 10°. The mixture was kept overnight at room temperature, and ethyl chloroformate (130 c.c.) then added slowly with stirring, the temperature being kept below 5°. The temperature of the mixture was then allowed to rise to 20°, water (2·5 l.) added, and the precipitated oil extracted with ether, dried (K_2CO_3), and distilled to give α-naphthyl *iso*thiocyanate as a white, waxy solid (208 g.), b. p. 190°/20 mm. m. p. 57—58°. An intimate mixture of α-naphthyl *iso*thiocyanate (88 g.) and sulphur (16 g.) was heated in a sealed tube for 5 hours at 240—250°. The brown amorphous product was extracted four times with 5% sodium hydroxide solution. The alkaline solution, on acidification with acetic acid, gave pale yellow rhombs (29 g.) which were crystallised from ethanol; m. p. 254°.

2-*Methylthio*-β-*naphthothiazole*.—2-Mercapto-β-naphthothiazole (70 g.) was dissolved in 5% sodium hydroxide solution (260 c.c.), and methyl sulphate (35 c.c.) added slowly with stirring, the temperature being kept below 45°. After one hour the precipitated oil was separated, dissolved in benzene, and dried (K_2CO_3), and the solvent removed. The residue was distilled (b. p. 246—248°/20 mm.) to give a yellow solid which on recrystallisation from ethanol formed pale yellow crystals (62 g.), m. p. 63° (Found : S, 27·6. Calc. for $C_{12}H_9NS_2$: S, 27·7%).

2-*Ethylthio*-β-*naphthothiazole*.—2-Mercapto-β-naphthothiazole (75 g.) was heated to boiling with a mixture of ethanol (128 c.c.) and 20% sodium hydroxide solution (91·5 c.c.). Ethyl bromide (46 c.c.) was run in slowly, the mixture being kept at boiling point during addition. After further heating of the mixture for 2 hours, water (2 l.) was added, and the precipitated oil separated and dried (K_2CO_3). Distillation yielded the product as a pale yellow oil (48·5 g.), b. p. 248—250°/18 mm. (Found : S, 25·8. Calc. for $C_{13}H_{11}NS_2$: S, 26·1%).

2-*Methylthio*-α-*naphthothiazole*.—2-Mercapto-α-naphthothiazole (200 g.) was dissolved in 2½% sodium hydroxide solution (1·6 l.), and methyl sulphate (80 c.c.) added slowly with stirring. After two hours the precipitated solid was filtered off, dried, and recrystallised from ethanol (50 c.c. per g.) to give pale yellow crystals (170 g.), m. p. 67—68° (Found : S, 27·5. Calc. for $C_{12}H_9NS_2$: S, 27·7%).

2-*Ethylthio*-α-*naphthothiazole*.—2-Mercapto-α-naphthothiazole (150 g.) was heated under reflux with ethanol (450 c.c.), and 20% sodium hydroxide solution (184 c.c.) and ethyl bromide (96 c.c.) were added slowly. The mixture was boiled for 2 hours and then cooled, and water (3 l.) was added. The product formed cream-coloured crystals (146 g.), m. p. 49°, b. p. 248—250°/18 mm. from ethanol (50 c.c. per g.) (Found : S, 25·9. Calc. for $C_{13}H_{11}NS_2$: S, 26·1%).

2-*Mercapto*-5 : 6-*dimethoxybenzthiazole*.—4-Bromo-5-nitroveratrole (230 g.) (Jones and Robinson, *J.*, 1917, **111**, 916) was suspended in boiling ethanol (600 c.c.), and sodium hydrogen sulphide (365 g.) in cold ethanol (365 c.c.) added slowly. The mixture was heated under reflux for 1 hour and then cooled; hydrogen sulphide was passed in during one hour. Carbon disulphide (106 c.c.) was added, and the brown mixture was then boiled for seven hours, and cooled, whereupon the sodium salt of the thiol, with some sodium bromide, was precipitated (302 g.). Addition of hydrochloric acid to a solution of the crude sodium salt gave 2-*mercapto*-5 : 6-*dimethoxybenzthiazole* which crystallised from ethanol as pale rhombs, m. p. 209° (Found : S, 27·8. $C_9H_9O_2NS_2$ requires S, 28·2%).

2-*Methylthio*-5 : 6-*dimethoxybenzthiazole*.—The above-mentioned crude sodium salt (200 g.) was dissolved in hot water (1 l.) and cooled to 85°, and methyl sulphate (55 c.c.) run in with stirring. 10% aqueous sodium hydroxide (100 c.c.) was added to decompose the excess of methyl sulphate, and the precipitated *methylthio*-compound filtered off and crystallised from ethanol (200 c.c.) to give almost colourless rhombs (92 g.), m. p. 115° (Found : S, 26·4. $C_{10}H_{11}O_2NS_2$ requires S, 26·5%).

2-*Ethylthio*-5 : 6-*dimethoxybenzthiazole*.—The crude sodium salt (92 g.) was suspended in ethanol (100 c.c.), ethyl bromide (71 c.c.) added gradually, and the solution boiled under reflux for 6 hours. Excess ethyl bromide and ethanol were distilled off, the residue diluted with water (2 l.), and the precipitated oil extracted with ether. The extracts were washed with water, and dried (K_2CO_3), and the solvent removed. The residual oil was distilled (b. p. 235—242°/12 mm.), and the *product* crystallised from ethanol to give colourless needles (29·1 g.), m. p. 63° (Found : S, 25·3. $C_{11}H_{13}O_2NS_2$ requires S, 25·10%).

2-*Mercapto*-5 : 6-*methylenedioxybenzthiazole*.—This was prepared as described for the 5 : 6-dimethoxy-analogue, from 4-bromo-5-nitropyrocatechol methylene ether (242 g.) (Jones and Robinson, *ibid.*, p. 919). 2-*Mercapto*-5 : 6-*methylenedioxybenzthiazole* crystallised from ethanol as buff-coloured rhombs, m. p. 263° (Found : S, 30·9. $C_8H_5O_2NS_2$ requires S, 30·3%).

2-*Methylthio*-5 : 6-*methylenedioxybenzthiazole*.—The crude sodium salt (160 g.) of 2-mercapto-5 : 6-methylenedioxybenzthiazole was dissolved in water (1·8 l.) and filtered from a little insoluble material. Methyl sulphate (62 c.c.) was added with stirring, the temperature being kept at about 30°. The *methylthio*-compound separated during the reaction as dull yellow crystals, which were filtered off after addition of aqueous sodium hydroxide (100 c.c. of 10% solution). Recrystallisation from ethanol, containing a little norite, gave the product as pale needles (64 g.), m. p. 160° (Found : S, 28·5. $C_9H_7O_2NS_2$ requires S, 28·5%).

2-*Ethylthio*-5 : 6-*methylenedioxybenzthiazole*.—The crude sodium salt of 2-mercapto-5 : 6-methylenedioxybenzthiazole (60 g.) was suspended in dry ethanol (700 c.c.) ethyl bromide (43 c.c.) added gradually, and the mixture boiled under reflux for 8 hours and filtered hot buff-coloured plates. Recrystallisation of the *product* which separated after cooling, from ethanol (1 g. in 5 c.c.) gave very pale-buff crystals (27 g.), m. p. 127—128° (Found : S, 26·8. $C_{10}H_9O_2NS_2$ requires S, 26·8%).

5 : 6-*Dimethoxy*-2-*methylbenzthiazole*.—4-Bromo-5-nitroveratrole (193 g.) was suspended in ethanol (1 l.) and treated gradually, with shaking, with a solution of sodium disulphide prepared from crystalline sodium sulphide (94 g.), sulphur (13·1 g.), and ethanol (120 c.c.). Addition of the disulphide solution caused a violent reaction, with dissolution of the bromonitroveratrole and precipitation of dark crystals which became bright yellow after the mixture had been boiled for 1½ hours. The precipitated 2 : 2′-dinitro-4 : 5 : 4′ : 5′-tetramethoxydiphenyl disulphide (153 g.) was filtered off after cooling, washed with hot water and then with ethanol, and dried; m. p. 219°. The crude disulphide was suspended in glacial acetic acid (1 l.) and acetic anhydride (565 c.c.) and reduced with zinc dust (320 g.). The mixture was filtered, excess of acetic acid and anhydride distilled off, and the residue distilled under reduced pressure; b. p. 188°/16 mm. The *product* formed buff-coloured needles, m. p. 65°, from ethanol (Found : S, 14·9. $C_{10}H_{11}O_2NS$ requires S, 15·3%).

5 : 6-*Methylenedioxy*-2-*methylbenzthiazole*.—4-Bromo-5-nitrocatechol methylene ether (125 g.) was treated, in ethanol (190 c.c.), gradually with frequent shaking, with a sodium disulphide solution prepared from crystalline sodium sulphide (62 g.), sulphur (9 g.), and ethanol (80 c.c.) (cf. above). A suspension of the crude 2 : 2′-dinitro-4 : 5-4′ : 5′-bis(methylenedioxy)diphenyl disulphide (m. p. 244°) (92 g.) thus produced, in glacial acetic acid (449 c.c.) and acetic anhydride (280 c.c.), was warmed to 80° and commercial zinc dust (151 g.) added in small portions. Working up as described above gave 5 : 6-*methylenedioxy*-2-*methylbenzthiazole* as colourless plates, m. p. 123—124° (from ethanol), b. p. 195—200°/20 mm. (Found : S, 16·9. $C_9H_7O_2NS$ requires S, 16·6%).

[3 : 4-*Dimethyloxazole*][3-*methylbenzthiazole*]*methincyanine Iodide*.—2 : 4-Dimethyloxazole (3 g.), 2-methylthiobenzthiazole (5·6 g.), and methyl toluene-*p*-sulphonate (11·5 g.) were fused together at 130—140° for three hours. Pyridine (20 c.c.) was added and the mixture boiled under reflux for 30 minutes. On pouring this into a warm aqueous solution of potassium iodide (8 g. in 50 c.c.), the *iodide* was precipitated; it crystallised from methanol as pale yellow prismatic needles (2 g.), m. p. 309° (decomp.) (Found : I, 33·0. $C_{14}H_{15}ON_2IS$ requires I, 32·9%).

[3 : 4-*Dimethylthiazole*][3-*methylbenzthiazole*]*methincyanine Bromide*.—This *bromide* was prepared by a process similar to that used for bis[3-methylbenzthiazole]methincyanine bromide, but from 2 : 4-dimethylthiazole (2·26 g.), 2-methylthiobenzthiazole (3·62 g.), and methyl toluene-*p*-sulphonate (7·44 g.). The dye was obtained from methanol (1 g. in 50 c.c.) as yellow rods and needles (2·7 g.), m. p. 298° (decomp.) (Found : Br, 22·7. $C_{14}H_{15}N_2S_2Br$ requires Br, 22·6%). It was also obtained from 3 : 4-dimethyl-1 : 2-dihydrothiazole-2-thione (1·44 g.), 2-methylbenzthiazole (1·49 g.), and methyl toluene-*p*-sulphonate (3·72 g.).

The following were similarly prepared. [4-*Methyl*-3-*ethylthiazole*][3-*ethylbenzthiazole*]*methincyanine iodide* [from 2 : 4-dimethylthiazole (2·26 g.), 2-ethylthiobenzthiazole (3·9 g.), and ethyl toluene-*p*-sulphonate (8 g.)], yellow prisms (1·8 g.), m. p. 297° (decomp.) [from methanol (1 g. in 200 c.c.)] (Found : I, 29·5. $C_{16}H_{19}N_2IS_2$ requires I, 29·6%). [3 : 4-*Dimethylthiazole*][1 : 6-*dimethyl*-2-*quinoline*]*methincyanine iodide* [from 2-methylthio-4-methylthiazole (Buckman, Reims, and Sargent, *J. Org. Chem.*, 1941, **6**, 764) (1·8 g.), *p*-toluquinaldine (1·95 g.), and methyl toluene-*p*-sulphonate (4·7 g.)], orange-red (1·5 g.), m. p. 238° (decomp.) [from methanol (1 g. in 50 c.c.)] (Found : I, 31·1. $C_{17}H_{19}N_2IS$ requires I, 30·9%). [3-*Phenyl*-4-*methylthiazole*][1-*methyl*-2-*quinoline*]*methincyanine iodide* [from quinaldine (1·43 g.), 3-phenyl-4-methyl-1 : 2-dihydrothiazole-2-thione (2·07 g.), and methyl toluene-*p*-sulphonate (3·72 g.)], reddish-brown (1 g.), m. p. 230° (decomp.) [from methanol (1 g. in 30 c.c.)] (Found : I, 27·6. $C_{21}H_{19}N_2IS$ requires I, 27·7%).

[3-*Phenyl*-4-*methylthiazole*][3-*methylbenzthiazole*]*methincyanine Iodide*.—3-Phenyl-4-methyl-1 : 2-dihydrothiazole-2-thione (2·07 g.), 2-methylbenzthiazole (1·49 g.), and methyl toluene-*p*-sulphonate (3·72 g.) were fused together at 150° for 4 hours; pyridine (25 c.c.) was added and the mixture boiled under reflux for 40 minutes; the yellow solution was poured into an aqueous solution of potassium iodide (5 g.), and the *dye* collected and washed with hot benzene, ethanol, and ether. It crystallised from methanol (1 g. in 10 c.c.) as pale yellow needles (2·9 g.), m. p. 264° (decomp.) (Found : I, 27·3. $C_{19}H_{17}N_2IS_2$ requires I, 27·4%).

The following were similarly prepared. [3-*Methylbenzoxazole*][3-*methylbenzthiazole*]*methincyanine iodide* [from 2-methylbenzoxazole (1·33 g.), 2-methylthiobenzthiazole (1·81 g.), and methyl toluene-*p*-sulphonate (3·72 g.)], pale-yellow rhombs (2·96 g.), m. p. 310° (decomp.) [from methanol (1 g. in 200 c.c.)] (Found : I, 30·3. $C_{17}H_{15}ON_2IS$ requires I, 30·1%). [3-*Ethylbenzoxazole*][3-*ethylbenzthiazole*]-*methincyanine iodide* [from 2-ethylthiobenzthiazole (1·95 g.), 1-methylbenzoxazole (1·33 g.), and ethyl toluene-*p*-sulphonate (4 g.)], yellow needles (2·27 g.), m. p. 309° (decomp.) [from methanol (1 g. in 200 c.c.)] (Found : I, 28·5. $C_{19}H_{19}ON_2IS$ requires I, 28·2%). [3-*Ethylnaphtho*(1′ : 2′-4 : 5)*oxazole*]-[3-*ethylbenzthiazole*]*methincyanine iodide* [from 2-ethylthiobenzthiazole (0·98 g.), 2-methylbenzoxazole (0·92 g.), and ethyl toluene-*p*-sulphonate (2·0 g.)], small straw-coloured needles (0·8 g.), m. p. 283° (decomp.) [from methanol (1 g. in 50 c.c.)] (Found : I, 25·4. $C_{23}H_{21}ON_2IS$ requires I, 25·4%). [3-*Ethylnaphtho*(2′ : 1′-4 : 5)*oxazole*][3-*ethylbenzthiazole*]*methincyanine iodide* [from 2-methylnaphtho(2′ : 1′-4 : 5)oxazole (3·6 g.), 2-methylthiobenzthiazole (3·8 g.), and ethyl toluene-*p*-sulphonate (8·3 g.)], bright yellow needles (0·6 g.), m. p. 298° (decomp.) [from methanol (1 g. in 400 c.c.)] (Found : I, 25·4. $C_{23}H_{21}ON_2IS$ requires I, 25·4%).

Bis-[3-*methylbenzthiazole*]*methincyanine Bromide*.—2-Methylthiobenzthiazole (3·1 g.), 2-methylbenzthiazole (2·5 g.), and methyl toluene-*p*-sulphonate (6·5 g.) were fused together at 140° for 2½ hours. Pyridine (30 c.c.) was added, and the mixture boiled gently for 45 minutes. A bright yellow solution formed and methylthiol was evolved. On pouring the solution into a warm aqueous solution of potassium bromide (10 g. in 100 c.c.), a yellow precipitate was obtained. This was filtered off, washed with water, hot benzene, and ether, and crystallised from methanol. The dye *bromide* was obtained as light yellow needles (4·5 g.), m. p. 303° (decomp.) (Found : Br, 20·7. $C_{17}H_{15}N_2BrS_2$ requires Br, 20·5%).

A small quantity of the dye iodide was obtained by pouring the original aqueous filtrate into a solution of potassium iodide (10 g. in 100 c.c.). The yellow precipitate crystallised from methanol in minute yellow needles, m. p. 306° (decomp.).

[3-*Ethylbenzthiazole*][3-*methylbenzthiazole*]*methincyanine Bromide*.—2-Methylthiobenzthiazole (1·81 g.) and methyl toluene-*p*-sulphonate (1·86 g.) were fused together for 3½ hours at 130°. A similar fusion was also carried out with 2-methylbenzthiazole (1·49 g.) and ethyl toluene-*p*-sulphonate (2·0 g.). The ethotoluene-*p*-sulphonate was then dissolved in pyridine (10 c.c.), and the solution poured into the 2-methylthiobenzthiazole methotoluene-*p*-sulphonate. The mixture was boiled for 45 minutes and then poured into potassium bromide (10 g.) in water (100 c.c.); and the yellow *bromide* was filtered off, washed with water, hot benzene, and ether, and crystallised from methanol; pale-yellow needles (2·5 g.), m. p. 283° (decomp.) (Found : Br, 19·9. $C_{18}H_{17}N_2BrS_2$ requires Br, 19·8%).

Bis-[3-*ethylbenzthiazole*]*methincyanine Bromide*.—This dye, prepared as described for the bis-3-methyl analogue, crystallised from methanol (40 c.c. per g.) as yellow needles (9·3 g.), m. p. 303° (decomp.). The derived yellow dye iodide crystallised from methanol (100 c.c. per g.); m. p. 314° (decomp.) (Found : I, 27·1. Calc. for $C_{19}H_{19}N_2IS_2$: I, 27·3%).

[3-*Methylbenzthiazole*][3-*methyl*-β-*naphthothiazole*]*methincyanine Bromide*.—2-Methyl-β-naphthothiazole with methyl toluene-*p*-sulphonate (3·7 g.), and 2-methylthiobenzthiazole (3·62 g.) with methyl *p*-toluenesulphonate (3·72 g.), similarly yielded a *dye*, yellow needles (5·6 g.), m. p. 250° (decomp.), from methanol (1 g. in 200 c.c.) (Found : Br, 17·9. $C_{21}H_{17}N_2BrS_2$ requires Br, 18·2%).

[3-*Ethylbenzthiazole*][3-*ethyl*-β-*naphthothiazole*]*methincyanine Bromide*.—2-Methyl-β-naphthothiazole (4 g.) and ethyl toluene-*p*-sulphonate (4 g.) were fused together for 3½ hours at 190°. A similar fusion was carried out with 2-ethylthiobenzthiazole (3·9 g.) and ethyl toluene-*p*-sulphonate (4 g.) at 140° for 3 hours. The 2-ethylthiobenzthiazole ethotoluene-*p*-sulphonate was cooled and dissolved in pyridine (30 c.c.), the solution poured on the 2-methyl-β-naphthothiazole salt, and the mixture heated under reflux for 45 minutes. On pouring the product into a warm aqueous solution of potassium bromide (10 g. in 100 c.c.), yellow crystals were obtained which were filtered off, washed with hot benzene, water, and ether, and recrystallised from methanol. The *product* consisted of yellow rhombs (2 g.), m. p. 252° (decomp.) (Found : Br, 16·8. $C_{23}H_{21}N_2BrS_2$ requires Br, 17·1%).

Similar preparations yielded: [3-*methylbenzthiazole*][3-*methyl*-5 : 6-*dimethoxybenzthiazole*]*methincyanine toluene*-p-*sulphonate*, from 5 : 6-dimethoxy-2-methylbenzthiazole (2·09 g.), 2-methylthiobenzthiazole (1·81 g.), and methyl toluene-*p*-sulphonate (37 g.), as yellow needles (3·1 g.), m. p. 315° (decomp.), from methanol (1 g. in 180 c.c.) (Found : S, 17·4, 17·5. $C_{26}H_{26}O_5N_2S_3$ requires S, 17·7%); [3-*ethylbenzthiazole*][5 : 6-*dimethoxy*-3-*ethylbenzthiazole*]*methincyanine bromide*, from 5 : 6-dimethoxy-2-methylbenzthiazole (1·2 g.), 2-ethylthiobenzthiazole (0·98 g.), and ethyl toluene-*p*-sulphonate (2 g.), as yellow rhombs (0·5 g.), m. p. 271° (decomp.), from methanol (1 g. in 100 c.c.) (Found : Br, 16·6. $C_{21}H_{23}O_2N_2BrS_2$ requires Br, 16·6%); [3-*methylbenzthiazole*][5 : 6-*methylenedioxy*-3-*methylbenzthiazole*]*methincyanine toluene*-p-*sulphonate*, from 5 : 6-methylenedioxy-2-methylbenzthiazole (3·86 g.), 2-methylthiobenzthiazole (3·62 g.), and methyl toluene-*p*-sulphonate (7·44 g.), as fine, deep-yellow needles (6·6 g.), m. p. 276° (decomp.), from methanol (1 g. in 100 c.c.) (Found : S, 16·7. $C_{25}H_{22}O_5N_2S_3$ requires S, 16·8%), [3-*ethylbenzthiazole*][5 : 6-*methylenedioxy*-3-*ethylbenzthiazole*]*methincyanine bromide*, from 5 : 6-methylenedioxy-2-methylbenzthiazole (3·86 g.), 2-methylthiobenzthiazole (3·8 g.), and ethyl toluene-*p*-sulphonate (8·3 g.), as yellow rods (4·4 g.), m. p. 301° (decomp.), from methanol (1 g. in 150 c.c.) (Found : Br, 17·4. $C_{20}H_{19}O_2N_2BrS_2$ requires Br, 17·3%); [3-*methylbenzthiazole*][5-*dimethylamino*-3-*methylbenzthiazole*]-*methincyanine bromide*, from 5-dimethylamino-2-methylbenzthiazole (Bogert and Updike, *J. Amer. Chem. Soc.*, 1927, **49**, 1373) (0·96 g.), 2-methylthiobenzthiazole (0·9 g.), and methyl toluene-*p*-sulphonate (1·86 g.), as dark-yellow rhombs (1 g.) m. p. 300° (decomp.), from methanol (1 g. in 50 c.c.) (Found : Br, 14·6. $C_{19}H_{20}N_3BrS_2$ requires Br, 14·3%), [3-*ethylbenzthiazole*][5-*dimethylamino*-3-*ethylbenzthiazole*]-

methincyanine iodide, from 5-dimethylamino-2-methylbenzthiazole (0·96 g.), 2-ethylthiobenzthiazole (0·98 g.), and ethyl toluene-*p*-sulphonate (2·0 g.), as ochre-coloured needles and rods (0·1 g.), m. p. 286° (decomp.), from methanol (60 c.c. for 1 g.) (Found: I, 24·7. $C_{21}H_{24}N_3IS_2$ requires I, 24·9%); [3-*methylbenzthiazole*][5-*diethylamino*-3-*methylbenzthiazole*]*methincyanine iodide*, from 5-diethylamino-2-methylbenzthiazole (2·2 g.), 2-methylthiobenzthiazole (1·81 g.), and methyl toluene-*p*-sulphonate (2·72 g.) yellow (2 g.), m. p. 267° (decomp.) [from methanol (1 g. in 25 c.c.)] (Found: I, 25·0. $C_{21}H_{24}N_3IS_2$ requires I, 24·9%), and [3-*ethylbenzthiazole*][5-*diethylamino*-3-*ethylbenzthiazole*]*methincyanine iodide*, from 5-diethylamino-2-methylbenzthiazole (Bogert and Updike, *loc. cit.*) (1·1 g.), 2-ethylthiobenzthiazole (0·98 g.), and ethyl toluene-*p*-sulphonate (2·0 g.), as orange rhombs (1 g.), m. p. 284° (decomp.), (from methanol (1 g. in 50 c.c.) (Found: I, 23·4. $C_{23}H_{28}N_3IS_2$ requires I, 23·6%).

[1 : 3 : 3-*Trimethylindolenine*][3-*methylbenzthiazole*]*methincyanine Iodide.*—2-Methylthiobenzthiazole (7·24 g.), finely powdered 1 : 3 : 3-trimethylindolenine methiodide (12 g.), and methyl toluene-*p*-sulphonate (7·44 g.) were fused together for 2 hours at 120°. Pyridine (100 c.c.) was added, and the mixture boiled for 45 minutes. The solution, on pouring into water (200 c.c.), afforded an orange-red *dye*, which was filtered off, washed with hot benzene, water, and ether, and recrystallised from methanol (1 g. in 20 c.c.); pale orange rhombs (5·25 g.), m. p. 262° (decomp.) (Found: I, 28·4. $C_{20}H_{21}N_2IS$ requires I, 28·4%).

Similarly were obtained [1 : 3 : 3-*trimethylindolenine*][3-*ethylbenzthiazole*]*methincyanine perchlorate*, from 2-ethylthiobenzthiazole (1·95 g.), finely powdered 1 : 3 : 3-trimethylindolenine methiodide (3·01 g.), ethyl toluene-*p*-sulphonate (2 g.), as orange-yellow rhombs (0·42 g.), m. p. 240° (decomp.), from a small quantity of methanol (Found: Cl, 8·3. $C_{21}H_{23}O_3NS$ requires Cl, 8·2%), [3-*methylbenzthiazole*][1-*methyl*-2-*pyridine*]*methincyanine iodide*, from α-picoline (3·72 g.), 2-methylthiobenzthiazole (3·62 g.), and methyl toluene-*p*-sulphonate (11·16 g.), as orange-red rhombs (1·7 g.), m. p. 296° (decomp.), from methanol (1 g. in 100 c.c.) (Found: I, 33·3. $C_{15}H_{15}N_2IS$ requires I, 33·5%), [3-*methylbenzthiazole*]-[1-*ethyl*-2-*pyridine*]*methincyanine iodide*, from α-picoline (3·72 g.), 2-ethylthiobenzthiazole (3·9 g.), and ethyl toluene-*p*-sulphonate (12 g.), as yellow-orange rhombs, m. p. 266° (decomp.) (0·3 g.), from methanol (1 g. in 100 c.c.) (Found: I, 30·6. $C_{17}H_{19}N_2IS$ requires I, 30·9%), [3-*methylbenzthiazole*][1 : 6-*dimethyl*-2-*pyridine*]*methincyanine iodide*, from 2 : 6-lutidine (2·14 g.), 2-methylthiobenzthiazole (3·62 g.), and methyl toluene-*p*-sulphonate (7·74 g.), as orange needles (1·55 g.) and rods, m. p. 243° (decomp.), from methanol (1 g. in 30 c.c.) (Found: I, 33·2. $C_{16}H_{17}N_2IS$ requires I, 32·1%), [3-*methylbenzthiazole*]-[1-*methyl*-2-*quinoline*]*methincyanine iodide*, from quinaldine (2·86 g.), 2-methylthiobenzthiazole (3·62 g.), and methyl toluene-*p*-sulphonate (7·44 g.), as scarlet needles (0·49 g.), m. p. 266° (decomp.), from methanol (1 g. in 160 c.c.) (Found: I, 29·3. Calc. for $C_{19}H_{17}N_2IS$.: I, 29·4%), and [3-*ethylbenzthiazole*]-[3-*ethyl*-2-*quinoline*]*methincyanine iodide*, from quinaldine (2·86 g.), 2-ethylthiobenzthiazole (3·9 g.), and ethyl toluene-*p*-sulphonate (8·0 g.), as crimson needles (1·4 g.), m. p. 286° (decomp.), from methanol (1 g. in 100 c.c.) (Found: I, 27·9. Calc. for $C_{21}H_{21}N_2IS$: I, 27·6%).

[3-*Methylbenzthiazole*][1-*methyl*-4-*quinoline*]*methincyanine Iodide.*—Lepidine (0·72 g.), 2-methylthiobenzthiazole (0·91 g.), and methyl toluene-*p*-sulphonate (1·86 g.) were fused together for 3½ hours at 150°. Pyridine (20 c.c.) was added, and the mixture heated under reflux for 30 minutes and poured into a warm aqueous solution of potassium iodide (5 g. in 200 c.c.). The orange *iodide* were filtered, washed with hot benzene, water, and ether, and recrystallised from methanol (1 g. in 50 c.c.); fine crimson needles (0·3 g.), m. p. 276° (decomp.) (Found: I, 29·7, 29·84. $C_{19}H_{17}N_2IS$ requires I, 29·4%).

[3-*Ethylbenzthiazole*][1-*ethyl*-4-*quinoline*]*methincyanine iodide* was prepared similarly from lepidine (0·72 g.), 2-methylthiobenzthiazole (0·91 g.), and ethyl toluene-*p*-sulphonate (2 g.). The orange crystals obtained were recrystallised from methanol (1 g. in 40 c.c.) to give orange-red needles (0·45 g.), m. p. 287° (decomp.) (Found: I, 27·1. $C_{21}H_{21}N_2IS$ requires I, 27·6%).

[3-*Ethylbenzthiazole*][1-*methyl*-4-*quinoline*]*methincyanine Iodide.*—A mixture of lepidine methiodide (2·85 g.), 2-methylthiobenzthiazole ethiodide (2·7 g.), and ethanol (40 c.c.) was boiled until solution was effected. Fused sodium acetate (0·82 g.) was added, and boiling continued for 30 minutes. The *dye* which precipitated during the reaction was filtered off, washed with hot benzene, water, and ether, and recrystallised from methanol (1 g. in 100 c.c.). It was obtained as fine, dark-red needles (3·15 g.), m. p. 270° (decomp.) (Found: I, 28·9. $C_{20}H_{19}N_2IS$ requires I, 28·5%).

[3-*Ethylbenzthiazole*][1 : 4-*dimethyl*-2-*quinoline*]*methincyanine Iodide.*—A mixture of 2 : 4-dimethylquinoline methiodide (3 g.) 2-methylthiobenzthiazole ethiodide (7·2 g.), and ethanol (80 c.c.) was heated to boiling, fused sodium acetate (1·64 g.) added, and the mixture boiled for a further 45 minutes. The red crystals which precipitated during the reaction were filtered, and recrystallised from methanol, in which the *dye* was only sparingly soluble, as red needles (3·6 g.) m. p. 291° (decomp.) (Found: I, 27·4. $C_{21}H_{21}N_2IS$ requires I, 27·6%).

[3-*Ethylbenzthiazole*][4-*methyl*-1-*ethyl*-2-*quinoline*]*methincyanine iodide.*—This *iodide*, prepared from 2 : 4-dimethylquinoline (0·79 g.), 2-ethylthiobenzthiazole (0·98 g.), and ethyl toluene-*p*-sulphonate (2·0 g.), was obtained as ochre crystals (0·32 g.), m. p. 278° (decomp.), from methanol (1 g. in 50 c.c.) (Found: I, 27·5. $C_{22}H_{23}N_2IS$ requires I, 26·8%).

[3-*Methylbenzthiazole*][6-*ethoxy*-1-*ethyl*-2-*quinoline*]*methincyanine Iodide.*—Starting materials were 6-ethoxyquinaldine (0·87 g.), 2-ethylthiobenzthiazole (0·98 g.), and ethyl toluene-*p*-sulphonate (2·0 g.). The resultant sticky mass was diluted with pyridine (20 c.c.), heated under reflux for 30 minutes, and poured into warm aqueous potassium iodide solution (5 g. in 50 c.c.). The orange precipitate was filtered off and washed with hot benzene, water, and ether. The *iodide* (0·9 g.) was obtained as orange rods, m. p. 270° (decomp.), from methanol (1 g. in 75 c.c.) (Found: I, 25·5. $C_{23}H_{25}ON_2IS$ requires I, 25·2%).

Bis-[3-*methyl*-β-*naphthothiazole*]*methincyanine Toluene*-p-*sulphonate.*—This salt was prepared from 2-methylthio-β-naphthothiazole (2·21 g.), 2-methyl-β-naphthothiazole (2·0 g.), and methyl toluene-*p*-sulphonate (3·72 g.). The *dye* was obtained by boiling out with methanol (in which it was only sparingly soluble) as minute yellow needles (2·23 g.), m. p. 293° (decomp.) (Found: S, 16·2. $C_{32}H_{26}O_3N_2S_3$ requires S, 16·5%).

Bis-[3-*ethyl*-β-*naphthothiazole*]*methincyanine Bromide.*—2-Ethylthio-β-naphthothiazole (2·35 g.), 2-methyl-β-naphthothiazole (2·0 g.), and ethyl toluene-*p*-sulphonate (4·0 g.) were used in this preparation. The *bromide* was obtained as yellow needles (1·35 g.), m. p. 263° (decomp.), from methanol (1 g. in 150 c.c.) (Found : Br, 15·5. $C_{27}H_{23}N_2BrS_2$ requires Br, 15·4%).

Bis-[3-*methyl-α-naphthothiazole*]*methincyanine Toluene-*p*-sulphonate.*—Similarly 2-methyl-α-naphthothiazole (1 g.), 2-methylthio-α-naphthothiazole (1·16 g.), and methyl toluene-*p*-sulphonate (2 g.) afforded a *dye,* which was obtained from methanol (1 g. in 100 c.c.) as orange-yellow needles (1·2 g.), m. p. 305° (decomp.) (Found : S, 16·6. $C_{32}H_{26}O_3N_2S_3$ requires S, 16·5%).

Bis-[3-*ethyl-α-naphthothiazole*]*methincyanine Bromide.*—This *salt,* prepared from 2-ethylthio-α-naphthothiazole (1·17 g.), 2-methyl-α-naphthothiazole (1·0 g.), and ethyl toluene-*p*-sulphonate (2 g.), crystallised from methanol, in which it was sparingly soluble, as yellow needles (1·4 g.), m. p. 296° (decomp.) (Found : Br, 15·5 g. $C_{23}H_{21}N_2BrS_2$ requires Be, 15·4%).

Bis-[5 : 6-*dimethoxy-*3-*methylbenzthiazole*]*methincyanine Toluene-*p*-sulphonate.*—2-Methylthio-5 : 6-dimethoxybenzthiazole (2·41 g.), 5 : 6-dimethoxy-2-methylbenzthiazole (2·09 g.), and methyl toluene-*p*-sulphonate (7·5 g.) were fused together for 3½ hours at 165—170°. Pyridine (40 c.c.) was added, and the mixture boiled for 30 minutes and poured into water; the *dye* was filtered off, washed with hot benzene, water, ethanol and ether, and crystallised from methanol (1 g. in 200 c.c.); orange rods (4·3 g.), m. p. 310° (decomp.) (Found : S, 15·9. $C_{28}H_{30}O_7N_2S_3$ requires S, 15·5%).

Similarly were prepared : *bis-*[5 : 6-*dimethoxy-*3-*ethylbenzthiazole*]*methincyanine bromide,* from 2-ethylthio-5 : 6-dimethoxybenzthiazole (2·55 g.), 5 : 6-dimethoxy-2-methylbenzthiazole (2·09 g.), and ethyl toluene-*p*-sulphonate (4·0 g.), as fine yellow needles (3·6 g.), m. p. 306° (decomp.), from methanol (1 g. in 60 c.c.) (Found : Br, 14·6. $C_{23}H_{27}O_4N_2BrS_2$ requires Br, 14·8%); [5 : 6-*dimethoxy-*3-*methylbenzthiazole*][1-*methyl-*2-*pyridine*]*methincyanine iodide,* from α-picoline (3·72 g.), 2-methylthio-5 : 6-dimethoxybenzthiazole (4·82 g.), and methyl toluene-*p*-sulphonate (11·2 g.), large orange-red needles and rods (2 g.), m. p. 291° (decomp.), from methanol (1 g. in 200 c.c.) (Found : I, 28·4. $C_{17}H_{19}O_2N_2IS$ requires I, 28·7%); [5 : 6-*dimethoxy-*3-*ethylbenzthiazole*][1-*ethyl-*2-*pyridine*]*methincyanine iodide,* from α-picoline (3·72 g.), 1-ethylthio-5 : 6-dimethoxybenzthiazole (7·65 g.), and ethyl toluene-*p*-sulphonate (12 g.), orange needles (1 g.), m. p. 243° (decomp.), from methanol (1 g. in 100 c.c.) (Found : I, 26·7. $C_{19}H_{23}O_2N_2IS$ requires I, 27·0%); and [5 : 6-*dimethoxy-*3-*methylbenzthiazole*][1-*methyl-*2-*quinoline*]-*methincyanine bromide,* from 2-methylthio-5 : 6-dimethoxybenzthiazole (1·21 g.), quinaldine (0·72 g.), and methyl toluene-*p*-sulphonate (1·86 g.), orange (1·7 g.), m. p. 242° (decomp.) [from methanol (1 g. in 60 c.c.)] (Found : Br, 18·0. $C_{21}H_{21}O_2N_2BrS$ requires Br, 18·0%).

[5 : 6-*Dimethoxy-*2-*ethylbenzthiazole*][1-*ethyl-*2-*quinoline*]*methincyanine Toluene-*p*-sulphonate.*—Quinaldine (4·29 g.), 2-methylthio-5 : 6-dimethoxybenzthiazole (7·23 g.), and ethyl toluene-*p*-sulphonate (12 g.) were fused together for 4 hours at 140°. The red solid obtained was boiled with ethanol (180 c.c.), anhydrous sodium acetate (3·28 g.) added, and the mixture heated under reflux for 15 minutes. The mixture was poured into water, and the precipitate filtered off, washed with hot benzene, ethanol, and ether, and recrystallised from methanol (1 g. in 150 c.c.) to give fine crimson needles (4·1 g.), m. p. 296° (decomp.) (Found : S, 11·6. $C_{30}H_{32}O_5N_2S_2$ requires S, 11·4%).

Similar preparations afforded : *bis-*[5 : 6-*methylenedioxy-*3-*methylbenzthiazole*]*methincyanine toluene-*p*-sulphonate,* from 2-methylthio-5 : 6-methylenedioxybenzthiazole (2·25 g.), 5 : 6-methylenedioxy-2-methylbenzthiazole (1·93 g.), and methyl toluene-*p*-sulphonate (3·75 g.), fine yellow needles (3·4 g.), m. p. 316° (decomp.), from methanol (1 g. in 200 c.c.) (Found : S, 16·7. $C_{26}H_{22}O_7N_2S_3$ requires S, 16·9%); *bis-*[5 : 6-*methylenedioxy-*3-*ethylbenzthiazole*]*methincyanine bromide,* from 2-ethylthio-5 : 6-methylenedioxybenzthiazole (2·39 g.), 5 : 6-methylenedioxy-2-methylbenzthiazole (1·93 g.), and ethyl toluene-*p*-sulphonate (4·05 g.), fine, ochre-coloured needles (1·3 g.), m. p. 360° (decomp.), from methanol (1 g. in 200 c.c.) (Found : S, 15·9. $C_{28}H_{26}O_9N_2S_3$ requires S, 16·0%); [5 : 6-*methylenedioxy-*3-*methylbenzthiazole*][1-*methyl-*2-*pyridine*]*methincyanine iodide,* from α-picoline (3·72 g.), 2-methylthio-5 : 6-methylenedioxybenzthiazole (4·5 g.), and methyl toluene-*p*-sulphonate (11·2 g.), sparingly soluble, brown rhombs (1·1 g.), m. p. 305° (decomp.), from methanol (1 g. in 200 c.c.) (Found : I, 30·0. $C_{16}H_{15}O_2N_2SI$ requires I, 29·8%); and [5 : 6-*methylenedioxy-*3-*ethylbenzthiazole*][1-*ethyl-*2-*pyridine*]-*methincyanine iodide,* from α-picoline (3·72 g.), 2-ethylthio-5 : 6-methylenedioxybenzthiazole (4·78 g.), and ethyl toluene-*p*-sulphonate (12 g.), orange needles (1·6 g.), m. p. 304° (decomp.), from methanol (Found : I, 28·2. $C_{18}H_{19}O_2N_2IS$ requires I, 28·0%).

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