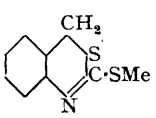
59. *Thiazinocyanines. Part IV. Simple Cyanines containing the 2 : 4-Benzthiazine Nucleus.*

By Bernard Beilenson, Frances M. Hamer, and Russell J. Rathbone.

Three 3-alkylthio-2 : 4-benzthiazine alkiodides were prepared. Five bases, of which methincyanines are quaternary salts, were synthesised from 3-alkylthio-2 : 4-benzthiazine and various heterocyclic quaternary salts having a reactive methyl group, followed by alkali. Another was prepared from 3-methyl-2 : 4-benzthiazine and a 2-methylthioquinoline quaternary salt. In these, the alkyldihydro-structure was in the nucleus other than benzthiazine. One of the alternative type was synthesised from 3-alkylthio-2 : 4-benzthiazine methiodide and quinaldine, and one having two benzthiazine nuclei from a 3-methylthio-2 : 4-benzthiazine salt and 3-methyl-2 : 4-benzthiazine. Ten simple cyanines of various types, but all having one 2 : 4-benzthiazine nucleus, were synthesised from 3-alkylthio-2 : 4-benzthiazine alkiodide and various heterocyclic quaternary salts having a reactive methyl group, in the presence of a condensing agent; one of them was also prepared from a dye base by the action of methyl sulphate and potassium iodide. Attempts to prepare methincyanines of this series by interaction of 3-ethylthio-2 : 4-benzthiazine, ethyl *p*-toluenesulphonate, and a heterocyclic base having a reactive methyl group, followed by potassium iodide, led to hydriodides and not ethiodides. These hydriodides were shown to have the alkyldihydro-structure in the nucleus other than benzthiazine. The absorption maxima of the various bases and dyes were compared and sensitising data are given.

In the first paper of this series (Beilenson and Hamer, J., 1942, 98), we mentioned 3-methylthio-2 : 4-benzthiazine (I) as an intermediate likely to give quaternary salts whence cyanine dyes containing the 2 : 4-benzthiazine nucleus might be obtained. We have prepared the necessary 3-thiol-2 : 4-benzthiazine, which Paal and Commerell called " thiocumothiazone," from *o*-aminobenzyl alcohol, by slightly modifying their method (*Ber.*, 1894, **27**, 2427), and whereas they subsequently used methyl iodide and alkali to convert it into the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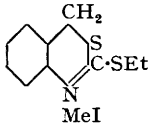
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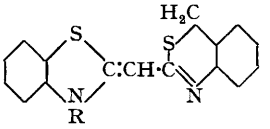
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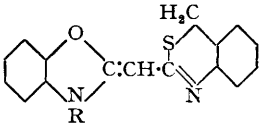
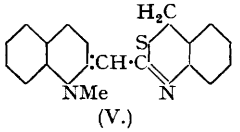

(IV.)

methylthio-compound (I), we used methyl sulphate and alkali. By the action of methyl iodide, (I) was converted into its *methiodide* but the action of ethyl iodide resulted in 3-*ethylthio*-2 : 4-*benzthiazine methiodide* (II). This is analogous with the rearrangement of alkyl groups that occurs when ethyl iodide acts upon 2-methylthioquinoline, 2-methylthiobenzthiazole, and 2-methylthiodihydro-1 : 3-thiazine, respectively (Beilenson and Hamer, J., 1939, 143; Sexton, J., 1939, 470; Hamer and Rathbone, J., 1943, 243). From 3-thiol-2 : 4-benzthiazine, ethyl sulphate and alkali, there was prepared 3-*ethylthio*-2 : 4-*benzthiazine*, which was converted into its *ethiodide*. It has been noted that in preparing 3-methyl-2 : 4-benzthiazine by the method of Gabriel and Posner (*Ber.*, 1894, **27**, 3509) the yields were erratic (Beilenson and Hamer, J., 1942, 98), but the method has now been modified to give consistently good yields.

By condensing (I) with 2-methylbenzthiazole metho-*p*-toluenesulphonate, and by condensing its ethyl analogue with 2-methylbenzthiazole etho-*p*-toluenesulphonate, methanethiol or ethanethiol, respectively, was eliminated, and by subsequent treatment with alkali, two *dye bases* were obtained (III; R = Me) and (III; R = Et). By use of 2-methyl-4 : 5-benzbenzthiazole etho-*p*-toluenesulphonate, the 4 : 5-benz-derivative of the latter was also prepared. The yields varied from 28—40%. However, we were unable to obtain a base isomeric with (III; R = Me), but carrying the *N*-methyl group in the benzthiazine nucleus, by condensing the methiodide of (I) with 2-methylbenzthiazole. By condensing (I) with 2-methylbenzoxazole methiodide and ethiodide, respectively, the *dye bases* (IV; R = Me) and (IV; R = Et) were prepared, the latter being purified through its *hydriodide*, but here again an attempt to obtain the isomer of the former, by condensing the metho-*p*-toluenesulphonate of (I) with 2-methylbenzoxazole, gave a negative result.

We failed to make the base (V) from (I) with quinaldine metho-*p*-toluenesulphonate, but were able to prepare it in 60% yield from 3-methyl-2 : 4-benzthiazine and 2-methylthioquinoline metho-*p*-toluene-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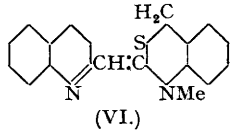
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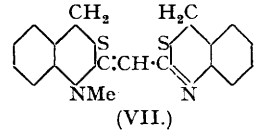

(VII.)

sulphonate, followed by alkali. In this case we were also successful in preparing the isomeric base (VI), although only in 14% yield, from (I) and methyl *p*-toluenesulphonate, followed by quinaldine. From (I)

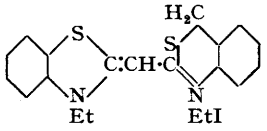
and methyl *p*-toluenesulphonate, followed by 3-methyl-2 : 4-benzthiazine, and by alkali, the base (VII), having two benzthiazine nuclei, was prepared in 30% yield; it was also prepared by condensing the methiodide of (I) with 3-methyl-2 : 4-benzthiazine, followed by alkali, this yield being 17%.

Absorption curves of methyl-alcoholic solutions of the bases were plotted, and the maxima determined. On passing from the oxa- to the thia-series, *i.e.*, from (IV; R = Me) to (III; R = Me) and from (IV; R = Et) to (III; R = Et), the maximum shifted 185 and 220 A. towards the red. Introduction of the 4 : 5-benz-group into (III; R = Et) caused a shift towards the red of 150 A. Acidification of the three thia-bases, namely (III; R = Me), (III; R = Et), and the 4 : 5-benz-derivative of the latter, caused shifts towards the red of 175, 210, and 160 A., respectively. Acidification of the two oxa-bases, namely, (IV; R = Me) and (IV; R = Et), caused shifts towards the red of 130 and 110 A., respectively. On passing from the thia-base (III; R = Me) to the 2'-cyanine base (V), the absorption maximum shifted 475 A. towards the red.

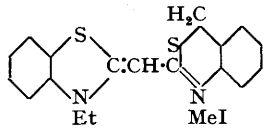
On passing from the 2'-cyanine base (VI) to its isomer (V), the shift towards the red was 600 A. Our colleague Dr. L. G. S. Brooker points out that such a difference in absorption indicates that the benzthiazine nucleus is less basic than the quinoline nucleus, the relationship between the two rings being similar to that between indole and benzthiazole or indole and quinoline, linked in the 4-position (Brooker, Sprague, Smyth, and Lewis, *J. Amer. Chem. Soc.*, 1940, **62**, 1116). Where the maximum of (V) shifted only 200 A. towards the red on acidification, the maximum of (VI) shifted 600 A. On acidifying the base (VII), which has two benzthiazine nuclei, the band became narrower and shifted 365 A. towards the red.

Three of these bases, namely (III; R = Et), its 4 : 5-benz-derivative, and (IV; R = Et), may be compared with three bases of the carbocyanine series, which have already been described (Beilenson and Hamer, J., 1942, 98) and which differ from them only in having two extra methin groups in the chain joining the nuclei. On passing from the present three cyanine bases to their higher vinylene homologues, the absorption maxima shifted 560, 560, and 470 A. towards the red.

By condensing 2-methylbenzthiazole ethiodide with 3-ethylthio-2 : 4-benzthiazine ethiodide, in the presence of triethylamine in alcohol, the simple cyanine (VIII) was prepared, ethanethiol and hydrogen iodide being eliminated. Use of 2-methyl-6 : 7-benzbenzthiazole ethiodide resulted in its 6 : 7-benz-derivative.



(VIII.)



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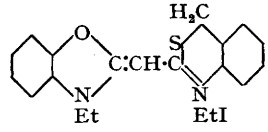

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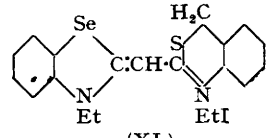
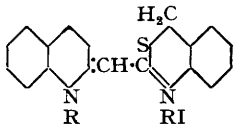


(XI.)

From 2-methylbenzthiazole ethiodide and the methiodide of (I), the simple cyanine (IX) was synthesised. (IX) also resulted on condensing 2-methylbenzthiazole ethiodide with the product obtained by interaction of (I) with ethyl iodide: our conclusion that this interaction involves rearrangement of alkyl groups, leading to (II), was based on this observation and on two other similar ones. By condensing 2-methylbenzoxazole ethiodide and 2-methylbenzselenazole ethiodide, respectively, with 3-ethylthio-2 : 4-benzthiazine ethiodide, (X) and (XI) were prepared, and the 6 : 7-benz-derivative of (X) was also similarly obtained. From quinaldine methiodide and the methiodide of (I), the 2'-cyanine (XII; R = Me) was prepared. From quinaldine ethiodide and lepidine ethiodide, respectively, with 3-ethylthio-2 : 4-benzthiazine ethiodide, the 2'-cyanine (XII; R = Et) and the 4'-cyanine (XIII) were prepared. From 2-methyldihydro-1 : 3-thiazine methiodide



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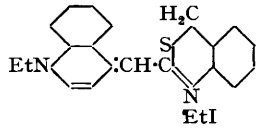

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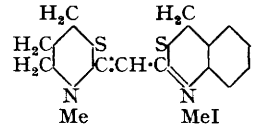


(XIV.)

(Hamer and Rathbone, J., 1943, 243) and the methiodide of (I), the cyanine (XIV) was obtained in 11% yield. For both oxa-dyes, the yields were 27%, for the 2'-cyanines they were 33% and 52%, 45% for the 4'-cyanine, 61% for the selena-compound, and 42—69% in the four preparations of thia-dyes.

An unsuccessful attempt was made to prepare the cyanine (VIII) from the base (III; R = Et) by heating the latter in a sealed tube with ethyl iodide. Similar negative results were also obtained when attempts were made to arrive at the ethiodide by use of ethyl *p*-toluenesulphonate or ethyl sulphate. However, although we failed to convert the base (III; R = Et) into its ethiodide, we did succeed in converting it into its methiodide (IX) by use of methyl sulphate, followed by potassium iodide. By means of methyl sulphate and potassium iodide we were also able to convert each of the pair of isomers (V) and (VI) into the 2'-cyanine (XII; R = Me). The yield of 2'-cyanine was 36% from (V) but only 20% from (VI) and in the latter case it was accompanied by a less soluble by-product.

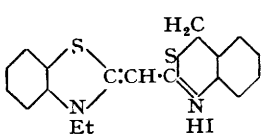
Absorption curves of methyl-alcoholic solutions of the methincyanines were plotted. On passing from the oxa-compound (X) to the thia-compound (VIII), the maximum shifted 400 A. towards the red, but on passing from thia-compound (VIII) to selena-compound (XI) the shift was only 140 A. in the same direction. Introduction of the 6 : 7-benz-group into (X) and (VIII) caused shifts of 210 and 200 A. towards the red.

An acid solution of the base (III; R = Et) had its absorption maximum 35 A. further towards the red than had the cyanine dye (VIII), which is the ethiodide of that base. On passing from the thia-dye (VIII) to the 2′-cyanine (XII; R = Et) and from that to the 4′-cyanine (XIII), the bathochromic shifts were 425 and 330 A. The absorption maximum of the 2′-cyanine (XII; R = Et) lay 75 A. on the short wave-length side of the maximum of an acidified solution of base (V), and 125 A. on the long wave-length side of the maximum of an acidified solution of base (VI).

On passing from the methincyanines (X) and (VIII) to the corresponding trimethincyanines, which have previously been described (Beilenson and Hamer, J., 1942, 98), introduction of the extra vinylene group caused a shift towards the red of 1200 A. in each instance.

Analogues of the present methincyanines have already been described, in which the part played by the 2 : 4-benzthiazine nucleus is taken by the dihydro-1 : 3-thiazine nucleus (Hamer and Rathbone, J., 1943, 243). The effect upon the absorption maximum of replacing that simple nucleus by the more complex one may now be found for eight pairs of dyes. The shift is in every instance a bathochromic one. In the oxa-series, on passing from the corresponding simple dyes to (X) and to the 6 : 7-benz-derivative of (X), the shifts are 140 and 240 A., respectively; in the thia-series, on passing from the corresponding simple dyes to (VIII) and to the 6 : 7-benz-derivative of (VIII), the shifts are 260 and 250 A., respectively; in the selena-series, on passing from the simple dye to (XI), the shift is 340 A.; in the 2′-cyanine series the shifts on passing to (XII; R = Me) and to (XII; R = Et) are 125 and 175 A., respectively; in the 4′-cyanine series the shift on passing from the simple dye to (XIII) is 205 A.

The preparation of simple cyanines by fusing together a heterocyclic base having a reactive alkylthio-group, a heterocyclic base having a reactive methyl group, and alkyl *p*-toluenesulphonate, followed by treatment with a solvent and an acid-binding agent, is one that has been patented (Kendall, B.P. 424,559/1933). In the present series, its attempted application led to curious results. It was noticed in the first place that a better product was obtained when no condensing agent was added after the fusion. The procedure adopted was therefore to fuse together equimolecular amounts of the two bases and 2 mols. of ethyl *p*-toluenesulphonate, dissolve the melt in spirit, and treat it with potassium iodide. Five such preparations yielded crystalline products, which did indeed look like the expected methincyanines, but analysis after recrystallisation showed them to be hydriodides and not ethiodides. Thus fusion of 2-methylbenzthiazole, 3-ethylthio-2 : 4-benzthiazine, and ethyl *p*-toluenesulphonate would have been expected to give the cyanine (VIII), ethanethiol and *p*-toluenesulphonic acid being eliminated: in fact, however, it gave a hydriodide, to which, at first sight, the constitution (XV) might be assigned, though (XVI) is also a possibility. That the constitution really is (XV) and not (XVI) was established, first by conversion of the hydriodide into the base (III; R = Et) by heating with alkali and benzene, and secondly by its preparation from (III; R = Et) by the action of hydriodic acid; in contrast to the breakdown of the hydriodide by alkali, the alkiodide (IX) was resistant to this treatment. Hydriodides were similarly obtained when 2-methylbenzthiazole was replaced by 2-methyl-6 : 7-benzbenzthiazole, 2-methylbenzselenazole, 2-methylbenzoxazole, and 2-methyl-6 : 7-benzbenzoxazole, respectively. The hydriodide obtained by use of 2-methylbenzoxazole proved to be identical with that isolated in the purification of the dye base (IV; R = Et) and was itself converted into that dye base, thus establishing a formula analogous with (XV) as opposed to (XVI). With the other three hydriodides an analogous structure was assumed. To explain the formation of a hydriodide, such as (XV), it may be supposed that 2-methylbenzthiazole etho-*p*-toluenesulphonate is first formed and condenses with 2-ethylthio-2 : 4-benzthiazine, which base is more reluctant to undergo quaternary salt formation; the product is the *p*-toluenesulphonic acid of (III; R = Et) and this, by the action of potassium iodide, is converted into the corresponding hydriodide. Although the hydriodides were the only products isolated and were certainly the main products, it is possible that small amounts of true cyanines were also formed. An exact comparison of the hydriodides and ethiodides as regards melting point, and solubility in methyl alcohol, showed that generalisations as to these properties were not justified. In plotting the absorption curves of the hydriodides it was noticed that sometimes the maximum approximated to that of the ethiodide but sometimes to that of the base. For this reason they were plotted both in basified and in acidified methyl alcohol. The change from alkalinity to acidity always caused a bathochromic shift. This was 130 A. with the oxa-compound, 120 A. with its 6 : 7-benz-derivative, 200 A. with the thia-compound, 250 A. with its 6 : 7-benz-derivative, and 300 A. with the selena-compound. Surprisingly, the absorption maximum of the basified solutions was, in four cases out of five, nearer to that of the ethiodide than was that of the acidified solution.



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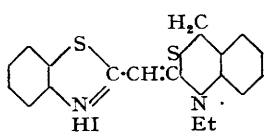

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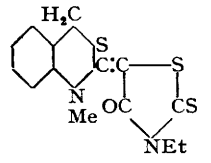

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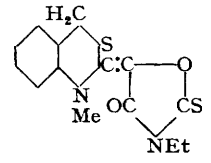

(XVIII.)

A pair of dyes, containing the 2 : 4-benzthiazine nucleus, but other than cyanines, was prepared by use of compounds containing a reactive cyclic methylene group (cf. Kendall, B.P. 426,718/1933; Kodak Ltd.,

B.P. 450,958/1934). Thus by condensing the methiodide of (I) with 3-ethylrhodanine and with 4-keto-2-thio-3-ethyltetrahydro-oxazole, respectively, dyes (XVII) and (XVIII) were obtained, in 50% and 49% yields. These same compounds were also prepared by using the salt which results by the action of ethyl iodide on 3-methylthio-2 : 4-benzthiazine, thus providing further evidence that this salt has the structure (II).

When the oxygen atom in the oxazole ring of (XVIII) is replaced by sulphur, giving (XVII), the absorption maximum shifts 330 A. towards the red. We have already described an analogue of (XVII) which contains the dihydro-1 : 3-thiazine nucleus instead of the 2 : 4-benzthiazine nucleus (Hamer and Rathbone, J., 1943, 243). On passing from this earlier dye to the present more complex one, the absorption maximum shifted 80 A. towards the red.

The behaviour of the various dyes towards a gelatino chloride photographic emulsion was examined and it was found that the group comprises some powerful sensitisers. Of the five hydriodides of the methin dye bases, four sensitised much more powerfully than did those methincyanines which were the corresponding ethiodides; with the fifth the action of the hydriodide was a little stronger than that of the ethiodide. It has already been recorded that in the 2 : 4-benzthiazine series the sensitising action of the carbocyanine ethiodides closely approximated to that of the corresponding bases (Beilenson and Hamer, J., 1942, 98). With carbocyanines of the *peri*naphtha-1 : 3-thiazine series it was noted that a methiodide and ethiodide had the same sensitising maximum as the corresponding hydrochloride and base, whilst another pair, consisting of carbocyanine base and hydrochloride, also showed identity of sensitising maxima (Hamer and Rathbone, J., 1943, 487). Our colleague, Dr. B. H. Carroll, has now straightened out what seemed anomalous. By examining the sensitising action of pairs of dye bases and hydrochlorides of other series, he found that the sensitisation appears to be dependent on pH only, regardless of whether the base or its salt is taken. In the present work the sensitising effect of each of the dye bases (III; R = Et) and (IV; R = Et) was found to be similar to that of the respective hydriodide and in the same region as that of the ethiodide, (VIII) and (X), respectively; also the base (III; R = Me) sensitised in the same region as its ethiodide (IX). The sensitising action of (XII; R = Me) resembled that of base (V) but not that of base (VI).

Experimental.

3-Thiol-2 : 4-benzthiazine.—*o*-Aminobenzyl alcohol, alcoholic potassium hydroxide, and carbon disulphide were heated together on the water-bath as described by Paal and Commerell (*Ber.*, 1894, **27**, 2427), but for 18 hours instead of 10. Excess of carbon disulphide was removed by distillation, instead of by steam-distillation, and the filtration before distillation was omitted. Afterwards the potassium salt which separated was filtered off. It was purified by their method of dissolving in dilute potassium hydroxide solution, filtering, and precipitating with acid. The thiol compound was almost white and was obtained in 79% yield, m. p. 160—162°. After recrystallisation from dilute spirit, the m. p. was 166°, as recorded by Paal and Commerell, who obtained 70—80% yields. It should be used at once, as it decomposes on keeping.

3-Methylthio-2 : 4-benzthiazine (I).—3-Thiol-2 : 4-benzthiazine (35 g.; 1 mol.) was dissolved in 10% sodium hydroxide solution (70 c.c.) and methyl sulphate (38 c.c.; 2 mols.) was gradually added with shaking; more sodium hydroxide solution (40 c.c.) was added to keep the mixture alkaline. The resultant solid was filtered off, heated on the water-bath under a vacuum to remove water, and finally vacuum-distilled, being obtained in 82% yield (31 g.). It was analysed by the method of Carius, which method was used throughout this work, except where otherwise stated (Found : S, 32·75. Calc. for $C_9H_9NS_2$: S, 32·85%). B. p. 192°/20 mm., m. p. 70—73°. Paal and Commerell, who prepared it by use of methyl iodide in the presence of alkali, recrystallised it from light petroleum and record an almost theoretical yield, m. p. 73° (*loc. cit.*).

3-Ethylthio-2 : 4-benzthiazine.—3-Thiol-2 : 4-benzthiazine (36·2 g.; 1 mol.) was dissolved in 10% sodium hydroxide solution (80 c.c.) and shaken with ethyl sulphate (26 c.c.; 1 mol.). After standing for an hour, with occasional shaking, the mixture was heated on the water-bath for 30 minutes. Excess of ammonia was added, and the oil extracted with ether. The residue from the dried ethereal extract, after removal of solvent, was vacuum-distilled and thus obtained in 76% yield (31·7 g.) (Found : S, 30·65. $C_{10}H_{11}NS_2$ requires S, 30·65%). The oil had b. p. 193°/14 mm.

3-Methylthio-2 : 4-benzthiazine Methiodide.—3-Methylthio-2 : 4-benzthiazine (5·86 g.; 1 mol.) and methyl iodide (4·5 c.c.; 2·4 mols.) were heated together under reflux for 4 days. The solid was ground with ether and 43% of unchanged base (2·5 g.) was recovered from the ethereal extract. The undissolved residue (5·5 g.) was recrystallised from methyl alcohol (5 c.c. per g.) and gave a 36% yield. Before analysis it was dried to constant weight in a vacuum at 60—80°, which method of drying solids was used throughout this work except where stated otherwise (Found : I, 37·65. $C_{10}H_{12}NIS_2$ requires I, 37·65%). The pale yellow substance had m. p. 163°.

3-Ethylthio-2 : 4-benzthiazine Methiodide (II).—After 3-methylthio-2 : 4-benzthiazine (9·9 g.; 1 mol.) and ethyl iodide (4·8 c.c.; 1·2 mols.) had been heated in a sealed tube at 100° for 16 hours, the dirty product was much improved by washing with acetone (13·1 g. obtained). By rapid recrystallisation from methyl alcohol (30 c.c.), it was obtained in 53% yield (9·6 g.) (Found : I, 36·35. $C_{11}H_{14}NIS_2$ requires I, 36·15%). The pale yellow prisms had m. p. 138° (decomp.).

3-Ethylthio-2 : 4-benzthiazine Ethiodide.—3-Ethylthio-2 : 4-benzthiazine (20·9 g.; 1 mol.), ethyl iodide (9·6 c.c.; 1·2 mols.), and a little quinol (0·05 g.) were heated together in a sealed tube at 100° for 2 days. The product was treated with absolute ether, and the resultant solid recrystallised from absolute alcohol (80 c.c.) with charcoal (1 g.). The yield of yellow crystalline product was 30% (22·5 g.) (Found : I, 34·9. $C_{12}H_{16}NIS_2$ requires I, 34·75%). M. p. 129° (decomp.).

3-Methyl-2 : 4-benzthiazine.—*o*-Aminobenzyl chloride hydrochloride (4 g.; 1 mol.), thioacetamide (2 g.; 1·2 mols.), anhydrous potassium carbonate (180-mesh; 13·6 g.; 4·4 mols.), and absolute ethyl alcohol (40 c.c.) were boiled together under reflux for 45 minutes. The alcohol was distilled off, and the residue steam-distilled. The resultant oil solidified on cooling and was filtered off and finally dried in a vacuum desiccator, being obtained in 64% yield (2·34 g.). It was almost colourless, m. p. 42—43°, whereas Gabriel and Posner give m. p. 45—46° for the base, which they prepared by heating the reactants without solvent or condensing agent (*Ber.*, 1894, **27**, 3509). By distillation in a vacuum, the yield was reduced to 47% but the m. p. was unchanged, b. p. 155—160°/15 mm. (Found for material dried in a vacuum to constant weight : S, 19·7. Calc. for C_9H_9NS : S, 19·65%).

Methin-[2-(*3-methyldihydrobenzthiazole*)][3-(2 : 4-*benzthiazine*)] (III; R = Me).—2-Methylbenzthiazole metho-*p*-toluenesulphonate (3·35 g.; 1 mol.) and 3-methylthio-2 : 4-benzthiazine (1·95 g.; 1 mol.) were fused together at 160° for 30 minutes. The product was heated with 10% sodium hydroxide solution and the resultant *base* when cold was filtered off and washed with water and with acetone (2·62 g. obtained). After two recrystallisations from acetone (20 c.c. per g.), the yield was

36% (1·12 g.) (Found : S, 20·55. $C_{17}H_{14}N_2S_2$ requires S, 20·7%). The lemon-yellow crystals had m. p. 154°. The absorption maximum of a methyl-alcoholic solution was at 4025 A. and shifted to 4200 A. on addition of sulphuric acid (5 g. per 100 c.c.). It is a good sensitiser for a gelatino silver chloride emulsion, giving a maximum at 4600, the sensitivity extending past 5100 A.

Methin-[(2-(3-*ethyldihydrobenzthiazole*)][3-(2 : 4-*benzthiazine*)] (III; R = Et).—The base, similarly prepared from 2-methylbenzthiazole etho-*p*-toluenesulphonate and 3-ethylthio-2 : 4-benzthiazine, followed by sodium hydroxide solution, was purified by washing with water and grinding with acetone. It was recrystallised from acetone (20 c.c. per g.) and thus obtained in 40% yield (Found : S, 20·0. $C_{18}H_{16}N_2S_2$ requires S, 19·75%). The lemon-yellow crystals had m. p. 143°. The absorption maximum was at 4090 A. and shifted to 4300 A. on addition of sulphuric acid (5 g. per 100 c.c.). It is a strong sensitiser for a chloride emulsion, having its maximum effect at 4700 A.

Methin-[2-(3-*ethyldihydro*-4 : 5-*benzbenzthiazole*)][3-(2 : 4-*benzthiazine*)].—In condensing 2-methyl-4 : 5-benzbenzthiazole etho-*p*-toluenesulphonate (3·99 g.) and 3-methylthio-2 : 4-benzthiazine, heating was at 145—150° for 2½ hours. The reaction mixture was subsequently heated with sodium hydroxide solution and extracted with benzene. The product obtained on removal of benzene from the dried extract was recrystallised from ethyl acetate (120 c.c.). After washing with cold spirit, the yield was 28% (Found : S, 17·3. $C_{22}H_{18}N_2S_2$ requires S, 17·15%). The brown crystals with a steely reflex had m. p. 206—207°. A methyl-alcoholic solution had its absorption maximum at 4240 A.; on addition of sulphuric acid (5 g. per 100 c.c.) the maximum shifted to 4400 A. The base sensitised a chloride emulsion strongly with a maximum at 4700 A., its action extending to 5200 for moderate exposures.

Methin-[2-(3-*methyldihydrobenzoxazole*)][3-(2 : 4-*benzthiazine*)] (IV; R = Me).—3-Methylthio-2 : 4-benzthiazine (1·95 g.) and 2-methylbenzoxazole methiodide were heated together at 155—160° for 2 hours, and the product was boiled and stirred with benzene (30 c.c.) and 40% sodium hydroxide solution (15 c.c.) for 15 minutes. The product (0·94 g.) obtained from the dried benzene extract was recrystallised from acetone (10 c.c.) and thus obtained in 17% yield (0·50 g.) (Found : S, 11·15. $C_{17}H_{14}ON_2S$ requires S, 10·9%). M. p. 150°. The absorption maximum of a methyl-alcoholic solution was at 3840 A. and on acidification shifted to 3970. The base was a powerful sensitiser towards a chloride emulsion. The maximum was at 4300 A. and its action extended to 4700.

Methin-[2-(3-*ethyldihydrobenzoxazole*][3-(2 : 4-*benzthiazine*)] (IV; R = Et).—After 3-methylthio-2 : 4-benzthiazine (3·90 g.; 1 mol.) had been similarly heated with 2-methylbenzoxazole ethiodide, and the product heated with benzene and alkali, the syrupy residue from the benzene extract was taken up in hot spirit, acidified with hydrochloric acid (1·2 mols.), and treated hot with aqueous potassium iodide (2 mols.). The precipitated *hydriodide* was washed with water and ground with acetone (12 c.c.), being obtained in 31% yield. After recrystallisation from methyl alcohol (85 c.c. per g.), the yield was 24% (Found : I, 28·95. $C_{18}H_{17}ON_2IS$ requires I, 29·1%). M. p. 278° (decomp.) with previous shrinking. The hydriodide (2·58 g.) was boiled and stirred with benzene and alkali. The residue from the dried benzene extract, after removal of solvent, was taken up in ethyl acetate (5 c.c.), precipitated with light petroleum (b. p. 40—60°) (25 c.c.), and finally recrystallised from spirit (2½ c.c.); the amount of *base* (0·78 g.) corresponded with a 43% conversion (Found : S, 10·3. $C_{18}H_{16}ON_2S$ requires S, 10·4%). The yellow product had no definite m. p. but softened at 74°, melted from 85—88° but not to a clear drop, and frothed up at about 110°. A methyl-alcoholic solution had its absorption maximum at 3870 A. On addition of sulphuric acid (5 g. per 100 c.c.) it shifted to 3980. The base was a good sensitiser towards a chloride emulsion. The maximum was at 4300 A. and its action extended to 4650. The spirit filtrate from the base was treated hot with concentrated hydrochloric acid (1 c.c.); the *hydrochloride* crystallised on cooling, the amount (0·40 g.) corresponding with a 20% conversion. It was recrystallised from methyl alcohol (2 c.c.) (0·20 g. obtained) (Found : Cl, 10·25. $C_{18}H_{17}ON_2ClS$ requires Cl, 10·3%). The yellow crystals melted at about 229° (decomp.) with previous softening.

Methin-[2-(1-*methyldihydroquinoline*)][3-(2 : 4-*benzthiazine*)] (V).—2-Methylthioquinoline (1·75 g.; 1 mol.) and methyl *p*-toluenesulphonate (1·86 g.; 1 mol.) were heated together at 145° for 1½ hours, 3-methyl-2 : 4-benzthiazine (1·63 g.; 1 mol.) then added, and heating continued for 10 minutes. The product was stirred with hot spirit (20 c.c.) and poured into aqueous ammonia (30 c.c.; *d* 0·880). The crude base was filtered off when cold and washed with water and spirit (2·55 g. obtained). It was recrystallised from spirit (20 c.c. per g.) and thus obtained in 60% yield (Found : S, 10·65. $C_{19}H_{16}N_2S$ requires S, 10·55%). The bright red crystals had m. p. 132°. The broad absorption band had its maximum at 4500 A. On addition of sulphuric acid (5 g. per 100 c.c.), the colour did not deepen, but the maximum shifted to 4700 A., with an inflexion at 4500, and the band became narrower. In a gelatino silver chloride emulsion the base sensitised with maxima at 4500 and 5000 A., the action extending to 5700. In a gelatino silver bromide emulsion the sensitising action extended to 5500 A.

Methin-[2-*quinoline*][3-(4-*methyldihydro*-2 : 4-*benzthiazine*)] (VI).—3-Methylthio-2 : 4-benzthiazine (1·95 g.) and methyl *p*-toluenesulphonate were heated together at 145—150°, then quinaldine was added and the mixture heated. The product was dissolved in hot spirit and poured into aqueous ammonia. When cold, the resultant oil was treated with cold spirit, which converted it into solid (0·86 g.). After recrystallisation from methyl alcohol (45 c.c.), the yield was 14% (0·44 g.) (Found : S, 10·6. $C_{19}H_{16}N_2S$ requires S, 10·55%). The yellow crystals had m. p. 139° (decomp.). The absorption maximum of the methyl-alcoholic solution was at 3900 A. On addition of sulphuric acid (5 g. per 100 c.c.) there was deepening in colour and the maximum shifted to 4500 with a secondary band at 4350 A. In a gelatino silver chloride emulsion the base was a good sensitiser with maxima at 4350 and 4700 A. Sensitisation was fairly even up to 4850, tailing off to 5150 A.

Methin-[3-(2 : 4-*benzthiazine*)][3-(4-*methyldihydro*-2 : 4-*benzthiazine*)] (VII).—3-Methylthio-2 : 4-benzthiazine (1·95 g.) and methyl *p*-toluenesulphonate were heated together at 150—160° for 3 hours, 3-methyl-2 : 4-benzthiazine added, and heating continued for one hour. The product was heated with sodium hydroxide solution, and the base extracted with benzene. After removal of solvent from the dried extract, the residual oil was dissolved in acetone (7 c.c.), and the solution treated with water (7 c.c.). The aqueous layer was decanted from the paste, which solidified on stirring with cold ethyl acetate (1·71 g. obtained). By crystallisation from ethyl acetate (27 c.c.), it was obtained in 30% yield (0·97 g.) (Found : S, 19·75. $C_{18}H_{16}N_2S_2$ requires S, 19·65%). The yellow crystals had m. p. 162° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 3780 A. On addition of sulphuric acid (10 g. per 100 c.c.), the yellow solution deepened in colour, the band became narrower, and the maximum shifted to 4145 A. The base sensitised a chloride emulsion strongly, the maximum lying at 4400 A. and sensitisation extending past 4900. It was also prepared from 3-methylthio-2 : 4-benzthiazine methiodide and 3-methyl-2 : 4-benzthiazine, followed by sodium hydroxide and chloroform; after recrystallisation from ethyl acetate it was obtained in 17% yield.

[2-(3-*Ethylbenzthiazole*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide* (VIII).—2-Methylbenzthiazole ethiodide (1·53 g.; 1 mol.), 3-ethylthio-2 : 4-benzthiazine ethiodide (1·83 g.; 1 mol.), and triethylamine (0·75 c.c.; 1·1 mols.) in absolute alcohol (20 c.c.) were boiled and stirred together for 2 minutes. The washed dye (2·12 g.) was recrystallised from methyl alcohol (40 c.c. per g.) and obtained in 65% yield (1·57 g.) (Found : I, 26·45. $C_{20}H_{21}N_2IS_2$ requires I, 26·45%). The orange-yellow crystals had m. p. 239° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4200 A. It was a moderate sensitiser with maximum at 4600.

[2-(3-*Ethyl*-6 : 7-*benzbenzthiazole*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide*.—When 2-methyl-6 : 7-benzbenzthiazole ethiodide was used instead of 2-methylbenzthiazole ethiodide and the washed product recrystallised from methyl

alcohol (410 c.c. per g.), the yield was 63% (Found: I, 24·05. $C_{24}H_{23}N_2IS_2$ requires I, 23·95%). The orange-yellow crystals had m. p. 270° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4400 A. It was a moderate sensitiser with its maximum at 4800 A., the sensitising action extending to 5200.

[2-(3-*Ethylbenzthiazole*)][3-(4-*methyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide* (IX).—The dye obtained by condensing 2-methylbenzthiazole ethiodide and 3-methylthio-2 : 4-benzthiazine methiodide in alcohol, in the presence of triethylamine, was recrystallised from methyl alcohol (130 c.c. per g.) and thus obtained in 69% yield (Found: I, 27·35. $C_{19}H_{19}N_2IS_2$ requires I, 27·2%). The bright yellow crystalline product had m. p. 238° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4200 A. It was a fairly good sensitiser with its maximum in a chloride emulsion at 4600 A.

The same dye was obtained by reaction of 2-methylbenzthiazole ethiodide and potassium carbonate in alcohol with the quaternary salt prepared from 3-methylthio-2 : 4-benzthiazine and ethyl iodide, being obtained in 42% yield after two recrystallisations (Found: I, 27·3%). M. p. and mixed m. p. with other specimen, 239° (decomp.). It was also prepared by heating methin-[2-(3-ethylbenzthiazole)][3-(2 : 4-benzthiazine)] (1·62 g.; 1 mol.) at 100° for an hour with methyl sulphate (0·62 g.; 1 mol.), which had been neutralised and dried by means of sodium bicarbonate and anhydrous sodium sulphate. The product was dissolved in hot spirit and treated with a hot solution of potassium iodide (4 g.) in water (10 c.c.). The orange solid was filtered off, washed with water (1·76 g. obtained), and recrystallised from methyl alcohol, being obtained in 58% yield (1·36 g.) (Found: I, 27·35%). The m. p., 222° (decomp.), was below that of the other sample, but the mixed m. p. was 222—224°. The absorption curves were identical.

To compare with the behaviour of the hydriodide, the present ethiodide (1 g.) prepared by the first method was boiled and stirred with benzene (20 c.c.) and 10% sodium hydroxide solution (20 c.c.) for an hour, but solution was incomplete and 30% of the dye was recovered unchanged. The benzene layer was washed and dried and the solvent was removed but only a sticky solid, m. p. about 98°, was obtained from it (0·5 g.).

[2-(3-*Ethylbenzoxazole*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide* (X).—After 2-methylbenzoxazole ethiodide (2·89 g.), 3-ethylthio-2 : 4-benzthiazine ethiodide, and triethylamine had been boiled together in absolute alcohol (10 c.c.) for 7 minutes, the liquid was cooled and treated with excess of ether. The resultant oil solidified on treatment with water. The solid was recrystallised from methyl alcohol (15 c.c.) and thus obtained in 27% yield (1·25 g.) (Found: I, 27·4. $C_{20}H_{21}ON_2IS$ requires I, 27·35%). The yellow crystals had m. p. 277° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 3800 A. It was a moderate sensitiser with its maximum at 4250 A., its action extending to 4500.

[2-(3-*Ethyl*-6 : 7-*benzbenzoxazole*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide*.—Prepared from 2-methyl-6 : 7-benzbenzoxazole ethiodide (3·39 g.), 3-ethylthio-2 : 4-benzthiazine ethiodide, and triethylamine in alcohol, with heating for 3 minutes, the washed solid (1·9 g.) was recrystallised from methyl alcohol (80 c.c. per g.) and thus obtained in 27% yield (1·37 g.) (Found: I, 24·6. $C_{24}H_{23}ON_2IS$ requires I, 24·7%). The yellow crystals had m. p. 257° (decomp.). The absorption maximum of their methyl-alcoholic solution was at 4010 A. It was a powerful sensitiser with its maximum at 4500 A. The sensitisation extended to 4800.

[2-(3-*Ethylbenzselenazole*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide* (XI).—On boiling 2-methylbenzselenazole ethiodide (3·52 g.) with 3-ethylthio-2 : 4-benzthiazine ethiodide, in the presence of triethylamine in alcohol, dye was at once precipitated, and boiling was continued for 1 minute only. The washed product (4·46 g.) was recrystallised from methyl alcohol (90 c.c. per g.) and thus obtained in 61% yield (3·21 g.) as yellow crystals (Found: I, 24·15. $C_{20}H_{21}N_2ISSe$ requires I, 24·05%). M. p. 234° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4340 A. The dye was a weak sensitiser with its maximum at 4750 A., the sensitisation extending to 5100.

[2-(1-*Methylquinoline*)][3-(4-*methyl*-2 : 4-*benzthiazine*)] *methincyanine Iodide* (XII; R = Me).—Methin-[2-(1-methylquinoline)][3-(2 : 4-benzthiazine)] (V) (1·52 g.; 1 mol.) was heated with dry, neutral methyl sulphate (0·5 c.c.; 1 mol.) on a steam-bath for an hour. The orange melt solidified on cooling. It was dissolved in hot spirit and treated with a hot solution of potassium iodide (3·3 g.; 4 mols.) in water (5 c.c.). The resultant solid was filtered off (2·1 g. obtained) and twice recrystallised from methyl alcohol (10 c.c. per g.), giving a 36% yield (0·8 g.) (Found for material dried in a vacuum at 60°: I, 28·55. $C_{20}H_{19}N_2IS$ requires I, 28·45%). The reddish-orange crystals had m. p. 107°, but subsequently solidification took place, followed by melting at 227° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4575 A. The dye was a weak sensitiser with maxima at 4450 and 4900 A., the action falling off gradually to 5400. When methin-[2-quinoline][3-(4-methyldihydro-2 : 4-benzthiazine)] (VI) was similarly heated with methyl sulphate, fusion did not occur. After heating at 120° for 2 hours, the product was converted into iodide (1·72 g. obtained). This was boiled out with methyl alcohol, leaving a sparingly soluble residue, and a 20% yield of dye crystallised from the filtrate. From m. p. and mixed m. p. determinations, it was concluded to be the same as the specimen prepared by the other method. It was also prepared from 3-methylthio-2 : 4-benzthiazine methiodide (1·69 g.), quinaldine methiodide, and triethylamine in alcohol. The crude, washed product (1·36 g.) was recrystallised from methyl alcohol (14 c.c.) and thus obtained in 33% yield (0·73 g.). M. p. 236° (decomp.), mixed m. p. with first specimen 227° (decomp.).

[2-(1-*Ethylquinoline*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide* (XII; R = Et).—Quinaldine ethiodide (1·5 g.) and 3-ethylthio-2 : 4-benzthiazine ethiodide were boiled and stirred together with triethylamine in ethyl alcohol for 4 minutes. The dye which crystallised on cooling was washed (1·43 g. obtained) and recrystallised from methyl alcohol (10 c.c. per g.), being obtained in 52% yield (1·24 g.) (Found: I, 26·75. $C_{22}H_{23}N_2IS$ requires I, 26·75%). The orange crystals had m. p. 212° (decomp.). The absorption maximum of their methyl-alcoholic solution was at 4625 A. with an inflexion at 4390 A. The dye was a weak sensitiser with the maximum effect at 4900 A., sensitisation extending to 5200.

[4-(1-*Ethylquinoline*)][3-(4-*ethyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide* (XIII).—Lepidine ethiodide (2·99 g.) and 3-ethylthio-2 : 4-benzthiazine ethiodide were boiled and stirred with triethylamine in alcohol for 3 minutes. On addition of ether to the deep red solution, a red oil separated. Treatment with water converted it into a solid (2·95 g. obtained). After crystallisation from methyl alcohol (10 c.c. per g.), it was obtained in 45% yield (2·13 g.) (Found for material dried to constant weight in a vacuum at 70°: I, 26·8. $C_{22}H_{23}N_2IS$ requires I, 26·75%). The bright red needles had m. p. 95° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4955 A. It was a moderate sensitiser with the maximum at 5250 A., its action extending to 5600.

[2-(3-*Methyldihydro*-1 : 3-*thiazine*)][3-(4-*methyl*-2 : 4-*benzthiazine*)]*methincyanine Iodide* (XIV).—2-Methyldihydro-1 : 3-thiazine methiodide (2·0 g.) and 3-methylthio-2 : 4-benzthiazine methiodide were boiled and stirred with triethylamine in alcohol for 7 minutes. Addition of ether precipitated a yellow oil, which solidified on treatment with water. After crystallisation from methyl alcohol (15 c.c.), the yield was 11% (0·35 g.) (Found: I, 30·2. $C_{15}H_{19}N_2IS_2$ requires I, 30·35%). The yellow crystals had m. p. 235° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 3790 A. The dye did not sensitise or depress blue sensitivity.

Methin-[2-(3-*ethyldihydrobenzthiazole*)][3-(2 : 4-*benzthiazine*)] *Hydriodide*.—2-Methylbenzthiazole (2·98 g.; 1 mol.), 3-ethylthio-2 : 4-benzthiazine (4·18 g.; 1 mol.), and ethyl *p*-toluenesulphonate (8 g.; 2 mols.) were heated together at 155—160° for 3 hours. The melt was dissolved in hot spirit (60 c.c.) and the crystals which separated on cooling were filtered off (5·62 g. obtained). They were dissolved in hot spirit and treated with a hot solution of potassium iodide (13·2 g.; 4 mols.) in water (40 c.c.). The resultant iodide (4·15 g.; 56% yield) was twice recrystallised from methyl

alcohol (160 c.c. per g.) and thus obtained in 38% yield (Found : I, 28·0. $C_{18}H_{17}N_2IS_2$ requires I, 28·05%). The golden-yellow crystals had m. p. 264—265° (decomp.). The methyl-alcoholic solution had its absorption maximum at 4090 in the presence of aqueous ammonia (5 c.c., *d* 0·880, per 100 c.c.) and at 4290 A. in the presence of sulphuric acid (5 g. per 100 c.c.). It was a strong sensitiser, sensitisation extending to 5000 A. with the maximum at 4600. This hydriodide (1 g.) was boiled and stirred for an hour with benzene (20 c.c.) and 10% sodium hydroxide solution (20 c.c.) : no solid was left undissolved. The benzene layer was washed and dried, and the solvent removed. The base was obtained in 88% yield (0·63 g.). Its m. p. and the mixed m. p. were identical with that of the specimen synthesised from 2-methylbenzthiazole etho-*p*-toluenesulphonate and 3-ethylthio-2 : 4-benzthiazine. The hydriodide was also prepared by adding a solution of the synthetic methin-[2-(3-ethyldihydrobenzthiazole)][3-(2 : 4-benzthiazine)] (3·24 g.; 1 mol.) in hot acetone (100 c.c.) to hydriodic acid (5·2 c.c.; *d* 1·5; 2 mols.) diluted with hot water. The iodide was filtered off, washed with water, and dried (4·63 g. obtained). On recrystallisation from methyl alcohol (180 c.c. per g.) it was obtained in 60% yield (2·71 g.) (Found : I, 28·15%). Its m. p. and absorption were identical with those of the other sample.

Methin-[2-(3-*ethyldihydro*-6 : 7-*benzbenzthiazole*)][3-(2 : 4-*benzthiazine*)] *Hydriodide.*—2-Methyl-6 : 7-benzbenzthiazole (1·99 g.), 3-ethylthio-2 : 4-benzthiazine, and ethyl *p*-toluenesulphonate were heated together at 150—160° for 4 hours. The hot melt was dissolved in hot absolute alcohol (10 c.c.) and treated with a hot solution of potassium iodide (3·3 g.) in water (20 c.c.). The dye was filtered off, washed, and ground with acetone (12 c.c.) (2·32 g. obtained; 46% yield). It was boiled out with methyl alcohol (20 c.c.), and the residue recrystallised from methyl alcohol (390 c.c. per g.). The yield of bright yellow crystals was 30% (1·51 g.) (Found : N, 5·55; I, 25·4; S, 12·7. $C_{22}H_{19}N_2IS_2$ requires N, 5·6; I, 25·3; S, 12·75%). M. p. 277° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 4270 in the presence of alkali and at 4450 A. in the presence of acid. It was a powerful sensitiser with its maximum at 4700 A., the sensitisation extending to 5250. In a similar preparation where 3-ethylthio-2 : 4-benzthiazine was heated with ethyl *p*-toluenesulphonate for 2 hours, and the melt heated with 2-methyl-6 : 7-benzbenzthiazole etho-*p*-toluenesulphonate for a further 2 hours, the resultant dye iodide (42% yield) gave only a 9% yield of hydriodide on recrystallisation. When the melt from a preparation such as the first one was dissolved in alcohol and boiled and stirred for 10 minutes with triethylamine (1·2 mols.), the crude iodide (29% yield) again gave only a 9% yield of hydriodide.

Methin-[2-(3-*ethyldihydrobenzoxazole*)][3-(2 : 4-*benzthiazine*)] *Hydriodide.*—The crude, washed iodide (34% yield) from 2-methylbenzoxazole ethiodide, 3-ethylthio-2 : 4-benzthiazine, and ethyl *p*-toluenesulphonate, followed by potassium iodide, was recrystallised from methyl alcohol (80 c.c. per g.) and thus obtained in 25% yield (Found : N, 6·45; I, 29·2; S, 7·3. $C_{18}H_{17}ON_2IS_2$ requires N, 6·45; I, 29·1; S, 7·35%). The yellow crystals had m. p. 277° (decomp.) and their mixed m. p. with hydriodide which had been prepared from synthetic base was 277° (decomp.). The absorption maximum of a methyl-alcoholic solution was at 3840 in the presence of alkali and at 3970 A. in the presence of acid. The hydriodide was a moderate sensitiser with its maximum at 4300 A., and its action extended to 4550. This hydriodide was converted into base by the action of benzene and alkali and the conversion proceeded exactly like that of the hydriodide from synthetic base, giving a 36% yield of recrystallised base and a 12% yield of hydrochloride. In simultaneous m. p. determinations this and the synthetic base behaved similarly.

Methin-[2-(3-*ethyldihydro*-6 : 7-*benzbenzoxazole*)][3-(2 : 4-*benzthiazine*)] *Hydriodide.*—This was similarly prepared (42% crude yield) by use of 2-methyl-6 : 7-benzbenzoxazole (3·66 g.). After boiling out with methyl alcohol (20 c.c.) and then recrystallising from methyl alcohol (50 c.c. per g.) the yield was 24% (Found : N, 5·55; I, 26·4; S, 6·45. $C_{22}H_{19}ON_2IS$ requires N, 5·75; I, 26·1; S, 6·6%). The dye from the boiling out (7% yield) appeared to consist of a mixture of hydriodide and ethiodide (Found : I, 25·15. $C_{24}H_{23}ON_2IS$ requires I, 24·7%). The main crop of yellow hydriodide had m. p. 254° (decomp.). The absorption maximum of its methyl-alcoholic solution was at 3970 in the presence of alkali and at 4090 A. in the presence of acid. It was a powerful sensitiser with its maximum effect at 4500 A., its action extending to 5000. In an experiment where boiling and stirring with triethylamine (1·2 mols.) in alcohol was applied after the fusion, the yield of hydriodide after recrystallisation was 19% (Found : I, 25·95%).

Methin-[2-(3-*ethyldihydrobenzselenazole*)][3-(2 : 4-*benzthiazine*)] *Hydriodide.*—2-Methylbenzselenazole (1·96 g.), 3-ethylthio-2 : 4-benzthiazine, and ethyl *p*-toluenesulphonate were heated together, and the gum was dissolved in hot alcohol and treated with aqueous potassium iodide. The crystalline solid was filtered off, washed with water, and ground with acetone (15 c.c.) (53% yield obtained). It was boiled out with methyl alcohol (8 c.c.), and the residue recrystallised from methyl alcohol (300 c.c. per g.), giving a 29% yield (Found : N, 5·85; I, 25·9. $C_{18}H_{17}N_2ISSe$ requires N, 5·6; I, 25·4%). The bright yellow crystalline substance had m. p. 272° (decomp.) with previous darkening. The absorption maximum of a methyl-alcoholic solution was at 4100 in the presence of alkali and at 4350 A. in the presence of acid. It was a powerful sensitiser with its maximum at 4650 A., the action extending to 5200. When the melt in such a preparation was dissolved in alcohol and boiled and stirred with triethylamine or anhydrous potassium carbonate, unsatisfactory products were obtained in small amount.

5-3′-(4′-*Methyldihydro*-2′ : 4′-*benzthiazylidene*)-3-*ethylrhodanine* (XVII).—3-Methylthio-2 : 4-benzthiazine methiodide (1·69 g.; 1 mol.), 3-ethylrhodanine (0·81 g.; 1 mol.), anhydrous potassium carbonate (180-mesh; 0·35 g.; 0·5 mol.), and absolute alcohol (12 c.c.) were boiled and stirred together for 5 minutes. The washed product (1·05 g.) was recrystallised from methyl alcohol (310 c.c.) and thus obtained in 50% yield (0·81 g.) (Found : S, 30·05. $C_{14}H_{14}ON_2S_3$ requires S, 29·85%). The golden-yellow crystals had m. p. 190°. The narrow absorption band had its maximum at 4200 A. and an inflexion at 4000. It sensitised a chloride emulsion strongly with a sharp maximum at 4600 A., sensitisation extending to about 4900. It was also obtained by use of the salt which had been prepared from 3-methylthio-2 : 4-benzthiazine and ethyl iodide, and was obtained, after recrystallisation, in 43% yield. After a second recrystallisation the yield was 29% (Found : S, 29·8; N, 8·7. $C_{14}H_{14}ON_2S_3$ requires S, 29·85; N, 8·7%).

5-3′-(4′-*Methyldihydro*-2′ : 4′-*benzthiazylidene*)-4-*keto*-2-*thio*-3-*ethyltetrahydro-oxazole* (XVIII).—2-Methylthio-2 : 4-benzthiazine methiodide (1·69 g.; 1 mol.), 4-keto-2-thio-3-ethyltetrahydro-oxazole, and triethylamine (0·75 c.c.; 1·1 mols.) in ethyl alcohol were boiled together under reflux for 25 minutes. The product was filtered off, washed with water, dried (0·9 g. obtained), and recrystallised from methyl alcohol (60 c.c.), being obtained in 49% yield (0·75 g.). M. p. 167°. In another preparation the salt which had been prepared from 3-ethylthio-2 : 4-benzthiazine and methyl iodide was similarly heated with 4-keto-2-thio-3-ethyltetrahydro-oxazole and anhydrous potassium carbonate in alcohol. The water-washed product was recrystallised from methyl alcohol (80 c.c. per g.) and thus obtained in 42% yield (Found : S, 20·7. $C_{14}H_{14}O_2N_2S_3$ requires S, 20·95%). The lemon-yellow crystals had m. p. 169° and the mixed m. p. with the other sample was 168°. The absorption maximum of a methyl-alcoholic solution was at 3870 A. The compound sensitised a chloride emulsion strongly, with a maximum at 4100 A., the action extending to 4500.

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