149. *Bases of which Methincyanines are the Quaternary Salts.*

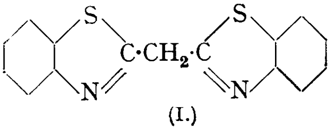
By Frances M. Hamer.

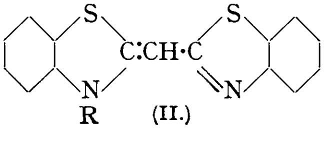
Known methods of preparing bases, of which methincyanines are quaternary salts, have been applied and extended. On passing from a base to the thiacyanine or selenathiacyanine which is its alkiodide, the shift of absorption maximum towards the red is about the same as on passing to the corresponding acid salt. There is a greater shift on passing from trimethin base to thiacarbocyanine (1020 A.) or to acid salt (950 A.). On passing from a thia-2′-cyanine base, having the alkyldihydro-structure in the benzthiazole nucleus, to the thia-2′-cyanine, the absorption maximum shifts further towards the red (about 600 A.) than on passing to an acid salt (about 450 A.). The hitherto unknown, isomeric bases, with the alkyldihydro-structure in the quinoline nucleus, have about the same absorption maximum as the thia-2′-cyanines themselves; it does not shift on addition of acid but shifts towards the blue on exposure to light.

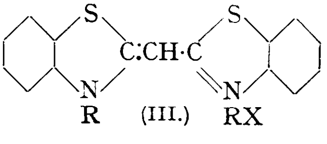
A thia-4′-cyanine base, with the alkyldihydro-structure in the benzthiazole nucleus, was isolated as its hydriodide. On treatment of the base with acid, the absorption maximum shifted towards the red. Whereas on passing from thia-2′- to thia-4′-cyanine, the maximum shifts towards the red, the base of thia-4′-cyanine has its maximum close to the maximum of that isomeric base of thia-2′-cyanine to which it is most nearly related.

A 2 : 2′-cyanine base showed a shift of absorption maximum towards the red with acetic acid but the solution was decolorised by an amount of sulphuric acid which, with the bases of thia-, thia-2′-, and thia-4′-cyanines, induced a shift towards the red.

Bases of which cyanines are the quaternary salts were first prepared by Mills, as the third stage in his four-stage synthesis of thiacyanines. Thus *o*-aminothiophenol was condensed with ethyl malonate to give dibenzthiazolylmethane (I), from the ethiodide of which, by the action of alkali, a base (II; R = Et) was produced. Its ethiodide proved to be the diethylthiacyanine (III; R = Et, X = I).

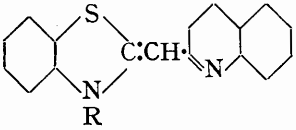

(I.)

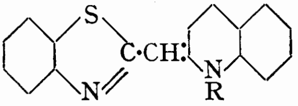

(II.)


(III.)

The methyl base (II; R = Me) and the dimethyl salt (III; R = Me, X = I) were also synthesised (J., 1922, **121,** 455). Several years later, Clark, from 2-imino-3-methyldihydrobenzthiazole * and quinaldine, prepared the base (IV; R = Me), of which thia-2′-cyanine is the quaternary salt (J., 1936, 507). Kendall noted that such bases have photographic sensitising properties, which are different from those of their quaternary salts. He patented the photographic use of a series of such bases, including those of which 2 : 2′-, oxa-2′-, selena-2′-, thia-2′-, and thia-4′-cyanines, also indo-2′-carbocyanine, are the quaternary salts. For making the bases of methincyanines, his method, which was not described in detail, was to condense a quinoline base, having a reactive methyl group, with a quaternary salt, having a reactive alkylthio-group or, for the trimethincyanine base, a reactive, substituted aminovinyl group (B.P. 456,362/1935). The preparations of the preceding types of bases, as also of one of which thia-2′-carbocyanine is the quaternary salt, were described by Barent and Kendall, a limitation being that that starting base, which has the reactive methyl group, must be a quinoline base (B.P. 477,983/1936).

(IV.)





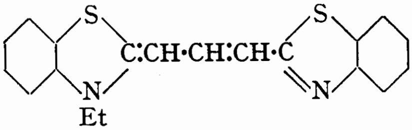
(V.)

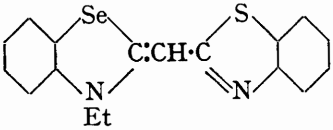
Gevaert Photo Producten, N.V. recorded that dye bases are produced by heating cyanines with a high-boiling base, such as diethylaniline, which has the effect of removing alkyl salt. In their examples, the starting points—thiacyanine, thiacarbocyanine, and 2 : 2′-carbocyanine—are all of the symmetrical cyanine type. They regarded as surprising their observation that solutions of the acid salts of the dye bases had about the same colour as those of the quaternary salts, and that the sensitising maxima of the acid salt and of the alkyl salt were the same (B.P. 477,990/1935).

There is in the literature no recorded instance of a cyanine dye base, comprising a quinoline and another heterocyclic nucleus, and having the alkyldihydro-structure in the quinoline nucleus: the known bases of the thia-2′-cyanine series are all of type (IV) and none of type (V). The present work was started with the object of comparing the colours of some dye bases with those of the simple methincyanines which are their alkyl salts. In the case of unsymmetrical cyanines, it seemed of especial interest to attempt the preparation and examination of both those types of base which can be formulated. In putting this plan into effect, it was found that the alkylthiol condensation of Barent and Kendall is capable of extension in two directions: in the first place, 2-methylbenzthiazole or 2-methylbenzselenazole may be used instead of methyl bases containing a quinoline nucleus; secondly, instead of condensing a heterocyclic quaternary salt having an alkylthio-group with a heterocyclic base containing a reactive methyl group, it is possible to condense a heterocyclic base, having an alkylthio-group, with a heterocyclic quaternary salt containing a reactive methyl group.

The methincyanine and trimethincyanine dye bases (II; R = Et, and VI) were prepared from the thiacyanine chloride (III; R = Et, X = Cl) and the thiacarbocyanine iodide, respectively, by the method of Gevaert Photo Producten, N.V. (*loc. cit.*). The methyl analogue (II; R = Me) of the former, however, was prepared by fusion of 2-methylthiobenzthiazole and 2-methylbenzthiazole metho-*p*-toluenesulphonate, followed by treatment with alkali, so that its preparation involved both of the new factors mentioned above. So also did the preparation of (VII) from 2-methylthiobenzthiazole and 2-methylbenzselenazole etho-*p*-toluenesulphonate; (VII) was first isolated as its *hydriodide* and, because of the insolubility of this salt, prolonged boiling and stirring with caustic alkali and benzene were necessary in order to liberate the base (VII). In the methin series, on

(VI.)





(VII.)

---

* The numbering of the benzthiazole ring now starts from the sulphur atom as 1.

passing from the methyl base (II; R = Me) to the thiacyanine which is its methiodide (III; R = Me, X = I), the maximum shifts 250 A. towards the region of longer wave-length; passing from the ethyl base (II; R = Et) to the thiacyanine which is its ethiodide (III; R = Et, X = I) the shift is 220 A. When the methyl base and the ethyl base are dissolved in methyl alcohol containing sulphuric acid, the maxima shift 230 and 200 A., respectively, towards the region of longer wave-length. The absorption maximum of base (II, R = Et) lies 30 A. further towards the red than that of base (VII). Passing from base (VII) to the selenathiacyanine which is its ethiodide, the shift is 300 A., and when the base is dissolved in acidified methyl alcohol, the shift is 260 A.; however, on passing from base to hydriodide, the shift is only 60 A., indicating that the hydriodide had dissociated in solution. In the trimethin series, in the one instance which has been examined, the shift of absorption maximum on passing from base to quaternary salt is much greater, being 1020 A. on passing from the ethyl base (VI) to the thiacarbocyanine which is its ethiodide. In passing from the ethyl base (VI) to an acid salt, the absorption maximum shifts 950 A. towards the region of longer wave-length. Thus with these representatives of the thiacyanine and thiacarbocyanine groups, the observation of Gevaert Photo Producten, N.V. (*loc. cit.*), that solutions of the acid salt and of the quaternary salt have the same colour, is borne out.

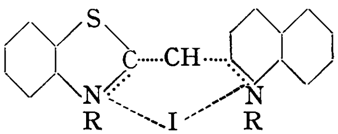
The two thiacyanine bases (II; R = Me or Et) and the thiacarbocyanine base (VI) possess photographic sensitising properties. The sensitising action of the last is weakened, and extended towards the red, by the addition of acid; as compared with the ethiodide, the acid salt is a poor sensitiser.

Clark's base (IV; R = Me) (*loc. cit.*) was prepared by Barent and Kendall's method (*loc. cit.*), but the ethyl base (IV; R = Et) was prepared by reaction of 2-methylthioquinoline with 2-methylbenzthiazole etho-*p*-toluenesulphonate, both the new factors again being involved. The hitherto unknown isomers (V; R = Me or Et) of these two bases were prepared by fusing 2-alkylthioquinoline alko-*p*-toluenesulphonate with 2-methylbenzthiazole, followed by treatment with alkali, which preparation involves the former of the two new points.

Alko-*p*-toluenesulphonates would appear to be more suitable than alkiodides as starting points in such fusions, since in two instances when alkiodides took their place the results were negative, and in a third instance the alkiodide gave a lower yield than did the alko-*p*-toluenesulphonate. In preparing quaternary salts of alkylthiol compounds, anomalies have been recorded. Thus on heating 2-methylthioquinoline with ethyl iodide the product is 2-ethylthioquinoline methiodide (Beilenson and Hamer, J., 1939, 143), whereas 2-methylthiobenzthiazole and ethyl iodide give 2-ethylthiobenzthiazole methiodide (Sexton, J., 1939, 470). When using alkylthiol compounds, it is, therefore, a desirable precaution to choose salts in which the alkyl groups which are attached to the nitrogen and sulphur atoms are the same: this precaution has been taken in the present work.

The bases of type (IV) were yellow, giving yellow alcoholic solutions, but those of type (V) were orange and gave orange solutions, resembling those of the thia-2'-cyanines (VIII; R = Me or Et) themselves. Solutions of both types showed on treatment with a large excess of mineral acid, *e.g.*, hydrochloric acid, the decolorisation which is a characteristic of cyanine dyes. With acetic acid, however, or with a moderate excess of mineral acid, the two types showed a striking and interesting difference in behaviour; solutions of the bases of type (IV) deepened in colour, now approaching the colour of the thia-2'-cyanines, whereas solutions of the bases of type (V) showed no preliminary deepening.

The behaviour of the bases of type (IV) is comparatively simple and will be discussed first. On addition of sulphuric acid to methyl-alcoholic solutions of Clark's base (IV; R = Me) and of its ethyl analogue (IV; R = Et), the absorption maximum shifts 440 and 460 A. respectively, towards the region of longer wave-length, whereas passage to the thia-2'-cyanines (VIII; R = Me or Et), which consists in addition to the bases of methyl iodide and ethyl iodide respectively, involves shifts of 590 and 600 A.



(VIII.)

In obtaining absorption curves of the two bases of type (V), the positions of the maxima as read from the wedge spectrograms lay at a shorter wave-length, by about 400 A. in each instance, than those obtained with the Hüfner spectrophotometer. The explanation of this result is that the bases are rapidly affected by light, the change consisting in a shift of the absorption maximum towards the region of shorter wave-length. The curves can be plotted by use of the Hüfner instrument, if special care be taken, but delay results in a certain shift of the maximum, whilst exposure to ultra-violet light gives the values recorded by use of the wedge spectrograph, where the source of light is stronger. The bases of type (IV), unlike those of type (V), do not show a shift of the maximum on similar exposure to light.

Measurements on the Hüfner instrument revealed that freshly prepared solutions of the bases of type (V; R = Me or Et) have almost the same absorption maxima as the thia-2′-cyanines (VIII; R = Me or Et), being only 50 and 40 A., respectively, on the shorter wave-length side; thus the methyl and ethyl bases of type (V) have their maxima 540 and 560 A., respectively, further towards the red than the isomeric bases of type (IV). After exposure to ultra-violet light they are only about 200 A. further. When some sulphuric acid is added in making up methyl-alcoholic solutions of the bases of type (V), it does not affect the position of the absorption maximum nearest the red, so that in this respect these bases differ strikingly from all the others. The action of light on acidified alcoholic solutions of the bases of type (V) resembles its action on their alcoholic solutions.

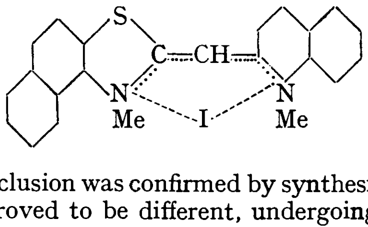
When tested in a gelatino chloride photographic emulsion, the sensitising action of the base of type (IV) was, with each pair, distinctly stronger than that of the isomeric base of type (V). So was it also with a pair of 6 : 7-benz-derivatives, described further on.

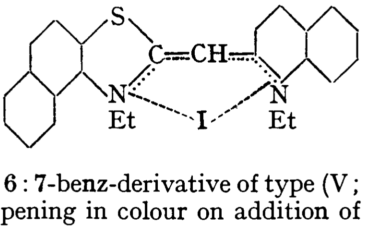
The *hydriodides* of three of these bases of types (IV) and (V) were prepared and the hydrochloride of the fourth. The principal absorption maximum of each salt proved to be in approximately the same position as the absorption maximum of an acidified solution of the corresponding base. The hydriodide of the methyl base of type (V) did not, whilst the hydrochloride of that of type (IV) did sensitise; the hydriodide of the ethyl base of type (V) had a weak sensitising action like that of the base itself, whilst that of the ethyl base of type (IV) sensitised more strongly although less extensively.

The thia-2′-cyanine (IX) was converted into a base by boiling with diethylaniline by the method which had previously been applied (Gevaert Photo Producten, N.V., *loc. cit.*) only to symmetrical cyanines. Since a methyl-alcoholic solution of this base did not deepen in colour when treated with acetic acid, it was concluded to be a 4 : 5-benz-derivative of the base of type (V; R = Me). This was confirmed by its synthesis from 2-methylthioquinoline metho-*p*-toluenesulphonate and 2-methyl-4 : 5-benzbenzthiazole. The diethyl analogue of (IX) also gave a base which did not deepen in colour on treatment with acid and was therefore also regarded as a 4 : 5-benz-derivative of the base of type (V; R = Et). On the other hand, the thia-2′-cyanine (X), on treatment with diethylaniline, yielded a base which did deepen in colour on treatment with acid.

It, therefore, was concluded to be the 6 : 7-benz-derivative of the base of type (IV; R = Et).

(IX.)





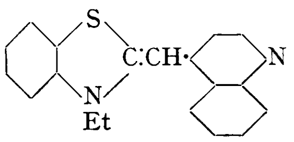
(X.)

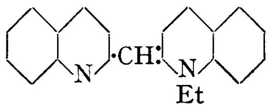
This conclusion was confirmed by synthesising the 6 : 7-benz-derivative of type (V; R = Et), which proved to be different, undergoing no deepening in colour on addition of excess of acetic acid; the synthesis consisted in fusion of 2-ethylthioquinoline etho-*p*-toluenesulphonate with 2-methyl-6 : 7-benzbenzthiazole. When the simple thia-2′-cyanine (VIII; R = Et) was boiled with diethylaniline, the product consisted of a mixture of the isomeric bases of types (IV; R = Et) and (V; R = Et). Therefore, after heating thia-2′-cyanines with diethylaniline, the product isolated may consist of either one of the two isomeric bases, or may be a mixture of the two. The important general conclusion that bases of type (IV) deepen in colour on addition of excess of acetic acid, whilst bases of type (V) do not, is now supported by a total of seven unequivocal instances.

With the preceding three benz-derivatives of bases of type (V), the absorption maxima as recorded by the wedge spectrograph are the same as those recorded by use of the Hüfner instrument. In one instance the use of the latter instrument showed also a second maximum, 280 A. further towards the red; because of this fact, and because the positions of the maxima are about the same as those given by wedge spectrograms of unsubstituted bases of type (V), it is concluded that the absorption maxima of these three benz-derivatives are those of solutions which have already changed in the light, though in the one case, with the Hüfner instrument, this change was incomplete. With the 6 : 7-benz-derivative of the base of type (V; R = Et) the absorption maximum, as recorded by the wedge spectrograph, is 250 A. further towards the red than that of the same derivative of the base of type (IV). The maximum of the latter is shifted 520 A. towards the red by addition of sulphuric acid, whereas the shift, involving addition of ethyl iodide, which occurs on passing to the thia-2′-cyanine, is 720 A. From these figures and from those for the two simple bases of type (IV), it is apparent that the absorption maxima of quaternary salt and acid salt are further apart than in previous instances.

To prepare the base (XI), of which thia-4′-cyanine is the quaternary salt, 2-ethylthiobenzthiazole etho-*p*-toluenesulphonate and lepidine were fused, the product was heated with alkali, and its acetic acid solution treated with potassium iodide to give the *hydriodide*, from which, by prolonged boiling and stirring with caustic alkali and benzene, the *base* was liberated. This base behaves like those of type (IV), to which it is related in structure, in that its alcoholic solution deepens in colour on treatment with excess of acetic acid. On passing from the base to the thia-4′-cyanine which is its ethiodide, the absorption maximum shifts 710 A. into the region of longer wave-length, whilst on passing from the base to the hydriodide the shift is 610 A. On passing from the thia-2′-cyanine, which is the ethiodide of (IV; R = Et) and (V; R = Et), to the thia-4′-cyanine which is the ethiodide of (X), the absorption maximum shifts 170 A. towards the region of longer wave-length; it is interesting that the shift on passing from (V; R = Et) to (XI) is in the opposite direction, being 500 A. towards the region of shorter wave-length, whilst the positions of the absorption maxima of (IV; R = Et) and (XI) are close together.

(XI.)





(XII.)

Two bases, of which 2 : 2′-cyanines are the quaternary salts, were prepared; *e.g.*, brief fusion of 2-ethylthioquinoline etho-*p*-toluenesulphonate and quinaldine, followed by treatment with alkali, gave (XII). Its orange alcoholic solution was completely decolorised by an amount of sulphuric acid which merely shifted the absorption maximum of each base of types (II), (IV), (VI), and (XI) towards the red; this accords with the fact that cyanines containing two quinoline nuclei are more readily decolorised by acid than those containing a benzthiazole nucleus. Addition of acetic acid reddened the solution of (XII), which colour change corresponded with a 450 A. shift of the absorption maximum into the region of longer wave-length; on passing from the base to its ethiodide the shift is 470 A. The base possesses two sensitising maxima, of which the one at the longer wave-length is attributed to an acid salt.

In working with the dye bases it has been found convenient to adopt a system of nomenclature suggested by Dr. J. T. Hewitt, F.R.S., in place of the more cumbersome chemical names. This system consists in stating simply the number of methin groups involved, followed by a description of each of the two nuclei. Thus, whereas the systematic chemical name of (II) is 2-benzthiazolyl-3′-alkyl-2′ : 3′-dihydro-2′-benzthiazolylidenemethane, its simplified name is methin[2-benzthiazole][2-(3-ethyldihydrobenzthiazole)].

EXPERIMENTAL.

Methin[2-*benzthiazole*][2-(3-*ethyldihydrobenzthiazole*)] (II; R = Et).—3 : 3′-Diethylthiacyanine chloride (III; R = Et, X = Cl) (3 g.) was boiled with freshly distilled diethylaniline (210 c.c.) for 4 hours (cf. Gevaert Photo Producten, N.V., B.P. 477,990/1935). The diethylaniline was removed by steam distillation, but, instead of following the Gevaert procedure, the residue was extracted with benzene. The dried benzene extract gave a tar, which was taken up in a few c.c. of hot acetone. An almost colourless substance crystallised on cooling, in 46% yield (1·14 g.); the filtrate was very dark. After recrystallisation from acetone (7 c.c.), the yield was 29% (0·71 g.). The base was dried in a vacuum desiccator and analysed by the method of Carius, which was used throughout this work, except where otherwise stated (Found : S, 20·7. Calc. for $C_{17}H_{14}N_2S_2$: S, 20·7%). If heated quickly, the very pale yellow crystals have m. p. 130°, but if heated slowly they do not melt until 162°; the substance may solidify after melting at 130° and melt again at 162°. Mills gives m. p. 163° (J., 1922, **121**, 455). The absorption maximum of the methyl-alcoholic solution lies at 4000 A., with an inflection at 3850; Fisher and Hamer (*Proc. Roy. Soc.*, 1936, *A*, **154**, 703) record 4220 A., for the corresponding thiacyanine iodide. When sulphuric acid is added to the methyl alcohol (10 g. per 100 c.c.) used for dissolving the base, the absorption maximum, for this compound and the next, lies at 4200 A. The base sensitised a gelatino silver chloride photographic emulsion, the maximum lying at 4300 A.

Methin[2-*benzthiazole*][2-(3-*methyldihydrobenzthiazole*)] (II_2; R = Me).—2-Methylthiobenzthiazole (3·62 g.; 1 mol.) and 2-methylbenzthiazole metho-*p*-toluenesulphonate (6·71 g.; 1 mol.) were ground together and heated at 165—175° for 1 hour. The product was heated with 40% sodium hydroxide solution and extracted with chloroform, and the extract dried over anhydrous sodium sulphate. After removal of the solvent, the liquid residue was treated with hot acetone (40 c.c.). Crystals separated on cooling (1·16 g.) and more on concentration (0·16 g.), making a total yield of 22%. After two more recrystallisations from acetone (35 c.c. per g.), the yield was 13% (Found for material dried in a vacuum desiccator : S, 21·95. Calc. for $C_{16}H_{12}N_2S_2$: S, 21·65%). The pale yellow crystals have m. p. 176°, whereas Mills (*loc. cit.*) gives m. p. 172°. The absorption maximum lies at 3970 A., with an inflection at 3830, and Mills (*loc. cit.*) records 4220 for the thiacyanine iodide. The base sensitises a silver chloride emulsion, the maxima lying at 4000 and 4300 A.

An attempt to bring about reaction between 2-methylthiobenzthiazole and 2-methylbenzthiazole methiodide gave a negative result.

Methin[2-*benzthiazole*][2-(3-*ethyldihydrobenzselenazole*)] *Hydriodide*.—2-Methylbenzselenazole (3·93 g.; 1 mol.) and ethyl *p*-toluenesulphonate (4·00 g.; 1 mol.) were fused together at 145—155° for 3 hours and the gum produced was boiled out twice with benzene (30 c.c. × 2) and heated with 2-methylthiobenzthiazole (3·6 g.; 1 mol.) at 165—175° for 1 hour. After heating with alkali, extraction with chloroform, drying, and removal of the solvent, the residue was dissolved in hot acetic acid (7 c.c.), and this solution treated with potassium iodide (6·64 g.; 2 mols.) dissolved in hot water (7 c.c.). After cooling, the brown sticky mass was washed with aqueous acetic acid and ground three times with acetone (15 c.c. × 3). The residue comprised a 27% yield (2·63 g.). It was recrystallised from methyl alcohol (415 c.c.), the yield then being 21% (2·02 g.) (Found : I, 26·1. $C_{17}H_{14}N_2SSe,HI$ requires I, 26·15%). The bright yellow *hydriodide* had m. p. 243° (decomp.). The absorption maximum lies at 4030 A. with an inflection at 4300. It sensitised a chloride emulsion, showing a broad maximum at 4300 A.

Methin[2-*benzthiazole*][2-(3-*ethyldihydrobenzselenazole*)] (VII).—The above hydriodide (1·84 g.) was boiled and stirred for 20 minutes with benzene (400 c.c.) and 20% sodium hydroxide solution (300 c.c.). After cooling, the solid was filtered off and boiled and stirred again with the same alkali and fresh benzene (400 c.c.). The *base* obtained from the dried benzene extracts (1·08 g.; 71% yield) was recrystallised from acetone (4 c.c.) and obtained in 55% yield (0·84 g.) (Found : S, 8·85. $C_{17}H_{14}N_2SSe$ requires S, 9·0%). The yellow solid had m. p. 134—135°. The absorption maximum was at 3970 A. and addition of sulphuric acid (10 g. per 100 c.c.) shifted it to 4230 A. Beilenson, Fisher, and Hamer record 4270 for the selenathiacyanine which is the ethiodide of this base (*Proc. Roy. Soc.*, 1937, *A*, **163**, 138).

Trimethin[2-*benzthiazole*][2-(3-*ethyldihydrobenzthiazole*)] (VI).—3 : 3′-Diethylthiacarbocyanine iodide (4 g.) was boiled with diethylaniline (200 c.c.) for 1 hour and the diethylaniline was removed by steam distillation (Gevaert Photo Producten, N.V., *loc. cit.*). The residue was extracted with benzene, and the extract dried. After removal of the solvent, the gummy residue solidified on grinding with light petroleum (b. p. 40—60°) (2·54 g. obtained, 93% yield). After recrystallisation from ethyl acetate (12 c.c.), the yield was 50% (1·37 g.). The product was dried for analysis in a vacuum at 60—80°, which method of drying was used throughout this work, except where otherwise stated (Found : S, 18·8. $C_{19}H_{16}N_2S_2$ requires S, 19·1%). The small red crystals have m. p. 136—137°. A wedge spectrogram showed the absorption maximum of a methyl-alcoholic solution at 4550 A.; Fisher and Hamer (*loc. cit.*) give 5570 A.

for the thiacarbocyanine iodide. By addition of acetic acid, the absorption maximum of the *base* was shifted to 5500 A. On a gelatino silver bromide photographic emulsion the base conferred extra-sensitivity, with a maximum at 5400 A.; in the presence of acid the sensitisation was weaker but extended to 6200 A, with an additional maximum at 6000. The base gave good sensitising of a silver chloride emulsion, but its action was weakened by the presence of acid.

Methin[2-*quinoline*][2-(3-*methyldihydrobenzthiazole*)] (IV; R = Me).—2-Methylthiobenzthiazole (3·62 g.) was fused with methyl *p*-toluenesulphonate at 150—160° for 3 hours. After addition of quinaldine (1 mol. of each reactant) to the resultant solid, it liquefied on heating, but after an hour at 150—160° was again solid. It was heated with sodium hydroxide solution and extracted with chloroform, and the extract was dried. The solvent was removed, and the residue cooled in a vacuum desiccator. After recrystallisation from acetone (45 c.c.), the yield (3·25 g.) was 56%. After a second recrystallisation from acetone, the yield was 44% (Found: S, 10·85. Calc. for $C_{18}H_{14}N_2S$: S, 11·05%). The deep yellow crystals have m. p. 162°, whereas Clark gives m. p. 165° (J., 1936, 507). The absorption maximum of a methyl-alcoholic solution lies at 4260 A., with a secondary maximum at 3370, and is shifted by addition of sulphuric acid (10 g. per 100 c.c.) to 4700 with a secondary maximum at 3150. For the thia-2′-cyanine which is the methiodide of this base and the next, Hamer gives 4850 A. for the absorption maximum (J., 1928, 206). On a silver chloride emulsion, the base confers strong extra-sensitivity extending to 5500 A., with maxima at 4700 and 5100.

When 2-methylthiobenzthiazole methiodide was used instead of the metho-*p*-toluenesulphonate, the dye base was not obtained.

Methin[2-*quinoline*][2-(3-*methyldihydrobenzthiazole*)] *Hydrochloride*.—The above base (2·85 g.) was suspended in hot spirit (6 c.c.) and treated with a hot mixture of concentrated hydrochloric acid (3 c.c.) and water (12 c.c.). The *hydrochloride* (3·51 g.) was recrystallised from methyl alcohol (21 c.c.) and obtained in 94% yield (3·0 g.) (Found: Cl, 10·9. $C_{18}H_{14}N_2S,HCl$ requires Cl, 10·9%). The red crystals gave a yellow methyl-alcoholic solution with its absorption maximum at 4720 A. and an inflection to the curve at 4400. The colour of the solution rapidly faded in daylight; after fading, the absorption maxima were those of the original base. The sensitising action in a gelatino bromide photographic emulsion extends to 5400 A. with a maximum at 5000.

Attempts to prepare the hydriodide by the action of aqueous potassium iodide, either on an alcoholic solution of the hydrochloride or on an acetic solution of the base, led to a product of lower iodine content than that calculated.

Methin[2-(1-*methyldihydroquinoline*)][2-*benzthiazole*)] (V; R = Me).—2-Methylthioquinoline (7 g.) and methyl *p*-toluenesulphonate were heated together at 140—150° for 1½ hours, 2-methylbenzthiazole added (1 mol. of each reactant), and heating continued for 3 hours. The red solid was heated with sodium hydroxide solution, and the *base* extracted with chloroform. After crystallisation from acetone (160 c.c.) it was obtained in 57% yield (Found: S, 11·05. $C_{18}H_{14}N_2S$ requires S, 11·05%). The bright red crystals melt at 140°, with previous softening. A freshly prepared methyl-alcoholic solution has its absorption maximum at 4800 A. with an inflection to the curve at 4550. After exposure to light the maximum is at 4600 with a secondary maximum at 3500, and after exposure to ultra-violet light, or in the wedge spectrograph, the maximum is at 4450. With addition of sulphuric acid (10 g. per 100 c.c.) there are maxima at 4650 and 4800, but the principal maximum is at 3230 A. Towards a silver chloride emulsion the sensitising is weak and extends to 5700 A. with a maximum at 5400.

Methin[2-(1-*methyldihydroquinoline*)][2-*benzthiazole*] *Hydriodide*.—The preceding base (2 g.) was dissolved in hot acetic acid (20 c.c.) and treated with a hot solution of potassium iodide (2 g.) in water (20 c.c.). The *hydriodide* (2·86 g.) after recrystallisation from methyl alcohol (100 c.c.) was obtained in 71% yield (2·01 g.) (Found: I, 30·25. $C_{18}H_{14}N_2S,HI$ requires I, 30·35%). M. p. 185° (decomp.). A methyl-alcoholic solution of the orange solid has absorption maxima at 4630 and 4800 A., but the principal maximum is at 3150. It gave no sensitisation of a gelatino bromide photographic emulsion and considerable depression of blue speed.

Methin[2-*quinoline*][2-(3-*ethyldihydrobenzthiazole*)] (IV; R = Et).—The base was prepared by fusion of 2-methylthioquinoline (1·75 g.) and 2-methylbenzthiazole etho-*p*-toluenesulphonate, followed by heating with aqueous sodium hydroxide and extraction with chloroform. After removal of the solvent, the sticky residue was crystallised from acetone (15 c.c.). The yield of crystallised *base* was 40% (1·21 g.); recrystallisation from acetone (10 c.c.) reduced it to 25% and another recrystallisation (8 c.c. per g.) to 19% (Found for material dried in a vacuum desiccator: S, 10·6. $C_{19}H_{16}N_2S$ requires S, 10·5%). M. p. 151° with softening from about 135°. The lemon-yellow crystals show in methyl-alcoholic solution an absorption maximum at 4260 A., with the maximum of a secondary band at 3390, and addition of sulphuric acid (10 g. per 100 c.c.) shifts the maximum to 4720, the maximum of the secondary band lying at 3200. For the thia-2′-cyanine which is the ethiodide of this base and the next, Beilenson, Fisher, and Hamer give 4860 A. for the absorption maximum (*Proc. Roy. Soc.*, 1937, *A*, **163**, 138). In a silver chloride emulsion, the weak sensitising action of the base extends from 4200—5300 A., with a maximum at about 5000.

Methin[2-*quinoline*][2-(3-*ethyldihydrobenzthiazole*)] *Hydriodide*.—A hot acetic acid solution of the preceding base was treated with a hot aqueous solution of potassium iodide. The *hydriodide* (93% yield) was recrystallised from methyl alcohol (190 c.c. per g.) and obtained in 83% yield (Found: I, 29·35. $C_{19}H_{16}N_2S,HI$ requires I, 29·4%). The scarlet crystals have m. p. 264° (decomp.), with previous softening. Their methyl-alcoholic solution has its absorption maximum at 4730 A., with the maximum of a secondary band at 3450. In a gelatino bromide photographic emulsion, the extra-sensitivity extends to 5400 A., the maximum lying at 5000.

Methin[2-(1-*ethyldihydroquinoline*)][2-*benzthiazole*] (V; R = Et).—2-Ethylthioquinoline etho-*p*-toluenesulphonate (3·89 g.) and 2-methylbenzthiazole (1 mol. of each) were heated together at 155—165° for 3 hours. The product was heated with sodium hydroxide solution, and the base extracted with chloroform. After removal of solvent from the dried extract, the residue was taken up in hot acetone (35 c.c.); the *base* crystallised on cooling, in 41% yield (1·25 g.) (Found: S, 10·5. $C_{19}H_{16}N_2S$ requires S, 10·5%). The orange crystals had m. p. 160°. The freshly prepared methyl-alcoholic solution had its absorption maximum at 4820 A., with the maximum of a weaker band at 4600. After exposure to light the maximum of the chief band lay at 4600 and that of a secondary band at 3350, and on exposure to ultra-violet light and in the wedge spectrograph the maxima were at 4550 and 4450 respectively. With addition of sulphuric acid (10 g. per 100 c.c.) the maximum was still at 4820, and gave place on fading to one at 4650, the principal one then lying at 3250. Upon a bromide emulsion the base confers weak extra-sensitivity extending to 5600 and with an indefinite maximum at 5250.

Methin[2(1-*ethyldihydroquinoline*)][2-*benzthiazole*]*Hydriodide*.—The preceding base, in acetic acid, was treated with aqueous potassium iodide. After recrystallisation from methyl alcohol (80 c.c. per g.), the yield of *hydriodide* was 81%, and after a second recrystallisation 67% (Found: I, 29·5. $C_{19}H_{16}N_2S,HI$ requires I, 29·4%). The red crystals have m. p. 223° (decomp.), with previous softening. The methyl-alcoholic solution has the maximum of its principal band at 4810 A. and that of a secondary band at 4600. Fading is produced by ultra-violet light, after which only the maximum at 4600 remains but the principal band is now at 3350. The sensitising action of the hydriodide is like that of the base itself.

Methin[2-(1-*methyldihydroquinoline*)][2-(4 : 5-*benzbenzthiazole*)].—3 : 1′-Dimethyl-4 : 5-benzthia-2′-cyanine iodide (3 g.) was boiled with diethylaniline and, after removal of the excess of the latter, the residual dye *base* was extracted with benzene. The solid from the extract was washed with light petroleum (b. p. 40—60°) (2·11 g. obtained). After recrystallisation from absolute alcohol (365 c.c. per g.), the yield was 47% (1 g.) (Found: S, 9·5. $C_{22}H_{16}N_2S$ requires S, 9·4%). The dull red crystals had m. p. 172°. A wedge spectrogram of their methyl-alcoholic solution showed an absorption maximum at 4500 A. On addition of excess of acetic acid, the colour did not deepen. For the thia-2′-cyanine which is the methiodide of this base, Hamer gives 5000 A. for the absorption maximum (J., 1929, 2598). In a chloride emulsion the sensitising maximum of the base was at 5200, in a bromide emulsion there was no maximum but only a tailing off of the sensitivity, and in the presence of acid a maximum appeared at 5400.

According to the synthetic method, 2-methylthioquinoline (3·5 g.) and methyl *p*-toluenesulphonate were heated together at 140—150° for 1½ hours; then 2-methyl-4 : 5-benzbenzthiazole was added and heating continued for 3 hours. After heating with hot alkali, the base was extracted with chloroform and, after removal of solvent, taken up in hot acetone (60 c.c.). It crystallised in 25% yield (1·72 g.), and was first recrystallised from acetone (80 c.c.), being thus obtained in 20% yield (1·38 g.), and then from benzene (8 c.c. per g.), the yield falling to 15% (Found: S, 9·5%). It and the base prepared by the preceding method and a mixture of the two melted simultaneously. Their solutions in spirit were identical in colour and behaved identically on treatment with acetic acid.

Methin[2-(1-*ethyldihydroquinoline*)][2-(4 : 5-*benzbenzthizole*)].—The *base* isolated after 3 : 1′-diethyl-4 : 5-benzthia-2′-cyanine iodide (3 g.) had been boiled with diethylaniline remained sticky even after washing with light petroleum. After crystallisation from ethyl acetate (10 c.c.) it resulted in 62% yield (1·29 g.), and after another recrystallisation the yield was 49% (1·02 g.) (Found: S, 9·1. $C_{23}H_{18}N_2S$ requires S, 9·05%). The red crystals had m. p. 133°. A wedge spectrogram of their orange methyl-alcoholic solution had its absorption maximum at 4600 A., and the colour did not deepen on addition of excess of acetic acid. As plotted by use of the Hüfner instrument, the principal maximum of the base was at 4600 and another at 4880. For the thia-2′-cyanine which is the ethiodide of this base, Beilenson, Fisher, and Hamer give 5030 for the absorption maximum (*Proc. Roy. Soc.*, 1937, *A*, **163**, 138). In a chloride emulsion the sensitising maximum of the base was at 5200, and in the presence of acid the sensitising was weaker, with maxima at 4850 and 5250; in a bromide emulsion the extra-sensitivity consisted only in a tailing off of the normal sensitivity, and in the presence of acid a maximum appeared at 5350.

Methin[2-*quinoline*][2-(3-*ethyldihydro*-6 : 7-*benzbenzthiazole*)].—The *base* prepared by boiling 3 : 1′-diethyl-6 : 7-benzthia-2′-cyanine iodide (3 g.) with diethylaniline, followed by steam distillation and extraction of the residue with benzene, was crystallised from acetone in two fractions (50 c.c., 50 c.c.), the total yield being 60% (1·26 g.). M. p. determinations showed the two fractions to be identical, so they were recrystallised together from acetone (75 c.c.), the yield then being 46% (0·96 g.) (Found : S, 9·3. $C_{23}H_{18}N_2S$ requires S, 9·05%). M. p. 204°. Its mixed m. p. with the following base was 178—185°, whence the bases were concluded to be non-identical and whence the constitution of the present base was deduced. The yellow crystals give a yellow solution in spirit, which deepens on adding excess of acetic acid. The absorption maximum of the base is at 4300 A., and in presence of acid at 4750. The thia-2′-cyanine which is the ethiodide of this base and the next has its maximum at 5020 (Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *A*, **163**, 138). This is a moderate sensitiser for chloride emulsions, its action extending to 5300 with a maximum at 4500.

Methin[2-(1-*ethyldihydroquinoline*)][2-(6 : 7-*benzbenzthiazole*)].—After fusion of 2-ethylthioquinoline etho-*p*-toluenesulphonate (3·89 g.) with 2-methyl-6 : 7-benzbenzthiazole at 150—160° for 7 hours, followed by heating with sodium hydroxide solution and extraction with chloroform, the resultant *base* was boiled out with acetone (80 c.c.), and the undissolved portion recrystallised from benzene (60 c.c.) (0·73 g. obtained). The product that crystallised from the acetone extract (0·17 g.) was recrystallised from benzene (25 c.c.) and the crystals thus obtained (0·06 g.) were added to the others, bringing the yield up to 22% (0·79 g.). After a second recrystallisation from benzene (40 c.c.) the yield was 18% (0·62 g.) (Found : S, 8·9. $C_{23}H_{18}N_2S$ requires S, 9·05%). The red crystals had m. p. 228° and gave a deep orange methyl-alcoholic solution, with an absorption maximum at 4550 A. as shown by a wedge spectrogram and at 4620 as plotted on the Hüfner spectrophotometer; the colour did not deepen on addition of acetic acid. The base conferred very weak sensitivity, extending to about 5600 for moderate exposures, and depressed blue sensitivity considerably.

Action of Diethylaniline on 3 : 1′-*Diethylthia*-2′-*cyanine Iodide*.—The crude base, which was the product of the reaction, was taken up in hot acetone; it separated, on cooling, as a solid, in 68% yield. After recrystallisation from acetone (4 c.c. per g.), the yield was 44% (Found : S, 10·6. Calc. for $C_{19}H_{16}N_2S$; S, 10·5%). The orange crystals melted at 115—120° and gave a deep yellow solution in spirit, the colour of which intensified on addition of excess of acetic acid. From m. p. determinations it is concluded to be a mixture of methin[2-quinoline][2-(3-ethyldihydrobenzthiazole)] and methin[2-(1-ethyldihydroquinoline)][2-benzthiazole].

Methin[4-*quinoline*][2-(3-*ethyldihydrobenzthiazole*)] *Hydriodide*.—2-Ethylthiobenzthiazole (3·9 g.; 1 mol.) and ethyl *p*-toluenesulphonate (4·0 g.; 1 mol.) were heated together at 155—165° for 3 hours. After being washed with absolute ether, the quaternary salt was heated with lepidine (2·7 c.c.; 1 mol.) at 140—150° for 30 minutes. The resultant red solid was heated with 40% sodium hydroxide solution, more water added, and chloroform extraction carried out. After removal of solvent from the dried extract, the residual tar was taken up in hot acetic acid (10 c.c.) and treated with a hot solution of potassium iodide (3 g.) in water (10 c.c.). After cooling, the *hydriodide* was filtered off and ground with acetone (20 c.c.); the yield was then 42% (3·67 g.). On recrystallisation from methyl alcohol (600 c.c.) the first crop (250 g.) amounted to a 29% yield (Found : I, 29·2. $C_{19}H_{16}N_2S,HI$ requires I, 29·4%). The bright red crystals melted at about 288° (decomp.). The absorption maximum was at 4930 A. For the thia-4′-cyanine which is the ethiodide, the absorption maximum is at 5030 (Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *A*, **163**, 138). For moderate exposures the hydriodide sensitised a bromide emulsion up to 5700 A., with a maximum at 5100.

Methin[4-*quinoline*][2-(3-*ethyldihydrobenzthiazole*)] (XI).—The above hydriodide (2·7 g.) was boiled and stirred mechanically with benzene (600 c.c.) and 20% sodium hydroxide solution (460 c.c.) for 30 minutes. After cooling, the layers were separated, and the undissolved solid again boiled with the alkali and a fresh lot of benzene (150 c.c.). Even after this treatment, some hydriodide (0·11 g.) was left undissolved. The benzene extracts were dried over sodium sulphate, and the solvent removed. The residue was crystallised from acetone (7 c.c.); the yield was 63% (1·19 g.). After a second crystallisation from acetone (6 c.c.), the yield was 45% (0·85 g.), after a third 33%, and after recrystallisation from ethyl acetate (5 c.c. per g.) 26% (Found : S, 10·35. $C_{19}H_{16}N_2S$ requires S, 10·5%). M. p. 131°. A methyl-alcoholic solution of the orange-yellow crystals, containing a few drops of triethylamine, has its absorption maximum at 4320 A. It sensitised a chloride emulsion strongly with maxima at 4400, 4700, and 5100.

Methin[2-*quinoline*][2-(1-*ethyldihydroquinoline*)] (XII).—2-Ethylthioquinoline etho-*p*-toluenesulphonate (3·89 g.; 1 mol.) and quinaldine (1·4 c.c.; 1 mol.) were heated together at 145—155° for 10 minutes. The product was heated with alkali and extracted with benzene, and the extract dried. After removal of solvent, the residue was taken up in hot acetone (7 c.c.) ; it crystallised in 47% yield (1·40 g.). After another crystallisation from acetone (10 c.c.) the yield was 36% (1·08 g.) (Found : N, 9·6. $C_{21}H_{18}N_2$ requires N, 9·4%). M. p. 140°, with previous softening. The bright red crystals gave an orange methyl-alcoholic solution having a broad absorption band with maximum at 4750 A. ; there was a secondary maximum at 4550, and an inflection to the curve at 5200. On addition of sulphuric acid (10 g. per 100 c.c.), the solution was decolorised. On addition of acetic acid (10 g. per 100 c.c.), the maximum of the principal band shifted to 5200 and there were secondary maxima at 4880 and 5300. The 2 : 2′-cyanine which is the ethiodide of the base has its absorption maximum at 5220 (Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703). In a gelatino bromide photographic emulsion containing the base, the sensitising maxima are at 5400 and 5800.

Methin[2-*quinoline*][2-(1-*methyldihydroquinoline*)].—2-Methylthioquinoline metho-*p*-toluenesulphonate was heated with quinaldine (1·4 c.c.), and the reaction mixture heated with alkali and extracted with chloroform. After being washed with light petroleum (b. p. 40—60°), the product was boiled out with benzene (20 c.c.), from which a 25% yield (0·72 g.) crystallised. A corresponding preparation with 2-methylthioquinoline methiodide gave only an 8% yield (Found : N, 9·9. $C_{20}H_{16}N_2$ requires N, 9·9%). The brick-red crystals had m. p. 154° with previous softening.

I am indebted to Mr. R. B. Morris for the extensive investigation of the absorption curves, to Dr. E. P. Davey for reports on the sensitising properties of the dye bases, to Dr. B. Beilenson for some preliminary chemical work, and to Dr. L. G. S. Brooker for his helpful criticism.

KODAK LIMITED, WEALDSTONE, HARROW, MIDDLESEX.

[*Received, April* 16*th*, 1940.]