34. *Preparation of Simple Cyanines.*

By Bernard Beilenson and Frances M. Hamer.

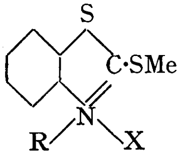
A critical review is given of the known methods for preparing monomethincyanines. Certain μ-alkylthiol derivatives of heterocyclic bases, and their quaternary salts, are described. 2-*Methylthiolquinoline* behaves anomalously on heating with ethyl iodide, in that 2-*ethylthiolquinoline methiodide* is the product. By heating 1-methylthiolbenzoxazole, or the α- and β-naphthoxazole derivatives, with alkyl iodide, *N*-alkyl-μ-thiones are prepared. A thione of this type, but not the keto-compound, can react with an ester to form a salt, which has the power of condensing with certain quaternary, heterocyclic salts having a μ-methyl group, to give a cyanine. The preparations of representatives of various types of monomethincyanines, by use of certain sulphur-containing intermediates, are described.

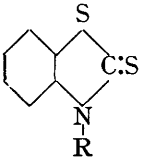
THERE are four important methods of preparing cyanines of the simplest type, in which the two heterocyclic nuclei are linked by a single methin group. These methods vary considerably in applicability, so that all known cyanine types are not obtainable by each of them. The first is restricted to the condensation of a limited number of heterocyclic quaternary ammonium salts, containing a reactive methyl group, with unsubstituted quinolinium salts. One mol. of acid and two hydrogen atoms are eliminated, and linking occurs, through the carbon of the reactive methyl group, with the 4-position of the quinoline nucleus. The preparations of the following comparatively few types of 4′-cyanines by this method are described in the scientific literature : 4 : 4′-cyanine (Hoogewerff and van Dorp, *Rec. Trav. chim.*, 1883, **2**, 28, 41, 317; 1884, **3**, 337), 2 : 4′-cyanine (*idem, ibid.*, 1883, **2**, 317; 1884, **3**, 337; Spalteholz, *Ber.*, 1883, **16**, 1847), thia-4′-cyanine (Braunholtz and Mills, J., 1922, **121**, 2004), thiazolo-4′-cyanine (Mills and Smith, J., 1922, **121**, 2724), and thiazolino-4′-cyanine (Brooker, *J. Amer. Chem. Soc.*, 1936, **58**, 662).

The second method consists in condensing certain heterocyclic quaternary ammonium salts, containing a reactive methyl group, with a 2-iodoquinolinium salt. Two mols. of acid are eliminated and linking occurs to the 2-position of the quinoline nucleus (Fischer and Scheibe, *J. pr. Chem.*, 1920, **100**, 86; Hamer, J., 1928, 206). Moreover, quaternary salts of 2-iodopyridine, 2-iodo-β-naphthaquinoline, and 1-iodo*iso*quinoline can be used in the same way, so that other types result (Hamer and Kelly, J., 1931, 777; Fisher and Hamer, J., 1934, 1905). For this 2′-cyanine condensation, triethylamine proved a better condensing agent than caustic alkali (Brooker and Keyes, *J. Amer. Chem. Soc.*, 1935, **57**, 2488) and, by its use, other difficultly accessible 2′-cyanines were obtained (Brooker, Keyes, and White, *ibid.*, p. 2492). More kinds of heterocyclic ammonium salts, containing a reactive methyl group, have been successfully subjected to the second type of condensation than to the first. Both iodine atoms in 2 : 4-di-iodoquinoline ethiodide undergo this second type of condensation (Brooker and Smith, *ibid.*, 1937, **59**, 67), but it is unknown with heterocyclic salts which contain more than one hetero-atom in the ring (*e.g.*, 1-iodobenzthiazole alkiodide).

In the third method, which has not yet appeared except in the patent literature, the part played by the reactive iodine atom in the second method is taken by the alkylthiol group; this condensation was applied to the production of a number of types of cyanines (Kendall, B.P. 424,559/1933; B.P. 425,609/1933). Alkiodides of 2-arylthiolpyridines or of 2-arylthiolquinolines have been prepared from the 2-iodo-compounds, for use in cyanine condensations (Kodak Ltd., Brooker, and Keyes, B.P. 454,687/1934). Instead of using a quaternary heterocyclic ammonium salt containing an alkylthiol group, *e.g.* (I), use of an alkyl salt of the corresponding μ-thio-*N*-alkyldihydro-base, *e.g.* (II), has been recorded (I.G. Farbenind. A.-G., B.P. 423,792/1932; Kendall, B.P. 438,420/1934).

(I.)





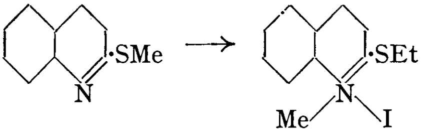
(II.)

For a recent study of the absorption spectra of symmetrical and unsymmetrical cyanine dyes in methyl-alcoholic solution (Fisher and Hamer, *Proc. Roy. Soc.*, 1936, *A*, **154**, 703; Beilenson, Fisher, and Hamer, *ibid.*, 1937, *A*, **163**, 138), the preparation of 45 simple cyanines, in a state of purity, was accomplished by one or other of these three methods. It seems of value to place on record a few examples of the successful application of the third method, together with certain anomalies which were observed.

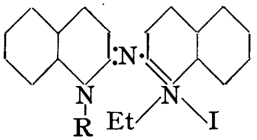
The fourth method of preparing simple cyanines, which was applied to the remaining

7 simple cyanines in the two papers, has already been discussed (Fisher and Hamer, J., 1930, 2502; 1934, 962; Kuhn, Winterstein, and Balser, *Ber.*, 1930, **63**, 176).

The published information about the intermediates for the third method is scanty. Although the preparation of 2-thiolquinoline (Roos, *Ber.*, 1888, **21**, 619; Fischer, *Ber.*, 1899, **32**, 1297) and its conversion into 2-*ethylthiolquinoline* have been described (Roos, *loc. cit.*), 2-*methylthiolquinoline* does not appear in the scientific literature. Its *methiodide* and *metho*-p-*toluenesulphonate* are obtainable by the normal methods, but an attempt to prepare the ethiodide by heating the base (III) with ethyl iodide led to 2-*ethylthiolquinoline methiodide* (IV). This unexpected result, which was, of course, not detectable on the analysis of the quaternary salt, was first suspected owing to the anomalous analyses obtained for the *azacyanine* (V), produced by condensing the salt with 2-aminoquinoline ethiodide. On the assumption that R in (V) was methyl, instead of ethyl, the analysis was satisfactory. The correctness of this assumption was shown when the identical azacyanine was prepared from 2-methylthiolquinoline methiodide and 2-aminoquinoline ethiodide. Further, 2-ethylthiolquinoline methiodide was prepared from 2-ethylthiolquinoline and methyl iodide and was found to be identical with the salt prepared by the anomalous method. 2-*Ethylthiolquinoline ethiodide* and *etho*-p-*toluenesulphonate* were also made. The dimethylazacyanine, which was the subject of the original synthesis (Hamer, J., 1924, **125**, 1348; cf. Fisher and Hamer, J., 1937, 307), has now been prepared through 2-methylthiolquinoline methiodide (cf. Kendall, B.P. 447,038/1934). In preparing cyanines by use of alkylthiol compounds, the condensing agent used throughout the present work was potassium carbonate (cf. Kodak Ltd. and Beilenson, B.P. 435,542/1933).



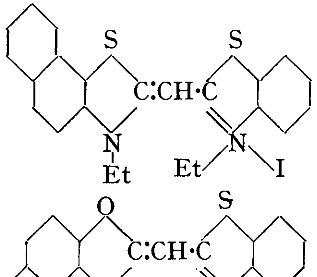
(III.) (IV.)

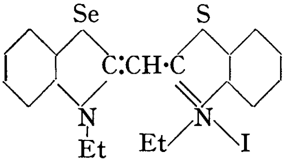


(V.)

The conversion of 1-thiolbenzthiazole into 1-methylthiolbenzthiazole, by the action of methyl iodide, is known (Hofmann, *Ber.*, 1887, **20**, 1788); we carried out the conversion with methyl sulphate in the presence of alkali, and subsequently prepared 1-*methylthiolbenzthiazole methiodide*, *ethiodide*, and *metho*-p-*toluenesulphonate*. The anomalous behaviour observed with 2-methylthiolquinoline and ethyl iodide has no parallel in the case of 1-methylthiolbenzthiazole and ethyl iodide: dyes (VI), (VII) and (VIII; R = Et, X = I), prepared from the latter reaction product, gave satisfactory analyses. 1-Ethylthiolbenzthiazole is known, having been prepared by the action of ethyl iodide, followed by alkali, on the thiol compound and also by the action of potassium cyanide and ethyl alcohol on di-1-benzthiazolyl disulphide (Levi, *Gazzetta*, 1931, **61**, 383). Here it was prepared from 1-thiolbenzthiazole, ethyl sulphate, and alkali, and was converted into 1-*ethylthiolbenzthiazole ethiodide*. 1-Methylthiolbenzthiazole ethiodide has been used in preparing dyes such as the unsymmetrical *thiacyanine* (VI), a *selenathiacyanine* (VII), and an *oxathiacyanine* (VIII; R = Et, X = I). Although it is usual, in preparing simple

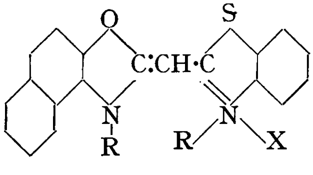
(VI.)

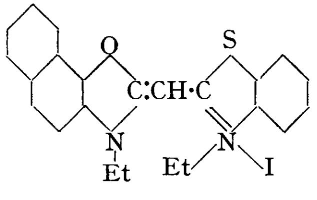




(VII.)

(VIII.)



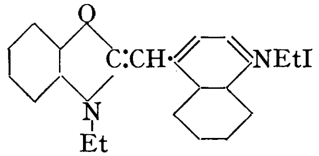


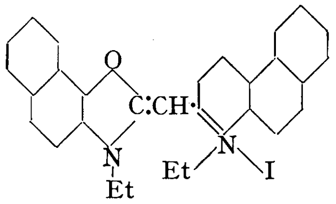
(IX.)

cyanine dyes, to condense together suitable pure quaternary salts, a recorded alternative method (Kendall, B.P. 424,559/1933) is to bring about reaction between two appropriate bases and alkyl *p*-toluenesulphonate, which method has been adopted for (IX), as also for (X) and (XI). The absorption maxima of methyl-alcoholic solutions of these six dyes have already been recorded (Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *A*, **163**, 138).

1-Thiolbenzoxazole (Dünner, *Ber.*, 1876, **9**, 465) was converted into 1-methylthiolbenzoxazole (cf. Desai, Hunter, and Khalidi, J., 1934, 1186). 2-Thiol-β-naphthoxazole was prepared by a modification of Jacobson's method (*Ber.*, 1888, **21**, 414) and converted into *2-methylthiol-β-naphthoxazole.* 1-Thiol-α-naphthoxazole was prepared in the same kind of way (cf. Jacobson and Schenke, *Ber.*, 1889, **22**, 3232) and converted into *1-methylthiol-α-naphthoxazole.* By reaction of such methylthiol compounds with ethyl *p*-toluenesulphonate and a base, containing a reactive methyl group, there were prepared difficultly accessible simple cyanines, *e.g.*, the *oxa-4'-cyanine* (X) and the *oxa-2'-cyanine* (XI).

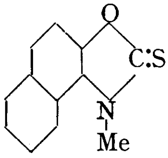
(X.)



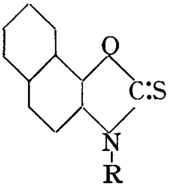


(XI.)

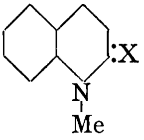
Although there was no difficulty in preparing quaternary salts of alkylthiol derivatives of quinoline and of benzthiazole bases, an anomaly was observed in the benzoxazole series : when 2-methylthiol-β-naphthoxazole was heated in a sealed tube with methyl iodide, with the object of preparing its methiodide, the product obtained, after recrystallisation from alcohol, was found to be free from iodine, and was finally identified as *2-thio-1-methyl-1 : 2-dihydro-β-naphthoxazole* (XII). So also, by heating 1-methylthiol-α-naphthoxazole with



(XII.)



(XIII.)



(XIV.)

methyl iodide or ethyl iodide, we obtained *1-thio-2-methyl-1 : 2-dihydro-α-naphthoxazole* (XIII ; R = Me) and *1-thio-2-ethyl-1 : 2-dihydro-α-naphthoxazole* (XIII ; R = Et), respectively; from 1-methylthiolbenzoxazole and methyl iodide there was obtained 1-thio-2-methyl-1 : 2-dihydrobenzoxazole, which had previously been prepared from *o*-methylaminophenol and thiocarbonyl chloride in ether (Seidel, *J. pr. Chem.*, 1890, **42**, 445). This conversion of alkylthiol derivatives of the benzoxazole series into thiones, simply by heating the base with alkyl iodide, is interesting in contrast with one recently patented (Kendall, B.P. 475,647/1936), in which a quaternary salt of a heterocyclic base is subjected to boiling with pyridine.

The thione (XII) was caused to react with methyl *p*-toluenesulphonate and 1-methylbenzthiazole (cf. Kendall, B.P. 438,420/1934) to give an *oxathiacyanine* (VIII ; R = Me, X = $C_6H_4Me\cdot SO_3$). As indicated in the patents (I.G. Farbenind. A.-G., B.P. 423,792/1932 ; Kendall, *loc. cit.*), it is not the thione, but its alkyl salt, that has the power of reacting with quaternary salts containing a reactive methyl group. This point was definitely put to the test here in the preparation of a thia-2'-cyanine. A negative result was obtained when an attempt was made to condense 2-thio-1-methyl-1 : 2-dihydroquinoline (XIV ; X = S) (Gutbier, *Ber.*, 1900, **33**, 3358) with 1-methylbenzthiazole methiodide in the presence of alkali, whereas the yield of thia-2'-cyanine was 65% when the thione was caused to react with methyl *p*-toluenesulphonate before attempting the dye condensation.

Following upon Decker's discovery of the alkylquinolinium ψ-bases (*Ber.*, 1891, **24**, 690), it was at that time supposed that *N*-alkylquinolones (*e.g.*, XIV; X = O) are intermediates in cyanine dye formation. It is now known, however, that this is not the case: they do not react with quaternary salts having a reactive methyl group. Since even the thio-compound (XIV; X = S) does not react except in the form of its alkyl salt, an attempt has now been made to bring about reaction with the quinolone (XIV; X = O) under those same conditions, but the result was again negative. Thus, although the thia-2′-cyanine was obtained in 32% yield by fusion of 2-thio-1-methyl-1 : 2-dihydroquinoline, 1-methylbenzthiazole, and methyl *p*-toluenesulphonate, yet fusion of 2-keto-1-methyl-1 : 2-dihydroquinoline, 1-methylbenzthiazole, and methyl *p*-toluenesulphonate gave no dye; this is probably because 2-keto-1-methyl-1 : 2-dihydroquinoline is unable to form a salt by addition of alkyl *p*-toluenesulphonate, whereas such a *salt* of the thio-compound was actually isolated.

EXPERIMENTAL.

2-*Methylthiolquinoline* (III).—2-Thiolquinoline (16 g.; 1 mol.) was dissolved in 5% sodium hydroxide solution (80 c.c.; 1 mol.), and methyl sulphate (19 c.c.; 2 mols.) added in small portions with vigorous shaking. To keep the reaction mixture alkaline, 10% sodium hydroxide solution was added from time to time. After an hour, the oil solidified; it was filtered off, washed with water, dried by heating in a vacuum, and distilled, being obtained in 75% yield (13·2 g.), b. p. 182—183°/22 mm. Recrystallised from spirit (1 c.c. per g.), it was obtained in white needles, m. p. 55°, in 56% yield. After drying in a vacuum desiccator, it was analysed by the method of Carius, which method of analysis was employed throughout this work (Found: S, 18·2. $C_{10}H_9NS$ requires S, 18·3%).

2-*Ethylthiolquinoline.*—2-Thiolquinoline was dissolved in 10% sodium hydroxide solution and shaken with ethyl sulphate, which was added gradually, the mixture being finally heated on the water-bath for 1½ hours. The product was extracted with ether, and on vacuum distillation was obtained in 78% yield as a very pale yellow oil, b. p. 177—178°/26 mm. (Found: S, 16·7. $C_{11}H_{11}NS$ requires S, 16·9%).

2-*Methylthiolquinoline Methiodide.*—2-Methylthiolquinoline (15 g.; 1 mol.) and methyl iodide (6·4 c.c.; 1·2 mols.) were heated together in a sealed tube at 100° for 24 hours. The crude product (26 g.; 96% yield) began to darken, so was at once recrystallised from absolute alcohol (100 c.c.); the yield was then 87% (23·7 g.). It was dried to constant weight in a vacuum at 60—80°, which method of drying was used for the salts and dyes throughout this work, except where otherwise stated (Found: I, 40·2. $C_{11}H_{12}NIS$ requires I, 40·0%). M. p. 193°, with softening from 187°.

2-*Methylthiolquinoline Metho*-p-*toluenesulphonate.*—2-Methylthiolquinoline (3·5 g.; 1 mol.) and methyl *p*-toluenesulphonate (3·7 g.; 1 mol.) were fused together at 145—150° for 3 hours. After the product had been ground to a powder with benzene and dried in a vacuum desiccator, the yield was 91% (6·6 g.). After recrystallisation from absolute alcohol and ether, the yield dropped to 37%, and after a second recrystallisation from absolute alcohol (3 c.c. per g.) to 25% (Found: S, 17·8. $C_{18}H_{19}O_3NS_2$ requires S, 17·7%). M. p. 160°, with softening from 155°.

2-*Ethylthiolquinoline Methiodide* (IV).—2-Methylthiolquinoline (9·6 g.; 1 mol.) and ethyl iodide (5·2 c.c.; 1·2 mols.) were heated together in a sealed tube at 100° for 24 hours, with the object of preparing 2-methylthiolquinoline ethiodide. The oily product was washed with absolute ether and recrystallised from absolute alcohol (80 c.c.). The yield of bright yellow crystals was 52% (9·4 g.); they rapidly darkened to an olive-yellow, but this was prevented by recrystallisation in the presence of a small amount of sulphur dioxide (cf. Browning, Cohen, Ellingworth, and Gulbransen, *Proc. Roy. Soc.*, 1931, *B*, **108**, 119) (Found: I, 38·5. $C_{12}H_{12}NIS$ requires I, 38·3%). M. p. 185° (decomp.). From the product obtained by its condensation with 2-aminoquinoline ethiodide, the salt was concluded to be 2-*ethylthiolquinoline methiodide*: this was confirmed by the following alternative method of preparation. 2-Ethylthiolquinoline (3·8 g.; 1 mol.) and methyl iodide (1·5 c.c.; 1·2 mols.) were heated together in a sealed tube at 100° for 2 days. The crude solid was obtained in theoretical yield after washing with ether and in 71% yield after recrystallisation from methyl alcohol (3 c.c. per g.) containing a little sulphur dioxide. M. p., and mixed m. p. with the product above, 185° (decomp.) (Found: I, 38·4%).

2-*Ethylthiolquinoline Ethiodide.*—2-Ethylthiolquinoline (4·7 g.; 1 mol.) and ethyl iodide (2·4 c.c.; 1·2 mols.) were heated together in a sealed tube at 100° for 2 days. After washing with ether, the yield was 85%. The *salt* was recrystallised from methyl alcohol (10 c.c.), but was greenish-yellow with a high iodine content (73% yield). After further crystallisation from methyl alcohol (12 c.c.) containing sulphur dioxide, with addition of ether (12 c.c.), it was obtained in 49% yield as a canary-yellow solid (Found : I, 36·75. $C_{13}H_{16}NIS$ requires I, 36·8%). M. p. 165° (decomp.).

2-*Ethylthiolquinoline Etho*-p-*toluenesulphonate*.—2-Ethylthiolquinoline (6·57 g.; 1 mol.) and ethyl *p*-toluenesulphonate (6·9 g.; 1 mol.) were heated together at 150—155° for 9 hours. On treatment with acetone (26 c.c.), transformation to a white solid took place, and this was filtered off and washed with acetone, being obtained in 68% yield (9·2 g.) (Found : S, 16·65. $C_{20}H_{23}O_3NS_2$ requires S, 16·5%). M. p. 116°.

1-*Methyl*-1′-*ethyl*-2 : 2′-*azacyanine Iodide* [(1-*Methyl*-2-*quinoline*)(1-*ethyl*-2-*quinoline*)*azamethincyanine Iodide*] * (V, R = Me).—2-Ethylthiolquinoline methiodide (3·3 g.; 1 mol.), obtained by the anomalous method described above, 2-aminoquinoline ethiodide (3 g.; 1 mol.), anhydrous potassium carbonate (180-mesh; 2·7 g.; 2 mols.), and absolute alcohol (10 c.c.) were boiled together under reflux for 3 hours, and the cooled reaction mixture was diluted with ether (30 c.c.). The liquid was decanted, and the sticky solid ground with water; it then became granular and was obtained in 49% yield (2·16 g.). After recrystallisation from methyl alcohol (20 c.c.), the yield was 31% (1·38 g.) [Found : I, 28·6. $C_{21}H_{20}N_3I$ requires I, 28·8%. But $C_{22}H_{22}N_3I$ (*i.e.*, V, R = Et) requires I, 27·9%]. By heating together appropriate amounts of 2-methylthiolquinoline methiodide, 2-aminoquinoline ethiodide, anhydrous potassium carbonate, and alcohol for an hour, filtering off the solid which separated on cooling, and washing the product with water, the yield was 42% and, after recrystallisation from methyl alcohol, 29% (Found : I, 28·7%). Both samples of *azacyanine*, separately or mixed, had m. p. about 235° (decomp.). The photographic sensitising action of the two also showed their identity.

1 : 1′-*Dimethyl*-2 : 2′-*azacyanine Iodide* [*Bis*-(1-*methyl*-2-*quinoline*)*azamethincyanine Iodide*].—2-Methylthiolquinoline methiodide, 2-aminoquinoline methiodide, anhydrous potassium carbonate, and absolute alcohol were boiled together for an hour. The yield of dye was 55%. After recrystallisation from methyl alcohol (17 c.c. per g.), the yield of bright yellow crystals was 43% (Found : I, 29·9. Calc. for $C_{20}H_{18}N_3I$: I, 29·7%). M. p. 273—275° (decomp.), with darkening from 267°. When heated simultaneously, the sample previously synthesised (Hamer, J., 1924, **125**, 1348) had the same m. p., and so had their mixture.

1-*Methylthiolbenzthiazole*.—1-Thiolbenzthiazole was shaken with 10% sodium hydroxide solution and methyl sulphate. After some hours, the resultant oil solidified on cooling with ice and was filtered off and washed with water. It was dried by heating in a vacuum and then distilled in a vacuum, being obtained in 87% yield (Found : S, 35·5. Calc. for $C_8H_7NS_2$: S, 35·4%). B. p. 165—166°/15 mm., m. p. 44—45°. Hofmann gives m. p. 52° (*Ber.*, 1887, **20**, 1788) and Levi gives m. p. 46° (*Gazzetta*, 1931, **61**, 383).

1-*Ethylthiolbenzthiazole*.—1-Thiolbenzthiazole was dissolved in 10% sodium hydroxide solution and shaken vigorously with ethyl sulphate for 40 minutes, then heated for 30 minutes on the water-bath. The oil was extracted with ether and obtained in 59% yield as a pale yellow oil, b. p. 174—176°/22 mm. M. p. 25—26°. Levi (*loc. cit.*) gives m. p. 26° (Found : S, 32·8. Calc. for $C_9H_9NS_2$: S, 32·85%).

1-*Methylthiolbenzthiazole Methiodide* (I; R = Me, X = I).—The base and methyl iodide were heated together in a sealed tube at 100° for 2 days. After ether extraction, the undissolved residue was recrystallised from methyl alcohol (10 c.c. per g.) containing a little sulphur dioxide. A 75% yield of bright yellow crystals was obtained (Found : I, 39·4. $C_9H_{10}NIS_2$ requires I, 39·3%). M. p. 146° (decomp.).

1-*Methylthiolbenzthiazole Ethiodide* (I; R = Et, X = I).—By heating the base and ethyl iodide under reflux for a day, only a 4% yield was obtained. 1-Methylthiolbenzthiazole (17·8 g.; 1 mol.) and ethyl iodide (1·2 mols.) were heated in a sealed tube for 2 days at 100°. The sticky mass crystallised on standing and was washed with ether (33 g. obtained). It was recrystallised from methyl alcohol (25 c.c.). Some undissolved oily residue gave a pale yellow solid (8·32 g.) on washing with acetone, and the recrystallised *salt* also was washed with acetone (11·60 g. obtained). Thus the total yield was 61% (19·92 g.) (Found after drying in a vacuum desiccator : I, 38·0. $C_{10}H_{12}NIS_2$ requires I, 37·65%). M. p. 135—137° (decomp.).

1-*Methylthiolbenzthiazole Metho*-p-*toluenesulphonate*.—1-Methylthiolbenzthiazole and methyl *p*-toluenesulphonate were heated together at 145° for 1½ hours. On treatment with acetone, crystallisation occurred and an almost white solid was obtained in 86% yield (Found : S, 26·2. $C_{16}H_{17}O_3NS_3$ requires S, 26·2%). M. p. 167—168° with previous softening.

1-*Ethylthiolbenzthiazole Ethiodide*.—After 1-ethylthiolbenzthiazole and ethyl iodide had been heated in a sealed tube at 100° for 2 days, and the resultant oil washed with cold acetone, a pale

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* The names of cyanines given in brackets are in accordance with the modern nomenclature for this class of compound.—Editor.

yellow powder was obtained in 48% yield. It was dissolved in hot methyl alcohol (1 c.c. per g.) and precipitated from the cooled solution with ether (1 c.c. per g.). The yield was 38%, and another crystallisation from absolute alcohol (1 c.c. per g.) gave a 33% yield of white solid (Found after drying in a vacuum desiccator: I, 35·9. $C_{11}H_{14}NIS_2$ requires I, 36·1%). M. p. 95—96°.

2 : 2′-*Diethyl*-5 : 6-*benzthiacyanine Iodide* [(2-*Ethyl*-1-*benzthiazole*)(2-*ethyl*-5 : 6-*benz*-1-*benzthiazole*)*methincyanine Iodide*] (VI).—1-Methylthiolbenzthiazole ethiodide (0·84 g.; 1 mol.), 1-methyl-α-naphthathiazole ethiodide (0·90 g.; 1 mol.), anhydrous potassium carbonate (180-mesh; 0·42 g.; 1·2 mols.), and absolute alcohol (15 c.c.) were boiled and stirred together for 20 minutes. The dirty greenish-yellow product was suspended in acetone and treated with sulphur dioxide; thereafter the solid was twice boiled out with methyl alcohol (20 c.c., 10 c.c.), and then with spirit (500 c.c.). The undissolved, canary-yellow solid amounted to a 75% yield (0·98 g.) (Found: I, 24·8. $C_{23}H_{21}N_2IS_2$ requires I, 24·6%). M. p. 299° (decomp.). The absorptions of methyl-alcoholic solutions of this and the following three compounds have already been recorded (Beilenson, Fisher, and Hamer, *Proc. Roy. Soc.*, 1937, *A*, **163**, 138).

2 : 2′-*Diethylselenathiacyanine Iodide* [(2-*Ethyl*-1-*benzthiazole*)(2-*ethyl*-1-*benzselenazole*)*methincyanine Iodide*] (VII).—1-Methylthiolbenzthiazole ethiodide and 1-methylbenzselenazole ethiodide were brought into reaction as above. The product, washed with water (yield, 88%), crystallised from methyl alcohol (145 c.c. per g.) in bright yellow needles in 65% yield (Found: I, 24·8. $C_{19}H_{19}N_2ISSe$ requires I, 24·7%). M. p. 284° (decomp.).

2 : 2′-*Diethyl*-3 : 4-*benzoxathiacyanine Iodide* [(2-*Ethyl*-3 : 4-*benz*-1-*benzoxazole*)(2-*ethyl*-1-*benzthiazole*)*methincyanine Iodide*] (VIII; R = Et, X = I).—1-Methylthiolbenzthiazole ethiodide (2 g.) was caused to react with 2-methyl-β-naphthoxazole ethiodide as above. The product was filtered off when cold and washed with water, and then thrice with hot acetone (20 c.c. × 3), being obtained in 17% yield (Found: I, 25·6. $C_{23}H_{21}ON_2IS_2$ requires I, 25·4%). M. p. 288° (decomp.).

2 : 2′-*Diethyl*-5 : 6-*benzoxathiacyanine Iodide* [(2-*Ethyl*-5 : 6-*benz*-1-*benzoxazole*)(2-*ethyl*-1-*benzthiazole*)*methincyanine Iodide*] (IX).—1-Methylthiolbenzthiazole (1·81 g.; 1 mol.), 1-methyl-α-naphthoxazole (1·83 g.; 1 mol.), and ethyl *p*-toluenesulphonate (4·04 g.; 2 mols.) were fused together at 160° for 3½ hours. The melt was dissolved in absolute alcohol (20 c.c.), treated with anhydrous potassium carbonate (180-mesh; 1·65 g.; 1·2 mols.), and heated on the steam-bath for 15 minutes. A solution of potassium iodide (4 g.) in water (7 c.c.) was added. After washing with water and spirit, a 41% yield (2·07 g.) of a bright yellow *compound* was obtained. It was recrystallised from pyridine (400 c.c.), a second crop being obtained by concentration (to 100 c.c.) and precipitation with ether (50 c.c.), making the total yield 28% (1·38 g.) (Found: I, 25·5. $C_{23}H_{21}ON_2IS$ requires I, 25·4%). M. p. 278° (decomp.).

1-*Methylthiolbenzoxazole*.—1-Thiolbenzoxazole (1 mol.) was dissolved in 10% sodium hydroxide solution (nearly 2 mols.) and gradually treated with methyl sulphate (2 mols.). After an hour, the *base* was extracted in ether, dried with potassium carbonate, and vacuum-distilled, being obtained as a colourless oil, b. p. 139—140°/21 mm., in 80% yield (Found: S, 19·2. C_8H_7ONS requires S, 19·4%).

2-*Thiol*-β-*naphthoxazole*.—1-Amino-2-naphthol hydrochloride (10 g.; 1 mol.) was heated with spirit (50 c.c.) and treated with 10% aqueous potassium hydroxide (29 c.c.; 1 mol.). Carbon disulphide (30 c.c.) was added, and the mixture refluxed on the steam-bath for 2 days. After distillation of the excess of carbon disulphide and spirit, the residual solid was filtered off, washed with water, and recrystallised twice from spirit. The yield was 65% and the m. p. 264°, with softening from 254°; Jacobson (*Ber.*, 1888, **21**, 417) gives m. p. 248—249° (Found: S, 16·1. Calc. for $C_{11}H_7ONS$: S, 15·9%).

1-*Thiol*-α-*naphthoxazole*.—2-Amino-1-naphthol hydrochloride was treated with spirit, aqueous sodium hydroxide, and carbon disulphide. The washed solid, obtained as in the previous preparation, was at first light in colour but rapidly darkened. Its solution in dilute aqueous sodium hydroxide was heated with charcoal, and the product recovered, in 61% yield, by precipitation with acetic acid. A sample recrystallised from methyl alcohol (12 c.c. per g.), with addition of charcoal, still darkened on standing (Found: S, 15·8. Calc. for $C_{11}H_7ONS$: S, 15·9%). M. p. 260—261° (decomp.). Jacobson and Schenke (*Ber.*, 1889, **22**, 3232) give m. p. 259—260°.

2-*Methylthiol*-β-*naphthoxazole*.—2-Thiol-β-naphthoxazole was dissolved in sodium hydroxide solution and gradually treated with methyl sulphate, with shaking; the resultant oil solidified (100% yield). After two vacuum distillations it was obtained as an amber liquid in 45% yield. B. p. 214°/2 mm., 225°/18 mm., m. p. 73° (Found: S, 14·8. $C_{12}H_9ONS$ requires S, 14·9%).

1-*Methylthiol*-α-*naphthoxazole*.—This was obtained by reaction of methyl sulphate and alkali on 1-thiol-α-naphthoxazole, and was recrystallised from spirit and water (charcoal). The yield was 63% and, after vacuum distillation, 50%. B. p. 222—230°/9 mm., m. p. 64° (Found: S, 14·7. $C_{12}H_9ONS$ requires S, 14·9%).

2 : 1′-*Diethyloxa*-4′-*cyanine Iodide* [(1-*Ethyl*-4-*quinoline*)(2-*ethyl*-1-*benzoxazole*)*methincyanine Iodide*] (X).—1-Methylthiolbenzoxazole (1·65 g.; 1 mol.), lepidine (1·43 g.; 1 mol.), and ethyl *p*-toluenesulphonate (4·04 g.; 2 mols.) were fused together at 150—160° for 3·5 hours. The yellow mass was dissolved in hot spirit (15 c.c.) and treated with potassium iodide (4 g.) dissolved in water (7 c.c.). The dye was filtered off and washed with water, and the treatment with potassium iodide repeated; the yield was then 26%. After recrystallisation from methyl alcohol (10 c.c. per g.), the yield was 11% (Found: I, 28·5. $C_{21}H_{21}ON_2I$ requires I, 28·6%). M. p. 233° (decomp.) with shrinking from 225°. The absorptions of methyl-alcoholic solutions of this and the following *compound* have already been recorded (Beilenson, Fisher, and Hamer, *loc. cit.*).

2 : 1′-*Diethyl*-5 : 6 : 5′ : 6′-*dibenzoxa*-2′-*cyanine Iodide* [(1-*Ethyl*-5 : 6-*benz*-2-*quinoline*)(2-*ethyl*-5 : 6-*benz*-1-*benzoxazole*)*methincyanine Iodide*] (XI).—1-Methylthiol-α-naphthoxazole (2·15 g.; 1 mol.), β-naphthaquinaldine (1·93 g.; 1 mol.), and ethyl *p*-toluenesulphonate (4·04 g.; 2 mols.) were heated together at 150—155° for 3 hours. The orange mass was dissolved in absolute alcohol (40 c.c.) and boiled with anhydrous potassium carbonate (180-mesh; 1·35 g.; 1 mol.) for 15 minutes. A solution of potassium iodide (5 g.) in water (5 c.c.) was added. The dye *iodide* was filtered off and washed with alcohol and then with water (29% yield). After recrystallisation from methyl alcohol (400 c.c.), the yield was 15% (Found: I, 23·2. $C_{29}H_{25}ON_2I$ requires I, 23·3%). M. p. 288° (decomp.).

2-*Thio*-1-*methyl*-1 : 2-*dihydro*-β-*naphthoxazole* (XII).—Freshly distilled 2-methylthiol-β-naphthoxazole (6·45 g.; 1 mol.) and methyl iodide (2·2 c.c.; 1·2 mols.) were heated together in a sealed tube at 100° for 2 days, with the object of preparing the methiodide of the base. The product, washed with ether (6·45 g. obtained) and recrystallised from spirit (800 c.c.), formed felted needles, m. p. 185—187°, which were free from iodine. From the analytical results, it was identified as 2-*thio*-1-*methyl*-1 : 2-*dihydro*-β-*naphthoxazole*, the yield of pure product being thus 78% (Found: C, 67·0; H, 4·8; N, 6·8; S, 14·5. $C_{12}H_9ONS$ requires C, 67·0; H, 4·8; N, 6·5; S, 14·9%).

1-*Thio*-2-*methyl*-1 : 2-*dihydro*-α-*naphthoxazole* (XIII; R = Me), obtained by heating 1-methylthiol-α-naphthoxazole in a sealed tube with methyl iodide, was washed with ether (100% yield). After being boiled out with a little methyl alcohol (solubility <1 g. per 500 c.c.), it was free from iodine, and after recrystallisation from pyridine (6 c.c. per g.), it was pure white (yield, 63%) (Found: S, 15·1. $C_{12}H_9ONS$ requires S, 14·9%). M. p. 226°.

1-*Thio*-2-*ethyl*-1 : 2-*dihydro*-α-*naphthoxazole* (XIII; R = Et), obtained by heating 1-methylthiol-α-naphthoxazole with ethyl iodide in a sealed tube, was washed with ether. After two recrystallisations from spirit (175 c.c. per g.), the yield was 32% (Found: S, 14·0. $C_{13}H_{11}ONS$ requires S, 14·0%). M. p. 215°.

1-*Thio*-2-*methyl*-1 : 2-*dihydrobenzoxazole*.—1-Methylthiolbenzoxazole and methyl iodide were heated together in a sealed tube and the ether-washed product was recrystallised from methyl alcohol (5 c.c. per g.). The yield was 42% and the solid was free from iodine. After a second recrystallisation from methyl alcohol (8 c.c. per g.) the yield was reduced to 28% (Found: S, 19·4. Calc. for C_8H_7ONS: S, 19·4%). M. p. 133°; Seidel (*J. pr. Chem.*, 1890, **42**, 445) gives m. p. 128°.

2 : 2′-*Dimethyl*-3 : 4-*benzoxathiacyanine* p-*Toluenesulphonate* [(2-*Methyl*-3 : 4-*benz*-1-*benzoxazole*)(2-*methyl*-1-*benzthiazole*)*methincyanine* p-*Toluenesulphonate*] (VIII; R = Me, X = $C_6H_4Me\cdot SO_3$).—2-Thio-1-methyl-1 : 2-dihydro-β-naphthoxazole (1·08 g.; 1 mol.), 1-methylbenzthiazole (0·75 g.; 1 mol.), and methyl *p*-toluenesulphonate (1·86 g.; 2 mols.) were heated together in an oil-bath at 150° for 1 hour. On treatment of the pasty mass with spirit (10 c.c.), a yellow dye separated; this was filtered off and washed with water, being obtained in 71% yield (1·83 g.). After recrystallisation from methyl alcohol (5 c.c.), the yield was 58% (Found: S, 12·2. $C_{28}H_{24}O_4N_2S_2$ requires S, 12·4%). M. p. 262° (decomp. from about 190°).

2 : 1′-*Dimethylthia*-2′-*cyanine Iodide* [(1-*Methyl*-2-*quinoline*)(2-*methyl*-1-*benzthiazole*)*methincyanine Iodide*].—2-Thio-1-methyl-1 : 2-dihydroquinoline (0·44 g.; 1 mol.) was heated with methyl *p*-toluenesulphonate (0·46 g.; 1 mol.) in an oil-bath at 150° for 1 hour. [The resultant *salt* solidified on treatment with acetone (3 c.c. per g.), being obtained in 73% yield. After solution in methyl alcohol (2½ c.c. per g.) and precipitation with ethyl acetate, the yield of white crystalline salt was 62%, m. p. 160—161° (Found: S, 17·85. $C_{18}H_{19}O_3NS_2$ requires S, 17·75%).] The crude salt was dissolved in absolute alcohol (15 c.c.) and treated with 1-methylbenzthiazole methiodide (0·73 g.; 1 mol.) and anhydrous potassium carbonate (180-mesh; 0·34 g.; 1 mol.).

The mixture was boiled and stirred for 3 minutes. After filtration and washing, the yield of crude dye was 84% (0·91 g.). Recrystallisation from methyl alcohol (140 c.c.) gave a 65% yield (Found : I, 29·45. Calc. for $C_{19}H_{17}N_2IS$: I, 29·4%). The physical properties were the same as those of the original specimen (Hamer, J., 1928, 206). When an attempt was made to condense 2-thio-1-methyl-1 : 2-dihydroquinoline (0·22 g.; 1 mol.) and 1-methylbenzthiazole methiodide (0·36 g.; 1 mol.), by heating with anhydrous potassium carbonate (180-mesh; 0·17 g.; 1 mol.) in absolute alcohol (8 c.c.), no thia-2′-cyanine was formed.

The dye was also prepared by fusing together 2-thio-1-methyl-1 : 2-dihydroquinoline (1·75 g.; 1 mol.), 1-methylbenzthiazole (1·3 c.c.; 1 mol.), and methyl *p*-toluenesulphonate (3·72 g.; 2 mols.) at 150° for 2 hours, without a condensing agent. The pasty reaction mixture was dissolved in hot spirit (30 c.c.) and treated with a hot solution of potassium iodide (3 g.) in water (6 c.c.). The yield of washed dye iodide was 36% (1·54 g.) and, after recrystallisation from methyl alcohol (375 c.c.), it was 32%.

An attempt to prepare the same compound by fusion of 2-keto-1-methyl-1 : 2-dihydroquinoline (1·59 g.; 1 mol.), 1-methylbenzthiazole (1·28 c.c.; 1 mol.), and methyl *p*-toluenesulphonate (3·72 g.; 2 mols.) gave a negative result

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