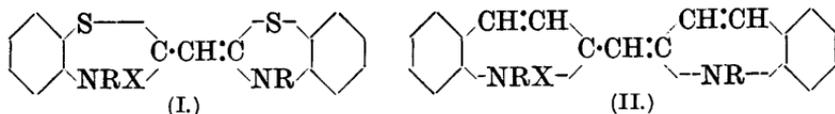


CCXL.—*The Cyanine Dyes. Part VI. Dyes containing a Quinoline and a Benzothiazole Nucleus. The Thioisocyanines.*

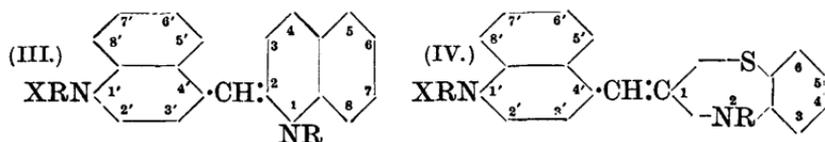
By WALTER THEODORE KARL BRAUNHOLTZ and WILLIAM HOBSON MILLS.

A SERIES of yellow photosensitising dyes, the thiocyanines, has recently been described by one of us (Mills, this vol., p. 455), the constitution of which is represented by the general formula I (in which R indicates an alkyl radicle and X an acid radicle). They

may accordingly be regarded as *pseudocyanines* * (II) in which the two quinoline nuclei are replaced by nuclei of benzothiazole.



In the present communication, a series of dyes is described which are intermediate between the thiocyanines and the *isocyanines* (III), in that they contain one quinoline and one benzothiazole nucleus. They are prepared by the action of sodium



hydroxide in alcoholic solution on a mixture of a quinoline alkylidide and a 1-methylbenzothiazole alkylidide. The method of their preparation thus corresponds exactly with that of the *isocyanines*; their composition is, moreover, analogous, differing from that of the *isocyanines* only in containing an atom of sulphur in place of the group $-C_2H_2-$, and their optical, photosensitising, and general chemical characters also show close relationships to those of the *isocyanines*. We therefore regard their formation as being due to an interaction between the reactive 1-methyl group of the 1-methylbenzothiazole alkylidide and the quinolinium *pseudo*-base, in which the latter plays the same part as in the *isocyanine* condensation. We accordingly consider that in these dyes the 1-methylbenzothiazole residue is linked to the 4-position of the quinoline nucleus and that their constitution is to be represented by formula IV. The acid radicle is regarded as being attached, in view of the virtual tautomerism of the cyanine dyes (this vol., p. 1489), to what is presumably the more basic part of the molecule (compare Mills and Wishart, T., 1920, 117, 579).

On account of their close correspondence with the *isocyanines*, the name *thioisocyanine* is proposed for the dyes of this series.

Although in the *isocyanine* condensation the quinaldinium salt can be replaced by a 1-methylbenzothiazole alkylidide, the converse replacement, namely, that of the quinolinium salt by a quaternary salt of benzothiazole, cannot be made. This appears to be due to the instability of the *pseudo*-bases derived from the benzothiazole alkylidides. It is, however, possible to bring about the

* These dyes, discovered by O. Fischer and Scheibe (*J. pr. Chem.*, 1919, [ii], 100, 86), were named by them *pseudoisocyanines*.

coupling of benzothiazole alkyliodides with quinaldinium or lepidinium salts indirectly by a method which we hope shortly to describe. From lepidine ethiodide and benzothiazole ethiodide, a dye is thus produced which is identical with the thioisocyanine formed from quinoline ethiodide and 1-methylbenzothiazole ethiodide by the action of alcoholic sodium hydroxide. This fact, together with those described in the present communication, establishes the constitution of the thioisocyanines (except for the question of the position of the acid radicle).

It is interesting that Hofmann, who first obtained cyanine dyes from the benzothiazole bases (the carbothiocyanines; this vol., p. 455)—although he regarded them incorrectly as analogues of cyanine itself (*Ber.*, 1887, 20, 2264)—apparently also observed the production of the thioisocyanines in an impure condition. He states (*loc. cit.*, p. 2265) that experiments to "cross" the amyliodides of the quinoline bases with those of the benzothiazole bases (by heating them together in presence of aqueous ammonia) yielded dyes which gave extraordinarily intense deep red solutions in alcohol, but could not be obtained in crystalline form.

The thioisocyanine iodides are bright red compounds which crystallise exceedingly well from alcohol. Their orange-red alcoholic solutions show a pair of overlapping absorption bands of unequal intensity in the green and bluish-green; the crest of the deeper band lies in the neighbourhood of wave-length λ 5000—5100, that of the less intense has a wave-length about λ 120—150 shorter. In general appearance, the absorption spectra of the thioisocyanines are very similar to those of the isocyanines, but the bands in the former lie nearer to the blue end of the spectrum—the difference in wave-length being roughly λ 500. This is in accordance with the fact, to which attention has recently been directed (this vol., p. 459), that benzothiazole derivatives are less deeply coloured than the corresponding quinoline compounds. The thioisocyanines are powerful photosensitisers for the green, giving an extra sensitisation to the gelatino-bromide plate extending to about λ 5800. As with other cyanine dyes, their aqueous-alcoholic solutions are decolorised by the addition of mineral acids.

EXPERIMENTAL.

2 : 1'-Diethylthioisocyanine Iodide.—Quinoline ethiodide (7.2 grams) and 1-methylbenzothiazole ethiodide (7.7 grams) were dissolved in hot alcohol (100 c.c.), and a solution of sodium (0.69 gram) in rectified spirit (40 c.c.) was added. The solution, which immediately developed a deep red colour, was boiled for fifteen minutes and then allowed to cool. Bright red needles

separated (1—1.5 grams), which, after repeated recrystallisation from methyl alcohol, melted and decomposed at 283°. The crystals were dried at 80°/11 mm. for analysis (Found: C = 54.60; H = 4.59; I = 27.75. $C_{21}H_{21}N_2IS$ requires C = 54.78; H = 4.57; I = 27.61 per cent.).

The sensitisation spectrum shows a powerful band in the green extending, for moderate exposures, as far as about λ 5800 with a maximum at λ 5250. There is an additional, very faint, band in the orange with a maximum at λ 6500. The absorption maxima lie at λ 5030 and about λ 4890, respectively.

5-Methyl-2 : 1'-diethylthioisocyanine iodide, obtained by condensing together equimolecular quantities of quinoline ethiodide and 1 : 5-dimethylbenzothiazole ethiodide as above, crystallises from methyl alcohol in bright red needles which melt and decompose at 269—270° (Found: I = 26.59. $C_{22}H_{23}N_2IS$ requires I = 26.80 per cent.).

The sensitisation spectrum shows only the one band in the green extending, for moderate exposures, to about λ 5800 with a crest at λ 5300. The two absorption bands have maxima at λ 5080 and about λ 4920, respectively.

1' : 6'-Dimethyl-2-ethylthioisocyanine Iodide.—This dye, which was prepared from a mixture of *p*-toluquinoline methiodide and 1-methylbenzothiazole ethiodide, is less soluble than the two preceding. It crystallises from methyl alcohol in dark red, prismatic needles, m. p. 306—307° (decomp.) (Found: I = 27.98. $C_{21}H_{21}N_2IS$ requires I = 27.61 per cent.).

The sensitisation spectrum resembles that of the parent substance. The band in the green extends, for moderate exposures, to about λ 5750, the maximum lying at λ 5270. There is a second, weak band which has a maximum at λ 6450 and is somewhat more pronounced than in the parent dye. The two absorption maxima lie at λ 5000 and about λ 4870, respectively.

5 : 1' : 6'-Trimethyl-2-ethylthioisocyanine Iodide.—The dye, obtained from *p*-toluquinoline methiodide and 1 : 5-dimethylbenzothiazole ethiodide, crystallises from methyl alcohol in dark red needles, m. p. 303° (decomp.) (Found: I = 26.81. $C_{22}H_{23}N_2IS$ requires I = 26.80 per cent.).

The extra-sensitisation comprises only the one band in the green, extending to about λ 5800 with its maximum at λ 5310. The crests of the two absorption bands occur at λ 5070 and about λ 4950, respectively.

6'-Ethoxy-2 : 1'-diethylthioisocyanine iodide was prepared from a mixture of *p*-ethoxyquinoline ethiodide and 1-methylbenzothiazole ethiodide. The dye is obtained as bright red needles when its hot

saturated methyl-alcoholic solution is rapidly cooled, and as short, triclinic prisms terminated by domal planes by slow crystallisation from the same solvent. These crystals are deep red with a brassy lustre and appear to contain a molecule of solvent of crystallisation, which is given up when they are heated at $80^{\circ}/12$ mm. (Loss in weight observed = 5.63. $C_{23}H_{25}ON_2IS, CH_3 \cdot OH$ requires $CH_3 \cdot OH = 5.97$ per cent.). Both modifications melt and decompose at 262° (Found : I = 25.45. $C_{23}H_{25}ON_2IS$ requires I = 25.20 per cent.).

The extra-sensitisation extends, for moderate exposures, to about $\lambda 5750$ with a maximum at $\lambda 5300$; there is also an extremely faint and indefinite continuation of the sensitisation into the orange, but no additional maximum is distinguishable. The two absorption bands have maxima at $\lambda 5060$ and about $\lambda 4930$, respectively.

6'-Ethoxy-5-methyl-2 : 1'-diethylthioisocyanine iodide, obtained from *p*-ethoxyquinoline ethiodide and 1 : 5-dimethylbenzothiazole ethiodide, crystallises from methyl alcohol in bright red needles, m. p. 269° (decomp.) (Found : I = 24.80. $C_{24}H_{27}ON_2IS$ requires I = 24.52 per cent.).

The sensitisation spectrum shows only the one band in the green, extending to about $\lambda 5800$, with its maximum at $\lambda 5350$. The two absorption maxima lie at $\lambda 5110$ and about $\lambda 4990$, respectively.

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UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

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