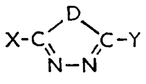
765. *The Structure and Reactivity of Pyridazine Quaternary Salts.**

By G. F. Duffin and J. D. Kendall.

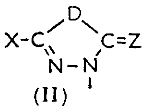
The rate and position of quaternization of a number of substituted pyridazines (III) and dihydropyridazines (VI) and (XI) have been studied and related to the electronic influences of the substituents. The structures of the salts (V) and (XII) so formed have been determined by study of their reactivities, degradation products, and alternative syntheses.

Cyanine dyes have been prepared from those salts containing reactive methyl or methylthio-groups.

In a number of investigations[1] which had as their object the synthesis of cyanine dyes containing new heterocyclic nuclei, the quaternisation of a variety of bases of the general formula (I) or (II) has been studied, where D is the residue of a heterocyclic ring, X and Y are substituents, and Z = O or S. On account of its ease of preparation and aromatic stability, the pyridazine ring appeared very suitable for a more detailed study of the effect of substituents on the rate and position of quaternization. It has been shown[2] that form (III) contributes more to the structure of pyridazine than does form (IV), and pyridazine compounds can be regarded as being of the general formula (I). The majority of the compounds studied contained a methyl or alkylthio-group which may therefore be activated, by suitable quaternization, to take part in the formation of cyanine dyes by reaction with another quaternary salt containing the suitable complementary group.[3]



(I)



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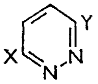
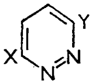


(III)



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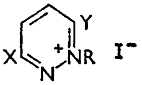

(V)

3-Methylpyridazine reacted rapidly with methyl iodide to give a methiodide which must be the salt (V; Y = R = Me, X = H), because treatment with 3-methyl-2-methylthiobenzothiazolium iodide gave a monomethincyanine. 1,6-Dihydropyridazin-6-one was converted into the mercapto-compound by treatment with phosphorus pentasulphide. Methylation then gave 3-methylthiopyridazine (III; X = MeS, Y = H) which reacted fairly slowly with methyl iodide, to give a salt which could not be condensed with 2,3-dimethylbenzothiazolium iodide and must therefore possess the structure (V; X = MeS, Y = H, R = Me). Methyl iodide and 1,6-dihydro-1-methyl-6-thiopyridazine (VI; X = H, Z = S, R = Me), prepared from the corresponding oxo-compound, reacted very rapidly, to give a quaternary salt which, with 2,3-dimethylbenzothiazolium iodide, gave the same dye as was prepared from 3-methylpyridazine methiodide. Further, the salt obtained from the thione (VI) was different from that from 3-methylthiopyridazine and therefore the salt from the thione must be (V; R = Me, X = H, Y = MeS) and the dye can only be (VII; R = Me, X = H). The methyl group (+*I*) is thus seen to activate the adjacent nitrogen atom whereas the alkylthio-group (—*I*) in the same position deactivates it. The inductive effect of the groups therefore appears to be the most important, because the mesomeric effects are of the same sign whereas the inductive effects are of opposite sign.[4]

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* Preliminary experiments were reported as part of a paper presented to the Fine Chemicals Group of the Society of Chemical Industry at King's College, London, December, 1954, and the complete paper was read at the XVIth Internat. Congr. Pure Appl. Chem., Paris, July, 1957.

[1a] Kendall and Duffin, B.P. 730,489; [b] Kendall, Duffin, and Waddington, B.P. 743,133; [c] *Idem.* B.P. 766,380; [d] Kendall and Duffin, B.P. 775,386; [e] Duffin, Fry, and Kendall, B.P. 785,939.

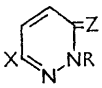
[2] Maccoll, *J.*, 1946, 671.

[3] Kendall and Suggate, *J.*, 1949, 1503.

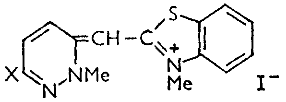
[4] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. (*a*) 71; (*b*) 77; (*c*) 735.

Mizzoni and Spoerri[5] reported, after this investigation had commenced, that 4-methylpyridazine gave 1,4-dimethylpyridazinium iodide and attributed the formation of the latter salt to the mesomeric effect of the methyl group which they believed acted by hyperconjunction.

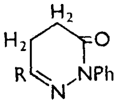
As was expected, 6-methyl-3-methylthiopyridazine, in which both of the above mentioned groups are operative, gave the salt (V; R = Y = Me, X = MeS). The structure of this salt was shown by its reaction with 3-methyl-2-methylthiobenzothiazolium iodide to give the dye (VII; X = MeS) and also because the salt was different from the salt (V; R = X = Me, Y = MeS) prepared by the very rapid reaction of methyl iodide with 1,6-dihydro-1,3-dimethyl-6-thiopyridazine (VI; R = X = Me, Z = S). The last salt condensed with 2,3-dimethylbenzothiazolium iodide to give the dye (VII; X = Me).



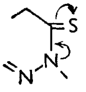
(VI)



(VII)



(VIII)



(IX)

3,6-Di(methylthio)pyridazine reacted very slowly with methyl iodide, to give the salt (V; R = Me, X = Y = MeS) from which the dye (VII; X = MeS) was obtained, while 3,6-dimethylpyridazine reacted rapidly, to give the salt (V; R = X = Y = Me) which gave the dye (VII; X = Me); and these dyes prepared from the symmetrical bases were identical with corresponding dyes obtained from the two isomeric salts (V; R = Y = Me, X = MeS) and (V; R = X = Me, Y = MeS).

Two pyridazine quaternary salts have already been described. 3-Chloro-6-methylpyridazine was reported[6] as giving the salt (V; R = Et, Y = Me, X = Cl) as the bromide. The corresponding methiodide has now been prepared and shown to be the salt (V; R = Y = Me, X = Cl) by its reaction with 3-methyl-2-methylthiobenzothiazolium iodide in ethanolic sodium acetate to give the dye (VII; X = Cl). The use of pyridine as the reaction medium gave a deep blue material which could not be purified but was suggestive of the formation of some tricarbocyanine-like substance (cf. the formation of tricarbocyanines from other heterocyclic chloro-compounds in presence of pyridine).[7] Again the $+I$ effect of the methyl group and the $-I$ of the chlorine atom control the quaternization.

Poppenberg[8] treated 3-phenylpyridazine with methyl iodide to obtain a salt of unknown structure. Oxidation of this salt with potassium ferricyanide has given 1,6-dihydro-1-methyl-3-phenylpyridazin-6-one (IV; R = Me, X = Ph, Z = O), which was then prepared unambiguously by the methylation of 1,6-dihydro-3-phenylpyridazin-6-one; the methiodide must therefore be (V; R = Me, X = Ph, Y = H). 6-Methyl-3-phenylpyridazine reacted at moderate speed with methyl iodide to give the salt (V; R = Y = Me, X = Ph), the structure of which was proved by reaction on the methyl group to give the dye (VII; X = Ph). 6-Methylthio-3-phenylpyridazine reacted slowly with methyl iodide, to give a salt containing a reactive methylthio-group and this, in turn, gave a dye identical with that obtained from the 6-methyl analogue, indicating that the latter methiodide was (V; R = Me, Y = MeS, X = Ph). This structure was proved by the formation of the identical product by the very rapid reaction of methyl iodide with 1,6-dihydro-1-methyl-3-phenyl-6-thiopyridazine (VI; R = Me, Z = S, X = Ph), prepared in turn by treatment of the corresponding oxo-compound with phosphorus pentasulphide. It would seem that the combined electronic[4c] and steric effects of the phenyl group more than offset the $-I$ effect of the methylthio-group.

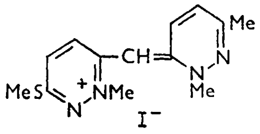
[5] Mizzone and Spoerri, *J. Amer. Chem. Soc.*, 1955, **76**, 2201.
[6] Halverson and Hirst, *J. Chem. Phys.*, 1951, **19**, 711.
[7a] Kendall, B.P. 424,264; [b] Ficken and Kendall, personal communication.
[8a] Poppenberg, *Ber.*, 1901, **34**, 3262; [b] Knorr, *Annalen*, 1886, **236**, 137.

1,4,5,6-Tetrahydro-3-methyl-1-phenyl- and -1,3-diphenyl-pyridazin-6-one (VIII; R = Me or Ph) were treated with phosphorus pentasulphide, but, even under the mildest conditions used, the extra hydrogen atoms were lost from the 4- and the 5-position and the corresponding 1,6-dihydro-6-thiopyridazines were formed. These compounds, in common with all the thiones (VI; Z = S), reacted very rapidly with methyl iodide, to give the quaternary salts (V; R = Ph, Y = MeS, X = Me or Ph) which contained reactive methylthio-groups and with 2,3-dimethylbenzothiazolium iodide gave cyanine dyes. The very high reactivity of the thiones is presumably due to mesomeric shift (IX) which possesses the additional driving force of making the ring truly aromatic.

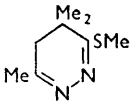
3-Methoxy-6-methylpyridazine reacted at moderate speed with methyl iodide, to give the salt (V; R = Y = Me, X = MeO) which contained a reactive methyl group and yielded cyanine dyes. 3-Methoxy-6-methylthiopyridazine reacted very slowly with methyl iodide and gave a salt which contained a reactive methylthio-group and so gave a cyanine dye; this proved identical with the corresponding dye obtained from 3-methoxy-1,6-dimethylpyridazinium iodide. The former salt must therefore be 3-methoxy-1-methyl-6-methylthiopyridazinium iodide (V; R = Me, X = MeO, Y = MeS). Once again, the methoxy-group, possessing a stronger $-I$ effect than the methylthio-group,[4a] results in quaternization on the N-atom remote from the methoxy in spite of the higher $+M$ effect of that group.[4b] The very strong influence of the methoxy-group to inhibit quaternization was finally shown by the very slow formation of the salt (V; R = Me, Y = Ph, X = MeO) from 3-methoxy-6-phenylpyridazine and methyl iodide. The structure of this product was assigned on the evidence of its failure to give 1,6-dihydro-1-methyl-3-phenylpyridazin-6-one when the salt was boiled with pyridine; this product would have been expected [8] to be formed from the isomeric material (V; R = Me, Y = MeO, X = Ph).

The dihydro-oxopyridazines (VI; Z = O) could not be brought into reaction with methyl iodide or methyl toluene-*p*-sulphonate even under drastic conditions. Fusion of 2-methylthiobenzothiazole, methyl toluene-*p*-sulphonate, and 1,6-dihydro-3-methylpyridazin-6-one gave the cyanine (VII; X = MeO), showing that O-methylation takes place under these conditions.

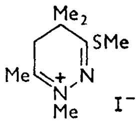
Although in no case could two methiodides be isolated from the same base, the " joint fusion " method [9] of preparing monomethincyanine dyes gave evidence that under these conditions 6-methyl-3-methylthiopyridazine yielded some of the isomeric salt (V; R = X = Me, Y = MeS). Thus fusion of that base with methyl toluene-*p*-sulphonate gave an orange melt which after being boiled with pyridine gave some of the dye (X) which must be formed by reaction between the toluene-*p*-sulphonates of the salts (V; R = Y = Me, X = MeS) and (V; R = X = Me, Y = MeS) and was indeed formed by the reaction between the two isolated salts. 6-Methyl-3-methylthiopyridazine, 2-methylbenzothiazole, and methyl toluene-*p*-sulphonate similarly gave 5% of the dye (VII; X = Me).



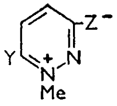
(X)



(XI)



(XII)



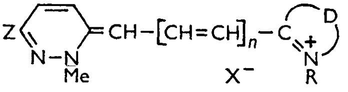
(XIII)

Although all attempts to obtain 4,5-dihydropyridazines free from substituents in the 4- and the 5-position were unsuccessful, the *gem*-dimethyl derivative (XI) was obtained. This compound behaved in a similar manner to 6-methyl-3-methylthiopyridazine, giving the salt (XII), which contained a reactive methyl group, and dyes were prepared by reaction on that group.[1d]

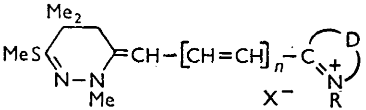
All the quaternary salts (V; Y = MeS) were readily converted into thiones (VI; Z = S)

[9] Kendall, B.P. 438,420.

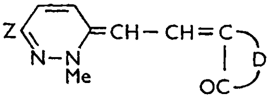
by treatment with boiling pyridine[10] or aqueous sodium sulphide,[11] and it was therefore of interest to see if those containing a methylthio- or methoxy-substituent in the *other* position relative to the nitrogen would give such compounds which could only be dipolar, *i.e.*, (XIII; Z = O or S). The action of boiling pyridine on these salts (V; X = MeS or MeO) gave very discoloured materials, but cold aqueous sodium sulphide rapidly gave a high yield of a white precipitate from the salts (V; X = MeS, Y = H; X = MeS, Y = Me; and X = MeO, Y = Me). The products, which all melted below 100° with decomposition, were insoluble in water and, though moderately soluble in most organic solvents, could not be crystallized: they analysed correctly for the salts minus MeI, but molecular-weight determination showed association. They decomposed in a few days and did not regenerate the salts (V; X = MeS or MeO) on treatment with methyl iodide, giving impure orange, cyanine-like materials. It seems unlikely therefore that these substances possess the structure (XIII).* It is noteworthy that the compound from the methoxy-salt contained no sulphur, indicating that the sodium sulphide was not attacking the ring. The action of sodium sulphide upon the methiodide of 3-methoxy-6-phenylpyridazine gave a product which, although it was not stable enough for analysis, resembled in properties the materials from the 6-methyl analogues and provides some support for the structure (V; X = MeO, R = Me, Y = Ph).



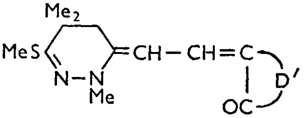
(XIV)



(XV)



(XVI)



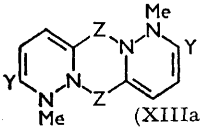
(XVII)

D = residue of five- or six-membered heterocyclic nucleus.

In addition to the monomethincyanines obtained in the elucidation of the structures of the salts, other monomethincyanines (XIV and XV; $n = 0$), trimethincyanines (XIV and XV; $n = 1$), and dimethinmerocyanines (XVI) and (XVII) were prepared from the salts (V; Y = Me) and (XII) by the usual methods. All the pyridazine monomethincyanines possess two widely spaced, rather broad maxima; *e.g.*, the dye (VII; R = X = Me) has maxima at 371 (ε 19,200) and 437 mμ (ε 22,100); those from the dihydro-*gem*-dimethylpyridazines show a single maximum of higher extinction coefficient, *e.g.*, (4,5-dihydro-1,4,4-trimethyl-3-methylthio-6-pyridazine)(3-methyl-2-benzothiazole)monomethincyanine has a maximum at 426 mμ (ε 50,100). The trimethincyanines, of both types, all show a single maximum of characteristic high extinction coefficient.

EXPERIMENTAL

3-*Mercapto*-6-*methylpyridazine*.—In spite of the statement by Gregory *et al.*,[12] the action of phosphorus pentasulphide on 1,6-dihydro-3-methylpyridazin-6-one was found to be the best method of preparing this mercapto-compound. The freshly dried pyridazinone[13] (132 g.), phosphorus pentasulphide (268 g.), and xylene (300 ml.) were stirred and heated under reflux



(XIIIa)

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* The authors are grateful for the suggestion by a referee that the formula (XIIIa) might represent these compounds. It is considered likely that some combination of this type, perhaps containing the residues from two or more molecules of quaternary salts, might explain the behaviour of these materials, but on the information at present available no final decision is possible.

[10] Kendall, B.P. 475,647.
[11] Sexton, *J.*, 1939, 470.
[12] Gregory, Overend, and Wiggins, *J.*, 1948, 2199.
[13] Overend and Wiggins, *J.*, 1947, 239.

for 3 hr. The xylene was then removed by evaporation and the residue decomposed with hot water (3 l.). After cooling, the precipitated solid was filtered off and the filtrate extracted with chloroform (4 × 400 ml.). The residue obtained by evaporation of the chloroform was combined with the first solid and recrystallized from ethanol, to give the mercapto-compound as deep yellow rhombic crystals, m. p. 203° (96 g., 64%).

3-*Methyl*-6-*methylthiopyridazine*.—3-Mercapto-6-methylpyridazine (56 g.) was dissolved in N-sodium hydroxide (444 ml.) and shaken with methyl iodide (28 ml.) for 1 hr. The resulting solution was extracted with chloroform (3 × 100 ml.) and the extracts were evaporated. The residue was distilled to give the *methylthio-compound* as a pale yellow oil, b. p. 135—141°/20 mm. (44 g., 70%) (Found: C, 51·15; H, 5·6. $C_6H_8N_2S$ requires C, 51·3; H, 5·7%).

1,6-*Dihydro*-3-*methyl*-1-*phenyl*-6-*thiopyridazine*.—1,4,5,6-Tetrahydro-3-methyl-1-phenylpyridazin-6-one [14] (9·4 g.) was dissolved in hot toluene (100 ml.), phosphorus pentasulphide (11 g.) was added, and the mixture boiled under reflux for 1 hr. The toluene was decanted while still hot and the residue extracted with boiling toluene (2 × 250 ml.). Evaporation of the combined toluene solutions gave a yellow oil which, when kept with ethanol, solidified. Recrystallization from ethanol gave the *thione* as yellow plates, m. p. 109° (6·1 g., 59%) (Found: N, 13·6; S, 15·9 $C_{11}H_{10}ON_2S$ requires N, 13·8; S, 15·8%).

3-*Mercaptopyridazine*.—1,6-Dihydropyridazin-6-one [15] (13·5 g.), pyridine (80 ml.), and phosphorus pentasulphide (12 g.) were boiled under reflux for 1 hr. Water (400 ml.) was added and the pyridine removed by evaporation. The resulting solid was filtered from the cooled residue and recrystallized from ethanol, to give the *thiol* as yellow needles, m. p. 170° (8·0 g., 51%) (Found: S, 28·6. $C_4H_4N_2S$ requires S, 28·5%).

3-*Methylthiopyridazine* was obtained from the mercapto-compound in the manner described for the 6-methyl analogue, and distilled to give a pale yellow solid, b. p. 138°/15 mm., m. p. 37—38° (65%) (Found: S, 25·5. $C_5H_6N_2S$ requires S, 25·4%).

1,6-*Dihydro*-1-*methylpyridazin*-6-*one*.—1,6-Dihydropyridazin-6-one (13·5 g.) was added to a solution from sodium (3·24 g.) in methanol (80 ml.), and methyl iodide (8·8 ml.) was then added. After refluxing for 1 hr., the solution was evaporated from a steam-bath, and the residue extracted with benzene (4 × 50 ml.). Evaporation of the benzene gave an oil which was distilled, to give the colourless *methyl compound*, m. p. 35°, b. p. 110°/15 mm. (8·7 g., 56%) (Found: C, 54·6; H, 5·3. $C_5H_6ON_2$ requires C, 54·4; H, 5·4%).

1,6-*Dihydro*-1-*methyl*-6-*thiopyridazine*.—1,6-Dihydro-1-methylpyridazin-6-one (3·7 g.), xylene (107 ml.), and phosphorus pentasulphide (7·4 g.) were boiled under reflux for 2 hr. After cooling, the tarry solid was filtered off and the filtrate evaporated to give a solid which recrystallized from cyclohexane to give the *thione* as yellow leaflets, m. p. 110° (1·75 g., 41%) (Found: S, 25·7. $C_5H_6N_2S$ requires S, 25·4%).

3-*Phenylpyridazine*.—3-Mercapto-6-phenylpyridazine (10 g.), water (50 ml.), aqueous ammonia (*d* 0·920; 10 ml.), and Raney nickel paste (40 g., prepared by Brown's method [16]) were heated on a steam-bath for 15 min. and then boiled under reflux for 1½ hr. The mixture was filtered hot and the filtrate cooled to give the product as colourless leaflets, m. p. 98° (cf. Poppenberg [8]) (4·1 g., 49%).

1,6-*Dihydro*-1-*methyl*-3-*phenylpyridazin*-6-*one*.—Sodium (1·15 g.) was dissolved in methanol (50 ml.), and 1,6-dihydro-3-phenylpyridazin-6-one [17] (8·6 g.) and methyl iodide (3·2 ml.) were added. After boiling under reflux for 2 hr., the solution was diluted with water and cooled, to precipitate the solid *product* which recrystallized from water as colourless needles, m. p. 116° (7·9 g., 85%) (Found: C, 70·75; H, 5·25. $C_{11}H_{10}ON_2$ requires C, 71·0; H, 5·4%).

1,6-*Dihydro*-1-*methyl*-3-*phenyl*-6-*thiopyridazine*.—1,6-Dihydro-1-methyl-3-phenylpyridazin-6-one (6·2 g.), xylene (40 ml.), and phosphorus pentasulphide (7·4 g.) were boiled under reflux for 2 hr. The xylene was decanted while still hot and, on cooling, gave the solid *thione* which was filtered off and recrystallized from ethanol as yellow needles, m. p. 151° (4·7 g., 70%) (Found: N, 13·6; S, 15·9. $C_{11}H_{10}N_2S$ requires N, 13·8; S, 15·9%).

3-*Chloro*-6-*methylthiopyridazine*.—Hydrogen sulphide was passed into a solution of sodium sulphide nonahydrate (55·3 g.) in water (175 ml.) until 8·4 g. had been absorbed. 3,6-Dichloropyridazine [18] (38 g.) was added, and the mixture shaken and set aside for 1 hr. Ethanol (175 ml.)

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[14] Fischer, *Annalen*, 1886, **236**, 147.

[15] Homer, Gregory, Overend, and Wiggins, *J.*, 1948, 2195.

[16] Brown, *J. Soc. Chem. Ind.*, 1950, **69**, 355.

[17] Gabriel and Colman, *Ber.*, 1899, **32**, 399.

[18] Mizzoni and Spoerri, *J. Amer. Chem. Soc.*, 1951, **73**, 1873.

was then added and the solution boiled under reflux for 1 hr. On cooling to 0° overnight, a solid was precipitated which was filtered off. The filtrate was acidified with concentrated hydrochloric acid (40 ml.), giving the crude mercapto-compound which was filtered off and dried in the air for 2 hr. (28·4 g.).[19] The mercapto-compound, in N-sodium hydroxide (201 ml.), was shaken with methyl iodide (11·4 g.) for 1 hr. The resulting solid was filtered off and recrystallized from light petroleum (b. p. 100—120°) to give 3-*chloro*-6-*methylthiopyridazine* as colourless needles, m. p. 103—104° (12·2 g., 30%) (Found: C, 37·6; H, 3·6; S, 20·0; Cl, 22·25. $C_5H_5N_2SCl$ requires C, 37·2; H, 3·1; S, 19·95; Cl, 22·15%).

3-*Methoxy*-6-*methylthiopyridazine*.—3-Chloro-6-methylthiopyridazine (15·0 g.) was added to a solution from sodium (2·16 g.) in methanol (66 ml.), and the whole was boiled under reflux for 2 hr. The methanol was then removed under reduced pressure, and water (100 ml.) added to the residue, to give the solid *methoxy-compound* which recrystallized from water as colourless needles, m. p. 87° (8·8 g., 60%) (Found: C, 45·9; H, 5·5; S, 20·6. $C_6H_8ON_2S$ requires C, 46·2; H, 5·3; S, 20·5%).

1,6-*Dihydro*-1,3-*dimethyl*-6-*thiopyridazine*.—1,6-Dihydro-1,3-dimethylpyridazin-6-one [20] (3·9 g.), xylene (100 ml.), and phosphorus pentasulphide (6·9 g.) were boiled under reflux for 2 hr., the mixture was cooled, and the liquid decanted. Evaporation of the xylene left a yellow oil which was distilled (b. p. 115—119°/0·8 mm.), to give the *thione* as a yellow solid, m. p. 91—93° (2·6 g., 59%). Recrystallization from ethanol gave yellow leaflets, m. p. 100° (Found: S, 22·75. $C_6H_8N_2S$ requires S, 22·8%).

1,6-*Dihydro*-1,3-*diphenyl*-6-*thiopyridazine*.—1,4,5,6-Tetrahydro-1,3-diphenylpyridazin-6-one [21] (12 g.), phosphorus pentasulphide (10·7 g.), and toluene (100 ml.) were boiled under reflux for 90 min. The resulting yellow solution was decanted from some tarry solid and evaporated under a vacuum, to leave a yellow solid *thione* which recrystallized from ethanol as bright yellow needles, m. p. 158—159° (7·2 g., 56%) (Found: C, 72·9; H, 5·0. $C_{16}H_{12}N_2S$ requires C, 72·9; H, 4·6%).

1,6-*Dimethyl*-3-*methylthiopyridazinium Iodide*.—3-Methyl-6-methylthiopyridazine (10 g.), dry benzene (20 ml.), and methyl iodide (10 ml.) were boiled under reflux. Some solid was deposited after 5 min. and at the end of 2 hr. the precipitated solid was filtered off and washed well with dry acetone and dried *in vacuo*, to give the yellow *salt*, m. p. 123° (18·2 g., 88%). Recrystallization from ethanol gave yellow needles, m. p. 132—134° (Found: C, 30·0; H, 4·1; S, 11·3. $C_7H_{11}N_2SI$ requires C, 29·75; H, 3·9; S, 11·35%).

The following quaternary salts were prepared by similar methods, reaction times are in parentheses: the salts formed yellow needles from ethanol unless otherwise stated:

1,6-Dihydro-1,3-dimethyl-6-thiopyridazine gave (½ hr.) 1,3-*dimethyl*-6-*methylthiopyridazinium iodide* (87%), m. p. 159° (Found: C, 29·5; H, 4·2; S, 11·4; I, 44·7. $C_7H_{11}N_2SI$ requires C, 29·75; H, 3·9; S, 11·35; I, 45·0%); 3-methylpyridazine [8] gave (1 hr.) 1,6-*dimethylpyridazinium iodide* (75%) (from acetone), m. p. 80° (Found: I, 53·4. $C_6H_9N_2I$ requires I, 53·8%); 3-methyl-6-phenylpyridazine [22] gave (1½ hr.) 1,6-*dimethyl*-3-*phenylpyridazinium iodide* (34%), m. p. 197° (Found: C, 46·25; H, 4·4; I, 39·7. $C_{12}H_{13}N_2I$ requires C, 46·2; H, 4·15; I, 40·8%); 3-phenylpyridazine gave (1 hr.) 1-*methyl*-3-*phenylpyridazinium iodide* (79%), m. p. 174° (cf. ref. 8); 3-methylthio-6-phenylpyridazine gave (2 hr.) 1-*methyl*-6-*methylthio*-3-*phenylpyridazinium iodide* (49%), m. p. 177° (Found: C, 41·7; H, 4·0. $C_{12}H_{13}N_2SI$ requires C, 41·8; H, 3·8%), the identical salt (m. p. and mixed m. p.) being obtained (¼ hr., 91%) from methyl iodide and 1,6-dihydro-1-methyl-3-phenyl-6-thiopyridazine; 3-methylthiopyridazine gave (1 hr.) 1-*methyl*-3-*methylthiopyridazinium iodide*, m. p. 147—148° (77%) (Found: C, 26·95; H, 3·5; S, 12·0. $C_6H_9N_2SI$ requires C, 26·9; H, 3·35; S, 11·95%); 1,6-dihydro-1-methyl-6-thiopyridazine gave (5 min.) 1-*methyl*-6-*methylthiopyridazinium iodide*, m. p. 188° (79%) (Found: C, 26·7; H, 3·4. $C_6H_9N_2SI$ requires C, 26·9; H, 3·35%); 1,6-dihydro-3-methyl-1-phenyl-6-thiopyridazine gave (15 min.) 3-*methyl*-6-*methylthio*-1-*phenylpyridazinium iodide*, m. p. 197—198° (73%) (Found: C, 41·9; H, 3·95. $C_{12}H_{13}N_2SI$ requires C, 41·8; H, 3·8%); 3-methoxy-6-methylpyridazine gave (2 hr.) 1,6-*dimethyl*-3-*methoxypyridazinium iodide*, needles, m. p. 160° (92%) (Found: C, 31·7; H, 4·5. $C_7H_{11}ON_2I$ requires C, 31·6; H, 4·15%); 3,6-di(methylthio)pyridazine [19] gave (2 hr.) 1-*methyl*-3,6-*di*(*methylthio*)*pyridazinium iodide* (from acetone), m. p. 160—162°

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[19] Cf. Druey, Meier, and Eichenberger, *Helv. Chem. Acta*, 1954, **37**, 121.

[20] Homer, Gregory, and Wiggins, *J.*, 1948, 2192.

[21] Pulvermacher, *Ber.*, 1893, **26**, 462.

[22] Paal and Dencks, *Ber.*, 1903, **36**, 492.

(59%) (Found: S, 20·3. $C_7H_{11}N_2S_2I$ requires S, 20·4%); 3-6-dimethylpyridazine [23] gave (30 min.) 1,3,6-*trimethylpyridazinium iodide* (from acetone), m. p. 110—111° (93%) (Found: I, 50·4. $C_7H_{11}N_2I$ requires I, 50·75%); 3-methoxy-6-methylthiopyridazine gave (4 hr.) 3-*methoxy*-1-*methyl*-6-*methylthiopyridazinium iodide*, m. p. 198° (51%) (Found: C, 27·8; H, 3·9; S, 11·0. $C_7H_{11}ON_2SI$ requires C, 28·2; H, 3·7; S, 10·7%); 1,6-dihydro-1,3-diphenyl-6-thiopyridazine gave (15 min.) 6-*methylthio*-1,3-*diphenylpyridazinium iodide*, m. p. 183° (45%) (Found: C, 49·9; H, 3·75; S, 8·15. $C_{17}H_{15}N_2SI$ requires C, 50·3; H, 3·7; S, 7·9%); 3-methoxy-6-phenylpyridazine [17] gave (4 hr.) 3-*methoxy*-1-*methyl*-6-*phenylpyridazinium iodide* (from ethyl acetate–ethanol), colourless needles, m. p. 153—154° (41%) (Found: C, 43·5; H, 4·0. $C_{12}H_{13}ON_2I$ requires C, 43·8; H, 3·95%); and 3-chloro-6-methylpyridazine [8] gave (1 hr.) 3-*chloro*-1,6-*dimethylpyridazinium iodide*, a yellow solid, m. p. 185° (68%), which could not be recrystallized (Found: N, 10·1. $C_6H_8N_2ClI$ requires N, 10·3%).

Oxidation of 1-*Methyl*-3-*phenylpyridazinium Iodide*.—The salt (1·5 g.) was dissolved in warm water (36 ml.) and added slowly with stirring to a solution of potassium ferricyanide (3·9 g.) and potassium hydroxide (1·3 g.) in water (35 ml.) at 5°. A solid was deposited fairly quickly. The temperature was allowed to rise to 10°. After 30 minutes' stirring, the mixture was warmed to 40° for a few minutes, cooled, and filtered, to give 1,6-dihydro-1-methyl-3-phenylpyridazin-6-one as buff needles, m. p. 114—115°, mixed m. p. with the authentic material 115—116° (0·67 g., 72%).

Action of Bases on 1-*Methyl*-6-*methylthio*-3-*phenylpyridazinium Iodide*.—(*a*) The methiodide (4·0 g.) and pyridine (20 ml.) were boiled under reflux for 2 hr. and diluted with water (150 ml.). The resulting solid was filtered off and recrystallized from ethanol, to give 1,6-dihydro-1-methyl-3-phenyl-6-thiopyridazine as yellow needles, m. p. 151° (0·95 g., 46%), identical with the material obtained as above. (*b*) The methiodide (2·0 g.) was dissolved in water (100 ml.), and sodium sulphide monohydrate (2·0 g.) in water (10 ml.) added. The mixture was left overnight and the resulting solid filtered off and recrystallized, to give the thione (0·42 g., 44%).

Preparation of Monomethincyanines.—(*a*) 3-Ethyl-2-methylbenzothiazolium iodide (0·76 g.), 1-methyl-6-methylthio-3-phenylpyridazinium iodide (0·81 g.), and ethanol (12 ml.) were boiled under reflux until all the solid had dissolved. Triethylamine (0·5 ml.) was added, giving an immediate orange-yellow colour, and, after a few minutes, solid began to be precipitated. After boiling for 10 min., the mixture was cooled, and the solid filtered off and recrystallized from methanol to give (1-*methyl*-3-*phenyl*-6-*pyridazine*)(3-*ethyl*-2-*benzothiazole*)*monomethincyanine iodide* (dye no. 1) as orange-red needles, m. p. 260° (0·43 g., 46%) (Found: C, 53·1; H, 4·4. $C_{21}H_{20}N_3SI$ requires C, 53·2; H, 4·25%).

The monomethincyanines in Table 1 were prepared by similar methods from the intermediates listed. The identity of the bracketed pairs provides evidence for the structures of the pyridazine salts from which the dyes are derived.

(*b*) 3-Methyl-6-methylthiopyridazine (0·75 g.), 2-methylthiobenzothiazole (0·9 g.), and methyl toluene-*p*-sulphonate (1·9 g.) were fused at 130° for 2 hr. Pyridine (10 ml.) was added and the mixture boiled under reflux for 1 hr., giving an orange solution which was poured into 4% aqueous sodium iodide (50 ml.). The resulting solid was filtered off and recrystallized from methanol, to give (1-methyl-3-methylthio-6-pyridazine)(3-methyl-2-benzothiazole)monomethincyanine iodide (dye no. 4′) as orange-red needles, m. p. 267° (0·92 g., 43%), identical with dye 4 of Table 1.

Similar experiments are summarized in Table 2.

(1,3-*Diphenyl*-6-*pyridazine*)(3-*ethyl*-2-*benzothiazole*)*monomethincyanine Iodide*.—1,3-Diphenyl-6-methylthiopyridazinium iodide (0·82 g.), 3-ethyl-2-methylbenzothiazolium iodide (0·61 g.), anhydrous sodium acetate (0·5 g.), and ethanol (20 ml.) were boiled under reflux for 1 hr., giving a deep orange solution. Pouring the mixture into water precipitated a solid which was filtered off and recrystallized from ethanol, to give the *dye* (no. 11) as red needles with a blue reflex, m. p. 248° (0·5 g., 47%) (Found: S, 6·15; I, 23·4. $C_{26}H_{22}N_3SI$ requires S, 6·0; I, 23·8%).

By a similar process, 3-chloro-1,6-dimethylpyridazinium iodide and 3-methyl-2-methylthiobenzothiazolium iodide gave (3-*chloro*-1-*methyl*-6-*pyridazine*)(3-*methyl*-2-*benzothiazole*)*monomethincyanine iodide* (dye no. 12) from methanol as orange needles, m. p. 254° (31%) (Found: S, 8·00. $C_{14}H_{13}N_3SClI$ requires S, 7·7%), but reaction between the same two salts in pyridine, in the manner used in the experiments of Table 1 gave only a deep blue tar.

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[23] Overberger, Byrd, and Mesrobian, *J. Amer. Chem. Soc.*, 1956, **78**, 1962.

Trimethincyanines.—The following exemplifies the procedure: 3-methoxy-1,6-dimethylpyridazinium iodide (0·51 g.) and 2,2′-acetanilidovinyl-1,3,3-trimethylindoleninium iodide (0·89 g.) were dissolved in hot ethanol (10 ml.), and triethylamine (0·5 ml.) was added. After boiling for 1 hr., the solution was added to 3% aqueous sodium iodide (50 ml.) to precipitate a solid which was filtered off and recrystallized from ethanol; this gave the *dye* (no. 13) as purple needles, m. p. 173—174° (Found: C, 53·7; H, 5·5; I, 27·8. $C_{20}H_{24}ON_3I$ requires C, 53·5; H, 5·35; I, 28·3%).

TABLE 1. *Monomethincyanines* (XIV; *n* = 0).

Dye no.	Pyridazine salt (V; R = Me) X	Pyridazine salt (V; R = Me) Y	Other inter-mediate	Dye (XIV; * *n* = 0) X	Dye (XIV; * *n* = 0) R	Yield (%)	M. p.	Found (%) S	Formula	Reqd. (%) S
2	H	Me	A	H	Me	73	265° [a]	8·5	$C_{14}H_{14}N_3SI$	8·35
2′	,,	MeS	B		,,	81		8·45		
3	Me	Me	A	Me	,,	75	289 [a]	7·9	$C_{15}H_{16}N_3SI$	8·05
3′	,,	MeS	B		,,	58		8·1		
4	MeS	,,	B	MeS	,,	90	267 [b]	14·7	$C_{15}H_{16}N_3S_2I$	14·9
4′	,,	Me	A		,,	50		15·0		
5	MeO	MeS	B	MeO	,,	23	232 [a]	7·6	$C_{15}H_{16}ON_3SI$	7·7
5′	,,	Me	A		,,	52		7·7		
6	Ph	,,	A	Ph	,,	84	278 [b]	7·2	$C_{20}H_{18}N_3SI$	7·0
6′	,,	MeS	B		,,	70		6·9		
7	MeO	,,	C	MeO	Et	21	225 [a]	[c]		

* D = 2-benzothiazole residue.

[a] Orange needles from methanol. [b] Red needles from methanol. [c] Found: C, 44·65; H, 5·05 $C_{16}H_{18}ON_3SI$ requires C, 44·8; H, 4·2%.

A = 3-Methyl-2-methylthiobenzothiazolium iodide. B = 2,3-Dimethylbenzothiazolium iodide. C = 3-Ethyl-2-methylbenzothiazolium iodide.

TABLE 2. *Dyes prepared by "joint-fusion."*

Dye no.	Pyridazine	Other inter-mediate	Dye (XIV;* *n* = 0) Z	Dye (XIV;* *n* = 0) X	Yield (%)	M. p.	Found (%)	Formula	Required (%)
8 †	VI; X = R = Me, Z = S	A	Me	Br	46	286°	S, 8·85	$C_{15}H_{16}N_3SBr$	S, 9·15
8′	III; X = Me, Y = MeS		,,	,,	3	,,	S, 9·2		
9	III; X = Ph, Y = Me	B		,,	58	257	S, 7·8; Br, 18·9	$C_{20}H_{18}N_3SBr$	S, 7·8 Br, 19·4
2′	III; X = H, Y = Me	B	H	I	29	267	Identical with no. 2 of Table 1		
10	III; X = OH, Y = Me	B	MeO	Br	19	202	S, 8·65 Br, 21·25	$C_{15}H_{16}ON_3SBr$	S, 8·6 Br, 21·4
10′	III; X = OMe, Y = Me	B	,,	,,	26	,,	S, 8·45 Br, 21·3		

* D = 2-benzothiazole residue. A = 2-Methylbenzothiazole. B = 2-Methylthiobenzothiazole. All the dyes crystallized as orange needles from methanol. † This dye is the bromide of dye no. 3 of Table 1; light-absorption data (Table 4) support this identity.

Other dyes prepared by similar methods are given in Table 3.

Self-condensation of Quaternized 3-Methyl-6-methylthiopyridazine.—The pyridazine (0·75 g.) and methyl toluene-*p*-sulphonate (1·00 g.) were fused as 180° for 5 min. The resulting orange melt was boiled in pyridine (5 ml.) for 1 hr., and poured into 5% aqueous potassium bromide to give an orange solid which recrystallized from methanol to give (1,3-*dimethyl*-6-*pyridazine*)(1-*methyl*-3-*methylthio*-6-*pyridazine*)*monomethincyanine bromide* (dye no. 20) as orange needles, m. p. 247° (decomp.) (0·14 g., 14%) (Found: C, 45·7; H, 5·1. $C_{13}H_{17}N_4SBr$ requires C, 45·8; H, 5·0%). The dye was identical with the product obtained by the following unambiguous method: 3-Methyl-6-methylthiopyridazine (0·35 g.) and 1,6-dihydro-1,3-dimethyl-6-thiopyridazine (0·35 g.) were each fused separately with methyl toluene-*p*-sulphonate (0·5 g.) at 120—130° for 1 hr. Each of the melts was dissolved in pyridine (2·5 ml.), and the solutions

TABLE 3. *Trimethincyanines.*

Dye no.	Pyridazine salt (V; R = Me)		Other intermediate	Dye (XIV; n = 1)	Yield (%)	M. p.	Found (%)	Formula	Reqd. (%)
	X	Y							
14	MeS	Me	A	Z = MeS, R = Et, X = 1, D = benzoxazole	40	250° [a]	S, 7·4	$C_{18}H_{20}N_3OSI$	S, 7·1
15	,,	,,	B	Z = MeS, R = Et, X = I, D = benzothiazole	72	238 [a]	S, 13·8	$C_{18}H_{20}N_3S_2I$	S, 13·6
16	,,	,,	C	Z = MeS, R = Me, X = I, D = 3,3-dimethylindolenine	54	191 [b]	S, 6·8	$C_{20}H_{24}N_3SI$	S, 6·9
17	,,	,,	D	Z = MeS, R = Me, X = I, D = quinoline-2	58	267 [b]	C, 49·9 H, 4·1	$C_{19}H_{20}N_3SI$	C, 50·8 H, 4·4
18	MeO	,,	A	Z = MeO, R = Et, X = ClO_4, D = benzoxazole	27	232 [c]		$C_{18}H_{20}O_6N_3Cl$	
19	,,	,,	B	Z = Me, R = Et, X = I, D = benzothiazole		197 [d]	C, 47·3 H, 4·5	$C_{18}H_{20}ON_3SI$	C, 47·7 H, 4·4

A = 2-2′-Acetanilidovinyl-3-ethylbenzoxazolium iodide. B = 2-2′-Acetanilidovinyl-3-ethylbenzothiazolium iodide. C = 2-2′-Acetanilidovinyl-1,3,3-trimethylindolenium iodide. D = 2-2′-Ethylthiovinyl-1-methylquinolinium iodide.

[a] Blue needles from methanol. [b] Green needles from methanol. [c] Purple needles from methanol. [d] Purple needles from ethanol.

were mixed and boiled for 15 min. Pouring the resulting orange solution into aqueous potassium bromide precipitated a solid, which on recrystallization from methanol gave the dye as orange needles, m. p. 247° (0·57 g., 68%).

1,4,5,6-*Tetrahydro*-3,5,5-*trimethyl*-6-*oxopyridazine*.—Mesitonic acid (the crude oily product prepared by Lapworth's method [24] was satisfactory and the difficulty accessible pure acid gave no better yield) (14 g.), hydrazine sulphate (14 g.), and 10% aqueous sodium hydroxide (86·5 ml.) were boiled under reflux for 1 hr. and evaporated to leave a white solid. This solid was extracted with hot ethanol (2 × 100 ml.), and the combined extracts were evaporated to an oil which was heated to 180° for 10 min. On cooling, the oil solidified and recrystallized from cyclohexane to give the *pyridazinone* as colourless needles, m. p. 110° (6·5 g., 47%) (Found: C, 60·15; H, 8·9. $C_7H_{12}ON_2$ requires C, 60·0; H, 8·7%).

4,5-*Dihydro*-3-*mercapto*-4,4,6-*trimethylpyridazine*.—The above pyridazinone (29·5 g.), dry xylene (295 ml.), and phosphorus pentasulphide (19 g.) were boiled under reflux for 2 hr. The hot xylene was decanted and the solid residue extracted with boiling benzene (200 ml.). The combined benzene extracts were evaporated to an oil which rapidly solidified. This material was purified by dissolution in N-sodium hydroxide and reprecipitation with hydrochloric acid, dried, and recrystallized from cyclohexane to give the pure *mercapto-compound* as pale yellow needles, m. p. 92° (18·9 g., 59%) (Found: S, 20·5. $C_7H_{12}N_2S$ requires S, 20·5%). This mercapto-compound was methylated, by the method described above for the other compounds, to give 4,5-*dihydro*-4,4,6-*trimethyl*-3-*methylthiopyridazine* as a yellow oil, b. p. 100—105°/0·7 mm. (68%) (Found: C, 56·3; H, 8·5. $C_8H_{14}N_2S$ requires C, 56·4; H, 8·25%), and this in turn gave 4,5-*dihydro*-1,4,4,6-*tetramethyl*-3-*methylthiopyridazinium iodide* as yellow needles (from ethanol), m. p. 213—214° (decomp.) (86%) (Found: C, 35·05; H, 5·55. $C_9H_{17}N_2SI$ requires C, 34·7; H, 5·45%).

(3-*Methyl*-2-*benzothiazole*)(4,5-*dihydro*-1,4,4-*trimethyl*-3-*methylthio*-6-*pyridazine*)*monomethincyanine Iodide*.—4,5-Dihydro-4,4,6-trimethyl-3-methylthiopyridazine (0·27 g.), 2-methylthiobenzothiazole (0·29 g.), and methyl toluene-*p*-sulphonate (0·60 g.) were fused for 90 min. at 130—140°. Pyridine (4·0 ml.) were added and the mixture boiled under reflux for 30 min. to give a yellow solution. Pouring this into aqueous potassium iodide precipitated a solid which was filtered off and recrystallized from methanol, to give the *dye* (no. 21) as orange leaflets, m. p. 266° (0·49 g., 56%) (Found: C, 44·6; H, 5·0. $C_{17}H_{22}N_3S_2I$ requires C, 44·45; H, 4·8%).

The following cyanines were prepared from the dihydropyridazine salt (XII) by the method used for the dyes of Table 3: 2-2′-acetanilidovinyl-3-ethylbenzoxazolium iodide gave dye no. 22 (3-*ethyl*-2-*benzoxazole*)(4,5-*dihydro*-1,4,4-*trimethyl*-3-*methylthio*-6-*pyridazine*)*trimethincyanine iodide*, purple plates (from ethanol), m. p. 251° (12%) (Found: S, 6·75. $C_{20}H_{26}ON_3SI$ requires

[24] Lapworth, *J.*, 1904, **85**, 1219.

S, 6·65%); 2-2′-acetanilidovinyl-3-ethylbenzothiazolium iodide gave dye no. 23 (3-*ethyl*-2-*benzothiazole*)(4,5-*dihydro*-1,4,4-*trimethyl*-3-*methylthio*-6-*pyridazine*)*trimethincyanine iodide*, purple plates (from methanol), m. p. 259° (10%) (Found: S, 13·0. $C_{20}H_{26}N_3S_2I$ requires S, 12·8%); 2-2-acetanilidovinyl-1,3,3-trimethylindolenium iodide gave dye no. 24 (1,3,3-*trimethyl*-2-*indolenine*)(4,5-*dihydro*-1,4,4-*trimethyl*-3-*methylthio*-6-*pyridazine*)*trimethincyanine iodide*, blue rhombs (from ethanol, m. p. 254° (32%) (Found: S, 6·5. $C_{22}H_{30}N_3SI$ requires S, 6·45%); and 3-ethyl-2-ethylthiobenzothiazolium iodide gave dye no. 25 (3-*ethyl*-2-*benzothiazole*)(4,5-*dihydro*-1,4,4-*trimethyl*-3-*methylthio*-6-*pyridazine*)*monomethincyanine iodide*, orange-yellow needles (from ethanol, m. p. 258° (8%) (Found: S, 13·5. $C_{18}H_{24}N_3S_2I$ requires S, 13·5%).

4-(1,6-*Dihydro*-1-*methyl*-3-*methylthio*-6-*pyridazinylidene-ethylidene*)-2-*phenyl*-5-*oxazolone*.—1,6-Dimethyl-3-methylthiopyridazinium iodide (1·5 g.), 4-ethoxymethylene-2-phenyl-5-oxazolone (1·09 g.), and pyridine (10 ml.) were boiled under reflux for 45 min. The resulting red solution was poured into water, precipitating a solid which was filtered off and recrystallized from methanol to give the pure *dye* (no. 26) as blue needles, m. p. 235—237° (0·4 g., 25%) (Found: S, 9·95. $C_{17}H_{15}N_3O_2S$ requires S, 9·85%).

By a similar process, 5-ethoxymethylene-3-ethyl-2-thiothiazolid-4-one gave 3-*ethyl*-4-(1,6-*dihydro*-1-*methyl*-3-*methylthio*-6-*pyridazinylidene-ethylidene*)-2-*thiothiazolid*-4-*one* (no. 27) which crystallized from ethanol in purple needles, m. p. 216—218° (78%) (Found: S, 29·4. $C_{13}H_{15}ON_3S_3$ requires S, 29·5%).

By similar processes, reaction of 4,5-dihydro-1,4,4,6-tetramethyl-3-methylthiopyridazinium iodide with 4-ethoxymethylene-4-phenyl-5-oxazolone gave 4-(1,4,5,6-*tetrahydro*-1,4,4-*trimethyl*-3-*methylthio*-6-*pyridazinylidene-ethylidene*)-2-*phenyl*-5-*oxazolone* (dye no. 28), red needles (from ethanol), m. p. 194° (39%) (Found: C, 64·2; H, 6·15; S, 9·0. $C_{19}H_{21}O_2N_3S$ requires C, 64·5; H, 5·95; S, 9·0%), and with 4-ethoxymethylene-3-ethyl-2-thiothiazolid-4-one gave a dye (no. 29), the 3-*ethyl*-2-*thiothiazolid*-4-*one analogue*, red needles (from ethanol), m. p. 194° (69%) (Found: C, 50·6; H, 6·0. $C_{15}H_{21}ON_3S_3$ requires C, 50·8; H, 5·9%).

TABLE 4. *Light-absorption of the dyes.*

These were determined in ethanol using a Unicam S.P. 500 spectrophotometer.

Dye no.	$\lambda_{max.}$ (mμ)	$10^{-4}E$	Dye no.	$\lambda_{max.}$ (mμ)	$10^{-4}E$	Dye no.	$\lambda_{max.}$ (mμ)	$10^{-4}E$
2	377, 435	2·13, 2·16	8′	371, 437	2·25, 2·70	23	552	11·7
2′	377, 435	2·13, 2·17	15	554	10·7	24	547	11·3
3	371, 438	2·24, 2·71	16	539	9·2	30	553, 570	6·82, 6·82
5	361, 450	2·08, 2·81	21	428	6·85	31	545	9·99
8	371, 437	2·25, 2·69	22	515	10·8			

Bis-(1-*methyl*-3-*methylthio*-6-*pyridazine*)*trimethincyanine Iodide*.—1,6-Dimethyl-3-methylthiopyridazinium iodide (1·8 g.), ethyl orthoformate (2·0 ml.), and pyridine (10 ml.) were boiled under reflux for 1 hr. The resulting purple solution was poured into 4% aqueous sodium iodide, precipitating a solid which was filtered off and recrystallized to give the pure *dye* (no. 30) as green leaflets, m. p. 268—269° (0·61 g., 28%) (Found: C, 40·1; H, 4·4. $C_{15}H_{19}N_4S_2I$ requires C, 40·1; H, 4·25%).

By a similar process, the dihydro-salt (XII) gave dye no. 31, *bis*-(4,5-*dihydro*-1,4,4-*trimethyl*-3-*methylthio*-6-*pyridazine*)*trimethincyanine iodide*, purple needles (from methanol), m. p. 282° (24%) (Found: C, 45·0; H, 6·1; S, 12·25. $C_{19}H_{27}N_4S_2I$ requires C, 45·1; H, 6·15; S, 12·6%).

Action of Sodium Sulphide on 1,6-*Dimethyl*-3-*methylthiopyridazinium Iodide*.—Sodium sulphide nonahydrate (5·0 g.) in water (25 ml.) was added to the iodide (2·82 g.) in water (25 ml.) at 20°. A solid was precipitated immediately and, after 5 min., was filtered off and washed with water, giving a material of unknown structure as a colourless solid, m. p. 60—62° (1·15 g., 82%) [Found: C, 51·3; H, 6·5; S, 23·0. $(C_6H_8N_2S)_n$ requires C, 51·4; H, 5·7; S, 22·9%]. A solution (1%) in boiling benzene gave no immediate elevation of the b. p. but after about 20 sec. the initially colourless solution became slowly brown and the elevation indicated $M \sim 620$. Similarly, 3-methoxy-1,6-dimethylpyridazinium iodide gave a colourless product, m. p. 94—96° (77%) [Found: C, 59·1; H, 6·8; S, 0. $(C_6H_8ON_2)_n$ requires C, 59·0; H, 6·6%]; M (in benzene) similar behaviour as above, $\sim$600]. 1-Methyl-3-methylthiopyridazinium iodide gave a colourless product, m. p. 59—61° (81%) [Found: C, 47·35; H, 4·85. $(C_5H_6N_2S)_n$ requires C, 47·6; H, 4·75%]; M (as before in benzene) $\sim$520]. 3-Methoxy-1-methyl-6-phenylpyridazinium iodide gave a similar product (73%) which decomposed rapidly.

All these materials became orange on storage or more rapidly on warming, and could not be recrystallized.

Similar treatment of 1-methyl-6-methylthiopyridazinium iodide gave 1,6-dihydro-1-methyl-6-thiopyridazine, m. p. and mixed m. p. 110° (68%); 1,3-dimethyl-6-methylthiopyridazinium iodide gave 1,6-dihydro-1,3-dimethyl-6-thiopyridazine, m. p. and mixed m. p. 100° (53%); 3-methoxy-1-methyl-6-methylthiopyridazinium iodide gave 1,6-*dihydro*-3-*methoxy*-1-*methyl*-6-*thiopyridazine*, yellow needles (from cyclohexane), m. p. 107° (67%) (Found: C, 46·0; H, 5·2. $C_6H_8ON_2S$ requires C, 46·2; H, 5·1%).

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