650. *Diazaindenes and Their Quaternary Salts. Part I. The Preparation of* 2,3,3-*Trimethyl*-3H-1,7-*diazaindene, and its Methiodides and Derived Cyanine Dyes.**

By G. E. Ficken and J. D. Kendall.

A Fischer indole synthesis with isopropyl methyl ketone 2-pyridylhydrazone gives 2,3,3-trimethyl-3*H*-1,7-diazaindene, which with methyl iodide yields largely the 7-methiodide. The isomeric 1-methiodide has been synthesised by way of 1,3,3-trimethyl-2-methylene-1,7-diazaindane. The methiodides yield two series of cyanine dyes, the light absorption of which is discussed.

3,3-DIALKYL-2-METHYL-3*H*-INDOLES (I) form quaternary salts which possess reactive methyl groups in the 2-position. They have consequently been frequently used for the preparation of cyanine and merocyanine dyes, the first recorded instance being König's synthesis of the symmetrical trimethincyanine from 1,2,3,3-tetramethyl-3*H*-indolium iodide

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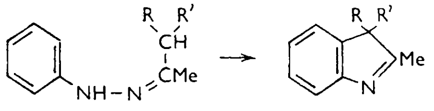
* A preliminary account was given at the VIII National Congress of the Società Chimica Italiana held jointly with the Society of Chemical Industry at Turin, May, 1958.

and ethyl orthoformate.[1] We have investigated the preparation of aza-analogues of (I) containing one nitrogen atom in each ring. A number of bases of this type, and derivatives thereof, have been described; *e.g.*, Robison and Robison [2] synthesised the base (II). However, as these all lack the characteristic *gem*-dialkyl group, the nitrogen atom of the five-membered ring carries a hydrogen atom, as in the true indoles.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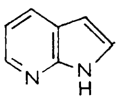
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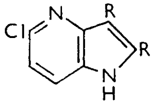
(IV)

3*H*-Indoles are generally prepared by Fischer's method [3] from a phenylhydrazone of type (III), cyclisation occurring on to the tertiary carbon atom in preference to the methyl group. Little has been reported, however, on the use of hydrazones of the heterocyclic series. However, the 2-chloro-5-pyridylhydrazones of acetone and propionaldehyde were reported to yield the chlorodiazaindenes (IV; R = H, R′ = Me and *vice versa* respectively) when heated with zinc chloride;[4] Clemo and Holt [5] cyclised cyclohexanone 2-methyl-3-pyridylhydrazone in low yield by zinc chloride; and Okuda and Robison [6] recently used polyphosphoric acid for the cyclisation of the 2-pyridylhydrazones of cyclohexanone and deoxybenzoin to diazaindenes. The present paper deals with the cyclisation of 2-pyridylhydrazones, and a later paper will describe the use of 3- and 4-pyridylhydrazones.

Okuda and Robison [6] obtained negative results with the 2-pyridylhydrazones of acetaldehyde, acetone, and pyruvic acid, as did Fargher and Furness [7] with acetone and propionaldehyde 2-pyridylhydrazones. We find, however, that heating isopropyl methyl ketone 2-pyridylhydrazone (V) with a catalytic amount of zinc chloride gives a mixture from which 2,3,3-trimethyl-3*H*-1,7-diazaindene (VI) can be isolated. Also formed in the reaction were 2-aminopyridine and a higher-boiling material, apparently possessing structure (VII). Compound (VII) could not be purified; it had evidently arisen by reaction of the diazaindene (VI) with unchanged pyridylhydrazone (V) under the action of the zinc chloride, 2-pyridylhydrazine being eliminated. The evidence for structure (VII) is discussed below. The mechanism of the Fischer synthesis (discussed in ref. 3) is generally considered to involve an electrophilic attack at the carbon atom adjacent to that carrying the -NH-N= group. In keeping with this, and with the well-known inertness of pyridines towards electrophilic substitution,[8] it was found that a considerably higher temperature (250°) was needed for the formation of the diazaindene (VI) than for that of 2,3,3-trimethyl-3*H*-indole (I; R = R′ = Me), which is formed from isopropyl methyl ketone phenylhydrazone and zinc chloride in refluxing ethanol.[9] Okuda and Robison [6] reported similar difficulty in cyclisation of 2-pyridylhydrazones with polyphosphoric acid.

The base (VI) with methyl iodide gave a mixture from which the 7-methiodide (VIII) was isolated as the major product; an ethiodide was also obtained. The position of quaternisation was proved by an unambiguous synthesis of the 1-methiodide (IX): *N*-methyl-*N*-2-pyridylhydrazine was synthesised, both by a modification of Tschitschibabin and Knunjanz's method [10] involving reduction of 2-(methylnitrosoamino)pyridine, and by

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[1] König, *Ber.*, 1924, **57**, 685.

[2] Robison and Robison, *J. Amer. Chem. Soc.*, 1955, **77**, 457.

[3] (*a*) Elderfield, " Heterocyclic Compounds," John Wiley and Sons, Inc., New York, 1952, Vol. III, Chapter 1; (*b*) Sumpter and Miller, " The Chemistry of Heterocyclic Compounds," Interscience Publ. Inc., New York, 1954, Vol. VIII, p. 3.

[4] Deutsche Gold-und Silberscheideanstalt, B.P. 259,982/1925.

[5] Clemo and Holt, *J.*, 1953, 1313.

[6] Okuda and Robison, *J. Amer. Chem. Soc.*, 1959, **81**, 740.

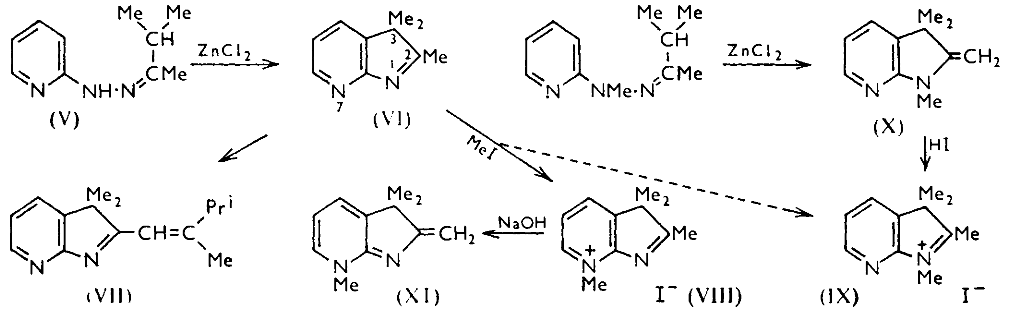
[7] Fargher and Furness, *J.*, 1915, **107**, 688.

[8] Elderfield, *op. cit.*, 1950, Vol. I, p. 401—410.

[9] Plancher, *Ber.*, 1898, **31**, 1488.

[10] Tschitschibabin and Knunjanz, *Ber.*, 1928, **61**, 2216.

reaction of 2-chloropyridine with methylhydrazine; reaction of 2-methylaminopyridine with chloramine[11] was unsuccessful, the amine being recovered. The *N*-methyl-*N*-2-pyridylhydrazone of isopropyl methyl ketone, with zinc chloride, gave 1,3,3-trimethyl-2-methylene-3*H*-1,7-diazaindane (X). As the anhydro-base of the 1-methiodide (IX), it added hydrogen iodide to give this quaternary salt, which differed from that obtained by quaternisation of the base (VI). Both methiodides had reactive methyl groups and they gave different series of cyanine and merocyanine dyes, *e.g.*, (XII) and (XIII; R′ = Me).



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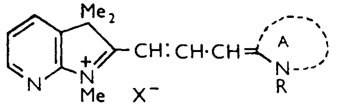

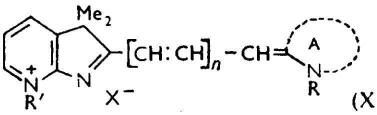

(XIII)

Both methiodides gave symmetrical trimethincyanines on reaction with ethyl orthoformate in pyridine. Apart from the difference in light absorption between corresponding dyes of the two series (to be discussed later), the most striking difference between the two series is the brilliant fluorescence of solutions of trimethincyanines of structure (XIII; $n = 1$). The monomethincyanines and merocyanines from the 7-methiodide, and all of the dyes from the 1-methiodide, fluoresce only feebly or not at all in solution.

Although the 1-methiodide (IX) could not be isolated from the product of quaternisation of base (VI), the presence of 5—10% of it was proved by reaction of the crude mixture with *p*-dimethylaminobenzaldehyde followed by chromatographic separation of the mixture of dyes. Formation of the 7-methiodide (VIII) preponderantly on quaternisation of the diazaindene (VI) implies that $N_{(7)}$ is more basic than $N_{(1)}$, in agreement with the known stronger basicity of pyridines than of 3*H*-indoles. Robison and Robison[12] showed that 1,7-diazaindene (II) reacts with methyl iodide exclusively on the nitrogen atom of the six-membered ring, but here the difference in basicity of the two nitrogen atoms (a pyridine and a virtually non-basic indole nitrogen) would be much more marked.

Table 1 gives some light absorptions for our compounds. Compared with 2,3,3-trimethyl-3*H*-indole, the diazaindene shows a bathochromic shift of the main absorption band of 23 mμ. The 1-methiodide (IX) shows a new absorption band at 317 mμ which is not present in the structurally similar tetramethyl-3*H*-indolium iodide. The main absorption maximum (277 mμ) of the latter corresponds, as expected, with the band at 274 mμ in the spectrum of trimethyl-3*H*-indole in acid solution. Likewise, in the case of diazaindene (VI), the spectrum in acid solution resembles quite closely that of the 7-methiodide, whilst the 1-methiodide has a rather different spectrum. This indicates that protonation of the base occurs largely on the pyridine-nitrogen atom, in agreement with the quaternisation. The spectrum of tetramethyl-3*H*-indolium iodide in alkaline solution,

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[11] Cf. Diamond and Audrieth, *J. Amer. Chem. Soc.*, 1955, **77**, 3131.

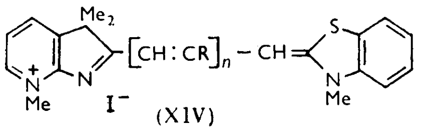
[12] Robison and Robison, *ibid.*, p. 6554.

TABLE 1. *Absorption spectra*, $\lambda_{max.}$ (mμ) *and* log ε *for ethanolic solutions* (*inflections in parentheses*).

	Neutral				Acid (HCl)		
2,3,3-Trimethyl-3*H*-indole	257				226	274	
	3·76				3·78	3·72	
The diazaindene (VI)	245	280			240	(282)	300
	3·61	3·87			3·75	(3·76)	3·89
	Alkaline (NaOH)				Neutral		
1,2,3,3-Tetramethyl-3*H*-indolium iodide		278	(308)			277	(299)
		4·34	(3·40)			3·97	(3·49)
The diazaindene 1-methiodide (IX)	249	274	313		248	274	317
	3·87	4·02	3·72		3·79	4·02	3·79
The diazaindene 7-methiodide (VIII)		293	345	362	(245)	(285)	304
		4·02	3·47	3·48	(3·66)	(3·76)	3·86

i.e., effectively a solution of 1,3,3-trimethyl-2-methyleneindoline (" Fischer's base "), is rather similar to that of the neutral solution, apart from a greater intensity of the main absorption band. The diazaindene 1-methiodide likewise shows little change of spectrum in alkaline solution, where the change (IX ⟶ X) presumably occurs. On the other hand, addition of alkali to a solution of the 7-methiodide results in a yellow coloration, due to the appearance of two new absorption bands above 300 mμ. This yellow colour, discharged by addition of excess of acid, must be ascribed to the formation of the methylene base (XI), which possesses an *ortho*-quinonoid pyridine ring.

To prove the structure (VII) assigned to the high-boiling by-product arising in the preparation of the diazaindene, the crude material was treated successively with methyl iodide and 3-methyl-2-methylthiobenzothiazolium iodide. The mixture of dyes obtained was separated chromatographically into the methincyanine (XIV; $n = 0$), derived from methiodide (VIII), and the trimethincyanine (XIV; $R = Pr^i$, $n = 1$), spectroscopically



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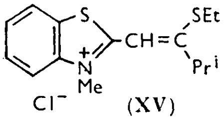

(XV)

closely similar to dye (XIV; $R = H$, $n = 1$). The structure of the new dye was proved by the following unambiguous synthesis. Reaction of 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate with isobutyryl chloride in pyridine,[13] and of the resulting 3-methyl-2-isobutyrylmethylenebenzothiazoline with ethanethiol in methanolic hydrogen chloride [14] gave the quaternary salt (XV). The use of intermediates of type (XV) for the preparation of trimethincyanines was first described by the I.G. Farbenindustrie; [15] reaction of the salt (XV) with the 7-methiodide (VIII) gave dye (XIV; $R = Pr^i$, $n = 1$), identical with that from (VII).

Light Absorption of the Dyes.—Amongst the dyes prepared were a number of trimethincyanines (XII; R = Me) and (XIII; $n = 1$, $R = R' = Me$) from the 3- and 4-methiodide respectively. The light-absorption data for these are given in Table 2(*b*), together with the figures for the symmetrical trimethincyanines (XVI) (only the principal maximum is given in each case, although most of the dyes possess a smaller maximum or inflection on the short-wavelength side of the principal maximum). In part (*a*) of the Table, data are given for the dimethincyanines (XVII and XVIII; B = 1,3,3- and 3,3,7-trimethyl-3*H*-1,7-diazaindene-2), for which the corresponding symmetrical dyes are (XIXa and b). The calculated value for each unsymmetrical dye is given, being the arithmetic mean of the

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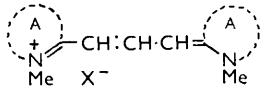
[13] Cf. Brooker, White, and Eastman Kodak Co., U.S.P. 2,112,139/1938.
[14] Cf. Gevaert Photo-Producten N.V., B.P. 637,182/1950.
[15] I.G. Farbenindustrie A.G., B.P. 412,309/1932.

wavelengths for the corresponding symmetrical dyes (XVI or XIX) and (XX or XXI). The difference between this calculated average and the observed value, the " deviation " of the dye, has been correlated by Brooker *et al.*[16,17,18] with the relative basicities of the heterocyclic nuclei. Table 2 (in which the nuclei in the first column are arranged in order of increasing basicity) shows that the deviations are small for the 7-methyldiazaindene nucleus in combination with nuclei from benzoxazole onwards. It follows therefore from Brooker's investigations[18] that $N_{(7)}$ in the diazaindene is itself strongly basic. In fact, the deviations obtained with the dyes of structure (XVII) and (XVIII) indicate that $N_{(7)}$ is intermediate in basicity between benzothiazole and β-naphthothiazole. The 1-quaternised diazaindene nucleus on the other hand gives large deviations in combination with the more basic nuclei, from which it appears to lie between nuclei (XXII) and (XXIII) in the basicity series. These facts are brought out in Table 3, where the deviations obtained from Table 2 are compared with Brooker's values[16,18] for a number of unsymmetrical cyanines not containing the diazaindene nucleus. The majority of these are trimethincyanines, but the dyes possessing styryl or pyrrole nuclei are dimethincyanines of type (XVII) and (XVIII). It is of interest that the unsymmetrical diazaindene trimethincyanine (XXIV) shows a considerable deviation, which is consistent with the other values given in Table 3. This dye was prepared by reaction of the 7-methiodide (VIII) with ethyl trithio-orthoformate to give an intermediate of the type described by Kendall and Majer,[19] which then reacted with the 1-methiodide (IX) to give dye (XXIV).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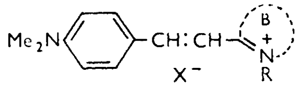
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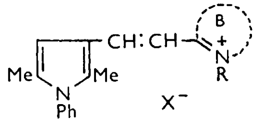
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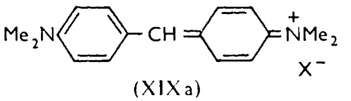
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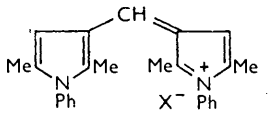
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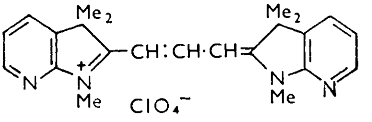
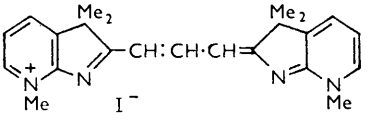
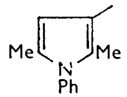

(XX)

$\lambda_{max.}$ 5360 Å, log ε 5·15


(XXI)

$\lambda_{max.}$ 6085 A, log ε 5·13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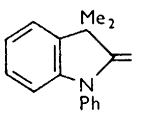
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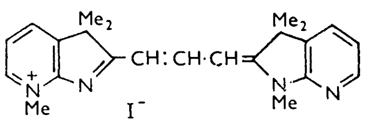
(XXIV)

$\lambda_{max.}$ 5580 Å, log ε 4·95

It should be noted that, except for nuclei (XXII) and (XXIII), Brooker's values refer to *N*-ethyl dyes, whereas the deviations for the diazaindene dyes refer to *N*-methyl dyes. Nevertheless, replacement of methyl by ethyl does not generally affect the wavelength

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[16] Brooker, Sklar, Cressman, Keyes, Smith, Sprague, Van Lare, Van Zandt, White, and Williams, *J. Amer. Chem. Soc.*, 1945, **67**, 1875.

[17] Brooker and Sprague, *ibid.*, p. 1869.

[18] Brooker, Sprague, and Cressman, *ibid.*, p., 1889.

[19] Kendall and Majer, *J.*, 1948, 687.

of maximum absorption by more than about 50 Å, so that the position of the diazaindene nitrogen atoms in the basicity series would not be significantly affected, since this position was determined by those dyes which gave the largest deviations.

Some facts of interest emerge from the above results:

TABLE 2. *Light absorption data for dye iodides* [$\lambda_{max.}$ (Å) *and* log ε].

(a) *Dimethincyanines.*

Formula	Symmetrical dye (XIX)	B = 1,3,3-Trimethyl-1,7-diazaindene obs.	calc.	B = 3,3,7-Trimethyl-1,7-diazaindene obs.	calc.
(XVII)	6100[b]	5590 4·84	5730	5390 4·78	6095
(XVIII)	4485[c]	4845[a] 4·62	4925	4760[a] 4·76	5285

(b) *Trimethincyanines.*

Nucleus A	Symmetrical dye (XVI)	1,3,3-Trimethyl dye (XII) obs.	calc.	3,3,7-Trimethyl dye (XIII; R′ = Me, *n* = 1) obs.	calc.
1,3,3-Trimethyl-3*H*-indole-2-[a]	5465[d] 5·18	5400 5·05	5415	5715 5·14	5775
3-Methyl-2-benzoxazole	4840[e] 4·97	4980 4·84	5100	5485 5·22	5465
3-Methyl-2-benzothiazole	5580[e] 5·09	5315 4·99	5470	5850 5·25	5835
3-Methylnaphtho[1′,2′:4,5]thiazole-2-	5980[f] 5·12	5360 4·90	5670	6020 5·16	6035
1-Methyl-2-quinoline	6050[g] 5·24	5400 4·93	5705	6060 5·08	6070
1-Methyl-4-quinoline	7070[h] 5·35	5700 4·79	6215	6510 4·99	6580

[a] Perchlorates. [b] Brooker, Sklar, Cressman, Keyes, Smith, Sprague, Van Lare, Van Zandt, White, and Williams, *J. Amer. Chem. Soc.*, 1945, **67**, 1875. [c] Brooker and Sprague, *ibid.*, p. 1869. [d] Hamer (*J.*, 1927, 2796) gives 5480 Å for the iodide. [e] König and Meier (*J. prakt. Chem.*, 1925, **109**, 324) give 4850 and 5580 Å respectively for these dyes. [f] Toluenesulphonate; Hamer (*J.*, 1929, 2598) gives 6000 Å for the iodide. [g] Brooker and Sprague (*J. Amer. Chem. Soc.*, 1941, **63**, 3203) give 6040 Å. [h] Hamer (*J.*, 1927, 2796) gives 7150 Å.

TABLE 3. *Deviations* (Å) *of dyes.*

Nucleus	1-Diaza	(XXIII)	Indo	Oxa	Thia	7-Diaza	Naphtho	2-Quino	4-Quino
(XVII)	140	170	290	455	555	705	720	820	1125
(XVIII)	80	140	260	345	375	525	540	525	730
1-Diaza[a]	(0)	—	15	120	155	145	310	305	515
(XXIII)		(0)	30	110	145	—	180	255	380
Indo[b]			(0)	65	100	60	110	145	220
Oxa[b]				(0)	0	−20	30	15	0
Thia[b]					(0)	−15	−5	30	15
7-Diaza[a]						(0)	15	10	70
Naphtho[b]							(0)	20	−20
2-Quino[b]								(0)	−5
4-Quino[b]									(0)

[a] 1,3,3-Trimethyl-1,7-diazaindene-2 and 3,3,7-trimethyl-1,7-diazaindene-2 respectively. [b] 3,3-Dimethyl-3*H*-indole-2-, 2-benzoxazole, 2-benzothiazole, naphtho(1′,2′:4,5)thiazole-2, 2-quinoline and 4-quinoline (all with an *N*-methyl or *N*-ethyl group).

First, $N_{(7)}$ in the diazaindene is considerably more basic than $N_{(1)}$, in agreement with the result of quaternisation of the base. Brooker[16] has, however, pointed out that basicities from deviation measurements are not necessarily strictly equivalent to the true basicities given by p*K* values, and in fact prefers to replace the basicities from deviations by the term "N^{IV}–N^{III} stabilisation." This implies that the 7-quaternised diazaindene displays less tendency to pass into a structure bearing a tervalent nitrogen atom than does the 1-quaternary salt. This is clearly related to the formation of an unstable *ortho*-quinonoid pyridine ring in the N^{III} form of the 7-methyl dyes, as in the methylene base (XI).

Secondly, $N_{(1)}$ and $N_{(7)}$ in the diazaindene are less basic than 3*H*-indole and pyridine respectively, pyridine being above all the nuclei shown in Table 3 in the basicity series.

This appears to be an instance of the well-known lowering of the basicity of a nitrogen heterocycle by the introduction of further nitrogen atoms (cf. Albert [20]).

EXPERIMENTAL

2-*Hydrazinopyridine*.—This was prepared by the method of Fargher and Furness.[7] The p-*nitrobenzylidene derivative* formed yellow needles, m. p. 241·5—242°, from ethanol (Found: C, 59·6; H, 4·4. $C_{12}H_{10}O_2N_4$ requires C, 59·5; H, 4·2%).

2,3,3-*Trimethyl*-3H-1,7-*diazaindene* (VI).—2-Hydrazinopyridine (77·0 g.), isopropyl methyl ketone (80 ml.), and benzene (250 ml.) were refluxed together, the water being removed by azeotropic distillation. The hydrazone remaining after distillation of the solvent was heated at 250° with anhydrous zinc chloride (2·0 g.) until ammonia evolution ceased (1 hr.). The dark brown product was fractionated under reduced pressure to give (i) b. p. 100°/17 mm. to 148°/21 mm. (14·4 g.), (ii) b. p. 112—120°/0·8 mm. (51·8 g.), and (iii) b. p. 130—200°/2 mm. (8·6 g.); all three fractions partially solidified on cooling. Fraction (i) consisted largely of 2-aminopyridine, m. p. and mixed m. p. 56—57° (from ethyl acetate); the methiodide had m. p. and mixed m. p. 152—153° (Tschitschibabin, Konowalowa, and Konowalowa [21] give m. p. 145—150°). Fraction (ii) crystallised from cyclohexane to give a solid (33·0 g.), m. p. 62—65°, further quantities of less pure material being obtained from the mother-liquors. Repeated recrystallisation from cyclohexane gave 2,3,3-*trimethyl*-3H-1,7-*diazaindene* as colourless needles, m. p. 77·5—78° (Found: C, 74·7; H, 7·5; N, 17·6. $C_{10}H_{12}N_2$ requires C, 75·0; H, 7·5; N, 17·5%). The compound slowly darkened and the m. p. fell several degrees during a year. Fraction (iii) of the distillation was a mixture, containing some of the diazaindene, but no pure material could be obtained from it.

The diazaindene (11·5 g.) was refluxed in acetone (50 ml.) with methyl iodide (9·0 ml.) for 1 hr. The solid (12·5 g.) which separated had m. p. 214—215° (decomp.); the 7-*methiodide* formed colourless prisms, m. p. 218—219° (decomp.), by crystallisation from propan-2-ol (Found: I, 41·8. $C_{11}H_{15}N_2I$ requires I, 42·0%). The mother-liquors on evaporation deposited a further crop (1·9 g.) of less pure material, and the final filtrate consisted of a mixture of the 1- and the 7-methiodide. Reaction of the base with ethyl iodide gave the 7-ethiodide as a deliquescent solid, m. p. 138—142°, which could not be recrystallised.

2-(*Methylnitrosoamino*)*pyridine*.—2-Aminopyridine (212 g.) was methylated with sodamide and dimethyl sulphate, according to the intructions of Tschitschibabin and Knunjanz; [10] purification *via* the benzoyl derivative was however unnecessary. Instead, the crude methylation product dissolved in concentrated hydrochloric acid (725 ml.) and water (390 ml.) was treated dropwise, with stirring, with an aqueous solution of sodium nitrite (130 g.), the temperature being kept below 10°. After the solution at room temperature had been stirred for 1 hr., excess of ammonia was added, the oil was separated and the aqueous solution was extracted three times with ether. After drying (K_2CO_3) of the combined extracts, the ether was removed and the product distilled. A fraction (21 g.), b. p. 70—90°/18 mm., was followed by the main fraction, b. p. 106—110°/12 mm., consisting of the nitrosamine (84 g., 27%); the picrate had m. p. 194—195° (Tschitschibabin and Knunjanz [10] give b. p. 123—124°/30 mm., yield 21%, picrate, m. p. 186—187°).

N-*Methyl*-N-2-*pyridylhydrazine*.—(a) *From the nitrosamine*. Reduction of the nitrosamine by zinc and acetic acid [10] proved unsatisfactory in our hands, the product appearing to contain large amounts of 2-methylaminopyridine. Reduction with hydrazine and Raney nickel gave this amine exclusively, but lithium aluminium hydride proved satisfactory. A solution of the nitrosamine (33 g.) in dry ether (100 ml.) was added slowly to a stirred solution of lithium aluminium hydride (10 g.) in ether (250 ml.). When the vigorous reaction had subsided, stirring was continued for a further 1 hr., then ethyl acetate (10 ml.) was added, followed by 40% aqueous sodium hydroxide solution (50 ml.). The ether layer was separated and the aqueous layer was extracted once with ether. After drying (K_2CO_3), the combined ether solutions were distilled to yield *N*-methyl-*N*-2-pyridylhydrazine (30·7 g.), b. p. 113—118°/12 mm. (Tschitschibabin and Knunjanz [10] give b. p. 105°/10 mm.); the p-*nitrobenzylidene derivative* formed orange needles, m. p. 137—137·5°, from ethanol (Found: C, 61·15; H, 4·7. $C_{13}H_{12}O_2N_4$ requires C, 60·9; H, 4·7%).

(b) *From methylhydrazine*. Isolation of methylhydrazine from its hydrochloride was found

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[20] Albert, *Chem. Soc. Special Publ.* No. 3, 1955, p. 124.

[21] Tschitschibabin, Konowalowa, and Konowalowa, *Ber.*, 1921, **54**, 814.

to be more satisfactory than the method of von Brüning [22] using the sulphate (we are indebted to Mr. D. J. Fry for suggesting this modification). A solution of methylhydrazine sulphate [23] (309 g.) in distilled water (1 l.) was added to a stirred solution of barium chloride dihydrate (525 g.) in warm water (2 l.). After a further hour's warming, the suspension of barium sulphate was filtered through kieselguhr, and the filtrate was evaporated to yield an almost colourless solid. *Methylhydrazine hydrochloride* formed colourless plates, m. p. 122—124°, from ethanol (Found: C, 15·1; H, 8·2; Cl, 43·6. CH_7N_2Cl requires C, 14·6; H, 8·55; Cl, 43·0%). The crude hydrochloride was dissolved in water (500 ml.), and the solution treated cautiously with a large excess of sodium hydroxide (flake), strong cooling being necessary. The oil which separated was poured off, and the aqueous layer (with much suspended sodium chloride) was evaporated at atmospheric pressure. The first 250 ml. of distillate was saturated with potassium carbonate, more oil separating. This was combined with the material obtained previously, dried (K_2CO_3), and distilled at 94—108°/756 mm.; the wide boiling range indicated that the methylhydrazine (72 g.) was still partially hydrated.

This material was refluxed for 48 hr. with 2-chloropyridine (54 g.) and 2-methoxyethanol. After distillation of as much volatile material as possible under reduced pressure on the steam-bath, excess of sodium hydroxide solution was added. The oil was separated and the aqueous layer extracted with ether (3 × 50 ml.). The combined oil and extracts were dried (K_2CO_3) and distilled, *N*-methyl-*N*-2-pyridylhydrazine being obtained at b. p. 116—122°/18 mm. (52·8 g.). The picrate had m. p. 166—167° (Found: C, 41·2; H, 3·7. Calc. for $C_{12}H_{12}O_7N_6$: C, 40·9; H, 3·4%), and the benzylidene derivative, m. p. 67—68° (Tschitschibabin and Knunjanz [10] give m. p.s 153—155° and 67—68° respectively). The *p*-nitrobenzylidene derivative had m. p. 136—137°, undepressed by that obtained from (*a*).

1,3,3-*Trimethyl*-2-*methylene*-1,7-*diazaindane* (X).—*N*-Methyl-*N*-2-pyridylhydrazine (52·5 g.), isopropyl methyl ketone (50 ml.), and benzene (150 ml.) were refluxed together until no more water was removed. The hydrazone was heated at 230° with anhydrous zinc chloride (2·0 g.) for 3 hr. and the product distilled. The material boiling between 73°/0·9 mm. and 130°/1·5 mm. (48·0 g.) was refractionated to give (i) 2-methylaminopyridine, b. p. 93°/14 mm. to 100°/13 mm. (18·0 g.) [picrate, m. p. and mixed m. p. 194—195°; and methiodide, m. p. 159·5—160·5° (Tschitschibabin, Konowalowa, and Konowalowa [21] give m. p.s 190° and 159—160°)]. An intermediate fraction (ii), b. p. 101°/13 mm. to 116°/11 mm. (7·0 g.), was followed by (iii), b. p. 117—120°/11 mm. (18·8 g.) consisting largely of 1,3,3-trimethyl-2-methylene-3*H*-1,7-diazaindane (X), b. p. 118°/12 mm., with a blue fluorescence; it contained a persistent impurity which could not be separated by repeated fractionation (Found: C, 73·95; H, 8·05. Calc. for $C_{11}H_{14}N_2$: C, 75·8; H, 8·1%). The base (6·66 g.) in propan-2-ol (60 ml.) was treated with freshly distilled hydriodic acid (*d* 1·70; 5·5 ml.). The solid which slowly crystallised was washed with a little cold propan-2-ol, and then with ether. The *hydriodide* (2,3,3-*trimethyl*-3H-1,7-*diazaindene* 1-*methiodide*) (7·57 g.) formed colourless needles, m. p. 240·5—241° (decomp.) (from ethanol) (Found: C, 44·0; H, 5·3; N, 9·1; I, 42·6. $C_{11}H_{15}N_2I$ requires C, 43·7; H, 5·0; N, 9·3; I, 42·0%).

Preparation of Diazaindene Dyes.—(a) *Mono- and tri-methincyanines.* The monomethincyanines, listed in Table 4, were prepared by reaction of the diazaindene 7-methiodide (VIII) or -ethiodide with the appropriate 2-methylthio-heterocyclic quaternary iodide in ethanol in the presence of triethylamine. If the cyanine iodide did not separate on cooling, the solution was poured into aqueous sodium perchlorate, and the dye was isolated as the perchlorate. The unsymmetrical trimethincyanines (Tables 5 and 6) were prepared by reaction of the diazaindene 1- or 7-alkiodide with an ω-ethylthiovinyl quaternary toluene-*p*-sulphonate or iodide in ethanol containing triethylamine, or with an ω-acetanilidovinyl quaternary iodide in pyridine; conversion into the perchlorate as above was sometimes necessary. The symmetrical trimethincyanines were prepared by reaction of the diazaindene alkiodide with ethyl orthoformate in pyridine. The yields, where given, refer to the crude and once recrystallised materials.

(b) *Dimethincyanines containing nuclei* (XVII) *and* (XVIII). The diazaindene 1-methiodide (0·60 g.) and *p*-dimethylaminobenzaldehyde (0·30 g.) were refluxed in ethanol (5·0 ml.) containing one drop of piperidine for one hour. The solid (0·35 g.) which separated on cooling was recrystallised from ethanol (12 ml.) to give 2-p-*dimethylaminostyryl*-3,3-*dimethyl*-3H-1,7-*diazaindene* 1-*methiodide* (0·14 g.) as blue needles, m. p. 264—265° (decomp.) (Found: I, 29·7.

[22] von Brüning, *Annalen*, 1889, **253**, 7.
[23] Hatt, *Org. Synth.*, **16**, 51.

TABLE 4. (A) (3,3-*Dimethyl*-7-R′-3H-1,7-*diazaindene*-2)*methincyanine dyes* (XIII; $n = 0$).

Nucleus A	R′	X	M. p. (decomp.)	Yield	Solvent [a]	Appearance	$\lambda_{max.}$ (Å)	log $\varepsilon_{max.}$	Formula	Found (%)	Reqd. (%)
1-Methyl-2-quinoline	Me	ClO_4	250—251° [b]	—	GM	Red needles	4990	4·88	$C_{21}H_{22}O_4N_3Cl$	Cl, 8·2	8·5
3,4-Dimethyl-2-thiazole	Et	ClO_4	203—204 [b]	—	E	Pale yellow plates	4470	4·51	$C_{16}H_{20}O_4N_3ClS$	N, 10·1	10·5
3-Methyl-4-phenyl-2-thiazole ...	Et	ClO_4	289—290	—	M	Yellow prisms	4500	4·82	$C_{21}H_{22}O_4N_3ClS$	N, 9·1	9·1
3-Methyl-2-benzothiazole	Me	I	313—314	47; 29	M	Yellow plates	4530	5·00	$C_{19}H_{20}N_3IS$	N, 9·6 I, 27·9	9·35 28·25
3-Ethyl-2-benzothiazole	Et	I	318—319	33; 17	M	Yellow prisms, blue reflex	4540	4·99	$C_{21}H_{24}N_3IS$	I, 26·3	26·6

[a] E = Ethanol, G = 2-Ethoxyethanol, M = Methanol. [b] Without decomp.

TABLE 5. (A) (1,3,3-*Trimethyl*-3H-1,7-*diazaindene*-2)*trimethincyanine iodides* (XII).

Nucleus A	M. p. (decomp.)	Yield (%)	Solvent [a] (ml./g.)	Appearance	Formula	Found (%)	Reqd. (%)
1,3,3-Trimethyl-3*H*-indole-2	241—242° [b]	14; 11	E(30)	Purple plates, silver reflex	$C_{24}H_{28}O_4N_3Cl$ [c]	N, 8·8	9·2
1-Methyl-2-quinoline	271—272 [b]	36; 22	M(55)	Green needles	$C_{23}H_{24}N_3I$	I, 26·6	27·0
1-Methyl-4-quinoline	326	64; 44	M(60)	Deep green plates	$C_{23}H_{24}N_3I,H_2O$	I, 25·6	26·0
1,3,3-Trimethyl-3*H*-1,7-diazaindene-2	272—273	33; 19	M(18)	Red plates, blue reflex	$C_{23}H_{27}O_4N_4Cl$ [c]	N, 12·2	12·2
3-Methyl-2-benzoxazole	292—293	39; 32	M(30)	Red-brown plates, blue reflex	$C_{21}H_{22}ON_3I$	I, 27·4	27·6
3-Methyl-2-benzothiazole	260—261	10; 6	M(30)	Green plates	$C_{21}H_{22}N_3IS,\frac{1}{2}H_2O$	C, 51·95 H, 5·3 I, 25·9	52·1 4·8 26·2
3-Methylnaphtho(1′,2′:4,5)thiazole-2	211—212 [b]	8; 5	G(50)	Red-brown prisms	$C_{25}H_{24}N_3IS$	I, 24·5	24·2

[a], [b] See Table 4. [c] Perchlorate.

TABLE 6. (A) (3,3-*Dimethyl*-7-R′-3H-1,7-*diazaindene*-2)*trimethincyanine iodides* (XIII; $n = 1$).

Nucleus A	R′	M. p. (decomp.)	Yield (%)	Solvent [a] (ml./g.)	Appearance	Formula	Found (%)	Reqd. (%)
1,3,3-Trimethyl-3*H*-indole-2	Me	271—272°	95; 40	M(55)	Brown prisms, blue reflex	$C_{24}H_{28}O_4N_3Cl$ [c]	N, 9·4	9·2
1-Methyl-2-quinoline	Me	250—251	45; —	E	Deep green	$C_{23}H_{24}N_3I$	I, 26·9	27·0
1-Methyl-4-quinoline	Me	297·5—298·5	53; —	M	Blue-green needles	$C_{23}H_{24}N_3I$	I, 26·9	27·0
3,3,7-Trimethyl-3*H*-1,7-diazaindene-2	Me	282	33; 29	E	Green plates	$C_{23}H_{27}N_4I$	I, 26·1	26·1
7-Ethyl-3,3-dimethyl-3*H*-1,7-diazaindene-2 [d]	Et	245—246	60; 33	E(30)	Bronze needles	$C_{25}H_{31}O_4N_4Cl$ [c]	Cl, 7·0	7·3
3-Methyl-2-benzoxazole	Me	268—269	44; 26	GM	Blue needles	$C_{21}H_{22}ON_3I,H_2O$ [e]	I, 26·4	26·6
3-Ethyl-2-benzoxazole	Et	252—253	94; 52	E	Purple	$C_{23}H_{26}ON_3I,HI$	I, 40·7	41·25
3-Methyl-2-benzothiazole	Me	269—270 [b]	73; 52	M	Indigo needles	$C_{21}H_{22}N_3IS$	I, 26·6	26·7
3-Methylnaphtho(1′,2′:4,5)thiazole-2	Me	236—237	23; 8	G(170)	Green	$C_{25}H_{24}N_3IS,H_2O$	I, 23·3	23·35

[a], [b] See Table 4. [c] Perchlorate. [d] $\lambda_{max.}$ 6090 Å (log ε 5·30). [e] Bromide, purple needles, m. p. 262° (Found: Br, 18·4. $C_{21}H_{22}ON_3Br,H_2O$ requires Br 18·6%).

$C_{20}H_{24}N_3I$ requires I, 29·3%). The three following dyes were obtained similarly. 3,3-*Dimethyl*-2-p-*dimethylaminostyryl*-3H-1,7-*diazaindene* 7-*methiodide* (38; 23%), bronze-green needles, m. p. 272—273° (decomp.), from methanol (1 in 20) (Found: C, 52·8; H, 5·9; I, 27·9. $C_{20}H_{24}N_3I,H_2O$ requires C, 53·2; H, 5·8; I, 28·1%). (1,3,3-*Trimethyl*-3H-1,7-*diazaindene*-2)-(2,5-*dimethyl*-1-*phenyl*-3-*pyrrole*)*dimethincyanine perchlorate* (53; 29%), orange needles with a steely reflex, m. p. 282° (decomp.), from methanol (1 in 60) (Found: N, 9·2. $C_{24}H_{26}O_4N_3Cl$ requires N, 9·2%). (3,3,7-*Trimethyl*-3H-1,7-*diazaindene*-2)(2,5-*dimethyl*-1-*phenyl*-3-*pyrrole*)*dimethincyanine perchlorate* (49; 12%), red prisms with a blue reflex, m. p. 259—260° (decomp.), from ethanol (1 in 55) (Found: N, 9·05. $C_{24}H_{26}O_4N_3Cl$ requires N, 9·2%). The last two dyes were prepared from 2,5-dimethyl-1-phenylpyrrole-3-aldehyde (cf. Brooker and Sprague [17]).

(c) *Merocyanines.* A solution of the diazaindene 1-methiodide (0·34 g.) and 5-ethoxymethylene-3-ethyl-2-thiothiazolid-4-one (ethoxymethylene-*N*-ethylrhodanic acid) (0·40 g.) in ethanol (5·0 ml.) was refluxed with one drop of piperidine for 1 hr. The solid (0·29 g.) which separated on cooling recrystallised from ethanol (35 ml.) to give 5-(1,2-*dihydro*-1,3,3-*trimethyl*-3H-1,7-*diazainden*-2-*ylidene*)*ethylidene*-3-*ethyl*-2-*thiothiazolid*-4-*one* (0·26 g.) as red needles and plates with a blue reflex, m. p. 223° (Found: S, 18·6. $C_{17}H_{19}ON_3S_2$ requires S, 18·6%), $\lambda_{\text{max.}}$ 4830 Å (log ε 4·84). Similarly prepared was 5-(2,7-*dihydro*-3,3,7-*trimethyl*-3H-1,7-*diazainden*-2-*ylidene*)*ethylidene*-3-*ethyl*-2-*thiothiazolid*-4-*one* (69; 58%), red plates with a blue reflex, m. p. 257—259° (from 2-methoxyethanol–methanol) (Found: S, 18·9. $C_{17}H_{19}ON_3S_2$ requires S, 18·6%), $\lambda_{\text{max.}}$ 5430 Å (log ε 4·83).

A solution of the diazaindene 1-methiodide (0·54 g.) and 3-methyl-1-phenylpyrazol-5-one (0·31 g.) in pyridine (3·0 ml.) was refluxed with ethyl orthoformate (1·0 ml.) for 45 min. The solid obtained by pouring the solution into water was chromatographed in chloroform on activated alumina. The main orange band was eluted and the eluate evaporated to yield a solid (0·37 g.) which gave 4-(1,2-*dihydro*-1,3,3-*trimethyl*-3H-1,7-*diazainden*-2-*ylidene*)*ethylidene*-3-*methyl*-1-*phenylpyrazol*-5-*one* (0·29 g.) as red rhombs, m. p. 187—188°, by crystallisation from ethanol (12 ml.) (Found: C, 73·4; H, 6·3. $C_{22}H_{22}ON_4$ requires C, 73·7; H, 6·2%), $\lambda_{\text{max.}}$ 4600 Å (log ε 4·68). Similarly prepared was 4-(2,7-*dihydro*-3,3,7-*trimethyl*-3H-1,7-*diazainden*-2-*ylidene*)-*ethylidene*-3-*methyl*-1-*phenylpyrazol*-5-*one*, obtained as red needles, m. p. 251—252°, by crystallisation from ethanol (Found: C, 73·2; H, 6·0. $C_{22}H_{22}ON_4$ requires C, 73·7; H, 6·2%), $\lambda_{\text{max.}}$ 5220 Å (log ε 4·89).

(d) *Dye* (XXIV). Diazaindene 7-methiodide (3·02 g.) was refluxed for 30 min. with acetic anhydride (10 ml.) containing ethyl trithio-orthoformate (2·2 ml.). The solvent was distilled off under reduced pressure and the residue was triturated with acetone to leave a sticky brown solid (1·78 g.). This crude ethylthiovinyl quaternary salt (0·84 g.) was refluxed for 45 min. with diazaindene 1-methiodide (0·75 g.) in ethanol (5·0 ml.) containing triethylamine (0·5 ml.). The solid (0·47 g.) which separated on cooling was recrystallised from ethanol (10 ml.) to give (1,3,3-*trimethyl*-3H-1,7-*diazaindene*-2)(3,3,7-*trimethyl*-3H-1,7-*diazaindene*-2)*trimethincyanine iodide* (0·33 g.) as lustrous blue prisms, m. p. 261—262° (decomp.) (Found: I, 25·8. $C_{23}H_{27}N_4I$ requires I, 26·1%).

Dye Preparation with the Crude Methiodide.—Diazaindene (VI) (160 mg., 0·01 mole) was refluxed for 1 hr. with dry methyl iodide (1·0 ml.). The residue remaining after distillation of the excess of methyl iodide was refluxed for 2 hr. with *p*-dimethylaminobenzaldehyde (0·30 g.) in ethanol (5·0 ml.) containing one drop of piperidine. After neutralisation with a little acetic acid, the solution was evaporated to dryness under reduced pressure, and the residue was chromatographed in chloroform on activated alumina. The first band (purple) was eluted and the eluate evaporated to dryness. A solution of the product in methanol (100 ml.; 2·5 ml. of solution diluted to 100 ml.) showed the absorption spectrum of the dye from the 1-methiodide, and had $E_{\text{max.}}$ 1·06 corresponding to a yield of 6·2%. The second band (red) similarly treated gave a solution in methanol (100 ml.; 0·5 ml. diluted to 100 ml.) which had the spectrum of the 7-methyl dye ($E_{\text{max.}}$ 1·66; yield 55%).

Dye Preparation from Compound (VII).—The high-boiling fraction (8·6 g.) from the previously described preparation of diazaindene (VI) was refluxed in acetone with methyl iodide (5·0 ml.) for 2 hr. Evaporation of the solution left a brown deliquescent powder (12·9 g.), from which no pure material could be isolated. This material (1·5 g.) and 3-methyl-2-methylthiobenzothiazolium toluene-*p*-sulphonate (1·8 g.) were refluxed for 2 hr. in ethanol (30 ml.) containing triethylamine (1·0 ml.). The solution was poured into aqueous potassium iodide, and the dyes were extracted with chloroform. The extracts were dried (Na_2SO_4) and evaporated to dryness, and the product was chromatographed in chloroform on activated alumina. The first, yellow band was eluted and the dye identified spectroscopically as the methincyanine (XIV; $n = 0$). Subsequently a purple band was eluted, the eluate was evaporated to dryness, and a solution of the product in ethanol was treated with an aqueous solution of sodium perchlorate. The precipitated solid (0·16 g.), m. p. 197—199°, recrystallised from ethanol to yield (3,3,7-*trimethyl*-3H-1,7-*diazaindene*-2)(3-*methyl*-2-*benzothiazole*)-β-*isopropyltrimethincyanine perchlorate* (XIV; $n = 1$, R = Pr^i) as green crystals, m. p. 217—218°, undepressed by a sample prepared by the method described below (Found: N, 8·6; Cl, 7·2; S, 6·9. $C_{24}H_{28}O_4N_3ClS$ requires N, 8·6; Cl, 7·2; S, 6·5%), $\lambda_{max.}$ 5740 Å (log ε 5·14).

2-*Isobutyrylmethylene*-3-*methylbenzothiazoline*.—Isobutyryl chloride (12·5 ml.) was added dropwise, with stirring to a solution/suspension of 2,3-dimethylbenzothiazolium toluene-*p*-sulphonate (33·5 g.) in dry pyridine (100 ml.), the temperature being kept below 0°. Then stirring was continued for successive 30-minute periods at 0°, room temperature, and 100°. The solvent was distilled off under reduced pressure and the residue was added to ice and water. The precipitated solid was washed with cold water, dried, and extracted (Soxhlet) with light petroleum (b. p. 60—80°). The extracts deposited a solid (17·0 g.), m. p. 120—124°, which yielded the *benzothiazoline* as cream-coloured plates, m. p. 131—132°, by crystallisation from dilute ethanol (Found: C, 67·1; H, 6·6; S, 13·2. $C_{13}H_{15}ONS$ requires C, 66·9; H, 6·5; S, 13·7%).

2-(2-*Ethylthio*-3-*methylbut*-1-*enyl*)-3-*methylbenzothiazolium Iodide* (XV).—The benzothiazoline was dissolved in methanol (150 ml.) containing ethanethiol (7·5 ml.). The solution, cooled in ice–salt, was saturated with dry hydrogen chloride. A solid separated but subsequently dissolved. The solution, after 16 hr. at room temperature, was treated with a saturated solution of potassium iodide (35 g.) in water, then diluted with water. The solid which separated (7·0 g.) was washed with water and recrystallised from ethanol to yield the *benzothiazolium iodide* as yellow needles, m. p. 150—151° (Found: I, 31·55; S, 15·4. $C_{15}H_{20}NIS_2$ requires I, 31·3; S, 15·8%).

Preparation of Dye from (XV).—A solution of the benzothiazolium iodide (1·01 g.) and 2,3,3-trimethyl-3*H*-1,7-diazaindene 7-methiodide (0·76 g.) in ethanol (10 ml.) was refluxed for 2 hr. with triethylamine, and the solution poured into aqueous sodium perchlorate solution. The dried precipitate was chromatographed to yield the trimethin-cyanine (XIV; $n = 1$, R = Pr^i), m. p. 219—220°, by crystallisation from ethanol. Its light absorption (visible and infra-red) was identical with that of the dye prepared from (VII).

Symmetrical Trimethincyanines.—The symmetrical trimethincyanines were prepared by refluxing the appropriate methyl heterocyclic quaternary salt with ethyl orthoformate in pyridine, according to the method of Hamer.[24] *Bis*-(1,3,3-*trimethyl*-3H-*indole*-2)*trimethincyanine perchlorate*, from 1,2,3,3-tetramethyl-3*H*-indolium iodide followed by treatment with aqueous sodium perchlorate solution, formed red plates with a blue reflex, m. p. 264°, by crystallisation from methanol (Found: N, 6·3. $C_{25}H_{29}O_4N_2Cl$ requires N, 6·1%). *Bis*-[3-*methylnaphtho*(1′,2′ : 4,5)*thiazole*-2]*trimethincyanine toluene*-p-*sulphonate* formed bronze needles, m. p. 269—270° (decomp.) (from ethanol) (Found: S, 15·4. $C_{34}H_{28}O_3N_2S_3$ requires S, 15·8%).

The light-absorption measurements were made in ethanolic solution on a Unicam S.P. 500 spectrophotometer.

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[24] Hamer, *J.*, 1929, 2598.