

*Anal.* Calcd. for  $C_{22}H_{23}IN_2$ : I, 27.95. Found: I, 27.60.

**1,1'-Diethyl-3,4-benzo-2,2'-cyanine Iodide (III).**—9-Methylphenanthridine ethiodide (1 g., 1 mol) was condensed with 2-iodoquinoline ethiodide (1.1 g., 1 mol) by refluxing with triethylamine (0.6 g., 2.1 mols) and ethyl alcohol (13 cc.) for twenty minutes; yield 46% (32%, 100 cc. per g.). After a further recrystallization (yield 23%) the dye formed garnet prisms with a greenish reflex and had m. p. 259–262° (dec.).

*Anal.* Calcd. for  $C_{27}H_{28}IN_2$ : I, 25.18. Found: I, 25.15.

**1,1'-Diethyl-3,4,5,6'-dibenzo-2,2'-cyanine Iodide (IV).**—Crude 9-methylphenanthridine etho-*p*-toluenesulfonate (1.95 g., 1 mol) was condensed with 2-iodo- $\beta$ -naphthoquinoline ethiodide (2.3 g., 1 mol) using triethylamine (1.05 g., 2.1 mols); yield 50% (22% after two recrystallizations; 100 cc. per g.). The minute greenish-bronze crystals had m. p. 250–251° (dec.).

*Anal.* Calcd. for  $C_{31}H_{27}IN_2$ : I, 22.91. Found: I, 22.93.

**1,1'-Diethyl-5,6-benzo-2,2'-cyanine iodide (VII).**—A higher yield of this dye than that previously recorded<sup>6</sup> was obtained as follows:  $\beta$ -naphthoquinaldine (0.97 g., 1 mol) was condensed with ethyl *p*-toluenesulfonate (1 g., 1 mol) by heating at 120–125° for six days. The solution of the product in ethyl alcohol (7 cc.) was boiled for twenty minutes with 2-iodoquinoline ethiodide (2.05 g., 1 mol) and triethylamine (1.05 g., 2.1 mols); yield 78% (63%, 200 cc. per g.).

**1,1'-Diethyl-5,6'-benzo-2-pyrido-2'-cyanine Iodide (VIII).**— $\alpha$ -Picoline ethiodide (5 g., 2 mols, *i. e.*, 100% excess), 2-iodo- $\beta$ -naphthoquinoline ethiodide (4.6 g., 1 mol), *N*-methylpiperidine (3 g., 3 mols) and *n*-propyl alcohol (20 cc.) were heated at 100° for one and one-half

hours; yield 51%. The dye was dissolved in hot methyl alcohol (200 cc.) and refluxed for one-half hour with one-twentieth of its weight of Norite. The crystals which separated from the filtrate were again recrystallized (yield 33%) and formed beautiful reddish-brown tablets with green reflex and had m. p. 268–270° (dec.).

*Anal.* Calcd. for  $C_{28}H_{28}IN_2$ : I, 27.95. Found: I, 27.90.

**1,1'-Diethyl-5,6,5',6'-dibenzo-2,2'-cyanine iodide<sup>5</sup> (IX)** was obtained in a yield of 78% (51%; 1230 cc. per g.) using triethylamine to effect the condensation.

**1,1'-Diethyl-3,4,3',4'-dibenzo-2,2'-carbocyanine iodide (X)** was prepared by refluxing crude 9-methylphenanthridine etho-*p*-toluenesulfonate (3.9 g.; 2 mols) with ethyl orthoformate (3.3 cc., 4 mols) and pyridine (20 cc.) for one and one-half hours. The dye was isolated as the iodide; yield 34% after recrystallization. After a further recrystallization (230 cc. per g.) the dark greenish crystals had m. p. 234–235° (dec.).

*Anal.* Calcd. for  $C_{33}H_{32}IN_2$ : I, 21.88. Found: I, 21.85.

### Summary

- Four cyanine dyes containing the phenanthridine nucleus have been prepared.
- In every case the absorption maximum of a dye containing a phenanthridine nucleus lies nearer the blue than that of the isomeric dye which contains a  $\beta$ -naphthoquinoline nucleus in place of phenanthridine.
- In all four cases the new dyes show no signs of photographic sensitizing action.

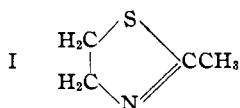
ROCHESTER, NEW YORK RECEIVED FEBRUARY 10, 1936

[CONTRIBUTION No. 580 FROM THE KODAK RESEARCH LABORATORIES]

## Studies in the Cyanine Dye Series. VI. Dyes Derived from 2-Methylthiazoline

By L. G. S. BROOKER

Up to the present only derivatives of completely unsaturated heterocyclic bases, such as those of the pyridine, quinoline, thiazole and benzothiazole series, have been used for the preparation of cyanine dyes. It was therefore of interest to examine the reactivity of the methyl group in quaternary salts of 2-methylthiazoline (I), since the nucleus of this base is partly saturated.



That this methyl group was indeed very reactive was demonstrated by the fact that the qua-

ternary salts underwent the commoner cyanine dye condensations.<sup>1,2</sup> Thus, 2-methylthiazoline ethiodide when treated with 2-iodoquinoline ethiodide in the presence of triethylamine gave 1',3-diethylthiazolino-2'-cyanine iodide (III) in excellent yield, and similar treatment with 2-iodopyridine ethiodide and with 2-iodo- $\beta$ -naphthoquinoline ethiodide gave 1',3-diethylthiazolino-2'-pyridocyanine iodide (II) and 1',3-diethyl-5',6'-benzo-thiazolino-2'-cyanine iodide (IV), respectively.

Alcoholic solutions of these dyes range in color from pale yellow (II) to orange-yellow (IV). The

- (1) Brooker, U. S. Patent 1,950,876; British Patent 385,320.
- (2) Cf. Fisher and Hamer, *J. Chem. Soc.*, 189 (1933).



TABLE I

Dye	Reactants, g.		Solvent, cc.	Heated, min.	Yield, %	Solvent, cc./g.	M. p., °C.	Formula	Analyses, %	
									Calcd.	Found
1',3-DiEt-thiazolino-2'-pyridocyanine iodide (II)	QS4	2.6	<i>n</i> -PrOH	35	18; 14	H <sub>2</sub> O	203-206	C <sub>13</sub> H <sub>19</sub> N <sub>3</sub> S	I, 35.05	35.04
	QS5	3.6				0.8				
	NEt <sub>3</sub>	2.1								
1',3-DiEt-thiazolino-2'-cyanine iodide (III)	QS4	2.6	EtOH	20	77; 61 <sup>a</sup>	MeOH	226-227	C <sub>17</sub> H <sub>21</sub> N <sub>3</sub> S	I, 30.80	30.89
	QS6	4.1				2.5				
	NEt <sub>3</sub>	2.1								
1',3-DiEt-5',6'-benzothiazolino-2'-cyanine iodide (IV)	QS4	2.6	EtOH	20	52; 25 <sup>a</sup>	MeOH	263-266	C <sub>21</sub> H <sub>23</sub> N <sub>3</sub> S	I, 27.46	27.38
	QS7	4.6				75				
	NEt <sub>3</sub>	2.1								
1',3-DiEt-thiazolino-4'-cyanine iodide (V)	QS4	2.6	EtOH	10	51; 38 <sup>c</sup>	<sup>d</sup>	223-224	C <sub>17</sub> H <sub>21</sub> N <sub>3</sub> S	I, 30.80	30.84
	QS8	5.7								
	KOH <sup>b</sup>	1.3								
2- <i>p</i> -NMe <sub>2</sub> -styrylthiazoline ethiodide (VI)	QS4	5.2	MeOH <sup>e</sup>	16 hrs.	63; 51	<sup>d</sup>	219-220	C <sub>18</sub> H <sub>19</sub> N <sub>3</sub> S	I, 32.70	32.80
	<i>p</i> -Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	3.0								
3,3'-DiMe-thiazolino-carbocyanine iodide	QS1	11.45	C <sub>6</sub> H <sub>5</sub> N	120	66 <sup>f</sup> ; 57	MeOH	250-252	C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> S <sub>2</sub>	I, 34.47	34.47
	CH(OEt) <sub>2</sub>	5.9				12				
3,3'-DiEt-thiazolino-carbocyanine iodide (VII)	QS4	5.15	C <sub>6</sub> H <sub>5</sub> N	120	68; 58	MeOH	256-258	C <sub>13</sub> H <sub>19</sub> N <sub>3</sub> S <sub>2</sub>	I, 32.03	32.03
	CH(OEt) <sub>2</sub>	2.2				3				
7-Et-3,3'-diMe-thiazolino-carbocyanine iodide	QS1	11.6	C <sub>6</sub> H <sub>5</sub> N	4 hrs.	35 <sup>f</sup> ; 29	MeOH	248-250	C <sub>13</sub> H <sub>19</sub> N <sub>3</sub> S <sub>2</sub>	I, 32.03	32.16
	CEt(OMe) <sub>2</sub>	10.8				35				
3,3',7-TriEt-thiazolinocarbocyanine iodide (VIII)	QS2	9.0	C <sub>6</sub> H <sub>5</sub> N	3 hrs.	27 <sup>f</sup> ; 13	MeOH	182-184	C <sub>15</sub> H <sub>21</sub> N <sub>3</sub> S <sub>2</sub>	I, 29.91	29.92
	CEt(OMe) <sub>2</sub>	8.1				10				

<sup>a</sup> After two recrystallizations. <sup>b</sup> 85% purity. <sup>c</sup> Two crops. <sup>d</sup> The dye was dissolved in very little hot methyl alcohol and acetone added. <sup>e</sup> A few drops of piperidine were added as a catalyst. <sup>f</sup> After conversion of the *p*-toluenesulfonate of the dye to iodide.

in the thiocarbocyanine series<sup>4</sup> where it was noted that 2,2'-diethylthiocarbocyanine dyes derived from 1-methylbenzothiazole invariably have their absorption maxima somewhat nearer to the red than the corresponding 2,2'-dimethyl dyes. However, it was found that 3,3',7-triethylthiazolino-carbocyanine iodide (VIII), in the preparation of which ethyl orthopropionate was used,<sup>4</sup> has its absorption maximum at 4600 Å., *i. e.*, introduction of a 7-ethyl group shifts the absorption maximum 165 Å. nearer to the red. This is the reverse of what was found under similar circumstances in the thiocarbocyanine series. 7-Ethyl-3,3'-dimethylthiazolinocarbocyanine iodide has its maximum absorption at 4550 Å.

The new dyes derived from 2-methylthiazoline are of special interest because they absorb at shorter wave lengths than the corresponding derivatives of any other heterocyclic base thus far applied to cyanine dye formation. This record was previously held by dyes derived from 1-methylbenzoxazole. The new dyes are also photographic sensitizers,<sup>5</sup> some being of considerable power.

We wish to acknowledge our debt to Mr. E. E. Richardson and Dr. L. A. Jones, who provided us with the absorption curves of methyl alcoholic solutions of all the dyes described in this and in the previous paper, and also to Dr. L. T. Hallett

(4) Brooker and White, *THIS JOURNAL*, **67**, 2480 (1935).

(5) Brooker, U. S. Patent 1,942,854; British Patent 385,332.

for the analytical results, and to several other colleagues for the photographic tests.

### Experimental

**Quaternary Salts.**—The quaternary salts used are numbered as follows:

- QS1: 2-methylthiazoline metho-*p*-toluenesulfonate
- QS2: 2-methylthiazoline etho-*p*-toluenesulfonate
- QS3: 2-methylthiazoline methiodide
- QS4: 2-methylthiazoline ethiodide
- QS5: 2-iodopyridine ethiodide
- QS6: 2-iodoquinoline ethiodide
- QS7: 2-iodo- $\beta$ -naphthoquinoline ethiodide
- QS8: quinoline ethiodide

The first two of these were obtained by heating equimolecular proportions of the compounds at 100° for one hour (metho-salt) or one day (etho-salt). These were used without purification.

**2-Methylthiazoline<sup>6</sup> methiodide** was prepared by heating the components under reflux on the water-bath overnight (initial reaction rapid); yield of washed (acetone) product 77%; colorless crystals *ex* methyl alcohol m. p. 241-242° (dec.).

*Anal.* Calcd. for C<sub>5</sub>H<sub>10</sub>INS: I, 52.20; S, 13.18. Found: I, 52.80; S, 13.20.

**2-Methylthiazoline ethiodide** was similarly prepared (refluxed one day); yield of washed (acetone) product 63%; colorless needles *ex* methyl alcohol-acetone, m. p. 190-193°.

*Anal.* Calcd. for C<sub>5</sub>H<sub>12</sub>INS: I, 49.37. Found: I, 49.36.

**Dyes.**—The dye condensations are summarized in Table I and were carried out in the usual fashions. Tri-

(6) Wenker [*THIS JOURNAL*, **67**, 1079 (1935)] has recently improved the preparation of the base.

ethylamine was used in the condensations of the 2'-cyanine type. In the preparation of V, a 100% excess of quinoline ethiodide and of potassium hydroxide was used, the yield being considerably higher (with respect to 2-methylthiazoline ethiodide) than when equimolecular proportions of the reactants were taken. The amount of solvent required for each reaction is shown as well as that required for the recrystallization of the product. The yield of crude washed dye is given, and also the yield after recrystallization.

In most cases the melting of a cyanine dye is accompanied by decomposition. However, it was noticed that II melted without decomposition. With III there was slight decomposition and IV melted with decomposition and gas evolution. Melting of the other dyes (Table I) was accompanied by more or less profound decomposition.

The appearance of the dyes was as follows: II, large pale yellow prisms; III, yellow-orange prisms; IV, scarlet needles; V, lustrous brown prisms; VI, orange powder; 3,3'-dimethylthiazolinocarbocyanine iodide, brownish amber prisms with blue reflex; VII, orange-brown needles with blue reflex; 7-ethyl-3,3'-dimethylthiazolinocarbo-

cyanine iodide, brown needles with blue reflex; VIII, orange powder.

The dyes were compared photographically by incorporation in a chloride emulsion. A list of wave lengths follows giving the approximate position of maximum sensitivity conferred by each dye, the order being that used above and the maxima being read directly from the individual wedge spectrograms: 4250, 4600, 4750, 4800, 5300, 4750, 4750, 4830 and 4830 Å.

### Summary

1. A base containing a partially saturated nucleus, 2-methylthiazoline, has been used for the preparation of cyanine dyes.

2. The new dyes are of special interest because their absorption bands lie at shorter wave lengths than those of corresponding derivatives of any other heterocyclic base thus far applied to cyanine dye formation.

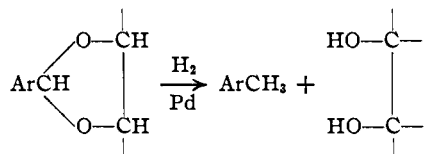
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

## Synthesis of 1,2-Monoacetone-5,6-benzophenone- $\alpha$ -*d*-glucofuranose. Catalytic Hydrogenation of Acetals of Aromatic Ketone Sugars

BY PHILIPPOS E. PAPADAKIS

It is known that acetals of aromatic aldehydes  $\text{ArCH}(\text{OR})_2$  on catalytic hydrogenation in the presence of palladium or platinum yield  $\text{ArCH}_3$  and the respective alcohols.<sup>1</sup> The application of catalytic hydrogenation to acetals of aromatic aldehydes and sugars or other polyhydroxy compounds has attracted considerable interest in the last few years.<sup>2</sup> The hydrogenation reaction takes place as follows

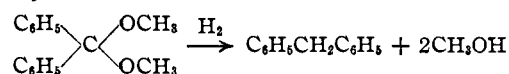


The splitting of the benzylidene residue by this method has been used advantageously, instead of acid hydrolysis, wherever the latter is objectionable. Thus sugars which have part of their hydroxyl groups blocked as above become convenient starting materials in synthetic work.

(1) T. Kariyone and Y. Kimura, *J. Pharm. Soc. Japan*, 51-52 (1923).

(2) K. Freudenberg, H. Toepffer and C. C. Andersen, *Ber.*, 61, 1759 (1928); N. M. Carter, *ibid.*, 63, 1684 (1930); M. Bergmann and N. M. Carter, *Z. physiol. Chem.*, 191, 211 (1930); L. Zervas and P. Sessler, *Ber.*, 66, 1326 (1933); L. Zervas, *ibid.*, 64, 2289 (1931).

In the present work, it is shown that acetals of aromatic ketones are affected similarly; the dimethyl acetal of benzophenone for example, gives on catalytic hydrogenation<sup>3</sup> diphenylmethane and methyl alcohol as follows



The acetals of aliphatic ketones do not show such reactions.

Since the benzophenone residue can be split off easily in this way, it was thought that benzophenone derivatives of sugars could be prepared and tested as above. Benzophenone derivatives, as far as the present author is aware, are not known. The methods used for the preparation of acetone sugars are neither convenient nor easy to use for the preparation of benzophenone sugars. The preparation of the latter is accomplished by allowing benzophenone chloride to react with sugar in dry pyridine at 0°. Thus benzophenone acetone glucose was prepared from 1,2-monoacetone glucose and benzophenone chloride. It was expected that the benzophenone residue would

(3) It is expected that the splitting of the benzophenone residue may be accomplished with sodium amalgam.