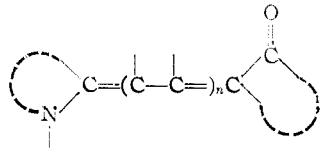
[COMMUNICATION NO. 1396 FROM THE KODAK RESEARCH LABORATORIES]

Studies in the Cyanine Dye Series. XI.[1] The Merocyanines

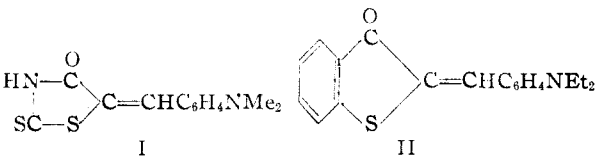
BY L. G. S. BROOKER, G. H. KEYES, R. H. SPRAGUE, R. H. VANDYKE, E. VANLARE, G. VANZANDT AND F. L. WHITE

Methods of preparation are described for a large group of un-ionized dyes, called *merocyanines*, characterized by the amide resonance system, $>N-(C=C-)_nC=O \longleftrightarrow >\overset{\oplus}{N}=(C-C=)_nC-\overset{\ominus}{O}$. In these new dyes the nitrogen and carbonyl "ends" of the amide system are generally included in rings, as shown in the general formula



although compounds having the carbonyl end in an open-chain system need not be excluded from the class. The colors of the dyes vary from almost colorless to greenish-blue; many of them are strong photographic sensitizers.

While searching for photographic sensitizing dyes of new types it was found that *p*-dialkylaminobenzylidene derivatives of certain keto-methylene compounds were sensitizers.[2] These dyes include, for example, 5-(*p*-dimethylaminobenzylidene)-rhodanine (I) (Feigl's reagent for silver) and 2-*p*-diethylaminobenzylidene - 3(2H) - thianaphthenone (II). The color-conferring system common to

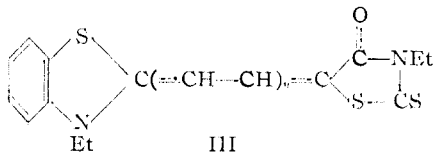


I II

these is the amidic grouping, $>N-(C=C-)_nC=O \longleftrightarrow >\overset{\oplus}{N}=(C-C=)_nC-\overset{\ominus}{O}$, and it was considered worthwhile to prepare other dyes containing this system, but in which the nitrogen atom formed part of a heterocyclic ring.

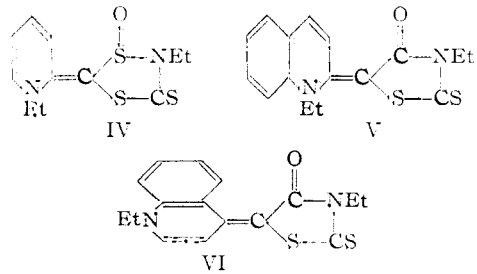
Many such dyes have now been prepared, and of a wide variety of types.[3] In general, they may be obtained by the condensation of keto-methylene compounds, which may be cyclic or otherwise, with cyclic intermediates which contribute the nitrogen end of the amidic chromophoric system. The new dyes thus formed include a number that are strong photographic sensitizers.[3a]

It is perhaps simplest to outline the nature of the reactions and the products which are formed, by citing specific examples. Thus, starting with the cyclic keto-methylene compound, 3-ethylrhodanine, and condensing this with intermediates which contribute the benzothiazole ring, it is possible to prepare the vinylogous series of dyes, III. Since a portion of the molecule of one of these dyes is identical with that present in a cyanine, the general name "merocyanine" (*μερος*, part) was suggested to us by Dr. Frances M. Hamer, and this name has now appeared in a number of publications.



III

The first member of the series, III (*i.e.*, $n = 0$), may be obtained in good yield by the condensation of 2-phenylmercaptobenzothiazole ethiodide with 3-ethylrhodanine in alcoholic solution using triethylamine as condensing agent. If the benzothiazole salt in this reaction is replaced by 2(or 4)-phenylmercaptopyridine ethiodide, the product is a compound such as IV, while use of 2(or 4)-phenylmercapto (or iodo)-quinoline ethiodide yields a quinoline derivative such as V or VI. Compounds of the latter type are also obtainable by condensing quinoline ethiodide with 3-ethylrhod-



IV V VI

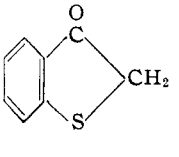
(1) Part X, THIS JOURNAL, **73**, 1094 (1951).

(2) L. G. S. Brooker, U. S. Patent 2,089,729 (1937); Kodak Ltd. British Patent 449,527 (1936). Observations in the same general field were made independently by J. D. Kendall, British Patents 428,222, 428,360 (1935).

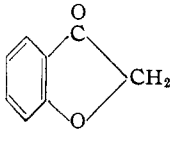
(3) (a) L. G. S. Brooker and collaborators, U. S. Patents 2,078,233 (1937). 2,153,169; 2,161,331; 2,165,219; 2,165,338; 2,170,803-2,170,807; 2,177,401-2,177,403 (1939). 2,185,182; 2,185,343; 2,186,624; 2,211,762 (1940). 2,231,659; 2,263,757 (1941). 2,282,116 (1942). 2,341,357 (1944). 2,409,189 (1946). 2,430,558 (1947). 2,441,530; 2,454,629 (1948). 2,493,747-2,493,748; 2,494,031; 2,519,001; 2,526,632 (1950). Kodak, Ltd., British Patents 450,958 (1936,). 466,097; 466,244; 470,726 (1937). 493,455 (1938). 518,904 (1940). 532,098 (1941). 557,294 (1943). 577,548 (1946). 599,631; 599,636; 603,492; 606,141 (1948). 618,073; 625,446 (1949). (b) The study of the merocyanines was well advanced in our laboratory when patents were issued from another source [J. D. Kendall, British Patents: 426,718; 428,222; 428,360; 428,359; 432,628 (1935)]. The present paper is a description of our entirely independent results. (c) Some merocarbocyanines derived from 3(2H)-thianaphthenone were also described by T. Ogata [*Bull. Inst. Phys. Chem. Res., Tokyo*, **13**, 556 (1934)] but dyes of this particular subgroup had already been made by us before Ogata's publication appeared. (d) G. Schwarz has described the independent preparation of dyes of certain types dealt with in the present paper [Beilage No. 1, p. 1, *Phot. Korr.*, **73** (1937)]. He appears to have considered that they offered no advantages as sensitizers over other known dyes . . . "weil wir diese Farbstoffe als Sensibilisatoren gegenüber anderen bekannten Farbstoffen als unvorteilhaft betrachtet haben."

anine in the presence of potassium hydroxide. Dyes such as the foregoing, in which the two-ring systems are linked together directly, may be called "simple merocyanines," though chemical names have been used in the experimental section for the individual compounds.

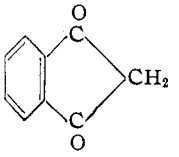
A number of cyclic keto-methylene compounds may similarly be linked with the basic nuclei of III–VI. These include the following



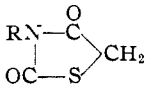
3(2H)-thianaphthenone



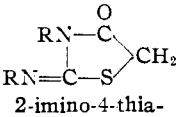
3(2H)-benzofuranone



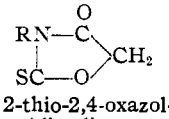
1,3-indandione



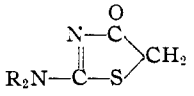
2,4-thiazolidinediones



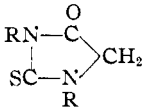
2-imino-4-thiazolidones



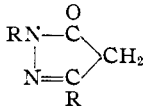
2-thio-2,4-oxazolidinediones



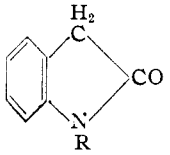
2-amino-4(5H)-thiazolones



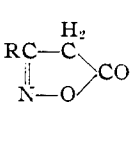
2-thiohydantoins



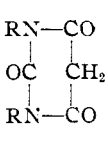
5-pyrazolones



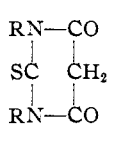
oxindoles



5(4H)-isoxazolones

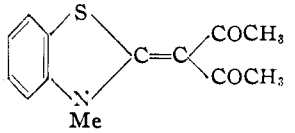


barbituric acids

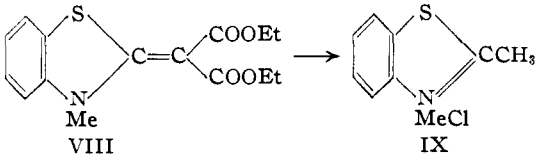


2-thiobarbituric acids

Non-cyclic keto-methylene compounds include the following: acetylacetone, ethyl malonate, malonanilide, cyanoacetamide, cyanoacetanilide, cyanoacetophenone, ethyl cyanoacetate. Thus, condensation of 2-methylmercaptobenzothiazole metho-*p*-toluenesulfonate with acetylacetone gives VII, an open-chain merocyanine that is useful in further reactions (*cf.* XII). The condensation product of the 2-methylmercaptobenzothiazolium



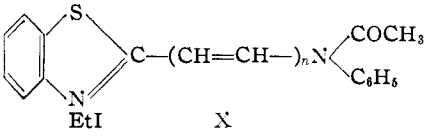
VII



VIII IX

salt with ethyl malonate gives VIII, a type which is also of interest as a dye intermediate, for hydrolysis with boiling hydrochloric acid is accompanied by spontaneous dicarboxylation, the product being 2-methylbenzothiazole methochloride (IX).[4] This reaction is of value for the conversion of quaternary salts of heterocyclic bases containing reactive alkylmercapto, or similar negative groups, into salts containing reactive methyl, when these latter are not otherwise accessible.[5] The rings which contain the nitrogen of the amidic chromophore include, besides the benzothiazole and the 2- and 4-pyridine and quinoline rings already mentioned, single-ring systems such as thiazoline, thiazole and pyrrole; condensed two-ring systems such as benzoxazole, benzoselenazole, 1-isoquinoline, pseudo-indole, benzimidazole; condensed three-ring systems such as the benzoquinolines and the naphthoxazoles and naphthothiazoles.

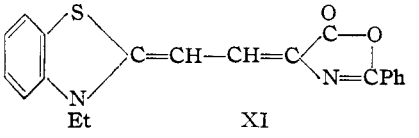
The next higher vinylogs of the simple merocyanines, such as III (n = 1) may be called "merocarbocyanines." The first representatives of this series were prepared by Rodd and Watts,[6] who treated pyrazolones containing a reactive methylene group with intermediates containing the β-anilino (or acetanilido)-vinyl group,[7] such as 2-β-acetanilidovinylbenzothiazole ethiodide (X, n = 1). However, many compounds other than pyrazolones may be employed. 3-Ethylrhodanine, for in-



EtI X

stance, condenses readily with X (n = 1), either in acetic anhydride solution in the presence of fused sodium acetate, or in alcoholic solution in the presence of triethylamine, to give III (n = 1) in high yield.

Hippuric and aceturic acids are open-chain keto-methylene compounds of a type that undergoes condensation in acetic anhydride with intermediates such as X (n = 1 or 2) with accompanying cyclization; the merocarbo(or dicarbo)-cyanines that result are derivatives of 5(4H)-oxazolones (*e.g.*, XI).[8,9]



Et XI

Merocarbocyanines containing substituents in the dimethine bridge include a number of strong sensitizers.[10] Dyes of this class, *e.g.*, XIII, may be prepared by the condensation in acetic anhydride of a reactive keto-methylene compound with a reactive pseudo-ketone such as XII. Compounds of this latter class are commonly prepared by the action of an acid chloride upon a quaternary salt containing reactive methyl (*e.g.*, IX) in cold pyridine suspension.[11] They may also be pre-

(4) L. G. S. Brooker and W. W. Williams, U. S. Patent 2,330,203 (1943).

(5) An example is given by L. G. S. Brooker, G. H. Keyes and W. W. Williams, THIS JOURNAL, **64**, 199 (1942).

(6) Imperial Chemical Industries, Ltd., E. H. Rodd and G. E. Watts, U. S. Patent 2,032,502 (1936); British Patent 366,964 (1932).

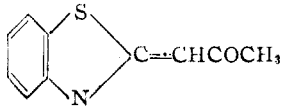
(7) Imperial Chemical Industries, Ltd., E. H. Rodd and G. E. Watts, British Patent 344,409 (1931).

(8) G. H. Keyes and L. G. S. Brooker, U. S. Patent 2,185,343 (1940).

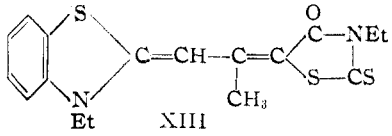
(9) See the azlactones of E. Erlenmeyer, Jr., *Ann.*, **275**, 1 (1893); *ibid.*, **337**, 265 (1904).

(10) L. G. S. Brooker and F. L. White, U. S. Patent 2,165,338 (1939).

(11) L. G. S. Brooker and F. L. White, U. S. Patent 2,112,139 (1938).



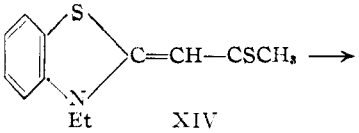
Et XII



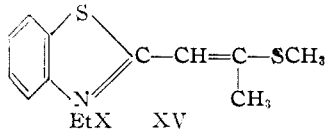
Et XIII

pared by the acid hydrolysis of acetylacetone condensation products of the type of VII.[12]

In certain cases it may be advantageous to convert the reactive pseudo-ketone (*e.g.*, XII) into the corresponding pseudo-thioketone (*e.g.*, XIV)[13] and

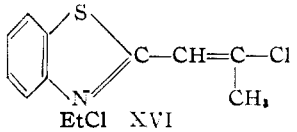


Et XIV



EtX XV

thence, by addition of alkyl *p*-toluenesulfonate or the like, into a reactive alkylmercapto intermediate (*e.g.*, XV), capable of condensing with a keto-methylene compound to give a chain-substituted merocarbocyanine (*e.g.*, XIII). Still another route to these latter dyes lies through reactive chloro(or bromo)-salts such as XVI, obtainable from the pseudo-ketones (*e.g.*, XII) by the action of phosphorus oxychloride (or oxybromide).[14]



EtCl XVI

Merodicarbocyanines such as III (n = 2) may be prepared by condensing the appropriate keto-methylene compound with acetanilidobutadienyl intermediates such as X (n = 2), and the merotricarbocyanines (*e.g.*, III, n = 3) result from the use of intermediates with still longer conjugated chains (*e.g.*, X, n = 3).

The absorption maxima of the merocyanines vary all the way from the near ultraviolet, where the dye is almost colorless, to the near infrared, where the dye is greenish-blue. A detailed examination of the relation between absorption and structure is reserved for the following paper.

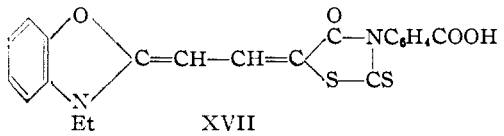
The relatively low solubility of many of the merocyanine dyes in the solvents commonly used in photographic work is sometimes a disadvantage. Increased solubility has been attained by the introduction of a carboxyl or sulfonic acid group into the keto-methylene component used in making the dyes.[15] Examples of dyes so obtained are XVII and XVIII.

(12) L. G. S. Brooker and F. L. White, U. S. Patent 2,341,357 (1944).

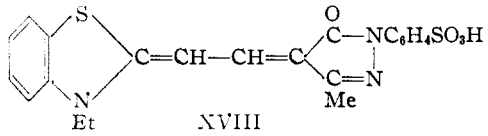
(13) L. G. S. Brooker and G. H. Keyes, U. S. Patent 2,369,647 (1945).

(14) L. G. S. Brooker and F. L. White, U. S. Patent 2,231,659 (1941).

(15) L. G. S. Brooker and F. L. White, U. S. Patent 2,526,632 (1950).



Et XVII



Et XVIII

In all cases, a merocyanine dye may be regarded as a resonance hybrid between an uncharged and a polar structure. The relative contributions of these extreme structures vary from dye to dye, and constitute a factor that not only governs the absorption, but strongly influences the dipole moment, solubility, and doubtless other physical properties (*cf.* following paper).

Because of the great number of possible merocyanine combinations, it is feasible to give the preparations of only a limited selection, even in tabular form. However, details are given in the experimental section of condensations undergone by all the keto-methylene compounds referred to.

Acknowledgment.—We wish to thank Dr. L. T. Hallett and Mr. Don Ketchum and their departments for the microanalyses.

Experimental

All melting points are corrected.

Quaternary salts used are listed below:

QS1	3-Ethyl-2-phenylmercaptobenzothiazolium iodide
QS2	2-(2-Acetanilidovinyl)-3-ethylbenzothiazolium iodide
QS3	2 (4-Acetanilido-1,3-butadienyl)-3-ethylbenzothiazolium iodide
QS4	2-(6-Acetanilido-1,3,5-hexatrienyl)-3-ethylbenzothiazolium iodide
QS5	1-Ethyl-2-iodopyridinium iodide
QS6*	1-Ethyl-2-phenylmercaptopyridinium *p*-toluenesulfonate
QS7	1-Ethyl-4-phenylmercaptopyridinium iodide
QS8	1-Ethyl-2-iodoquinolinium iodide
QS9*	1-Ethyl-2-phenylmercaptoquinolinium iodide
QS10*	1-Ethyl-4-phenylmercaptoquinolinium *p*-toluenesulfonate
QS11	1-Ethylquinolinium iodide
QS12*	3-Methyl-2-methylmercaptobenzothiazolium *p*-toluenesulfonate
QS13	2-(2-Acetanilidovinyl)-3-ethylbenzoxazolium iodide
QS14*	3-Ethyl-2-(2-methylmercaptopropenyl)-benzothiazolium *p*-toluenesulfonate
QS15*	2-(2-Chloropropenyl)-3-ethylbenzothiazolium chloride

Keto-methylene compounds used are:

KM1	3-Ethylrhodanine
KM2	Acetylacetone
KM3	Ethyl malonate
KM4	3(2H)-Thianaphthenone
KM5	5-Methoxy-3(2H)-benzofuranone
KM6	1,3-Indandione
KM7	3-Phenyl-2,4-thiazolidinedione
KM8	3-Phenyl-2-phenylimino-4-thiazolidone
KM9	3-Ethyl-2 thio-2,4-oxazolidinedione
KM10	2-Diphenylamino-4(5H)-thiazolone
KM11*	3-Ethyl-1-phenyl-2-thiohydantoin
KM12	3-Methyl-1-phenyl-5-pyrazolone
KM13	1-Ethyloxindole
KM14	Hippuric acid
KM15	3-Phenyl-5(4H)-isoxazolone
KM16	1,3-Diethylbarbituric acid
KM17*	1,3-Diethyl-2-thiobarbituric acid
KM18	Malonanilide

KM19 Cyanoacetamide
KM20 Cyanoacetanilide
KM21 Benzoylacetonitrile
KM22 Ethyl cyanoacetate
KM23* 3-*p*-Carboxyphenylrhodanine
KM24 3-Methyl-1-*p*-sulfophenyl-5-pyrazolone

Details of the preparation of the nine compounds marked with an asterisk follow, together with those of certain necessary intermediates.

2-Phenylmercaptopyridine.—Triethylamine (178 g., 2 mols.) was added in small portions, with shaking, to a mixture of 2-chloropyridine (100 g., 1 mol.) and of thiophenol (194 g., 2 mols.). The reaction mixture became warm and was heated for 2 days at 100°. After the mixture had been made alkaline, it was extracted four times with 500 ml. of benzene, the combined extracts were washed and the solvent was evaporated. After distillation, the product formed a colorless oil, b.p. 160–162° (8 mm.); yield 93%; it was used directly for the next step.

1-Ethyl-2-phenylmercaptopyridinium *p*-Toluenesulfonate (QS6).—A mixture of 2-phenylmercaptopyridine (18.7 g., 1 mol.) and ethyl *p*-toluenesulfonate (20 g., 1 mol.) was heated for 42 hours in an oil-bath at 135–140°. The solid was pulverized, well washed with acetone and dried; yield 85%. A sample recrystallized from acetone formed colorless crystals, m.p. 142–144°.

Anal. Calcd. for $C_{20}H_{21}NO_3S_2$: C, 61.97; H, 5.47. Found: C, 62.0; H, 5.2.

2-Phenylmercaptoquinoline.—Triethylamine (328 g., 1.1 mols.) was added in several portions, with shaking, to a mixture of 2-chloroquinoline (500 g., 1 mol.) and thiophenol (650 g., 2 mols.). Much heat now developed and solid separated. The mixture was heated on a steam-bath for 2 days. The solid was treated with water, made alkaline, extracted with ether, the ether solution dried over anhydrous potassium carbonate and distilled. The nearly colorless oil had b.p. 190° (1 mm.), yield 681 g. (93%).

1-Ethyl-2-phenylmercaptoquinolinium Iodide (QS9).—A mixture of 2-phenylmercaptoquinoline (237 g., 1 mol.) and ethyl iodide (300 g., 2 mols.) was heated on a steam-bath for 2 days. The solid cake was pulverized, washed with acetone and dried; yield 80%. After recrystallization from ethyl alcohol, the bright yellow crystals had m.p. 180–181° dec.

Anal. Calcd. for $C_{17}H_{16}INS$: I, 32.29. Found: I, 32.5.

4-Phenylmercaptoquinoline.—Thiophenol (22.4 g., 2 mols.) was added slowly to 4-chloroquinoline (16.7 g., 1 mol.) with shaking; considerable heat was evolved. Triethylamine (20.6 g., 2 mols.) was then added in four portions and the mixture heated overnight on a steam-bath. The product was dissolved in 500 ml. of water, made alkaline and extracted with ether, the extract dried over calcium chloride and distilled. The colorless oil, b.p. 214–221° (8 mm.), yield 90%, was used directly for the next step.

1-Ethyl-4-phenylmercaptoquinolinium *p*-Toluenesulfonate (QS10).—A mixture of 4-phenylmercaptoquinoline (21.8 g., 1 mol.) and ethyl *p*-toluenesulfonate (18.5 g., 1 mol.) was heated for 24 hours at 110°. The product was cooled, pulverized, and washed with acetone; yield 93%. After recrystallization from acetone, the colorless crystals had m.p. 151–153°.

Anal. Calcd. for $C_{24}H_{23}NO_3S_2$: C, 65.86; H, 5.30. Found: C, 66.1; H, 5.4.

3-Methyl-2-methylmercaptobenzothiazolium *p*-Toluenesulfonate (QS12).—A mixture of 2-methylmercaptobenzothiazole (36.2 g., 1 mol.) and methyl *p*-toluenesulfonate (37.2 g., 1 mol.) was heated for 16 hours at 110°. The solid cake was pulverized, washed with acetone, and dried. The light grayish crystals (yield 99%) were used without further purification.

3-Ethyl-2-thioacetylmethylenebenzothiazoline (XIV).—2-Acetylmethylene-3-ethylbenzothiazoline (XII, 43.8 g., 1 mol.) was dissolved in dry pyridine (100 ml.) and phosphorus pentasulfide (22.2 g., 0.5 mol.) added in portions with shaking. The mixture was refluxed for 13 minutes and poured into 3 l. of water containing 1 g. of detergent (Dreft). The product separated immediately as a dark powder. It was filtered off, washed well with water and dried; yield 60%. The product was used without further purification. It could be purified by extraction with ligroin (b.p. 90–120°), and was then obtained as bright yellow crystals with m.p. 142–144° dec.

Anal. Calcd. for $C_{12}H_{13}NS_2$: C, 61.22; H, 5.57. Found: C, 61.14; H, 5.59.

3-Ethyl-2-(2-methylmercaptopropenyl)-benzothiazolium *p*-Toluenesulfonate (QS14).—A mixture of 3-ethyl-2-thioacetylmethylenebenzothiazoline (XIV) (117 g., 1 mol.) and methyl *p*-toluenesulfonate (186 g., 2 mols.) was heated for 18 hours at 100°. The solid cake was pulverized, washed with ether and then acetone, yield 143 g. (68%) of white crystals, suitable for further use without additional purification. A portion converted to the iodide consisted of colorless crystals with m.p. 234–236° dec.

Anal. Calcd. for $C_{13}H_{16}INS_2$: I, 33.65. Found: I, 33.69.

2-(2-Chloropropenyl)-3-ethylbenzothiazolium Chloride (QS15).—Phosphorus oxychloride (68.8 g., 1.5 mols.) was added to a suspension of 2-acetylmethylene-3-ethylbenzothiazoline (65.7 g., 1 mol.) in dry benzene (200 ml.), with stirring, and stirring maintained for an additional 10 minutes. The solid which separated was filtered off and washed well with acetone. The colorless solid (yield 74 g., 90%) was used without further purification.

3-Ethyl-1-phenyl-2-thiohydantoin (KM11).—A mixture of phenylglycine ethyl ester (17.9 g., 1 mol.) and ethyl isothiocyanate (8.7 g., 1 mol.) was heated at 100° for 4 days. The solid product was pulverized under methyl alcohol and filtered off; yield 12.5 g. (57%). After recrystallization from methyl alcohol, the yield was 9.7 g. (44%) of almost colorless glistening plates, m.p. 125.5–128.5°.

Anal. Calcd. for $C_{11}H_{12}N_2OS$: N, 12.73. Found: N, 12.74.

1,3-Diethyl-2-thiobarbituric Acid (KM17).—A solution of sodium ethylate was prepared by dissolving sodium (110 g., 1 mol. + 100% excess) in absolute ethyl alcohol (1500 ml.). Ethyl malonate (768 g., 1 mol. +100% excess) was added to this solution, with stirring, followed by the addition of symmetrical diethylthiourea (317 g., 1 mol.). The mixture was then heated on a steam-bath with stirring for 8 hours and without stirring for a further 72 hours. The reaction mixture was cooled somewhat and water (1500 ml.) added carefully. Most of the alcohol was then removed by distillation under reduced pressure. The residue was poured into cold water (2 l.), chilled and filtered. The filtrate was acidified with dilute hydrochloric acid, and the product filtered off, washed with water and dried; yield 99% of nearly colorless crystals. A sample recrystallized from ethyl alcohol had m.p. 103–105°.

Anal. Calcd. for $C_8H_{12}N_2O_2S$: C, 47.98; H, 6.04. Found: C, 48.3; H, 6.3.

3-*p*-Carboxyphenylrhodanine (KM23) was made by the method of Holmberg.[16] *p*-Aminobenzoic acid (13.7 g., 1 mol.) was dissolved in a solution of anhydrous sodium carbonate (5.3 g.) in water (100 ml.). To this solution was added di-(carboxymethyl)-trithiocarbonate[17] (22.6 g., 1 mol.) and the mixture heated on a steam-bath overnight. The solution was chilled, acidified with dilute sulfuric acid, filtered and the residue washed with water and dried. A yield of 21.3 g. (96%) of a slightly yellow powder of m.p. 268–270° dec. was obtained. It was used without further purification.

2-Acetylmethylene-3-ethylbenzothiazoline (XII).—A suspension of 3-ethyl-2-methylbenzothiazolium *p*-toluenesulfonate (87 g., 1 mol.) in pyridine (200 ml.) was cooled to 0° and acetyl chloride (29.4 g., 1.5 mols.) added slowly, with stirring. The stirring was continued for an additional 15 minutes, the reaction mixture allowed to come to room temperature and then heated on a steam-bath for 10 minutes. Most of the pyridine was removed under reduced pressure and the residue stirred with water (one liter). The product was filtered off, washed with water and dried; yield 47.8 g. (87%) of pinkish solid. The product was purified by extraction with hot ligroin (b.p. 60–90°) from which it separated in pale yellow needles, m.p. 111–113°; yield 34.2 g. (63%).

Anal. Calcd. for $C_{12}H_{13}NOS$: C, 65.72; H, 5.69; N, 6.39. Found: C, 65.35; H, 5.69; N, 6.30.

2-Acetylmethylene-3-methylbenzothiazoline (*cf.*, **XII**).—2-Diacetylmethylene-3-methylbenzothiazoline (VII) (0.25 g., 1 mol.) was heated on a steam-bath for 50 minutes with concentrated hydrochloric acid (5 ml.). The cooled reac-

(16) B. Holmberg, *J. prakt. Chem.*, **81**, 451 (1910).
(17) B. Holmberg, *ibid.*, **71**, 264 (1905).

TABLE I

DETAILS OF DYE SYNTHESES

Dye no.	Name	Formula	Reactants, g.		Medium, ml.		Refluxed, min.	Yield, %	Solvent, ml./g.		M.p., °C. dec.	Formula	Analyses, % Calcd.	Found
Simple merocyanines														
M1	3-Et-5-(3-Et-2(3H)-benzothiazolylidene)-rhodanine	III (n = 0)	QS1 KM1	2.0 0.8	EtOH	50	10	71, 34	C_5H_5N	13	246–248	$C_{14}H_{14}N_2OS$	C, 52.12 H, 4.38	52.0 4.24
M2a	3-Et-5-(1-Et-2(1H)-pyridylidene)-rhodanine	IV	QS5 KM1	3.6 1.6	EtOH	35	15	55, 22	MeOH	45	144·145	$C_{12}H_{14}N_2OS_2$	C, 54.08 H, 5.30	54.16 5.23
M2b	3-Et-5-(1-Et-2(1H)-pyridylidene)-rhodanine	IV	QS6 KM1	1.9 0.8	EtOH	15	15	61, 52	MeOH	45	145–146	$C_{12}H_{14}N_2OS_2$	C, 54.08 H, 5.30	54.4 5.4
M3	3-Et-5-(1-Et-4(1H)-pyridylidene)-rhodanine		QS7 KM1	3.5 1.6	EtOH	20	30	74, 45	MeOH	210	233–235	$C_{12}H_{14}N_2OS_2$	N, 10.52	10.45
M4a	3-Et-5-(1-Et-2(1H)-quinolylidene)-rhodanine	V	QS8 KM1	4.1 1.6	EtOH	30	15	84, 60	HOAc	20	194–196	$C_{16}H_{16}N_2OS_2$	N, 8.86	8.99
M4b	3-Et-5-(1-Et-2(1H)-quinolidene)-rhodanine	V	QS9 KM1	2.0 0.8	EtOH	15	20	91, 72	HOAc	20	194–196	$C_{16}H_{16}N_2OS_2$	C, 60.70 H, 5.10	60.9 5.1
M5a	3-Et-5-(1-Et-4(1H)-quinolylidene)-rhodanine	VI	QS10 KM1	2.2 0.8	EtOH	30	15	92, 78	HOAc	300	203–205	$C_{16}H_{16}N_2OS_2$	C, 60.7 H, 5.1	61.1 5.2
M5b	3-Et-5-(1-Et-4(1H)-quinolylidene)-rhodanine	VI	QS11 KM1 KOH	5.7 1.6 1.4	EtOH	50	10	60, 27	HOAc	300	204–206	$C_{16}H_{16}N_2OS_2$	N, 8.86	8.82
M6	2-Diacetylmethylene-3-Me-benzothiazoline	VII	QS12 KM2	7.34 6.0	EtOH	10	10	67, 38	EtOH 95%	4	140–141	$C_{13}H_{13}NO_2S$	C, 63.11 H, 5.30	62.61 5.38
M7	2-Di(ethoxycarbonyl)-methylene-3-Me-benzothiazoline	VIII	QS12 KM3	12.3 10.7	EtOH	30	30	72, 50	EtOH	7	121–122	$C_{15}H_{17}NO_4S$	N, 10.44	10.42
Merocarbocyanines														
M8	3-Et-5-[(3-Et-2(3H)-benzothiazolylidene)-ethylidene]-rhodanine	III (n = 1)	QS2 KM1	4.5 1.6	EtOH	30	15	86, 60	HOAc	140	268·270	$C_{16}H_{16}N_2OS_4$	N, 8.04	8.06
M9	2-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-3(2H)-thianaphthenone		QS13 KM4	2.2 0.75	EtOH	25	13	81, 65	MeOH	150	209–210	$C_{19}H_{16}NO_2S$	C, 70.98 H, 4.71	71.03 4.48
M10	2-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-5-MeO-3(2H)-benzofuranone		QS13 KM5	4.3 1.6	EtOH	50	45	69, 57	MeOH	175	217·219	$C_{20}H_{17}NO_4$	C, 71.63 H, 5.12	71.38 5.46
M11	2-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-1,3-indandione		QS13 KM6	1.1 0.4	EtOH	15	15	94, 75	MeOH	350	286–287	$C_{20}H_{13}NO_3$	N, 4.42	4.58
M12	5-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-3-Ph-2,4-thiazolidinedione		QS13 KM7	2.2 1.0	EtOH	20	15	56, 47	HOAc	50	272–273	$C_{20}H_{16}N_2O_3S$	N, 7.70	7.63
M13	3-Et-5-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-2-thio-2,4-oxazolidinedione		QS13 KM9	2.2 0.7	EtOH	20	15	56, 25	HOAc	50	273–276	$C_{15}H_{16}N_2O_3S$	N, 8.86	8.61
M14	5-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-3-Ph-2-PhN-4-thiazolidone		QS13 KM8	2.2 1.35	EtOH	20	120	60, 27	EtOH	125	236–239	$C_{26}H_{21}N_3O_2S$	N, 9.57	9.55
M15	2-Ph_2N-5-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-4(5H)-thiazolone		QS13 KM10	2.2 1.35	EtOH	25	10	36, 20	MeOH	250	248–250	$C_{26}H_{21}N_3O_2S$	N, 9.57	9.46
M16	3-Et-5-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-1-Ph-2-thiohydantoin		QS13 KM11	4.3 2.2	EtOH	35	15	61, 36	HOAc	25	266·268	$C_{22}H_{21}N_3O_2S$	N, 10.74	10.58
M17	4-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-3-Me-1-Ph-5-pyrazolone		QS13 KM12	4.3 1.7	EtOH	20	15	83, 63	MeOH	13	210·213	$C_{23}H_{19}N_3O_2$	N, 12.17	12.02
M18	1-Et-3-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-oxindole		QS13 KM13	2.2 0.8	EtOH	10	30	30, 9	MeOH	160	196–198	$C_{21}H_{20}N_2O_2$	N, 8.43	8.41

TABLE I (*Continued*)

Dye no.	Name	Formula	Reactants, g.		Medium, ml.		Refluxed, min.	Yield, %	Solvent, ml./g.		M.p., °C. dec.	Formula	Analyses, % Calcd.	Found
M19	4-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-2-Ph-5(4H)-oxazolone	XI	QS13 KM14 NaOAc (fused)	2.2 0.9 0.4	Ac_2O	15	10	70, 29	HOAc	25	233–235	$C_{20}H_{16}N_2O_3$	N, 8.44	8.50
M20	4-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-3-Ph-5(4H)-isoxazolone		QS13 KM15	2.2 0.8	C_5H_5N	10	10	77, 59	MeOH	130	252–253	$C_{20}H_{16}N_2O_3$	N, 8.44	8.56
M21	1,3-DiEt-5-[(3-Et-2(3H)-benzothiazolylidene)-ethylidene]-barbituric acid		QS2 KM16	2.2 0.9	C_5H_5N	20	10	81, 70	HOAc	100	325–327	$C_{19}H_{21}N_2O_3S$	C, 61.42 H, 5.70	61.44 5.84
M22	1,3-DiEt-5-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-2-thiobarbituric acid		QS13 KM17	2.2 1.0	EtOH	35	30	80, 43	C_5H_5N·MeOH[a]		302–303	$C_{19}H_{21}N_3O_2S_2$	C, 61.41 H, 5.70	61.40 5.68
M23	2-[3,3-Di-(phenylcarbamyl)-allylidene]-3-Et-benzothiazoline		QS2 KM18	2.25 1.3	EtOH	20	10	86, 37	HOAc	20	244–245	$C_{26}H_{23}N_3O_2S$	N, 9.52	9.76
M24	2-(3-Carbamyl-3-cyanoallylidene)-3-Et-benzothiazoline		QS2 KM19	4.5 0.85	EtOH	25	10	88, 63	MeOH	210	255–256	$C_{14}H_{13}N_3OS$	N, 15.49	15.29
M25	2-(3-Cyano-3-phenylcarbamylallylidene)-3-Et-benzothiazoline		QS2 KM20	2.25 0.8	EtOH	20	15	92, 58	HOAc	20	240–243	$C_{20}H_{17}N_3OS$	N, 12.10	11.83
M26	2-(3-Benzoyl-3-cyanoallylidene)-3-Et-benzothiazoline		QS2 KM21	2.25 0.7	EtOH	20	15	93, 51	HOAc	10	215–216	$C_{20}H_{16}N_2OS$	N, 8.44	8.40
M27	2-(3-Cyano-3-ethoxycarbonylallylidene)-3-Et-benzothiazoline		QS2 KM22	4.5 1.1	EtOH	25	10	86, 68	MeOH	180	172–174	$C_{16}H_{16}N_2O_2S$	N, 9.34	9.21
M28a	3-Et-5-[(3-Et-2(3H)-benzothiazolylidene)-isopropylidene]-rhodanine	XIII	XII KM1	2.2 1.6	Ac_2O	10	30	22, 15	HOAc	75	219–220	$C_{17}H_{18}N_2OS_3$	C, 56.30 H, 5.00	56.24 5.12
M28b	3-Et-5-[(3-Et-2(3H)-benzothiazolylidene)-isopropylidene]-rhodanine	XIII	QS14 KM1	4.2 1.6	EtOH	15	45	68, 48	HOAc	75	215–216[d]			
M28c	3-Et-[(3-Et-2(3H)-benzothiazolylidene)-isopropylidene]-rhodanine	XIII	QS15 KM1	3.6 1.6	EtOH	15	20	58, 43	HOAc	75	215–216	$C_{17}H_{18}N_2OS_3$	C, 56.3 H, 5.0	56.3 5.1
M29	3-*p*-Carboxyphenyl-5-[(3-Et-2(3H)-benzoxazolylidene)-ethylidene]-rhodanine	XVII	QS13 KM23	2.2 1.1	EtOH	25	30	71, 64	MeOH[b]		>300	$C_{21}H_{16}N_2O_4S_2$	S, 15.11	15.00
M30	4-[(3-Et-2(3H)-benzothiazolylidene)-ethylidene]-3-Me-1-*p*-sulfophenyl-5-pyrazolone	XVIII	QS2 KM24	4.5 2.54	EtOH	25	20	66, 36	H_2O[c]		>325	$C_{21}H_{19}N_3O_4S_2$	C, 57.11 H, 4.34	57.46 4.25
								Merodicarbocyanine						
M31	3-Et-5-[(3-Et-2(3H)-benzothiazolylidene)-2-butenylidene]-rhodanine		QS3 KM1	1.2 0.4	EtOH	20	10	91, 21	HOAc	53	239–241	$C_{18}H_{18}N_2OS_3$	C, 57.74 H, 4.84	57.98 4.80
								Merotricarbocyanine						
M32	3-Et-5-[(3-Et-2(3H)-benzothiazolylidene)-2,4-hexadienylidene]-rhodanine		QS4 KM1	1.25 0.4	EtOH	10	15	25, 15	C_5H_5N·MeOH[a]		231–233	$C_{20}H_{20}N_2OS_3$	C, 59.94 H, 5.03	59.78 4.89

[a] Dissolved in C_5H_5N and pptd. with MeOH. [b] Dissolved in MeOH with NEt_3 and pptd. with HOAc. [c] Dissolved in H_2O as C_5H_5N salt and pptd. with concd. HCl. [d] M.p. and mixed m.p. with authentic specimen.

tion mixture was made alkaline with aqueous sodium hydroxide, filtered and washed with water; yield 0.2 g. (97.5%) of colorless crystals. After recrystallization from ligroin (b.p. 90–120°), the product melted at 160–161°.

Anal. Calcd. for $C_{11}H_{11}NOS$: C, 64.34; H, 5.40 Found: C, 64.01; H, 5.64.

2,3-Dimethylbenzothiazolium Perchlorate (IX).—2-(Diethoxycarbonyl)-methylene-3-methylbenzothiazoline (VIII) (5.0 g., 1 mol.) was refluxed for 20 minutes with 15% hydrochloric acid (25 ml.). After evaporation to dryness, the residue was dissolved in hot water, filtered and converted to the perchlorate using sodium perchlorate; yield 4.1 g. (95%) of colorless crystals. After recrystallization from ethyl alcohol, the m.p. of 124–125° was identical with that of a specimen obtained from 2,3-dimethylbenzothiazolium iodide. The mixed m.p. showed no depression.

Details of the preparation of the dyes are listed in Table I.

The necessary reactants were heated together in the specified medium for the period indicated. Triethylamine (5% excess above the calculated amount) was used as the condensing agent in all cases except two (M5b, M19), where another condensing agent is given and three (M20, M21, M28a), where no condensing agent was required beyond the solvent used for the reaction. Merocyanine dye (M1–M32) separated either spontaneously or on cooling. The yield of crude, but washed, dye is given, followed by the yield after two recrystallizations from the solvent indicated. All of the dyes except M6 and M7 melted with decomposition.

The dyes appear as follows: M1, yellow crystals with blue reflex; M2, brownish needles with green reflex; M3, yellowish-orange flakes; M4, garnet crystals with green reflex; M5, red needles with blue reflex; M6, very pale yellow needles; M7, colorless crystals; M8, reddish-brown needles with blue and green reflex; M9, reddish-brown prisms with green reflex; M10, red needles with blue reflex; M11, orange-red needles with blue reflex; M12, orange crystals with blue reflex; M13, yellow-orange needles; M14, orange crystals; M15, lustrous yellow-orange plates; M16, orange needles with blue reflex; M17, red crystals with green reflex; M18, orange crystals; M19, red powder; M20, orange-yellow needles with blue reflex; M21, reddish-orange crystals; M22, orange crystals; M23, fine orange crystals; M24, brownish-golden plates; M25, orange-brown prisms with blue reflex; M26, garnet needles with blue reflex; M27, brownish-orange needles; M28, dark needles with blue reflex; M29, red crystals with golden reflex; M30, yellow-orange crystals; M31, minute blue-green crystals; M32, emerald green crystals.

ROCHESTER 4, NEW YORK RECEIVED APRIL 11, 1951

[COMMUNICATION NO. 1397 FROM THE KODAK RESEARCH LABORATORIES]

Color and Constitution. X.[1] Absorption of the Merocyanines[2]

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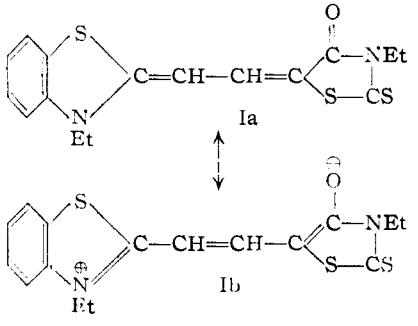
In a merocyanine an additional double bond enters *each* of the two rings of the dye in the dipolar resonance structure with $>\overset{\oplus}{N}=C(-C=C)_n-\overset{\ominus}{O}$. Depending on the rings paired in the dye, stabilization thus acquired may be low, or high, or have any intermediate value. If such stabilization is low, the dye has low intrinsic polarity: it will show large $\lambda_{max.}$ deviations in all solvents and $\lambda_{max.}$ will tend to shift to longer wave lengths with increasing polarity of the solvent, especially for the higher vinylogs of a series. If the stabilization is moderate, the dye may show a negligible deviation in a solvent of moderate polarity such as methanol and $\lambda_{max.}$ will be relatively insensitive to change of solvent. If the stabilization is great, the dye has high intrinsic polarity and will show small deviations only in solvents of low polarity, and will exhibit extraordinary shifts of $\lambda_{max.}$ to *shorter* wave lengths with increasing polarity of the solvent, these shifts increasing with chain length. Thus the hypsochromic shifts $\lambda_{max.}$ pyridine → $\lambda_{max.}$ water for the series XII (n = 0, 1, 2, 3) are 365, 800, 1400 and 2200 Å., respectively.

(1) **Introduction.**—When the absorptions of the merocyanines first began to be examined between one and two decades ago, many of the relationships were incomprehensible. At that time a great quantity of data showing non-convergence of the $\lambda_{max.}$ values of symmetrical[3] and certain unsymmetrical vinylogous cyanine series had been published,[4] but convergence in more highly unsymmetrical cyanine series had not then been noted,[5c] and was actually first observed in a vinylogous series of merocyanines, where it struck a puzzling new note. Also, just as the absorptions of many unsymmetrical cationic dyes could not be reconciled with those of structurally related symmetrical dyes until the introduction of the "deviation" concept,[5] so the absorptions of many merocyanines seemed anomalous when they were first compared with those of structurally related symmetrical cyanines.

The resonance theory has now been used successfully for interpreting the absorptions of ionized dyes such as the symmetrical[1] and unsymmetrical cyanines[5f] and *p*-dimethylaminostyryl derivatives.[5a,e] The merocyanines,[6] being un-ionized, present several special problems, but it will be shown that the resonance treatment gives a self-consistent qualitative account of their absorptions also.

(2) **Deviations in the Merocyanines.**—The key to the spectra of the merocyanines consists in regarding them, in each case, as a resonance hybrid between an uncharged and a dipolar structure, as illustrated by Ia↔Ib. In this dye a benzothiazole ring is linked to one derived from 3-ethylrhodanine; the resonance is of the amidic type $>N-\overset{|}{C}=O \longleftrightarrow >\overset{\oplus}{N}=\overset{|}{C}-\overset{\ominus}{O}$. Three possibilities arise: (1) the extreme resonance structures,



Ia and Ib, may have the same energy; (2) Ia may be of higher energy than Ib, or, (3) it may be of lower energy than Ib. Selection of the third possibility as the correct one has been reached in the

† Deceased, October 15, 1951.

(1) Part IX, THIS JOURNAL, **73**, 1087 (1951).

(2) Presented before the Organic Section of the American Chemical Society, March 28, 1949, at San Francisco, Calif.

(3) N. I. Fisher and F. M. Hamer, *Proc. Roy. Soc. (London)*, **A154**, 703 (1936).

(4) B. Beilenson, N. I. Fisher and F. M. Hamer, *ibid.*, **A163**, 138, (1937).

(5) (a) Part III, THIS JOURNAL, **63**, 3203 (1941); (b) Part IV, *ibid.*, **63**, 3214 (1941); (c) Part V, *ibid.*, **64**, 199 (1942); (d) Part VI, *ibid.*, **67**, 1869 (1945); (e) Part VII, *ibid.*, **67**, 1875 (1945); (f) Part VIII, *ibid.*, **67**, 1889 (1945).

(6) Preceding paper, *ibid.*, **73**, 5326 (1951).