SYNTHESIS AND INVESTIGATION OF MEROCYANINE DYES

I. 3,4-PYRROLINE-2,5-DIONE DERIVATIVES

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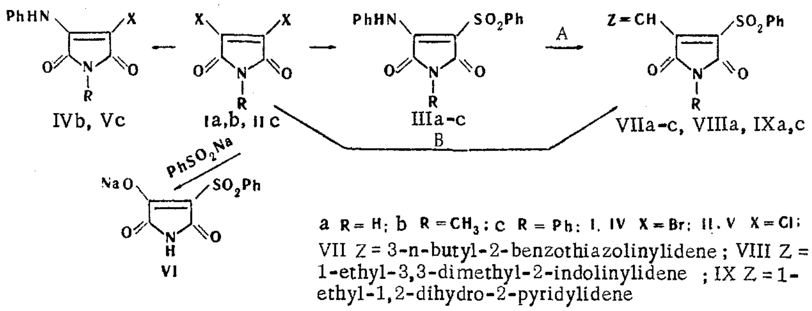
New merocyanine dyes – derivatives of 1-unsubstituted, 1-methyl-, and 1-phenyl-3,4-pyrroline-2,5-diones – were synthesized by the reaction of quaternary salts of 2-methyl-substituted heterocyclic nitrogen bases with the appropriate 3,4-dihalopyrrolinedione and sodium benzenesulfinate or with 3-phenylamino-4-phenylsulfonylpyrroline-2,5-diones. The effect of substituents attached to the nitrogen atom of 3,4-dihalo-3,4-pyrroline-2,5-diones on the nature of the products formed by reaction with aniline and sodium benzenesulfinate was investigated.

It was recently established [1,2] that 3,4-dihalo-3,4-dihydrofuran (or 3,4-pyrroline)-2,5-diones readily react with a mixture of sodium benzenesulfinate and a tertiary aromatic amine in dimethylformamide. The 3-(p-dialkylaminoaryl)-4-arylsulfonyl derivatives of the indicated dihydrofuran- or pyrrolinediones that are formed are a new class of dyes for synthetic fibers.

The reaction of 3,4-dihalo-3,4-dihydrofuran-2,5-dione, sodium p-toluenesulfinate, and 1,3,3-trimethyl-2-methyleneindoline under similar conditions yielded a mixture of blue 3-(1,3,3-trimethyl-2-methyl-6-indolinyl)-4-(p-tolylsulfonyl)-3,4-dihydrofuran-2,5-dione and red 3-(1,3,3-trimethyl-2-indolinolidenemethyl)-4-(p-tolylsulfonyl)-3,4-dihydrofuran-2,5-dione [1]. The latter can be assigned to the broad class of merocyanine dyes and is distinguished by the fact that a portion of its polymethine chromophore, which contains an electronegative substituent, is included in the dihydrofurandione ring. Since such merocyanines were heretofore unknown, it seemed of interest to us to synthesize a number of such dyes and investigate them by spectroscopy. For this, we prepared 3,4-pyrroline-2,5-diones of general structures VII-IX. Dyes with 3-n-butylbenzothiazole and 1-ethyl-3,3-dimethylindolenine residues (Z) were obtained by the reaction of a mixture of the appropriate 3,4-dibromo (or dichloro)pyrroline-2,5-diones (Ia,b and IIc) and the n-butyl iodide of 2-methylbenzothiazole or 1-ethyl-3,3-dimethyl-2-methyleneindolenine and sodium benzenesulfinate in dimethylformamide (method B, see [1]).



a R = H; b R = CH_3; c R = Ph; I, IV X = Br; II, V X = Cl;
VII Z = 3-n-butyl-2-benzothiazolinylidene; VIII Z = 1-ethyl-3,3-dimethyl-2-indolinylidene; IX Z = 1-ethyl-1,2-dihydro-2-pyridylidene

α-Picoline ethiodide does not undergo this reaction; the pyrido-2-merocyanines (IXa,c) were therefore obtained by heating the indicated quaternary salt with 3-phenylamino-4-phenylsulfonyl-3,4-pyrroline-2,5-dione (IIIa) and its 1-phenyl derivative (IIIc) (method A, usually employed for the synthesis of polymethine dyes).

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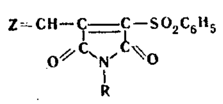
TABLE 1



VIIa-c, VIIIa, IXa,c

Comp.	R	Starting pyrrolinedione	Yield, %*	Mp, °C	Crystalline solvent, ml/g	Empirical formula	S, %		λ max, nm (log ε)
							found	calc.	
VIIa	H	III a (Ia)	61(23)	202—203	Alcohol, 220	$C_{22}H_{20}N_2O_4S_2$	14,3	14,5	538(4,64)
VIIb	CH_3	IIIb (Ib)	64(15)	194—196	Benzene, 330	$C_{23}H_{22}N_2O_4S_2$	14,0	14,1	543(4,63)
VIIc	C_6H_5	IIIc (IIc)	81(8,2)	171—173	Alcohol, 330	$C_{26}H_{24}N_2O_4S_2$	13,0	13,0	544(4,56)
VIIIa	H	(Ia)	(26)	158—160	50% Alcohol, 100	$C_{23}H_{22}N_2O_4S$	7,8	7,6	526(4,60)
IX a	H	IIIa	35	193—195	Alcohol, 1000	$C_{18}H_{16}N_2O_4S$	9,1	9,0	492(4,06)
IX c	C_6H_5	IIIc	51	208—210	Alcohol, 500	$C_{24}H_{20}N_2O_4S$	N 6,4	N 6,5	492(4,04)

*2-Methylbenzothiazole n-butyliodide was used to synthesize VIIa, 1-ethyl-3,3-dimethyl-2-methyleneindoline was used to prepare VIIIa, and α-picoline ethiodide was used to synthesize IXa,c. The starting pyrrolinedione and the yield from the synthesis via method B are indicated in parentheses.

The starting dihalopyrrolinediones were obtained by known methods: 3,4-dibromo-3,4-pyrroline-2,5-dione (Ia) was obtained by bromination of succinimide at 160° [3]; the 1-methyl derivative (Ib) [4] was isolated by heating in acetone solution of Ia with dimethyl sulfate in the presence of potassium carbonate.

1-Phenyl-3,4-dibromopyrroline-2,5-dione (IIc) was obtained by heating dichloromaleic anhydride with aniline in acetic acid [5]; the formation of a more soluble side product – 1-phenyl-3-phenylamino-4-chloro-3,4-pyrroline-2,5-dione (Vc), the structure of which was confirmed by alternative synthesis from IIc and aniline – was observed in the process.

The 3-phenylamino-4-phenylsulfonyl-3,4-pyrroline-2,5-dione (IIIa) necessary for the synthesis of merocyanines by method A was obtained by heating a mixture of dibromopyrroline-2,5-dione (Ia) sodium benzenesulfinate, and aniline in methanol (75% yield) and, judging from the absorption spectrum and elementary analysis, was a pure substance (λ_{max} 370 nm). At the same time, the formation of significant amounts of the corresponding 3-phenylamino-4-halo derivatives (IVb and Vc), the structures of which were confirmed by alternative synthesis and comparison of the melting points and absorption spectra, was observed in the preparation of 1-methyl and 1-phenyl derivatives (IIIb and IIIc). The yields of IIIb and IIIc were only 17.5% (λ_{max} 380 nm).

In order to increase the yields of intermediates IIIb and IIIc, this reaction was investigated in greater detail. It was found that replacement of the second halogen atom in IVb and Vc by a phenylsulfonyl group or an aniline residue does not occur, which is in agreement with the results in [1,3]. This is possibly explained by the deactivating effect of a phenylamino group in the 3 position. In addition, 3,4-dibromopyrrolinedione readily enters into the reaction on heating with sodium benzenesulfinate in methanol. The substance obtained (according to elementary analysis) was the sodium salt of structure VI. The introduction of a phenylsulfonyl group probably activates the adjacent halogen atom to such an extent that it is hydrolyzed (see [6]).

Although the reasons for the formation of the side products in the synthesis of IIIb and IIIc, in contrast to IIIa, are still not sufficiently clear, it can nevertheless be assumed that the reaction of 3,4-dibromopyrrolinedione with aniline and sodium benzenesulfinate initially gives 3-bromo-4-phenylsulfonyl derivative (see [1]), the activated halogen atom of which is then readily replaced by a phenylamino group to form IIIa. At the same time, in the case of 1-substituted pyrrolinediones (Ib and IIc), 3-phenylamino-4-halo- and 3-halo-4-phenylsulfonyl-3,4-pyrroline-2,5-diones are formed in the first stage of the reaction. Moreover, because of deactivation of the halogen atom, as indicated above, the former remains unchanged in the reaction mixture, while the latter is converted to 3-phenylamino-4-phenylsulfonylpyrrolinediones (IIIb and IIIc).

EXPERIMENTAL

1-Phenyl-3,4-dichloro-3,4-pyrroline-2,5-dione (IIc). A mixture of 1.67 g (0.01 mole) of dichloromaleic anhydride, 0.93 g (0.01 mole) of aniline, and 10 ml of glacial acetic acid was heated for 15 min on a boiling-water bath. The resulting yellow precipitate (2.25 g) was removed by filtration after 2 h, washed with water, and dried to give a product with mp 178-198°. Washing with boiling alcohol (three 5-ml portions) and crystallization from benzene gave 1.8 g (75%) of shiny, colorless platelets of IIc with mp 205-207° (208-210° [5]). The solid that was isolated from the wash alcohol was removed by filtration and crystallized twice from alcohol to give 0.1 g of Vc, which was identical to an authentic sample.

1-Phenyl-3-phenylamino-4-chloro-3,4-pyrroline-2,5-dione (Vc, see [6,7]). Aniline [0.18 g (0.002 mole)] was added to a boiling solution of 0.24 g (0.001 mole) of IIc in 20 ml of methanol, and the mixture was refluxed for 20 min and cooled. The resulting precipitate was removed by filtration, washed with alcohol, and crystallized from alcohol to give 0.2 g (66%) of yellow needles with mp 189-191°, λ_{max} 396 nm, and log ε 4.32. Found: Cl 11.9%. $C_{16}H_{11}ClN_2O_2$. Calculated: Cl 11.9%.

1-Methyl-3-phenylamino-4-bromo-3,4-pyrroline-2,5-dione (IVb). This compound was similarly obtained from Ib in 78% yield as yellow needles from alcohol with mp 182-183°, λ_{max} 396 nm and log ε 4.36. Found: Br 28.6%. $C_{11}H_9BrN_2O_2$. Calculated: Br 28.4%.

3-Phenylamino-4-phenylsulfonyl-3,4-pyrroline-2,5-dione (IIIa). Aniline [0.93 g (0.01 mole)] and 1.27 g (0.005 mole) of 3,4-dibromo-3,4-pyrroline-2,5-dione [3] were added to a hot suspension of 0.8 g (0.005 mole) of sodium benzenesulfinate in 7 ml of methanol, and the mixture was refluxed for 5 min. The yellow needles that developed during heating were removed by filtration, washed with alcohol, and crystallized from alcohol to give 1.24 g (75%) of a product with mp 225-227°, λ_{max} 370 nm, and log ε 4.44. Found: N 8.5%. $C_{18}H_{12}N_2O_4S$. Calculated: N 8.5%.

1-Methyl-3-phenylamino-4-phenylsulfonyl-3,4-pyrroline-2,5-dione (IIIb). Sodium benzenesulfinate [0.18 g (0.001 mole)] and 0.18 g (0.002 mole) of aniline were added to a boiling solution of 0.27 g (0.001 mole) of 1-methyl-3,4-dibromo-3,4-pyrroline-2,5-dione in 4 ml of methanol, and the mixture was refluxed for 20 min and cooled. It was then diluted with water, and the precipitate (0.15 g with mp 160-165°) was removed by filtration, washed with water, and dissolved in 20 ml of benzene. The benzene solution was filtered through a layer of aluminum oxide. A yellow side product was eluted with chloroform–benzene (1 : 4), and IIIb was eluted with chloroform–alcohol (9 : 1). Evaporation of the solution in vacuo and crystallization of the residue from alcohol gave 0.06 g (17.5%) of yellowish plates of IIIb with mp 190-191°, λ_{max} 380 nm, and log ε 4.56. Found: N 8.0%. $C_{17}H_{14}N_2O_4S$. Calculated: N 8.2%.

The solution of yellow side products was vacuum-evaporated, and the residue was crystallized from alcohol to give 0.05 g (18%) of IVb with mp 178-180°, which was identical to the sample described above.

1-Phenyl-3-phenylamino-4-phenylsulfonyl-3,4-pyrroline-2,5-dione (IIIc). A total of 0.3 g of a mixture of IIIc and Vc with mp 170-190° was similarly obtained from 0.24 g of 1-phenyl-3,4-dichloropyrroline-2,5-dione. Chromatography yielded 0.1 g (33%) of Vc, which was identical to the sample described above, and 0.07 g (17.5%) of light-yellow plates of IIIc with mp 208-209° (from alcohol), λ_{max} 380 nm, and log ε 4.63. Found: S 7.8%. $C_{22}H_{16}N_2O_4S$. Calculated: S 7.9%.

Sodium Salt of 3-Hydroxy-4-phenylsulfonyl-3,4-pyrroline-2,5-dione (VI). A mixture of 0.5 g (0.002 mole) of 3,4-dibromo-3,4-pyrroline-2,5-dione, 0.54 g (0.003 mole) of sodium benzenesulfinate, and 5 ml of methanol was refluxed for 30 min. The precipitate was removed by filtration, washed with water, and crystallized from 10% alcohol to give 0.25 g (45%) of colorless needles of VI with mp 305-310°, λ_{max} 328 nm, and log ε 4.12. Found: C 43.5; H 2.3; N 5.1; S 11.9%. $C_{10}H_6NNaO_5S$. Calculated: C 43.6; H 2.2; N 5.1; S 11.6%.

Synthesis of Dyes (Table 1). A) A mixture of equimolecular amounts (0.5 mmole) of 3-phenylamino-4-phenylsulfonyl-3,4-pyrroline-2,5-dione, the quaternary salt of the 2-methyl-substituted heterocyclic nitrogen base, and 5 ml of pyridine (triethylamine and acetic anhydride were added in some cases) was refluxed for 5 min. The mixture was diluted with 10 ml of ice water, and the resulting precipitate was removed by filtration and purified by crystallization from alcohol or benzene or by chromatography on silica gel with subsequent crystallization.

B) Sodium benzenesulfinate (1 mmole) was added to a mixture of equimolecular amounts (1 mmole each) of 3,4-dihalo-3,4-pyrroline-2,5-dione, the quaternary salt of the 2-methyl-substituted heterocyclic nitrogen base, and 10 ml of dimethylformamide heated to 50°, and the mixture was heated for another 30-60 min. The dye was isolated and purified as indicated above.

The absorption spectra of alcohol solutions of all of the compounds were measured.

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