MONOMETHYLIDYNECYANINES WITH UNSYMMETRICAL STRUCTURES AND DIMETHYLIDYNEMEROCYANINES FROM N-METHYL-2-ARYL-5,6-BENZOLEPIDINIUM SALTS

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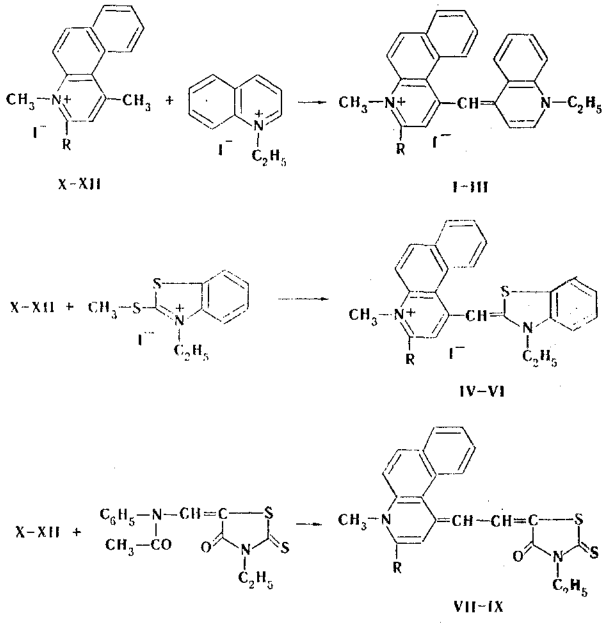
N-Methyl-2-aryl-5,6-benzolepidinium quaternary salts undergo cyanine condensation with quinoline and 2-methylmercaptobenzothiazole ethiodides to give monomethylidynecyanines and also with 3-ethyl-5-N-phenylacetamidomethylenerhodanine to give dimethylidynemerocyanines. The introduction of a phenyl group into the 2 position of the quinoline ring causes a bathochromic shift of the absorption maxima of the dyes.

Monomethylidynecyanine dyes of the quinoline series and dimethylidynemerocyanines are used as sensitizers for silver halide emulsions [1]. As previously demonstrated [2], the catalytic condensation of arylidene-2-naphthylamines with acetone in acid media gives 2-aryl-4-methyl-5,6-benzoquinolines, which are readily quaternized with methyl iodide [3].

The goal of the present study was the preparation of unsymmetrical monomethylidynecyanines (I-VI) and dimethylidynemerocyanines (VII-IX) by condensation of 2-aryl-4-methyl-5,6-benzoquinoline methiodides (X-XII) with quinoline and 2-methylmercaptobenzothiazole ethiodides and also with 3-ethyl-5-N-phenylacetamidomethylenerhodanine via the following schemes:



$R = C_6H_5$; $p\text{-}CH_3OC_6H_4$; $3,4\text{-}(OCH_2O)\,C_6H_3$

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TABLE 1. Monomethylidynecyanines and Dimethylidynemerocyanines

Comp.	R	Mp, °C	Empirical formula	Found, %		Calc., %		λ_{max}, nm	lg ε	Yield, %
				N	S	N	S			
I	C_6H_5	150—152	$C_{32}H_{27}N_2I$	5,1 5,1		4,9		615	4,47	82
II	p-$CH_3OC_6H_4$	151—153	$C_{33}H_{29}N_2OI$	4,9 4,7		4,7		615	4,30	51
III	3,4(OCH_2O)C_6H_3	178—180	$C_{33}H_{27}N_2O_2I$	4,3 4,2		4,6		617	4,98	33
IV	C_6H_5	227—229	$C_{30}H_{25}N_2SI$		5,2		5,6	521	5,10	40
V	p-$CH_3OC_6H_4$	247—248	$C_{31}H_{27}N_2OSI$		5,3		5,3	521	5,18	20
VI	3,4(OCH_2O)C_6H_3	245—246	$C_{31}H_{25}N_2O_2SI$		5,6		5,2	521	5,20	10
VII	C_6H_5	242	$C_{27}H_{22}N_2OS_2$		14,2		14,0	637	5,15	30
VIII	p-$CH_3OC_6H_4$	222	$C_{28}H_{24}N_2O_2S_2$		12,9		13,1	645	5,27	12
IX	3,4(OCH_2O)C_6H_3	211—212	$C_{28}H_{22}N_2O_3S_2$		12,8		12,8	637	4,54	36

The physical constants of the synthesized dyes and the analytical data are presented in Table 1.

The dyes obtained are violet (I-III), red (IV-VI), and green (VII-IX) crystalline substances. Monomethylidynecyanines I-VI are quite soluble in alcohols, acetone, pyridine, and acetic anhydride but insoluble in ether, water, hydrocarbons, CCl_4, and dioxane. Dimethylidynemerocyanines VII-IX are soluble in all of the solvents indicated above except for water.

A small bathochromic shift of the absorption maximum is observed when one compares the absorption spectra of dyes I-III (λ_{max} 615, 617 nm) with the corresponding unsubstituted (in the 2 position of the quinoline ring) monomethylidynecyanine (λ_{max} 608 nm), which was previously obtained in [4]. The presence of a bathochromic effect as compared with the corresponding 2-unsubstituted dyes is also characteristic for quinothiacyanines and dimethylidynemerocyanines. The shift in the absorption maximum to the long-wave region of the spectrum is apparently due to the introduction of an additional phenyl group into the dye molecules. The introduction of substituents (CH_3O and $-OCH_2O-$) into the phenyl ring is, except for VIII, only slightly reflected in the position of the absorption maximum.

EXPERIMENTAL

The starting heterocyclic bases (2-phenyl-, p-methoxyphenyl-, and piperonyl-4-methyl-5,6-benzoquinolines) were obtained via the method in [2].

The methiodides of the bases were obtained by heating the latter with methyl iodide and acetic anhydride in an ampule via the method in [3].

The dyes were obtained via the methods in [5,6,7].

1-Methyl-2-piperonyl4-[(1'-ethyldihydro-4'-quinolylidene)methyl]-5,6-benzoquinolinium Iodide (III). A mixture of 0.23 g (1 mmole) of 2-piperonyl-4-methyl-5,6-benzoquinoline methiodide, 0.28 g (2 mmole) of quinoline ethiodide, 0.14 g (1 mmole) of anhydrous K_2CO_3, and 4 ml of absolute ethanol was heated on a water bath for 2 h. The dye was precipitated by the addition of ether, removed by filtration, and washed with water. Two crystallizations from alcohol gave 0.1 g of III (Table 1).

Compounds I and II (Table 1) were similarly obtained.

1-Methyl-2-(p-methoxyphenyl)-4-[(3'-ethyl-2'-benzothiazolinylidene)methyl]-5,6-benzoquinolinium Iodide (V). A mixture of 0.22 g (0.5 mmole) of 2-(p-methoxyphenyl)-4-methyl-5,6-benzoquinoline methiodide, 0.17 g (0.5 mmole) of 2-methylmercaptobenzothiazole ethiodide, 0.14 g (1 mmole) of anhydrous K_2CO_3, and 4 ml of absolute ethanol was refluxed for 1.5 h. The mixture was cooled, and the precipitate was removed by filtration and washed with water, alcohol, and ether. Crystallization from alcohol gave 0.06 g of V (Table 1).

Compounds IV and VI (Table 1) were similarly obtained.

3-Ethyl-5-(1'-methyl-2'-phenyl-5',6'-benzodihydroquinolylidene-4'-ethylidene)thiazolidine-2-thion-4-one (VII). A mixture of 0.2 g (0.5 mmole) of 2-phenyl-4-methyl-5,6-benzoquinoline methiodide, 0.15 g (0.5 mmole) of 3-ethyl-5-N-phenylacetamidomethylenerhodanine, 0.2 g of anhydrous sodium acetate, and 4 ml of absolute ethanol was refluxed for 1.5 h. The mixture was cooled, and the crystals were removed by filtration and washed with water and alcohol to give 0.12 g of a product with mp 203°. Crystallization from alcohol gave 0.7 g of VII (Table 1).

Dyes VIII and IX (Table 1) were similarly obtained.

The absorption spectra of ethanol solutions of the dyes were recorded with a Specord UV VIS spectrophotometer.

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