STUDIES IN THE FIELD OF SYNTHETIC DYES

LXXII. Reaction of Quaternary Salts of Quinaldine and Lepidine with Methenylbis-1, 3-indandione*

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A number of dimethinequinomerocyanines containing the indandione nucleus has been synthesized. The influence of the substituents in the quinoline nucleus and on the hetero nitrogen atom on the absorption maximum, the deviation, and the solvatochromic properties of the dyes has been studied.

As an active compound, indandione is used for many reactions [1], including the preparation of merocyanine dyes [2-7]. The present work was devoted to the synthesis and to a study of the properties of dimethinequinomerocyanines containing an indandione nucleus. 1, 3-Indandione reacts with orthoacetic ester in the absence of a solvent to form 2-(1'-ethoxyethylidene)-1, 3-indandione, an intermediate for the synthesis of merocyanines substituted in the chain [8]. Under the same conditions, orthoformic ester forms only a monomethineoxonol [9,10]. Some oxonols have been used successfully to obtain merocyanines [11]. We have carried out the reaction of quaternary salts of quinaldine and lepidine with methylenebis-1, 3-indandione in ethanol in the presence of an excess of triethylamine. For comparison, a number of syntheses were carried out with 2-anilinomethylene-1, 3-indandione [12], which was condensed with the quaternary salts in ethanol but in the presence of an equimolecular amount of a basic agent. The time required for the performance of the reaction was shortened by a factor of 10-12 and the yield of product rose somewhat. The properties and the results of elementary analysis of the dyes obtained are given in Table 1.

As can be seen from Table 2, positive substituents in the 2-quinolylidene and particularly in the 4-quinolylidene nucleus have a weak influence on the absorption maximum, causing a small bathochromic shift. The replacement of the ethyl radical attached to nitrogen in the quinoline nucleus (IX, X) by phenyl (I, II) leads to a bathochromic shift. A nitro group in the quinoline nucleus (XI) also gives a bathochromic effect as compared with the unsubstituted dye X.

The deviation of the quinomerocyanines derived from indandione is small and increases with an increase in the basicity of the quinoline nucleus. Its value is higher the stronger the electron-donating properties of the substituents in the quinoline nucleus and in the phenyl radical attached to the nitrogen. The low value of the deviation indicates the closeness of the indandione dyes to a state intermediate between the ionic and covalent forms. For those dyes in which the basicity of the quinoline nucleus is raised by the presence of substituents the bipolar form probably predominates somewhat.

Table 3 characterizes the solvatochromic properties of the indandione dyes. The change in the absorption maximum takes place more sharply in polar solvents, small changes being observed in solvents of low polarity. The majority of the merocyanines exhibit intermediate solvatochromism with the deepest coloration in chloroform or in benzene. By comparing the increase in the deviation of the dyes V-VII (Table 2) with their solvatochromic properties (Table 3), it can be seen that with an increase in the deviation from 0 to 6 nm there is a transition from the dye with intermediate solvatochromism V to the dye VII exhibiting negative solvatochromism. It can be said that the bipolar form of the dye VII predominates in all the solvents selected.

EXPERIMENTAL

General method of preparing the dyes (Table 1). A mixture of 0.001 mole of the quaternary salt, 0.001 mole of methenylbisindandione, 0.002 mole of triethylamine, and 2-4 ml of ethanol was heated in the water bath for 1 hr 30 min to 2 hr. The reaction product that precipitated on cooling was washed with ethanol and ether.

The following quaternary salts were used for the syntheses: 1-phenylquinaldinium perchlorate [13], 1-p-tolyl-6-methylquinaldinium perchlorate [14], 1-phenyl-5, 6-benzoquinaldinium iodide [15], 1-p-methoxyphenyl-6-methoxyquinaldinium perchlorate [16], 1-phenyllepidinium perchlorate [17], 1-p-tolyl-6-methyllepidinium perchlorate [18], 1-p-methoxyphenyl-6-methoxylepidinium iodide [19], and 1-β-naphtyl-5, 6-benzoquinaldinium iodide [14].

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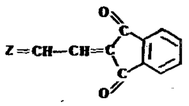
*For part LXXI, see [20].

Table 1



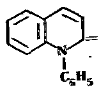
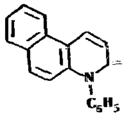
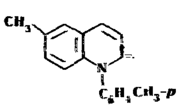
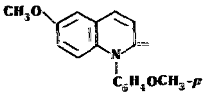
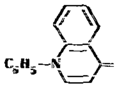
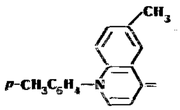
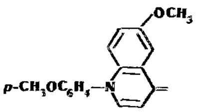
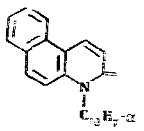
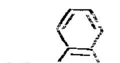
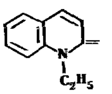
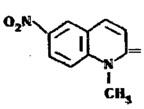
Compound	Z	Mp, °C (solvent for crystallization)	External form	Empirical formula	N, %		Yield %
					found	calculated	
I		310—312 (i-C_4H_9OH)	Lustrous claret-colored crystals	$C_{26}H_{17}NO_2$	3.99 4.01	3.73	80.0
II		348—350 (CH_3COOH+ $+C_2H_5OH$)	Gray needles	$C_{30}H_{19}NO_2$	3.16 3.25	3.30	59.5
III		323—325 (CH_3COOH+ $+C_2H_5OH$)	Lustrous dark blue needles	$C_{28}H_{21}NO_2$	3.67 3.73	3.47	67.5
IV		291—293 (n-C_4H_9OH)	Lustrous green crystals	$C_{28}H_{21}NO_4$	3.01 2.98	3.22	55.0
V		279—281 (i-C_4H_9OH)	Dark green needles with a reddish tinge	$C_{26}H_{17}NO_2$	3.71 3.55	3.73	96.0
VI		286—287 (n-C_4H_9OH)	Lustrous green crystals	$C_{28}H_{21}NO_2$	3.55 3.33	3.47	65.0
VII		285—287 (i-C_4H_9OH)	Lustrous green needles	$C_{28}H_{21}NO_4$	3.35 3.51	3.22	51.7
VIII		230—232 (i-C_4H_9OH)	Lustrous gray-blue crystals	$C_{34}H_{21}NO_2$	3.19 3.22	2.94	46.0
IX		270—271 (n-C_4H_9OH)	Lustrous dark green needles	$C_{22}H_{17}NO_2$	4.36 4.47	4.28	76.0
X		273—274[2] (C_2H_5OH)	Dark blue needles	—	—	—	42.0
XI		>300 (C_5H_5N+ $+C_2H_5OH$)	Dark blue crystals	$C_{21}H_{14}N_2O_4$	7.62 7.70	7.82	90.0

Table 2

Optical Properties of Ethanolic Solutions of the Indandione Dyes

Compound	Absorption maximum, nm of the carbocyanine	Absorption maximum, nm of the monomethineoxonol	Calculated value of the absorption of the merocyanine, nm	Absorption maximum of the merocyanine, nm	Deviation, nm	Shift in comparison with the unsubstituted dye	Shift in comparison with the alkyl-containing dye
I	614	462	538	543	−5	—	10
II	644	—	553	553	0	10	—
III	622	—	542	543	−1	0	—
IV	638	—	550	548	2	5	—
V	718	—	590	590	0	—	8
VI	728	—	595	591	4	1	—
VII	738	—	600	594	6	4	—
VIII	650	—	556	554	2	11	—
IX	705	—	583.5	582	1.5	—	—
X [2]	604	—	533	534	−1	—	—
XI	632	—	547	551	−4	17	—

Table 3

Solvatochromism of the Indanione Dyes

Compound	λ_{max}, nm					
	methanol	ethanol	acetone	chloroform	benzene	tetrachloromethane
I	538	543	520, 546	523, 556	527, 562	529, 565
II	549	553	561	540, 571	547, 583	551, 589
III	538	543	550	526, 557	531, 566	534, 570
IV	545	548	555	534, 565	539, 575	543, 580
V	586	590	592	563, 600	560, 599	557, 596
VI	587	591	595	571, 603	564, 603	566, 603
VII	588	594	600	572, 608	570, 609	570, 611
VIII	549	554	560	541, 572	548, 583	552, 590
IX	580	582	593	565, 601.	564, 603	561, 601
X	532	534	512, 540	519, 549	522, 555	523, 556
XI	550	551	524, 555	529, 562	531, 564	527, 560*

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* In dioxane.

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