RESEARCHES ON SYNTHETIC DYES

LXIII. Styrenes From Derivatives Of 1-Arylquinaldinium Salts*

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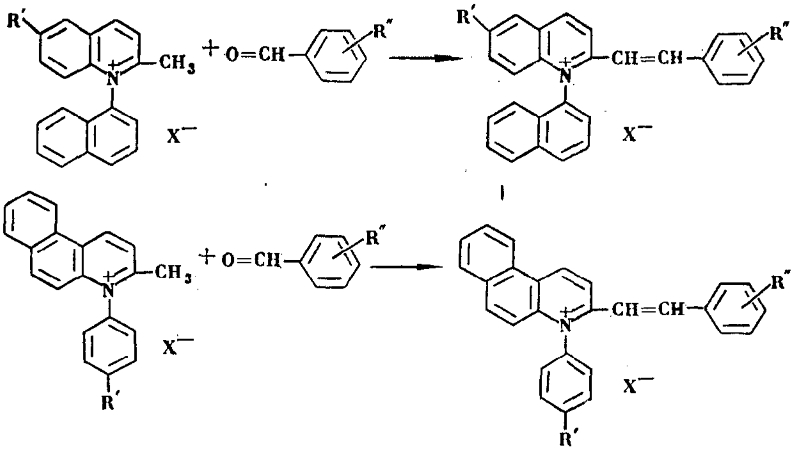
In order to study the effects of OMe and OH groups at various positions in the benzene ring on the optical properties of dyes, 13 styrene-type dyes are prepared by condensing a number of 1-arylquinaldinium salts with anisaldehyde, salicylaldehyde, β-resorcylaldehyde, and 2,4-dimethoxybenzaldehyde in anhydrous pyridine or ethanol plus piperidine. The absorption spectra of the dyes obtained are determined in the visible region, and the spectroscopic data analyzed.

Developing our work on synthesizing and investigating styrene dyes which are 1-arylquinaldinium derivatives [1,2], we have prepared a number of hydroxy and methoxy styrenes by condensing 1-α-napthylquinaldinium perchlorate, 1-α-napthyl-6-methoxyquinaldinium iodide, and 1-p-methoxyphenyl-5,6-benzoquinaldinium perchlorate with anisaldehyde, salicylylaldehyde, β-resorcylaldehyde, and 2,4-dimethoxybenzaldehyde:



$R' = H$, CH_3, OCH_3; $R'' = o\text{-}OH$, $p\text{-}OCH_3$, $o\text{-}OH$, $p\text{-}OH$, $o\text{-}OCH_3$, $p\text{-}OCH_3$; $X = ClO_4$, I

The absorption spectra of the styrenes were determined in ethanol using a SF–2 spectrophotometer. Table 1 shows the spectroscopic characteristics of these styrenes.

The data of Table 1 show that introduction of a second substitutent into the benzene ring of the dye molecules leads to a bathochromic shift of the absorption maximum relative to the corresponding monosubstituted dyes. With p-hydroxy substitution the shift is 34 mμ, with o-hydroxy substitution it is 43–47 mμ, with styrenes which are derivatives of 1-α-naphthylquinldinium salts. With styrenes which are derivatives of 5,6-benzoquinaldinium salts, is 27–30 mμ and 32–40 mμ in the cases of those substituted in the p and o positions respectively [2]. In the case of methoxystyrenes, the bathochromic shift of the absorption maxima for disubstituted ones compared with monosubstituted ones is 24–25 mμ with derivatives of 1-α-naphthylquinaldinium salts and 20–25 mμ [2] for derivatives of 5,6-benzoquinaldinium salts. Comparison of hydroxy-with methoxystyrenes shows a hypsochromic 23–27 mμ shift of the absorption maximum for disubstituted styrenes, and an 18 mμ one for monosubstituted styrenes.

This absorption maximum shift is in line with the electronic structure of the dyes compared. Thus a second substituent introduces an additional pair of free electrons of the oxygen atom into conjugation with the π electrons of the main conjugated chain of the dye molecule, which also causes a shift of absorption maximum in the longer wavelength region. The value of the shift depends on the degree of mobility of this electron pair, and this is higher at the oxygen atom of the hydroxyl group. The more marked electron-donating properties of the hydroxy group also explain the deepening of the color of this group of styrenes as compared with the corresponding methoxystyrenes. In the case of monosubstituted dyes introduction of an electron-donating substituent at the ortho position instead of at the para one results in "contraction" of the conjugated chain, decreases the constant shift of electrons in the latter, and is accompanied by increased coloration. Thus on passing from p-hydroxy- to o-hydroxystyrenes,

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*For Part LXII see [2].

Table 1

Spectroscopic Properties of the Dyes

Name of heterocyclic ring	R′	X	λ_{max}, mμ				
			o-OCH$_3$ p-OCH$_3$	o-OH p-OH	p-OCH$_3$	o-OH	p-OH[1]
Quinaldine	H	ClO$_4$	465	492	440		458
Quinaldine	CH$_3$	ClO$_4$	463	489		442	455
Quinaldine	OCH$_3$	I	465	488	441	445	
5, 6-Benzoquinaldine	OCH$_3$	ClO$_4$	456	480.		448	

Table 2

Dyes Synthesized

Dye name	Mp, °C (decomp),	λ_{max}, mμ		Formula	N, %		Yield, %
		EtOH	pH>7		Found	Calculated	
(1-α-Naphthylquinoline-2)-2, 4-dimethoxystyrene perchlorate	241	465		$C_{29}H_{24}ClNO_6$	2.96 2.58	2.70	87
(1-α-Naphthylquinoline-2)-2, 4-dihydroxystyrene perchlorate	238	492	566	$C_{27}H_{20}ClNO_6$	3.00 2.94	2.86	54.3
(1-α-Naphthylquinoline-2)-p-methoxystyrene perchlorate	227—228	440		$C_{28}H_{22}ClNO_5$	2.95 2.80	2.87	72
(1-α-Naphthyl-6-methoxyquinoline-2)-2, 4-dimethoxystyrene perchlorate	235	463		$C_{30}H_{26}ClNO_6$	2.90 2.79	2.63	76.7
(1-α-Naphthyl-6-methoxyquinoline-2)-2, 4-dihydroxystyrene perchlorate	200	489	568	$C_{28}H_{22}ClNO_6$	2.80 3.00	2.78	48
(1-α-Naphthyl-6-methoxyquinoline-2)-o-hydroxystyrene perchlorate	239	442	580	$C_{28}H_{22}ClNO_5$	2.56 2.61	2.86	79
(1-α-Naphthyl-6-methoxyquinoline-2)-2, 4-dimethoxystyrene iodide	260	465		$C_{30}H_{26}INO_3$	2.80 2.74	2.43	59.1
(o-α-Naphthyl-6-methoxyquinoline-2)-2, 4-dihydroxystyrene iodide	195	488	577	$C_{28}H_{22}INO_3$	2.14 2.83	2.56	50
(1-α-Naphthyl-6-methoxyquinoline-2)-p-methoxystyrene iodide	235—236	441		$C_{29}H_{24}INO_2$	2.84 2.90	2.57	73.6
(1-α-Naphthyl-6-methoxyquinoline-2)-o-hydroxystyrene iodide	245—246	445	576	$C_{28}H_{22}INO_2$	2.52 2.78	2.63	53
(1-p-Methoxy-5, 6-benzoquinoline-2)-2, 4-dimethoxystyrene perchlorate	248—249	456		$C_{30}H_{26}ClNO_7$	2.66 2.89	2.57	91
(1-p-Methoxy-5, 6-benzoquinoline-2)-2, 4-dihydroxystyrene perchlorate	240—241	480	580	$C_{28}H_{22}ClNO_7$	2.78 2.91	2.69	89
(1-p-Methoxy-5, 6-benzoquinoline-2)-o-hydroxystyrene perchlorate	255 -256	448	570	$C_{28}H_{22}ClNO_6$	2.81 2.91	2.77	49.2

the absorption maximum of the latter is found to undergo a hypsochromic shift of 13 mμ. In ethanolic alkali the absorption maximum of all the hydroxystyrenes is shifted towards the long wave region.

EXPERIMENTAL

The 1-arylquinaldinium quaternary salts were prepared as described in [3–5]. The styrene dyes were prepared by condensing equimolecular amounts of 1-α-naphthylquinaldinium perchlorate, 1-α-naphthyl-6-methylquinaldinium perchlorate, 1-α-naphthyl-6-methoxyquinaldinium iodide, and 1-p-methoxyphenyl-5, 6-benzoquinaldinium perchlorate with anisaldehyde, salicylaldehyde, β-resorcylaldehyde, and 2,4-dimethoxybenzaldehyde in dry pyridine or ethanol plus piperidine, by gentle refluxing for 40–90 min. At the end of the reaction 1–2 drops of HCl were added to the hydroxystyrenes. The dyes were washed with ether and hot water, and recrystallized from EtOH. Data regarding the styrenes are given in Table 2.

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