## CONDENSATION OF 2-(3,4-METHYLENEDIOXYPHENYL)-5,6-BENZOLEPIDINE METHIODIDE WITH AROMATIC ALDEHYDES

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2-(3,4-Methylenedioxyphenyl)-5,6-benzolepidine methiodide enters into condensation with aromatic aldehydes in absolute alcohol in the presence of piperidine to give styryl dyes. The effect of various substituents in the styryl residue on the position of the absorption maxima of the dyes was studied.

Styryl derivatives of quinoline are promising compounds for practical use as physiologically active substances and sensitizers and desensitizers of photoemulsions [1]. The aim of the present study was to obtain styryl derivatives of 2-(3,4-methylenedioxyphenyl)-5,6-benzolepidine methiodide (1) and to investigate their optical properties.



Styryl derivatives (II-XI) were obtained by condensation of equimolecular amounts (1 mmole) of I with aromatic aldehydes in absolute alcohol in the presence of 1-1.5 mmole of piperidine. This amount of condensing agent is minimal for carrying out the reaction, and practically no condensation occurs in pyridine or acetic anhydride. The slowed-down course of the condensation (2-3 h) and the necessity of an equimolecular amount of condensing agent are apparently associated with the presence of steric hindrance between the 5,6-benzo group and the methyl group in the 4 position of the quinoline ring. Since partial splitting out of the elements of hydrogen iodide and the formation of merocyanines [2] are possible under the conditions of the alkali medium created by piperidine (pH 8), one to two drops of concentrated HCl (to pH 5-7) are added to the reaction mixture at the end of the condensation reaction to isolate the o-hydroxy- and dihy-droxystyryls.

A product, the elementary composition of which corresponds to a molecular compound of o-hydroxystyryl and merocyanine (XII) [2], is isolated in the reaction of equimolecular amounts of I, salicylaldehyde, and piperidine in absolute alcohol without acidification of the reaction mixture:



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10	P	°C,	Empirical formula	Found, %				Calculated, %				-		1. %
Con				с	н	I	N	с	н	I	N	hmas nm	lg e	Yield
11 111	4-OH 2-OH	192 198 200	C <sub>29</sub> H <sub>22</sub> INO <sub>3</sub> C <sub>29</sub> H <sub>22</sub> INO <sub>3</sub>	62,1 62,5	3,9 3,9	22,7 22,8	2,2 2,8	62,3 62,3	3,9 3,9	22,7 22,7	2,5 2,5	407	4,73	48 18
· IV V	4-OCH₃ 4-N (CH₃) ₂	158 191	C <sub>30</sub> H <sub>24</sub> INO <sub>3</sub> C <sub>31</sub> H <sub>27</sub> IN <sub>2</sub> O <sub>2</sub>	62,6 63,3	4,4 4,8	21,7 22,1	2,1 4,5	62,8 63,5	4,2 4,6	22,1 21,7	2,4 4,7	413 413 549	4,40 4,75 4,72	26 55
VI	2,4- (OH) 2	180	C <sub>29</sub> H <sub>22</sub> INO <sub>4</sub>	60,9	4,2	21,8	2,4	60,5	3,8	22,1	2,4	483;	4,87;	35
VII	2-OH-3-OCH₃	174	C <sub>30</sub> H <sub>24</sub> INO <sub>4</sub>	61,3	4,2	20,9	2,4	61,1	4,1	21,2	2,4	412;	4,14 4,79;	42
VIII IX	3,4- (OCH <sub>2</sub> O) 3,4- (OCH <sub>3</sub> ) <sub>2</sub>	189 157— 158	C <sub>30</sub> H <sub>22</sub> INO <sub>4</sub> C <sub>31</sub> H <sub>26</sub> INO <sub>4</sub>	61,1 61,7	3,7 4,4	21,8 21,2	2,5 2,5	61,3 61,7	3,7 4,3	21,6 21,1	2,4 2,3	429 417	5,25 5,71 4,76	50 51
х	2-OH-5,6 <b>-</b> benzo	222	$C_{33}H_{24}INO_3$	65,3	3,9	21,0	2,3	65,0	3,9	20,9	2,3	412;	4,44;	60
XI	3,4-(OH)2	154— 155	C <sub>29</sub> H <sub>22</sub> INO <sub>4</sub>	60,2	4,1	22,5	2,6	60,5	3,8	22,1	2,4	477 456; 640	4,52 4,18; 3,58	29

The addition of triethylamine to the reaction mixture presented above leads to the isolation of 2-(3,-4-methylenedioxyphenyl)-5,6-benzolepidine in addition to XII. Spiropyrans do not form from o-hydroxystyryl derivatives of I, as was also previously noted [3] relative to o-hydroxystyryl derivatives of quinaldine and lepidine. We were unable to isolate the merocyacanine in the pure state, since it decomposes in solution.

A molecular compound (XIII) similar to XII was also obtained on reaction of I with 3,4-dihydroxy-benzaldehyde.

Partial splitting out of HI was observed for 2,4-dihydroxystyryl VI in several experiments. Hydroxystyryl derivatives II, VII, and X are stable compounds.

The styryls obtained are crystalline substances of yellow (II, III), orange (IV, VII-XI), red-brown (VI), green (VII), and violet (V) color that are soluble in alcohols, acetone, and pyridine, and insoluble in ether, hydrocarbons, and CCl<sub>4</sub>. The hydroxy- and methylenedioxystyryls dissolve in water on heating. Alcohol solutions of the hydroxystyryls in alkaline media are deep blue.

## EXPERIMENTAL

2-(3,4-Methylenedioxyphenyl)-5,6-benzolepidine [4]. This compound was obtained by the method in [5]. A 22-ml (0.3 mole) sample of acetone, 5 ml of concentrated HCl, and 3 ml of nitrobenzene were added to a Schiff base obtained by heating equimolecular amounts (0.1 mole) of 2-naphthylamine and piperonal in alcohol, and the mixture was refluxed for 2 h. It was then cooled and neutralized with 10% NH<sub>4</sub>OH, and the precipitate was removed by filtration, washed with water, and crystallized from alcohol -benzene (1:1) to give colorless needles with mp 159-160° in 33% yield. UV spectrum:  $\lambda_{max}$ , nm (log  $\varepsilon$ ), in alcohol (c 1  $\cdot$  10<sup>-4</sup> M): 235, 258, 280, 318, 348, 364 (4.59, 4.56, 4.59, 4.40, 4.07, 4.05).

2-(3,4-Methylenedioxyphenyl)-5,6-benzolepidine Methiodide (1). A mixture of 3.14 g (10 mmole) of 2-(3,4-methylenedioxyphenyl)-5,6-benzolepidine, 7 ml (100 mmole) of methyl iodide, and 5 ml of acetic anhydride was heated in a sealed ampul at 100° for 10 h. Treatment of the product with boiling toluene and crystallization from alcohol-acetone (1:2) gave yellow needles of I (85%) with mp 211°. Found: N 2.8%.  $C_{22}H_{18}INO_2$ . Calculated: N 3.1%.

The styryls were obtained by the methods in [2, 6].

4-(3,4-Methylenedioxystyryl)-2-(3,4-methylenedioxyphenyl)-5,6-benzoquinoline Methiodide (VIII). A mixture of 0.46 g (1 mmole) of I, 0.2 g (1.3 mmole) of piperonal, and five drops (1.5 mmole) of piperidine was refluxed in 5 ml of absolute alcohol for 3 h. The dye was precipitated with ether, and the oily mass was triturated until it was converted to a powder. The powder was removed by filtration and crystallized from alcohol to give 0.29 g of orange prisms (Table 1).

Styryls II, IV, V, VII, and IX (Table I) were similarly obtained; II and V were isolated from the reaction mixture on cooling.

4-(2-Hydroxy-5,6-benzostyryl)-2-(3,4-methylenedioxyphenyl)-5,6-benzoquinoline Methiodide (X). A mixture of 0.46 g (1 mmole) of I, 0.23 g (1.3 mmole) of 2-hydroxynaphthaldehyde, and five drops of piperidine (pH 8) was refluxed in 4 ml of absolute alcohol for 2 h. At the end of the condensation, one drop of concentrated HCl was added to bring the pH to 7. The subsequent isolation and purification were carried out as in the preceding experiment.

Compound VI was similarly obtained.

4-(2-Hydroxystyryl)-2-(3,4-methylenedioxyphenyl)-5,6-benzoquinoline Methiodide (III). A mixture of 0.46 g (1 mmole) of I, 0.18 g (1.5 mmole) of silicylaldehyde, and five drops (1.5 mmole) of piperidine (pH 8) was refluxed in 5 ml of absolute alcohol for 2 h. The mixture was acidified to pH 5 with two drops of concentrated HCl, and the precipitate was removed by filtration, washed with water and ether, and crystallized from alcohol to give 0.1 g of yellow needles.

Molecular Compound of III with Merocyanine (XII). A. The above mixture of I, salicylaldehyde, and piperidine was heated for 2.5 h, and the resulting slightly soluble precipitate was, without subsequent acidification, removed by filtration and washed with alcohol and ether. To purify it, it was refluxed with alcohol to give 0.26 g (52%) of XII with mp 219°. Recrystallization from alcohol-acetone (1:5) gave dark-green prisms with mp 220° that were only slightly soluble in the usual solvents.  $\lambda_{max}$ , nm (log  $\varepsilon$ ) in dimethyl-formamide (DMF): 406, 685 (3.78, 3.42). Found: C 70.2; H 4.6; I 12.6%. C<sub>58</sub>H<sub>43</sub>IN<sub>2</sub>O<sub>6</sub>. Calculated: C 70.2; H 4.4; I 12.8%.

B. The reaction mixture indicated above was heated for 2 h to precipitate a dark-green substance, which dissolved in alcohol to give a yellow solution. A 1-ml (7 mmole) sample of triethylamine was added to the reaction mixture, and it was refluxed for another 30 min. The precipitate was removed by filtration and refluxed with alcohol to give 0.2 g (40%) of XII with mp 219°. Cooling of the alcohol mother liquor gave 0.1 g of 2-(3,4-methylenedioxyphenyl)-5,6-benzolepidine with mp 159-160°.

4-(3,4-Dihydroxystyryl)-2-(3,4-methylenedioxyphenyl)-5,6-benzoquinoline Methiodide (XI). A mixture of 0.46 g (1 mmole) of I, 0.18 g (1.4 mmole) of 3,4-dihydroxybenzaldehyde, and 1.5 mmole of piperidine (pH 8) was refluxed in 5 ml of absolute alcohol for 2.5 h. The mixture was then acidified with two drops of concentrated HCl to pH 5, and the styryl was precipitated with aqueous KI. The precipitate was removed by filtration, washed with water and ether, and crystallized from alcohol to give 0.17 g of fine orange crystals.

Molecular Compound of XI with Merocyanine (XIII). The above mixture of I, 3,4-dihydroxybenzaldehyde, and piperidine was heated for 2 h, and the resulting black resinous precipitate was converted to a yellow-brown powder (48%) with mp 187° (from alcohol) after acidification with one drop of concentrated HCl, trituration, and washing with ether.  $\lambda_{max}$ , nm (log  $\varepsilon$ ) in DMF 405, 706 (4.80, 5.04). Found: C 67.9; H 4.5; I 12.9; N 2.7%. C<sub>58</sub>H<sub>43</sub>IN<sub>2</sub>O<sub>8</sub>. Calculated: C 68.0; H 4.3; I 12.4; N 2.7%.

The absorption spectra of alcohol solutions (c  $1 \cdot 10^{-4}$  M) of II-XI were recorded with a Specord UV VIS spectrophotometer.

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