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RESEARCHES ON SYNTHETIC DYES

LVIII. Synthesis of N-2,5-Dichlorophenyl-5,6-benzolepidinium Salts and Their Conversion to Cyanine Dyes*

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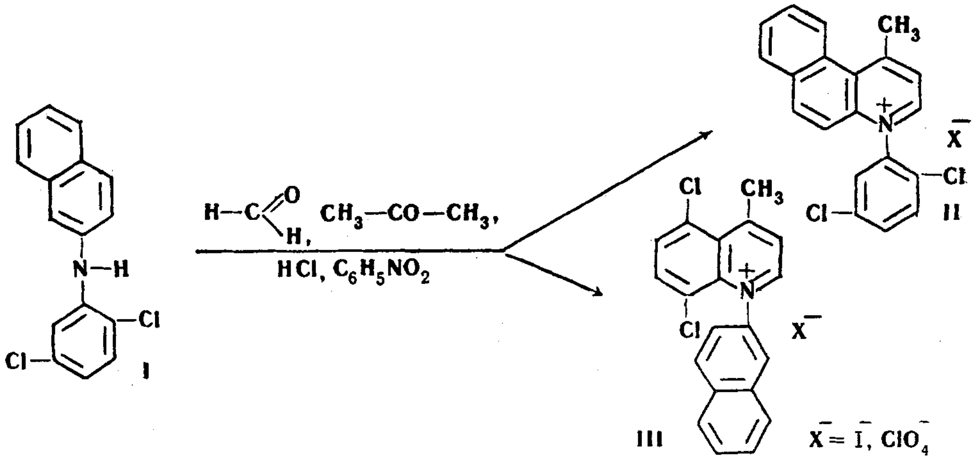
N-2,5-Dichlorophenyl-5,6-benzolepidinium perchlorate and iodide quaternary salts, not described in the literature, are synthesized. Carbocyanine and 4-styryl dyes, based on N-2,5-dichlorophenyl-5,6-benzolepidinium perchlorate, are obtained.

We have previously converted 2,5-dichlorophenyl-β-naphthylamine (I) by the Doebner-Miller reaction into N-arylquinaldinium quaternary salts [1]. The preparation of some lepidinium salts from unsymmetrical secondary amines has also been described [2].

In the present paper, 2,5-dichlorophenyl-β-naphthylamine is condensed with formaldehyde and with a ten-fold excess of acetone in dioxane, in the presence of nitrobenzene plus hydrochloric acid. In this reaction, ring closure can take place in two ways



Investigation showed that only isomer II was formed.

This is first and foremost indicated by the UV absorption spectrum of the quaternary salt isolated. It has three absorption bands in the ultraviolet, λ_{max} 377 mμ (lg ε 3.911), 280 mμ (lg ε 4.25), and 220 mμ (lg ε 4.601). The

Properties of Dyes Prepared

Compound number	λ_{max}, mμ	Mp °C (decomp)	Formula	N, % Found	N, % Calc.	Yield, %
IV	739	250	$C_{41}H_{25}Cl_5N_2O_4$	3.79 3.98	3.58	50
VI	592	216—217	$C_{29}H_{23}Cl_3N_2O_4$	5.17 5.01	4.91	62
VII	602	218—220	$C_{31}H_{27}Cl_3N_2O_4$	4.50 4.53	4.69	70
VIII	550	216	$C_{27}H_{19}Cl_3N_2O_4$	5.29 5.38	5.17	81
IX	459	213	$C_{27}H_{18}Cl_3NO_5$	2.81 2.78	2.56	80

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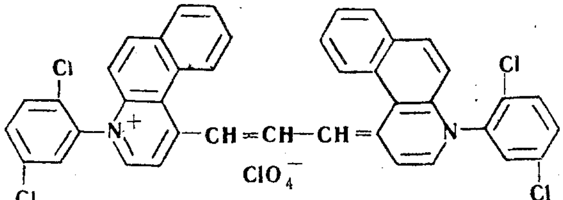
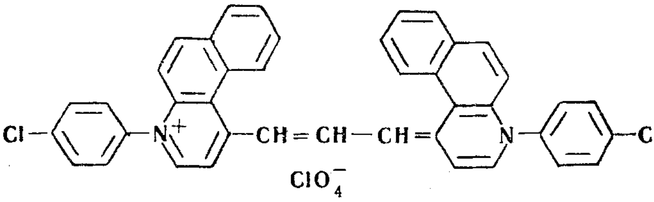
*For Part LVII see [1].

presence of three absorption bands with maxima close to those indicated, is characteristic of N-aryl-5, 6-benzoquinaldinium and N-aryl-5, 6-benzolepidinium salts [3, 4].

A further argument in favor of structure II for the salt is the position of the absorption maximum of the carbocyanine dye IV (739 mμ) derived from it, this corresponding to an absorption maximum position of a compound of similar structure, bis (1-p-chlorophenyl-5, 6-benzoquinoline-4) trimethinecyanine perchlorate (V) (733 mμ) [5].



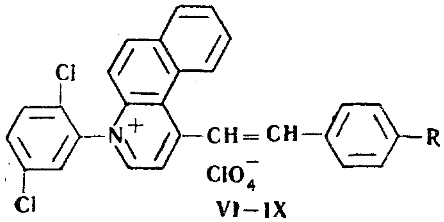
IV



V

An isocyanine could not be obtained from the salts which we isolated, though one is found for all 5, 6-benzolepidinium salts, and arises through steric hindrance due to the benzene ring at positions 5 and 6 of the quinoline ring.

The styryl dyes VI-IX (table) were prepared by condensing N-2, 5-dichlorophenyl-5, 6-benzolepidinium perchlorate with p-amino-p-dimethylamino-, p-diethylamino-, and p-hydroxybenzaldehyde (table)



VI–IX

$R = -NH_2, -N(CH_3)_2, -N(C_2H_5)_2, -OH;$

Experimental

N-2, 5-Dichlorophenyl-5, 6-benzolepidinium perchlorate (II, X = ClO_4). A mixture of 2 g (7 mmole) 2, 5-dichlorophenyl-β-naphthylamine, 0.5 ml 40% formaldehyde, 10 ml acetone, 1 ml nitrobenzene, 0.5 ml HCl (d 1.19), and 8 ml dioxane was sealed up in a tube, which was then heated for 18 hr in a boiling water bath. The dioxane, nitrobenzene, and residual acetone and formaldehyde were steam-distilled off. The quaternary chloride formed was converted into perchlorate by adding a concentrated solution of $NaClO_4$. Yield 0.75 g (27%). Pale yellow powder, mp 200° (ex water). Found: N 3.09, 3.27%. Calculated for $C_{20}H_{14}Cl_3NO_4$: N 3.18%.

N-2, 5-Dichlorophenyl-5, 6-benzolepidinium iodide (II, X = I). The quaternary chloride was prepared in the same way, and converted to iodide by adding a saturated KI solution. Yellow powder mp 160° C, yield 0.8 g (22%). Found: N 2.98, 3.12%. Calculated for $C_{20}H_{14}Cl_2IN$: N 3.09%.

Bis (N-2, 5-dichlorophenyl-5, 6-benzoquinoline-4) trimethinecyanine perchlorate (IV). 0.2 g (0.5 mmole) N-2, 5-dichlorophenyl-5, 6-benzolepidinium perchlorate, 0.1 ml orthoformic ester, and 1 ml pyridine were refluxed together moderately for 60 min. The reaction products were poured into water. Recrystallized from EtOH, the dye formed a pale-green powder.

(N-2, 5-Dichlorophenyl-5, 6-benzoquinoline-4)-p-dimethylaminostyryl perchlorate (VI). A mixture of 0.2 g (0.5 mmole) N-2, 5-dichlorophenyl-5, 6-benzolepidinium perchlorate, 0.1 g (0.7 mmole) p-dimethylaminobenzaldehyde, 1.5 ml Ac_2O, was refluxed for 40 min. The violet solution was transferred to a beaker, and precipitated with water. The dye, after recrystallizing from EtOH, formed a dark-violet finely-divided crystalline powder.

(N-2, 5-Dichlorophenyl-5, 6-benzoquinoline-4)-p-diethylaminostyryl perchlorate (VII). A mixture of 0.2 g (0.5 mmole) N-2, 5-dichlorophenyl-5, 6-benzolepidinium perchlorate, 0.2 g (1.1 mmole) p-diethylaminobenzaldehyde, and 2 ml Ac_2O was heated in a small flask. The dye formed was precipitated with ether, washed with hot water and recrystallized from EtOH. It formed dark-blue crystals.

(N-2, 5-Dichloro-5, 6-benzoquinoline-4)-p-aminostyryl perchlorate (VIII). 0.2 g (0.5 mmole) N-2, 5-dichloro-5, 6-benzolepidinium perchlorate, 0.06 g (0.05 mmole) p-aminobenzaldehyde, and 1.5 ml pyridine were refluxed together for 30 min. The dye was precipitated with water, and recrystallized from iso-BuOH. The dye formed a crimson powder.

(N-2, 5-Dichloro-5, 6-benzoquinoline-4)-p-hydroxystyryl perchlorate (IX). A mixture of N-2, 5-dichloro-5, 6-benzolepidinium perchlorate, 0.06 (0.5 mmole) p-hydroxybenzaldehyde, and 1 ml pyridine was heated, precipitated with water, and recrystallized from iso-BuOH. The dye was a dark-brown powder.

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