STUDIES IN THE FIELD OF SYNTHETIC DYES

LXVIII. Synthesis of N-Arylquinaldinium Salts and Their Conversion into Cyanine Dyes*

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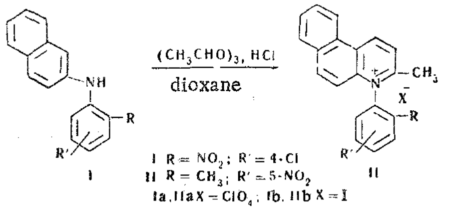
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 2, pp. 319–320, 1968

UDC 547.831.542:668.8

N-arylquinaldinium iodides and perchlorates have been obtained by the condensation of 2-methyl-5-nitrophenyl- and 4-chloro-2-nitrophenyl-β-naphthylamines with paraldehyde. Carbocyanines and styryls have been synthesized from these salts.

Only a few N-arylquinaldinium salts with two substituents in the nucleus are known [1]. Only recently have N-arylquinaldinium salts with electron-accepting substituents been obtained [2–4]. In order to study compounds with such a structure further, we have prepared N-(4-chloro-2-nitrophenyl)-5,6-benzoquinaldinium perchlorate (Ia) and N-(2-methyl-5-nitrophenyl)-5,6-benzoquinaldinium perchlorate (IIa) by condensing the corresponding amines with paraldehyde in hydrochloric acid.

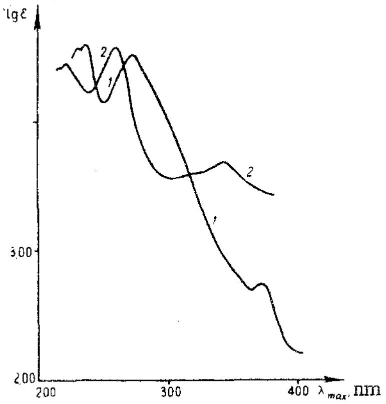


Confirmation of the structure of the salts isolated is given by their UV spectra, which have the three absorption bands characteristic for 5,6-benzoquinaldinium salts [5] (see figure) and differ from the UV spectra of the N-naphthylquinaldinium salts [6] that could be formed if cyclization took place in a different direction. The presumed structure of the salts obtained is confirmed to some extent also by the position of the absorption maxima of the carbocyanine dyes synthesized from these salts (~650 nm). If the naphthylquinaldinium salts had been formed, the maxima of the absorption spectra of the corresponding carbocyanines would be approximately in the 625–630 nm region [7], which is not the case.

We have also obtained styryls by condensing the benzoquinaldinium salts I and II with p-dimethylaminobenzaldehyde in acetic anhydride. The introduction of a nitro group into the phenyl nucleus leads to a displacement of the absorption maximum in the shortwave direction of the spectrum by 11–20 nm as compared with the unsubstituted compound, the hypsochromic shift differing from the additive figure by 85–95 nm.

EXPERIMENTAL

N-(4-Chloro-2-nitrophenyl)-β-naphthylamine was obtained by heating 15 g (0.087 mole) of 4-chloro-2-nitroaniline, 12 g (0.083 mole) of β-naphthol, and 0.1 g of crystalline iodine at 180°–200° C for 15 hr. The reaction mixture was washed with 10% HCl solution and with NaOH, dissolved in benzene, dried with $CaCl_2$, and distilled in vacuum. Bp 175° C (1 mm). Small light-yellow needles, mp 82°–83° C (from petroleum ether). Yield 6 g (20%). Found, %: Cl 12.27, 11.76; N 9.51, 9.77. Calculated for $C_{16}H_{11}ClN_2O_2$, %: Cl 12.21; N 9.38.



Absorption curves of quaternary salts in ethanol: 1) N-(4-chloro-2-nitrophenyl)-5, 6-benzoquinaldinium perchlorate (λ_{max} 235, 275, 374 nm; log ε 4.60, 4.56, 2.73); 2) N-(2-methyl-5-nitrophenyl)-5, 6-benzoquinaldinium perchlorate (λ_{max} 220, 260, 346 nm; log ε 4.45, 4.58, 3.63).

N-(2-Methyl-5-nitrophenyl)-β-naphthylamine was obtained similarly. Bp 156° C (2–3 mm). Small light-yellow needles, mp 74°–75° C (from petroleum ether). Yield 35%. Found, %: N 10.47, 10.64. Calculated for $C_{17}H_{14}N_2O_2$, %: N 10.09.

N-(4-Chloro-2-nitrophenyl)-5,6-benzoquinaldinium perchlorate (Ia). With cooling, 2 ml of paraldehyde was added to 2 g (6.7 mM) of N-(4-chloro-2-nitrophenyl)-β-naphthylamine, 1 ml of hydrochloric acid (d 1.19), and 10 ml of dioxane. The mixture was heated in a sealed tube in the water bath for 10 hr. The dioxane was distilled off with steam and the unchanged secondary amine was separated off. The chloride was converted into the less water-soluble perchlorate by the addition of a saturated solution of sodium perchlorate. The perchlorate Ia was obtained in the form of a light-yellow powder with mp 280° C (from water). Yield 0.54 g (18%). Found, %: N 6.45, 6.76. Calculated for $C_{20}H_{14}Cl_2N_2O_6$, %: N 6.46.

N-(4-Chloro-2-nitrophenyl)-5,6-benzoquinaldinium iodide (Ib). The chloride, obtained similarly, was converted into the iodide by the addition of a saturated solution of potassium iodide. Mp 245° C (from water). Yield 0.64 g (20%). Found, %: N 6.12, 6.16. Calculated for $C_{20}H_{14}N_2O_2$, %: N 5.87.

N-(2-Methyl-5-nitrophenyl)-5,6-benzoquinaldinium perchlorate (IIa). was obtained as described previously [8]. A mixture of 2 g of N-(2-methyl-5-nitrophenyl)-β-naphthylamine, 1 ml of hydrochloric acid (d 1.19), and 2 ml of paraldehyde in dioxane was heated at 100° C

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*For communication LXVII, see [9].

in a sealed tube for 15 hr. The product was worked up by the method described above. Mp 226° C. Yield 0.7 g (23.3%). Found, %: N 6.37, 6.45. Calculated for $C_{21}H_{17}ClN_2O_6$, %: N 6.53. Then the chloride was converted into the iodide IIb by the addition of a saturated solution of potassium iodide. Mp 134° C. Yield 0.96 g (30%). Found, %: N 6.05, 5.97. Calculated for $C_{21}H_{17}IN_2O_2$, %: N 6.13.

Bis[1-(2-methyl-5-nitrophenyl)-5, 6-benzoquinoline-2]trimethinecyanine perchlorate (III). A mixture of 0.2 g (0.45 mM) of the perchlorate Ia, 0.1 ml of orthoformic ester, and 1.5 ml of dry pyridine was heated to a moderate boil for 3 hr. The dye was precipitated from solution with ether, washed with water, and crystallized from ethanol. Mp 251° C. Yield 0.115 g (32%), λ_{max} 647 nm (in ethanol). Found, %: N 7.03, 6.80. Calculated for $C_{41}H_{25}Cl_3N_4O_8$, %: N 6.90.

Bis[1-(2-methyl-5-nitrophenyl)-5, 6-benzoquinoline-2]trimethinecyanine perchlorate (IV). A mixture of 0.3 g (0.7 mM) of the perchlorate IIa, 0.12 ml of orthoformic ester, and 2 ml of pyridine was heated for an hour. Yield 0.2 g (41%). Mp 231°–232° C (from 50% ethanol). λ_{max} 650 nm (in ethanol). Found, %: N 7.28, 7.33. Calculated for $C_{43}H_{31}ClN_4O_3$, %: N 7.31.

[1-(4-Chloro-2-nitrophenyl)-5,6-benzoquinoline-2]-p-dimethylaminostyryl perchlorate (V). A mixture of 0.3 g (0.67 mM) of the perchlorate Ia, 0.1 g (0.67 mM) of p-dimethylaminobenzaldehyde, and 2.5 ml of acetaldehyde was heated under reflux. The dye was obtained in the form of small crystals with mp above 300° C (from isobutanol). Yield 0.3 g (77%); λ_{max} 543 nm. Found, %: N 7.31, 7.29. Calculated for $C_{29}H_{23}ClN_3O_6$, %: N 7.35.

[1-(2-Methyl-5-nitrophenyl)-5,6-benzoquinoline-2]-p-dimethylaminostyryl iodide (VI) was obtained by heating by 0.3 g (0.66 mole) of the iodide IIB, 0.09 g (0.6 mM) of p-dimethylaminobenzaldehyde, and 2.5 ml of acetic anhydride for 45 min. The dye was precipitated with ether and crystallized from ethanol. Mp 282° C; yield 0.2 g, 54%. λ_{max} in ethanol 534 mμ. Found, %: N 7.01, 6.98. Calculated for $C_{29}H_{26}IN_3$, %: N 7.15.

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10 September 1968

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