

2-BENZOPYRYLIUM SALTS

XVI.* REACTION OF 3-CARBALKOXY-2-BENZOPYRYLIUM SALTS WITH SOME DIAMINES

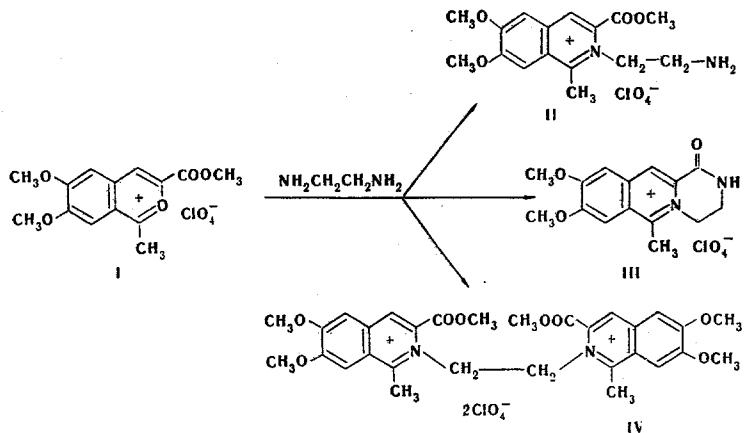
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The condensation of 1-alkyl-3-carbalkoxy-2-benzopyrylium salts with diamines leads to the synthesis of piperazino[3,4-b]- and quinoxalino[3,4-b]isoquinolinium perchlorates.

One of the most important transformations of 2-benzopyrylium salts is their reaction with nitrogen bases, which leads to the formation of isoquinolines or isoquinolinium salts — close analogs of natural alkaloids [2]. Recently it has been shown [3] that 2-benzopyrylium salts react with diamines (hexamethylene-diamine, p-phenylenediamine, and benzidine) to give isoquinolinium bisquaternary salts.

We have studied the reaction of 2-benzopyrylium salts that have two reactive centers with some diamines. For this purpose, we carried out the reaction of 1-methyl-3-methoxycarbonyl-6,7-dimethoxy-2-benzopyrylium perchlorate (I) (which we synthesized in [4]) with an equimolecular amount of ethylenediamine, which proceeds readily to give one individual product. The final products of the reaction might have been II-IV:

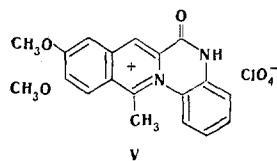


A study of the IR spectrum [5-7] of the product showed that there is an absorption band of the NH group of a cyclic lactam at 3200 cm^{-1} and a strong absorption band at 1715 cm^{-1} , which is characteristic for the carbonyl group of a cyclic imide (imide I band); however, there is no absorption band at 1735 cm^{-1} (ester group). On the basis of a study of the IR spectrum of the compound obtained, we decided in favor of structure III. This conclusion was also confirmed by the PMR spectra. The chemical shifts (δ scale) were as follows: singlet at 2.28 ppm (CH_3 group), singlet at 3.03 ppm (two OCH_3 groups), triplets at 2.94 and 3.69 ppm (CH_2CH_2 group), and singlets at 5.78, 5.93, and 6.80 ppm (aromatic protons). The absence in the spectrum of signals of the protons of another methoxy group confirms proposed structure III [8].

*See [1] for communication XV.

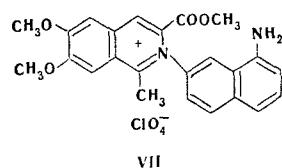
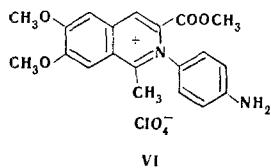
Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 3, pp. 342-344, March, 1974. Original article submitted March 15, 1973.

Perchlorate I reacts similarly with o-phenylenediamine to give V:



The data from the PMR spectrum are as follows: 2.58 ppm (CH₃ group), 3.04 ppm (two OCH₃ groups), and multiplet at 5.64–6.18 and 7.06 ppm (aromatic protons). These data confirm structure V, which was proposed on the basis of the IR spectroscopic data. Thus we have shown that this method can be used to synthesize the previously unknown condensed bisheterocyclic systems – piperazino[3,4-b]- and quinoxaline-[3,4-b]-isoquinolinium salts.

Only replacement of the heterocyclic oxygen atom by nitrogen without ring closing occurs in the reaction of perchlorate I with 1,8-diaminonaphthalene or p-phenylenediamine, and N-substituted isoquinolinium salts VI and VII are formed:



The IR spectra of VI and VII contain absorption bands at 3455, 3370 (VI) and 3435, 3355 cm⁻¹ (VII), which are related to the stretching vibrations of an unsubstituted primary amino group [6] [$\nu_S VI = 345.53 + (0.876 \cdot 3455) = 3372.11$; $\nu_S VII = 345.53 + (0.876 \cdot 3435) = 3354.59$], and the absorption band of an ester group (1730 cm⁻¹).

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of CF₃COOH solutions were recorded with a Tesla BS 487c spectrometer at 80 MHz and 50°.

1-Methyl-6,7-dimethoxy-2-ketopiperazino[3,4-b]isoquinolinium Perchlorate (III). A mixture of 0.45 g (1.24 mmole) of perchlorate I, 0.14 g (2.8 mmole) of ethylenediamine, and 4 ml of alcohol was refluxed for 30 min, after which it was cooled and filtered to give 0.3 g (65%) of colorless crystals with mp 287° (dec., from alcohol-nitromethane). Found: C 48.2; H 4.7; Cl 9.3; N 7.6%. C₁₅H₁₇N₂O₇Cl. Calculated: C 48.3; H 4.6; Cl 9.5; N 7.5%. IR spectrum, cm⁻¹: 3200 m, 1715 s, 1605 s, 1570 m, 1525 s, 1290 s, 1265 m, 1235 m, 1100 s, and 1000 s.

1-Methyl-6,7-dimethoxy-1H-2-ketoquinoxalino[3,4-b]isoquinolinium Perchlorate (V). This compound was similarly obtained from 0.5 g (1.38 mmole) of perchlorate I, 0.12 g (1.11 mmole) of o-phenylenediamine, and 4 ml of alcohol. The yield of yellow crystals with mp 280° (dec., from nitromethane) was 0.35 g (60%). Found: C 53.9; H 4.2; Cl 8.1%. C₁₉H₁₇N₂O₇Cl. Calculated: C 54.2; H 4.0; Cl 8.4%. IR spectrum, cm⁻¹: 3270 m, 1695 s, 1595 s, 1555 m, 1520 w, 1500 w, 1275 s, 1230 s, 1100 s, and 1020 m.

1-Methyl-2-(4-aminophenyl)-3-methoxycarbonyl-6,7-dimethoxyisoquinolinium Perchlorate (VI). This compound was similarly obtained from 0.5 g (1.38 g mmole) of perchlorate I, 0.14 g (1.11 mmole) of p-phenylenediamine, and 4 ml of alcohol. The yield of yellow crystals with mp 226° (dec., from nitromethane) was 0.3 g (50%). Found: C 52.7; H 4.5; Cl 7.6%. C₂₀H₂₁N₂O₈Cl. Calculated: C 53.0; H 4.6; Cl 7.8%. IR spectrum, cm⁻¹: 3455 m, 3370 m, 1730 s, 1610 s, 1560 m, 1515 s, 1275 s, 1230 s, 1210 s, 1170 s, 1100 s, and 1020 m.

1-Methyl-2-[1-(8-aminonaphthyl)]-3-methoxycarbonyl-6,7-dimethoxyisoquinolinium Perchlorate (VII). This compound was similarly obtained from 0.5 g (1.38 mmole) of perchlorate I, 0.19 g (1.2 mmole) of 1,8-diaminonaphthalene, and 4 ml of alcohol. The yield of yellow crystals with mp 247° (dec., from nitromethane) was 0.4 g (66%). Found: C 57.5; H 4.7; Cl 7.2; N 5.6%. C₂₄H₂₃N₂O₈Cl. Calculated: C 57.8; H 4.6; Cl 7.2; N 6.0%. IR spectrum, cm⁻¹: 3355 m, 3435 m, 1730 s, 1640 w, 1605 s, 1580 s, 1515 s, 1275 m, 1235 s, 1210 s, 1100 s, and 1015 w.

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