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## CONDENSATION OF 6-METHYL-3-AZAPYRYLIUM SALTS TO PYRIDO[1,2-C]PYRIMIDINIUM DERIVATIVES

N. V. Shibaeva, I. I. Nechayuk, S. V. Borodaev, D. S. Yufit, Yu. T. Struchkov, A. I. Pyshchev, and S. M. Luk'yanov

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Under the influence of  $DMF/Ac_2O$  2,4-diphenyl-6-methyl-3-azapyrylium perchlorates undergo condensation to give pyrido[1,2-c]pyrimidinium perchlorates. The structure of one of the perchlorates was proved by x-ray diffraction analysis.

Little study has been devoted to the properties of 3-azapyrylium salts. We have recently observed [1] that the acid-catalyzed acylation of 4-methyl-substituted 3-azapyrylium salts at the methyl group is accompanied by a previously unknown recyclization to give difficult-to-obtain 4-acylaminopyrylium salts. This opens up prospects for the profound modification of 3-azapyrylium salts by the action of not only nucleophilic reagents but also electrophilic reagents.

Our recently developed [2] method for obtaining 6-alkyl-3-azapyrylium salts has made it possible to begin a systematic study of the reactivities of the alkyl groups of this class of heterocyclic cations, viz., pathways of functionalization and subsequent transformations of the products formed.

We found that pyrido[1,2-c]pyrimidinium salts IIIa, b are formed when 3-azapyrylium perchlorates Ia, b are refluxed in DMF/Ac<sub>2</sub>O, which is normally used to obtain N,N-dimethylaminovinyl-substituted pyrylium salts [3]. Carrying out this reaction at 20°C probably gives N-benzoylaminovinyl derivatives B of pyridine, which are converted to pyridines IVa, b by the action of aqueous alkali, whereas they are converted to salts IIIa, b by heating in acetic anhydride.

The formation of perchlorates IIa, b can be explained by a scheme that provides for deprotonation of 3azapyrylium salts Ia, b to anhydro bases IIa, b. The latter are capable of reacting with electrophilic reagents, which in this case are starting salts Ia, b. Reactions of this sort in series of other heterocyclic systems have been previously described [4-6]. The subsequent recyclization of adducts A leads to perchlorates B, which undergo cyclization to salts IIIa, b on heating (see Table 1).

The scheme presented below is confirmed by the fact that the same products IIIa, b and IVa, b were synthesized in the reactions of salts Ia, b with anhydro bases IIa, b. The latter were obtained by deprotonation of the starting perchlorates Ia, b with triethylamine.

The structure of product IIIb was proved unequivocally by an x-ray study of its perchlorate (see Fig. 1 and Tables 2 and 3), which was also of independent structural-chemical interest, since, according to the Cambridge structural data base [7], the structure of pyrido[1,2-c]pyrimidinium derivatives has not been previously studied.

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The distribution of the bond lengths in the bicyclic fragment of the IIIb cation is similar to the distribution characteristic for derivatives of naphthalene and isoquinoline — isoelectronic (with respect to the investigated cation)  $10\pi$ -electron aromatic systems (for example, see [8]): the  $C_{(1)}$ — $N_{(2)}$ ,  $C_{(3)}$ — $C_{(4)}$ ,  $C_{(5)}$ — $C_{(6)}$ , and  $C_{(7)}$ — $C_{(8)}$  bonds are somewhat shortened as compared with the remaining bonds of the corresponding types. However, whereas the above-mentioned aromatic systems have planar structures, the planarity of the bicyclic system is appreciably disrupted in the IIIb cation. Pyridinium ring A has a flattened sofa conformation with 0.144 Å deviation of the  $N_{(9)}$  atom from the plane (realized with an accuracy of 0.013 Å) of the remaining atoms of this ring. The inflection of the A ring along the  $C_{(4a)}$ … $C_{(8)}$  line is 11.5°. Pyrimidine ring B is also substantially nonplanar and exists in a boat conformation [the N<sub>(9)</sub> and C<sub>(3)</sub> atoms deviate 0.198 Å and 0.142 Å, respectively, from the N<sub>(2)</sub>C<sub>(1)</sub>C<sub>(4)</sub>C<sub>(4a)</sub> plane (realized with an accuracy of 0.010 Å); the inflection of the B ring along the N<sub>(2)</sub>… $C_{(4)}$  line is 11.6°, while the deviation along the  $C_{(1)}$ … $C_{(4a)}$  line is 15.6°]. In addition, in the IIIb cation one observes uncharacteristic (for naphthalene and isoquinoline derivatives) relative shortening of the central N<sub>(9)</sub>— $C_{(4a)}$  bond common to the A and B rings. These characteristics of the structure of the IIIb cation make it possible, in our opinion, to speak of nonaromatic character of the investigated bicyclic system and localization of the positive charge of the cation on the N<sub>(9)</sub> atom.

The reason for the unexpected nonplanarity of the heterocyclic system of the IIIb cation is evidently its steric strain, which leads to the development of a number of intramolecular, short, nonvalent contacts between the atoms of the substituents:  $C_{(10)}\cdots C_{(27)} 2.843(6)$ ,  $C_{(10)}\cdots C_{(28)} 3.192(7)$ ,  $C_{(15)}\cdots C_{(27)} 3.033(7)$ ,  $C_{(15)}\cdots C_{(32)} 3.005(7)$ ,  $C_{(27)}\cdots C_{(25)} 3.00(7)$ ,  $C_{(25)}\cdots C_{(24)} 2.918(7)$ ,  $C_{(16)}\cdots C_{(22)} 3.124(7)$  Å. These short contacts, which are substantially smaller than twice the van der Waals radius of the carbon atom (3.42 Å) [9], in addition to disruption of the planarity of the bicyclic system of the IIIb cation, give rise to significant rotation of the phenyl rings, as well as appreciable inequality of the exocyclic bond angles at the  $C_{(1)}$ ,  $C_{(3)}$ ,  $C_{(4)}$ ,  $C_{(7)}$ , and  $C_{(8)}$  atoms and, to a lesser extent, at the  $C_{(6)}$  atom.

The remaining geometrical parameters of the IIIb molecule have the usual values, and shortened intermolecular contacts are absent in the structure.

## **EXPERIMENTAL**

The IR spectra of suspensions of the compounds in mineral oil were recorded with a Specord IR-75 spectrometer. The mass spectra were obtained with a Finnigan 4021 mass spectrometer at an ionization energy of

| Com-<br>pound | Empirical<br>formula  | ™mp, °C           | IR spec-<br>trum, cm <sup>-1</sup>       | PMR spectrum,* δ, ppm   | Yield,<br>% |
|---------------|---|-------------------|--|---|-------------|
| Ib            | C <sub>19</sub> H <sub>18</sub> CINO <sub>5</sub>               | 193195<br>( dec•) | 1600, 1585,<br>1565, 1080                | _   | 43          |
| ]]a           | C <sub>18</sub> H <sub>15</sub> NO                              | 76 7 <b>8</b>     | 1640, 1607,<br>1574                      | 1,84 (3H, s 5-CH <sub>3</sub> ); 4,10 and 4,48<br>(1H each $dJ = 2$ Hz =CH <sub>2</sub> ); 7,0<br>8 20 (10H m arcm)   | 73          |
| IIb           | C <sub>19</sub> H <sub>17</sub> NO                              | 8890              | 1638, 1608,<br>1572                      | 1.13 (3H, t $J=7$ Hz 5-CH <sub>2</sub> CH <sub>3</sub> );<br>2,30 (2H, q $J=7$ Hz, 5-CH <sub>2</sub> CH <sub>3</sub> );<br>4,18 and 4,50 (1H each, d $J=2$ Hz,<br>=CH <sub>2</sub> ); 7 0 8 20 (10H m arom.)                      | 68          |
| IIIa          | C <sub>29</sub> H <sub>25</sub> C1N <sub>2</sub> O <sub>4</sub> | 215220<br>(dec.)  | 1609, 1591,<br>1581, 1567,<br>1553, 1080 | 2,24 (3H, S CH <sub>3</sub> ); 2,69 (3H, S,<br>CH <sub>3</sub> ); 2,78 (3H, S CH <sub>3</sub> ); 6,70<br>8,10 (15H, m, atom: 8,35 (1H,<br>S 5-H)  | 73          |
| IIIp          | C <sub>31</sub> H <sub>29</sub> CIN <sub>2</sub> O <sub>4</sub> | 178 179           | 1607, 1579,<br>1564, 1539,<br>1073       | 0.63 (3H, t $J=7$ Hz $CH_2CH_3$ );<br>1.06 (3H, t $J=7$ Hz $CH_2CH_3$ );<br>2.43 (2H, q $J=7$ Hz $CH_2CH_3$ );<br>2.52 (3H, 6-CH <sub>3</sub> ); 2.90 (2H, q)<br>$J=7$ Hz $CH_2CH_3$ ); 6.207,50<br>(15H m arcm $= 8.06$ (1H 5-H) | 48          |
| IVa*3         | $C_{29}H_{26}N_2O$  | 6264              | 1687, 1281,<br>1244                      | 2,0 (6H, s $CH_3$ ); 2,13 (3H, s $CH_3$ ); 6,757,75 (16H, m, arom.  | 69, 71      |
| IV b*4        | $C_{31}H_{30}N_2O$  | 125 127           | 1687, 1639,<br>1279, 1241                | $\begin{array}{cccccccccccccccccccccccccccccccccccc$  | 57, 54      |

TABLE 1. Characteristics of I-IV

\*The following solvents were used to record the spectra:  $CDCl_3$  for IIa, b and IVa, b, d<sub>5</sub>-nitrobenzene for IIIa, and  $CF_3COOH$  for IIIb.

\*\*The yields of IVa, b obtained by method B.

\*\*\*\*Mass spectrum, m/z ( $I_{rel}$ , %): 418 (2.08), 400 (2.43), 313 (7.26), 183 (2.57), 122 (25.29), 115 (9.39), 105 (79.13), 103 (63.85), 77 (100).

\*\*\*\*Mass spectrum, m/z ( $I_{rel}$ , %): 446 (2.64), 428 (24.38), 341 (5.98), 197 (2.72), 129 (2.73), 122 (30.19), 105 (100), 103 (12.72), 77 (73.76).

TABLE 2. Bond Lengths d in the IIIb Cation

| Bond   | <i>d</i> , Å   | Bond  | d, Å   | Bond  | d, Å  |
|--|--|---|--|---|---|
| $\begin{array}{c} N_{(2)} - C_{(1)} \\ N_{(2)} - C_{(3)} \\ N_{(9)} - C_{(4)} \\ N_{(9)} - C_{(4)} \\ N_{(9)} - C_{(4)} \\ C_{(3)} - C_{(10)} \\ C_{(3)} - C_{(10)} \\ C_{(3)} - C_{(4)} \\ C_{(4)} - C_{(22)} \\ C_{(4)} - C_{(22)} \\ C_{(4)} - C_{(5)} \\ C_{(5)} - C_{(6)} \\ C_{(6)} - C_{(7)} \end{array}$ | $1,273(6) \\1,381(6) \\1,413(5) \\1,384(6) \\1,411(5) \\1,475(7) \\1,381(6) \\1,483(7) \\1,424(6) \\1,511(6) \\1,408(6) \\1,352(7) \\1,422(6)$ | $\begin{array}{c} \bullet & C_{(6)} C_{(24)} \\ & C_{(7)} C_{(8)} \\ & C_{(7)} - C_{(25)} \\ & C_{(10)} - C_{(11)} \\ & C_{(10)} - C_{(11)} \\ & C_{(10)} - C_{(15)} \\ & C_{(11)} - C_{(12)} \\ & C_{(12)} - C_{(13)} \\ & C_{(13)} - C_{(14)} \\ & C_{(14)} - C_{(15)} \\ & C_{(16)} - C_{(17)} \\ & C_{(16)} - C_{(21)} \end{array}$ | $\begin{array}{c} 1,492(6)\\ 1,368(6)\\ 1,510(7)\\ 1,501(6)\\ 1,404(6)\\ 1,392(7)\\ 1,394(8)\\ 1,339(9)\\ 1,386(7)\\ 1,370(8)\\ 1,357(8)\\ 1,402(7) \end{array}$ | $\begin{array}{c} C_{(17)} - C_{(18)} \\ C_{(18)} - C_{(19)} \\ C_{(19)} - C_{(20)} \\ C_{(20)} - C_{(21)} \\ C_{(22)} - C_{(23)} \\ C_{(25)} - C_{(26)} \\ C_{(27)} - C_{(26)} \\ C_{(27)} - C_{(32)} \\ C_{(28)} - C_{(29)} \\ C_{(29)} - C_{(30)} \\ C_{(30)} - C_{(31)} \\ C_{(31)} - C_{(32)} \end{array}$ | $\begin{array}{c} 1,412(8)\\ 1,382(8)\\ 1,374(9)\\ 1,390(7)\\ 1,504(9)\\ 1,500(9)\\ 1,390(7)\\ 1,389(8)\\ 1,410(7)\\ 1,388(9)\\ 1,354(9)\\ 1,382(7)\end{array}$ |

70 eV. The PMR spectra were recorded with a Tesla 487C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard.

The IIIb crystals ( $C_{31}H_{29}CIN_2O_4$ ) were monoclinic and had the following parameters at 20°C: a = 11.749(2), b = 15.498(3), c = 15.659(2) Å,  $\beta = 110.68(1)^\circ$ , Z = 4, space group P2<sub>1</sub>/n. The cell parameters and the intensities of 3216 independent reflections with I >  $2\sigma(I)$  were measured with a Syntex P2<sub>1</sub> automatic diffractometer ( $\lambda_{Mo} K_{\alpha}$ , graphite monochromator,  $\theta/2\theta$  scanning,  $\theta < 30^\circ$ ). The structure was decoded by the direct method and was refined by the completely matrix method of least squares within the anisotropic approximation for all of the nonhydrogen atoms. The oxygen atoms of the perchlorate anion in the IIIb structure were disordered with respect to two positions and were refined isotropically using half masses. Despite this, the geometry of the anion was determined extremely imprecisely: the Cl—O bond lengths were 1.32-1.55 Å. The disorderliness of the anion

TABLE 3. Bond Angles  $\omega$  in the IIIb Cation

| Angle   | ω°  | Angle  | ω°  | Angle  | ω°   |
|---|---|--|---|--|--|
| $\begin{array}{c} C_{(1)}N_{(2)}C_{(3)}\\ C_{(1)}N_{(9)}C_{(4a)}\\ C_{(1)}N_{(9)}C_{(8)}\\ C_{(4a)}N_{(9)}C_{(8)}\\ N_{(2)}C_{(1)}N_{(9)}\\ N_{(2)}C_{(1)}C_{(10)}\\ N_{(9)}C_{(1)}C_{(10)}\\ N_{(9)}C_{(1)}C_{(10)}\\ N_{(2)}C_{(3)}C_{(4)}\\ N_{(2)}C_{(3)}C_{(4)}\\ C_{(3)}C_{(4)}C_{(3)}\\ C_{(4)}C_{(3)}C_{(16)}\\ C_{(3)}C_{(4)}C_{(22)}\\ C_{(4a)}C_{(4)}C_{(22)}\\ C_{(4a)}C_{(4)}C_{(22)}\\ N_{(9)}C_{(4a)}C_{(4)}\\ N_{(9)}C_{(4a)}C_{(5)}\\ C_{(4a)}C_{(5)}\\ C_{(4a)}C_{(5)}\\ C_{(5)}C_{(6)}C_{(7)}\\ \end{array}$ | $\begin{array}{c} 122,7(4)\\ 116,2(4)\\ 123,2(4)\\ 120,5(4)\\ 121,0(4)\\ 121,0(4)\\ 121,8(4)\\ 118,9(4)\\ 113,7(4)\\ 126,9(4)\\ 117,0(4)\\ 124,2(4)\\ 120,3(4)\\ 117,4(4)\\ 122,3(4)\\ 122,2(4)\\ 119,4(4)\\ \end{array}$ | $\begin{array}{c} C_{(5)}C_{(6)}C_{(24)}\\ C_{(7)}C_{(6)}C_{(24)}\\ C_{(6)}C_{(7)}C_{(8)}\\ C_{(6)}C_{(7)}C_{(25)}\\ C_{(8)}C_{(7)}C_{(25)}\\ C_{(8)}C_{(7)}C_{(25)}\\ N_{(9)}C_{(8)}C_{(27)}\\ C_{(7)}C_{(8)}C_{(27)}\\ C_{(7)}C_{(8)}C_{(27)}\\ C_{(1)}C_{(10)}C_{(11)}\\ C_{(10)}C_{(10)}C_{(15)}\\ C_{(11)}C_{(10)}C_{(15)}\\ C_{(11)}C_{(10)}C_{(15)}\\ C_{(11)}C_{(12)}C_{(13)}\\ C_{(12)}C_{(13)}C_{(14)}\\ C_{(13)}C_{(14)}C_{(15)}\\ C_{(13)}C_{(14)}C_{(15)}\\ C_{(13)}C_{(14)}C_{(15)}\\ C_{(13)}C_{(14)}C_{(15)}\\ C_{(13)}C_{(14)}C_{(15)}\\ C_{(13)}C_{(14)}C_{(15)}\\ C_{(13)}C_{(14)}C_{(15)}\\ C_{(13)}C_{(14)}C_{(15)}\\ C_{(13)}C_{(14)}C_{(17)}\\ \end{array}$ | $\begin{array}{c} 119,5(5)\\ 120,9(4)\\ 119,4(4)\\ 118,8(4)\\ 121,8(4)\\ 121,8(4)\\ 119,8(4)\\ 116,2(4)\\ 123,6(4)\\ 117,6(4)\\ 122,3(4)\\ 117,9(5)\\ 121,9(5)\\ 120,6(5)\\ 119,5(5)\\ 120,5(4)\\ 122,5(4)\\ \end{array}$ | $\begin{array}{c} C_{(3)}C_{(16)}C_{(21)}\\ C_{(17)}C_{(16)}C_{(21)}\\ C_{(16)}C_{(17)}C_{(18)}\\ C_{(17)}C_{(18)}C_{(19)}\\ C_{(18)}C_{(19)}C_{(20)}\\ C_{(19)}C_{(20)}C_{(21)}\\ C_{(16)}C_{(21)}C_{(20)}\\ C_{(16)}C_{(22)}C_{(23)}\\ C_{(17)}C_{(25)}C_{(26)}\\ C_{(8)}C_{(27)}C_{(22)}\\ C_{(28)}C_{(27)}C_{(32)}\\ C_{(28)}C_{(29)}C_{(30)}\\ C_{(29)}C_{(30)}C_{(31)}\\ C_{(30)}C_{(31)}C_{(32)}\\ C_{(31)}C_{(31)}\\ C_{(31)}C_{(31)}\\ C_{(31)}\\ C$ | $\begin{array}{ c c c c c c c c c c c c c c c c c c c$ |

TABLE 4. Coordinates ( $\cdot 10^4$ ) and Equivalent Isotropic (isotropic for the O atoms) Temperature Factors B (Å<sup>2</sup>) of the Atoms in the IIIb Structure

| Atom   | x   | y  | z   | <i>B</i> , Å <sup>2</sup>                              | Atom   | x  | y  | z  | <i>B</i> , Å <sup>2</sup>   |
|--|---|--|---|--|--|--|--|--|---|
| $\begin{array}{c} N_{(2)} \\ N_{(9)} \\ C_{(3)} \\ C_{(4)} \\ C_{(4)} \\ C_{(5)} \\ C_{(6)} \\ C_{(7)} \\ C_{(11)} \\ C_{(12)} \\ C_{(13)} \\ C_{(14)} \\ C_{(15)} \\ C_{(16)} \\ C_{(16)} \\ C_{(16)} \\ C_{(19)} \\ \end{array}$ | $\begin{array}{c} 3604 (3) \\ 3843 (3) \\ 3965 (4) \\ 3156 (3) \\ 3314 (4) \\ 3856 (5) \\ 4120 (4) \\ 4131 (4) \\ 3950 (4) \\ 4686 (4) \\ 4311 (5) \\ 5070 (5) \\ 6137 (5) \\ 6528 (5) \\ 5798 (4) \\ 2689 (4) \\ 1778 (5) \\ 1353 (5) \\ 1854 (5) \end{array}$ | 10115 (2)<br>8737 (2)<br>9643 (3)<br>9777 (3)<br>8909 (3)<br>8380 (3)<br>7484 (3)<br>6974 (3)<br>7335 (3)<br>1074 (3)<br>10898 (3)<br>11355 (3)<br>11036 (3)<br>10231 (3)<br>9750 (3)<br>10277 (3)<br>10913 (4)<br>11721 (4) | $\begin{array}{c} 3748 (2) \\ 3229 (2) \\ 3228 (3) \\ 4383 (3) \\ 4589 (3) \\ 3988 (3) \\ 4118 (3) \\ 3512 (3) \\ 2680 (3) \\ 2532 (3) \\ 2532 (3) \\ 2532 (3) \\ 2036 (3) \\ 2036 (3) \\ 2055 (3) \\ 2764 (3) \\ 2764 (3) \\ 5179 (3) \\ 5640 (3) \\ 5755 (4) \end{array}$ | $\begin{array}{ c c c c c c c c c c c c c c c c c c c$ | $\begin{array}{c} C(21)\\ C(22)\\ C(23)\\ C(24)\\ C(25)\\ C(26)\\ C(27)\\ C(28)\\ C(29)\\ C(31)\\ C(31)\\ C(32)\\ C(31)\\ C(32)\\ C(31)\\ O(1-2)\\ O(2-2)\\ O(2-1)\\ O(2-2)\\ O(3-2)\\ O(3-2)$ | $\begin{array}{c} 3198 (5) \\ 3152 (5) \\ 2022 (6) \\ 4312 (6) \\ 4309 (5) \\ 5622 (6) \\ 3706 (4) \\ 2591 (5) \\ 2333 (6) \\ 3180 (6) \\ 4241 (6) \\ 42530 (5) \\ 5311 (2) \\ 6375 (8) \\ 5925 (9) \\ 5329 (11) \\ 5585 (9) \\ 5919 (11) \\ 4475 (10) \\ 4225 (13) \end{array}$ | $\begin{array}{c} 11268 (3)\\ 8499 (3)\\ 7959 (4)\\ 6031 (3)\\ 6743 (3)\\ 6534 (4)\\ 8621 (3)\\ 9033 (3)\\ 9439 (3)\\ 9439 (3)\\ 9431 (4)\\ 9002 (4)\\ 8598 (3)\\ 13775 (1)\\ 13257 (6)\\ 13557 (7)\\ 14066 (6)\\ 14618 (8)\\ 14386 (7)\\ 13679 (8)\\ \end{array}$ | 4966 (3)<br>5414 (3)<br>5204 (4)<br>3698 (4)<br>1972 (3)<br>2161 (4)<br>1621 (3)<br>1229 (3)<br>375 (3)<br>- 58 (3)<br>330 (3)<br>1167 (3)<br>2937 (1)<br>2879 (6)<br>2483 (6)<br>3821 (6)<br>3821 (6)<br>3821 (6)<br>3821 (6)<br>3821 (7)<br>2333 (7)<br>2301 (9) | $\begin{array}{c c} & 3,1 (2) \\ & 3,4 (2) \\ & 4,8 (2) \\ & 4,7 (2) \\ & 3,8 (2) \\ & 5,8 (2) \\ & 5,8 (2) \\ & 2,7 (1) \\ & 3,6 (2) \\ & 5,0 (2) \\ & 5,2 (2) \\ & 4,8 (2) \\ & 5,2 (2) \\ & 4,8 (2) \\ & 5,2 (2) \\ & 4,8 (2) \\ & 5,2 (2)$ |

TABLE 5. Coordinates (·10<sup>3</sup>) of the Hydrogen Atoms in the IIIb Structure

| Atom   | x  | y  | z  | Atom  | x   | y   | z   |
|--|--|--|--|---|---|---|---|
| $\begin{array}{c} H_{(5)} \\ H_{(11)} \\ H_{(12)} \\ H_{(14)} \\ H_{(13)} \\ H_{(15)} \\ H_{(17)} \\ H_{(18)} \\ H_{(19)} \\ H_{(20)} \\ H_{(22.1)} \\ H_{(22.2)} \\ H_{(23.1)} \\ H_{(23.2)} \end{array}$ | $\begin{array}{c} 377 (4) \\ 347 (4) \\ 488 (4) \\ 672 (4) \\ 750 (4) \\ 608 (4) \\ 140 (4) \\ 75 (4) \\ 322 (4) \\ 391 (4) \\ 386 (4) \\ 315 (4) \\ 196 (4) \\ 137 (4) \end{array}$ | $\begin{array}{c} 723  (3) \\ 1110  (3) \\ 1180  (3) \\ 995  (3) \\ 9924  (3) \\ 972  (3) \\ 1072  (3) \\ 1214  (3) \\ 1238  (3) \\ 1140  (3) \\ 817  (3) \\ 892  (3) \\ 742  (3) \\ 823  (3) \end{array}$ | $\begin{array}{c} 467(3)\\ 240(3)\\ 173(3)\\ 182(3)\\ 241(3)\\ 301(3)\\ 510(3)\\ 584(3)\\ 603(3)\\ 547(3)\\ 547(3)\\ 547(3)\\ 575(3)\\ 584(3)\\ 485(3)\\ 483(3)\\ \end{array}$ | $\begin{array}{c} H_{(23.3)} \\ H_{(24.1)} \\ H_{(24.2)} \\ H_{(24.2)} \\ H_{(25.2)} \\ H_{(25.2)} \\ H_{(25.2)} \\ H_{(26.1)} \\ H_{(26.2)} \\ H_{(26.3)} \\ H_{(28)} \\ H_{(29)} \\ H_{(30)} \\ H_{(31)} \\ H_{(32)} \end{array}$ | $192(4) \\ 515(4) \\ 437(4) \\ 375(4) \\ 385(4) \\ 393(4) \\ 568(4) \\ 621(4) \\ 617(4) \\ 210(4) \\ 163(4) \\ 303(4) \\ 467(4) \\ 527(4) \\ \end{array}$ | $\begin{array}{c} 773 (3) \\ 580 (3) \\ 594 (3) \\ 567 (3) \\ 628 (3) \\ 697 (3) \\ 622 (3) \\ 640 (3) \\ 692 (3) \\ 903 (3) \\ 976 (3) \\ 974 (3) \\ 896 (3) \\ 829 (3) \end{array}$ | $\begin{array}{c} 567(3)\\ 368(3)\\ 422(3)\\ 334(3)\\ 197(3)\\ 145(3)\\ 165(3)\\ 262(3)\\ 217(3)\\ 144(3)\\ 144(3)\\ -72(3)\\ 16(3)\\ 144(3) \end{array}$ |



Fig. 1. General form of the cation of salt IIIb and numbering of the atoms.

and the strong thermal vibrations of the peripheral atoms of the substituents in the cation affect the accuracy of the determination of the bond lengths and bond angles in which they participate. The hydrogen atoms were revealed from a differential series and were refined isotropically with fixed  $B_{iso} = 5 \text{ Å}^2$ . The final values of the divergence factors R = 0.089 and  $R_W = 0.092$ . All of the calculations were made with an ECLIPSE S/200 computer by means of INEXTL programs [10]. The coordinates of the nonhydrogen atoms are presented in Table 4, while the coordinates of the hydrogen atoms are presented in Table 5.

The results of elementary analysis of Ib and II-IVa, b for C, H, Cl, and N were in agreement with the calculated values.

2,4-Diphenyl-5-R-6-methyl-3-azapyrylium perchlorates Ia, b were synthesized by the method in [2].

2,4-Diphenyl-5-R-6-methylene-6H-1,3-oxazines IIa, b. A mixture of 20 ml of absolute triethylamine and 10 ml of the corresponding perchlorate I was stirred for 1 h at 20°C, after which 100 ml of ether was added, and the solution was separated by decantation from the oily triethylamine perchlorate and evaporated in vacuo. The crystalline residue was washed with ethanol and dried in vacuo.

1,3,8-Triphenyl-6-methyl-4,7-R-pyrido[1,2-c]pyrimidinium Perchlorates IIIa, b. A mixture of 10 ml of acetic anhydride, 2 ml of DMF, and 5 mmole of the corresponding perchlorate I was refluxed for 5-7 min, after which it was cooled and diluted to 10 times its original volume with ether. The resulting oily precipitate was separated by decantation and crystallized by trituration with water or ethanol. The product was removed by filtration. Compound IIIa was recrystallized from acetic acid, while IIIb was recrystallized from ethanol.

2-Phenyl-3-R-4-methyl-6-( $\alpha$ -R- $\beta$ -benzoylaminostyryl)pyridines IVa, b. A. A mixture of 10 ml of acetic anhydride, 2 ml of DMF, and 5 mmole of perchlorate Ia, b was maintained at 20°C for 48 h, after which 100 ml of ether was added. The resulting precipitate was removed by filtration and washed with ether (3 × 20 ml) (as described in the preceding method, salts IIIa, b were isolated when the perchlorates obtained were heated in acetic anhydride). The precipitate was then stirred for 4 h at 20°C in a mixture of 100 ml of 5% aqueous NaOH solution and 50 ml of ether. The ether layer was separated and evaporated, and the residue was chromatographed with a column packed with Al<sub>2</sub>O<sub>3</sub> (with a 30 cm sorbent layer, a column diameter of 1.6 cm, and elution with chloroform) with collection of the first fraction with R<sub>f</sub> 0.8. Recrystallization from heptane gave colorless crystals of IVa, b.

**B**. A 5-mmole sample of the corresponding anhydro base IIa, b was added to a suspension of 5 mmole of perchlorate Ia, b in 15 ml of dichloroethane. After 10 h, the mixture was diluted with 100 ml of ether, and the resulting precipitate was removed by filtration. Pyridines IVa, b were isolated as described above.

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