2-BENZOPYRYLIUM SALTS

XII.* SYNTHESIS OF BIS-2-BENZOPYRYLIUM SALTS

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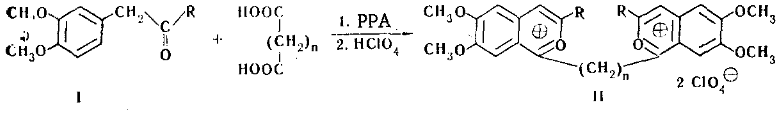
The previously unknown bis-2-benzopyrylium salts and 2-benzopyrylium salts containing an alkylcarboxy group were synthesized by the acylation of some alkoxy-substituted deoxybenzoins and phenylacetones with dibasic aliphatic acids in polyphosphoric acid. The effect of the structure of the dicarboxylic acid on the structure of the reaction products was followed. The IR spectra of the synthesized salts are presented.

Despite the extensive investigations carried out with respect to the synthesis and study of the properties of pyrylium salts, compounds with two or more pyrylium cations in the molecules have received little study, and methods for their synthesis [1-3] need further development.

We have previously demonstrated that the introduction of aromatic, aliphatic-aromatic [4,5], or heterocyclic [6] residues into the 1 position of the 2-benzopyrylium cation can be accomplished by the acylation of alkoxy-substituted deoxybenzoins or phenylacetones with the appropriate acids in polyphosphoric acid (PPA).

In a continuation of these investigations to synthesize 2-benzopyrylium salts, we studied the acylation of 3-methoxydeoxyanisoin (Ia) and 3,4-dimethoxyphenylacetone (Ib) with dibasic acids in the presence of PPA.

As should have been expected, the structures of the reaction products are determined by the length of the hydrocarbon chain of the reacting acid. When dibasic acids with n ≥ 3 (glutaric, adipic, and pimelic) were introduced into the reaction, the previously unknown bis-2-benzopyrylium salts (II) were obtained in 20-60% yields.



a $R = p\text{-}CH_3OC_6H_4$; b $R = CH_3$; $n = 3, 4, 5$; $R = CH_3$, $p\text{-}CH_3OC_6H_4$

The same system of bands that is present in the spectra of the corresponding mono-2-benzopyrylium salts [4,7] (1616-1640, 1600-1610, 1540-1560, 1230-1280, and 1080-1100 cm^{-1}) is retained in the IR spectra of all of the synthesized bis-2-benzopyrylium salts.

The acylation of Ia with succinic acid gave 1-(2-carboxyethyl)-3-(4-methoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorate (III) in 30% yield. The IR spectrum of the salt contains a strong band at 1712 cm^{-1}, which corresponds to the stretching vibrations of a free carboxyl group, and the characteristic absorption bands of the 2-benzopyrylium cation [4,7].

Malonic acid is decarboxylated under the reaction conditions; the acylation of Ia by the acetic acid formed leads to a previously synthesized salt (IV) [4]. A comparison of the melting points and IR spectra of this and previously obtained samples confirms that they are identical.

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*See [8] for communication XI.

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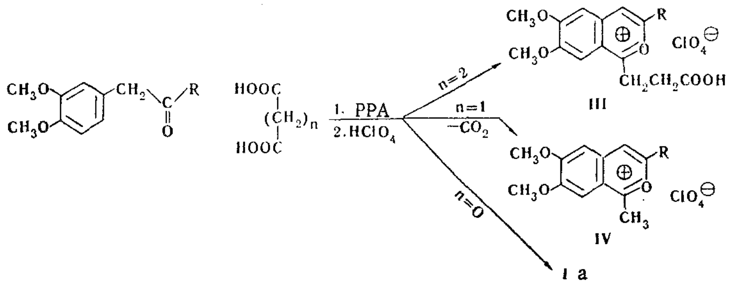

Attempts to acylate Ia with oxalic acid were unsuccessful, since the latter decomposes completely under the reaction conditions.

It must be noted that the structure of the starting ketone also has an appreciable effect on the course of the reaction. For example, in the acylation of ketone Ia with glutaric acid (n = 3), the presence of a structure containing a carboxyl group (an absorption band at 1710 cm^{-1} in the IR spectrum, the intensity of which is markedly reduced) was qualitatively proved to be in the reaction mixture along with the bisacylation products. However, this band is absent in the IR spectrum of the salt obtained from the reaction of ketone Ib and glutaric acid.

EXPERIMENTAL

1,1'-Pentamethylenebis[3-(4-methoxyphenyl)-6,7-dimethoxy-2-benzopyrylium] Diperchlorate (II, R = p-$CH_3OC_6H_4$, n = 5). A mixture of 0.7 g (2.5 mmole) of 3-methoxydeoxyanisoin (Ia), 0.16 g (1.25 mmole) of pimelic acid, and 10 g of PPA was heated for 2.5 h at 95-100°. The mixture was poured into cold water and acidified with 30% $HClO_4$, and the precipitated product was removed by filtration and dried. Reprecipitation from nitromethane solution by the addition of ether (to remove unchanged ketone) and recrystallization from nitromethane gave 0.62 g (58%) of yellow crystals with mp 220°. Found: C 55.9; H 5.0; Cl 8.0%. $C_{41}H_{42}Cl_2O_{16}$. Calculated: C 56.0; H 4.9; Cl 8.3%. IR spectrum, cm^{-1}: 1616, 1602, 1566, 1236, and 1099.

1,1'-Tetramethylenebis[3-(4-methoxyphenyl)-6,7-dimethoxy-2-benzopyrylium] Diperchlorate (II, R = p-$CH_3OC_6H_4$, n = 4). This compound was similarly obtained in 48% yield as dark-yellow crystals with mp 240° by acylation of Ia with adipic acid. Found: C 56.3; H 4.8, Cl 8.7%. $C_{40}H_{40}Cl_2O_{16}$. Calculated: C 56.5; H 4.7; Cl 8.4%.

1,1'-Trimethylenebis(3-methyl-6,7-dimethoxy-2-benzopyrylium) Diperchlorate (II, R = CH_3, n = 3). This compound was obtained by heating a mixture of 0.78 g (4 mmole) of Ib, 0.16 g (2 mmole) of glutaric acid, and 5 g of PPA at 95-100° for 30 min. The dark-green crystals [0.29 g (23%)] had mp 217° (from acetic acid). Found: C 49.8; H 4.5; Cl 10.8%. $C_{27}H_{30}Cl_2O_{14}$. Calculated: C 49.9; H 4.6; Cl 10.9%. IR spectrum, cm^{-1}: 1640, 1602, 1540, 1500, 1284, and 1076.

1,1'-Tetramethylenebis(3-methyl-6,7-dimethoxy-2-benzopyrylium) Diperchlorate (II, R = CH_3, n = 4). This compound was similarly obtained in 33% yield by acylation of Ib with adipic acid. The dark-gray crystals melted above 280°. Found: C 50.7; H 4.8; Cl 11.2%. $C_{28}H_{32}Cl_2O_{14}$. Calculated: C 50.7; H 4.8; Cl 10.7%. IR spectrum, cm^{-1}: 1634, 1608, 1434, 1284, 1083.

1-(2-Carboxyethyl)-3-(4-methoxyphenyl)-6,7-dimethoxy-2-benzopyrylium Perchlorate (III) (R = p-$CH_3OC_6H_4$). This compound was obtained in the usual manner in 30% yield by acylation of Ia with succinic acid at 100° for 3 h; the product had mp 222°. Found: C 54.2; H 4.6; Cl 8.0%. $C_{21}H_{21}ClO_{10}$. Calculated: C 53.7; H 4.5; Cl 7.6%. IR spectrum, cm^{-1}: 1720, 1610, 1602, 1556, 1508, 1232, and 1080.

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