2-BENZOPYRYLIUM SALTS CONTAINING THIOPHENE SUBSTITUENTS IN POSITIONS 1 AND 3

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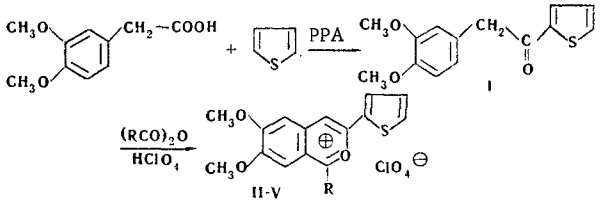
2-Benzopyrylium salts containing heterocyclic substituents have not previously been known. In order to obtain 2-benzopyrylium salts containing thiophene substituents in position 3, we have studied the acylation of 3,4-dimethoxybenzyl 2-thienyl ketone (I), which was obtained with a yield of 36% by the acylation of thiophene (at 75°C) with homoveratric acid in the presence of polyphosphoric acid (PPA). Compound I forms yellow crystals with mp 74-75°C (from benzene), bp 220°C (6 mm). Found %: C 63.40; H 5.38; S 13.55. $C_{11}H_{13}O_3S$. Calculated %: C 64.12; H 5.34; S 13.21.

The acylation of I with aliphatic acid anhydrides in the presence of 70% $HClO_4$ under mild conditions gave 1-alkyl-6,7-dimethoxy-3-(α-thienyl)-2-benzopyrylium salts (II-V) according to the following scheme:



II R=CH_3; III R=C_2H_5; IV R=C_3H_7; V R=C_4H_9

The properties and yields of the salts obtained are given in Table 1.

To obtain 2-benzopyrylium salts having a thiophene substituent in position 1 we used a method proposed previously [1]. In this way, by acylating 3,4-dimethoxyphenylacetone with thiophene-2-carbonyl chloride in the presence of anhydrous $AlCl_3$ we obtained a tetrachloroaluminate. The latter was converted by treatment with perchloric acid into 6,7-dimethoxy-3-methyl-1-(α-thienyl)-2-benzopyrylium perchlorate. It formed orange crystals with mp 309°C (from nitromethane). Found %: C 49.81; H 3.98; Cl 9.18; S 8.35. $C_{16}H_{15}O_7ClS$. Calculated %: C 49.67; H 3.88; Cl 9.18; S 8.27.

The structure of the salts obtained was confirmed by IR spectroscopy.

TABLE 1. 2-Benzopyrylium Salts

Compound	mp, °C	Empirical formula	Found, %				Calc., %				Yield, %
			C	H	Cl	S	C	H	Cl	S	
II	360	$C_{16}H_{15}O_7ClS$	49,06	4,00	9,18	8,00	49,67	3,88	9,18	8,27	75
III	217	$C_{17}H_{17}O_7ClS$	51,22	3,98	7,79	8,65	50,94	4,24	8,05	7,99	68
IV	246	$C_{18}H_{19}O_7ClS$	51,78	4,83	8,40	8,00	52,12	4,59	8,45	7,75	50
V	237	$C_{19}H_{21}O_7ClS$	53,15	5,13	8,28	6,93	53,20	4,90	8,28	7,46	70

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