PYRILOCYANINES.

24.* SYMMETRICAL TETRA-tert-BUTYL SUBSTITUTED PYRILO-2-CYANINES

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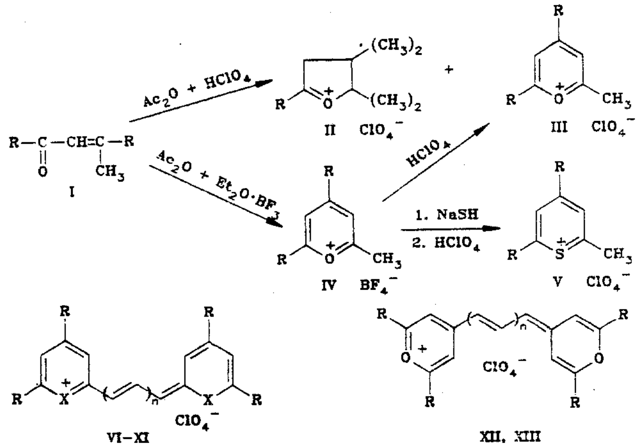
2,4-di-tert-butyl-6-methylpyrilium and -thiopyrilium salts were synthesized. From them were obtained symmetrical tetra-tert-butyl substituted α-pyrilocarbo- and dicarbocyanines and their sulfur analogs. The α-pyrilocyanines were converted to symmetrical α-pyridocyanines. The effects of heteroresidue structure, length of polymethine chain, and solvent on the location and shape of the absorption bands of these dyes were studied. Their experimental spectral properties were compared with the results of quantum chemical calculations of average band locations, second-power changes of bond order upon excitation, and theoretical electron donor capabilities.

The features of the absorption spectra of pyrilo-2-cyanines and their heteroanalogs, as exemplified by tetraphenyl-substituted dyes [1-3], have been studied in detail. But in those compounds the phenyl substituents are located (depending on the heteroatom) at various angles to the chromophore plane [4] and consequently show different effects on the color. The dependence of color on the electron structure of the heteroresidue should be followed more distinctly by using tetraalkyl-substituted pyrilo-2-cyanines and their heteroanalogs as examples. Such dyes with methyl substituents are practically unavailable, because 2,4,6-trimethylpyrilium salts undergo the cyanine condensation because of the methyl group at position 4 [5]; consequently, the present work has undertaken the problem of synthesizing 2,4-di-tert-butyl-6-methylpyrilium and -thiopyrilium salts and symmetrical polymethine dyes based on them.



II—XIII R=C(CH$_3$)$_3$; VI, VII X=O, VIII, IX X=S, X, XI, X=NCH$_3$; VI, VIII, X, XII n=1, VII, IX, XI, XIII n=2, VI BF$_4$- anion

In [6] it was shown that when 2,2,5,6,6-pentamethylhept-4-en-3-one (I) reacts with perchloric acid the only product is the dihydrofurylium salt II. We have found that when the same ketone I is treated with a mixture of acetic anhydride and perchloric acid, along with compound II 2,4-di-tert-butyl-6-methylpyrilium perchlorate (III) forms in 26% yield. The reaction of a mixture of acetic anhydride and boron trifluoride etherate with substance I gave only pyrilium tetrafluoroborate IV. By treatment with perchloric acid compound IV was

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*For Communication 23, see [1].

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TABLE 1. Properties of Long-Wave Absorption Bands of Dyes VI-XIII

Dye	X	n	Solvent*	λ_{max}, nm	lg ε	M^{-1}, nm	f	σ, cm^{-1}	γ_1	γ_2	F	M_{th}^{-1}, nm	δ	Φ_0
VI	O	1	1	616, 668	4,77; 5,09	631,6	0,81	1058	1,36	2,8	0,091	619	0,1705	40,0
			2	611, 660	4,74; 4,95	618,4	0,71	1235	1,46	3,5	0,089			
VII	O	2	1	700, 763	4,71; 5,07	731,3	0,85	970	1,41	3,2	0,089	725	0,1315	41,1
			2	695, 755	4,87; 5,07	704,5	1,09	1260	1,35	2,9	0,080			
VIII	S	1	1	782	4,85	732,1	0,70	910	1,30	2,5	0,056	718	0,1490	37,9
			2	747	4,68	713,4	0,67	1200	1,16	2,4	0,048			
IX	S	2	1	876	5,03	832,5	0,80	925	1,39	3,4	0,068	827	0,1210	39,0
			2	854	4,85	778,6	0,95	1455	1,39	3,6	0,077			
X	NCH_3	1	1	575	4,81	554,8	0,63	1030	1,30	2,2	0,044	486	0,1615	66,5
			2	572	4,70	548,0	0,62	1180	1,50	2,4	0,062			
XI	NCH_3	2	1	675	5,34	658,7	1,21	890	2,07	7,3	0,113	577	0,1286	67,8
			2	666	5,19	638,0	1,09	1160	2,06	6,9	0,126			
XII	—	1	1	607	5,40	593,3	1,00	751	1,82	4,8	0,130	593	0,1222	38,0
			2	598	5,34	581,9	1,03	842	1,74	4,4	0,118			
XIII	—	2	1	715	5,54	699,7	1,32	754	1,96	5,9	0,135	707	0,0977	39,7
			2	703	5,35	676,7	1,26	970	1,72	4,4	0,116			

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*1) Methylene chloride; 2) acetonitrile.

converted to perchlorate III, while reaction with sodium hydrosulfide gave the corresponding thiopyrilium salt V.

Carbocyanines VI and VIII were obtained by condensation of salts IV and V with ethyl orthoformate. Dicarbocyanines VII and IX were synthesized from salts IV and V and (3-phenylaminopropene-2-ylidene)phenyl ammonium chloride. The symmetrical pyridocarbo- and -dicarbocyanines X and XI were obtained by treatment of pyrilocyanines VI and VII with methylamine. For comparison of spectral data, the isomeric pyrilo-4-carbocyanine XII [7] and, by analogy with compound VII, dicarbocyanine XIII [8] were also synthesized.

For solutions of the synthesized dyes in weakly polar methylene chloride and strongly polar acetonitrile, Table 1 shows besides λ_{max} and log ε (as in [1-3]), the average positions of the absorption bands M^{-1} (determined by the method of moments), the oscillator forces f, and the properties of the band shape, viz., the width σ, and the coefficients of asymmetry γ_1, of excess γ_2, and fine structure F. Besides the experimental data Table 1 also shows the results of quantum chemical calculations by a simple Hückel molecular orbital (HMO) method with the following parameters [9]: average bond positions M_{th}^{-1}, second-power changes of bond order upon excitation δ [10], and theoretical electron donor capabilities Φ_0 [11] of these compounds. The value of δ is determined by the expression

$$\delta=\sqrt{\sum_{i}^{m}(p^0-p^*)_i^2},$$

where p^0 and p^* are the bond orders of the ground and excited states, respectively; i, bond number; and m, number of bonds. In the absence of strong solvation effects this property, being a quantitative measure of vibrational interactions, changes symbatically with the experimental band width [10].

Since in the present work we consider only the first transition, which is one-electron and to which the contribution of higher configurations is small [11, 12], we were limited to calculations for the test dyes by the method described above. Moreover, comparison of the calculations in HMO, CNO, and CNDO/2 approximations for a number of polymethine dyes showed that all these methods not only validly convey the tendency of cyanine bond orders and charges to change, but also give close to the absolute values for these quantities [11, 12]. In the calculation no account was taken of the tert-butyl group. The value of β is $-28{,}624$ cm^{-1}.

From comparison of the spectral properties of the synthesized dyes (Table 1) and their phenyl substituted analogs [2], it follows that the former are substantially more highly colored and have narrower absorption bands. Moreover, the tert-butyl substituted dye bands are distinguished by greater asymmetry, sharpness of peak, and structurization. This is evidenced by the higher numerical values of γ_1, γ_2, and F of compounds VI-XIII as compared with those of dyes described in [2]. The differences in band location and shape of the dyes mentioned above are related to the participation of phenyl groups in conjugation with the basic chromophore, which lengthens and strengthens the vibrational interactions (VI). This reflected correspondingly in the increase of M_{th}^{-1} and δ in going from tert-butyl dyes (Table 1) to phenyl substituted [3]. (For the latter M_{th}^{-1} and δ were calculated only for the carbocyanines.)

From the data of the quantum chemical calculations of M_{th}^{-1} (Table 1), it follows that replacement of oxygen by sulfur in the pyrilocyanines should cause a deepening of color by ~100 nm. Indeed in the dyes containing tert-butyl substituents, the value of the bathochromic shift calculated from M_{th}^{-1} in the weakly solvating methylene chloride practically coincides with that calculated by theory in going from pyrilo- to thiopyrilocyanines. In the case of the tetraphenyl-substituted compounds [2] a similar change of heteroatom also causes a deepenin of color, but in smaller amount (~80 nm) than the dyes mentioned above. The explanation may be that phenyl groups in the 6,6' positions, due to large steric hindrance by the sulfur of the thiopyrilocyanines, is taken out of the chromophore plane and consequently out of conjugation to a greater extent than in the case of the dyes containing oxygen [4]. Quantum chemical calculations of M_{th}^{-1} for the tetraphenyl substituted analogs VI and VIII at resonance integral values of the $C-C_6H_5$ that correspond to the phenyl group rotation angles in these compounds [4] are in good agreement with experimental values [3].

The replacement of the heteroatom, as with the tetraphenyl-substituted dyes [2], is accompanied by a narrowing of the absorption bands in methylene chloride. The symbatic change of σ and δ (Table 1) is evidence that this is due to a weakening of VI. In the tert-butyl substituted dyes the narrowing bands when oxygen is replaced by sulfur is accompanied by a decrease in the asymmetry, excess, and fine structure coefficients. Such changes cannot be due only to VI [10], but should be determined by some other kind of factor acting in the opposite direction. For the synthesized dyes the course of σ, γ_1, γ_2, and F is the same as for the corresponding phenyl substituted compounds.

Most probably, for both types of dyes it is due to intensification of interactions with the solvent (nucleophilic solvation [13]), which always increase as the deviation of the heter oresidue from average electron donor capability ($\Phi_0 = 45°$) and the length of the polymethine chain [14] increase (thiopyrilium Φ_0 < pyrilium $\Phi_0 < 45°$, see Table 1). Indeed, as n increase the amount of narrowing in going from pyrilo- to thiopyrilocyanine decreases. This tendency can be followed even more distinctly in the strongly polar acetonitrile. There the solvation effects are so pronounced that replacement of oxygen by sulfur in pyrilodicarbocyanines is accompanied not by band narrowing, but strong broadening (Table 1 and [15]).

Thus, replacement of oxygen by sulfur in pyrilocyanines deepens the color practically by the same amount as lengthening the polymethine chain by one vinyl group. The use of a weakly nucleophilic solvent permits simultaneous increase of absorption selectivity and decrease of σ; in theory this is impossible to achieve with increase of n, due to the increase in solvation, especially if the heteroresidue deviates from the average electron donor capability [14]. On the other hand, a strongly nucleophilic solvent makes it possible to significantly broaden the thiopyrilocyanine absorption bands at practically the same value of bathochromic shift (λ_{max} is less sensitive to change in solvent nucleophilicity than are M^{-1} and σ) [13].

Theoretical calculations with the parameters of [9], although they give M_{th}^{-1} values for pyridocyanines that are much too low, enable us to predict the hypsochromic band shift when the oxygen in pyrilo-2-cyanines is replaced by nitrogen (Table 1). To account for the increased coloration caused by similar replacement as exemplified by tetraphenyl-substituted dyes is extremely difficult. On the one hand, it may be due to lesser participation of pyridine nucleus C—C bonds in conjugation than that of pyrilium bonds [2]; on the other hand, it may be due to stronger rotation of the phenyl groups at the 6,6' pyridocyanine positions (the angle of rotation reaches 60° [4]) as compared with pyrilocyanines. In going from tert-butyl substituted pyrilocyanines VI and VII to their nitrogen analogs X and XI the hypsochromic shift indicates unequivocally that it is due to the former cause. This is confirmed by the fact that for the isomeric alkyl-substituted γ-series dyes, in which the heteroresidue C—O bond takes an equal part in the conjugated system, the pyrilocyanines are nevertheless more deeply colored that the pryidocyanines [7].

With the α-series phenyl-substituted dyes as an example, starting from what has been presented above, it is also complicated to elucidate the factors that determine the absorption band narrowing when oxygen is replaced by nitrogen. Such a change in breadth is moreover quite unusual, because Φ_0 of the pyridinium series differs from 45° to a very much greater extent than does pyrilium Φ_0 (Table 1). In such cases the alternation of the bonds from heteroresidue to the center of the chain increases [12]. Consequently, the transition from pyrilo- to pyridocyanine should be accompanied by intensification of VI and band broadening. Indeed the latter appears distinctly for the corresponding γ-series dyes [2]. But as the values of σ and δ show, for compounds VI, VII and X, XI the picture is quite the opposite. In order to resolve this contradiction, it is necessary to take into account that a substantial contribution to the overall δ value of the α-pyrilocyanines and their homologs comes from the change in $C_{(3)}$–$C_{(4)}$ bond order upon excitation [15]. The lesser participation of this bond and the adjacent nuclear bonds in conjugation in the nitrogen dyes, as compared with the oxygen analog compensates for the VI increase due to increased bond alternation in going from pyrilo- to pyridocyanine. Indeed the contribution of the $C_{(3)}$–$C_{(4)}$ bonds in dye VI to the total value of δ is 33%, whereas in dye X, it is only 16%. Consequently in the pyridocyanines these bonds are isolated to a significant extent from the main chromophore, whereas in the pyrilo- and thiopyrilocyanines they constitute a continuation of the polymethine chain.

The pyrilo- and thiopyrilocyanines are significantly more solvatochromic than are the pyridocyanines (Table 1). For example, in going from methylene chloride to acetonitrile the bands broaden and their average location shifts toward the high-frequency region of the spectrum (for dye VI, by 177 and 338; for dye VIII, by 290 and 358; and dye X, only by 150 and 224 cm^{-1}, respectively). The weakening of nucleophilic solvation in going from α-pyrilo- and thiopyrilocyanines to their nitrogen analogs is also related to the longer conjugation chain in the former; due to the greater deviation of Φ_0 of the pyridinium series from 45° than that of pyrilium and thiopyrilium, the opposite result should be expected [14].

Table 1 shows that the Φ_0 values of the heteroresidues of isomeric dyes differ little from one another, while the α-pyrilium nucleus is somewhat closer to 45° than its γ-isomer. Hence it can be assumed that the pyrilo-2-cyanines will solvate more weakly than the γ-series dyes. But also in the present case, in going from methylene chloride to acetonitrile the reverse picture appears (for pyrilo-4-carbocyanine XII, $\Delta\sigma = 91$, $\Delta M^{-1} = 330\ cm^{-1}$). The greater tendency of pyrilo-2-cyanines to undergo nucleophilic solvation as compared with their 4-isomers is yet another confirmation of the presence in the former of a longer chromophore.

Thus our investigation enables us to unequivocally relate the location and shape of the absorption bands of dyes VI-XIII with the heteroresidue structure; this makes it possible to synthesize pyrilocyanines and their hetero analogs with specific spectral properties.

EXPERIMENTAL

Absorption band moments were determined analogously to [1-3] on the basis of the absorption spectra obtained with a SF-4A spectrophotometer in methylene chloride stabilized with 1% absolute ethanol and in acetonitrile. Absorption spectra of dye solutions ranged over at least two orders of magnitude with respect to intensity. The numerical values in Table 1 have a precision corresponding to the size of the measurement error of the spectra. UV spectra were obtained with the same instrument in methylene chloride. The dyes were carefully purified until the absorption curve became constant. Purity of preparations was monitored by TLC on Silufol-254 plates, with acetonitrile eluent. PMR spectra were determined with a Tesla BS-467 spectrometer (60 MHz) at 20° in CF_3CO_2H, with HMDS internal standard.

2,4-Di-tert-butyl-6-methylpyrilium Perchlorate (III). To a solution of 1.82 g (10 mmole) of 2,2,5,6,6-pentamethylhept-4-en-3-one (I) in 10 ml of acetic anhydride was added a mixture of 10 ml of acetic anhydride and 1.5 ml (25 mmole) of 70% perchloric acid (prepared with cooling) with stirring at 0°. The mixture was heated at 100° for 5 min. The precipitate of salt II was filtered off and the mother liquor was diluted with ether. The reaction product was reprecipitated from acetone with ether (Table 2).

2,4-Di-tert-butyl-6-methylpyrilium Tetrafluoroborate (IV). To a solution of 1.4 g (7.7 mmole) of ketone I in 5 ml of acetic anhydride was added 3 g (2.1 mmole) of boron trifluoride etherate and the mixture was boiled for 3 min. The reaction mixture was cooled and diluted with ether. UV spectrum, λ_{max} (log ε): 240 (3.92), 288 nm (4.11). PMR spectrum: 1.06 [9H, s, γ-$C(CH_3)_3$]; 1.15 [9H, s, α-$C(CH_3)_3$]; 2.55 (3H, s, α-CH_3); 7.57 ppm (2H, s, β-H).

Tetrafluoroborate IV was converted by 20% perchloric acid to perchlorate III in 90% yield

2,4-Di-tert-butyl-6-methylpyrilium Perchlorate (V). To a solution of 0.294 g (1 mmole) of salt IV in 4 ml of acetonitrile was added 3 ml (3 mmole) of a saturated solution of NaSH in absolute ethanol. The mixture was stirred for 20 min and filtered, and to the filtrate were added 1.3 ml (2.2 mmole) of 70% perchloric acid and 100 ml of ether. The white crystalline

TABLE 2. Properties of Synthesized Compounds

Compound	mp,* °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	Cl (F)	N (S)		C	H	Cl (F)	N (S)	
III	142—144	54,6	7,9	11,6	—	$C_{14}H_{23}ClO_5$	54,8	7,5	11,6	—	26
IV	123—124	57,1	8,2	(25,5)	—	$C_{14}H_{23}BF_4O$	57,2	7,8	(25,9)	—	53
V	140—141	—	—	11,0	(10,1)	$C_{14}H_{23}ClO_4S$	—	—	11,0	(9,9)	52
VI	212—214	68,3	8,6	(14,5)	—	$C_{29}H_{43}BF_4O_2$	68,3	8,4	(14,9)	—	58
VII	177—178	68,1	8,1	6,6	—	$C_{31}H_{45}ClO_6$	67,8	8,2	6,5	—	35
VIII	209—210	—	—	6,4	(11,5)	$C_{29}H_{43}ClO_4S_2$	—	—	6,4	(11,5)	35
IX	201—203	—	—	6,1	(10,7)	$C_{31}H_{45}ClO_4S_2$	—	—	6,1	(11,0)	28
X	115—117	—	—	6,5	5,1	$C_{31}H_{49}ClN_2O_4$	—	—	6,5	5,1	55
XI	194—195	—	—	6,4	5,2	$C_{33}H_{51}ClN_2O_4$	—	—	6,2	4,9	32

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*Compounds III-V reprecipitated from acetone with ether; VII, X from acetone with n-hexane; compound VI crystallized from ethanol; VIII, IX, XI from 1:5 ethanol—tert-butanol.

precipitate was filtered off and washed with water and ether. UV spectrum, λ_{max} (log ε): 269 (4.01), 305 nm (3.88). PMR spectrum: 1.09 [9H, s, γ-$C(CH_3)_3$]; 1.22 [9H, s, α-$C(CH_3)_3$]; 2.70 (3H, s, α-CH_3); 8.10 (1H, s, β-H); 8.25 ppm (1H, s, β'-H).

2-[3-(4,6-Di-tert-butylpyranilidene-2)propen-1-yl]-4,6-di-tert-butylpyrilium Tetrafluoroborate (VI). A mixture of 0.294 g (1 mmole) of salt IV and 0.74 g (5 mmole) of ethyl orthoformate in 3.5 ml of dry pyridine was heated at 120° for 2 h. After cooling the mixture was diluted with aqueous HBF_4.

2-[5-(4,6-Di-tert-butylpyranylidene-2)pentadien-1,3-yl-1]-4,6-di-tert-butylpyrilium Perchlorate (VII). A mixture of 0.294 g (1 mmole) of salt IV, 0.129 g (0.5 mmole) of phenyl[(3-phenylamino)-2-propenylidene]ammonium chloride, and 0.1 g (1.2 mmole) of anhydrous sodium acetate in 5 ml of acetic anhydride was boiled for 3 min, cooled, and diluted with aqueous sodium perchlorate.

2-[3-(4,6-Di-tert-butylthiopyranylidene-2)propen-1-yl-1]-4,6-di-tert-butylthiopyrilium Perchlorate (VIII). A mixture of 0.323 g (1 mmole) of salt V, 0.74 g (5 mmole) of ethyl orthoformate, and 0.1 g (1.2 mmole) of anhydrous sodium acetate in 3 ml of acetic anhydride was boiled for 3 min. The mixture was diluted with aqueous sodium perchlorate.

2-[5-(4,6-Di-tert-butylthiopyranylidene-2)pentadien-1,3-yl-1]-4,6-di-tert-butylthiopyrilium Perchlorate (IX). This was obtained similarly to compound VII by using salt V.

1-Methyl-2-[3-[1-methyl-4,6-di-tert-butyl-1,4-dihydropyridinylidene-2)propen-1-yl-1)-4,6-di-tert-butylpyridinium Perchlorate (X). A mixture of 0.149 g (0.3 mmole) of pyrilocyanine VI and 1 ml (3.3 mmole) of 10% methanolic methylamine in 1.5 ml of dimethyl sulfoxide was heated at 90° for 1 h. The dye was precipitated by aqueous sodium perchlorate.

1-Methyl-2-[5-(1-methyl]4,6-di-tert-butyl-1,4-dihydropyridinylidene-2)pentadien-1,3-yl-1]-4,6-di-tert-butylpyridinium Perchlorate (XI). This was obtained similarly to X from the respective pyrilocyanine VII.

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SYNTHESIS AND RECYCLIZATION OF 4-CHLOROMETHYLFLAVYLIUM AND 4-CHLOROMETHYLBENZOTHIAPYRILIUM SALTS

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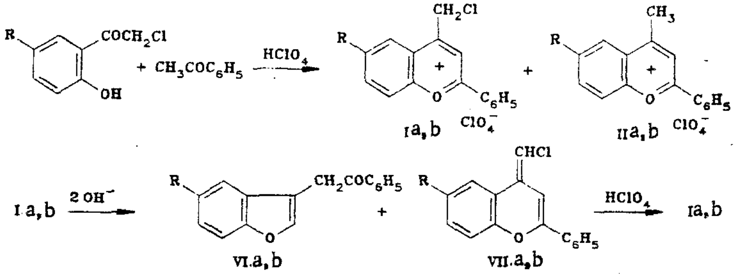
Condensation of α-chloro-o-hydroxyacetophenones in the presence of perchloric acid yields 4-chloromethylflavylium perchlorates. 4-Chloromethylbenzothiapyrilium perchlorates were obtained by intramolecular cyclization of 2-arylmercapto-5-chloropentanones-4. In the reaction of 4-chloromethylflavylium salts with aqueous alkali, chloromethyleneflavenes (the anhydro bases of the starting salts) and 3-phenacylbenzo[b]furanes were separated.

A feature of pyrilium salts is their ability to undergo ring contraction by the action of inorganic nucleophiles. Thus 2,3,4,6-tetraphenylpyrilium perbromide is converted by alkali to 2-benzoyl-3,4,5-triphenylfurane [1]. Later Balaban and Nenitzescu observed recyclization of trialkyl-substituted pyrilium salts to furanes by means of hydrogen peroxide [2]. Analogous ring contraction takes place during the oxidation of thiapyrilium cation and 1-benzothiapyrilium salts by manganese dioxide [3, 4]. Pyrilium ring contraction by recyclization of 4-chloromethylpyrilium salts to furylketones (the starting compounds for furopyrilium cation synthesis) in alkaline medium was recently reported [5]. The extension of this method to 4-chloromethylflavilium and 4-chloromethylbenzothiapyrilium salts would permit synthesis of the respective ketones of the benzo[b]furane and benzo[b]thiophene series.

The 4-chloromethylflavylium and 4-chloromethyl-1-benzothiapyrilium perchlorates have not been described. We find that the former can be obtained by the method used for the synthesis of 4-methylflavylium salts [6]. Indeed, condensation of α-chloro-o-hydroxyacetophenone with acetophenone in glacial acetic acid in the presence of perchloric acid gives 4-chloromethylflavylium perchlorates Ia,b. According to the PMR spectra, the respective 4-methylflavylium salts IIa,b form as byproducts, due to heterocyclic scission of the C—Cl bond in salts Ia,b. The amount of IIa,b depends on the duration of the reaction and is no more than 5% (the ratio is determined from the integrated intensities of the CH$_3$ and CH$_2$ signals).



I, II, VI, VII a R=H, b R=CH$_3$

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