sodium carbonate solution, water until the wash waters were neutral, and ethanol to give 0.7 g (21%) of a product with mp 319-320°C (from dimethylformamide). Found, %: C 75.2; H 5.8; N 8.6. $C_{20}H_{18}N_2O_2$. Calculated, %: C 75.4; H 5.7; N 8.8.

4-Nitro-4'-dimethylaminostilbene was obtained by the method in [11]; the synthesis of 2-(p-nitrophenyl)-5-(p-dimethylaminophenyl)-1,3,4-oxadiazole was described in [1].

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SYNTHESIS AND REACTIONS OF THIENO[2',3':5,4]THIENO[2,3-c]- AND THIENO[2',3':4,5]THIENO[2,3-c]PYRYLIUM SALTS

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N. N. Alekseev

UDC 547.737'816'83.07:543.422

Methods for the synthesis of isomeric thienothiophenes by cyclization of methyl γ-thienylmercaptoacetoacetates in polyphosphoric acid (PPA) were developed. It is shown that the acylation of the acetonyl derivaties of isomeric thienothiophenes in an aliphatic acid anhydride—70% perchloric acid system leads to the corresponding pyrylium salts. Some reactions of the latter with nucleophilic reagents were studied. The structures of the substance obtained were confirmed by the IR and PMR spectra.

In a continuation of our research on the synthesis and properties of pyrylium salts condensed with heterocyclic systems [1-3] we have realized the synthesis of thieno[2',3':5,4]-thieno[2,3-c]pyrylium and thieno[2',3':4,5]thieno[2,3-c]pyrylium perchlorates.*

We have observed that 5-alkylthieno[2,3-b]thiophen-3-ylacetic acid esters IIa,b and 5-methylthieno[3,2-b]thiophen-3-ylacetic acid ester IVa (Table 4) are formed in good yields in the intramolecular cyclization of γ-thienylmercaptoacetoacetic acid esters in polyphosphoric acid (PPA). The cyclization takes place under mild conditions only when substituent R is present in one of the α positions of the thiophene ring. Only resinification

*See [4] for our preliminary communication.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 37-41, January, 1983. Original article submitted December 9, 1981; revision submitted May 24, 1982.

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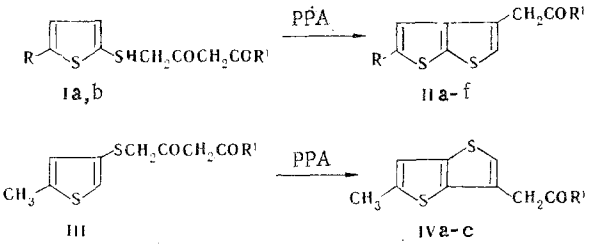
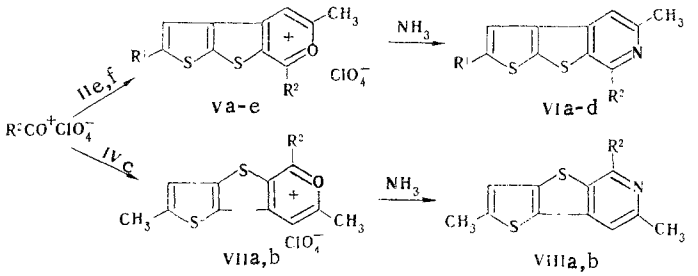


I a R=CH_3, R^1=OCH_3; b R=C_2H_5, R^1=OCH_3; II a R=CH_3, R^1=OCH_3; b R=C_2H_5, R^1=OCH_3; c R=CH_3, R^1=OH; d R=C_2H_5, R^1=OH; e R=CH_3, R^1=CH_3; f R=C_2H_5, R^1=CH_3; III R^1=OCH_3; IV a R^1=OCH_3, b R^1=OH, c R^1=CH_3

products were isolated in the cyclization of unsubstituted methyl γ-(2-thienylmercapto)acetoacetate. It must be noted that the formation of isomers of IIa,b and IVa is possible in the cyclization of the type used [5]. We showed by means of gas–liquid chromatography (GLC) and PMR spectroscopy that individual products are formed. Alkaline hydrolysis of IIa,b and IVa leads to the corresponding 5-alkylthieno[2,3-b]thiophen-3-ylacetic acids (IIc,d) and 5-methylthieno[3,2-b]thiophen-yl-acetic acid (IVb).

The acetonyl derivatives of isomeric thienothiophenes IIe,f and IVc were obtained by the same method as that used for the acetonyl derivatives of benzo[b]thiophene [6]. We demonstrated the formation of mixtures of the ketones and the acyl derivatives of the enols of the ketones by spectroscopy.

The acylation of 5-alkyl-3-acetonylthieno[2,3-b]thiophene (IIe, f) and 5-methyl-3-acetonylthieno[3,2-b]thiophene (IVc) in an aliphatic acid anhydride–perchloric acid system takes place in the free α position of the thienothiophene ring with subsequent cyclization to give thieno[2',3':5,4]thieno[2,3-c]pyrylium (Va-e) and thieno[2',3':4,5]thieno[2,3-c]pyrylium (VIIa,b) perchlorates.



V, VI a R^1=CH_3, R^2=CH_3; b R^1=CH_3, R^2=C_2H_5; c R^1=C_2H_5, R^2=CH_3; d R^1=C_2H_5, R^2=C_2H_5; e R^1=C_2H_5, R^2=C_4H_9; VII, VIII a R^2=CH_3, b R^2=C_2H_5

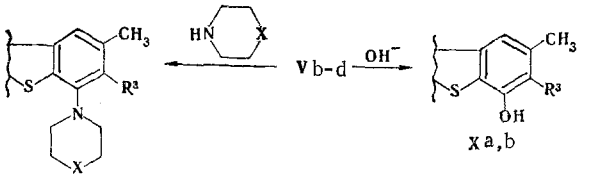
Reaction products Va-e to VIIa, b are stable crystalline compounds, the structures of which were proved by the results of elementary analysis and IR and PMR spectroscopy (Tables 1 and 5).

Thus in the PMR spectrum of perchlorate Va the chemical shifts of the protons of the methyl groups are observed at 3.16, 2.94, and 2.75 ppm, whereas they are observed at 2.94 and 2.75 ppm and at 3.16 and 2.75 ppm, respectively in the PMR spectra of perchlorates Vb and Vc. Thus the chemical shift of the protons of the methyl groups in the 1, 3, and 6 positions are, respectively, 3.16, 2.94, and 2.75 ppm. The weak-field shift of the signals of the methyl groups in the 1 and 3 positions is due to their deshielding by the positively charged heteroatom of the pyrylium ring. The aromatic protons are observed at 7.46 and 7.99 ppm. The chemical shifts of the methyl groups in 1,3,5-trimethylthieno[2',3':4,5]thieno[2,3-c]pyrylium perchlorate were similarly established (Table 5).

The IR spectra of Va-e and VIIa, b contain absorption bands at 1620, 1550, 1300, and 1090 cm^{-1}, which are characteristic for the pyrylium and thienothiophene rings, as well as the ClO_4^- anion.

Owing to the presence of a pyrylium ring, V and VII can be converted to various compounds of the heteroaromatic series by the action of nucleophilic agents. When ammonia is passed into alcohol suspensions of perchlorates Va-d and VIIa, b the latter are converted to the corresponding pyridine bases VIa-d and VIIIa, b in good yields (Table 2).

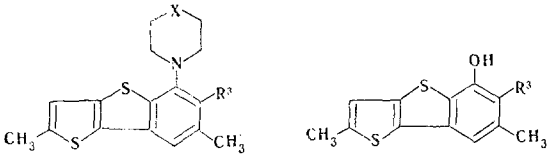
Hydroxy and amino derivatives of thieno[2,3-b]benzo[b]thiophene were isolated in the reaction of perchlorates Vb-d with aqueous alcohol solutions of alkalis and secondary cyclic amines (piperidine and morpholine) (Table 3).



IXa-d Xa,b

IX a $R^1=R^3=CH_3$, X=O; b $R^1=C_2H_5$, $R^3=H$, $X=CH_2$; c $R^1=C_2H_5$, $R^3=CH_3$, $X=CH_2$; d $R^1=C_2H_5$, $R^3=CH_3$, X=O; X a $R^1=C_2H_5$, $R^3=H$; b $R^1=C_2H_5$, $R^3=CH_3$

Compounds VIIa, b react similarly under these conditions to give the corresponding thieno[3,2-b]benzo[b]thiophene derivatives XIa-d and XIIa, b.



XIa-d XIIa,b

XI a $R^3=H$; b $R^2=CH_3$; c $R^3=H$; d $R^3=CH_3$; a, b $X=CH_2$; c, d X=O; XII a $R^3=H$; b $R^3=CH_3$

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds obtained were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz) with tetramethylsilane as the standard. The spectra of pyrylium salts were recorded in CF_3COOH, while the spectra of the hydroxy and dialkylamino derivatives of thienobenzo[b]thiophene were recorded in CCl_4.

Methyl γ-Thienylmercaptoacetoacetates (Ia, b, III). A 0.1-mole sample of mercaptothiophene was added at room temperature to a solution of sodium methoxide obtained from 2.3 g (0.1 mole) of sodium in 100 ml of methanol, after which a solution of 0.1 mole of methyl γ-chloroacetoacetate in 20 ml of methanol was added dropwise, and the reaction mixture was refluxed for 1 h, and 80 ml of methanol was removed by distillation. The residue was poured into 0.5 liter of cold water, and the aqueous mixture was extracted with ether. The extract was dried over calcium chloride, the ether was removed, and the residue was distilled *in vacuo* (Table 4).

Methyl Thieno[2,3-b]thiophen-3-yl- and Thieno[3,2-b]thiophen-3-ylacetates (IIa, b, IVa). A solution of 0.1 mole of ester Ia, b or III in 150 ml of chlorobenzene was added with vigorous stirring to 250 g of polyphosphoric acid (PPA), and the reaction mixture was heated at 55°C for 3 h. It was then poured over 1 kg of ice, and the product was extracted with chlorobenzene. The extract was dried over calcium chloride, the chlorobenzene was removed at reduced pressure, and the residue was distilled *in vacuo* (Table 4).

TABLE 1. Characteristics of V and VII

Compound	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	Cl	S		C	H	Cl	S	
Va	198—199	43,4	3,0	11,0	19,4	$C_{12}H_{11}ClO_5S_2$	43,3	3,3	10,6	19,1	84
Vb	166—167	45,2	4,0	10,0	18,0	$C_{13}H_{13}ClO_5S_2$	44,8	3,7	10,2	18,4	86
Vc	169—170	45,1	4,0	10,6	18,1	$C_{13}H_{13}ClO_5S_2$	44,8	3,7	10,2	18,4	86
Vd	146—147	46,0	4,4	9,5	18,1	$C_{14}H_{15}ClO_5S_2$	46,4	4,1	9,8	17,7	84
Ve	145—146	49,6	4,6	9,4	16,0	$C_{16}H_{19}ClO_5S_2$	49,2	4,9	9,0	16,4	81
VIIa	230—231	43,5	3,5	10,9	18,8	$C_{12}H_{11}ClO_5S_2$	43,1	3,3	10,6	19,1	89
VIIb	210—211	44,5	3,4	9,8	18,0	$C_{13}H_{13}ClO_5S_2$	44,8	3,7	10,2	18,4	87

TABLE 2. Characteristics of VI and VIII

Compound	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %	mp of the picrate, °C
		C	H	N	S		C	H	N	S		
VIa	108—109	61,5	4,9	6,4	27,7	$C_{12}H_{11}NS_2$	61,8	4,7	6,1	27,4	91	241—242
VIb	66—67	63,2	5,5	5,9	25,6	$C_{13}H_{13}NS_2$	63,1	5,3	5,7	25,9	90	236—237
VIc	56—57	62,8	5,0	5,4	25,6	$C_{13}H_{13}NS_2$	63,1	5,3	5,7	25,9	92	215—216
VId	—	64,9	5,3	5,0	24,9	$C_{14}H_{15}NS_2$	64,4	5,7	5,3	24,6	93	207—208
VIIIa	103—104	61,4	4,5	6,0	27,6	$C_{12}H_{11}NS_2$	61,8	4,7	6,1	27,4	92	243—244
VIIIb	73—74	63,4	5,5	5,9	25,7	$C_{13}H_{13}NS_2$	63,1	5,3	5,7	25,9	91	229—230

TABLE 3. Characteristics of IX-XII

Compound	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	N	S		C	H	N	S	
IXa	144—145	64,7	6,4	4,8	20,4	$C_{17}H_{19}NOS_2$	64,4	6,0	4,4	20,2	51
IXb	157—158	69,0	6,9	4,8	20,5	$C_{18}H_{21}NS_2$	68,6	6,7	4,4	20,3	44
IXc	123—124	69,7	7,4	4,7	19,2	$C_{19}H_{23}NS_2$	69,2	7,0	4,3	19,4	52
IXd	165—166	65,8	6,0	4,6	20,0	$C_{18}H_{21}NOS_2$	65,3	6,3	4,2	19,4	48
Xa	144—145	63,2	5,3	—	25,4	$C_{13}H_{12}OS_2$	62,8	4,9	—	25,8	40
Xb	151—152	63,9	5,8	—	24,8	$C_{14}H_{14}OS_2$	64,1	5,4	—	24,4	47
XIa	96—97	68,0	6,5	4,9	21,6	$C_{17}H_{19}NS_2$	67,8	6,3	4,7	21,2	43
XIb	100—101	68,9	6,4	4,7	20,1	$C_{18}H_{21}NS_2$	68,6	6,7	4,4	20,3	54
XIc	135—136	63,8	5,3	4,8	20,9	$C_{16}H_{17}NOS_2$	63,4	5,6	4,6	21,1	44
XId	193—194	64,2	6,3	4,2	20,3	$C_{17}H_{19}NOS_2$	64,4	6,0	4,4	20,2	56
XIIa	157—158	61,1	4,5	—	27,1	$C_{12}H_{10}OS_2$	61,5	4,3	—	27,4	41
XIIb	172—173	63,0	5,2	—	26,0	$C_{13}H_{12}OS_2$	62,8	4,9	—	25,8	50

TABLE 4. Characteristics of I-IV

Compound	bp, °C (mm) (mp, °C)	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	S		C	H	S	
Ia	175—180 (2)	49,8	5,3	26,6	$C_{10}H_{12}O_3S_2$	49,2	4,9	26,2	70
Ib	175—182 (2)	51,6	5,1	25,3	$C_{11}H_{14}O_3S_2$	51,2	5,4	24,8	72
IIa	165—170 (3)	53,3	4,8	28,0	$C_{10}H_{10}O_2S_2$	53,1	4,4	28,3	58
IIb	160—165 (2)	54,5	5,4	27,2	$C_{11}H_{12}O_2S_2$	55,0	5,0	26,7	57
IIc	(82—83)	50,4	3,4	30,4	$C_9H_8O_2S_2$	50,9	3,8	30,2	90
IId	(68—69)	53,4	4,8	28,0	$C_{10}H_{10}O_2S_2$	53,1	4,4	28,3	87
IIe	135—140 (1)	57,6	4,4	31,0	$C_{10}H_{10}OS_2$	57,1	4.8	30,5	51
IIf	140—143 (1)	59,3	5,2	28,2	$C_{11}H_{12}OS_2$	58,9	5,4	28,6	52
III	176—181 (2)	49,7	5,4	26,4	$C_{10}H_{12}O_3S_2$	49,2	4,9	26,2	73
IVa	175—180 (3)	52,7	4,0	28,5	$C_{10}H_{10}O_2S_2$	53,1	4,4	28,3	63
IVb	(104—105)	50,6	4,2	30,5	$C_9H_8O_2S_2$	50,9	3,8	30,2	80
IVc	138—140 (1)	57,4	5,1	30,8	$C_{10}H_{10}OS_2$	57,1	4,8	30,5	52

TABLE 5. PMR Spectra of V-IX, XI, and XII

Compound	δ, ppm			
	2-Me	5-Me	7-Me (6-Me)	aromatic protons
Va	2,75	2,94	3,16	7,99; 7,46
Vb	2,76	2,94	—	8,00; 7,50
Vc	—	2,94	3,17	7,99; 7,50
VIa	2,56	2,63	2,65	7,26; 7,10
VIc	—	2,55	2,64	7,30; 7,10
VIIa	2,86	2,90	3,14	7,84; 7,46
VIIb	2,86	2,90	—	7,84; 7,46
VIIIa	2,66	2,69	2,69	7,27; 7,00
IXd	—	2,52	(2,63)	7,26; 7,93
XIc	2,63	—	2,46	7,20; 6,89; 6,65
XId	2,74	—	(2,63); 2,57	7,10; 7,85
XIIb	2,60	—	(2,38); 2,25	—

Thieno[2,3-b]thiophen-3-yl- and Thieno[3,2-b]thiophen-3-ylacetic Acids (IIc, d, IVb). These compounds were obtained by hydrolysis of IIa, b and IVa by the method in [7] (Table 4).

3-Acetonylthieno[2,3-b]- and Thieno[3,2-b]thiophenes (IIe, f, IVc). These compounds were obtained from IIc, d and IVb by the method in [6] (Table 4).

Thieno[2',3':5,4]- and Thieno[2',3':4,5]thieno[2,3-c]pyridium Perchlorates (Va-e, VIIa, b). An acylating mixture prepared from 0.05 mole of the corresponding anhydride and 0.01 mole of 70% perchloric acid was added with stirring at 0°C to 0.01 mole of IIc, d or IVb, during which the mixture warmed up and solidified after a certain time. After 10 min, 50 ml of ether was added to the reaction mixture, and the precipitate was removed by filtration, washed with cold alcohol and ether, dried, and crystallized from glacial acetic acid (Table 1).

Thieno[2',3':5,4]- and Thieno[2',3':4,5]thieno[2,3-c]pyridines (VIa-d, VIIIa, b). Gaseous ammonia was passed at 20°C into a suspension of 0.01 mole of Va-e or VIIa, b in 30 ml of alcohol in the course of 20 min, after which a solution was refluxed for 10 min and poured into water containing ice. The product was extracted with ether, the extract was dried over sodium hydroxide, the ether was evaporated, and the residue was crystallized from hexane (Table 2).

Hydroxy Derivatives of Thieno[2,3-b]- and Thieno[3,2-b]benzothiophene (Xa, b, XIIa, b). A solution of 0.07 mole of sodium hydroxide in 6 ml of water was added to a solution of 0.01 mole of Vb, d or VIIa, b in 30 ml of alcohol, and the reaction mixture was refluxed for 6 h. It was then cooled and poured into 100 ml of water. The aqueous mixture was extracted with ether, and the aqueous layer was separated and acidified with hydrochloric acid. The precipitate was removed by filtration and crystallized from aqueous alcohol (Table 3).

Dialkylamino Derivatives of Thieno[2,3-b]- and Thieno[3,2-b]benzothiophene (IXa-d, XIa-d). A mixture of 0.01 mole of Vb-d or VIIa, b and 15 ml of the secondary amine was refluxed for

5 h, after which the excess secondary amine was removed by vacuum distillation, and the residue was dissolved in ether. The ether solution was washed thoroughly with an alkaline solution to remove the hydroxy compounds, and the ether layer was dried over sodium hydroxide. The ether was removed, and the residue was crystallized from hexane (Table 3).

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CONDENSED HETEROCYCLES WITH A THIAZOLE RING

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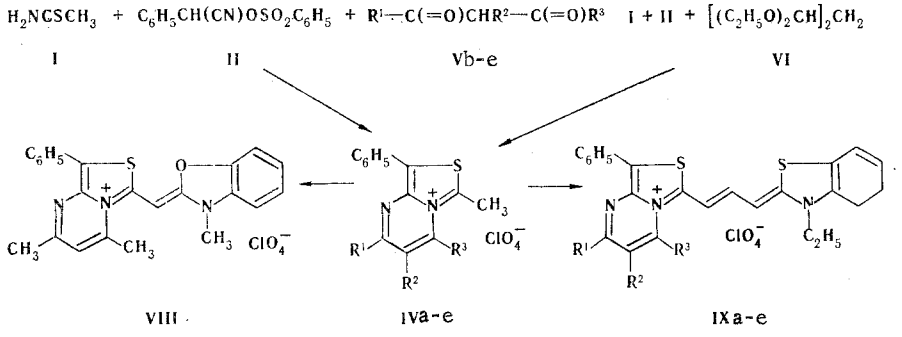
UDC 547.859'789.61.07:543.422

Previously unknown 6-methylthiazolo[3,4-a]pyrimidinium salts that can be used to obtain cyanine dyes were synthesized. The spectral characteristics of the compounds obtained were investigated.

Monomethylidynecyanine dyes have been previously synthesized from 6-methylthio-substituted thiazolo[3,4-a]pyrimidinium salts [2]. It was noted that the absorption spectra of such derivatives contain two bands, the positions and intensities of which are determined by the substituents in the thiazolopyrimidine ring. It seemed of interest to obtain a larger number of polymethine dyes that contain a thiazolopyrimidine ring.



a $R^1=R^2=R^3=H$; b $R^1=R^3=H$, $R^2=C_6H_5$; c $R^1=R^3=CH_3$, $R^2=H$; d $R^1=C_6H_5$, $R^2=H$, $R^3=CH_3$; e $R^1=R^3=C_6H_5$, $R^2=H$

This objective could have been realized on the basis of 6-methylthiazolo[3,4-a]pyrimidinium salts, the synthesis of which still had to be worked out. We were able to accomplish this by extending the method proposed in [3] for 6-phenyl-substituted thiazolopyrimidinium salts after its appropriate modification. Taking into account the indications in [4] that the 4-amino-2-methyl-5-phenylthiazolium salt (III) that should have been the starting substance in the method in [3] could not be obtained by the reaction of thioacetamide (I) with cyanobenzyl benzenesulfonate (II), we carried out the reaction between I and II in the presence

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 42-45, January, 1983. Original article submitted April 27, 1982.