## PECULIARITIES OF THE REACTION OF CYCLOALKA[b]THIOPYRYLIUM SALTS AND THEIR HETERO ANALOGS WITH BASES

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The reaction of aryl-substituted cycloalka[b]thiopyrylium salts, as well as their O and N analogs, with bases (pyridine, NaOH, NaHCO<sub>3</sub>) was studied. The formation of 6,6',7,7'-tetrahydro-2,2',4,4'-tetraarylbis(5H-1-benzothiopyrans) through the intermediate anhydro bases was established for the cyclohexa[b]thiopyrylium salts, while the formation of 2,4-diphenyl-7-(2,4-diphenyl-8-cyclopenta[b]thiopyranyl)- $\Delta^{7,8}$ -cyclopenta[b]thiopyran was established for 2,4-diphenylcyclopenta[b]thiopyrylium perchlorate. The peculiarities of the behavior of the O and N analogs of the cycloalka[b]thiopyrylium salts in reactions with bases were ascertained. The investigation was carried out using electronic, IR, and PMR spectroscopy.

It is known that the alkaline hydrolysis of 4-aryl- or 4-thienyl-substituted thiochromylium salts leads to mixtures of thiochromenes and thiocoumarins. The latter develop as a result of oxidation of the intermediate  $\alpha$ -pseudobases due to hydride transfer in their reaction with the starting cations [1, 2]. 4-Methylthiochromylium and 4-methylthioflavylium perchlorates are deprotonated by the action of bases [3, 4]; 4-methylthioflavylium salts form (1,2-ethanediylidene)bisflavenes [4]. It was assumed that the dimerization proceeds through a step involving the formation of the anhydro bases; however, the mechanism of the reactions was not studied.

We have previously shown that 2,4-diphenyl- (Ia) and 2-phenyl-4-(p-methoxyphenyl)cyclohexa[b]thiopyrylium (Ib) tetrafluoroborates form the corresponding 2,2',4,4'-tetraaryl-substituted 6,6',7,7'-tetrahydro-bis(5H-1-benzothiopyrans) IIa, b in quantitative yields in an aqueous alcohol solution of sodium hydroxide in the presence of potassium hexacyanoferrate [6]. We assumed an ion-radical mechanism for this transformation and proposed a scheme with the participation of the anhydro bases [6]. To confirm the proposed mechanism we made a detailed study of the reaction of some cycloalka[b]thiopyrylium salts, as well as their O and N analogs, with organic and inorganic bases. The results of the investigations are presented in this paper.

In the reaction of thiopyrylium salts Ia-c with sodium hydroxide and sodium bicarbonate in aqueous alcohol media one might have expected attack by the nucleophile at the  $C_{(2)}$  or  $C_{(6)}$  atom of the heteroring; however, the formation of pseudobases is not observed (see Table 1). The reaction of tetrafluoroborate Ia with sodium bicarbonate (experiments 1 and 2) leads to dimer IIa; an increase in the temperature significantly increases the yield of the latter. The action of sodium hydroxide in aqueous ethanol solution on salts Ia and Ib (experiments 3 and 4) leads to the development of dimers IIa and IIb in 4% and 35% yields, respectively. Salts Id and Ih undergo resinification under these conditions.

Tetrafluoroborates Ia, b react with pyridine (experiments 8 and 9) to give dimers IIa, b in 50% yield. The use of an excess amount of pyridine and raising the temperature of the reaction mixture from 20°C to 70°C shortens the reaction time substantially. For perchlorate Id, with a free position at the  $C_{(4)}$  atom, in reactions with bases one might have expected both dimerization at the  $C_{(8)}$  atom to give a dimer of the II type and nucleophilic attack of the anhydro bases at the  $C_{(4)}$  or  $C_{(6)}$  atom. A complex mixture of products, from which only dimer IId was isolated by column chromatography, is formed in the reaction of salt Id with pyridine.

N. G. Chernyshevskii Saratov State University, Saratov 410026. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 26-31, January, 1992. Original article submitted November 25, 1990; revision submitted November 7, 1991.

Expt. No.	Starting salt	Reagent	Solvent	T <sub>reac</sub> , °C	Reaction time, h	Product	Yield, %
I	la	NaHCO <sub>3</sub>	сн₃он	65	10	IIa	69
2	Ia	NaHCO3	сн3он	20	24	IIA	35
3	Ia	NaOH	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O (4:1)	50	2	II.a	4
4	IЪ	NaOH	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O (4:1)	50	2	Пр	35
5	Ia	NaOH / K <sub>3</sub> Fe(CN) <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O (4:1)	50	2	lla	90
6	Ŀр	NaOH / K <sub>3</sub> Fe(CN) <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O (4:1)	50	2	IIC	90
7	Ic	NaOH / K <sub>3</sub> Fe(CN) <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O (4:1)	50	2	IIa	96
8*	Ia	Ру	CH <sub>2</sub> Cl <sub>2</sub>	20	48	nb	50
9**	Ŀр	Ру	CH <sub>2</sub> Cl <sub>2</sub>	20	48	IIa	50
10**	Ia	Ру	-	70	8	IIA	49
11	Id	Ру	—	70	0,4	IId	17
12	Ih	Ру	-	70	0,4	IIh	80

TABLE 1. Conditions and Products of the Oxidative Dimerization of  $2-R^1-4-R^2$ -Cycloalka[b]thiopyrylium Tetrafluoroborates Ia-d, h

\*A fivefold to tenfold excess of the base was used in experiments 1-7 and 10-12, while the starting salt:pyridine ratio in experiments 8 and 9 was 1:1. \*\*The reaction was carried out in a stream of argon.

0	Chemical shifts, ppm								
Compound	3-H. 3'-H <b>*</b>	3-H	R <sup>1</sup>	R <sup>2</sup>	Alicycle				
IIIa	6,29 S(iH)	5,62t(1H)		7,30 m(10H)	2,422.07 m (4H); 1,63 m (2H)				
ШЪ	6,47 S (1H)	5,65 t (1H)	3.70 \$ (3H); 7.23d.d (4H)	7,41 m (5H)	2,421,97 m (4H); 1,571,49 m (2H)				
Шe	5,87 S (1H)	5,07t (1H)	3,77 S (3H); 7,24 d.d (4H)	7,34 m (5H)	2,471,37 m (6H)				
Пq	6,05 d.d(2H)		7,30 m (5H)		2,40 m (8H); 1,81 m (4H)				
Vh	6,31s (1H); 6,85 s (1H)	-	7,28 m (20H)		2,802,32 m (10H)				

TABLE 2. PMR Spectra of Anhydro Bases IIIa, b, e and Compounds IId and Vh

\*For IId and Vh.

When we carried out the reaction of salts Ia, b with  $d_5$ -pyridine in the ampul of an NMR spectrometer we were able to record the formation of intermediate anhydro bases — 2,4-diaryl-substituted 6,7-dihydro-5H-1-benzothiopyrans IIIa, b (see scheme at the top of the next page.)

Evidence for the structure of anhydro bases IIIa, b is provided by the presence in the PMR spectra of these compounds, recorded immediately after dissolving, of a triplet of a vinyl proton (8-H) at 5.62 and 5.65 ppm, respectively (Table 2); signals that are characteristic for any other compounds were not detected. These bases are unstable compounds that are readily oxidized in air, and only product IIIa could therefore be isolated by column chromatography.



I--IV X-S, Y=BF4, n=2; a  $R^{1}=R^{2}=C_{6}H_{5}$ ; b  $R^{1}=C_{6}H_{4}OCH_{3-p}$ ,  $R^{2}=C_{6}H_{5}$ ; c  $R^{1}=R^{2}=C_{6}H_{4}OCH_{3-p}$ ; Id-IIIdX-S, Y=ClO4, n=2;  $R^{1}=C_{6}H_{5}$ ,  $R^{2}=H_{1}$ ; le IIe X=O, Y=BF4, n=2,  $R^{1}=C_{6}H_{4}OCH_{3-p}$ ,  $R^{2}=C_{6}H_{5}$ ; IfX=NH, n=2;  $R^{1}=C_{6}H_{4}OCH_{3-p}$ ,  $R^{2}=C_{6}H_{5}$ ; If X=NC<sub>6</sub>H<sub>5</sub>; Y=BF4, n=2;  $R^{1}=C_{6}H_{4}OCH_{3-p}$ ,  $R^{2}=C_{6}H_{5}$ ; If V h X=S, Y=ClO4, n=1,  $R^{1}=R^{2}=C_{6}H_{5}$ 

In contrast to cyclohexa[b]thiopyrylium salts, their oxygen analogs undergo resinification in the presence of pyridine. The formation of 2-(p-methoxyphenyl)-4-phenyl-6,7-dihydro-5H-1-benzopyran (IIIe) (Table 2), the PMR spectrum of which contains a triplet of a vinyl proton (8-H) at 5.07 ppm, was detected in the reaction of 2-(p-methoxyphenyl)-4-phenylcyclohexa[b]pyrylium tetrafluoroborate (Ie) in  $d_3$ -acetonitrile with an equimolar amount of triethylamine in the ampul of the NMR spectrometer. A product of subsequent dimerization of IIIe was not detected.

The nitrogen analogs of the cyclohexa[b]thiopyrylium salts -2-(p-methoxyphenyl)-2-phenylcyclohexa[b]pyridinium (If) and 1-phenyl-2-(p-methoxyphenyl)-2-phenylcyclohexa[b]pyridinium (Ig) tetrafluoroborates - do not give anhydro bases and do not dimerize under the conditions described above: they were isolated unchanged from the reaction mixtures.

It is known that the rate of detachment of a proton from the alkyl group in methyl derivatives of pyrylium, thiopyrylium, and N-methylpyridinium salts by means of bases depends on the character of the heteroatom and decreases in the order O, S, and N derivatives [7]. This may serve as an explanation of the inertness of the investigated cyclohexa[b]pyridinium salts If, g with respect to bases. The high reactivity in the case of oxygen analog Ie evidently leads to very rapid and complete deprotonation and the development of anhydro base IIIe, which is not capable of dimerization because of the absence of the starting Ie cation in the reaction medium.

The proposed scheme for the conversion of salts of the I type to dimers of the II type includes deprotonation of salts I to anhydro bases III, their oxidation with the participation of salts I to cation radicals of the A type, and then dimerization of the latter to dications IV with subsequent deprotonation to dimers II (Scheme 2).

The low yields of dimers IIa, b, d in experiments 1-4 and 8-9 should be noted. The yields become quantitative (experiments 5-7) when one uses an excess amount of a one-electron oxidizing agent (potassium hexacyanoferrate), which converts radical B to the starting cation (Scheme 2). The possibility of oxidation directly of the anhydro base by this oxidizing agent is also not excluded.



When 2,4-diphenylcyclopenta[b]thiopyrylium perchlorate (Ih) is dissolved in excess pyridine (Table 1, experiment 12), it forms product Vh as a result of nucleophilic attack of the intermediate anhydro base at starting perchlorate Ih, which is present in excess amounts. The 2,4-diphenyl-7-(2,4-diphenyl-8-cyclopenta[b]thiopyranyl)- $\Delta^{7,8}$ -cyclopenta[b]thiopyran structure was assigned to Vh on the basis of PMR spectral data. The PMR spectrum contains two singlets of 3-H and 3'-H vinyl protons at 6.31 and 6.85 ppm, which are characteristic for thiopyrans with conjugated double bonds in the heteroring [8]. The multiplet at 2.80-2.32 ppm, the integral intensity of which corresponds to 10 protons, indicates the presence of a bond at the C<sub>(7)</sub> atom of one of the alicycles (Table 2). The data presented above provide evidence that, in contrast to sym-octahydrothioxanthylium salts [9], attack of the anhydro base in the case of salt Ih is realized not at the C<sub>(4)</sub> atom of the heteroaromatic cation but rather at the C<sub>(6)</sub> atom, which corresponds to the direction of nucleophilic attack in series of 2,4-diaryl-substituted cycloalka[b]thiopyrylium salts [10, 11]. The different ratios of the dimers of the II and V types to perchloric acid should be noted. As we have previously shown, dimers IIa, b form the corresponding dimers IVa, b under the influence of this acid [6], while Vh reacts with it with cleavage of the C<sub>(7)</sub>--C<sub>(8)</sub> bond and gives starting perchlorate Ih.

Thus we have discovered a dependence of the direction of the reaction of condensed heteroaromatic salts of the Ia-h type with bases on the heteroatom; in the case of salt Ih we observed specific behavior in these reactions of thiopyrylium salts with a condensed five-membered alicycle.

The possibility of the existence of radical and ion-radical particles that act as intermediates in the formation of the dimers (Scheme 2) was previously substantiated by electrochemical and EPR methods [17].

## EXPERIMENTAL

The electronic spectra of solutions of the compounds in methylene chloride were recorded with a Specord M-40 spectrophotometer. The PMR spectra of solutions in CDCl<sub>3</sub> or  $d_5$ -pyridine were recorded with a Varian FT-80 A spectrometer with tetramethylsilane (TMS) as the internal standard. The IR spectra of suspensions in mineral oil and hexachlorobutadiene were obtained with a UR-20 spectrometer. The starting thiopyrylium salts Ia-d, h were obtained by the methods described in [12, 13]; tetrafluoroborate Ie was also obtained by a known method [14]. Pyridinium salts If, g were synthesized as described in [15, 16] with the subsequent action of tetrafluoroboric or perchloric acid on the intermediate nitrogen bases. A known method [6] was used to obtain dimers IIa-c and diperchlorates IVa, b.

The results of elementary analysis for C, H, and S for IIc, d, IIIa, and Vh were in agreement with the calculated values.

6,6',7,7'-Tetrahydro-2,2'-diphenyl-8,8'-bis(5H-1-benzothiopyran) (IId,  $C_{30}H_{26}S_2$ ) (Experiment 11). Pyridine (10 ml) was added to 2 g (7.6 moles) of perchlorate Id, the mixture was heated until Id dissolved, and the resulting solution was cooled and poured into water. The resulting precipitate was removed by filtration, washed with water, dried, and chromatographed with a column (25 by 2.5 cm) packed with  $Al_2O_3$  [elution with hexane—ether (6:1)] to give 0.28 g of red crystals of dimer IId with mp 123-126°C. IR spectrum: 1600, 1580, 1510 cm<sup>-1</sup> (C=C).

**Reaction of Tetrafluoroborates Ia, b with Pyridine (Experiments 8 and 9).** Pyridine (5 ml) was added at  $20^{\circ}$ C in a stream of argon to a solution of 1.95 g (5 mmole) of salt Ia or to 2.10 g (5 mmole) of salt Ib in 20 ml of methylene chloride. After 48 h, the precipitated dimer IIa or IIb was separated, washed with water, and dried. The dimers were identical to those previously obtained [6]. The yields were 0.75 g (IIa) and 0.82 g (IIb).

Reaction of Tetrafluoroborate Ia with Sodium Hydroxide (Experiment 5). A solution of 0.96 g (24 mmole) of sodium hydroxide in 25 ml of water was added at 50°C to a solution of 1.95 g (5 mmole) of salt Ia in 100 ml of ethanol. After 2 h, the reaction mixture was poured into water, and the precipitated dimer IIa was separated and washed with water. The product was identical to the compound previously obtained [6]. The yield was 0.06 g.

**Reaction of Tetrafluoroborate Ia with Sodium Bicarbonate (Experiment 2).** A 0.34-g (4 mmole) sample of sodium bicarbonate was added at 20°C to a solution of 1.56 g (4 mmole) of salt Ia in 15 ml of methanol, after which stirring was continued for 24 h. The precipitated dimer IIa was separated, washed with water, and air dried. The yield was 0.42 g.

2,4-Diphenyl-6,7-dihydro-5H-1-benzothiopyran (IIIa,  $C_{21}H_{18}S$ ). Pyridine (5 ml) was added with stirring to 1.95 g (5 mmole) of salt Ia, and the resulting solution was poured immediately over crushed ice. The liberated red oil was extracted with chloroform, and 0.05 g (3.6%) of red crystals of IIIa, with mp 57-58°C, was isolated with a column packed with  $Al_2O_3$  (elution with hexane).

2-(p-Methoxyphenyl)-4-phenyl-6,7-dihydro-5H-1-benzothiopyran (IIIb). A 0.03-g (0.07 mmole) sample of salt lb was dissolved in 0.5 ml of  $d_3$ -acetonitrile and 0.0055 g (0.07 mmole) of  $d_5$ -pyridine in the ampul of the NMR spectrometer, and the PMR spectrum was recorded immediately. The PMR spectrum of IIIb is presented in Table 2.

2-(p-Methoxyphenyl)-4-phenyl-6,7-dihydro-5H-1-benzopyran (IIIe). A 0.028-g (0.07 mmole) sample of salt Ie was dissolved in 0.5 ml of  $d_3$ -acetonitrile and 0.07 g (0.07 mmole) of triethylamine in the ampul of the NMR spectrometer, and the PMR spectrum was recorded immediately. The PMR spectrum of IIIe is presented in Table 2.

2,4-Diphenyl-7-(2,4-diphenyl-8-cyclopenta[b]thiopyranyl)- $\Delta^{7,8}$ -cyclopenta[b]thiopyran (Vh, C<sub>40</sub>H<sub>32</sub>S<sub>2</sub>). A 2-g (5 mmole) sample of perchlorate Ih was dissolved in 10 ml of pyridine, the resulting solution was immediately poured into water, and 1.15 g (80%) of a light-brown precipitate of Vh, with mp 90-93°C (benzene), was separated. IR spectrum: 1600, 1580, 1540, 1490 cm<sup>-1</sup>.

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