REACTIONS OF 1-ARYLTHIONIACYCLOALKANE SALTS WITH NUCLEOPHILIC AGENTS

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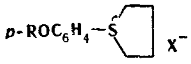
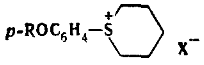
Depending on the structures of the salt and the nucleophilic agent, replacement of the anion of the sulfonium salt or expansion of the heteroring at the C—S bond to give substituted alkyl aryl sulfides occurs in the reaction of 1-(p-hydroxyphenyl)- and 1-(p-methoxyphenyl)thioniacyclopentane (I, III) and -thioniacyclohexane perchlorates (II, IV) in aqueous or alcohol solutions with potassium halides and potassium hydroxide. The ease of cleavage of the C—S bond as a function of the nature of the nucleophilic agent decreases in the order KOH > Cl > Br. The strength of the C—S bond of the heteroring decreases in the order II > I >IV > III. All of the heterocycles (I-IV) are stable with respect to the action of picric acid and potassium iodide, and 1-(p-hydroxyphenyl)thioniacyclohexane perchlorate (II) is stable with respect to the other investigated nucleophiles.

The formation of sulfonium salts from thiacycloalkanes leads to a decrease in the strength of the ring C—S and makes it possible to pass to polyfunctional acyclic sulfides on the basis of a ring-opening reaction. Thus aminoalkyl aryl sulfides are formed by the action of nitrogen bases, particularly secondary amines, on 1-arylthioniacycloalkane salts (I-III) [1]. The reactions of salts I-III proceed quantitatively with opening of the heteroring [1]; this makes it impossible to draw a conclusion regarding the relative strengths of the C—S bonds in salts with different structures. For this, one must investigate the reaction of 1-arylthioniacycloalkane salts with weaker nucleophilic agents than amines.

We have studied the reaction in aqueous and alcohol solutions of four 1-arylthioniacycloalkane perchlorates (IA-IVA), which differ with respect to the size of the heteroring and the substituent in the aromatic ring, namely, 1-(p-hydroxyphenyl)- and 1-(p-methoxyphenyl)-thioniacyclopentane (I, III) and 1-(p-hydroxyphenyl)- and 1-(p-methoxyphenyl)thioniacyclohexane perchlorates (II, IV), with potassium halides, potassium hydroxide, and picric acid. All of the heterocycles were found to be stable with respect to the action of potassium iodide and picric acid, and the cation of II was found to be stable with respect to the action of the remaining investigated nucleophiles (only replacement of the perchlorate ion occurs).



I, III



II, IV

I, II R=H, X=A—F III $R=CH_3$, X=A, D, E IV $R=CH_3$, X=A—E A $X=ClO_4$; B X=Cl; C X=Br; D X=I; E $X=OC_6H_2(NO_2)_3$; F X=OH

In the remaining cases reductive cleavage of the C—S bond of the heteroring occurs to a greater or lesser extent, depending on the structures of the heterocation (I-IV) and the nucleophilic agent (X^-). In addition to the alkyl aryl sulfides $[ArS(CH_2)_nX]$ formed in this case, either the starting heterocation perchlorates (IA-IVA) or their salts with other anions (Het^+X^-) can usually be isolated. The yields and properties of the products of these reactions are presented in Tables 1 and 3.

The reaction of IA with a solution of potassium hydroxide in methanol or in water leads to 1-(p-hydroxyphenyl)thioniacyclopentane hydroxide IF [1-(p-hydroxyphenyl)thiophanium hydroxide], which was isolated in the hydrated form. Products of opening of the heteroring

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TABLE 1. Yields of ω-X-Alkyl Aryl Sulfides and 1-Arylthioniacycloalkane Salts (Het^+X^-) in the Reaction of Perchlorates IA-IVA with KX[a]

X	$ArS(CH_2)_nX$			Het^+X^-			
	I	III	IV	I	II	III	IV
OCH_3	0	81	73	37^b	83^b	15^c	14^c
OH	0	72	31	42	79	$8{,}5^c$	40^c
Cl	(16)	86	60	74	91	0	2
Br	0	81 + (10)	(6)	97	73	0	93

[a] The reactions were carried out with KOH in CH_3OH at 20°C with KOH, KCl (for IA), and KBr in water at 100°C (the yields of the hydroxyalkyl aryl sulfides are indicated in parentheses) and with KCl (for IIIA and IVA) in aqueous alcohol. [b] X = OH. [c] $X = ClO_4$.

TABLE 2. Chemical Shifts (δ, ppm) of the Protons of ω-X-Alkyl p-Methoxyphenyl Sulfides (V-X)

Compound	X	$(CH_2)_{n-2}$	CH_2S	CH_2X
Va	OH	1,57 (br)[a]	2,83 (br)	3,48 (t)[b]
Vb	OCH_3	1,60 (m)	2,57 (t)	~3,3[c]
VIb	OCH_3	1,48 (m)	2,75 (t)	~3,3[c]
VII	Cl	1,50 (m)	2,75 (t)	3,45 (t)
VIII	Cl	1,55 (m)	2,72 (t)	3,42 (t)
IX	Br	1,55 (m)	2,75 (t)	3,32 (t)
X	F	1,65 (br)	2,75 (t)	4,25 (dt)

[a] Abbreviations in parentheses: s is singlet, br is broad unresolved signal, t is triplet, and dt is doublet of triplets. [b] δ(OH) 2.73 ppm (s). [c] The position and character of the signal could not be accurately determined because of the superimposition of the singlet of X (OCH_3), for which δ 3.23 and 3.22 ppm are observed in the case of Vb and VIb, respectively.

were not detected for IIa even in the case of refluxing with a solution of potassium hydroxide in methanol — 1-(p-hydroxyphenyl)thioniacyclohexane hydroxide IIf [1-(p-hydroxyphenyl)-thianium hydroxide] was obtained in 83% yield. The hydroxides of the cations of I and II are converted to the corresponding previously described [2] salts (IA, B, E and IIA, B, E) in alcohol or aqueous solutions when they are treated with perchloric, hydrochloric, or picric acid; this confirms the presence of an unopened heteroring in these bases.

In the case of salts III and IV the strength of the ring C—S bond is weakened substantially. This is a consequence of the weaker electromeric effect of the p-methoxy group as compared with $p\text{-}O^-$ in the phenyl ring. Replacement of the anion in IIIA and IVA without expansion of the heteroring occurs only under the influence of picric acid or potassium iodide.

$$\underset{\text{VII, VIII}}{ArS(CH_2)_nCl} \xleftarrow{KCl} \text{III A, IV A} \xrightarrow[ROH]{KOH} \underset{\text{Va,b VIa,b}}{ArS(CH_2)_nOR}$$

$$\underset{\text{X}}{ArS(CH_2)_4F} \xleftarrow{KF} \text{III A} \xrightarrow[H_2O]{KBr} \text{III C} \underset{\leqslant 20^\circ}{\overset{\geqslant 100^\circ}{\rightleftarrows}} \underset{\text{IX}}{ArS(CH_2)_4Br} \xrightarrow{H_2O} \text{Va}$$

$Ar = p\text{-}CH_3OC_6H_4$; V, VII $n = 4$; VI, VIII $n = 5$; a $R = H$; b $R = CH_3$

Compound IIIA is converted almost completely to p-methoxyphenyl 4-methoxybutyl sulfide (Vb) on reaction with potassium hydroxide in methanol at room temperature. A similar reaction leading to p-methoxyphenyl 4-hydroxybutyl sulfide (Va) occurs with an aqueous solution of potassium hydroxide only when the mixture is heated. p-Methoxyphenyl 5-hydroxyamyl sulfide (VIa) is obtained when IVA is heated for a long time with an aqueous solution of

TABLE 3. 1-Arylthioniacycloalkane Salts and Hydroxides (I-IV) and ω-X-Alkyl p-Methoxyphenyl Sulfides (V-X)[a]

Compound	R	X	mp or bp, °C (mm); n_D^{20}	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	S or Hal		C	H	S or Hal	
IC	H	Br	145—146	—	—	Br 30,3	$C_{10}H_{13}BrOS$	—	—	Br 30,6	97
ID	H	I	159—160	39,7	4,3	I 38,8	$C_{10}H_{13}IOS$	39,0	4,2	I 41,3	73
IF	H	OH	146—147	55,8	7,4	15,0	$C_{10}H_{14}O_2S \cdot H_2O$	55,5	7,4	14,8	37
IIC	H	Br	182—183	—	—	Br 28,4	$C_{11}H_{15}BrOS$	—	—	Br 29,0	73
IID	H	I	174—175	40,5	4,8	I 37,5	$C_{11}H_{15}IOS$	40,9	4,7	I 39,3	86
IIF	H	OH	143—144 (dec.)	62,2	7,6	14,6	$C_{11}H_{16}O_2S$	62,2	7,5	15,0	83
IIIC	CH_3	Br	93—95	—	—	Br 28,7	$C_{11}H_{15}BrOS$	—	—	Br 29,0	—
IIID	CH_3	I	97—98	39,6	5,3	I 35,0	$C_{11}H_{15}IOS \cdot H_2O$	38,9	4,9	I 37,3	90,5
IIIE	CH_3	$OC_6H_2(NO_2)_3$	128—132	48,6	4,5	7,9	$C_{17}H_{17}N_3O_8S$	48,3	4,0	7,6	66,5
IVC	CH_3	Br	124—126	46,7	6,1	Br 25,3	$C_{12}H_{17}BrOS \cdot H_2O$	46,9	6,2	Br 26,0	93
IVD	CH_3	I	129,5—131	—	—	I 37,5	$C_{12}H_{17}IOS$	—	—	I 37,8	100
IV E	CH_3	$OC_6H_2(NO_2)_3$	130—132	48,8	4,0	—	$C_{18}H_{19}N_3O_8S$	49,3	4,3	—	57

$p\text{-}CH_3OC_6H_4S(CH_2)_nX$

	n	X									
Va	4	OH	41—42	62,8	7,3	15,3	$C_{11}H_{16}O_2S$	62,2	7,5	15,0	72
Vb	4	OCH_3	131—137 (1); 1,5461	63,6	8,0	13,2	$C_{12}H_{18}O_2S$	63,7	7,9	14,4	81
VIa	5	OH	45—48	64,4	7,9		$C_{12}H_{18}O_2S$	63,7	7,9		31
VIb	5	OCH_3	1,5438	66,5	8,4	13,1	$C_{13}H_{20}O_2S$	64,9	8,3	13,3	73
VII	4	Cl	141 (1); 1,5634	57,9	6,2	13,2	$C_{11}H_{15}ClOS$	57,2	6,5	13,9	86
VIII	5	Cl	$n_D^{22,5}$ 1,5562	59,3	7,0	12,9	$C_{12}H_{17}ClOS$	58,9	7,0	13,0	60
IX	4	Br	156—157 (1); 1,5765	48,3	5,7	Br 28,7	$C_{11}H_{15}BrOS$	47,9	5,5	Br 29,0	81
X	4	F	1,5485	—	—	15,0	$C_{11}H_{15}FOS$	—	—	15,0	12,5

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[a] The compositions of IIIE and IVE were also confirmed by determination of the nitrogen content, and the compositions of VII, VIII, and X were confirmed by determination of the halogen content.

potassium hydroxide; the yield of VIa is lower than in the case of the analogous transformations of salt IIIA. Salt IVA is converted to p-methoxyphenyl 5-methoxyamyl sulfide (VIb) on reaction with potassium hydroxide in methanol at room temperature.

As shown in [2], a small amount of p-hydroxyphenyl 4-hydroxybutyl sulfide is formed when IA is heated with a saturated aqueous solution of potassium chloride. When IIIA is heated briefly with a solution of potassium chloride, it is converted completely to p-methoxyphenyl 4-chlorobutyl sulfide (VII). This compound does not undergo any changes during prolonged storage, in contrast to ethyl 4-chlorobutyl sulfide, which is converted to 1-ethylthiophanium chloride [3] during storage. Compound IVA, like IIA, gives mainly p-methoxyphenyl 5-chloroamyl sulfide (VIII) when it is treated with a solution of potassium chloride; however, the yield of VIII is lower than the yield of VII formed from IIIA.

Only the product of opening of the heteroring — p-methoxyphenyl 4-bromobutyl sulfide (IX) — and a small amount of the product of its saponification — p-methoxyphenyl 4-hydroxybutyl sulfide (Va) — are also formed when IIIA is heated with an aqueous solution of potassium bromide. Compound IX readily undergoes cycloisomerization: when it is stored even at −8 to −10°C, it is gradually (and finally completely) converted to 1-(p-methoxyphenyl)-thiophanium bromide (IIIC). Heating the latter converts it to IX, which, in contrast to its salt precursor, undergoes vacuum distillation but rapidly recyclizes after distillation at room temperature. In contrast to IIIA, IVA reacts with potassium bromide to give mainly the stable p-methoxyphenylthianium bromide (IVC). A small amount of ring-opening product — p-methoxyphenyl 5-hydroxyamyl sulfide (VIa) — is formed.

The reaction of even the most reactive cation (III) with potassium fluoride proceeds sluggishly — p-methoxyphenyl 4-fluorobutyl sulfide (X) is formed in only low yield, a sulfonium fluoride is not formed at all, and the unchanged IIIA is recovered. This result evidently should be explained by the high solvation energy of F^- in a protic solvent.

The material set forth above leads to the conclusion that the ease of cleavage of the heteroring C—S bond in 1-arylthioniacycloalkane salts under the influence of nucleophilic agents in protic solvents decreases in the order $CH_3O^- > OH^- > Cl^- > Br^- > F^- \geqslant I^-$, $^-OC_6H_2(NO_2)_3$.

The strength of the C—S bond in the cations of I-IV decreases in the order II > I > IV > III. In this series the six-membered heteroring is more stable than a strained five-membered heteroring in the case of identical aryl groups. Replacement of the methoxy group in the aryl ring by a hydroxy group increases the stability of the heteroring to such an extent that the five-membered heteroring with a p-hydroxyphenyl group becomes more stable than a six-membered heteroring with a p-methoxyphenyl group.

Some of the investigated reactions of p-methoxyphenylthioniacycloalkane salts with nucleophilic agents may constitute the basis for new preparative methods for the synthesis of polyfunctional aryl alkyl sulfides of the V-IX type.

The structures of the compounds that we obtained were established by means of IR, PMR, and mass spectrometry. The phenyl ring in sulfonium salts I, IIA-E, IIIA, D, E, and IVA-E and in aryl alkyl sulfides V-VIII is characterized by three bands of skeletal vibrations at 1590-1605, 1575-1587, and 1498-1504 cm^{-1}. Bands at 1575 and 1503 cm^{-1} and an extremely weak band at 1521 cm^{-1} are observed in the spectra of the sulfonium bases (IF, IIF). The intensities of the phenyl bands in the IR spectra of the aryl alkyl sulfides listed above are lower by a factor of two to three than the intensities of the bands at 1220-1270 cm^{-1} due to the deformation vibrations of the methylene groups bonded to the sulfur atom [4]. On the other hand, the intensities of the phenyl bands in the spectra of sulfonium salts IA, IIA-E, IIIA, D, E, and IVA-E and sulfonium bases IF and IIF are two to three times higher than the intensities of the bands at 1220-1270 cm^{-1}. Both groups of bands have approximately equal intensities only in the case of IB-E.

Hydroxyl-containing compounds Va, VIa, IA-F, and IIA-F are associated due to the formation of hydrogen bonds: frequencies of OH stretching vibrations corresponding to the centers of gravity of unsymmetrical or slightly structured absorption bands are observed at 2800-3450 cm^{-1}.

The PMR spectra of the alkyl aryl sulfides (Table 2) were analyzed as first-order spectra [5], and the results of their assignment are in agreement with the data obtained for similar compounds [1, 6, 7]. The chemical shifts and the character of the signals for the protons of the methoxy groups bonded to the phenyl rings (δ 3.72-3.73 ppm), p-substituted phenyl rings (AB quartet, 6.72-6.75 and 7.23-7.26 ppm), and methylene groups bonded to the sulfur atom are virtually identical for all of the compounds (V, VIb, and VII-X). A difference is observed for the signals of the protons of the methylene groups in the 4 or 5 position bonded to halogens or with the oxygen atom of the hydroxy or methoxy group: the shift to weak field follows the trend of the electronegativities of these atoms (F > Cl $\geqslant$ O > Br). The magnitude of the geminal J_{HF} constant (48 Hz) in the spectrum of X is in agreement with the data in [8]. The spectrum of IIF in CF_3COOH does not contain an individual peak corresponding to a phenolic hydroxyl group, since an averaged signal of the protons of the carboxyl group, water, and a hydroxyl group is formed above 10 ppm because of rapid exchange in strongly acidic media [9, 10]. The signals of the protons of the other groups in the cation of II are shifted to weaker field than in the case of the sulfides: 3.17 ($CH_2\overset{+}{S}$, t), 6.86 and 7.38 (C_6H_4, AB quartet), and 1.8 ppm [$(CH_2)_3$, broad and unresolved].

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene (in the case of the sulfonium salts and bases and hydroxyalkyl aryl sulfides) were recorded with a Carl Zeiss Jena UR-20 spectrometer. The PMR spectra of 10% solutions of the compounds in CCl_4 were recorded with a Varian T-60 spectrometer at 35°C with hexamethyldisiloxane as the internal standard. The mass spectra* were recorded with an LKB-2091 spectrometer; the ionization-chamber temperature was 250°C, the emission current was 50 μA, and the ionizing-electron energy was 70 eV.

The starting 1-arylthioniacycloalkane perchlorates (IA-IVA) were obtained by the methods in [1, 2].

p-Methoxyphenylthianium Perchlorate (IVA). This compound, with mp 110-112°C (from aqueous alcohol), was obtained in 60% yield from anisole, perchloric acid, thiacyclohexane, and hydrogen peroxide by the method in [2]. Found: C 46.5; H 5.6; Cl 11.6%. $C_{12}H_{17}ClO_5$. Calculated: C 46.7; H 5.5; Cl 11.5%. This salt was obtained in 44% yield in the case of synthesis from thiacyclohexane 1-oxide by the method in [1].

Reaction of Arylthioniacycloalkane Perchlorates with Potassium Hydroxide (Tables 1 and 3). A) A solution of 1.93 g (6.8 mmole) of IA in 10 ml of methanol was added to a solution of 0.38 g (6.7 mmole) of potassium hydroxide in 10 ml of methanol, the precipitated potassium perchlorate was removed by filtration, and the filtrate was vacuum evaporated without heating. The yield of crude p-hydroxyphenylthiophanium hydroxide (IF) was quantitative. For purification, the product was dissolved in 3 ml of methanol, the solution was filtered, and acetone was added to the filtrate to precipitate the hydrated base (0.55 g).

B) A 2.8-g (10 mmole) sample of perchlorate IA was added to a solution of 0.56 g (10 mmole) of potassium hydroxide in 65 ml of water, and the mixture was concentrated in vacuo at no higher than 50°C to a volume of 5-10 ml. The precipitated potassium perchlorate was removed by filtration, the filtrate was vacuum evaporated to dryness, acetone was added immediately to the residue, and the mixture was worked up as in method A. The yield of IF was 0.90 g. Hydrated IF loses water at 64-75°C, during which it undergoes polymerization.

C) A solution of 0.27 g (4.8 mmole) of potassium hydroxide was added to a solution of 2.86 g (9.7 mmole) of IIA in 180 ml of methanol, the mixture was filtered, and the solvent was removed from the filtrate by distillation. The residue was dissolved in the minimum amount of methanol, an equal volume of acetone was added, and ether was added until the mixture became turbid. The mixture was then filtered to give 0.89 g of base IIF.

D) A solution of 1.68 g (30 mmole) of potassium hydroxide in 12 ml of water was added to 8.84 g (30 mmole) of IIA in 140 ml of water, and the mixture was refluxed for 13 h. It was then concentrated in vacuo with removal of the potassium perchlorate by filtration from time to time. The concentrate was evaporated to dryness, and the residual IIF was purified as in method C. Found: M 201 (by ebullioscopy in methanol). Calculated: M 212.

E) Perchlorate IIIA did not react with an aqueous solution of potassium hydroxide at 20°C. A 3.74-g (12.7 mmole) sample of IIIA was heated with an aqueous solution of potassium hydroxide as in the case of IIA, after which the mixture was cooled to precipitate 2.06 g

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of p-methoxyphenyl 4-hydroxybutyl sulfide (Va), which was crystallized from hexane. The mother solution after separation of Va was evaporated to dryness, and the residual IIIA was extracted with methanol.

F) A solution of 5.89 g (0.02 mole) of IIIA in 56 ml of methanol and a solution of 1.12 g (0.02 mole) of potassium hydroxide in 24 ml of methanol were mixed, and the mixture was filtered. The methanol was removed from the filtrate in vacuo without heating, and the residue (a mixture of oil Vb and crystals of IIIA) was extracted with ether to give p-methoxyphenyl 4-methoxybutyl sulfide (Vb).

G) An aqueous solution of IVA and potassium hydroxide was heated as indicated for IIA, after which it was cooled and extracted with benzene to give p-methoxyphenyl 5-hydroxyamyl sulfide (VIa), which was crystallized from hexane. Unchanged IVA was isolated from the aqueous layer as described for IIIA.

H) p-Methoxyphenyl 5-methoxyamyl sulfide (VIb) was obtained in the reaction of IVA in methanol with potassium hydroxide as in the case of IIIA.

p-Methoxyphenyl 4-Fluorobutyl Sulfide (X). A solution of 0.94 g (0.01 mole) of potassium fluoride dihydrate in 3 ml of water was added to a solution of 2.94 g (0.01 mole) of IIIA in a mixture of 3 ml of alcohol and 2 ml of water, and the precipitated mixture of IIIA and potassium perchlorate was removed by filtration. The filtrate was evaporated in vacuo without heating, and the residue — a mixture of liquid and crystals — was filtered. The filtered crystals were washed with benzene, and the wash benzene was added to the filtrate, and the mixture was again evaporated as described above. This treatment was repeated many times until sulfide X was free of IIIA and KF remained after evaporation of the benzene extract. The yield was 0.27 g.

p-Methoxyphenyl 4-Chlorobutyl Sulfide (VII). A 2.82-g (9.5 mmole) sample of IIIA was dissolved by heating in a mixture of 3 ml of alcohol and 2 ml of water, 3 ml (13 mmole) of a saturated solution of potassium chloride was added, and the mixture was heated to the boiling point. The potassium perchlorate was removed by filtration, the filtrate was concentrated, and the VII was removed from the residue by extraction with ether and distilled (Tables 1-3). Mass spectrum, m/e (relative intensity, %): 232 (46), 230 (100), 195 (8), 153 (62), 140 (68), 139 (61), 126 (4), 125 (43).

p-Methoxyphenyl 5-Chloroamyl Sulfide (VIII) (Tables 1-3). This compound was obtained by the method used to prepare VII. The reaction mixture was extracted with ether, and the ether was removed by distillation. The residue, which was insoluble in ether, consisted of a mixture of salts IVA and IVB. The percentage of the latter was determined by titration of a solution of a weighed sample of the mixture in acetic acid with perchloric acid in dioxane in the presence of mercury(II) acetate.

p-Methoxyphenyl 4-Bromobutyl Sulfide (IX) and p-Methoxyphenyl 4-Hydroxybutyl Sulfide (Va). A 5.89-g (0.02 mole) sample of IIIA was heated with a solution of 12 g of potassium bromide (0.1 mole) in 18 ml of water at 100°C for 6 h, after which the mixture was allowed to stand at room temperature for 10 days (in order to convert IX completely to IIIC). The liquid layer and the supernatant crystals of VA were decanted from the potassium perchlorate and extracted with benzene. Removal of the benzene by distillation gave 0.46 g of Va. The aqueous layer after treatment with benzene was evaporated to dryness, during which the IIIC was converted to IX. The latter was extracted with benzene, or, preferably, the residue after evaporation of the aqueous layer was vacuum distilled to give IX. The product was soluble in nonpolar solvents and did not give a precipitate with a solution of silver nitrate. After 24 h at −30°C, bromo sulfide IX was converted to salt IIIC. The latter was soluble in benzene but insoluble in polar solvents and had mp 93-95°C (after precipitation from alcohol solution by the addition of ether). After heating at 100°C for 1 h, salt IIIC was converted to sulfide IX. If a 2-3% aqueous solution of salt IIIC is refluxed, hydroxybutyl sulfide Va (26%) can be extracted from it after 18 h. Starting bromide IIIC (72%) was obtained from the washed (with ether) aqueous solution after evaporation and allowing the residue to stand for 10 days.

p-Methoxyphenyl 5-Hydroxyamyl Sulfide (VIa). p-Methoxyphenyl 5-hydroxyamyl sulfide (VIa) (6%) was extracted with benzene after heating IVA with an aqueous solution of potassium bromide, as described for IIIA, and decantation. The aqueous layer was evaporated, and hydrated IVC (93%) was extracted from the residue with alcohol (the product was crystallized from a mixture of alcohol and ether). The absorption bands at 3400, 3490, and 450-600 cm^{-1} in the IR spectrum of IVC are associated with the presence of water of hydration.

1-Arylthioniacycloalkane Iodides (ID-IVD, Table 3). A hot solution of 1.7 g (0.01 mole) of potassium iodide in a mixture of 10 ml of alcohol and 1 ml of water was added to a hot solution of 0.01 mole of the corresponding perchlorate (IA-IVA) in a mixture of 3 ml of alcohol and 2 ml of water, and the mixture was refluxed for 1 min. After a few hours, the precipitated $KClO_4$ was separated and washed with water and alcohol. The wash liquid was combined with the filtrate, and the mixture was evaporated. The residue was recrystallized from alcohol (ID, IID), water (IIID), or acetone—alcohol—ether (IVD). The IR spectrum of hydrated IIID contains absorption bands at 3420, 3500, and 440-490 cm^{-1}.

1-(p-Methoxyphenyl)-1-thioniacycloalkane Picrates (IIIE and IVE, Table 3). Alcohol solutions of equivalent amounts of the corresponding perchlorates (IIIA and IVA) and picric acid were mixed with heating, and the precipitated picrates (IIIE and IVE) were separated and crystallized from alcohol.

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ACYLATION OF BENZOTHIOPHENE IN THE PRESENCE OF SMALL AMOUNTS OF FERRIC CHLORIDE

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The corresponding ketones were obtained by reaction of acetyl, benzoyl, and 4-methyl- and 4-methoxybenzoyl chlorides with benzothiophene in the presence of $1 \cdot 10^{-3}$-$1 \cdot 10^{-4}$ mole of ferric chloride. It was found by gas—liquid chromatography that ∿1:4 mixtures of 2- and 3-acylbenzothiophenes are formed in all cases.

Little study has been devoted to the synthesis of ketones of the thiophene series by acylation of benzothiophene, although sulfur-containing heterocyclic carbonyl compounds are potential physiologically active substances. The acetylation [1-3] and benzoylation [3-4] of benzothiophene in the presence of various catalysts have been described. The o-methylbenzoylation [5] and p-methoxybenzoylation [6] of benzothiophene in the presence of equimolar amounts of aluminum chloride and stannic chloride are also known. It is apparent from the results of these studies that 3-acylbenzothiophenes are formed exclusively in the acylation of benzothiophene. The 2 isomer was isolated along with the 3-acyl product only in [3].

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