the concentrated solution was allowed to stand at 0-3° for 16 h. The resulting precipitate was removed by filtration to give 0.72 g (87%) of colorless needles with mp 195-196° (from methanol) and R_f 0.85 [elution with an n-butyl alcohol–amyl alcohol–water–acetic acid system (20 : 20 : 12 : 1) and development with a 0.2% solution of potassium permanganate]. Found: 49.1; H 5.9; S 13.0%. $C_{10}H_{15}NO_4S$. Calculated: C 49.0; H 6.2; S 13.1%.

dl-trans-6-(4-Carboxybutyl)-2-oxo-cis-hexahydrothieno[3,4-d]oxazole (VIII). Under conditions similar to those in the preparation of IV, 0.75 g (90%) of colorless needles with mp 180-181° (from methanol) and R_f 0.83 (in the same system as in the case of IV) was obtained from 1 g (3 mmole) of VIIa (or VIIb, c). Found: C 49.2; H 6.3; S 12.6%. $C_{10}H_{15}NO_4S$. Calculated: C 49.0; H 6.2; S 13.1%.

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MASS SPECTRA OF 4-ACYLAMINO-3-HYDROXY(OR ACYLOXY)THIOPHANS

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UDC 547.732 : 543.51 : 547.634

The mass spectra of cis- and trans-4-acylamino-3-hydroxy(or acyloxy)thiophans were investigated. The general principles of fragmentation under the influence of electron impact were established. A difference in the intensities of the peaks of the fragments formed at an ionizing-electron energy of 14 eV was observed for some of the cis and trans isomers of 3,4-substituted thiophans.

Up to now, only individual mass-spectrometric studies of thiophans were known; for example, unsubstituted thiophans [1] and α-alkylthiophans [2] have been studied. In connection with our investigation of the stereochemistry of di- and trisubstituted thiophans [3-6], it was of interest to study the fragmentation of cis- and trans-4-acylamino-3-hydroxy(or acyloxy)thiophans. A total of 25 thiophan derivatives, of which 11 were cis- and trans-isomeric pairs, were studied.

As a result of the study we established the general principles for I-XIV and the effect of the type of substituent on the fragmentation process. The relative intensities of the ion peaks of hydroxyaminothiophans are presented in Table 1.

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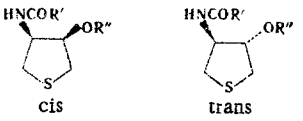
TABLE 1. Relative Intensities of the Peaks of Ions Formed in the Fragmentation of Disubstituted Thiophans I-XIV

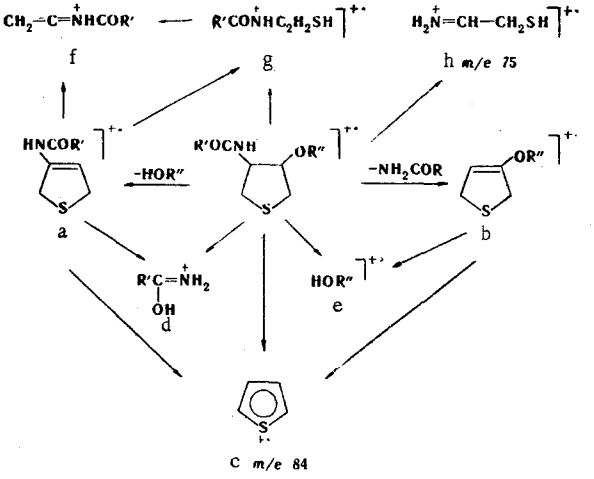
Compound	m/e Values and relative intensities (%) at 75 and 14 eV																													
	M^+			a			b			c			d			e			f			g			h		
	m/e	75eV	14eV	m/e	75eV	14eV	m/e	75eV	14eV	m/e	75eV	14eV	m/e	75eV	14eV	m/e	75eV	14eV	m/e	75eV	14eV	m/e	75eV	14eV	m/e	75eV	14eV
I cis	161	—	—	143	66	84	102	95	100	84	67	69	60	64	46	18	—	—	84	66	69	117	4	4	75	100	33
I trans	161	5	4	143	54	61	102	100	100	84	63	55	60	66	46	18	—	—	84	64	55	117	4	4	75	95	26
II cis	203	—	—	143	49	100	144	8	15	84	100	7	60	3	—	60	3	—	84	100	7	117	—	—	75	—	—
II trans	203	—	16	143	48	100	144	16	9	84	100	10	60	2	—	60	2	—	84	100	10	117	—	—	75	—	—
III cis	223	2	—	205	48	100	102	26	35	84	27	63	122	36	68	18	—	—	146	6	8	179	—	—	75	—	—
III trans	223	5	2	205	44	100	102	26	47	84	24	35	122	40	94	18	—	—	146	6	6	179	—	—	75	—	—
IV cis	265	—	—	205	54	100	144	1	2	84	100	35	122	35	29	60	—	—	146	7	—	179	—	—	75	1	—
IV trans	265	—	—	205	77	100	144	2	2	84	100	24	122	50	18	60	1	—	146	6	—	179	—	—	75	1	—
V cis	327	—	—	205	75	100	206	9	12	84	100	13	122	40	10	122	40	10	146	5	—	179	—	—	75	—	—
V trans	327	—	—	205	63	100	206	9	14	84	100	19	122	32	15	122	32	15	146	3	—	179	—	—	75	—	—
VI cis	162	—	—	144	100	100	102	65	20	84	62	29	61	51	—	18	—	—	85	24	6	118	6	—	75	57	12
VI trans	162	1	3	144	100	100	102	75	41	84	69	52	61	63	35	18	—	—	85	26	16	118	7	—	75	65	10
VII trans	204	—	—	144	51	100	144	51	100	84	100	46	61	27	10	60	5	2	85	20	5	118	3	3	75	25	10
VIII cis	266	—	—	144	93	100	206	3	5	84	100	12	61	32	—	122	4	2	85	23	—	118	5	—	75	26	3
IX cis	246	—	—	186	32	100	144	1	1	84	100	83	103	14	11	60	24	—	127	4	1	160	2	—	75	8	—
IX trans	246	3	8	186	27	97	144	2	3	84	100	100	103	23	29	60	15	4	127	4	2	160	9	2	75	8	2
X cis	219	—	2	159	48	100	144	5	—	84	100	7	76	14	—	60	3	—	100	30	—	133	10	—	75	—	—
X trans	219	5	14	159	72	100	144	6	5	84	100	10	76	15	—	60	2	—	100	25	—	133	8	—	75	—	—
XI cis	191	—	—	173	100	100	102	58	8	84	51	8	152	—	—	18	—	—	176	—	—	209	—	—	75	—	—
XI trans	191	23	34	173	100	100	102	29	7	84	59	3	152	2	7	18	—	—	176	—	—	209	—	—	75	—	—
XII cis	233	—	—	173	84	100	144	20	7	84	100	22	90	17	7	60	2	—	114	17	1	147	10	4	75	9	—
XII trans	233	6	15	173	63	100	144	16	9	84	100	34	90	27	10	60	1	—	114	10	1	147	8	4	75	8	—
XIII cis	253	—	—	235	2	4	102	10	2	84	3	—	152	—	—	18	—	—	176	—	—	209	—	—	75	—	—
XIII trans	253	1	7	235	—	2	102	7	6	84	—	—	152	2	7	18	—	—	176	—	—	209	—	—	75	—	—
XIV cis	295	—	—	235	9	27	144	91	100	84	22	—	152	—	—	60	—	—	176	—	—	209	—	—	75	5	—

The fragmentation of I-XIV, which are amino alcohols of the thiophan series, is characterized by primary detachment of the substituents (hydroxy, acyloxy, or acylamino), during which one hydrogen atom is detached simultaneously from the thiophan ring and the substituents are split out in the form of a neutral particle. Ions b and *a* are formed by cleavage of the bond between the oxygen atom of the hydroxyl group (or acyloxy group) and the C_3 atom and also by cleavage of the bond between the nitrogen atom of the acylamino group and the C_4 atom. The intensities of the peaks of ion *a* for most of the investigated compounds exceed the intensities of the peaks of ions b. The difference in the surpassing of the intensities of the peaks of ions *a* as compared with ions b is particularly large for compounds with an acyloxy group as a substituent in the 3 position (II, IV, V, VIII-X, and XII). An electron-acceptor substituent evidently markedly weakens the C–O bond, and cleavage of the carbon–oxygen bond in 4-acylamino-3-acyloxythiophans (II, IV, V, VIII and IX) is therefore the determining factor upon electron impact.



R"	R'						
	CH_3	C_6H_5	NH_2	$NHCOCH_3$	OCH_3	OC_2H_5	$OCH_2C_6H_5$
H	I	III	VI			XI	XIII
$COCH_3$	II	IV	VII	IX	X	XII	XIV
COC_6H_5		V	VIII				

Compound I, which has a free hydroxyl group and an acetamido group as substituents, does not follow the above-described principles, and primary cleavage of the C–N bond, to which the high intensity of the peak of ion b (m/e 102) as compared with the intensity of ion *a* (m/e 143) corresponds, is characteristic for it. The relative intensity of the peaks of ions *a* (m/e 235) and b (m/e 102 and 144) is weak for 4-benzyloxycarbonylamino-3-hydroxy(or acyloxy)thiophans (XIII, XIV), apparently because of the prevailing fragmentation in the benzyloxycarbonyl group.



The elimination of a substituent from ions *a* or b or of both substituents from molecular ion M^+ leads to the formation of thiophanium ion c (m/e 84). The formation of an ion analogous to ion c was also observed in the case of α-alkylthiophans [2]. The relative intensity of the peak of ion i (m/e 58), which is evidently formed from thiophanium ion c (m/e 84), is insignificant (< 1.5%) and is not included in Table 1, although the peak of fragment i is a primary peak in the mass spectrum of unsubstituted thiophan [1].

Fragmentation with splitting out of substituents is also realized with charge localization of the departing hydroxyl and amide substituents. In this case, the acylamino substituent from the 4 position departs with two hydrogen atoms to give ion b, whereas the hydroxyl or acyloxy group departs from the 3 position with one hydrogen atom to give ion e. From the relative intensities of the peaks of ions b and e one can form a judgment that the probability of the formation of ion d is higher than the probability of the formation of ion e. The primary formation of ion d can be explained by the presence in it of a nitrogen atom, which has greater electron-donor properties than the oxygen atom in the hydroxyl or acyloxy groups.

Fragmentation of thiophan hydroxyamides I-X with cleavage of the thiophan ring leads to the formation of ions f, g, and h, which can be formed from the molecular ion or ion *a*, which contains an amide sub-

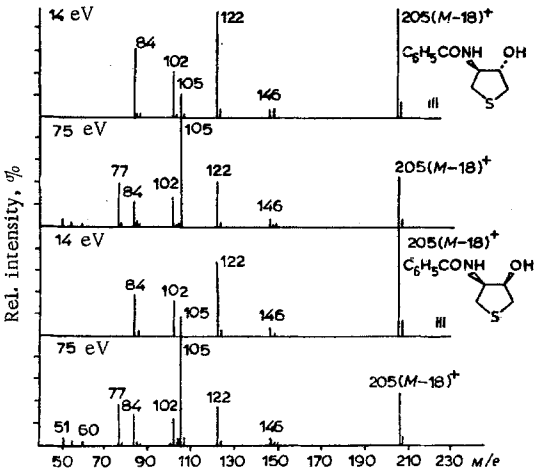


Fig. 1. Mass spectra of I, II, VI, and IX.

TABLE 2. Elementary Compositions of the Ions Formed in the Fragmentation of I, III-VI, and XII

Fragment	Compound											
	I		III		IV		V		VI		XII	
	m/e		m/e		m/e		m/e		m/e		m/e	
a	143	C_6H_9NOS	205	$C_{11}H_{11}NOS$	205	$C_{11}H_{11}NOS$	205	$C_{11}H_{11}NOS$	144	$C_5H_8N_2OS$	173	$C_7H_{11}NO_2S$
b	102	C_4H_6S	102	C_4H_6S			206	$C_{11}H_{10}O_2S$	102	C_4H_6OS	144	$C_6H_8O_2S$
		C_4H_6NO										
c*	84	C_4H_4S	84	C_4H_4S	84	C_4H_4S	84	C_4H_4S	84	C_4H_4S	84	C_4H_4S
d			122	C_7H_8NO	122	C_7H_8NO	122	C_7H_8NO	61	CH_5N_2O	90	$C_3H_8NO_2$
e							122	$C_7H_6O_2$				
f	84	C_4H_6NO	146	C_9H_8NO	146	C_9H_8NO	146	C_9H_8NO	85	$C_3H_5N_2O$	114	$C_5H_8NO_2$
g	117	C_4H_7NOS	179	C_9H_9NOS					118	$C_3H_6N_2OS$	147	$C_5H_9NO_2S$
h	75	C_2H_5NS	75	C_2H_5NS			75	C_2H_5NS	75	C_2H_5NS		

*Ion c is a doublet with the additional composition C_4H_6NO; this corresponds to ion f, which is formed by fragmentation with cleavage of the thiophan ring.

stituent. Ions g are formed by cleavage of the thiophan ring at the C_3-C_4 and $S-C_2$ bonds, and its mass number and elementary composition depend on the substituent attached to the amide group (R' = CH_3, C_6H_5, NH_2, and $NHCOCH_3$). Ions f and h can also apparently be formed by cleavage of the thiophan ring at the C_3-C_4 and $S-C_5$ bonds of ion *a* or from the molecular ion. The elementary composition of ion f also depends on the substituent (R') attached to the amide group, whereas ion h has an identical structure for all of the investigated compounds. Thus the fragmentation under consideration is characteristic for cyclic amides [7]. The relative intensities of ions f, g, and h are weak for all of the investigated compounds except for 4-ureido-3-hydroxythiophan (VI) and 4-acetamido-3-hydroxythiophan (I), for which, as indicated above, fragmentation with cleavage of the C–N bond predominates.

When the ionizing-electron energy is increased from 14 to 75 eV, the intensities of the peaks of ion *a* decrease, whereas the intensities of the peaks of fragments g, h, and f (for I, VII-X, and XII) increase. The reason for this may be the fact that fragmentation with cleavage of the thiophan ring proceeds through the open form of the molecular ion at the C_3-C_4 bond and possibly also through ion *a*. It should be noted that opening of the thiophan ring to give oxygen-containing fragments does not occur.

Ions *a*, b, c, d, e, f, g, and h were identified in the case of I, III-VI, and XII from data from the high-resolution mass spectra. The accurate measurement of the masses of these ions made it possible to determine their elementary compositions (Table 2).

A molecular ion peak of weak intensity shows up primarily in the case of the trans configuration of the hydroxyaminothiophans.

An examination of the spectra of the cis and trans isomers of disubstituted thiophans I-XIV at 12-14 eV shows that there are considerable differences in the intensities of the peaks of fragments *a*, b, c, and d, formed in the splitting out of substituents, for a number of the isomers (I, III, VI, IX, and XII) (Table 3).

TABLE 3. Relative Intensities of the Peaks of the Fragments of the cis and trans Isomers of Disubstituted Thiophans

Compound	m/e	Fragment	Relative intensities (%) at 14 eV for isomers	
			cis	trans
I	143	a	84	61
	84	b	69	55
III	102	b	35	47
	84	c	63	35
	122	d	68	94
IV	84	c	35	24
	122	d	29	18
V	84	c	13	19
	122	d	10	15
	122	e	10	15
VI	102	b	20	40
	84	c*	29	52
IX	186	a	100	97
	84	c	83	100
	103	d	11	29
XII	84	c	22	34

*One must bear in mind that this ion is a composite ion.

The differences in the intensities of these fragments can apparently be associated with the conformational state of the cis and trans isomers [8]. In the present research we used disubstituted thiophans I-IV, VI-VIII, IX, XI, and XIII, the synthesis of which was described in [3, 4, 6]. The cis-V, trans-V, cis-X, trans-X, and cis-XIV compounds were obtained for the first time in the present study.

EXPERIMENTAL METHOD

The mass spectra were obtained with a JMS-01-JC-2 high-resolution spectrometer with direct introduction of the sample into the ion source; the ionizing voltages were 75 and 14 eV, the temperature of the sample support was varied from 60 to 80°, and the temperature of the ionization chamber ranged from 120 to 140°. The high-resolution spectra were recorded on photographic plates of the Q type and were interpreted with a JMD-2M and JEC-6 microphotometer-computer system.

cis-4-Ureido-3-benzoxythiophan (cis-V). A 3.8-ml (10 mmole)-sample of a 4 N sodium hydroxide solution and 1.12 ml (10 mmole) of benzoyl chloride were added simultaneously at 0° to a solution of 0.8 g (5 mmole) of cis-4-ureido-3-hydroxythiophan in 8 ml of 50% aqueous dioxane at 0°, after which the mixture was stirred for 1 h, and the resulting precipitate was removed by filtration and washed with water to give 1.3 g (98%) of white prisms with mp 174-175° (from alcohol). Found: C 53.6; H 5.6; N 10.8%. $C_{12}H_{14}N_2O_3S$. Calculated: C 54.1; H 5.3; N 10.5%.

trans-4-Ureido-3-benzosythiophan (trans-V). As in the preceding experiment, this compound, with mp 187-188° (from alcohol), was obtained as white needles in 91% yield from trans-4-ureido-3-hydroxythiophan [3]. Found: C 53.5; H 5.5; N 10.5%. $C_{12}H_{14}N_2O_3S$. Calculated: C 54.1; H 5.3; N 10.5%.

cis-4-Methoxycarbonylamino-3-acetoxythiophan (cis-X). Acetic anhydride (1.5 ml) and 1.5 ml of acetyl chloride were added to 1 g (5.6 mmole) of cis-4-methoxycarbonylamino-3-hydroxythiophan [6], and the mixture was cooled to 0° and treated with 0.5 ml (6.2 mmole) of pyridine. The mixture was then stirred at 18-20° for 3 h, after which it was concentrated to dryness, and the residue was dissolved in chloroform. The chloroform solution was washed with water, the chloroform was removed, 3-4 ml of methanol was added to the residue, and the mixture was allowed to stand at 0° for 18-20 h. The resulting precipitate was separated to give 0.7 g (56.7%) of white prisms with mp 97-98° (from methanol). Found: C 43.8; H 5.9; N 6.6%. $C_8H_{13}NO_4S$. Calculated: C 43.8; H 6.0; N 6.4%.

trans-4-Methoxycarbonylamino-3-acetoxythiophan (trans-X). As in the preparation of cis-X, 0.8 g (64.7%) of white plates with mp 59-61° (from methanol) was obtained from trans-4-methoxycarbonylamino-3-hydroxythiophan [6]. Found: C 43.4; H 6.0; N 6.1%. $C_8H_{13}NO_4S$. Calculated: C 43.8; H 6.0; N 6.4%.

cis-4-Benzylcarbonylamino-3-acetoxythiophan (cis-XIV). A 0.4-ml (5.4 mmole) sample of acetyl chloride was added at 0° to a solution of 0.4 g (1.6 mmole) of cis-4-benzylcarbonylamido-3-hydroxythiophan (XII) [6] in 3 ml of chloroform and 0.4 ml (5.4 mmole) of pyridine, and the mixture was stirred at 20°

for 2 h. Water (20 ml) was added, and the mixture was extracted with chloroform. The chloroform was removed from the extract, 2 ml of alcohol was added to the residue, and the mixture was allowed to stand at 0° for 24 h. The resulting solid was removed by filtration to give 0.3 g (64%) of white needles with mp 64-65° (from alcohol). Found: C 56.9; H 5.8; N 10.7%. $C_{14}H_{17}NO_4S$. Calculated: C 56.9; H 5.8; N 10.9%.

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REACTION OF 1,5-DIKETONES

XIX.* 2,2'-DICYCLOHEXANONYL SULFIDE: SYNTHESIS, ISOMERIZATION TO A CYCLOKETOL, AND CONVERSION TO PERHYDROPHENOTHIAZINE

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UDC 547.869.2.07:542.952.1

2,2'-Dicyclohexanonyl sulfide and the isomeric 2-thiatricyclo[7.2.1.$0^{3,8}$]tridecan-8-ol-13-one were synthesized by reaction of α-chlorocyclohexanone with $Na_2S \cdot 9H_2O$. Both compounds form the same perhydrophenothiazine isomers under the conditions of the Leuckart reaction.

The previously undescribed 2,2'-dicyclohexanonyl sulfide (I) is a peculiar 1,5-diketone and the thia analog of the known [2] 2,2'-dicyclohexanonylmethane. In the present communication we present data that confirm that the structural analogy between these diketones also extends to some of their reactions.

Depending on the reaction conditions, diketone I or isomeric ketol II is obtained in the reaction of α-chlorocyclohexanone with sodium sulfide. When the temperature is lowered, one can obtain diketone I in yields up to 40%. Diketone I is unstable and can be stored only at low temperature in the dark. In light it decomposes after a few days. Ketol II, which is formed in 80% yield when a solution of sodium sulfide and α-chlorocyclohexanone is allowed to stand at room temperature for 2 days, is completely stable on storage.

The IR spectrum of diketone I contains an intense absorption band at 1710 cm^{-1} (C=O), and the IR spectrum of ketol II, in addition to this band, also contains absorption bands at 3600 and 3450 cm^{-1} (OH). The presence of two carbonyl groups in diketone I is confirmed by the formation of a bis derivative (III) on reaction of diketone I with malononitrile under the conditions of the Knoevenagel reaction. We were unable to obtain a dioxime from diketone I.

*See [1] for communication XVIII.

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