was filtered, the chlorobenzene was removed by distillation, and the residue was dissolved in ether. The ether solution was cooled to 0°C and filtered, the ether was removed by distillation, and the residue was dissolved in acetone–hexane (1:5) and purified by passage through a column filled with silica gel. PMR spectrum: 7.44 (5H, m, C_6H_5), and 2.43 ppm (3H, s, CH_3).

Benzothieno[2,3-b]dihydrothiopyran (VI). PMR spectrum: 7.44 (4H, m, C_6H_4), 2.63 (4H, m, $-CH_2CH_2-$), and 1.70 ppm (2H, m, $-CH_2-$).

Allyl 3-Methyl-2-benzothienyl Sulfide (VII). This compound was obtained in 52% yield by the method described for sulfide I starting from 3-methylbenzothiophene and had n_D^{20} 1.5492 and d_4^{20} 1.2018. PMR spectrum: 7.55 (4H, m, C_6H_4), 5.7 (1H, m, $-CH=$), 5.04 (2H, m, $=CH_2$), 3.36 (2H, d, $-CH_2-$), and 2.33 ppm (3H, s, CH_3). Found: C 65.3; H 5.6; S 29.4%. $C_{12}H_{12}S_2$. Calculated: C 65.4; H 5.4; S 29.2%.

Sulfide VII was heated at 150-190°C in a sealed ampul in an argon atmosphere for 1 h, after which the mixture was dissolved in ether, and the ether solution was washed with 10% KOH solution. The ether was removed from the residue by distillation, and the residue was dissolved in hexane and chromatographed on silica gel elution with CCl_4–hexane–ether (47:43:10). Removal of the solvent gave sulfide VIII. PMR spectrum: 7.55 (8H, m, $C_{16}H_8$) and 2.55 ppm (6H, s, $2CH_3$).

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MASS-SPECTROMETRIC STUDY OF SUBSTITUTED TETRAHYDRO-4-THIOPYRONES

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UDC 543.51:547.818

The mass spectra of 16 methyl- and phenyl-substituted tetrahydro-4-thiopyrones that differ with respect to the position of the substituents in the ring and some of their deutero derivatives were studied. The principal pathways of dissociative ionization of these compounds are due to cleavage of the α bonds with respect to the heteroatom and the carbonyl group. Analytical features that make it possible to determine the position of the substituents in the tetrahydro-4-thiopyrone ring and distinguish the structural and spatial isomers in this series of compounds were found.

In [1-5] we described new simple and convenient methods for the preparation of various derivatives of tetrahydro-4-thiopyrones from the bases and salts of alkenyl and styryl β-dialkylaminoalkyl ketones [1-3], as well as from 4-ketodecahydroquinolines [4, 5]. In the present research we studied the mass-spectral behavior of the tetrahydro-4-thiopyrones obtained by the indicated methods [1-5] and their previously known representatives and established the principles of the dissociative ionization of these compounds under the influence of electron impact. Up until now, data on the mass spectra of compounds of this type were limited to the data in [6-9], in which the fragmentation of unsubstituted tetrahydro-4-thiopyrone and its sulfoxide [6] and sulfone [6, 7] is described. Data on the mass spectra of 2,2-di and 2,3-dimethyl-, 2,2,6,6-tetramethyl-, and trans-2,5-dimethyltetrahydro-4-thiopyrone are presented in [8, 9] without analysis and discussion. The mass-spectral

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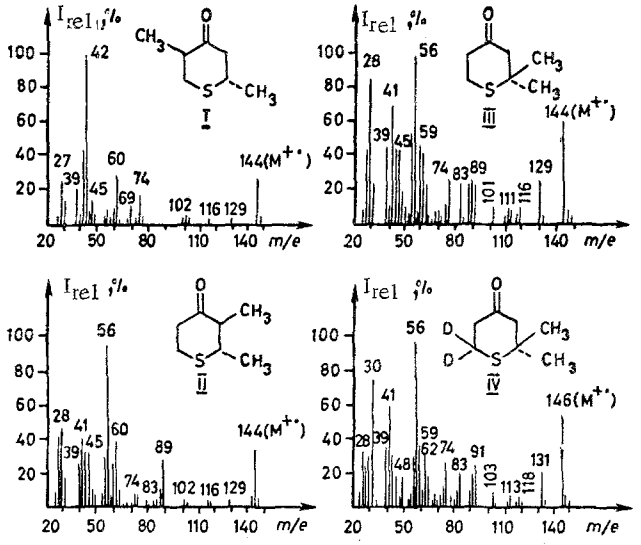
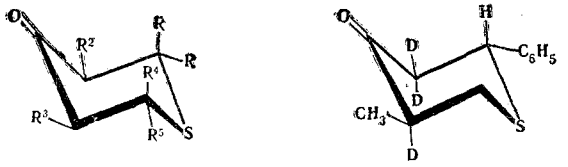


Fig. 1. Mass spectra of thiopyrones I-IV (70 eV).

behavior of oxygen- and silicon-containing analogs of tetrahydro-4-thiopyrone has been previously studied in [10-12]. No systematic mass-spectrometric study of substituted tetrahydro-4-thiopyrones and their two-ring analogs has yet been made.

The following series of compounds were investigated:



I-VIII, X-XVI IX

I $R=R^3=CH_3$, $R^1=R^2=R^4=R^5=H$; II $R=R^2=CH_3$, $R^1=R^3=R^4=R^5=H$; III $R=R^1=CH_3$, $R^2=R_3=R^4=R^5=H$; IV $R=R^1=CH_3$, $R^2=R^3=H$, $R^4=R^5=D$; V $R=C_6H_5$, $R^1=R^2=R^3=R^4=R^5=H$; VI $R=C_6H_5$, $R^1=R^2=R^3=H$, $R^4=R^5=D$; VII $R=C_6H_5$, $R^1=R^2=R^4=R^5=H$, $R^3=CH_3$; VIII $R=C_6H_5$, $R^1=R^2=H$, $R^3=CH_3$, $R^4=R^5=D$; X $R=C_6H_5$, $R^1=R^3=R^4=R^5=H$, $R^2=CH_3$; XI $R=C_6H_5$, $R^1=R^4=R^5=H$, $R^2=R^3=CH_3$; XII $R=C_6H_5$, $R^1=R^2=R^3=H$, $R^4=R^5=CH_3$; XIII $R=R^5=C_6H_5$, $R^1=R^2=R^3=R^4=H$; XIV $R=R^4=C_6H_5$, $R^1=R^2=R^3=R^5=H$; XV $R=R^5=C_6H_5$, $R^1=R^3=R^4=H$, $R^2=CH_3$; XVI R and $R^2=-(CH_2)_4-$, $R^1=R^3=R^4=R^5=H$

Compounds II and VII are a mixture of the cis and trans isomers, while the remaining thiopyrones are individual compounds and are stereohomogeneous; this was confirmed by means of the PMR spectra and thin-layer chromatography (TLC). The configurations and conformations of some of the compounds were established in [4] by means of the PMR spectra, which will be examined in detail in one of our subsequent communications.

The mass spectra of I-XVI are presented in Figs. 1-3. The molecular-ion peaks of the investigated compounds are quite intense, whereas in the spectrum of octahydro-4-thiochromanone XVI they are the maximum peaks (Figs. 1-3, Table 1).

The dominant pathway of fragmentation of I-XVI is the simultaneous cleavage of the S—C_6 and C_5—C_4 or S—C_2 and C_3—C_4 bonds; the positive charge is localized primarily on the hydrocarbon fragment (Scheme 1, pathway A or B). The cleavage of the ring proceeds symmetrically relative to the sulfur atom and the carbonyl group; this is characteristic for the fragmentation of tetrahydro-4-thiopyrone [6-8], its sulfoxide and sulfone [6, 7], and 3,3-dimethyl- and 2,2,6,6-tetramethyltetrahydro-4-thiopyrone [8], as well as for the oxygen- and silicon-containing heteroanalogs [10-12].

The fragmentation of I-XVI via pathways A and B is confirmed by the shift of the peaks of the a and b ions by the corresponding atomic mass unit when methyl substituents and a phenyl group are present in the molecule and by 1 or 2 amu in the mass spectra of the deutero derivatives IV, VI, VIII, and IX. The peaks of the indicated ions generally have the highest intensities in the mass spectra of the investigated compounds (Table 1).

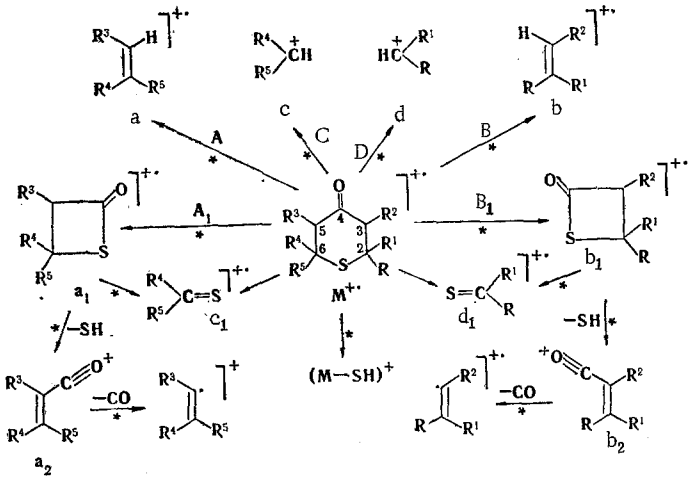
TABLE 1. Stabilities of the Molecular Ions and Relative Intensities of the Peaks of the Principal Characteristic Fragments (% of the maximum peak) in the Mass Spectra of Substituted Tetrahydro-4-thiopyrones

Compound	W_{M^+}, %	a		b		a_2		b_2		c		d		$I_{[M-SH]^+}/I_{M^+}$*
		m/e	I_a	m/e	I_b	m/e	I_{a_2}	m/e	I_{c_2}	m/e	I_c	m/e	I_d	
I	7,9	42	100	42	100	69	10	69	10	46	5,0	60	30	4
II	5,9	28	50	56	100	55	32	83	4,0	46	12	60	39	2
III	6,1	28	88	56	100	55	56	83	23	46	20	74	25	13
IV	6,4	30	76	56	100	57	37	83	20	48	18	74	26	13
V	10,3	28	22	104	100	55	3,6	131	4,1	46	7,1	122	9,0	3
VI	10,8	30	20	104	100	57	3,4	131	3,9	48	7,1	122	8,8	3
VII	9,2	42	29	104	100	69	3,2	131	6,1	46	3,6	122	13	4
VIII	9,6	44	31	104	100	71	3,2	131	6,0	48	3,0	122	15	4
IX	9,8	43	29	106	100	70	3,2	132	4,9	46	3,7	122	17	1
X	11,1	28	22	118	100	55	7,9	145	2,0	46	5,4	122	20	1
XI	6,8	42	23	118	100	69	6,1	145	3,2	46	2,0	122	14	1
XII	11,1	56	17	104	100	83	10	131	15	74	11	122	41	2
XIII	10,1	104	100	104	100	131	9,8	131	9,8	122	29	122	29	14
XIV	8,3	104	100	104	100	131	8,1	131	8,1	122	19	122	19	6
XV	10,4	104	100	118	66	131	5,7	145	3,4	122	37	122	37	2
XVI	11,9	28	56	82	28	55	19	109	14	46	22	—	—	6

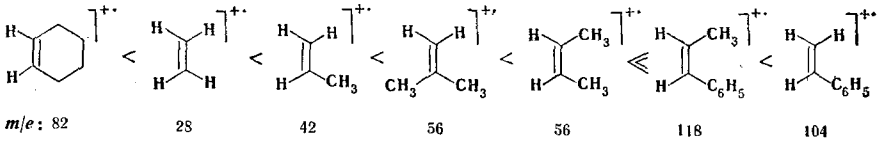
*The intensities are indicated in percent with respect to the intensity of the molecular-ion peak.

The fraction of the a and b ions and their daughter fragments with respect to the total ion current is 40-60%. The maximum contribution to the total ion current (50-60%) of these ions is observed in the case of monophenyl derivatives V-XI.

Scheme 1



The ratio of the intensities of the peaks of the a and b ions is determined by the character of the substituents attached to the C_6 and C_5 or C_2 and C_3 carbon atoms and increases as a function of the number and position of these substituents in the following order:



m/e: 82 28 42 56 56 118 104

When one or two methyl groups are present in the a and b ions, the relative intensities of their peaks increase, and this is so to an even greater degree when the methyl substituents are replaced by phenyl substituents. The simultaneous presence in the a and b ions of methyl and phenyl substituents gives rise to higher intensities of the peaks of these

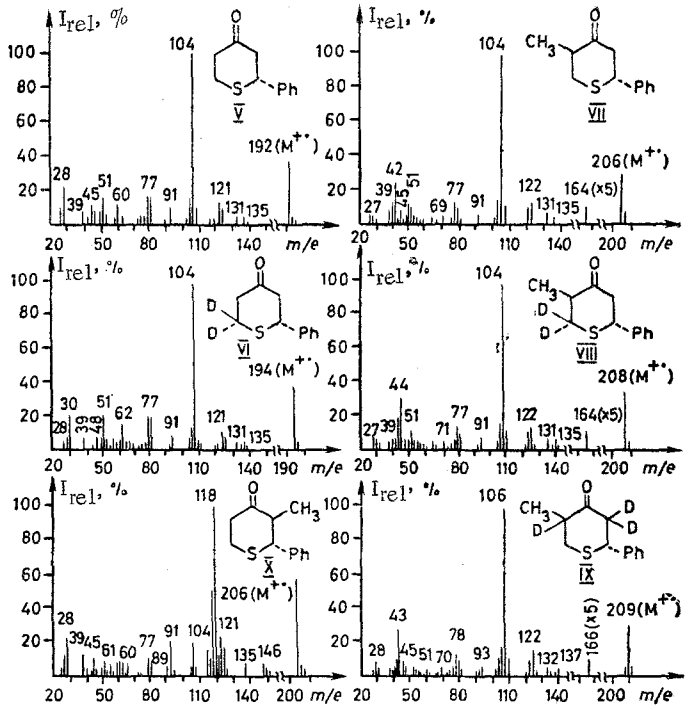


Fig. 2. Mass spectra of thiopyrones V–X (70 eV).

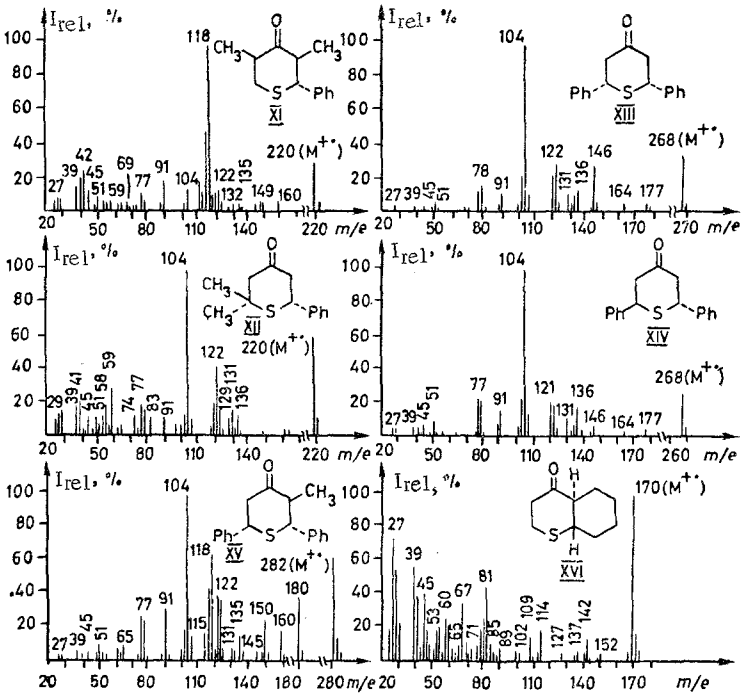


Fig. 3. Mass spectra of thiopyrones XI–XVI (70 eV).

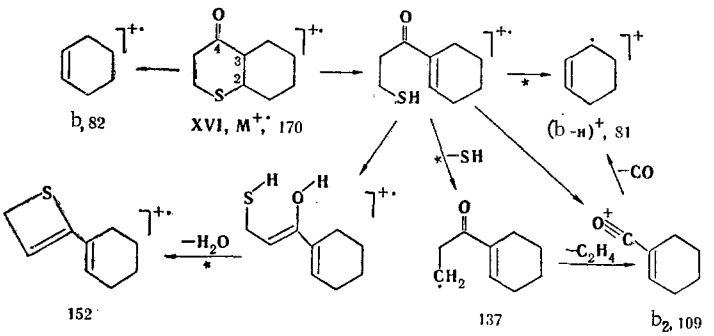
fragments as compared with the ions that contain two methyl groups, but somewhat lower intensities as compared with the ions that contain only a phenyl group.

The peaks of the a_1 and b_1 ions that are formed in fragmentation via pathways A_1 and B_1, respectively (Scheme 1), have very low intensities. In contrast to the peaks of the a and b ions, their intensities decrease as methyl or phenyl substituents are introduced in the tetrahydro-4-thiopyrone ring. The subsequent fragmentation of the a_1 and b_1 ions (Scheme 1) leads to a_2 and b_2 fragments and sulfur-containing c_1 and d_1 ions (Table 1). The a_2 and b_2 ions make it possible to establish the presence in the investigated molecules of a carbonyl group via elimination of a CO particle during subsequent fragmentation.

Sulfur-containing c_1 and d_1 fragments determine the presence or absence of substituents in the α position relative to the sulfur atom (attached to the C_6 or C_2 atoms) from the shift of the peaks by the number of the atomic mass unit that is determined by the mass of these substituents. For example, the b ion (104*) in the mass spectrum of VII attests to the presence of a phenyl substituent attached to the cyclic C_2 or C_3 atom, while the d_1 ion (122) indicates unambiguously that this substituent is attached to the C_2 atom. Consequently, the peaks of a, b, c_1, and d_1 ions observed in the mass spectra of I-XVI (Scheme 1) make it possible to establish the number and position of the methyl or phenyl substituents in the tetrahydro-4-thiopyrone ring and, in particular, to readily distinguish the structural isomers I, II, and III, VII and X, XI, and XII.

It is interesting to note the peculiarity of the fragmentation of XVI, which contains condensed tetrahydrothiopyrone and cyclohexane rings fused in the 2 and 3 positions. In addition to simple synchronous cleavage of the S—C_2 and C_3—C_4 bonds, their cleavage, accompanied by migration of a hydrogen atom (evidently from the α position relative to the carbonyl group) to the sulfur atom (Scheme 2), very likely also occurs. Thus the intensity of the peak of the $[b-H]^+$ fragment (81), the formation of which from the molecular ion is confirmed by the appearance of a metastable ion, exceeds the intensity of the peak of the b fragment (82) by a factor greater than 1.5.

Scheme 2



The cleavage of the S—C bond, which is accompanied by migration of the hydrogen atom to the sulfur atom, also gives rise to elimination of an SH particle directly from the molecular ion (Scheme 1). The formation of $[M-SH]^+$ ions and sulfur-containing c_1 and d_1 fragments, as well as the thioformyl $CH{\equiv}S^+$ (45) that is typical for cyclic sulfides [13], determines the presence of a sulfur atom in the molecule.

When methyl or phenyl substituents attached to the cyclic C_2 or C_6 atoms are present, cleavage of the S—C_2 or S—C_6 bond may be accompanied by migration of hydrogen atoms to one of these atoms, as a result of which $R-\overset{+}{C}H-R^1$ (c) or $R^4-\overset{+}{C}H-R^5$ (d) fragments, respectively, are formed during the subsequent fragmentation (Scheme 1, pathway C or D). In particular, a peak of $C_7H_7^+$ ions (91), which are characteristic for the dissociative ionization of alkylbenzenes [14-16], is observed in the mass spectra of all of the α-phenyl-substituted thiopyrones V-XV. A vicinal methyl group adjacent to the α-phenyl substituent intensifies the formation of $C_7H_7^+$ ions. Thus, for example, in the mass spectrum of X the intensity of the peak of these ions exceeds the intensity of the peak of the same fragment in the mass spectrum of isomeric VII by a factor of almost four.

The participation of the hydrogen atoms in the α positions relative to the carbonyl group in the examined rearrangement processes was established by means of the deutero derivative IX, which was obtained by deuteration of thiopyrone VII. In its mass spectrum the peaks of the rearranged $C_6H_6^+$ ions (78) and $C_7H_7^+$ ions (91) are shifted by 1 and 2 amu to the higher m/e region, while in the case of 6,6-dideutero derivatives VI and VIII shifts of the peaks of the indicated ions are not observed. The shift of the peaks of the 78 and 91 ions by 2 amu in the mass spectrum of trideutero analog IX constitutes evidence for exchange of the hydrogen atoms in the 2 and 3 positions of the heteroring with the hydrogen atoms of the phenyl substituent during the rearrangement.

*Here and subsequently, the numbers that characterize the ions are the mass-to-charge ratios.

The peak of an $[M-28]^+$ fragment, which may be formed as a result of ejection of CO or C_2H_4 molecules from the molecular ion, is observed in the mass spectra of some of the investigated compounds (I-V, X, XIII, XV, and XVI). By comparison of the mass spectra of 2,2-dimethyl-substituted thiopyrone III and its deutero derivative IV it was established that the $[M-28]^+$ ion is a component ion and is formed as a result of both processes (ejection of CO and C_2H_4), while in [6-8] its formation is ascribed as being due only to elimination of a molecule of ethylene from the molecular ion. In the general case the peaks of the $[M-28]^+$ ions observed in the mass spectra of the investigated compounds cannot be regarded as an ambiguous confirmation of the presence of a carbonyl group in their molecules.

The presence in the octahydro-4-thiochromanone (XVI) molecule of an oxygen atom leads, in addition to a_2 and b_2 ions, to the formation of a low-intensity $[M-H_2O]^+$ fragment (152), while peaks of the $[M-H_2O]^+$ ion are absent in the mass spectra of the remaining compounds. The dehydration of the molecular ion of XVI is explained by the increased migrational lability of its hydrogen atoms, which was previously noted in a discussion of the deviation of the dissociative ionization of XVI from the principal fragmentation pathway (Scheme 2).

A study of the character of the fragmentation of I-XVI associated with cleavage of the heteroring revealed predominance of the contribution to the overall ion current of the sulfur-containing fragments as compared with oxygen-containing fragments. Consequently, localization of the positive charge in the molecular ions of these compounds occurs primarily on the sulfur atom; this is characteristic for the dissociative ionization of thiacycloalkanones [6].

One should note the peculiarities of the mass-spectrometric behavior of individual compounds that are associated with the presence and orientation in the heteroring of methyl and phenyl substituents. Thus an intense peak of an $[M-CH_3]^+$ ion, which is due to the presence in the molecules of a gem-dimethyl grouping, appears in the mass spectra of 2,2-dimethyltetrahydro-4-thiopyrone (III) and its deutero derivative IV, and this may serve as a mass-spectrometric sign [17] of its location in the α position relative to the ring heteroatom. According to the data presented in [8], the formation of an intense $[M-CH_3]^+$ ion peak is also observed in the fragmentation of 2,2,6,6-tetramethyltetrahydro-4-thiopyrone, while the presence of a gem-dimethyl grouping in the α position relative to the carbonyl group in the case of the 3,3-dimethyl-substituted analog does not lead to the formation of a sufficiently intense peak of this ion. The intensity of the $[M-CH_3]^+$ ion peak is also considerably lower in the mass spectrum of 2,2-dimethyl-6-phenyltetrahydro-4-thiopyrone XII ($I_{[M-CH_3]^+}/I_{M^+} = 0.42$ for III, whereas $I_{[M-CH_3]^+}/I_{M^+} = 0.025$ for thiopyrone XII); this is evidently associated with the stabilizing effect of the phenyl substituent in the α position relative to the sulfur atom (the W_{M^+} value for XII is higher by a factor of approximately two for XII than for III). The peaks of the $[M-CH_3]^+$ fragment in the mass spectra of dimethyl-substituted thiopyrones I, II, and XI have considerably lower intensities and are virtually absent in the mass spectra of the remaining investigated compounds.

The presence of a phenyl substituent in phenyl-substituted thiopyrones V-XI is detected from the appearance in the mass spectra of a doublet of peaks of $C_6H_5^+$ (77) and $C_6H_6^+$ (78) ions. In contrast to α-monophenyl-substituted thiopyrones, the presence in thiopyrones XIII, XIV, and XV of two phenyl substituents attached to the ring C_2 and C_6 atoms leads to the appearance in the mass spectra of rather intense $[M-C_6H_5CHS]^+$ and $[M-C_6H_5C_2H_3CO]^+$ ion peaks. Similar fragmentation is also observed in the case of 2,2-dimethyl-6-phenyltetrahydro-4-thiopyrone (XII). It is important to note that the probability of the fragmentation of 2,6-diphenyl-substituted compounds via these pathways depends on the spatial orientation of the substituents and their mutual orientation. In contrast to the mass spectrum of cis-2e,6e-diphenyltetrahydro-4-thiopyrone (XIII), in the mass spectrum of its trans-2e,6a-diphenyl-substituted stereoisomer XIV the peaks of the $[M-C_6H_5CHS]^+$ (146) and $C_6H_5CHS^+$ (122) ions have appreciably lower intensities, whereas the intensity of the $[M-C_6H_5C_2H_3CO]^+$ (136) ion peak in the mass spectrum of XIV is higher. In other words, in the case of the trans isomer the formation of $[M-C_6H_5CHS]^+$ and $C_6H_5CHS^+$ fragments is less likely, and ejection of a $C_6H_5C_2H_3CO$ particle occurs more readily. In addition, the trans orientation of the phenyl substituents attached to the heteroring C_2 and C_6 atoms is responsible for the appreciable decrease in the stability of the molecular ion of the trans isomer (Table 1). This difference in the mass-spectral behavior of stereoisomers XIII and XIV, which is evidently associated with interaction of the axial substituent and the carbonyl group in trans

isomer XIV, makes it possible to easily identify these stereoisomeric compounds and by the mass-spectrometric method to determine the configuration and mutual spatial orientation of their phenyl substituents.

Thus the mass-spectrometric study of substituted tetrahydro-4-thio-pyrones I-XVI showed that their fragmentation under the influence of electron impact is monotypic and is associated primarily with cleavage of the heteroring of the symmetrically endocyclic sulfur atom and the carbonyl group. The mass spectra of most tetrahydro-4-thipyrones give complete information regarding the character, number, and position of the substituents in the heteroring and make it possible to readily distinguish structural isomers of compounds of this type and in a number of cases determine the configurations of stereoisomeric compounds and the mutual spatial orientation of their substituents.

EXPERIMENTAL

The synthesis of I-III, V, VII, X, XI, and XVI was carried out by the methods in [2-4]. Compounds XII-XV were obtained by condensation of phenyl-substituted divinyl ketones with hydrogen sulfide, as indicated in [4, 18-20].

Deutero derivatives IV, VI, and VIII were synthesized by aminomethylation of the corresponding alkyl styryl ketones by reaction with deuteroparaformaldehyde and dimethylamine hydrochloride with subsequent cyclization of the resulting deuterated styryl β-dimethylaminoethyl ketones with an aqueous methanol solution of sodium sulfide [2, 3]. Deutero derivative IX was obtained by heating a solution of 2-phenyl-5-methyltetrahydro-4-thiopyrone (VII) with excess CH_3OD in the presence of sodium methoxide on a boiling water bath for 10 h.

The purity and stereohomogeneity of the synthesized compounds were monitored by thin-layer chromatography (TLC), by data from the IR and PMR spectra, and analysis of their mass spectra.

The mass spectra of I-XVI were obtained with an MKh-1303 apparatus equipped with a system for direct introduction of the samples into the ion source at an ionizing voltage of 70 V and a sample-input temperature of 30-40°C.

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SYNTHESIS OF SOME 4-THIAZOLIDONE DERIVATIVES FROM 4-(CYCLO-3-ALKENYL)THIOSEMICARBAZONES

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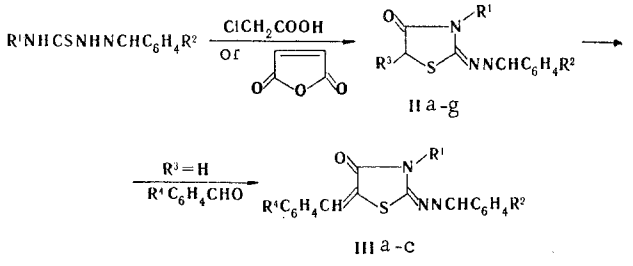
The reaction of 4-(cyclo-3-pentenyl)- and 4-(cyclo-3-hexenyl)thiosemicarbazones with chloroacetic acid gave 2-hydrazono derivatives of 3-cyclo-pentenyl(cyclohexenyl)thioazolid-4-one, the condensation of which with aromatic aldehydes gave 5-benzylidene derivatives. Representatives of 4-thiazolidone with a carboxy group in the 5 position were synthesized by condensation of the same thiosemicarbazones with maleic anhydride. Some of the substances obtained have bactericidal activity.

Pseudothiohydantoin derivatives that have a broad range of antimicrobial and pharmacological activity because of their structural similarity to a number of the most important antibiotics have been obtained by condensation of thiosemicarbazones with α-halo carboxylic acids [1-4]. 4-Thiazolidine derivatives that contain a carboxymethyl group in the 5 position have been obtained by the reaction of thiosemicarbazones with maleic anhydride [5, 6]. It is also known [2, 7] that the introduction of alkyl or aryl substituents in molecules of medicinals is often accompanied by a significant increase in their physiological effect.

In this connection, we synthesized pseudothiohydantoin derivatives (IIa-g) that contain a cycloalkenyl grouping by condensation of 4-(cyclo-3-pentenyl)- and 4-(cyclo-3-hexenyl)-thiosemicarbazones (I) with chloroacetic acid and maleic anhydride.

5-Benzylidene derivatives (IIIa-c), which were also obtained in one step by condensation of thiosemicarbazone Ia with chloroacetic acid and aromatic aldehydes, were synthesized by condensation of derivatives II with aromatic aldehydes, respectively.



I R^1=cyclo-3-pentenyl or cyclo-3-hexenyl; ; II a R^1=cyclo-3-pentenyl, $R^2=R^3=H$; b R^1=cyclo-3-pentenyl R^2=OH-2, R^3=H; c R^1=cyclo-3-pentenyl R^2=H, $R^3=CH_2COOH$; d R^1=cyclo-3-pentenyl, R^2=OH-2, $R^3=CH_2COOH$; e R^1=cyclo-3-pentenyl, $R^2=NO_2$-3, $R^3=CH_2COOH$; f R^1=cyclo-3-pentenyl, R^2=OH-2, R^3=H; g R^1=cyclo-3-hexenyl $R^2=N(CH_3)_2$-4, R^3=H; III R^1= cyclo-3-pentenyl, a $R^2=R^4=H$; b R^2=H, R^4=OH-2; c R^2=OH-2, R^4=H

The identical character of III obtained by the different variants is confirmed by data from their IR spectra. Thus absorption bands at 670 (δ_{C-H} in the benzene ring), 760 (γ_{C-S-C}), 990 (δ_{C-H} in C=CH), 1330 and 1340 (δ_{C-OH}), 1400 (δ_H in C=CH), 1500 (aromatic ring), 1550 ($\gamma_{C=N}$), and 1580 cm^{-1} (conjugated $\gamma_{C=C}$).

Compounds I have bactericidal activity. The preparations had a selective effect on microbes that use molecular oxygen for oxidative processes.

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