3.12 g (88%) of a product with mp 172-173°C (from ethanol). Found: C 66.4; H 3.5; S 23.7%. $C_{15}H_{10}OS_2$. Calculated: C 66.7; H 3.7; S 23.7%.

B) A 1-g (0.01 mole) sample of triethylamine was added with stirring at 20°C to a solution of 1 g (5 mmole) of X in 15 ml of ethanol, after which 0.71 g (5 mmole) of II was added slowly dropwise, and the mixture was stirred for 2 h. It was then cooled to 0°C, and the precipitate was removed by filtration to give 1.6 g (94%) of a product with mp 173-174°C (from ethanol).

<u>2-Thenoylmethylenebenzo-1,3-dithiole (IXb).</u> This compound was similarly obtained from 2.15 g (0.01 mole) of 1-(2-thienyl)-3-bromo-2-propyn-1-one (VIIIb) and 1.42 g (0.01 mole) of II. Workup gave 2.29 g (83%) of a product with mp 185-187,C (from acetone). Found: C 56.8; H 2.9; S 34.7%. $C_{13}H_8OS_3$. Calculated: C 56.8; H 2.9; S 34.8%.

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EFFECTS OF STEREOISOMERISM IN THE MASS SPECTRA OF 2,4-DISUBSTITUTED THIACYCLOHEXANES*

A. I. Mikaya, E. A. Trusova,
L. I. Perepelitchenko, and V. G. Zaikin

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The mass spectra of cis- (Ia-c) and trans-2-methyl-4-R-thiacyclohexanes (IIa-c; a R = n-C_4H_9, b R = n-C_5H_{11}, c R = Ph) were studied. It was established that $[M-CH_3]^+$ ions, which correspond to the loss of a methyl group from the 2 position, are formed more readily in the case of the less stable trans isomers IIa-c than in the case of cis isomers Ia-c. The three-dimensional structures of the substances have no effect on the degree of elimination of the R substituent. The relative ionization energies (RIE) for Ia,b and IIa,b and the relative appearance energies (RAE) of the $[M-CH_3]^+$ ions were measured by the electron impact method. It was found that the RIE are almost 0.05 eV lower and that the RAE of the $[M-CH_3]^+$ ions are ~0.1 eV lower for trans isomers IIa,b than for cis isomers Ia,b.

The stereospecificity of the fragmentation under electron impact of geometrical isomers that differ with respect to the configuration of the alkyl-substituted centers is associated mainly with the different ease of elimination of the substituting alkyl groups. The available relatively small number of papers devoted to the mass-spectrometric study of such stereoisomers shows that the character of the stereospecificity of the fragmentation reactions differs for heterocyclic and carbocyclic compounds. In the case of carbocyclic methyldecalins [2], which have a conformationally rigid system, as well as dialkylcyclohexanes [3] with a loose conformation, an alkyl substituent is unexpectedly readily ejected from the molecular ions of the thermodynamically more stable stereoisomers. The opposite principle is observed in series of heterocyclic compounds with a fixed conformation (sub-

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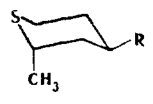
TABLE 1. Mass Spectra of 2,4-Dialkylthiacyclohexanes Ia-c and IIa-c (intensities in percent of the maximum peak)

m/e	Compound						*m/e*	Compound					
	Ia	Ib	Ic	IIa	IIb	IIc		Ia	Ib	Ic	IIa	IIb	IIc
51	4	2	10	3	2	11	110	7	4	—	6	4	—
52	4	2	3	3	<1	4	111	4	3	—	3	3	—
53	15	15	5	16	16	6	112	3	1	—	3	1	—
54	8	9	—	9	10	2	113	2	3	2	3	5	2
55	100	100	3	100	100	4	114	—	1	3	—	1	16
56	11	13	—	12	15	—	115	24	27	18	22	25	20
57	8	10	—	8	11	—	116	6	5	8	5	6	10
58	2	2	—	3	2	2	117	2	2	41	2	2	47
59	17	16	6	18	16	8	118	—	—	20	—	—	45
60	17	16	5	18	16	6	119	—	—	3	—	—	5
61	29	30	9	29	30	10	121	—	—	4	—	—	4
62	2	2	2	2	2	2	122	—	—	6	—	—	6
63	2	2	5	3	2	6	123	6	8	1	5	8	3
65	5	5	8	5	5	10	124	—	4	—	—	4	—
66	2	2	—	3	2	—	125	—	2	—	—	2	—
67	30	31	2	31	33	4	126	—	2	—	—	2	—
68	11	13	—	11	15	—	128	—	—	7	—	—	7
69	50	55	—	51	58	—	129	38	48	16	39	47	16
70	11	12	—	10	12	—	130	5	5	6	5	5	6
71	3	5	—	2	5	—	131	2	3	55	3	3	52
73	13	14	13	15	13	17	132	—	—	20	—	—	17
74	16	16	7	15	15	12	133	—	—	3	—	—	2
75	22	23	11	20	22	13	135	—	—	4	—	—	4
76	3	2	3	2	2	4	136	—	—	2	—	—	2
77	6	5	14	5	5	16	137	—	3	3	—	3	3
78	12	3	11	10	2	13	143	73	15	40	68	23	37
79	6	7	4	6	8	4	144	9	3	6	8	4	6
80	2	2	—	2	3	—	145	4	1	8	4	2	7
81	61	65	2	58	65	2	149	—	—	8	—	—	7
82	22	12	—	22	13	—	150	—	—	4	—	—	3
83	18	21	—	19	20	—	157	72	70	3	75	65	3
84	4	4	—	5	6	—	158	8	9	6	8	9	5
85	5	5	—	5	5	—	159	4	4	1	4	3	2
86	2	2	2	2	2	2	163	—	—	25	—	—	14
87	37	40	6	40	45	7	164	—	—	5	—	—	4
88	8	8	6	9	9	17	165	—	—	2	—	—	2
89	4	5	4	5	5	5	171	4	68	—	4	84	—
91	1	1	39	1	2	42	172	73	9	—	64	10	—
92	—	—	4	—	—	4	173	9	4	—	8	4	—
95	17	21	—	18	24	—	174	4	—	—	3	—	—
96	15	23	2	14	23	2	177	—	—	5	—	—	11
97	7	12	—	8	12	—	178	—	—	1	—	—	2
98	2	2	—	2	3	—	185	—	4	—	—	4	—
99	4	5	2	4	4	4	186	—	68	—	—	70	—
101	25	26	3	23	26	3	187	—	10	—	—	10	—
102	2	3	4	3	3	4	188	—	4	—	—	4	—
103	1	2	15	2	2	17	191	—	—	3	—	—	3
104	—	—	25	—	—	26	192	—	—	100	—	—	100
105	—	—	10	—	—	13	193	—	—	13	—	—	14
109	16	16	—	15	15	—	194	—	—	5	—	—	5

stituted 2-methyldecahydroquinolines [4] and 2-methyl-1-thiadecalins [5]). Since the literature does not contain information regarding the character of the stereospecificity of the fragmentation of the spatial isomers of the heterocyclic series with a conformationally labile system, we undertook a mass-spectrometric study of the cis and trans isomers of 2,4-disubstituted thiacyclohexanes Ia-c and IIa-c.

I a-c



II a-c

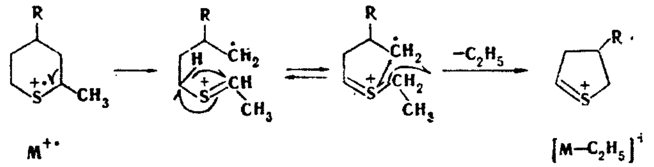
a $R=n\text{-}C_4H_9$; b $R=n\text{-}C_5H_{11}$; c $R=C_6H_5$

The mass spectra of these compounds obtained at an ionizing-electron energy of 70 eV are presented in Table 1. We will not begin to discuss the pathways of fragmentation of the investigated thiacyclohexanes under the influence of electron impact in detail, but we will deal only with those peculiarities that may be useful in the subsequent examination of the effect of the stereochemistry on the mass-spectral fragmentation. The M^+ ion peaks have high intensities in all cases, and they are the maximum peaks in the spectra of 4-phenyl-substituted derivatives Ic and IIc. In the case of thiacyclohexanes Ia,b and IIa,b, which have an alkyl group in the 4 position, the fragments due to ejection of CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, and other hydrocarbon radicals constitute a significant fraction of the total ion current. In principle, the elimination of these radicals may be realized as a result of cleavage of both the substituting alkyl groups and the ring. However, an analysis of the mass spectra shows that each specific radical is ejected from a definite part of the molecule.

It has been established [6] that monosubstituted thiacyclohexanes that contain alkyl groups in the α and γ positions eject an alkyl substituent from the molecular ions via different pathways. Ejection of the alkyl substituent as a whole is characteristic for α-alkylthiacyclohexanes, and the peak of the resulting $[M{-}alkyl]^+$ ion is the maximum peak in the spectrum. In the case of α-alkyl derivatives, in addition to elimination of an alkyl group as a whole, one observed more facile ejection of a part of the group with retention of one methylene link in the composition of the charged fragment. A similar picture is also apparent for the investigated 2,4-dialkylthiacyclohexanes Ia,b and IIa,b, which contain an alkyl residue in the γ position relative to the sulfur atom. The peaks of $[M{-}alkyl]^+$ ions (m/e 115) in their mass spectra are substantially less intense than the peaks of the homologous $[M{-}(alkyl{-}CH_2)]^+$ ions (m/e 129). Thus it may be assumed with confidence that the $[M{-}C_4H_9]^+$ and $[M{-}C_3H_7]^+$ ions in the case of Ib and IIb are formed by elimination of a 4-alkyl group or a fragment of it. In confirmation of this one may also cite the fact that the peaks of analogous ions have extremely low intensities in the spectra of 4-phenyl derivatives Ic and IIc.

The intensities of the $[M{-}CH_3]^+$ and $[M{-}C_2H_5]^+$ ion peaks in the mass spectra of Ia,b and IIa,b are close to the intensities of the M^+ ion peaks. One can state with confidence that the development of the first ion is associated with ejection of a methyl group from the 2 position, since the elimination of an alkyl substituent from the α position of the thiacyclohexane ring is an extremely favorable process that leads to the formation of a thionium ion [6]. The assumption that the ejection of a CH_3 radical may be realized due to cleavage of the terminal C—C bond in the 4-alkyl group should be rejected, since this process was not observed in the fragmentation of the previously investigated γ-alkylthiacyclohexanes [6]. The low intensities of $[M{-}CH_3]^+$ ion peaks in the spectra of Ic and IIc are associated with the fact that the benzene ring stabilizes the molecular ion and blocks its fragmentation via all the pathways.

The origin of the $[M{-}C_2H_5]^+$ ion is less obvious. One might have assumed that it arises as a result of detachment of an ethyl radical from the 4-alkyl group as a consequence of the anchimeric effect of the sulfur atom. However, in this case a C_3H_7 radical should be readily lost in the fragmentation of 4-pentyl derivatives (Ib and IIb), but this does not actually occur. In addition, the $[M{-}C_2H_5]^+$ ion peak is rather intense in the spectra of Ic and IIc, which do not contain an alkyl substituent in the 4 position. The formation of the $[M{-}C_2H_5]^+$ ion is most likely associated with a complex rearrangement process that is accompanied by ejection of the group of the C_2 atom with a methyl substituent and an additional hydrogen atom from the 6 position. The driving force of this reaction may be the formation of a five-membered thionium ion, which has high stability:



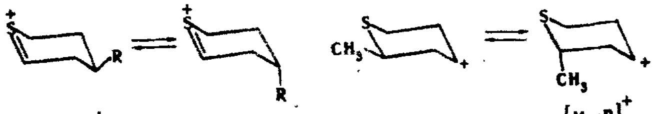
Before we turn to an examination of the stereospecificity of the fragmentation under electron impact, we must note that the cis isomers of 2,4-disubstituted thiacyclohexanes Ia-c have lower enthalpies of formation (they are thermochemically more stable) than trans isomers IIa-c, i.e., for these compounds with a 1,3 orientation of the substituents the difference in the stabilities of the spatial isomers is similar to that observed for 1,3-dialkylcyclohexanes. Under the conditions of gas chromatography cis isomers Ia-c have shorter retention times than trans isomers IIa-c.

As we have already noted above, in the case of stereoisomers that differ with respect to the orientation of the alkyl groups differences in the internal energies (ΔH) may affect the rates of reactions due to elimination of the substituting groups as a result of simple cleavage of the bonds. This is completely natural, since the source of nonbonded interactions, which determines the differences in the heats of formation of the stereoisomers, dis-

TABLE 2. Ratios of the Intensities of the Ion Peaks ($I_{[M-CH_3]^+}/I_{[M]^+}$) in the Mass Spectra of 2,4-Disubstituted Thiacyclohexanes Ia-c and IIa-c

	Compound					
	Ia	IIa	Ib	IIb	Ic	IIc
$\frac{I_{[M-CH_3]^+}}{I_{[M]^+}}$	0,99±0,02	1,18±0,02	1,00±0,02	1,20±0,03	0,05±0,01	0,11±0,01

appears in the case of ejection of an alkyl substituent from the M^+ ions; the resulting ions may have identical structures, while surplus internal energy of the less stable epimer is realized as a consequence of the more facile ejection of a substituent. In the case of the dialkylthiacyclohexanes that we investigated the elimination of any alkyl group removes the differences in the character of the nonbonded interactions, since the resulting $[M-CH_3]^+$ and $[M-R]^+$ ions for the stereoisomers may have identical structures:



$[M-CH_3]^+$ $[M-R]^+$

A comparison of the ratios of the intensities of the ion peaks [$I_{[M-CH_3]^+}/I_{M^+}$ (A) and $I_{[M-R]^+}/I_{M^+}$ (B)], which can be conveniently used in the analysis of the mass spectra of the geometrical isomers, shows that only the A values differ for the Ia-c and IIa-c stereoisomers. The absence of a difference in the B values may be associated with the fact that the ions formed for the stereoisomers have different structures or undergo fragmentation via different pathways. At the same time, the structures of the $[M-CH_3]^+$ thionium ions should be identical for the stereoisomers, and the difference in the internal energies of the latter should be manifested in the different ease of elimination of methyl groups from the 2 position. It is apparent from Table 2 that the A values are higher in the mass spectra of the thermochemically less stable trans isomers IIa-c. Thus the character of the stereospecificity of the fragmentation of the heterocyclic diastereomers with a conformationally labile system is the same as for compounds with a rigid conformation. At the same time, it differs from the stereospecificity observed in the case of conformationally labile 1,3-dialkylcyclohexanes.

It has been previously established that the ionization energies (IE) of organic compounds and the appearance energies (AE) of the characteristic ions depend on the three-dimensional structures of the molecules. However, most of the observed correlations of the IE and AE with the stereostructures have been qualitative in nature, since these values could not be measured with sufficiently high accuracy even by the photoionization method. It has been shown relatively recently by Jalonen and Pihlaja [7] and by us [1, 8] that the IE and AE can be measured with very high reproducibility with ordinary mass spectrometers with electron impact; it was emphasized repeatedly that such values, which we have termed "relative," may differ from the absolute values, but their differences are equal to the true differences in the ionization or appearance energies for identical ions formed in the fragmentation of the stereoisomers. In a continuation of our research to ascertain the possibilities of the application of the IE and AE to the solution of stereochemical problems we measured the "relative" IE (RIE) for the investigated cis (Ia,b) and trans (IIa,b) isomers of 2,4-dialkylthiacyclohexanes, as well as the "relative" AE (RAE) of $[M-CH_3]^+$ ions, the ease of elimination of which, as demonstrated above, depends on the three-dimensional structures of these compounds.

It is apparent from Table 3 that the RIE are almost 0.05 eV lower in the case of trans isomers IIa,b. Thus in this series the less stable stereoisomers have lower ionization energies than the more stable cis isomers Ia,b. A similar dependence of the RIE on the enthalpies of formation of the ground states was also noted for stereoisomeric oxathians [9] and decahydroquinolines [8]. The combination of these results makes it possible to propose that this effect of the thermochemical stability on the REI will be observed for all heterocyclic stereoisomers that contain an unshared pair of electrons on the heteroatom, due to which their primary ionization under electron impact is realized.

TABLE 3. Relative Ionization Energies and Relative Appearance Energies of $[M-CH_3]^+$ Ions (eV) for 2,4-Dialkylthiacyclohexanes Ia,b and IIa,b

	Compound			
	Ia	IIa	Ib	IIb
RIE	$7{,}63_5 \pm 0{,}003_3$	$7{,}58_0 \pm 0{,}00_5$	$7{,}75_0 \pm 0{,}00_2$	$7{,}70_5 \pm 0{,}00_5$
RAE of $[M-CH_3]^+$ ions	$10{,}28_0 \pm 0{,}003_3$	$10{,}17_7 \pm 0{,}00_4$	$10{,}34_5 \pm 0{,}00_5$	$10{,}25_0 \pm 0{,}00_3$
ΔRAE of $[M-CH_3]^+$ ions	$0{,}10_3 \pm 0{,}01$		$0{,}09_5 \pm 0{,}01$	

The appearance energies of the $[M-CH_3]^+$ ions, the formation of which, as pointed out above, is associated with ejection of a methyl group from the 2 position, also depend on the three-dimensional structures of the investigated compounds. The RAE of these ions are ∿0.1 eV lower in the case of trans isomers IIa,b, which have higher enthalpies of formation of the ground states than their cis isomers Ia,b (Table 3). The equality

$$AE[F]_I^+ - AE[F]_{II}^+ = \Delta H_f[M_{II}] - \Delta H_f[M_I],$$

which quantitatively links the difference in the AE of the $[F]^+$ fragment ions with the difference in the heats of formation of the ground states of the stereoisomers, was derived and experimentally confirmed in [7-9]. However, this equality is not valid for all of the fragment ions but only for those that have identical structures for the stereoisomers and in the formation of which neutral fragments with identical structures are eliminated. The $[M-CH_3]^+$ ions satisfy all these requirements: A CH_3 radical is eliminated during their formation for each pair of stereoisomers, and the ions themselves most likely have the thionium structure presented above. In this case the difference in the RAE of the $[M-CH_3]^+$ ions (see the ΔRAE values for $[M-CH_3]^+$ ions in Table 3) should be equal to the difference in the heats of formation of the stereoisomers, which should amount to 9.94 ± 0.96 kJ/mole for Ia and IIa and 9.17 ± 0.16 kJ/mole for Ib and IIb. Unfortunately, the differences in the ΔH_f values of these geometrical isomers have not yet been determined by other methods; however, the $\Delta\Delta H_f$ values that we obtained by means of the RAE of $[M-CH_3]^+$ ions are close to the values and have the same sign as in the case of the related dialkylcyclohexanes.

EXPERIMENTAL

The mass spectra of Ia,b and IIa,b were obtained with an LKB-2091 spectrometer with a system for introduction of the samples through a heatable cylinder (200°C) at an ionizing-electron energy of 70 eV, an emission current of 25 μA, and an ionization chamber temperature of 200°C. The mass spectra of Ic and IIc were obtained with the same apparatus and under the same conditions with gas-chromatographic analysis of a mixture of them (with a 50 m × 0.5 mm steel column, OV-17 as the stationary phase, and helium as the carrier gas). The errors in the measurement of the $I_{[M-CH_3]^+}/I_{[M]^+}$ ratios of the intensities of the ion peaks in the spectra of the stereoisomers were obtained on the basis of four to five independent experiments.

The "relative" IE and AE were obtained with the same apparatus by the method described in [1, 8]. For their measurement a sample in a mixture with a standard (benzene, IE = 9.25 eV) was introduced into the ion source of the mass spectrometer through a heatable inlet cylinder. The RIE and RAE were obtained from linear graphs of the log (I/I_{50}) dependence (I is the height of the ion peak at the low accelerating electron voltage, and I_{50} is the height of the same peak at a normalizing voltage of 50 V) with reference to the analogous graphs for the standard at the arbitrary level log $(I/I_{50}) = -2.30$. The standard errors for the RIE and RAE, which are presented in Table 3, were obtained from five to six independent measurements.

The method of synthesis and the proof of the configuration of the compounds investigated in this research will be presented separately. The individual stereoisomers, which were isolated by preparative GLC, had the following constants: (Ia) n_D^{20} 1.4810, d_4^{20} 0.9070; (Ib) n_D^{20} 1.4810, d_4^{20} 0.9018; (IIa) n_D^{20} 1.4858, d_4^{20} 0.9198; (IIb) n_D^{20} 1.4840, d_4^{20} 0.9129. Compounds Ic and IIc were analyzed in the form of a mixture; their configurations were assigned on the basis of the relative retention times during GLC.

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SYNTHESIS AND REACTIONS OF 3-AMINOTHIAZOLIDINE-2-THION-4-ONE DERIVATIVES.

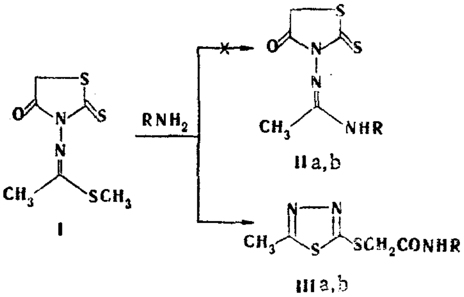
3.* REACTION OF 3-[N-(α-METHYLTHIO)ETHYLIDENE] AMINOTHIAZOLIDINE-2-THION-4-ONE WITH AMINES

E. K. Mikitenko, N. N. Romanov,
and I. S. Shpileva

UDC 547.789'794.3.07:543.422.25'51

It is shown that recyclization leading to the formation of 1,3,4-thiadiazole derivatives occurs in the reaction of 3-[N-(α-methylthio)ethylidene]aminothiazolidine-2-thion-4-one with amines. The structures of the compounds obtained were established by spectral methods and were confirmed by alternative synthesis.

Continuing our research on the reactions of 3-aminothiazolidine-2-thion-4-one derivatives [1] we have studied the reaction of 3-[N-(α-methylthio)ethylidine]aminothiazolidine-2-thion-4-one (I) with ammonia and aniline; the formation of diverse products is possible in this case, since there are three electrophilic centers in the starting compound. Since rhodanine I can be regarded as a substituted thioimino ester from which amidines are formed by the action of amines [2], in our case one might have expected the production of derivatives of the II type or their transformation products.



a R=H; b R=C$_6$H$_5$

In fact, we found from the results of elementary analysis that the methylthio group is replaced by an amine residue in the compounds obtained. The same conclusion also follows from the PMR spectra, in which singlets of C-methyl and methylene groups (2.67 and ~4.0 ppm), as well as signals of protons of amino or phenylamino groups, are observed (see the experimental section).

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*See [1] for Communication 2.

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