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MASS SPECTROMETRIC STUDY OF MONOALKYL-SUBSTITUTED THIACYCLANES

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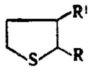
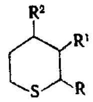
Monosubstituted α- and β-alkylthiophans and α-, β-, and γ-alkylthiacyclohexanes were subjected to a comparative mass spectrometric study. The stability of the M^+ ion increases on passing from α- to β-alkylthiophans and from α- to β- and γ-alkylthiacyclohexanes. In the case of α-alkylthiophans and α- and β-alkylthiacyclohexanes the principal process is associated with ejection of the substituent as a whole, whereas a portion of the alkyl substituent, with retention of one CH_2 group in the composition of the charged fragment, is eliminated from the molecular ions of β-alkylthiophans and γ-alkylthiacyclohexanes.

There have been several reports of the mass spectrometric study of cyclic sulfides. The mass spectra of ethylene sulfide [1], unsubstituted thiophan [2], α-alkylthiophans [3], α,α'-dialkylthiophans [4], α-alkylthiacyclohexanes [5], and some saturated two-ring and three-ring sulfides [6] have been analyzed in detail. However, in the case of alkylthiacyclanes only compounds that contain a substituent attached to the α-C atom with respect to the sulfur atom have been investigated. This orientation of the substituent determines the principal pathway of fragmentation under electron impact, which involves the ejection of an alkyl radical as a whole and the formation of an onium ion. The literature contains virtually no mass spectrometric data on β-alkylthiacyclopentanes or β- and γ-alkylthiacyclohexanes (some spectra of the lower homologs can be found in [7, 8]). However, data of this sort are necessary in the solution of structural analysis problems in the chemistry of sulfur-containing compounds of petroleum and in the chemistry of cyclic sulfides.

In the present research we made a comparative mass spectrometric study of monoalkyl-substituted thiacyclopentanes (I-X) and thiacyclohexanes (XI-XX) with substituents in different positions in the ring. The mass spectra of investigated compounds are presented in Table 1.



I-X



XI-XX

I $R=CH_3$, $R^1=H$; II $R=H$, $R^1=CH_3$; III $R=C_2H_5$, $R^1=H$; IV $R=H$, $R^1=C_2H_5$; V $R=n\text{-}C_4H_9$, $R^1=H$; VI $R=H$, $R^1=n\text{-}C_4H_9$; VII $R=n\text{-}C_6H_{13}$, $R^1=H$; VIII $R=H$, $R^1=n\text{-}C_6H_{13}$; IX $R=H$, $R^1=n\text{-}C_5H_{11}$; X $R=H$, $R^1=c\text{-}C_6H_{11}$; XI $R=CH_3$, $R^1=R^2=H$; XII $R=R^2=H$, $R^1=CH_3$; XIII $R=R^1=H$, $R^2=CH_3$; XIV $R=C_2H_5$, $R^1=R^2=H$; XV $R=R^2=H$, $R^1=C_2H_5$; XVI $R=R^1=H$, $R^2=C_2H_5$; XVII $R=R^2=H$, $R^1=C_4H_9$; XVIII $R=R^1=H$, $R^2=n\text{-}C_4H_9$; XIX $R=R^1=H$, $R^2=n\text{-}C_6H_{13}$; XX $R=R^1=H$, $R^2=c\text{-}C_6H_{11}$

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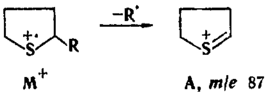
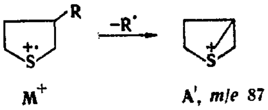
The mass spectra of the isomers in the thiophan series (I-X) are qualitatively close but differ markedly in a quantitative respect. We will not deal with the general principles of the fragmentation of these compounds under the influence of electron impact in detail, since they have already been examined in other studies; we will discuss only the quantitative differences in the spectra that can be used for identification of the isomers. One should first of all note the increase in the intensity of the molecular ion peak on passing from α- to β-alkylthiophans. In fact, the highest intensity of the M^+ ion peak in the α-alkylthiophan series is observed for the α-methyl derivative (I) ($\sim$40% of the maximum peak in the spectrum) and decreases to 10% in the case of α-hexylthiophan (VII) as the length of the alkyl chain increases. At the same time, the minimum value of the M^+ peak observed for the β isomers is observed in the spectrum of β-hexylthiophan (VIII) and amounts to >50% of the maximum peak, whereas the M^+ ion peak is the major peak in the spectrum for β-ethylthiophan (III) and β-methylthiophan (II). It is customary to assume that the fraction of current of the M^+ ions expressed in percent of the total ion current ($I_{M^+}/\Sigma I \cdot 100$) reflects the stability of the molecular ion. In this case, it is evident from Table 2 that the stabilities of the molecular ions of β-alkylthiophans are higher than the stabilities of their α-isomers.

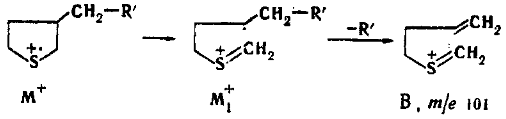
The isomeric alkylthiophans differ most markedly with respect to the character of the fragmentation of the alkyl substituent. As we have already noted above, the principal process in the fragmentation of α-alkylthiophans is ejection of the entire alkyl group from the molecular ion. The peaks of the resulting ions (A) are the maximum peaks in the spectra, while the intensities of the peaks of the remaining fragments do not, as a rule, exceed 30% of the maximum peak.



In the case of β-alkylthiophans ejection of the entire alkyl group takes place less intensively, and the principal fragmentation pathway is elimination of a portion of the alkyl substituent with retention of one CH_2 group in the composition of the charged fragment. The decrease in the intensity of the $[M - \text{alkyl}]^+$ ion peaks in the spectra of β-alkylthiophans may be associated with an increase in the distance from β-C— to the S atom, and, as a consequence of this, to the lower probability of the formation of an onium ion of the A' type:



At the same time it may be assumed that in the case of β-alkylthiophans the C—C bond adjacent to the S atom in the M^+ ion may readily undergo cleavage to give an isomeric ion (M_1^+), which is then capable of ejecting an alkyl group via the scheme



The resulting B ions are the principal ions in the spectra. Fragmentation associated with ejection of a portion of the alkyl substituent is also observed in the case of α-alkylthiophans, but the peaks of the resulting ions have low intensities (Table 2). The mass

TABLE 1. Mass Spectra of Alkylthiophans and Alkylthiacyclohexanes (intensities of the ion peaks in percent of the maximum peak)

m/e	I	II	III	IV	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX
51	1	—	—	—	—	—	—	—	2	3	—	—	—	3	—	—	—	—
53	7	8	6	15	3	10	10	17	6	12	10	—	13	12	6	12	8	12
54	2	9	2	16	2	15	14	17	7	8	12	3	14	21	6	14	8	8
55	11	34	5	64	9	47	49	60	24	32	54	19	57	97	28	87	50	66
56	5	46	—	9	—	12	14	4	3	9	11	3	9	15	13	17	8	5
57	2	7	—	—	—	8	9	—	1	23	—	4	2	3	10	9	7	—
58	6	5	2	6	—	—	2	—	4	7	—	2	3	4	2	2	—	—
59	20	27	5	21	4	10	11	8	22	28	16	7	16	18	11	14	9	8
60	19	95	3	69	3	29	31	21	26	37	38	4	22	28	10	18	11	6
61	8	14	2	31	2	13	14	8	22	41	58	5	18	5	12	37	23	13
62	1	5	—	5	—	—	2	—	2	4	—	—	—	4	—	—	—	—
65	—	—	—	—	—	—	2	6	1	2	—	—	4	4	3	—	—	6
66	—	—	—	—	—	—	1	4	—	2	—	—	3	6	—	—	—	2
67	5	10	5	35	6	22	21	68	38	45	75	20	40	75	25	46	31	46
68	6	13	—	14	3	17	14	13	3	13	13	4	9	30	10	21	17	23
69	4	15	3	51	3	37	36	10	6	47	38	6	7	33	19	50	34	13
70	—	—	—	22	—	—	6	—	1	5	14	2	12	13	3	12	8	—
71	1	—	—	7	—	—	—	—	2	5	—	3	11	3	2	—	2	—
73	3	5	2	10	2	7	6	—	6	10	11	9	9	13	5	12	7	—
74	16	48	1	14	2	6	6	—	9	12	14	6	5	14	3	11	8	—
75	—	2	—	5	—	—	—	—	13	11	—	2	3	8	2	—	—	—
76	—	3	—	—	—	—	—	—	—	—	—	—	—	2	—	—	—	—
77	—	—	—	—	—	—	—	—	—	1	—	2	—	2	1	—	—	6
79	—	—	—	—	—	—	—	19	—	1	—	2	—	—	2	—	—	12
80	—	—	—	—	—	—	—	11	—	—	—	—	—	—	—	—	—	4
81	—	—	1	7	2	29	26	67	4	6	10	4	20	34	9	34	23	37
82	—	—	2	25	—	10	9	19	12	10	18	2	6	8	5	36	22	16
83	—	—	—	10	—	13	4	13	6	2	—	3	17	23	3	11	16	31
84	—	—	—	2	—	—	—	—	—	—	—	—	2	6	—	—	3	—
85	3	3	3	10	—	10	6	13	—	3	—	—	3	3	3	—	3	5
86	—	1	—	2	—	—	3	13	—	—	—	—	1	—	1	—	2	—
87	100	31	100	54	100	60	54	79	37	14	—	9	49	16	45	36	27	41
88	5	2	5	25	11	15	13	20	6	4	—	1	5	4	4	5	4	—
89	4	—	4	4	7	—	4	13	2	—	—	2	4	3	3	—	2	—
91	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	—	—	6
93	—	—	—	—	—	—	—	13	—	—	—	—	—	—	—	—	—	7
94	—	—	—	—	—	—	—	13	—	—	—	—	—	—	—	—	—	5
95	—	—	—	—	11	26	34	22	—	—	—	—	1	6	6	41	19	16
96	—	—	—	—	—	6	9	8	—	—	—	—	4	23	2	11	5	6
97	—	—	—	—	—	—	5	3	—	—	—	—	—	5	—	8	5	4
98	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1	6	—	—
99	—	—	—	—	—	5	—	6	—	1	—	—	—	4	3	3	5	10
100	—	—	—	—	—	—	—	6	—	—	—	—	—	—	—	—	37	15
101	4	10	2	61	22	100	100	20	100	100	96	100	100	56	100	45	10	20
102	42	100	—	6	2	14	11	—	6	7	6	8	8	16	7	11	3	13
103	3	7	—	4	1	6	6	—	5	4	4	6	5	3	5	4	—	—
104	2	5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
107	—	—	—	—	—	—	—	—	—	—	—	3	—	—	—	—	—	—
108	—	—	—	—	—	—	—	—	—	—	—	3	—	—	—	—	—	—
109	—	—	—	—	—	19	—	—	—	—	—	2	—	—	—	2	8	—
110	—	—	—	—	—	6	—	13	—	—	—	—	—	—	—	—	3	—
111	—	—	—	—	—	3	—	—	—	—	—	—	—	—	3	—	—	—
113	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	—	—	20
114	—	—	—	—	—	—	—	40	—	—	—	—	—	—	—	—	—	8
115	—	—	1	6	12	35	25	10	3	3	8	3	9	100	8	100	100	12
116	—	—	22	100	—	4	—	—	55	76	100	—	1	8	1	9	9	—
117	—	—	2	7	—	2	—	11	4	6	7	—	—	5	—	5	5	—
118	—	—	1	5	—	—	—	10	3	3	4	—	—	—	—	—	—	—
120	—	—	—	—	—	—	—	8	—	—	—	—	—	—	—	—	—	—
121	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	8
122	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	—	—	6
123	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	7	6
124	—	—	—	—	—	—	4	—	—	—	—	—	—	—	—	—	3	11
127	—	—	—	—	—	—	—	73	—	—	—	—	—	—	—	—	—	6
128	—	—	—	—	—	—	—	17	—	—	—	—	—	—	—	—	—	7
129	—	—	—	—	12	8	7	6	—	—	—	—	—	22	4	80	15	6
130	—	—	—	—	1	—	—	—	—	—	—	20	43	94	—	—	2	—
131	—	—	—	—	—	—	—	—	—	—	—	—	8	8	—	—	—	—
132	—	—	—	—	—	—	—	—	—	—	—	—	2	5	—	—	—	—
135	—	—	—	—	—	—	—	5	—	—	—	—	—	—	—	—	—	4
136	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	—	—	4
137	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	5
141	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	—	—	29
142	—	—	—	—	—	—	—	9	—	—	—	—	—	—	—	—	—	5
143	—	—	—	—	1	4	3	—	—	—	—	—	—	—	4	32	4	2
155	—	—	—	—	—	—	—	9	—	—	—	—	—	—	—	—	—	10

TABLE 1 (Continued)

m/e	I	II	III	IV	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX
156	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	14
157	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	6	2
158	—	—	—	—	—	—	56	—	—	—	—	—	—	—	30	86	2	—
159	—	—	—	—	—	—	—	—	—	—	—	—	—	—	4	—	—	—
169	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	11
170	—	—	—	—	—	2	—	100	—	—	—	—	—	—	—	—	—	4
171	—	—	—	—	—	3	—	13	—	—	—	—	—	—	—	—	18	—
172	—	—	—	—	16	52	—	6	—	—	—	—	—	—	—	—	5	—
173	—	—	—	—	2	6	—	—	—	—	—	—	—	—	—	—	—	—
174	—	—	—	—	—	3	—	—	—	—	—	—	—	—	—	—	—	—
183	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	47
184	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	100
185	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	6	16
186	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	54	6
187	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	7	—

TABLE 2. Fractions of the M^+ Ion Current in the Total Ion Current and Intensities of the Peaks of the A, A', and B Fragments in Percent of the Maximum for I-IX.

Compound	I	II	III	IV	V	VI	VII	VIII	IX
Substituent	CH_3		C_2H_5		n-C_4H_9		n-C_6H_{13}		β-C_5H_{11}
	α	β	α	β	α	β	α	β	
$I_{M^+}/\Sigma I$ (%)	13,3	19,8	9,7	10,0	7,7	10,1	5,6	7,7	9,0
Ions A or A'	100	32	100	54	100	64	100	60	54
Ions B	—	—	2	62	25	100	13	100	100

TABLE 3. Fractions of the M^+ Ion Current in the Total Ion Current and Intensities of the Peaks of the C and D Fragments in Percent of the Maximum for XI-XIX

Compound	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
Substituent	CH_3			C_2H_5			n-C_4H_9		γ-C_6H_{13}
	α	β	γ	α	β	γ	β	γ	
$I_{M^+}/\Sigma I$ (%)	12,4	13,5	15,0	2,6	6,3	9,0	7,0	9,3	8,0
Ions C	100	100	96	100	100	56	100	45	37
Ions D	—	—	—	4	9	100	8	100	100

spectra of α- (V) and β-butylthiophan (VI), which graphically show the differences in the character of the fragmentation of isomeric alkylthiophans under the influence of electron impact, are presented in Fig. 1.

The M^+ ion peak is the maximum peak in the mass spectrum of β-cyclohexylthiophan (X). Although ejection of a cyclohexyl group from the M^+ ion takes place quite intensively, the intensity of the corresponding peak does not exceed 80%. Relatively intense peaks with m/e 114 and 127 are formed by ejection of C_4H_8 and C_3H_7 particles, most likely through fragmentation of the naphthene ring.

It should be noted that the peaks of fragments that are formed as a result of successive cleavage of the molecular ions, which bypasses the step involving the formation of $[M - \text{alkyl}]^+$ ions, increase, along with an increase in the intensity of the M^+ peak, in the spectra of β-alkylthiophans as compared with the spectra of their α-isomers.

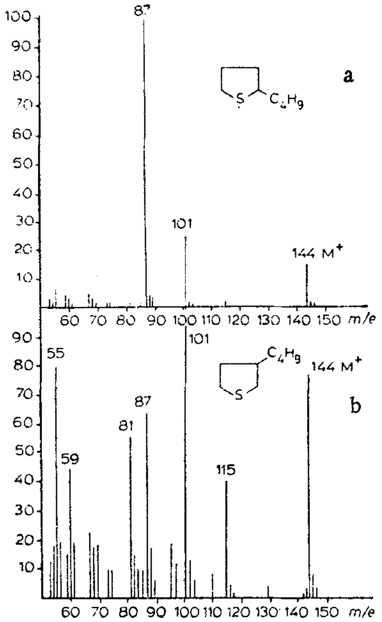
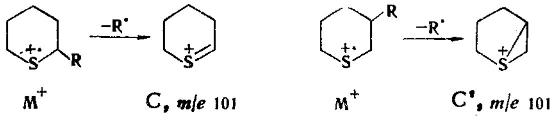


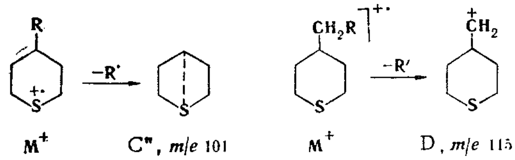
Fig. 1. Mass spectra: a) α-n-butylthiophan (V); b) β-n-butylthiophan (VI).

In the alkylthiacyclohexane series the intensity of the M^+ ion peak increases as the distance between the substituent and the heteroatom increases. Thus in the case of methylthiacyclohexanes (XI-XIII) on passing from the α to the β and γ isomers the intensity of M^+ (in percent of the maximum peak in the spectrum) is 55, 75, and 100%, respectively, as compared with 20, 43, and 94%, respectively, for ethylthiacyclohexanes (XIV-XVI). The stabilities of the molecular ions ($I_{M^+}/\Sigma I$) also increase in the indicated order (Table 3).

With respect to the fragmentation of the alkyl substituent, in the case of α- and β-alkylthiacyclohexanes it is primarily eliminated in its entirety, and the peaks of the corresponding ions (C and C') are the maximum peaks in the spectra (Table 3). This fragmentation pathway is characteristic for derivatives with both a relatively short alkyl chain (XIV and XV, R = C_2H_5) and a longer chain (XVII, R = C_4H_9).



γ-Alkylthiacyclohexanes remind one of β-alkylthiophans with respect to the character of the fragmentation of the alkyl group. In fact, a portion of the substituent is most easily ejected from the molecular ion in this case with retention of one of its CH_2 groups in the composition of the charged fragment. The peaks of the resulting ions (D) are the maximum peaks in the spectra, whereas the peaks of the [M – Alkyl]$^+$ ions (C") are less intense (Table 3):



We proposed a more or less rational mechanism above for the formation of ion B from β-alkylthiophans. If it is assumed that ion D is formed from γ-alkylthiacyclohexanes as a result of primary ionization of the molecule at the S atom, it is difficult to imagine a similar mechanism for this ion. The possibility therefore cannot be excluded that the different behavior of the alkyl substituents in the case of α-alkylthiophans and α- and β-alkylthiacyclohexanes, on the one hand, and β-alkylthiophans and γ-alkylthiacyclohexanes, on the other, may be due to the distance between the S atom and the C atom, adjacent to which cleavage occurs, and to the flexibility of the cyclic system. In fact, in the case of the markedly compressed thiacyclopentane ring only a portion of the β-alkyl substituent is primarily ejected, whereas the entire β-alkyl substituent is eliminated in the case of the more flexible thiacyclohexane system, and partial ejection is observed only for the γ-alkyl group. An examination of Dreiding models of alkylthiacyclopentanes and thiacyclohexanes showed that for all the compounds the distance between the S atom and the primary atom of the alkyl substituent is greater than the distance between the S atom and the ring C atom to which this substituent is attached. These distances are close only for the boat conformation in γ-alkylthiacyclohexanes and can be compared in the case of substantial ring deformation. Thus the distance factor only decreases the probability of the formation of A' and C" ions; the driving force of the competitive processes that lead to B or D ions is completely unclear.

The molecular ion peak is the principal peak in the mass spectra of γ-cyclohexylthiacyclohexane (XX), and ejection of a cyclohexyl group from M^+ is minimal (the intensity of the corresponding peak is on the order of 20% of the M^+ peak). Low-intensity peaks of fragments formed in the fragmentation of the cyclohexyl ring are also present in the spectrum (elimination from the M^+ ion of CH_3, C_2H_4, C_3H_7, C_4H_8, C_4H_9, and C_5H_{11}); $[M - CH_3]^+$ and $[M - C_2H_4]^{+\cdot}$ ions may also be formed in the cleavage of the thiacyclohexane ring.

EXPERIMENTAL

The mass spectra were obtained with an LKB-2091 mass spectrometer with a heatable inlet system (200°C) at an ionizing-electron energy of 70 eV, an emission current of 25 μA, and an ion source temperature of 200°C.

The alkylthiophans and alkylthiacyclohexanes were obtained by the method in [9] and were purified by preparative gas—liquid chromatography.

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