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50 EV MASS SPECTRA OF 1- AND 3-*n*-ALKYL-SUBSTITUTED CYCLOPENT-1-ENES

In literature there are few mass spectral data available for hydrocarbons of the cyclopentene series.

Praet [1] has investigated the fragmentation of 1-methylcyclopentene, methylenecyclopentane and other isomeric to them C_6H_{10} unsaturated hydrocarbons at various energies of bombarding electrons. The API catalog [2] and other compilations [3, 4] include mass spectra of 1-, 3-, 4-methyl- and 1- and 3-ethylcyclopentenes. The base peak in their spectra corresponds to an ion $(C_5H_7)^+$ formed by the elimination of the methyl or ethyl group from the molecular ion. Since the mass spectra of isomeric methyl- and ethylcyclopentenes are very similar, the common degradation paths of molecular ions, supposed to undergo double bond isomerization via hydrogen rearrangements before fragmentation, may be assumed, analogically to positional isomers of many other olefins [5–8].

The fragmentation regularities observed for methyl- and ethylcyclopentenes only, are inadequate for elucidating principal fragmentation paths and identifying possibilities of higher isomeric homologs in this series. The fundamental data for solving these problems — mass spectra of higher cyclopentenes — have not been described so far. As they are of considerable theoretical and practical interest, we have recorded mass spectra of various monosubstituted cyclopentenes at various energies of bombarding electrons and investigated the effect of the side chain length, structure and position on the fragmentation process. In this report, the regularities found in 50 eV mass spectra of 1- and 3-*n*-alkylcyclopentenes C_6—C_{12} with the position and length of the *n*-alkyl group in a side chain, are presented. This work was carried out as a part of the program of a systematic investigation of the physico-chemical properties of unsaturated hydrocarbons. The mass spectra obtained can be used for the identification of individual compounds when analysing complex olefinic mixtures by chromato-mass-spectrometry.

Experimental

The compounds investigated were *n*-alkylcyclopentanes, 1- and 3-*n*-alkylcyclopent-1-enes with methyl . . . *n*-hexyl group in a side chain and 1-*n*-heptylcyclopentene-1-ene.

1-*n*-alkylcyclopent-1-enes were prepared by dehydration with iodine of the corresponding 1-*n*-alkylcyclopentan-1-ols, obtained by the Grignard reaction on cyclopentanone [9, 10].

3-*n*-alkylcyclopent-1-enes were prepared by interaction of corresponding Grignard reagents with 3-chlorocyclopent-1-ene [11].

n-Alkylcyclopentanes were obtained by hydrogenation of *n*-alkylcyclopentenes.

The synthesized hydrocarbons were purified by rectification and preparative gas chromatography on 1, 2, 3-tris-(2-cyanoethoxy)-propane or apiezon *L* [12]. Their purity, determined on capillary columns (45—80 m; 0.25 mm) coated with squalane, apiezon *L* or polyethylene glycol 4000, varied within the limits of 97.4—99.9 per cent.

The mass spectra were run on a modified [13, 14] MH-1303 mass spectrometer with an oscillographic recorder. The electron beam energy was 50 eV, ion accelerating voltage 2.2 kV, emission current 0.75 mA, temperature in the inlet reservoir and ion source — 200° C. For every compound at least 3 mass spectra were recorded. Parallel spectra showed differences within the limits of 1—2.5 per cent (relative). The differences in the spectra taken through longer time intervals were on an average 5—10 per cent (rel.). MINSK 22 or 23 computer was used to calculate and tabulate the mass-spectral data. The relative peak intensities were calculated as a percentage of the base peak (B) and of the total ion intensities (Σ) in the mass range from 12 mass units (m. u.) up to two m. u. higher of the molecular ion peak ($M+2$). Stability of the molecular ion (W_m) was calculated from the formula:

$W_m = \frac{I_{mol}}{I_{mol} + \Sigma I_{frag}}$, where I_{mol} — total intensity of the molecular ion, included its isotopic ^{13}C ion [15],

ΣI_{frag} — sum of peak heights of all fragment ions.

In addition, total intensities of homologous series of ions $(C_nH_{2n+1})^+$, $(C_nH_{2n})^+$, $(C_nH_{2n-1})^+$, $(C_nH_{2n-2})^+$ and $(C_nH_{2n-3})^+$ — Σ43, Σ42, Σ41, Σ68 and Σ67 and total intensities of ions with the same number of carbon atoms — ΣC_1, ΣC_2, etc., were calculated. From published data available for some compounds, the same characteristics were calculated, too. The latter coincided well with our experimental data. The peak intensities in the text, if not indicated otherwise, are expressed in per cent of the total ion intensities.

Results and discussion

Mass spectra obtained are given in Tables 1—3. Peaks with intensities less than 1 per cent (in B) are omitted.

Mass spectra of *n*-alkylcyclopentenes reveal great differences in fragment ion distribution and in molecular ion intensity, as compared to those of *n*-alkylcyclopentanes with an identical side chain.

Due to the stabilizing effect of double bond π-electrons, the W_m values of 1-*n*-alkylcyclopentenes are on an average three times higher than those of *n*-alkylcyclopentanes with an identical side chain (Fig. 1).

1- and 3-methyl- as well as 1- and 3-ethylcyclopentenes have close W_m values, but there are certain differences between the W_m values of higher 1- and 3-*n*-alkylcyclopentenes, showing higher stability (up to 1.5 times) of 1-*n*-alkylcyclopentene molecular ions.

In accordance with the general rule, the relative abundances of molecular peaks decrease with the lengthening of *n*-alkyl side chain

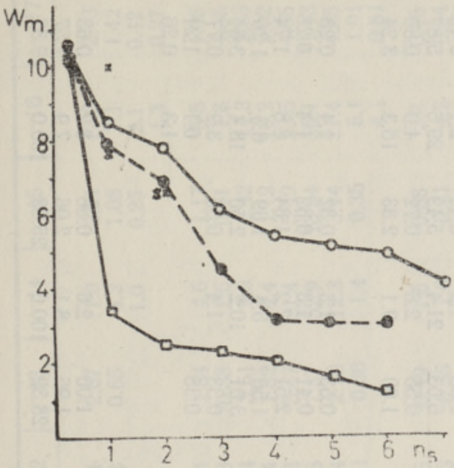

Fig. 1. Stability W_m of *n*-alkylcyclopentenes and -pentanes upon electron impact at 50 eV.
n_s — number of carbon atoms in a side chain, ○ — 1-*n*-alkylcyclopent-1-enes, ● — 3-*n*-alkylcyclopent-1-enes, ⊕ — cyclopentene, □ — *n*-alkylcyclopentanes, ⊞ — cyclopentane, +, * — literature data for 1- and 3-alkylcyclopentenes.

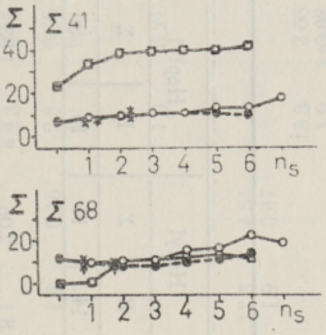

Fig. 2. Dependences of Σ41 and Σ68 on the number of carbon atoms in a side chain n_s.
Designation as in Fig. 1.

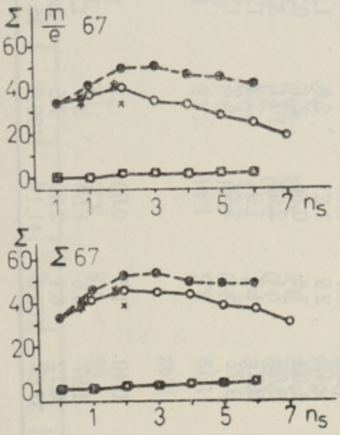

Fig. 3. Dependence of the intensity of the peak with m/e 67 and of Σ67 on the number of carbon atoms in a side chain n_s.
Designation as in Fig. 1.

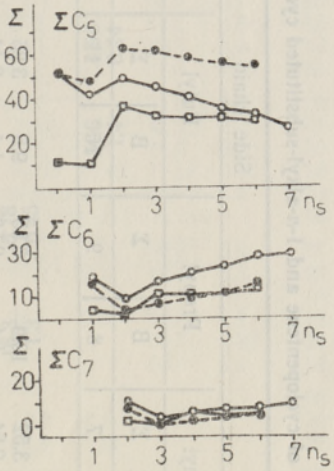

Fig. 4. Dependences of ΣC_5, ΣC_6 and ΣC_7 on the number of carbon atoms in a side chain n_s.
Designation as in Fig 1.

$C_1 \ldots C_6$ from 3 to 1 and from 8 to 3 per cent for *n*-alkylcyclopentanes and -pentenes, respectively (Fig. 1).

More intensive peaks in the mass spectra of *n*-alkylcyclopentanes with two to six carbon atoms in a side chain correspond to ions $(C_nH_{2n-1})^+$ with m/e 41, 55, 69, etc. The sums of their intensities — Σ41 make about 40 per cent (Fig. 2), and exceed four times those of 1- and 3-*n*-alkylcyclopentenes with the same n_s* (10—13%). The intensities of base peaks — m/e 41 and 69 vary in the limits of 10—15 per

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* n_s — number of carbon atoms in a side chain.

Table 1

Mass spectra of cyclopentene and 1-n-alkyl-substituted cyclopentenes

m/e	Cyclopentene		Side chain														
			Methyl		Ethyl		Propyl		Butyl		Pentyl		Hexyl		Heptyl	
	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
26	2.4	0.83	1.4	0.52												
27	12.5	4.28	12.8	4.82	8.6	3.52	10.9	3.85	9.5	3.25	8.9	2.53	8.1	2.06	8.2	1.63
28	3.9	1.33	2.0	0.76	1.6	0.64	1.4	0.50	1.4	0.44	4.8	1.35	3.9	1.00		
29	1.0	0.35	2.0	0.76	3.4	1.38	3.5	1.23	5.1	1.73	8.9	2.53	8.2	2.10	10.2	2.03
31	1.3	0.46														
37	2.3	0.77														
38	6.4	2.19	1.7	0.64	1.1	0.46										
39	34.8	11.93	22.1	8.33	14.0	5.74	14.0	4.95	11.3	3.85	9.9	2.81	7.5	1.93	9.2	1.82
40	15.0	5.14	3.5	1.31	2.7	1.12	2.6	0.92	2.1	0.70	1.9	0.55	1.9	0.49	2.1	0.42
41	17.9	6.15	19.8	7.45	14.0	5.74	21.7	7.70	21.5	7.35	21.3	6.03	21.4	5.49	29.6	5.87
42	7.5	2.57	2.2	0.84	1.2	0.50	1.5	0.52	1.3	0.46	1.9	0.55	2.8	0.72	4.0	0.80
43			1.6	0.60			1.3	0.45	1.7	0.56	3.5	1.00	9.1	2.33	16.3	3.24
50	1.7	0.60	3.3	1.23	1.1	0.46										
51	2.6	0.89	5.6	2.12	2.9	1.21	2.9	1.04	1.7	0.56	1.9	0.53	1.3	0.32	1.4	0.28
52	1.2	0.42	2.7	1.03	1.6	0.66	2.1	0.75	1.2	0.42	1.4	0.41	1.3	0.32	1.4	0.28
53	21.1	7.23	9.6	3.63	7.1	2.92	10.1	3.58	8.4	2.86	8.8	2.51	7.2	1.84	8.8	1.74
54	1.0	0.34	6.0	2.27	4.7	1.91	3.2	1.14	4.4	1.51	5.3	1.50	5.4	1.39	6.3	1.26
55			2.4	0.92	8.1	3.32	4.3	1.52	6.4	2.17	10.6	3.01	10.2	2.60	18.4	3.64
56											1.1	0.33	1.4	0.35	3.9	0.77
57											1.3	0.38			6.1	1.21
58															1.3	0.26
62	1.6	0.54														
63	2.3	0.80	1.1	0.40	1.5	0.60										
65	6.1	2.09	5.2	1.97	3.6	1.50	3.7	1.33	3.6	1.23	3.5	1.00	2.6	0.66	3.2	0.63
66	5.3	1.81	1.9	0.72	6.1	2.52	7.5	2.66	6.1	2.07	6.9	1.96	8.1	2.06	7.9	1.57
67	100,0	34.28	100.0	37.67	100.0	41.11	100.0	35.46	100.0	34.13	100.0	28.32	100.0	25.63	100.0	19.82

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
68	34.8	11.93	4.4	1.66	7.8	3.22	11.0	3.89	8.1	2.76	9.4	2.67	11.0	2.91	12.2	2.43
69	1.6	0.57					2.9	1.04	1.1	0.39	2.3	0.65	4.2	1.08	7.1	1.42
70													1.0	0.25	2.1	0.42
71			1.1	0.42											1.3	0.27
77			3.2	1.19	3.5	1.44	4.5	1.61	4.75	1.62	5.4	1.54	4.6	1.17	5.5	1.08
78					1.0	0.41	1.1	0.37	1.0	0.34	1.3	0.38	1.6	0.41	1.8	4.35
79			7.2	2.72	5.1	2.11	10.9	3.85	11.3	3.85	12.4	3.51	9.5	2.42	14.3	2.83
80			1.4	0.52	1.0	0.40	2.1	0.75	2.6	0.88	6.4	1.82	4.4	1.12	10.2	2.02
81			11.6	4.38	8.8	3.62	20.2	7.15	15.0	5.13	19.3	5.47	21.4	5.49	23.5	4.65
82			22.1	8.33			4.5	1.61	21.3	7.28	27.8	7.87	52.9	13.54	56.1	11.13
83			1.4	0.52					2.5	0.85	7.4	2.10	12.3	3.14	21.4	4.25
84											1.1	0.30	1.4	0.35	5.1	1.01
85															4.1	0.81
91					1.0	0.41	1.3	0.45	1.3	0.43	1.6	0.49	1.5	0.38	2.3	0.45
93									1.2	0.42	2.3	0.65	1.6	0.41	4.2	0.84
94													1.6	0.42	2.6	0.52
95					3.6	1.47	5.9	2.09	13.0	4.44	15.9	4.49	21.1	5.64	27.6	5.46
96					18.0	7.41			1.4	0.49	3.4	0.95	4.2	1.08	6.3	1.26
97					1.3	0.53					1.8	0.50			6.5	1.29
98															2.5	0.49
109							1.0	0.35			1.6	0.45	3.2	0.81	4.2	0.84
110							16.3	5.78					1.9	0.48	2.8	0.56
111							1.3	0.45							2.3	0.45
123													1.8	0.46	2.8	0.56
124									14.6	4.98					1.1	0.21
125									1.4	0.44						
136											1.0	0.28				
137											1.3	0.37			1.0	0.21
138											16.3	4.63				
139											2.1	0.58				
152													17.6	4.51		
153													1.9	0.47		
166															18.3	3.63
167															1.9	0.38

Table 2

Mass spectra of 3-*n*-alkyl-substituted cyclopentenes

m/e	Side chain											
	Methyl		Ethyl		Propyl		Butyl		Pentyl		Hexyl	
	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ
26	1.2	0.53										
27	10.3	4.39	6.2	3.18	6.0	3.06	5.9	2.78	4.5	2.07	3.7	1.60
28	1.2	0.51					2.9	1.36	2.4	1.11	2.5	1.10
29	1.8	0.76	2.4	1.24	1.7	0.86	3.5	1.66	3.9	1.79	5.2	2.27
38	1.7	0.73	1.0	0.50								
39	20.6	8.79	10.9	5.54	9.8	5.01	9.4	4.44	4.8	2.23	4.6	2.02
40	3.3	1.39	2.1	1.07	1.9	0.96	1.8	0.85	1.3	0.58	1.0	0.43
41	18.9	8.06	13.3	6.77	16.3	8.35	17.3	8.21	14.3	6.64	11.9	5.19
42	1.7	0.73			1.0	0.53	1.0	0.48	1.6	0.74	1.1	0.48
43									3.2	1.47	4.1	1.77
50	2.3	1.00										
51	4.1	1.77	1.8	0.91	1.6	0.83	1.2	0.58				
52	1.9	0.80			1.0	0.51						
53	6.8	2.90	3.4	1.73	3.7	1.92	3.0	1.44	2.8	1.32	2.5	1.10
54	4.4	1.89	2.9	1.46	1.9	0.96	2.0	0.93	1.8	0.84	1.6	0.71
55	1.6	0.70	3.6	1.84	1.7	0.96	2.9	1.36	4.5	2.06	3.3	1.43
63	1.0	0.43	1.2	0.61								
65	5.3	2.27	4.0	2.02	3.7	1.92	4.6	2.16	2.8	1.32	2.7	1.18
66	1.9	0.83	6.4	3.27	7.6	3.90	10.3	4.87	10.2	4.72	11.9	5.19
67	100.0	42.71	100.0	50.90	100.0	51.24	100.0	47.39	100.0	46.30	100.0	43.64
68	4.4	1.89	5.9	2.98	7.1	3.62	7.1	3.36	6.7	3.10	7.6	3.30
69					1.2	0.61			1.1	0.50	1.8	0.77
77	2.2	0.90	1.7	0.88	1.9	0.99	2.0	0.96	2.2	1.00	2.3	1.01
79	3.8	1.64	1.9	0.96	3.4	1.73	3.4	1.62	3.8	1.77	5.4	2.36
80									2.5	1.16	3.7	1.60
81	9.2	3.92	3.6	1.83	4.9	2.50	3.8	1.78	3.1	1.43	5.2	2.27
82	18.0	7.69			1.6	0.81	9.3	4.38	10.5	4.87	14.6	6.37
83	1.2	0.50					1.1	0.53	3.0	1.37	3.5	1.52
93											1.0	0.46
95			1.2	0.61	1.3	0.66	2.7	1.28	3.8	1.74	5.4	2.36
96			12.7	6.45					1.7	0.79	2.5	1.10
109											1.0	0.46
110					8.15	4.17					1.0	0.43
124							6.1	2.88				
138									6.1	2.80		
152											6.4	2.78

cent. The total intensity of ions $(C_nH_{2n})^+$ accompanying the above-mentioned ions is 20 per cent.

The most abundant peaks in the mass spectra of *n*-alkylcyclopentenes correspond to the ions $(C_nH_{2n-3})^+$ with m/e 67, 81, etc. The sums of their intensities — Σ67 decrease slightly with the lengthening of the side chain $C_3 \ldots C_6$ from 45 to 38 per cent in 1-*n*-alkyl- and from 55 to 49 per cent in 3-*n*-alkylcyclopentene series, being higher for the latter by about 10 per cent (abs., Fig. 3). *n*-Alkylcyclopentanes have small Σ67 values that increase up to 4 per cent for *n*-hexylcyclopentane. Two other homologous series of more abundant ions in *n*-alkylcyclopentene spectra are $(C_nH_{2n-1})^+$ and $(C_nH_{2n-2})^+$ with total intensities 10—13 (Σ41) and 9—22 per cent (Σ68), as seen from Fig. 2.

From 1-*n*-alkylcyclopentenes with $n_s=4-6$ the "pseudomolecular" ions $(C_nH_{2n-2})^+$ are formed in slightly higher quantities ($\Sigma68=15$—20%) as compared to 3-*n*-alkylcyclopentenes (11—14%). *n*-Alkylcyclopentanes reveal close Σ68 values with 3-*n*-alkylcyclopentenes (Fig. 2).

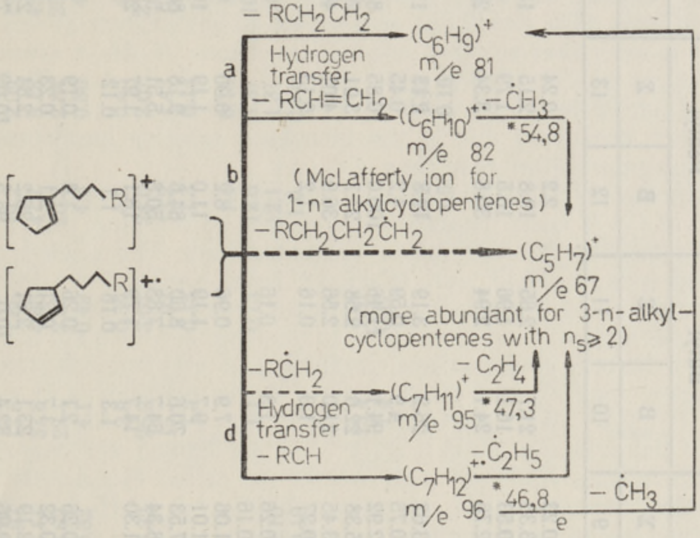

Fig. 5. Possible principal degradation reactions of *n*-alkylcyclopentenes ($n_s \geqslant 3$) upon electron impact, resulting in principal fragment ions $(C_5H_7)^+$ and ions $(C_6H_9)^+$. Metastable ions, observed for most compounds, are given in figure. Dotted line — metastable ions absent.

m_a: 59.7 (110 $\xrightarrow{-29}$ 81, 3-*n*-propylcyclopentene);
m_b: 61.1 (110 $\xrightarrow{-28}$ 82, 3-*n*-propylcyclopentene);
m_d: 74.3 (124 $\xrightarrow{-28}$ 96, 3-*n*-butylcyclopentene);
60.6 (152 $\xrightarrow{-56}$ 96, *n*-hexylcyclopentenes);
m_e: 68.3 (96 $\xrightarrow{-15}$ 81, 1-*n*-heptylcyclopentene);
m_a, m_b, m_d, m_e — metastable ions, observed for reaction a, b, d, e, R=H, CH_3, C_2H_5, C_3H_7, C_4H_9.

In mass spectra of *n*-alkylcyclopentenes alkyl ions present in small quantities and Σ43 are less than 1 per cent for lower homologs. Lengthening of the side chain $C_4 \ldots C_6$ increases the abundance of alkyl ions in the mass spectra of cyclopentenes from 1 to 2—3 per cent.

High intensity of the base peak m/e 67 (20—50%) points to the more selective fragmentation process of *n*-alkylcyclopentenes upon electron impact, as compared to *n*-alkylcyclopentanes.

In general, the mass spectra of higher 1- and 3-*n*-alkylcyclopentenes are very similar. For this reason, equally to isomeric methyl- and ethylcyclopentenes, the similar principal fragmentation paths of their molecular ions undergoing double bond isomerization before fragmentation, are to be cosidered, too.

Table 3

Mass spectra of cyclopentane and *n*-alkyl-substituted cyclopentanes

m/e	Cyclopentane		Side chain											
			Methyl		Ethyl		Propyl		Butyl		Pentyl		Hexyl	
	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ	B	Σ
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
26	1.4	0.59					1.7	0.23			2.2	0.24	1.1	0.13
27	10.5	4.31	11.3	3.68	23.0	3.55	24.5	3.36	21.7	2.65	19.8	2.15	18.3	2.24
28	7.6	3.14	4.9	1.59	18.2	2.80	3.9	0.53	16.1	1.96	16.5	1.79	4.0	0.49
29	4.1	1.71	7.8	2.54	18.8	2.89	20.1	2.76	24.1	2.94	30.8	3.34	28.3	3.46
38	1.2	0.51												
39	15.7	6.48	17.0	5.52	28.5	4.39	26.3	3.62	26.2	3.19	19.8	2.15	17.2	2.11
40	5.7	2.33	3.7	1.19	5.6	0.86	5.4	0.75	4.9	0.59	4.2	0.45	3.8	0.46
41	25.7	10.58	56.5	18.34	86.4	13.33	94.1	12.92	94.1	11.46	100.0	10.85	85.0	10.38
42	100.0	41.21	19.1	6.21	47.5	7.32	39.2	5.38	22.0	2.68	27.7	3.01	20.1	2.46
43	2.0	0.81	7.8	2.53	8.5	1.31	25.1	3.45	21.0	2.56	36.9	4.01	41.7	5.09
44					1.8	0.28	2.0	0.27	1.3	0.16	1.2	0.13	1.2	0.15
51			1.2	0.40			1.9	0.26	1.3	0.16				
52					1.0	0.16	1.2	0.16						
53	1.6	0.65	3.0	0.96	7.7	1.19	7.7	1.06	7.9	0.96	8.2	0.90	7.3	0.91
54	1.0	0.42	2.5	0.81	6.9	1.06	7.4	1.01	9.7	1.19	11.0	1.19	10.9	1.33
55	31.5	12.96	19.1	6.21	55.9	8.62	54.9	7.53	70.6	8.60	84.6	9.18	80.0	9.77
56	1.2	0.48	100.0	32.44	47.5	7.32	60.8	8.34	64.7	7.88	50.8	5.51	51.7	6.31
57			3.2	1.03	7.9	1.21	9.5	1.30	14.7	1.79	18.1	1.97	20.0	2.44
58									1.3	0.16	1.1	0.12		
65					1.7	0.26	1.9	0.26	2.1	0.26	1.8	0.19	1.5	0.18
66					1.4	0.21	2.3	0.32	1.7	0.21	2.1	0.23	1.6	0.19
67	1.4	0.59	1.9	0.61	12.1	1.87	15.9	2.19	23.1	2.81	26.2	2.84	21.8	2.67
68			2.6	0.86	67.8	10.45	72.5	9.96	82.4	10.0	98.5	10.69	75.0	9.16
69	1.0	0.40	27.6	8.96	100.0	15.42	100.0	13.72	100.0	12.18	100.0	10.85	100.0	12.21
70	24.0	9.89	1.4	0.44	56.9	8.77	39.2	5.38	45.1	5.49	50.8	5.51	36.7	4.48
71	1.1	0.45			2.6	0.40	4.2	0.58	6.0	0.73	7.7	0.84	6.9	0.84
77							1.2	0.16	1.3	0.16	1.1	0.12		
79							1.3	0.17	1.6	0.20	1.7	0.19	1.4	0.17

Tabel 3

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
81							1.5	0.21	2.0	0.25	2.8	0.31	8.0	0.98
82							9.3	1.27	13.6	1.66	19.2	2.09	19.0	2.31
83					7.9	1.21	37.3	5.11	37.8	4.60	47.7	5.18	43.3	5.29
84			9.9	3.22			26.3	3.62	23.1	2.81	26.2	2.84	25.0	3.05
85							2.3	0.32	4.1	0.49	4.6	0.50	4.7	0.57
96									2.9	0.36	4.2	0.45	4.2	0.52
97							2.4	0.32	25.2	3.07	24.6	2.67	21.7	2.65
98					15.1	2.33			15.7	1.92	13.2	1.43	10.3	1.26
99									1.2	0.15	1.3	0.14		
110											1.4	0.15	1.4	0.17
111									1.1	0.13	12.6	1.37	10.3	1.26
112							15.3	2.10			12.1	1.31	4.5	0.55
113							1.4	0.19			1.0	0.11		
125													4.5	0.55
126									15.4	1.87			6.3	0.77
127									1.4	0.17				
140											13.2	1.43		
141											1.5	0.16		
154													8.6	1.05

There appear some differences in fragment ion intensity distribution between 1- and 3-*n*-alkylcyclopentenes with three and more carbon atoms in a side chain. The main fragmentation path in both cases is the elimination of the *n*-alkyl group from the molecular ion, but the degradation of 1-*n*-alkylcyclopentenes results in lower quantities (about 1.5 times) of ions $(C_5H_7)^+$ as well as ions with five carbon atoms (ΣC_5), and in higher quantities of ions with six (ΣC_6) and seven (ΣC_7) carbon atoms (Fig. 4). In Fig. 3 it is seen that relative intensities of ions $(C_5H_7)^+$ diminish with the lengthening of the *n*-alkyl side chain $C_3 \ldots C_6$ in 1-*n*-alkylcyclopentene series from 36 to 26 per cent, in 3-*n*-alkylcyclopentene series from 51 to 44 per cent, obviously due to the increased relative importance of the side chain fragmentation reactions.

As the formation of the principal fragment ions $(C_5H_7)^+$ proceeds with the rupture of C—C bond located in β-position to the ring double bond in 3-alkylcyclopentenes, it is obviously promoted here. The slightly favoured formation of ions $(C_6H_9)^+$ and $(C_6H_{10})^+$ from higher 1-*n*-alkylcyclopentenes as compared to 3-*n*-alkylcyclopentenes seems, in turn, to reveal the promoted cleavage of C—C bond beta to the ring double bond in this case.

As shown before, cyclopentene, methyl- and ethylcyclopentenes eliminate hydrogen, methyl and ethyl groups correspondingly, to give principal ions $(C_5H_7)^+$. Metastable ions show that from higher homologs with $n_s \geqslant 3$ the principal ions $(C_5H_7)^+$ may be formed via degradation of larger fragment ions $(C_6H_{10})^+$ with m/e 82 (so called McLafferty ion from 1-*n*-alkylcyclopentenes), $(C_7H_{11})^+$ with m/e 95 and $(C_7H_{12})^+$ with m/e 96 by elimination of the methyl group, ethylene molecule or ethyl group, respectively, as it is seen from Fig. 5. These results are in agreement with the data of K. Mayer and C. Djerassi [8], who found in the mass spectra of 1-*n*-butyl- and 1-*n*-pentylcyclohexenes metastable ions, indicating the loss of the methyl group from the McLafferty ion. Larger fragment ions originate from molecular ions that primarily eliminate smaller alkyl groups or alkene molecules (ethylene, butylene).

The abundant ions $(C_5H_8)^+$, $(C_6H_{10})^+$ with m/e 68, 82, etc., show a relatively great importance of hydrogen atom rearrangements in the whole fragmentation scheme of the *n*-alkylcyclopentenes $(n_s \geqslant 4)$.

Many metastable ions presented in the mass spectra of most *n*-alkylcyclopentenes and indicating the loss of H_2 (or 2H), methyl group, acetylene or ethylene molecules a.o. from various fragment ions are characteristic for many other hydrocarbons, too.

Specific fragmentation features of *n*-alkylcyclopentenes appear in plots, showing the distribution of ion intensities with the number of carbon atoms in the ion n_i (Fig. 6). Besides differences between *n*-alkylcyclopentane and -pentene spectra, these plots reveal some differences between 1- and 3-*n*-alkylcyclopentene fragmentation patterns, too. All these graphs have three common maxima (when $n_s \geqslant 2$), corresponding to the ions with three and five carbon atoms and to the group of ions, including molecular ion. When $n_s \geqslant 2$, the highest maxima (sums of intensities of ions with five carbon atoms) decrease in the following order: 3-*n*-alkylcyclopent-1-enes (54—62%), 1-*n*-alkylcyclopent-1-enes (33—50%, e. g. about 1.5 times lower than for 3-substituted isomers). *n*-alkylcyclopentanes (30—37%). ΣC_5 for cyclopentane, methyl- and ethylcyclopentanes are smaller (12, 11, 37%) than for cyclopentene, methyl- and ethylcyclopentenes (53, 43—60%) and vary within the limits of 30—32 per cent for propyl ... *n*-hexylcyclopentanes.

Isomeric cyclopentenes have identical values of ΣC_3 (at $n_s \geqslant 3$ — 10—15%), which are about two times lower as compared to those of

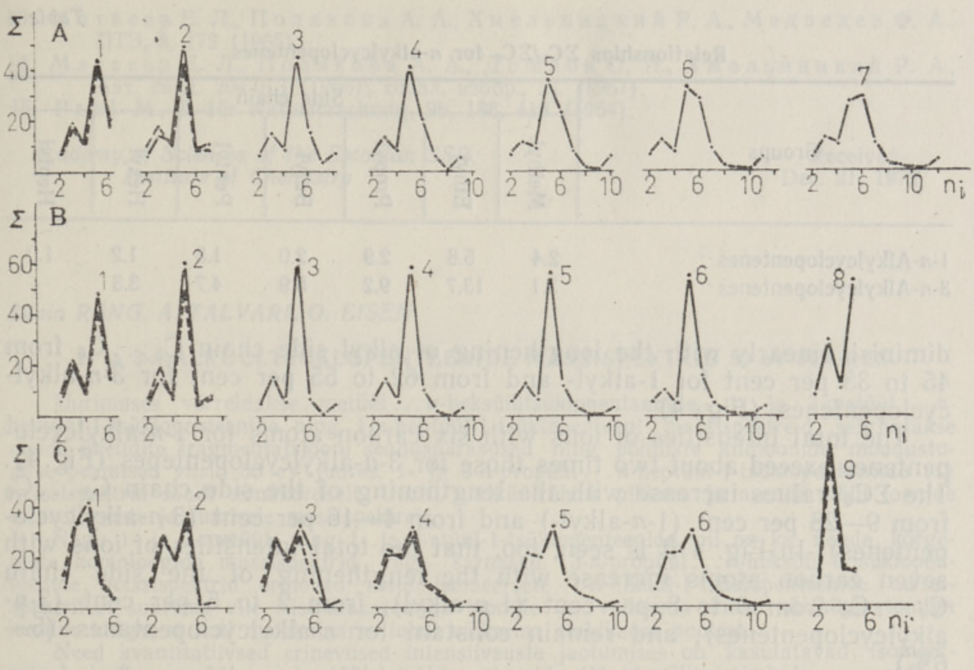

Fig. 6. Distributions of peak intensities according to the number of carbon atoms in an ion n_i. A — 1-*n*-alkylcyclopent-1-enes, B — 3-*n*-alkylcyclopent-1-enes, C — *n*-alkylcyclopentanes with following side chains: 1 — methyl, 2 — ethyl, 3 — *n*-propyl, 4 — *n*-butyl, 5 — *n*-pentyl, 6 — *n*-hexyl, 7 — *n*-heptyl, 8 — cyclopentene, 9 — cyclopentane. Dotted lines — literature data.

n-alkylcyclopentanes (21—26%). As seen from Fig. 7, the ΣC_3 values decrease markedly with the addition of a methyl group to cyclopentane or cyclopentene ring (from 62 to 34% and 30 to 20%, respectively) and remain constant at $n_s=4$—6.

Ethyl- and propylcyclopentanes show close ΣC_3 and ΣC_5 values (26—28 and 33—38%, Fig. 6), but higher homologs of this series — 20—21 and 30—32 per cent, e. g. for the higher *n*-alkylcyclopentanes, the ΣC_5 is about 1.5 times higher as compared to the ΣC_3. *n*-Alkylcyclopentenes differ by about 3—5 times higher total intensities of ions with five carbon atoms (33—62%) as compared to those of ions with three carbon atoms (10—15%).

Accordingly, the maximum, corresponding to ΣC_5 on the intensity distribution curve of cyclopentenes is about 3—5 times higher as compared to that of ΣC_3, the latter being about two times higher for *n*-alkylcyclopentanes (when $n_s \geqslant 4$).

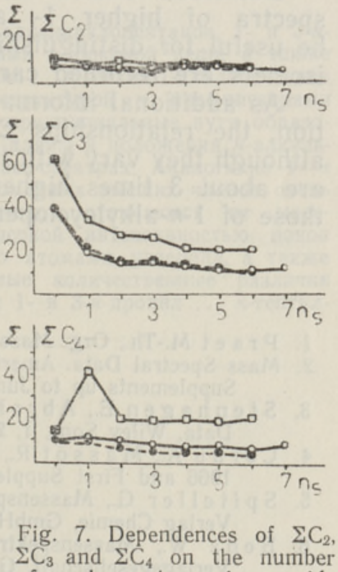

Fig. 7. Dependences of ΣC_2, ΣC_3 and ΣC_4 on the number of carbon atoms in a side chain n_s. Designation as in Fig. 1.

Higher ΣC_6, ΣC_7 and lower ΣC_5 values make intensity distribution curves for 1-*n*-alkylcyclopentenes more diffuse as compared to those of 3-*n*-alkylcyclopentenes, differing by sharp high maxima at ΣC_5. The ΣC_5 values

Table 4

Relationships $\Sigma C_5/\Sigma C_6$ for *n*-alkylcyclopentenes

Groups	Side chain						
	Methyl	Ethyl	Propyl	Butyl	Pentyl	Hexyl	Heptyl
1-*n*-Alkylcyclopentenes	2.4	5.8	2.9	2.0	1.5	1.2	1.0
3-*n*-Alkylcyclopentenes	3.1	13.7	9.2	5.9	4.7	3.3	—

diminish linearly with the lengthening of alkyl side chain $C_3 \ldots C_6$ from 45 to 33 per cent for 1-alkyl- and from 62 to 55 per cent for 3-*n*-alkylcyclopentenes (Fig. 4).

The total intensities of ions with six carbon atoms for 1-*n*-alkylcyclopentenes exceed about two times those for 3-*n*-alkylcyclopentenes (Fig. 4). The ΣC_6 values increase with the lengthening of the side chain $C_2 \ldots C_6$ from 9—28 per cent (1-*n*-alkyl-) and from 4—16 per cent (3-*n*-alkylcyclopentenes). In Fig. 4 it is seen, too, that the total intensities of ions with seven carbon atoms increase with the lengthening of the side chain $C_4 \ldots C_6$ from 6 to 8 per cent (1-*n*-alkyl), from 2 to 5 per cent (3-*n*-alkylcyclopentenes), and remain constant for *n*-alkylcyclopentanes (5—6%).

The ΣC_2 and ΣC_4 do not markedly depend on the n_s and vary within the limits of 6—9 and 19—21 per cent for *n*-alkylcyclopentanes ($n_s \geqslant 2$), 5—6 and 5—11 per cent for *n*-alkylcyclopentenes (Fig. 7). ΣC_8, ΣC_9, etc. are lower than 3 per cent when molecular ions are omitted.

Described differences in ion intensity distribution between mass spectra of higher 1- and 3-*n*-alkylcyclopentenes ($n_s \geqslant 2$) seem to be useful for distinguishing isomeric molecules if mass spectra of both isomers are recorded carefully at equal working conditions.

As additional information, for the determination of double bond position, the relationships $\Sigma C_5/\Sigma C_6$ are perhaps most suitable (Table 4), although they vary with the length of the side chain. On an average, they are about 3 times higher for 3-*n*-alkylcyclopent-1-enes as compared to those of 1-*n*-alkylcyclopent-1-enes (when $n_s \geqslant 3$).

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1- ja 3-*n*-ALKÜÜLTSÜKLOPENTEENIDE MASSISPEKTRID 50 eV JUURES

Uurimuses võrreldakse metüül ... *n*-heksüültsüklopentaanide, 1- ja 3-metüül ... *n*-heksüül-1-tsüklopenteenide ning 1-*n*-heptüül-1-tsüklopenteeni massispektreid, selgitatakse nende ühendite fragmentatsiooni seaduspärasused ning põhiliste kildioonide moodustumise peamised viisid 50 eV juures. 1- ja 3-*n*-propüül ... *n*-heptüül-1-tsüklopenteenide (1) massispektrid saadi esmakordselt. Uuriti *n*-alküülrühma pikkuse ja asendi mõju ioonide intensiivsuste jaotumisele massispektreis.

Nagu 1- ja 3-metüül- ning 1- ja 3-etüül-1-tsüklopenteenide, nii on ka nende kõrgemate homoloogide massispektrid väga sarnased. 3-*n*-propüül ... *n*-heksüül-1-tsüklopenteenide massispektrid erinevad neile isomeersete 1-*n*-alküül-1-tsüklopenteenide massispektritest suurema viie süsinikuaatomiga ioonide ja väiksema kuue süsinikuaatomiga ioonide hulga, samuti molekulaarse iooni väiksema stabiilsuse poolest.

Need kvantitatiivsed erinevused intensiivsuste jaotumises on kasutatavad isomeersete 1- ja 3-*n*-propüül ... *n*-heptüül-1-tsüklopenteenide (1) identifitseerimisel.

Сильвия РАНГ, А. ТАЛВАРИ, О. ЭЙЗЕН

50 *эв* МАСС-СПЕКТРЫ 1- И 3-*н*-АЛКИЛЗАМЕЩЕННЫХ ЦИКЛОПЕНТЕНОВ

Исследованы и сопоставлены 50 *эв* масс-спектры *н*-алкилциклопентанов, 1- и 3-*н*-алкилциклопентенов с метильной ... *н*-гексильной группами в боковой цепи, а также 1-*н*-гептил-1-циклопентена. Масс-спектры 1- и 3-*н*-пропил ... *н*-гептил-1-циклопентенов получены впервые. Установлены корреляции между структурой и масс-спектрами изомерных *н*-алкилциклопентенов и показаны вероятные принципиальные пути образования основных осколочных ионов. Рассмотрено влияние длины и положения *н*-алкильной боковой цепи на распределение интенсивностей в масс-спектрах. Аналогично 1- и 3-метил- и 1- и 3-этил-1-циклопентенам масс-спектры изомерных высших членов очень схожи. Масс-спектры 3-*н*-пропил ... *н*-гексил-1-циклопентенов отличаются от масс-спектров изомерных 1-*н*-алкил-1-циклопентенов более высокой интенсивностью ионов с пятью и более низкой интенсивностью ионов с шестью атомами углерода, а также меньшей стабильностью молекулярного иона. Найденные количественные различия могут быть использованы при идентификации изомерных 1- и 3-*н*-пропил ... *н*-гептил-1-циклопентенов.