

Mass Spectral Data of Cyclooctyl Derivatives

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The mass spectra of some cyclooctyl derivatives are reported. The main fragmentation processes observed are loss of C₂H₅, loss of C₂H₄, and where appropriate, loss of water. High-resolution mass measurements define the exact composition of some of the principal fragment peaks.

In the course of work on bicyclononane derivatives, it was considered to be of interest to prepare some cyclooctyl derivatives and to examine their mass spectral fragmentations. The mass spectra of the prepared derivatives (Table I) reported here are: methylenecyclooctane (I), 5-methylenecyclooctene (II), 5-hydroxymethylcyclooctene (III), 5-formylcyclooctene (IV), 5-acetylcyclooctene (V), 5-propionylcyclooctene (VI), and cyclooctene-5-carboxylic acid (VII).

The cyclooctyl derivatives were prepared from 2-(*N*-pyrrolidiny)bicyclo[3,3,1]nonan-9-ene. The conversions of the ketoamine to IV and VII have been described pre-

viously (1, 3). The compounds V (2) and VI were prepared from the ketoamine by the method used for compound IV after reaction of the ketoamine with methyl magnesium iodide or ethyl magnesium iodide. Lithium aluminum hydride reduction of the methyl ester of VII afforded the hydroxymethyl compound (III) (2). The hydrocarbon (II) was prepared from the hydroxymethyl compound (III) by reaction with triphenyl phosphite and bromine. Treatment of the subsequent bromide with 2,4,6-trimethylpyridine eliminated hydrogen bromide giving an exocyclic double bond. The saturated hydrocarbon (I) (2) was prepared in an analogous manner from 5-hydroxymethylcyclooctane, obtained from the carboxylic acid (VII) after catalytic hydrogenation, esterification, and lithium aluminum hydride reduction. All the compounds were purified by fractional distillation.

The mass spectra were recorded at the PCMU, Harwell, England, on an AEI MS-902 spectrometer at an ionizing voltage of 70 eV. The accuracy of the high-resolution data is ± 0.005 over the range of mass values given.

Results and Discussion

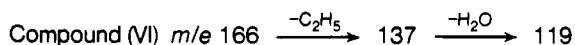
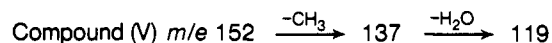
With the one exception of the carboxylic acid (VII), all the cyclooctyl derivatives gave a clear indication of the

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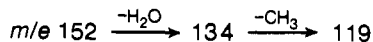
Table I. Fragmentation Pattern of Cyclooctyl Derivatives

<i>m/e</i>	I	II	III	IV	V	VI	VII	<i>m/e</i>	I	II	III	IV	V	VI	VII
39	48	30	32	37	36	50	47	87						6	
40	11	14	7	7	7	10		91	11	7		28	8	17	28
41	60	6	61	50	57	54	52	92			17	22		5	
42	14	5	11	12	10	9		93	16	7	42	9	10	46	60
43	84		29	100	69	27		94	24	100	39	11	14	18	
44	6		10	9	15	10		95	21	8	10	12	10	10	
50		7				5		96	48		12	9		5	
51	9	7	7	6	5	12		97			17	12	21	6	
52	5					7		98			5		100	23	21
53	22		21	15	15	20	28	99					7		
54	32		36	30	20	21	27	105			10	6	5	5	
55	44	9	52	30	48	29	62	107			24	5		8	
56	22		15	7				108				6	6	18	59
57	7		55	30		50		109	7		31	26	20	38	
58	25		8	66		10		110			8	8		5	
63		9						111			7		8		
65	10	27	9		5	11		112			15		6		
66	11	35	12	8	5	17		117	8	9					
67	64	7	100	62	60	100	72	118	5	7					
68	40		39	20	10	22	26	119					7	12	
69	27		18	9	7	8		120				26			
70	6		22	11	36	10		121			7				
71			23	7	16		20	122	9	5P	24				
72			6					123					7		
73				8				124	4P						
77	13	5	15	8	8	19	27	131			11				24
78	5		11	8	5	9		134					15		
79	36	13	58	32	22	71	100	136				5		58	61
80	28	9	48	15	8	46	95	137					6	18	9
81	100	9	71	30	17	19	25	138			12	9P			
82	24		31	24	6	7	18	140			10P				
83	6		33	10	21	8		152					15P		
84			10	6	8			154							4P
85			14			10		166						1P	

loss of a C₂H₅ fragment upon electron impact. The loss of C₂H₅ from the ethyl ketone (VI) is no doubt due to both loss from the ring, as has occurred with the other compounds, and loss from the side chain. The corresponding loss of a methyl unit from the methyl ketone (V) was observed. Another linking feature of these ketones is the loss of H₂O subsequent to the loss of the hydrocarbon fragment from the side chain.



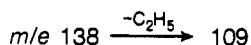
A metastable peak at m/e 105.7 corresponding to the breakdown m/e 137 to m/e 119 was observed in the spectrum of (V). The alternative sequence was only apparent in (V), i.e.,



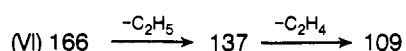
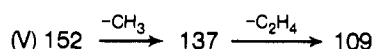
The ethyl ketone (VI) was the only oxygenated compound examined that did not lose water as an initial fragmentation process. The breakdown in the acid (VII) is accompanied by the formation of a metastable ion at m/e 120.2 (Table II). High resolution (Table III) upon the (M-18) fragments of the aldehyde (IV) and the methyl ketone (V) show them to be due to hydrocarbon fragments only.

The formation of the ion m/e (M-28) is apparent only in the two hydrocarbons (I and II), the alcohol (III), and the aldehyde (IV). In the two oxygenated compounds this could be due to loss of CO. However, it could be due to the loss of C₂H₄ from the parent, or the sequential loss of H₂ and C₂H₂, as is undoubtedly the case with the hydrocarbon (I).

The hydrocarbon (II) appears to lose C₂H₄ from the parent, but here, contrary to the compounds just mentioned, there is a loss of 2H₂ from the parent. Possibly, this is due to the fact that such a loss, with a rearrangement would bring the resulting double bonds formed into a cyclic conjugated system. This result could also account for the loss of 3H₂ from the hydrocarbon (I), m/e 124 → 122 → 118. The fragment ion at m/e 109 in the spectrum of the compounds I, III, IV, V, and VI has some duality associated with it. In the case of the hydrocarbon (I), it is due to a straight loss of a methyl group. However, in the oxygenated compounds III, IV, V, and VI, it would appear to be due to loss of side chain or loss of a hydrocarbon fragment either directly as in (IV),



or by a sequential process as indicated:



High resolution (Table III) upon m/e 109 indicates that the structure of the parent has an influence upon the rel-

Table II. Metastable Ions

Compound	Metastable ions				
I	68.3	66.3			
III	77.1	66.4	54.8	52.5	
IV	104.4	77.1	70.5	66.2	54.7
V	105.7	96.4	77.1	70.5	66.5
VI	89.0	80.0	78.1		
VII	120.2	89.1	78.4	66.4	59.2

Table III. High-Resolution Mass Measurement

Compound	m/e	Com- position	Multiplet ratio	Measd mass	Calcd mass	
IV	120	C ₉ H ₁₂		120.0935	120.0939	
	109	C ₈ H ₁₃	1	109.1016	109.1017	
	109	C ₇ H ₉ O	1	109.0647	109.0653	
	92	C ₇ H ₈		92.0624	92.0626	
	79	C ₆ H ₇		79.0546	79.0548	
	58	C ₅ H ₆ O		58.0419	58.0419	
	43	C ₄ H ₇	1	43.0549	43.0548	
	43	C ₂ H ₃ O	2	43.0184	43.0184	
	V	134	C ₁₀ H ₁₄		134.1095	134.1095
		109	C ₈ H ₁₃	2	109.1020	109.1017
109		C ₇ H ₉ O	1	109.0655	109.0653	
98		C ₆ H ₁₀ O		98.0733	98.0732	
79		C ₆ H ₇		79.0549	79.0548	
67		C ₅ H ₇		67.0547	67.0548	
VII		108	C ₈ H ₁₂	4	108.0941	108.0939
	108	C ₇ H ₈ O	1	108.0577	108.0575	
	93	C ₇ H ₉	4	93.0704	93.0704	
	93	C ₆ H ₅ O	1	93.0341	93.0340	
	80	C ₆ H ₈		80.0624	80.0626	
	79	C ₆ H ₇		79.0547	79.0548	
	67	C ₅ H ₇		67.0550	67.0548	

ative abundance of the oxygenated as opposed to the hydrocarbon fragment (Table I).

Similarly, the ion m/e 108 in the spectra of compounds IV, V, VI, and VII could be due to the loss of a hydrocarbon fragment or of the side chain plus a hydrogen atom to give the molecules formaldehyde, acetaldehyde, propionaldehyde, and formic acid, respectively. That this latter process is the major route is shown by the multiplet ratios of the ions at m/e 108 (Table III).

The alcohol (III) did not give rise to a fragment ion at m/e 108 corresponding to the loss of methanol which would bring its behavior into line with the other oxygenated compounds studied.

Acknowledgment

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