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 C_2H_5, loss of C_2H_4, 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*-pyrrolidinyl)bicyclo[3,3,1]nonan-9-ene. The conversions of the ketoamine to IV and VII have been described previously (*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

Table I. Fragmentation Pattern of Cyclooctyl Derivatives

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

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loss of a C_2H_5 fragment upon electron impact. The loss of C_2H_5 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 H_2O subsequent to the loss of the hydrocarbon fragment from the side chain.

$$\text{Compound (V) } m/e\ 152 \xrightarrow{-CH_3} 137 \xrightarrow{-H_2O} 119$$

$$\text{Compound (VI) } m/e\ 166 \xrightarrow{-C_2H_5} 137 \xrightarrow{-H_2O} 119$$

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.,

$$m/e\ 152 \xrightarrow{-H_2O} 134 \xrightarrow{-CH_3} 119$$

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 C_2H_4 from the parent, or the sequential loss of H_2 and C_2H_2, as is undoubtedly the case with the hydrocarbon (I).

The hydrocarbon (II) appears to lose C_2H_4 from the parent, but here, contrary to the compounds just mentioned, there is a loss of $2H_2$ 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 $3H_2$ 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),

$$m/e\ 138 \xrightarrow{-C_2H_5} 109$$

or by a sequential process as indicated:

$$\text{(III) } 140 \xrightarrow{-H_2} 138 \xrightarrow{-C_2H_5} 109$$

$$\text{(V) } 152 \xrightarrow{-CH_3} 137 \xrightarrow{-C_2H_4} 109$$

$$\text{(VI) } 166 \xrightarrow{-C_2H_5} 137 \xrightarrow{-C_2H_4} 109$$

High resolution (Table III) upon *m/e* 109 indicates that the structure of the parent has an influence upon the relative abundance of the oxygenated as opposed to the hydrocarbon fragment (Table I).

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*	Composition	Multiplet ratio	Measd mass	Calcd mass
IV	120	C_9H_{12}		120.0935	120.0939
	109	C_8H_{13}	1	109.1016	109.1017
	109	C_7H_9O	1	109.0647	109.0653
	92	C_7H_8		92.0624	92.0626
	79	C_6H_7		79.0546	79.0548
	58	C_3H_6O		58.0419	58.0419
	43	C_3H_7	1	43.0549	43.0548
	43	C_2H_3O	2	43.0184	43.0184
V	134	$C_{10}H_{14}$		134.1095	134.1095
	109	C_8H_{13}	2	109.1020	109.1017
	109	C_7H_9O	1	109.0655	109.0653
	98	$C_6H_{10}O$		98.0733	98.0732
	79	C_6H_7		79.0549	79.0548
	67	C_5H_7		67.0547	67.0548
VII	108	C_8H_{12}	4	108.0941	108.0939
	108	C_7H_8O	1	108.0577	108.0575
	93	C_7H_9	4	93.0704	93.0704
	93	C_6H_5O	1	93.0341	93.0340
	80	C_6H_8		80.0624	80.0626
	79	C_6H_7		79.0547	79.0548
	67	C_5H_7		67.0550	67.0548

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.

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