Mass Spectral Data of Some Bicyclo(3,3,1) Compounds

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The mass spectra of some bicyclo(3,3,1)nonanes are reported. The main fragmentation processes observed are rupture of one of the bridges containing three carbon atoms by loss of either a C_2H_5 or CHO unit, or the loss of a C_3H_6 or C_2H_2O unit. Significant differences in the abundance of $(M—H_2O)^+$ ions for stereoisomeric alcohols were noticed. High-resolution mass measurements define the exact composition of some of the principal fragment peaks.

This mass spectrometric study of bicyclo(3,3,1)nonanes was undertaken as it had been noticed that no systematic study had been previously carried out, despite chemical interest in the system over a number of years. However, since the commencement of this work, some studies have been initiated in the field of bicyclo(3,3,1)nonanes (*2, 7*).

The derivatives whose mass spectra are reported here (Tables I and II) are:

I bicyclo(3,3,1)nonane
II bicyclo(3,3,1)non-2-ene (*1*)
III exo-2-hydroxybicyclo(3,3,1)nonane (*1*)
IV endo-2-hydroxybicyclo(3,3,1)nonane (*1*)
V exo-2-hydroxybicyclo(3,3,1)non-3-ene (*4*)
VI bicyclo(3,3,1)nonan-2-one (*1*)
VII 2-hydroxy-2-methylbicyclo(3,3,1)nonane
VIII 9-hydroxybicyclo(3,3,1)nonane (*6*)
IX syn-9-hydroxybicyclo(3,3,1)non-2-ene (*5*)
X 9-ketobicyclo(3,3,1)non-2-ene (*6*)
XI 9-hydroxy-9-methylbicyclo(3,3,1)nonane (*6*)
XII 9-hydroxy-9-methylbicyclo(3,3,1)non-2-ene (*6*)

Bicyclo(3,3,1)nonane (I) was prepared by catalytic reduction of II. The material prepared by this route was identical with that prepared by Cope and Synerholm (*3*). 2-Hydroxy-2-methylbicyclo(3,3,1)nonane (VII) was prepared from VI by a Grignard reaction with methyl magnesium iodide. All the compounds were purified by vacuum sublimation. 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

Compounds I, II, V, VI, VIII, and X gave a clear indication of the loss of 29 mass units upon electron impact. In the case of hydrocarbons I and II, this is obviously due to loss of a C_2H_5 fragment.

The oxygenated compounds show evidence of loss of both C_2H_5 and CHO fragments. High-resolution mass measurement (Tables III and IV) on compound V shows that the loss of CHO vs. C_2H_5 is 10 to 1. A metastable peak at *m/e* 86.2 corresponding to the transition *m/e* 138 to *m/e* 109 occurs in the spectrum of V (Table V). Compounds II, III, IV, V, VIII, and XI all show loss of 31 mass units. It is evident that this loss can be either a concerted or a sequential loss of H_2 and 29 mass units. The sequential loss is apparent in compounds III, V, and

Table I. Fragmentation Pattern of (3,3,1) Bicyclononyl Derivatives (I–VII)

m/e	I	II	III	IV	V	VI	VII
39	22	20	36	35	26	18	10
40		6	7	6	5		
41	31	24	48	54	31	27	19
42				6	5		
43			24	16	14		35
44				8			
51		6	10	6	10		
52			6		5		
53	13	13	24	22	20	11	7
54	28	11	13	33	10	24	6
55	31	13	45	67	43	19	21
56			10	6	5		
57			24	23	14		6
58				30			18
59							7
65		13	12	8	9		
66	6	26	17	10	14	5	
67	66	12	42	84	31	60	19
68	27		29	28	21	15	7
69	6		13	9	8	6	9
70			48	11	34		
71			26		18		100
72							21
77	6	17	22	15	19	5	6
78		13	15	8	13		
79	11	85	52	86	43	25	24
80	6	100	32	84	29	6	7
81	100	54	39	91	26	38	21
82	64	7	14	21	9	14	
83	13	5	47	35	46	9	
84			10				6
85			11				
91		11	23	9	19	5	5
92		5	14		11		
93		22	16	37	8		11
94		15	24	100	20	100	49
95	22	9	32	15	27	15	10
96	47	8	100	62	100	12	34
97		5	23	13	20		11
99			6				
105			7		6		
107		7	7	23	5		8
108			14		5		
109			36	15	31	8	
110			10		7		5
120			7			2.5	
121							16
122		33P		62			
123			7	8	5		
124	50P						
125							6
136			20		15		
137			8		6		14
138			18		17P	24P	
140			1P	11P			12
154							6P

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Table II. Fragmentation Pattern of (3,3,1) Bicyclononyl Derivatives (VIII–XII)

m/e	VIII	IX	X	XI	XII	m/e	VIII	IX	X	XI	XII
39	18	24	51	24	10	85				12	7
40			15		6	91	35	100	23	17	12
41	32	30	35	52	30	92	24	76	6		8
42		5		9		93	29	12	80	36	36
43		13		88	100	94	22	6	9	25	32
44			27		6	95	5	7	6	44	34
50			7			96				17	7
51		7	15			97	6	6		38	7
52			9			105	5	15		10	15
53	9	11	20	15	9	106					6
54	11	10	12	15	8	107	10		6		
55	21	13	14	100	26	108			20	50	66
56				14		109	10			40	53
57	17	21		21	9	110					8
65		7	17			111				13	8
66	6	10	20			119				14	16
67	45	28	60	60	53	120	29	92			
68	13	7	17	21	11	121		10			
69	7	6		23	9	122	52				
70	11	16			6	123				10	
71	6			28	32	124					5.5
77	9	14	34	12	12	134				27	46
78	9	24	12			136		6	62P	5	
79	37	44	100	30	29	137				14	13
80	45	11	71	15		138		2P			
81	100	12	7	44	21	140	8P				
82	10	7		32	10	152				10	12P
83	9	8		11	6	154				1P	
84					10						

Table III. High-Resolution Mass Measurement (III–VII)

Compound	m/e	Composition	Multiplet ratio	Measd mass	Calcd mass
III	109	C_8H_{13}	10	109.1017	109.1017
	109	C_7H_9O	1	109.0654	109.0653
	96	C_7H_{12}	10	96.0939	96.0939
	96	C_6H_8O	1	96.0573	96.0575
	83	C_6H_{11}	20	83.0857	83.0860
	83	C_5H_7O	1	83.0492	83.0497
	79	C_6H_7		79.0548	79.0548
IV	122	C_9H_{14}		122.1092	122.1095
	96	C_7H_{12}	20	96.0935	96.0939
	96	C_6H_8O	1	96.0571	96.0575
	81	C_6H_9	20	81.0705	81.0704
	81	C_5H_5O	1	81.0341	81.0340
V	109	C_8H_{13}	10	109.1019	109.1017
	109	C_7H_9O	1	109.0649	109.0653
	96	C_7H_{12}	10	96.0933	96.0939
	96	C_6H_8O	1	96.0573	96.0575
	94	C_7H_{10}	10	94.0780	94.0783
	94	C_6H_6O	1	94.0420	94.0419
	83	C_6H_{11}	20	83.0857	83.0861
	83	C_5H_7O	1	83.0492	83.0479
VI	120	C_9H_{12}		120.0939	120.0939
	96	C_7H_{12}	1	96.0939	96.0939
	96	C_6H_8O	1	96.0574	96.0575
	81	C_6H_9	1	81.0704	81.0704
	81	C_5H_5O	1	81.0341	81.0340
VII	137	$C_{10}H_{17}$		137.1324	137.1330
	121	C_9H_{13}		121.1023	121.1017
	96	C_7H_{12}		96.0940	96.0939
	94	C_7H_{10}		94.0788	94.0782
	80	C_6H_8		80.0626	80.0626
	71	C_4H_7O		71.0500	71.0497

Table IV. High-Resolution Mass Measurement (VIII–XII)

Compound	m/e	Composition	Multiplet ratio	Measd mass	Calcd mass
VIII	122	C_9H_{14}		122.1095	122.1095
	120	C_9H_{12}		120.0937	120.0939
	94	C_7H_{10}		94.0780	94.0783
	81	C_6H_9		81.0705	81.0704
IX	120	C_9H_{12}		120.0933	120.0939
	105	C_8H_9		105.0707	105.0704
	92	C_7H_8		92.0625	92.0626
	79	C_6H_7		79.0549	79.0548
	67	C_5H_7		67.0547	67.0548
X	108	C_8H_{12}	5	108.0935	108.0939
	108	C_7H_8O	1	108.0571	108.0575
	93	C_7H_9		93.0705	93.0704
	80	C_6H_8		80.0622	80.0626
	79	C_6H_7		79.0549	79.0548
	77	C_6H_5		77.0395	77.0391
XI	134	$C_{10}H_{14}$		134.1092	134.1095
	109	C_8H_{13}	10	109.1020	109.1017
	109	C_7H_9O	1	109.0657	109.0653
	108	C_8H_{12}		108.0942	108.0939
	95	C_7H_{11}		95.0858	95.0861
	81	C_6H_9	18	81.0705	81.0704
	81	C_5H_5O	1	81.0341	81.0340
XII	137	$C_9H_{13}O$		137.0957	137.0966
	134	$C_{10}H_{14}$		134.1090	134.1095
	119	C_9H_{11}		119.0860	119.0861
	109	C_8H_{13}	10	109.1011	109.1017
	109	C_7H_9O	1	109.0656	109.0653
	108	C_8H_{12}		108.0941	108.0939
	95	C_7H_{11}	15	95.0858	95.0861
	95	C_6H_7O	1	95.0496	95.0497

Table V. Metastable Ions

Compound	Metastable ions					
I	77.1	68.4	54.7	54.3		
II	77.1	52.5				
III	94.8	94.1	77.1	66.4		
IV	106.4	77.1	68.4	66.4	52.5	36.5
V	94.8	94.1	86.2	77.1	66.8	46.8
VI	77.1	68.4	66.4	54.7		
VII	107.8	105.4	66.4			
VIII	90.2	77.1	72.5	66.4	52.5	
IX	91.9	90.1	77.1	70.5	54.8	50.7
X	89.2	80.0	78.9	75.1		
XI	105.7	80.1	77.1	66.4		
XII	118.2	105.7	89.2	82.2	80.1	78.1
	77.1	66.4	63.1	47.3	41.2	

XI and that of the concerted loss of II, IV, and VIII. In the case of hydrocarbon (II), it is a loss of H_2 and C_2H_5. In the oxygenated compounds, however, competition arises between loss of CHO and loss of C_2H_5. High resolution on III shows that the resultant ion is the consequence of a 10 to 1 loss of CHO over C_2H_5. A similar pattern is observed for the loss of water followed by C_2H_5, sequential in compounds IV, VI, VIII, XI, and XII and concerted in compounds III and VII.

The observation of the loss of a C_3H_6 unit from hydrocarbons I and II (meta peak at *m/e* 54.3 and *m/e* 52.5, respectively), gives rise to the possibility of an identical loss from the oxygenated compounds. A metastable peak at *m/e* 66.8 in the spectrum of V indicates the transition P-42. That this is a loss of C_3H_6 and of C_2H_2O is shown by high resolution on the P-42 peak. The major occurrence is the loss of the oxygenated fragment. Compounds VI, X, and XII all show a P-42 peak. High resolution shows that in the case of VI, it is due to loss of C_3H_6 and of C_2H_2O. The sequential loss of H_2 and 42 mass units is observed in compounds III, V, and IX, and the corresponding concerted loss could be occurring in compounds I, II, IV, VI, VII, X, and XII. High-resolution mass measurement shows that the P—H_2—C_2H_2O route takes place preferentially to P—H_2—C_3H_6 in compounds III, IV, and V and exclusively in compound XII.

The sequential loss of P—H_2O—42 is evidenced in compounds IV and VIII by metastable peaks at *m/e* 106.4 and *m/e* 52.5 in the spectrum of IV and at *m/e* 52.5 in the spectrum of VIII. Possibly, this also occurs in compounds IX and XII. The concerted loss could be occurring in compounds III, VII, and XI. High resolution shows that the resultant fragment ion from VII is a hydrocarbon. Loss of OH from the parent is not so characteristic in the series. This has only been observed in compounds III, IV, VII, IX, and XI. Similarly P—CH_3 is only observed in compounds II, V, and XII.

The observation that the endo-2-ol (IV) suffers loss of water from the parent ion, whereas the exo-2-ol (III) and exo-2-ol-3-ene (VI) do not, is a direct consequence of the stereochemistry of the compounds concerned, since in the endo compound a 1,2 trans élimination can occur, whereas in the exo compounds it cannot.

Confirmation of the loss of H_2O from the parent ion in compounds IV, VI, VIII, IX, and XII is given by high-resolution mass measurement (Tables III and IV) and by the observation of metastable peaks associated with the fragmentation (*m/e* 106.4, compound IV, and *m/e* 118.2, compound XII).

All the 9-hydroxy compounds undergo a P—H_2O fragmentation. The abundance of the resulting ions varies considerably but does indicate a preferential loss of H_2O from the unsaturated compounds.

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