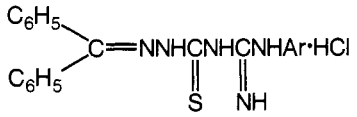
Table II. *N*-Arylformamidino-*N'*-diphenylthiosemicarbazone Hydrochlorides[a]



No.	Ar	Mp, °C	Yield, %	Formula
1.	Phenyl	202–203	68	$C_{21}H_{20}ClN_5S$
2.	2-MePh	198–199	70	$C_{22}H_{22}ClN_5S$
3.	3-MePh	150–152	62	$C_{22}H_{22}ClN_5S$
4.	4-MePh	200–201	71	$C_{22}H_{22}ClN_5S$
5.	2-MeOPh	195–196	67	$C_{22}H_{22}ClN_5OS$
6.	4-MeOPh	197–198	65	$C_{22}H_{22}ClN_5OS$
7.	4-EtOPh	160–162	72	$C_{23}H_{24}ClN_5OS$
8.	2-ClPh	175–176	64	$C_{21}H_{19}Cl_2N_5S$
9.	3-ClPh	155–156	69	$C_{21}H_{19}Cl_2N_5S$
10.	4-ClPh	182–183	73	$C_{21}H_{19}Cl_2N_5S$
11.	4-BrPh	205–206	60	$C_{21}H_{19}BrClN_5S$
12.	2,5-Me_2Ph	204–205	66	$C_{23}H_{24}ClN_5S$
13.	1-Naphthyl	207–208	67	$C_{25}H_{22}ClN_5S$

[a] All of the compounds gave elemental analyses (C, H, N, S) within ±0.30 of the calculated values.

was dissolved in acetone (20.0 ml) and the solution was cooled in freezing mixtures. To this cooled solution, phenylcyanamide hydrochloride (2.4 g, 0.015 mol) dissolved in acetone (10.0 ml) was added slowly with constant shaking. After keeping it in a freezing mixture for 1 h, crystalline pure *N*-phenylformamidino-*N'*-dimethylthiosemicarbazone hydrochloride was separated, filtered, and washed with acetone and petroleum ether to remove any unreacted constituents, yield 3.3 g, 80%, mp 203–204.

Other *N*-arylformamidino-*N'*-dimethlthiosemicarbazone hydrochlorides, prepared by condensing dimethylthiosemicarbazone with different arylcanamides hydrochloride are summarized in Table I.

Using similar procedure as above several *N*-arylformamidino-*N'*-diphenylthiosemicarbazone hydrochlorides, described in Table II, were obtained.

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Mass Spectral and Nuclear Magnetic Resonance Data of Some Bicyclo[3.2.1] Compounds

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The mass spectra and NMR spectra of some bicyclo[3.2.1]-octanes are reported. The main fragmentation process observed is the loss of a C_2H_5 or CHO unit. The abundance of $(P - H_2O)^+$ ions in the spectra of the alcohols was found to be related to their stereochemistry and based upon these observations a structure is suggested for one of the alcohols whose stereochemistry was initially undefined. High resolution mass measurement define the exact composition of some of the principal fragment peaks.

This mass spectrometric and NMR study of selected bicyclo[3.2.1]octanes was undertaken as an extension of the work previously reported (*5*) on the related bicyclo[3.3.1] system. Kwart and Blazer (*6*) have reported on the mass spectrum of 2-hydroxybicyclo[3.2.1]octane, and the present paper also extends their field of investigation.

The derivatives whose mass spectra are reported here (Tables I–III) are: I, bicyclo[3.2.1]octane (*5*); II, bicyclo[3.2.1]oct-2-ene (*1, 5*); III, *endo*-2-hydroxybicyclo[3.2.1]octane (*1, 5*); IV, *exo*-2-hydroxybicyclo[3.2.1]oct-3-ene (*2, 5*); V, 2-hydroxy-2-methylbicyclo[3.2.1]octane (*5*); VI, bicyclo[3.2.1]octan-2-one (*1, 5*); VII, *syn*-8-hydroxybicyclo[3.2.1]octane (*4, 5*); VIII, *syn*-8-hydroxybicyclo[3.2.1]oct-2-ene (*3, 5*).

These compounds were prepared by methods analogous to those used for the bicyclo[3.2.1]nonyl series previously reported.[5] From the preparative methods employed and analysis of the products, compounds III and IV were assigned the endo and exo configurations, respectively.

Compound VIII was prepared from a mixture of 2-*exo*-morpholino-8-ketobicyclo[3.2.1]octane and 2-*endo*-morpholino-8-ketobicyclo[3.2.1]octane by $LiAlH_4$ reduction followed by amine oxide pyrolysis. This procedure led to a mixture of the *syn*- and *anti*-8-hydroxybicyclo[3.2.1]oct-2-enes, the syn isomer accounting for 95% of the yield.

Table I. Fragmentation Pattern of Bicyclo[3.2.1]octyl Derivatives

m/e	I	II	III	IV	m/e	I	II	III	IV
39	18	12	22	17	79	10	100	38	17
40	21				80	11	38	97	100
41	26	11	38	26	81	65		12	66
42	5				82	72		37	9
43	6			6	83	100			29
44	21				91		8		90
51	5	5		5	93		21	29	
53	7			11	95	26			26
54	21	13	13	18	96				8
55	17		17	27	97	6			
56	6				105	12			
57	8		40		106				
58			26		107				7
59		5			108		42P	29	
65		6			109		3.8		31
66	8	58	20	7	110	41P			
67	72	36	100	42	111	3.8			
68	18		15	17	122				6
69	15		15	5	123				4
70				6	124				53P
71	5				125				4.5
77		16		7	126			10P	
78		14		7	127			0.8	

Table II. Fragmentation Pattern of Bicyclo[3.2.1]octyl Derivatives

m/e	V	VI	VII	VIII	m/e	V	VI	VII	VIII
39	8	17	20	18	79	12	8	50	18
41	12	17	29	15	80	28	100	43	7
42			6		81	9	13	10	6
43	28		6		82	14		22	
51				6	83	5		26	5
53	5	8	10	8	84			9	
54		8		5	91				20
55	9	20	25	7	93	10		53	10
56			5		94			6	
57			40	80	95		11	43	9
58	8		5		96			5	
59	5				97			10	
65				6	98			8	
66	5	18	13	6	106		2		36
67	20	70	67	32	108			25	
68		22	10	100	122	9			
69		5	7		124		28P		28P
70			20		125	9	2.5		2.5
71	100		9		126			100P	
72	11				127			8.9	
77			8	15	140	6P			
78			6	92	141	0.6			

Compound VII was prepared directly from compound VIII by catalytic reduction in quantitative yield and the authors assumed the same relative isomeric ratio for the products.

2-Hydroxy-2-methylbicyclo[3.2.1]octane (V) was prepared from VI by a Grignard reaction with methyl magnesium iodide. The stereochemistry of V is commented upon in the discussion.

All the compounds were purified by vacuum sublimation. The mass spectra were recorded at the P.C.M.U., 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 amu. The NMR spectra were recorded in these laboratories on a JEOL 60HL spectrometer.

Results and Discussion

With the exception of the *exo*-2-ol-3-ene (IV) all the oxygenated compounds show evidence of loss of a H_2O unit from the parent ion. The spectra of compounds III, V, VII, and VIII show metastable peaks at *m/e* 92.6, 106.3, 92.6, and 90.7, respectively (Table IV), corresponding to the fragmentation P − H_2O.

The fact that the exo compound IV does not lose water is to be expected since the stereochemistry of the compound is such that a 1,2 trans elimination of the water cannot occur. (*5*) The stereochemistry of the 2-hydroxy-2-methyl compound V is assigned as an *endo*-2-hydroxy-*exo*-2-methyl compound on the basis that it does lose water and hence the hydroxyl group must be in the endo position. This assignment accords with the expected mode of attack by a Grignard reagent on a ketone during the preparation of the alcohol.

The compounds III, VII, and VIII gave a clear indication of the loss of 33 mass units upon electron impact. That these are sequential losses of the type P − H_2O − CH_3 is evidenced by high resolution of the P − 33 ions (Table III), the presence of the metastable ions at *m/e* 80.1 and 78.1 in the spectra of compounds VII and VIII, respectively, corresponding to the fragmentation (P − H_2O) − CH_3.

The same three compounds also show evidence of the sequential loss P − H_2O − C_2H_4. High resolution on the resulting ions for compounds III, VII, and VIII (Table III) confirm that they are hydrocarbons. Metastable ions corresponding to the tran-

Table III. High Resolution Mass Measurement

Compound	m/e	Composition	Multiplet rel abund	Measd mass	Calcd mass
III	108	C_8H_{12}		108.0931	108.0939
	93	C_7H_9		93.0698	93.0704
	82	C_6H_{10}		82.0780	82.0783
	80	C_6H_8		80.0622	80.0626
	79	C_6H_7		79.0544	79.0548
	67	C_5H_7		67.0543	67.0548
IV	124	$C_8H_{12}O$		124.0886	124.0888
	109	C_7H_9O		109.0658	109.0653
	95	C_6H_7O	4	95.0497	95.0497
	95	C_7H_{11}	1	95.0859	95.0861
	81	C_5H_5O	1	81.0337	81.0340
	81	C_6H_9	1.5	81.0699	81.0704
	80	C_6H_8		80.0625	80.0626
	67	C_5H_7		67.0548	67.0548
V	125	$C_8H_{13}O$		125.0968	125.0966
	122	C_9H_{14}		122.1093	122.1096
	93	C_7H_9		93.0702	93.0704
	82	C_6H_{10}		82.0777	82.0783
	81	C_6H_9		81.0700	81.0704
	80	C_6H_8		80.0623	80.0626
VI	95	C_6H_7O	1	95.0496	95.0497
	95	C_7H_{11}	2	95.0859	95.0861
	81	C_6H_9		81.0673	81.0704
	80	C_6H_8		80.0616	80.0626
	68	C_4H_4O	1	68.0262	68.0262
	68	C_5H_8	10	68.0624	68.0626
	67	C_5H_7		67.0543	67.0548
VII	108	C_8H_{12}		108.0949	108.0939
	95	C_7H_{11}		95.0856	95.0861
	93	C_7H_9		93.0704	93.0704
	80	C_6H_8		80.0621	80.0626
	79	C_6H_7		79.0551	79.0548
	67	C_5H_7		67.0545	67.0548
VIII	106	C_8H_{10}		106.0785	106.0782
	93	C_7H_9		93.0705	93.0704
	91	C_7H_7		91.0548	91.0548
	78	C_6H_6		78.0470	78.0469
	68	C_5H_8		68.0623	68.0626
	57	C_3H_5O		57.0350	57.0340

Table IV. Metastable Ions

Compound	Metastable ions					
II	40.3	63.1	89.0			
III	54.8	59.3	63.1	92.6		
IV	54.8					
V	52.5	71.0	106.3			
VI	54.7	78.1				
VII	54.4	55.9	59.3	80.1	89.2	92.6
VIII	57.4	78.1	90.7			

Table V. NMR Data of Bicyclo[3.2.1]octyl Derivatives[a]

I	H_1, H_5	7.85	umc
	H_8	8.20	umc
	H_6, H_7	8.45	umc
	H_2, H_3, H_4	8.55	umc
II	H_2, H_3	4.17,4.66	d (pairs)
	H_1, H_5	7.71	umc
	H_4, H_6, H_7, H_8	80–8.8	bumc
III endo	H_2	6.30	umc
	HO	7.58	s
	H_1, H_5	7.83	umc
	H_3, H_4, H_6, H_7, H_8	8.0–8.8	bumc
IV exo	H_3, H_4	4.05	mc → q
	H_2	6.15	d
	HO	7.53	s
	H_1, H_5	8.00	bumc
	H_6, H_7, H_8	8.3–8.8	bumc
V	H_1, H_5	7.95	umc
	HO	8.28	s
	H_3, H_4, H_6, H_7, H_8	8.2–8.8	bumc
	H_9	8.88	s
VI	H_5	7.3	umc
	H_1, H_3	7.45–7.9	bumc
	H_4, H_6, H_7, H_8	7.95–8.5	bumc
VII syn	H_8	5.95	umc
	H_1, H_5	7.70	umc
	HO	7.95	s
	H_2, H_3, H_4, H_6, H_7	8.2–8.8	bumc
VIII syn	H_2, H_3	4.35	mc → q
	H_8	5.95	umc
	H_1, H_5	7.65	umc
	HO	7.95	s
	H_4, H_6, H_7	8.0–8.4	bumc

[a] s = singlet, d = doublet, q = quartet, mc = multiple complex, umc = unresolved multiple complex, bumc = broad unresolved multiple complex. All spectra were run at 60 MHz; chemical shifts are given in τ values relative to Me_4Si; approximately 10% solutions in $CDCl_3$ or CCl_4 (II and VIII).

sition (P − H_2O) to (P − H_2O − C_2H_4) were observed in the spectra of these compounds (Table IV).

The high resolution data (Table III) suggests a sequential loss P − H_2O − C_2H_5 occurring in the compounds III, VI, VII, and VIII. However, this is not substantiated by appropriate metastable ions.

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

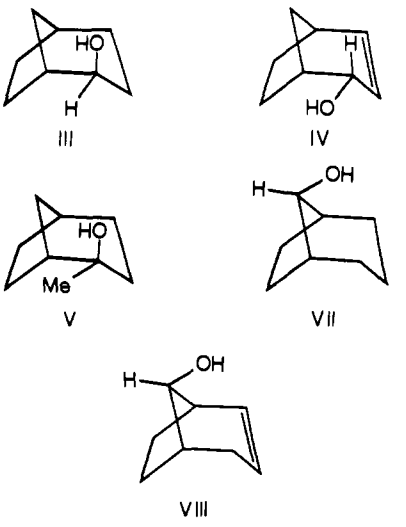

Figure 1.

The oxygenated compounds show evidence of loss of both C_2H_5 and CHO fragments. High resolution mass measurement (Table III) shows that in IV the loss of CHO vs. C_2H_5 is 1 to 4, while in VI the ratio is 2 to 1.

The compounds I, II, VII, and VIII all showed a loss of 31 mass units. It is evident that this is a concerted loss of H_2 and 29 mass units. In the case of the hydrocarbons I and II it is obviously a loss of H_2 and C_2H_5. In the oxygenated compounds high resolution (Table III) shows that it is exclusively a loss of H_2 and CHO.

A loss of a 15 mass unit is shown by the compounds I, II, IV, and V. It is not shown by the 8-hydroxy compounds. It may be noted that there is a similar loss of 15 mass units occurring in the analogous bicyclononanes (*5*).

As in the case of the bicyclononanes (*5*) the loss of an OH unit is not characteristic of this series, being shown only the *exo*-2-ene (IV).

The NMR spectra reported (Table V) appeared mainly as unresolved multiplets. However, certain structural features of the molecules were clearly identifiable. The OH peaks appeared as singlets and were identified using deuterium oxide. Configurations where known are shown in Figure 1.

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