An Electron-Impact Study of Norbornane Derivatives[1]

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The principal peaks in the mass spectra of a variety of norbornane derivatives are discussed. The 2-norbornanol derivatives lose carbon atoms 2 and 3 (as the enol form of an aldehyde or ketone), along with a hydrogen atom or methyl radical at C-1 or C-7, to give a cyclopentenyl ion. Depending upon substitution at C-1 and C-4-7, this ion will appear as a strong peak at either *m/e* 67, 81, 95, or 109. The fragmentation trends observed for the alcohols can be extended to include a large variety of other norbornane derivatives.

Our need for a method to help elucidate the structures of bicyclic terpenes related to and derived from the camphene sultones[3] has led us to undertake a comprehensive mass spectral study of norbornane derivatives. The conclusions derived from analysis of a large variety of methyl substituted bicyclic alcohols (Table I) should find application to other bicyclo[2.2.1]heptane derivatives (Table II).

Except for the recent studies with camphor[4,5] and isoborneol,[5] the spectra of bicyclic terpenes have been presented with relatively little discussion of the origin of their major peaks.[6-11] The reason for this is the unusually complicated fragmentation reactions that occur upon electron-impact of these molecules, which are so prone to undergo carbonium ion or free-radical rearrangements.

The studies with $\Delta^{4(8)}$-menthene,[4] camphor,[4,5] and isoborneol[5] have shown the importance of employing extensive deuterium labeling in drawing precise conclusions regarding fragmentation pathways. Con-

Table I

The Important Peaks in the Mass Spectra of 2-Norbornanols[a]

		m/e (% of base peak)									
Compound[b]	Registry No.	Parent	Base	2nd	3rd	4th	5th	6th	7th	8th	9th
2,3,3-*exo*		154 (5)	43	71 (88)	41 (61)	69 (43)	28 (43)	86 (36)	93 (34)	96 (33)	39 (32)
2,3,3-*endo*	1342-57-7	154 (5)	43	71 (91)	41 (48)	69 (40)	28 (41)	86 (35)	96 (32)	84 (25)	67 (23)
1,7,7-*exo*		154 (2)	95	41 (38)	43 (24)	55 (22)	110 (22)	93 (20)	39 (17)	28 (17)	67 (16)
1,7,7-*endo*	507-70-0	154 (2)	95	41 (30)	110 (25)	43 (18)	55 (16)	39 (13)	27 (12)	67 (11)	29 (11)
1,3,3-*endo*	512-13-0	154 (5)	81	80 (69)	41 (51)	43 (45)	29 (44)	95 (37)	69 (32)	55 (31)	67 (28)
3,3,4-*exo*	13144-40-6	154 (9)	41	43 (90)	93 (80)	55 (72)	57 (71)	81 (68)	84 (66)	82 (64)	39 (61)
3,3,4-*endo*	13144-44-0	154 (15)	41	43 (80)	55 (71)	93 (68)	81 (65)	57 (65)	84 (60)	83 (57)	82 (54)
1,4,7,7-*exo*	3588-29-2	168 (4)	109	41 (55)	43 (33)	55 (32)	124 (27)	107 (25)	39 (24)	84 (23)	135 (21)
3,3-*endo*	13429-63-5	140 (24)	41	57 (95)	69 (79)	43 (58)	39 (53)	55 (50)	67 (47)	84 (46)	107 (43)
1,2-*exo*		140 (2)	43	80 (87)	122 (70)	81 (69)	41 (56)	28 (55)	107 (51)	67 (49)	39 (37)
1,2-*endo*		140 (4)	43	80 (80)	81 (73)	122 (66)	107 (54)	67 (50)	41 (44)	39 (36)	55 (35)
2-*exo*		126 (10)	43	59 (74)	58 (4)	71 (45)	67 (37)	41 (35)	39 (33)	66 (31)	83 (27)
2-*endo*		126 (13)	43	59 (74)	58 (44)	71 (45)	67 (37)	41 (35)	39 (31)	66 (28)	83 (26)
4-*exo*		126 (7)	81	67 (63)	41 (53)	93 (43)	80 (43)	39 (42)	108 (37)	55 (31)	27 (31)
exo	497-37-0	112 (3)	94	67 (82)	79 (78)	66 (78)	68 (66)	39 (57)	41 (57)	27 (39)	57 (35)
endo	497-36-9	112 (3)	94	67 (81)	79 (80)	66 (74)	68 (64)	39 (55)	41 (55)	27 (37)	57 (35)

[a] Tables I and II show the ranking of the peaks in each spectra. [b] The numbers refer to positions occupied by methyl groups and the *exo* or *endo* refers to the position of the 2-hydroxyl group relative to the bridgehead methylene.

Table II

The Important Peaks in the Mass Spectra of Some Norbornane Derivatives[a]

		m/e (% of base peak)						
Compound[b]	Parent	Base	2nd	3rd	4th	5th	6th	7th
Camphene	136	93	121 (60)	41 (43)	79 (36)	39 (35)	67 (27)	91 (27)
Sultone **32**	216	43	67 (100)	148 (64)	66 (63)	41 (58)	109 (54)	84 (46)
Bornyl bromide	218 216	81	137 (96)	95 (60)	69 (29)	41 (25)	39 (15)	136 (15)
3-Methyl-3-propyl-2-norbornanone	166	55	97 (80)	67 (63)	41 (46)	96 (30)	124 (27)	39 (27)
3-Oxocamphor	166	95	83 (61)	41 (55)	69 (53)	55 (47)	39 (32)	138 (23)
Bromo lactone **12**	234 232	109	41 (67)	125 (65)	93 (40)	39 (28)	67 (27)	91 (27)
Bromo anhydride **9**	262 260	137	69 (60)	41 (43)	39 (24)	94 (16)	175 (15)	173 (15)
Acid lactone **2**	198	41	109 (94)	83 (83)	55 (67)	39 (59)	139 (51)	170 (43)
9-Hydroxycamphor	168	95	41 (46)	108 (42)	43 (38)	39 (32)	67 (28)	109 (27)
8-Hydroxycamphor-8,8-d_2	170	109	95 (44)	94 (36)	41 (35)	110 (26)	39 (25)	27 (19)
Diacid **21**	200	95	41 (62)	83 (48)	55 (47)	138 (41)	39 (32)	67 (22)

[a] See footnote *a*, Table I. [b] Refer to text for the exact structures.

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(1) Abstracted from part of the thesis submitted by D. R. D. in partial fulfillment of the requirements for the Ph.D. degree, Purdue University, Aug 1966.

(2) National Institutes of Health Predoctoral Fellow, 1964–1966.

(3) J. Wolinsky, D. R. Dimmel, and T. W. Gibson, *J. Org. Chem.*, **32**, 2087 (1967).

(4) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

(5) D. Dimmel and J. Wolinsky, *ibid.*, **32**, 410 (1967).

(6) A. F. Thomas and B. Willhalm, *Helv. Chim. Acta*, **47**, 475 (1964).

(7) R. Ryhage and E. von Sydow, *Acta Chem. Scand.*, **17**, 2025 (1963).

(8) E. von Sydow, *ibid.*, **17**, 2504 (1963).

(9) (a) E. von Sydow, *ibid.*, **18**, 1099 (1964); (b) *ibid.*, **18**, 1791 (1964).

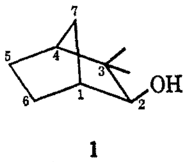
(10) B. Willhalm, A. F. Thomas, and M. Stoll, *ibid.*, **18**, 1573 (1964).

(11) A. F. Thomas and B. Willhalm, *J. Chem. Soc.*, 219 (1966).

sequently, the following discussion is not intended to be definitive and will only concern itself with the qualitative interpretation of the major fragmentation trends observed in over 50 compounds.

exo-endo **Isomers.**—A comparison of the spectra of six pairs of *exo* and *endo* alcohols shows that it is difficult to distinguish between the two isomers.[12] Biemann[13] claims that a distinction can be made by comparing the relative intensities of the very weak parent peaks and the M − 18 peak. From a practical standpoint, we find that this type of comparison should be used with a great deal of caution.

The *m/e* **41 Peak.**—All norbornane derivatives exhibit a *m/e* 41 peak. Although there are many sources for the $C_3H_5^+$ ion, the presence of a *gem*-dimethyl group greatly enhances the relative abundance of this fragment. For instance, the *m/e* 41 fragment is the base peak in the spectra of camphenilol (**1**) and the acid lactone **2**.[14] It is the second or third most abundant peak in the spectra of isoborneol (**3**), camphor (**4**), camphene hydrate (**5**), fenchyl alcohol (**6**), 4-methylisoborneol (**7**),[3] 3-oxocamphor (**8**),[14] and the bromo acid anhydride **9**.[14]



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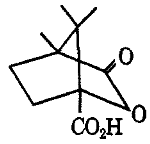

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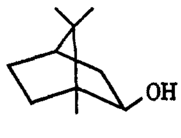

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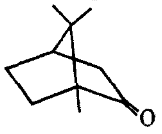

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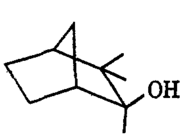

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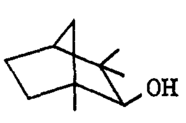

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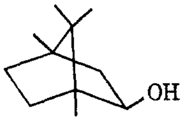

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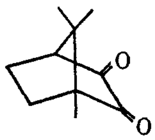

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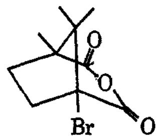

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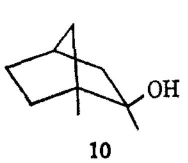
The *m/e* **43 Peak.**—Except in one case, all of the compounds possessing a CH_3CO grouping showed a base peak of *m/e* 43, attributed to an acylium ion. For example, camphene hydrate (**5**), 1,2-dimethyl-2-norbornanol (**10**), and 2-methyl-2-norbornanol (**11**) all show base peaks of *m/e* 43. The lone exception, the bromo lactone **12**,[14] shows the *m/e* 43 peak as the second most abundant to the base peak at *m/e* 109 (M − CO_2 and Br·). A high-resolution mass spectrum of camphene hydrate (low-resolution spectrum, Figure 1) indicated that its *m/e* 41 peak was hydrocarbon, while its *m/e* 43 was 80% $C_2H_3O^+$ ions and 20% $C_3H_7^+$ ions. In summary, although the *m/e* 43 peak is found in the spectra of most of the norbornane derivatives, only in those cases where it is base peak or stronger than the *m/e* 41 peak can one conclude that there is a CH_3CO moiety present.



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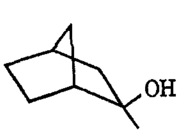

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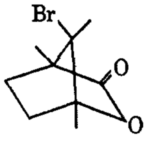

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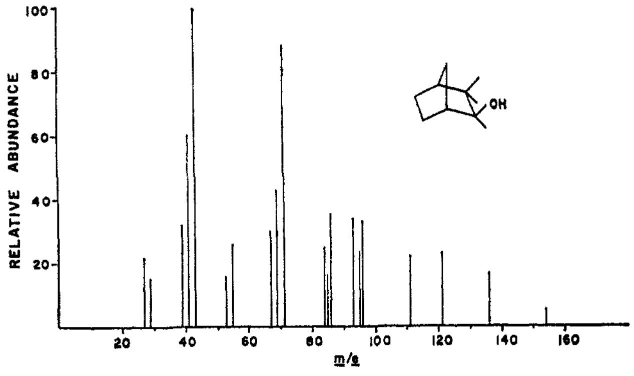


Figure 1.—The mass spectrum of camphene hydrate.

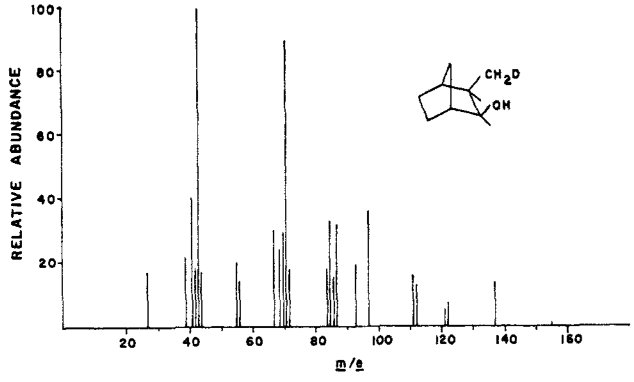
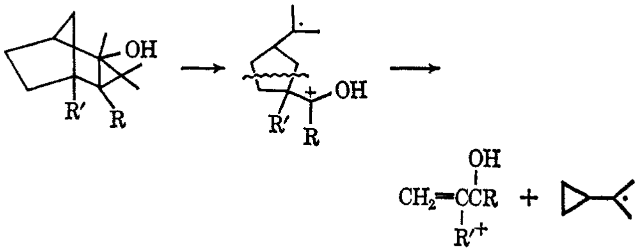


Figure 2.—The mass spectrum of camphene hydrate-9-*d*.

The *m/e* **57 and 71 Peaks.**—Compounds containing *gem*-dimethyl groups in the 3 position fragment to yield abundant *m/e* 57 or 71 peaks, depending on the methyl substitution at C-1 and C-2. The *m/e* 71 peak does not shift (Figures 1 and 2) when camphene hydrate is deuterated in the 9 position (**13**),[15] indicating that the *gem*-dimethyl groups do not contribute to this fragment. This type of breakdown pattern (Scheme I) appears to be analogous to the manner in which camphor fragments to the *m/e* 69 ion.[5]

SCHEME I
FRAGMENTATION OF 2-NORBORNANOLS TO *m/e* 57 AND 71



	m/e
R = R′ = H	57
R = H; R′ = CH_3	71
R = CH_3; R′ = H	71

Fenchyl alcohol (**6**) shows a somewhat weak (tenth most abundant) *m/e* 71 peak, suggesting that α cleavage of the C-1,2 bond overrides cleavage of the C-2,3 bond. Thus, apparently this type of cleavage will

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[12] For an example, see ref 5.

[13] K. Biemann and J. Seibl, *J. Am. Chem. Soc.*, **81**, 3149 (1959).

[14] We are grateful to Dr. W. Meyer and to Dr. A. Lobo of the University of Arkansas for a sample of this compound.

[15] The deuterated derivative was obtained[4] by lithium aluminum deuteride desulfurization of camphene sultone (**32**).

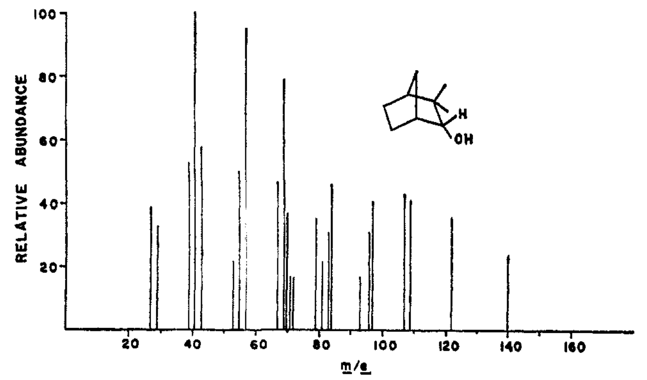
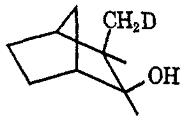


Figure 3.—The mass spectrum of camphenilol (3,3-dimethyl-*exo*-2-norbornanol).

only be of major importance for those compounds containing a greater degree of substitution at C-3 compared to C-1. Further support for this general fission reaction is shown in the spectrum of camphenilol (Figure 3), which shows an abundant *m/e* 57 peak, 2-ethylcamphenilol (**14**), an intense *m/e* 85 peak, and 3-methyl-3-propyl-2-norbornanone (**15**), which exhibits a base peak at *m/e* 55.



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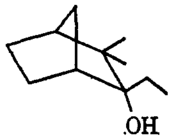

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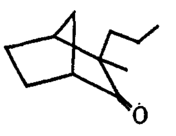

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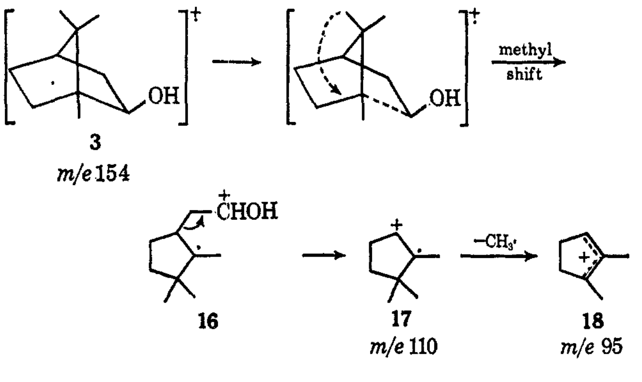
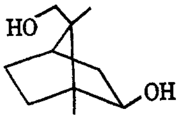
The *m/e* 67, 81, 95, and 109 Peaks.—It has been suggested that the *m/e* 95 peak of isoborneol (**3**) arises by means of the fragmentation shown in Scheme II.[5] In general there appears to be a strong tendency for the 2-norbornyl *alcohols* and *ketones* to fragment to a cyclopentenyl ion similar to **18**. The loss of C-2 and C-3 has been suggested by Thomas[6] and von Sydow[8] to explain the breakdown of fenchane and fenchol.

SCHEME II
FRAGMENTATION OF ISOBORNEOL TO *m/e* 95



Besides the borneols, other trisubstituted derivatives, such as camphor (**4**),[4,5] 9-hydroxyisoborneol (**19**),[14] 9-hydroxycamphor (**20**), and 3-oxocamphor (**8**) show base peaks of *m/e* 95. The dicarboxylic acid **21**[14] also gives a base peak of *m/e* 95, while bornyl bromide **22** shows a substantial *m/e* 95 peak. In each of these cases, one can imagine initial cleavage of the C-1,2 bond, followed by loss of carbons 2 and 3 and a methyl (or hydroxymethyl) group. The *m/e* 109 peak is base peak in the spectra of tetrasubstituted derivatives such as 4-methylisoborneol (**7**) and the bromo lactone **12** and is second largest for the acid lactone **2**. This fragment would correspond to the trimethylcyclopentenyl ion **23**.



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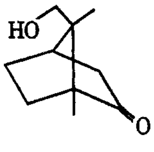

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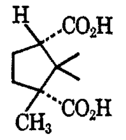

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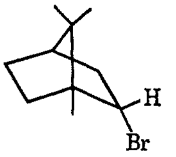

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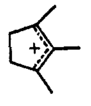

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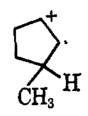

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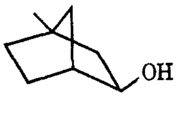

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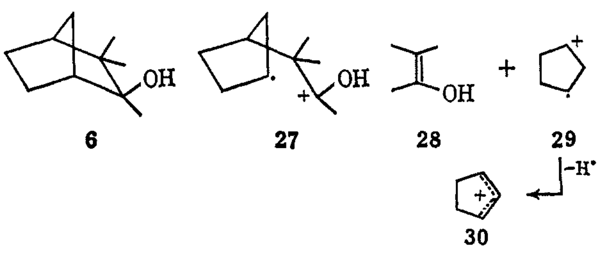
Norbornane derivatives monomethylated in the 1 or 4–7 positions show an intense *m/e* 81 peak corresponding to the cyclopentenyl ion **25**. Thus, fenchyl alcohol (**6**) and 4-methyl-2-norbornanol (**26**) show base peaks at *m/e* 81, whereas 1,2-dimethyl-2-norbornanol (**10**) shows a relatively intense *m/e* 81 peak. In order to obtain a better estimate of the importance of the fission leading to this fragment, it is necessary to include the *m/e* 67 peak, which could arise by loss of a methyl group, instead of a hydrogen atom, from the intermediate ion **24**. The *m/e* 67 peak is of major importance in the spectra of alcohols **7**, **31**, **11**, and **2**. The combination of *m/e* 67 and 81 peaks would represent base peak in each of these spectra and is taken as evidence for the favorable formation of a cyclopentenyl ion.

If there are no methyl groups attached to the 1 and 4–7 position, the unsubstituted cyclopentenyl ion, *m/e* 67, is found (Scheme III). The intensity of this fragment varies because, in the absence of a C-1 substituent, α cleavage at C-2,3 may be preferred to C-1,2 bond breaking. The relative abundance of the *m/e* 67 ion in compounds which fall into this category are camphene hydrate (**5**) eighth, camphenilol (**1**) seventh, 2-methyl-2-norbornanol (**1**) fifth, and 2-norbornanol (**31**) second.

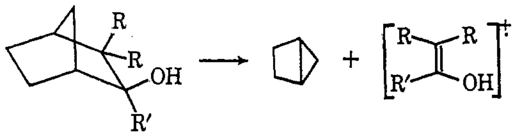
SCHEME III
FRAGMENTATION OF CAMPHENE HYDRATE TO *m/e* 67



In summary, a strong *m/e* 109 peak would mean that three or four methyl groups are attached at C-1 or -4–7. An intense *m/e* 95 peak implies two or three methyl groups at C-1 or 4–7. A *m/e* 81 peak indicates only one methyl group at C-1 or 4–7, whereas the absence of the *m/e* 109, 95, and 81 peaks and the presence of a substantial *m/e* 67 peak suggests the absence of substituents at these positions. A note of caution should be extended when applying these conclusions to norbornane derivatives possessing strong fragmentation-directing group; for instance, the bromo anhydride **9** shows a very weak *m/e* 109 peak.

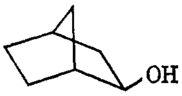
We now turn to the neutral fragment, containing carbons 2 and 3, which is sometimes ejected as an ion (Scheme IV) and can appear either as a weak or strong peak, depending upon the particular compound in question. The enol form of acetaldehyde, *m/e* 44 peak, does not appear as a positive ion in the spectra of isoborneol and its derivatives. This should be contrasted to the enol of acetone which appears as an intense peak (55 and 33% relative abundance) in the spectra of 2-methyl-2-norbornanol (**11**) and 1,2-dimethyl-2-norbornanol (**10**). The *m/e* 86 peak is of major importance in the spectrum (Figure 1) of camphene hydrate (**5**) and would correspond to the ionized form of **28**. This peak shifts one unit in the 9-d_1 analog of camphene hydrate (Figure 2). In comparison with the other fragments, the *m/e* 72 peak is rather weak (approximately 20% of base) in the spectra of camphenilol (Figure 3) and fenchyl alcohol (**6**).

SCHEME IV



	m/e
R = R' = H	44
R = H; R' = CH_3	58
R = CH_3; R' = H	72
R = R' = CH_3	86

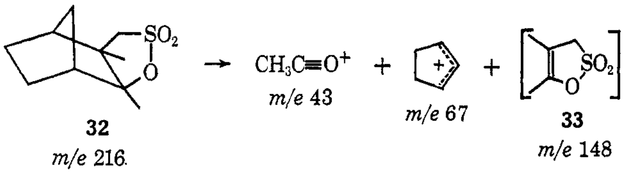
The M − 18 Peak.—The peak due to loss of water from these alcohols becomes increasingly more abundant as the number of methyl substituents decreases. For example, 2-norbornanol (**31**) exhibits a base peak at *m/e* 94, corresponding to loss of water. Consequently, without methyl groups to direct fragmentation, loss of water predominates. In addition to increasing amounts of water elimination, the spectrum becomes more and more dominated by fragmentations characteristic of the dehydration product.



31

Applications

In this section, specific examples of the use of the generalizations just described are cited. An especially straightforward case is that of camphene sultone (**32**),[16]



whose three most abundant fragments are *m/e* 43, 67, and 148. The strength of these peaks allow the assignment of a CH_3CO grouping, a norbornyl ring unsubstituted at C-1 and -4–7, and the ion **33**.

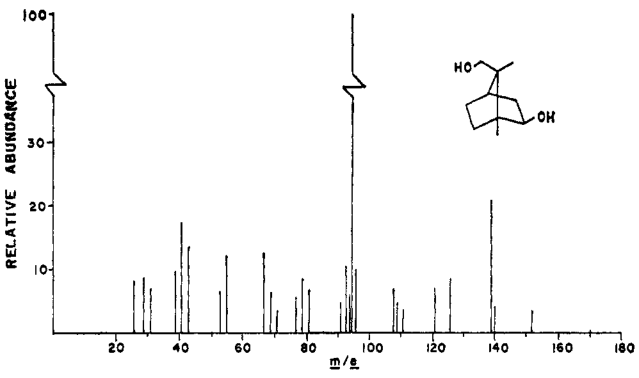
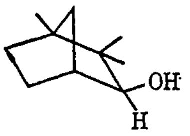


Figure 4.—The mass spectrum of 9-hydroxyisoborneol.

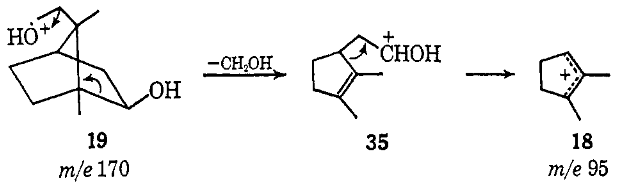
In connection with work in this laboratory, an unknown bicyclic alcohol was obtained by desulfurization of a sultone.[3] Its mass spectrum showed a base peak of *m/e* 41 and an abundant *m/e* 57 fragment. These peaks suggest a 3,3-dimethyl-2-norbornanol derivative and the absence of a methyl group at C-1, which would have displayed a *m/e* 71 peak instead of the observed *m/e* 57 peak. Abundant *m/e* 81 and 67 peaks placed the other methyl group at C-4–7 and, since the three methyl groups were observed as singlets in the nmr spectrum of the alcohol, the third methyl group could be assigned unambiguously to the 4 position. Thus, the compound must be 4-methylcamphenilol (**34**). A synthesis of 4-methylcamphenilol demonstrated the correctness of this spectral assignment.[3]



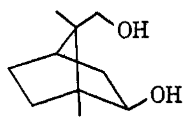
34

The mass spectrum (Figure 4) of 9-hydroxyisoborneol (**19**)[14] is dominated by a *m/e* 95 peak. This peak does not shift in the 9,9-d_2 analog,[14] demonstrating that the C-9 carbon atom is quantitatively lost during the formation of the cyclopentenyl ion **18**. The ion **18** could arise in a manner similar to that shown by isoborneol (Scheme II) or, alternately, by a reverse Prins-type reaction (Scheme V).

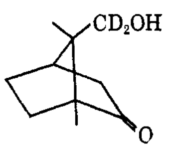
SCHEME V
FRAGMENTATION OF 9-HYDROXYISOBORNEOL TO *m/e* 95



The spectrum (Figure 5) of 8-hydroxyisoborneol (**36**)[14] shows dual base peaks of *m/e* 95 and 108 ($C_8H_{12}^+$) and many supporting fragments with a relative abundance > 40%. Clearly the fragmenta-



36



37

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(16) The exact stereochemistry of this compound has been established by independent means.[3]

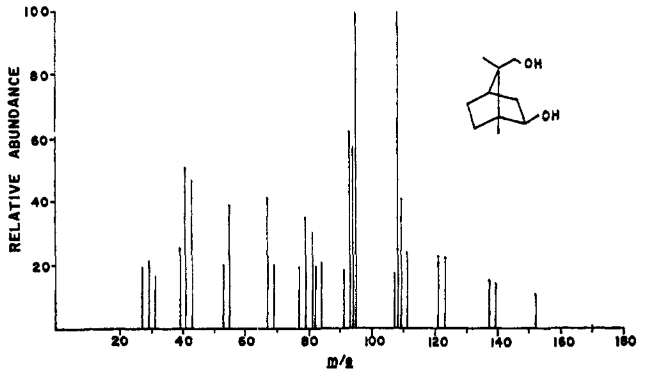

Figure 5.—The mass spectrum of 8-hydroxyisoborneol.

tion of this compound is not dominated by fission to the *m/e* 95 peak as was the case of 9-hydroxyisoborneol. These observations are remarkably similar to the selective elimination of the C-9 *vs.* the C-8 methyl group of isoborneol.[5] The corresponding camphor derivatives show a similar phenomenon; 9-hydroxycamphor (**20**) displays a base peak of *m/e* 95 and a *m/e* 108 ion of 42%, while 8-hydroxycamphor-8,8-d_2 (**37**)[14] exhibits a base peak of *m/e* 109 and a *m/e* 95 ion of 54% abundance.

Conclusions

A comparison of the mass spectra of many different norbornane derivatives points out the importance of several trends.

1. A very large *m/e* 41 peak suggests the presence of a *gem*-dimethyl group.
2. A base peak of *m/e* 43 correlates with the presence of a CH_3CO moiety.
3. Abundant peaks at *m/e* 57 and 71 indicate a 3,3-dimethyl-2-norbornanol derivative (peaks at *m/e* 55 and 69 for the norbornanone case).
4. The number of methyl groups attached to carbons 1 and 4–7 can be determined by their respective *m/e* peaks: *m/e* 109, three or four[17] methyl groups; 95, two or three;[17] 81 (with 67), one; 67 (with no 109, 95, or 81), zero.
5. The presence of a substantial peak at *m/e* 58, 72, or 86, taken together with the above conclusions, demonstrates the number of methyl groups at C-2 and C-3.

When used in conjunction with other spectral tools, mass spectrometry provides a powerful method for establishing the structures of norbornyl ketones and alcohols. In the absence of other strong fragmentation-directing groups, these conclusions should find application to other norbornane derivatives.

Experimental Section[18]

2-Norbornanols.—Samples of alcohols **5**,[19] **10**,[20] **11**,[19] **26**,[21] and **31**[19] and their corresponding *endo* isomers were supplied to us by Dr. H. C. Brown of Purdue University. Isoborneol, borneol, fenchyl alcohol,[22] and camphenilol[22] were readily available. The *exo*- and *endo*-4-methylcamphenilols, 4-methylisoborneol, and camphene hydrate-9-d_1 were obtained in connection with other work in this laboratory.[3] The purity of most of these compounds was checked by vapor phase chromatography using 150-ft capillary columns.

Norbornane Derivatives.—Samples of **2**, **8**, **9**, **12**, **19**, **20**, **21**, **36**, and **37** were supplied to us by Meyer[23] of the University of Arkansas. Camphene sultone (**32**) and 3-methyl-3-propyl-2-norbornanone (**15**) were obtained in connection with other work in this laboratory.[3] Bornyl bromide (**27**)[24] was prepared by Dr. Robert Novak.

Registry No.—**1**, 5957-68-6; **2**, 13429-83-9; **3**, 124-76-5; **5**, 13429-40-8; **6**, 470-08-6; **8**, 465-29-2; **9**, 13441-28-6; *exo* **10**, 13429-43-1; *endo* **10**, 13429-45-3; *exo* **11**, 6197-16-6; *endo* **11**, 6196-84-5; **12**, 13444-33-2; **13**, 13429-47-5; **14**, 13429-48-6; **15**, 13296-20-3; **19**, 13429-50-0; **20**, 3751-95-9; **21**, 10334-27-7; **22**, 13429-53-3; *exo* **26**, 13429-54-5; **32**, 13131-58-3; **37**, 13429-56-6; camphene, 79-92-5; 8-hydroxyisoborneol, 1925-38-8.

Acknowledgments.—We wish to thank Dr. F. W. McLafferty and his co-workers, Mr. C. Smith and Mr. J. Bantjes, for making it possible to obtain the mass spectra. We are indebted to Dr. W. Meyer and Dr. A. Lobo for their gift of the various 8- and 9-substituted norbornane derivatives and to Dr. H. C. Brown and colleagues for their samples of bicyclic alcohols.

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(17) Depending upon disubstitution at C-7.

(18) The mass spectra were recorded on two Hitachi mass spectrometers, Models RMU-6A and RMU-6D. The all glass inlet system was heated to 185°, the source temperature was 160°, and the ionizing energy was maintained at 75 ev.

(19) H. C. Brown, F. J. Chloupek, and M. H. Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

(20) H. C. Brown and M. H. Rei, *ibid.*, **86**, 5004 (1964).

(21) P. Von R. Schleyer, unpublished results.

(22) H. C. Brown and H. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).

(23) W. Meyer and A. Lobo, *ibid.*, **88**, 3181 (1966).

(24) I. L. Kondakow and S. Saprikin, *Bull. Soc. Chim. France*, (4), **37**, 735 (1925).