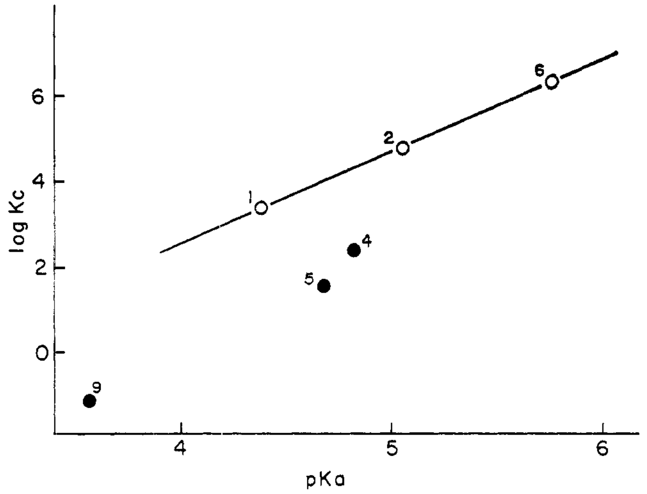

Figure 2.—Plot of pK_a (in 50% aqueous ethanol) of pyridines *vs.* log K for methanol–pyridine complexes. Based on data in Table I.

values[18] and the values of $\Delta\nu$ shows a reasonable linear correlation. In this sort of a relationship steric effects would not be expected except in exceptional circumstances, *e.g.*, the reaction between *t*-butyl alcohol and 2,6-di-*t*-butylpyridine. There is, however, definite evidence for steric effects in certain of these systems. We attribute the quantitative differences between 2,6-lutidine and 2,6-diisopropylpyridine to steric hindrance. It is suggested that the decreased $-\Delta S$ of complexion for the 2,6-lutidine system reflects an increased electron density at the nitrogen atom resulting from the (+I) inductive effect of the methyl groups and that the increased steric requirements of 2,6-diisopropylpyridine lead to steric strains in the complex and cause the $-\Delta S$ to be large. Observations with molecular models bear out this suggestion of strain. However, it is more profitable to compare the equilibrium constants at 25° in order to demonstrate trends in inductive and steric effects. From such a comparison it appears that hydrogen bonding ability is determined by a synthesis of the electronic and steric effects in a given system. In Figure 2, the values of log K_c are plotted against pK_a for the pyridines in 50% aqueous ethanol solution. The points for pyridine, 2-picoline and 2,6-lutidine describe a straight line. This is in agreement with the proposal[19] that the pK_a of organic bases is correlatable with hydrogen-bonding ability when the bases are closely related in structure. The data indicate that the effects of methyl groups in the 2 and 2,6 positions on basicity and hydrogen bonding ability are largely electronic in nature. It is seen from Figure 2 that introduction of other alkyl groups at these same positions results in points which clearly depart from the relation and demonstrate that some other factor governs the degree of association in these cases. We suggest this to be steric hindrance.

Acknowledgment.—It is a pleasure to acknowledge Dr. Reisuke Soda and Miss Charlotte M. Schmidt for their help and valuable discussions.

(18) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953).

(19) (a) M. Tamres, S. Searles, E. M. Leighly, and D. M. Mohrman, *ibid.*, **76**, 3983 (1954); (b) A. Halleux, *Bull. Soc. Chim. Belges*, **63**, 381 (1959).

Preferential Methyl Eliminations in Camphor and Isoborneol on Electron Impact[1]

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Received August 26, 1966

The mass spectra of isoborneol and camphor were studied by the deuterium-labeling technique. The base peak in these compounds (*m/e* 95) corresponds to a dimethylcyclopentenyl ion (**5**) and arises from loss of carbon atoms 2 and 3, together with a selective loss of the C-9 and C-10 methyl groups. The mechanism of this fragmentation is discussed in terms of a preferred *trans*-methyl migration to an adjacent, electron-deficient carbon atom. The C-8 and C-9 methyl groups are lost more frequently than the C-10 methyl group when isoborneol fragments to *m/e* 139 and 121 ions. The origin of the other principal fission products is also discussed.

Until recently very little has been published on the mass spectra of bicyclic terpenes. In most cases the spectra have been presented with little or no discussion of the origin of the major peaks.[3–6] 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 single attempt[7] to explain the breakdown of camphor upon electron impact could not be substantiated by deuterium-labeling experiments.[8] Our need for a method to help elucidate the structures of bicyclic terpenes related to and derived from the camphene sultones[9] led us to undertake a detailed mass spectral analysis of camphor (**1**) and isoborneol (**31**). The results reported herein further point out[8] the importance of employing extensive deuterium labeling in gaining an understanding of the fission reactions of these compounds.

Camphor.—Weinberg and Djerassi[8] have reported the mass spectra of camphor and its 3,3-d_2 and 10-d_1 analogs. Their conclusions regarding the fragmentation reactions of camphor are reproduced in Scheme I. They have also shown that the *m/e* 110, 109, 108, 95, 83, and 81 peaks are composed of hydrocarbon ions.

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

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

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

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

(5) (a) E. von Sydow, *ibid.*, **17**, 2504 (1963); (b) *ibid.*, **18**, 1099 (1964); (c) *ibid.*, **18**, 1791 (1964).

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

(7) (a) R. I. Reed, "Ion Production by Electron Impact," Academic Press Inc., New York, N. Y., 1962, pp 204–206; (b) R. I. Reed, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 13.

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

(9) J. Wolinsky, D. R. Dimmel, and T. W. Gibson, "The Chemistry of Camphene Sultones," to be published.

Scheme I
Fragmentation Reactions of Camphor

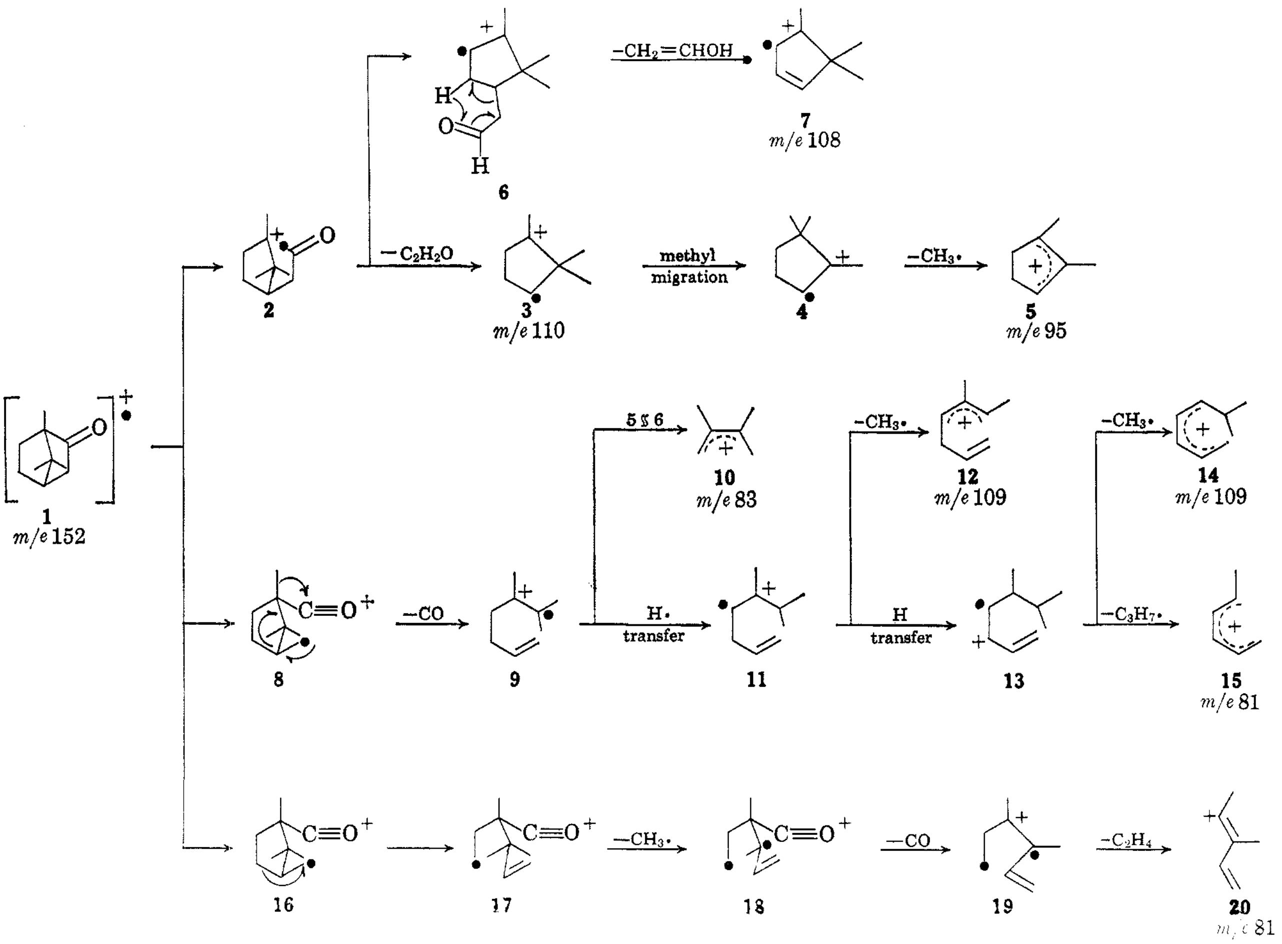
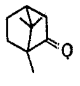
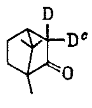
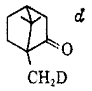
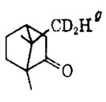
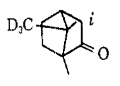


Table I
Principal Mass Spectra Peaks of Camphor and Its Deuterated Analogs[a]

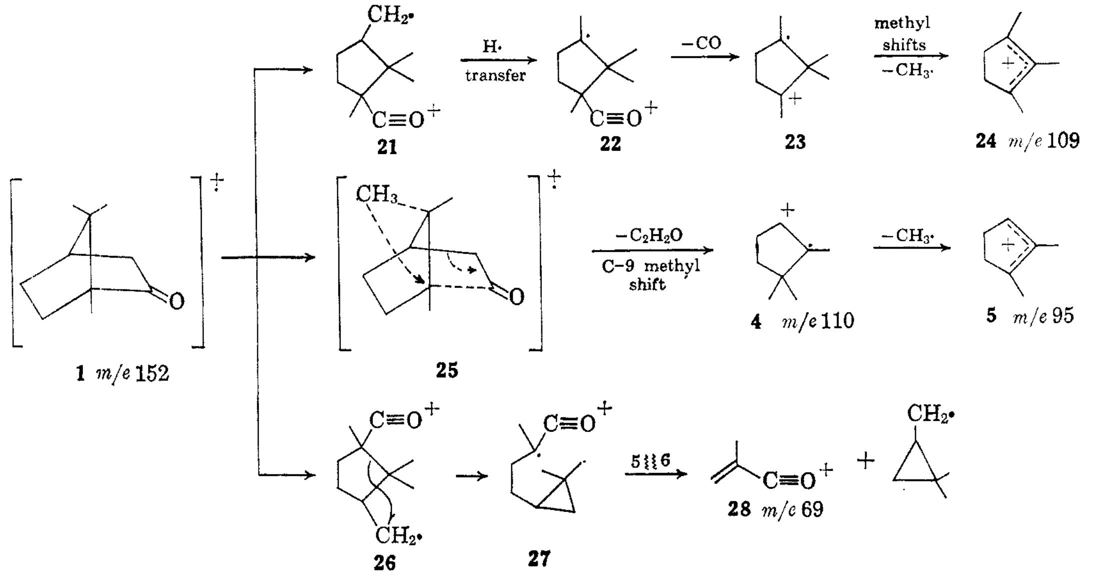
Compound	m/e (% shift)							
	M − 15	M − 42	M − 43	M − 44	M − 57[b]	M − 69	M − 71	M − 83
	137	110	109	108	95	83	81	69
 [c]	139 (q)	110 (q)	109 (25) 111 (75)	108 (q)	95 (q)	83 (q)	83 (80)	69 (q)
 [d]	137 (40) 138 (60)	111 (q)	109 (31)[e] 110 (69)	109 (q)	95 (50) 96 (50)[f]	84 (q)	82 (q)	70 (q)
 [g]	137 (31) 139 (69)	112 (q)	109 (35) 111 (65)	110 (q)	95 (23)[h] 97 (77)	85 (q)	81 (q)	69 (q)
 [i]	137 (41) 140 (59)	113 (q)	109 (32) 112 (68)	111 (q)	95 (37) 98 (63)	86 (q)	81 (q)	69 (q)

[a] Tables I and II show the per cent shift of the compounds discussed when specifically labeled with deuterium. The symbol q refers to a quantitative transfer (*i.e.*, 95%). [b] See Table III for relative abundance of m/e 92–99 ions in the spectra of camphor and its deuterated analogs. [c] 95.5% D_2. [d] 88.8% D. [e] Estimated by subtracting the amount of m/e 108 that shifts to m/e 109. [f] Corrected for the M + 1 peak of the m/e 95 peak. [g] 96.6% D_2. [h] Corrected for some m/e 93 peak shifting to m/e 95. [i] 99% D_3.

Our examination of camphor-8,8-d_2 and camphor-9,9,9-d_3 substantiate many of the conclusions of these workers, and provide sufficient new information to warrant further discussion. The principal mass spectral fragmentation peaks of camphor and its deuterated analogs, as determined in our laboratory, are listed in Table I. Our spectrum of camphor compares favorably with that published by Weinberg and Djerassi.[8]

Camphor-3,3-d_2 was prepared in the manner reported by Weinberg and Djerassi.[8] The 10-d_1 species was

SCHEME II
FURTHER FRAGMENTATION REACTIONS OF CAMPHOR

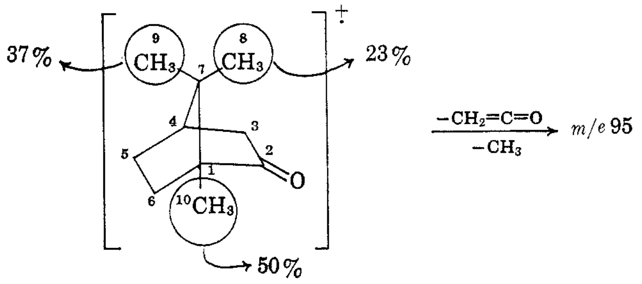


prepared by reductive desulfurization of 10-camphorsulfonyl chloride with lithium aluminum deuteride to a mixture of borneol-2,10-d_2 and isoborneol-2,10-d_2,[10] which was then oxidized to camphor-10-d_1. Camphor-8,8-d_2 was synthesized from 8-hydroxycamphor-8,8-d_2[11] by (a) conversion into the 8-bromo compound[12] and (b) catalytic hydrogenation to remove the bromine atom.[12] A sample of camphor-9,9,9-d_3 was kindly supplied by Dr. W. Meyer.[13]

Our data verify that the methyl groups of camphor are lost statistically from the molecular ion to give the *m/e* 137 peak. Our labeling shows that both methyl groups at C-7 are lost during the formation of the *m/e* 81 ion, and requires that this fragment, now assigned to the ion **15**, be formed by the scheme **8** → **9** → **11** → **13** → **15**. The alternate pathway (**16** → **20**) to the *m/e* 81 fragment need no longer be considered. The retention of the *gem*-dimethyl group in the breakdown of camphor to the *m/e* 110, 108, and 83 ions is in accordance with Djerassi's conclusions regarding the formation of these peaks.

Uncertainty still surrounds the *m/e* 109 peak, which corresponds to loss of carbon monoxide and a methyl group from camphor. In addition to a statistical loss of the methyl groups, the C-3 carbon is also lost part of the time.[14] An alternative side pathway (**21** → **24**), involving elimination of carbon 3, should therefore be considered (Scheme II).

The base peak (*m/e* 95) corresponds to an ion produced by the loss of ketene and a methyl group. The variation of the *m/e* 95 peak with deuteration presents some interesting data concerning methyl fragmentations. The various methyl cleavages (given in percentages) which occur during the formation of the *m/e* 95 fragment are shown in A.[15]



A

The observed 50% loss of the C-10 methyl group requires the breaking of two bonds at C-1. The loss of a methyl radical or carbon monoxide from a positively charged site is energetically unlikely,[8] and, as a consequence, it is reasonable to assume the intervention of a methyl migration from C-7 to C-10 to produce **4**, which can then lose either methyl group at C-1 to give the stable species **5**. The preferred loss of a C-9 methyl, compared with a C-8 methyl group, can be explained in terms of a *trans* migration of the C-9 methyl group to C-1 as the C-1,2 bond breaks (**1** →→ **25**, Scheme II). Because the selectivity of this process is only 1.6 in favor of C-9 over C-8 methyl loss, the alternate pathway, **1** →→ **4** (Scheme I), may occur simultaneously.

Djerassi[8] makes no mention of the *m/e* 69 peak, third most abundant in camphor's spectrum. This peak shifts one unit in the 10-d_1 analog, but remains constant in the 3,3-d_2, 8,8-d_2, and 9,9,9-d_3 species. This suggests that the *m/e* 69 fragment is due to the four-carbon oxygenated ion **28** (Scheme II). This type of cleavage is also prominent in the spectra of many other

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(10) We have found[9] that lithium aluminum hydride will desulfurize sultones and sulfonyl chlorides.

(11) We are grateful to Dr. W. Meyer and Dr. A. Lobo of the University of Arkansas, for a sample of this compound.

(12) We wish to thank Dr. Walter Meyer for supplying us with the details for this transformation which was originally carried out by Dr. W. R. Vaughan of the University of Michigan.

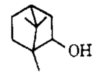
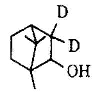
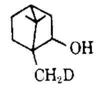
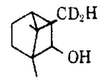
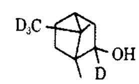
(13) W. Meyer and A. Lobo, *J. Am. Chem. Soc.*, **88**, 3181 (1966).

(14) Our figures indicate a 25% loss of C-3, while Djerassi[8] reports a 12% loss. The fact that some C-3 is lost is incompatible with the statistical loss of the methyl groups.

(15) The spectra were recorded several times and in some cases on two different mass spectrometers to give reproducible results. Consequently, the percentages are good to within ±2–3%. We are unable to explain why the percentages do not total 100%. Possibly, there is a deuterium isotope effect; or more likely, there is a residual *m/e* 95 fragment which does not shift with deuteration.

Table II

Principal Mass Spectra Peaks of Isoborneol and Its Deuterated Analogs[a]

Compound	m/e (% shift) M − 15	M − 18	M − 33	M − 44	M − 59	M − 72
	139	136	121	110	95[b]	82
	141 (q)	137 (50) 138 (50)	122 (56) 123 (44)	110 (q)	95 (q)	82 (q)
	139 (25) 140 (75)	136 (14) 137 (86)	121 (18) 122 (82)	111 (q)	95 (50)[c] 96 (50)	82 (q)
	139 (40) 141 (60)	138 (q)	121 (42) 123 (58)	112 (q)	95 (15)[d] 97 (85)	84 (q)
	140 (43)[e] 143 (57)	140 (q)	122 (46) 125 (54)	113 (q)	95 (43) 98 (57)	85 (q)

[a] See footnote *a*, Table I. [b] See Table III for per cent abundance of *m/e* 92–99 ions in the spectra of isoborneol and its deuterated analogs. [c] See footnote *f*, Table I. [d] See footnote *h*, Table I. [e] Estimated by subtracting the amount of M − 18 which also contributes to this peak.

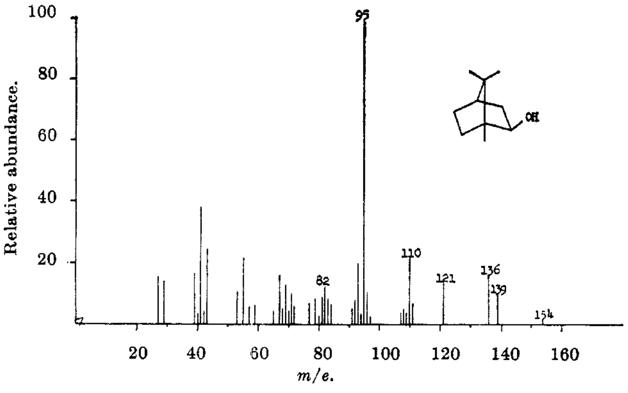


Figure 1. The mass spectrum of isoborneol.

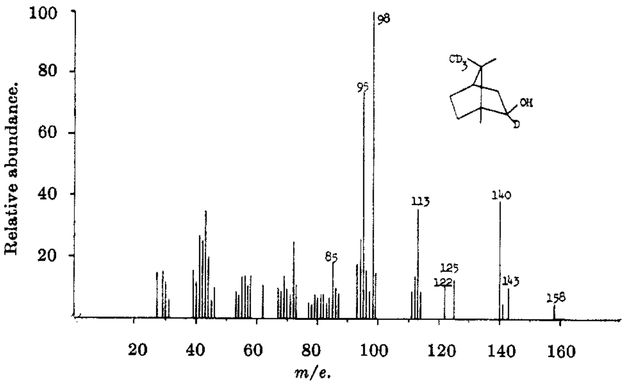


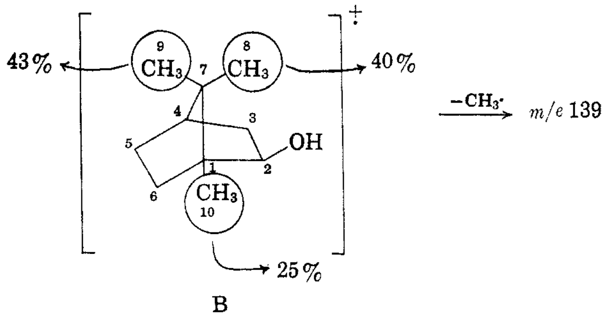
Figure 2.—The mass spectrum of isoborneol-9,9,9,2-d_4.

bicyclic ketones and alcohols.[16] The actual abundance of this peak is probably masked by the fact that it can lose carbon monoxide to give a $C_3H_5^+$ ion, *m/e* 41, as is the case with fenchone.[5b]

Isoborneol.—The deuterated isoborneol derivatives employed in this study were the 3,3-d_2, 10-d_1, 8,8-d_2, and 9,9,9,2-d_4 analogs. The spectra of isoborneol and its 9,9,9,2-d_4 derivative are reproduced in Figures 1 and 2. The principal mass spectra peaks of isoborneol and its deuterated analogs are presented in Table II.

The deuterated isoborneols were prepared by lithium aluminum hydride reduction of the corresponding deuterated camphors. The 9,9,9,2-d_4 compound was kindly donated by Dr. W. Meyer.[13] The isoborneols are contaminated with 10%[17,18] of the corresponding deuterated borneol derivatives. Since the mass spectrum of borneol (Figure 3) is nearly identical with that of isoborneol, this impurity does not lead to complications.

Unlike camphor, isoborneol does not lose a methyl group statistically from the molecular ion, but rather ejects a C-8 or C-9 methyl in preference to a C-10 methyl group. The various methyl cleavages (given in percentages) are shown in B.



B

Loss of a methyl group from the bridgehead position of an intact 2.2.1-bicyclic system should be less favorable than loss of a methyl group from one of the other positions.[19a] If the ring opened at C-1,2 simultaneously with methyl ejection, the C-10 methyl should still be largely retained. Our data suggest that either or both of these conditions apply to isoborneol.

The statistical loss of a methyl group from the molecular ion of camphor would correspond to a larger amount of C-2,3 α cleavage leading eventually to ion

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(16) J. Wolinsky and D. R. Dimmel, "An Electron Impact Study of Norbornane Derivatives," to be published.

(17) S. Beckmann and R. Mezger, *Chem. Ber.*, **89**, 2738 (1956).

(18) P. Hirsjarvi, *Ann. Acad. Sci. Fenicae Ser. A II*, **No. 81**, 16 (1957); **No. 84**, 15 (1957).

(19) K. Bieman, "Mass Spectroscopy: Organic Chemical Applications," McGraw Hill Book Co., Inc., New York, N. Y., 1962: (a) pp 136, 137; (b) p 109; (c) p 95.

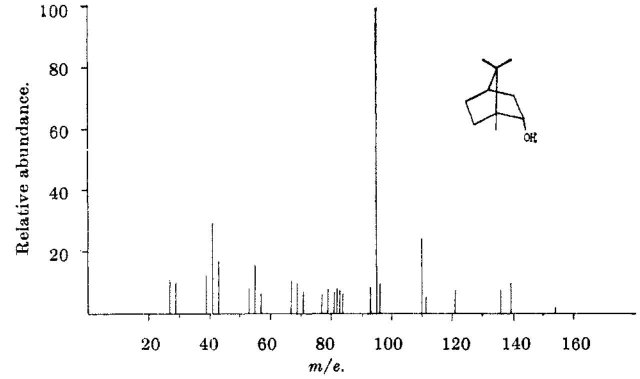
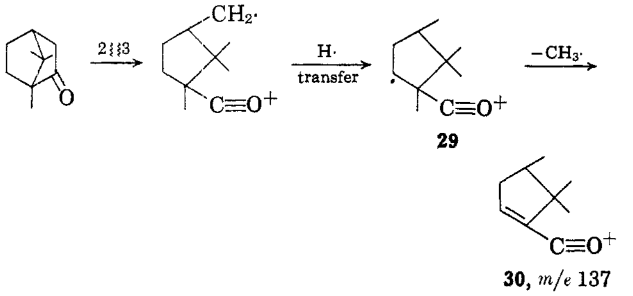


Figure 3.—The mass spectrum of borneol.

30, which loses the C-10 methyl group (Scheme III). Camphor seems to show a number of abundant ions which can be attributed to α cleavage of the C-2,3 bond, whereas isoborneol does not. Cleavage of C-2,3 compared with C-1,2 generates a 1° radical (or ion) in contrast to a 3° radical. However, it should be noted that α cleavage of cyclohexanone derivatives is controlled more by subtle differences two or three carbons removed rather than the immediate substitution of the α carbon.[20a]

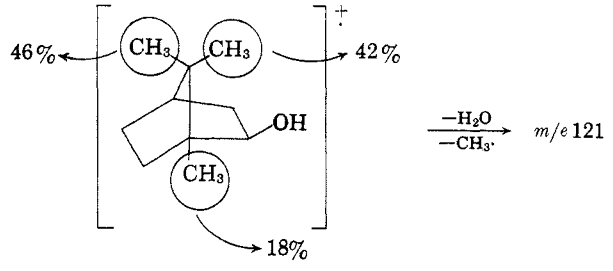
SCHEME III



The loss of water from isoborneol results in a m/e 136 fragment. The equal distribution of the m/e 137 and 138 peaks in the spectrum of the 3,3-d_2 analog suggests that one-half of the water elimination involves a proton in the 3 position. Since loss of water from alcohols does not normally involve 1,2 eliminations,[19b,20b] we propose that isoborneol first undergoes α cleavage[19c] and then loss of water to afford ion **35** (Scheme IV).

Some rearrangement to camphene (**32**) must also occur since a m/e 136 peak remains in the spectrum of the 10-d_1 analog. In fact, with the aid of the known deuterium isotope effect of 1.15 in favor of C–H bond cleavage *vs.* C–D cleavage,[21] it is estimated that nearly 50% of the m/e 136 peak is due to camphene.

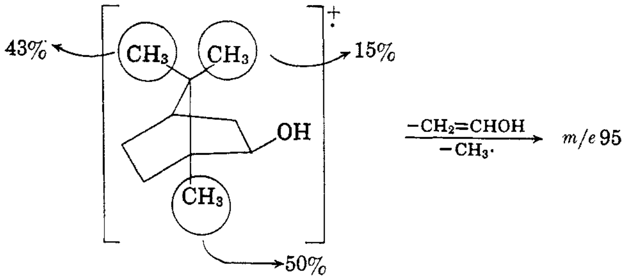
The appearance of a peak at m/e 121 indicates that a methyl group and a water molecule are readily lost from the isoborneol molecular ion. This fragment could arise by methyl cleavage from the m/e 136 ions since camphene and other $C_{10}H_{16}$ hydrocarbons show abundant m/e 121 peaks.[4,5] Our data do not allow us to conclude which is lost first—the methyl group or the water molecule. Regardless of this, there is a strong preference for losing the *gem*-dimethyl groups as compared to the C-10 methyl. The various per cent cleavages are shown in C.[22]



C

Carbon atoms 2 and 3 are lost as the enol form of acetaldehyde to afford the m/e 110 (M − 44) fragment, which is not shifted in the 3,3-d_2 analog, but is shifted 1, 2, and 3 units in the 10-d_1, 8,8-d_2, and 9,9,9,2-d_4 derivatives, respectively. This same hydrocarbon peak is prominent in the spectrum of camphor and is formed in much the same manner (Scheme IV).

The most interesting feature of the isoborneol spectra involves the origin of the base peak, m/e 95. It seems reasonable to assume that this peak corresponds to the same hydrocarbon ion **5**, found in the breakdown of camphor, and arises by loss of a methyl group from the m/e 110 ion. Quantitative determination of the per cent methyl cleavage in these cases was rendered somewhat more difficult owing to overlap of peaks as lower molecular weight fragments are transferred to the m/e 95–98 region when deuterium atoms are present. The percentage loss of each methyl group in the fragmentation to the m/e 95 ion is shown in D.[15]



D

There is a definite preference for loss of a C-9 methyl group in comparison with a C-8 methyl group. This specificity is again believed to be due to a *trans* migration of the C-9 methyl group to an electron-deficient C-1 carbon atom generating ion **4** directly. One of the methyl groups at C-1 in ion **4** is then ejected to give the cyclopentyl cation **5**, m/e 95 (Scheme IV). This mechanism is in accord with the 50% loss of the C-10 methyl group.

The m/e 93 peak, which is 20% of the base peak in isoborneol, probably arises, in large part, by a further fragmentation of the m/e 136 ion. This m/e 93 fragment represents the base peak in the spectra of a large number of monoterpene hydrocarbons, including camphene.[4,5] Because a portion of the m/e 93 peak shifts in the 8,8-d_2 and 9,9,9,2-d_4 derivatives of isoborneol,

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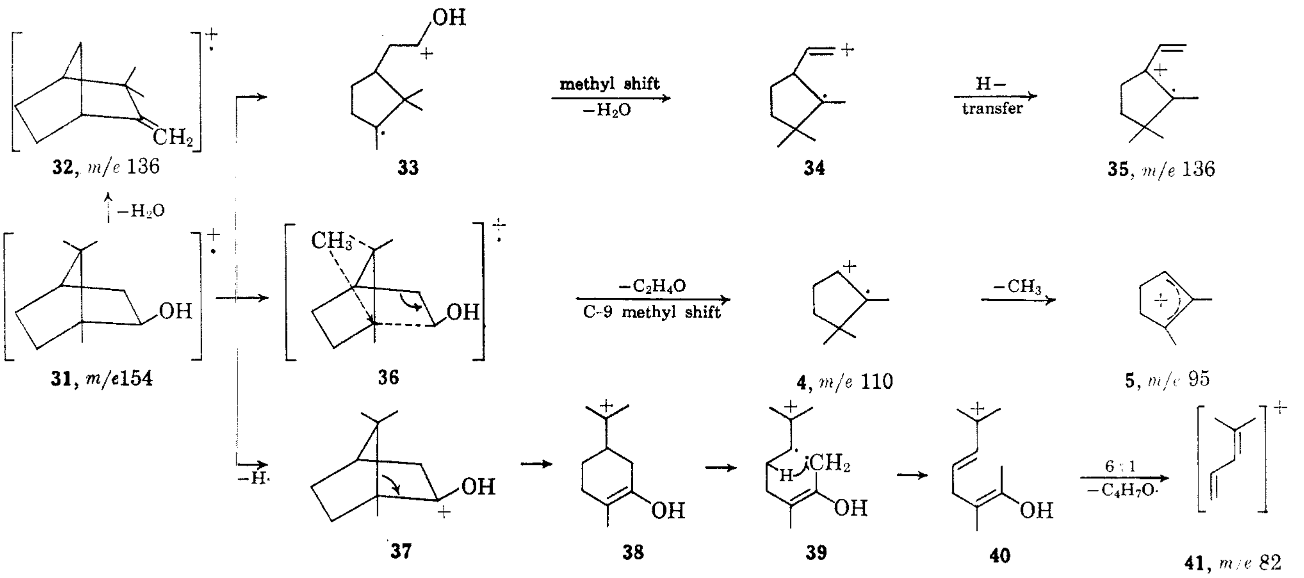
(20) H. Budzikiewicz, C. Djerassi, and D. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964: (a) pp 22–26; (b) pp 33, 43.

(21) D. H. Williams, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 284 (1964).

(22) The m/e 121 peak in the 10-d_1 analog can arise by loss of HOH and $\cdot CH_2D$ or loss of HOD and $\cdot CH_3$ and, therefore, must be corrected to determine only $\cdot CH_2D$ loss. With the aid of the m/e 136 to 137 ratio, it was calculated that 43% of the m/e 121 peak was a result of HOD loss.

Scheme IV

Fragmentation Reactions of Isoborneol



there may be another unknown source of the m/e 93 ion.

The relative abundance of m/e ions in the mass spectra of camphor and isoborneol is given in Table III.

Table III

Relative Abundance of m/e 92–99 Ions in the Mass Spectra of Camphor and Isoborneol

Compound	Abundance, % at m/e 92	93	94	95	96	97	98	99
Camphor		12		100	12	8		
Camphor-3,3-d_2		11		88[a]	11	11		
Camphor-10-d_1		9	12	73[b]	84	18		
Camphor-9,9,9-d_3		8		48[c]	13	7	83	11
Camphor-8,8-d_2		9		40	9	100	12	
Isoborneol	8	20	3	100	10	2		
Isoborneol-3,3-d_2		8	9	100	10			
Isoborneol-10-d_1	8	26	32	87	100	16		
Isoborneol-3,9,9,9-d_4		18	26	73	16	9	100	15
Isoborneol-8,8-d_2	8	18	6	27	7	100	11	

[a] At m/e 83, 100%. [b] At m/e 82, 100%. [c] At m/e 81, 100%

Deuterium labeling shows that the *gem*-dimethyl groups (C-9 and C-8) are retained in the formation of the m/e 82 fragment, while C-2, C-3, and C-10 are lost. Since it seems unlikely that two bonds would break around C-1, we assume that this carbon atom is also lost. Scheme IV outlines a pathway by which the m/e 82 ion (**41**) could arise.

Conclusions

Camphor and isoborneol undergo extensive and complicated rearrangements during electron impact; however, in spite of this, there is a great deal of specificity in their fission reactions, especially with isoborneol. The reason for this greater selectivity is not well understood. A possible explanation may be that camphor undergoes α cleavage at C-2,3 more readily than isoborneol and, thereby, requires less assistance (C-9 methyl migration) in the bond-breaking step(s). In line with this reasoning, camphor shows a number of abundant peaks which, presumedly, arise by α cleavage of the C-2,3 bond generating a primary radical, while isoborneol exhibits few, if any, fragments owing to this type of cleavage.

This appears to be the first known example of a preferential shift of one *gem*-dimethyl group relative to another upon electron impact. Thus, as in ground-state chemistry, migrations of groups *trans* to a leaving substituent may also be important in mass spectroscopy.

Experimental Section[23]

Camphor-3,3-d_2.—A solution of 0.43 g (2.5 mmoles) of camphor, 2.6 g (12.5 mmoles) of freshly distilled trifluoroacetic anhydride, and 3.0 g (150 mmoles) of deuterium oxide was heated at 130° in a sealed tube for 8 days.[8] The reaction mixture was basified with anhydrous potassium carbonate and extracted with pentane. The extract was dried and filtered; the solvent was removed to give 480 mg of solid. Sublimation afforded a colorless solid, mp 176–179°. A comparison of the nmr spectra of the product to that of camphor's established that two protons α to the carbonyl had been completely replaced by deuterium atoms. The mass spectrum of the solid had a parent ion at 154 and fragmentation ions expected for camphor-3,3-d_2.

Isoborneol-3,3-d_2.—A solution of 154 mg (1 mmole) of camphor-3,3-d_2 in anhydrous ether was added to a stirred suspension of 100 mg (2.5 mmoles) of lithium aluminum hydride in anhydrous ether. The mixture was stirred at room temperature overnight and quenched with 0.5 ml of deuterium oxide. The salts were filtered and washed with fresh ether. The ethereal filtrate was washed with water to convert any OD bonds into OH bonds. The ether was dried and evaporated to give a colorless solid, which as further purified by sublimation, mp 210–212°. An infrared spectrum (Nujol mull) showed bands at 2.9, 9.3 (>CHOH), and 4.5–4.8 μ (CD). The mass spectrum showed a parent peak of mass 156, indicative of a dideuterioisoborneol.

Isoborneol-2,10-d_2.—To a stirred suspension of 0.4 g (10 mmoles) of lithium aluminum deuteride in anhydrous ether was added 0.5 g (2 mmoles) of 10-camphorsulfonyl chloride dissolved in ether. The mixture was stirred at room temperature for 18 hr and quenched with saturated, aqueous sodium sulfate solution. The aluminum salts were filtered and washed several times with fresh ether. The combined ether washings were dried with magnesium sulfate and evaporated to give a mushy

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(23) The mass spectra were measured by Mr. T. Wachs with a Hitach, RMU-6D mass spectrometer, using an all-glass inlet system heated at 180°i a source temperature of 155°, an ionizing current of 52 μa, and an ionization energy of 75 ev. Nmr spectra were determined at 60 Mc by Mrs. Robert Hutchins on a Varian Associates A-60 spectrometer, using carbon tetrachloride as the solvent and tetramethylsilane as an internal reference. Infrared spectra were measured with a Perkin-Elmer Infracord spectrometer, Model 137-B.

solid. Sublimation afforded 100 mg (32%) of colorless solid, mp 209.5–217°. The mass spectrum displayed a parent ion of 156 and other fragmentation ions indicative of a mixture of borneol and isoborneol-2,10-d_2.

When this same reaction was carried out on 10-camphorsulfonyl chloride, only using lithium aluminum *hydride* as the reducing agent, a 47% yield of sublimed, colorless solid was obtained. Analysis by vpc, using a 150-ft capillary poly(propylene glycol) UC oil LB 550-X column, proved that the solid was a 2:1 mixture of isoborneol and borneol, respectively, by comparing retention times with authentic samples.

Camphor-10-d_1.—To a solution of 85 mg (0.54 mmole) of a mixture of borneol and isoborneol-2,10-d_2 in acetone was added 0.2 ml of 8 *N* CrO_3 in sulfuric acid–water. After standing for a few minutes, the solvent was decanted from the chromium salts and diluted with water. The aqueous acetone solution was extracted with ethyl ether, which, in turn, was washed with water, dried, and evaporated to give a colorless solid. Except for a C–D bond stretch absorption at 4.55 μ, the infrared spectrum (Nujol mull) resembled that of camphor. The sublimed ketone was free of impurities as shown by vpc analysis and was shown to be a monodeuterated camphor by its molecular weight of 153 (mass spectrometry).

Isoborneol-10-d_1.—A mixture of 60 mg of camphor-10-d_1 and 100 mg of lithium aluminum hydride in anhydrous ether was stirred at room temperature for 3 hr. After quenching with aqueous sodium sulfate solution, the aluminum salts were filtered and washed with fresh ether. The filtrate was dried with magnesium sulfate and evaporated. The residue was sublimed to give a colorless solid, mp 207.5–210°, whose infrared spectrum (Nujol mull) resembled that of isoborneol's except for a C–D stretch at 4.55 μ.[24] Its mass spectrum showed a parent ion of 155.

Isoborneol-8,8-d_2.—A mixture of about 18 mg of camphor-8,8-d_2 and a small amount of lithium aluminum hydride in anhydrous ether was stirred at room temperature overnight. After the addition of water, the salts were filtered and washed with fresh ether several times. The ether washings were dried with magnesium sulfate and concentrated in a sublimer. Sublimation gave about 10 mg of colorless solid, mp 205–208°. An infrared spectrum (CCl_4 solution) showed hydroxyl (2.8, 2.9) and C–D stretch (4.5–4.7), but no carbonyl or *gem*-dimethyl absorptions. The mass spectrum showed a parent ion of mass 156 (two deuteriums) and other ions characteristic of an isoborneol derivative.

8-Bromocamphor-8,8-d_2.—Following a procedure described by Sommer,[25] 130 mg (0.77 mmole) of 8-hydroxycamphor-8,8-d_2,[11] 130 mg (1.0 mmole) of quinoline, 220 mg (0.81 mmole) of phosphorus tribromide in 2 ml of bromobenzene were stirred and refluxed at 180° for 1 day. Work-up gave 104 mg (60%) of an oily solid, which showed a strong carbonyl band and no hydroxyl absorption in its infrared spectrum (Nujol mull). The mass spectrum showed a dual parent peak of *m/e* 232 and 234.

Camphor-8,8-d_2.—Using a microhydrogenation apparatus, 560 mg of 5% palladium on charcoal in 0.8 ml of water, 0.6 ml of ethanol, and 30 mg (0.56 mmole) of potassium hydroxide were stirred in a hydrogen atmosphere for 3 hr. To this mixture was added 90 mg (0.4 mmole) of 8-bromocamphor-8,8-d_2 in 2.5 ml of ethanol. After stirring for 18 hr, the catalyst was filtered and washed with ether. The ether filtrate was washed with water, dried, and evaporated in a sublimer to give an oily solid. Sublimation afforded a colorless solid (22 mg). Analysis by vpc showed that the product was free of impurities and had a retention time identical with that of camphor. Its mass spectrum displayed a parent ion of mass 154 (two deuteriums).

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[24] The purity of all the deuterated isoborneol derivatives was checked by vpc using a 150-ft capillary poly UC oil column. The only impurities present were the corresponding borneol derivatives.

[25] L. H. Sommer, H. D. Blackman, and P. C. Miller, *J. Am. Chem. Soc.*, **76**, 803 (1954).

Low-Temperature Fluorination of Schiff Bases[1]

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Controlled addition of elemental fluorine to the carbon–nitrogen double bond of benzilidenealkylamines provides a synthetic route to α,α-difluoro secondary fluoramines. Some properties and reactions of these fluoramines are discussed.

It has been demonstrated that the addition of elemental fluorine to complex and reactive organic substrates, such as olefins,[2,3] may be controlled. The process utilizes a combination of low temperatures and inert diluents and provides a convenient synthetic method for vicinal difluorides. The extension of such a process to the carbon–nitrogen double bond, which produces secondary fluoramines, is reported here.

The addition of fluorine to carbon–nitrogen unsaturation has received scant attention and has centered mostly upon the nitrile group. One example is acetonitrile which may be fluorinated with mercuric fluoride at 150 to 180° to produce a host of N-fluoramines, difluoramines, and generally rearranged and variously substituted products.[4] Direct fluorination with elemental fluorine is usually[4] quite destructive and causes extensive cleavage and substitution of the attached organic moiety. Relatively simple substrates had to be used to reduce the number of possible side products.

The method employed successfully[2,3] for the fluorination of olefins was used without modification on the Schiff bases and produced primarily α,α-difluoro secondary fluoramines (I). The additions were conducted at $-78°$ with the substrate as a 10% solution in Freon 11 (CCl_3F). Pure, undiluted fluorine was metered to the solution in such a manner that the partial pressure never exceeded 50 mm. Care must be taken as the reaction can easily become quite violent even at $-78°$. An inorganic HF scavenger was usually included, and sodium fluoride was found to be marginally effective. Compounds more basic than NaF will react with fluorine or dehydrofluorinate the product.

A number of equivalents of fluorine admitted to the reactor were controlled from pressure-drop measurements. This fluorine/substrate ratio will determine

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[2] R. F. Merritt and T. E. Stevens, *J. Am. Chem. Soc.*, **88**, 1822 (1966).

[3] R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966).

[4] For a general review of this area, see M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The MacMillan Co., New York, N. Y., 1962, p 71, and references therein.