In the presence of large quantities of starting olefin the π-complexed product from **2** is displaced and excluded from the surface and, therefore, does not undergo further exchange; *e.g.*, toluene solvent does not affect the deuterium distributions.

Variation of R (OCH_3, H, NO_2) results in no change in deuterium distributions. It would seem that R should influence **2**; however, such electronic effects in similar models are known to be small[12] or lacking.[13]

Acknowledgment. This investigation was supported in part by Public Health Service Research Grant GM 10664 from the National Institute of General Medical Sciences.

(12) J. R. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 304 (1959).
(13) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

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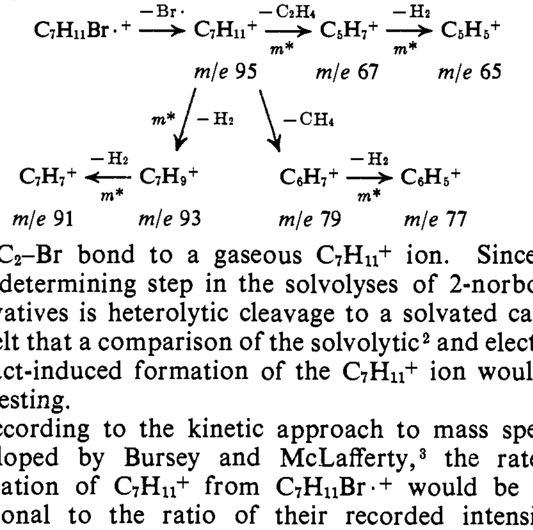
A Mass Spectral Study of *exo*- and *endo*-2-Norbornyl Bromides[1]

Sir:

The mass spectra of *exo*- and *endo*-2-norbornyl bromides are identical except for the intensity of the molecular ion peak, $C_7H_{11}Br\cdot^+$, relative to that of the base peak, $C_7H_{11}^+$. These spectra are summarized in Scheme I and do not change from 20 to 70 ev. The only fragmentation of the molecular ion is cleavage of the C_2–Br bond to a gaseous $C_7H_{11}^+$ ion. Since the rate-determining step in the solvolyses of 2-norbornyl derivatives is heterolytic cleavage to a solvated cation, we felt that a comparison of the solvolytic[2] and electron-impact-induced formation of the $C_7H_{11}^+$ ion would be interesting.

Scheme I



According to the kinetic approach to mass spectra developed by Bursey and McLafferty,[3] the rate of formation of $C_7H_{11}^+$ from $C_7H_{11}Br\cdot^+$ would be proportional to the ratio of their recorded intensities. Therefore, if the molecular ions from *exo*- and *endo*-2-norbornyl bromides fragment to the same $C_7H_{11}^+$ ion, the peak–intensity relationship in Scheme II may be derived.[3] The intensities of the two molecular ion peaks and the two fragment ion peaks are experimentally measurable quantities which allow calculation of the ratio of rate constants. In Table I, this ratio, determined from electron-impact studies in the gas phase, is compared to the corresponding ratio obtained from solvolytic studies by Roberts, *et al.*[4]

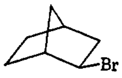
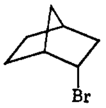
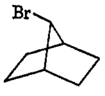
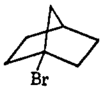
Scheme II

$$exo\text{-}C_7H_{11}Br\cdot^+ \xrightarrow{k} [C_7H_{11}^+]_{exo} + Br\cdot$$

$$endo\text{-}C_7H_{11}Br\cdot^+ \xrightarrow{k'} [C_7H_{11}^+]_{endo} + Br\cdot$$

$$\frac{[C_7H_{11}^+]_{exo}/[exo\text{-}C_7H_{11}Br\cdot^+]}{[C_7H_{11}^+]_{endo}/[endo\text{-}C_7H_{11}Br\cdot^+]} = \frac{k}{k'}$$

Table I

Compd	$[C_7H_{11}^+]/[C_7H_{11}Br\cdot^+]$[c]	k/k', electron impact	k/k', solvolysis	AP($C_7H_{11}^+$), ev
	264	10	10[a]	10.27 ± 0.05
	26.4	1	1[a,b]	10.26 ± 0.05
	5.92	(0.22)		
	3.22	(0.12)		

[a] In 80% aqueous ethanol at 55°.[4] Internal return, if any, has not been measured and compensated for in these values. [b] Twenty per cent impurity of a more reactive bromide, presumably the *exo* isomer.[4] [c] Relative intensity ratio.

No quantitative significance can be assigned to the observation of an identical (10:1) rate from the two processes, but the fact that *exo*-Br is lost faster than *endo*-Br represents a striking correlation. Our data can be explained in terms of steric deceleration of fragmentation in the *endo* isomer as well as in terms of nonclassical anchimeric assistance in the *exo* isomer, as have been used to rationalize the larger rates of solvolysis of *exo*-2-norbornyl derivatives relative to their *endo* isomers.[2,4]

Appearance potential measurements of the intense $C_7H_{11}^+$ ions, *m/e* 95, by the semilog matching technique for evaluation of appearance potential curves, are also summarized in Table I. These figures are likely reliable to ±0.15 ev. Due to the low abundance of the corresponding molecular ions, ionization potential measurements were not made. The similarity of the mass spectra of the *exo* and *endo* isomers together with these appearance potential data indicate that the same $C_7H_{11}^+$ ion with the same energy distribution is formed from both compounds, a requirement for the kinetic approach to be valid.[3]

We have also studied the fragmentation of the two remaining norbornyl bromides, namely the 1 and 7 isomers. A fragmentation of their molecular ions which competes with the loss of a bromine radical is elimination of the ethylene bridge. The relative intensity ratios given in Table I indicate that these lose a bromine radical more slowly than do their 2-bromo isomers, paralleling solvolytic behavior.[2] The relative rate ratios shown in parentheses would represent the k/k' ratios *only* if the $C_7H_{11}^+$ ion is identical from all

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(1) Presented in part at the 14th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, May 22–27, 1966.
(2) For a compilation of publications in this area see P. D. Bartlett, "Nonclassical Ions: Reprints and Commentary," W. A. Benjamin, Inc., New York, N. Y., 1965.
(3) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).
(4) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

four compounds. The nmr spectrum of the 2-norbornyl cation as the hexafluoroantimonate salt has been observed in SbF_5–liquid SO_2 solution;[5] it was noted that both the 1- and 7-norbornyl cations rapidly rearranged to the more stable 2-norbornyl cation at $-10°$. Thus, it is probable that the gaseous $C_7H_{11}^+$ ions formed upon electron impact from the four norbornyl bromides are identical, and that the values in Table I reflect the k/k' ratios.

Additional data obtained with the isomeric 2,3-dibromo- and 2,3-bromochloronorbornanes indicate that the more facile loss of *exo*-Br relative to *endo*-Br is general for the norbornyl system.[6] These and further studies will be described in the full article.

Acknowledgment. The mass spectrometer was purchased by Wayne State University with funds from a National Science Foundation Chemical Research Instrument grant.

(5) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964).

(6) D. C. DeJongh, S. R. Shrader, and N. A. LeBel, to be published.

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The Isolation and Structure of Echinodol, a Triterpene Acetate

Sir:

Echinodontium tinctorium Ellis and Ev. (Polyporaceae) is a wood-rotting fungus commonly found on conifers, particularly in the Northwest. According to French[1] the plant has been used as a bactericidal agent by the Wasco Indians, and preliminary tests of crude material also indicate tumor-inhibiting activity.[2] Petroleum ether extraction of the dried fungus afforded a good yield of crude material, shown by tlc to consist of at least ten components. Careful chromatography on alumina or repeated recrystallizations afforded the major component, Ia, named echinodol, in pure form.

Echinodol, $C_{32}H_{50}O_4$,[3] mp 236–238°, $[\alpha]^{25}D$ +48°, $\lambda_{\max}^{CHCl_3}$ 3605, 3450 (broad), 1735, and 1240 cm^{-1}, was clearly an hydroxy acetate, confirmed by its nmr spectrum (Table I, and three-proton singlet at δ 2.01) and further chemical transformations. Acetylation gave the diacetate Ib, $C_{34}H_{52}O_5$,[4] mp 270–271°, $[\alpha]^{25}D$ +51°, which showed no hydroxyl group even when the infrared spectrum was taken using a concentrated solution. Saponification or lithium aluminum hydride reduction afforded the diol Ic, $C_{30}H_{48}O_3$, mp 228–229°, $[\alpha]^{25}D$ +47°, which showed no carbonyl band in the infrared. The above data suggest the presence of one ether linkage in these compounds. The nmr spectra of these compounds all showed the presence of one vinyl hydrogen, confirmed by catalytic reduction to a dihydro derivative, $C_{32}H_{52}O_4$, IIa, mp 186–187°, which formed a diacetate IIb, $C_{34}H_{54}O_5$, mp 178–180°. The presence of an isopropylidene group in I, suggested by the nmr six-proton doublet at about δ 1.7 (Table II), was confirmed by isolation of acetone[5] upon ozonolysis of Ia. The presence of a nonreducible, tetrasubstituted double bond in IIb was shown by chromic acid–acetic acid oxidation of IIb to a yellow diketone, mp 179–182°, $\lambda_{\max}^{alc}$ 270 mμ (ε 9200), $\lambda_{\max}^{CHCl_3}$ 1739, 1671, and 1240 cm^{-1}, indicative of a Δ^2-ene-1,4-dione.[6] These data, coupled with the nmr evidence (Table II) showing six angular methyl groups and two vinyl methyl groups, clearly suggested a lanosterol skeleton. The nmr chemical shifts of the angular methyl groups in particular are in excellent agreement with those predicted on the basis of earlier data.[7]

Table I. Nmr Data (δ 3.0–5.5) on Echinodol Derivatives[a]

Compd	C_3–H	C_{16}–H	C_{22}–H	C_{23}–H	C_{24}–H
Ia	3.20 (m)	3.74 (m)	4.51 (t)[b]	4.10 (t)[b]	5.16 (bd)
Ib	4.50 (m)	3.74 (m)	4.52 (t)[b]	4.05 (t)[b]	5.16 (bd)[b]
Ic	3.20 (m)	3.70 (m)	2.96 (t)[b]	3.97 (t)[b]	5.20 (bd)[b]
Id	...	3.75 (m)	4.50 (t)[b]	4.04 (t)[b]	5.16 (bd)[b]
Ie	...	4.20 (m)	...	4.52 (d)[c]	5.31 (bd)[c]
If	...	3.80 (m)	2.97 (t)[b]	3.93 (t)[b]	5.19 (bd)[b]
IIa	3.20 (m)	3.50 (m)	4.48 (t)[b]	3.67 (q)[b]	...

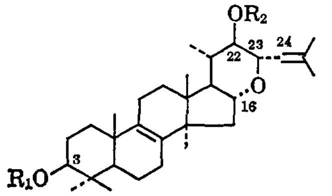
[a] All spectra were recorded in $CDCl_3$. Chemical shifts are given in parts per million relative to internal tetramethylsilane. Chemical shifts of multiplets are approximate. Abbreviations: bd, allylically broadened doublet; d, doublet; q, quartet; t, triplet; m, multiplet. [b] $J = 9$ cps. [c] $J = 8$ cps.

Table II. Chemical Shifts of Angular Methyl Groups

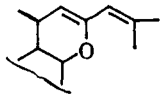
Compd	C_{18}	C_{19}	C_{21}	$C_{26,27}$	C_{30}	C_{31}	C_{32}
Ia	0.69	1.00	0.90 (d)[a]	1.69 (d)[b]	0.82	1.00	1.05
Ib	0.68	1.00	0.90 (d)[a]	1.67 (d)[b]	0.87	0.87	1.05
Ic	0.68	0.99	Obs[c]	1.67 (d)[b]	0.82	0.99	1.03
Id	0.70	1.07	0.92 (d)[a]	1.70 (d)[b]	1.08	1.08	1.06
Ie	0.82	1.08	Obs[c]	1.70 (d)[b]	1.08	1.08	1.13
If	0.71	1.08	Obs[c]	1.70 (d)[b]	1.08	1.08	1.08

[a] $J = 7$ cps. [b] $J = 1.5$ cps. [c] Obs, obscured by other peaks.

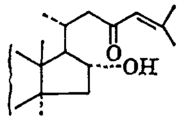
The position and nature of the acetate and ether linkages[8] were shown by further degradation and extremely informative nmr data. Jones oxidation of Ia afforded the 3-keto derivative Id, $C_{32}H_{48}O_4$, mp 227–229°, whereas similar oxidation of Ic gave the valuable diketone Ie, $C_{30}H_{44}O_3$, mp 168–171°, $\lambda_{\max}^{CHCl_3}$ 1698 cm^{-1}.



Ia, $R_1 = H$, $R_2 = Ac$
b, $R_1 = Ac$, $R_2 = Ac$
c, $R_1 = H$, $R_2 = H$
d, 3-keto, $R_2 = Ac$
e, 3-keto, 22-keto
f, 3-keto, $R_2 = H$



III (3-keto)



IV (3-keto)

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(1) Private communication from Dr. D. H. French, Reed College, Portland, Ore.

(2) Private communication from Dr. J. L. Hartwell, National Cancer Institute, Bethesda, Md.

(3) Satisfactory microanalyses have been obtained for all compounds with cited empirical formulas.

(4) Molecular weight confirmed by mass spectrometry.

(5) As its 2,4-dinitrophenylhydrazone derivative in 46% yield.

(6) J. Fried, P. Grabowich, E. F. Sabo, and A. I. Cohen, *Tetrahedron*, **20**, 2297 (1964).

(7) A. I. Cohen, D. Rosenthal, G. W. Krakower, and J. Fried, *ibid.*, **21**, 3171 (1965).

(8) The nmr data in Tables I and II, as well as molecular rotational changes, clearly point to the presence of a C-3 hydroxyl group.