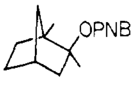
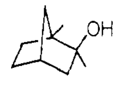
Table II. Rotations[a] and Optical Purities (DP) of Solvolysis Products Derived from Optically Active Ib-PNB

$[\alpha]^{30}$D, deg (OP, %)			
			
(+)-Ib-PNB	(−)-Ib-OH	(+)-IV	V
	A. Aqueous Acetone,[b] 100.07°		
+13.1 (26)[c]	−2.2[d] (2.5)	+16.6 (16)	−3.9
+37.5 (75)[c]	−5.3[d] (6.2)	+49.9 (47)	−10.9
	B. Methanol[b], 78.48°		
+24.7 (40)[c]	+1.06 (3.0)[e]	+25 (24)	−5.3

[a] Rotations are for chloroform solutions. [b] Solvent contained 0.14 M 2,6-lutidine. [c] Average optical purity determined by multiplying OP of starting ester by k_t/k_α.[14] [d] Rotation is $[\alpha]^{30}_{365}$. [e] Optical activity of methyl ether.

dently lutidine has no important effect on the rate or nature of solvolysis because k_α (lutidine present) corresponds to $k_t + k_{rac}$ (lutidine absent).

Solvolysis of Ib-OPNB in 90% acetone containing 0.14 M lutidine at 100° gives about 11% Ib-OH, 35% 1-methyl-2-methylenenorbornane (IV), and 54% 1,2-dimethyl-2-norbornene (V). Methanolysis at 78.5° gives about 37% Ib-OCH_3, 26% IV, and 37% V.[13] Unlike the parent norbornyl system (Ia),[2,3] optically active substrate gives active products.

For substrates that undergo simultaneous racemization and solvolysis the average optical purity for complete solvolysis is k_t/k_α times the initial value.[14] Initial rotations and average optical purities of samples of (+)-Ib-OPNB used in the product studies are shown in Table II together with rotations and optical purities of the products derived from these samples.[12]

The two experiments in part A of the table show that Ib-OH and the exocyclic olefin IV are formed with about 9 and 63% retention of configuration, respectively (the absolute rotation of V has not been established). Control experiments with ^{18}O-labeled ester showed that Ib-OH results from alkyl oxygen cleavage. The results for methanolysis are similar; the ether, Ib-OCH_3, and olefin IV are formed with 8 and 60% retention of optical activity, respectively.

These results show that ionization of Ib-OPNB gives an asymmetric carbonium ion. It should be noted that in each solvent the elimination product is about seven times more active than the substitution product, which means that they are derived from different intermediates. A possible interpretation is that most, or all, of the olefin is derived from an initially formed asymmetric ion pair[15] and that racemization of the dissociated ion IIIb competes with solvent capture. In this case ionization is at least 60% unassisted. Alternatively, active olefin may result from a parallel elimination reaction superimposed on the carbonium ion process, in which case unassisted ionization could be as low as 10%.

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[13] Compositions based on capillary gc peak areas.

[14] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952).

[15] See R. L. Buckson and S. G. Smith, *J. Org. Chem.*, **32**, 634 (1967); M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, **85**, 1702 (1963); D. J. Cram and M. R. Sahyan, *ibid.*, **85**, 1257 (1963); and P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963), for similar interpretations.

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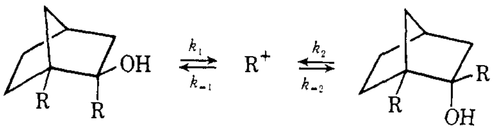
On the Norbornyl and 1,2-Dimethylnorbornyl Cations[1]

Sir:

The preceding communication reports that solvolysis of optically active 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate, unlike the parent norbornyl system,[2] gives active products. Thus, unassisted ionization to give the classical ion is involved in the tertiary system. We now report a comparison of the difference in (a) *exo* and *endo* transition-state energies, (b) reactivity ratios (k_1/k_2), and (c) partition ratios (k_{-1}/k_{-2}) for the acid-catalyzed *exo* ⇄ *endo* equilibration of norbornanol (R_sOH) and dimethylnorbornanol (R_tOH) in 80% (v/v) dioxane.



exo-R_sOH, R = H
exo-R_tOH, R = CH_3

endo-R_sOH, R = H
endo-R_tOH, R = CH_3

The method is the same as has been applied to other systems[3] and involves comparing rates (and activation parameters) of three reactions associated with the equilibration. These are loss of optical activity (eq 1) and the forward and reverse reactions for equilibration (eq 2).

$$\text{active } exo\text{-ROH} \xrightarrow{K\alpha} \text{inactive products} \quad (1)$$

$$exo\text{-ROH} \underset{k_{i\text{-}endo}}{\overset{k_{i\text{-}exo}}{\rightleftarrows}} endo\text{-ROH} \quad (2)$$

Reactions were followed by methods described earlier[3] and $k_{i\text{-}exo}$ and $k_{i\text{-}endo}$ were determined from the rate constant for irreversible equilibration (eq 3; $k_i = k_{i\text{-}exo} + k_{i\text{-}endo}$) and the equilibrium constant for eq 2 ($K_{eq} = k_{i\text{-}exo}/k_{i\text{-}endo}$). In both systems, K_{eq} and k_i were the same for the two isomers.

$$exo\text{- or } endo\text{-ROH} \xrightarrow{k_i} \text{equilibrium mixture} \quad (3)$$

Rate constants for reactions 1 and 2 are presented in Table I. Both are cleanly pseudo first order and rates are proportional to acid concentration over the range 0.01–0.23 M. The constants in the table have been normalized for $[HClO_4] = 1\ M$ (*i.e.*, $k_{obsd}/[HClO_4]$) and most are averages of several independent determinations for two acid concentrations. The ionic strength was constant, $[HClO_4] + [LiClO_4] = 0.232\ M$, and solvent (containing acid and salt) from the same batch was used for the two systems.

In the norbornyl system k_α measures the rate of generation of the symmetrical norbornyl cation (R_s^+), and thus $k_\alpha = k_1$. For the tertiary system k_α probably does not measure total ionization because in a similar aqueous solvent the dimethylnorbornyl cation (R_t^+) is generated and captured with about 9% survival of activity.[4]

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[1] This research was supported by the Air Force Office of Scientific Research (AFOSR-847-67) and the National Institutes of Health (G. M. 14134).

[2] S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, **87**, 376 (1965); J. A. Berson in "Molecular Rearrangements, Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3; G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

[3] (a) H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87**, 3516 (1965); (b) H. L. Goering and R. R. Josephson, *ibid.*, **84**, 2779 (1962); H. L. Goering and R. E. Dilgren, *ibid.*, **82**, 5744 (1960).

[4] H. L. Goering and K. Humski, *ibid.*, **90**, 6213 (1968).

Table I. Pseudo-First-Order Constants for Acid-Catalyzed Transformations of Norbornanol and 1,2-Dimethylnorbornanol in 80% Dioxane[a]

Temp, °C	$10^3 k_\alpha$, M^{-1} min^{-1}	$10^4 k_{i\text{-}exo}$, M^{-1} min^{-1}	$10^2 K_{eq}$
	A. 1,2-Dimethylnorbornanol[b]		
19.67	12.26 ± 0.03		
29.85	57.2 ± 0.2		
40.14	232 ± 1.2		
49.04	738 ± 2[c]	7.24 ± 0.16[d]	51.5 ± 0.3[e]
64.95		67.5 ± 1.1	51.0 ± 0.2
78.47		392 ± 10	52.3 ± 0.2
	B. Norbornanol[f]		
78.47	0.879 ± 0.004		
99.40	15.7 ± 0.1		
119.83	194 ± 4[g]	1.69 ± 0.06[h]	25.9 ± 2[i]
145.27		50.8 ± 1.4	29.7 ± 0.5
159.32		276 ± 9	30.2 ± 0.5

[a] [HClO$_4$] = 0.014 − 0.23; concentrations (25°) not corrected for thermal expansion of solvent; [HClO$_4$] + [LiClO$_4$] = 0.232 M. [b] [R$_t$OH] = 0.11 M. [c] E_a = 26.17 ± 0.03 kcal mole^{-1}. [d] E_a = 30.56 ± 0.44 kcal mole^{-1}. [e] K_{eq} = 51.3 ± 0.9 at 145.27°, ΔH = 0.0 ± 0.1, kcal mole^{-1}, ΔG = 0.424 ± 0.006 kcal mole^{-1}, ΔS = −1.3 ± 0.3 eu. [f] [R$_s$OH] = 0.18 M. [g] E_a = 35.8 ± 0.2 kcal mole^{-1}. [h] E_a = 43.5 ± 0.7 kcal mole^{-1}. [i] ΔH = 1.4 ± 0.5 kcal mole^{-1}, ΔG = 1.06 ± 0.01 kcal mole^{-1}, ΔS = 1.0 ± 1.3 eu.

Table II. Partition (k_{-1}/k_{-2}) and Reactivity (k_1/k_2) Ratios for Isomerization of Norobornanol and 1,2-Dimethylnorbornanol in 80% Dioxane

Temp, °C	k_{-1}/k_{-2}[a]	k_1/k_2[a]
	A. 1,2-Dimethylnorbornanol	
19.67	2030 ± 160[b]	1039 ± 49
29.85	1620 ± 80	833 ± 25
40.14	1240 ± 30	639 ± 12
49.04	1020 ± 30	525 ± 8
64.95	750 ± 14	386 ± 4
78.47	577 ± 17	297 ± 6
	B. Norbornanol	
78.47	3650 ± 480[c]	775 ± 71
99.40	1960 ± 120	466 ± 20
119.83	1148 ± 67	298 ± 16
120.73	1170 ± 60	303 ± 11
145.27	616 ± 26	183 ± 5
159.32	457 ± 26	138 ± 6

[a] Uncertainties estimated from limiting values of constants. [b] ΔE_a = 4.35 ± 0.34 kcal mole^{-1}, $\Delta\Delta S^{\ddagger}$ = −0.3 ± 1.1 eu. [c] ΔE_a = 7.8 ± 0.6 kcal mole^{-1}, $\Delta\Delta S^{\ddagger}$ = 5.8 ± 1.6 eu.

However, any discrepancy in k_α and k_1 is small and has no important effect on the present interpretations.[5] The constants in Table I are related to the partition (k_{-1}/k_{-2}) and reactivity ratios (k_1/k_2) in Table II as follows.[3a]

$$k_\alpha/k_{i\text{-}exo} = (k_{-1}/k_{-2}) + 1$$

$$(k_{-1}/k_{-2})K_{eq} = k_1/k_2$$

Apparent activation energies (E_a) and ΔH for norbornanol (dashed lines) and 1,2-dimethylnorbornanol (solid lines) are shown in Figure 1. These parameters were determined as outlined earlier.[3a] In all cases logarithmic plots were linear.

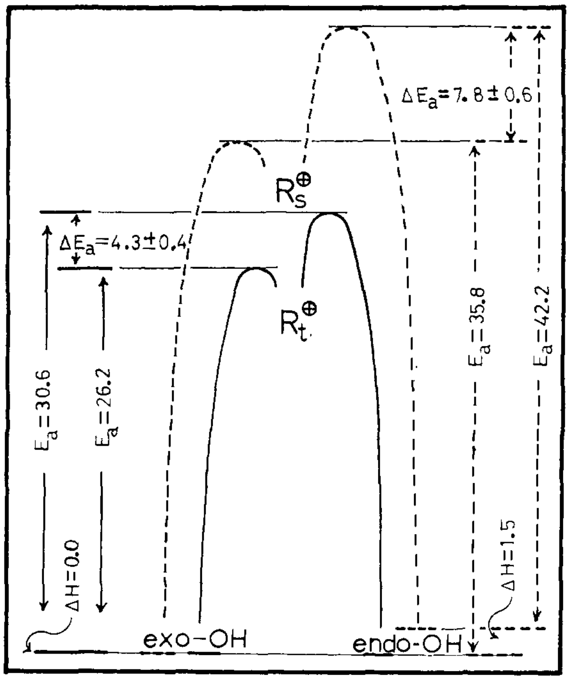

Figure 1. Energy diagrams for acid-catalyzed equilibration of norbornanol (dashed lines) and 1,2-dimethylnorbornanol (solid lines).

Table II shows that reactivity and partition ratios do not differ greatly for the two systems; at 78.5° k_1/k_2 is less than three times larger in the norbornyl than in the dimethylnorbornyl system. Similar *exo-endo* rate ratios for secondary and tertiary norbornyl systems have been noted earlier[6] and have been interpreted[6b] as indicating that σ participation is unimportant in either case. However, Figure 1 shows that there is an important difference in the two systems. The activation energy gap for the *exo* and *endo* transition states, ΔE_a, is substantially larger in the norbornyl than in the 1,2-dimethylnorbornyl system.[7]

In the tertiary system, which undergoes unassisted ionization,[4] ΔE_a presumably results from steric[6] or torsional[8] effects or from a combination of the two. Nonbonded steric interactions (involving the leaving group and the *endo*-6-hydrogen) in the *endo* transition state[6] would be expected to make similar contributions to ΔE_a in the two systems. Torsional effects, if involved, are more important in the tertiary than in the secondary system; judging from the rotational barriers for ethane (3 kcal) and the central bond of butane (4.4–6.1 kcal),[9] torsional effects would be expected to contribute from 1 to 3 kcal less to ΔE_a in the norbornyl system than in the dimethylnorbornyl system. From this analysis it is evident that some factor other than torsional and steric effects make an important contribution (at least 3.5 kcal) to ΔE_a in the norbornyl system,

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(5) The rate of exchange (k_{exc}) associated with the equilibration of *exo*-R$_t$^{18}OH at 40.14° has also been determined and k_α/k_{exc} = 1.7. Thus, k_α is a better measure of ionization than k_{exc}. This k_α/k_{exc} ratio is similar to that observed in other cases in which the carbonium ion is known to be symmetrical.[3]

(6) (a) H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 5004 (1964); **88**, 5335 (1966); H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964); (b) H. C. Brown, *Chem. Eng. News*, **45**, 87 (1967); *Chem. Brit.*, **2**, 199 (1966).

(7) The difference in ΔE_a for the two systems is much larger than the difference in $\Delta\Delta F^{\ddagger}$ for the temperature range in Table II. This is the reason that the important difference in ΔE_a for the two systems is not reflected in the partition and reactivity ratios.

(8) P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

(9) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. M. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, pp 6–10.

and σ delocalization in the *exo* transition state[2,3a] seems to be the most satisfactory explanation.

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The Goering–Schewene Diagram for the 1,2-Dimethylnorbornyl System. A Remarkable Similarity in the Diagrams for Classical Tertiary Norbornyl Cations and the Secondary Norbornyl Species

Sir:

There is growing acceptance for the position that tertiary norbornyl cations are classical. Thus Bunton originally argued that resonance cannot be important between canonical structures represented by a secondary norbornyl cation and the related tertiary cation, so that cations such as the 2-methylnorbornyl should be essentially classical.[1a] Brown and Rei observed that a methyl group in the 1 position of 2-methylnorbornyl had the same effect on the rate for the *endo* isomer (× 4.8) as for the *exo* isomer (× 4.3).[1b] This was not compatible with a σ-bridged transition state in which charge would be delocalized to the 1 position in the *exo*, but not in the *endo*, isomer. Sargent concluded that 2-methyl-*exo*-norbornyl derivatives solvolyze without σ participation since he could calculate the observed rates without allowing for that factor.[1c] Brown and Liu observed that the hydrochlorination of 1-methyl-d_3-2-methylenenorbornane can be controlled to yield predominantly unscrambled 1-methyl-d_3-2-methyl-*exo*-norbornyl chloride. Consequently, the symmetrical intermediate, the 1,2-dimethylnorbornyl nonclassical cation, cannot be a significant intermediate in this typical electrophilic reaction.[1d] Sunko has observed that deuterium substituents in the 3 position produce the same rate-retarding effect in the solvolysis of *exo*- and *endo*-2-methylnorbornyl. He also concludes that the 2-methylnorbornyl cation must be classical.[1e] Then Schleyer, from a consideration of all of the available evidence, reached the same conclusion.[1f]

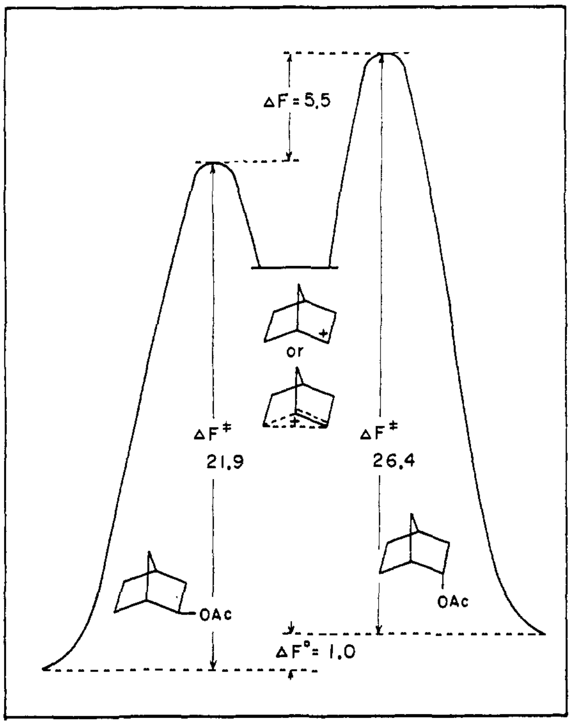

Figure 1. Goering–Schewene diagram for the acid-catalyzed acetolysis of *exo*- and *endo*-norbornyl acetates at 75°. (All numbers are in kilocalories per mole.)

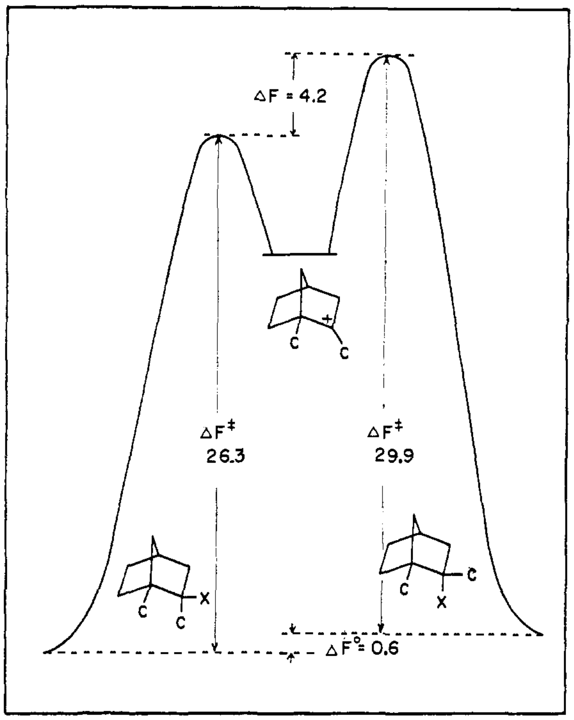

Figure 2. Goering–Schewene diagram for the solvolyses of 1,2-dimethyl-*exo*- and -*endo*-norbornyl *p*-nitrobenzoates in 60% aqueous dioxane at 75°. (X = OH or OPNB; all numbers are in kilocalories per mole.)

This position has now been elegantly confirmed by the successful trapping of the optically active 1,2-dimethylnorbornyl cation by Goering and his coworkers in the solvolysis of optically active 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate.[2]

We are now in a position to examine the properties of such classical tertiary norbornyl cations and to compare them with the corresponding properties of the secondary norbornyl derivatives. The structure of the secondary norbornyl cation is still undecided.[3]

The Goering–Schewene diagram for the acetolysis of the 2-norbornyl acetates (Figure 1) provides a quantitative picture of the relationship between the ground-state energies of the *exo* and *endo* isomers, the *exo–endo* rate ratio, and the *exo–endo* product ratio.[4] These authors observed that the *exo* transition state was more stable than the *endo* by 5.5 kcal/mole.[5] They stated

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[1] (a) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 62; (b) H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 5004 (1964); (c) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (d) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 466 (1967); (e) J. M. Jerkunica, S. Borčić, and D. E. Sunko, manuscript in publication; (f) P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

[2] H. Goering and K. Humski, *ibid.*, **90**, 6213 (1968).

[3] S. Winstein, *ibid.*, **87**, 381 (1965).

[4] H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

[5] The authors[4] actually formulated their diagram in terms of *E*, rather than *F*. Their diagram shows the two transition states to differ by $\Delta E = 4.4$ kcal/mole, rather than $\Delta F = 5.5$ kcal/mole in our diagram. We prefer to use free energy because it is more precise, being directly related to the measured rate and equilibrium constants, and because