Communications to the Editor

Solvolysis of Optically Active 1,2-Dimethyl-*exo*-2-norbornyl *p*-Nitrobenzoate. Evidence for Involvement of a Classical Carbonium Ion[1]

Sir:

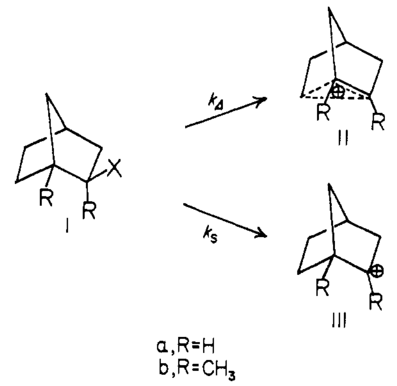
Solvolysis of *exo*-2-norbornyl derivatives (Ia) evidently involves assisted ionization (k_Δ) leading directly to the symmetrical nonclassical ion IIa.[2,3] The pertinent evidence in this connection is (a) the only capturable intermediate appears to be symmetrical[2a] and (b) the *exo* transition state for generation and capture of the carbonium ion is of lower energy than the *endo* transition state.[4,5]

The situation is less clear for tertiary norbornyl systems. An *endo*-2 electron-releasing substituent would be expected to increase k_s more than k_Δ,[7] and the point at which unassisted ionization takes over is an important unanswered question. On the basis of relative reactivities and *exo–endo* rate ratios it has been concluded that participation is unimportant in the 2-methyl- and 1,2-dimethyl-*exo*-2-norbornyl systems.[6c,8] However, the evidence is indirect and of the type that has been shown[9] to be misleading with regard to participation in the *exo*-benzonorbornen-2-yl system.[6a,c] Additional evidence concerning the 1,2-dimethylnorbornyl system (Ib) is the interesting observation that addition of hydrogen chloride to 1-methyl-2-methylenenorbornane (IV) does not pass through a symmetrical intermediate.[10] However, this evidence is also indirect because it is not certain that addition and solvolysis involve the same intermediate(s).

Table I. Rate Constants for Solvolysis (k_t), Racemization (k_{rac}), and Loss of Optical Activity (k_α) of Ib-OPNB[a]

Temp, °C	$10^4 k_t$, min^{-1}	$10^4 k_{rac}$,[b] min^{-1}	$10^4 k_\alpha$, min^{-1}	k_α/k_t
		A. 90% Aqueous Acetone		
78.45	7.42 ± 0.07[c]	3.1 ± 0.3	10.34 ± 0.02[d]	1.39 ± 0.02
100.07	79.9 ± 0.6[e]		107.4 ± 1.3[f]	1.34 ± 0.02
		B. Methanol		
65.02	8.83 ± 0.07[e]		14.84 ± 0.01[f]	1.68 ± 0.02
78.48	46.0 ± 0.0[e]		74.8 ± 0.4[f]	1.63 ± 0.01

[a] Constants independent of substrate concentration over the range 0.02–0.10 *M*. [b] Determined directly from optical purity of isolated unsolvolyzed ester. [c] Average, and average deviation, of four independent kinetic experiments. [d] Solvent contained 0.15 *M* lutidine. [e] Average of two independent experiments. [f] Solvent contained 0.04 *M* lutidine.



We now report direct evidence that ionization (alkyl oxygen cleavage) of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (Ib-OPNB) gives, at least in part, the asymmetric classical ion IIIb. In this work we have investigated the rates and products of solvolysis of optically active Ib-OPNB in 90% (v/v) aqueous acetone and methanol. The resolution of the dimethylnorbornyl system (Ib) and determination of absolute configurations and rotations of Ib-OPNB and the solvolysis products will be reported elsewhere.[11,12] Titrimetric (k_t) and polarimetric (k_α) rate constants are given in Table I. These data show that ion-pair return results in racemization of the unsolvolyzed ester, *i.e.*, $k_\alpha > k_t$. The titrimetric rate is first order in each solvent; however, the polarimetric rate is not because initially formed active products undergo subsequent acid-catalyzed changes. The rate constant for first-order racemization of the unsolvolyzed ester, k_{rac}, was determined directly from the activities of isolated samples of ester.

In the presence of a slight excess of 2,6-lutidine (to neutralize the acid produced by solvolysis), the products are optically stable and the polarimetric rates are first order. The polarimetric experiments and product studies were carried out under these conditions. Evi-

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[1] This research was supported by the National Science Foundation (GP-6555X) and the National Institutes of Health (G.M. 14134).

[2] (a) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, **87**, 376 (1965); (b) S. Winstein, *ibid.*, **87**, 381 (1965).

[3] J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3; P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

[4] H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87**, 3516 (1965).

[5] It has been proposed[6] that the energy difference for the transition states results from destabilization of the *endo* isomer by steric strain instead of from stabilization of the *exo* isomer by delocalization.

[6] (a) H. C. Brown and G. L. Tritle, *J. Am. Chem. Soc.*, **88**, 1320 (1966); (b) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 6378 (1967), and references therein; (c) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); *Chem. Eng. News*, **45**, 87 (Feb 13, 1967).

[7] S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948); S. Winstein, B. K., Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

[8] H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5004 (1964).

[9] D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968); H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, **90**, 2688 (1968); H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968).

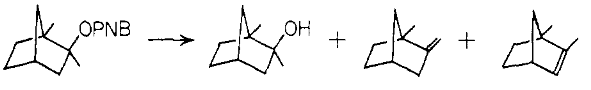
[10] H. C. Brown and K.-T. Liu, *ibid.*, **89**, 466 (1967).

[11] H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and K. Humski, *J. Org. Chem.*, in press.

[12] Optically active compounds had the same infrared and nmr spectra as authentic racemic samples.

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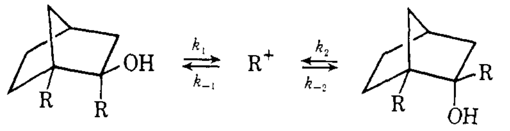
On the Norbornyl and 1,2-Dimethylnorbornyl Cations[1]

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).

$$\text{active } exo\text{-ROH} \xrightarrow{K_\alpha} \text{inactive products} \tag{1}$$

$$exo\text{-ROH} \underset{k_{i\text{-}endo}}{\overset{k_{i\text{-}exo}}{\rightleftarrows}} endo\text{-ROH} \tag{2}$$

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.

$$exo\text{- or } endo\text{-ROH} \xrightarrow{k_i} \text{equilibrium mixture} \tag{3}$$

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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[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).