red spectra of the *d*-norbornenes indicates *exo–endo* scrambling of the D at C-6 corresponding to 15 ± 5% of the olefin having been formed *via* an E1 path and 85 ± 5% *via* E2. The deuterated ethers and olefins from the "high base" runs had the same D content[6] as their tosylate precursors. However, the nortricyclene from each labeled tosylate had lost an appreciably different fraction of deuterium (*cf.* 33.4 and 52.9%) and so the cyclopropane ring can arise from a precursor in which *exo–endo* distinction at C-6 is preserved. This finding strengthens further the conclusion that at "high base" concentration the bulk of each hydrocarbon is derived from an E2-like process. The greater D loss from the 6-*endo*-*d*-tosylate reveals a preference for the *exo*-S geometry over the W geometry in these eliminations.[9,10]

(9) Contrast J. K. Stille and F. M. Sonnenberg, *J. Am. Chem. Soc.*, **88**, 4915 (1966); *Tetrahedron Letters*, 4587 (1966); F. M. Sonnenberg and J. K. Stille, *J. Org. Chem.*, **31**, 3441 (1966).

(10) We wish to emphasize that the E2-like 1,3 eliminations need not involve attack on a covalent substrate, but could involve partially or fully developed charged species that preserve original stereochemical differences.

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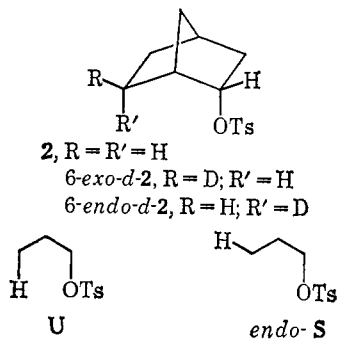
1,3 Eliminations. III. Preference for the U over the *endo*-S Geometry in *endo*-Norbornyl Tosylates[1,2]

Sir:

We wish to describe studies with *endo*-norbornyl tosylate (**2**)[3] and the labeled analogs 6-*exo*-*d*-**2** and 6-*endo*-*d*-**2** on treatment with potassium *t*-butoxide in *t*-butyl alcohol at "low" and "high" base concentrations at 135 ± 5°. Our results indicate that an initial U geometry is favored over an initial *endo*-S geometry in the 1,3 elimination to form nortricyclene.



2, R = R′ = H
6-*exo*-*d*-**2**, R = D; R′ = H
6-*endo*-*d*-**2**, R = H; R′ = D

U

endo-S

The products were *exo*-norbornyl *t*-butyl ether, norbornene, and nortricyclene, whose ratios at "low," and "high" base concentrations are summarized in Table I.

The *exo* ether could arise by preliminary ionization of the tosylate or by a direct displacement. At low base concentration (0.054 *M*) the fraction derived from the ionization path was found to be 0.25 ± 0.05 from the infrared spectrum of the deuterated ether, because this path permits the C-6 *exo* and *endo* positions to become equivalent, an event that was identifiable by characteristic changes in the fingerprint region of the infrared spectrum. Using this fraction as a measure of the E1 component of the reaction and knowing from earlier work[2] with the *exo*-tosylate the average product ratio (75:8:17) from the ionization path at the same base concentration, we can estimate the fraction of norbornene (0.17 ± 0.03) and of nortricyclene (0.10 ± 0.02) that arose from the ionization path. The former fraction was confirmed independently by isolation of sufficient norbornene from the run with 6-*endo*-*d*-**2** for an infrared analysis, which revealed 15 ± 5% of the olefin was formed after the D at C-6 had lost its original *endo* configurational identity. Clearly, even at low alkali concentration the three products are derived largely by a process other than the E1 limiting type.

Table I. Action of Potassium *t*-Butoxide on *endo*-Norbornyl Tosylates in *t*-Butyl Alcohol at 135 ± 5°

Substrate	Initial concn, *M* ROTS	Initial concn, *M* KO-*t*-Bu	Relative % products *exo*-*t*-Butyl ether	Relative % products Norbornene	Relative % products Nortricyclene	Fractional % D loss in nortricyclene
2	0.024	0.035	49	9	42	
6-*exo*-*d*-**2**[a]	0.034	0.054	57	8	35	15.8
6-*endo*-*d*-**2**[a]	0.034	0.054	57.5	10	32.5	50.5
2	0.25	0.91	39	44.5	16.5	
6-*exo*-*d*-**2**	0.19	0.89	34.5	50	15.5	24.5
6-*endo*-*d*-**2**	0.19	0.89	28	51	21	48.3

[a] Obtained from the same deuterio ketones used earlier.[2]

At high butoxide concentration (0.89 *M*) the products arose almost exclusively by a bimolecular process, as evidenced by the infrared spectra of the *t*-butyl ether and norbornene from each labeled precursor. In each product the D at C-6 had the same configuration as that in its starting tosylate, with no indication of *exo–endo* scrambling.[4] It follows that very little of the nortricyclene could have been produced by an E1 path.[5]

The ether and the olefin from the low and high base runs contained the same amount of deuterium as their tosylate precursors. Importantly, at both concentrations of potassium *t*-butoxide the fraction of the original deuterium lost in the nortricyclene from 6-*endo*-*d*-**2** was considerably greater than that from 6-*exo*-*d*-**2**.[6] Consequently, there was a preference for the U over the *endo*-S arrangement when *endo*-norbornyl tosylate underwent this 1,3 elimination.[7] The deuterium loss in generation of nortricyclene cannot be reasonably accounted for in terms of an α elimination to give a carbene at C-2 (or its equivalent) followed by insertion into the C–H bond at C-6 because such insertions are

(1) Supported by the National Science Foundation and by the Petroleum Research Fund (administered by the American Chemical Society).

(2) Part II: A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 3915 (1967).

(3) The *endo*-tosylates are numbered **2** to facilitate comparisons with the *exo*-tosylates, which were numbered **1** in the preceding communication.[2]

(4) The nmr spectrum of the *t*-butyl ether from 6-*exo*-*d*-**2** showed no D at C-2 or C-1 by area integration, thereby precluding any appreciable 6,2-hydride shifts.

(5) The *t*-butyl ether/nortricyclene ratio from 6-*endo*-*d*-**2** (1.33) was unexpectedly lower than that from 6-*exo*-*d*-**2** (2.22) or from **2** (2.36). Whether any significance should be attached to this difference is presently not clear. Controls showed that all products were stable to the reaction conditions.

(6) P. G. Gassman and F. V. Zalar, *J. Am. Chem. Soc.*, **88**, 3070 (1966), established that no deuterium loss from nortricyclene is expected under our reaction conditions.

(7) *Cf.* F. M. Sonnenberg and J. K. Stille, *J. Org. Chem.*, **31**, 3441 (1966); J. K. Stille and F. M. Sonnenberg, *J. Am. Chem. Soc.*, **88**, 4915 (1966).

known to proceed with little or no isotope effect and with no D loss.[8,9]

The data in this and the previous paper[2] can be analyzed in a more quantitative way. Let P be the ratio of the rate of abstraction of a C-6 *endo* hydrogen to that of a C-6 *exo* hydrogen; let Y_{exo} and Y_{endo}, respectively, represent the positive isotope effects (k_H/k_D) for loss of a C-6 *exo* deuterium and a C-6 *endo* deuterium; and let F be the fraction of nortricyclene produced by an E1 path (therefore $30.6F$ is the deuterium lost by the E1 path).[2]

For the bimolecular path to nortricyclene from 6-*exo*-*d*-**2** at low base concentration eq 1 may be written, and for 6-*endo*-*d*-**2** similar considerations lead to eq 2. The value of F is 0.10 (obtained as described above) and solution of eq 1 and 2 leads to $Y_{exo}Y_{endo} = 7.63$. If Y_{exo} is essentially the same as Y_{endo}, then this isotope effect (Y) is 2.8, and P becomes 2.5. Similar treatment of the entire data[2] leads to Table II.[10] The preference

$$\frac{\%\ endo\text{-H lost}}{\%\ exo\text{-D lost}} = \frac{100 - (15.8 - 30.6F)}{15.8 - 30.6F} = PY_{exo} \quad (1)$$

$$\frac{\%\ endo\text{-D lost}}{\%\ exo\text{-H lost}} = \frac{50.5 - 30.6F}{100 - (50.5 - 30.6F)} = \frac{P}{Y_{endo}} \quad (2)$$

(P) for abstraction of an *endo* hydrogen over that of an *exo* hydrogen represents the net outcome of steric and stereoelectronic factors in the norbornyl systems, and these *endo* preferences could be considerably higher in the absence of a steric disadvantage.[11] Cyclic or quasi-cyclic transition states could be important in the U system.[12]

Table II. Nortricyclene Formation from Norbornyl Tosylates in *t*-BuOH–KO-*t*-Bu

Approx concn of KO-*t*-Bu, *M*	Substrate (temp, °C)	Approx amount of Nortricyclene from E1 and E2 paths	*P*	*Y*
	exo-Tosylate (60)	100% E1	1[a]	2.1[2]
	endo-Tosylate (135)	10% E1	1[a]	2.1[b]
		90% E2	2.5	2.8
0.9	*exo*-Tosylate (60)	13% E1	1[a]	2.1[b]
		87% E2	1.5	1.6
	endo-Tosylate (135)	100% E2	1.7	1.8

[a] In a bridged norbornyl cation the *exo–endo* distinction at C-6 is lost, and so $P = 1$. [b] Value taken to be the same as for *exo*-tosylate at 60° at low base concentration.[2]

(8) A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **88**, 4543 (1966).

(9) (a) A carbene that is protonated to the norbornyl cation should lead to the same consequences as a conventional E1 path. (b) For α eliminations see: W. Kirmse, *Angew. Chem.*, 77, 1 (1965); *Angew. Chem. Intern. Ed. Engl.*, 4, 1 (1965); G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **87**, 4270 (1965); M. J. Goldstein and W. R. Dolbier, Jr., *ibid.*, **87**, 2293 (1965).

(10) In this treatment we must assume that a norbornyl cation produced in the E1 component at "high" base concentration behaves quantitatively the same as the norbornyl cation produced in the "low base" solution.

(11) A. F. Thomas and B. Willhalm, *Tetrahedron Letters*, 1309 (1965); J. M. Jerkunica, S. Borčić, and D. E. Sunko, *ibid.*, 4465 (1975); A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Am. Chem. Soc.*, **89**, 68 (1967).

(12) *Cf.* 1,2 eliminations [J. Zavada, J. Krupicka, and J. Sicher, *Chem. Commun.*, 66 (1967)].

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Hydrolysis of Esters of Bicycloheptyl- and -heptenylphosphinic Acids[1]

Sir:

The rate of hydrolysis of five-membered cyclic phosphates (such as methyl ethylene phosphate) is accelerated as much as a millionfold not only with ring opening but also with hydrolysis of the ester group external to the ring.[2,3] The rapid hydrolysis external to the ring has been explained[3] by assuming that the ring strain in the five-membered ring is diminished, without ring opening, in a transition state that has a naturally small (*e.g.*, 90°) O–P–O bond angle; the complete mechanism involves a "pseudo-rotation"[3,4] between two trigonal-bipyramidal intermediates. Furthermore, esters of simple five-membered cyclic phosphinic acids do not show enhanced rates of hydrolysis[3,5] relative to their acyclic analogs, presumably because the formation of trigonal-bipyramidal phosphorane intermediates[6] in this case demands that an alkyl group be placed in apical position. This configuration is energetically unfavorable[3,7,8] and could explain a lowered rate. The structure is, however, not forbidden,[8,9] so that one may predict that trigonal bipyramids with alkyl substituents in apical positions may still be favored for those cases where an especially large diminution in ring strain accompanies the formation of the intermediate. Such strained compounds have now been prepared;[10] the predicted rate enhancements have been observed and are reported in Table I. (The structures of II and III are presented in the accompanying communication.[10])

Inspection of Table I shows that, in acid, the first ester group of II is hydrolyzed 100 times faster at 26° than the second ester group at 100°; the rate difference, at a common temperature, is probably of the order of 10^5. The rate of acid hydrolysis of the first ester group of II, extrapolated to a common temperature, is probably about 10^5 times that of an appropriate monocyclic analog, whereas the rate of the hydrolysis of the second ester group is comparable to that of its monocyclic analog. In alkali, the rate of hydrolysis of the first ester group is nearly 10^3 times that of the second, and almost 10^5 times that of its monocyclic analog; the hydrolysis of the second ester group is retarded by a factor of about 30 relative to a comparable monocyclic ester.

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(2) P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961); F. Covitz and F. H. Westheimer, *ibid.*, **85**, 1773 (1963).

(3) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3431, 3432 (1966).

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(5) G. Aksnes and K. Bergesen, *Acta Chem. Scand.*, **20**, 2508 (1966).

(6) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965); F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); *Bull. Soc. Chim. France*, 2443 (1966).

(7) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 20, 245 (1966); R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **4**, 496 (1965).

(8) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(9) D. Gorenstein, and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967).

(10) R. Kluger, F. Kerst, D. G. Lee, and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 3919 (1967).