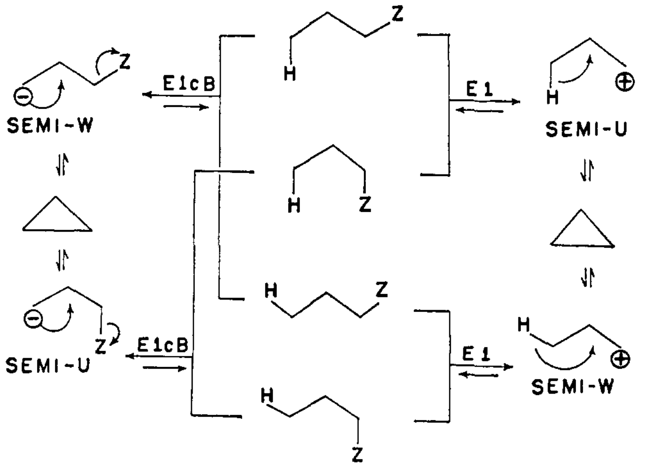
and Z is the departing group. The electronegativity distinction may be necessary when both X and Z can serve as leaving groups (*e.g.*, when X and Z are different halogens). In the special case where $X = Z$, structures **3** and **4** are geometrically equivalent, and the *exo–endo* prefixes are dropped. The *apo*-S form **5** refers only to the staggered precursor because it must twist to one of the other four transition states **1b**–**4b** for ring closure. Arrangement **2a** is the only one that can go to product without conformational rotation (*viz.*, **2a** → **2b**), and arrangement **1** is the only one in which X and Z can partake in cyclic transition states.

With respect to the atoms bearing X and Z, it is relevant to note that in the U path both centers undergo formal retention of configuration, and in the W path both undergo inversion. In the *exo*-S path there is retention at X and inversion at Z, and *vice versa* for the *endo*-S path. The over-all stereochemical outcome from the *apo*-S array will depend on which of the four transition states the *apo*-S form adopts during reaction.

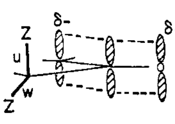
Arrangements **1**–**4** are clearly defined in a chair cyclohexane ring where the U forms utilizes 1,3-diaxial bonds, the W form utilizes 1,3-diequatorial bonds, and each of the two S forms involves one axial and one equatorial bond. Other common instances of U, W, *exo*-S, and *endo*-S geometries, or slight distortions thereof, include various boat-type molecules like bicyclo[2.2.1]heptanes, as well as puckered cyclobutanes,[5] bicyclo[*n*.1.1] systems, and appropriate conformations of cyclopropylmethanes that are precursors of bicyclo[1.1.0]butanes. *apo*-S units exist in these cyclic systems but involve endocyclic ring bonds, which must rupture during formation of a new three-membered ring.

With slight adaptation this terminology readily accommodates stepwise 1,3 eliminations in which stereochemistry at one center is lost prior to the ring closure. Since U and W are associated, respectively, with retention and with inversion at both centers, stepwise 1,3 eliminations (and the reverse ring cleavages) are termed semi-U and semi-W according to whether formal retention or inversion of configuration, respectively, occurs at the remaining center in the ring-forming step. Common situations are those that involve loss of HZ *via* cationic (E1 type) and anionic (E1cB type) intermediates (see Scheme I), but the nomenclature serves equally well for ions and radicals derived other ways (*e.g.*, by addition to various multiply bonded systems).

Scheme I. Stepwise 1,3 Eliminations and Cyclopropane Ring Cleavages



Delocalization of electrons can affect the geometry of nearby centers. However, even when the mesomerism implicates a pair of adjacent atoms in the A–B–C unit, only two extreme cyclopropyl transition states appear attainable, closely akin to semi-U and semi-W, and so no additional names are necessary. Structure **6** depicts an enolate ion as a precursor to a cyclopropanone (as in a Favorskii reaction). In the semi-U array the C–Z bond is initially more nearly parallel to the p orbitals of the enolate system, and in the semi-W form the orientation is more nearly orthogonal. The corresponding abbreviated notations are **7** and **8**, but it must be kept in mind that any single structure cannot accurately portray the dynamic situation, which demands appreciable conformational change from start to finish. For a half-chair cyclohexanone enolate, semi-U corresponds to Z initially quasi-axial and semi-W corresponds to Z initially quasi-equatorial. Similar considerations apply to allylic cations or radicals that lose a hydrogen to form methylenecyclopropane systems.



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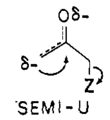
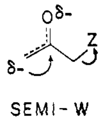


7



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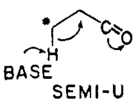

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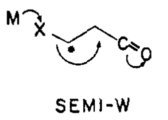

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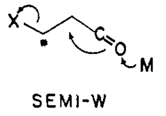

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Finally, we illustrate uses of semi-U and semi-W for neutral molecules with trigonal centers. Thus, the abstraction of homoenolic hydrogens by alkali[6] as in **9** and the generation of homoenolate ions by metal (M) reductions (*e.g.*, **10** or **11**) would be classed as shown in accord with the retention or inversion criterion at the relevant center (*).

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(5) I. Lillien and R. A. Doughty, *J. Am. Chem. Soc.*, **89**, 155 (1967); K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(6) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Wertiuk, *J. Am. Chem. Soc.*, **88**, 3354 (1966).

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1,3 Eliminations. II. Behavior of *exo*-Norbornyl Tosylate in Alkaline Media and Preference for *exo*-S over W Geometry[1]

Sir:

We present evidence that the *exo*-S arrangement is favored over the W arrangement when *exo*-norbornyl

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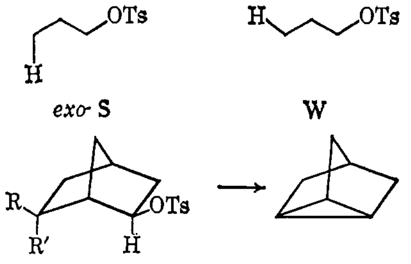
(1) Supported by the National Science Foundation and the Petroleum Research Fund (administered by the American Chemical Society). Part I: A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 3914 (1967).

tosylate (**1**) undergoes 1,3 elimination to nortricyclene with potassium *t*-butoxide in *t*-butyl alcohol under E2-like conditions.



1, R = R' = H
6-*exo*-*d*-**1**, R = D; R' = H
6-*endo*-*d*-**1**, R = H; R' = D

In principle, bimolecular reaction of 6-*exo*-*d*-**1** and 6-*endo*-*d*-**1**[2] with potassium *t*-butoxide could give nortricyclene whose deuterium content would reveal any preference for cleavage of the *exo* or *endo* C–H (or C–D) bond. In practice even at high base concentration (0.9 *M*) a small proportion of the nortricyclene arose by an ionization (E1) mechanism. Consequently, it became essential to establish the behavior of **1** and its deuterated analogs at low base concentrations (<0.05 *M*) so that the results at high base concentrations could be more fully interpreted.[4]

exo-Norbornyl tosylate (**1**, *ca.* 0.017 *M*) was solvolyzed at 60° in *t*-butyl alcohol and in *t*-butyl alcohol containing three different low, initial concentrations of potassium *t*-butoxide (0.013–0.055 *M*). Good first-order plots were obtained,[5] with results shown in Table I. The slight increase in k_1 with initial base concentration is attributable to an ionic strength effect or to a bimolecular component whose contribution is slight enough not to affect the linearity of the first-order plots. The products were *exo*-norbornyl *t*-butyl ether, norbornene, and nortricyclene, whose approximate ratios (upper half of Table II) were typical for base concentrations from 0.03 to 0.06 *M*. The high proportion of *exo* ether, which can arise reasonably from an *exo*-tosylate only by an ionization mechanism, corroborates that the reaction at "low base" concentrations is virtually entirely of the SN1 (or E1) type. Independent evidence stems from the following arguments.

Table I. First-Order Rate Constants for Solvolysis of *exo*-Norbornyl Tosylate (0.017 *M*) in *t*-Butyl Alcohol at 60°

Initial concn of KO-*t*-Bu, *M*	$k_1 \times 10^5$, sec^{-1}
0.00	1.29
0.013	1.30
0.024	1.36
0.055	1.53

Table II. Behavior of *exo*-Norbornyl Tosylates in *t*-Butyl Alcohol–Potassium *t*-Butoxide at 60°

			Relative % products			Fractional % D loss in nortricyclene
Substrate	Initial concn, *M* ROTS	KO-*t*-Bu	*exo*-*t*-Butyl ether	Norbornene	Nortricyclene	
1	0.032	0.061	70	10	20	
6-*exo*-*d*-**1**	0.043	0.054	76	7	17	29.7
6-*endo*-*d*-**1**	0.043	0.052	74	9	17	31.6
1	0.31	0.93	11	64.5	24.5	
6-*exo*-*d*-**1**	0.29	0.93	13	64.5	22.5	33.4[a]
6-*endo*-*d*-**1**	0.28	0.93	13.5	64	22.5	52.9[a]

[a] Deuterium losses determined in separate experiments at these concentrations: 6-*exo*-*d*-**1**, 0.26 *M*, KO-*t*-Bu, 0.93 *M*; 6-*endo*-*d*-**1**, 0.19 *M*, KO-*t*-Bu, 0.97 *M*.

Formation of a norbornyl cation (bridged or rapidly equilibrating) by any process prior to final proton abstraction removes the stereochemical distinction between the *exo* and *endo* hydrogens at C-6, so that 6-*exo*-*d*-**1** and 6-*endo*-*d*-**1** should give the same product ratio (confirmed in Table II) and the same deuterium outcome in each product. We found that the *t*-butyl ether from each labeled precursor had virtually identical fingerprint infrared spectra. The infrared spectrum of the olefin from 6-*endo*-*d*-**1** revealed the composition 65 ± 5% *endo*-*d*- and 35 ± 5% *exo*-*d*-norbornene. Therefore, about 70 ± 10% (*i.e.*, 2 × 35%) of the olefin was derived from an E1 path. The *t*-butyl ethers and the norbornenes had the same deuterium content as did their respective deuterated tosylates, and the fractional per cent deuterium lost in the nortricyclene (Table II) was virtually the same for each precursor.[6] Therefore, at "low base" concentrations ionization to a norbornyl cation precedes formation of the three products for the most part. It it be assumed that the cyclopropane ring arises from a carbon-bridged or hydrogen-bridged norbornyl cation by competitive H and D abstraction, the D loss (average value 30.6%; Table II) leads to a value of $k_H/k_D = 2.26$ (2.12 when corrected for scrambling)[7] for the primary isotope effect for such a process.[8]

Kinetic studies at 60° were conducted at "high base" concentrations (0.63—0.93 *M* KO-*t*-Bu; 0.32–0.38 *M* ROTs). The reactions were clearly not first order, and second-order plots had some curvature, which was least at 0.93 *M* base. The formation of 11–13.5% *exo* ether (bottom half of Table II) demonstrates that at least this fraction of the molecules undergoes preliminary ionization, even at the "high base" concentration. In confirmation, the infrared spectra of the deuterated *t*-butyl ethers from both labeled tosylates were identical with those of the ether from the "low base" runs. The infra-

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(2) The 6-*exo*-*d*-1 (89.7% D; stereochemical purity 95–98%) and 6-*endo*-*d*-1 (86.6% D; stereochemical purity 90–95%) were prepared conventionally[3] and no corrections for stereochemical purity were applied.

(3) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963); A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

(4) Compare H. Kwart, T. Takeshita, and J. L. Nyce, *ibid.*, **86**, 2606 (1964).

(5) C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

(6) The accuracy of the mass spectroscopic deuterium assays is approximately ±1% for the ether, ±2% for nortricyclene, and ±3% for norbornene.

(7) Scrambling by 6,2-hydride and -deuteride shifts was estimated by integration of the C-2 and bridgehead protons in the nmr spectra of the *t*-butyl ether from each tosylate. Equal probability for H and D shifts was assumed, and 3,2 shifts were ignored in view of their known lesser importance [J. D. Roberts, C. C. Lee, and W. A. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954)].

(8) Compare k_H/k_D values for cyclopropane formation by deamination of 1-aminopropane [A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964)] and for olefin formation from classical ions [V. J. Shiner, *ibid.*, **75**, 2925, (1953); **76**, 1603 (1954); C. E. Boozer and E. S. Lewis, *ibid.*, **76**, 794 (1954); M. S. Silver, *ibid.*, **83**, 3487, (1961)].

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]

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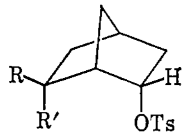
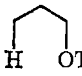
1,3 Eliminations. III. Preference for the U over the *endo*-S Geometry in *endo*-Norbornyl Tosylates[1,2]

Sir:

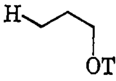
We wish to describe studies with *endo*-norbornyl tosylate (**2**)[3] and the labeled analogs 6-*exo*-*d*-**2** and 6-*endo*-*d*-**2** on treatment with potassium *t*-butoxide in *t*-butyl alcohol at "low" and "high" base concentrations at 135 ± 5°. Our results indicate that an initial U geometry is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

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

	Initial concn, *M*		Relative % products			Fractional % D loss in nortricyclene
Substrate	ROTS	KO-*t*-Bu	*exo*-*t* Butyl ether	Norbornene	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]

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.

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

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(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).