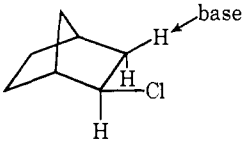
Communications to the Editor

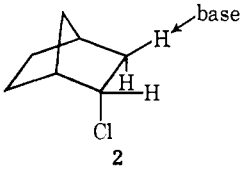
Stereochemistry of β Elimination in 2-Norbornyl and 7,7-Dimethyl-2-norbornyl Tosylates. Evidence for the Preferential Attack by Base on the *exo*-3-Hydrogen in Both Systems

Sir:

The 2,3-dihalonorbornanes[1,2] undergo preferential *exo-cis* bimolecular elimination, rather than *endo-cis* or *trans* elimination. The same phenomenon is also observed in the β elimination of *exo*-norbornyl tosylate,[3] bromide,[3,4] and chloride.[4] However, under E2 reaction conditions, *trans* elimination is strongly favored (84%) over *endo-cis* elimination (16%) in *endo*-norbornyl chloride.[4,5] These results suggest that the most important factor in the stereochemistry of β elimination in 2-norbornyl derivatives may be preferential attack of the base on the less hindered *exo*-3-hydrogen (**1**, **2**).

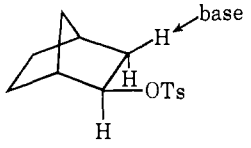


1
(*exo-cis* elimination)

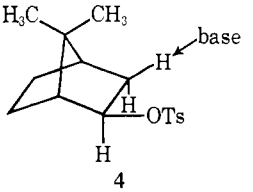


2
(*trans* elimination)

In view of the importance of attaining an understanding of the steric effect of 7,7-dimethyl substituents on the reactions of the norbornyl system,[6,7] we undertook a study of β elimination in *exo*-norbornyl and 7,7-dimethyl-*exo*-norbornyl tosylates. In both cases we observed predominant *exo-cis* elimination, with the *exo*-3-hydrogen being removed preferentially (**3**, **4**).



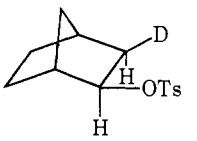
3
(*exo-cis* elimination)



4
(*exo-cis* elimination)

Consequently, in this reaction the presence of the 7,7-dimethyl substituents fails to alter the preferential attack by the base on the *exo*-3-hydrogen. This system thus joins the base-catalyzed deuteration of camphor in exhibiting a higher reactivity of the *exo*-3-hydrogen even in the presence of 7,7-dimethyl substituents.[8,9]

exo-Norbornyl tosylate (**3**), *exo*-norbornyl-*exo*-3-*d* tosylate (**5**), 7,7-dimethyl-*exo*-norbornyl tosylate (**4**),



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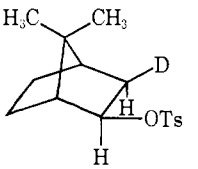

6

and 7,7-dimethyl-*exo*-norbornyl-*exo*-3-*d* tosylate (**6**) were subjected to β elimination. After some experimentation, treatment of 0.1 *M* solutions of the tosylates in triglyme with 1 *M* solutions of the sodium salt of 2-cyclohexylcyclohexanol in the same solvent at 80° was selected as providing relatively clean β eliminations with minimum complication from concurrent solvolysis. The hydrocarbon product was isolated in approximately 60% yield and its composition was established by glpc examination.[10] The stereochemistry of the elimination was determined by integrating the area of the olefinic protons and the area of the bridgehead protons on 60-MHz pmr spectra.[11] The results are summarized in Table I.

Table I. Product and Stereochemistry of Elimination of *exo*-Norbornyl and 7,7-Dimethyl-*exo*-norbornyl (Apoisobornyl) Tosylates

Products	% from norbornyl **3**	% from norbornyl **5**	% from apoisobornyl **4**	% from apoisobornyl **6**
Norbornene	99.5	98.0		
Nortricyclene	0.5	2.0		
7,7-Dimethylnorbornene			81	59
2,2-Dimethylnortricyclene			16	34
5,5-Dimethylnorbornene			3	7
Stereochemistry of β elimination, *cis*:*trans*		≥98:2[a]		95:5

[a] Pmr analysis indicated equal intensity of both olefinic and bridgehead protons. The maximum possibility for the existence of norbornene-2-*d* (from *trans* elimination) would be 2%, as estimated from the sensitivity of the electronic integration.

The increase in the formation of nortricyclene and 2,2-dimethylnortricyclene in the deuterium derivatives presumably arises as a result of a decrease in the rate of β elimination resulting from a primary isotope effect. Indeed, on this basis the observed products indicate an isotope effect of 2–4, which is in line with the value, 3.5, observed for E2 elimination of the 2,3-dihalonorbornanes.[2] The norbornene obtained from the elimination of **5** retained only 6% of the deuterium, as indicated by mass spectral analysis,[12] and pmr analysis revealed that the deuterium was located at the *syn*-7 position.[13] Therefore, we may conclude that the reaction involves predominantly a simple E2 elimination, without serious scrambling due to ionization and internal return prior to elimination.[14]

(1) S. J. Cristol and E. F. Hoegger, *J. Am. Chem. Soc.*, **79**, 3438 (1957).
(2) N. A. LeBel, *et al.*, *ibid.*, **85**, 3199 (1963); **86**, 4144 (1964).
(3) H. Kwart, T. Takeshita, and J. L. Nyce, *ibid.*, **86**, 2606 (1964).
(4) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).
(5) J. K. Stille and F. M. Sonnenberg, *Tetrahedron Lett.*, 4587 (1966).
(6) J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 123–133.
(7) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 378 (1965); R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, **87**, 379 (1965).
(8) A. F. Thomas, *et al.*, *Tetrahedron Lett.*, 1309 (1965); *J. Am. Chem. Soc.*, **89**, 68 (1967).
(9) T. T. Tidwell, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 14–18, 1969, Abstract ORGN-42.
(10) We used a Perkin-Elmer Model 226 gas chromatograph with either a 150 ft × 0.01 in. "R" or squalane column.
(11) These were taken with a Varian A-60A spectrometer using carbon tetrachloride solutions. Average values of ten or more integrations were recorded.
(12) The analysis was performed on a Hitachi Perkin-Elmer RMU-6A mass spectrometer at 5.5 eV.
(13) K. Tori, *et al.*, *Can. J. Chem.*, **42**, 926 (1964); *Tetrahedron Lett.*, 9 (1966).

Under the same reaction conditions *endo*-norbornyl-*exo*-3-*d* tosylate yielded 15% of the elimination product. The pmr analysis indicated that only 20% of the norbornene contained vinylic deuterium, similar to the results realized with *endo*-2-chloronorbornane-*exo*-2,3-d_2.[4,5] Again the removal of the *exo*-3-deuterium is preferred (80%) in spite of the unfavorable primary isotope effect and an unfavorable dihedral angle of approximately 120° between the two groups undergoing elimination.[14]

From these results it appears that the predominant *exo-cis* elimination observed for the tosylates **3–6** must be primarily a consequence of the greater accessibility of the *exo* hydrogen or deuterium and not due to any stereoelectronic factor favoring *cis* eliminations. Moreover, the 95:5 ratio of *exo-cis vs. trans* elimination of **6** clearly indicates a marked preference for the base to attack the *exo*-3-deuterium even in the face of an unfavorable primary isotope effect and the presence of the sterically hindering 7,7-dimethyl substituents. Consequently, it would appear that for reagents of modest steric requirements the nearer *endo*-6 position must be sterically far more demanding than the more distant *syn*-7-methyl substituent for reactions involving an attack at the 3-hydrogen atoms. Possibly it is the exceptionally large steric requirements of the complex hydrides which is responsible for the observed inversion of the direction of attack in 2-norbornanone brought on by 7,7-dimethyl substituents,[15] and it was dangerous to adopt this reaction as a model for extrapolation to all other reactions of the 7,7-dimethylnorbornyl system.[6,7]

(14) For a discussion of the advantages of coplanarity of the departing groups in bimolecular elimination of alicyclic tosylates, see C. H. DePuy, *et al.*, *J. Am. Chem. Soc.*, 87, 2421 (1965). See also J. Hine, *ibid.*, 88, 5525 (1966); W. T. Dixon, *Chem. Commun.*, 402 (1967).

(15) Indeed, we have observed that reduction of camphor by H_3B in THF results in a 50:50 formation of the two isomers.

(16) The Proctor and Gamble Fellow at Purdue University, 1967–1968.

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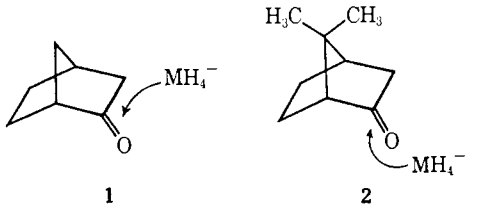
Stereochemistry of Additions to Norbornene and 7,7-Dimethylnorbornene. A New Interpretation of the Steric Influence of 7,7-Dimethyl Substituents on Reactions of the Norbornyl System

Sir:

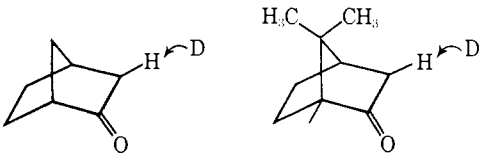
In the reaction of complex hydrides with norcamphor (**1**) and apocamphor (**2**) it has long been recognized that the presence of the 7,7-dimethyl substituents in the latter molecule brings about a change in the direction of preferential attack of the reagent from *exo* to *endo*.[1]



1 2

It was argued that a similar inversion in the direction of attack should be expected in the norbornyl and apobornyl cations (or ion pairs), so that the observed almost exclusive *exo* substitution in the solvolysis of these derivatives requires a "special" feature, σ-bridged cations.[2,3]

This is a reasonable argument. However, as was pointed out, it rests on largely unexplored foundations.[4] The danger in extrapolating from such a narrow base is illustrated by the observation that base-catalyzed deuteration of both norcamphor (**3**) and camphor (**4**) involves the *exo*-3-hydrogen preferentially.[5]

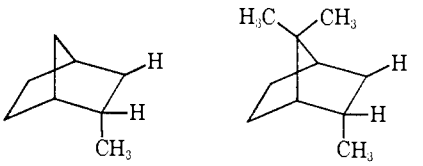


3 4

It appeared desirable to subject the steric influence of the 7,7-dimethyl substituents to a much broader examination. Accordingly, we undertook to examine the comparative behavior of norbornene (**5**) and apobornene (**6**) toward a number of representative addition reactions: hydrogenation, hydroboration, epoxidation, silver ion complexation, oxymercuration, hydrochlorination, and free-radical addition of thiophenol.

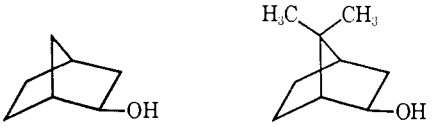
5 6

Hydrogenation over the borohydride-reduced platinum catalyst[6] of 2-methylnorbornene gave 90% *endo*-2-methylnorbornane, indicating 90% *exo* addition of hydrogen (**7**). Hydrogenation of ζ-fenchene (2,7,7-trimethylnorbornene) gave 90% *endo* addition[7] (**8**).



7, 90% 8, 10%

Hydroboration–oxidation of norbornene gave 99.5% of *exo*-norbornanol (**9**), whereas apobornene revealed only 22% *exo*-hydroboration (**10**).



9, 99.5% 10, 22%

Epoxidation of norbornene gave 99.5% of the *exo* epoxide (**11**), whereas apobornene gave only 10% *exo* (90% *endo*) (**12**).[8]

(2) J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 123–133.

(3) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, 87, 378 (1965); R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, 87, 379 (1965).

(4) H. C. Brown, *Chem. Brit.*, 2, 199 (1966).

(5) A. F. Thomas and B. Willham, *Tetrahedron Lett.*, 1309 (1965); A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Am. Chem. Soc.*, 89, 68 (1967).

(6) C. A. Brown and H. C. Brown, *J. Org. Chem.*, 31, 3989 (1966).

(7) H. M. Bell, Ph.D. Thesis, Purdue University.

(8) The structures of the epoxides were confirmed by conversion to the corresponding alcohols by treatment with lithium in ethylenediamine.