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]

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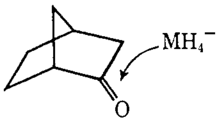
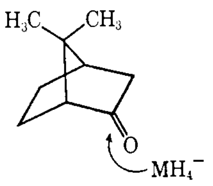
Stereochemistry of Additions to Norbornene and 7,7-Dimethylnorbornene. A New Interpretation of the Steric Influence of 7,7-Dimethyl Substituents on Reactions of the Norbornyl System

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]



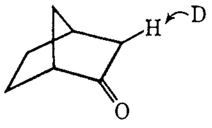
1



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]



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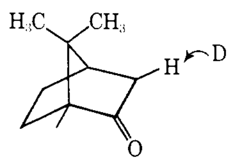
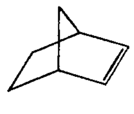


4

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.



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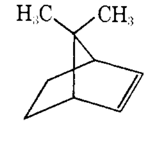
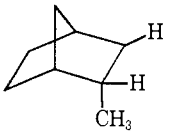
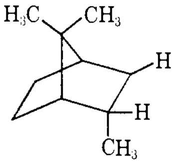


6

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**).

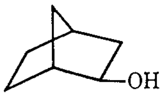


7, 90%

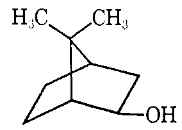


8, 10%

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]

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(1) S. Beckmann and R. Mezger, *Chem. Ber.*, **89**, 2738 (1956).

(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).

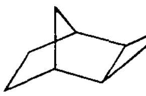
(4) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(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).

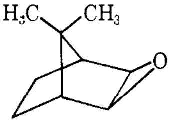
(6) C. A. Brown and H. C. Brown, *J. Org. Chem.*, 31, 3989 (1966).

(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.



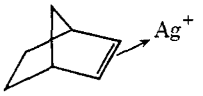
11, 99.5%



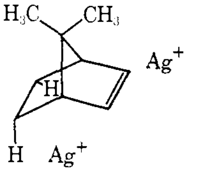
12, 10%

Silver nitrate forms an unusually stable complex with norbornene.[9] On the other hand, we observed that apobornene fails to exhibit the slightest interaction with silver ion. For example, the glpc retention time for norbornene increased from 7.0 to 35.1 min in changing from an ethylene glycol to an ethylene glycol–silver nitrate column. Under the same conditions the retention times for apobornene were 10.3 and 10.9 min. Apocamphane exhibited times of 10.3 and 10.9 over these same columns. Moreover, a mixture of apobornene and apocamphane exhibited a single symmetrical peak over the silver nitrate column.

These results are explicable only if we assume that norbornene coordinates with silver ion from the *exo* direction (**13**). The 7,7-dimethyl substituents must sterically prevent such complexation from the *exo* direction in apobornene (**14**). Evidently, complexing from the *endo* direction must likewise be forbidden for steric reasons.

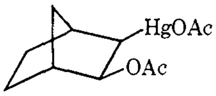


13

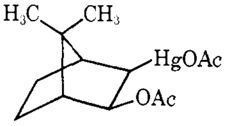


14

Oxymercuration is believed to involve a mercurinium ion intermediate,[10] similar to the silver ion complex. Yet oxymercuration of apobornene proceeds readily and produces the *exo-cis* adduct[11] **15**, similar to that observed for norbornene[12,13] (**16**). Reduction of this mercurial (**16**) with sodium borohydride gives apoisoborneol of ≥99.8% isomeric purity.[14] Addition of deuterium chloride to apobornene also proceeds to give predominantly *exo-cis* addition[15] (**17**, **18**).

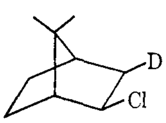


15

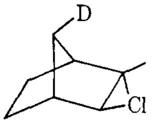


16

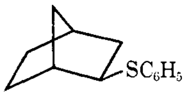
Finally, the photochemical free-radical addition of thiophenol at 0° to norbornene gives 99.5% *exo*-2-norbornyl phenyl thioether (**19**). The addition to apobornene is slower by a factor of approximately 10, as shown by a competitive experiment. However, here also the *exo* product (**20**) is predominant (95% *exo*:5% *endo*).[16]



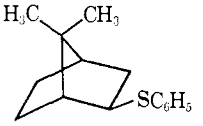
17, 90%



18, 10%



19, 99.5%



20, 95%

It is evident from these results that the 7,7-dimethyl substituents control sterically the addition reactions involving (1) hydrogenation, (2) hydroboration, (3) epoxidation, and (4) silver ion complexation. They fail to control sterically the (5) oxymercuration, (6) hydrochlorination, and (7) free-radical addition of thiophenol. We wish to propose that reactions of the first class proceed through essentially one-stage additions involving cyclic transition states which place the adding species in the immediate environment of the 7,7-dimethyl substituents. On the other hand, reactions which proceed in two stages, involving reaction intermediates of small or moderate steric requirements, attack at the corners of the bicyclic structure and are not seriously influenced sterically by the 7,7-dimethyl substituents. This picture would include the observed *exo* deuteration of norcamphor (**3**) and camphor (**4**), as well as the *exo-cis* β elimination in apoisobornyl tosylate.[17] Two-stage reactions involving attack by intermediates of very large steric requirements may come under steric control of the 7,7-dimethyl substituents in the same way that these substituents alter the direction of attack of complex hydrides on the carbonyl groups (**1**, **2**).

Fortunately, this proposal appears capable of being subjected to experimental test by establishing that the reactions of the first group (1–4) really involve essentially single-stage additions, whereas reactions of the second group (5–7) involve two-stage additions in which it may be possible to trap the intermediate between the two successive stages.

It should be emphasized that the present development does not disprove σ bridging in the norbornyl and apobornyl cations. However, it does render doubtful the original argument that *exo* substitution in the solvolysis of apobornyl derivatives is completely inexplicable and requires a "special" explanation.[18]

A detailed study of such epoxidation of bicyclic systems and the opening of the epoxides by this convenient procedure has been completed by Dr. S. Ikegami and will shortly be reported.

(9) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962). Among the large number of olefins examined, only *trans*-cyclooctene formed a more stable complex.

(10) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

(11) We used infrared and pmr techniques similar to those pioneered by Traylor[12] to establish the structure.

(12) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963).

(13) Oxymercurations of 1,4,7,7-tetramethylnorbornene and *syn*-7-bromonorbornene also yield the *exo-cis* adduct: T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968). The present results confirm the conclusion that the earlier observations must be general and not the result either of enhanced torsional effects in the 1,4,7,7 derivative or of coordination effects in the *syn*-7-bromo compound.

(14) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

(15) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 3900 (1967).

(16) The addition of thiophenol to a mixture of apobornene and apocyclene at 80° under the influence of azobisisobutyronitrile also produces the *exo* isomer predominantly. However, the *exo*:*endo* ratio was not established: D. I. Davies and P. J. Rowley, *J. Chem. Soc.*, 1832 (1968).

(17) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **92**, 200 (1970).

(18) The original argument was essentially qualitative, based essentially on the direction of substitution.[2] However, even if the argument shifts to the unusually high degree of *exo* substitution in the solvolysis of apoisobornyl derivatives,[3] we are faced with the fact that oxymercuration appears to be equally stereospecific,[13,14] but apparently cannot involve a σ-bridged intermediate.[14]

(19) Research assistant on grants (G 19878 and GP 6492X) supported by the National Science Foundation.

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