and σ delocalization in the *exo* transition state[2,3a] seems to be the most satisfactory explanation.

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The Goering–Schewene Diagram for the 1,2-Dimethylnorbornyl System. A Remarkable Similarity in the Diagrams for Classical Tertiary Norbornyl Cations and the Secondary Norbornyl Species

Sir:

There is growing acceptance for the position that tertiary norbornyl cations are classical. Thus Bunton originally argued that resonance cannot be important between canonical structures represented by a secondary norbornyl cation and the related tertiary cation, so that cations such as the 2-methylnorbornyl should be essentially classical.[1a] Brown and Rei observed that a methyl group in the 1 position of 2-methylnorbornyl had the same effect on the rate for the *endo* isomer (× 4.8) as for the *exo* isomer (× 4.3).[1b] This was not compatible with a σ-bridged transition state in which charge would be delocalized to the 1 position in the *exo*, but not in the *endo*, isomer. Sargent concluded that 2-methyl-*exo*-norbornyl derivatives solvolyze without σ participation since he could calculate the observed rates without allowing for that factor.[1c] Brown and Liu observed that the hydrochlorination of 1-methyl-d_3-2-methylenenorbornane can be controlled to yield predominantly unscrambled 1-methyl-d_3-2-methyl-*exo*-norbornyl chloride. Consequently, the symmetrical intermediate, the 1,2-dimethylnorbornyl nonclassical cation, cannot be a significant intermediate in this typical electrophilic reaction.[1d] Sunko has observed that deuterium substituents in the 3 position produce the same rate-retarding effect in the solvolysis of *exo*- and *endo*-2-methylnorbornyl. He also concludes that the 2-methylnorbornyl cation must be classical.[1e] Then Schleyer, from a consideration of all of the available evidence, reached the same conclusion.[1f]

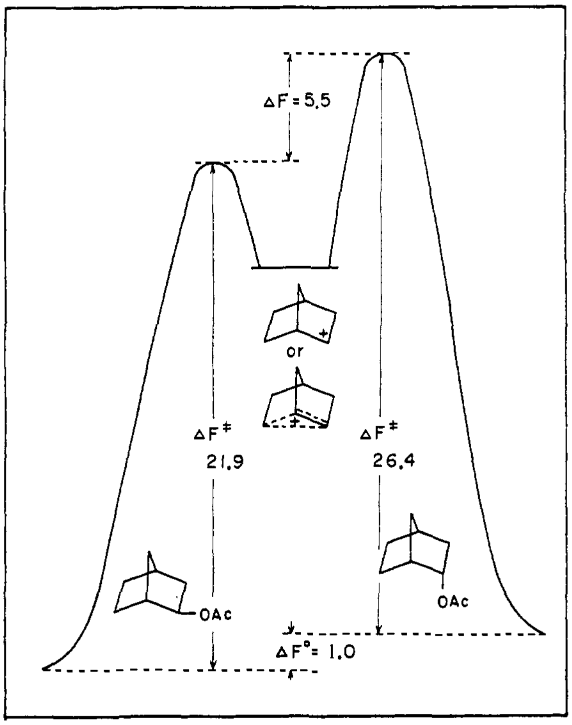

Figure 1. Goering–Schewene diagram for the acid-catalyzed acetolysis of *exo*- and *endo*-norbornyl acetates at 75°. (All numbers are in kilocalories per mole.)

This position has now been elegantly confirmed by the successful trapping of the optically active 1,2-dimethylnorbornyl cation by Goering and his coworkers in the solvolysis of optically active 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate.[2]

We are now in a position to examine the properties of such classical tertiary norbornyl cations and to compare them with the corresponding properties of the secondary norbornyl derivatives. The structure of the secondary norbornyl cation is still undecided.[3]

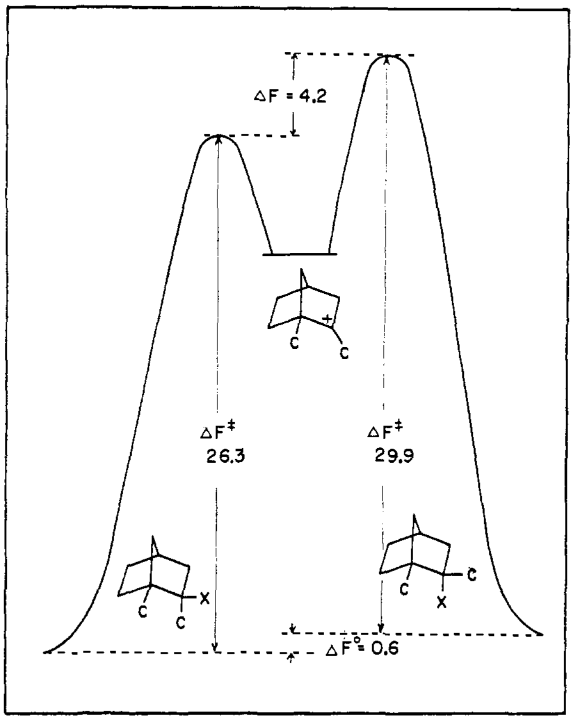

Figure 2. Goering–Schewene diagram for the solvolyses of 1,2-dimethyl-*exo*- and -*endo*-norbornyl *p*-nitrobenzoates in 60% aqueous dioxane at 75°. (X = OH or OPNB; all numbers are in kilocalories per mole.)

The Goering–Schewene diagram for the acetolysis of the 2-norbornyl acetates (Figure 1) provides a quantitative picture of the relationship between the ground-state energies of the *exo* and *endo* isomers, the *exo–endo* rate ratio, and the *exo–endo* product ratio.[4] These authors observed that the *exo* transition state was more stable than the *endo* by 5.5 kcal/mole.[5] They stated

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(1) (a) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 62; (b) H. C. Brown and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 5004 (1964); (c) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (d) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 466 (1967); (e) J. M. Jerkunica, S. Borčić, and D. E. Sunko, manuscript in publication; (f) P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

(2) H. Goering and K. Humski, *ibid.*, **90**, 6213 (1968).

(3) S. Winstein, *ibid.*, **87**, 381 (1965).

(4) H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

(5) The authors[4] actually formulated their diagram in terms of *E*, rather than *F*. Their diagram shows the two transition states to differ by $\Delta E = 4.4$ kcal/mole, rather than $\Delta F = 5.5$ kcal/mole in our diagram. We prefer to use free energy because it is more precise, being directly related to the measured rate and equilibrium constants, and because

that this greater stability of the *exo* transition state was consistent with the nonclassical interpretation, but failed to consider any other alternatives.

It has been pointed out that there are other alternatives to consider:[6] (1) the *exo* transition state is stabilized by nonclassical resonance, with the *endo* being normal; (2) the *endo* transition state is destabilized by steric strain, with the *exo* transition state being normal; (3) a combination of 1 and 2; or (4) some new factor not now recognized by current theory.

Since the successful trapping of the optically active 1,2-dimethylnorbornyl cation appears to establish beyond reasonable doubt the classical nature of this intermediate,[2] it appeared particularly appropriate to construct a Goering–Schewene diagram for this system. Rate data for the *p*-nitrobenzoates[1b] and equilibrium data for the alcohols (72% *exo*-OH, 28% *endo*-OH)[7] were available. The diagram is shown in Figure 2.

The solvolysis at 75° of carefully purified 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate yielded 99.65% *exo* and 0.35 ± 0.5% *endo* alcohol (plus hydrocarbon). The free-energy difference of 4.2 kcal/mole predicts 0.23% *endo*.[8]

The similarity in the two diagrams is noteworthy and significant. The two diagrams involve different solvents and different leaving groups. We must consider the possibility that the similarity is fortuitous.

However, we now have a great deal of data for secondary and tertiary norbornyl systems which indicate that the *exo–endo* rate ratio does not vary significantly with solvent (acetic acid, methanol, aqueous acetone) or with leaving group (OBs, OTs, OMs, Cl). We undertook to confirm this position by comparing the *exo–endo* rate ratio for 2-norbornyl chloride with that for 1,2-dimethylnorbornyl chloride, both in ethanolic solvents.

Treatment of 1,2-dimethyl-*exo*-norborneol with hydrogen chloride in the automatic hydrochlorinator[9] gives initially 1,2-dimethyl-*exo*-norbornyl chloride. However, continued treatment in the presence of a minute amount of zinc chloride rapidly converts the product to an equilibrium mixture (64% *exo*-Cl, 36% *endo*-Cl) of the epimeric chlorides, as identified by pmr examination. Solvolysis in ethanol by the differential technique[10] established the *exo–endo* rate ratio to be 180 at 25°. Similarly, the *exo–endo* rate ratio for the corresponding bromides (equilibrium: 50% *exo*-Br, 50% *endo*-Br) was established as 210. The rates of solvolysis of *exo*- and *endo*-norbornyl chlorides at 85° in 80% ethanol were previously determined.[11] Extrapolation of the observed *exo–endo* rate ratio of 70 at 85° down to 25°[12] yields the value 167. These data support the position that the similarity in the two diagrams (Figures 1 and 2) is not fortuitous.

Goering and Schewene had previously stated that the difference in energy between the two transition states for norbornyl was consistent with the nonclassical interpretation.[4] In view of Goering's own results with 1,2-dimethylnorbornyl,[2] the same position cannot be taken for this system. We are thus forced to conclude that in this tertiary system the *exo* transition state is normal, with the *endo* transition state being destabilized by some factor.

One possibility to consider is that torsional effects[1f] play a dominant role in the destabilization of the transition state for the 1,2-dimethyl derivative.

At first sight this latter interpretation appears quite reasonable, since torsional effects might be expected to be of enhanced importance in this system with its possibilities for large interactions of the two methyl groups. However, the available data[1b] permit us to eliminate this factor as a major contributor. First, the *exo–endo* rate ratio in 1,2-dimethylnorbornyl derivatives is no larger than in 2-methylnorbornyl, where such torsional interactions between two methyl groups are absent. Second, large torsional effects would predict a greatly retarded rate for 1,2-dimethyl-*endo*-norbornyl *p*-nitrobenzoate, since ionization would require the 2-methyl to move toward opposition to the 1-methyl. However, the observed rate is not slower, but faster (× 4.8).[1b]

With torsional effects ruled out as a major contributor in these systems, we are left with steric effects as the sole remaining explanation now available for the higher energy of the *endo* transition state in the tertiary system. There appears to be no reason not to expect similar steric effects to be involved also in the higher energy of the *endo* transition state of the secondary norbornyl system.[13] Whether it is the entire factor remains to be decided.[14] Clearly these developments force us to the conclusion that the long-accepted theory that σ participation is the sole factor responsible for high *exo–endo* rate and product ratios in the norbornyl system must be revised.[15]

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the *exo*/*endo* product ratio is directly related to ΔF for the two transition states.

[6] H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966).

[7] M.-H. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).

[8] Strictly speaking, this figure is the predicted value for the capture of the *p*-nitrobenzoate anion by the cation. However, there are considerable data to support the position that the steric requirements of OH and OCOR are not very different in these reactions.

[9] H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

[10] H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845 (1949).

[11] J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

[12] For this extrapolation we made the reasonable assumption that the entropies of activation for the two compounds are the same.

[13] It is becoming apparent that all reactions of the norbornyl system and similar U-shaped structures show a preference for reaction at the *exo* face, similar to that observed in solvolysis: H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. VanderJagt, *J. Am. Chem. Soc.*, **89**, 6381 (1967).

[14] The appreciable difference in ΔF for the two transition states, 5.5 *vs.* 4.2 kcal/mol, might be interpreted to indicate an added factor in the norbornyl system. However, the transition state for the secondary derivative would be expected, on the basis of Hammond's postulate, to lie further along the reaction coordinate than in the case of the more reactive tertiary derivative. This could result in significantly larger steric interactions in the *endo* secondary than in the *endo* tertiary. However, we cannot now rule out the possibility that σ participation might make a minor contribution to the *exo–endo* ratio in the secondary derivative.

[15] NOTE ADDED IN PROOF. Goering and Sehewene have now revised their original position.[4] They point out that σ participation cannot be significant in the high *exo–endo* rate and product ratios for 1,2-dimethylnorbornyl and conclude, as we do here, that whatever the factor other than σ participation that is responsible for these characteristics in the tertiary derivative must also contribute to the high *exo–endo* rate and product ratios for norbornyl itself (H. L. Goering, C. Brown, and C. B. Schewene, *J. Am. Chem. Soc.*, **90**, 6214 (1968)). Attention is also called to the recent conclusion that σ participation is not a factor in the fast rates of solvolysis of tri-*t*-butylcarbinyl and related derivatives (P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968)).

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