The Question of σ Bridging in the Solvolysis of 2-Norbornyl Derivatives[†,1]
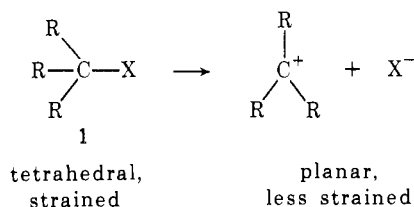
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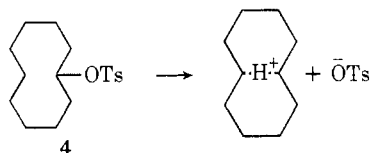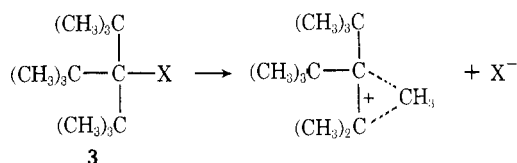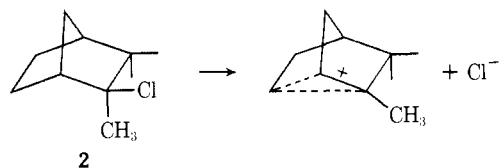
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Origins of the Problem

In 1946 the author proposed that the solvolysis of highly branched tertiary alkyl derivatives (1) should

tetrahedral,   planar,
strained   less strained

be facilitated by the relief of steric strain.[2] A number of systems were examined. The results appeared to support the proposal.[3] The concept appeared to receive general acceptance.[4] Consequently, we left this area for other problems.

Soon thereafter, examples of fast solvolysis rates involving highly strained systems began to appear in the literature. These enhanced rates were attributed not to relief of steric strain but to a new phenomenon, σ participation.[5] Typical examples were cam-

phene hydrochloride[6] (2), tri-*tert*-butylcarbinyl esters[7] (3), and cyclodecyl tosylate[8] (4).

It seemed a remarkable coincidence that all such cases of enhanced rates attributed to σ participation involved strained molecules where relief of steric strain might have been expected to be a major contributory factor. A thorough examination of the evidence advanced for σ participation proved not convincing. Consequently, a detailed experimental program was undertaken to test this proposal.

The Experimental Approach

There appeared to be general agreement that the norbornyl system provided the best, most clear-cut example for σ participation[9] (5). Accordingly, this system was selected for intensive study.

A detailed examination of the literature revealed three major foundations for the proposal of σ participation in the solvolysis of 2-norbornyl derivatives: (A) unusual fast rates of solvolysis for the exo derivatives, as illustrated by a rate for camphene hydrochloride (2) 13,600 larger than that for *tert*-butyl chloride;[6] (B) high exo:endo rate ratios, as indicated by a value of 350 for the acetolysis of the 2-norbornyl brosylates;[5] (C) high exo:endo product ratios in the

(1) (a) For a more detailed discussion of the nonclassical ion problem, see H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, Chapters IX–XI. For earlier reviews, see (b) H. C. Brown, *Chem. Brit.*, 2, 199 (1966); (c) *Chem. Eng. News*, 45, 87 (Feb. 13, 1967).

(2) H. C. Brown, *Science*, 103, 385 (1946).

(3) H. C. Brown and R. S. Fletcher, *J. Amer. Chem. Soc.*, 71, 1845 (1949); H. C. Brown and H. L. Berneis, *ibid.*, 75, 10 (1953).

(4) E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley, New York, N. Y., 1956, Chapter 2.

(5) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, 74, 1147 1154 (1952).

(6) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature (London)*, 168, 65 (1951).

(7) P. D. Bartlett, *J. Chem. Educ.*, 30, 22 (1953).

(8) R. Heck and V. Prelog, *Helv. Chim. Acta*, 38, 1541 (1955).

(9) J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3.
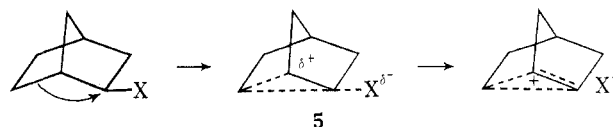
Herbert C. Brown was born in London, England. He started undergraduate studies at Chicago City Junior College and continued at the University of Chicago, where he took his B.S. in 1936 and his Ph.D. (with H. I. Schlesinger) in 1938. He then spent a year in postdoctoral work with M. S. Kharasch and 4 years as research assistant to Schlesinger. After 4 years at Wayne State University, he moved in 1947 to Purdue, where he is now R. B. Wetherill Research Professor. He is renowned for his quantitative studies of steric strains, for developing the σ+ scale of substituent constants and applying them to aromatic electrophilic substitution reactions, for studies in organic synthesis utilizing borohydride, diborane, and organoborane reagents, and for studies in carbonium ion chemistry, one phase of which is the subject of this Account. Professor Brown has been honored by election to the National Academy of Sciences (1957) and the American Academy of Arts and Sciences (1966), and has been the recipient of numerous awards, including the Medal of Science (1969), the Roger Adams Medal (1971), and the Charles Frederick Chandler Medal (1973).

solvolysis of both exo and endo derivatives,[5] including compounds containing 7,7-dimethyl substituents.[9]

Each of these indicated foundations was subjected in turn to intensive examination.

Are Exo Rates Unusually Fast?

The magnitude of the enhanced rate of solvolysis exhibited by camphene hydrochloride (13,600)[10] as compared to *tert*-butyl chloride (1.00) was considered to be not compatible with relief of steric strain.[6] Consequently, the enhanced rate was attributed to the driving force associated with the formation of a stabilized mesomeric cation[6] (2).

In such analyses it is always important to select suitable models.[11] The question may be raised as to the suitability of *tert*-butyl chloride as a model for the highly congested molecule, camphene hydrochloride. A more suitable molecule would doubtless be the pentamethylcyclopentyl chloride realized by opening the 5,6-ethylene bridge (6). This structure

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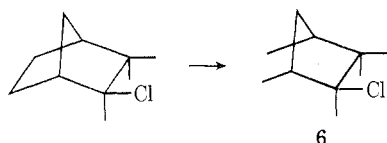
has not yet been synthesized. However, many of the other methylsubstituted 1-methylcyclopentyl chlorides have been prepared and their rates of ethanolysis at 25° determined.[10] The data do not support the conclusion that the rates for the norbornyl derivatives are exceptional.
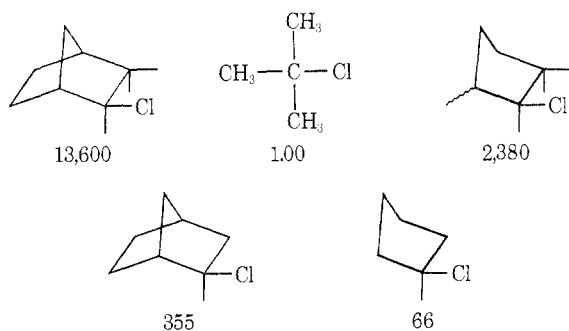
Quite clearly the results are in accord with the postulated effect of increasing steric strain in enhancing the rates of solvolysis of highly branched tertiary chlorides.[2,3] Similar results have been realized in other comparisons.[12]

These results do not disprove the formation of mesomeric norbornyl cations in the solvolysis of 2-norbornyl derivatives. However, they do eliminate the original argument that the rates of solvolysis of camphene hydrochloride and other *exo*-norbornyl derivatives are too fast to be explicable on any basis other than the formation of mesomerically stabilized cations.

Do the High Exo:Endo Rate Ratios Require σ-Bridged Cations?

The precise problem of the 2-norbornyl solvolysis
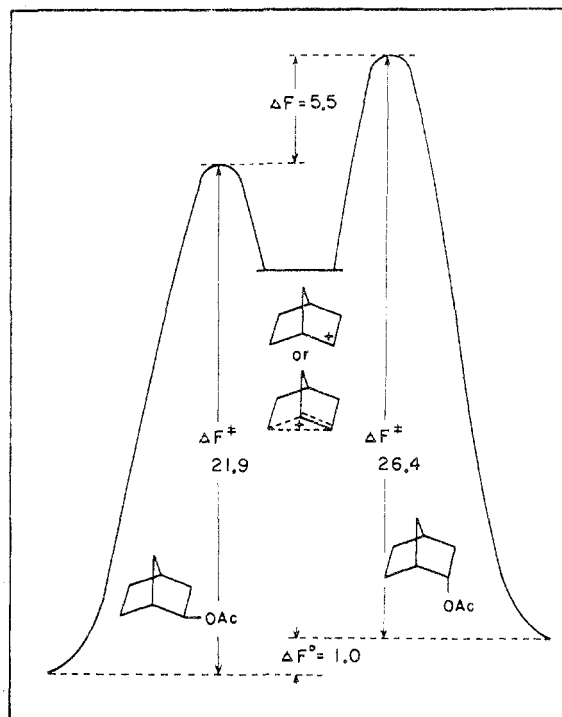
Figure 1. Goering–Schewene diagram for the acid-catalyzed acetolyses of *exo*- and *endo*-norbornyl acetates at 75° (all numbers are in kcal mol⁻¹).

is defined by the Goering–Schewene diagram[13] (Figure 1). The free energy of activation for the exo isomer is 4.5 kcal mol⁻¹ lower than that for the endo isomer. Corrected for the higher ground-state energy of the endo isomer (1.0 kcal mol⁻¹), the difference between the two transition states becomes 5.5 kcal mol⁻¹.

The crucial problem is to define the factor or factors responsible for the major difference of 5.5 kcal mol⁻¹ between the energies of the two transition states. Is the transition state for the exo derivative stabilized by σ participation and charge delocalization, or is the transition state for the endo derivatives destabilized by steric hindrance to ionization or some related factor?

A novel approach to this question was suggested by a comment of one of the referees of the camphene hydrochloride study.[10] In addition to the usual recommendation in this area that the manuscript not be accepted, he made the point that a tertiary carbonium ion is so stable as not to require further stabilization from the 1,6 σ bond. In his opinion, the original authors[6] had been seriously in error in proposing a σ-bridged intermediate as their explanation for the fast solvolysis rate of camphene hydrochloride. Why not prepare highly stabilized tertiary norbornyl derivatives and observe whether or not the exo:endo rate ratio decreases to unity?

The 2-*p*-Anisylnorbornyl Derivatives

It has long been accepted that the more stable the carbonium ion center, the less demand that center will make upon neighboring groups for additional

(10) H. C. Brown and F. J. Chloupek, *J. Amer. Chem. Soc.*, **85**, 2322 (1963).
(11) See ref 1a, p 155.

(12) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1246, 1247, 1248 (1964).
(13) H. L. Goering and C. B. Schewene, *J. Amer. Chem. Soc.*, **87**, 3516 (1965).

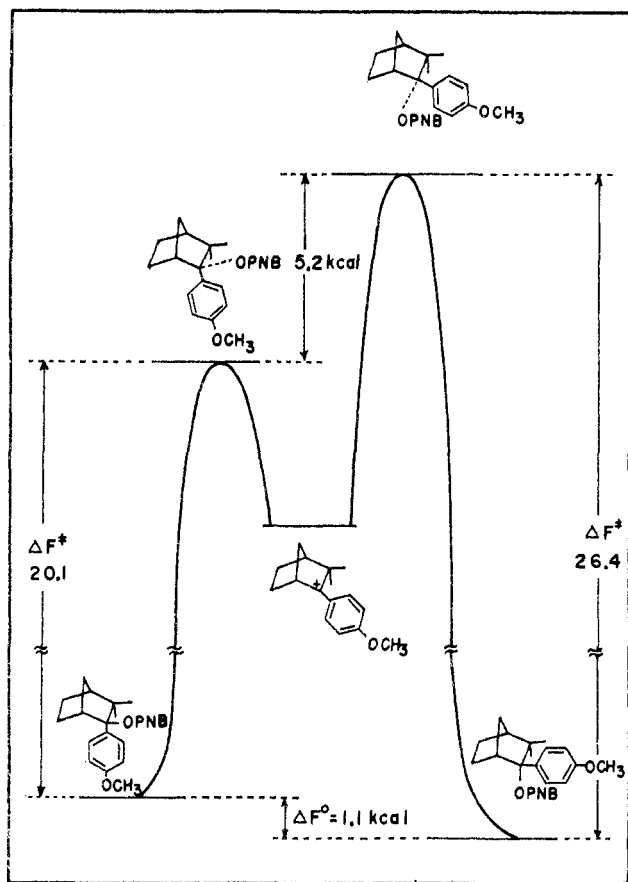**Figure 2.** Free-energy diagram for the solvolyses of 2-*p*-anisyl-camphenilyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.
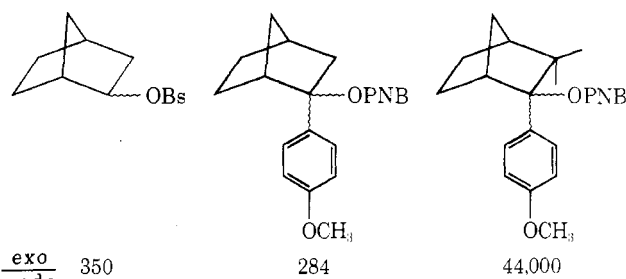
stabilization through participation.[14] Thus, the presence of *p*-anisyl at the 7 position causes the 10^{11} acceleration arising from participation of the double bond in the solvolysis of *anti*-7-dehydronorbornyl derivatives essentially to vanish[14] (**7, 8**).
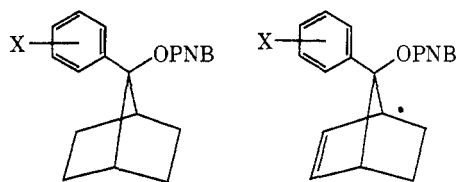
X	7	8
p-CH$_3$O	1.00	3.4
p-H	1.00	41.5
p-CF$_3$	1.00	34,500
m,m'-(CF$_3$)$_2$	1.00	255,000

If *p*-anisyl can cause the truly enormous participation ($\times 10^{11}$) observed in *anti*-7-dehydronorbornyl to vanish, surely it should also cause the much smaller σ participation ($\times 350$) proposed for *exo*-norbornyl to vanish. However, the exo:endo rate ratio in the solvolysis of 2-*p*-anisylnorbornyl *p*-nitrobenzoates is comparable, 284.[15]

Indeed, if methyl groups are introduced in the 3 position, a greatly enhanced exo:endo rate ratio is observed, 44,000.[16] The product is essentially pure ($\geq 99.5\%$) exo alcohol.[16]

(14) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549 (1970).

(15) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **90**, 2691 (1968).

$\dfrac{\text{exo}}{\text{endo}}$ 350	284	44,000

Note the similarity in the characteristics of the free-energy diagram for such a classical 2-anisylnorbornyl system (Figure 2) to that for norbornyl itself (Figure 1).

A careful pmr examination of the 2-phenylnorbornyl cation has revealed no evidence for charge delocalization from the 2 to the 1 and 6 positions.[17] If the 2-phenylnorbornyl cation is classical, there can be no question about the 2-anisyl derivatives. Since σ participation with accompanying charge delocalization cannot be involved in these high exo:endo rate ratios, some other factor must be responsible for the difference in the energies of the two transition states (Figure 2).

Do the High Exo:Endo Product Ratios Require σ-Bridged Cations?

It was recognized early that the acetolysis of either *exo*- or *endo*-norbornyl brosylate yields >99% exo acetate.[5] This was considered to represent a major argument favoring the σ-bridged norbornyl cation (**9**).

exo attack by nucleophile strongly favored
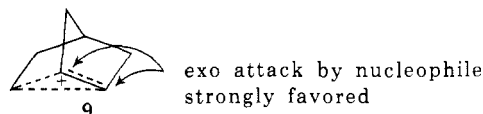
It was originally considered that the high exo:endo rate and product ratios represented two characteristics which provided independent support for the σ-bridged intermediate. However, the free-energy diagrams (Figures 1 and 2) reveal that these are not independent phenomena. The ion in the central well must pass over almost identical transition states (identical in the case of Figure 1) to generate the product. Clearly the formation of exo product will be strongly favored energetically.

Consequently, whatever the factor which stabilizes the exo transition state (or destabilizes the endo transition state) in Figures 1 and 2, it is responsible both for the high exo:endo rate ratio and the high exo:endo product ratio. In the 2-anisylnorbornyl derivatives (Figure 2), this factor cannot be σ participation. We must explore other factors which can be responsible.

Stereochemical Characteristics of the Norbornyl Structure

At a time when little was known about the stereochemical characteristics of the norbornyl structure, it was considered that the high stereoselectivity exhibited in the reaction of the cation with solvent rep-

(16) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **90**, 5268, 5270 (1968).

(17) D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969).

Brown Accounts of Chemical Research

resented a special phenomenon which required a special explanation. However, with the growth of knowledge about the norbornyl system, it has become evident that many reacti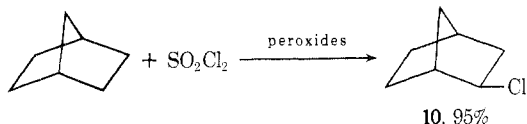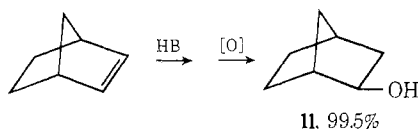ons not involving carbonium ions exhibit a similar strong preference for substitution in the exo direction. Thus free-radical chlorination of norbornane with sulfuryl chloride yields 95% exo chloride[18] (10). Similarly, hydroboration–oxida-

10, 95%

tion of norborene yields 99.5% exo[19] (11). Finally,


11, 99.5%

the base-catalyzed deuterium exchange of norcamphor gives an exo:endo ratio of 715[20] (12).

12
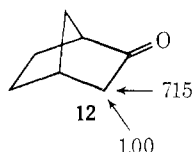
Therefore, the faster rate of solvolysis of the exo isomer and the exo stereochemistry of the product are not unique, but conform to the same reactivity pattern exhibited by the norbornyl system in varying degree in all of its reactions.

Stereochemical Characteristics of the 7,7-Dimethylnorbornyl Structure

It was originally believed that 7,7-dimethyl substituents would dominate the stereochemistry of all reactions of the norbornyl system and force such reactions to take a preferential endo course in the absence of σ bridging. However, data now accumulating require modification of that assumption. Thus, the base-catalyzed deuteration of camphor shows an exo:endo ratio of 21[20] (13).

13
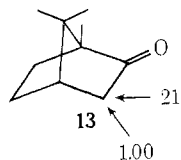
Many other reactions which involve attack by moieties of small steric requirements also go preferentially exo[21] (14).

14, >99.8% exo
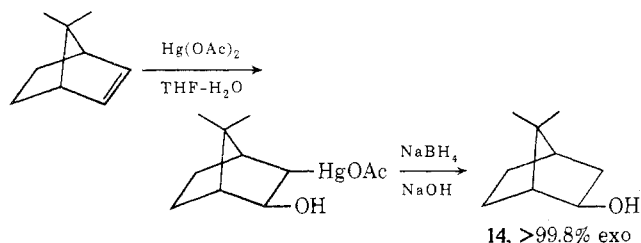
The evidence favors the view that reactions involving reagents of very large steric requirements, such as the reduction of apocamphor by lithium aluminum hydride, or those proceeding through cyclic processes, such as hydroboration or epoxidation of apobornene, are forced by the 7,7-dimethyl substituents to go endo. However, many other reagents go preferentially exo (13, 14), similar to the corresponding reactions of the parent norbornyl system.

Steric Hindrance to Ionization

Steric hindrance to ionization has been suggested as a factor destabilizing the *endo*-norbornyl transition states, both for secondary and tertiary. The norbornane system has a rigid U-shaped structure. Attack of the endo positions is very difficult (10-12). Consequently, it appears reasonable to consider the possibility that departure of the leaving group in a typical ionization will likewise be difficult. Indeed, consideration of molecular models for hypothetical intimate ion pairs for two possible reaction paths reveals major steric difficulties (Figure 3).
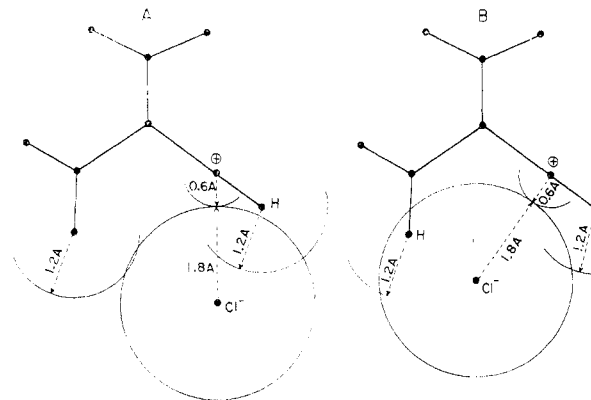
Figure 3. Molecular models for the hypothetical intimate ion pairs from the two postulated reaction paths.

This concept was tested by examining the relative stereoselectivities exhibited by three different bicyclic systems of gradually increasing U-shaped character and rigidity.[22] The results are summarized in Table I. Although individual reactions evidently differ considerably in the stereoselectivities they exhibit, the results reveal a consistent pattern. In all cases, the *cis*-bicyclo[3.3.0]octane system exhibits the least preference for exo attack, presumably because of its higher flexibility, and the *endo*-5,6-trimethylenenorbornane system exhibits the highest stereoselectivity for exo attack. In all cases, the norbornane system is intermediate.

The exo:endo rate ratios exhibited by the corresponding tertiary 2-methyl p-nitrobenzoates exhibit the same pattern of behavior. Is it reasonable then to continue to treat solvolysis as though this reaction obeyed totally different physical laws than other representative reactions?

(18) P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, 3, 177 (1970).

(19) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 92, 1990 (1970).

(20) T. T. Tidwell, *J. Amer. Chem. Soc.*, 92, 1448 (1970).

(21) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *J. Amer. Chem. Soc.*, 95, 2209 (1973).

(22) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *J. Amer. Chem. Soc.*, 89, 6381 (1967).

Table I
**Comparison of the Relative Stereoselectivities Exhibited by
Three Representative U-Shaped Systems**

	Exo:endo ratios		
Reaction			
Hydroboration–oxidation of olefin	24	200	>1000
Epoxidation of olefin	6.7	200	>1000
Oxymercuration–demercuration of olefin	8	>500	
Lithium aluminum hydride reduction of ketone (X = O)	3	8.1	>1000
Addition of CH_3MgX to ketone (X = O)	50	200	>1000
Oxymercuration–demercuration of methylene derivatives (X = CH_2)	8.1	200	>1000
Solvolysis of the tertiary 2-methyl p-nitrobenzoates (X = CH_3, OPNB)	17	885	4300

Effect of Increasing Electron Demand

The free-energy diagrams for norbornyl (Figure 1) and 2-anisylcamphenilyl (Figure 2) are remarkably similar. Ordinarily, in science, such similarity in the behavior of the two systems would favor an interpretation based upon the operation of similar physical factors. However, the situation is different here. It is argued that steric hindrance to ionization should be much less important in secondary derivatives, such as norbornyl, than in tertiary derivatives, such as 2-anisylnorbornyl.[23] Consequently, the difference in energy between the two transition states is attributed primarily to nonclassical stabilization of the exo transition state in norbornyl (Figure 1) and to steric destabilization of the endo transition state in 2-anisylnorbornyl (Figure 2). The problem is how to test this proposal.

One approach which we have explored is to increase the electron demand at the developing carbonium ion center by introducing appropriate substituents in the aromatic ring. Increasing electron demand might result in increasing electron supply from the 1,6 bond, resulting in significant increases in the observed exo:endo rate ratios.

In the 7-aryl-7-*anti*-norbornenyl p-nitrobenzoates increasing electron demand results in major increases in participation[14] (7, 8). However, the 2-aryl-norbornyl derivatives fail to exhibit any increase in the exo:endo rate ratios[24] (15, 16).

One might question whether the demonstration that this tool is capable of revealing π participation[14] (7, 8) can be extrapolated to such a test for σ

X	15	16
p-CH_3O	1.0	284
p-H	1.0	143
p-CF_3	1.0	188
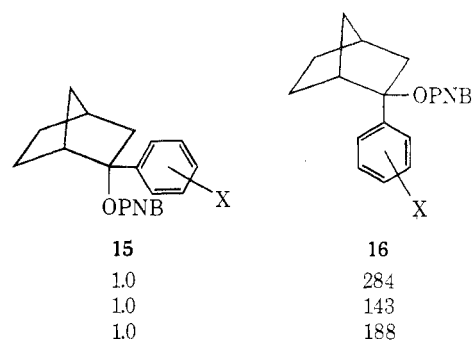
participation from a strained σ bond. Accordingly, we examined the effect of increasing electron demand on the rates of solvolysis of the 2-aryl-3-methyl-2-butyl and 1-aryl-1-cyclopropyl-1-ethyl p-nitrobenzoates[25] (17).

X	17a	17b
p-CH_3O	1.0	505
p-H	1.0	25,300
p-CF_3	1.0	285,000
m,m'-$(CF_3)_2$	1.0	1,210,000
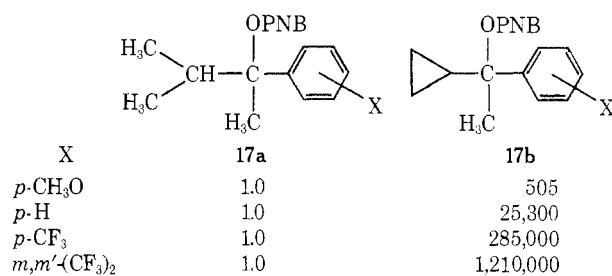
Even in a case involving much smaller electron supply, as in the 3-nortricyclyl system, application of the tool reveals unambiguously increasing electron supply with increasing electron demand[26] (18).

X	18a	18b
p-CH_3O	1.0	2.36
p-H	1.0	38.4
p-CF_3	1.0	270
m,m'-$(CF_3)_2$	1.0	682
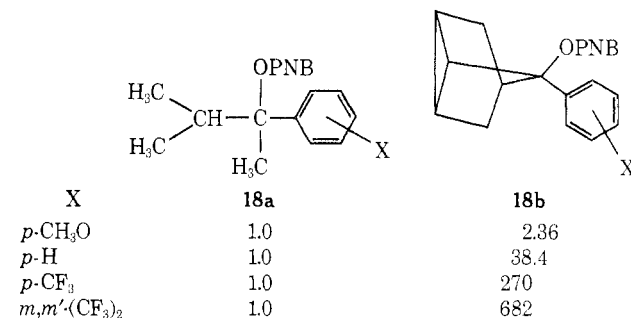
We can only conclude that over this range of electron demand there is no evidence for electron supply as a significant factor in the exo:endo rate ratio.

The 1,2-Dimethylnorbornyl System

As was pointed out earlier, the faster rate of solvolysis of the exo isomer and the exo stereochemistry of the product are not unique, but conform to the same reactivity pattern exhibited by the norbornyl system in varying degree in all of its reactions. It is not the reactivity or the stereochemistry of solvolysis that is unique, but the symmetry properties of the cation[5] (19).

(no plane of symmetry)

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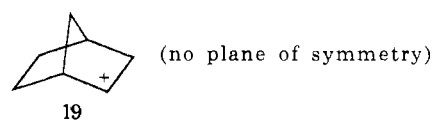
(23) P. v. R. Schleyer, private communication.
(24) K. Takeuchi and H. C. Brown, *J. Amer. Chem. Soc.*, 90, 2693 (1968).

(25) E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, 95, 2397 (1973).
(26) E. N. Peters and H. C. Brown, unpublished research.
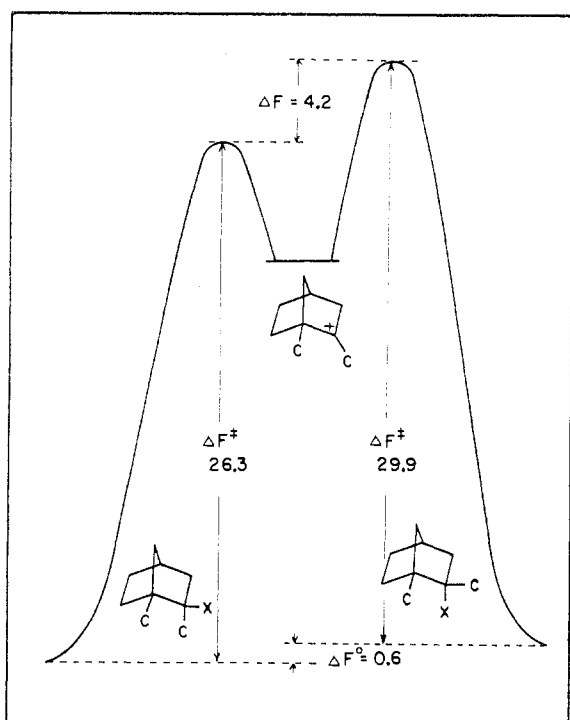
Figure 4. Free-energy diagram for the solvolyses of 1,2-dimethyl-*exo*- and -*endo*-norbornyl *p*-nitrobenzoates in 60% aqueous dioxane at 75° (X = OH or OPNB; all numbers are in kcal mol^{-1}).

The nonclassical structure 5 possesses such a plane of symmetry. However, this characteristic would also be duplicated by a pair of classical ions or ion pairs which equilibrated rapidly compared to the rate of reaction with solvent (20).
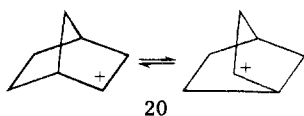
1,2-Disubstituted norbornyl derivatives are of special interest both because the effect of the 1 substituent on the rate possesses diagnostic significance[1b] and because they can be prepared in optically active form and examined to see if they undergo racemization during solvolysis.

1,2-Dimethylnorbornyl *p*-nitrobenzoate exhibits an exo:endo rate ratio at 50° of 185.[27] The product is 99.7% exo, 0.3% endo.[28] The system provides a free-energy diagram (Figure 4) that is also remarkably similar to that for norbornyl (Figure 1). Again the question arises whether the difference in energy arises from nonclassical stabilization of the exo, or steric destabilization of the endo. Fortunately, in this case it is now possible to give an unambiguous answer.

Solvolysis of optically active 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate in 90% aqueous acetone gives alcohol with 9% retention.[29] Similarly, methanolysis of optically active 1,2-dimethyl-*exo*-norbornyl chloride gives methyl ether with 14% retention.[30] Goering and Clevenger[30] conclude that

they are trapping a rapidly equilibrating classical ion or ion pair before it has completely equilibrated (21).
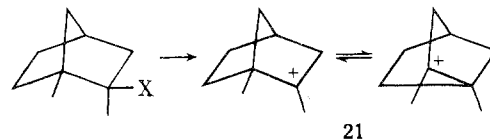
Although these authors conclude that the minor difference in the energies of the two transition states (Figures 1 and 4) support the conclusion that totally different physical interactions are involved in the two systems, it appears to this author more reasonable to conclude that the phenomena involved must be quite similar, with equilibration in the norbornyl system sufficiently faster or the lifetime of a tight ion pair sufficiently longer so as to frustrate such trapping of an unsymmetrical species.

The 2,7,7- and 2,6,6-Trimethylnorbornyl Systems

If the exo:endo rate ratio is the result of steric forces, it should be possible to vary these ratios in a predictable manner by varying the steric environment. Thus an increase in the steric crowding of the exo environment should lead to a decrease in the exo:endo rate ratio. Similarly, an increase in the steric crowding of the endo environment might be expected to result in an increase in the exo:endo rate ratio. Indeed, the exo:endo rate ratio of 855 for 2-methylnorbornyl *p*-nitrobenzoate decreases to 6.1 with the presence of two methyl groups in the 7 position, and increases to 3,630,000 with the methyl groups in the 6 position. These major changes in the exo:endo rate ratios are readily explicable in terms of the effects of the *gem*-dimethyl groups in either facilitating or hindering the rates of solvolysis[31] (22).


strain	strain
enhanced exo rate	diminished endo rate
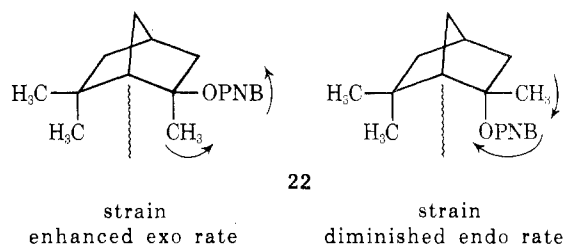
Note the major changes in the magnitude of the difference in energy of the two transition states (Figures 5 and 6) of the corresponding Goering–Schewene diagrams. Certainly in these cases the difference cannot be solely the result of stabilization by σ bridging in the exo isomer.

The Parent Norbornyl System

The data show that these tertiary norbornyl derivatives exhibit exo:endo rate and product ratios comparable to those exhibited by norbornyl itself. Is it reasonable to account for such similar phenomena in terms of the operation of totally different forces, steric in the tertiary derivatives, σ bridging in the secondary? Reasonable or not, let us examine the data to see if we can find independent evidence confirming the presence of σ bridging in the parent norborn-

(27) H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 86, 5004 (1964).
(28) H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 90, 6216 (1968).
(29) H. Goering and K. Humski, *J. Amer. Chem. Soc.*, 90, 6213 (1968).
(30) H. L. Goering and J. V. Clevenger, *J. Amer. Chem. Soc.*, 94, 1010 (1972).

(31) H. C. Brown and S. Ikegami, *J. Amer. Chem. Soc.*, 90, 7122 (1968); S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, 90, 7124 (1968).
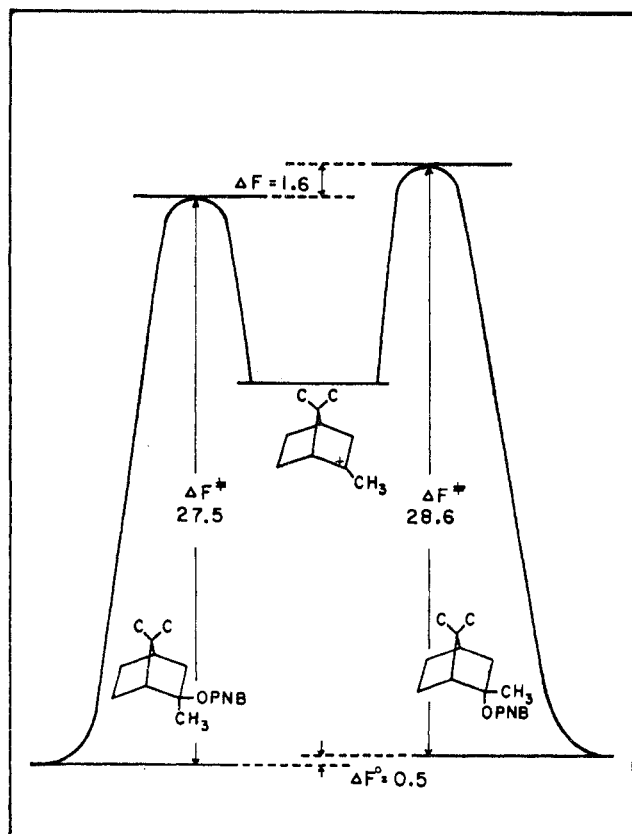
Figure 5. Free-energy diagram for the solvolyses of 2,7,7-trimethyl-*exo*- and -*endo*-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25° (all numbers are in kcal mol^{-1}).
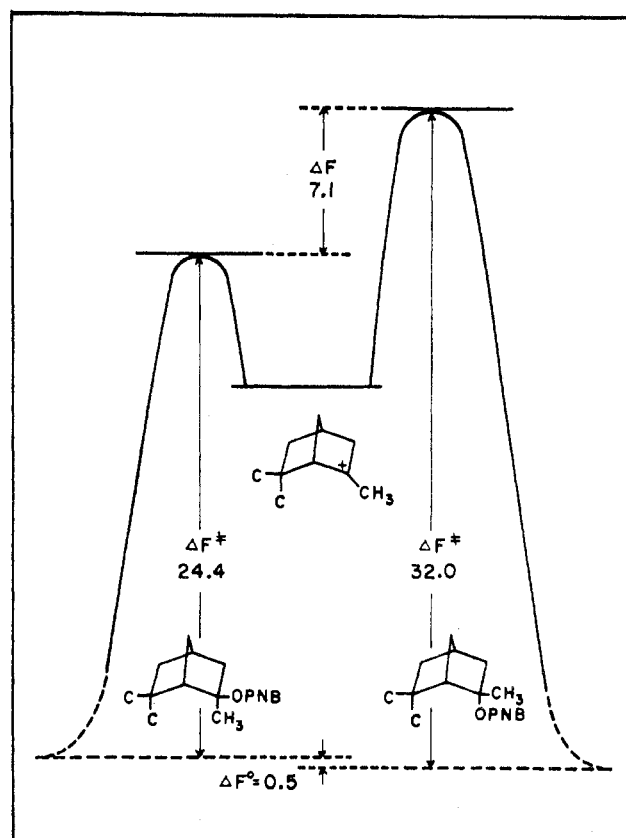

Figure 6. Free-energy diagram for the solvolyses of 2,6,6-trimethyl-*exo*- and -*endo*-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25° (all numbers are in kcal mol^{-1}).

yl system with concurrent charge delocalization from the 2 to the 1 and 6 positions. However, first it is desirable to consider the precise implications of the Goering–Schewene diagram (Figure 1).

Implications of the Goering–Schewene Diagram

The acetolysis of 2-norbornyl derivatives exhibits an extraordinarily high preference for exo product: 99.98% *exo*-, 0.02% *endo*-norbornyl acetate at 25°.[13] Does this remarkably high stereospecificity require the formation of a σ-bridged intermediate? The Goering–Schewene diagram provides a definitive answer. Indeed, a careful examination of the implications of the diagram can eliminate much of the confusion in the literature provided by earlier qualitative discussions.

The exo and endo isomeric acetates pass over the two transition states to form the same intermediate, the norbornyl cation (Figure 1). The principle of microscopic reversibility requires that in the symmetrical system, which was the subject of the original study, the norbornyl intermediate, in reacting with acetic acid, must pass over the same two transition states involved in the ionization of the reactants. The authors established that the difference in the energies of the two transition states actually corresponds to the observed distribution of the intermediate to the products: 99.98% exo, 0.02% endo.[32]

It follows that the factor responsible for the difference in energy between the exo and endo transition states of the norbornyl system must be responsible for the stereoselectivity leading to the almost exclusive formation of the exo product. Unfortunately, the fact that we recognize this point does not aid us in understanding just what that factor may be.

The remarkable stereoselectivity exhibited in the solvolysis of norbornyl derivatives had been considered to require σ bridging in the norbornyl cation. The literature is replete with arguments of this kind.[33] However, the diagram makes it clear that the amount of bridging that may or may not be present in the free ion is not directly involved in the stereoselectivity of the substitution. *It is the amount of bridging in the exo transition state, or whatever the factor responsible for the difference in stability of the two transition states, that will control the distribution of the norbornyl cation or ion pair between exo and endo products.*

Consequently, it is difficult to understand the rationale behind the proposal that bridging may lag behind ionization.[34] Such bridging following the transition state would appear to have nothing to do with the high exo:endo rate and product ratios.

Let us consider what might be the factor or factors responsible for the difference in energy between the exo and endo transition states. Four possibilities might be pointed out: (1) the exo transition state is stabilized by nonclassical resonance, with the endo

(32) The authors[13] constructed their diagram utilizing enthalpies. They calculated a ΔE for the two transition states of 4.4 kcal mol^{-1}. In order to compare the diagram for norbornyl with those for other derivatives (Figures 2, 4–6), we have utilized free energy data. We have also made the assumption that the steric requirements of an acyloxy group, such as *p*-nitrobenzoate, will not differ significantly from those of hydroxyl.

(33) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965.

(34) S. Winstein, *J. Amer. Chem. Soc.*, 87, 381 (1965).

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.[35]

Let us consider some of the approaches which have been made in an attempt to confirm the proposed stabilization of the *exo*-norbornyl transition state.

Application of the Foote–Schleyer Correlation

The Foote–Schleyer correlation was proposed as a means of calculating the rates of acetolysis of secondary tosylates.[36] Clearly, if such a calculation could be relied upon to reveal that the endo isomer is normal, whereas the exo isomer is 350 times more reactive than the calculated value, the problem could be considered resolved. Indeed, this claim was made.[36]

A possible difficulty with this approach appeared to be the treatment of steric hindrance to ionization in developing the correlation. In principle the non-bonded strain term ($GS_{strain} - TS_{strain}$) in Schleyer's correlation should be capable of handling steric hindrance to ionization ($GS_{strain} < TS_{strain}$), as well as steric assistance to ionization ($GS_{strain} > TS_{strain}$). However, in practice the expediency was adopted of assuming TS $\approx$ 0 for leaving groups.

Accordingly, in collaboration with Schleyer, we undertook to test the ability of the correlation to predict the rates of certain *endo*-norbornyl derivatives where large steric hindrance to ionization might be anticipated (23). Discrepancies of 8,000 to 100,000

    23a   23b   23c
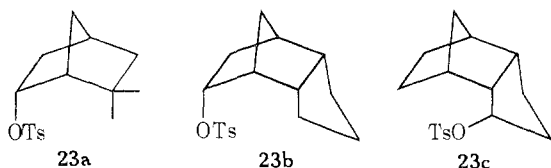
between the predicted and observed rates were realized.[37] It was concluded that this approach could not resolve the problem.

Effect of Substituents

The nonclassical norbornyl cation has been represented as a resonance hybrid of three structures[5] (24). According to this formulation, charge is delo-

calized from the 2 to the 1 and 6 positions. If the lower energy of the exo transition state is the result of the fact that the stabilized σ-bridged norbornyl cation is partially formed in that transition state, it should be possible to obtain evidence for such charge delocalization by using the classical tool of the organic chemist, the effect of substituents in appropriate positions.
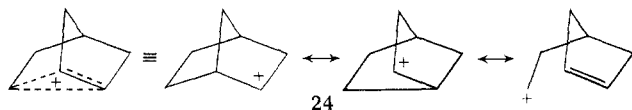
For example, the fast rate of solvolysis of cyclopropylcarbinyl derivatives is attributed to the ability of the cyclopropyl ring to delocalize charge from the carbonium ion center. In confirmation, the introduction of a methyl and an ethoxy substituent results in large rate increases.[38]

    1.00   11.0   940
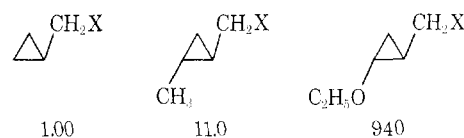
If charge were similarly delocalized to the 6 position of the norbornyl system in the transition state, then the introduction of methyl and methoxy groups into that position should result in similar rate increases. However, such rate increases are not observed.[39]

    1.00   (0.5)[39]

    0.04[40]   0.14[41]
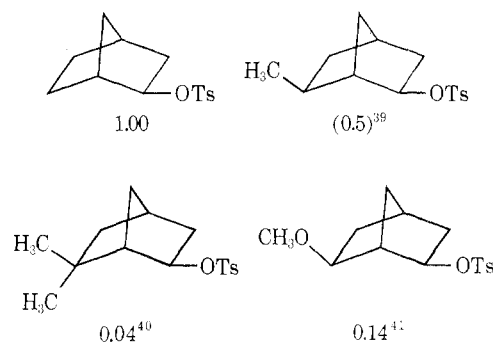
It has been suggested that "there are good reasons to expect carbon bridging to lag behind C–X ionization at the transition state."[34] However, if σ bridging in the transition state is responsible for the 5.5 kcal mol^{-1} difference in energy of the two transition states (Figure 1), as the proponents of the nonclassical norbornyl cation have long argued,[13] it is difficult to understand how one can achieve stabilization of this magnitude in the transition state while arguing that carbon bridging largely follows ionization. As has been pointed out, the Goering–Schewene diagram makes it clear that the amount of carbon bridging in the free ion has nothing to do either with the exo:endo rate ratio or the exo:endo product ratio. It is the amount of bridging in the exo transition state, or whatever the factor responsible for the difference in energy of the two transition states, that is the controlling factor.

If the norbornyl cation is really a resonance-stabilized species, the effect of substituents in the 2 position should be greatly decreased over their effect in a typical aliphatic or alicyclic system. However, we observe very similar effects.[1b,42]

There is a difficulty in introducing substituents into the 1 position as a test for charge delocalization to that position. Norbornyl derivatives containing alkyl or aryl substituents in the 1 position solvolyze

(35) It has been suggested that torsional effects may contribute to the exo:endo ratio in norbornyl derivatives. However, the factor resulting from such torsional effects cannot be large (P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 89, 701 (1967)).

(36) C. S. Foote, *J. Amer. Chem. Soc.*, 86, 1853 (1964); P. v. R. Schleyer, *ibid.*, 86, 1854, 1856 (1964).

(37) H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Nat. Acad. Sci. U. S.*, 56, 1653 (1966).

(38) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, 88, 2321 (1966).

(39) The value for the 6-methyl is a tentative value: private communication from P. v. R. Schleyer.

(40) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, 87, 375 (1965).

(41) P. v. R. Schleyer, P. J. Stang, and D. J. Raber, *J. Amer. Chem. Soc.*, 92, 4725 (1970).

(42) H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 86, 5008 (1964); H. C. Brown and K. Takeuchi, *ibid.*, 88, 5336 (1966).

with rearrangement to tertiary norbornyl cations. This should provide a driving force which would enhance the effect of the 1 substituent. Nevertheless, the data reveal major differences in the effects of substituents in the 1 and 2 positions.[42,43]

1.00   7.8   500,000,000,000

At the present time substituent effect data do not appear to be available to confirm the presence of the oft-postulated nonclassical resonance. The numerous explanations which have been advanced to account for the repeated failure of this major tool to detect the presence of delocalized charge in the norbornyl system[34,40,41] make interesting reading.

Other Carbonium Ion Studies

The deamination of optically active *exo-* and *endo*-norbornylamine yields *exo*-norbornanol with considerable retention of activity.[44] The reaction presumably involves the classical norbornyl cation as an intermediate.[44,45]

The addition of acids to olefins under ionic conditions is a representative process involving carbonium ions.[46] Yet the addition of various deuterated acids (DCl,[47] CD_3CO_2D,[48,49] CF_3CO_2D[49]) yields results which appear to require the intermediacy of the classical norbornyl cation.

61%   32%   7% hydride shifted product

It has been argued that these results should not be extrapolated to the interpretation of solvolytic data.[44,50,51] However, perhaps we should consider the possibility that it is solvolysis that is unique and not the other carbonium ion reactions of the norbornyl system. Conceivably, solvolysis of 2-norbornyl derivatives may produce tight ion pairs[52] whose lifetime

might be relatively long, permitting equilibration of isomeric ion pairs before they react with solvent. Deamination and the addition of acids may produce 2-norbornyl cations which are less tightly associated with anions than those produced in solvolytic processes, facilitating capture of the intermediates before they have fully equilibrated.

Other Studies

A detailed discussion of the 2-norbornyl cation by G. D. Sargent has recently appeared.[53] The author accepts the position that tertiary norbornyl cations are classical, so that the high exo:endo rate and product ratios in these systems must have a steric origin. However, he concludes, in spite of the similarity of the Goering–Schewene diagrams, that σ participation must be the dominant factor in the secondary norbornyl derivatives. It is interesting to note how time has answered many of the arguments that Sargent and others have used to support this position.

Berson originally argued that the preference for exo,exo 3,2 migrations in norbornyl cations strongly supported a σ-bridged formulation.[54] More recently, an endo,endo 3,2 migration was described.[55] Sargent, following a review of the evidence, concludes that the phenomenon "fails to provide conclusive evidence for a bridged structure for the ion."[53]

At one time the Foote–Schleyer correlation was utilized to support the σ-bridged formulation.[36] However, it proved incapable of handling steric hindrance to ionization, and it was concluded that the correlation could not resolve the problem.[37] It now appears to be in even more serious difficulty.[56] Early calculations favored the σ-bridged structure for the norbornyl cation.[57] However, a recent, presumably more precise, approach favors the classical structure.[58]

It was originally argued that the very similar effects of one and two methyl substituents on the rate of solvolysis of the 2-(3-cyclopentenyl)ethyl arenesulfonates required that both the transition states and intermediates be symmetrical, i.e., nonclassical.[59] However, Goering's recent success in trapping the optically active 1,2-dimethylnorbornyl cation[29,30] makes it necessary to reconsider this argument.

Secondary isotope effects have been utilized.[60] For example, a deuterium substituent in the 6 position gives $k_H/k_D = 1.10$ for *exo-*, but 1.00 for *endo*-norbornyl brosylate. This is considered to support σ participation. At one time it was reported that there was a reduced σ deuterium effect ($k_H/k_D = 1.11$) in

(43) D. C. Kleinfelter and P. v. R. Schleyer, quoted in ref 9.

(44) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *J. Amer. Chem. Soc.*, 85, 169 (1963); J. A. Berson and A. Remanick, *ibid.*, 86, 1749 (1964).

(45) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, 92, 3182 (1970).

(46) P. E. Peterson, *et al.*, *J. Amer. Chem. Soc.*, 89, 5902 (1967).

(47) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, 89, 3898 (1967).

(48) E. Vogelfanger, Ph.D. Thesis, University of California, Los Angeles, Calif., 1963.

(49) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *J. Amer. Chem. Soc.*, 92, 5536 (1970).

(50) R. C. Fahey, *Top. Stereochem.*, 3, 253 (1969).

(51) However, the distribution of the ^{14}C in the *exo*-norbornyl acetate produced in the solvolysis of 2-(3-cyclopentenyl)ethyl-2-^{14}C brosylate is in better agreement with the classical formulation: C. J. Collins and M. H. Lietzke, *J. Amer. Chem. Soc.*, 89, 6565 (1967).

(52) R. A. Sneen, *Accounts Chem. Res.*, 6, 46 (1973).

(53) G. D. Sargent in "Carbonium Ions," Vol. III, G. Olah and P. v. R. Schleyer, Ed., John Wiley, New York, N. Y., 1972, Chapter 24.

(54) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, 89, 2561, 2590 (1967).

(55) A. W Bushell and P. Wilder, Jr., *J. Amer. Chem. Soc.*, 89, 5721 (1967).

(56) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 92, 2538 (1970). See footnote 21.

(57) G. Klopman, *J. Amer. Chem. Soc.*, 91, 89 (1969).

(58) D. W. Goetz and L. C. Allen, *Proc. Int. Congr. Pure Appl. Chem.*, 26, 51 (1971).

(59) P. D. Bartlett, *et al.*, *J. Amer. Chem. Soc.*, 87, 1288, 1297 (1965).

(60) D. E. Sunko and S. Borčić in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N. Y., 1970, Chapter 3. For a discussion of the difficulties involved in interpreting these deuterium isotope effects in norbornyl derivatives, see S. E. Scheppele, *Chem. Rev.*, 72, 511 (1972).

exo-norbornyl but a normal effect (k_H/k_D = 1.21) in *endo*-.[61] This result was also interpreted as favoring a nonclassical intermediate. However, it is now reported that this earlier result was a consequence of scrambling, so that both isomers actually yield the same value, 1.21, for k_H/k_D.[60] What conclusion can be safely drawn?

It has been argued that low exo:endo rate ratios observed for the solvolyses of certain modified norbornyl derivatives represent the true behavior of classical norbornyl cations.[62-67] Space does not permit a detailed discussion of the evidence and interpretation of all these cases.[65a] However, it can be pointed out briefly that in the case of 7-oxonorbornyl Gassman has concluded that the unusual exo:endo rate ratio is the result of participation of the 7-oxo group, greatly enhancing the rate of the endo tosylate.[68] In the case of 6-carbomethoxynorbornyl, the products from the exo and endo brosylates are very different[67] and do not conform to the behavior anticipated for a system giving a common cation or ion pair (Figure 1).

Observations of the norbornyl cation in strong acids at low temperatures have been interpreted as requiring a σ-bridged species.[69,70] However, there is by no means agreement as to the precise interpretation of the data.[71] For example, Kramer points out that the published ESCA spectrum[69] corresponds to a 6:1 distribution of carbon atoms, rather than the 5:2 required by the σ-bridged interpretation.[71] However, interesting as these studies are, they are not pertinent to the question of what is responsible for the high exo:endo rate and product ratios in the solvolysis of norbornyl derivatives, a point which Olah, *et al.*,[69] have stated.

Finally, a major piece of evidence favoring the absence of significant σ participation is provided by the observation that the exo:endo rate ratio for norbornyl tosylate in acetic acid (k_t = 281; k_α = 1600) shows no major change in formic acid ($k_t \approx k_\alpha$ = 1600)[72] or in trifluoroacetic acid (k_t = 1120).[73] In systems where participation is known to occur, major increases in rates resulting from such participation are observed in shifting from acetic acid to less nucleophilic solvents.[74]

Conclusions

Twelve years have passed since we first began a systematic search for σ participation in camphene hydrochloride and related tertiary norbornyl derivatives. There now appears to be considerable agreement that such tertiary norbornyl cations are largely, if not entirely, classical. Yet they exhibit exo:endo rate and product ratios comparable to the corresponding ratios exhibited by the parent secondary systems. The similarities in the Goering–Schewene diagrams (Figures 1, 2, 4–6) are obvious. Is it reasonable to continue to interpret such similar phenomena in terms of totally different physical bases? We believe that it is not, unless some definitive piece of experimental evidence to support σ bridging in secondary norbornyl derivatives is forthcoming.

As was pointed out earlier, our interest in the question of σ participation was initiated by proposals that such σ participation provided an alternative explanation to relief of steric strain for certain enhanced rates: (1) camphene hydrochloride, (2) tri-*tert*-butylcarbinyl *p*-nitrobenzoate, and (3) cyclodecyl tosylate. It is of interest to observe what has happened to these three original cases in the intervening years. In the case of cyclodecyl tosylate, it was observed that the introduction of transannular deuterium failed to affect the rate significantly. Consequently, the transannularly bridged formulation (4) was withdrawn.[75] A detailed study of the products from the solvolysis of tri-*tert*-butylcarbinyl *p*-nitrobenzoate failed to support the σ-bridged formulation (3), and it has been withdrawn.[76] Finally, if one can extrapolate the conclusions of Goering and Humski about the essentially classical nature of the 1,2-dimethylnorbornyl cation[29,30] to the 2,3,3-trimethylnorbornyl (hydrocamphenilyl) cation, then this σ-bridged cation is no longer with us.

We have come a long way since the era when complex nonclassical structures were considered for cations as stable as that derived from 2-*p*-anisylcamphenilol in formic acid[77] (**25**). We are now reduced to

25
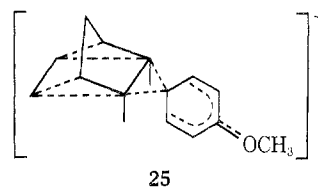
the parent secondary system as a place where σ participation is still being proposed as a contributing factor to the observed exo:endo rate and product ratios. However, even here we must give serious consideration to the question of why all experimental efforts to find independent confirmation for the oft-postulated presence of σ bridging and charge delocalization from the 2 to the 1 and 6 positions in solvolytic reactions have uniformly failed.

(61) C. C. Lee and E. W. C. Wong, *J. Amer. Chem. Soc.*, **86**, 2752 (1964).

(62) K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Jap.*, **38**, 1318 (1965).

(63) E. J. Corey and R. S. Glass, *J. Amer. Chem. Soc.*, **89**, 2600 (1967).

(64) C. F. Wilcox, Jr., and R. G. Jesaitis, *Chem. Commun.*, 1046 (1967).

(65) C. F. Wilcox, Jr., and R. G. Jesaitis, *Tetrahedron Lett.*, 2567 (1967). The 7-spiro derivative reveals no rate acceleration corresponding to stabilization accompanying charge delocalization to the 1 position.

(65a) Note Added in Proof. The low exo:endo rate ratios observed for the 3-methylene[64] and 3-spirocyclopropane[65] derivatives appear to reflect operation of the Selectivity Principle: H. C. Brown and E. N. Peters, *Proc. Nat. Acad. Sci. U. S.*, in press.

(66) P. G. Gassman and J. L. Marshall, *J. Amer. Chem. Soc.*, **88**, 2822 (1966).

(67) G. W. Oxer and D. Wege, *Tetrahedron Lett.*, 457 (1971).

(68) P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. M. Hornback, *J. Amer. Chem. Soc.*, **91**, 4282 (1969).

(69) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Liu, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

(70) G. A. Olah, G. D. Mateescu, and J. L. Riemenschneider, *J. Amer. Chem. Soc.*, **94**, 2529 (1972).

(71) G. Kramer, *Advan. Phys. Org. Chem.*, in press.

(72) Unpublished work with F. J. Chloupek.

(73) J. E. Nordlander, R. E. Gruetzmacher, W. J. Kelley, and S. P. Jindal, in press.

(74) For example, the 1-phenyl-2-propyl:2-propyl tosylate ratio is 0.4 in acetic acid, 0.58 in formic acid, and 17.1 in trifluoroacetic acid: J. E. Nordlander and W. J. Kelly, *J. Amer. Chem. Soc.*, **91**, 996 (1969).

(75) V. Prelog, *Rec. Chem. Progr.*, **18**, 247 (1957). See also V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 9.

(76) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968).

(77) P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, Jr., *Justus Liebigs Ann. Chem.*, **623**, 217 (1959).