The Energy of the Transition States and the Intermediate Cation in the Ionization of 2-Norbornyl Derivatives. Where is the Nonclassical Stabilization Energy?[1]

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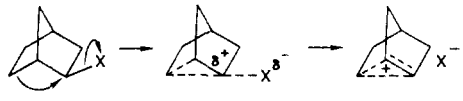
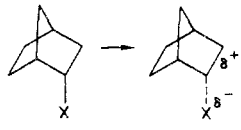
The Problem

An early application of the nonclassical carbonium ion concept was made by Winstein.[2] He proposed to account for both the high exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives and the racemization of *exo*-norbornyl *p*-bromobenzenesulfonate (brosylate) in the solvolytic process by proposing that the exo isomer **1** undergoes solvolysis with σ-bridging by the 1,6-bonding pair, stabilizing the exo transition state **2** as the system proceeds through the σ-bridged exo transition state **2** to the symmetrical nonclassical cation



1 2 3

3. The endo isomer **4** was considered to be stereoelectronically unsuited for such σ-participation. In this isomer, solvolysis was postulated to proceed through an unbridged transition state **5**.



4 5

The free energy diagrams for the solvolysis of 2-norbornyl derivatives reveal that the energies of the two transition states differ by approximately 6.0 kcal/mol (Figure 1[3]). Essentially identical diagrams are realized for data under a wide range of conditions.[4–6] Accordingly, this interpretation requires that there be present in the exo transition state **2** 6.0 kcal/mol of nonclassical stabilization energy not present in the endo transition state **5**.

We tried very early to detect this nonclassical stabilization by comparing $\Delta\Delta G^{\ddagger}$ for the solvolysis of secondary/tertiary pairs: *i*-PrCl/*t*-BuCl, CpCl/1-MeCpCl, 2-NbCl/2-Me-2-NbCl.[7] However, the difficulty of correcting for solvent participation in the solvolysis of the secondary derivatives made the results and conclusions uncertain.

In the last several years there have been four major developments that make it possible now to determine the nonclassical stabilization energy in the transition-state **2** or the fully developed ion **3**.

1. Schleyer and his co-workers have established that solvolysis of secondary *p*-toluenesulfonates (tosylates) in trifluoroacetic acid (TFA)[8] and hexafluoroisopropyl alcohol (HFIP)[6] are limiting.[9b]
2. He and his co-workers have developed a precise method for calculating the limiting rates in other solvents, such as EtOH.[9a]
3. Harris and Brown and their co-workers have independently established that the solvolysis of *endo*-norbornyl derivatives proceed with little solvent participation.[10]
4. Arnett and Petro developed a calorimetric method for determining the heats of ionization and applied the method to the alkyl chlorides of interest.[11]

For the first time we can search for the nonclassical stabilization energy under both solvolytic and stable ion conditions. Three independent aproaches show negligible nonclassical stabilization.

How Did I Get Involved?

In 1946 I proposed that the solvolysis of highly branched tertiary alkyl derivatives should be facilitated by relief of steric strain.[12] A number of systems was examined. The results appeared to support the proposal.[13] The concept appeared to receive general acceptance.[14] Consequently, we left this area for other problems.

Soon thereafter, examples of fast solvolysis rates in-

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(1) (a) For a broader review, see: Brown, H. C. *Acc. Chem. Res.* **1973**, *6*, 377. (b) For a detailed discussion of the 2-norbornyl problem, see: Brown, H. C. "The Nonclassical Ion Problem", with comments by Schleyer, P. v. R.; Plenum Press: New York, 1977.

(2) Winstein, S.; Trifan, D. S. *J Am. Chem. Soc.* **1952**, *74*, 1147, 1154.

(3) Brown, H. C. *Chem. Br.* **1966**, *2*, 199.

(4) Goering, H. L.; Schewene, C. B. *J Am. Chem. Soc.* **1965**, *87*, 3516. Acetolysis of 2-NbOAc.

(5) Bentley, T. W.; Bowen, C. T.; Brown, H. C.; Chloupek, F. J. *J. Org. Chem.* **1981**, *46*, 38. Hydrolysis of 2-NbOMs in H_2O.

(6) Bentley, T. W.; Bowen, C. T.; Morton, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466. Solvolysis of 2-NbOTs in HFIP.

(7) (a) Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* **1964**, *86*, 5008. (b) Cp stands for cyclopentyl and Nb for norbornyl.

(8) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658.

(9) (a) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667; (b) "Limiting" solvolyses involve insignificant nucleophilic participation by solvent during the ionization step.

(10) (a) Harris, J. M.; Mount, D. L.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 3139. (b) Brown, H. C.; Ravindranathan, M.; Chloupek, F. J.; Rothberg, I. *Ibid.* **1978**, *100*, 3143. (c) Also see: Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1980**, *45*, 2113.

(11) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5402, 5408.

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

(13) (a) Brown, H. C.; Fletcher, R. S. *J. Am. Chem. Soc.* **1949**, *71*, 1845. (b) Brown, H. C.; Berneis, H. L. *Ibid.* **1953**, *75*, 10.

(14) Eliel, E. L. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 2.

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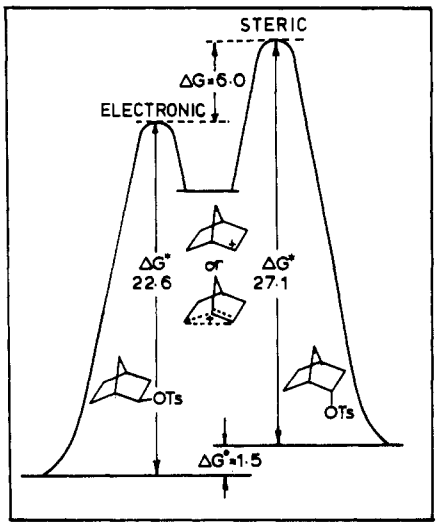


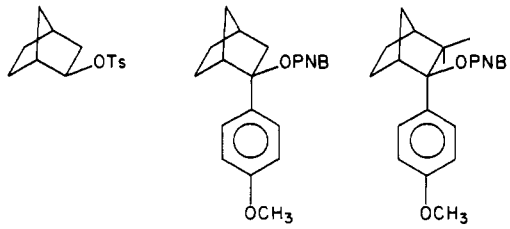
Figure 1. Free energy diagram for the acetolysis of *exo*- and *endo*-norbornyl tosylates at 25 °C (all numbers in kilocalories/mole).

volving 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.[2] Typical examples were camphene hydrochloride,[15] tri-*tert*-butylcarbinyl esters,[16] and cyclodecyl tosylate.[17]

These were soon withdrawn, largely by their own authors.[18-20] At this stage, I could have withdrawn from the field. However, Schleyer persuaded me to examine both secondary and tertiary 2-norbornyl derivatives as providing the most favorable case for rate enhancements arising from σ-participation.

Tertiary 2-Norbornyl Derivatives

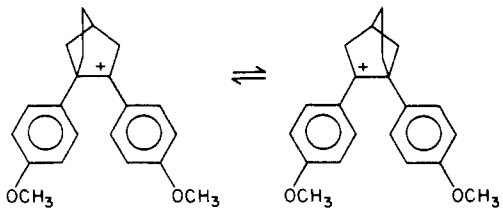
Simple experiments soon established that tertiary 2-norbornyl derivatives undergo solvolysis with high exo/endo rate ratios, comparable to those of the secondry derivatives.[21] Moreover, Winstein concluded



exo/endo	280	284	44 000

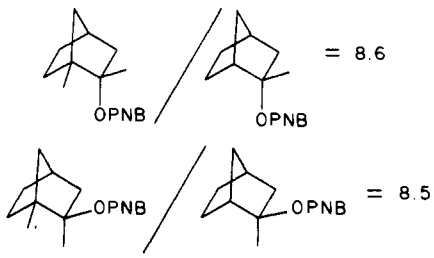
that "the older evidence for typical tertiary norbornyl cations is in line with preferred bridged structures".[22]

A number of developments soon convinced nonclassical adherents that tertiary 2-norbornyl cations must be classical. For example, Schleyer and his co-workers subjected the 1,2-di-*p*-anisyl-2-norbornyl cation to intensive study.[23] They concluded that their thermochemical, chemical reactivity, and UV and NMR spectral data support the existence of the ion **6** as a rapidly equilibrating pair rather than as a resonance hybrid.

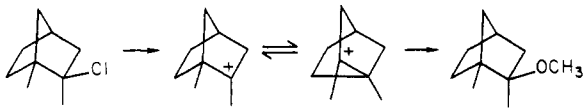


6

It appeared that a comparison of the rates of solvolysis of 2-methyl- and 1,2-dimethyl-2-norbornyl *p*-nitrobenzoates should provide evidence for the presence of nonclassical resonance. This should be much more important in the symmetrical species than in the unsymmetrical one. Moreover, it should be present in the exo derivatives but not in the endo. However, the experimental data did not confirm the presence of such nonclassical resonance.[24] Then, Goering and his co-

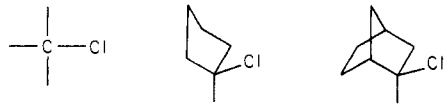


workers solvolyzed optically active 1,2-dimethyl-*exo*-norbornyl chloride (**7**) and successfully captured up to 14% of the optically active methyl ether[25] (**8**).



7 **8**

The solvolysis of simple tertiary chlorides is essentially a k_c process.[25c] Consequently, simple rate data revealed that there was no major stabilization present in 2-methyl-*exo*-norbornyl chloride not present in 1-methylcyclopentyl chloride.[18] $\Delta\Delta G^{\ddagger}$ for the first two



rel rate	1.00	66	355

members is 2.3 kcal/mol; for the last two, it is 1.0.

(15) Brown, F.; Hughes, E. D.; Ingold, C. K.; Smith, J. F. *Nature (London)* **1951**, *168*, 65.
(16) Bartlett, P. D. *J. Chem. Educ.* **1953**, *30*, 22.
(17) Heck, R.; Prelog, V. *Helv. Chim. Acta* **1955**, *38*, 1541.
(18) Brown, H. C.; Chloupek, F. J. *J. Am. Chem. Soc.* **1963**, *85*, 2322.
(19) Bartlett, P. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1968**, *90*, 4421.
(20) Prelog, V. *Rec. Chem. Prog.* **1957**, *18*, 247. See also Prelog, V.; Traynham, J. G. In "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963; Vol. 1, Chapter 9. J. E. Nordlander has recently argued for a revival of such transannularly bridged cations: Nordlander, J. E.; Owuor, P. O.; Cabral, D. J.; Haky, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 201. However, H.-J. Schneider has recently reported that he has been unable to find any significant stabilization for such cations: Schneider, H.-J.; Schmidt, G.; Thomas, F. *J. Am. Chem. Soc.* **1983**, *105*, 3556. These authors report "...any nonclassical participation in the tosylate solvolysis...for medium rings to be unrecognizable ($\Delta\Delta G^{\ddagger} \leq 0.5$ kcal/mol)."
(21) (a) Brown, H. C.; Takeuchi, K. *J. Am. Chem. Soc.* **1968**, *90*, 2691, 5268, 5270. (b) PNB stands for the *p*-nitrobenzoyl group.
(22) Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 381.
(23) Schleyer, P. v. R.; Kleinfelter, D. C.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 479.
(24) Brown, H. C.; Ravindranathan, M.; Rao, C. G.; Chloupek, F. J.; Rei, M.-H. *J. Org. Chem.* **1980**, *43*, 3667.
(25) (a) Goering, H. L.; Humski, K. *J. Am. Chem. Soc.* **1968**, *90*, 6213. (b) Goering, H. L.; Clevenger, J. V. *Ibid.* **1972**, *94*, 1010. (c) k_c is a rate constant for solvolysis not assisted by solvent or neighboring group nucleophilic participation.

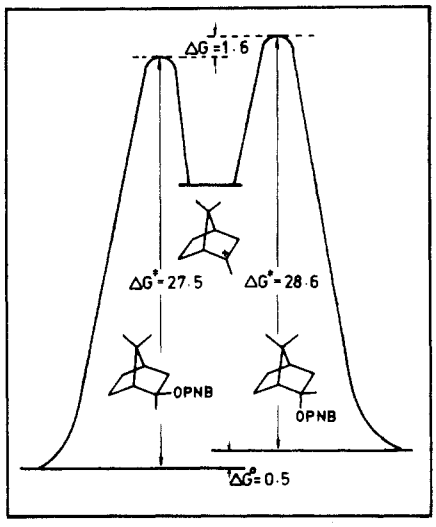
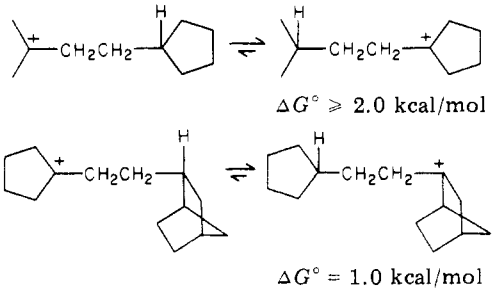


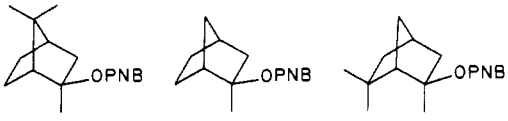
Figure 2. Free energy diagram for the hydrolysis in 80% acetone of 2,7,7-trimethyl-2-norbornyl *p*-nitrobenzoate at 25 °C (all numbers in kilocalories/mole).

A related comparison under stable ion conditions (−90 °C) gives data in excellent agreement.[26]



These data emphasize the importance of having a suitable model compound for comparison with the norbornyl derivative. As in the case of camphene hydrochloride discussed previously, the direct comparison with *tert*-butyl chloride gives an enormous relative rate factor, 13 600.[15,18] Yet, comparison with a methylated 1-methylcyclopentyl chloride gives only a relative reactivity of 5.[18] Likewise, in Sorensen's equilibrium study[26] the direct comparison of 2-norbornyl with isopropyl gives an equilibrium strongly favoring the positive charge on norbornyl. No measurable equilibrium can be detected. Yet in the literature, the 2-norbornyl cation is frequently compared with the isopropyl rather than the cyclopentyl cation.

Finally, the importance of steric effects in influencing the exo/endo rate ratio in such tertiary 2-norbornyl derivatives is indicated by a comparison of the following systems:[27]



exo/endo	6.1	885	3 630 000

Note the similarities and differences of the free energy diagrams (Figures 2 and 3), with that for 2-norbornyl (Figure 1). Clearly the differences in the energies of the two transition states vary in a predictable manner with the exo/endo rate ratios.

(26) Okazawa, N.; Sorensen, T. S. *Can. J. Chem.* **1982**, *60*, 2180.
(27) (b) Brown, H. C.; Ikegami, S. *J. Am. Chem. Soc.* **1968**, *90*, 7122. (b) Ikegami, S.; Vander Jagt, D. L.; Brown, H. C. *Ibid.* **1968**, *90*, 7124.

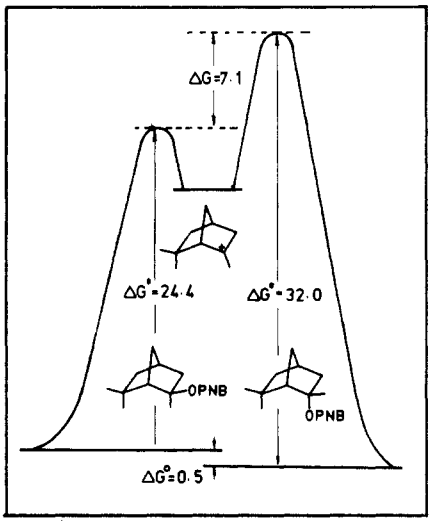


Figure 3. Free energy diagram for the hydrolysis in 80% acetone of 2,6,6-trimethyl-2-norbornyl *p*-nitrobenzoate at 25 °C (all numbers in kilocalories/mole).

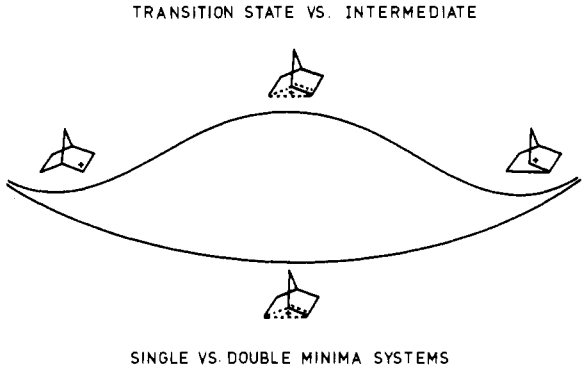
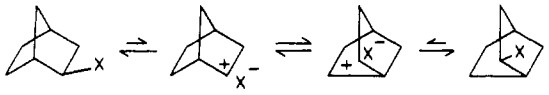


Figure 4. Proposed transformation of the relatively stable transition state for the rapid equilibration of 2-norbornyl cations into a stabilized symmetrical intermediate sufficiently stable so as to make it unnecessary for further consideration of unsymmetrical 2-norbornyl cations as intermediates.

Consequently, now there appears to be general agreement that tertiary 2-norbornyl cations are classical, with only the secondary 2-norbornyl cations being retained in the nonclassical fold.[28]

Single vs. Double Minima

The heart of the Winstein proposal was that the 2-norbornyl cationic intermediate be considered to be a single minimum system rather than a rapidly equilibrating double minimum system (Figure 4). The sta-



bilization of the fully developed cation by σ-bridging would largely be present in the exo transition state, not in the endo.

The Free Energy Diagram

The free energy diagram (Figure 1) provides a rigorous basis to calculate the nonclassical stabilization energy of the exo transition state. It is clear (Figure 1) that the exo transition state is 6.0 kcal/mol lower in energy than the endo transition state. If this difference in energy is due to σ-participation in the exo transition

(28) (a) Walling, C., accompanying paper in this issue. (b) See also comments by P. v. R. Schleyer, ref 1b.

state and its absence in the endo, then there is 6.0 kcal/mol of nonclassical stabilization in the exo transition state. This stabilization is absent in the endo transition state or in the tertiary 2-methyl-*exo*-norbornyl transition state. One means of solving the problem is to detect this 6.0 kcal/mol of nonclassical stabilization in the exo transition state and to show its absence in the related tertiary derivatives. That is the main focus of the present study.

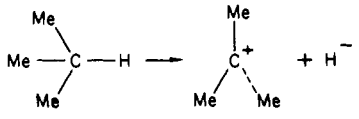
If the difference in energy is 6.0 kcal/mol in the two transition states, the difference in the energies of the nonclassical cation and the classical cation should be somewhat larger. We have taken 8.0 kcal/mol as a conservative estimate.

Nonclassical ions with delocalized charge should be much more weakly solvated than classical cations with more localized charge.[29] Consequently, the difference in energy between the nonclassical and classical structures of the 2-norbornyl cations should be considerably larger for the unsolvated cations in the gas phase.

Stability of Carbocations

Inductive effects [Ingold, 1926], direct field effects [Ingold, 1928], and hyperconjugation [Mulliken, 1939] were introduced early and used to account for the stabilities of carbocations and their ease of formation.[30]

Let us consider how the early effects were applied. The removal of H^- from isobutane produces the *tert*-butyl cation. The interaction of the positive charge



with the three methyl groups (inductive effect) stabilizes the system. Furthermore, hyperconjugation delocalizes charge to the nine hydrogen atoms. In this case, the direct field effect would be expected to be small.

The resulting ion is planar and highly stablized. It is generally considered to be a representative classical cation.

In the case of cyclopentane, removal of a hydride ion produces the cyclopentyl cation. Again, the inductive effect will stabilize the cationic center. The direct field effect (polarization) will be quite important as the cationic center interacts with the four other carbon atoms of the ring. The strain in the five-membered ring should be especially effective in facilitating polarization interactions. Finally, hyperconjugation would be expected to delocalize charge into the α-positions.

Why should this cation be more stable than the 2-propyl cation? Clearly, the two additional carbon atoms, their geometrical arrangement surrounding the cationic center, and the strain in the ring facilitating polarization interactions should all lead to considerably larger stabilization in the cyclopentyl cation than in the 2-propyl cation.

Removal from norbornane of the 2-hydrogen as hydride produces the 2-norbornyl cation. Again we have inductive effects stabilizing the system. Hyperconjugation will also delocalize charge into the α-positions.

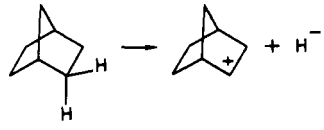
(29) Jorgensen, W. L.; Munroe, J. E. *Tetrahedron Lett.* **1977**, 581.
(30) For an early discussion of how these concepts were applied, see: Remick, A. E. "Electronic Interpretations of Organic Chemistry"; Wiley: New York, 1943.

Table I
Relative Rates of Solvolysis at 25 °C

solvent	X	*i*-PrX	CpX	*exo*-2-NbX	*endo*-2-NbX
MeOH[a]	OMs	1.00	8.40	30.9	0.0497
		0.12	1.00	3.70	0.0090
				412.0	1.00
HOAc[b]	OTs	1.00	21.0	301.0	1.07
		0.048	1.00	14.3	0.05
				281.0	1.00
TFA[c]	OTs	1.00	128.0	21900.0	19.5
		0.008	1.00	171.0	0.15
				1121.0	1.00
HFIP[d]	OTs	1.00	377.0	156000.0	99.10
		0.0027	1.00	413.0	0.026
				1572.0	1.00

[a] Unpublished research with F. J. Chloupek. [b] Reference 10b. [c] Reference 38. [d] Reference 6.

Finally, the direct field effect (polarization) should further stabilize the cation.



How would the effect compare with the stabilization of the cyclopentyl cation? Clearly, the presence of two more carbon atoms surrounding the cationic center should greatly stabilize the system over that achieved with cyclopentyl. The strain in the system should be favorable for polarization interactions.

Clearly the cation will undergo major readjustments as these interactions of the cationic center with the structure occur. It is puzzling to see in the literature statements that the classical 2-norbornyl cation should have the structure of norbornane.

Clearly, the 2-propyl cation is not a reasonable model for the 2-norbornyl cation. They are far separated in the stability spectrum. Interestingly, the 7-norbornyl cation is less stable than the 2-propyl cation by an amount that is even larger than the difference in stability of 2-propyl and 2-norbornyl. In view of these facts, it is puzzling that nonclassical supporters have often stated that all secondary cations possess the same stability, with only 2-norbornyl being exceptional.[31]

Solvolysis of 2-Norbornyl and Related Derivatives

Can we obtain evidence for the presence of nonclassical resonance energy in *exo*-norbornyl by examining its rate of solvolysis? In Table I we have summarized the data for the rates of solvolysis of *exo*-norbornyl and related alkyl methanesulfonates and toluenesulfonates in representative solvents.

In each solvent the rates increase: *i*-PrX < CpX < *exo*-NbX. This agrees with the discussion of how we might expect the stabilities of the *i*-Pr^+, Cp^+, 2-Nb^+ cations to vary.

The effects increase from MeOH to HOAc to TFA to HFIP. Again, the less nucleophilic the solvent, the greater the charge at the developing cationic center and the greater the effects of the structure in stabilizing the cation.

(31) Olah, G. A.; Prakash, G. K. S. *Prep. Div. Pet. Chem., Am. Chem. Soc.* **1982**, *28*, 366: "If the classical structure were correct, the 2-norbornyl cation would be a regular secondary carbocation with no additional stabilization provided by σ-delocalization such as the cyclopentyl cation."

The results with HFIP are especially interesting. The solvolysis of secondary tosylates in this solvent has been established to be limiting.[6] Cyclopentyl undergoes solvolysis at a rate 377 that of 2-propyl. Presumably, the two additional carbon atoms surrounding the cationic center and the greater polarizability of the five-membered ring contribute to the greater rate, as discussed earlier. Bond opposition forces will also contribute.

exo-Norbornyl tosylate undergoes solvolysis at a rate 156 000 that of 2-propyl. At first sight, this would appear to be a huge rate enhancement attributable to σ-participation. However, the observed rate is only 413 times that of cyclopentyl tosylate. Clearly, we might anticipate comparable factors for cyclopentyl (with two more carbon atoms surrounding the cationic center) and for *exo*-norbornyl (with two additional carbon atoms surrounding the cationic center). The greater strain of the ring system and the larger bond opposition forces are also favorable. It should be noted that the incremental $\Delta\Delta G^{\ddagger}$ is 3.5 kcal/mol for 2-propyl/cyclopentyl and the same for cyclopentyl/2-norbornyl. In the gas phase, the increments indicated by the hydride affinity values of Solomon and Field are considerably larger: 5.9 and 11.4 kcal/mol.[32]

It is noteworthy that the rate of solvolysis of the endo isomer is slow, which we attribute to steric hindrance to ionization. However, the endo isomer in HFIP shows a large increase over the rate in acetic acid. (As discussed later, the solvolyses are essentially limiting for *endo*-norbornyl tosylate in both solvents.) The large increase is most reasonably attributed to the interaction of the developing charge with the six carbon atoms surrounding the developing cationic center. The exo/endo rate ratio does not change greatly.

In his discussion of the 2-norbornyl question, Walling has proposed that the cationic center at C-2 must interact with the electron cloud of C-6.[28a] He does not consider similar interaction of the charge with C-4 and C-7, situated at the same distance from C-2. The direct field effect would favor comparable interactions with C-4, C-6, and C-7, with a smaller, but significant, interaction with the more distant C-5.

Analysis of the solvolysis data by Bentley has persuaded him that in the solvolysis of the endo derivative there is a retardation, which he prefers to term "steric hindrance to solvation of the leaving group" (included in our more general term.) However, his calculations lead him to conclude that half of the exo/endo rate ratio is due to this term and half to σ-participation.[33]

Solvolysis of 6-Substituted 2-Norbornyl Derivatives

In recent years, Grob and his co-workers have examined the solvolysis of 6-substituted 2-norbornyl derivatives.[34] He has been able to change the exo/endo rate ratio in a major way with changes of the substituent. Consequently, he concludes that steric hindrance to ionization cannot be a significant factor in such ratios.

In contrast to the 2-norbornyl solvolyses, he does not obtain the same products from the exo and endo isomers. Consequently, he concludes that he is not obtaining the symmetrically bridged cation of Winstein. Instead, he proposes that the solvolysis proceeds through the formation of rapidly equilibrating cations that are captured before they are fully equilibrated.

He prefers to represent these as σ-bridged equilibrating cations. However, as was pointed out earlier, it is not clear how this differs from the operation of the field effect, or why the interaction of the charge is restricted to the electron cloud at C-2 and does not involve the electron clouds at the equidistant C-4 and C-7.

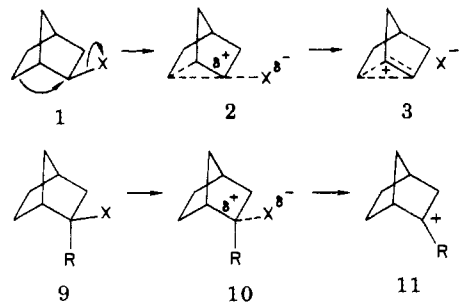
One problem is the question of whether these solvolyses with deactivating substituents involve true k_c or k_Δ[35] processes, a problem discussed earlier for such derivatives.[36]

It should be pointed out that all of the secondary and tertiary derivatives that we examined,[37] and for which we have given free energy diagrams (Figures 1–3), yielded essentially identical products from the exo and endo derivatives.

It is clear that Grob's experiments throw doubt on the present nonclassical position that the solvolysis of all secondary 2-norbornyl derivatives, in contrast to the behavior of tertiary, proceed to the formation of symmetrical bridged 2-norbornyl cations.

Search for Nonclassical Stabilization

The nonclassical interpretation of the exo/endo rate ratio in the ionization of secondary and tertiary *exo*-norbornyl derivatives involves an interesting dichotomy.[28] In spite of the similarity in the chemical phenomena and the free energy diagrams (Figures 1 and 3), the behavior of these two systems is accounted for in terms of totally different phenomena. The high exo/endo rate ratio in secondary *exo*-norbornyl is attributed to the stabilization provided by σ-bridging, both in the transition state and in the free ion or ion pair. In the tertiary derivative, the high exo/endo rate ratio is attributed to steric hindrance to ionization in the endo isomer. Thus we have an electronic explanation for the secondary and a steric explanation for the tertiary to account for phenomena that appear remarkably similar (Figures 1 and 3).



This position offers the possibility for simple quantitative tests. A comparison of the energies of the two transition states **2** and **10** should reveal a difference that is 6.0 kcal/mol smaller than that of other comparable secondary and tertiary transition states not involving σ-bridging. A comparison of the energies of the two cations **3** and **11** with other systems not involving σ-bridging should reveal a modestly larger discrepancy

(32) Solomon, J. J.; Field, F. *J. Am. Chem. Soc.* **1976**, *101*, 4067.
(33) Bentley, T. W. *Ann. Rep. B* **1974**, 119.
(34) Grob, C. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 87; accompanying paper in this issue.
(35) k_Δ is the part of the overall solvolysis rate constant due to neighboring group participation.
(36) Reference 1b, pp 206–209.
(37) Reference 1b.

Table II
Rates of Ethanolysis of Alkyl Chlorides

substituent/substrate	rate constants at 25 °C, 10^6k, s^{-1}			
	2-R-2-PrCl	1-R-1-CpCl	2-R-*exo*-NbCl	2-R-*endo*-NbCl
R = hydrogen	?[a,c]	?[b,d]	5.42×10^{-4}	3.20×10^{-6}
relative rate			170.0	1.00
R = methyl	0.086	5.60	30.0	0.18
	1.00	65.0	348.8	2.1
relative rates	0.015	1.00	5.3	0.032
	0.48	31.1	170.0	1.00
R = phenyl	394.0	21100.0	158000.0	930.0
	1.00	54.0	401.0	2.4
relative rates	0.019	1.00	7.4	0.044
	0.42	22.7	170.0	1.0

[a-d] Limiting rate constant (10^6k) for 2-PrCl and CpCl: [a] $k = 1.6 \times 10^{-7}$, calculated from 2-PrOTs in TFA. [b] $k = 8.6 \times 10^{-6}$, calculated from CpOTs in TFA. [c] $k = 2.7 \times 10^{-8}$, calculated from 2-PrOTs in HFIP. [d] $k = 4.8 \times 10^{-6}$, calculated from CpOTs in HFIP.

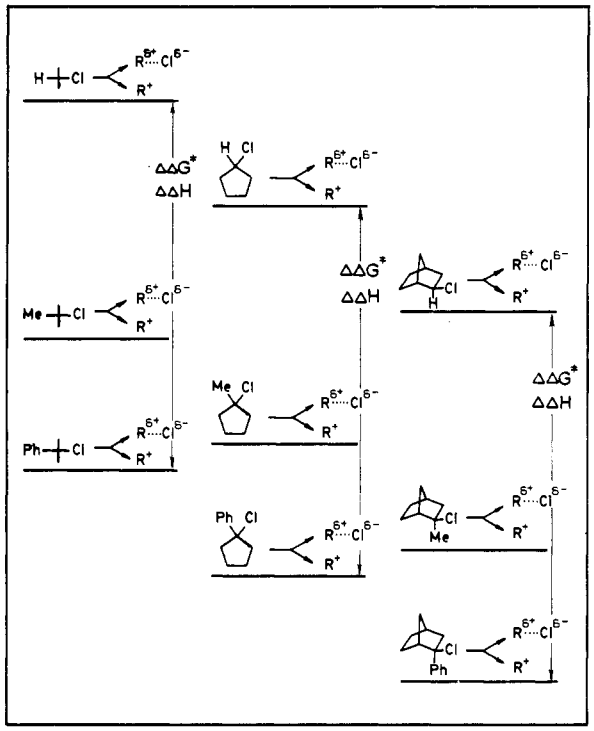


Figure 5. Predicted behavior of representative secondary and tertiary systems assuming 2-norbornyl is classical.

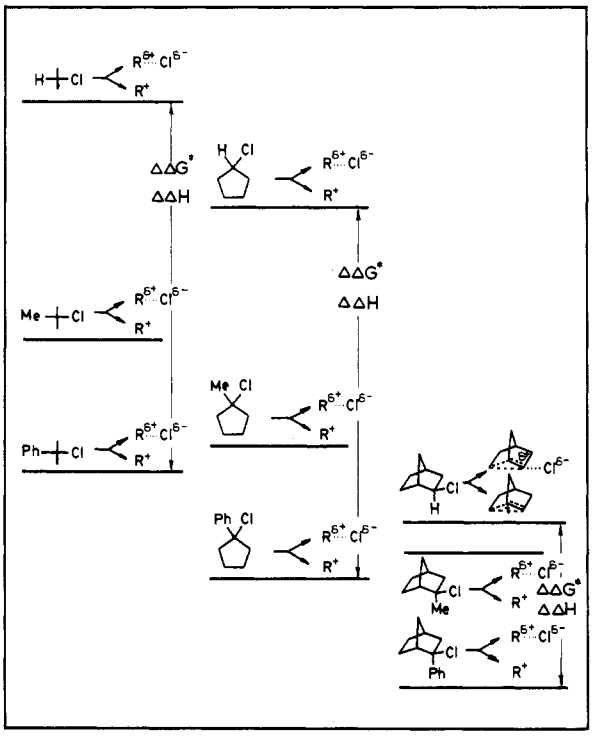


Figure 6. Predicted behavior of representative secondary and tertiary systems assuming 2-norbornyl is nonclassical.

~8 kcal/mol. This approach is indicated by Figures 5 and 6.

Search for Nonclassical Stabilization. Solvolytic Data

We have long wanted to test for the presence in the transition state for solvolysis of *exo*-norbornyl derivatives of 6.0 kcal/mol of nonclassical stabilization, not present in related tertiary transition states. As is pointed out above, it appeared that a comparison of $\Delta G^{\ddagger}$ for secondary and tertiary derivatives should establish that norbornyl derivatives show a $\Delta\Delta G^{\ddagger}$ that is 6.0 kcal/mol less than that in other representative systems (Figures 5 and 6).

We had reliable data for the enthanolysis of tertiary chlorides.[7,24] The difficulty was the lack of reliable values for the limiting rates of ethanolysis of isopropyl chloride and cyclopentyl chloride (Table II). This problem has now been solved by Schleyer and his coworkers.[8,9]

We took the rates of solvolysis of isopropyl, cyclopentyl, and *exo*-norbornyl tosylate in the limiting solvents, TFA[38] and HFIP.[6] These limiting rate constants were then converted to the limiting rates in ethanol by using the Schleyer correlation,[9] the conversion factor for ROTs/RCl,[7] and the appropriate m values (0.64 for *i*-Pr, 0.70 for Cp, and 0.80 for *exo*-Nb) for use in the correlation equation.

Limiting rate constants for ethanolysis of these alkyl chlorides had previously been calculated by Arnett et al.[39] Our values were somewhat higher than theirs. Investigation revealed that they had used $m = 1.00$ for all alkyl groups, whereas we had used the experimental m values.

We also examined a simplified method for proceeding from the rate constants for the tosylates in TFA and HFIP to those for the chlorides in ethanol. As pointed out earlier, the solvolyses of *endo*-norbornyl derivatives are essentially limiting.[10] Consequently, we calculated

(38) Nordlander, J. E.; Gruetzmacher, R. R.; Kelly, W. J.; Jindal, S. P. *J. Am. Chem. Soc.* **1974**, *96*, 181.
(39) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522.

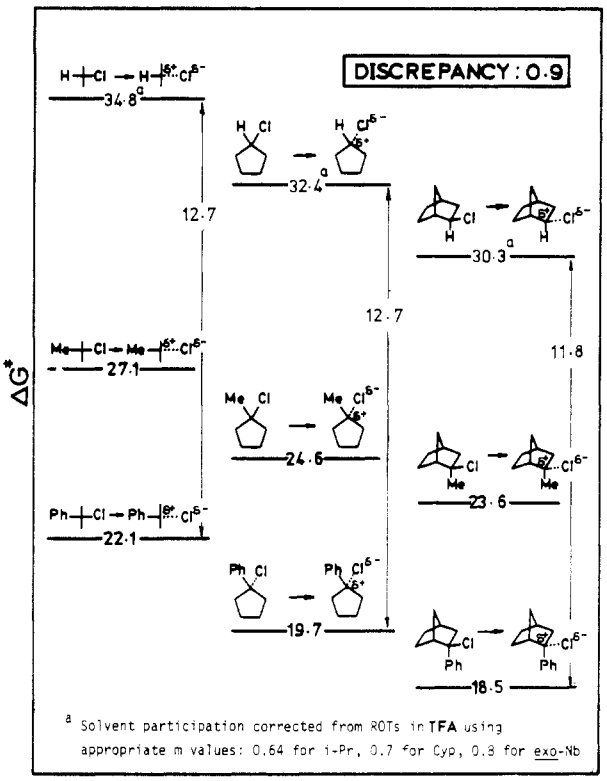


Figure 7. $\Delta\Delta G^{\ddagger}$ for ethanolysis of representative secondary and tertiary chlorides using limiting rates for *i*-PrCl and CpCl (from TFA).

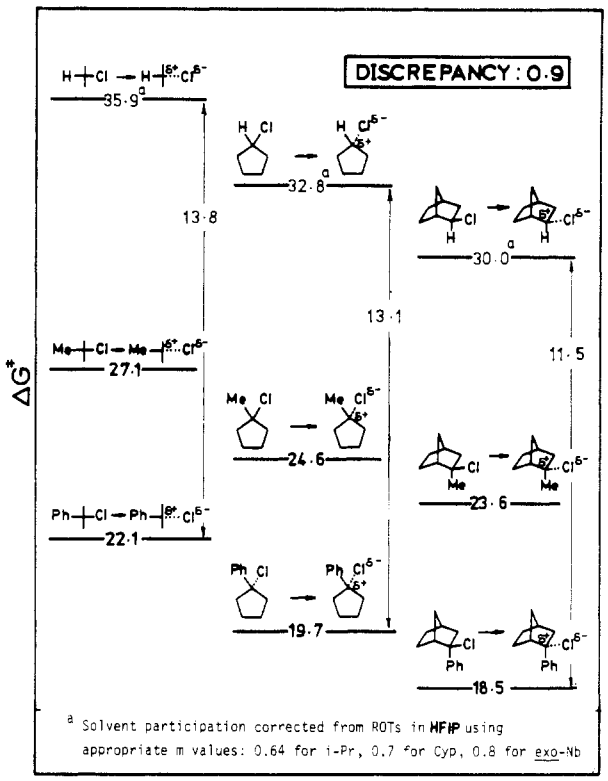


Figure 8. $\Delta\Delta G^{\ddagger}$ for ethanolysis of representative secondary and tertiary chlorides using limiting rates for *i*-PrCl and CpCl (from HFIP).

a conversion factor from the rate constants for *endo*-NbOTs in TFA or HFIP and the rate constant for *endo*-NbCl in EtOH. We then applied this conversion factor to proceed from secondary ROTs in TFA or HFIP to RCl in ethanol. We realized excellent agreement between the two approaches.

The results of this treatment are shown in Figure 7. $\Delta\Delta G^{\ddagger}$ for *i*-PrCl → *t*-CuCl[40] is 12.7 kcal/mol. $\Delta\Delta G^{\ddagger}$ for the related cyclopentane system is also 12.7. The critical case is 2-norbornyl. Will it be 6.7 kcal/mol as the 6.0 kcal/mol of nonclassical stabilization in *exo*-norbornyl vanishes in 2-phenyl-*exo*-norbornyl chloride? Obviously not. There is a decrease of 0.9 kcal/mol to 11.8, not the 6.0 kcal/mol we are seeking.

For the data in HFIP (Figure 8), the $\Delta\Delta G^{\ddagger}$ values are 13.8 for the acyclic system and 13.1 for the cyclopentyl system. This extrapolates to a predicted value of 12.4 or 6.4 kcal/mol for the 2-norbornyl system, for the classical and nonclassical cations, respectively. Again there is a minor discrepancy from the classical ion expectation of 0.9 kcal/mol, not the 6.0 kcal/mol we are seeking.

Search for Nonclassical Stabilization. Solvolytic Data for *exo*- and *endo*-Norbornyl

Since the very beginning, the solvolysis of *exo*-norbornyl has been considered to proceed by a k_{Δ} and that of *endo*-norbornyl by a k_s process.[2] However, the observation that the exo/endo rate ratio is not changed greatly by a huge range of solvents (EtOH, AcOH, MeOH, 80% EtOH, 60% Me_2CO, TFE, HCO_2H, HFIP, TFA, and H_2O) persuaded us that the solvolysis of *endo*-norbornyl must be essentially limiting.[10b] A more systematic study was made by Harris and his co-workers. Application of nine probes of nucleophilic solvent assistance persuaded them that solvent assistance must be small.[10a] This fortunate development suggested the feasibility of an alternative probe for the presence of the 6.0 kcal/mol of nonclassical resonance energy in the transition state for solvolysis of *exo*-norbornyl chloride and its absence, either in the endo or a highly stabilized tertiary derivative, such as 2-phenyl-*exo*-norbornyl chloride.

This procedure involves a determination of $\Delta\Delta G^{\ddagger}$ for *endo*-norbornyl chloride → 2-phenyl-*endo*-norbornyl chloride, followed by a comparison with $\Delta\Delta G^{\ddagger}$ for *exo*-norbornyl chloride → 2-phenyl-*exo*-norbornyl chloride. All rate constants are available in ethanolic solvents, with only minor extrapolations occasionally necessary.[24] Consequently, this procedure avoids the large extrapolations necessitated by the previous procedure in order to obtain the limiting rates of solvolysis for the secondary derivatives.

The results are summarized in Figure 9. $\Delta\Delta G^{\ddagger}$ for *endo*-norbornyl chloride → 2-phenyl-*endo*-norbornyl chloride amounts to 11.6 kcal/mol. If the *exo*-norbornyl transition state is stabilized by 6.0 kcal/mol and this vanishes in the stabilized 2-phenyl-*exo*-norbornyl chloride, $\Delta\Delta G^{\ddagger}$ for the exo pair of compounds should be 6.0 kcal/mol smaller, or 5.6. Instead, the observed value is 11.6 kcal/mol. There is no evidence for a nonclassical stabilization of *exo*-norbornyl chloride, which vanishes in the more stable tertiary derivatives.

Search for Nonclassical Stabilization. Calorimetric Heats of Ionization

The development of a suitable calorimeter and the determination of the heats of ionization of alkyl chlorides under stable ion conditions (such as in SO_2ClF) makes it possible to probe for the presence of the

(40) *t*-CuCl is *tert*-cumyl chloride, 2-chloro-2-phenylpropane.

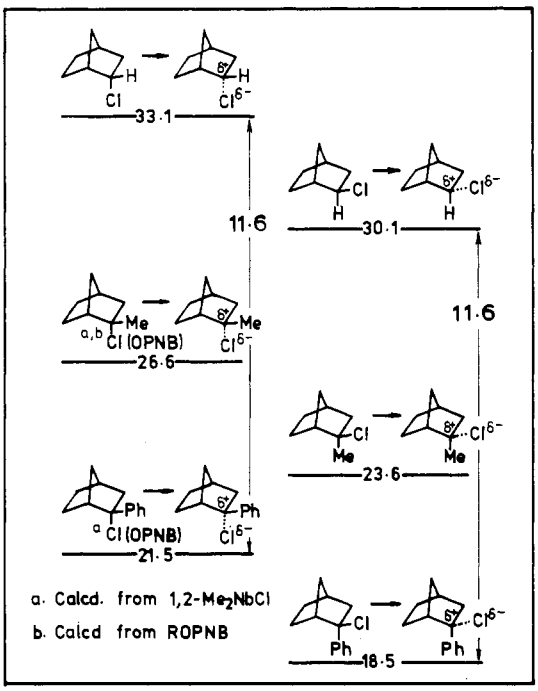


Figure 9. $\Delta\Delta G^{\ddagger}$ of ethanolysis of representative secondary and tertiary *endo*- and *exo*-norbornyl chlorides.

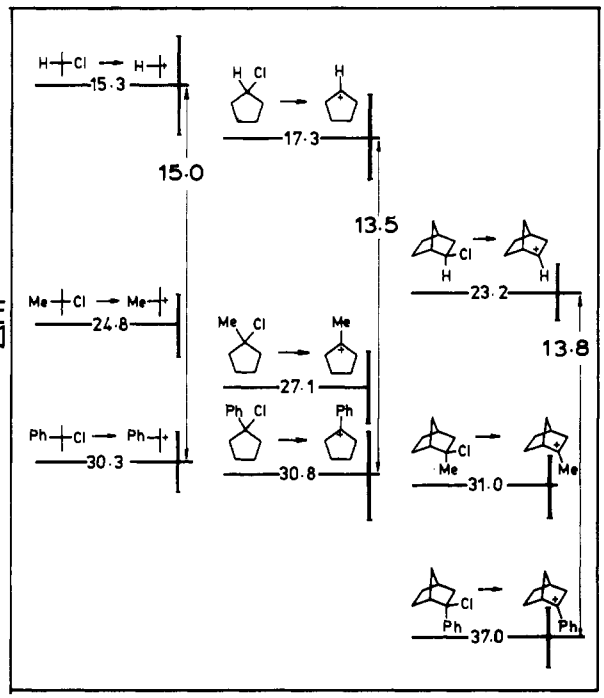


Figure 10. $\Delta\Delta H_i$ for the calorimetric heats of ionization of representative alkyl chlorides in SO_2ClF (with SbF_5). Heavy vertical lines indicate the error bars.

nonclassical stabilization in the fully developed ions.[11] Here we are seeking the disappearance of an even larger energy quantity, about 8.0 kcal/mol.

The results are shown in Figure 10. Note the fairly large error bars. Some people have tried to discuss these results by comparing the secondaries as a group or by comparing the tertiary methyl derivatives. This is hazardous. The differences in energy are comparable to the sums of the error bars. Consequently, there is a major advantage in our procedure of comparing the first and last compound in each series. This provides a large Δ, which minimizes the possible effect of the large error bars.

$\Delta\Delta H_i$ between 2-propyl chloride and *tert*-cumyl chloride[40] is 15.0 kcal/mol. $\Delta\Delta H_i$ between cyclopentyl chloride and 1-phenylcyclopentyl chloride is 13.5 kcal/mol. A linear extrapolation to the 2-norbornyl system predicts a value of 12.0 kcal/mol or a value of 4.0 kcal/mol (if the 8.0 kcal/mol of nonclassical resonance energy in the 2-norbornyl cation vanishes in the highly stable 2-phenyl-2-norbornyl cation). In actual fact, the experimental value is 13.8 kcal/mol.

All three probes agree—there is no evidence for the 6.0 kcal/mol nonclassical stabilization energy in the transition state for 2-norbornyl chloride solvolysis or for 8.0 kcal/mol nonclassical stabilization energy in the fully developed 2-norbornyl cation. There is no evidence for the differential stabilization energy of 2-norbornyl derivatives over tertiary.

Isodesmic Equations

Let us write isodesmic equations comparing the norbornyl derivative with the aliphatic derivative (Figure 10).

	ΔH_i, kcal/mol
i-Pr$^+$ + *exo*-NbCl → *i*-PrCl + 2-Nb$^+$	7.9
t-Bu$^+$ + 2-Me-*exo*-NbCl → *t*-BuCl + 2-Me-*exo*-Nb$^+$	6.2
t-Cu$^+$ + 2-Ph-*exo*-NbCl → *t*-CuCl + 2-Ph-*exo*-Nb$^+$	6.7

The ΔH_i values fail to reveal a discrepancy of 8 kcal for the secondary 2-norbornyl ionization.

Calculated Heats of Ionization

The difference in the calorimetric heats of ionization (Figure 10) for 2-PrCl/*t*-CuCl is 15.0 and for CpCl/1-PhCpCl 13.5 kcal/mol. Let us take 14 kcal/mol as the average difference in the heats of ionization of a simple secondary alkyl chloride and the corresponding stabilized benzylic derivative.

The heat of ionization of 2-phenyl-2-norbornyl chloride is 37 kcal/mol. There is general agreement that this derivative ionizes to the classical cation. Subtraction of 14 kcal/mol gives 23 kcal/mol as the calculated heat of ionization of *exo*-norbornyl chloride to the classical cation. The calculated heat of ionization to the nonclassical cation must be 8 kcal/mol greater, or 31 kcal/mol. What does experiment show? Arnett and Petro report 23 kcal/mol![11]

Conclusion

It is now some 20 years since I first spoke up to question the proliferation of nonclassical ion structures in accounting for solvolytic behavior.[41] I was concerned over the growing application of σ-bridging to account for fast rates of solvolysis, many of the cases readily accounted for in terms of relief of steric strains.[12,13]

What has happened in the intervening years? As discussed, all of the original cases attributing fast rates of solvolysis to σ-participation were withdrawn, the majority by the original proponents. The high exo/endo rate ratio observed in the solvolysis of 2-norbornyl derivatives was considered to be the best case for σ-participation. Yet, now all of the tertiaries, with their high exo/endo rate ratios, are considered classical.[28] Indeed, the leading proponent for nonclassical cations has acknowledged, "Nonclassical carbonium ions are not

(41) Brown, H. C. *Spec. Publ.-Chem. Soc.* **1962**, *6*, 140.

as prevalent as once believed".[42a] We are really left only with the question of the factor responsible for the high exo/endo rate ratio in 2-norbornyl and related secondary derivatives, a very small fragment of the original question.

For some 20 years I have been carefully examining many pieces of evidence purporting to support the formation of a highly stabilized 2-norbornyl cation. Invariably, the arguments and evidence have crumpled after careful study.[1b]

The heart of the 2-norbornyl question appears to be the thermochemistry. The nonclassical interpretation of the high exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives requires nonclassical stabilization of the exo transition state by 6.0 kcal/mol and a somewhat larger stabilization of the free ion (~8.0 kcal/mol).

None of the three independent experimental approaches has detected any significant stabilization of either the transition states for secondary *exo*-norbornyl not present in the corresponding tertiary derivatives or in the free secondary cation not present in the tertiary cation. The 6.0–8.0 kcal/mol of nonclassical stabilization energy cannot be detected.

On the other hand, unsymmetrical 2-norbornyl cations have been captured in a number of reactions.[42b]

Meanwhile, various workers continue to publish papers purporting to have established the nonclassical nature of the 2-norbornyl cation in the gas phase (calculation,[43,44] stability,[32,45]), in the solid state (ESCA,[46] low-temperature NMR[47]), and in solution under stable ion conditions, (NMR,[48] isotope perturbation[49]). It is an interesting question as to what is the structure of the 2-norbornyl cation under these special conditions. However, I do not see that the results are pertinent to the question as to what is responsible for the high exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives.[50]

None of the workers in this area has addressed the thermodynamic dilemma that has been the major point made in this Account. It will be of intense interest to see if any of the papers in this Symposium-In-Print addresses this question.

I believe that our data clearly reveal that the 2-norbornyl cation can be prepared and captured in an unsymmetrical state.[42b] It clearly does not have the nonclassical stabilization energy that has been postulated for so long. It ill befits serious scientific workers in this area to ignore these data and results.

(42) (a) Reference 1b, p 259. (b) Reference 1b, Chapter 12.
(43) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983** *105*, 5915. See also: Yoshimine, M.; McLean, A. D.; Lin, B.; Defrees, D. J.; Binkley, J. S. *Ibid.* **1983**, *105*, 6185.
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(45) Saluja, P. P. S.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1084.
(46) Olah, G. A.; Mateescu, D. G.; Riemeneschneider, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2529. It has been pointed out that the published spectrum analyzes for a 1:6 distribution of carbon atoms corresponding to a classical ion, not 2:5, as claimed. Kramer, G. *Adv. Phys. Org. Chem.* **1975**, *11*, 177.
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(48) Olah, G. A.; Surya Prakash, G. K.; Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7105.
(49) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 3571.
(50) In ref 49, the authors conclude that the cation under stable ion conditions differs considerably from the transition state under solvolytic conditions.

Conclusion of the Classical–Nonclassical Ion Controversy Based on the Structural Study of the 2-Norbornyl Cation†

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Facile skeletal rearrangements in the bicyclo[2.2.1]-heptyl system attracted the interest of chemists, most notably Wagner,[1] who as early as 1899 studied the borneol–camphene rearrangement. The actual ionic nature of the camphene hydrochloride (1)–isobornyl chloride (2) rearrangement was first recognized by Meerwin and Van Emster in 1922.[2] Their interpretation replaced Ruzicka's earlier suggested neutral tricyclane type mechanism for the process.[3] This ionic path is now known as the Wagner–Meerwin rearrangement. Thus Meerwein's studies laid the foundation for modern carbocation chemistry.

George A. Olah is a native of Hungary, where he received his university education. He emigrated in 1956, was for 8 years with Dow Chemical Co. in Canada, and in 1965 moved to Western Reserve University as Professor of Chemistry. After the amalgamation he was C. F. Maybery Professor of Chemistry and Department Chairman at Case Western Reserve University. In 1977, he moved to the University of Southern California where he is Loker Distinguished Professor of Organic Chemistry and Scientific Co-Director of the Hydrocarbon Research Institute.

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† Stable Carbocations. 249.
(1) Wagner, G.; Brickner, W. *Ber.* **1899**, *32*, 2307. *J. Russ. Phys. Chem. Soc.* **1899**, *31*, 680.
(2) Meerwein, H.; Van Emster, K. *Chem. Ber.* **1922**, *55*, 2500.
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