Structural Effects in Solvolytic Reactions. 52. Direct Search for the Nonclassical Stabilization Energy in the Ionization of 2-Norbornyl Derivatives. Consistent Absence of Nonclassical Stabilization in the Ionization of 2-Norbornyl Derivatives in Solvolytic or Superacid Media

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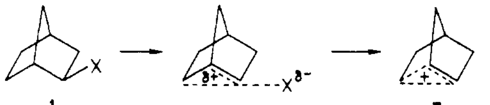
Winstein's explanation for the large exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives in terms of a nonclassical stabilization of the exo transition state requires a nonclassical stabilization energy of 6.0 kcal/mol. For the fully formed cation, the nonclassical stabilization energy will be somewhat larger, estimated as approximately 8.0 kcal/mol. To test the nonclassical proposal, we have made a search for this nonclassical stabilization energy in solvolytic media and stable ion conditions by using three probes. Since tertiary 2-norbornyl cations are classical, we compared the $\Delta\Delta G^{\ddagger}$ (or $\Delta\Delta H_i$) for the pair *exo*-norbornyl/2-methyl(or 2-phenyl)-*exo*-norbornyl chloride with pairs such as isopropyl/*tert*-butyl or *tert*-cumyl chlorides and cyclopentyl/1-methyl(or 1-phenyl)cyclopentyl chlorides. If the 2-norbornyl cation were nonclassical, $\Delta\Delta G^{\ddagger}$ (or $\Delta\Delta H_i$) for the norbornyl pair must be much smaller than that for the latter pairs since the latter two pairs are doubtlessly classical. All of our probes consistently give the same values for the three systems, the results supporting the absence of nonclassical stabilization energy in the required magnitude, 6–8 kcal/mol. This investigation clearly disproves the presence of highly stabilized σ-bridged transition states and nonclassical cations in the ionization of secondary *exo*-norbornyl derivatives, a stabilization presumed to be absent in the relatively stable tertiary *exo*-norbornyl derivatives.

Winstein and Trifan[2] proposed that the large exo/endo rate ratio in the acetolysis of 2-norbornyl tosylate is due to a nonclassical stabilization of the exo transition state by participation of the C_1–C_6 σ-electron cloud (eq 1).



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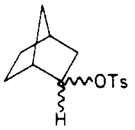
We initiated a program[3] on the effects of structure on the solvolytic behavior of 2-norbornyl and related derivatives to test Winstein's proposal. A major step in that direction was the study of solvolysis of tertiary 2-norbornyl derivatives.[4] The solvolyses of tertiary 2-norbornyl derivatives also exhibit large exo/endo rate ratios comparable to that of the secondary analogues (**4**, **5**, **6**). More interesting is the fact that even those tertiary derivatives, such as **6**, which involve highly stabilized cationic intermediates, exhibit large exo/endo rate ratios, indicating that large exo/endo rate ratios, per se, do not imply σ-bridging. In fact, detailed studies soon revealed that tertiary 2-norbornyl cations were classical.[5] For example, Paul von R. Schleyer has stated that it is "the now established position that tertiary 2-norbornyl cations are classical or nearly so."[5a]



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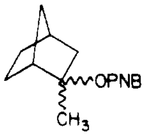

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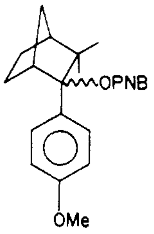

6

exo/endo 280 885 44000

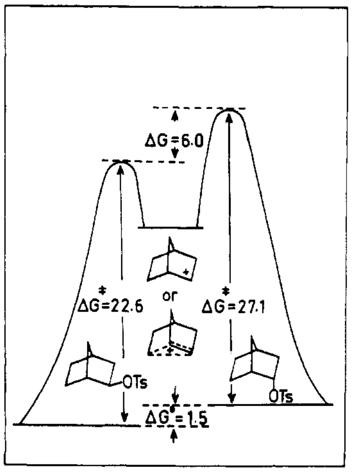

Figure 1. Free-energy diagram for acetolysis of *exo*- and *endo*-2-norbornyl tosylates at 25 °C.

Our explanation for the large exo/endo rate ratios in the solvolysis of 2-norbornyl derivatives is that the exo isomer solvolyzes at the normal rate while the endo isomer solvolyzes unusually slowly, due to steric retardation of ionization caused by the U-shape character of the norbornyl skeleton.[6] Using tertiary systems, we showed that exo/endo rate ratio is strongly affected by steric congestion on the exo and endo face,[7] as well as by the U-shape character of the bicyclic skeleton.[6]

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[1] Postdoctoral research associates on grants from (a) the National Science Foundation; (b) the National Science Foundation; and (c) the United States Army Research Office.

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

[3] For a complete survey, see the four preceding papers in this series.

[4] Brown, H. C.; Takeuchi, K. *J. Am. Chem. Soc.* **1968**, *90*, 2691, 5268, 5270.

[5] (a) Schleyer, P. v. R.; Kleinfelter, D. C.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 479. (b) Brown, H. C.; Ravindranathan, M.; Rao, C. G.; Chloupek, F. J.; Rei, M.-H. *J. Org. Chem.* **1980**, *43*, 3667. (c) Goering, H. L.; Humski, K. *J. Am. Chem. Soc.* **1968**, *90*, 6213. (d) Goering, H. L.; Clevenger, J. V. *Ibid.* **1972**, *94*, 1010. (e) See: P. v. R. Schleyer's comments in: Brown, H. C. (with comments by Schleyer, P. v. R.) "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; p 119.

[6] Brown, H. C.; Vander Jagt, D. L.; Rothberg, I.; Hammar, W. J.; Kawakami, J. H. *J. Org. Chem.*, in press.

[7] Brown, H. C.; Ikegami, S.; Vander Jagt, D. L. *J. Org. Chem.* **1985**, *50*, 1165.

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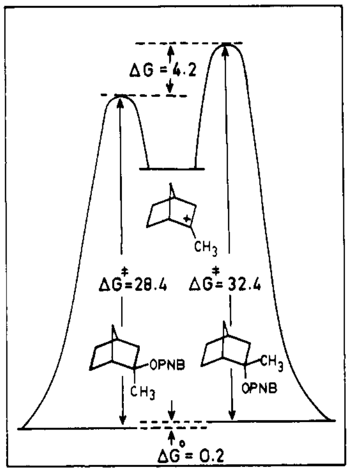

Figure 2. Free-energy diagram for the solvolysis of *exo-* and *endo*-2-methyl-2-norbornyl p-nitrobenzoates at 25 °C.

Even though all of these studies with the tertiaries clearly proved that steric factors play a major role in governing the exo/endo rate ratios in the solvolysis of tertiary 2-norbornyl derivatives, there has been considerable reluctance to extend this proposal to account for the high exo/endo rate ratios in secondary 2-norbornyl.[8]

We are thus left with an interesting mechanistic dichotomy. Both secondary and tertiary 2-norbornyl derivatives solvolyze with large exo/endo rate ratios. The Goering–Schewene diagrams for the solvolysis of secondary 2-norbornyl and tertiary 2-methyl-2-norbornyl derivatives are remarkably similar (Figures 1 and 2). Yet, it is believed that in the secondaries, it is the nonclassical participation and in the tertiaries, the steric retardation of ionization which is the governing factor for the large exo/endo rate ratios.

We decided to examine this dichotomy in closer detail. If σ-bridging is a major factor in the ionization of secondary 2-norbornyl derivatives, as proposed by Winstein, the resulting nonclassical stabilization should manifest itself on comparing with classical models. Consequently, we made a direct search for the nonclassical stabilization energy in the ionization of 2-norbornyl derivatives by using three independent probes. Our search has revealed the consistent absence of nonclassical stabilization energy in the ionization of 2-norbornyl derivatives in solvolytic or superacid media. We discuss the details of this study in this paper.

Results and Discussion

Nonclassical Stabilization Energy. The free-energy diagram for the acetolysis of *exo-* and *endo*-norbornyl tosylates at 25 °C (Figure 1) shows 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-bridging, there is 6.0 kcal/mol of nonclassical stabilization energy in the exo transition state, which is absent in the endo transition state. Since tertiary 2-norbornyl cations are classical,[5e] this nonclassical stabilization energy must be absent in the ionization of tertiary 2-norbornyl derivatives.

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

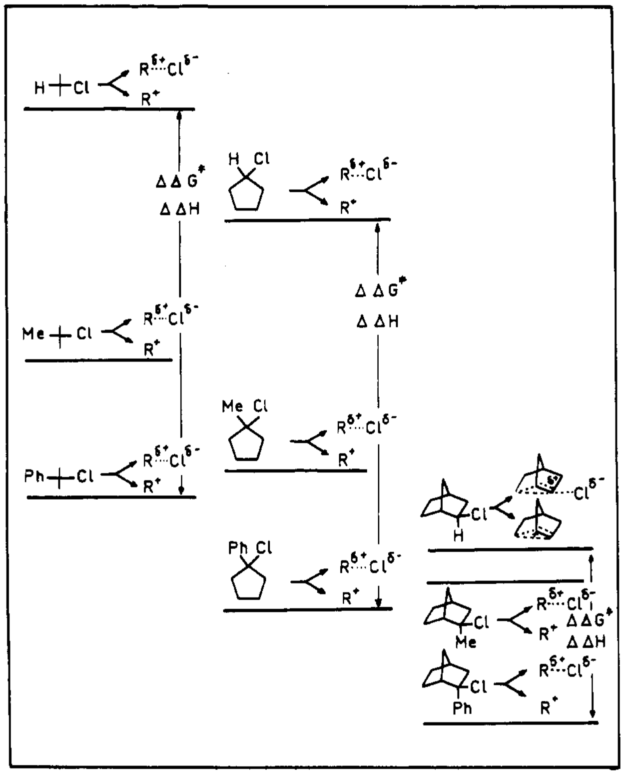

Figure 3. Predicted behavior of representative secondary and tertiary systems assuming that 2-norbornyl is nonclassical.

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

Search for Nonclassical Stabilization. As mentioned before, according to Winstein's proposal, the nonclassical stabilization energy must be present in the ionization of *exo*-norbornyl chloride, but absent in the ionization of the corresponding tertiary derivatives substituted by methyl or phenyl. Consequently, we used the following strategy to search for the nonclassical stabilization energy. We compared the $\Delta\Delta G^{\ddagger}$ (or $\Delta\Delta H_i$) for the ionization of the pair: *exo*-norbornyl/*exo*-2-methyl (or 2-phenyl)-2-norbornyl chlorides with that for representative model pairs such as isopropyl(*i*-Pr)/*tert*-butyl(*t*-Bu) and cyclopentyl(Cp)/1-methylcyclopentyl(Me-Cp), which are doubtless classical (see Figures 3 and 4). In case the 2-norbornyl cation were nonclassical, the $\Delta\Delta G^{\ddagger}$ ($\Delta\Delta H_i$) for the norbornyl pair must be much less than that for the model pairs and the difference in $\Delta\Delta G^{\ddagger}$ (or $\Delta\Delta H_i$) must give the nonclassical stabilization energy (Figure 3); otherwise, the $\Delta\Delta G^{\ddagger}$ (or $\Delta\Delta H_i$) must be essentially the same for all pairs (Figure 4). We applied this tool to the solvolytic rate data and to Arnett's thermochemical data on the ionization of the relevant chlorides.

(a) Solvolytic Data. The rate data for the ethanolysis of 2-norbornyl and model chlorides[9] are provided in Table I. The ethanolysis of the tertiary chlorides and that of *exo-* and *endo*-2-norbornyl chlorides occurs by a k_c process with insignificant nucleophilic participation by the solvent.[10,11] Consequently, we can use the experimental rate

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[8] For example, see: P. v. R. Schleyer's comments in: Brown, H. C. (with comments by Schleyer, P. v. R.) "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; pp 33, 146–149.

[9] (a) Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* **1964**, *86*, 5008. (b) Reference 5b.

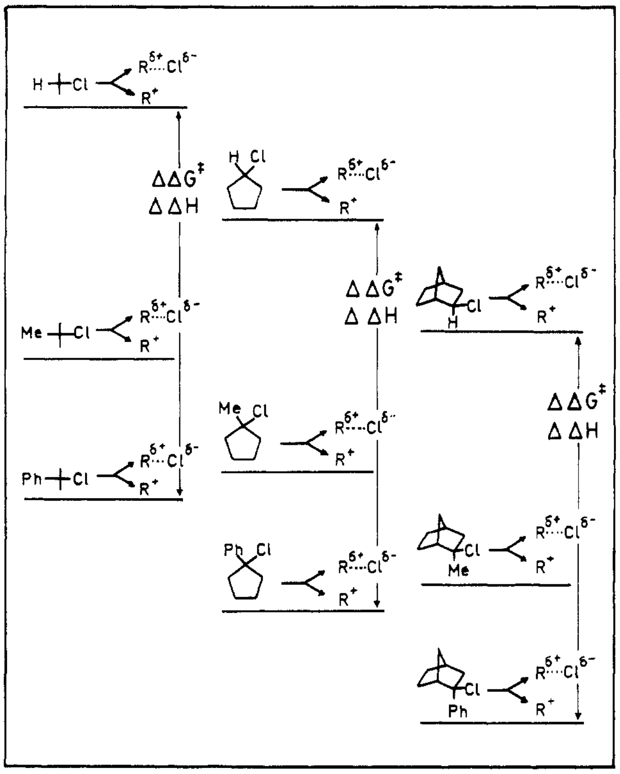

Figure 4. Predicted behavior of representative secondary and tertiary systems assuming that 2-norbornyl is classical.

Table I. 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]	?[b,d]	?[c,e]	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] The limiting rate constants for *i*-PrCl and CpCl were calculated using Schleyer's procedure. [b] $k = 1.6 \times 10^{-7}$ calculated from *i*-PrOTs in TFA. [c] $k = 8.6 \times 10^{-6}$ calculated from CpOTs in TFA. [d] $k = 2.7 \times 10^{-8}$ calculated from *i*-PrOTs in HFIP. [e] $k = 4.8 \times 10^{-6}$ calculated from CpOTs in HFIP.

constants directly for calculating the $\Delta G^{\ddagger}$. On the other hand, nucleophilic solvent participation is very significant in the solvolysis of unhindered secondary derivatives.[12] Hence, the experimental rate constants cannot be used for the present study. We calculated the limiting rates for the ethanolysis of *i*-PrCl and CpCl by Schleyer's procedure.[13] We took the rates of solvolysis of isopropyl and cyclopentyl tosylates in the limiting solvents, TFA[4] and HFIP.[15] These limiting rate constants were then converted to the limiting rates in ethanol by using the Schleyer correlation, the conversion factor for k_{ROTs} to k_{RCl} and the appropriate *m* values (0.64 for *i*-Pr; 0.70 for Cp; and 0.80 for *exo*-2-Nb) for use in the correlation equation.

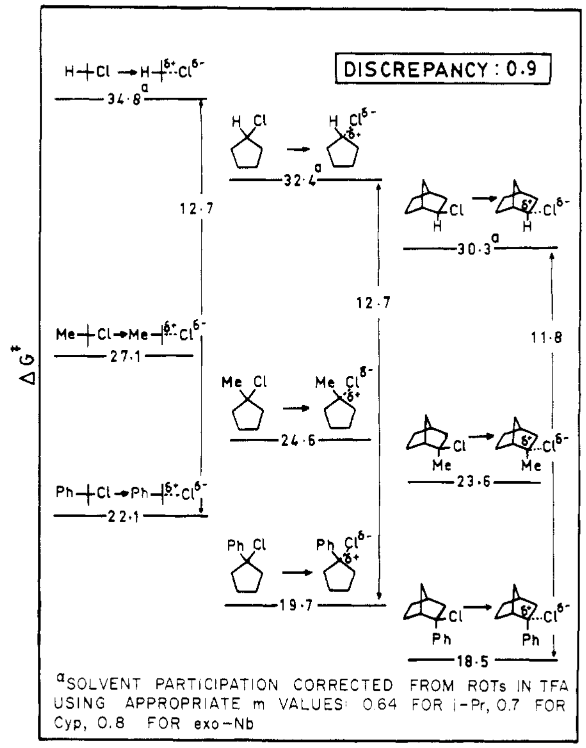

Figure 5. $\Delta\Delta G^{\ddagger}$ for ethanolysis of representative secondary and tertiary chlorides using limiting rates for *i*-PrCl and CpCl (from TFA).

Limiting rate constants for ethanolysis of these alkyl chlorides had previously been calculated by Arnett et al.[15] 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.[11] Consequently, we calculated 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 5, $\Delta\Delta G^{\ddagger}$ for *i*-PrCl → *t*-CuCl[16] 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 6), 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

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(10) (a) Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 2700. (b) Fort, R. C., Jr.; Schleyer, P. v. R. *Adv. Alicycl. Chem.* **1966**, *1*, 283. (c) Raber, D. J.; Bingham, R. C.; Harris, J. M.; Fry, J. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 5977.

(11) (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.

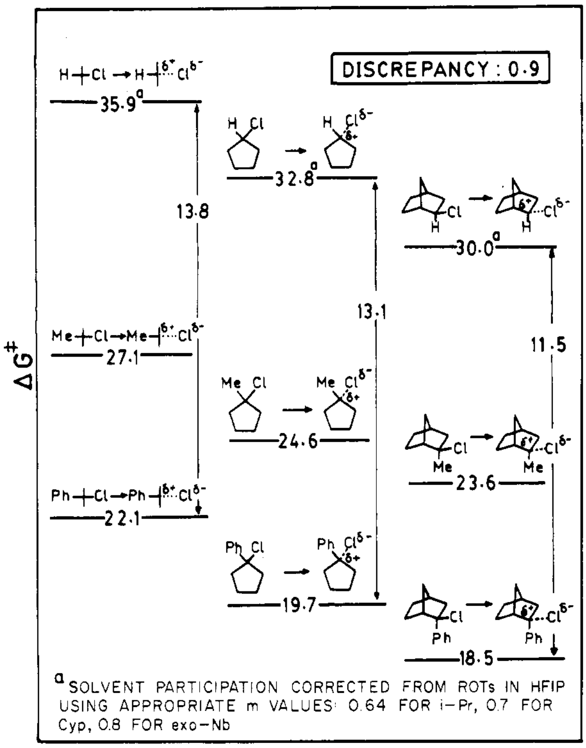
(12) (a) Fry, J. L.; Lancelot, D. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2538. (b) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *Ibid.* **1970**, *92*, 2540. (c) Schleyer, P. v. R.; Fry, J. L.; Lam, L. K. M.; Lancelot, C. J. *Ibid.* **1970**, *92*, 2542.

(13) (a) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658. (b) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7667.

(14) Nordlander, J. E.; Bruetzmacher, R. R.; Kelly, W. J.; Jindal, S. P. *J. Am. Chem. Soc.* **1974**, *96*, 181.

(15) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522.

(16) *t*-CuCl stands for *tert*-cumyl chloride, 2-chloro-2-phenylpropane.



a SOLVENT PARTICIPATION CORRECTED FROM ROTs IN HFIP USING APPROPRIATE m VALUES: 0.64 FOR i-Pr, 0.7 FOR Cyp, 0.8 FOR exo-Nb

Figure 6. $\Delta\Delta G^{\ddagger}$ for ethanolysis of representative secondary and tertiary chlorides using limiting rates for *i*-PrCl and CpCl (from HFIP).

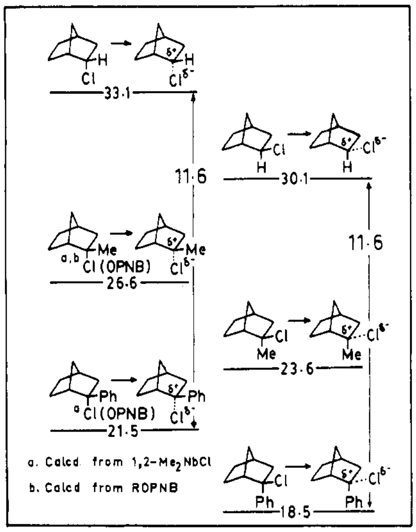
and nonclassical cations, respectively. Again there is a minor discrepancy from the classical ion expectation of 0.9 kcal/mol, not the 6.0 kcal/mol we are seeking.

The above procedure involves rather large extrapolations for obtaining the limiting rates for the ethanolysis of the secondary derivatives. Consequently, we decided to use an alternate procedure for searching for the nonclassical stabilization energy.

As mentioned earlier, the solvolysis of both *exo*- and *endo*-2-norbornyl derivatives has been clearly established to be essentially limiting by Harris and co-workers and us independently.[11] Since the tertiary solvolyses are also limiting,[10] it is possible to compare $\Delta\Delta G^{\ddagger}$ for the pairs, *exo*-norbornyl chloride/2-phenyl-*exo*-norbornyl chloride and *endo*-norbornyl chloride/2-phenyl-*endo*-norbornyl chloride. The results are summarized in Figure 7. $\Delta\Delta G^{\ddagger}$ 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 participation in the ionization of *exo*-norbornyl chloride, which vanishes in the ionization of the more stable tertiary derivatives.

(b) 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 nonclassical stabilization in the fully developed ions.[17] Here we are seeking the disappearance of an even larger energy quantity, about 8.0 kcal/mol.

The results are shown in Figure 8. Note the fairly large error bars. Some people have tried to discuss these results by comparing the secondaries as a group or by comparing



a. Calcd from 1,2-Me$_2$NbCl
b. Calcd from ROPNB

Figure 7. $\Delta\Delta G^{\ddagger}$ for ethanolysis of representative secondary and tertiary *endo*- and *exo*-norbornyl chlorides.

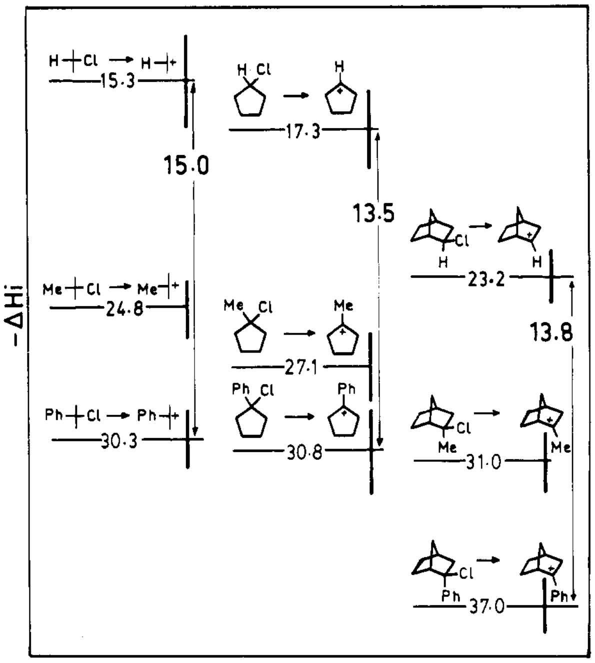


Figure 8. $\Delta\Delta H_i$ for the calorimetric heats of ionization of representative alkyl chlorides in SO_2ClF (with SbF_5). Heavy vertical lines indicate the error bars.

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 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 or 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 differ-

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

ential stabilization energy of 2-norbornyl derivatives over tertiary.

Isodesmic Equations. Let us write isodesmic equations comparing the norbornyl derivative with the aliphatic derivative (Figure 8).

	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 8) 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![17]

Other Studies

Our attention was mainly focused on the factor responsible for the high exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives. Meanwhile, numerous workers have applied other methods to explore the 2-norbornyl cation for evidence of the oft-postulated σ-participation. The stability and structure of the cation in the gas phase has been calculated.[18,19] The structure in the solid state has been explored by ESCA[20] and NMR[21] spectroscopy. The nature of the ion in solution under stable ion conditions has been explored by NMR[22] and isotope perturbation studies.[23]

At the time these studies were reported, each of them appeared to provide distinctive unambiguous evidence for σ-bridging. However, these studies have not yet been subjected to critical scrutiny. Any further examination of these studies so far reported appears to indicate a clear need for a close examination. For example, the original ESCA spectrum was interpreted as showing a carbon distribution of 2:5 corresponding to that anticipated for a nonclassical ion. However, Kramer reexamined the published spectrum and concluded that it really showed a carbon distribution of 1:6 corresponding to that anticipated for a classical ion.[24]

The low-temperature NMR on the solid 2-norbornyl salts indicated the formation either of a symmetrical cation or of a rapidly equilibrating pair of classical cations with a very low barrier. Originally, the results appeared unambiguously in favor of the symmetrical structure. However, recently the authors have published some observations which are difficult to understand.[25] They report that at low temperatures they observe in the 2,3,3-trimethyl-2-butyl cation both static classical and equilibrating classical systems "in apparent coexistence," which they attribute to differing constraints on the rate of degenerate rearrangement imposed by different sites in the amorphous SbF_5 solid. We do not know the type and nature of the effect of the matrix on 2-norbornyl cation. Until the phenomena in simple systems are well understood, it appears dangerous to apply the procedure to interpret phenomena in complex systems such as 2-norbornyl cation.

Recently, Goldstein and his co-workers[26] achieved markedly improved resolution of the ^{13}C NMR spectrum of 2-norbornyl cation and have reassigned many of the peaks.[22] Of special interest is the fact that they find the chemical shifts of C_5 and C_6 to be very close and almost identical with that of a typical carbon in a secondary cation. Surely if C_6 were σ-bridged, it would be expected to show a chemical shift much different from that for the unbridged C_5.

Dewar has questioned the reliability of Saunders' isotope perturbation studies on the grounds that "secondary deuterium isotope effects in unsymmetrical structures can mimic those expected for symmetrical ones because there is not a 1:1 correspondence between the geometry (i.e., hybridization) of a carbon atom and the strengths of partial bonds formed by it."[27]

It is certainly interesting to know what the structure of 2-norbornyl cation is under these special, nonsolvolytic conditions. However, these studies do not appear to be pertinent to establishing the factor responsible for the high exo/endo rate ratio in the solvolysis of 2-norbornyl derivatives.

Conclusions

At the time we began to question the proliferation of nonclassical ion structures as solvolytic intermediates, we were confronted by three major foundations supporting that concept: (i) unusually fast solvolysis rates for the exo isomers, such as camphene hydrochloride; (ii) large exo/endo rate ratios for the solvolysis of 2-norbornyl derivatives; (iii) large exo/endo product ratios in the solvolysis of both *exo*- and *endo*-norbornyl derivatives.

By a proper choice of models, we convincingly demonstrated that there is nothing unusual in the solvolysis of camphene hydrochloride.[28] Thus foundation i is no longer valid. Foundations ii and iii are essentially the same. We have proved that large exo/endo rate ratios per se do not imply σ-bridging since many classical tertiary 2-norbornyl derivatives also exhibit high exo/endo rate ratios. In this paper we illustrate that three independent probes consistently show the absence of nonclassical stabilization energy in the ionization of *exo*-norbornyl chloride in solvolytic and stable ion conditions. Consequently, foundations ii and iii vanish as well.

This leaves us with the question: What is the factor, or factors, responsible for the large exo/endo rate ratio in the

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solvolysis of 2-norbornyl derivatives? We believe that steric retardation of ionization of the endo isomer can account for this phenomenon.[6] In fact, Bentley has proposed that "steric hindrance to solvation" of the leaving group in the endo isomer (included in our more general term, steric retardation of ionization) contributes significantly ($\sim$50%) to the exo/endo rate ratio with the rest coming from σ-bridging in the exo isomer.[29] Regretably, the present study does not allow for even 50% of the effect being attributed to σ-participation.

We point out that we are not against the existence of σ-bridged cations. As H. C. Brown has pointed elsewhere, "I wish to make it clear that...I did not deny the whole concept. (It would be unscientific to take a dogmatic position that any particular phenomenon is incapable of existence in this fascinating, versatile world of ours.) My position then and now is merely that my students and I have been unable to find any experimental evidence whatsoever for σ-bridging in the solvolysis of norbornyl derivatives."[30]

It is now clear that the 2-norbornyl cation can be prepared and captured in an unsymmetrical state.[31] It clearly does not have the nonclassical stabilization energy that has been postulated for so long. It ill befits serious scientific workers interested in the factor responsible for the high exo/endo rate ratios to ignore these data and results.

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Hydroboration. 73. Relative Rates of Hydroboration of Representative Heterocyclic Olefins with 9-Borabicyclo[3.3.1]nonane

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Relative reactivity studies using the competitive method showed that hydroboration of 2,3-dihydrofuran in THF at 25 °C with 9-borabicyclo[3.3.1]nonane (9-BBN) is 106 times faster than that of cyclopentene, whereas Δ^2-dihydropyran and 2,3,4,5-tetrahydrooxepin react at rates that are 6.4 and 0.034 times those of their corresponding carbocyclic analogues. On the other hand, both 2,3-dihydrothiophene and Δ^2-dihydrothiopyran react slower than cyclopentene and cyclohexene, respectively. In the hydroboration of all of these heterocyclic olefins, boron is exclusively directed to the 3-position. To understand whether the rate differences are due to electronic or steric factors or both, we determined the ^{13}C chemical shifts of the olefinic carbons of the heterocycles. The ^{13}C chemical shifts show a substantial mesomeric contribution in the ground state in all three oxygen heterocycles and only negligible contribution by sulfur. It is probable that there is a strong mesomeric contribution from oxygen and sulfur to the 3-position in the transition state that controls the direction of hydroboration, giving the 3-substituted boron derivative, and the observed rate, modified by individual conformational effects in each system. The mesomeric effects in the ground state, as indicated by the ^{13}C NMR shifts, evidently do not play a significant role either in the reactivity or in the directive effect.

Recently, we undertook a systematic investigation of the hydroboration of heterocyclic olefins with representative hydroborating agents to establish optimum conditions for the hydroboration.[3] It appeared during the course of the investigation that 2,3-dihydrofuran undergoes hydroboration unexpectedly fast. In order to understand the role of the heteroatom on the rate of hydroboration, we undertook a more quantitative study of the relative rates of hydroboration of representative heterocyclic olefins such as 2,3-dihydrofuran, Δ^2-dihydropyran (DHP), 2,3,4,5-tetrahydrooxepin, 2,3-dihydrothiophene, and Δ^2-dihydrothiopyran in comparison with the corresponding carbocyclic analogues. We chose 9-borabicyclo[3.3.1]nonane (9-BBN) as the hydroborating agent, since it is stable, commercially available, and has been more thoroughly studied[4] than other, less stable hydroborating agents. The relative rates were determined at 25 °C in order to permit comparison with the large amount of data available for relative reactivities with 9-BBN at this temperature. It may be noted that a similar relative reactivity study of some of these heterocyclic olefins as compared to their carbocyclic analogs utilizing disiamylborane (Sia_2BH) as the hydroborating agent at 0 °C has been described earlier by Zweifel and Plamondon.[5] We present the results of our study in this paper.

Results and Discussion

The competitive method reported earlier[6] to determine the relative reactivity of two olefins toward hydroboration was adopted for this study. The two olefins to be compared were mixed in equimolar amounts (0.5 M in THF) and reacted with 1 equiv of 9-BBN (0.5 M in THF) at 25 °C. An inert hydrocarbon was added as internal standard. After the hydroboration was complete, the mixture was analyzed by GC for residual olefins. A stripper column ($^1/_8$ in. × 12 in.—20% THEED on Chromosorb W, 80–100

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