

major issue of the high exo/endo rates in solvolysis, and related energetics. Some years ago one of us¹⁰ commented, "Knowing the structure of the intermediate in any reaction, including solvolysis, has obvious significance to understanding of the path and mechanism of the whole process. What can be argued is to what degree the transition state will resemble the intermediate". Nothing further needs to be added.

More importantly, rather than being rare, two-electron, three (or multi)-center bonding is characteristic of electron-deficient molecules, including nonclassical carbocations.¹¹ The real significance of the very thorough study of the nonclassical norbornyl cation lies in

that it helped to establish that carbocations, the positive ions of hydrocarbons that play the key role in their acid-catalyzed reactions, belong to two major subclasses:⁶⁶ (a) trivalent ions such as the parent CH_3^+ or the *tert*-butyl cation, $^+\text{C}(\text{CH}_3)_3$, and (b) ions containing five- or six-coordinate carbons, of which the parent is CH_5^+ . It also provided evidence for the close similarity of π - and σ -bond donor ability and thus helped to open the door to the general utilization of single-bond reactivity in electrophilic reactions of saturated hydrocarbons (including methane).

(66) Olah, G. A. *J. Am. Chem. Soc.* 1972, 94, 808.

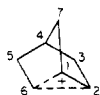
An Innocent Bystander Looks at the 2-Norbornyl Cation

CHEVES WALLING

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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In 1949 Winstein and Trifan first reported the now long familiar facts about the acetolysis of 2-norbornyl arenesulfonates: exo isomers react much more rapidly than endo, both give solely exo products, and the products from optically active exo starting material are completely racemized.¹ They then stated "The facts are at present best accommodated by formulation of the intermediate ion from exo norbornyl derivatives as II".



II

Such a formulation was a plausible extension of Winstein's previous interpretation of neighboring-group effects, and the authors noted that such "bridged ions" had, in fact, been proposed or mentioned as possibilities by others in connection with several Wagner-Meerwein rearrangements. The next 15 years were very active ones in the study of both solvolyses and carbocation rearrangements, and similar structures were frequently invoked to account for the results in a variety of systems. As the field developed, so did the nomenclature. Winstein had originally referred to his postulated structure as "bridged" and, later, to the whole process of such neighboring-group interaction as "anchimeric assistance". Ingold proposed the name "synartetic ions" for such bridged species. However, the term "nonclassical ions" introduced by Roberts and Lee in 1951² has been most popular, at least in this country. Originally, its meaning was rather ill-defined, and it still

seems to be used in two senses: to refer specifically to a symmetric bridged structure such as II or more generally to any cationic center on carbon, bonded to (or perhaps only interacting with) more than three other atoms. This leads to difficulties,³ and I shall simply refer to all such structures as "bridged species".

By the 1960s, interest in such bridging phenomenon might have leveled off had it not been for a vigorous attack on the whole concept of "nonclassical" ions launched by Brown in 1962.⁴ The number of contentious communications published in the next 10 years gives one some idea of the intensity of feeling aroused. The debate was vigorously pursued verbally in lectures, meetings, and seminars all over the U.S. and even abroad. The controversy has been fed by continual additional research, and, as other papers in this issue indicate,⁵⁻⁷ interest in the subject continues to this day.

All this attention and activity has had consequences within the chemical community considerably beyond the significance of the question immediately involved. On the positive side, besides providing material for innumerable Ph.D. theses, it has clarified concepts, led to improved kinetic techniques, encouraged the gathering of thermochemical data, and, perhaps most important, sparked the development of techniques for the study of the NMR spectra of carbocations under "stable" conditions in highly acidic nonnucleophilic solvents over a wide range of temperature. On the negative side, the position of the chemical community as a whole appears to have moved from interest to a

(1) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* 1949, 71, 2953.

(2) Roberts, J. D.; Lee, C. C. *J. Am. Chem. Soc.* 1951, 73, 5009.

(3) As in the familiar question, "is the 2-norbornyl cation nonclassical or two rapidly equilibrating classical ions?". A better form of the question would be "is it a symmetric bridged species, or two rapidly equilibrating species that may also be significantly bridged?".

(4) Brown, H. C. *Spec. Publ.-Chem. Soc.* 1962, 16, 140.

(5) Brown, H. C., accompanying paper in this issue.

(6) Grob, C. A., accompanying.

(7) Olah, G. A.; Prakash, G. K. S.; Saunders, M., accompanying paper in this issue.

Cheves Walling is Distinguished Professor of Chemistry at the University of Utah. He received his A.B. degree from Harvard (in 1937) and his Ph.D. at the University of Chicago with M. S. Kharasch. Although his chief field of research is free-radical reactions, he has been struggling to understand the broader aspects of physical organic chemistry and to explain them to students ever since. As Editor of the *Journal of the American Chemical Society*, 1975-1981, he estimates he had to make decisions on over 3000 physical organic manuscripts, not all (fortunately, in his view) involving 2-norbornyl systems.

measure of either boredom or exasperation. In part, this has been the consequence of the sheer mass of data and arguments generated. No one has ever counted the number of publications touching on the 2-norbornyl cation problem, but they include a number of reviews, chapters, and books, and a typical research paper may well include references to over 100 others.⁸ Unfortunately, the tone of the debate has also contributed. There have been claims of "final solutions" that failed to gain general acceptance, authors have sometimes ignored data contrary to their viewpoint, and a reader might be excused for sensing that different protagonists attached quite different meanings to the words they use. Since a significant fraction of the efforts of physical organic chemists was drawn into the problem, an unhappy consequence was a feeling on the part of many (including some of those concerned with the distribution of research funds) that physical organic chemistry was in danger of withdrawing into a world of its own.

For over 30 years I have been an innocent, but interested, bystander of all this turmoil, reading papers, listening to talks, attempting to discuss the matter comprehensibly in graduate courses, and more recently, trying to evaluate manuscripts as an editor of *J. Am. Chem. Soc.* The questions I would like to address are as follows.

1. Can a few pieces of data that give clear-cut answers be extracted from the confusion of information so that the subject can be made understandable and significant to the nonexpert?

2. What are these answers?

3. Where does the problem stand in our overall picture of structure and reactivity and the way chemical reactions take place?

I will start by stating a personal opinion. While Winstein's original proposal was certainly consistent with his data, in a way, he, and most of the subsequent discussion, put the cart before the horse. If the 2-norbornyl cation is unusually stable and easily formed, and if it has the symmetric structure (II), the former is not necessarily a consequence of the latter. Rather, both arise from interaction between the positive center and the electron cloud around C-6. Much of the rhetoric in the literature has unfortunately been based on this misconception, so that any evidence of unusual stability or other striking property was taken ipso facto as evidence for a symmetric, bridged structure. The confusion this has generated has been considerable. With this prejudice, three points should really be considered separately and in turn.

1. Is there evidence that the 2-norbornyl cation is unusually stable relative to other secondary cations, and if so, is there specific evidence that this is due to interaction with the electron cloud around C-6?

2. Aside from stability, what can be said about the actual structure (i.e., geometry) of the parent 2-norbornyl cation?

3. To what extent does this stabilization extend to tertiary 2-substituted-2-norbornyl cations? This point is important chiefly because of the emphasis H. C.

(8) Brown, H. C. (with comments by Schleyer, P. v. R.) "The Non-classical Ion Problem"; Plenum Press: New York, 1977 (covers much of the literature through 1976 and contains 559 references). While there is some duplication between chapters, many references are to several original articles. Because of this proliferation, I have here only cited reviews and sources of specific data.

Brown has given to such tertiary systems.

Does Bridging Stabilize the 2-Norbornyl Cation?

Winstein's original observation of a high exo/endo rate ratio for the solvolysis of 2-norbornyl arenesulfonates has been confirmed for several leaving groups in a variety of solvents. Further, in those solvents where the matter has been investigated, exo compounds exhibit significant internal return (with optically active starting materials, polarographic rate constants are higher than titrimetric ones by factors of 2-4) so the differences in actual ionization rates may be higher than those usually reported.

Early in his attack on the nonclassical ion concept, Brown suggested that, in 2-norbornyl and similar systems, high exo/endo rate ratios arose not because exo solvolyses were accelerated by bridging but because endo solvolyses were sterically retarded. The suggestion was plausible at the time and has taken some time to evaluate, since there has been debate as to suitable models for comparison and since the relative rates of solvolysis of different secondary *p*-toluenesulfonates, often known as "tosylates" (and similar derivatives), vary greatly with solvent. The most successful explanation of this variation is that it arises from different sensitivity to two solvent properties: solvating ability (chiefly solvation of the leaving anion) and nucleophilicity (chiefly interaction with the backside of the developing carbocation).

As Schadt et al. and Bentley et al.^{9,10} have shown, solvolysis rates of tosylates of widely varying structure in a number of solvents can be well-correlated by a four-parameter linear free energy equation of the sort originally proposed by Swain et al.¹¹ and by Winstein et al. (eq 1).¹² Here k_0 refers to a reference solvent, N

$$\log k/k_0 = lN + mY \quad (1)$$

and Y measure nucleophilicity and solvating power of a particular solvent, and l and m are the sensitivity of a particular tosylate to these properties.¹³ Thus, in comparison to 2-adamantyl tosylate, $l = 0$, $m = 1$, simple monocyclic secondary tosylates are more sensitive to nucleophilicity, N ($l = 0.25-0.5$), and less sensitive to solvating power, Y ($m = 0.6-0.8$).¹⁰ Table I gives typical data collected from recent reviews.^{8,11,14} We see that 2-adamantyl is a relatively reactive tosylate in CF_3COOH and $(\text{CF}_3)\text{CHOH}$, strongly solvating, non-nucleophilic media, but relatively unreactive in nucleophilic, weakly solvating solvents such as ethanol and

(9) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1976, 98, 7667.

(10) Bentley, T. W.; Bowen, C. T.; Morton, D. H.; Schleyer, P. v. R. *J. Chem. Soc.* 1981, 103, 5466.

(11) Swain, C. G.; Moseley, R. B.; Brown, D. E. *J. Am. Chem. Soc.* 1955, 77, 3731.

(12) Winstein, S.; Fainberg, A. H.; Grunwald, E. *J. Am. Chem. Soc.* 1957, 79, 4146.

(13) It is worth noting that in developing such an equation some arbitrary values must be assigned as anchor points and to set scales. These choices have no effect on the goodness of the correlation and are basically made to make the parameters fit to plausible preconceived ideas. Thus 2-adamantyl tosylate is assigned $l = 0$, $m = 1$. Interestingly, Swain has recently published a general correlation in the same form for a much more extensive variety of reactions and media. He again finds two solvent properties (which he calls acidity and basicity) but uses different anchor points and obtains different sensitivity factors: Swain, S. G.; Swain, M. S.; Power, A. L.; Alumni, S. *J. Am. Chem. Soc.* 1983, 105, 502.

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

Table I
Solvolysis Rates of Tosylates R-OTs, (25 °C)

R	HOAc	EtOH	MeOH	H ₂ O	HCOOH	(CF ₃) ₂ CHOH	CF ₃ COOH
2-propyl	0.0077 ^b	0.039 ^b	0.118 ^a	41.1 ^a	2.38 ^b	0.11 ^b	2.49 ^b
3-pentyl	0.0243 ^b (0.00053) ^d	0.067 ^b (5 × 10 ⁻⁵) ^d	0.273 ^a	296 ^a	14.08 ^b	8.36 ^a	76.8 ^b
cyclopentyl	0.165 ^b (0.0016) ^d	0.269 ^b (0.00016) ^d	0.985 ^a	1150 ^a	72.2 ^b	41.5 ^a	240 ^b
cyclohexyl	0.00488 ^b	0.0046 ^b	0.016 ^a	89.5 ^a	3.98 ^b	2.64 ^a	27 ^b
2-adamantyl	0.00059 ^b	0.00043 ^b	0.00029 ^a	31.5 ^a	2.65 ^b	14.7 ^a	90 ^b
endo-2-norbornyl	0.00828 ^c	0.00156 ^a	0.0102 ^a	26.9 ^a	3.01 ^c	10.9 ^a	41.7 ^c
exo-2-norbornyl	2.33 ^c	0.439 ^c	3.48 ^a	68500 ^a	5125 ^c	17100 ^a	46800 ^c
exo/endo	355 (1.228) ^e	297 (740) ^e	341	2346	1703	1569	1122

^a Reference 10, Table V. ^b Reference 14, Table II. ^c Reference 8, p 193. ^d Corrected for nucleophilic participation (see text). ^e Corrected for internal return (see text).

acetic acid. Brown¹⁵ has recently placed *endo*- and *exo*-2-norbornyl tosylates in this model by showing that both give good linear plots of solvolysis rates vs. 2-adamantyl tosylate in a wide range of solvents *but not* with other secondary tosylates, indicating that the norbornyl compounds are quite insensitive to solvent nucleophilicity.¹⁶ If so, I suggest that comparisons should best be made in strongly solvating, nonnucleophilic media such as CF₃COOH and (CF₃)₂CHOH (large l , small N) where l values are unimportant, since m values for 2-norbornyl and most other secondary tosylates are quite similar. Here, as Table I shows, the *endo* isomer lies near the middle in reactivity of the tosylates listed. Another approach, which is less convincing since it depends more on theory, is to also look at the data in the more nucleophilic solvents but correct the rates for the nucleophilic contribution.¹⁷ This has been done in Table I for 3-pentyl and cyclopentyl tosylates in ethanol and acetic acid (figures in parentheses), and the results indicate that, were it not for the nucleophilic contribution, *endo*-2-norbornyl would be faster than either. Without belaboring the data further, I think Brown's original question is answered. There is no good evidence that *endo*-2-norbornyl solvolyses are actually slow. They are certainly not slow enough to account for more than a small fraction of the *exo/endo* rate differences (which, as the table shows, are quite solvent independent).

If *exo*-2-norbornyl solvolyses are therefore fast, the explanation in terms of "bridging" has been that their structure is ideally disposed for backside nucleophilic attack by the electron cloud around C-6. (Winstein and others originally discussed this interaction primarily as participation by the electron pair of the 1,6- σ bond, but I agree with Grob⁶ that this is an unnecessary limitation.) Indeed, the importance of internal return indicates that the transition state for *exo* solvolysis is little higher in energy than the resulting stabilized carbocation-anion pair.

From Goering-Schewene diagrams, which correct rate data for differences in energy of starting materials, the (free) energy of the *endo* transition state lies about 5.5 kcal higher than that of the *exo*.⁸ Simple considerations of geometry show that in the *endo* case the transition state is much less well-arranged for interaction of the developing positive charge with the C-6 electron cloud, but simply to equate this energy difference to the bridging stabilization of the 2-norbornyl cation, implying that just beyond the transition state lies a hypothetical "classical ion" in which no interaction with C-6 electron cloud exists, is at best a crude approximation. Nevertheless the idea that in the *exo* solvolysis most of any stabilization due to bridging has been reached by the transition state, while in the *endo* case for steric reasons little if any has, sets a slower limit for the stabilization of about 6 kcal. Once over the transition state, the cation from the *endo* solvolysis presumably "slides down" to the same ion as from the *exo* case, but since slightly different product distributions

(15) Brown, H. C.; Ravindranathan, M.; Chloupek, F. J.; Rothberg, I. *J. Am. Chem. Soc.* 1978, 100, 3143.

(16) The good linear fit with a slope of 0.69 for *endo*-2-norbornyl tosylate is consistent with $l = 0$, $m = 0.69$. The slope for *exo* compound is 0.81.

(17) To keep abreast of current nomenclature, the lN term in eq 1 corresponds to contribution of a k_a process and mY corresponds to $k_c + k_\Delta$.

Table II
Gas-Phase Hydride Affinities (ΔH for $\text{RH} \rightarrow \text{R}^+ + \text{H}^-$)²⁰

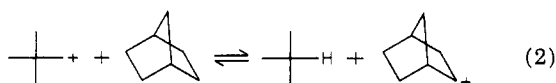
R	ΔH , kcal/ mol	R	ΔH , kcal/ mol
isopropyl	251.7	<i>tert</i> -butyl	235.9
cyclopentyl	245.8	1-methylcyclopentyl	229.5
2-norbornyl	234.4	2-methyl-2-norbornyl	228.4

have sometimes been reported, it may be that this process is impeded as long as the system exists as an ion pair with the counterion on the endo side.¹⁹

Several investigators have attempted to obtain further evidence for or against bridging by examining the solvolyses of 2-norbornyl derivatives with substituents elsewhere in the molecule. Some results are equivocal, but, to me, by far the most convincing are the detailed studies of the effect of substituents of different polarity at C-6 by Grob and his colleagues. Since they are clearly and comprehensively reviewed elsewhere in this issue,⁶ I will simply summarize their major conclusion. Exo (and, to a lesser extent, endo) substitution of C-6 greatly influences the rate of solvolysis of *exo*-2-norbornyl derivatives. The effect is much less with endo solvolyses so that, with electron-withdrawing groups *exo/endo* rate ratios drop to less than unity. The results are large and in the direction expected if bridging were important in the *exo* transition state, and they seem to admit of no alternative explanation involving steric hindrance.

The second approach to detecting stabilization of the 2-norbornyl cation has been through thermochemical measurements, either ion equilibria in the gas phase or heats of ionization of halides (or other derivatives) in strongly acid media where the resulting carbocations are stable.

The most convincing and direct of the ion-equilibria measurements are those of Solomon and Field²⁰ who directly measured equilibria of the type given in eq 2



by mass spectrometric determination of the relative concentrations of the two ions over a temperature range so that both ΔG and ΔH could be calculated. Since ΔS values vary little, differences in ΔG and ΔH values are reasonably comparable. For reaction 1 as written, $\Delta G = -2.3$ kcal/mol: the 2-norbornyl cation is more "stable" than the *tert*-butyl cation.²¹ Their results for a number of hydrocarbons, tabulated as heterocyclic bond dissociation energies are listed in Table II. It is important to note that the *relative* values (which are presumably good measures of relative ion stabilities or delocalization energies, the quantities in which we are interested) involve only the direct measurements and the *difference* in heterolytic bond dissociation energies of propane and isobutane, which is known with con-

(18) Such corrections are listed in Table IV of ref 9.

(19) Similarly there are a number of reactions of 2-norbornyl compounds, presumably proceeding through the development of a cationic center, which fail to give wholly racemized or solely *exo* products. A number of examples are given in ref 8.

(20) Solomon, J. J.; Field, F. H. *J. Am. Chem. Soc.* 1976, 98, 1567.

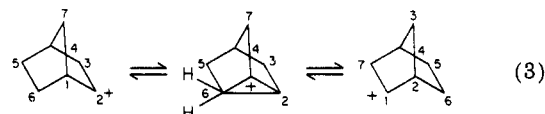
(21) As Arnett has frequently pointed out, such comparisons really involve "stabilities" of all four species. However, heats of formation of isomeric carbocations vary much more with structure than do those of their parent hydrocarbons. Accordingly, when differences are large, it is reasonable to attribute most of them to differences in the cation.

siderable precision. Although the stabilization energies of ions are known to increase somewhat with size (compare isopropyl and cyclopentyl), the increase in going to norbornyl from cyclopentyl, 11.4 kcal/mol, is so large that it clearly implies there is something unusual about the norbornyl structure.

Heats of ionization of alkyl chlorides in solvents such as SO_2FCl , measured by Arnett,²² lead to similar conclusions; see Table III. Again the heat of ionization of 2-norbornyl chloride is close to that of *tert*-butyl chloride and notably larger than the other secondary chlorides studied. Differences are smaller than those between the gas-phase data, as might be expected since any stabilization of the cation due to charge delocalization should be partially offset by less effective solvation of the more dispersed charge.

What Is the Structure of the 2-Norbornyl Cation?

While much can be inferred from reaction rates about the stability of intermediates, conclusions about their structures are much more tenuous and appropriate physical measurements more reliable. Before discussing these, however, I should state a second prejudice. I firmly believe that molecules exist as specific arrangements of atomic nuclei around which a cloud of electrons is arranged in a configuration of minimum energy. Thus there is a real distinction between two equilibrating ions and a symmetric intermediate arrangement that is also an energy minimum, e.g., whether in process 3 the center structure is a transition state or actually



represents the most stable structure of the ion. However, how chemists choose to describe this electron cloud—in terms of resonance structures, dashed lines, arrows, overlapping orbitals, or what not—are human inventions and largely a matter of taste. Thus, if we speak of bridging as lowering the energy of the transition state in an *exo*-2-norbornyl solvolysis, we are trying to describe how the electrons around C-6 may rearrange themselves to shield and lower the energy of the developing positive charge, and I doubt that it makes much difference whether we call it orbital overlap, induced dipole interaction, or a direct field effect.²³ Similarly, there are many ways of representing the postulated symmetric "nonclassical" structure of the 2-norbornyl cation.²⁴ I think they only differ operationally in regard to where the fourth H is placed with respect to the triangle of C's—at one corner as I have done here (a corner protonated cyclopropane), between two C's (an edge protonated cyclopropane), or sus-

(22) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* 1978, 100, 5408. Ionizations of other starting materials and in other media give qualitatively similar results.

(23) To illustrate this point, a direct field effect is intended to describe the effect of a dipole or charge, acting through space (and any intervening electron cloud) on the electrons in another part of a molecule. The dipoles associated with C-H bonds are normally small, so to produce the large effects observed here, a considerable induced dipole would seem to be required. Producing such a dipole implies shifting the electron cloud around C-6 toward C-1. Since these nuclei are already held close together, I find it hard to tell this description from orbital overlap or Winstein's original dashed lines.

(24) H. C. Brown collects these, and a number are depicted on p 85 of ref 8.

Table III^a
 Heats of Ionization for RCl (SO₂ClF at -55 °C)²²

R	ΔH, kcal/mol	R	ΔH, kcal/mol	R	ΔH, kcal/mol
isopropyl	-15.3	cyclopentyl	-17.3	2-norbornyl	-23.6
<i>tert</i> -butyl	-25.4	1-MeCP	-27.1	2-Me-2-NB	-31.0
2-phenyl-2-propyl	-30.3	1-PhCP	-30.8	2-Ph-2-NB	-37.0

^a CP stands for cyclopentyl and NB for norbornyl.

pended above the middle (Roberts' "nortricyclonium ion").

The key to investigating the properties of the 2-norbornyl cation was the discovery²⁵ that it (and a great many other carbocations) is sufficiently persistent in strongly acidic nonnucleophilic media, such as SbF₅-SO₂ or SO₂ClF, for NMR examination. Two approaches have, I believe, provided the most definitive data, and since both are discussed in detail by Olah et al.,⁷ I shall merely summarize them briefly. The first is study of the temperature dependence of ¹H and ¹³C spectra. At room temperature the proton spectrum is a single broad line due to rapid 2,3 and 1,2,6 hydride shifts (plus any Wagner-Merwein rearrangement if the ion is actually two equilibrating species). At -80 °C the 2,3-shift is frozen out to give a three-line spectrum, and at -150 °C the 1,2,6-shift is also suppressed, giving five lines. Now the two protons at C-6 are clearly distinguished from those at C-1 and C-2, but the latter are not separated, indicating that any equilibration, if occurring, is still too rapid to be detected on the NMR time scale. The ¹³C spectra give similar results, and measurements have recently been extended by Yannoni et al.²⁶ to the solid state all the way down to 5 K. Even here C-1 and C-2 are not differentiated, and the authors conclude that either the ion is symmetric or consists of two equilibrating species separated by a barrier of no more than 200 cal/mol. At this point, I think most readers would conclude that the problem had evaporated, although a distinction, in principle, still exists.²⁷

The temperature-dependent spectra provide other information. The spectrum at -150 °C, if that of a single species, clearly indicates the corner-protonated cyclopropane structure rather than the other alternatives mentioned. The 2,3 hydride shift, $E_a = 10.8$ kcal/mol, is quite slow compared to that in, e.g., the cyclopentyl cation, which cannot be frozen out in solution, indicating considerable loss of some sort of stabilization in its transition state. Finally, the much faster 1,2,6 hydride shift, $E_a = 5.9$ kcal/mol, is hard to picture as a low activation energy process if we are dealing with equilibrating ions but becomes a simple 1,2-shift in a protonated cyclopropane.

The second convincing piece of NMR evidence involves the effect on deuterium substitution on the ¹³C NMR of two otherwise identical equilibrating carbocations, as developed by Saunders. If equilibration is rapid on the NMR time scale, the two carbons bearing the positive charges (which, if resolved, would show lines separated by ~300 ppm) give a single line of av-

eraged position. Deuterium substitution near one of the centers, however, shifts the equilibrium constant from unity by an equilibrium isotope effect (presumably because the cationic carbon is an sp² hybrid and the other sp³); one carbon has the positive charge more than half the time and is shifted downfield, while the other is shifted up. The resulting splitting is temperature dependent and, at low temperatures, very large, ~100 ppm. In contrast, in a delocalized system such as an allylic cation, hybridization of the two carbons is identical. Deuterium substitution may still produce splitting, but it is very small (~1 ppm or less in cases that have been examined).²⁸

Saunders and Kates²⁹ have applied this test to the 2-norbornyl cation substituted with deuterium at either C-2 or C-3 by generating the cation at -150 °C and taking its spectrum at that temperature. No splitting of the merged signal for C-1 and C-2 was detected and, from the line width observed, the authors concluded that, if any splitting existed, it amounted to <2 ppm. While this evidence is convincing and straightforward, I can add two comments. First, the situation is actually a bit more complicated than is indicated in Saunders and Kates' original paper.³⁰ Second, if equilibration is between two strongly bridged ions, as should be the case here, the cation is closer to an sp³ hybrid and the isotope effect should be reduced. Such cases are known, but they do not approach the small splitting found here. In short I think the situation is much the same as with low-temperature NMR. The data are consistent with a single symmetric structure but do not rule out equilibration between two *very* strongly bridged species separated by a *very* small barrier.

A third piece of evidence that has been presented as conclusive is the ESCA spectrum of the 2-norbornyl cation.^{31a} Since the data analysis has been questioned³² and a reported confirmation has not yet been published, I find it hard to evaluate. However, I should point out that no critic has proposed that the reported data are, in fact, more consistent with a pair of equilibrating ions.

A number of other physical measurements—NMR chemical shifts, Raman spectra, etc.—have been presented as supporting a symmetric structure for the 2-norbornyl cation and have been reviewed by Olah.^{7,31b} All indicate that the 2-norbornyl cation is "different" and thus support the idea that it is "bridged", but they are basically arguments by analogy about somewhat

(28) The sensitivity of this technique is impressive. A 1-ppm splitting corresponds to $K_H/K_D \sim 1.017$.

(29) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* 1980, 102, 6867.

(30) Although the 1,2,6 hydride shift was frozen out on the NMR time scale, it was not on the time scale of the experiment. Accordingly, for C-3 substitution the measurement was actually carried out on equal mixture of isomers labeled at C-3, C-5, and C-7. That at C-5 would produce no splitting, so a "split" spectrum should actually show three peaks of equal area. Similarly, labeling C-2 should give a central peak with double the area of the others. This does not vitiate the experiment but slightly decreases its sensitivity.

(31) (a) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* 1973, 12, 173. (b) Olah, G. A. *Acc. Chem. Res.* 1976, 9, 41.

(32) Kramer, G. M. *Adv. Phys. Org. Chem.* 1975, 11, 177.

(25) Saunders, M.; Schleyer, P. v. R.; Olah, G. A. *J. Am. Chem. Soc.* 1964, 86, 5680.

(26) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* 1982, 104, 7380.

(27) The situation is much like the question of the structure of the methyl radical. A variety of physical evidence shows that it is either planar or a very flat, rapidly inverting pyramid. However, it has never become a cause celebre and is generally treated as flat except by the most *recherché* commentators.

Table IV
Solvolytic Rates of 2-Substituted-2-norbornyl *p*-Nitrobenzoates^a (80% Acetone, 25 °C)

R	10 ³ k, s ⁻¹	R	10 ³ k, s ⁻¹
1-methylcyclopentyl ³⁴	2.11	1-phenylcyclopentyl ³⁵	2.6
2-Me- <i>endo</i> -2-NB ³⁴	0.0113	2-Ph- <i>endo</i> -2-NB ³⁶	0.059
2-Me- <i>exo</i> -2-NB ³⁴	855	2-Ph- <i>exo</i> -2-NB ³⁶	7.56
exo/endo	855		128

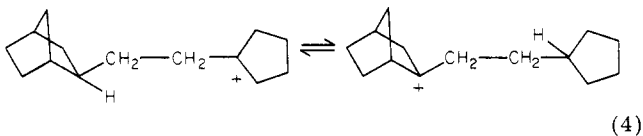
^a The stereochemical designator, *endo* or *exo*, refers to the situation of the *p*-nitrobenzoyloxy group.

indeterminate standards and thus do not distinguish as acutely between a symmetric structure and an appreciably bridged equilibrating pair as do the data I have selected.

What About 2-Substituted-2-norbornyl Cations?

Here I shall restrict myself to the two simplest cases, the 2-methyl and 2-phenyl species, on which the first kinetic data were published by Brown in 1964.³³ Results, actually taken from later full papers where they are sometimes extrapolated from high temperatures, are summarized in Table IV. They show that higher *exo* rates persist, although less than in Table I and with methyl > phenyl. If one believes that high *exo/endo* ratios arise from transition-state bridging, the phenomenon must accordingly extend to unsymmetric structures. On the other hand, *exo* rates are only 2–4 times faster than those for the corresponding cyclopentyl derivatives and *endo* are very much slower. The measurements were made in 80% aqueous acetone, a moderately nucleophilic medium, but since tertiary derivatives show little sensitivity to nucleophilicity, the comparison is probably valid. As far as I know, a similar comparison has not been carried out in a low *N*, high *Y* solvent such as CF₃COOH.

Equilibrium and thermochemical data throw further but rather confusing light on the matter. Solomon and Field's gas-phase data, Table II, indicate that the 2-methylnorbornyl ion is only 1.1 kcal/mol more stable than methylcyclopentyl, compared with 11.4 kcal/mol for the unsubstituted compounds. Arnett's heats of ionization data, Table III, similarly show a difference of 3.9 kcal/mol between methylnorbornyl and methylcyclopentyl in comparison with 6.3 for the unsubstituted compounds. However, the data on phenyl-substituted compounds are puzzling since now the differences become larger, and if one compares 2-*propyl* with norbornyl derivatives, differences between unsubstituted, methyl, and phenyl compounds decrease only slightly.³⁷ Other measurements exist, and a particularly clean-cut one is the equilibrium directly measured by NMR in acid media by Okazawa and Sorenson³⁸ for which $\Delta G \approx -1.0$ kcal.



(33) Brown, H. C.; Chloupek, F. J.; Rei, M. H. *J. Am. Chem. Soc.* 1964, 86, 1248.

(34) Ikegami, S.; Vander Jagt, D. L.; Brown, H. C. *J. Am. Chem. Soc.* 1968, 90, 7124.

(35) Brown, H. C.; Ravindranathan, M.; Takeuchi, K.; Peters, E. N. *J. Am. Chem. Soc.* 1975, 97, 2899.

(36) Brown, H. C.; Takeuchi, K.; Ravindranathan, M. *J. Am. Chem. Soc.* 1977, 99, 2894.

(37) Arnett gives a ± 0.6 kcal uncertainty to his heats of ionization, but if the value for methylcyclopentyl were 3 kcal/mol larger, the whole data set would appear more consistent.

Admittedly the data are not very consistent, but taken all together, they seem to say that stabilization, presumably due to bridging, in 2-substituted-norbornyl cations still persists but is very much less than in the unsubstituted case.

NMR studies of structure yield results paralleling measurements of stability. NMR spectra of cations that might have symmetric structures—1,2-dimethyl- and 1,2-diaryl-2-norbornyl—show rapidly equilibrating pairs; although, for the 1,2-dimethyl case, deuterium substitution leads to a ¹³C spectrum in which C-1 and C-2 are split by only 12–23 ppm depending on the temperature (–21 to –127 °C),³⁹ pointing to some bridging in the equilibrating species. NMR data on simple 2-substituted-2-norbornyl cations are consistent with a single quite asymmetric stable species, and chemical shifts can be interpreted as showing varying amounts of bridging.

Conclusions

I think I can now answer the Innocent Bystander's earlier questions. A few clear-cut and definitive sets of data can indeed be isolated from the welter of information. They are as follows.

1. The *endo* and *exo* solvolysis rates of secondary 2-norbornyl derivatives, interpreted in terms of what we now know about the nucleophilic and solvolytic properties of different media and the response of different substrates to these properties, and the effect of C-6 substitution on these rates.

2. Equilibrium and thermochemical measurements comparing the 2-norbornyl cation with other secondary and tertiary cations.

3. Low-temperature and isotope-perturbed NMR spectra of the 2-norbornyl cation under stable ion conditions, which give the most direct information as to its structure.

The firm conclusions that can be reached from these and that are consistent with an enormous amount of "softer" data available I consider to be the following. For simplicity and clarity I omit the whole series of minor *caveats* that experts like to attach to each, although I have already indicated some of them.

1. The 2-norbornyl cation is significantly stabilized relative to open chain and monocyclic secondary cations (by 6–12 kcal/mol vs. cyclopentyl) so that its properties resemble a simple tertiary cation. All evidence indicates that this stability arises from interaction with the electron cloud around C-6, which I have termed "bridging" but which is quite as effective under other names.

2. The 2-norbornyl cation is best thought of as a corner-protonated cyclopropane. All physical measurements and a mass of "soft" data are consistent with

(38) Okazawa, N.; Sorenson, T. S. *Can. J. Chem.* 1982, 60, 2180.

(39) Saunders, M.; Telkowski, L. A.; Kates, M. R. *J. Am. Chem. Soc.* 1977, 99, 8070.

this. The most discriminating measurements permit as an alternative only a pair of ions of "almost" this structure in extraordinarily rapid equilibrium.

3. Since the energy difference between exo and endo transition states is close to the "unusual" stabilization of the 2-norbornyl cation,⁴⁰ since there is no good evidence that endo solvolyses are slow, and since exo/endo ratios respond to substitution at C-6 as would be expected, the high exo/endo rate ratios observed must be attributed primarily to bridging in the exo transition state.

4. In tertiary 2-norbornyl reactions and ions, stabilization due to bridging decreases, much as (and for the same reasons as) was discussed by Winstein and Grunwald in 1948 in connection with bridging by neighboring atoms with unshared electron pairs.⁴¹ As a consequence, symmetrically 1,2-disubstituted ions exist as rapidly equilibrating pairs rather than as protonated cyclopropanes. Put another way, tertiary and particularly tertiary benzylic systems are a poor place to look for σ bridging and, since they are relatively crowded, a good place to find steric effects. Although sorting out steric and electronic effects is particularly difficult in systems where substituents are changed in the immediate vicinity of reaction sites,⁴² I think most workers agree with Brown that high exo/endo rate ratios in such systems are, in fact, largely steric in origin. However, how this steric effect should be apportioned between retardation of the solvolysis of compounds with endo leaving groups (perhaps by steric interference with solvation of the leaving group) and acceleration of solvolysis of compounds with exo leaving groups due to relief of steric repulsion between the 2-endo-substituent and the C-6 CH_2 group is not at all clear.

In these conclusions, I have implicitly given the Innocent Bystander's answer to the more limited and historical question that Brown emphasizes: "Are the high exo/endo rate ratios in unsubstituted 2-norbornyl solvolyses electronic or steric in origin?". His argument for a steric origin, as I see it, has been that, since there was plausible evidence for steric hindrance accounting for high exo/endo ratios in tertiary systems, why should

(40) A true enthusiast can waste a lot of time quibbling about this statement, but I have tried to indicate some of the difficulties earlier.

(41) Winstein, S.; Grunwald, E. *J. Am. Chem. Soc.* 1948, 70, 828.

(42) A point clearly made by Hammett when he developed his σ - ρ relation for side-chain reactions of aromatics: Hammett, L. P. *J. Am. Chem. Soc.* 1937, 59, 96.

not the same explanation be applied to the unsubstituted system as well? When first posed, the question was plausible, and a conclusive answer has required not only solvolysis rate data but an understanding of solvent-reactant interactions, thermochemical data, and suitable and conclusive structural information on the carbocations involved. While these have only become available during the 1970s, I will note that Brown's alternative "endo solvolysis is slow" was never supported by convincing data, and only endured as a hypothesis for 20 years because of uncertainty as to proper models and suitable conditions for making the rate comparisons.⁴³

Finally, what is the place of all this in chemistry? Aside from the historical and sociological interest of the long debate and the enjoyment of some of the circuses it has provided, the problem has certainly supplied a testing ground for a variety of techniques and concepts. As for broadening our understanding of the principles underlying physical organic chemistry, its resolution provides another and particularly striking example of how one part of a molecule affects another, a central theme in modern chemistry.⁴⁴ Involvement of the electron cloud around a neighboring carbon with a positive center is well-known as hyperconjugation and must be related to the extreme ease of 1,2 hydride shifts. Involvement of electron clouds around more remote carbons has entropy working against it and, to be really effective as here, requires that the molecule take an enzymelike grip on itself and force the remote carbon and the positive center into close proximity with proper geometry. Nevertheless, as NMR studies show,⁴⁵ degenerate 1,2 alkyl migrations in open-chain systems are also rapid (but slower than hydride shifts). In such systems the protonated cyclopropane intermediate lies a few kilocalories/mole above the secondary cation and exists only as a transition state. In the 2-norbornyl system, the peculiar geometry evidently makes it of lower energy and the stable species, even compared with a possible strongly bridged unsymmetric structure.

(43) It may well turn out that the coup de grace to this "endo is slow" hypothesis is the correlation of solvolysis rates presented in ref 14, although the authors have never developed the argument.

(44) This idea is elegantly expressed by Morrison and Boyd in their preface: Morrison, R. T.; Boyd, R. N. "Organic Chemistry", 4th ed.; Allyn and Bacon: Boston, 1983.

(45) Thus, in the 2-butyl cation, the 2,3 hydride shift has $E_a < 6$ kcal, while for carbon scrambling via methyl shifts $E_a = 7.5$ kcal. Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* 1973, 6, 53.