THE NONCLASSICAL ION PROBLEM - TWENTY YEARS LATER*

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Abstract - Twenty years have passed since the author first questioned the
importance of nonclassical structures for carbonium ions at the 1962
Symposium on "The Transition State" at Sheffield. At that time nonclassical
structures were being advanced for essentially all carbocations known to
man. There appeared to be general agreement that the 2-norbornyl cation
was the most favorable example of a nonclassical ion. Accordingly, this
cation was made the central feature of a careful reexamination of the evid-
ence. After 20 years study, it is possible to say that many of the argu-
ments and experimental evidence advanced to support the symmetrical σ-
bridged structure for the 2-norbornyl cation are no longer valid. Indeed,
at this time, there is no definitive evidence which requires the nonclassical
structure for the 2-norbornyl cation. Moreover, there are many experimental
results which are clearly incompatible with this structure.

INTRODUCTION

In 1937 there was a famous Discussion of the Faraday Society on the topic, "Reaction Kinetics."
This discussion was very influential in stimulating the development of our current ideas about
the mechanisms of chemical reactions. To celebrate the twenty-fifth anniversary of this re-
nowned Discussion, in 1962 The Chemical Society (London) sponsored a Symposium on the topic,
"The Transition State," at the University in Sheffield, England. There I presented an invited
lecture on the topic, "Strained Transition States" (Ref. 1).

The main topic of my lecture was the role of steric strains in influencing the rate and course
of chemical reactions (Ref. 2). However, I also discussed some of the unease I felt toward
the rapidly proliferating nonclassical structures for carbocations which had been appearing
in the literature for the past ten or so years. This lecture brought about a vigorous reac-
tion from supporters of the nonclassical position. Unfortunately, many of the papers published
by these supporters appeared to have as their objective proving me wrong, rather than provid-
ing an irrefutable experimental basis for the concept.

It was not possible for one individual with a few coworkers in this area to undertake to
examine all of the nonclassical structures which had been proposed. There appeared to be
general agreement that the 2-norbornyl cation represented the best possible example for a
nonclassical ion (Ref. 3). Accordingly, we decided to concentrate our efforts on this system.

HOW DID I GET INVOLVED?

In 1946 the author proposed that the solvolysis of highly branched tertiary alkyl derivatives
should be facilitated by the relief of steric strain (Eqn. 1) (Ref. 4).

$$\begin{array}{ccc}
R & & R \\
\diagdown & & | \\
R-C-X & \longrightarrow & C^+ + X^- \\
\diagup & & \diagup\diagdown \\
R & & R \quad R
\end{array} \qquad (1)$$

tetrahedral,   planar,
  strained   less strained

_____

The experimental results supported the proposal (Ref. 5), and the concept received wide
acceptance (Ref. 6). Consequently, we left this area for other problems.

Soon thereafter a number of examples of fast solvolysis rates involving highly strained
systems began to appear in the literature. These enhanced rates were attributed not to
relief of steric strain but to a new phenomenon, σ-participation (Ref. 7). Typical examples
were camphene hydrochloride (Eqn. 2) (Ref. 8), tri-*tert*-butylcarbinyl esters (Eqn. 3) (Ref.
9), and cyclodecyl tosylate (Eqn. 4) (Ref. 10).

(2)

(3)

(4)
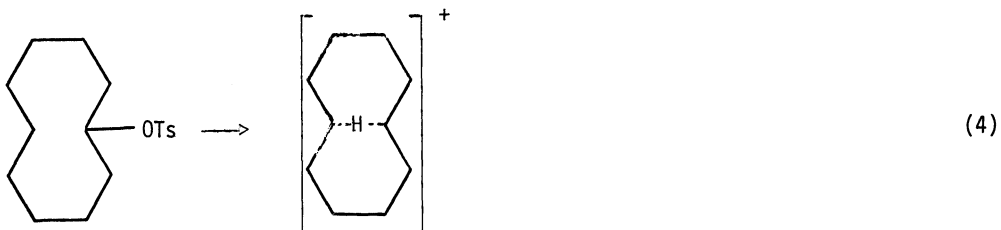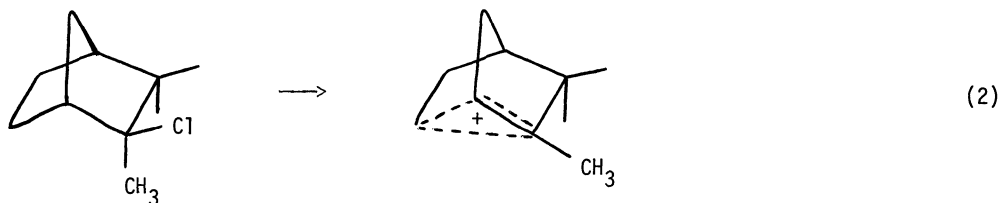
It appeared to be a remarkable coincidence that all such cases of enhanced rates attributed to
σ-participation involved strained molecules where relief of steric strain might have been
expected to be a major contributory factor. A thorough examination of the evidence advanced
for σ-participation proved not convincing. Consequently, a detailed experimental program was
undertaken to test this proposal.

THE EXPERIMENTAL APPROACH

As discussed earlier, it appeared that the 2-norbornyl system provided the best, most clear-
cut example for σ-participation (Ref. 3, 11) (Eqn. 5).

(5)
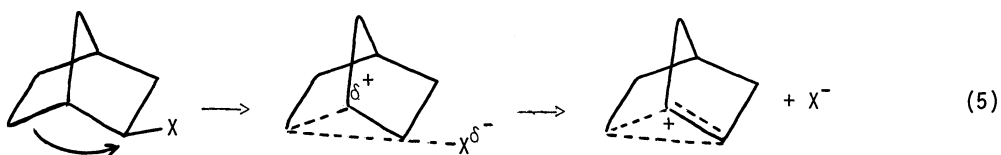
There appeared to be three major foundations for the proposal of σ-participation in the solvo-
lysis of 2-norbornyl derivatives: (a) unusually fast rates of solvolysis for the exo deriva-
tives, as illustrated by a rate for camphene hydrochloride, 13,600 larger than that for *tert*-
butyl chloride (Ref. 8, Eqn. 2); (b) high exo:endo rate ratios, as indicated by a value of
350 for the acetolysis of the 2-norbornyl brosylates (Ref. 7, Eqn. 5); (c) high exo:endo
product ratios, in the solvolysis of 2-norbornyl derivatives (Ref. 3, Eqn. 5). It was pro-
posed that in the exo isomer, the Cl-C6 carbon bond can participate to assist the departure
of X. In the nonclassical cation, solvent can react only to regenerate the exo derivative.

Each of these indicated foundations was subjected in turn to intensive examination. The
detailed evidence is summarized in my book on the subject and need not be repeated here (Ref.
12). Here I shall merely touch on a few critical points which appear to refute these proposed
foundations.

ARE EXO RATES UNUSUALLY FAST?

The magnitude of the enhanced rate of solvolysis exhibited by camphene hydrochloride (13,600) (Ref. 13), as compared to *tert*-butyl chloride (1.00), was considered to be not compatible with relief of steric strain (Ref. 8). Consequently, the enhanced rate was attributed to the driving force associated with the formation of a stabilized mesomeric cation (Eqn. 2).

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

$$(6)$$
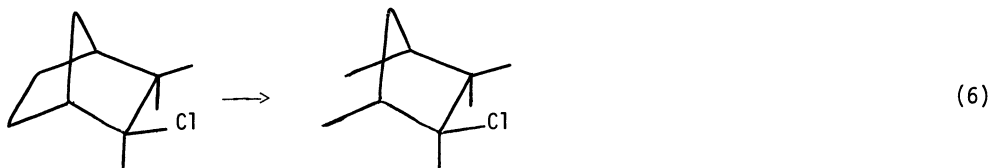
This structure has not yet been synthesized. However, many of the methyl substituted 1-methyl-cyclopentyl chlorides were prepared and their rates of ethanolysis at 25°C determined. The data do not support the conclusion that the rates of solvolysis for the *exo*-norbornyl deriva-tives are exceptional (Fig. 1).

13,600   1.00   2,380

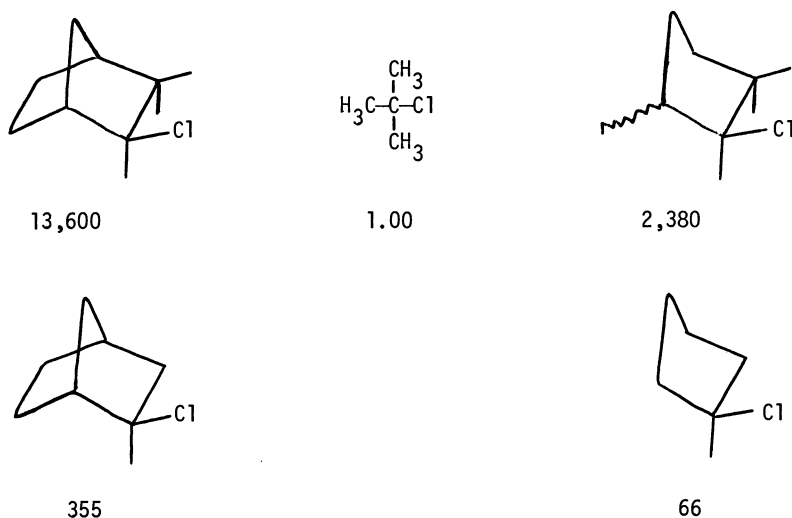355   66

Fig. 1. Effect of methyl substituents on solvolytic reactivities of
tertiary 2-norbornyl and cyclopentyl derivatives.

Quite clearly these results are in better accord with the postulated effect of increasing steric strain in enhancing the rates of solvolysis of highly branched tertiary chlorides (Ref. 2, 5) than with σ-participation. Note that the rates of the *exo*-norbornyl derivatives are faster than the corresponding cyclopentane derivatives by factors of less than six, a modest factor on which to justify such a major change in the course of the reaction.

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

DO THE HIGH EXO:ENDO RATE RATIOS REQUIRE σ-BRIDGED CATIONS?

The precise problem of the 2-norbornyl solvolysis is defined by the Goering-Schewene diagram for the acid-catalyzed acetolysis of *exo*- and *endo*-norbornyl acetates (Fig. 2) (Ref. 14).
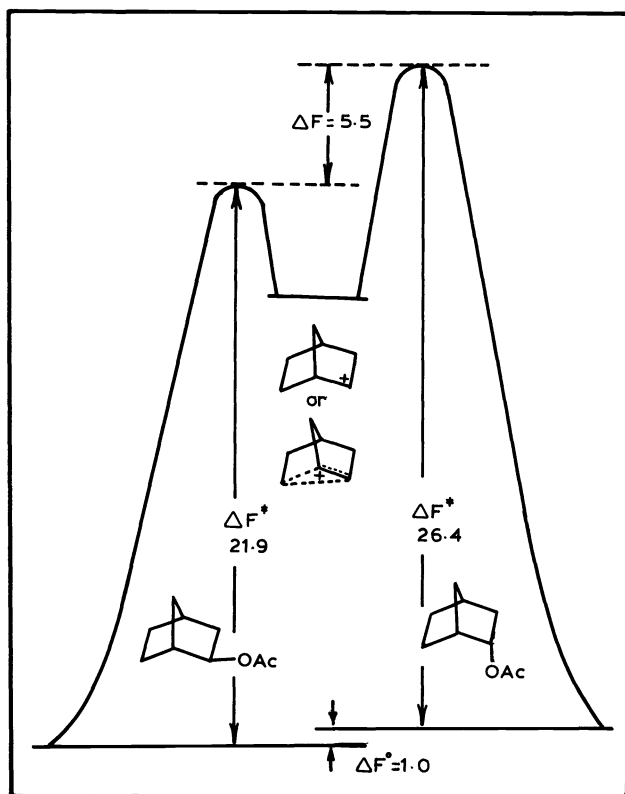
Fig. 2. Goering-Schewene diagram for the acid-catalyzed acetolysis of
*exo-* and *endo*-norbornyl acetates at 75°C (all numbers in kcal mol-1).

The free energy of activation for the ionization of the exo isomer is 4.5 kcal mol^{-1} lower
than that for the endo isomer. Correcting for the higher ground-state energy for the endo
isomer, 1.0 kcal mol-1, results in a difference of 5.5 kcal mol-1 for the difference in the
energies of the two transition states.

The crucial problem is to define the factor or factors responsible for the major differences
in energy of 5.5 kcal mol-1 between the energies of the two transition states. Is the transi-
tion state for the exo derivative stabilized by σ-participation and charge delocalization, as
postulated by nonclassical supporters, or is the transition state for the endo derivatives
destabilized by steric hindrance to ionization (Ref. 12), or some unrecognized factor?

Until we raised the question, it had been considered axiomatic that the difference in energy
must be attributed only to stabilization of the exo transition state by σ-bridging (Ref. 14).
Fortunately, a suggestion by one of the referees of the camphene hydrochloride study indicated
a means of testing this position.

DO THE HIGH EXO:ENDO PRODUCT RATIOS REQUIRE σ-BRIDGED CATIONS?

It was recognized early that the acetolysis of either *exo-* or *endo*-norbornyl brosylate yields
> 99% exo acetate. This was considered to represent a major argument favoring the σ-bridged
2-norbornyl cation (Str. 1) (Ref. 7).

exo attack by
nucleophiles
strongly favored

1
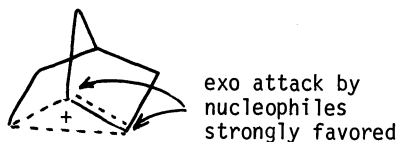
It was originally considered that the high exo:endo rate and product ratios represent two different characteristics which provided independent support for the σ-bridged intermediate. However, the free energy diagram (Fig. 2) reveals that these are not independent phenomena. The ion in the central well must pass over the same two transition states to generate the products. Clearly the formation of exo product will be strongly favored energetically.

Consequently, whatever the factor that stabilizes the exo transition state, or destabilizes the endo transition state in Figure 2 must be responsible both for the high exo:endo rate ratio and the high exo:endo product ratio.

HIGHLY STABILIZED 2-NORBORNYL DERIVATIVES

As was mentioned earlier, the referee of the camphene hydrochloride paper made a most important suggestion (in addition to the customary one in this area that the manuscript not be published). He pointed out that tertiary carbocations are quite stable. He argued, therefore, that in the camphenilyl cation the tertiary center should be incapable of acquiring further stabilization from the C1-C6 carbon-carbon bond. In his opinion, the original authors (including C. K. Ingold) had been seriously in error in proposing a σ-bridged transition state and intermediate as their explanation for the fast solvolysis rate of camphene hydrochloride.

This comment suggested a new approach to the problem. Why not prepare highly stabilized tertiary 2-norbornyl cations? If the high exo:endo rate ratio and high exo:endo product ratio observed in the solvolysis of 2-norbornyl tosylate were due to σ-bridging, such σ-bridging should be negligible in highly stabilized tertiary 2-norbornyl cations. In these cations, both the exo:endo rate ratio and the exo:endo product ratio should tend toward unity, with the energy levels of the exo and endo transition states approaching the same value.

Accordingly, we synthesized 2-p-anisyl-2-norbornyl (Ref. 15) and 2-p-anisyl-2-camphenilyl p-nitrobenzoates (Ref. 16) and measured their rates of solvolysis in 80% aqueous acetone. The results (Fig. 3) reveal a very high exo:endo rate ratio for 2-p-anisyl-2-norbornyl and an even higher value for the camphenilyl derivative.

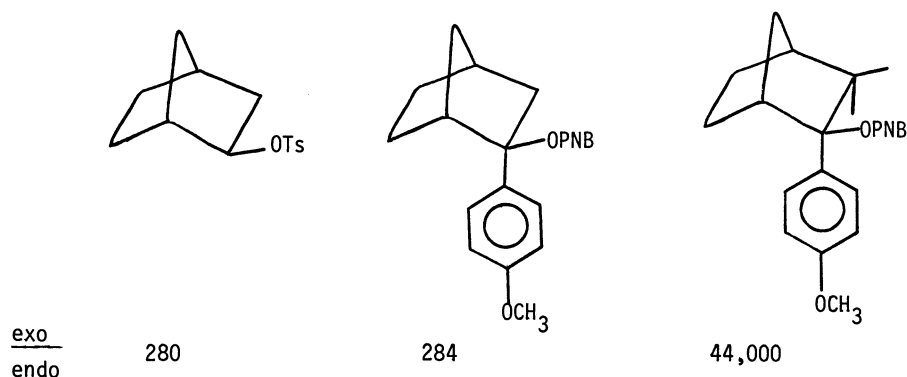$$\frac{exo}{endo}$$ 280   284   44,000

Fig. 3. Exo:endo rate ratios in the solvolysis of 2-norbornyl and highly stabilized 2-norbornyl derivatives.

Note the similarity in the characteristics of the free-energy diagram for such a classical 2-anisyl-2-norbornyl system (Fig. 4) to that for 2-norbornyl itself (Fig. 2).

As anticipated from the energy diagram, the products from the solvolysis of these highly stabilized tertiary 2-norbornyl derivatives involve capture of solvent or other nucleophile almost exclusively from the exo direction.
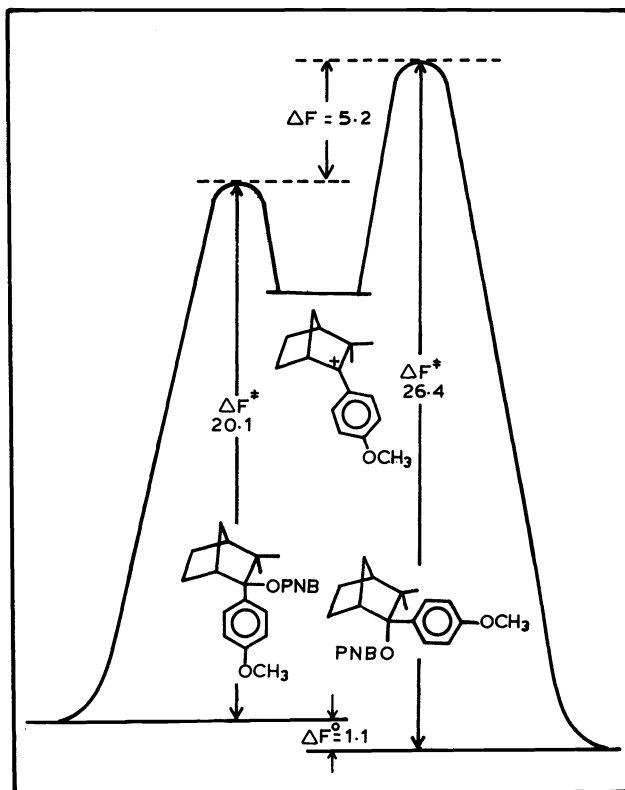
Fig. 4. Free energy diagram for the solvolyses of 2-p-anisylcamphenilyl p-nitrobenzoates in 80% aqueous acetone at 25°C.

STERIC HINDRANCE TO IONIZATION

Steric hindrance to ionization has been suggested as a factor destabilizing the *endo*-norbornyl transition states, both for secondary and tertiary. The norbornane system has a rigid U-shaped structure. Attack of the endo positions is very difficult. Consequently, it appears reasonable to consider the possibility that departure of the leaving group in a typical ionization will likewise be difficult. Indeed, consideration of molecular models for hypothetical intimate ion pairs for two possible reaction paths reveals major steric difficulties (Fig. 5).
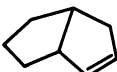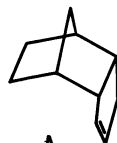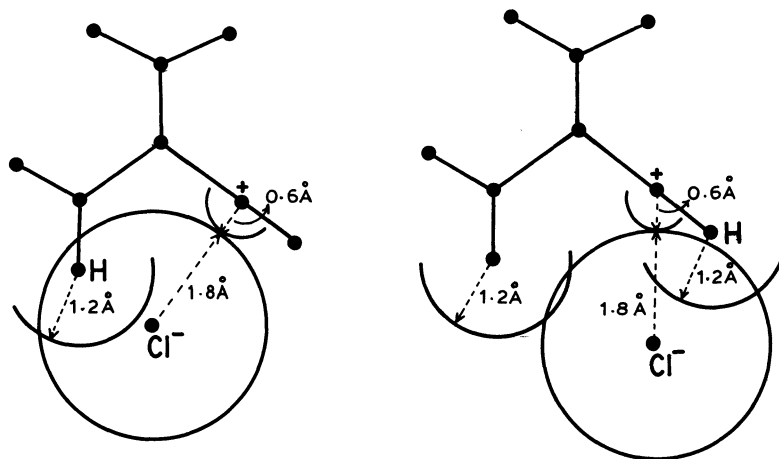

Fig. 5. Molecular models for the hypothetical intimate ion pairs from the two postulated reaction paths.

This concept was tested by examining the relative stereoselectivities exhibited by three different bicyclic systems of gradually increasing U-shaped character and rigidity (Ref. 17) (Table 1).

TABLE 1.   Comparison of the relative stereoselectivities exhibited by three representative U-shaped systems

Reaction	exo: endo ratio		
Hydroboration-oxidation of olefin	24	200	> 1000
Epoxidation of olefin	6.7	200	> 1000
Oxymercuration-demercuration of olefin	8	> 500	
Lithium aluminum hydride reduction of ketone (X = 0)	3	8.1	> 1000
Addition of CH_3MgX to ketone (X = 0)	50	200	> 1000
Oxymercuration-demercuration of methylene derivatives (X = CH_2)	8.1	200	> 1000
Solvolysis of the tertiary 2-methyl-p-nitrobenzoates (X = CH_3, OPNB)	17	855	4300

Although individual reactions evidently differ considerably in the stereoselectivities they exhibit, the results reveal a consistent pattern. In all cases, the cis-bicyclo[3.3.0]-octane system exhibits the least preference for exo attack, presumably because of its higher flexibility, and the $endo$-5,6-trimethylenenorbornane system exhibits the highest stereoselectivity for exo attack. In all cases, the norbornane system is intermediate.

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

THE 2,7,7- AND 2,6,6-TRIMETHYLNORBORNYL SYSTEMS

If the exo:endo rate ratio is the result of steric forces, it should be possible to vary these ratios in a predictable manner by varying the steric environment. Thus an increase in the steric crowding of the exo environment should lead to a decrease in the exo:endo rate ratio. Similarly, an increase in the steric crowding of the endo environment might be expected to result in an increase in the exo:endo rate ratio. Indeed, the exo:endo rate ratio of 855 for 2-methylnorbornyl p-nitrobenzoate decreases to 6.1 with the presence of two methyl groups in the 7-position, and increases to 3,630,000 with the methyl groups in the 6-position (Fig. 6).
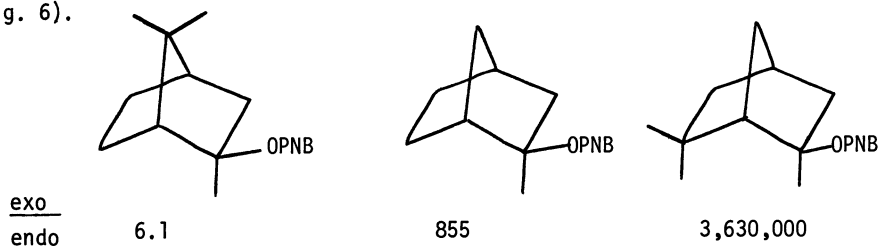
$\dfrac{exo}{endo}$ 6.1   855   3,630,000

Fig. 6.   Modification of the exo:endo rate ratios by appropriate methyl substitution.

These major changes in the exo:endo rate ratios are readily explicable in terms of the effects of the *gem*-dimethyl groups in either facilitating or hindering the rates of solvolysis (Ref. 18) (Fig. 7).
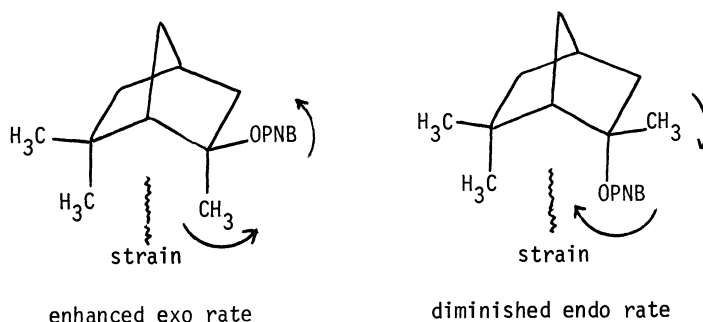

Fig. 7. Effect of 6,6-dimethyl substituents in the enormous increase in the exo:endo rate ratio.

Note the major changes in the magnitude of the difference in energy of the two transition states (Fig. 8 and 9) of the corresponding Goering-Schewene diagrams. Certainly in these cases the difference cannot be solely the result of stabilization by σ-bridging in the exo isomer.

Fig. 8. Free-energy diagram for the solvo-
lyses of 2,7,7-trimethyl-*exo*- and
-*endo*-2-norbornyl *p*-nitrobenzoates
in 80% aqueous acetone at 25°C (all
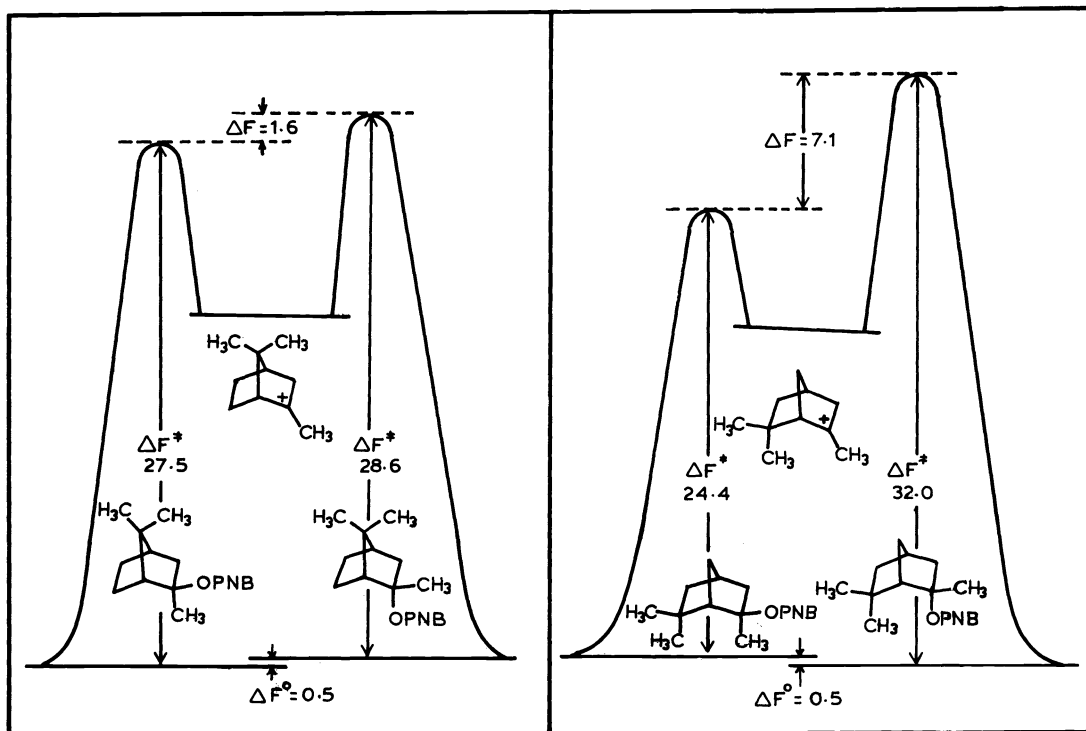numbers are in kcal mol-1).

Fig. 9. Free-energy diagram for the solvo-
lyses of 2,6,6-trimethyl-*exo*- and
-*endo*-norbornyl *p*-nitrobenzoates in
80% aqueous acetone at 25°C (all
numbers are in kcal mol-1).

IMPLICATIONS OF THE GOERING-SCHEWENE DIAGRAM

The acetolysis of 2-norbornyl derivatives exhibits an extraordinarily high preference for exo product: 99.98% *exo*-, 0.02% *endo*-norbornyl acetate at 25°C (Ref. 14). Does this remarkably high stereospecificity require the formation of a σ-bridged intermediate? The Goering-Schewene diagram provides a definitive answer. Indeed, a careful examination of the implications of the diagram can eliminate much of the confusion in the literature provided by earlier qualitative discussions.

The exo and endo isomeric acetates pass over the two transition states to form the same intermediate, the norbornyl cation (Fig. 2). The principle of microscopic reversibility requires that in the symmetrical system, which was the subject of the original study, the norbornyl intermediate, in reacting with acetic acid, must pass over the same two transition states involved in the ionization of the reactants. The authors established that the difference in the energies of the two transition states actually corresponds to the observed distribution of the intermediate to the products: 99.98% exo, 0.02% endo.

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

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

The Goering-Schewene diagram allows us to calculate the difference in energy between the solvated classical 2-norbornyl cation (or ion-pair) and the proposed solvated nonclassical structure (or ion-pair). The free energy diagram for the acetolysis of *exo-* and *endo-*norbornyl tosylate reveals a difference in the energies of the two transition states of 6.0 kcal mol^{-1} (Fig. 10). According to the nonclassical interpretation, the transition state for the exo isomer is stabilized by partial σ-bridging and such σ-bridging increases as the ion proceeds past the transition state to the σ-bridged nonclassical ion intermediate. The endo isomer is stereoelectronically unsuited for such σ-participation. Consequently, the transition state is unbridged and the reaction proceeds past the transition state to the classical unbridged cation, with bridging occurring subsequently.
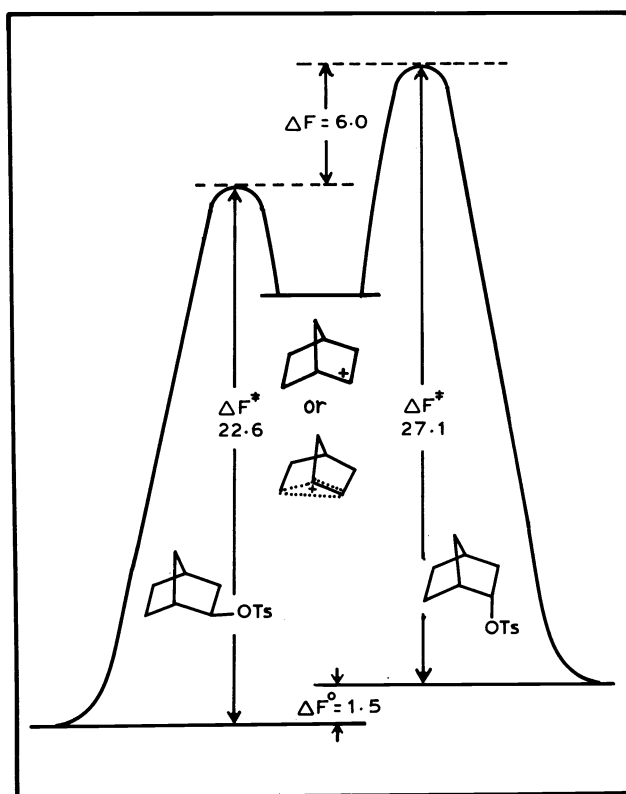

Fig. 10. Free energy diagram for the acetolysis of *exo-* and *endo-*norbornyl tosylates at 25°C (all numbers in kcal mol^{-1}).

If the two transition states differ by 6.0 kcal mol^{-1}, the nonclassical and classical ions should differ in energy by a quantity somewhat larger than this quantity. If we make the usual assumption that the transition states will resemble the two intermediates, the difference in energies for the solvated classical and nonclassical ions will be modestly greater than 6 kcal mol^{-1}. For convenience we will use a value of 8 kcal mol^{-1}.

It should be recognized that the classical ion, with its less delocalized charge, will be more strongly solvated than the nonclassical ion, with its delocalized charge. Consequently, in the gas phase these two structures should differ in energy by considerably more than 8 kcal mol^{-1}.

PROPOSED DICHOTOMY OF CATIONS

One attempt made by nonclassical supporters has been to propose a dichotomy of cations. They accept the evidence that stabilized tertiary 2-norbornyl cations are classical, but propose that secondary 2-norbornyl cations are nonclassical. (The clearest exposition of this position is by Paul von R. Schleyer in his comments in Ref. 12.) According to this position, the high exo:endo rate and product ratios in tertiary 2-norbornyl derivatives is due to steric inhibition of ionization. On the other hand, the high exo:endo rate and product ratios in secondary 2-norbornyl derivatives is attributed to σ-bridging in the exo isomer.

Can we test this proposal?

THE ARNETT CALORIMETRIC DATA

The recent calorimetric data of E. M. Arnett (Ref. 18) appear to offer an unambiguous refutation of this position. This author and his coworkers measured the heats of ionization of three series of organic chlorides (Fig. 11).
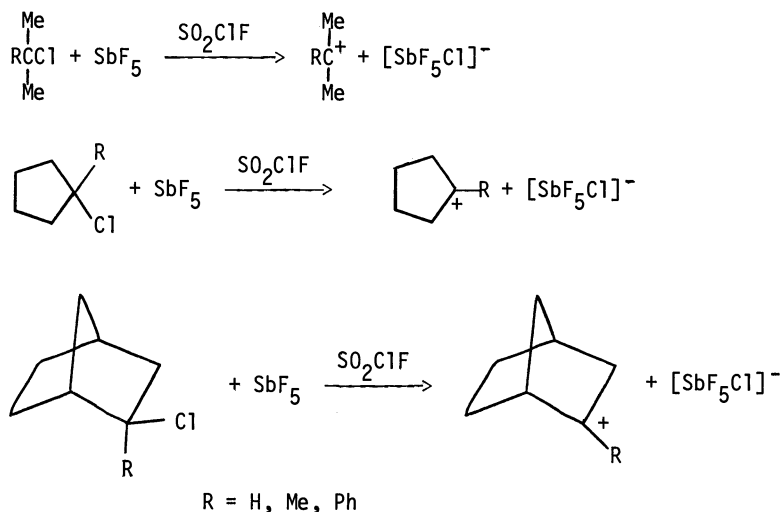

R = H, Me, Ph

Fig. 11. Heats of ionization of three selected series of organic chlorides.

We now have considerable data which indicate that the more carbon atoms situated around a carbocationic center, the more stable the cation. The more bond opposition forces, the easier the ionization. Both factors predict that the ease of ionization should increase as we proceed to the right for a particular R (Fig. 12).
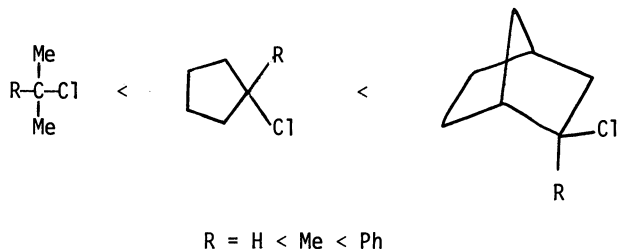

R = H < Me < Ph

Fig. 12. Predicted variation in the calorimetric heats of ionization.

We should anticipate the following behavior in the observed heats of ionization, provided both secondary and tertiary 2-norbornyls are classical (Fig. 13).
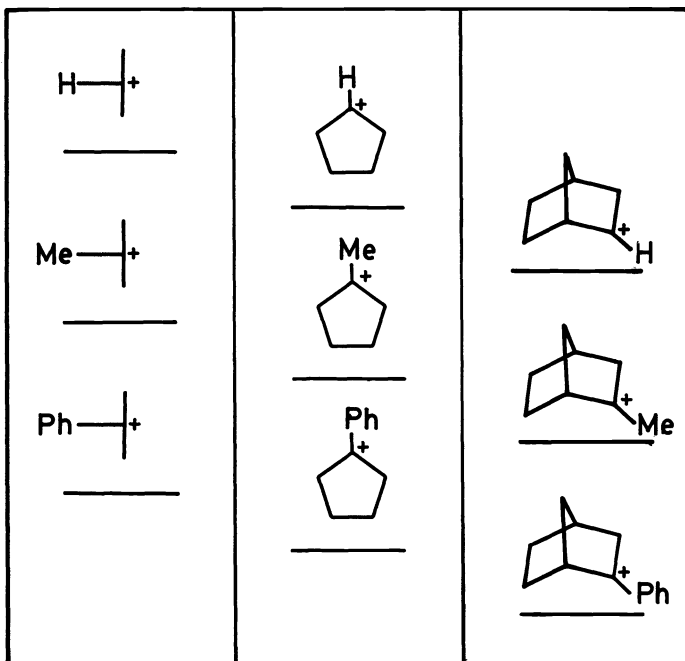
Fig. 13. Predicted changes in the calorimetric heats of ionization
with structure of the system and variation in R (H < Me < Ph),
assuming a classical secondary 2-norbornyl cation.

On the other hand, if 2-norbornyl is nonclassical, stabilized by $\sim$ 8 kcal mol^{-1}, whereas 2-methyl-2-norbornyl and 2-phenyl-2-norbornyl are classical, we should expect the behavior shown in Fig. 14.
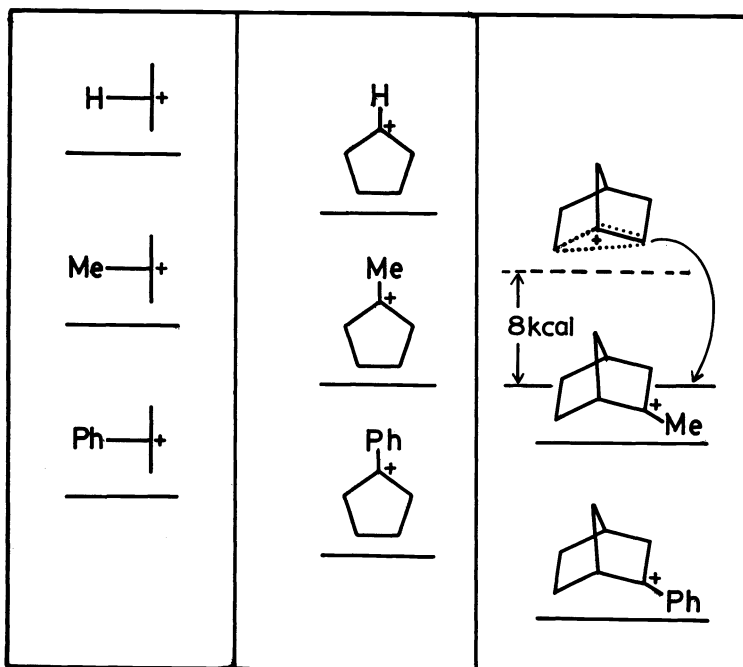

Fig. 14. Predicted changes in the heats of ionization with structure
of the system and variation in R (H < Me < Ph) assuming a nonclassical
secondary 2-norbornyl cation.

What do his data (Fig. 15) actually show?

They clearly conform to Fig. 13, not Fig. 14. Clearly there is no evidence for the nonclassical resonance energy so long postulated for the 2-norbornyl cation.
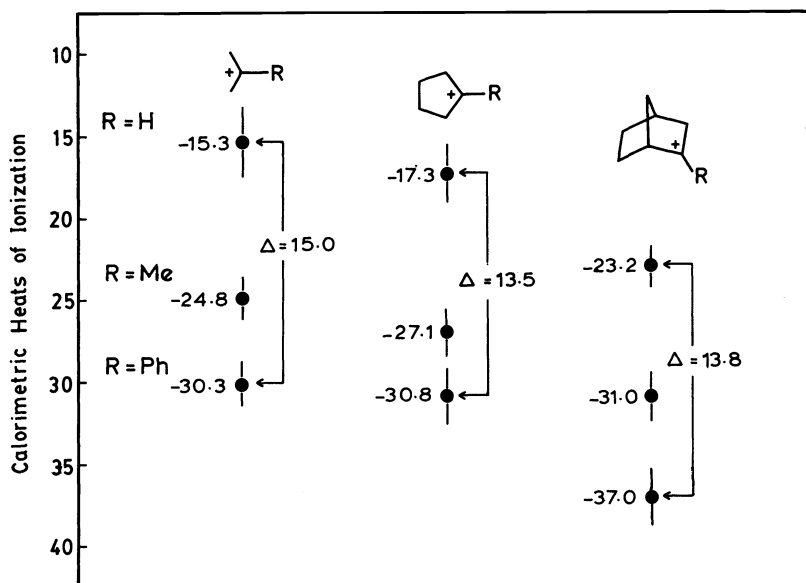

Fig. 15. Calorimetric heats of ionization in SO₂ClF for the selected organic chlorides.

A plot of Arnett's data for the heats of ionization in SO₂ClF against the rates of ethanolysis of the chlorides (corrected for solvent participation in the case of 2-propyl chloride, 2-butyl chloride, and cyclopentyl chloride) reveals a reasonable linear relationship. Only the endo points deviate, presumably the result of steric hindrance to ionization (Fig. 16).
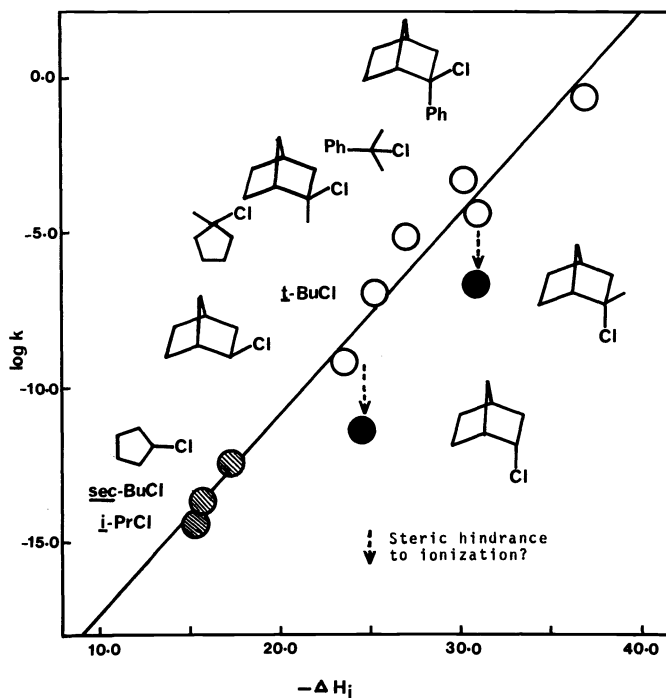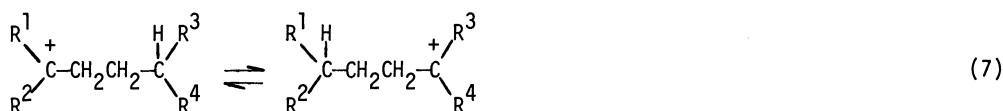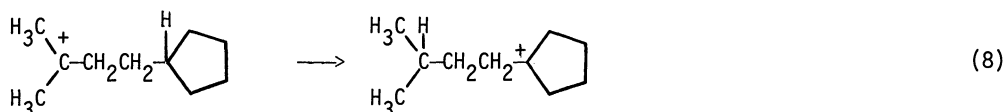

Fig. 16. Linear free energy plot of the calorimetric heats of ionization of alkyl chlorides in SO₂ClF and their rates of ethanolysis at 25°C. (The shaded points are corrected for solvent participation.)

The conclusion that there is no major stabilization energy in 2-norbornyl has been recently confirmed by T. S. Sorenson (Ref. 19). He detected a simple equilibration between two tert-iary positions joined by an ethano bridge (Eqn. 7).

$$R^1\!\!\!\underset{R^2}{\overset{+}{\diagdown}}\!\!C\!-\!CH_2CH_2\!-\!\underset{R^4}{\overset{H\;R^3}{\diagup}}\!C \rightleftharpoons R^1\!\!\!\underset{R^2}{\overset{H}{\diagdown}}\!\!C\!-\!CH_2CH_2\!-\!\underset{R^4}{\overset{+\;R^3}{\diagup}}\!C \tag{7}$$

The equilibrium was sufficiently slow so that the spectrum revealed the presence of both cations, if both were of comparable stability, permitting a simple quantitative determination of the equilibrium position.

The equilibrium between 2-propyl and cyclopentyl strongly favored cyclopentyl, in accordance with the opposition forces mentioned earlier (Eqn. 8)

$$\underset{H_3C}{\overset{H_3C}{\diagdown}}\!\!\overset{+}{C}\!-\!CH_2CH_2\!-\!\overset{H}{\underset{}{\bigcirc}} \longrightarrow \underset{H_3C}{\overset{H_3C}{\diagdown}}\!\!\overset{H}{C}\!-\!CH_2CH_2\!-\!\overset{+}{\underset{}{\bigcirc}} \tag{8}$$

Cyclopentyl and 2-norbornyl revealed a measurable equilibrium (Eqn. 9).

$$\overset{+}{\bigcirc}\!\!-CH_2CH_2\!-\!\overset{H}{\diagup} \rightleftharpoons \overset{H}{\bigcirc}\!\!-CH_2CH_2\!-\!\overset{+}{\diagup} \tag{9}$$
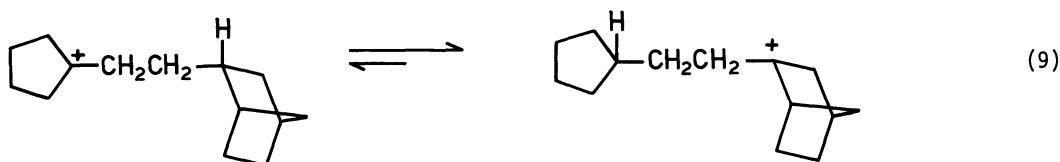
Measurement of the relative concentration of the two cations resulted in an equilibrium constant which favors the 2-norbornyl cation, corresponding to a $\Delta F°$ of 1.0 kcal mol^{-1} at $-90°C$.

Again, there is no evidence for the large stabilization, ~ 8.0 kcal mol^{-1}, of the 2-norbornyl cation required by the nonclassical interpretation of the free energy diagram for the solvolysis of 2-norbornyl.

CONCLUSION

For 20 years many organic chemists have sought for a definitive answer to the question as to whether the 2-norbornyl cation is classical or nonclassical. Numerous ingenious approaches have been used. Many difficult techniques have been applied. There is far more material now available than can be handled in a lecture of reasonable length. For the present discussion I decided to restrict myself to presenting simple, clear experiments and results, which, in my opinion, provide a definitive answer to the question. No supporter of the nonclassical interpretation has attempted a refutation of these data and arguments. Before we consider the results of far more complex experiments and techniques, we should ask those who urge them upon us to consider these simple results and implications and to rebut the obvious implication.

This is not to take the position that nonclassical ions may not exist. Certainly, Coates' cation appears to satisfy the critical criteria we have applied (Ref. 20). However, this system involves participation by a cyclopropyl ring ($\pi\sigma$-participation). We have no case at present which clearly supports simple σ-participation in the formation of a stabilized nonclassical ion.

Before closing, it might be appropriate to call attention to the fate of the three nonclassical ions (Eqns. 2,3,4) which started us on our quest. None are now with us, largely withdrawn by their own authors (Refs. 12,21,22,23). A comparison of the literature of today with that of twenty years ago reveals a major change. At that time, nonclassical structures were being used for nearly all carbocations. Today, one finds only an occasional carbocation, usually one with exceptionally complex structures, being represented in the nonclassical form.

We should recognize that the nonclassical ion problem is related to a much broader problem that has long occupied chemists. Is a particular system better represented as a single minimum or as a rapidly equilibrating double-minimum? When I was an undergraduate at the University of Chicago (1935), benzene was treated as a double-minimum system, rapid equilibrating between two Kekulé structures. Cyclohexane was considered to be planar--a single minimum system. Now we hold the opposite view for these two systems. The hydrogen bond was originally treated as a single-minimum system. Now most are considered to be double-minimum systems.

It was Winstein's proposal (Ref. 7) that the Meerwein proposal of a rapidly equilibrating pair of 2-norbornyl cations (Ref. 24) (double-minimum) be considered to possess a symmetrical non-classical structure (single-minimum). However, as here described, the experimental probes applied to this system fail to detect the 7-8 kcal mol^{-1} stabilization energy required by the nonclassical interpretation. Until this discrepancy is accounted for, there appears to be little point in considering seriously new proposals for the nonclassical structure for the 2-norbornyl cation.

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