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TETRAHEDRON REPORT

EXPLORATIONS IN THE NONCLASSICAL ION AREA

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Abstract—Intensive investigations over the past twenty-five years have failed to provide confirmation for the proposal that σ-bridges in aliphatic and alicyclic cations play an important role in the chemistry and stability of such cations.

Twenty-five years ago the term "nonclassical" was first used by Roberts in referring to his proposed tricyclobutonium structure **2** for the cyclopropylcarbinyl cation **1**.[1]

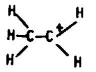
2

The structure proposed **2** was clearly different from the classical structure **1** for the intermediate cation. The second appearance of the term is apparently that of Winstein, who refers to the "nonclassical structures" of norbornyl **4** and other cations in contrast to their "classical structures" **3**.[2]

3

4

The third such reference is apparently due again to Roberts:[3] "Recent interest in the structures of carbonium ions has led to speculation as to whether the ethyl cation is most appropriately formulated as a simple solvated electron-deficient entity **5**, a "nonclassical" bridged ethylene protonium ion **6**, or possibly as an equilibrium mixture of the two ions."[3]



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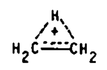

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Although the term in the past has also been applied to π-bridged species, such as the phenonium ion,[2] it has been urged by both Bartlett[4] and Sargent[5] that the term nonclassical be restricted to electron deficient ions, such as **2**, **4** and **6**. After all, there is nothing nonclassical about a protonated aromatic[6] **7** or the heptamethylbenzene cation[7] **8**.

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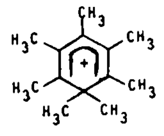

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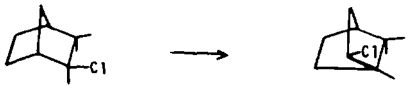
Actually there would be major advantages in restricting the term nonclassical ion to cations containing σ-bridges **2**, **4**, **6**. Then a nonclassical ion could be defined as a cation containing one or more such σ-bridges. Ions such as **2** and **4** would have the characteristic structural feature of possessing at least one carbon atom bonded to five atoms including the carbonium carbon. Ions such as **6** would possess at least one hydrogen atom bound to two carbon atoms including the carbonium carbon.

It was easy to propose such nonclassical structures. It has proven extraordinarily difficult to confirm their existence.[8–12]

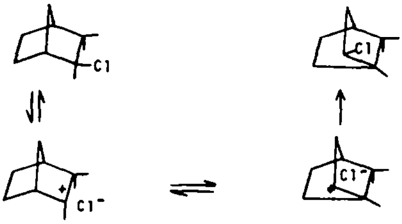
ORIGINS

The camphene hydrochloride-isobornyl chloride rearrangement (1) has played a major role in carbonium ion chemistry.



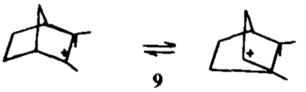
(1)

Thus Meerwein's proposal in 1922 that this rearrangement involves the prior formation of a carbonium ion[13] (2) appears to be the first application of carbonium ion intermediates to account for such a molecular transformation.



(2)

In 1939, Wilson *et al.* suggested that such a rapidly equilibrating pair of ions **9** might exist instead as the mesomeric species[14] **10**.



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10

Wilson's proposal lay fallow for some ten years, until Winstein and Roberts applied it actively in the early 1950s to interpret the structures of carbonium ions **2**, **4** and **6**.

THE NONCLASSICAL ERA OF CARBONIUM ION CHEMISTRY

The proposal that σ-bridges can exist in even simple aliphatic and alicyclic cations caught the fancy of physical organic chemists and the concept was widely adopted and used. Indeed, with the possible exception of the methyl cation, nonclassical structures apparently have been considered for every known aliphatic, alicyclic and bicyclic carbonium ion.[4] Representative systems for which nonclassical ions have been considered are shown in Fig. 1.

Such was the enthusiasm that customary scientific caution was often ignored. For example, at a *Symposium*

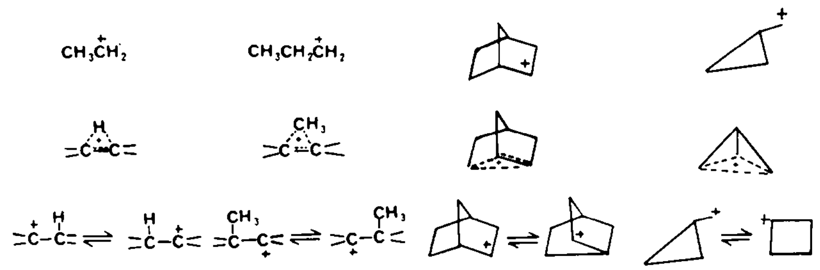


Fig. 1. Representative carbonium ions for which σ-bridged nonclassical structures have been considered.

on Carbonium Ions held at the Meeting of the American Chemical Society in St. Louis in 1961 one speaker, questioned as to why he proposed a particular nonclassical ion, replied, "Because it is fashionable". Another speaker advanced as his reason for proposing a given structure, "Because it looks so nice".[11]

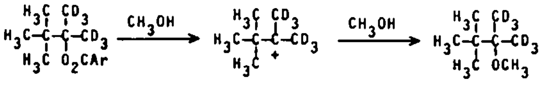
We then passed through what might be termed the rococco period of carbonium ion structures in which highly elaborate "structures" were advanced[11] (Fig. 2). Clearly, inadequate heed was being paid to the counsel of R. B. Woodward that the mere fact that one is dealing with fugitive intermediates should not convey license to propose highly fanciful structures without adequate experimental support.[15]

σ-BRIDGED VS EQUILIBRATING CATIONS

In those cases for which symmetrical nonclassical structures have been considered (such as **2**, **4**, **6**), it is also possible to represent the intermediate as a rapidly equilibrating pair of cations (Fig. 1). On this basis the nonclassical structures would represent the transition states for the equilibrating systems. The problem is then that of deciding in individual systems whether the structure is best represented in its classical form, or as an equilibrating pair (or set) of cations or ion-pairs, or as a resonance hybrid so stable that these prior alternative structures need not be considered.

By using isotopic tags, it has been possible to demonstrate in a large number of systems that the carbonium ions can be generated and transformed into products without the equilibration of the carbon atoms required by the bridged structures. Roberts *et al.* have been especially active in this area.[3,16]

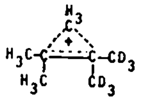
For example, solvolysis of the tagged 2,3,3-trimethyl-2-butyl 3,5-dinitrobenzoate in methanol at 100° produces the methyl ether product with negligible scrambling of the tag[17] (3).



$$(H_3C)_3C-C(CD_3)_2O_2CAr \xrightarrow{CH_3OH} (H_3C)_3C-\overset{+}{C}(CD_3)_2 \xrightarrow{CH_3OH} (H_3C)_3C-C(CD_3)_2OCH_3 \quad (3)$$

11

Clearly the reaction cannot involve the symmetrical methyl bridged intermediate **12**.



12

The intermediate must be the essentially static classical cation **11**, which under these conditions is captured much faster than it can equilibrate.

Such cases are readily resolved. The problem is how do we resolve other cases, such as cyclopropylcarbinyl and 2-norbornyl, where equilibration of the tag approaches

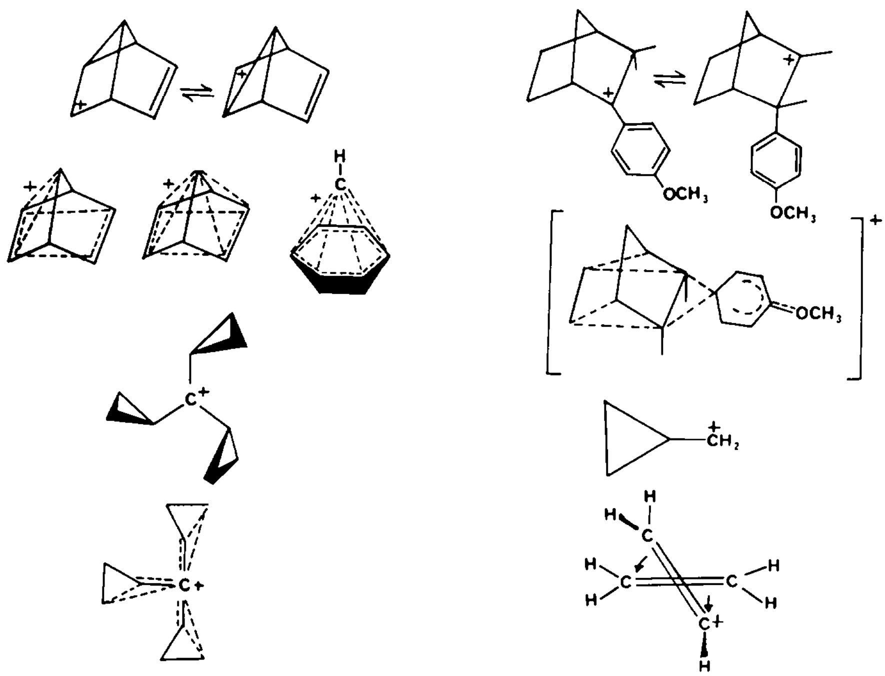


Fig. 2. Representative examples of the rococo period of carbonium ion structures.

that anticipated on the basis of the nonclassical structure. Such systems cannot be represented as involving static classical cations. Rather they must involve either bridged ions or their kinetic equivalent, a rapidly equilibrating pair (or set) of cations. The problem then becomes one of deciding between these two alternatives.

σ-BRIDGING—TRANSITION STATE OR INTERMEDIATE?

It has long been recognized that the rearrangements of cationic intermediates in bicyclic systems of the norbornyl type are extraordinarily facile.[13] If σ-bridged species are not involved, the barrier for such interconversions must be very low. If the rate of interconversion of such ions or ion pairs is to be fast relative to the rate of their capture by solvent, the barrier to the interconversion must indeed be low, not greater than a few kcal mol^{-1}.

In essence the nonclassical proposal was that those electronic effects which served to lower the barrier for the interconversion of two cations (Fig. 3) could further stabilize this species so that it produced a symmetrical intermediate sufficiently stable that there was no longer any need to consider the original equilibrating unsymmetrical cations.

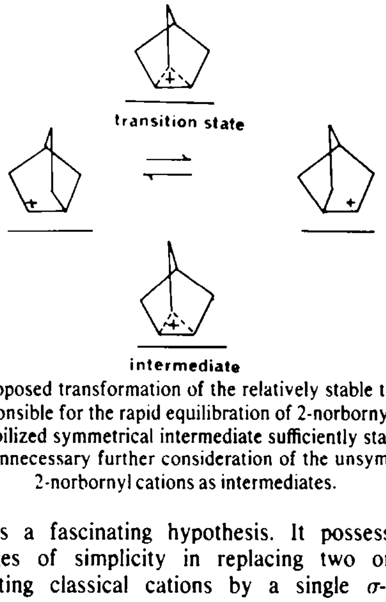


Fig. 3. Proposed transformation of the relatively stable transition state responsible for the rapid equilibration of 2-norbornyl cations into a stabilized symmetrical intermediate sufficiently stable so as to make unnecessary further consideration of the unsymmetrical 2-norbornyl cations as intermediates.

This is a fascinating hypothesis. It possesses the advantages of simplicity in replacing two or more equilibrating classical cations by a single σ-bridged species. However, chemistry is still an experimental science—no matter how reasonable and attractive such a proposal may appear, it is still necessary to subject such proposals to experimental test.

EQUILIBRATING CATIONS

In recent years the pioneering work of Olah, Saunders, Brouwer and Hogeveen has made possible the direct spectroscopic observation of many cations.[18] One remarkable development from these studies has been the conclusion that many cations, such as 2,3,3-trimethyl-2-butyl, which can readily be captured in solvolysis without equilibration,[17] undergo very rapid equilibration under stable ion conditions. Such equilibration often cannot be frozen out even at temperatures as low as −150°. Representative examples are summarized in Table 1.

Consequently, of all these carbonium ions, for many of which nonclassical ionic structures were previously considered,[4] only cyclopropylcarbinyl and 2-norbornyl are still assigned σ-bridged structures.

It should be pointed out that nonclassical structures have been proposed recently for additional systems.[19,20] However, these systems have not yet been subjected to detailed study. On the other hand, we now have an immense amount of data for the cyclopropylcarbinyl and 2-norbornyl cations. If we cannot reach a decision for these systems with all of the immense amount of data available for them, there appears to be little point to examining additional systems for which there is available only a minute fraction of comparable pertinent data.

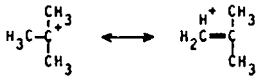
σ-BRIDGING VS HYPERCONJUGATION

One of the difficulties in this area has been the failure to differentiate clearly between hyperconjugation and σ-bridging.[21] Indeed, it has been suggested that mere σ-delocalization be utilized as a basis for assignment to the nonclassical ion group.[4] This would have the effect of including essentially all cations other than methyl, with and without σ-bridges in the nonclassical group.

In my opinion, this represents a distortion of the original proposal. The term nonclassical was originally used for structures in which the presence of σ-bridges was postulated (2, 4, 6). Such structures often possesed a symmetry not present in the corresponding open classical structures. In order to clarify the situation, it may be appropriate to review briefly the theoretical situation as it existed just prior to the introduction of the nonclassical concept.

In the 1940s, electronic effects, such as inductive, inductomeric, field, mesomeric, and hyperconjugative, were generally recognized and utilized to interpret structural effects in organic chemistry. The book by my former colleague at Wayne University, A. E. Remick,[22] *Electronic Interpretations of Organic Chemistry*, published in 1943, can be utilized as a convenient summary of the *status quo* prior to the nonclassical ion proposal.

The t-butyl cation is more stable than the methyl cation. We account for this today in terms of the hyperconjugative contributions which stabilize the t-butyl cation and delocalize charge from the carbonium carbon into the methyl groups (4).



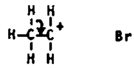
$$(CH_3)_3C^+ \longleftrightarrow H_2C{=}C(CH_3)_2\ H^+ \qquad (4)$$

(9 structures)

Does such delocalization of charge into a saturated alkyl group correspond to the new concept proposed in the 1950s and attributed to nonclassical carbonium ions?

Let us see what Remick had to say on the subject in 1943 (p. 394).

"On the basis of these arguments, one might wonder how a secondary or tertiary alkyl halide can yield a carbonium ion which is sufficiently stable to permit of a S_N1 reaction. The explanation is readily found in the concept of hyperconjugation. Thus no stabilization by resonance is possible in the carbonium ion produced from methyl bromide, whereas in ethyl bromide it becomes conceivable and in secondary and tertiary

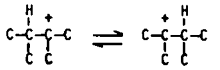
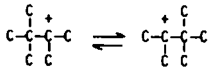
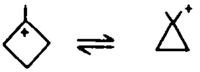
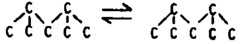
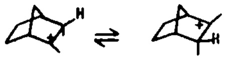
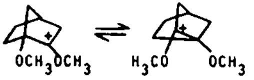
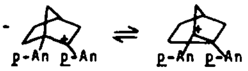
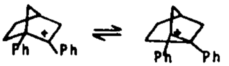
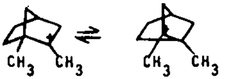
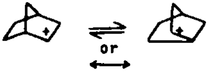
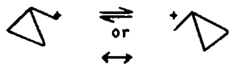


$$H_3C{-}CH_2^+ \quad Br^-$$

halides it becomes still more probable owing to the increasing number of contributing structures".

Consequently, to avoid further confusion, it appears desirable to restrict the term nonclassical cation to a species possessing one or more σ-bridges with the

Table 1. Representative equilibrating classical cations under stable ion conditions

Cation	Structure	Assignment	Ref.
2-Butyl		Equil. class.	Brouwer[a] Olah[b] Saunders[c]
2,3-Dimethyl-2-butyl		Equil. class.	Brouwer[a] Olah[b] Saunders[c]
2,3,3-Trimethyl-2-butyl		Equil. class.	Brouwer[a] Olah[b] Saunders[c]
Cyclopentyl		Equil. class.	Brouwer[a] Olah[b]
1-Methyl-cyclobutyl		Equil. class.	Saunders[d]
2,4-Dimethyl-2-pentyl		Equil. class.	Brouwer[a] Saunders[c]
2,3-Dimethyl-2-norbornyl		Equil. class.	Olah[e] Sorensen[f]
1,2-Dimethoxy-2-norbornyl		Equil. class.	Nickon[g]
1,2-Di-p-anisyl-2-norbornyl		Equil. class.	Schleyer[h]
1,2-Diphenyl-2-norbornyl		Equil. class.	Olah[i]
1,2-Dimethyl-2-norbornyl		Equil. class	Olah[j]
2-Norbornyl		Nonclassical	Olah[k]
Cyclopropyl-carbinyl		Nonclassical Equil. class.	Olah[l] Kelly[m]

[a] D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.* **9**, 179 (1972).

[b] G. A. Olah, *Carbocations and Electrophilic Reactions*. Wiley, New York (1974).

[c] M. Saunders, P. Vogel and J. Rosenfield, *Accounts Chem. Res.* **6**, 53 (1973).

[d] M. Saunders and J. Rosenfield, *J. Am. Chem. Soc.* **92**, 2548 (1970).

[e] G. A. Olah and G. Liang, *Ibid.* **96**, 189 (1974).

[f] A. J. Jones, E. Huang, R. Haseline and T. S. Sorensen, *Ibid.* **97**, 1133 (1975).

[g] A. Nickon and Y. Lin, *Ibid.* **91**, 6861 (1969).

[h] P. v. R. Schleyer, D. C. Kleinfelter and H. G. Richey, Jr., *Ibid.* **85**, 479 (1963).

[i] G. A. Olah and G. Liang, *Ibid.* **96**, 195 (1974).

[j] G. A. Olah, J. R. DeMember, C. Y. Lui and R. D. Porter, *Ibid.* **93**, 1442 (1971).

[k] G. A. Olah, *et al.*, *Ibid.* **90**, 3882 (1968); **92**, 4627 (1970); **94**, 2529 (1972); **95**, 8698 (1973).

[l] G. A. Olah, C. L. Jeuell, D. P. Kelly and R. D. Porter, *Ibid.* **94**, 146 (1972).

[m] D. P. Kelly and H. C. Brown, *Ibid.* **97**, 3897 (1975).

symmetry properties corresponding to the presence of that bridge.

THE CYCLOPROPYLCARBINYL CATION

The cyclopropylcarbinyl cation possesses features which are especially helpful in clarifying the difference between hyperconjugation or σ-delocalization on the one hand and σ-bridging on the other.

The fast rates of solvolysis of cyclopropylcarbinyl tosylate and other related derivatives were originally attributed to the stabilization of the transition states leading to the formation of the presumably highly stabilized symmetrical tricyclobutonium ion[1] **2**. This species is σ-bridged. Note that it contains three carbon atoms each bonded to five atoms.

Later it was observed that the reactions of tagged cyclopropylcarbinyl derivatives fail to show the full equilibration of the tag required by the tricyclobutonium ion.[23] It was therefore proposed that the cyclopropylcarbinyl cation exists instead as a rapidly equilibrating set of three equivalent bicyclobutonium cations **13**.

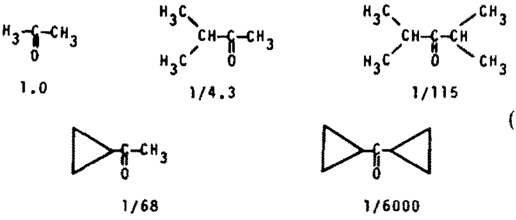
13

The bicyclobutonium ion is a σ-bridged species with one carbon atom bonded to five nearest neighbors.

The question we must decide is whether the rate acceleration involves the postulated formation of a σ-bridge through space to one or two of the far carbon atoms of the cyclopropane ring, or whether it is the result of a favorable hyperconjugative electron supply from the cyclopropane ring. Considerable evidence has accumulated that it is the latter.

For example, Hart and Sandri showed that a number of secondary and tertiary derivatives containing cyclopropyl groups undergo solvolysis with similar rate enhancements but without rearrangements.[24] Consequently, the cyclopropyl group is capable of providing electron density to stabilize a carbonium ion without rearrangement of the structure.

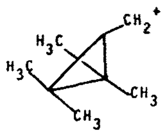
Similarly, a study of the rates of reaction of sodium borohydride with ketones containing cyclopropyl groups established that these rates are quite low[25] (5).



(5)

Clearly, the cyclopropyl group is capable of providing electron density to the carbonyl group in these ketones, as well as to the electron deficient centers of carbonium ions.

The introduction of a methyl group into the cyclopropylcarbinyl system results in an increase in the rate of solvolysis by a factor of approx. 10.[26] The authors observed a reasonably good additivity with the introduction of one, two, three or four methyl groups into the ring at C2 and C3. They concluded that electron supply from the cyclopropane ring must involve a symmetrical contribution, not compatible with the bicyclobutonium ion formulation. Indeed, the bicyclobutonium ion for the tetramethyl derivative (**14**) would require a σ-bridge to a fully substituted carbon atom.



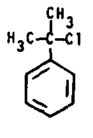
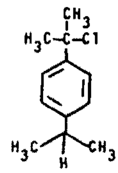
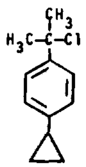
14

This appears highly improbable on steric grounds.

Especially convincing are the results of a study of the solvolysis of optically active cyclopropylmethylcarbinyl derivatives. A σ-bridged intermediate would have been expected to shield the asymmetric center and retain asymmetry. However, the products are inactive.[27] More recently an optically active primary derivative was prepared and solvolyzed.[28] Again the products are inactive.

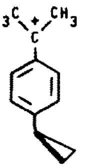
The electronic contributions of substituents are conveniently explored in the t-cumyl system, without concern about possible complications resulting from σ-bridging.[29] Accordingly, we undertook to compare the electronic contributions from isopropyl and cyclopropyl and the steric requirements of those contributions.[30]

A p-isopropyl group increases the rate of solvolysis of t-cumyl chloride (**15**) in 90% aqueous acetone at 25° by a factor of 18 (**16**). On the other hand, a p-cyclopropyl group is much more effective—it increases the rate by a factor of 157 (**17**).

Relative rate 1·00 18 157
15 **16** **17**

A single m-methyl substituent decreases the effect of the p-cyclopropyl group by a relatively small factor. However, two m-methyl groups, ortho to the cyclopropyl substituent, decrease the effect of the p-cyclopropyl group to a factor of only 9, even less than the effect of an isopropyl group. The results are readily accounted for on the basis that the cyclopropyl group provides electrons best to the electron deficient center when it can adopt the bisected conformation as in **18** and **19**, but not **20**.



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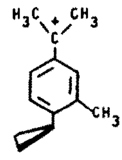

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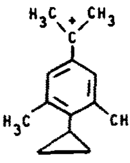
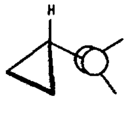


20

There is now a huge mass of data to support the position that electron contributions from the cyclopropane ring to an electron deficient center occurs best from the bisected arrangement[31] **21**.



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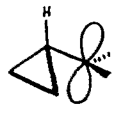


22

The σ-bridged structure would require a rotation of the carbonium carbon away from this stabilized conformation toward the parallel arrangement where one lobe of the p-orbital is directed toward the cyclopropane ring **22**.

The existence of the cyclopropylcarbinyl cation as a rapidly equilibrating set of open cations in the bisected arrangements is supported by recent *ab initio* calculations.[32]

In view of all of the evidence favoring the existence of cyclopropylcarbinyl cation in the stabilized bisected conformation, distinctly unfavorable for the proposed σ-bridge, what is the basis for the proposal that under stable ion conditions the cation exists in its nonclassical σ-bridged form (Table 1)?[33] It is based on a discrepancy between the observed ^{13}C shift and that estimated for an equilibrating set of open cations. As will be discussed later, there are serious uncertainties in this procedure. Indeed, of the two NMR criteria proposed by Olah,[33] one, ^{13}C shifts, favors the σ-bridged structure for the cyclopropylcarbinyl cation,[33] while the second, J_{HC}, favors the open structure.[34]

To sum up, under solvolytic conditions the evidence strongly favors the existence of cyclopropylcarbinyl cations in the bisected arrangement. That structure is evidently favorable for electron supply from the cyclopropyl moiety to the electron deficient center. That structure is not compatible with the proposed σ-bridge from the carbonium carbon to one or both carbon atoms of the three-membered ring. Consequently, it can be concluded that σ-bridges through space are not involved in the fast rates of solvolysis of cyclopropylcarbinyl derivatives.

THE NORBORNYL CATION

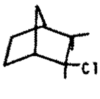
At the time we undertook our reexamination of the validity of the proposals that σ-bridging represented a major factor in the rates of solvolysis, there was general acceptance for the position that cyclopropylcarbinyl[1] and 2-norbornyl[2] provided the strongest available cases for this phenomenon.[4]

Fortunately, it is now clear that the unusual stereochemical requirements for electron supply from the cyclopropyl group to the electron deficient center are in direct opposition to those required for a σ-bridge. This feature greatly simplified the task of reaching a decision for that system. At this time there appears to be little remaining support for the significance of a σ-bridged species in the solvolysis of cyclopropylcarbinyl derivatives.[24–28,30–32]

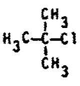
2-Norbornyl has provided a much more difficult case to resolve. In this case the stereochemical requirements for a σ-bridge are very nicely met by the bicyclo[2.2.1]heptane structure. Consequently, it has been necessary to employ more subtle probes.

What were the experimental bases for the proposed σ-bridged structure of the 2-norbornyl cation?

1. Ingold observed that the rate of solvolysis of camphene hydrochloride **23** was 6000 times that of t-butyl chloride **24**.[35]



23
6000

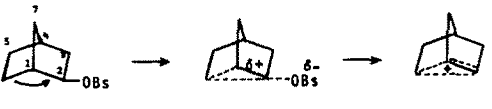


$$H_3C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl$$

24
1·00

He argued that in his opinion such a fast rate could not be the result of relief of steric strain,[36,37] but must arise from what we now term σ-participation, resulting in the formation of a stabilized σ-bridged cation **10**.

2. Winstein and Trifan pointed out that *exo*-norbornyl brosylate **25** undergoes acetolysis (6) at a rate 350 times that of the *endo* isomer.[2]



(6)

25 **4**

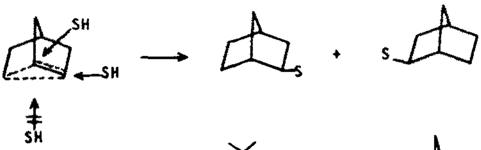
It was postulated that the 1,6-bonding pair is in ideal position to participate in the displacement of the *exo*-OBs group, but it is in an unfavorable position to assist the ionization of the *endo* isomer **26**.

26

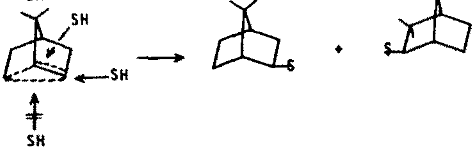
3. Acetolysis of optically active *exo*-norbornyl brosylate yields optically inactive acetate.[2] (Acetolysis of optically active *endo*-norbornyl brosylate yields *exo*-acetate with 7% retained activity.[2]) The proposed nonclassical ion intermediate **4** possesses a plane of symmetry. The classical ion **3** does not. To account for the racemization in terms of the formation of a classical ion, one must postulate a rate of equilibration of the ion or ion-pair that is fast compared to the rate of reaction with solvent (Fig. 3).

The rate of racemization of the brosylate in acetic acid is considerably faster ($k_\alpha \approx 4k_t$) than the titrimetric rate of conversion to product. This is attributed to recapture of the anion by the cation from the first formed bridged or rapidly equilibrating ion pair to reform racemized brosylate. If the rate of racemization of the *exo* isomer, k_α, is taken as equal to the rate of ionization, then the *exo* : *endo* rate ratio becomes 1600.[2]

4. Almost exclusive formation of *exo* acetates in the solvolysis of both *exo* and *endo* derivatives[2] (7), especially for compounds containing 7,7-dimethyl substituents[38] (8).



(7)

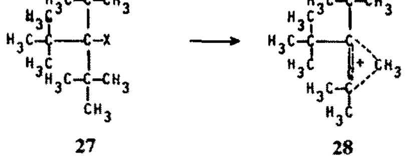


(8)

σ-BRIDGING AND FAST RATES

This proposal of a σ-bridged species appeared to provide a simple, ideal explanation for the observed phenomena. At first, there appeared to be no reason to question it. However, it began to be applied to account for enhanced rates in more and more systems which could be interpreted alternatively as involving relief of steric strain.[36,37]

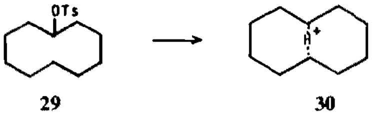
Thus the fast rate of solvolysis of camphene hydrochloride **23** could be interpreted as involving relief of steric strain as the chloride ion, surrounded by three methyl groups, departed the highly congested 2-position of the norbornane structure. Similarly, the fast rate of solvolysis of tri-t-butylcarbinyl *p*-nitrobenzoate **27**, which Bartlett suggested could be due to stabilization of the intermediate carbonium ion through σ-bridging[39] **28**, could alternatively be ascribed to relief of steric strain in the ionization process.



(9)

27 **28**

Again, the fast rate of solvolysis of cyclodecyl tosylate **29** was attributed to transannular σ-bridging[40] **30** and not to the relief of non-bonded interactions (10).



(10)

29 **30**

It appeared to be a remarkable coincidence that all such cases of enhanced rates of solvolysis attributed to σ-participation involved strained molecules, where relief of steric strain might be considered a major contributing factor. It may be appropriate to point out the essential difference in the two proposals.

The solvolysis of t-cumyl chloride in 90% aqueous acetone proceeds at a rate some 6000 times greater than t-butyl chloride (11).

(11)

The enhanced rate of solvolysis of the t-cumyl chloride is attributed to resonance stabilization by the phenyl group of the incipient carbonium ion in the transition state. Such resonance stabilization is greater than the hyperconjugative stabilization provided by the methyl group. Consequently, the enhanced rate is primarily the result of the existence of a transition state which is lower in energy than the corresponding transition state in t-butyl chloride (Fig. 4).

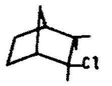
It was proposed that an increase in the steric requirements of the three alkyl groups of tertiary chloride could result in steric strain, increasing the ground state energy. Since such strain should be decreased in the transition state leading to the planar carbonium ion, solvolysis of such derivatives should be facilitated (Fig. 5). The alternative proposal was that σ-bridging could occur in the transition state, stabilizing that state and facilitating solvolysis (Fig. 5).

It was clearly impractical to examine every system where such σ-bridging has been proposed. We concentrated our efforts on the two most favorable cases, cyclopropylcarbinyl and 2-norbornyl, in an effort to establish conclusive evidence for the existence of such σ-bridges and their role in the solvolytic behavior of these systems. For reasons discussed earlier, the cyclopropylcarbinyl system has proven to be a much simpler case. It is now clear that while σ-delocalization plays a role in the unique reactivity of cyclopropylcarbinyl cations, σ-bridges through space from the carbonium carbon to the far carbon atoms of the cyclopropane ring do not. The 2-norbornyl question has been a more difficult one to resolve.

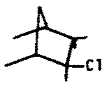
THE FAST RATE OF CAMPHENE HYDROCHORIDE

Ingold had taken the position that the magnitude of the observed rate of solvolysis of camphene hydrochloride (6000[35] or 13,600[41]), as compared to t-butyl chloride (1·00) was too large to be attributed to relief of steric strain. Consequently, he attributed the enhanced rate to the driving force associated with the formation of a stabilized mesomeric cation[35] **10**.

One possible difficulty is the unsuitability of t-butyl chloride as a model for the highly congested structure of camphene hydrochloride **23**. We came to the conclusion that methyl substituted 1-methylcyclopentyl chlorides, such as **31**, involving an opening of the 5,6-ethylene bridge, might be more suitable models.



23



31

The results[41] do not support the conclusion that the rates for the norbornyl derivatives are exceptional (12).

It should be noted that the removal of the gem-dimethyl substituents, **23**→**32**, **33**→**34**, reduces the rates by approximately the same factor in both systems. Clearly the results are in better agreement with the postulated effect of increasing steric strain in enhancing the rates of solvolysis of highly branched tertiary chlorides.[36,37]

It is not argued that these results disprove the formation of mesomeric norbornyl cations in the solvolysis of camphene hydrochloride and related *exo*-norbornyl derivatives. However, they do eliminate the original

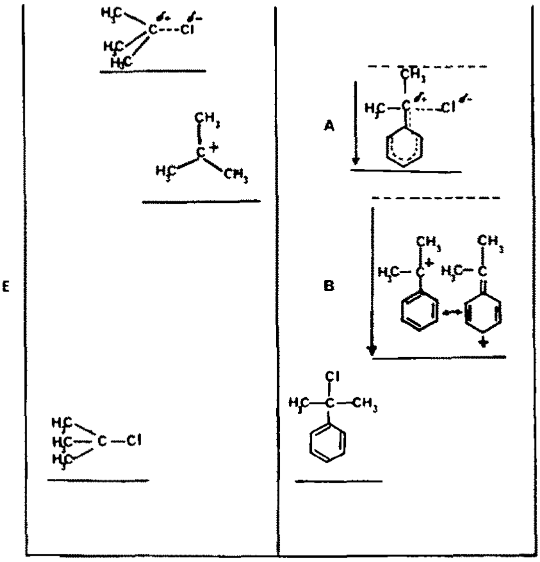


Fig. 4. Effect of classical resonance in facilitating solvolysis through stabilization of the transition state A and the carbonium ion intermediate B.

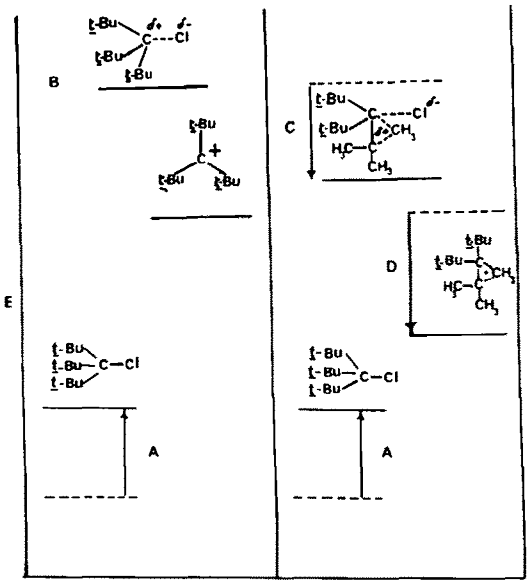
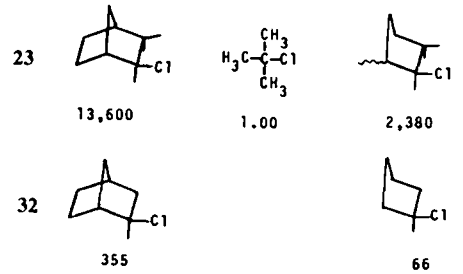


Fig. 5. Effect of steric strain in the ground state A facilitating solvolysis either by relief of strain in the less strained transition state B or by stabilization via σ-bridging in the transition state C and in the carbonium ion intermediate D.



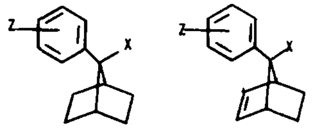
(12)

argument that the rates of solvolysis of these derivatives are too fast to be explicable on any basis other than the formation of mesomerically stabilized cations.

CLASSICAL 2-ANISYLNORBORNYL CATIONS

Ideally, one would like to have a slightly modified 2-norbornyl system which definitely produces a classical (unbridged) 2-norbornyl cation for comparison with the postulated bridged system. Would such a system exhibit low *exo* : *endo* rate ratios? Would such a system produce low *exo* : *endo* product ratios?

One approach to such classical ions is suggested by the Gassman-Fentiman study of the *anti*-7-norbornenyl system.[42] It has long been accepted that the more stable the cationic center the less demand that center will make upon a neighboring group for additional stabilization through participation. This is clearly revealed in the study of the 7-arylnorbornyl 35 and 7-arylnorbornenyl derivatives 36.



Z	35	36
p-CH_3O	1·00	3·4
p-H	1·00	41·5
p-CF_3	1·00	34,500
3,5-$(CF_3)_2$	1·00	255,000
7-H	1·00	10^{11}

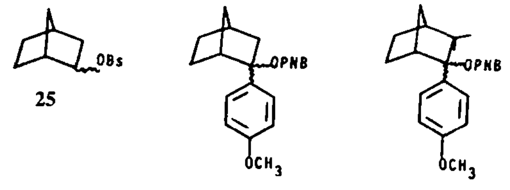
The presence of *p*-anisyl at the 7-position causes the truly enormous participation factor of 10^{11} exhibited by the secondary derivative essentially to vanish.

If *p*-anisyl can achieve this, should not the presence of a *p*-anisyl group at the 2-position of norbornyl cause the much smaller σ-participation (×350) postulated for the secondary derivative to vanish? Indeed, a careful PMR examination of the 2-phenylnorbornyl cation has revealed no evidence for charge delocalization from the 2- to the 1- and 6-positions.[43] If the 2-phenyl-2-norbornyl cation is classical, there surely cannot be any argument about the more stable 2-*p*-anisyl derivative.

Yet the solvolysis of the 2-*p*-anisyl-2-norbornyl *p*-nitrobenzoates 37 yields an *exo* : *endo* rate ratio of 284,[44] not significantly different from the value of 350 exhibited by *exo*-norbornyl 25 itself. Even more remarkable, the *exo* : *endo* rate ratio of the related 2-*p*-anisyl-2-camphenilyl *p*-nitrobenzoate 38 is 44,000![45]

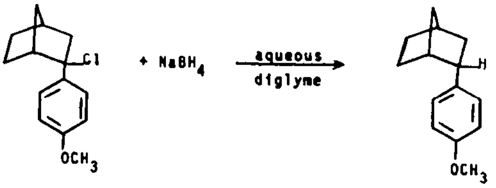
As will be discussed later, the increase in the *exo* : *endo* rate ratio from 284 for 37 to 44,000 for 38 arises not because of any significant change in the rates of solvolysis of the *exo* isomers, but results from a marked decrease in the rate of the *endo* isomer corresponding to 38.

The capture of the 2-*p*-anisyl-2-norbornyl cationic intermediate by sodiumborohydride yields essentially pure



	25	37	38
exo *endo*	350	284	44,000

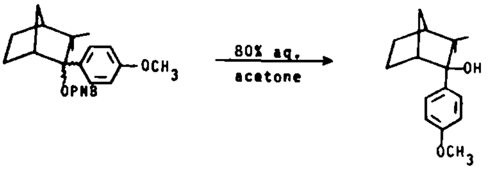
endo-*p*-anisylnorbornane, involving capture of hydride from the *exo* direction (13).



(13)

≥98%

Similarly, the solvolysis of 2-*p*-anisyl-*exo*- and -*endo*-camphenilyl *p*-nitrobenzoates give the *exo* alcohol essentially exclusively (14).



(14)

≥99·5%

Consequently, even these highly stabilized 2-norbornyl derivatives exhibit the high *exo* : *endo* rate and product ratios previously considered to represent a major argument favoring the σ-bridged formulation. If we accept both the theoretical and the experimental evidence that highly stabilized cations, such as 2-phenyl- and 2-*p*-anisyl-2-norbornyl, cannot involve σ-bridging, it follows that high *exo* : *endo* rate and product ratios are not evidence for such σ-bridging. More logically, there must be some feature characteristic of the norbornyl structure other than σ-bridging that is responsible for the observed high *exo* : *endo* rate and product ratios.

FREE ENERGY DIAGRAMS FOR THE 2-*p*-ANISYL DERIVATIVES

The free energy of activation for the solvolysis of 2-*p*-anisyl-*exo*-norbornyl *p*-nitrobenzoate in 80% aqueous acetone is 20·1 kcal mol^{-1}.[44] The corresponding value for the *endo*-isomer is 23·4 kcal mol^{-1}. Both isomers yield the same intermediate, the 2-*p*-anisyl-2-norbornyl cation. Equilibration of the two epimeric alcohols in the case of the phenyl derivatives established that they are of comparable stabilities, with the ground state of the *endo* derivative being higher in energy by a relatively small factor of 0·4 kcal mol^{-1}.[46] Finally, the available evidence indicates that there is no significant difference in the steric requirements of the acyloxy and hydroxyl groups in the norbornyl system.[46]

With these approximations in mind, it is possible to construct a free-energy diagram[47] for the solvolysis of this *exo* : *endo* pair (Fig. 6). This diagram reveals a difference in energy of the two transition states of 3·7 kcal mol^{-1}.

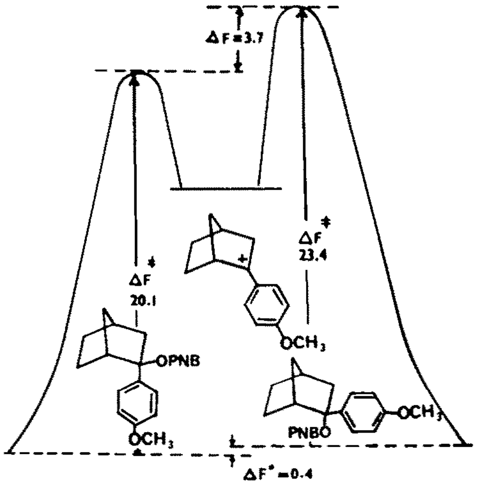


Fig. 6. Free energy diagram for the solvolysis of 2-*p*-anisyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

It is clear that the cation once formed will react with the anion (or the solvent) to pass over the same (or similar) transition states, to give the two epimeric derivatives in a ratio determined by the difference in energy in the respective transition states. The reaction will evidently proceed in the case of both isomers to give the *exo* derivative predominantly.

The problem is that of accounting for the major difference in the energies of the two transition states. Is the *endo* transition state normal, with the *exo* transition state stabilized by some factor, or is the *exo* transition state normal with the *endo* transition state destabilized by some factor?

In the case of the parent system, 2-norbornyl itself, it has been customary to argue that the *exo* transition state must be stabilized by σ-bridging over the corresponding *endo* transition state. However, this explanation cannot be utilized for the 2-*p*-anisyl derivative. There appears to be considerable experimental evidence and general agreement that a cationic center highly stabilized by a 2-*p*-anisyl group cannot engage in such σ-bridging.

This leaves us with the possibility that the *exo* transition state must be considered normal, with the *endo* transition state destabilized by some factor. Steric hindrance to ionization has been suggested as that factor and will be discussed later.[48]

In the case of 2-*p*-anisyl-*exo*-camphenilyl *p*-nitrobenzoate, the free energy of activation is the same, 20·1 kcal mol^{-1}, as for the corresponding 2-norbornyl derivative.[45] However, the free energy of activation for the *endo* isomer is 26·4 kcal mol^{-1}, considerably larger than the value for the corresponding 2-norbornyl derivative. Consequently, the major increase in the *exo* : *endo* rate ratio observed for the 2-*p*-anisylcamphenilyl derivatives (44,000), as compared with the 2-*p*-anisylnorbornyl derivatives (284), comes about primarily because of a major decrease in the rate of solvolysis of the *endo* isomer of the camphenilyl system. As will be discussed later, this decrease in rate is readily accounted for in terms of an additional hindrance by the *endo*-3-methyl substituent to the ionization and departure of the *endo* leaving group.

Construction of the free energy diagram (Fig. 7) reveals a difference in the energies of the two transition states of 5·2 kcal mol^{-1}, considerably larger than in the related 2-*p*-anisyl-2-norbornyl system (Fig. 6). It follows that the partition of the cationic intermediate between *exo* and *endo* product should be more stereoselective for *exo* in the case of the camphenilyl derivative than in the case of the corresponding norbornyl derivative (Figs. 6 and 7).

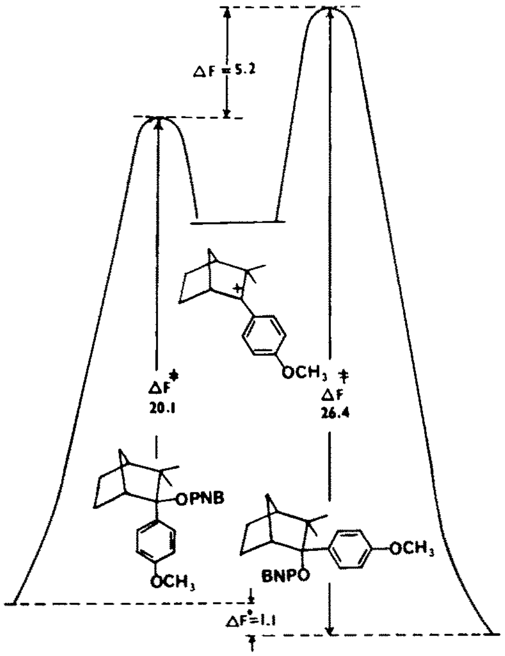


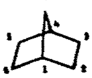
Fig. 7. Free energy diagram for the solvolysis of 2-*p*-anisylcamphenilyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

STERIC CHARACTERISTICS OF THE NORBORNYL SYSTEM

At the time the high *exo* : *endo* rate ratio of 350 for 2-norbornyl brosylate was observed,[2] little was known about the remarkable steric characteristics of the norbornane structure. Consequently, it was not unreasonable to conclude that this high rate ratio was a unique phenomenon requiring a unique explanation, σ-bridging.

With the years, considerable additional data have become available bearing on the stereochemistry of reactions involving the norbornane structure. It has become evident that all reactions of norbornane exhibit a marked preference for reaction from the *exo* direction over reaction from the *endo* direction. The precise preference can vary considerably with the particular reaction utilized, but there appears to be no exception to the rule of preferential *exo* attack.

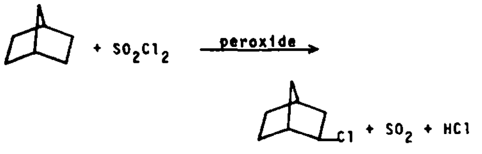
The origin of this preference for *exo* reaction appears to lie in the rigid U-shaped structure of the norbornane system **39**.



39

Carbon atoms 1–6 constitute a cyclohexane structure in the higher energy boat conformation. Moreover, the 7-methylene group not only locks this ring system into a rigid boat conformation, but the constraint so produced accentuates the steric crowding within the *endo* moiety of the boat structure (Fig. 8).

For example, free radical chlorination of norbornane with sulfuryl chloride yields 95% *exo* chloride[49] (15).



(15)

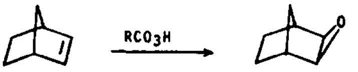
95% *exo*

Similarly, hydroboration-oxidation of norbornene yields 99·5% *exo* product[50] (16).

(16)

99·5% *exo*

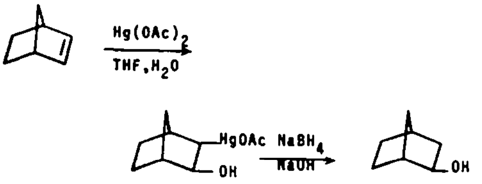
Epoxidation of norbornene gives 99·5% of the *exo* epoxide[51] (17).



(17)

99·5% *exo*

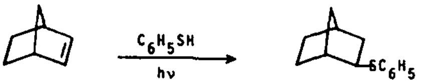
Oxymercuration-demercuration of norbornene gives ≥99·8% *exo* (18).



(18)

≥99·8%

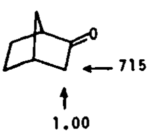
Free radical addition of thiophenol at 0° gives 99·5% *exo*[53] (19).



(19)

99·5% *exo*

Finally, the base-catalyzed deuterium exchange of norcamphor yields an *exo* : *endo* ratio of 715[54] **40**.



40

Therefore, the faster rate of solvolysis of the *exo*-norbornyl derivatives, both secondary and tertiary, and the *exo* stereochemistry of the solvolytic products are not unique, but conform to the same reactivity pattern exhibited by the norbornyl system in varying degree in all of its reactions.

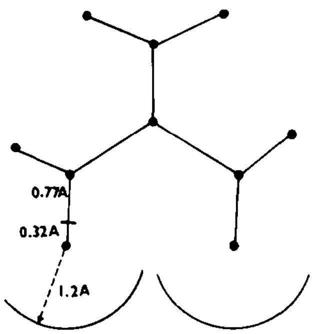
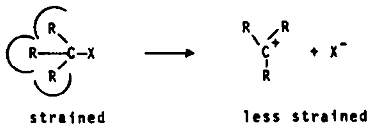


Fig. 8. End-on view of the norbornane molecule.

STERIC HINDRANCE TO IONIZATION

The data reveal that all reactions of the norbornyl system exhibit high *exo* : *endo* ratios. These high ratios are presumably the result of decreased rates of reaction in the sterically hindered *endo* direction of the U-shaped norborane structure (Fig. 8). Consequently, it appeared appropriate to consider the possibility that the high *exo* : *endo* rate ratio in the solvolysis of the tertiary 2-*p*-anisyl-2-norbornyl and the parent secondary 2-norbornyl derivatives may actually be the result of a normal *exo* rate combined with a very slow *endo* rate.

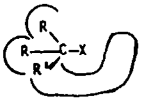
The concept of steric assistance to ionization was introduced in 1946.[36] It was proposed that tertiary derivatives carrying bulky substituents would undergo solvolysis with relief of steric strain and would therefore exhibit enhanced rates (20).



(20)

This concept was explored and has received general acceptance.[49]

The proposal of steric hindrance to ionization[48] has encountered much more resistance. Yet it appears quite reasonable that the structure of the compound undergoing solvolysis may be so shaped that the departure of the leaving group may be hindered, as indicated in **41**.



41

Indeed, *endo*-norbornyl derivatives would appear to possess this feature. Consider the *endo*-norbornyl chloride structure (Fig. 9). In the ionization process the chlorine substituent would be expected to move along a curved path away from the carbon atom at the 2-position, maintaining the chlorine substituent perpendicular to the face of the developing carbonium ion so as to retain maximum overlap of the orbitals undergoing separation. In this way the system should pass through the transition state to the first intermediate, the idealized ion-pair shown iin Fig. 10. Clearly there would be major steric overlap of the chlorine substituent with the *endo*-6-hydrogen. Moreover, the group undergoing ionization should be strongly solvated by the medium, yet the U-shaped structure obviously makes difficult such solvation of the developing anion.

An alternative model for ionization has been

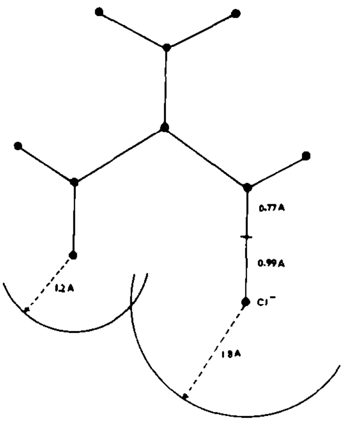


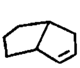
Fig. 9. End-on view of the *endo*-norbornyl chloride molecule.

suggested.[55] In this model the departing group would move initially along the direction of the C–X bond leading to the first intermediate, the idealized intimate ion-pair shown in Fig. 10. This path does not avoid the steric difficulty, although in this model it is largely transferred to the hydrogen atom or other group at the 2-position.

The large steric interactions of both models will presumably cause some other path, providing decreased steric interactions at the cost of poorer overlap, to be selected as a compromise. Such a compromise would still result in an increase in the energy of the transition state as compared to that for a derivative without this structural feature.

STERIC EFFECTS IN U-SHAPED SYSTEMS

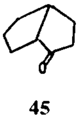
The idea that it was the rigid U-shaped structure of the norbornane skeleton that was responsible for the marked *exo* preference, both in representative non-carbonium reactions and in solvolysis, was subjected to experimental test. We selected three representative bicyclic systems of increasing U-shaped character (21), *cis*-bicyclo[3.3.0] octane > norbornane > *endo*-5,6-trimethylenenorbornane, and examined representative reactions of the olefins **42, 43, 44**, as well as of the related ketones **45, 46, 47**.[56]



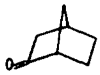
42

43

44



45



46

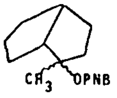
47

(21)

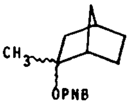
These results are summarized in Table 2.

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 **42**, **45** exhibits the least preference for *exo* attack presumably because of its higher flexibility and relatively less inaccessible *endo* face, whereas the *endo*-5,6-trimethylenenorbornane system exhibits the highest stereoselectivity of the three systems examined. Indeed, an examination of a molecular model reveals that in this rigid U-shaped structure the *endo* face is highly hindered to the approach of reagents. In all cases, the stereoselectivities indicated by the norbornane system are intermediate.

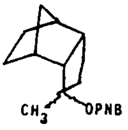
The corresponding tertiary methyl *p*-nitrobenzoates **48**, **49**, **50** were then synthesized and the rates of solvolysis in 80% aqueous acetone determined.



48



49



50

The tertiary ester from the bicyclo[3.3.0]octane system **48** reveals an *exo* : *endo* rate ratio of 17. The norbornyl system reveals an *exo* : *endo* rate ratio of 885. Finally, the *endo*-5,6-trimethylenenorbornane **50** reveals an *exo* : *endo* rate ratio of 4300.

The corresponding tertiary phenyl derivatives exhibit the same pattern of reactivity.[57] It is of interest to note the similarity in the free energy diagram for the solvolysis of the 8-phenyl-*endo*-5,6-trimethylene-8-norbornyl *p*-nitrobenzoates (Fig. 11) with that for the 2-arylnorbornyl derivatives (Fig. 6).

These results establish the existence of an excellent correlation within these three systems as to the stereoselectivities they show toward the various representative reagents and the stereoselectivities they reveal in the solvolysis of the related tertiary esters. This common pattern of reactivity for the carbonium ion and non-carbonium ion reactions supports the position we have

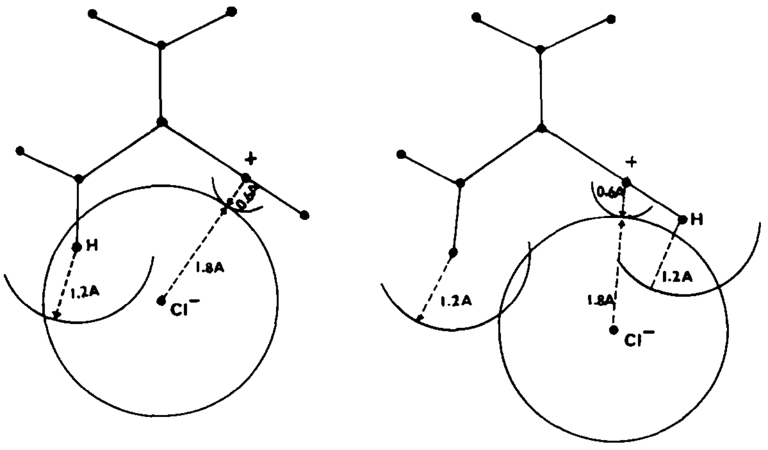
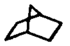


Fig. 10. Molecular models for the hypothetical intimate ion-pairs from the two postulated reaction paths.

Table 2. Comparison of the relative stereoselectivities exhibited by three representative U-shaped systems

Reaction	Exo:endo ratios for the U-shaped systems  42, 45, 48	 43, 46, 49	 44, 47, 50
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	3	8.1	> 1000
Addition of CH_3MgX to ketone	50	200	> 1000
Oxymercuration of methylene derivatives	8.1	200	> 1000
Solvolysis of tertiary 2-methyl p-nitrobenzoates	17	885	4300
Solvolysis of tertiary 2-phenyl p-nitrobenzoates	10	143	11,000

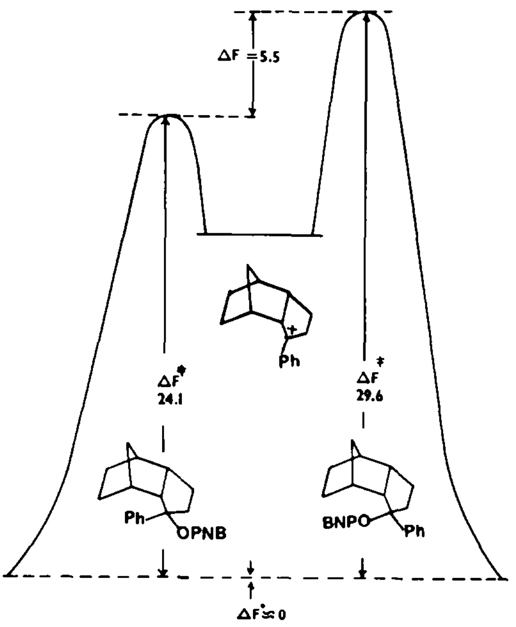


Fig. 11. Free energy diagram for the solvolysis of the 8-phenyl-*endo*-5,6-trimethylene-8-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

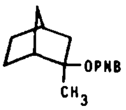
been led to: the *exo*:*endo* rate and product ratios in norbornyl must be largely, if not entirely, steric in origin.

EXO:*ENDO* RATE AND PRODUCT RATIOS AS A STERIC PHENOMENON

The data presented lead to the conclusion that in the tertiary norbornyl derivatives we have examined the *exo* : *endo* rate ratio must be predominantly the result of steric forces. If this interpretation is valid, we should be able to introduce substituents into the *exo* face or the *endo* face of the norbornyl system and vary both the steric environment and the *exo* : *endo* rate and product ratios in a consistent predictable manner.[58,59]

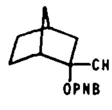
For example, the *exo* : *endo* rate ratio in the solvolysis of the 2-methyl-2-norbornyl *p*-nitrobenzoates **51**, **52** in 80% aqueous acetone is 885.[59]

51



885

52



1·00

The steric requirements of the methyl and *p*-nitrobenzoate groups are very similar.[46] Consequently, the ground state energies for the *exo* **51** and *endo* **52** isomers are almost the same (Fig. 12). The high *exo* : *endo* rate ratio is then ascribed to the fact that the *exo* face is more open sterically than the *endo* face. The greater

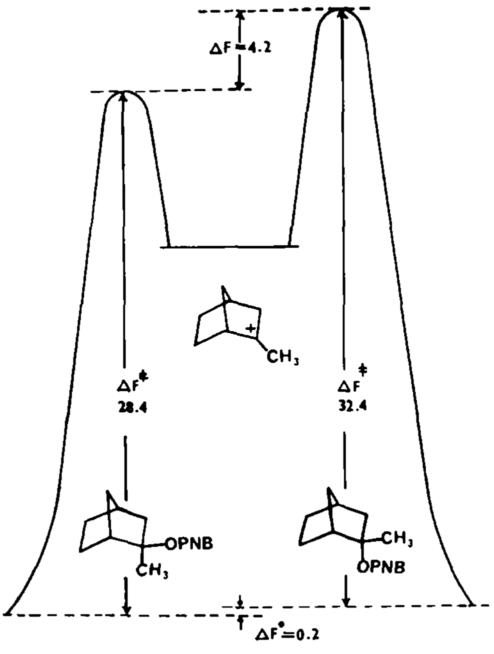


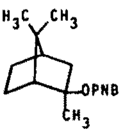
Fig. 12. Free energy diagram for the solvolysis of 2-methyl-2-nrobornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

steric availability of the *exo* face facilitates solvation of the incipient anion and its more ready ionization to the ion-pair as compared to the more crowded steric environment of the *endo* face.

On this basis, an increase in the steric requirements of the *exo* face, while maintaining constant those of the *endo* face, should result in a major decrease in the *exo* : *endo* rate ratio. Contrariwise, maintaining the steric requirements of the *exo* face constant while increasing those of the *endo* face should bring about a significant increase in the *exo* : *endo* rate ratio.

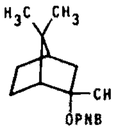
Indeed, we observed that the presence of *gem*-dimethyls in the 7-position decreases the *exo* : *endo* rate ratio from the 885 value observed in the parent compounds **51**, **52** to a value of 6·1 in **53**, **54**.[58]

53



6·1

54



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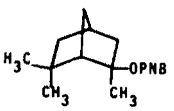
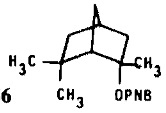
On the other hand, the presence of *gem*-dimethyls in the 6-position (**55**, **56**) increases the *exo* : *endo* rate ratio to 3,630,000[59]

55



3,630,000

56



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Thus the *exo* : *endo* rate ratio changes by a factor of 600,000 merely through a shift of the methyl substituents from the 7- to the 6-position—a truly remarkable effect. As discussed earlier, a similar increase in the *exo* : *endo* rate ratio occurs in 2-*p*-anisyl-2-norbornyl with the introduction of methyl substituents in the 3-position.[45]

The free energy diagrams for the two trimethylnorbornyl systems are given in Figs. 13 and 14.

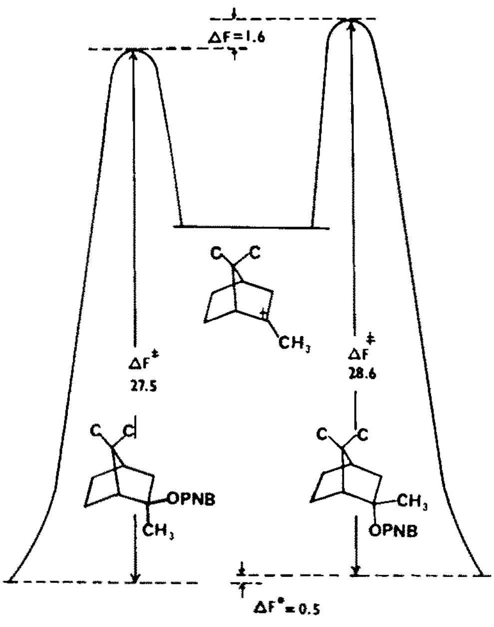


Fig. 13. Free energy diagram for the solvolysis of 2,7,7-trimethyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

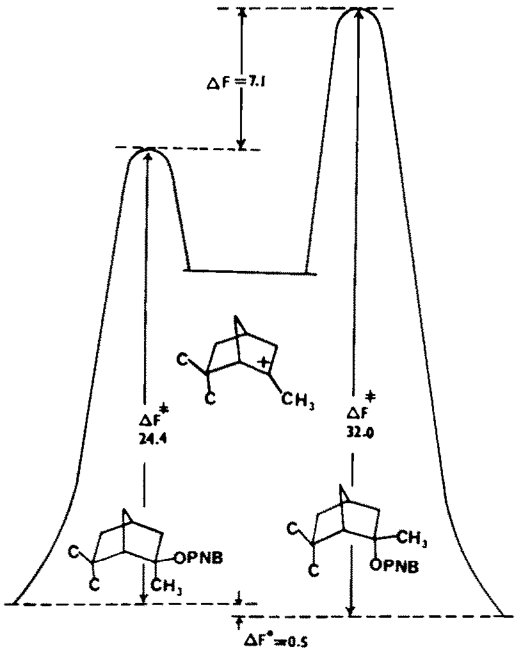


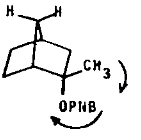
Fig. 14. Free energy diagram for the solvolysis of 2,6,6-trimethyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

A comparison of the three diagrams, Figs. 12–14, is instructive. The difference in the energies of the two transition states in the three systems changes from 1·6 to 4·2 to 7·1 kcal mol^{-1}. Thus the ions produced in the solvolysis of each epimeric pair will distribute themselves to product in a ratio determined by this quantity. The products from the solvolysis of these compounds correspond to those predicted from the free-energy diagrams. Thus the alcohol product from **55** is exclusively (≥99·9%) *exo*-, whereas that from **53** contains ~10% *endo*-.

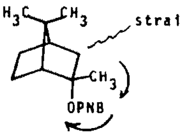
An examination of the actual rate constants is instructive (Table 3).

It should be noted that the rate constant for 2-methyl-*exo*-norbornyl is modestly greater than that for 1-methylcyclopentyl. However, the *endo*-isomer is much slower. This is consistent with the proposed interpretation in terms of steric hindrance to ionization.

The low *exo* : *endo* rate ratio in the 2,7,7-trimethylnorbornyl system arises from a small increase in the rate of the *exo* isomer (4) and a large increase in the rate of the *endo* isomer (580). Obviously, this marked increase is readily accounted for in terms of relief of steric strain accompanying rotation of the 2-methyl substituent away from the *gem*-dimethyl group during the ionization process **57**, **58**.



57

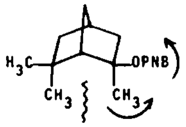


58

The very fast rate of 2,6,6-trimethyl-*exo*-norbornyl *p*-nitrobenzoate (726 greater than that of the parent compound) is again attributed to relief of steric strain **59**, **60**.

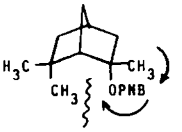
Table 3. Rates of solvolysis of 2,7,7-trimethyl-2-norbornyl and 2,6,6-trimethyl-2-norbornyl *p*-nitrobenzoates and related derivatives in 80% aqueous acetone at 25°

p-Nitrobenzoate	10^6k sec^{-1}	Relative rate
1-Methylcyclopentyl	2.11×10^{-3}	1.00
2-Methyl-*exo*-norbornyl	1.00×10^{-2}	4.74
2-Methyl-*endo*-norbornyl	1.13×10^{-5}	0.00536
2,7,7-Trimethyl-*exo*-norbornyl	4.01×10^{-2}	19.0
2,7,7-Trimethyl-*endo*-norbornyl	6.54×10^{-3}	3.1
2,6,6-Trimethyl-*exo*-norbornyl	7.26	3440
2,6,6-Trimethyl-*endo*-norbornyl	2.00×10^{-6}	0.000948



strain

59



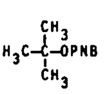
strain

60

As was pointed out earlier, the steric requirements of a methyl and *p*-nitrobenzoate group are quite similar.[46] Consequently, **60** should be just as strained as **59**. Yet **60** reacts not faster, but slower than the much less strained parent compound **57**. This is readily accounted for on the basis that the natrual reaction path for ionization of the *p*-nitrobenzoate group does not allow for relief of steric strain.

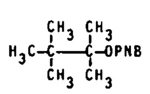
We have proposed that steric effects in rigid bicyclic systems should be much more important than in flexible aliphatic or alicyclic systems. This proposal was tested by comparing the relative effects of a t-butyl group versus a methyl group on the rates of solvolysis in acyclic, alicyclic, and bicyclic systems.[60a]

It was observed that the rate of solvolysis in 80% aqueous acetone of t-butyldimethylcarbinyl *p*-nitrobenzoate **62** is faster than that of t-butyl *p*-nitrobenzoate **61** by a factor of 4·4.



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OPNB$

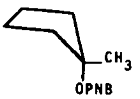
61
1·00



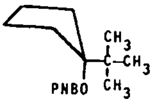
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-OPNB$

62
4·36

In representative alicyclic systems **63**, **64**, the factor is considerably larger, in the neighborhood of 100.

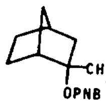


63
1·00

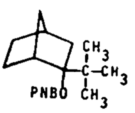


64
112

In the more rigid norbornyl system, **65**, **66**, the observed rate enhancement is 39,600.

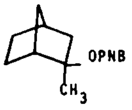


65
1·00

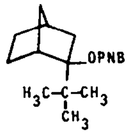


66
39,600

The factor is almost as large for the *exo* isomers[60b] **67**, **68**.



67
1·00



68
21,000

In spite of these large changes in the individual rates, the *exo* : *endo* rate ratio is 470, not greatly different from the 885 value observed for **67**:**65**. However, the introduction of the t-butyl group does have a large effect on the relative ground state energies of the *exo* and *endo* isomers. This results in a free energy diagram (Fig. 15) which reveals a relatively small difference, 1·7 kcal mol^{-1}, in the energies of the two transition states. This difference predicts an *exo* : *endo* product ratio of 17·6; a value of 19 was observed.

As a result of these many studies, it has become apparent that the behavior of such tertiary norbornyl derivatives can be fully understood in terms of the effect of steric interactions, without the need to postulate σ-bridging. The question remaining is whether the

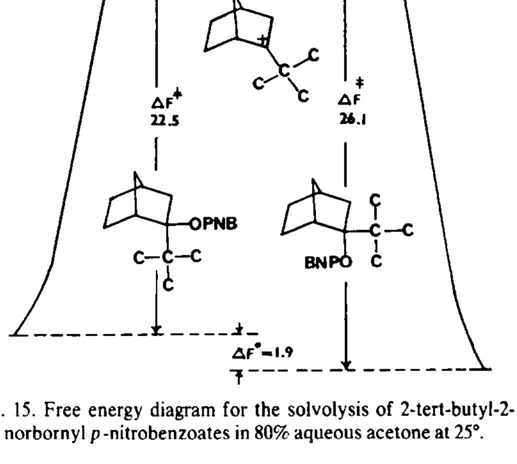


Fig. 15. Free energy diagram for the solvolysis of 2-tert-butyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

secondary norbornyl system can be similarly interpreted, or do we need to include the σ-bridging factor.

THE SECONDARY 2-NORBORNYL SYSTEM

In 1965 Goering and Schewene introduced a means of looking at the norbornyl system that is especially helpful in visualizing the relationship between the *exo* : *endo* rate ratio and the *exo* : *endo* product ratio.[47] We have utilized such free energy diagrams in this review for the various tertiary 2-norbornyl systems that have been discussed. Let us examine the corresponding diagram for the secondary system.

The rate of acetolysis of *exo*-norbornyl brosylate is 350 times that for the corresponding *endo*-derivative.[2] If the data are corrected for internal return in the *exo*-isomer, then the *exo* : *endo* rate ratio becomes 1600. The relative rate of 1600 corresponds to a difference in the free energy of activation of 4·5 kcal mol^{-1}. The strain in *endo*-norbornyl arenesulfonates is estimated to be 1·3 kcal mol^{-1}.[61] This leads to a difference in the energies of the two transition states of 5·8 kcal mol^{-1} (Fig. 16).

The problem is clearly that of defining what factor or factors are responsible for the difference in energies of the two transition states. Is the transition state for the *exo* isomer stabilized by σ-participation, or is the *endo* transition state destabilized by steric hindrance to ionization? Once ionization occurs, the ion or ion-pair will be in the central well. Recombination will obviously occur much more readily to produce the *exo* ester as compared to the *endo* ester.

What we would like to know is not the relative rates at which the cationic intermediate reacts with the anion to reform the original esters, but the relative rates at which the intermediate captures the solvent acetic acid to form the two products, *exo*- and *endo*-norbornyl acetate. Fortunately, the data are available. Goering and Schewene[47] measured the rates of racemization, the rates of exchange, and the equilibration of *exo*- and *endo*-norbornyl acetate. The results of their study are shown in the free energy diagram (Fig. 17).

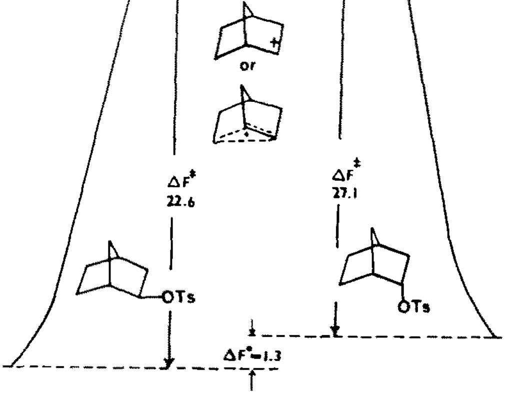


Fig. 16. Free energy diagram for the acetolysis of *exo*- and *endo*-norbornyl tosylate.

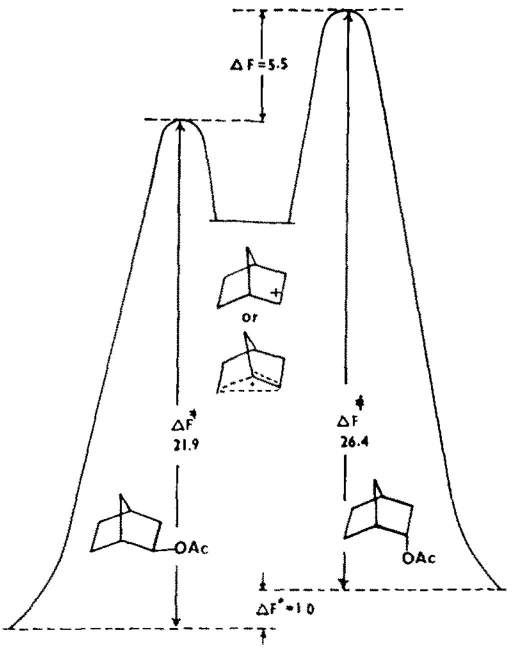


Fig. 17. Free energy diagram for the acetolysis of *exo*- and *endo*-norbornyl acetate.

We are now in a position to consider what happens to the cationic intermediate in reacting with acetic acid solvent to form the two acetates.

The energy of activation of the ionization of the *endo* acetate is 4·5 kcal mol^{-1} higher than for the *exo*. If we correct for the higher ground-state energy of the *endo* isomer, 1·0 kcal mol^{-1}, the difference in the energies of the two transition states becomes 5·5 kcal mol^{-1}.

The two reactants pass over these two transition states to form the same intermediate, the norbornyl cation (or ion-pair). The principle of microscopic reversibility requires that in the symmetrical system (the subject of this discussion) the norbornyl intermediate, in reacting with the solvent, must pass over the same two transition states that are involved in the solvolysis of the reactants. The authors establish that the product from the solvolysis of norbornyl brosylate consists of 99·98% *exo*- and 0·02% *endo*-norbornyl acetate. This is in reasonable agreement with the distribution predicted for a difference of 5·5 kcal mol^{-1} in the energies of the two transition states.

It follows that the factor responsible for the difference in energy between the transition states for the *exo*- and *endo*-isomers must be largely responsible for the difference in the *exo*- and *endo*- rates of solvolysis. (The difference in ground-state energies also contributes, but this difference is relatively small in the present cases compared to the much larger difference in the energies of the transition states.) It also follows that the factor responsible for the difference in energy between the *exo* and *endo* transition states 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 has been considered to require bridging in the norbornyl cation.[2,47] 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 between* exo *and* endo *product.*

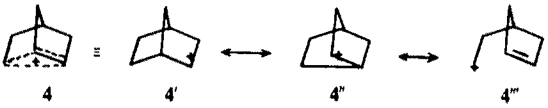
It is instructive to compare the diagrams for 2-anisylcamphenilyl (Fig. 7) with that for norbornyl (Fig. 17). The similarity is evident. Yet σ-bridging cannot be involved in the difference in energies of the two transition states in Fig. 7. Consequently, it is reasonable to consider the possibility that the difference in energy of the two transition states in Fig. 17 may be due to some factor other than σ-participation.

Let us consider what might be the factor or factors responsible for the difference in energy between the *exo* and *endo* transition states for the secondary system. Four possibilities may be pointed out: (1) the *exo* transition state is stabilized by σ-participation, with the endo being normal; (2) the *endo* transition state is destabilized by steric strain, with the *exo* transition state being normal; (3) a combination of (1) and (2); or (4) some new factor, such as torsional effects,[62] not now considered by current theory.

We have already established that steric hindrance to ionization must be the dominant factor in the *exo* : *endo* rate and product ratios in the tertiary 2-norbornyl systems. The similarity in the two diagrams, Fig. 7 and Fig. 17, would normally be considered to involve similar physical foundations. However, let us give serious consideration to the proposal that these similar behavior patterns possess different origins, with the transition state for the tertiary *endo*-norbornyl derivatives being destabilized by steric strain and that for the secondary *exo*-norbornyl derivative being stabilized by σ-bridging.[8]

SUBSTITUENT EFFECTS IN THE SEARCH FOR σ-PARTICIPATION

The nonclassical 2-norbornyl cation was originally formulated as a resonance hybrid of three canonical structures (22).

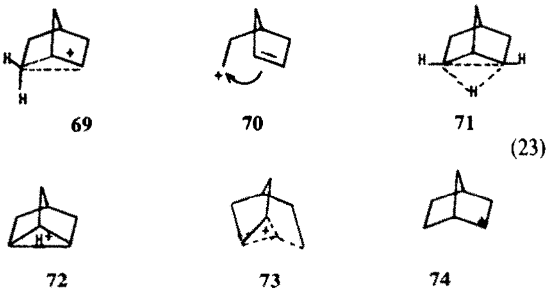


4 4′ 4″ 4‴

(22)

On this basis, charge should be delocalized from the 2- to the 1- and 6-positions.

More recently, numerous other structures have been proposed (23).



69 70 71

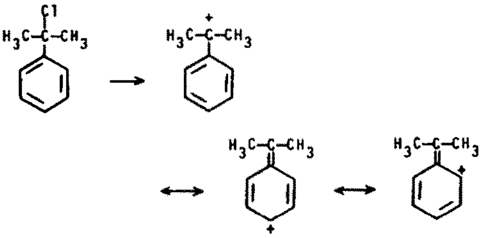
(23)

72 73 74

Thus, Dewar favored a structure based on his π-complex concept **70**.[63] Klopman's calculation favored the edge-protonated species **71** over the face protonated species **72**.[64] Olah, however, has favored a formulation as a corner-protonated nortricylene **69**,[65] deleting the dashed double bond of Winstein **4**.[2] More recently, he has favored still another formulation **73**.[66] Finally, Traylor has supported a formulation of the 2-norbornyl cation as involving vertical stabilization by the C1–C6 bonding pair but without σ-bridging or movement of the atoms. In other words, the structure **74** would be that of the classical ion **3** but stabilized by an electronic contribution that does not alter the geometry.[67]

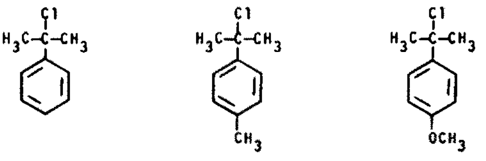
Irrespective of which formulation is preferred, it is common to all that charge is delocalized from the 2- to the 1- and 6-positions. If the lower energy of the *exo* transition state is the result of the fact that the stabilized σ-bridged norbornyl cation is partially formed in that transition state, it should be possible to obtain evidence for such charge delocalization by using the classical reliable tool of the organic chemist, the effect of substituents in appropriate positions.

For example, the fast rate of solvolysis of t-cumyl chloride as compared to t-butyl chloride (11) is attributed to stabilization of the incipient cation in the transition state through charge delocalization into the aromatic ring (24). (For simplicity, the fully formed cation is shown.)



(24)

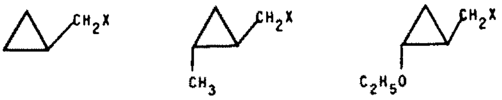
Introduction of electron supplying substituents into the *meta* position has relatively little effect on the rate.[29,68,69] However, the introduction of such electron supplying substituents into the *para* position of t-cumyl chloride results in major increases in rate (25).



(25)

1·00 26 3360

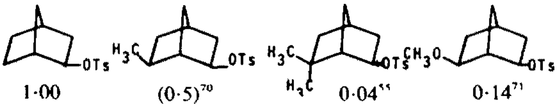
Similarly, the fast rate of solvolysis of cyclopropylcarbinyl derivatives is attributed to the ability of the cyclopropyl ring to delocalize charge from the carbonium ion center. In support of this interpretation, the introduction of the methyl or the ethoxy substituent results in large rate increases (26).[26]



(26)

1·00 11·0 940

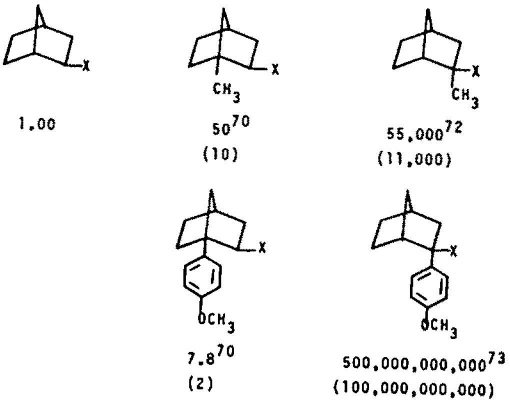
If charge were similarly delocalized in the transition state to the 6-position of the norbornyl system, then the introduction of methyl and methoxyl groups into that position should result in similar rate increases. However, such rate increases are not observed (27).



(27)

The introduction of a methyl group into the central carbon atom of benzhydryl chloride has a much smaller effect on the rate of hydrolysis than the analogous introduction of a methyl group into isopropyl chloride to form t-butyl chloride. This is attributed to a "leveling effect". The stabilized benzhydryl cation makes a much smaller demand upon the new methyl substituent for additional stabilization than does the relatively hungry less stabilized isopropyl cation.[72] Consequently, if the 2-norbornyl cation is really a resonance-stabilized species, the effect of substituents in the 2-position should be greatly decreased over their effect in a typical aliphatic or alicyclic system. However, very similar effects are observed (Table 4).[72,73]

There is a difficulty in introducing substituents into the 1-position as a test for charge delocalization to that position. 2-Norbornyl derivatives containing alkyl or aryl substituents in the 1-position solvolyze with rearrangement to tertiary norbornyl cations. This should provide a driving force which should enhance the effect of the 1-substituent. Nevertheless, the data reveal major differences in the effects of substituents in the 1- and 2-positions (28).



(28)

Since the 1- and 2-substituted derivatives doubtless undergo solvolysis without internal return, the observed rates should be compared with 2-norbornyl corrected for internal return. This correction, if valid, reduces the effect of the substituents by a factor of approx. 5, as shown by the values in the parentheses.

Finally, it has been suggested that "there are good reasons to expect carbon bridging to lag behind C–X ionization at the transition state".[74] However, if σ-bridging in the transition state is responsible for the 5·5 kcal mol^{-1} difference in energy of the two transition states (Fig. 17), as proponents of the nonclassical norbornyl cation have long argued,[47] it is difficult to understand how one can achieve stabilization of that magnitude in the transition state while arguing that carbon bridging largely follows ionization. As has been pointed out, the free energy diagram (Fig. 17) makes it clear that the amount of carbon bridging in the free ion has nothing to do either with the *exo* : *endo* rate ratio or the *exo* : *endo* product ratio. It is the amount of bridging in the *exo* transition state, or whatever the factor responsible for the difference in energy of the two transition states, that is the controlling factor.

THEORETICAL AND EMPIRICAL APPROACHES TO THE STABILITY OF THE CATION

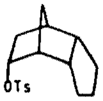
Another possible approach to resolve the problem would be by a theoretical calculation of the energies of the two transition states in Fig. 17. However, this appears to be beyond us at the present time. Even the apparently simpler problem of calculating the relative energies of the unsolvated classical and σ-bridged 2-norbornyl cation has proven difficult to achieve. Thus Klopman calculated that the σ-bridged structure was more stable than the classical structure by some 40 kcal mol^{-1}.[64] On the other hand, Allen reports that a more rigorous *ab initio* calculation favors the classical structure by some 5 kcal mol^{-1}.[75]

At one time the Foote-Schleyer correlation appeared to offer hope of solving the problem.[61] This empirical correlation provides a means of calculating the rates of acetolysis of secondary tosylates. Clearly, if the treatment could be relied upon to reveal that the *endo* isomer is normal, whereas the *exo* isomer is 350 times more reactive than the calculated value, the problem could be considered solved. Indeed, the initial application of the correlation appeared to point to that conclusion.[61]

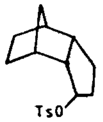
Study of the correlation indicated that a possible difficulty lay in the treatment of steric hindrance to ionization. In principle, the non-bonded strain term ($GS_{strain} - TS_{strain}$) in the correlation should be capable of handling steric hindrance to ionization ($GS_{strain} < TS_{strain}$) as well as steric assistance to ionization ($GS_{strain} > TS_{strain}$). However, in practice the expediency had been adopted of assuming $TS_{strain} \approx 0$ for leaving groups.

Accordingly, a joint program was undertaken with Schleyer to test the ability of the correlation to predict the rates of certain *endo*-norbornyl derivatives where the steric hindrance to ionization might be expected to be relatively large in terms of the considerations presented earlier **75**, **76**, **77**.

75



76

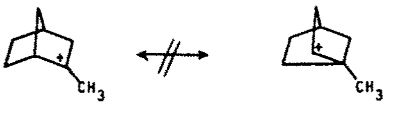


77

The discrepancies between the predicted and the observed rates were 8000 for **75**, 10,000 for **76**, and 100,000 for **77**. It was concluded that the correlation in its present state of development could not be relied upon to provide a definitive answer to the nonclassical ion problem.[76]

SYMMETRICALLY SUBSTITUTED 1,2-NORBORNYL DERIVATIVES

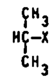
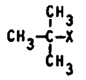
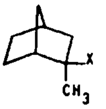
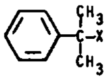
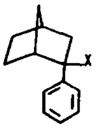
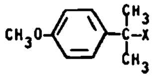
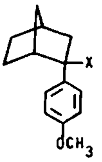
The large difference in stability between secondary **79** and tertiary **78** cations would appear to preclude resonance between canonical structures differing so much in energy (29).



78 **79**

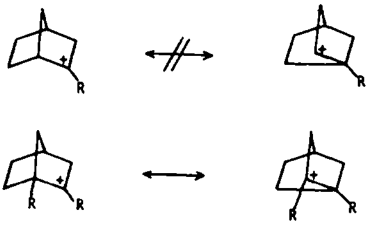
(29)

Table 4. Effect of substituents on the rates of solvolysis

Acyclic derivative	Rel. rate	2-Norbornyl derivative	Rel. rate
 $\underset{CH_3}{\overset{CH_3}{HC}}{-}X$	1.00		1.00
 $CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}X$	55,000		55,000
	(x 4,600) 2.6 x 10^8		(x 5,300) 2.9 x 10^8
	(x 3,400) 8.5 x 10^{11}		(x 1,700) 5.0 x 10^{11}

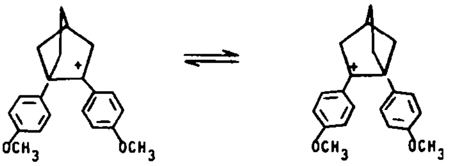
Consequently, it was suggested that a tertiary norbornyl cation, such as 2-methylnorbornyl, should be essentially classical in nature.[77] The same argument would predict classical structures for the 2-phenyl and 2-*p*-anisylnorbornyl cations.

By introducing an identical substituent in the 1-position, we again introduce the possibility for resonance between identical structures (30), such as is postulated in the nonclassical formulation of the 2-norbornyl cation (22).



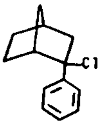
(30)

The 1,2-di-*p*-anisylnorbornyl cation was subjected to intensive study by Schleyer *et al.*[78] They concluded that their thermochemical, chemical reactivity, UV and NMR spectral data support the existence of the ion as a rapidly equilibrating pair, rather than as a resonance hybrid (31).

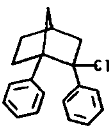


(31)

Similarly, a phenyl substituent in the 1-position **81** retards, rather than enhances, the rate of solvolysis of 2-phenylnorbornyl chloride **80**.[79]



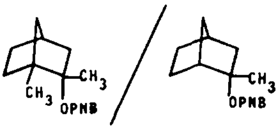
80
1·00



81
1/16

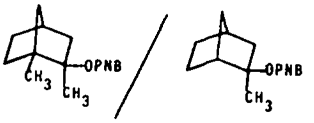
NMR examination of the 1,2-diphenylnorbornyl cation under stable ion conditions reveals it to be a rapidly equilibrating pair even at low temperatures (Table 1).

A possible difficulty with these systems is the argument that it may be impossible, for steric reasons, to place both aryl groups into the orientation required to permit them to participate in resonance stabilization of the ion. This difficulty does not arise in the 1,2-dimethylnorbornyl derivatives.[80,81] Here the introduction of a methyl group in the 1-position increases the rate of solvolysis in 80% aqueous acetone[82] over that shown by the parent system by a factor of 8·6 (32).



= 8.6 (32)

The question is as to the effect of a 1-methyl substituent in the *exo* isomer. If the 1-methyl group were to cause resonance to return, its effect should be far greater. However, the effect is the same[82] (33).



= 8.5 (33)

In spite of the failure to detect any resonance in the system, 1,2-dimethyl-2-norbornyl *p*-nitrobenzoate exhibits an *exo* : *endo* rate ratio at 25° of 564 (875 corrected for internal return[83]). The product is ≥99·7% *exo*, ≤0·3% *endo*.[81] The system provides a free energy diagram (Fig. 18) that is also remarkably similar to that for norbornyl (Fig. 17). Again the question arises as to whether the difference in the energy of the two transition states arises from nonclassical stabilization of the *exo*, or from steric destabilization of the *endo*. In this case, it is possible to give an unambiguous answer. The similarity in the substituent effect in the *exo* (33) and *endo* (32) isomers can only mean that there is no significant charge delocalization from the 2- to the 1-position. Without such charge delocalization, it is pointless to attribute the lower

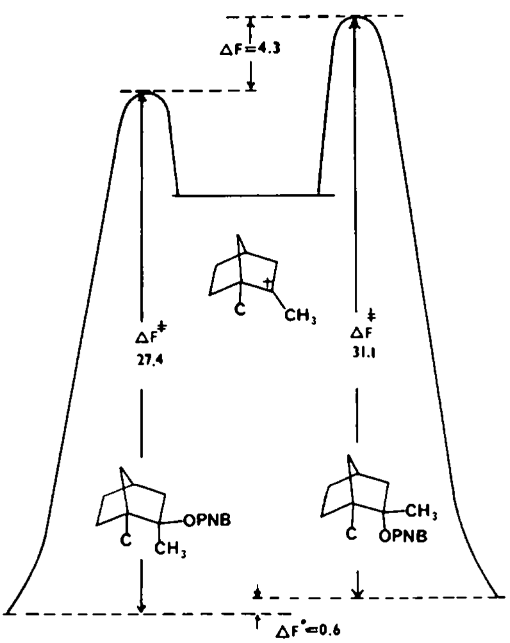
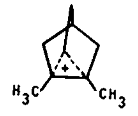


Fig. 18. Free energy diagram for the solvolysis of 1,2-dimethyl-*exo*- and *endo*-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25°.

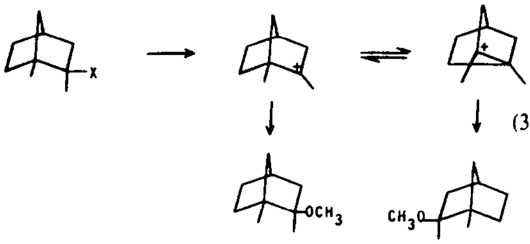
energy of the *exo* transition state to its stabilization by σ-bridging.

In this system it is further possible to establish that the intermediate formed is not the symmetrical σ-bridged nonclassical ion **82**.



82

Solvolysis of optically active 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate in 90% aqueous acetone gives alcohol with 9% retention.[83] Similarly, methanolysis of optically active 1,2-dimethyl-*exo*-norbornyl chloride gives methyl ether with 14% retention.[84] Goering and Clevenger conclude that they are trapping a rapidly equilibrating classical ion or ion pair before it has completely equilibrated[84] (34).



(34)

It is evident from their results that the rate of equilibration of the 1,2-dimethyl-2-norbornyl cation or ion pair must be approx. 10 times the rate of solvent capture. No one has yet described a successful trapping of the unsymmetrical 2-norbornyl cation produced in a solvolytic process. (As will be discussed later, the unsymmetrical 2-norbornyl, produced in other processes, has been trapped on numerous occasions.) Is it reasonable to postulate a rate of equilibration so fast that it frustrates the attempts to trap it in solvolytic reactions?

The solvolysis of optically active 2-norbornyl brosylate produces acetate which is >99·95% racemic.[2] Consequently, the rate of equilibration would need to exceed the rate of collapse of the 2-norbornyl cation by a factor greater than 2000.[74] The rate of ion or ion pair collapse in aqueous acetone is faster than the 6,2-hydrogen shift. The rate constant for the latter process at 25° in NMR solvents[85] was estimated as 10^9 sec^{-1} at 25°. On the assumption that this rate will be the same in acetic acid, the rate of equilibration has been estimated to be in the neighborhood of $\geq 2 \times 10^{12}$ sec^{-1}.[4,74] Bartlett[4] concluded that a rate constant of this order of magnitude "happens to be about the rate of passage of a transition state over the barrier in rate theory". In his view, "any reaction occurring so fast has zero activation energy and the migrating carbon would be at just as low an energy when midway in its migration as at the beginning or end". He concluded that "no such picture of decaying molecular structure results if we attribute the racemization to the direct formation of the bridged ion with planar symmetry, and no absurdly high rate constants are required".

Recently, Fong has applied the principles of the quantum statistical mechanical theory of relaxation to elucidate the general properties of intramolecular rearrangement processes in carbonium ions.[86] As a result of his analysis he concludes that a rate of equilibration of 10^{12} sec^{-1} lies well within the expectation of his analysis. Consequently, he concludes that "when the barrier to intramolecular rearrangement is low (i.e. $Ea \leqslant h\omega$), as indeed appears to be the case in the 2-norbornyl cations, we envision a most elegant mode of quantum shuttling between two "classical" wells, far from Bartlett's vision of a "decaying molecular structure" in which "C-6 flops about randomly" as if "in an untidy box"."

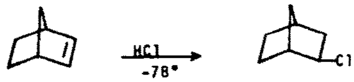
Consequently, even a rate of equilibration as high as 10^{12} sec^{-1} is not incompatible with the Fong treatment. However, there are reasons for believing that this estimate is on the high side. First, the rate of the 6:2 hydrogen shift at 25° in NMR solvents has now been determined to be 10^8 sec^{-1}[87] (not 10^6 sec^{-1}, as given in the publication[87]), a factor of 10 lower than the earlier estimate.[74] Second, there are good reasons to expect that the rate of equilibration of cations, such as are shown in Table 1, should be considerably slower in the usual solvolytic media than in systems used for NMR observations of carbonium ions. Consequently, the original estimate of $\geq 10^{12}$ sec^{-1} should be lowered to $\geq 10^{11}$ sec^{-1}, and may be lowered considerably further by the solvation factor.

An additional factor to consider is the possibility that solvolysis may produce not the free carbonium ion, but a relatively tight ion pair.[88] The reaction of such an ion pair with solvent may be considerably slower than the rate achieved with free carbonium ions. In view of the difficulties in trying to answer such questions from theoretical considerations, we decided to explore other methods of generating 2-norbornyl cations in a freer state in the hope of achieving a successful trapping of the ions in unsymmetrical form before they had fully equilibrated.

ADDITION OF ACIDS TO NORBORNENE AND RELATED OLEFINS

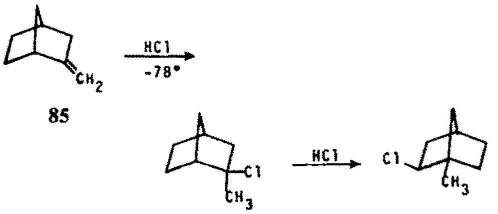
A detailed examination of the addition of hydrogen chloride,[89] trifluoroacetic acid,[90] and acetic acid,[91] with their deuterio analogues, to norbornene and variously substituted norbornene was undertaken.

The addition of hydrogen chloride to norbornene in ethyl ether, methylene chloride or pentane proceeds rapidly at −78° to yield *exo*-norbornyl chloride **84** in an isomeric purity of at least 99·5% (35).



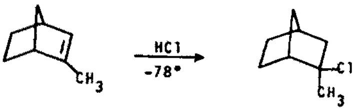
83 **84** ≥99·5% (35)

2-Methylenenorbornane **85** adds hydrogen chloride rapidly to give the tertiary chloride **86** as the initial product. This is rapidly converted to the secondary chloride **87** on further treatment with hydrogen chloride (36).



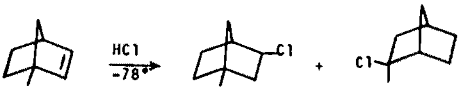
85 **86** **87** (36)

Similarly, 2-methylnorbornene **88** is converted initially into the same tertiary chloride (37).



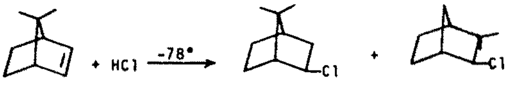
88 (37)

Remarkably, 1-methylnorbornene **89** adds hydrogen chloride to give a mixture of 45% of 4-methyl-*exo*-norbornyl chloride **90** and 55% of the tertiary chloride **86** (38).



89 **90**, 45% **86**, 55% (38)

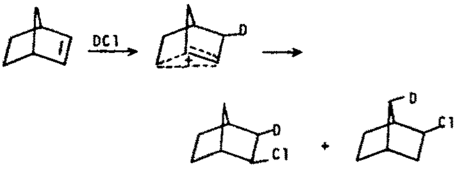
Finally, the addition of hydrogen chloride to 7,7-dimethylnorbornene **91** yields 90% of 7,7-dimethyl-*exo*-norbornyl chloride **92** and 10% of the Wagner-Meerwein shifted product, 3,3-dimethyl-*exo*-norbornyl chloride **93** (39).



91 **92**, 90% **93**, 10% (39)

The strong directive influence leading to the exclusive formation of the tertiary chlorides from **85** and **88** are characteristic of carbonium ion processes. Molecular addition of hydrogen chloride cannot be significant because such an addition would give the two secondary chlorides from **89**. Both secondary chlorides are stable to the reaction conditions. Moreover, molecular addition to **91** would be expected to give the *endo* isomer predominantly.[53]

The critical experiment involves the addition of deuterium chloride to norbornene. A nonclassical ion intermediate requires that the tag be equally distributed between the *exo*-3 **94** and *syn*-7 **95** positions (40).

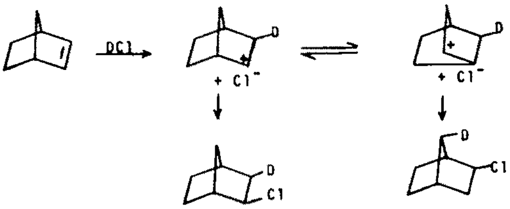


94, X% **95**, X% (40)

hydride shifted products

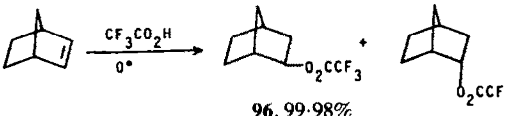
The results of a variety of analyses reveal the formation of 57–61% of *exo*-3*d* **94**, 32 to 41% *syn*-7*d* **95**, with 2–7% of hydride shifted material. Very similar results were realized by Stille and Hughes in the addition of hydrogen chloride to 2,3-dideuterionorbornene.[92]

These results cannot be accounted for in terms of the sole formation of a nonclassical intermediate (40). They are readily accounted for in terms of the formation of a rapidly equilibrating pair of classical cations which are captured short of full equilibration (41).



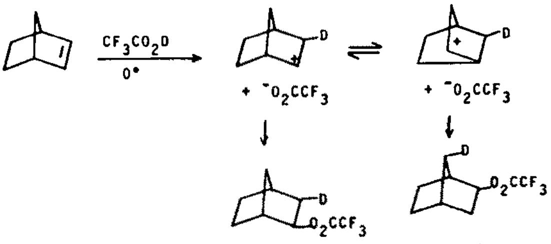
94, 57% **95**, 41% (41)

The addition of trifluoroacetic acid to norbornene is exceptionally fast at 0°, requiring only 1–2 min for completion.[90] The reaction product is 99·98% *exo*-norbornyl trifluoroacetate **96**, 0·02% *endo*-**97** (42).



96, 99·98% **97**, 0·02% (42)

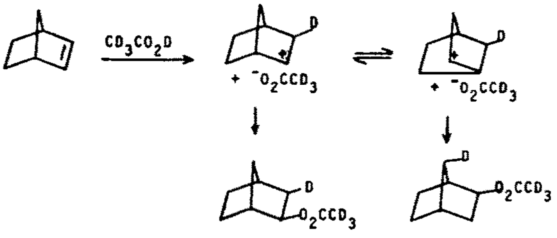
The same tests were applied as were used in the hydrogen chloride study to establish that the addition proceeds through carbonium ion intermediates and does not involve a cyclic molecular addition to any significant extent. Addition of trifluoroacetic acid-d_1 to norbornene again gave the product containing *exo*-3-*d* **98** in excess over the Wagner-Meerwein shifted product, *syn*-7-*d* **99**. The results are compatible with the formation of a rapidly equilibrating pair of cations which is captured prior to full equilibration (43).



98, 37% **99**, 26%

(43)

Finally, the addition of acetic acid to norbornene proceeds relatively slowly at 100°.[91] The product is 99·98% *exo*-, 0·02% *endo*-norbornyl acetate, a stereoselectivity comparable with that realized in the acetolysis of the brosylate.[47] Addition of perdeuterioacetic acid to norbornene provides 67% of the *exo*-3-*d* isomer **100**, and 20% of *syn*-7-*d* **101** with a small amount of hydride shifted products. Again the results are compatible with the formation of a rapidly equilibrating pair of cations which is captured prior to full equilibration (44).



100, 67% **101**, 20%

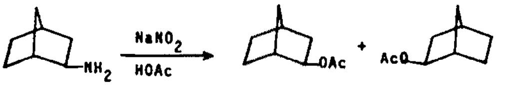
(44)

These results clearly establish that the rapidly equilibrating 2-norbornyl cations can be captured prior to full equilibration. It is pertinent to inquire as to why it is possible to achieve such capture here, whereas it has not yet been achieved in representative solvolytic processes. The difference may lie in the nature of the tight ion pair produced in such solvolyses. However, solvolysis is only one of many carbonium ion substitution processes. Perhaps one should examine the behavior of the 2-norbornyl cation under a wide variety of reaction conditions.

CAPTURE OF UNSYMMETRICAL 2-NORBORNYL CATIONS

The fact is that there are now a number of studies which point to the capture of the norbornyl cation in an unsymmetrical form. The difficulty has been that the proposal that the norbornyl is a symmetrical σ-bridged species has been accepted for so long that investigators have often refused to accept the actual implications of their experiments. Let us summarize the available results.

1. Deamination of optically active *exo*-norbornylamine gives *exo*-norbornanol with approx. 10% of residual activity (45).[93,94]



(45)

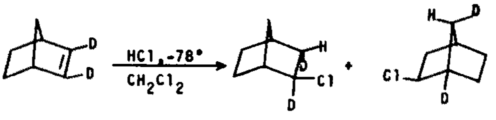
(optically active)

54·5% 44·5%
(98% *exo*-, 2% *endo*-)

It was accepted that the reaction had generated and trapped the optically active classical 2-norbornyl cation. But this was considered to be a special feature of the exothermic decomposition of the *exo*-norbornyldiazonium ion intermediate which permits at least some of the classical ion to be formed without σ-bridging. On this basis the classical cation must be separated by an energy barrier from the symmetrical σ-bridged species.

Alternatively, one can account for the results on the basis that rapidly equilibrating classical 2-norbornyl cations are formed and their capture by solvent proceeds at rates comparable to the rate of equilibration. The difference in behavior from that observed in solvolysis would then be attributed to the formation of the cation in a relatively free state, facilitating capture by the solvent.

2. Addition of hydrogen chloride to 2,3-dideuterionorbornene gives an excess of the isomer **102** with retained structure (46).[92]

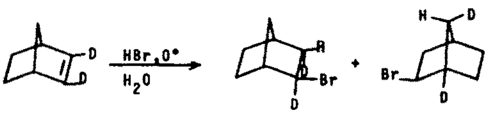


(46)

102, 56% **103**, 42%

The results are most simply accounted for by the mechanism shown in (41).

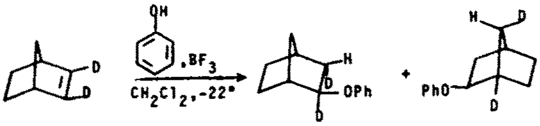
3. Reaction of 2,3-dideuterionorbornene with hydrobromic acid again gives an excess of the isomer **104** with retained structure[92] (47).



(47)

104, 52% **105**, 35%

4. The acid-catalyzed reaction of 2,3-dideuterionorbornene with phenol produces the O-alkyl isomer **106** with an excess of retained structure[92] (48).



106, 47% **107**, 39%

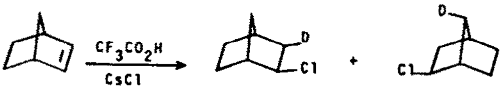
(48)

Again the results are consistent with a trapping of the unsymmetrical cation before it has become fully equilibrated.

5. The addition of deuterium chloride to norbornene at −78° in methylene chloride produces 57% of *exo*-3-*d* isomer **94** in excess to 41% of the rearranged *syn*-7-*d* **95** isomer.[89] As was pointed out earlier, the result is consistent with the trapping of an equilibrating pair of cations prior to full equilibration (41).

6. Addition of deuteriotrifluoroacetic acid to norbornene proceeds very rapidly at 0° and yields 99·98% *exo* isomer, a stereoselectivity considered characteristic for reactions involving the σ-bridged cation.[90] Yet the two principle isomers resulting from the addition, unrearranged **98** and the Wagner-Meerwein shifted product **99**, are not produced in equal amounts. Here also the preferred mechanism involves trapping of an equilibrating pair prior to full equilibration (43).

7. The reaction of norbornene with trifluoroacetic acid containing dissolved cesium chloride gives the chloride as major product, the trifluoroacetate as minor product.[90] An increase in the concentration of the dissolved cesium chloride results in an increase in the yield of chloride and a decrease in that of the trifluoroacetate (49).



(49)

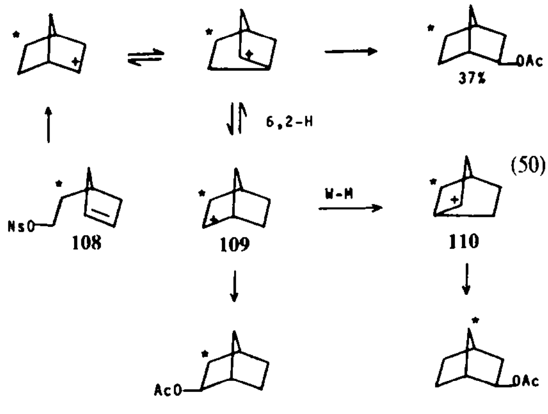
94, 61% **95**, 34%

The presence of cesium chloride decreases the amount of hydride shifted material from 37% in ordinary trifluoroacetic acid to as little as 5% in the presence of the chloride. The system behaves as though the chloride were trapping the equilibrating intermediate considerably faster than the less nucleophilic trifluoroacetate ion (compare **94**:**95** in (49) with that of **98**:**99** in (43)).

8. The addition of acetic acid to norbornene[91] results in far less hydride shifted material, consistent with the more favorable nucleophilic characteristic of the reagent. Moreover, the addition of perdeuterioacetic acid involves much less of the Wagner-Meerwein shifted isomer (44), again consistent with the more favorable nucleophilic characteristics of acetic acid as compared with trifluoroacetic acid.

The reaction proceeds to give 99·98% *exo*-, 0·02% *endo*-. The two tagged isomers are produced in a ratio of the unrearranged acetate **100** to Wagner-Meerwein shifted product **101** of 67:20. These results create a difficulty for the suggestion that such additions may involve a considerable amount of concurrent molecular addition. To achieve the observed distribution would require that approx. 50% of the reaction goes through a carbonium ion process and 50% goes through the proposed cyclic addition. However, this proposal then requires that the cyclic addition process must proceed with an exceptionally high stereoselectivity, a stereoselectivity previously considered to be a diagnostic characteristic for the σ-bridged cation.[47]

9. The capture of the hydride-shifted tagged 2-norbornyl cation in the acetolysis of 2-(Δ^3-cyclopentenyl)ethyl-2-^{14}C *p*-nitrobenzenesulfonate **108** provides a case where the 2-norbornyl cation has been trapped in an unsymmetrical form in a solvolytic process, presumably because the anion is not in position to form the usual tight ion pair[96,97] (50).

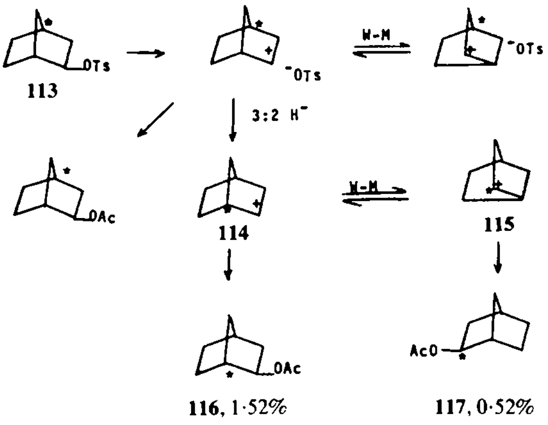


(50)

If **109** and **110** were the resonance hybrids, equal amounts of **111** and **112** should form. However, the results reveal an excess of **111** corresponding to the first formed ion of the Wagner-Meerwein pair.

10. This result has been confirmed by a study of the capture of the hydride shifted 2-norbornyl cation from the solvolysis of *exo*-norbornyl-4-^{14}C tosylate **113** in acetic acid[98] (51).

Again, if the ions produced in the 3:2 hydrogen shift, **114** and **115**, were a resonance hybrid, the yields of **116** and **117** would be identical. However, once again there is realized a larger yield of that ion which would be the first formed member of a Wagner-Meerwein equilibrating pair.



(51)

All of these data support the conclusion that a σ-bridge may not be the factor responsible for the high *exo* : *endo* rate and product ratios observed in the solvolysis of 2-norbornyl derivatives. The intermediate produced is evidently not the symmetrical σ-bridged (nonclassical) species, but a rapidly equilibrating pair of unsymmetrical (classical) cations.

EQUILIBRATING CATIONS UNDER STABLE ION CONDITIONS

Recent advances in the preparation and study of cations in super acids have greatly advanced our knowledge of rapidly equilibrating cations.[99-101] Indeed, many cations, such as 2,3,3-trimethyl-2-butyl, which can be generated and captured in a solvolytic process without equilibration[17] (3), are revealed to be rapidly equilibrating classical cations under stable ion conditions.

A representative series of such ions are listed in Table 1.

It was an unexpected development that so many cations which can be formed and captured without significant equilibration in solvolytic processes are observed to exist as rapidly equilibrating pairs or sets of ions even at very low temperatures. It appears that the new theoretical analysis by Fong may provide the explanation for this development.

In any event, Table 1 may place things in proper perspective. If one accepts Olah's evidence and arguments, then only the cyclopropylcarbinyl and the 2-norbornyl cation exist as σ-bridged species under the favorable conditions of superacid low nucleophilic media. It is appropriate to turn our attention to the evidence and arguments used to arrive at this conclusion.

Olah *et al.* concluded that the cyclopropylcarbinyl cation must exist as a nonclassical σ-bridged species on the basis of a discrepancy between the observed ^{13}C shift and the value calculated for a set of rapidly equilibrating classical cations.[33,102] This is a surprising conclusion in view of the huge amount of evidence that the cyclopropyl group best stabilizes the cationic center in the bisected form **21**, whereas a σ-bridged structure would require the less favorable parallel conformation **22**. Consequently, it appears desirable to subject the arguments and evidence used to arrive at this surprising conclusion to careful scrutiny.

There are major uncertainties in the arguments. First, the ^{13}C shift for the carbonium carbon of the primary cation in cyclopropylcarbinyl is estimated from a linear extrapolation of the values for the nonequilibrating secondary and tertiary cyclopropylmethylcarbinyl cations. It has not been established that such a linear extrapolation is valid. Secondly, it is not possible to confirm the conclusion by calculating and demonstrating agreement of the observed ^{13}C shift with the proposed σ-bridged structure. No basis now exists for such calculations.

Fortunately, in the case of cyclopropylcarbinyl, another independent criterion has been suggested for the formation of a σ-bridge. Such a σ-bridge would cause the carbonium carbon to move toward the cyclopropyl ring. There is considerable evidence that such decrease in the dihedral angle and increase in strain will be reflected in major increases in the coupling constants, as shown by **118**, **119**, and bicyclobutane itself **120**.[103]

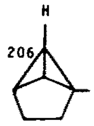
118

119

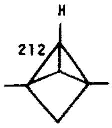
120

The same effect is shown in the bicyclobutane derivatives **121**–**123** where the increase in strain increases the apical methine coupling from 200 Hz in **121** to 212 Hz in **123**.[104]

121

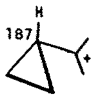


122

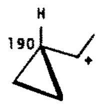


123

It was on this basis that it was predicted that the coupling constant for the apical methine hydrogen would increase from the normal values anticipated for cyclopropyldimethylcarbinyl **124** and cyclopropylmethylcarbinyl **125** to a much higher value, in the neighborhood of 200 Hz, for the σ-bridged primary ion **126**. However, experiment does not bear out that prediction.[34] The value shows a small decrease rather than the increase expected.



124



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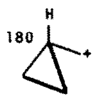


126

These results have important implications. Two major NMR criteria have been proposed by Olah to distinguish the formation of σ-bridged nonclassical ions in super acids. The first is the agreement between calculated and observed values for ^{13}C shifts. A failure to obtain agreement has been used as a basis to argue for the formation of a σ-bridged species.[100,102] The second has been an increase in the ^{13}C–H coupling constant postulated to accompany an increase in strain with the formation of the σ-bridge.[33] Failure to observe a substantially different coupling constant has been used to argue for a classical cationic intermediate.[105]

In the case of the cyclopropylcarbinyl cation, these criteria now lead to conflicting interpretations. The earlier chemical shift data led to a preference for the σ-bridged structure, in spite of the mass of data favoring the bisected conformation in this system.[102] The present coupling constant data supports a structure without such a σ-bridge. Clearly it is necessary to proceed with caution before using either NMR criterion as a basis for a decision.

Disagreement between the calculated value for the ^{13}C shift in equilibrating classical ions and the observed value has been used to argue for the nonclassical structure of 2-norbornyl,[87] **4**, **69**, **70**, **71**, **72**, **73** or **74**. However, this procedure suffers from the difficulties previously discussed. The ^{13}C shift for the static classical 2-propyl cation is used as an estimate for the ^{13}C shift to be expected for the static classical 2-norbornyl cation. This is an enormous extrapolation. Kramer has pointed out that the value for 2-propyl cannot be utilized in this way to calculate the observed shift in the equilibrating classical 2-butyl cations[106] (Table 1). If this minor extrapolation causes difficulty, what confidence can be placed on the much greater extrapolation from 2-propyl to 2-norbornyl?

In theory at least the ESCA spectrum offers more hope for a definitive answer. Indeed, study of the ESCA spectrum has led Olah *et al.* to deduce that the 2-norbornyl cation is a σ-bridged species in super acid media[107,108] and to extrapolate their ESCA results in such super acid media to the solvolytic field to conclude "... the long standing controversy as to the nature of the norbornyl cation is unequivocally resolved in favor of the nonclassical carbonium ion".[107,108] Is this a reliable conclusion?

Unfortunately, there are serious problems with the ESCA technique as applied to the study of carbonium ions. Thus in a private communication from Prof. Martin Saunders of Yale University, he states: "I agree with you that the published ESCA data are not conclusive. In our own ESCA studies we have observed that the peaks vary considerably from experiment to experiment. I believe that the variability arises from surface effects since the ESCA experiment only looks at about the first 30 angstroms of material. It is extremely difficult to prevent small amounts of contamination from entering an ESCA instrument during the sample preparation or afterward. These impurities could very easily destroy carbonium ions. It is regrettable that no one has yet repeated any of Olah's ESCA experiments in this area".

In earlier discussions with Olah and Mateescu, they have agreed that there are major experimental difficulties. Indeed, they advised the author that only one of many spectra run is "acceptable". Unfortunately, these difficulties are not pointed out or discussed in the publications.[107,108]

It has been noted that the original ESCA spectrum corresponds to a 6 : 1 distribution of carbon atoms, rather than the 5 : 2 reported by the authors and required by the σ-bridged formulation.[106] The later ESCA spectrum appears to be that of a mixture.[106]

In addition to these technical difficulties, there is a further problem. It has recently been discovered that such solutions of carbonium ions can involve a number of equilibria.[109] Consequently, there is no certainty as to the precise solid phase that separates on freezing the solution, the solid phase which is then subjected to ESCA examination.

The ESCA technique in principle should be capable of solving the problem of the 2-norbornyl cation.[86] In actual fact the available results do not give one confidence that such a solution is at hand.

Finally, it is desirable to retain proper perspective. Numerous such cations have been subjected to NMR examination (Table 1). Almost all of them have been assigned static classical or equilibrating classical structures. Only one of the ions in Table 1, 2-norbornyl, may exist in σ-bridged form in super acid media, although a sound decision cannot be reached on the basis of the data now available. Clearly, the problem has become shrunken to a size where it is no longer of significance to the advance of chemistry.

OTHER STUDIES

Numerous other techniques and procedures have been applied to the question.[8,12] Thus secondary isotope effects have been utilized.[110] For example, a deuterium substituent in the 6-position gives $k_H/k_D = 1{\cdot}10$ for *exo*-, but 1·00 for *endo*-norbornyl brosylate. This is considered to support σ-participation. However, there are major difficulties in interpreting such secondary isotope effects.[111] These difficulties are illustrated by the following example. At one time it was reported that there was a reduced 2-deuterium effect ($k_H/k_D = 1{\cdot}11$) in *exo*-norbornyl but a normal effect ($k_H/k_D = 1{\cdot}21$) in *endo*.[112] This result was also interpreted as favoring a nonclassical intermediate. However, it is now reported that this early result was a consequence of scrambling (internal return) in the solvolysis of the *exo*-, so that if this difficulty is avoided, both isomers actually yield the same value, 1·21, for k_H/k_D.[110] What conclusion can be safely drawn?

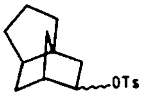
It has been argued that the low *exo* : *endo* rate ratios observed for the solvolysis of certain modified norbornyl derivatives **127**, **128** represent the true behavior of classical norbornyl cations.[113,114]

127

128

However, it has been suggested that in these cases the low *exo* : *endo* rate ratios appear to reflect operation of the Selectivity Principle.[115]

The low *exo* : *endo* rate ratios, ~10, observed for 4,5- **129** and 5,6-trimethylene-2-norbornyl **130** derivatives has also been interpreted as favoring σ-bridging in the parent system.[116,117]



129

130

It is argued that the trimethylene bridge resists formation of the σ-bridged transition state and therefore essentially removes this contribution to the *exo* : *endo* rate ratio. The higher *exo* : *endo* rate ratio observed in 2-norbornyl is then taken as evidence for the presence of σ-bridging in that species.

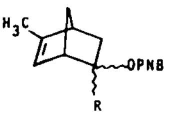
This is a reasonable argument. At the present time I have no other satisfactory explanation for the low *exo* : *endo* rate ratio in **129** and **130**. Possibly the trimethylene rings so distort the parent structure as to modify the solvolytic process. Obviously, this system should be subjected to more intensive study.

It may be worthwhile to point out a weakness of the nonclassical theory. It is, after all, a qualitative theory. Suppose experiment had shown that the *exo* : *endo* rate ratio in **129** and **130** was huge, in the neighborhood of 10,000. The nonclassical theory could have readily accommodated even this result. It would have been suggested that the strain in the trimethylene bridge polarizes the C1–C6 bonding pair, making it better able to supply electrons to the developing electron deficiency at the 2-position.

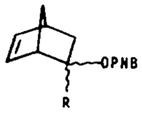
In other words, one can use either an increase or a decrease in the *exo* : *endo* rate ratio in these systems to argue that the results support σ-participation.

Finally, we have been engaged in a major effort exploring the tool of increasing electron demand to probe for participation in the manner utilized by Gassman and Fentiman for the 7-norbornenyl system **35**, **36**.[42]

The tool reveals major π-contributions from the 5-methyl-2-norbornenyl system **131**, as revealed by the changes in the *exo* : *endo* rate ratios[118] (Fig. 19).



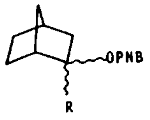
131



132

On the other hand, 2-norbornenyl **132** appears to be a borderline case. There is no significant change with the first three less electron demanding groups. Only with the more demanding groups are there observed increases in the *exo* : *endo* rate ratios corresponding to the inception of π-participation[118] (Fig. 19).

In the case of 2-norbornyl **133**, no significant change in the *exo* : *endo* rate ratio is observed over the full range of electron demand explored[119] (Fig. 19).



133

Evidently, σ-participation is far more difficult to achieve than π-participation.

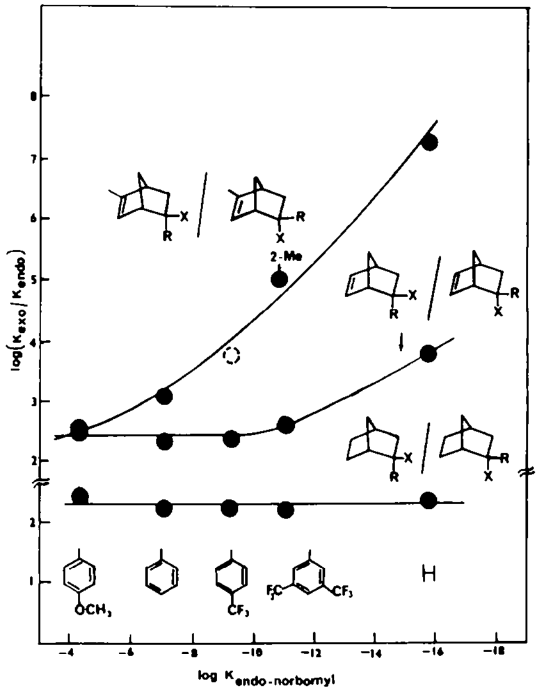


Fig. 19. Effect of increasing electron demand on *exo* : *endo* rate ratio.

CONCLUSIONS

In 1960 we undertook our first tentative experiments to confirm the presence of σ-bridging as a major factor in the high solvolytic reactivity exhibited by many highly branched organic derivatives. These early experiments failed to confirm the proposed σ-bridging. Accordingly, we decided to concentrate our examination on the two cases which were then considered to constitute the strongest, most reliable examples of this new phenomenon—cyclopropylcarbinyl and 2-norbornyl.

Now, some fifteen years later (at the time of this writing) it would appear that the situation should be ripe for a definitive decision. However, this has proven difficult to achieve. It is always a struggle to obtain reconsideration of a generally accepted concept. The non-classical ion area has been no exception—indeed, it may be the prime example of such difficulties.

In all the years that our reexamination was taking place, the pros and cons of the alternative interpretations were never made the subject of an open discussion among those interested in the question. Even the attempts to hold Symposia-in-Print[11,12] failed.

In spite of these difficulties, progress has been made. In Fig. 20 I have tried to represent the changes in the situation as they appear to me. In the 1950–60 era, nonclassical ions were at least considered for every carbonium ion known with the possible exception of methyl. Now the discussion appears to be primarily restricted to secondary 2-norbornyl as a vestigial member of the class.

As was pointed out earlier, the interest of my group in the question of σ-participation was initiated by proposals that such σ-participation provided an alternative factor to relief of steric strain for certain enhanced rates. Representative cases of this kind, discussed earlier, were camphene hydrochloride,[35] tri-tert-butylcarbinyl derivatives,[39] and cyclodecyl tosylate.[40] It is pertinent to point out what has happened to these three cases in the intervening years. In the case of cyclodecyl tosylate, it was observed that the introduction of transannular deuterium failed to affect the rate significantly. Consequently, the transannularly bridged formulation **30** was withdrawn. A detailed study of the products from the solvolysis of tri-tert-butylcarbinyl p-nitrobenzoate failed to support the σ-bridged formulation **28**, and it has been withdrawn.[121] Finally, if one can extrapolate the conclusions of Goering about the essentially classical nature of the 1,2-dimethylnorbornyl cation[83,84] to the 2,3,3-trimethylnorbornyl (hydrocamphenilyl) cation, then this σ-bridged cation **10** is no longer with us.

It has been a long and difficult journey from the time when complex nonclassical structures were considered for cations as stable as that derived from 2-p-anisylcamphenilol in formic acid **134**.[122]

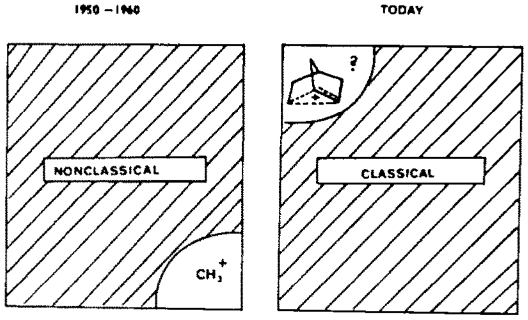
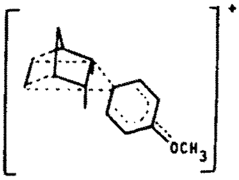


Fig. 20. Graphical representation of the change in the accepted scope of σ-bridged nonclassical ions.



134

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

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