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Author's Review

Participation in Solvolysis: A Look Back*

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From the beginning, the »carbonium ion controversy« of yesteryear was characterized and skewed by a series of assumptions, definitions and antecedents the significance of which was not fully realized at the time by many principals involved in it. An attempt is made here to illuminate these aspects in the light of new developments in our laboratory and elsewhere.

The »carbonium ion controversy« has passed into history. Most of those participants who are still active in chemistry have turned their attention to other pursuits, and the carbocation researchers now comprise only a small group.

Professor Sunko's 70th birthday is a most appropriate occasion for a look back at those heady days when few if any organic chemists failed to express their opinions about the merits of the contending points of view. The author well remembers the impact of the communications by Sunko[1] and Nickon,[2] in which they reported large deuterium isotope effects in the solvolysis of 6-deuterio-2-*exo*-norbornyl esters, and their absence in the *endo*-epimers. This observation proved to be one of the most convincing and enduring arguments in favor of Winstein's proposal[3] that the solvolysis rate of this *exo* isomer is enhanced by »sigma participation«. I begin my Monday-morning quarterbacking about that episode by recalling some of the events and concepts that helped shape it in important ways.

The famous 1935 paper by Baker and Nathan[4] reported the first instance of the idea that the stability of a carbocation might be strongly affected by distant aliphatic substituents. Benzyl cations appeared to form more easily if an alkyl group was present in the *para* position, and this enhancement varied in the order methyl > ethyl > isopropyl > *tert*-butyl. No-bond resonance structures were proposed to account for this effect, which implied that C–H bonds served as better donors than C–C bonds. No-bond structures had been proposed even earlier by G. N. Lewis, to account for the existence of diborane.[5] The phenomenon was examined by Mullikan[6] in molecular orbital terms; the word hyperconjugation was coined by him in 1941.[7] Remick's widely used book »Electronic Interpretations of Organic Chemistry«, published ten years later,[8] appeared to provide a solid foundation for this extension of the concept of conjugation.

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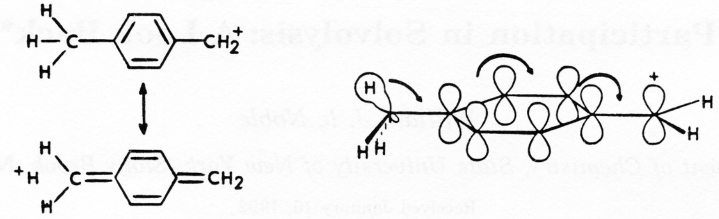
* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday

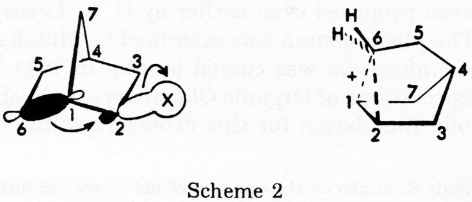
Yet, the proposal did not become widely popular. Chemists looked askance at the strange new structures, and did not find them appealing, or easy to use. A number of suggestions were made subsequently concerning possible hyperconjugation effects in molecular spectroscopies; however, these effects were generally small and not well-known. In 1959, a symposium on the topic was held at Indiana University in Bloomington; it received decidedly mixed reviews.[9] A book under the same title by Dewar[10] concluded essentially that the concept was supported by little evidence, and not really needed.



Scheme 1

Meanwhile, however, a related idea was gaining strength. Lucas had demonstrated that the bromination of *cis*- and *trans* stilbene leads to dibromides the identities of which were determined by an intermediate cation capable of retaining the original olefin configuration.[11] Winstein greatly elaborated the proposal of neighboring group assistance to include solvolytic carbocation formation and capture. His early work involved distant atoms carrying unshared pairs,[12] but in 1951, he went a long step further by proposing that in the solvolysis of the relatively unstrained *exo*-2-norbornyl esters, ionization was assisted by the antiperiplanar C_1–C_2 bond. The assistance was thought to be so strong (rate several hundred times faster than that of the presumably unassisted *endo* epimer) that C_6 took up a position symmetrically below the midpoint of the C_1–C_2 bond, and thus became pentacoordinated (Scheme 2).[3] The terms »sigma delocalization« and »non-classical ions« came into use, as did dotted lines signifying partial bonds. However, these notions were stoutly resisted by some chemists, notable among them H. C. Brown.[13] The resulting dispute went on for a quarter of a century, and ended unsatisfactorily with most of the participants still living once more restating their positions before ending their involvements.[14] A review of this episode by the author has appeared elsewhere.[15] In recent times, elegant experiments by Grob,[16] Saunders[17] and Yannoni,[18] essentially decided the matter in the late Winstein's favor. My present purpose is not to recite the details of this history once again, but to point out some of the pitfalls that characterized the dispute.

1. The first of these is a matter of definition: what exactly is sigma delocalization (or sigma participation), and what is its relation to hyperconjugation? Even a casual glance at Schemes 1 and 2 should suffice to convince almost anyone that these con-



Scheme 2

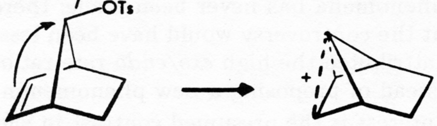
cepts are so similar as to leave one wondering whether they are not actually identical. However, it is hard to find evidence of recognition of this similarity in the literature. Winstein did not cite the Baker-Nathan or Mullikan papers, and did not use the term hyperconjugation. Conversely, not one of the papers contributed at the Bloomington Symposium mentioned Winstein's papers, nor was Winstein's work either discussed or cited in Dewar's book. In fact, the whole voluminous literature on the subject seems devoid of any realization that these two concepts might be the same, or if they were different, that the difference should be precisely defined. It was not until 1969 that Jensen and Smart discussed this relation in print, in paper[19] reporting that *exo*-2-norbornyl was especially effective as a *para* substituent in processes believed to be promoted by hyperconjugation, when it was compared with other alkyl groups. After that, little more was written in this vein, although the question was raised now and then in seminars and discussions. In 1984, Brown at last addressed the question in his book. »The Nonclassical Ion Problem«, stating that »Unfortunately, in the literature there has not been the same care in differentiating between σ-participation and σ-conjugation (hyperconjugation). We shall attempt to avoid this ambiguity by using the term »σ-participation« for a direct interaction through space of a *p*-orbital with the electrons in a carbon-carbon bond... On the other hand, interaction of the carbonium ion center...does not involve such a σ-bridge through space, but sideways interaction of orbitals...«[20] Schleyer commented: »I agree with Brown that the hyperconjugative model does not provide a satisfactory explanation for 2-norbornyl behavior. Although hyperconjugation and σ-electron participation are closely related phenomena, the former implies insignificant nuclear movement towards bridging.«[20] However, there are neither claims nor evidence in the original literature – beginning with Baker and Nathan – to the effect that hyperconjugation does *not* involve distortions. It seems only natural to suppose that it *does* so, in fact, just as does conjugation itself. Traylor has proposed the term vertical stabilization[21] for a hyperconjugative interaction that does not involve distortion; however, this notion has not received convincing experimental support.

Since no one seemed to have any quarrel with Baker and Nathan, one might ask: if delocalization of the electrons in a C–H bond in a methyl group to a cationic site separated from it by a phenyl ring is acceptable, why shouldn't a directly neighboring group be able to do so in the same manner? Indeed, many textbooks now attribute the S_N1 solvolysis sequence *t*-butyl > *i*-propyl > ethyl (>>> methyl) more to increased opportunities for hyperconjugation than for relief of steric strain. A strong experimental case for two different phenomena has never been made; there are only assertions to that effect. I believe that the controversy would have been less acrimonious and much briefer if Winstein had attributed the high *exo/endo* rate ratio to an extreme example of hyperconjugation, instead of proposing a new phenomenon.

2. A second point of interest is the presumed contrast in sigma participation (or, as we see it, in hyperconjugation) between secondary and tertiary norbornyl ions, and the related matter of a symmetrical, single (»non-classical«) cation *vs.* a pair of (»classical«) equilibrating ones. From the early 1960's on, Brown's strategy was based on the assumption that tertiary 2-norbornyl ions, which might be expected to be more stable than the secondary ones, should behave in a different manner: the *exo/endo* rate ratio should be reduced, even to unity. But he found that this was not the case; thus, the ρ^+ values for *exo*- and *endo*-2-phenyl-2-norbornyl sulfonate solvolysis are the same, and the rate ratio is essentially the same as for the parent substrate.

Was Brown's basic assumption justified? Winstein alone at one time pointed out[22] that it was an *assumption*, but even he subsequently appeared to acquiesce. A probable reason for the absence of demurral was Schleyer's demonstration[23] that in superacid medium, the 1,2-di-*p*-2-norbornyl ion is clearly an equilibrating degenerate pair, as shown by proton NMR. In the parlance of those days, that ion was so stable that it did not »need« sigma delocalization. The word »need« is, of course, an anthropocentric term the use of which is risky in chemistry! To embroider on this phrase, ions and molecules are greedy creatures that will avail themselves of any opportunity to lower their energies further no matter how stable we judge them to be already. It would be more reasonable to examine whether the opportunity for further stabilization might involve a *cost*, for example, in terms of strain. Thus, it is conceivable that the solvolysis of 1,2-dianisyl-*exo*-2-norbornyl esters is promoted hyperconjugatively but that the intermediate ion is not quite symmetrical because of the strain from two eclipsed anisyl groups. In any event, Brown's case seemed powerful: tertiary ions were seen to equilibrate, and hence were deemed to be »classical«, equilibrating ions were accepted as too stable to »need« participation, and the secondary ions solvolyzed with the same epimeric rate ratio as the tertiaries. A high rate ratio could therefore not be used as an argument for participation.

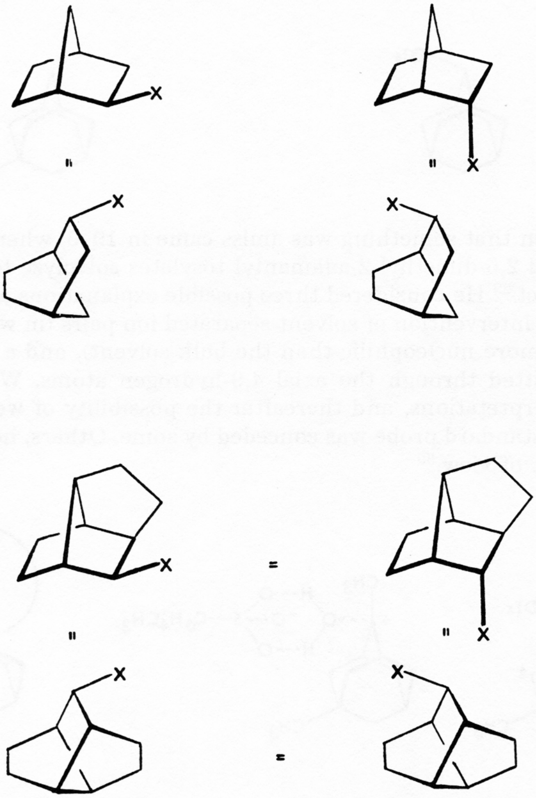
3. A third psychological millstone universally carried around by those so anxious to solve the problem was the unquestioned assumption that sigma participation was only an extension of the already well-established n- and π types of participation. As an example, let us consider Gassman's demonstration that the enormous rate acceleration (10^{11}) afforded by the *anti*-homoallylic double bond in 7-norbornenyl ester solvolysis[24] is completely swamped by the presence of a 7-anisyl group.[25] The concept of π participation, proposed by Winstein and Woodward to account for this rate acceleration, was thus further supported. When Brown, who accepted π participation (though not the presumably resulting symmetrical »non-classical« ion) applied the Gassman criterion to the 2-norbornyl esters, it failed to diminish the rate ratio, and he thus seemed justified in rejecting sigma participation. In doing so, he treated π and σ participation as slightly different versions of the same phenomenon (carbon participation) that could be tested by the same means. Indeed, Winstein had pointed out that many »non-classical« ions could be generated by either the »sigma route« or the »pi route«, thus contributing to the notion that these two types of assistance were but different facets of the same gem.



4. Another circumstance contributing in a major way to the indecisive nature of the carbonium ion dispute was the very choice of the 2-norbornyl cation as the battlefield. The notions that sigma assistance would convert the chiral 2-norbornyl precursor into a C_2-symmetrical intermediate (first suggested parenthetically by Wilson[26]), and that the structure of this intermediate might be provable by physical means were certainly fascinating, and they have produced a rich harvest of chemical knowledge; however, this also meant that, what was basically a problem in face selection, was doomed to be studied by means of a probe in which the two faces were different *both electronically AND sterically*. The norbornyl structure did not have the undisputable absence of

steric factors that are seen, for example, in the *m*- and *p*-substituted benzene derivatives which made the Hammett analysis so useful. Any difference between *exo* and *endo* could be attributed to either an electronic or a steric factor. Was *exo* unusually fast because of sigma delocalization, or was *endo* unusually slow because of steric inhibition? The 2-norbornyl probe was tailor-made for perpetual argument.

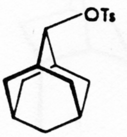
An ingenious attempt was made by Nickon[27] to end this duality, by means of his brexyl-substrate in which the incipient cationic site is both *exo* and *endo* (Scheme 3). Unfortunately, partial rearrangement occurs during solvolysis of this substrate, and the results proved indecisive.

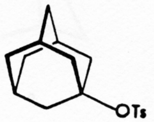


Scheme 3

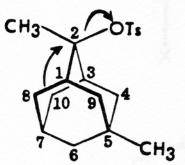
5. A further obstacle was the result of a search for secondary and tertiary substrates that could be used as the ultimate examples of *unassisted* heterolysis.[28] In this connection, a distinction was made between k_Δ, k_s and k_c processes, which were meant to symbolize carbon-assisted, solvent-assisted and unassisted processes. A variety of methods was used to compare candidates for the ideal substrate roles in which *tert*-butyl and isopropyl substrates had hitherto been used; among these methods, solvent

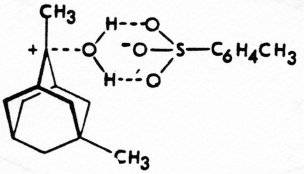
and substituent effects, product analyses with various nucleophiles, and leaving group effects were prominent. On the basis of these studies, the secondary 2-adamantyl and tertiary 1-adamantyl substrates emerged as the ideal examples of k_c behavior. Because of the symmetries of these substrates, C_2 and C_3 respectively, the solvolysis stereochemistry could not be included among the methods. This was unfortunate; had it been so included, the 2-adamantyl cation might have replaced the norbornyl cation as the probe with which to study sigma participation, preferred because the faces of the incipient cationic site could be made *sterically equivalent.* As it was, the 2-adamantyl cation instead became *the* example of unassisted solvolysis, producing a symmetrical, classical cation; thus, a 1974 Abstract states categorically: »Tertiary 2-adamantyl cations are classical«.[28b]

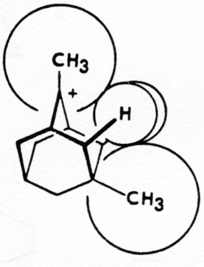




One indication that something was amiss came in 1975, when Whiting found that the 5-methyl- and 2,5-dimethyl-2-adamantyl tosylates solvolyze to give a small excess of retained product.[29] He considered three possible explanations at great length: sigma participation, the intervention of solvent-separated ion pairs (in which the trapped solvent molecule is more nucleophilic than the bulk solvent), and a long range steric interaction transmitted through the axial 4,9-hydrogen atoms. Whiting preferred the first of these interpretations, and thereafter the possibility of weak assistance in the solvolysis of this standard probe was conceded by some. Others, however, have favored the ion-pair point of view.[30]







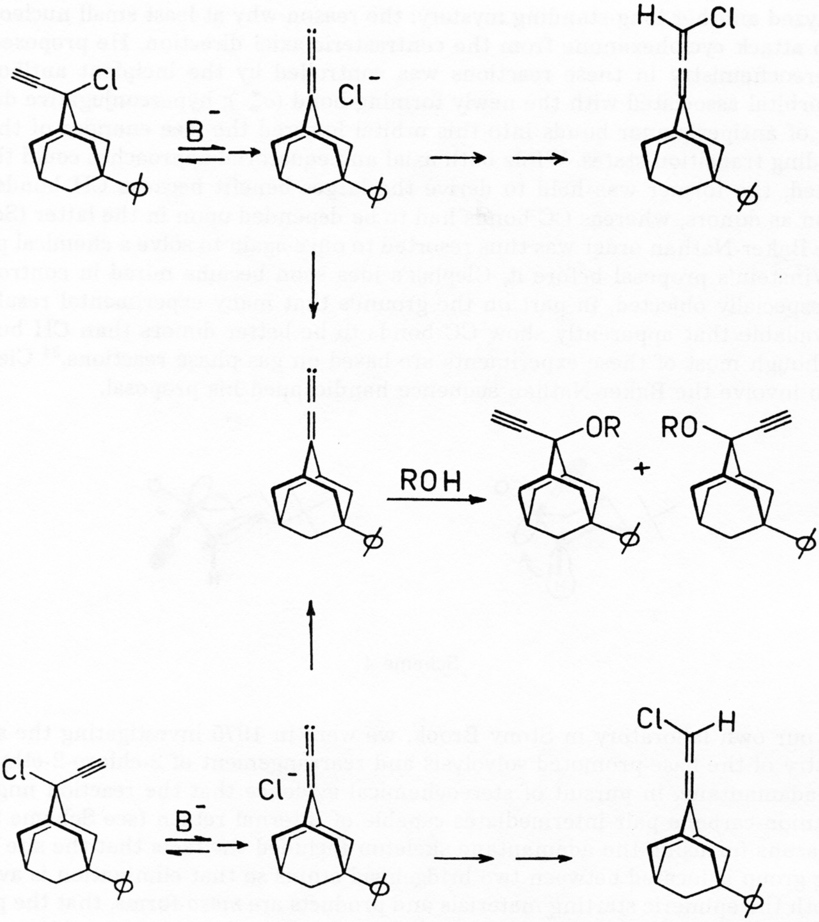
6. Another factor in this tumultuous disagreement was Brown's demonstration that reactions apparently unrelated to solvolysis, such as the reduction of 2-norbornanone and the capture of carbenes by norbornene, were also characterized by a preference for exo attack.[31] This tended to support his contention that exo cleavage and capture were preferred sterically, since no common electronic factor could be discerned in all of these reactions.

* * *

In 1981, an apparently unrelated proposal by Cieplak[32] provided the key that ultimately helped us understand the nature of these puzzles and inconsistencies. Cieplak re-analyzed another long-standing mystery: the reason why at least small nucleophiles tend to attack cyclohexanone from the contrasteric axial direction. He proposed that the stereochemistry in these reactions was controlled by the incipient antibonding sigma orbital associated with the newly forming bond ($\sigma^*_{\neq}$); hyperconjugative delocalization of antiperiplanar bonds into this orbital lowered the free energies of the corresponding transition states. While both axial and equatorial approaches could thus be stabilized, the former was held to derive the larger benefit because CH bonds then function as donors, whereas CC bonds had to be depended upon in the latter (Scheme 4). The Baker-Nathan order was thus resorted to once again to solve a chemical puzzle. Like Winstein's proposal before it, Cieplak's idea soon became mired in controversy. Houk especially objected, in part on the grounds that many experimental results are now available that apparently show CC bonds to be better donors than CH bonds.[33] Even though most of these experiments are based on gas phase reactions,[34] Cieplak's need to involve the Baker-Nathan sequence handicapped his proposal.

Scheme 4

In our own laboratory in Stony Brook, we were in 1975 investigating the stereochemistry of the base-promoted solvolysis and rearrangement of 2-chloro-2-ethynyl-5-phenyladamantane, in pursuit of stereochemical evidence that the reaction might involve anion-carbene pair intermediates capable of internal return (see Scheme 5).[35,36] Our reasons for using the adamantane skeleton included the facts that the site of the leaving group is located between two bridgehead atoms so that elimination is avoided, that both the epimeric starting materials and products are *meso*-forms, that the phenyl label is too far to exert steric effects, and that no uncertainties due to conformational motion arise. The possibility of an electronic effect of the phenyl group did not occur to us: no one had ever suggested that this function, so often used as a locking group in the 4-position of cyclohexanone and its derivatives, might affect the stereochemistry of addition from its trans-annular equatorial location. Yet we ran into two facts that clearly refuted our supposition.[37] Firstly, the preparation of the starting material involved the ethynylation of 5-phenyladamantanone. The ratio of the *E*- to *Z*-propargyl alcohols was not exactly 50:50 as we had expected, but rather 75:25! Secondly, the allenic isomers shown in Scheme 5 appeared to form with excess retention and the ether mixtures obtained from either initial propargyl chloride were identical as we hoped; however, this mixture did not have a 50/50 composition either, but rather 75:25. The *Z*-ether was the major product. In both the ketone and the carbene, the phenyl group strongly directed the nucleophiles, the ethynyl anion and methanol, to the zu face of the trigonal carbon. Subsequent investigation with other 5-substituted adamantanones and other nucleophiles showed this phenomenon to be without exception so long as the substituent is an electron-withdrawing one; electron donors lead the reagent to attack the en face.[38] All these results support Cieplak's account of the stereoselectivity



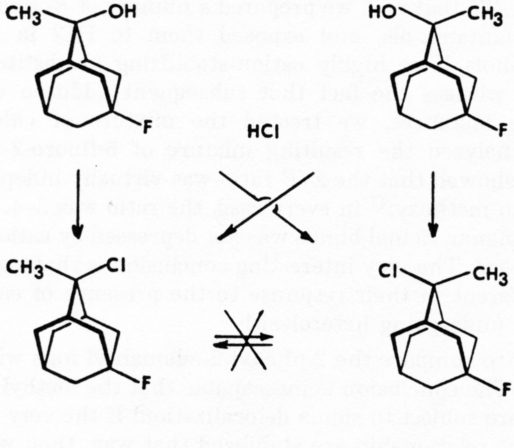
Scheme 5

observed in cyclohexanone. More important, they do not depend on the correctness of the Baker-Nathan order, as the structure in Scheme 6 may show.

Cieplak's suggestion can be extrapolated to electrophilic attack on olefins,[39,40] since the identity of the species contributing the electrons for the newly forming bond is immaterial and only the $\sigma^*_{\neq}$ matters. Indeed, the same stereochemistry is observed; the electrophiles add to that face which is antiperiplanar to the electron-richer vicinal bonds. Extensions to several other types of addition have been made; these include thermal[41] and photo[42] cycloadditions, sigmatropic shifts,[43] radical capture,[44] and metal complexation.[45] All of these studies can be successfully incorporated into the same hyperconjugative model.

These results led us to new experiments in carbocation chemistry which clarified our understanding of this field. First of all, we found that *E*-5-deuterio-2-adamantyl tosylate solvolyzes in aqueous acetone with 95% retention.[38a] The possibility that steric effects can always account for retentive stereochemistry in solvolysis is thus laid to

Scheme 6



Scheme 7

rest, once and for all. In another experiment, we studied the product mixtures resulting from the exposure of a number of epimeric pairs of 5-substituted tertiary 2-adamantanols to HCl gas dissolved in methylene chloride (see Scheme 7).

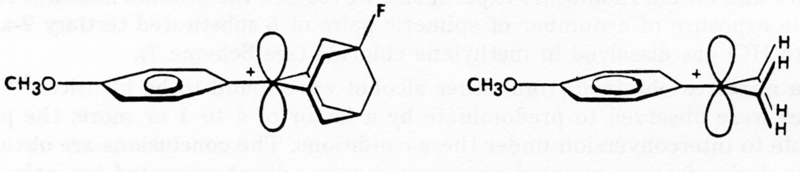
The mixtures obtained from either alcohol were found to be identical.[38a] The *Z*-dihalides were observed to predominate by a factor of 4 to 1 or more; the products are stable to interconversion under these conditions. The conclusions are obvious: the products derive from a common precursor, hence solvent-separated ion pairs cannot be held responsible for the selectivity. If 5-fluoro-2-methyleneadamantane was used instead of the alcohols, the *Z*/*E* ratio was as much as 200;[39] in this case, there isn't any trapped solvent molecule at all. Whiting's preferred possibility of sigma participation remains as the only viable explanation of retentive solvolysis. It was amazing to see how easily the notion of sigma participation could be proved once a probe was used free from steric prejudice toward one of the two faces of the trigonal carbon site. A structure was now available in which sigma participation had no rival to account for face selection. And that structure was the one that had earlier been touted as *the* example of k_c solvolysis![28b]

Clearly, the tertiary ion was subject to this effect just as much as the secondary one, even though a 2-methyl group accelerates the solvolysis of 2-adamantyl esters by as much as 10^8. Thus, our findings substantiate Grob's earlier claim[46] that tertiary 2-norbornyl ions seem to be formed with sigma participation just like the parent cation.

We also understand now why reagents in nucleophilic addition to 2-norbornanone and in electrophilic addition to norbornenes, so strongly prefer the exo face. One should not conclude from this that the solvolysis of 2-norbornyl esters is unassisted, but rather that these addition reactions are assisted also! The Cieplak and Winstein types of assistance are basically the same: both have their origin in hyperconjugation. In Winstein's case, the delocalization occurs into the empty p-orbital, in Cieplak's, into the empty $\sigma^*_{\neq}$.

Having once convinced ourselves of the reality of sigma participation in solvolysis and in its reverse, the nucleophilic capture of carbocations, we were then in a position to test the validity of Brown's use of the Gassman-Fentiman tool to judge the existence of this phenomenon. To that end, we prepared a number of *E*- and *Z*-5-fluoro-2-(*p*-substituted)phenyladamantan-2-ols, and exposed them to HCl in methylene chloride. Some of these alcohols have highly cation-stabilizing *p*-substituents which lead to labile chlorides, as witness the fact that subsequent addition of HBr gave mostly bromides. In those instances, we treated the mixture of chlorides with sodium borohydride, and analyzed the resulting mixture of 5-fluoro-2-phenyladamantanes. These experiments showed that the *Z*/*E* ratio was virtually independent of the *p*-substituent, from CF_3 to methoxy;[47] in every case, the ratio was 3–4. Thus, the participation by the antiperiplanar vicinal bonds was *not* depressed by cation-stabilizing groups, as Brown had supposed. The very interesting conclusion is that sigma and pi participation are utterly different in their response to the presence of cation stabilizing substituents at the site undergoing heterolysis!

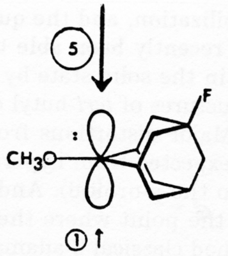
It is fascinating to compare the 2-phenyl-2-adamantyl ions with the parent cumyl cations (Scheme 8). The conclusion is inescapable that the methyl groups in the cumyl cations *themselves* are subject to sigma delocalization! If the very molecules which are the basis of the $\sigma^+\rho^+$ relationship are stabilized that way, then we obviously have no business to use them in any investigation the objective of which is to see whether sigma participation exists.



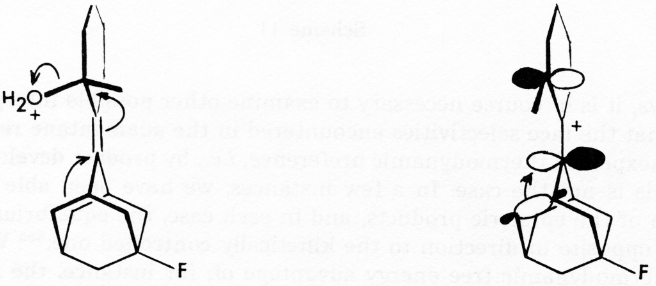
Scheme 8

One is left wondering whether true k_c processes really exist. We found[47] that even a 2-adamantyl cation in which a methoxy group is directly bound to the cationic site captures borohydride to give a mixture of epimeric methyl ethers in which the *E*-isomer predominates by a margin of 5:1. Indeed, if we consider ketones in essence to be carbocations with an α-oxide function, we find that even *they* show a prejudice toward reduction to give *E*-alcohols. That leaves us with no hope that a true and ideal k_c process will ever be seen. The only possible candidate would now seem to be the methyl cation, in which vicinal bonds are lacking altogether; it has not been possible to generate it in solution.

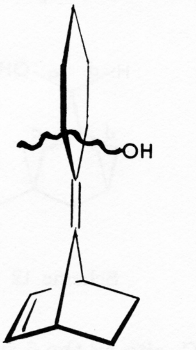
If cumyl cations are subject to sigma delocalization from antiperiplanar vicinal bonds, the same attribute should also be possessed by allylic cations, and this moved us to



wonder whether the stereochemistry might be reversed in cases where the delocalization occurs at the γ rather than the α site. Accordingly, we have studied[48] the acid catalyzed dehydration of the alcohols shown in Scheme 9, and find that the E-isomer is now more reactive than the Z. The rate ratio was found to be somewhat variable (between factors of 2–45, probably due to difficulties in reproducing the exact conditions); however, there is no doubt that this type of orbital symmetry is involved in the generation of allylic carbocations. The epimers shown in Scheme 10 dehydrate at exactly the same rate, showing once again that σ and π participation do not respond in the same way to stabilizing features (in this case: homo-allylic conjugation).[49]

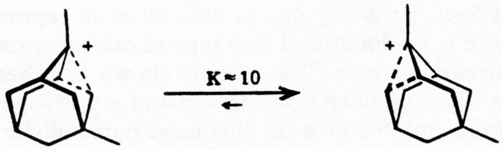


Scheme 9



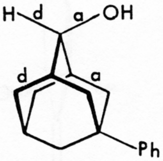
Scheme 10

What about the vertical stabilization, and the question of hyperconjugation in undistorted structures? Laube has recently been able to determine the fine-structure of several simple carbocation salts in the solid state by means of X-ray diffraction,[50] and Yannoni has contributed the structures of *tert*-butyl cation in solid superacid media by means of magic angle NMR.[51] Major distortions from the simple classical structures were seen, all of the type to be expected from hyperconjugation (short C_α-bonds, long C_β bonds made nearly parallel to the p-orbital). And just so as the presumed classical norbornyl ions are distorted to the point where they come together as a single symmetrical structure, so the presumed classical 2-adamantyl ion is distorted into an equilibrating pair of less symmetrical species, as Sorensen has demonstrated from the temperature dependence of the ^{13}C NMR spectra of 2,5-dimethyladamant-2-yl cation (Scheme 11).[52]



Scheme 11

As always, it is of course necessary to examine other possible interpretations. One of these is that the face selectivities encountered in the adamantane reactions are driven by an unexpected thermodynamic preference, *i.e.*, by product development control. However, this is not the case. In a few instances, we have been able to bring about equilibration of the epimeric products, and in each case, the equilibrium preference is smaller and opposite in direction to the kinetically controlled one.[38a] We suspect that the small thermodynamic free energy advantage of, for instance, the *Z*-alcohols over their epimers derives from the more favorable hyperconjugative interactions between antiperiplanar vicinal acceptor and donor bonds (Scheme 12). The newly formed C–H bond in reduction, for example, is electron-deficient in the transition state but not in the product, and hence kinetic and thermodynamic preferences tend to be opposite.



Scheme 12

Skeletal distortions of the C_2 site by the 5-substituent are sometimes put forward as possibly responsible for the face selectivities observed.[53] The cations, for example, are indeed distorted, as shown by Sorensen, but in fact, hyperconjugation is itself responsible. It seems unlikely, however, that the ketones are significantly distorted. We have not been able to apply X-ray diffraction to this question because all of the adamantanones of which we could prepare single crystals to date are characterized by disorder problems preventing adequate refinement of the crystal structures. However, with a number of other adamantane derivatives, we did obtain crystal structures, and none showed systematic distortions attributable to 5-substituents such as fluoro.[41] In the same vein, ion-dipole and/or dipole-dipole interactions have been suggested to be responsible.[53] Apart from the fact that it would be a tall order to explain all of our results in that way, such interactions should be demonstrable by virtue of their solvent sensitivity – but no such solvent effects have been noticed. An interesting example is provided by the isoelectronic pair of molecules shown below; we recently examined the latter in the hope that our generally small E/Z product ratios might be larger if C_5 were replaced by positive nitrogen (Scheme 13). Indeed, we found the preference for *syn*-attack in reduction and in methylation in this case to reach values of 20–30. This type of substrate would seem to be tailor-made for dipole-ion interactions;[54] however, the ratio is the same in methanol, water and saturated aqueous sodium chloride.[55].

A different kind of objection that is sometimes made[56] is that it is difficult to understand why electron delocalization into an antibonding orbital should occur even as the bond is forming. However, this apparently reasonable argument is mostly the result of false intuitions fed by too literal an interpretation of such words as »anti-bonding« and »bond formation.« If we apply the same intuitions to the elimination process, we would be led to think that such hyperconjugation is reasonable in that reaction since the terms »anti-bonding« and »bond-cleavage« are not so awkwardly juxtaposed. However, the transition states for addition and elimination are the same, by virtue of microscopic reversibility, and what's reasonable in one direction must be reasonable in both. Rather than be concerned about the »paradoxical« nature of the electron flow, we should accept[55] that free energies can be lowered by hyperconjugative delocalization of electrons, and obviously they can and are.

Finally, a question might be raised about the possibility of hyperconjugation in the opposite direction, from the occupied $\sigma_{\neq}$ orbital into the antiperiplanar σ^* orbitals as proposed by Anh, and about the interaction between the filled σ and $\sigma_{\neq}$ orbitals as proposed by Felkin. Consideration of these questions would take us too far afield; however, we have considered them elsewhere.[57]

We conclude as follows. All additions, and all eliminations are accelerated to various degrees by hyperconjugation between the bond in transition and the antiperiplanar vicinal sigma bond(s). Included especially are the heterolytic formation and nucleophilic capture of carbocations. Such hyperconjugation is not different from sigma participation or sigma delocalization. All carbocations are affected by it, tertiary as well as secon-

Scheme 13

dary, and the distinction between »classical« and »non-classical ions« is not useful. Nevertheless, one question remains: does non-hyperconjugative sigma participation exist? Sorensen's trans-annular C-H bond assistance in the solvolysis of cyclodecyl sulfonates would seem to be a very clear example.[58] On the other hand, the Adcock-Shiner advocacy of *extended* hyperconjugation to explain the effect of a 5-trimethylstannyl group on the solvolysis rate ratio of 2-adamantyl esters[59] makes one hesitate even then. The last word on this topics has not been said.

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SAŽETAK

Participacija u solvolizi: pogled unatrag

William J. le Noble

Kritički se razmatraju koncepti koji su doveli do distinkcije karbokationa na klasične i neklasične. Autor zaključuje da sve adicije i eliminacije u stanovitoj mjeri uključuju hiperkonjugativnu interakciju veze koja se tijekom reakcije mijenja i antiperiplanarne vicinalne sigma veze(a). To posebno dolazi do izražaja pri heterolitičkom nastajanju i nukleofilnim reakcijama hvatanja karbokationa. Navedena se interakcija u biti ne razlikuje od sigma participacije ili sigma delokalizacije.