7533-40-6; **1g**, 24629-25-2; **1h**, 2899-37-8; **1i**, 85803-42-5; **1j**, 85803-43-6; **1k**, 56613-80-0; **1l**, 3182-95-4; **1m**, 5034-68-4; **1n**, 20989-19-9; **1o**, 85803-44-7; **1p**, 4836-52-6; **1q**, 2899-29-8; **1r**, 46032-98-8; **2a**, 67928-34-1; **2b**, 67928-33-0; **2d**, 85879-93-2; **2f**, 85803-45-8; **2k**, 85803-46-9; leucinol-d_2, 76427-93-5; N-(p-methoxybenzylidene)-2-amino-4-methyl-1-pentanol-d_2, 85803-47-0; N-(p-methoxybenzylidene)-p-n-butylaniline, 26227-73-6; L-norvaline, 6600-40-4; L-norleucine, 327-57-1; D-ethionine, 535-32-0; S-benzyl-L-cysteine, 3054-01-1; O-methyl-L-tyrosine, 6230-11-1; O-benzyl-L-tyrosine, 16652-64-5; (R)-**1b**, 5856-63-3.

Comments on the Application of the Gassman–Fentiman Tool of Increasing Electron Demand to the Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Substituted 2-Aryl-2-norbornyl Cations[1a]

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This paper is a rebuttal to the recent paper by Brown and co-workers entitled "Anomalous Carbon-13 Chemical Shifts with Increasing Electron Demand in the 2-Aryl-2-norbornyl Cations and Related Systems. Evidence That These Anomalous Shifts Are Not Diagnostic for the Onset of Nonclassical σ Bridging".[2] Our critical examination of all the available data clearly reveals that the deviation from linearity observed in the chemical shift plots of 2-aryl-2-norbornyl cations and related systems with more electron demanding substituents is uniquely consistent with the onset of nonclassical σ bridging. The Gassman–Fentiman tool of increasing electron demand, although coarse, is also capable of detecting the onset of enhanced π, $\pi\sigma$, and cyclopropyl conjugation in a wide variety of phenyl- and cyclopropyl-substituted cationic systems.

Recently Brown and co-workers[2] published a paper entitled "Anomalous Carbon-13 Chemical Shifts with Increasing Electron Demand in the 2-Aryl-2-norbornyl Cations and Related Systems. Evidence That These Anomalous Shifts Are Not Diagnostic of the Onset of Nonclassical σ Bridging". In this paper we present a rebuttal of Brown's criticism of our previous work. It is our contention that a more comprehensive examination of the data and a proper understanding of the method render Brown's conclusions invalid.

The Gassman–Fentiman tool of increasing electron demand was first applied to chemical shifts by Gassman, Richey, and Winstein[4] to measure the electron demand of the electron-deficient cationic center of 7-aryl-7-norbornenyl cations. Subsequently, it has been extensively used (notably by Brown) to probe the onset of σ, π, and $\pi\sigma$ participation in the solvolytic transition states of a large number of systems.[5] Indeed, the application of this probe in solvolysis has confirmed the onset of π participation in 7-aryl-7-norbornenyl[4] and 2-aryl-5-norbornen-2-yl systems[6] and the onset of $\pi\sigma$ participation in Coates' 9-aryl-9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl system.[7] The application of the same tool to the 2-aryl-2-norbornyl system in solvolytic studies failed to reveal the onset of σ participation[7,8] which led Brown to conclude that no such participation occurs in the parent 2-norbornyl system.

Extending the application of the same tool coupled with ^{13}C NMR spectroscopy as the structural probe under stable ion conditions allowed our groups to detect the onset of π, $\pi\sigma$, and σ delcoalization in a variety of systems.[9-15] The ^{13}C NMR chemical shifts of the cationic carbons of a series of arylcyclopentyl **2**, arylcyclohexyl **3**, 2-aryl-2-adamantyl **4**, 6-aryl-6-bicyclo[3.2.1]octyl **5**, and 7-aryl-7-norbornyl **6** cations (Chart I) correlate linearly with the observed cationic chemical shifts of substituted cumyl cations **1** over a range of substituents[16,17] (generally from the most electron releasing p-OCH_3 to the most electron withdrawing 3,5-$(CF_3)_2$ groups). However, systems such as the 7-norbornenyl **13**,[12] 5-norbornen-2-yl **14**,[10,11] 2-norbornyl **15**,[9] 8-tricyclo[5.2.1.0^{2,6}]decyl **16**,[11] and 9-aryl-9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl **17**[13] cations show deviations from linearity in such chemical shift plots with electron demanding substituents or show negative slope throughout the range of substituents considered. Brown and coworkers[17] recently developed σ^{C^+} substituent constants (based on a modified Hammett–Brown equation) which

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[1] (a) Stable Carbocations. 247. For part 246, see: Mertens, A. L.; Olah, G. A. *Chem. Ber.*, in press. (b) University of Southern California. (c) Michigan State University.

[2] Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089.

[3] Although Prof. Brown is kind enough to send us preprints of some of his articles, we were disappointed that we did not receive a preprint of this particular paper, nor were any of us selected as reviewers.

[4] (a) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 1545; **1970**, *92*, 2549. (b) Richey, H. G., Jr.; Nichols, D.; Gassman, P. G.; Fentiman, A. F., Jr.; Winstein, S.; Brookhart, M.; Lustgarten, R. K. *Ibid.* **1970**, *92*, 3783.

[5] Brown, H. C. "The Nonclassical Ion Problem"; Plenum: New York, 1977; Chapter 10.

[6] Brown, H. C.; Ravindranathan, M.; Peters, E. M. *J. Am. Chem. Soc.* **1975**, *97*, 2900.

[7] Coates, R. M.; Fretz, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 2538; **1977**, *99*, 297. Brown, H. C.; Ravindranathan, M. *Ibid.* **1977**, *99*, 299.

[8] Brown, H. C.; Ravindranathan, M.; Takeuchi, K.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 2899. Brown, H. C.; Rei, M. H. *Ibid.* **1964**, *86*, 5008.

[9] Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 5683.

[10] Farnum, D. G.; Botto, R. E. *Tetrahedron Lett.* **1975**, *46*, 4013.

[11] (a) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847. For preceding H^1 studies see: (b) Farnum, D. G.; Wolf, A. D. *J. Am. Chem. Soc.* **1974**, *96*, 5166.

[12] Olah, G. A.; Berrier, A. L; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 1122.

[13] Farnum, D. G.; Clausen, T. P. *Tetrahedron Lett.* **1981**, *22*, 549.

[14] For a comprehensive evaluation of the method see: Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998.

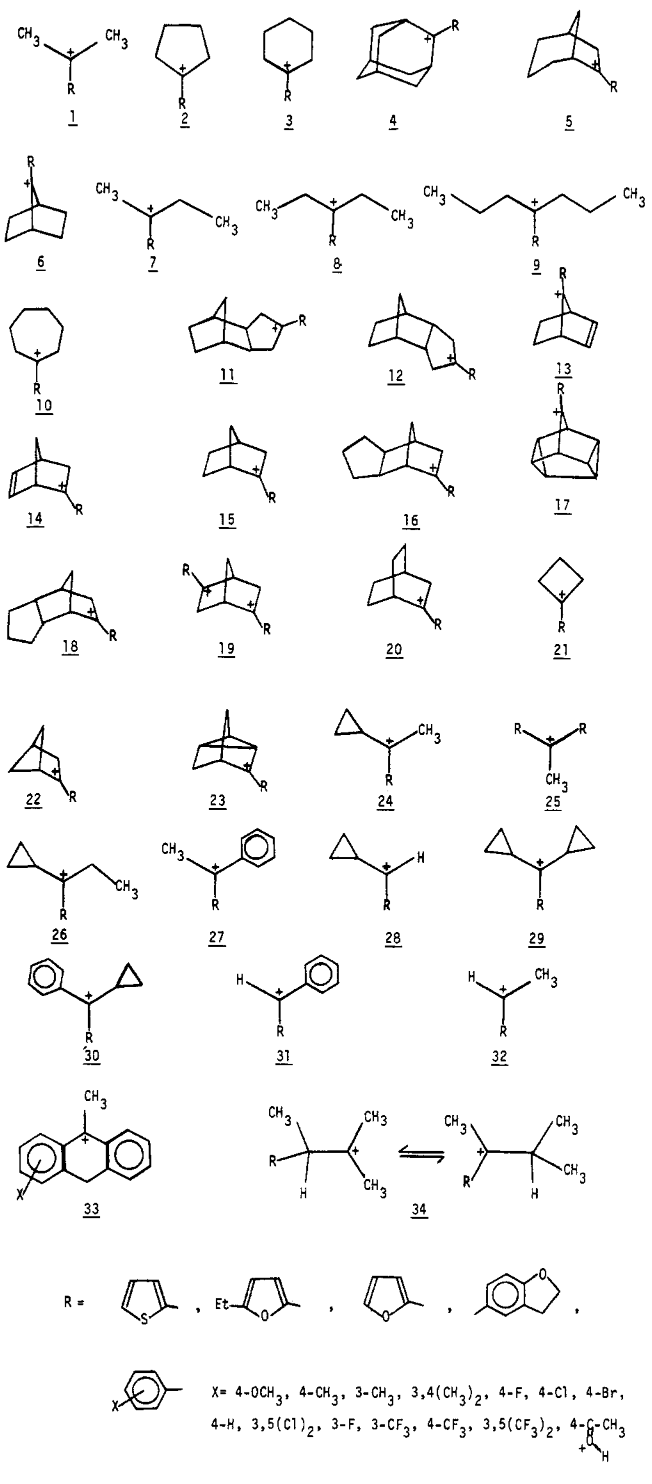
[15] Olah, G. A.; Berrier, Al. L.; Prakash, G. K. S. *J. Org. Chem.* **1982**, *47*, 3903.

[16] Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94* 2044.

[17] Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956.

0022-3263/83/1948-2146$01.50/0

Chart I



are considered to take into account the true electron demand of a carbocationic center in the superacid media. Since the σ^{C^+} constants were defined by a linear relationship with the ^{13}C NMR chemical shifts of the cationic carbon of 1-aryl-1-cyclopentyl cations **2**,[11b] Brown's approach provides no more information than the previously employed method of Farnum[11] and Olah[12] in which the ^{13}C chemical shifts of the cationic carbons of the arylcyclopentyl cations rather than σ^{C^+} values were used as reference values.[14] Since then, Brown, Kelly, and Co-workers published several papers[18–21] emphasizing the usefulness of the newly derived σ^{C^+} substituent constants in analyzing a series of ordinary trivalent cations. Since in most of these cases the cations had already been correlated with the arylcyclopentyl cations, it was no surprise that they also correlated with σ^{C^+}. In the course of their work they also developoed $\sigma^{C^+\alpha}$ substituent constants to correlate the chemical shifts of the neighboring carbon of the cationic center.[21] Their most recent paper analyzed the data for several systems such as **15**, **16**, **18** and **20–23**. However, their analysis disregarded systems such as **13**, *14*, **17**, and **19** which are quite relevant to the problem.

The general principle basic to the application of the Gassman–Fentiman tool of increasing electron demand is simply this: if a parameter for a number of structurally related systems shows a linear correlation with all of them and another apparently structurally related system is found in which this parameter deviates from linearity, then there *must* be some mechanism operating in the new system which is not *common* to all the others to account for the deviation. Note that the principle does *not* state that if a deviation is *not* found the mechanism is not operating. Nor does it state that if two systems show the same or similar deviations the same mechanism must be operating in both cases. A proper understanding of the general principle will help considerably to clarify the confusion introduced by Brown's interpretation of the data.

It is the objective of this paper to examine critically the paper of Brown and co-workers[2] point by point, and show their inappropriate selection of data and their misapplication of th Gassman–Fentiman tool of increasing electron damand which invalidate their conclusins. In our discussion we will try to avoid a detailed review of our previously published work in this area.[9–15]

Discussion

Points of Agreement. There are a number of points about which all three of our groups agree. First, and perhaps most significant for the scientific community, we agree on the data for all of the systems **1–34** in the many instances where duplicate (and even triplicate!) determinations have been made. Second, we agree that plots of the cationic carbon ^{13}C chemical shifts against σ^+ are not relevant—a point which Brown has made repeatedly and need make no more. Third, we all agree that plots of the cationic carbon ^{13}C chemical shift of the 2-arylnorbornyl cations against relevant parameters (1-arylcyclopentyl[15] and 6-aryl-6-bicyclo[3.2.1]octyl[11] cation chemical shifts, σ^{C^+})[17] show a deviation from the linearity as against the linearity observed in cations **1–12**.

Points of Disagreement. Brown's arguments against our interpretation of the anomalous behavior of 2-aryl-2-norbornyl cation as evidence for the onset of σ bridgeing fall into three categories: (1) Variations in the other chemical shifts (notably C_1 and C_6) with increasing electron demand are not consistent with the onset of σ bridging. (2) The deviation from linearity observed for the 2-arylnorbornyl cations is not observed for other cations claimed to the "nonclassical". (3) A number of other cations for which nonclassical character is either absent or claimed to be less pronounced do show the same or similar deviations. We will take up these arguments in order.

(1) Other Chemical Shifts. Although Brown is quite correct in pointing out that the chemical shift of the

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[18] Kelly, D. P.; Jensins, M. J.; Mantello, R. A. *J. Org. Chem.* **1981**, *46*, 1650.

[19] Brown, H. C.; Periasamy, M.; Liu, K. T. *J. Org. Chem.* **1981**, *46*, 1646.

[20] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3166.

[21] Brown, H. C.; Kelly, D. P.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3170.

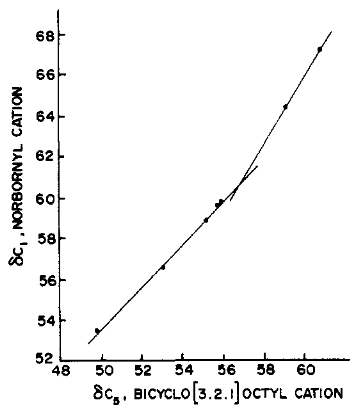

Figure 1. ^{13}C chemical shift of C_1 for the arylnorbornyl cations as a function of δC_5 for the 6-arylbicyclo[3.2.1]octyl cation.

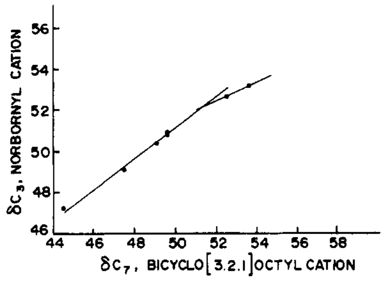

Figure 2. ^{13}C chemical shift of C_3 for the arylnorbornyl cation as a function of δC_7 for the 6-arylbicyclo[3.2.1]octyl cation.

bridgehead C_1 in the 2-arylnorbornyl cations shows a linear correlation with that of the methyl carbon in tertiary cumyl cations, hence also with his $\sigma^{C^{+}\alpha}$, the signifncance of this observation is not at all clear. Aside from the fact that an α-CH_3 group is a poor model for an α-CH at a bridgehead, the expected behavior of the chemical shift at C_1 with the onset of σ bridging is difficult to define. Although it is true that more positive charge is delocalized to C_1 with σ bridging, it is also true that the geometry, and therefore the shape of the electron distribution around it, may change, resulting in ill-defined changes in the chemical shift. For this reason, we plotted the chemical shift of C_1 vs. that of C_3 in both the 2-arylnorbornyl and 6-aryl-6-bicyclo[3.2.1]octyl cations[11] as a better probe. The results are entirely consistent with the onset of σ bridging in the norbornyl cation for electron-withdrawing substituents as revealed by a change in slope of the otherwise linear relationship—a change which is not observed for the classical model bicyclooctyl system. A further dissection of the change in slope can be obtained by plotting C_1 and C_3 of the 2-arylnorbornyl cation against, respectively, C_5 and C_7 (the α-carbons) of the bicyclooctyl model (Figures 1 and 2). These plots reveal that the change in slope has two components, a minor one from C_1 and a larger change from C_3, probably reflecting the fact that positive charge is being delocalized away from C_3 without any compensating changes in hydridization.

Thus Brown's objection can be rejected on two grounds: an inappropriate choice of a model system and a misapplication of the tool in regard to the conclusion that because a linear correlation *is* observed between two systems, the nonclassical mechanism is *not* operating.

Brown is also correct in pointing out that the regular downfield chemical shift of C_6 in the 2-arylnorbornyl cations correlates linearly with the chemical shift of the β-CH_2 group in the 1-cyclohexyl cations. He concludes that "the mechanism of charge attenuation is not different" in the two cations and that the onset of σ bridging should result in an *upfield* shift of the β-CH_2. Here again, however, although it is true that the bridging carbon in a fully developed σ-bridged ion shows a larger upfield shift, it is not possible at this time to predict the effect of the *onset* of σ bridging. The absence of a change in slope in no way precludes the onset of σ bridging. It simply indicates that the probe has not detected σ bridging. The fact that the β-CH_2 chemical shift changes by only 8 ppm compared with the α-carbon chemical shift variation of 14 ppm is an indication that it is less sensitive to changes in charge distribution and hybridization in these ions.

(2) Other Nonclassical Ions. The essence of Brown's argument here is contained in the following quote from his paper:[2] "In all of five cases, 2-norbornyl, 1-cyclobutyl, 2-bicyclo[2.2.1]hexyl, 2-bicyclo[2,2.2]octyl, and 6-bicyclo-[3.2.1]octyl, σ-bridged nonclassical cations have been proposed for the secondary cations. However, the plots of $\Delta\delta C^{+}$ against $\sigma^{C^{+}}$ for the last four aryl tertiary cations all show excellent linear correlations. Accordingly, the deviation observed for the 2-aryl-2-norbornyl case is not characteristic of systems considered to be nonclassical". It is clear that this argument misunderstands the principle basic to the application of the Gassman–Fentiman tool of increasing electron demand. There are many reasons why the tool might not detect the onset of σ bridging in the tertiary aryl cation, even though the parent secondary ion might give evidence of σ bridging. Among them are poor geometry for σ-orbital overlap in the tertiary ion, a sharp increase in steric strain with the onset of bridging, too little energy gain upon bridging, and compensating chemical shift changes upon bridging. It is not neccessary to understand the reasons for the absence of a deviation from linearity in each case to identify σ bridging as the only acceptable explanation for the deviation observed in the 2-arylnorbornyl case. In fact, the chemical shift additivity relationship used effectively by Olah and Schleyer[22] implies that the parent, secondary, 2-norbornyl cation is "more fully σ bridged" than either the cyclobutyl or bicyclohexyl system. The bicyclo[3.2.1]octyl and bicyclo[2.2.2]octyl cations have never given evidence of the extensively developed σ bridging present in the norbornyl cations. The 2-methylbicyclo[2.2,2]oct-2-yl cation gives no evidence for σ bridging,[22] in contrast to the 2-methylnorbornyl cation.[22] To expect to detect the onset of σ bridging in the arylbicyclooctyl systems is totally unrealistic.

Not only has Brown misapplied the tool in this argument but he has also failed to emphasize that the onset of bridging has been detected by the tool in a number of systems generally agreed to be bridged based on other criteria. Thus, the π-bridged norbornenyl systems **13**[12] and **14**[13] show deviations from linearity as expected, and the σ-bridged Coates cation shows a reverse slope over the entire range of aryl substituents.[17] In fact, of the 34 cationic systems given, 19 show a linear relationship over the entire range of substituents studied, including the especially significant dication **19**,[23] which serves as a good model for the geometry of the norbornyl cation. For only two of these have the parent secondary catins been shown to exhibit significant σ bridging (**21** and **22**). Of the 15 systems that do show a deviation from linearity, the parent secondary cations of six (**13**–**18**) have shown evidence for significant σ bridging. The deviations observed for most of the remaining nine have been accounted for on other grounds.[11,14,24-26]

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(22) Schleyer, P. v. R.; Lenoir, D.; Mison, P.; Liang, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1980**, *102*, 683.

(23) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Am .Chem. Soc.* **1980**, *102*, 6127.

(24) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666.

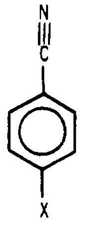
We therefore propose that Brown's claim that the deviation from linearity observed in the 2-aryl-2-norbornyl cations is not characteristic of σ bridging is in error. Interpretation of the deviation as evidence for the onset of σ bridging is entirely consistent with the behavior of other cations, both normal and bridged.

(3) Nonlinear Behavior of Other Ions. Brown cites three types of ions as evidence of systems where the Gassman–Fentiman tool of increasing demand detects nonlinear behavior, yet σ bridging is either absent or considerly attenuated: 2-aryl-*exo*/*endo*-5,6-trimethylene-2-norbornyl cations (**16**, **18**), the aryl cyclopropylcarbinyl cations (**23**, **24**, **26**, **28**), and the diarylcarbinyl cations (**27**, **31**). We quote his conclusion: "Thus there are three different molecular systems, 2-norbornyl, cyclopropylcarbinyl, and diarylalkyl, which all show similar (in some cases, almost identical) deviations in the plots of $\Delta\delta C^+$ against σ^{C^+}. In each of the three cases, three different reasons have been proposed previously for these deviations: onset of σ bridging, onset of cyclopropyl conjugation (ill-defined) and steric inhibition of resonance. In addition, a variety of other alicyclic cationic systems which have been suggested to have nonclassical, σ-bridged, secondary, cationic structures do not show deviations in the plots of their aryl derivatives. Accordingly, we conclude that the anomaly in the plots of the cationic carbon chemical shifts against σ^{C^+} is not diagnostic for the onset of nonclassical σ bridging in 2-aryl-2-norbornyl cations". The error in this line of reasoning should now be clear. It is not at all necessary, nor even likely, that every deviation from the linear relationship observed for ordinary cations have the same origin. The problem of interpretation is to identify all plausible causes of the deviation in a given case and then, by careful experiment and reasoning, to eliminate those that are not significant. We have done this for the 2-arylnorbornyl cations and are left with σ bridging as the only satisfactory explanation for the results. The fact that the *exo*- and *endo*-trimethylenenorbornyl systems show a similar deviation from linearity, even though it has been suggested that σ bridging in the endo cation is sterically hindered, presents a different problem for interpretation. There may be any number of explanations for this observation, but it seems to us most likely that σ bridging in these tertiary aryl cations, even with electron-withdrawing substituents, is not very far advanced. Therefore steric hindrance is not significant. The cyclopropylcarbinyl systems present yet a different problem for an interpretation in which σ bridging is probably not the explanation. Whatever the explanation, be it cyclopropyl conjugation, dynamic equilibrium, or some combination of factors,[27] it need have nothing to do with the origin of the phenomenon in the norbornyl system. The same can be said for the diarylcarbinyl cations, for which Brown[2] has stated our interpretation in terms of steric hindrance to coplanarity[11] very clearly. We see no reason to alter that interpretation. Nor do we see any reason to alter the different interpretation in the norbornyl system.

Other Possible Reasons for Deviations from Linearity. It should be apparent from the above that Brown has presented no valid argument against σ bridging as a possible explanation for the deviation from expected linearity observed in some of the ^{13}C NMR correlations for the 2-arylnorbornyl cations. The question to be dealt with here is: "Are there reasonable alternative explanations?" In our earlier work we considered equilibrating cations as the most commonly offered alternative and ruled it out on the basis of both theoretical and experimental considerations.[11] Brown has recently reported a definitive experiment which distinguishes between a rapidly equilibrating cation pair (e.g. **34**) and a statric cation based upon temperature effects on chemical shifts.[26] He agrees that the arylnorbornyl cation system is not a rapidly equilibrating pair.

In order to limit the number of plausible alternative explanations, we chose cations as close as possible in structure to the norbornyl cation for classical models. Thus the arylbicyclooctyl cations (**5** and **20**) and especially the diarylbicycloheptyl dications (**19**) were shown to be normal in their ^{13}C NMR correlations.[11] These cations mimic very closely the geometry, steric requirements, and substitution patterns in the 2-arylnorbornyl cations, yet do not shown deviations from linearity. Any reasonable alternative explanations must account for these facts.

(1) Single Substituent Parameter. Brown's discussion of the Hammett single and double substituent parameter (DSP) treatments is quite irrelevant to our treatment, since our corrlatins use ^{13}C NMR chemical shifts of closely related model cations as reference values. He himself recognizes that the use of the DSP treatment is not "likely to substantially improve the correlations". He does suggest that the inductive π-polarization phenomenon observed by Brownlee and co-workers[28] in neutral para-substituted benzonitriles, styrenes, acetophenones, benzophenones, etc. may explain our results. In the case of para-substituted benzonitriles **35**, Brownlee and co-workers[28] observed a reversal of chemical shifts of the nitrile carbon with increasing electron demand of the para substituent (i.e., from gradual deshielding to shielding with increasing electron demand). However, the ipso carbon is gradually deshielded with increasing electron demand. Similar observations were made on acetophenones, styrenes, and benzophenones. In the case of styrenes **37**, the α-carbon undergoes a downfield shift from Z = p-OCH_3 to X = H and then an upfield shift from X = H to X = p-CF_3. The β-carbon, however, underwent a regular deshielding. Interestingly, in the case of styrenes, the C_α chemical shift spread is less than 2 ppm whereas C_β varies by almost 7 ppm. A similarly large spread of 13 ppm is observed for the ipso carbon of the aromatic ring (Table II). A similar comparison (Table I) of the 2-aryl-2-norbornyl system **15** reveals, however, extraordinarily large changes for the C_2 chemical shifts over the range of substituents studied (~40 ppm).



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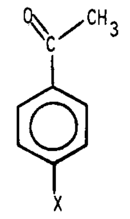

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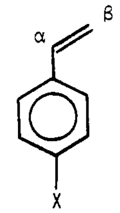

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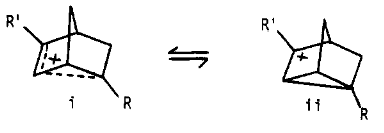
[25] Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 4742.

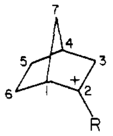
[26] Brown, H. C.; Periasamy, M., submitted for publication in *J. Org. Chem.* (paper no. 43, personal communication).

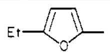
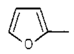
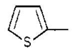
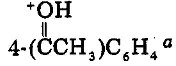
[27] The deviation from linearty observed in **23** and other cyclopropyl carbinyl cations presents a complex, fascinating puzzle. We intend to publish a separate paper presenting arguments in support of an equilibrating pair of ions (e.g.; i ⇄ ii) to account for the phenomenon.



[28] Bromilow, J.; Brownlee, R. T. C. *Tetrahedron Lett.* **1975**, *25*, 2113.

Table I. Relevant ^{13}C NMR Chemical Shifts of 2-Substituted 2-Norbornyl Cations in FSO_3H/SO_2ClF or $SbF_5:FSO_3H/SO_2ClF$ at −80 °C



R	shift, ppm			
	C_1	C_2	C_3	C_6
	49.4	195.0, 194.4	42.6, 41.8	29.9, 29.2
	50.5	206.7, 206.1	43.2, 42.6	29.2, 28.5
	55.2, 53.9	223.7, 223.4	46.0, 46.7	30.7, 30.6
4-$(OCH_3)C_6H_4$	52.0	238.3	45.6	30.4
4-$(CH_3)C_6H_4$	56.3	252.3	48.6	32.4
3-$(CH_3)C_6H_4$	58.3	258.8	49.8	33.4
C_6H_5	59.3	260.5	50.5	34.3
4-$(CF_3)C_6H_4$	63.6	264.5	51.9	36.3
4-$NH^+(CH_3)_2C_6H_4$	65.5	264.6	53.2	37.8
3,5-$(CF_3)_2C_6H_3$	66.2	262.8	52.4	38.0
 $4\text{-}(\overset{{}^{+}OH}{\overset{\|}{C}}CH_3)C_6H_4$ [a]		255.0		

[a] Equilibrating system.

Table II. Selected ^{13}C NMR Chemical Shifts of Para-Substituted Styrenes[a]

$4\text{-}XC_6H_4C_\alpha H{=}C_\beta H_2$

X	shift, ppm		
	C_1	C_α	C_β
4-OCH_3	130.23	136.29	110.98
4-CH_3	134.78	136.73	112.20
4-H	137.40	136.96	113.20
4-Cl	135.69	135.69	113.97
4-F	133.95	136.11	113.43
4-CF_3	140.68	135.64	116.02
4-$C(O)CH_3$	141.35	136.07	115.91
4-NO_2	143.08	135.03	117.90

[a] Reference 31b.

It is not at all clear how the Brownlee explanation in terms of inductive π polarization can even be applied to the cations, which have no π electrons to polarize. In fact, in a subsequent paper Brownlee and co-workers[29] have observed that the reversal of the chemical shift trend seen in neutral para-substituted acetophenones almost diminishes in the case of protonated acetophenones (decrease in polarization due to decrease in carbonyl π-bond character upon protonation). Hence even in more electron-deficient π systems contributions from such inductive π polarization becomes negligible. Furthermore, no such effect is observed in the case of normal tertiary aryl cations, including the 2,5-norbornyl dications. We conclude that the Brownlee π-polarization explanation is not applicable to these tertiary aryl cations.

(2) Decreased Electron Demand by the Carbocations. Brown suggests that stabilizing groups on carbocations would result in polar substituent effects becoming more important relative to conjugative effects for aryl rings containing electron-withdrawing substituents. As a result the carbocationic center chemical shift would become more shielded instead of deshielded, as in the case of the substituted styrenes. If this were true one would expect cations of similar stability to show similar deviations. Brown's ρ values, which measure the sensitivity of the ^{13}C NMR chemical shift to substituent effect, can be taken as a good measure of cation electron demand. Why then do the arylnorbornyl cations ($\rho = -14.03$) show a deviation, while the arylbicyclohexyl cations (**22**, $\rho = -14.4$) do not? Or, why do the arylphenylethyl cations (**27**, $\rho = -10.9$) show a deviation, while the symmetrically substituted diarylethyl cations ($\rho = -13.3$) do not? Or why do the arycyclopropylmethylcarbinyl cations (**24**, $\rho = -10.5$) show a deviation, while the aryldicyclopropylcarbinyl cations (**29**, $\rho = -.65$) do not? There is clearly no correlation betwen simple cation stability and nonlinearity. The ρ value for the norbornyl cation (−14.03) is, in fact, not terribly different from the ρ values for the closely related classical bicyclic models (−17.1, −15.4).

(3) Steric Hindrance to Coplanarity. Brown also suggests that steric hindrance to coplanarity of the aryl group in the 2-arylnorbornyl cations would make the polar effect of the substituent more important compared to the resonance effect for the electron-withdrawing aryl groups. However, no deviation is observed in the closely related bicyclic cations (**5** and **20**), and especially the diarylbicyclo[2.2.1]heptyl dication (**29**), where the steric requirements must be nearly identical. In fact, Brown himself has shown that, in the hindered *o*-methyl-*tert*-cumyl cations, hindrance to coplanarity does *not* lead to a deviation from linearity in the plot of $\Delta\delta C^+$ against σ^{C^+}.[30] This explanation of Brown's is closely related to our interpretation of the deviation observed for the arylphenylethyl cation (**27**). However, in the symmetrical diarylethyl cations, where the aryl groups are also not coplanar, no deviation is observed. Again the steric hindrance to coplanarity argument can be rejected as inconsistent with the facts.

Conclusions

In the present paper we have shown major flaws in the arguments put forth by Brown and co-workers[2] against our earlier reported application of the Gassman–Fentiman tool

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of increasing electron demand to detect the onset of σ bridging in 2-aryl-2-norbornyl system **15** and related systems **16** and **18** with substituents more electron demanding than phenyl. We have also shown that in some cases with similar deviations the origin of such effects may be entirely different. Judicious application of the Gassman–Fentiman tool of increasing electron demand coupled with ^{13}C NMR spectroscopy as the structural probe is useful to determine the onset of π, πσ, or σ delocalization provided alternative explanations for the data are ruled out. No claim was ever made by the originators that the method was selective for σ delocalization. However, it should be reemphasized that, since phenyl groups even with electron-withdrawing substituents can still delocalize charge into the π system, the method is not sensitive enough to detect bridging in cases where structural changes are limited, including systems which are partially bridged or delocalized. For the same reasons the method must be considered ineffective in may solvolytic studies, since solvation significantly masks the electron demand of the cationic center in the solvolytic transition state unless the structural change is significant (as in the case of the 7-norbornenyl, 5-norbornen-2-yl, or pentacyclononyl systems).

We make no sweeping new claims for the Gassman–Fentiman tool of increasing electron demand. Nonetheless, in the midst of the polemics, the clear fact remains that the norbornyl cation, when probed with this tool, responds in a way qualitatively different from a large number of normal cations. That difference begs to be explained and is uniquely consistent with the onset of σ bridging. Until a definitive experiment appears which is inconsistent with that interpretation or an acceptable alternate explanation appears which is consistent with all the facts we see no reason to alter our conclusion.

We are therefore amused to read Brown's concluding statement[2] "We have now shown that such deviations are not diagnostic of nonclassical σ bridging. Thus this criterion must join the huge graveyard of disproved criteria for nonclassical structures." It seems to us that this criterion, along with many others "laid to rest" by Brown, will, like Lazarus, refuse to accept this premature consignment to the tomb.

Mercury in Organic Chemistry. 24.[1] Mercuration and Subsequent Carbonylation of 4-Hydroxy-2-alkyn-1-ones: A Novel Route to Furans

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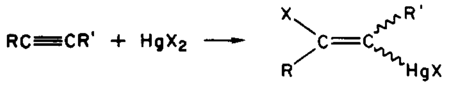
Mercuric chloride readily adds to the carbon–carbon triple bond of certain 4-hydroxy-2-alkyn-1-ones (**3a**, **3b**, and **3e**) to give vinylmercurials which appear to be the first syn addition compounds of mercuric chloride. These vinylmercurials readily dehydrate to 3-furylmercurials. Palladium-promoted carbonylation of these compounds affords 3-furyl carbonyl compounds.

Mercury(II) salts are known to readily add to a variety of acetylenes to afford vinylmercurials (eq 1). Thus,



(1)

X = F, Cl, OAc, SCN

mercuric halides are reported to add to acetylene (anti),[2-7] propyne (anti),[8] cyclooctyne,[9] vinylacetylene (anti?),[8,10-12] alkynyl ethers,[13-15] propargylic alcohols (anti)[16-18] and halides (anti),[16,19] and α,β-unsaturated ketones,[20] acids (anti),[21-23] and esters (anti?)[21,24,25] with the stereochemistry

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