Structural Effects in Solvolytic Reactions. 46. Carbon-13 NMR Studies of Carbocations. 11.[1] Anomalous Carbon-13 Chemical Shifts with Increasing Electron Demand in a Model Classical 2-Norbornyl System, the 2-Aryl-3-methylene-2-norbornyl Cations

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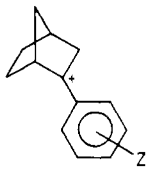
Abstract: The 3-methylene-2-norbornyl cation has long been accepted as a model "classical" 2-norbornyl system. Allylic resonance involving the 3-methylene group stabilizes the positive charge, rendering σ-bridging in this system insignificant. Accordingly, the ^{13}C NMR spectra of a series of 2-aryl-3-methylene-2-norbornyl cations (**4**) were measured in $SbF_5/FSO_3H/SO_2ClF$ at −80 °C to test the proposal that deviations from linearity in plots of the ^{13}C NMR shifts of the cationic carbon ($\Delta\delta C^+$) in the 2-aryl-2-norbornyl cations vs. the σ^{C^+} constants provide evidence for σ-bridging in the parent cation. In fact, the observed shifts ($\Delta\delta C^+$) give a linear correlation for the electron-donating substituents, with $r = 0.998$ and $\rho^{C^+} = -10.0$. On the other hand, the points for the electron-withdrawing substituents deviate upward from this line. No correlation has been observed for the presence (D) or absence of such deviations (ND) in the 2-aryl derivatives of parent systems that are accepted as being classical cations (C) or those that are postulated to be nonclassical cations (NC): 1-aryl-1-cyclobutyl (NC, ND), 2-aryl-2-bicyclo[2.1.1]hexyl (NC, ND), 3-aryl-3-nortricyclyl (C, D), 2-aryl-*exo*-5,6-trimethylene-2-norbornyl (C, D), 2-aryl-*endo*-5,6-trimethylene-2-norbornyl (NC, D), 2-aryl-2-bicyclo[2.2.2]octyl (NC, ND), 2-aryl-2-bicyclo[3.2.1]octyl (NC, ND), 2-aryl-2-norbornyl (NC, D), 2-aryl-3-methylene-2-norbornyl (C, D).

Application of the tool of increasing electron demand to the study of fully formed carbocations in superacids requires the plotting of carbon-13 chemical shifts against some quantitative measure of electron demand. The use of Hammett–Brown σ^+ constants has been shown to be inappropriate for this purpose,[3] and new enhanced σ^{C^+} constants have now been developed.[4] When applied to a range of acyclic, cyclic, and polycyclic dialkylaryl systems, these σ^{C^+} constants give excellent linear correlations for the cationic carbon substituent chemical shifts ($\Delta\delta C^+$).[5-10] However, when $\Delta\delta C^+$ values for the 2-aryl-2-norbornyl cations **1** are plotted against σ^{C^+}, the plot is linear for the electron-donating substituents but deviates from linearity for substituents more electron demanding than H, the deviation taking the form of an upward curve due to an increase in shielding of C^+ with increasing electron demand.[11] This phenomenon has been attributed by both Farnum and Olah and their co-workers to the onset of nonclassical σ-bridging in these tertiary cations.[12,13] However, other cationic systems for which nonclassical σ-bridged structures have also been proposed for the secondary cations, such as 1-cyclobutyl and 2-bicyclo[2.1.1]hexyl, fail to exhibit these deviations in the $\Delta\delta C^+$–σ^{C^+} plots.[11a]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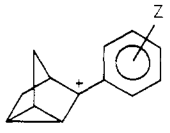
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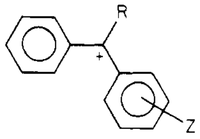
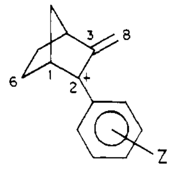

3a, R = H
b, R = CH_3

The deviation from linearity observed in the plot for **1** is also observed in those for **2** and **3**, in which σ-bridging is impossible. The "onset of increased cyclopropyl conjugation" (not further defined) was given as the reason for the deviation in **2**[14] and steric hindrance to coplanarity as the reason for the deviation in **3**,[12,15-17] yet all three plots are qualitatively similar.[11a]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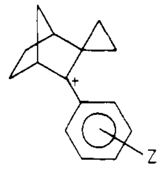
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It appeared that the 2-aryl-3-methylene-2-norbornyl (**4**) and the 2-aryl-3-spirocyclopropane-2-norbornyl (**5**) cations should provide a valuable test of these alternative interpretations. It was previously noted that the solvolyses of the parent secondary 2-norbornyl derivatives containing either a methylene or a spiral cyclopropane moiety in the 3-position exhibit low exo/endo rate

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(1) For parts 45 and 9 in the respective series, see ref 24. For part 10, see ref 17.

(2) Postdoctoral research associates on a grant provided by Exxon Research and Engineering Co.

(3) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1978**, *31*, 1209–1221.

(4) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956–6960.

(5) Brown, H. C.; Periasamy, M.; Liu, K.-T. *J. Org. Chem.* **1981**, *46*, 1646–1650.

(6) Kelly, D. P.; Jenkins, M. J.; Mantello, R. A. *J. Org. Chem.* **1981**, *46*, 1650–1653.

(7) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3161–3165.

(8) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3166–3170.

(9) Giansiracusa, J. J.; Jenkins, M. J.; Kelly, D. P. *Aust. J. Chem.* **1982**, *35*, 443–450. Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 5–8.

(10) The substituent chemical shift is defined as $\Delta\delta C^+ = [\delta C^+(H) - \delta C^+(Z)]$ in order to reproduce the form of the Hammett–Brown equation with ρ negative.

(11) (a) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089–2101. (b) For a recent rebuttal, see: Olah, G. A.; Surya Prakash, G. K.; Farnum, D. G.; Clausen, T. P. *Ibid.* **1983**, *48*, 2146–2151.

(12) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847–3855.

(13) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998–2002.

(14) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 1122–1128.

(15) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1983**, *47*, 4740–4742.

(16) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1983**, *47*, 4742–4745.

(17) Kelly, D. P.; Jenkins, M. J. *J. Org. Chem.* **1984**, *49*, 409–417.

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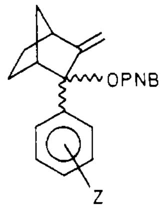
Table I. ^{13}C NMR Shifts of 2-Aryl-3-methylene-2-norbornyl Cations in $SbF_5/FSO_3H/SO_2ClF$ at −80 °C

	chemical shift[a]														
substituent (Z)	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_1'	C_2'	C_3'	C_4'	C_5'	C_6'	C_Z
p-OCH_2CH_2-*m*	52.1	207.1	156.4	48.1	25.0	31.0	41.4	137.3	128.9	138.5, 137.4^b	136.2	181.8	115.7	146.7, 147.9^b	27.4, 78.9
p-OCH_3	53.0	211.8	156.6	48.1	24.8	31.3	41.5	138.8	127.9	145.8^b	119.9^c	179.4	119.4^c	144.3^b	58.8
p-CH_3	56.5	225.9	158.3	48.5	24.2	32.4	42.5	147.2	131.5	142.3^b	134.0^c	166.2	133.7^c	139.8^b	23.9
p-F	58.0	227.4	158.8	48.7	24.0	32.8	42.7	149.5	130.1	146.1^b (14)	121.1^c (22)	176.7 (282)	120.7^c (22)	143.6^b (14)	
p-Cl	58.4	229.0	159.1	48.7	24.0	33.0	43.0	150.5	131.5	142.6^b	133.3	157.6	133.3	140.0^b	
m-CH_3	58.0	230.4	159.0	48.5	24.0	32.7	42.8	150.1	132.3	139.7 141.9^b	143.9, 143.6^c	150.4	133.6, 132.6^c	138.9, 136.7^b	20.8
H	58.3	231.1	158.9	48.4	23.8	32.7	42.7	151.3	133.0	141.9^b	132.4^c	148.6	132.4^c	139.1^b	
m-F	60.0	232.6	159.6	48.8	23.8	33.5	43.2	153.7	134.1	124.1 (21)	164.2 (253)	137.0 (21)	134.5	135.2	
m-Cl	60.0	232.5	159.6	48.8	23.7	33.5	43.3	153.8	133.7	139.4^b	138.6	146.7	133.9	138.3^b	
m-CF_3	60.7	233.8	159.9	48.8	23.7	33.8	43.4	155.1	133.5	135.3	136.1 (34)	142.6	133.3	132.6	123.6 (272)
3,5-Cl_2	61.5	233.3	160.1	48.9	23.5	34.2	43.6	156.1	134.1	140.5^b	139.1	144.7	139.1	136.5^b	
p-CF_3	61.4	234.9	160.2	48.8	23.6	33.9	43.6	156.2	134.6	139.9	128.7	144.8 (34)	128.7	139.9	123.5 (274)
3,5-$(CF_3)_2$	62.9	234.7	160.4	49.1	23.4	34.8	43.9	158.4	132.8	137.9	135.3 (35)	137.9	135.3 (35)	137.9	122.9 (273)

[a] Chemical shifts are in parts per million downfield from external Me_4Si (capillary). The signals were assigned on the basis of off-resonance experiments and by comparison with the data reported for the 2-aryl-2-norbornyl cation (ref 11). [b] Assignments may be interchanged. [c] Assignments may be interchanged.

ratios.[18] It was argued that the delocalization of charge from C2 in these derivatives makes impossible the type of σ-bridging proposed for 2-norbornyl itself. Consequently, on the basis of the Olah–Farnum interpretation, in the absence of other controlling factors, no deviations in the ^{13}C shifts should be anticipated. It should be recalled that the solvolyses of the 2-aryl derivatives **6** and **7** yield high exo/endo rate ratios[19] similar to those observed for the 2-aryl-2-norbornyl system, a powerful argument for the steric interpretation of the high exo/endo rate ratios in the solvolysis of tertiary 2-norbornyl derivatives (**8**).[20]



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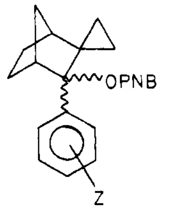

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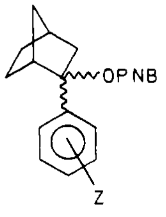

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Results

2-Aryl-3-spirocyclopropane-2-norbornyl and 2-Aryl-3-methylene-2-norbornyl Cations. The cations **4** and **5** were prepared by ionization of the corresponding endo alcohols at −78 °C in excess SbF_5/FSO_3H (1:1) diluted with SO_2ClF. The alcohols were prepared by standard Grignard reactions of 3-methylene-2-norbornanone or 3-spirocyclopropane-2-norbornanone with the appropriate aryllithium or arylmagnesium bromide. Use of the latter reagent with the 3-methylene derivative resulted in the formation of substantial amounts (20–30%) of the 1,4-addition product, 8-aryl-2-norbornanone, which was removed by semicarbazone formation. The ^{13}C NMR data of the cations are summarized in Table I.

Unfortunately, preparation of the cations **5** was accompanied by rapid opening of the spirocyclopropane moiety in the case of derivatives containing electron-withdrawing substituents. Consequently, the ^{13}C shifts in this system could not be followed for the substituents of special interest, so the study was necessarily limited to the 3-methylene derivatives.

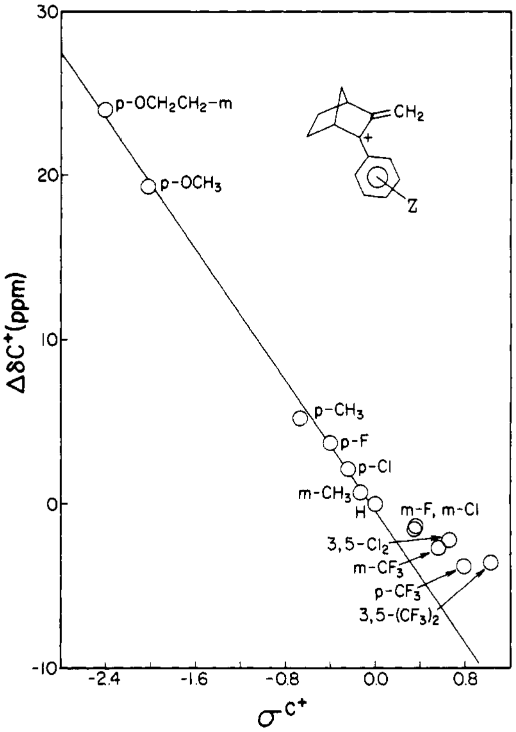

Figure 1. Plot of $\Delta\delta C^+$ against σ^{C^+} values for 2-aryl-3-methylene-2-norbornyl cations: correlation coefficient, $r = 0.998$; slope, $\rho^{C^+} = -10.0$ (correlation analysis for electron-donating substituents only).

A plot of the $\Delta\delta C^+$ values against σ^{C^+} constants[21] gives a linear correlation for the points for the electron-donating substituents with $\rho^{C^+} = -10.0$ and $r = 0.998$ (Figure 1). However, the points for the electron-withdrawing substituents deviate upward from this correlation line in a qualitatively similar fashion to that observed in the plot of the 2-aryl-2-norbornyl cations (**1**).[11a] If this deviation observed for **1** were due to the onset of nonclassical σ-bridging, the deviation should be absent in the case of the 3-methylene-2-norbornyl cations **4**, since such nonclassical σ-bridging would surely be swamped by allylic conjugation. Clearly

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(18) (a) Wilcox, C. F., Jr.; Jesaitis, R. G. *Chem. Commun.* **1967**, 1046–1047. (b) Wilcox, C. F., Jr.; Jesaitis, R. G. *Tetrahedron Lett.* **1967**, 2567–2572.

(19) Brown, H. C.; Gundu, Rao, C. *J. Org. Chem.* **1979**, *44*, 3536–3540.

(20) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432–440.

(21) Since $\Delta\delta C^+$ for 1-aryl-1-cyclopentyl cations plot linearly against σ^{C^+} ($r = 0.999$), a plot of $\Delta\delta C^+$ values against σ^{C^+} is equivalent to a plot of $\Delta\delta C^+$ values for a system against the values for 1-aryl-1-cyclopentyl.[12,13]

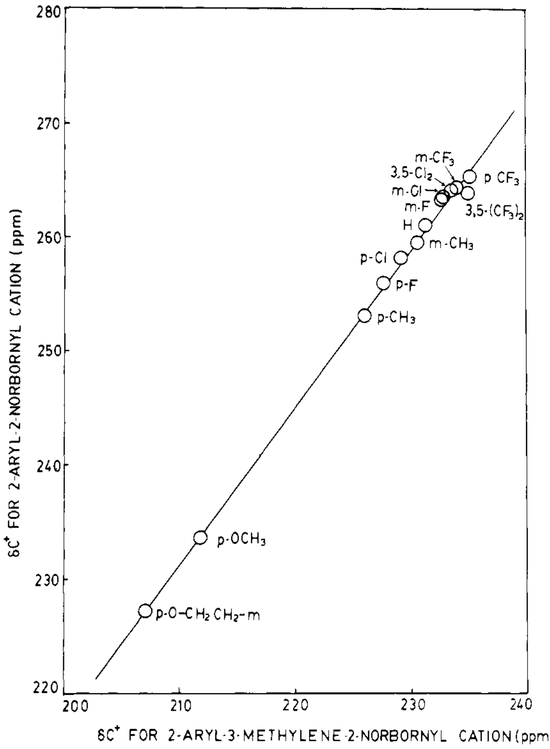


Figure 2. Plots of δC^+ for the 2-aryl-3-methylene-2-norbornyl cations against δC^+ for the 2-aryl-2-norbornyl cations (slope = 1.39; r = 0.998).

this is not the case, and the plots for all four systems, **1**, **2**, **3**, and **4**, are very similar.

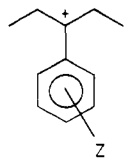
Indeed, a plot of δC^+ for the 2-aryl-3-methylene-2-norbornyl cations against δC^+ for the 2-aryl-2-norbornyl cations (Figure 2) reveals a reasonably good linear relationship, with only the point for 3,5-$(CF_3)_2$ exhibiting a minor deviation.

Discussion

There has long been a need for an objective means of testing different cationic systems for the oft-postulated presence of σ-bridging.[22a] For a number of years we explored the use of the tool of increasing electron demand[22b] as a means for such testing. With one exception, this tool indicated the absence of such bridging in many systems where it had been postulated.[22b]

The Olah/Farnum proposal that the deviation observed in the plot of $\Delta\delta C^+$ vs. σ^{C^+} for the 2-aryl-2-norbornyl cations indicated the onset of σ-bridging with the more electron-withdrawing substituents[12,13] suggested that this phenomenon might provide a valuable basis for testing for the presence of σ-bridging in other systems where it has been proposed. Accordingly, we undertook to apply this procedure to a number of recognized classical systems as well as to representative systems for which nonclassical (σ-bridged) structures have been proposed. It is appropriate to summarize our findings.

Classical Systems/No Deviations. A range of ten different cations representative of acyclic (e.g., 3-aryl-3-pentyl (**9**)), cyclic (e.g., 1-aryl-1-cyclopentyl (**10**)), and polycyclic (e.g., 2-aryl-2-adamantyl (**11**)) systems all give excellent correlations ($r \geq 0.998$) when their $\Delta\delta C^+$ values are plotted against the enhanced substituent constant σ^{C^+}.[5-10] The slopes of the plots are all strongly negative (ρ^{C^+} = −14 to −18, Table II) and are consistent with a normal electronic effect of the substituent; that is, increasing electron demand results in deshielding of the cationic carbon (type A, Figure 3).



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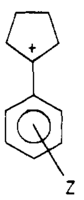

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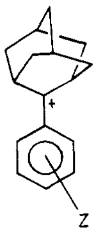

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Table II. ρ^{C^+} Values for Some Aryldialkyl Carbocations[a]

system	ρ^{C^+}
substituted *tert*-cumyl	−18.2[a]
2-aryl-2-butyl	−18.0
3-aryl-3-pentyl	−17.0
4-aryl-4-heptyl	−14.6
1-aryl-1-cyclopentyl	−17.1
1-aryl-1-cyclohexyl	−17.4
1-aryl-1-cycloheptyl	−16.5
9-aryl-*exo*-5,6-trimethylene-9-norbornyl	−16.3
9-aryl-*endo*-5,6-trimethylene-9-norbornyl	−16.0
2-aryl-2-adamantyl	−16.5

[a] This ρ^{C^+} value was taken from ref 4. All of the other values were taken from ref 11.

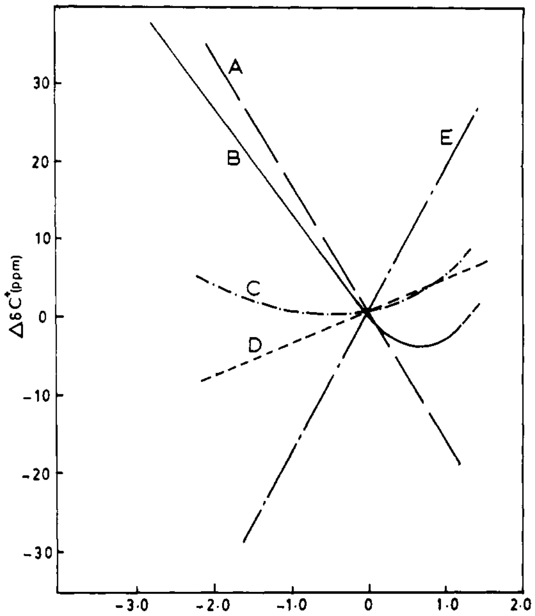

Figure 3. Plots of cationic carbon substituent chemical shifts ($\Delta\delta C^+$) against electron demand (σ^{C^+}) for different types of arylcarbocationic systems:[10] (A) "normal", e.g., 1-aryl-1-cyclopentyl (**10**); (B) "deviant", e.g., 2-aryl-2-norbornyl (**1**); (C) "highly deviant", e.g., 1-(4-methoxyphenyl)-1-aryl-1-ethyl; (D) "reverse", e.g., benzoyl (**20**); (E) "reverse" $\sigma\pi$-bridged, e.g., 9-aryl-9-pentacyclo$[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonyl (**21**).

Postulated Nonclassical Systems/Deviations. The $\Delta\delta C^+$–σ^{C^+} plot for 2-aryl-2-norbornyl cations (**1**) shows a straight line for the electron-donating substituents Z = H to 3,4-CH_2CH_2O- with ρ^{C^+} = −14.0, but the points for the electron-withdrawing substituents fall above the correlation line in the form of a curve (type B, Figure 3). As was pointed out, this increased shielding of the cationic carbon has been attributed previously to the onset of nonclassical σ-bridging.[12,13] We believe this to be improbable for the following reasons. (a) Carbons 1 and 6 exhibit regular deshielding with increasing electron demand (linear plots are obtained against an appropriate measure of electron demand).[11a] (b) No exceptionally shielded carbon is observed, such as might be expected for a penta-coordinated carbon in a σ-bridged structure; (c) The 2-aryl-*exo*- and -*endo*-5,6-trimethylene-2-norbornyl cations **12** and **13** both show similar (but slightly lower) deviations compared to **1**, although the *exo*-trimethylene ring has been proposed to hinder σ-bridging while the endo ring should correspondingly enhance σ-bridging.[11a] The deviations in the plots for **1**, **12**, and **13** all start at the same point, yet one should expect

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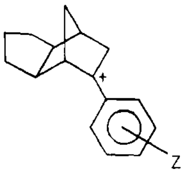
[22] (a) Brown, H. C. "The Nonclassical Ion Problem"; Plenum: New York, 1977. (b) See Chapter 10.



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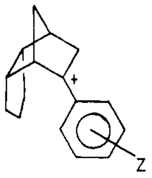

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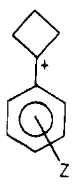
major differences between the three systems on the basis of the σ-bridging argument.

Postulated Nonclassical Systems/No Deviations. Four different systems were examined in which the parent secondary ions have been postulated to be nonclassical (σ-bridged).[22a] These include the 1-aryl-1-cyclobutyl (**14**), 2-aryl-2-bicyclo[2.1.1]hexyl (**15**), 2-aryl-2-bicyclo[2.2.2]octyl (**16**), and 2-aryl[3.2.1]bicyclooctyl (**17**) cations. However, none of these cations exhibit deviations of the kind observed for **1**, **12**, and **13**. That is, their plots correspond to type A, Figure 3.



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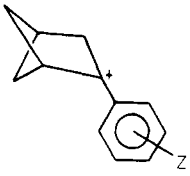

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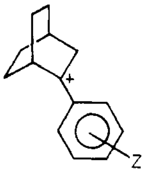

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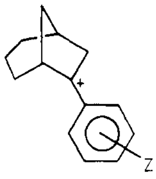

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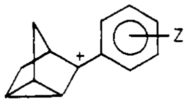
Postulated Classical Cations/Deviations. The 3-nortricyclyl cation is geometrically unsuited to form a σ-bridge either to the cyclopropyl ring or to the transannular carbon atom.[22a] Its stabilization is evidently provided by hyperconjugative interaction of the positive charge with the three-membered ring. Yet the 3-aryl-3-nortricyclyl cations (**18**) exhibit deviations that are qualitatively similar to those for **1**[11] (type B, Figure 3). 1-Aryl-1-cyclopropylethyl (**19**) constitutes a similar case where σ-bridging appears improbable, but deviations in the plot are observed.[11]



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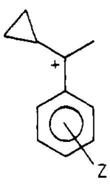

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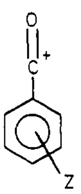
Finally, the 2-aryl derivatives of the 3-methylene-2-norbornyl cation (**4**), long considered to be a model classical 2-norbornyl cation,[18] reveal deviations comparable to those observed for **1**. Indeed, a plot of the δC^+ values for **4** against those for **1** reveals a reasonable linear correlation with only one minor discrepancy, 3,5-$(CF_3)_2$.

Other Deviations. Our studies have revealed deviations arising from many different origins. For example, the equilibration in the 2-aryl-3-methyl-2-butyl cations causes a comparable deviation in the $\Delta\delta C^+ - \sigma^{C^+}$ plots.[23]

The benzhydryl cations (**3**) also exhibit such deviation in their plots. In these derivatives, σ-bridging cannot be a factor. The deviation has been attributed to steric hindrance to coplanarity. Introduction of strongly electron-releasing substituents greatly increases the deviations[17,24] (type C, Figure 3).

Quite different behavior is observed in the plot for the benzoyl cations[25,26] **20** (type D, Figure 3). Finally, in plots of the data for **21**[27] and **22**,[14] for which there is general agreement that $\pi\sigma$-bridging occurs in **21**[27–29] and π-bridging in **31**,[14,30] very steep, positive slopes are obtained (type E, Figure 3).



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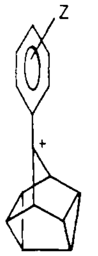

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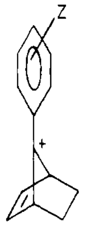

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We have been attempting to utilize inductive π-polarization as a means of accounting for these various types of deviations.[31] However, the referees have recommended that the discussion be limited to a consideration of the argument that such deviations can be considered to be evidence for σ-bridging. The results with respect to this question appear quite clear.

The referees have also stated that ^{13}C shifts are strongly influenced by many different factors so that it is questionable whether they can be used to establish charge densities. Of course, the use of ^{13}C shifts as a measure of charge densities is not our proposal, and numerous papers have appeared in the literature based upon such a relationship. Even though no sound theoretical basis exists between ^{13}C shifts and charge density, it is possible that a useful empirical correlation exists and can be used to corroborate proposals for σ-bridging. That is the question we have been exploring. However, we have been unable to confirm the use of such deviations in the $\Delta\delta^{13}C/\sigma^{C^+}$ plots as a diagnostic tool to corroborate σ-bridging in representative systems where such bridging has been postulated.

Conclusion

It has been proposed that the deviations observed in plots for $\Delta\delta C^+/\sigma^{C^+}$ for substituted 2-aryl-2-norbornyl cations arise from the onset of σ-bridging in the derivatives with the more strongly electron-withdrawing substituents. The generality of this proposal has been examined in a number of systems previously postulated to have nonclassical σ-bridged structures. No such deviations were observed. Similarly, the 2-aryl derivatives of the 3-methylene-2-norbornyl cation, long considered to be a model for a classical 2-norbornyl system, exhibit deviations comparable to those in the parent system. Accordingly, it is concluded that the proposal has no predictive value and cannot be used to test for the presence or absence of σ-bridging in individual systems.

Experimental Section

2-Aryl-3-methylene-*endo*-2-norbornanols. These precursors were prepared by addition of 3-methylene-2-norbornanone (Aldrich) to the Grignard reagent or aryllithium reagent prepared from the corresponding bromo- or iodobenzenes. The material obtained in the Grignard reaction was found to contain a substantial amount (20–30%) of the 1,4-addition product. This ketone impurity can be conveniently removed by forming the corresponding semicarbazone. All alcohols were purified by distillation. The derivatives Z = 3,4-CH_2CH_2O-, mp 110–111 °C, Z = H, bp 90–91 °C/0.05 mm, Z = p-CF_3, bp 100–101 °C/0.05 mm, and Z = 3,5-$(CF_3)_2$, bp 90–92 °C/0.01 mm, were available from previous work in our laboratories.[19] The physical constant data for the other precursors are as follows (Z, bp, °C/mm): p-OCH_3, 126–128/0.05; p-CH_3, 110–112/0.01; p-F, 96–98/0.05; p-Cl, 118–120/0.1; m-CH_3, 108–109/0.15; m-F, 94/0.15; m-Cl, 125–126/0.15; m-CF_3, 92/0.15; and 3,5-Cl_2, mp 80–81 °C. All of these precursors gave ^{13}C NMR spectral data in accordance with their structures. Satisfactory (C, H, F, and Cl ±0.3%)

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analytical data were obtained for all new compounds.

Carbocations. The ions **4** were prepared by slow addition of the appropriate precursor, either as a solution in SO_2ClF at ~−78 °C or as a powder to a solution of FSO_3H/SbF_5 (1:1 M)/SO_2ClF cooled to −78 °C, with rapid vortex mixing. The concentration of the "magic acid" was 3 M and those of the ions were ~0.5 M based on the assumption of complete ionization of the alcohol.[32] The resulting solutions were transferred to NMR tubes via a precooled double-ended syringe, as detailed previously.[32]

NMR Spectra. ^{13}C NMR spectra were recorded at −80 °C of solutions in 8-mm NMR tubes containing a concentric capillary (3-mm o.d.) of acetone-d_6 and Me_4Si on a Varian CFT-20 spectrometer, using 8192 data points, 6000-Hz spectral width, and a 45° pulse angle. Chemical shifts are ±0.1 ppm from external Me_4Si.

Registry No. **4** (Z = *p*-OCH_2CH_2-*m*), 89164-88-5; **4** (Z = *p*-OCH_3), 89164-89-6; **4** (Z = *p*-CH_3), 89164-90-9; **4** (Z = *p*-F), 89164-91-0; **4** (Z = *p*-Cl), 89164-92-1; **4** (Z = *m*-CH_3), 89164-93-2; **4** (Z = H), 89164-94-3; **4** (Z = *m*-F), 89164-95-4; **4** (Z = *m*-Cl), 89164-96-5; **4** (Z = *m*-CF_3), 89164-97-6; **4** (Z = 3,5-Cl_2), 89164-98-7; **4** (Z = *p*-CF_3), 89164-99-8; **4** (Z = 3,5-$(CF_3)_2$), 89165-00-4.

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Photochemical [3 + 2] Cycloaddition Reactions of Alkynones. Diverse Fates of Two Similar Vinylcarbene Intermediates and Reactions of a Cyclopropenol

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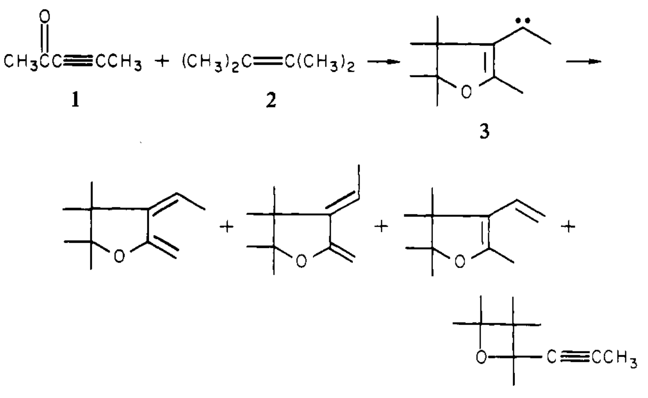
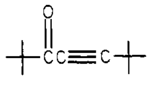
Received July 11, 1983

Abstract: Irradiation of alkynone **4** with tetramethylethylene (**2**) in wet benzene furnishes in high yield the simple cyclopropenol **11a**. Thermolysis of **11a** gives the conjugated allenic ketone **5** with loss of C_3H_6; treatment of **11a** with sodium hydride leads to **19**, and on standing in inert solvent at room temperature **11a** ejects acetone. In contrast the related alkynone **7** adds **2** photochemically to yield **25**, which rearranges at 75 °C to **8**. In explanation of the difference in reaction paths of **4** and **7** it is suggested that carbene **12** cyclizes to a cyclopropene from the singlet, while carbene **26** abstracts hydrogen intramolecularly from the triplet state.

Photochemical reaction of conjugated alkynones with several simple olefins yields novel [3 + 2] cycloaddition products for which a carbene intermediate has been proposed,[1] as well as the expected[2] oxetanes; this is illustrated for 3-pentyn-2-one (**1**) and tetramethylethylene (**2**). More recently we found that the oxetanes arise from the excited singlet state of the alkynone and that the [3 + 2] products come from a quenchable triplet.[3] There is also good experimental evidence for the carbenes (as **3**), including isolation of products of O–H bond insertion in alcoholic solvents.[3] In the present work we have now explored addition of tetramethylethylene to two α,β-acetylenic ketones in which no simple 1,2 or 1,4 hydrogen shifts are available for carbene stabilization. Irradiation of **4** with **2** in benzene, followed by removal of solvent, distillation, and preparative vapor-phase chromatography (VPC) of the volatile products furnished allenic ketone **5** in ~25% yield along with a small amount of oxetane **6a**. The constitution of **5** formally requires the surprising addition to **4** of *one-half* molecule of tetramethylethylene. In the course of elucidating the mechanism of this apparently extraordinary transformation, we examined the reaction of the closely related trimethylsilyl-substituted ketone **7** with **2**. Here the same procedure yields some **6b** and 68% of **8**, in which rearrangement of the *tert*-butyl group has occurred. Further investigation has provided explanations for these and other unusual transformations, as well as insight into the interesting question of the spin state of the reactive carbene and its influence on the course of subsequent reaction. Details are presented below.

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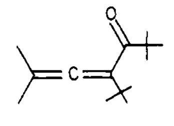
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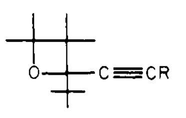
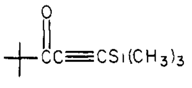

6a, R = $C(CH_3)_3$
b, R = $Si(CH_3)_3$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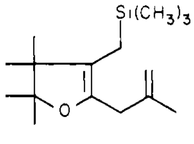
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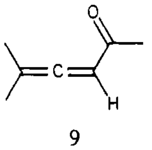
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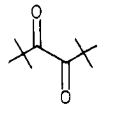
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Ketone **4** was available through reaction of pivalaldehyde with the Grignard reagent formed from *tert*-butylacetylene followed by oxidation with Jones's reagent.[4] Following the procedure

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