of fractional distillation with a 20-cm Vigreux column (bp max 98 °C), affording 1–2 mL of a *n*-heptane solution. This solution was processed by preparative GC with column B to isolate the C_5 fraction with a retention time of 2.3 min. Characterization was achieved by ^{1}H NMR and ^{2}H NMR, respectively. Relative product yields and deuterium distributions were obtained by means of electronic integration of the ^{1}H NMR or ^{2}H NMR resonances (Table II).

Time Dependence of the Exo/Endo Ratio during 185-nm Photolysis of 2,3-Dideuteriobicyclo[2.1.0]pentane. Three solutions (25 mL, 0.0171 M) of *exo/endo*-bicyclo[2.1.0]pentane (exo/endo ratio = 2.94) in *n*-heptane were photolyzed under exactly the same conditions for 20, 40, and 60 min, respectively. The C_5-product fraction was isolated as described above and analyzed by means of ^{2}H NMR spectroscopy. The actinometric measurement[9] was conducted by irradiating a 0.040 M solution of *cis*-cyclooctene and *n*-nonane as GC standard (0.027 M) in *n*-pentane in the same vessel and under the same conditions. The cistrans isomerization was monitored by GC with column A (but column temperature 72 °C and carrier gas flow (N_2) = 1.1 mL/min). The quantum yield of exo/endo isomerization (ϕ_{iso}) was calculated according to eq 7 with $\phi_{Z\to E}$ = 0.32,[3d] the quantum yield of formation of *trans*-cyclooctene,

$$\phi_{iso} = \frac{R_{iso}\phi_{Z\to E}}{R_{Z\to E}} \tag{7}$$

R_{iso} = (2.1 ± 0.1) × 10^{-5}, the rate of exo/endo isomerization of bicyclo[2.1.0]pentane-*2,3-d_2*, and $R_{Z\to E}$ = (2.4 ± 0.1) × 10^{-4}, the rate of formation of *trans*-cyclooctene (M^{-1} min^{-1}).

Registry No. Bicyclo[2.1.0]pentane, 185-94-6; *exo*-5,6-dideuteriobicyclo[2.2.1]hept-2-ene, 3675-40-9; *exo*-2,3-dideuteriobicyclo[2.1.0]-pentane, 51794-28-6; *endo*-2,3-dideuteriobicyclo[2.1.0]pentane, 60426-74-6; bicyclo[2.1.0]pentane-*2,3-d_2*, 96442-65-8; *cis*-3,4-dideuteriocyclopentene, 96349-02-9; glutaric acid-d_2, 96349-03-0; *cis*-glutaric-*3,4-d_2* anhydride, 96349-04-1; glutaconic anhydride, 5926-95-4; cyclopentene, 142-29-0.

Application of the Gassman–Fentiman Tool of Increasing Electron Demand to the ^{13}C NMR Spectroscopic Study of 1-Aryl-3-methylbut-2-enyl (Allylic) and 2-Arylpent-3-yn-2-yl (Propargylic) Cations[1]

G. K. Surya Prakash, V. V. Krishnamurthy, George A. Olah,* and **D. G. Farnum**

Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and the Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, and the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. Received July 31, 1984. Revised Manuscript Received March 4, 1985

Abstract: The Gassman–Fentiman tool of increasing electron demand has been applied to 1-aryl-3-methylbut-2-enyl (allylic) and 2-arylpent-3-yn-2-yl (propargylic) cations **2** and **3**, using ^{13}C NMR spectroscopy as the structural probe. A plot of C_α and C_γ chemical shifts of **2** and **3** vs. the cationic center chemical shifts of model 1-aryl-1-cyclopentyl cations **8** indicates deviations which can be rationalized by an increased resonance effect (allylic resonance in **2** and mesomeric vinyl cation character in **3**).

Although the Gassman–Fentiman tool of increasing electron demand[2] has been used extensively in conjunction with ^{13}C NMR spectroscopy to probe the structures of a variety of "ordinary" and "extraordinary" unconjugated carbocations, as well as some aryl conjugated carbocations,[3–22] no systematic study of the tool applied

to ordinary conjugated allylic cations has been reported. Since there is dispute over the interpretation of the response of the diarylcarbenium ions to the probe,[9,21] and since the probe has been applied to the allylic carbocation 2-aryl-3-methylenenorbornyl (**1**),[22] and an interpretation offered, we thought that it is imperative to determine the response of an "ordinary" conjugated system to the probe to serve as a model for detection of "extraordinary" conjugated carbocations. It is well-known that ^{13}C NMR shifts cannot be directly equated with charge densities and[2a] such

(1) Considered Stable Carbocations. 259. For Part 258 see: Olah, G. A.; Prakash, G. K. S.; Shih, J. G.; Krishnamurthy, V. V.; Mateescu, G. D.; Liang, G.; Sipos, G.; Buss, V.; Gund, T. M.; Scleyer, P. v. R. *J. Am. Chem. Soc.*, in press.

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

(3) Brown, H. C. "The Nonclassical Ion Problem"; Plenum: New York, 1977; Chapter 10.

(4) Brown, H. C.; Ravindranathan, M.; Peters, E. M. *J. Am. Chem. Soc.* **1975**, *97*, 2900.

(5) 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.

(6) 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.

(7) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 5683.

(8) Farnum, D. G.; Botto, R. E. *Tetrahedron Lett.* **1975**, *46*, 4013.

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

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

(11) Farnum, D. G.; Clausen, T. P. *Tetrahedron Lett.* **1981**, *22*, 549.

(12) 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.

(13) (a) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *J. Org. Chem.* **1982**, *47*, 3903. (b) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *J. Am. Chem. Soc.* **1980**, *102*, 6127.

(14) (a) Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044. (b) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666.

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

(16) Kelly, D. G.; Jenkins, M. J.; Mantello, R. A. *J. Org. Chem.* **1981**, *46*, 1650.

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

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

(19) Brown, H. C.; Kelly, D. P.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3170.

(20) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089.

(21) Brwon, H. C.; Periasamy, M.; Perumal, P. T.; Kelly, D. P.; Giansiracusa, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 6300.

(22) Brown, H. C.; Periasamy, M.; Perumal, P. T.; Kelly, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 2359.

Table I. Physical Properties and ^{1}H NMR Chemical Shifts of 1-Aryl-3-methylbut-1-en-3-ol (4)

R	bp,[a] °C (pressure, torr)	^{1}H NMR chemical shifts[b]
4-OCH$_3$	108–110 (0.15)	7.32 (d, 2 H, J = 9.0, H$_2$H$_6$), 6.87 (d, 2 H, J = 9.0, H$_3$H$_5$), 6.55 (d, 1 H, J = 16.0, H$_\alpha$), 6.24 (d, 1 H, J = 16.0, H$_\beta$), 3.82 (s, 3 H, OCH$_3$), 1.44 (s, 6 H, CH$_3$)
3,4-(CH$_3$)$_2$	103–105 (0.3)	7.30 (complex, 3 H, aromatic), 6.70 (d, 1 H, J = 16.0, H$_\alpha$), 6.45 (d, 1 H, J = 16.0, H$_\beta$), 2.30 (s, 6 H, C$_3$-CH$_3$, C$_4$-CH$_3$), 1.45 (s, 6 H, CH$_3$)
4-CH$_3$	95–96 (0.6)	7.30 (d, 2 H, J = 8.5, H$_2$H$_6$), 7.13 (d, 2 H, J = 8.5, H$_3$H$_5$), 6.57 (d, 1 H, J = 16.1, H$_\alpha$), 6.31 (d, 1 H, J = 16.1, H$_\beta$), 2.36 (s, 3 H, C$_4$-CH$_3$), 1.44 (s, 6 H, CH$_3$)
3-CH$_3$	94–96 (0.3)	7.22 (complex, 4 H, aromatic), 6.59 (d, 1 H, J = 16.1, H$_\alpha$), 6.37 (d, 1 H, J = 16.1, H$_\beta$), 2.37 (s, 3 H, C$_3$-CH$_3$), 1.45 (s, 6 H, CH$_3$)
H	74–75 (0.2)	7.31 (complex, 5 H, aromatic), 6.61 (d, 1 H, J = 16.1, H$_\alpha$), 6.37 (d, 1 H, J = 16.1, H$_\beta$), 1.45 (s, 6 H, CH$_3$)
3-CF$_3$	75 (0.15)	7.52 (complex, 4 H, aromatic), 6.65 (d, 1 H, J = 16.0, H$_\alpha$), 6.43 (d, 1 H, J = 16.0, H$_\beta$), 1.45 (s, 6 H, CH$_3$)
4-CF$_3$	77 (0.15)	7.53 (AB quartet, 4 H, J = 8.4, aromatic), 6.65 (d, 1 H, J = 16.0, H$_\alpha$), 6.45 (d, 1 H, J = 16.0, H$_\beta$), 1.45 (s, 6 H, CH$_3$)
3,5-(CF$_3$)$_2$	100 dec (0.15)	7.80 (s, 2 H, H$_2$H$_6$), 7.73 (s, 1 H, H$_4$), 6.70 (d, 1 H, J = 16.0, H$_\alpha$), 6.50 (s, 1 H, J = 16.0, H$_\beta$), 1.46 (s, 6 H, CH$_3$)

[a] All boiling points and pressures are uncorrected. [b] ^{1}H NMR chemical shifts are with respect to external Me$_4$Si and measured in CDCl$_3$ at room temperature.

Table II. Physical Properties and ^{1}H NMR Chemical Shifts of 4-Arylpent-2-yn-4-ol (5)

R	bp,[a] °C (pressure, torr)	^{1}H NMR chemical shifts[b]
4-OCH$_3$	100 dec (0.1)	7.64 (d, J = 9.0, 2 H, H$_2$H$_6$), 7.00 (d, J = 9.0, 2 H, H$_3$H$_5$), 3.85 (s, 3 H, OCH$_3$), 1.95 (s, 3 H, C$_\alpha$-CH$_3$), 1.77 (s, 3 H, C$_\gamma$-CH$_3$)
3,4-(CH$_3$)$_2$	96–98 (0.5)	7.60 (s, 1 H, H$_2$), 7.40 (AB quartet, J = 8.0, 2 H, H$_5$H$_6$), 2.30 (s, 6 H, C$_3$-CH$_3$, C$_4$-CH$_3$), 1.95 (s, 3 H, C$_\alpha$-CH$_3$), 1.77 (s, 3 H, C$_\gamma$-CH$_3$)
4-CH$_3$	87 (0.15)	7.56 (d, J = 8.0, 2 H, H$_2$H$_6$), 7.18 (d, J = 8.0, 2 H, H$_3$H$_5$), 2.38 (s, 3 H, C$_4$-CH$_3$), 1.93 (s, 3 H, C$_\alpha$-CH$_3$), 1.77 (s, 3 H, C$_\gamma$-CH$_3$)
3-CH$_3$	90 (0.25)	7.49 (s, 1 H, H$_2$), 7.46 (d, J = 7.0, 1 H, H$_4$ or H$_6$), 7.27 (t, J = 7.0, 1 H, H$_5$), 7.11 (d, J = 7.0, 1 H, H$_6$ or H$_4$), 2.40 (s, 3 H, C$_3$-CH$_3$), 1.94 (s, 3 H, C$_\alpha$-CH$_3$), 1.76 (s, 3 H, C$_\gamma$-CH$_3$)
H	89 (0.5)	7.40 (complex multiplet, 5 H, aromatic H), 1.94 (s, 3 H, C$_\alpha$-CH$_3$), 1.77 (s, 3 H, C$_\gamma$-CH$_3$)
3-CF$_3$	68–70 (0.1)	7.93 (s, 1 H, H$_2$), 7.84 (d, 1 H, J = 7.0, H$_4$ or H$_6$), 7.50 (complex, 2 H, H$_4$ or H$_6$ and H$_5$), 1.94 (s, 3 H, C$_\alpha$-CH$_3$), 1.76 (s, 3 H, C$_\gamma$-CH$_3$)
4-CF$_3$	72 (0.1)	7.77 (d, 2 H, J = 8.0, H$_3$H$_5$), 7.62 (d, 2 H, J = 8.0, H$_2$H$_6$), 1.93 (s, 3 H, C$_\alpha$-CH$_3$), 1.75 (s, 3 H, C$_\gamma$-CH$_3$)
3,5-(CF$_3$)$_2$	71–72 (0.1)	8.11 (s, 2 H, H$_2$H$_6$), 7.81 (s, 1 H, C$_4$), 1.95 (s, 3 H, C$_\alpha$-CH$_3$), 1.77 (s, 3 H, C$_\gamma$-CH$_3$)

[a] All boiling points and pressures are uncorrected. [b] ^{1}H NMR chemical shifts are with respect to external Me$_4$Si and measured in CDCl$_3$ at room temperature.

Table III. ^{13}C NMR Chemical Shifts of 1-Aryl-3-methylbut-1-en-3-ols[b]

X	C$_1$	C$_2$	C$_3$	C$_4$	C$_\alpha$	C$_\beta$	C$_\gamma$	CH$_3$	other
4-OCH$_3$	129.5	127.3	113.8	158.8	125.5	135.4	70.6	29.7	OCH$_3$: 55.0
3,4-(CH$_3$)$_2$	135.3[a]	123.6	134.4[a]	136.1[a]	125.9	136.3	70.5	29.5	C$_5$: 129.5;[a] C$_6$: 127.4;[a] CH$_3$: 19.4, 19.1
4-CH$_3$	134.0	129.2	126.2	137.1	126.1	136.4	70.9	29.8	CH$_3$: 21.1
3-CH$_3$	136.7	122.4	135.8	126.9[a]	125.9[a]	136.3	69.8	28.6	C$_5$: 127.2, C$_6$: 125.1;[a] CH$_3$: 20.1
H	136.8	126.1	128.2	127.0	126.0	137.4	70.6	29.6	
3-CF$_3$	137.9	122.5 (3.9)	130.5 (31.9)	123.2 (3.4)	124.6	139.8	70.3	29.3	C$_5$: 122.6; C$_6$: 129.2; CF$_3$: 124.6 (272.6)
4-CF$_3$	140.6	126.4	125.3 (3.6)	128.9 (31.9)	125.0	140.3	70.9	29.6	CF$_3$: 124.2 (272.8)
3,5-(CF$_3$)$_2$	139.2	125.9	131.6 (32.7)	120.2 (3.8)	123.6	141.8	70.6	29.3	CF$_3$: 123.2 (272.5)

[a] Assignments interchangeable. [b] Chemical shifts in ppm from tetramethylsilane. Carbon–fluorine coupling constants are in parentheses (in Hz).

charge-shift comparisons have been earlier criticized.[23a] The basic assumption in the application of the Gassman–Fentiman tool of electron demand using ^{13}C NMR spectroscopy is that in a series of closely related homologous ions with similar enough nature considerable cancellation of factors other than charge distribution occurs which enters into the makeup of chemical shifts. On the basis of this presumption we herein report the effect of the application of the tool of increasing electron demand on the ^{13}C NMR spectra of the 1-aryl-3-methylbut-2-enyl (allylic) and 2-arylpent-3-yn-2-yl (propargylic) cations (2 and 3). We have also analyzed cations 2 and 3 in light of localized inductive π-polarization phenomenon, first explored by Brownlee and co-workers[23b] to explain the ^{13}C chemical shift shielding effects of α-carbons of a series of substituted benzonitriles, acetophenones, benzophenones, and styrenes, and shown that such effects are unimportant in the case of fully developed carbocations contrary to such claims.[21,24,25]

Results and discussion

Carbocations 2 and 3 were prepared by the ionization of the corresponding *trans*-1-aryl-3-methylbut-1-en-3-ols, 4, and 4-arylpent-2-yn-4-ols, 5, in FSO$_3$H–SbF$_5$/SO$_2$ClF solutions at –78 °C. Further details are given in the Experimental Section. The ^{13}C and ^{1}H NMR spectroscopic data and the physical constants (bp) of precursor alcohols are listed in Tables I–IV.

The ^{13}C NMR spectra of ions 2 and 3 were recorded at –85 °C, and the data are summarized in Tables V and VI. Assignment of the chemical shifts were made based on both proton coupled spectra as well as APT (attached proton test) experiments.[26]
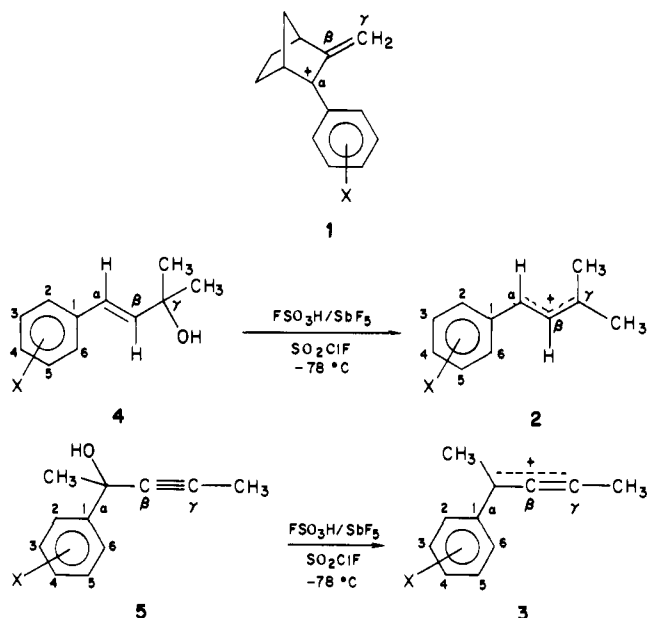
1-Aryl-3-methylbut-2-enyl Cations. Allylic (alkenyl) cations are the simplest conjugatively stabilized carbocations and have been the subject of many experimental and theoretical investigations.[27] The distribution of charge in allylic cations has been

(23) (a) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159. (b) Bromilow, J.; Brownlee, R. T. C.; Craik, D.; Fiske, P. R.; Rowe, J. E.; Sadek, M. *J. Chem. Soc., Perkins Trans. 2* **1981**, 753.

(24) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1983**, *48*, 3386.
(25) Kelly, D. P.; Jenkins, M. J. *J. Org. Chem.* **1984**, *49*, 409.
(26) (a) Anet, F. A. L.; Jaffer, N.; Strouse, J. 21st ENC, 1980. (b) LeCoca, C.; Lalemand, J.-Y. *J. Chem. Soc., Chem. Commun.* **1981**, 150.

Figure 1. A plot of C_α [a] and C_γ [b] chemical shifts of 1-aryl-3-methylbut-2-enyl cations (2) vs. carbocationic center chemical shifts of 1-aryl-1-cyclopentyl cations (8).

a subject of some controversy, particularly regarding the importance of 1,3-overlap (6c) relative to the classical resonance structures 6a and 6b. Many recent molecular orbital calculations have suggested that 1,3-overlap is not of any significance for acyclic allylic cations.[28-31] However, there is convincing evidence that cyclobutenyl cations 7, wherein the proximity of C_1 and C_3 permits greater overlap between the π-orbitals on these carbon atoms, have strong 1,3-overlap.[32]
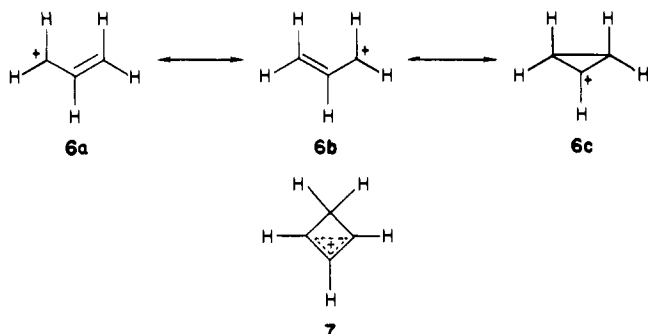
To understand the nature of classical resonance stabilization (6a ↔ 6b) on the ^{13}C NMR chemical shifts of acyclic allylic cations, we investigated a series of 1-aryl-3-methylbut-2-enyl cations 2. The *trans* configuration of the hydrogens in the ion was established by the observation of a large *trans* coupling in the proton spectrum ($J_{H-H} \simeq 14$ Hz). The electron demand of the fully developed carbocationic center at the C_α position has been systematically varied by varying the nature of the substituents on the aryl ring.

From the ^{13}C NMR data (Table V), it is apparent that there is a change in C_α as well as C_γ chemical shifts going from the most electron donating 4-OCH$_3$ substituent to the most electron demanding 3,5-(CF$_3$)$_2$ group. The ^{13}C NMR chemical shift of C_α is gradually deshielded up to the parent phenyl system 2-H. Upon introducing more electron demanding substituents, such as

Figure 2. A plot of δ_{C_β}'s in 1-aryl-3-methylbut-2-enyl cations (2) [a] and 2-arylpent-3-yn-2-yl cations (3) [b] vs. δ_{C_2} in 1-aryl-1-cyclopentyl cations (8).

3-CF$_3$, 4-CF$_3$, and 3,5-(CF$_3$)$_2$ groups, there is a shielding effect observed. A plot of the C_α chemical shifts in 2 vs. the carbocationic center chemical shifts of 1-aryl-1-cyclopentyl cations (8)[9] (Figure 1a) indicates a deviation from linearity with groups more electron demanding than the hydrogen substituent. On the other hand, C_γ is progressively deshielded up to the ion 2-H, and the deshielding effect with more electron demanding substituents such

(27) Deno, M. C. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R. Eds.; Wiley-Interscience: New York, 1970; Vol. 2, Chapter 18.

(28) (a) Katz, T. J.; Gold, E. H. *J. Am. Chem. Soc.* **1964**, *86*, 1600. (b) Olah, G. A.; Clifford, P. R.; Halpern, Y.; Johanson, R. A. *J. Org. Chem.* **1971**, *93*, 4219.

(29) (a) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1972**, *94*, 6434. (b) Olah, G. A.; Liang, G.; Mo, Y. K. *Ibid.* **1972**, *94*, 3544.

(30) Carpenter, B. K. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1.

(31) Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1539.

(32) (a) Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 6233. (b) Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, G. *Ibid.* **1975**, *97*, 5489. (c) Smart, B. E.; Reddy, G. S. *Ibid.* **1976**, *98*, 5593.
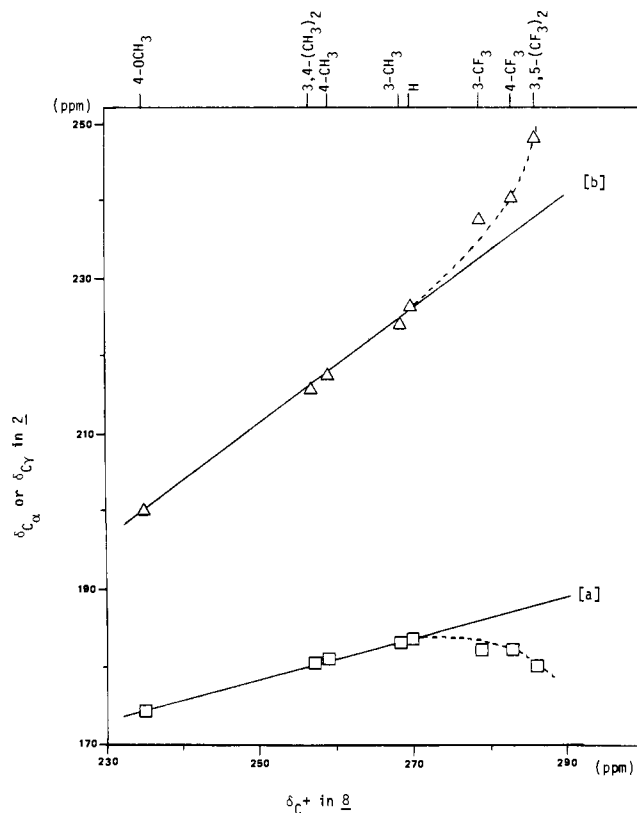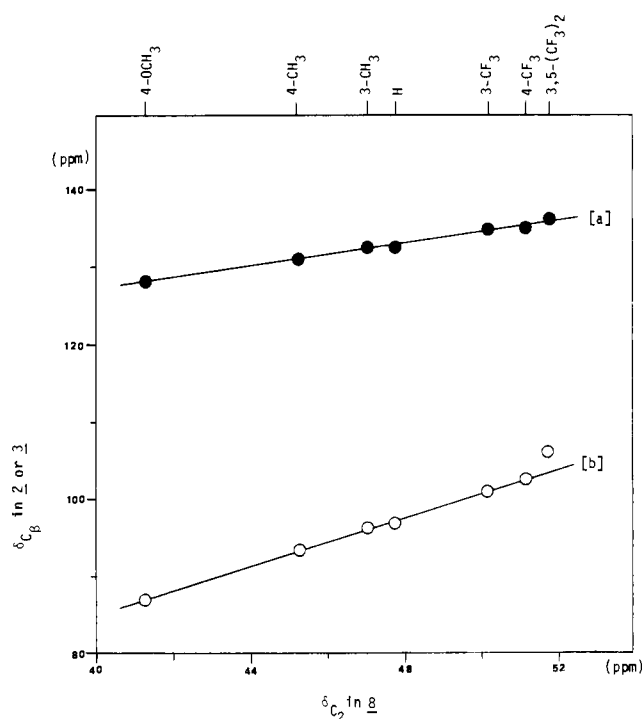
Table IV. ^{13}C NMR Chemical Shifts of 4-Arylpen-2-yne-4-ols[b]

X	C_1	C_2	C_3	C_4	C_α	C_β	C_γ	C_α–CH_3	C_γ–CH_3	others
4-OCH$_3$	138.6	126.1	113.5	158.6	69.1	83.4	80.2	33.3	3.3	OCH$_3$: 55.0
3,4-(CH$_3$)$_2$	143.6	122.1	135.0	135.6	69.2	83.2	79.9	33.0	3.2	C$_5$: 128.9; C$_6$: 125.8; CH$_3$: 19.5, 18.9
4-CH$_3$	143.2	128.6^a	124.7^a	136.8	69.6	83.1	80.5	33.2	3.4	CH$_3$: 20.8
3-CH$_3$	145.9	121.8	137.1	127.6^a	69.4	83.1	80.2	33.1	3.1	C$_5$: 127.6; C$_6$: 125.3; CH$_3$: 21.1
H	146.0	128.0	124.9	127.4	69.9	82.9	80.9	33.3	3.5	
3-CF$_3$	147.9	121.4 (3.6)	129.8 (32.6)	123.4 (3.5)	68.4	82.5	80.0	33.2	2.8	C$_5$: 128.3; C$_6$: 128.0 CF$_3$: 123.9 (272.2)
4-CF$_3$	150.2	125.3	125.0 (3.7)	129.5 (33.1)	69.4	82.4	81.3	33.4	3.3	CF$_3$: 124.1 (272.2)
3,5-(CF$_3$)$_2$	149.5	125.3	131.0 (33.0)	120.9	68.6	81.7	81.4	33.5	3.1	CF$_3$: 123.2 (272.6)

^{a} Assignments interchangeable. ^{b} Chemical shifts in ppm from external tetramethylsilane. Carbon–fluorine coupling constants in parentheses (in Hz).

Table V. ^{13}C NMR Chemical Shifts of 1-Aryl-3-methylbut-2-enyl Cations **2** in FSO$_3$H:SbF$_5$/SO$_2$ClF at −80 °C^a

| X	C_1	C_2	C_3	C_4	C_5	C_6	C_α	C_β	C_γ	CH$_3$ (anti)	CH$_3$ (syn)	others	$\delta_{C_T} = \delta_{C_\alpha} + \delta_{C_\gamma}$
4-OCH$_3$	129.2	138.7*	119.6*	176.8	117.4*	150.2*	174.1	128.4	200.2	30.8	22.3	57.6	374.3 [−35.7]
3,4-(CH$_3$)$_2$	133.2	134.4 133.2	141.6 141.5	163.2 162.9	133.2 132.9	145.9 144.5	180.6	131.3	215.4	32.5	24.0	21.5; 21.4 18.6; 18.1	396.0 [−14.0]
4-CH$_3$	132.5	155.2*	132.6	163.2	132.6	145.9*	181.0	131.5	217.7	32.8	24.3	22.4	398.7 [−11.3]
3-CH$_3$	134.5	133.9 131.8	142.2	147.7 147.3	131.2	145.5 143.3	183.1	132.8	223.9	33.6	25.2	19.7; 19.4	407.0 [−3.0]
H	134.2	145.3	131.4	145.9	131.2	134.2	183.4	133.2	226.6	34.1	25.7		410.0 [0.0]
3-CF$_3$	133.7						182.2	134.9	237.7	35.6	27.3	122.5 (271.9)	419.9 [+9.9]
4-CF$_3$	135.7		127.4	141.8 (34.9)	127.4		182.1	135.5	240.3	36.0	27.6	122.4 (273)	422.4 [+12.4]
3,5-(CF$_3$)$_2$	134.0		133.7 (30.0)	134.3	133.7 (30.0)		179.7	136.4	247.5	37.2	28.8	122.0 (272.7)	427.2 [+17.2]

^{a} Chemical shifts are in ppm with respect to external tetramethylsilane. Carbon–fluorine coupling constants are in parentheses (in Hz). Values in brackets are $\Delta\delta_T = \delta_T(X) - \delta_T(H)$. Assignments with * and * are interchangeable.

Table VI. ^{13}C NMR Chemical Shifts of 2-Arylpent-3-yn-2-yl Cations **3** in FSO$_3$H:SbF$_5$/SO$_2$ClF at −80 °C^a

X	C_1	C_2	C_3	C_4	C_5	C_6	C_α	C_β	C_γ	C_α–CH_3	C_γ–CH_3	other	$\delta_{C_T} = \delta_{C_\alpha} + \delta_{C_\gamma}$
4-OCH$_3$	137.1	147.0	118.9	184.9	118.9	142.7	180.9	87.5	142.0	25.7	6.7	58.8	322.9 [−52.9]
3,4-(CH$_3$)$_2$	142.4 142.3	138.5 137.5	141.4 141.3	171.1	133.6 133.5	142.4 141.6	202.1	92.9	160.0 159.3	28.4	8.4 8.3	18.5 18.2, 22.5	361.8 [−24.0]
4-CH$_3$	140.7	143.0	133.0	171.1	133.0	139.0	203.8	93.4	161.9	28.6	8.5	23.8	365.7 [−20.1]
3-CH$_3$	143.1	138.5 136.8	142.6	153.8 153.6	131.6	142.4 140.8	210.7	96.2 96.3	171.0 170.4	30.4 30.0	9.4 9.3	19.7 19.5	381.4 [−4.4]
H	142.2	142.8	131.8	152.1	131.6	138.8	212.4	96.9	173.4	30.2	9.6		385.8 [0.0]
3-CF$_3$	141.3 141.2	144.4 140.7		145.2	132.2	137.1 133.7	218.0 217.9	101.3 101.2	187.3 187.2	31.7 31.4	10.9 10.7	121.9 (272.4)	405.3 [+19.5]
4-CF$_3$	142.9	141.8	127.7	146.6 (35.2)	127.7	138.1	220.3	103.0	191.7	32.2	11.3	121.4 (273.7)	411.0 [+24.2]
3,5-(CF$_3$)$_2$	141.0	139.9	134.3 (36.1)	139.2	134.3	136.2	222.0	106.1	200.6	33.3	12.5	121.4 (273.2)	422.6 [+36.8]

^{a} Chemical shifts in ppm from external capillary tetramethylsilane. Carbon–fluorine coupling constants in parentheses (in Hz). Values in brackets are $\Delta\delta_T = \delta_T(X) - \delta_T(H)$.

as 3-CF$_3$, 4-CF$_3$, and 3,5-(CF$_3$)$_2$ groups is much more pronounced. This can be readily seen from a plot of δ_{C_γ} vs. δ_{C^+} of **8** in Figure 1b. With electron-demanding substituents, the observed deviation (Figure 1b) is in the opposite direction from that in Figure 1a. These effects can be readily rationalized by simple resonance (**2a** ↔ **2b**).
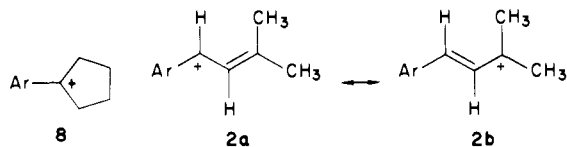
The central C$_\beta$ carbon chemical shift, however, experiences a much smaller gradual deshielding from **2**-OCH$_3$ to **2**-3,5-(CF$_3$)$_2$.

This can be understood by the fact that C$_\beta$ is adjacent to both C$_\alpha$ and C$_\gamma$ centers simultaneously. A plot of C$_\beta$ chemical shifts vs. δ_{C_2} of 1-aryl-1-cyclopentyl cations **8** shows a linear correlation ($r^2 = 1$, Figure 2a) of gentle slope as expected. To demonstrate the ordinary nature of these allylic cations (involving π-resonance interaction, **2a** ↔ **2b**), we also plotted the following differential sum, $\Delta\delta_T$ ($=\Delta\delta_{C_\alpha^+} + \Delta\delta_{C_\gamma}$)[33] vs. $\Delta\delta_{C^+}$,[33] of 1-aryl-1-cyclopentyl cations **8**. The plot (Figure 3a) reveals an excellent linear correlation ($r^2 = 1$), indicating the regular trivalent carbenium nature of **2**, and also attests to the fact that there is very little 1,3-overlap

(33) $\Delta\delta_{C_T}$ for **1**, **2**, and **3** = $[\delta_{C_\alpha} + \delta_{C_\gamma}(X \neq H)] - [\delta_{C_\alpha} + \delta_{C_\gamma}(X = H)]$. $\Delta\delta_{C_T}$ for **12–17** = $[\delta_{C^+} + \delta_{C_2} + \delta_{C_4} + \delta_{C_6}(Z \neq H)] - [\delta_{C^+} + \delta_{C_2} + \delta_{C_4} + \delta_{C_6}(Z = H)]$. $\Delta\delta_{C_T}$ for **19** = $[\delta_{C^+} + \delta_{C_{5a}} + \delta_{C_6} + \delta_{C_8}(Z \neq H)] - [\delta_{C^+} + \delta_{C_{5a}} + \delta_{C_6} + \delta_{C_8}(Z = H)]$.
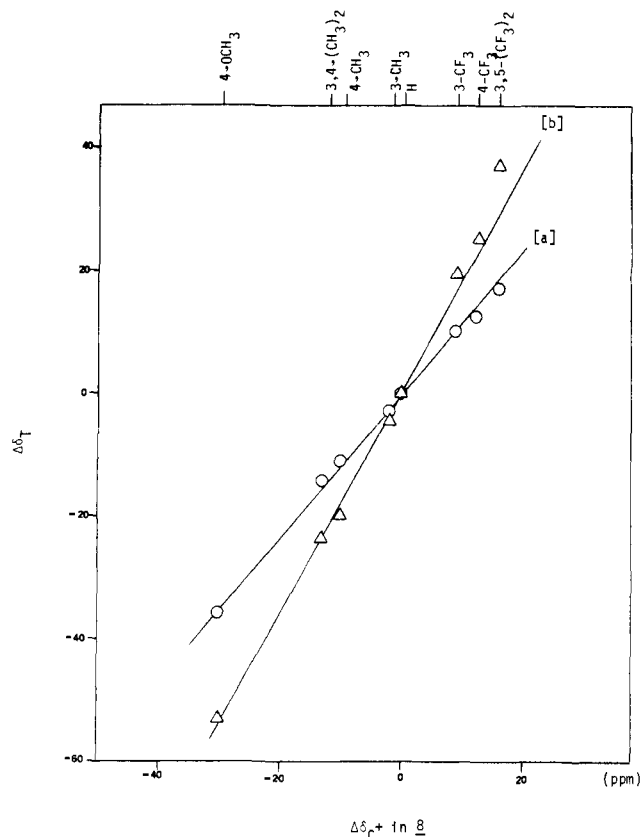
Figure 3. A plot of the differential sum of C_α and C_γ chemical shifts of 1-aryl-3-methylbut-2-enyl cations (2) [a, O] and 2-arylpent-3-yn-2-yl cations (3) [b, Δ] vs. differential carbocationic center chemical shifts of 1-aryl-1-cyclopentyl cations (8).

in these acyclic allylic cations involving structures similar to 6c.

Brown has recently reported[22] that the 2-aryl-3-methylene-2-norbornyl cations (1) show a deviation from linearity like that of the 2-arylnorbornyl cation when their cationic carbon (C_2) NMR chemical shifts are plotted against σC^+. We have previously noted that, since σC^+ is derived from and linearly related to the cationic carbon chemical shifts of the arylcyclopentyl cations, Brown's analysis is equivalent to our procedure of plotting against δ_{13C^+} of the arylcyclopentyl cations. From the above discussion of the delocalized allylic cations 2 it is apparent that plotting one nominally cationic carbon chemical shift against δ_{C^+} (arylcyclopentyl) is not a satisfactory procedure for revealing abnormal behavior in aryl-substituted allylic cations. A plot of the differential sum of chemical shifts of the allylically related cationic carbon of the methylene norbornyl system 1 ($\Delta\delta_{C_T}$) against $\Delta\delta_{13C^+}$[33] (arylcyclopentyl) is given in Figure 4 for comparison with a similar plot for the delocalized system 2 in Figure 3a. Again a linear relationship is observed with $r^2 = 0.99$ indicating that 1 is an ordinary π-delocalized system just like system 2.

The very fact that Brown reports[22] a colinear relationship ($r = 0.998$) between the cationic center chemical shifts of 1 vs. those of the 2-aryl-2-norbornyl system seems to indicate that the extent of the onset of σ-delocalization (i.e., increased positive charge dispersal to the C_1 carbon) with electron-withdrawing groups in the latter is as powerful as π-conjugation.

2-Arylpent-3-yn-2-yl Cations. Whereas bona fide vinyl cations have not been experimentally observed under stable ion conditions, the mesomeric vinylic cation forms of propargylic cations (alkynyl carbenium ions) have been shown to contribute extensively to the total ion structure.[34] Ions such as 9 have been thoroughly studied with a variety of substituents, including the trimethylsilyl group, at the γ-position.[35] Similarly, allenylcarbinyl cations 10 have
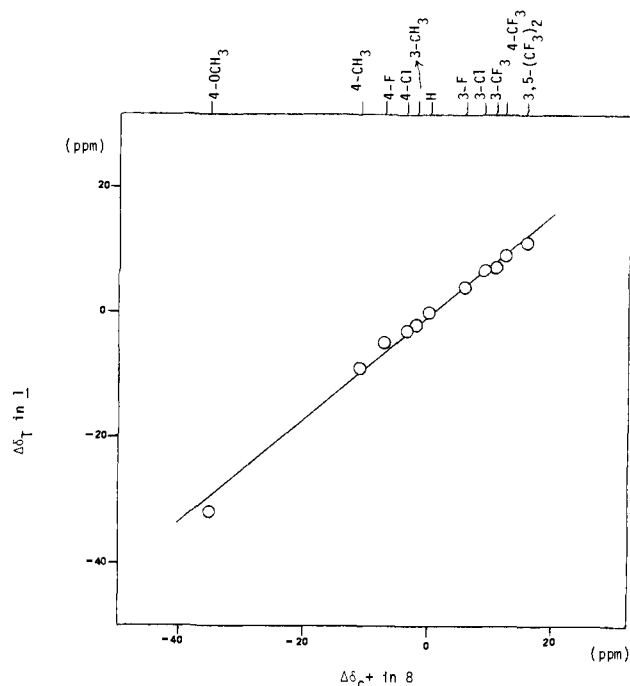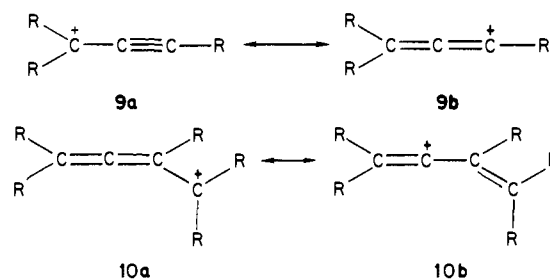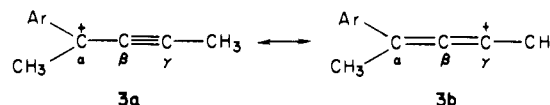

Figure 4. A plot of the differential sum of C_α and C_γ chemical shifts of 1 vs. the differential carbocationic center chemical shifts of 1-aryl-1-cyclopentyl cations in 8.

been studied[36] and again show substantial mesomeric vinyl ion character.

Interested in the extent of mesomeric vinyl ion character of alkynyl cations, we prepared a series of 2-arylpent-3-yn-2-yl cations 3. The electron demand at the C_α position was varied by changing the nature of the substituent on the aryl ring. The C_α carbon in 3 varies from δ_{13C} 180.9 to 222.0 on going from the 4-OCH$_3$ to the 3,5-(CF$_3$)$_2$ group. Similarly, the C_γ carbon shows a corresponding chemical shift change from δ_{13C} 142.0 to δ_{13C} 200.6. This deshielding of the C_γ carbon with an increase in electron demand at the cationic center is consistent with increased mesomeric vinyl cation character (increased contribution of 3b). This can also be observed in the plots of C_α and C_γ chemical shifts vs. the cationic center chemical shifts of the model 1-aryl-1-cyclopentyl cations[9] (Figure 5, a and b). As in the allylic cation 2, the C_α plot shows a deviation (shielding effect) with substituents more electron demanding than hydrogen, while C_γ shows increased deshielding with an increase in electron demand. We also plotted the dif-

ferential sum $\Delta\delta_{C_T}$[33] vs. the $\Delta\delta_{C^+}$[33] of 8 (Figure 3b). Up to the 4-CF$_3$ substituent an excellent linear relationship is observed ($r^2 = 1$). However, a small deviation may be appearing for the

---

(34) (a) Olah, G. A.; Spear, R. J.; Westerman, P. W.; Dennis, J.-M. *J. Am. Chem. Soc.* **1974**, *96*, 5855. (b) Prakash, G. K. S. Ph.D. Thesis, University of Southern California, 1978.

(35) Olah, G. A.; Berrier, A. L.; Field, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1349.

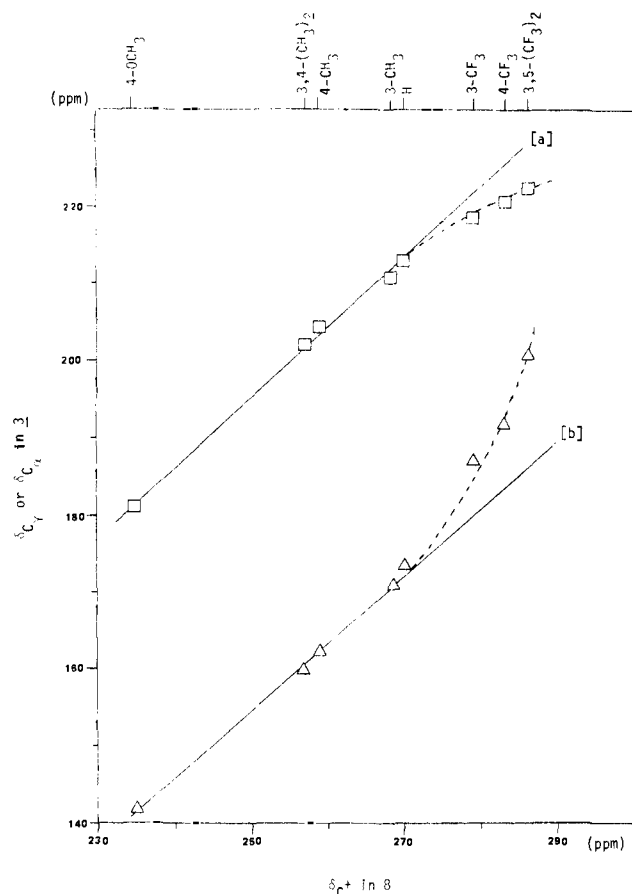(36) Siehl, H.-U.; Mayr, H. *J. Am. Chem. Soc.* **1982**, *104*, 909.

Figure 5. A plot of C_α [a] and C_γ [b] chemical shifts of 2-arylpent-3-yn-2-yl cations (3) vs. carbocationic center chemical shifts of 1-aryl-1-cyclopentyl cations (8).

3,5-$(CF_3)_2$ substituent. On the other hand, previously discussed allylic cations 2 showed a linear behavior throughout in such a plot. To rationalize the anomaly in 3 we will have to take into account changes around C_α and C_β in 3 as a consequence of increased mesomeric vinyl cation character with increase in electron demand (structure 3b). Due to increased contribution of 3b to the total ion structure of 3, the ring current shielding effect of the acetylenic group is lost. Hence C_α carbon shows less shielding effect than expected with increase in electron demand. Such an effect is also apparent by a plot of δ_{C_β} vs. δ_{C_2} of 8[9] (Figure 2b). The plot shows deviation (deshielding) with the 3,5-$(CF_3)_2$ group (up to 4-CF_3, $r^2 = 1.0$). In fact, with increase in electron demand C_β becomes increasingly an allenyl carbon. The middle carbon atom in neutral allene is observed at δ_{13C} 228.0 which is substantially deshielded from that in propyne (ca. 110 ppm).

It could, however, also be argued that there may be some other explanation for the above anamoly such as inductive π-polarization suggested by Brown et al.[21] in their studies.

Let us, therefore, analyze inductive π-polarization[23b] as a possible factor in the behavior of the allylic and propargylic cations (2 and 3). With an increase in electron demand, the following structures (11a and 11b) could be written to indicate the onset of an inductive localized π-polarization effect. A glance at these structures would indicate that any onset of inductive π-polarization
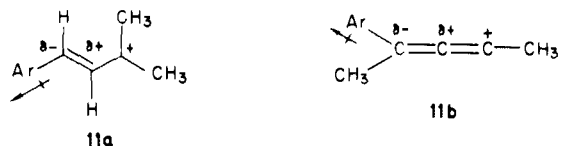

with increase in electron demand would result in a polarization of the developing double bond with increased positive charge adjacent to the highly electropositive carbocationic center. This seems unlikely. Moreover, in the allylic cation series 2, the $\Delta\delta_{C_\gamma}$[33]

vs. the $\Delta\delta_{C^+}$ of 1-aryl-1-cyclopentyl cations 8[9] shows an excellent linear relationship, clearly ruling out any onset of inductive π-polarization with increase in electron demand. It appears that a simple resonance effect involving structures 2a ↔ 2b is operative. This interpretation is further supported by the regular linear behavior of the C_β chemical shifts vs. those of C_2 of 8 (Figure 2a). In the propargylic series 3, however, some anomalies were observed in C_α and C_β chemical shifts in the case of the 3,5-$(CF_3)_2$ substituent. This is readily rationalized by an increased contribution of mesomeric vinyl cation character (3b) resulting in an allenyl framework. Moreover, inductive π-polarization should have resulted in more shielding of the C_α carbon. However, this is not reflected in Figure 3b.

In an earlier paper, one of us reported a limited study of the SCS for some 1,1-diarylethyl cations[9] as "a simple test" of the Gassman–Fentiman tool of increasing electron demand. It was concluded that the results were readily accommodated by the intuitively reasonable proposals that (a) for cations with one electron donating substituent (e.g., 15, X = H, Z = OCH_3), the substituted aryl group was coplanar with the cationic carbon, while the unsubstituted phenyl group was twisted out of the plane, (b) for cations with one electron withdrawing substituent (e.g., 15, X = H, Z = 4-CF_3) the substituted aryl group was twisted, while the unsubstituted one was coplanar, and (c) for symmetrically substituted cations (X = Z), both aryl groups were twisted. In an independent and more thorough study, Ancian, Membrey, and Doucet determined SCS for many more derivatives of these cations in fluorosulfonic acid and concluded that the data could be interpreted adequately without invoking unsymmetrically twisted cations.[37] On the basis of proton NMR studies, they concluded that all cations had essentially the same geometry, a symmetrically twisted propellor,[38] and found that most of the chemical shifts correlated well with INDO calculations for this geometry. For those cases which did not correlate well (a particularly striking example is the pair X = Z = 4-CH_3O, $\Delta\delta_{C^+}$ = -25.8 ppm and X = 4-CH_3O, Z = 4-NO_2, $\Delta\delta_{C^+}$ = -27.3 ppm, that is, the chemical shifts of the cationic carbons in these two ions are nearly the same), the authors proposed substituent-substituent interactions,[37] which were discussed in detail. In a later analysis, they concluded that π-polarization was not a factor affecting the chemical shifts of the cationic carbon in these systems.[39]

In later work, Brown and co-workers determined SCS for a still more comprehensive series of diarylethyl cations in SbF_5/FSO_3H/SO_2ClF (12–17).[21] Since a reversal of slope was observed in the cationic center shifts vs. σ_{C^+} plot with an increase in electron demand, they concluded that the data were best interpreted by invoking inductive localized π-polarization of the double bond between the cationic carbon and the ipso carbon (C'_1) of the aryl group bearing the fixed substituent, X, in resonance contributor 18.[16]

12. X = 3',4'-CH_2CH_2O
13. X = 4'-OCH_3
14. X = 4'-CH_3
15. X = H
16. X = 4'-CF_3
17. X = 3',5'-(CF_3)

18
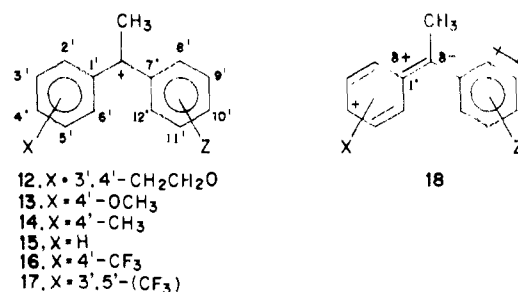
In view of the current results with the conjugated cations 2 and 3, it is reasonable to question the importance of π-polarization in the diarylethyl cations. A close examination of the variations of other chemical shifts in the systems studied by Brown reveals

(37) Ancian, B.; Membrey, F.; Doucet, J. P. *J. Org. Chem.* **1978**, *43*, 1509.
(38) Ancian, B.; Doucet, J. P.; Dubois, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4764.
(39) Membrey, F.; Ancian, B.; Doucet, J. P. *Org. Magn. Reson.* **1978**, *11*, 580.

Table VII. Sum of Ortho, Para, and Cationic Carbon Chemical Shifts in 1,1-Diaryl-1-ethyl Cations (**12-17**) and 9-Methyl-9-anthracenium Cations (**19**)ᵃ

	total chemical shiftsᵇ⁻ᵈ									
cations	Z = p-OCH₃	Z = p-CH₃	Z = p-F	Z = p-Cl	Z = m-CH₃	Z = H	Z = m-Cl	Z = m-CF₃	Z = p-CF₃	Z = 3,5-(CF₃)₂
12	662.9	673.0	673.0	673.4	675.9	676.1	674.4	674.4	675.1	672.1
	(-13.2)	(-3.1)	(-3.1)	(-2.7)	(-0.2)		(-1.7)	(1.7)	(-1.0)	(-4.0)
13	664.0	679.0	680.2	681.0	683.0	683.5	683.0	683.6	684.2	681.9
	(-19.5)	(-4.5)	(-3.3)	(-2.5)	(-0.5)		(-0.5)	(+0.1)	(+0.7)	(-1.6)
14	638.3	665.5	670.5	670.1	673.7	673.0	682.3	684.0	685.9	688.5
	(-34.7)	(-7.5)	(-2.5)	(-2.9)	(+0.7)		(+9.3)	(+11.0)	(+12.9)	(+17.3)
15	620.0	649.1				659.5		670.7	673.1	676.8
	(-39.5)	(-10.4)						(+11.2)	(+13.6)	(+17.3)
16	609.9	633.9	646.2	650.9	652.6	655.5	662.8	667.4	671.3	676.3
	(-45.6)	(-11.6)	(-9.3)	(-4.6)	(-2.9)		(+7.3)	(+11.9)	(+15.8)	(+20.8)
17	595.2	627.5				642.3			659.6	662.2
	(-47.1)	(-14.8)							(+17.3)	(+19.9)
19	609.1	627.1		633.6		635.3	638.5	642.2	644.0	
	(-26.2)	(-8.2)		(-1.7)			(+3.2)	(+6.9)	(+8.7)	

ᵃChemical shifts are in ppm with respect to external Me₄Si and are taken from ref 21 (for **12-17**) and 24 (for **19**). ᵇ$\delta_T = \delta_{C^+} + \delta_{C'_2} + \delta_{C'_4} + \delta_{C'_6}$ for **12-17** and $\delta_T = \delta_{C^+} + \delta_{C_{5a}} + \delta_{C_6} + \delta_{C_8}$ for **19**. ᶜValues in parentheses are $\Delta\delta_T = \delta_T(Z) - \delta_T(Z = H)$. ᵈm, p, and 3, 5 represent 9', 10' and 9', 11', respectively, in **12-17** and 2, 3 and 2, 4 in **19**.
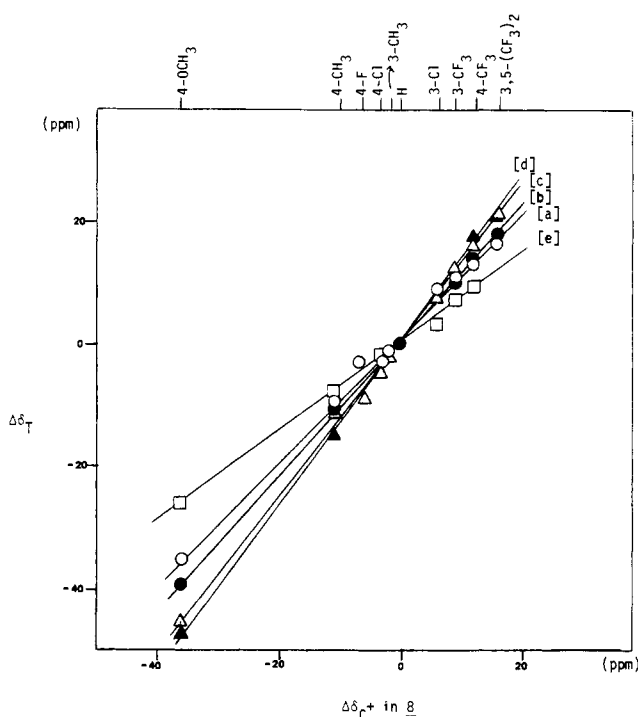

Figure 6. A plot of the differential sum of ortho, para, and carbocationic center chemical shifts of diarylethyl cations (**14** [a, O], **15** [b, ●], **16** [c, Δ], **17** [d, ▲]) and 9-methylanthracenium cations (**19**) [e, □] vs. the differential carbocationic center chemical shifts of 1-aryl-1-cyclopentyl cations (**8**).

Figure 7. A plot of the differential sum of ortho, para, and carbocationic center chemical shifts of diarylethyl cations (**12** [a, O] and **13** [b, Δ]) vs. differential carbocationic center chemical shifts of 1-aryl-1-cyclopentyl cations (**8**).

inconsistencies which are not reconcilable with π-polarization. In fact, the chemical shifts of the ortho and para carbons of the fixed aryl ring in each series can be interpreted quite satisfactorily in terms of simple π-delocalization. Inductive π-polarization is unnecessary. Table VII lists the sum of ortho, para, and cationic carbon chemical shifts of the fixed aryl ring in 1,1-diaryl-1-ethyl cations **12-17**. A plot of the differential sum³³ of all four centers vs. the Δδ_C+ of **8** (Figure 6) reveals an excellent linear relationship for all systems except **12** and **13** (correlation coefficients: **14**, 0.99; **15**, 1.0; **16**, 0.99; **17**, 1). That the systems **12** and **13** (Figure 7) still show deviations with an increase in electron demand can be accounted for by the fact that the positive charge is delocalized onto the heteroatom oxygen. This is not reflected in C′₂, C′₄, C′₆, and C⁺ chemical shifts.

The above plots (Figures 6 and 7) demonstrate that only resonance interaction is necessary to account for the results over the entire range of substituents studied. Depending on the nature of
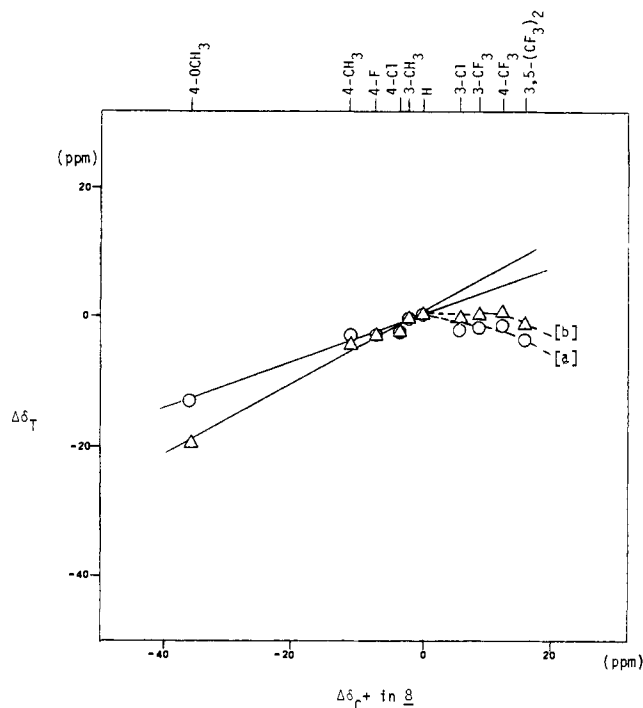
the Z substituent, the positive charge can reside either at ortho and para carbons or on oxygen (as in **12** and **13**) of the fixed aryl ring to varying degrees. Similarly, the previously studied 9-methyl-9-anthracenium ions (**19**) also show a linear plot ($r^2 = 0.98$, Figure 6) indicating again the unimportance of inductive π-polarization in these resonance stabilized systems.⁴⁰ The same arguments can be extended to diphenylmethyl cations **20** studied recently by Kelly and co-workers.⁴¹

(40) Craik, D. J.; Brownlee, T. C. *Prog. Phys. Org. Chem.* **1983**, *14*, 1.
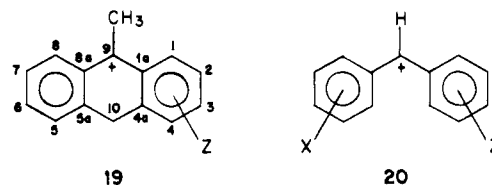
The unimportance of inductive localized π-polarization on ^{13}C NMR chemical shifts in protonated acetophenones was first discussed by Craik and Brownlee, the orginators of the inductive localized π-polarization phenomenon.[40] However, Brown et al.[21,22,25] have attempted to use this effect as a possible explanation for the observed deviations in the application of the "tool of increasing electron demand" in the ^{13}C NMR spectroscopic study of certain carbocations. We believe that our studies emphasizes the unimportance of such effects on ^{13}C NMR chemical shifts in fully developed carbocations under superacid conditions.

Conclusion

We conclude that use of the Gassman–Fentiman tool of increasing electron demand, coupled with ^{13}C NMR, to probe for extraordinary behavior in π-conjugated cations is reliable only if the chemical shifts of *all* conjugatively related cationic carbon sites are taken into account. The attempt to correlate ^{13}C$^+$ NMR chemical shifts of the arylcyclopentyl cations and the σ_{C^+} parameters derived from them with only on nominally cationic carbon of a conjugated system will give misleading results. When the representative conjugated cations described in this paper are probed considering all involved carbons, they are seen to be ordinary conjugated systems, requiring only π-delocalization. There is no evidence requiring inductive localized π-polarization.

There is, therefore, no reason to doubt the reliability of the probe to detect extraordinary behavior in cyclopropyl conjugated systems (e.g., 3-aryl-3-nortricyclyl), homoallylically conjugated systems (e.g., 5-aryl-2-norbornen-5-yl), or σ-bridged systems (e.g., 2-aryl-2-norbornyl).[7-10,42]

---

(41) Kelly, D. P.; Jenkins, M. J. *J. Org. Chem.* **1984**, *49*, 409.
(42) Olah, G. A.; Prakash, G. K. S.; Farnum, D. G.; Clausen, T. P. *J. Org. Chem.* **1983**, *48*, 2146.

Experimental Section

The precursor alcohols, *trans*-1-aryl-3-methylbut-1-en-3-ols (**4**), were prepared by the reaction of methyllithium with either the corresponding *trans*-benzalactones or the *trans*-ethyl cinnamate in ethereal solutions. The 4-arylpent-2-yn-4-ols (**5**) were prepared by the addition of propynyllithium to the respective substituted acetophenones in refluxing tetrahydrofuran solutions. The ^{1}H NMR spectral data and the physical constants of precursor alcohols are listed in Tables I and II. The ^{13}C NMR data are listed in Tables III and IV.

Carbocations. The ions were prepared by the addition of the appropriate precursor dissolved in SO$_2$ClF to a fivefold excess of FSO$_3$H:SbF$_5$ dissolved in SO$_2$ClF precooled at −78 °C so as to obtain a 15% solution of the carbocations.

NMR Spectra. The ^{1}H and ^{13}C NMR spectra were obtained on a Varian Associates Model XL-200 NMR spectrometer equipped with variable-temperature probes. The field lock was held by a 2.5-mm capillary containing acetone-d_6. The chemical shifts are referenced to external tetramethylsilane.

Silacyclopropylcarbinyl and Cyclopropylsilylenium Cations in the AlCl$_3$-Induced Rearrangements of (Chloromethyl)vinylsilanes[1]
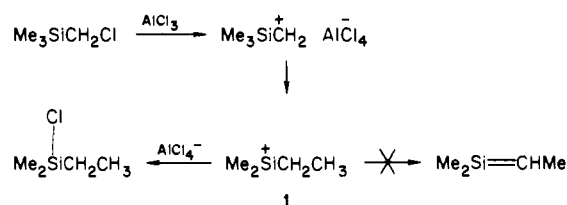
Larry R. Robinson, Gary T. Burns, and Thomas J. Barton*

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011. Received November 5, 1984

Abstract: Reaction of a variety of (chloromethyl)vinylsilanes and AlCl$_3$ affords cyclopropylchlorosilane products. These reactions are most economically viewed as proceeding via β-closure of the initially formed carbocation to produce silacyclopropylcarbinyl cations which either rearrange to cyclopropylsilylenium ions or can be quenched directly by chloride to yield allylic chlorosilanes. Alkyl substitution at the terminal position of the vinyl group induces a shift to allylic products consistent with stabilization of the initial silacyclopropylcarbinyl cation relative to the rearranged ion or a silacyclobutyl cation formed from γ-closure.

The first observation of AlCl$_3$-induced rearrangements of α-chloroalkylsilanes was by Whitmore,[2] who in 1947 reported that treatment of (chloromethyl)trimethylsilane with AlCl$_3$ produced ethyldimethylchlorosilane in 79% yield. It was assumed that this reaction proceeded in a fashion analogous to the AlCl$_3$-induced rearrangement of neopentyl chloride with chloride quenching of the corresponding silylenium ion **1** rather than loss of a proton

to produce the then unknown silicon–carbon double bond.

$$Me_3SiCH_2Cl \xrightarrow{AlCl_3} Me_3Si\overset{+}{C}H_2 \; AlCl_4^-$$

$$\downarrow$$

$$\underset{\overset{|}{Me_2SiCH_2CH_3}}{\overset{Cl}{|}} \xleftarrow{AlCl_4^-} Me_2\overset{+}{Si}CH_2CH_3 \xcancel{\longrightarrow} Me_2Si{=}CHMe$$

1

Although the AlCl$_3$-induced rearrangement has often been employed for synthetic purposes,[3] there has been surprisingly little

---

(1) Presented at the VII International Symposium on Organosilicon Chemistry, Kyoto, Japan, September 11, 1984.
(2) Whitmore, F. C.; Sommer, L. H.; Gold, J. *J. Am. Chem. Soc.* **1947**, *69*, 1976.