Use of 2-Thienyl, 2-Furyl, 5-Ethyl-2-furyl, and Protonated 4-Acetylphenyl Substituents in Carbon-14 Nuclear Magnetic Resonance Chemical Shift Correlations[1]

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The application of the tool of increasing electron demand has been extended by employing increased electron-withdrawing as well as electron-donating substituents. In combination with the electron-withdrawing 4-protonated acetylphenyl substituent and the electron-donating 2-thienyl, 2-furyl, and 5-ethyl-2-furyl groups, the ^{13}C NMR chemical shift range is nearly doubled over that of previously studied substituent effects. Observation of large deviations in the ^{13}C NMR chemical shift plots of the cationic center of 2-aryl-2-norbornyl and 8-aryl-8-tricyclo[5.2.1.$0^{2,6}$]decyl cations vs. those of model 1-aryl-1-cyclopentyl cations, which includes the presently developed protonated 4-acetylphenyl substituent, further supports the earlier interpretations of the onset of nonclassical σ delocalization in these systems.

Although it is only one of the many techniques available to study carbocations generated under stable-ion conditions, the tool of increasing electron demand has in recent years been extensively used.[2-5] Coupled with ^{13}C NMR spectroscopy it has been applied to many systems such as the 7-norbornenyl,[4c] 9-pentacyclononyl,[3e] and 2-norbornyl[3d,4b,d] cations. Recently we reported a comprehensive evaluation of the tool of increasing electron demand applied to 22 aryl-substituted carbocationic systems.[4d] It was observed that slopes of less than unity in the ^{13}C NMR chemical shift correlations could be attributed to additional charge-delocalizing mechanisms present in the system such as cyclopropyl or π conjugation.

However, the values of the slopes of these chemical shift correlations depended to a large extent upon the strong electron-donating *p*-methoxy substituent.[6] This fact, along with the notorious behavior of the *p*-methoxy substituent in the superacid media, prompted us to investigate several other possibilities for electron-donating substituents.

The tool of increasing electron demand has also revealed the onset of nonclassical σ delocalization in the 2-aryl-2-norbornyl and 8-aryl-8-tricyclo[5.2.1.$0^{2,6}$]decyl cations.[3d,4b,d] In contrast to the linear behavior observed between classical systems,[3d] a plot of the cationic carbon (C-2) chemical shifts of the 2-aryl-2-norbornyl cations vs. those of model systems shows a distinct break with the electron-withdrawing 4-(trifluoromethyl)phenyl and 3,5-bis(trifluoromethyl)phenyl substituents. This deviation in linearity has been attributed to the onset of σ bridging. A similar deviation was observed in a plot of the 8-aryl-8-tricyclo-[5.2.1.$0^{2,6}$]decyl cations. However, in the latter system, the break is less pronounced, indicating a smaller degree of σ delocalization.

When applied to other systems whose parent cations have been depicted as σ bridged such as the bicyclo-[2.1.1]hexyl or cyclobutyl cations, a similar deviation was not observed.[4c] The cations displayed classical (i.e., linear) behavior over the range of substituents employed [*p*-methoxy to 3,5-bis(trifluoromethyl)] indicating the lack of sufficient electron demand necessary for the onset of σ bridging. The need for a stronger electron-withdrawing group than the bis(trifluoromethyl)phenyl substituent was obvious.

In this paper we report our findings on such greatly increased electron-withdrawing and electron-donating substituents.

Electron-Donating Substituents

The *p*-methoxy group has proven to be the most strongly electron-donating aryl substituent suitable for stable ion studies. Indeed, *p*-methoxyphenyl-substituted cations are extremely stable and have been extensively studied.[7] Most of the data available on the *p*-methoxy substituent has been generated in connection with the tool of increasing electron demand studies. It has been shown in several of these studies that a wide variation in the chemical shifts of the cationic carbons occur with changes in the acid concentration. For example, a variation of 42 ppm is observed for the 2-(*p*-methoxyphenyl)-2-adamantyl cation.[3e] Presumably, this is due to either protonation or Lewis acid complexation of the oxygen's lone pair of electrons, thereby decreasing or eliminating the ability of the aryl ring to

(1) Stable Carbocations. 224. For part 243 see: Olah, G. A. *Chem. Scr.* **1981**, *18*, 97-125.

(2) Richey, H. G., Jr.; Nichols, D.; Gassman, P. G.; Fentiman, A. F., Jr.; Winstein, S.; Brookhart, M.; Lustgarten, R. K. *J. Am. Chem. Soc.* **1970**, *92*, 3783-3784.

(3) (a) Farnum, D. G.; Wolf, A. D. *J. Am. Chem. Soc.* **1974**, *96*, 5166-5175. (b) *Ibid.* **1974**, *96*, 5175-5181. (c) Farnum, D. G.; Botto, R. E. *Tetrahedron Lett.* **1975**, 4013-4016. (d) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am Chem. Soc.* **1978**, *100*, 3847-3855. (e) Farnum, D. G.; Clausen, T. P. *Tetrahedron Lett.* **1981**, 549-552.

(4) (a) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 5683-5687. (b) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N. *Ibid.* **1980**, *102*, 6127-6130. (c) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Prakash, G. K. S. *Ibid.* **1981**, *103*, 1122-1128. (d) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998-2002. (e) Olah, G. A.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 1628-1631.

(5) (a) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956-6960. (b) Brown, H. C.; Periasamy, M.; Liu, K. T. *J. Org. Chem.* **1981**, *46*, 1646-1650. (c) Kelly, D. P.; Jenkins, M. J.; Mantello, R. A. *Ibid.* **1981**, *46*, 1650-1653. Brown, H. C.; Periasamy, M. *Ibid.* **1981**, *46*, 3161-3165. (e) *Ibid.* **1981**, *46*, 3166-3170. (f) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Ibid.* **1981**, *46*, 3170-3174. (g) Kelly, D. P.; Farquharson, G. J.; Giansiracusa, J. J.; Jensen, W. A.; Hugel, H. M.; Porter, A. P.; Rainbow, I. J.; Timewell, P. H. *J. Am. Chem. Soc.*, **1981**, *103*, 3539-3543. (h) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1982**, *47*, 5-8.

(6) The cationic chemical shift difference between the *p*-methoxyphenyl substituted cyclopentyl cation and the *p*-methylphenyl substituted cyclopentyl cation (the next strongest electron donating substituent commonly used) is 24 ppm, nearly the same as the chemical shift difference between the para-methylphenyl and the 3,5-bis(trifluoromethyl)phenyl substituted cyclopentyl cations (27 ppm).

(7) See, for example: Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284. Jost, R.; Sommer, J.; Engdahl, C. E.; Ahlberg, P. *Ibid.* **1980**, *102*, 7663-7667.

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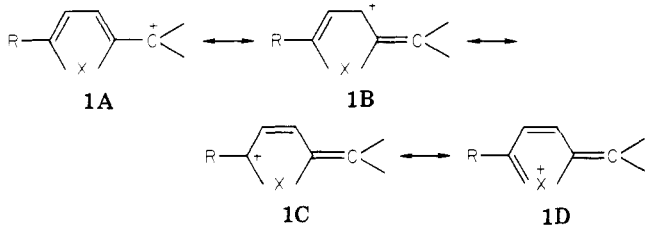
Table I. ^{13}C NMR Chemical Shifts of the 2-Thienyl-Substituted Carbocations

cation	chemical shift, ppm					
	C^+	C_2'	C_3'	C_4'	C_5'	other
2a	225.1	143.3	153.5	136.7	174.1	Cα, 41.2, 42.4; Cβ, 25.1
3a	210.2	150.0	153.9	139.0	177.4	CH_3, 30.8, 28.2
4a	215.9	145.6	151.6	138.0	175.8	Cα, 41.9, 38.9; Cβ, 32.3, 32.1; Cγ, 24.5
5a	218.0		152.6	138.2	176.7	Cα, 35.4, 32.2; Cβ, 14.9
6a	215.0	148.9	152.1	138.0	176.0	Cα, 44.1, 41.0; Cβ, 25.8, 25.3; Cγ, 13.1
7a	213.7, 213.9		153.1, 152.1	138.0	176.3, 176.6	Cα, 37.6, 34.6; Cβ, 13.6, 13.8; Cα, 28.1, 25.4
8a	226.4	143.8	149.8	137.8	173.1	Cα, 48.1, 44.8; Cβ, 43.7, 43.4; Cγ, 34.8; Cδ, 27.5
9a	223.7, 223.4		153.1	137.2, 136.5	172.1, 172.6	C_1, 55.2, 53.9; C_4, 37.4; C_6, 30.7, 30.6; C_3, 46.0, 46.7; C_5, 25.0; C_7, 46.3
10a	222.7, 223.0	142.0, 142.8	153.7, 153.4	137.6, 136.7	172.7, 173.6	

delocalize the charge. With this in mind we investigated other potential electron-releasing groups suitable for use in superacidic media.

2-Thienyl System. There is much experimental evidence indicating the substantial stabilizing ability of a 2-thienyl substituent in electrophilic reactions.[8] When the solvolytic rates for substituted 1-(2-thienyl)ethyl *p*-nitrobenzoates are plotted against the σ^+ substituent constants,[8] an excellent correlation is obtained with an extremely negative ρ value of –6.79 which is indicative of substantial charge development in the transition state. Likewise, it was found by ^{13}C NMR chemical shift response patterns that C_5 in (2-thienyl)carbenium ions has nearly twice as much positive charge as the para carbon in analogous phenyl systems.[9] This increase in charge delocalization can be explained on the basis of the resonance structures **1A–D** (X = S, R = H).



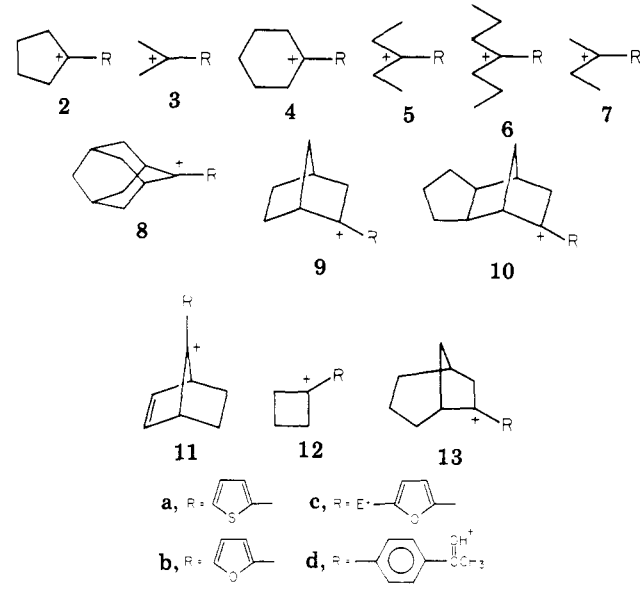
1A 1B 1C 1D

X = S, O; R = H, C_2H_5

The slow addition of alcohols **2a**-OH–**10a**-OH to FSO_3H/SO_2ClF at –78 °C led to dark red solutions of the corresponding cations **2a–10a** (Chart I). These ions were conveniently studied at –60 °C and showed no apparent rearrangement or decomposition. The ^{13}C NMR chemical shifts obtained for ions **2a–10a** are given in Table I. The cationic carbons of ions **2a–10a** are significantly shielded (7–15 ppm) when compared to the analogous *p*-methoxyphenyl-substituted ions.

There is substantial π-bond character between C-2 of the thienyl moiety and the cationic carbon due to the substantial π-electron donation from the thienyl ring to the highly electron-deficient carbocationic center [involving resonance structures **1B–1D** (X = S, R = H)]. This causes a high rotational barrier about the C–C bond and brings about a nonequivalance of the carbons in the side chain.[10] For example, the two Cα's in the dimethyl (2-thienyl) cation **3a** are observed at 30.8 and 28.2 ppm. A similar nonequivalence is also observed in the case of β-carbons, although the chemical shift difference is smaller.

Chart I

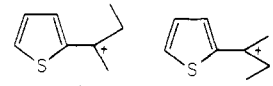


2 3 4 5 6 7 8 9 10 11 12 13

a, R = c, R =

b, R = d, R =

For systems containing nonsymmetrical substituents such as cations **7a**, **9a**, and **10a**, there exists two possible isomers both of which are observed. Cation **7a** exists as conformers **7a′** and **7a″** in approximately equal amounts.



7a′ 7a″

The cationic carbons of the two isomers differ only slightly in chemical shift (<1 ppm), and an average value was used in the ^{13}C NMR chemical shift correlations.

2-Furyl and 5-Ethyl-2-furyl Systems. The charge-delocalizing ability of the 2-furyl system has been demonstrated by the rates of solvolysis of several (2-furyl)-methylcarbinol derivatives which were found to be greater than the rates for the related *p*-methoxybenzyl compounds.[11] However, the use of furan as a substituent in stable-ion studies has not been widely exploited.[9]

The treatment of the 2-furyl-substituted alcohols **2b**-OH–**10b**-OH with FSO_3H/SO_2ClF at –78 °C led to the formation of the corresponding cations **2b–10b**. The chemical shifts of these ions are given in Table II. The cationic carbons for ions **2b–10b** are significantly shielded when compared to the 2-thienyl- or *p*-methoxyphenyl-substituted cations which is indicative of substantial charge delocalization. In agreement with this idea is the pronounced deshielding of C-5 in the furyl ring resulting from

(8) Noyce, D. S.; Lipinski, C. A.; Nichols, R. W. *J. Org. Chem.* **1972**, *37*, 2615–2620 and references therein.
(9) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1979**, *101*, 5309–5416.
(10) Similar high rotational barriers have been observed previously. See for example: Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044–2052.
(11) Noyce, D. S.; Kaiser, G. V. *J. Org. Chem.* **1969**, *34*, 1008–1012. Noyce, D. S.; Pavez, H. J. *Ibid.* **1972**, *37*, 2623–2625.

Table II. ^{13}C NMR Chemical Shifts of the 2-Furyl- and 5-Ethyl-2-Furyl-Substituted Carbocations

cation	chemical shift, ppm					other
	C^+	C_2'	C_3'	C_4'	C_5'	
2b	207.2	155.6	150.8	125.0	175.7	Cα, 38.6, 38.3; Cβ, 25.1, 24.4
3b	193.1	159.8	152.1	126.9	179.0	CH_3, 25.8, 24.6
4b	199.8	156.7	150.0	125.8	177.9	Cα, 36.1, 34.7; Cβ, 31.3, 31.0; Cγ, 24.2
5b	201.5	158.3	150.9	126.0	178.2	Cα, 30.1, 28.6; Cβ, 13.2, 12.4
6b	198.9	159.2	150.8	125.1	178.1	Cα, 38.9, 27.7; Cβ, 24.0, 23.8; Cγ, 13.3
7b	197.5	158.7	151.7, 150.9	126.3	178.6, 178.2	
8b	210.7	154.8	148.5	125.4	177.0	
9b	206.7, 206.1	153.7, 153.6	149.7, 149.9	124.1, 124.4	174.7, 174.1	C_1, 50.5; C_4, 36.0, 36.3; C_6, 29.2, 28.5; C_3, 43.2, 42.6; C_5, 24.4, 24.0; C_7, 39.9, 39.3
10b	206.6 206.0	154.9 154.4	150.3, 151.0	124.8, 125.2	175.7, 174.8	
2c	193.1	154.5	150.2	123.8	197.9	Cα, 36.5, 36.0; Cβ, 24.6, 24.3; CH_2, 25.2; CH_3, 8.1
3c	179.5	158.2	150.6	125.4	200.4	Cα, 23.8, 22.9; CH_2, 25.2; CH_3, 8.5
4c	187.1	156.3	150.3	125.7	200.8	Cα, 35.4, 34.1; Cβ, 30.9, 30.4; Cγ, 25.5; CH_2, 25.7; CH_3, 8.9
5c	187.8	156.7	149.7	124.7	199.8	Cα, 28.0, 26.7; Cβ, 12.7, 11.9; CH_2, 24.6; CH_3, 7.7
9c	195.0, 194.4	153.8, 153.9	150.7, 151.0	124.1, 124.6	198.2, 197.5	C_1, 49.4; C_4, 36.9, 37.1; C_6, 29.9, 29.2; C_3, 42.6, 41.8; C_5, 26.1, 25.8; C_7, 40.9, 40.3; CH_2, 25.2; CH_3, 9.2

Table III. ^{13}C NMR Chemical Shifts of the Protonated 4-Acetylphenyl-Substituted Carbocations

cation	chemical shift, ppm			other
	C^+	$>C=OH^+$		
2d	293.2	225.5	26.6	Cα, 54.0; Cβ, 25.6
3d	284.8	226.2	27.3	Cα, 39.6
9d	255.0	224.7	26.3	
10d	267.6	225.3	26.9	
11d	63.0	220.7	25.0	$C_{1,4}$, 56.5; $C_{2,3}$, 135.9, $C_{5,6}$, 25.0

resonance structures **1C,D** (X = O).

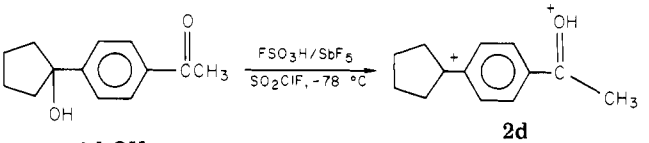
Employing a furyl ring with a C-5 substituent capable of dispersing positive charge should increase the amount of charge delocalization.[11,12] This was indeed the case for the 5-ethyl-2-furyl-substituted cations studied (**2c–5c** and **9c**) in this investigation. All these cations show highly shielded cationic centers (approximately 14-ppm shielded with respect to the analogous furyl systems) and highly deshielded C-5 carbons. The deshielding of C-5 indicates that the resonance form **1C** (X = O, R = C_2H_5) contributes signficantly to the overall ionic structure.

Similar to the 2-thienyl-substituted cations, the 2-furyl- and 5-ethyl-2-furyl-substituted systems also show isomeric behavior in the case of nonsymmetrical substituents (**7b,c, 9b,c, 10b,c**). In the case of symmetrically substituted cations (**2–6, 8**) nonequivalence of side-chain carbons is observed. Again, the cationic chemical shifts of the isomeric cations differ only slightly, and an average was used in the chemical shift correlations.

Electron-Withdrawing Groups

The 3,5-bis(trifluoromethyl)phenyl group is the most common electron-withdrawing substituent used in stable-ion studies at the present time. Even though it has two strongly electron-demanding trifluoromethyl substituents, the 3,5-bis(trifluoromethyl)phenyl group still acts as a 6-π-electron system and thus delocalizes the charge. Other electron-withdrawing groups used are the *p*-trifluoromethyl and *p*-dimethylammonium[4a] substituents. However, the last two substituents are not as electron demanding as the 3,5-bis(trifluoromethyl) group.

Of several possible candidates for highly electron-withdrawing substituents,[14] the protonated acetyl group $^+HO{=}CCH_3$ proved to be the most successful. The treatment of the keto alcohol **2d**-OH with FSO_3H/SbF_5 in SO_2ClF at −78 °C led to the formation of the corresponding protonated dication **2d**.



2d-OH 2d

The carbocationic center of **2d** is significantly deshielded compared to other aryl-substituted cyclopentyl cations.[3d] The cationic carbon was observed at δ(^{13}C) 293.2, 7.0 ppm downfield with respect to the cationic chemical shift of the 1-[3,5-bis(trifluoromethyl)phenyl]-1-cyclopentyl cation.[3d] The protonated carbonyl carbon also reveals the effect of two positive charges in this molecule, the chemical shift being 225.5 ppm, nearly 6 ppm deshielded with respect to protonated acetophenone.[15]

The substituted cumyl system **3d** was also generated for this study. The chemical shift of the carbenium carbon in **3d** again reveals the substantial electron-withdrawing capacity of the protonated acetyl moiety. There is a 10.4-ppm deshielding upon going from the bis(trifluoromethyl)phenyl-substituted cumyl[3d] cation to cation **3d**. Attempts to prepare other classical model systems such as the cyclohexyl and bicyclo[3.2.1]octyl cations failed. Instead, unidentified rearranged products were obtained.

Cationic systems indicating σ or π delocalization such as **9–11** and **12** were also investigated. The ^{13}C NMR data for the generated cations are given in Table III.

^{13}C NMR Chemical Shift Correlations

The ^{13}C NMR chemical shift correlation plots including the newly developed substituents are presented in Figures

(12) Substantial positive charge is localized at C-5 as indicated by both ^{13}C NMR chemical shift response patterns[9] and chemical studies.[13]

(13) Divald, S.; Chunand, M. C.; Joullie, M. M. *J. Org. Chem.* **1976**, *41*, 2835–2846.

(14) Other potential electron-withdrawing substituents considered were the *p*-[bis(trimethylsilyl)ammonium] and *p*-nitro groups.

(15) Forsyth, D.; Spear, R. J.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 2512–2518.

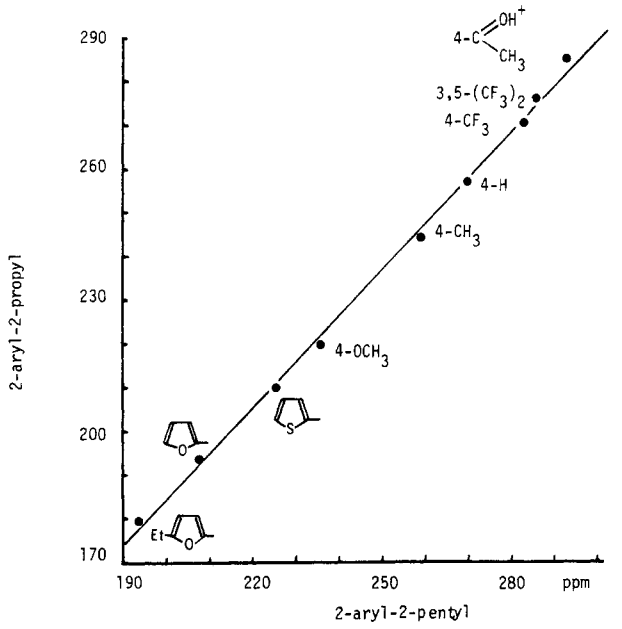


Figure 1. Plot of the ^{13}C NMR chemical shifts of the cationic center of the 2-aryl-2-propyl cations **3** vs. those of the model 1-aryl-1-cyclopentyl cations **2**.

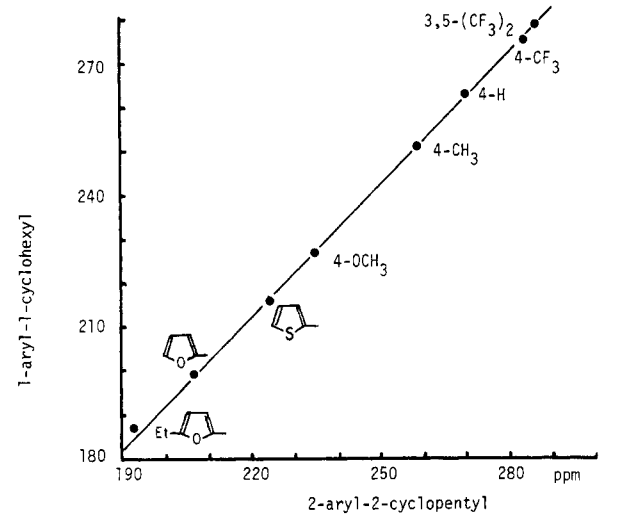


Figure 2. Plot of the ^{13}C NMR chemical shifts of the cationic center of the 1-aryl-1-cyclohexyl cations **4** vs. those of the model 1-aryl-1-cyclopentyl cations **2**.

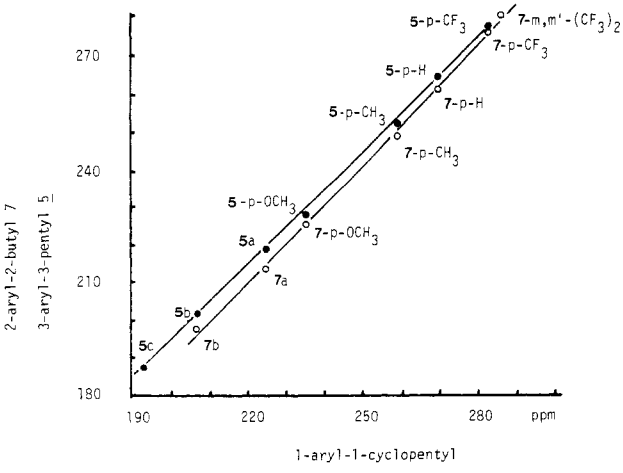


Figure 3. Plot of the ^{13}C NMR chemical shifts of the cationic center of the 3-aryl-3-pentyl cations **5** and 2-aryl-2-butyl cations **7** vs. those of the model 1-aryl-1-cyclopentyl cations **2**.

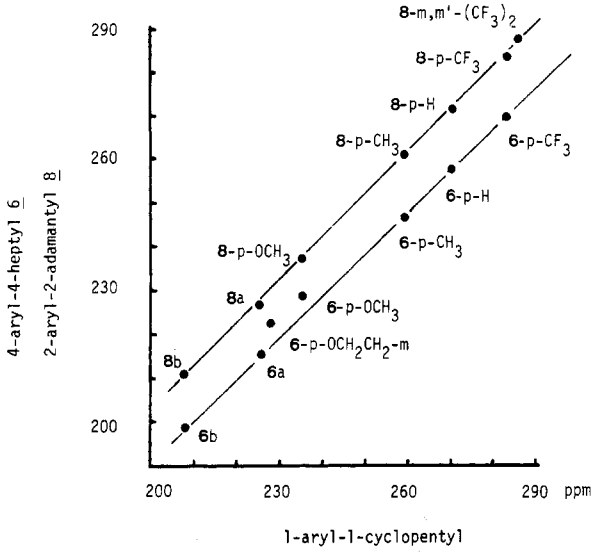


Figure 4. Plot of the ^{13}C NMR chemical shifts of the cationic center of the 4-aryl-4-heptyl cations **6** and the 2-aryl-2-adamantyl cations **8** vs. those of the model 1-aryl-1-cyclopentyl cations **2**.

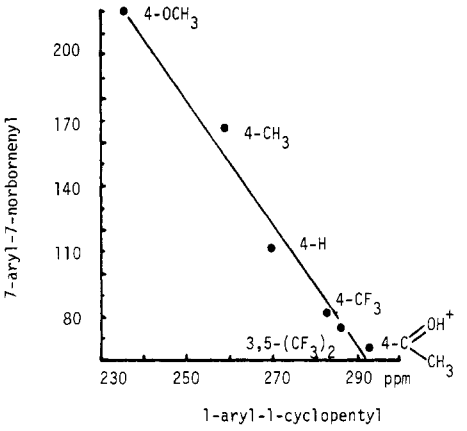


Figure 5. Plot of the ^{13}C NMR chemical shifts of the cationic center of the 7-aryl-7-norbornenyl cations **11** vs. those of the model 1-aryl-1-cyclopentyl cations **2**.

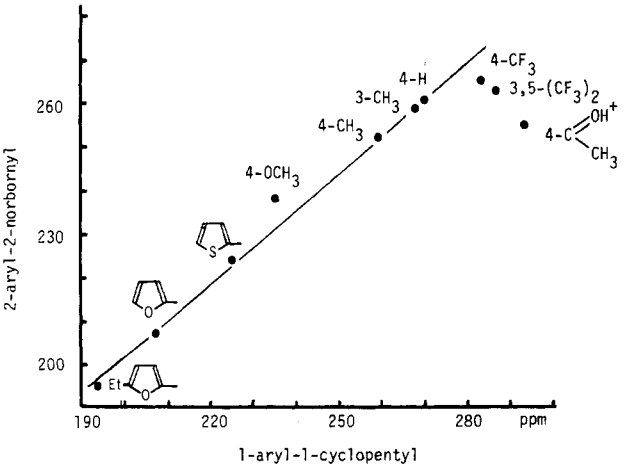


Figure 6. Plot of the ^{13}C NMR chemical shifts of the cationic center of the 2-aryl-2-norbornyl cations **9** vs. those of the model 1-aryl-1-cyclopentyl cations **2**.

1–7. The 2-thienyl, 2-furyl, 5-ethyl-2-furyl, and protonated *p*-acetyl substituents expand the chemical shift range previously studied by nearly twofold. For the model cyclopentyl system, the chemical shift difference from the 5-ethyl-2-furyl to the para $^{+}HO{=}CCH_3$ substituent is 100.1

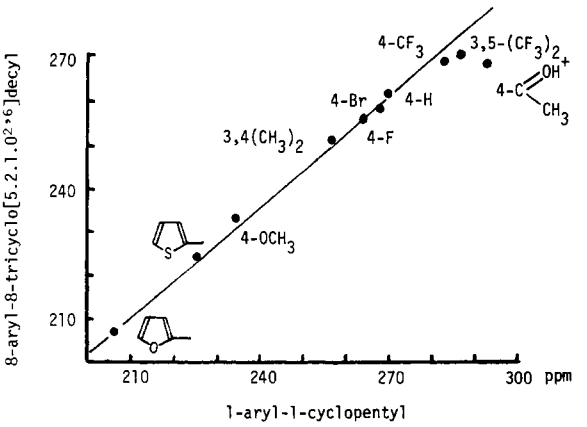
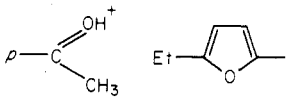


Figure 7. Plot of the ^{13}C NMR chemical shifts of the cationic center of the 8-aryl-8-tricyclo[5.2.1.0^{2,6}]decyl cations **10** vs. those of the model 1-aryl-1-cyclopentyl cations **2**.

ppm, while from *p*-methoxy to 3,5-bis(trifluoromethyl) is 51 ppm.[3d,4d] Similarly, the chemical shift difference of the cumyl system with the extended-range substituents is 105.3 ppm while the difference from *p*-methoxy to 3,5-bis(trifluoromethyl) is 55.4 ppm.[3d,4d] Most of this increase in range is due to the electron-releasing substituents.

It is evident from Figures 1–4 that the newly developed substituents nicely correlate the cationic shifts in classical systems. Excellent correlation coefficients are observed even with the highly electron demanding (I) and electron



I II

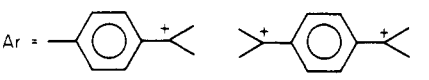
releasing (II) substituents included in the analysis. This indicates the general validity of using these substituents in stable-ion studies. It is interesting to note the apparent aberrant behavior of the *p*-methoxyphenyl and the 5-coumaranyl[5h] substituents in the 4-aryl-4-heptyl cations (Figure 4). The deviation of these two points from the normally excellent linear relationship indicates the caution needed when using the *p*-methoxyphenyl and 5-coumaranyl substituents. The deviation is probably due to protonation or complexation of the oxygen by the acid system as discussed earlier.

Figure 5 depicts the plot of the cationic carbons of the 7-aryl-7-norbornenyl and the 1-aryl-1-cyclopentyl cations including the data of the protonated acetyl substituent. It is obvious from the good correlation observed that the para-protonated acetyl group is very useful as an electron-withdrawing group in stable-ion studies. The negative slope of the ^{13}C NMR correlation was described earlier[4c] as due to nonclassical π delocalization. Surprisingly, the cationic chemical shift of the para-protonated acetyl-substituted cation **11d** is $\delta(^{13}C)$ 63.0, 8.9-ppm shielded with respect to the 7-methyl-7-norbornenyl cation [$\delta(^{13}C)$ 71.9],[16] indicating that even the aryl-substituted ion is enormously π delocalized.

The plots of the 2-aryl-2-norbornyl and 8-aryl-8-tricyclo[5.2.1.0^{2,6}]decyl cations employing the newly developed substituents are shown in Figures 6 and 7. It has been shown that both of these systems have deviations in the chemical shift correlation plots with electron-withdrawing substituents, indicating the onset of σ bridging (delocalization).[3d,4a] Such deviations are more pronounced in the present plots which include the protonated acetyl substituent in the analysis (Figures 6 and 7). This continuation of nonclassical behavior in these plots reveals the usefulness of the protonated acetyl group as a highly electron-demanding substituent as well as verifies the earlier interpretations.[3d,4a]

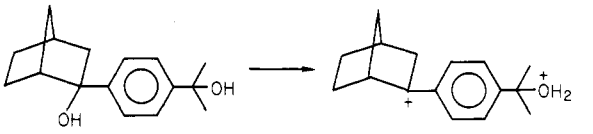
One system for which the parent cation has been interpreted to involve nonclassical σ bridging but for which the tool of increasing electron demand has failed to reveal such behavior is the cyclobutyl cation.[4c] An attempt was made to generate para-protonated (acetylphenyl)cyclobutyl cation **12d** with the hope of observing a deviation due to the onset of σ bridging. However, cation **12d** could not be prepared from the corresponding alcohol under several superacid conditions, and no discernible peaks in the ^{13}C NMR spectrum were observed.

In hopes of obtaining a "super" electron-demanding group, we investigated the possibility of using a para-substituted cumyl cation as a substituent. The tetramethyl-substituted dication **14** was generated previously



14

from the diol precursor in SbF_5/SO_2ClF.[16] It showed substantial charge–charge repulsion as evidenced by the significant deshielding of the methyl carbons in the ^{13}C NMR spectrum. However, the dication system could not be generated either from the cyclopentyl- or 2-norbornyl-substituted diols **15** and **16** under a variety of conditions. The 2-norbornyl system underwent monoionization and O-protonation to give **17**.



16 17

The failure to observe cations **4d**, **12d**, and the bicyclo[3.2.1]octyl derivative indicates the destabilizing nature of the protonated acetophenone group inspite of the presence of the aromatic π system which is capable of electron donation. This destabilizing behavior has also been observed in several 3,5-bis(trifluoromethyl)phenyl- and pentafluorophenyl-substituted cations.[18] It appears that there is a limit to the electron-demanding ability of the aromatic substituents. The use of too strong of an electron-withdrawing group may cause decomposition, rearrangement, or failure of the precursor to fully ionize.

σ^{c+} Values

Brown has introduced σ^{c+} constants with which he correlates the cationic carbon chemical shifts of aryl-substituted carbocations.[5a] The values ranged from −2.02 for the *p*-methoxy substituent to 1.03 for the 3,5-bis(trifluoromethyl) substituent. Later, Brown and Kelly investigated the 5-coumaranyl moiety as an electron releasing group which was found to have a σ^{c+} value of −2.4.[5g] The newly developed electron-donating substituents presented in this paper have substantially more negative values of −2.53, −3.44, and −4.19 for the 2-thienyl, 2-furyl, and 5-ethyl-2-furyl systems, respectively. The electron-demanding protonated acetyl group has a σ^{c+} value of 1.60,

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(18) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S., unpublished results.

larger than the value of the 3,5-bis(trifluoromethyl) group (1.03).

Conclusion

The development of the protonated acetyl group, which is significantly more electron-withdrawing than the aryl substituents previously used, further verifies the onset of nonclassical behavior in the 2-aryl-2-norbornyl and 8-aryl-8-tricyclo[5.2.1.$0^{2,6}$]decyl cations. The electron-demanding nature of this substituent is fully revealed by the observed ^{13}C NMR chemical shift deshieldings of the cationic centers. In combination with the protonated acetyl substituent, the electron-donating 2-thienyl, 2-furyl, and 5-ethyl-2-furyl groups nearly double the ^{13}C NMR chemical shift range previously studied.

Experimental Section

Preparation of the 2-Thienyl-Substituted Alcohols 2a-OH–10a-OH. To a cooled (0 °C) solution of 2.3 g (0.027 mol) of thiophene and ether (20 mL) was added *n*-BuLi in hexane (0.020 mol) dropwise. The resulting mixture was stirred at 0 °C for 1 h after which was added an etheral solution of the corresponding ketone (0.017 mol). After being stirred overnight, the reaction mixture was quenched with water (2 mL). After the ether layer was decanted and dried (over anhydrous $MgSO_4$), the ether solvent was removed under reduced pressure. The obtained crude product was purified either by distillation or recrystallization.

The furyl- and 5-ethyl-2-furyl-substituted alcohols 2b-OH–10b-OH, 2c-OH–5c-OH, and 9c-OH were prepared analogously by using 2.0 g of furan or 2.5 g of 2-ethyl furan, respectively.

The keto alcohols 2d-OH, 3d-OH, 9d-OH, 10d-OH, 11d-OH, 12d-OH, and 13d-OH were prepared by the addition of the appropriate ketone to the Grignard reagent generated from the ethylene ketal of *p*-bromoacetophenone in THF and subsequent deprotection.

The diols 15 and 16 were prepared from keto alcohols **2d**-OH and **9d**-OH by excess methyllithium addition in ether solution.

The physical constants and the ^{13}C NMR spectral data of the newly synthesized alcohols are the following (the melting and boiling points are uncorrected).

1-(2-Thienyl)-1-cyclopentanol (2a-OH): bp 53–55 °C (2.3 mm); ^{13}C NMR ($CDCl_3$) δ 152.3 (s), 126.2 (d), 123.3 (d), 121.8 (d), 81.0 (s), 42.2 (t), 23.2 (t).

1-(2-Furyl)-1-cyclopentanol (2b-OH): bp 78–80 °C (0.5 mm); ^{13}C NMR ($CDCl_3$) δ 159.2 (s), 141.0 (d), 109.7 (d), 103.8 (d), 79.1 (s), 38.0 (t), 23.3 (q).

1-(5-Ethyl-2-furyl)-1-cyclopentanol (2c-OH): bp 84–86 °C (0.5 mm); ^{13}C NMR ($CDCl_3$) δ 157.2 (s), 156.3 (s), 104.2 (d), 103.9 (d), 79.1 (s), 39.1 (t), 23.3 (t), 21.1 (t), 11.7 (q).

1-(*p*-Acetylphenyl)-1-cyclopentanol (2d-OH): decomposes upon heating; ^{13}C NMR ($CDCl_3$) δ 195.9 (s), 151.3 (s), 131.1 (s), 126.5 (d), 126.3 (d), 123.3 (d), 80.8 (s), 40.2 (t), 24.4 (q), 22.1 (t).

1-(α-Hydroxycum-4-yl)-1-cyclopentanol (15): mp 90.0 °C; ^{13}C NMR ($CDCl_3$) δ 147.5 (s), 145.3 (s), 128.3 (d), 125.2 (d), 124.9 (d), 124.2 (d), 83.2 (s), 72.2 (s), 40.2 (t), 24.4 (q), 22.1 (t).

2-(5-Ethyl-2-furyl)-2-propanol (3c-OH): bp 48–49 °C (0.5 mm); ^{13}C NMR ($CDCl_3$) δ 158.9 (s), 155.9 (s), 104.1 (d), 103.9 (d), 68.4 (s), 28.6 (t), 21.3 (q), 12.0 (q).

***p*-Acetylcumyl alcohol (3d-OH)**: mp 101–103 °C (0.07 mm); ^{13}C NMR ($CDCl_3$) δ 197.9 (s), 154.7 (s), 134.1 (s), 128.0 (d), 124.5 (d), 72.0 (s), 31.3 (q), 26.2 (q).

1-(2-Thienyl)-1-cyclohexanol (4a-OH): bp 78–81 °C (0.08 mm); ^{13}C NMR ($CDCl_3$) δ 154.5 (s), 126.3 (d), 123.3 (d), 121.7 (d), 71.7 (s), 39.7 (t), 25.2 (t), 22.1 (t).

1-(2-Furyl)-1-cyclohexanol (4b-OH): bp 58–59 °C (0.12 mm); ^{13}C NMR ($CDCl_3$) δ 159.9 (s), 140.8 (d), 109.6 (d), 104.0 (d), 77.6 (s), 36.3 (t), 25.2 (t), 21.9 (t).

1-(5-Ethyl-2-furyl)-1-cyclohexanol (4c-OH): bp 77–80 °C (0.1 mm); ^{13}C NMR ($CDCl_3$) δ 158.0 (s), 156.6 (s), 104.9 (d), 104.2 (d), 69.9 (s), 36.5 (t), 25.6 (t), 23.3 (t), 21.3 (t), 12.0 (q).

1-(*p*-Acetylphenyl)-1-cyclohexanol (4d-OH): decomposes upon heating; ^{13}C NMR ($CDCl_3$) δ 197.6 (s), 151.2 (s), 135.0 (s), 128.2 (d), 124.7 (d), 72.7 (s), 38.3 (t), 26.2 (t), 25.2 (q), 21.6 (t).

3-(2-Thienyl)-3-pentanol (5a-OH): bp 58–60 °C (0.07 mm); ^{13}C NMR ($CDCl_3$) δ 151.5 (s), 126.2 (d), 123.2 (d), 122.4 (d), 76.5 (s), 34.7 (t), 7.7 (q).

3-(2-Furyl)-3-pentanol (5b-OH): bp 44–46 °C (0.1 mm); ^{13}C NMR ($CDCl_3$) δ 160.8 (s), 143.3 (d), 111.9 (d), 107.5 (d), 77.0 (s), 33.9 (t), 9.9 (q).

3-(5-Ethyl-2-furyl)-3-pentanol (5c-OH): bp 50–51 °C (0.08 mm); ^{13}C NMR ($CDCl_3$) δ 156.5 (s), 156.3 (s), 105.6 (d), 103.9 (d), 74.5 (s), 31.5 (t), 21.2 (t), 13.9 (q), 7.7 (q).

4-(2-Thienyl)-4-heptanol (6a-OH): bp 75–77 °C (0.06 mm); ^{13}C NMR ($CDCl_3$) δ 152.4 (s), 126.4 (d), 123.3 (d), 122.3 (d), 76.4 (s), 45.2 (t), 16.8 (t), 14.2 (q).

4-(2-Furyl)-4-heptanol (6b-OH): bp 54–56 °C (0.1 mm); ^{13}C NMR ($CDCl_3$) δ 159.1 (s), 140.9 (d), 109.8 (d), 104.9 (d), 74.3 (s), 42.1 (t), 16.7 (t), 14.2 (q).

2-(2-Thienyl)-2-butanol (7a-OH): bp 55–57 °C (0.6 mm); ^{13}C NMR ($CDCl_3$) δ 153.0 (s), 126.3 (d), 123.4 (d), 122.2 (d), 73.8 (s), 37.3 (t), 29.2 (q), 8.4 (q).

2-(2-Furyl)-2-butanol (7b-OH): bp 40–42 °C (0.8 mm); ^{13}C NMR ($CDCl_3$) δ 159.4 (s), 140.9 (d), 109.6 (d), 104.3 (d), 71.5 (s), 34.0 (t), 25.4 (q), 8.1 (q).

2-(2-Thienyl)-2-adamantanol (8a-OH): mp 78 °C; ^{13}C NMR ($CDCl_3$) δ 152.2 (s), 126.2 (d), 123.8 (d), 123.0 (d), 74.3 (s), 38.0 (d), 37.6 (t), 34.9 (t), 32.6 (t), 27.0 (d).

2-(2-Furyl)-2-adamantanol (8b-OH): mp 67 °C; ^{13}C NMR ($CDCl_3$) δ 150.9 (s), 140.6 (d), 109.8 (d), 105.3 (t), 73.3 (s), 37.6 (t), 35.3 (d), 34.9 (t), 32.1 (t), 27.0 (d).

***exo*-2-(2-Thienyl)-2-norborneol (9a-OH)**: mp 82–86 °C (0.12 mm); ^{13}C NMR ($CDCl_3$) δ 154.9 (s), 126.2 (d), 123.9 (d), 122.7 (d), 78.9 (s), 49.7 (d), 47.7 (t), 38.5 (t), 37.0 (d), 28.5 (t), 22.1 (t).

***exo*-2-(2-Furyl)-2-norborneol (9b-OH)**: mp 78–80 °C (0.7 mm); ^{13}C NMR ($CDCl_3$) δ 160.0 (s), 141.2 (d), 109.6 (d), 104.5 (d), 76.9 (s), 46.6 (d), 43.8 (t), 38.2 (t), 36.6 (d), 28.7 (t), 21.5 (t).

***exo*-2-(5-Ethyl-2-furyl)-2-norborneol (9c-OH)**: bp 89–91 °C (0.6 mm); ^{13}C NMR ($CDCl_3$) δ 158.1 (s), 157.0 (s), 105.5 (d), 104.2 (d), 77.2 (s), 46.9 (d), 43.9 (t), 38.5 (t), 36.9 (d), 29.0 (t), 21.8 (t), 21.4 (t), 12.0 (q).

***exo*-2-(*p*-Acetylphenyl)-2-norborneol (9d-OH)**: mp 64–65 °C; ^{13}C NMR ($CDCl_3$) δ 198.3 (s), 155.0 (s), 135.3 (s), 128.3 (d), 126.3 (d), 80.4 (s), 47.4 (s), 46.7 (t), 38.9 (t), 37.6 (d), 29.0 (t), 26.6 (q), 22.5 (t).

***exo*-2-(α-Hydroxycum-4-yl)-2-norborneol (16)**: mp 100 °C; ^{13}C NMR ($CDCl_3$) δ 147.5 (s), 147.3 (s), 125.7 (d), 124.2 (d), 80.5 (s), 72.3 (s), 47.2 (d), 46.4 (t), 38.6 (t), 37.5 (d), 31.6 (q), 29.1 (t), 22.1 (t).

***exo*-8-(2-Thienyl)-8-tricyclo[5.2.1.$0^{2,6}$]decanol (10a-OH)**: bp 119–121 °C (0.12 mm); ^{13}C NMR ($CDCl_3$) δ 154.9 (s), 126.1 (d), 123.9 (d), 122.8 (d), 78.5 (s), 54.0 (d), 47.2 (t), 47.0 (d), 41.5 (d), 39.3 (t), 32.4 (d), 32.3 (t), 31.6 (t), 27.1 (t).

***exo*-8-(2-Furyl)-8-tricyclo[5.2.1.$0^{2,6}$]decanol (10b-OH)**: bp 110–113 °C (0.12 mm); ^{13}C NMR ($CDCl_3$) δ 160.1 (s), 141.3 (s), 109.7 (d), 104.7 (d), 76.5 (s), 50.9 (d), 47.2 (d), 43.5 (t), 41.2 (d), 38.8 (t), 32.4 (t), 32.1 (d), 31.5 (t), 27.1 (t).

***exo*-8-(*p*-Acetylphenyl)-8-tricyclo[5.2.1.$0^{2,6}$]decanol (10d-OH)**: mp 126.0 °C; ^{13}C NMR ($CDCl_3$) δ 197.9 (s), 154.3 (s), 135.3 (s), 128.2 (d), 124.9 (d), 80.1 (s), 51.5 (d), 47.4 (d), 46.2 (t), 41.9 (d), 39.3 (d), 32.5 (t), 32.4 (t), 31.7 (t), 27.2 (t), 26.5 (q).

***anti*-7-(*p*-Acetylphenyl)-7-norbornenol (11d-OH)**: mp 87.5 °C; ^{13}C NMR ($CDCl_3$) δ 197.8 (s), 148.9 (s), 135.1 (s), 134.7 (d), 127.9 (d), 127.6 (d), 92.0 (s), 48.5 (d), 26.2 (q), 23.2 (t).

1-(*p*-Acetylphenyl)-1-cyclobutanol (12d-OH): decomposes upon heating; ^{13}C NMR ($CDCl_3$) δ 197.9 (s), 151.9 (s), 135.0 (s), 128.0 (d), 124.8 (d), 76.0 (s), 36.7 (t), 26.1 (q), 12.7 (t).

***exo*-6-(*p*-Acetylphenyl)-6-bicyclo[3.2.1]octanol (13d-OH)**: mp 147 °C; ^{13}C NMR ($CDCl_3$) δ 197.7 (s), 155.8 (s), 135.1 (s), 128.0 (d), 125.7 (d), 82.9 (s), 45.5 (d), 44.6 (t), 38.1 (t), 34.7 (d), 32.5 (t), 28.0 (t), 26.4 (q), 19.1 (t).

Preparation of Carbocations. The 2-thienyl-, 2-furyl-, and 5-ethyl-2-furyl-substituted cations were prepared by the addition of the precursor to a −78 °C solution of FSO_3H in SO_2ClF. The liquids were generally frozen onto the sides of the NMR tube containing the FSO_3H/SO_2ClF and slowly dissolved into the acid solution with vigorous stirring so as to obtain 20% solution of the ion. The protonated acetyl-substituted cations were prepared in $FSO_3H/SbF_5/SO_2ClF$ solution at −78 °C.

^{13}C NMR spectra were obtained with the use of a Varian Associates Model FT-80 spectrometer equipped with a multinuclei broad-band variable-temperature probe. The chemical shifts were referenced from an external capillary of tetramethylsilane.

Acknowledgment. Support of our work by the National Science Foundation and National Institutes of Health is gratefully acknowledged.

Registry No. 2a, 82732-48-7; **2a**-OH, 82732-52-3; **2b**, 82732-49-8; **2b**-OH, 79575-90-9; **2c**, 82732-50-1; **2c**-OH, 82732-53-4; **2d**, 82732-51-2; **2d**-OH, 82732-54-5; **3a**, 71939-89-4; **3b**, 71939-86-1; **3c**, 82732-55-6; **3c**-OH, 82732-57-8; **3d**, 82732-56-7; **3d**-OH, 54549-72-3; **4a**, 82732-58-9; **4a**-OH, 17138-80-6; **4b**, 82732-59-0; **4b**-OH, 36169-67-2; **4c**, 82732-60-3; **4c**-OH, 82732-61-4; **4d**-OH, 82732-62-5; **5a**, 82732-63-6; **5a**-OH, 82732-66-9; **5b**, 82732-64-7; **5b**-OH, 82732-67-0; **5c**, 82732-65-8; **5c**-OH, 82732-68-1; **6a**, 82732-69-2; **6a**-OH, 82732-71-6; **6b**, 82732-70-5; **6b**-OH, 82732-72-7; **7a**, 82732-73-8; **7a**-OH, 82740-51-0; **7b**, 82732-74-9; **7b**-OH, 4229-86-1; **8a**, 82732-75-0; **8a**-OH, 82740-53-2; **8b**, 82740-52-1; **8b**-OH, 82740-54-3; **9a**, 82732-76-1; **9a**-OH, 82732-80-7; **9b**, 82732-77-2; **9b**-OH, 82732-81-8; **9c**, 82732-78-3; **9c**-OH, 82732-82-9; **9d**, 82732-79-4; **9d**-OH, 82732-83-0; **10a**, 82732-84-1; **10a**-OH, 82732-87-4; **10b**, 82732-85-2; **10b**-OH, 82732-88-5; **10d**, 82732-86-3; **10d**-OH, 82732-89-6; **11d**, 82732-90-9; **11d**-OH, 82732-91-0; **12d**-OH, 82732-92-1; **13d**-OH, 82732-93-2; **15**, 82732-94-3; **16**, 82732-95-4.

Syntheses of Arborescin, 1,10-Epiarborescin, and (11*S*)-Guaia-3,10(14)-dieno-13,6α-lactone, the Key Intermediate in Greene and Crabbé's Estafiatin Synthesis, and the Stereochemical Assignment of Arborescin[1]

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Arborescin (**2**), 1,10-epiarborescin (**3**), and (11*S*)-guaia-3,10(14)-dieno-13,6α-lactone (**33**), the key intermediate in Greene and Crabbé's synthesis of estafiatin (**4**), have been synthesized from (11*S*)-1,1-(ethylenedioxy)eudesm-3-eno-13,6α-lactone (**6**) in 12 steps and 11 steps, respectively. The key step involves the solvolytic rearrangement of (11*S*)-3α-(benzoyloxy)-1β-(mesyloxy)eudesmano-13,6α-lactone (**18**). The stereochemistry of the epoxide ring of arborescin has been determined to be β orientation from this synthesis.

Guaianolides are a rapidly expanding group of natural products, comprising to date ca. 200 varieties.[2] Some of them have been shown to possess high antitumor,[3,4] allergenic,[3,5] antischistosomal,[3,6] antihelmintic,[7] contraceptive,[8] root growth stimulatory,[3,9] root growth and germination inhibitory activities.[3,10] Because of their high biological activities and because they are available from natural sources often only in small quantities, their efficient syntheses are a synthetic challenge that has received much attention during the past few years.[11]

Chart I

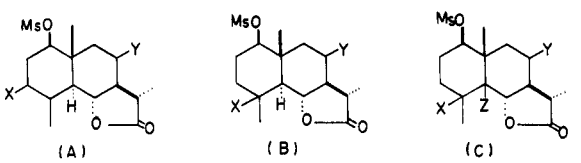
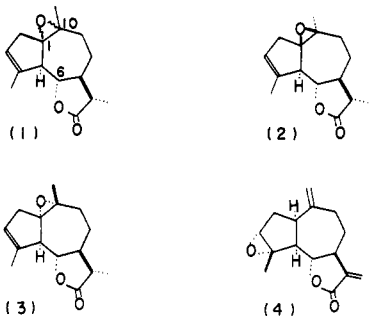


Chart II



With only a few exceptions guaianolides possess a cis-fused (α-H) hydroazulene skeleton and a functionality at C_{10} (double bond, hydroxyl or epoxide group). Furthermore, most have the γ-lactone moiety closed in a trans

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