Carbon-13 NMR Studies of Carbocations. 12.[1] Effect of Increasing Electron Demand on the ^{13}C Chemical Shifts of 1-Aryl-1-cycloalkyl-1-ethyl and 1-Aryl-2-methyl-1-cycloalkyl Cations

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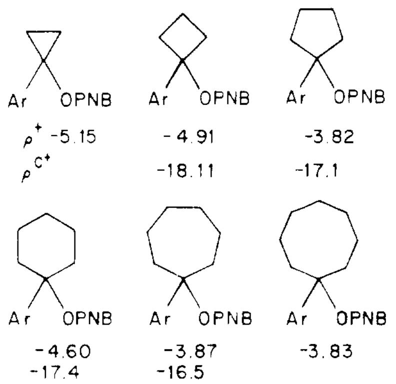
Four different series of 1-aryl-1-cycloalkyl carbocations (**8**, **9**, **11**, **14**) have been prepared in $SbF_5/FSO_3H/SO_2ClF$ solutions and their ^{13}C NMR spectra measured at −80 °C. From the plots of $\Delta\delta C^+$ vs. σ^{C+} for 1-aryl-1-cyclopentyl-1-ethyl (**8**) and 1-aryl-1-cyclohexyl-1-ethyl cations (**9**) the ρ^{C+} values were obtained and, when compared with data available for 2-aryl-3-methyl-2-butyl (**18**) and 1-aryl-1-cyclopropyl-1-ethyl cations (**6**), provided evidence for the stabilizing abilities of adjacent groups: cyclopropyl > cyclopentyl > cyclohexyl > isopropyl (ρ^{C+} −10.5, −17.1, −17.6, −18.2, respectively). This parallels the order determined from solvolysis of the corresponding *p*-nitrobenzoates. When cation **8** is substituted with electron-withdrawing groups, an irreversible rearrangement occurs to give a 1-aryl-2-methyl-1-cyclohexyl cation (**14**). Ionization of the 1-aryl-2-methyl-1-cyclohexanols (**15**) also yields **14**, and 1-aryl-2-methyl-1-cyclopentanols (**12**) yield 1-aryl-2-methyl-1-cyclopentyl cations (**11**). The plots of $\Delta\delta C^+$ vs. σ^{C+} and of $\Delta\delta C^\alpha$ vs. $\sigma^{\alpha C+}$ for cations **9**, **11**, and **14** bearing electron-withdrawing substituents show upward ($\Delta\delta C^+$) and downward ($\Delta\delta C^\alpha$) deviations consistent with the incursion of equilibration.

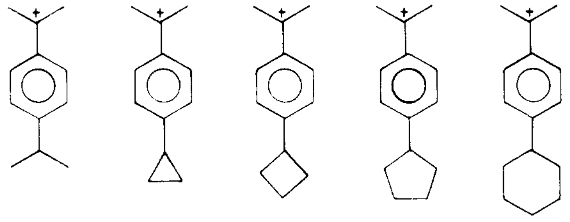
The effect of positive charge in and adjacent to cycloalkyl groups has been examined by the tool of increasing electron demand, both via solvolysis[3,4] and via ^{13}C NMR spectroscopy.[5] The extent of charge development in the transition states of the series of *p*-nitrobenzoates, 1-aryl-1-cyclopropyl to 1-aryl-1-cyclooctyl, as measured by ρ^+, approximately parallels the values of ρ^{C+} obtained directly from the carbocations.[3,5]



Although the stabilization of charge is not favored in the case of cyclopropyl and cyclobutyl,[3] the situation is reversed when these groups are placed adjacent to the developing cationic center, as shown by ρ^+ for the series of 1-substituted 1-(arylethyl)-*p*-nitrobenzoates[4] isopropyl −4.76, cyclopropyl −2.78, cyclobutyl −3.94, cyclopentyl −4.48, and cyclohexyl −4.71.

The cyclopropyl group provides the greatest stabilization and furthermore retains its ability to release electron density when placed para to the developing cationic center, as shown by the enhanced rate of solvolysis of *p*-(cyclopropyl)cumyl chloride over the *p*-isopropyl analogue.[6]

In an attempt to determine the relative electron-releasing ability of cycloalkyl groups, some of us measured the cationic-carbon shifts for the series of para-substituted cumyl cations **1**–**5**.[7] Whereas the stabilizing ability of the cyclopropyl group is evident from the relatively shielded cationic carbon in the case of the *p*-(cyclopropyl)cumyl cation **2**, the differences in the chemical shifts in the other cases are too small to draw any firm conclusions. We have therefore investigated the series of cations **6**–**9** where the cycloalkyl moieties are attached directly to the cationic carbon.



1 δC^+ 244.0 2 231.6 3 241.6 4 241.6 5 242.8

Results and Discussion

1-Aryl-1-cycloalkyl-1-ethyl Cations. The data for cations **6** are available from previous work.[5] Generation of the cations **7**, **8**, and **9** was attempted by ionization of the corresponding alcohols **10**, **13**, and **16** in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C. The spectrum obtained from **10** under these conditions was consistent with the rearranged ion **11** and not **7**. Confirmation of this was provided when ionization of alcohols **12** yielded identical ^{13}C spectra (Table I).

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[1] For Part 11, see: Brown H. C.; Periasamy, M.; Perumal, P. T.; Kelly, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 2359–2363.

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[3] Brown, H. C.; Ravindranathan, M.; Peters, E. N.; Gundu Rao, C.; Rho, M. M. *J. Am. Chem. Soc.* **1977**, *99*, 5373–5378.

[4] Brown, H. C.; Ravindranathan, M.; Gundu Rao, C. *J. Am. Chem. Soc.* **1978**, *100*, 1218–1222.

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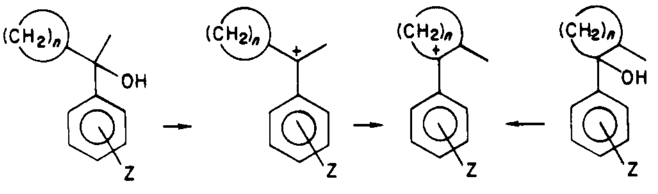
Table I. Selected ^{13}C NMR Chemical Shifts of Carbocations in $SbF_5/FSO_3H/SO_2ClF$ at -80 °C[a]

	cation							
	8		9		11		14	
substituent Z	C_1^+	C_3	C_1^+	C_3	C_1^+	C_2	C_1^+	C_2
p-OCH_3	226.9	51.3	227.1	50.7	237.1[b]	46.3	231.5	41.0
p-CH_3	250.3	55.1	251.1	54.5	260.5[b]	49.7	256.6	44.8
p-F	254.5	56.7	255.5	56.1	264.6	51.0	261.5	46.3
p–Cl	257.4	57.3	258.6	56.7	267.5[b]	51.5	264.9	46.9
m-CH_3	259.2	57.0	260.5	56.6	269.3	51.2	266.8	46.9
H	261.3	57.6	262.5	56.9	271.3[b]	51.6	269.1	47.2
m-F			267.9	59.2	276.8	53.5	275.4	49.7
m-Cl			267.9	59.2	276.6	53.2	275.4	49.7
m-CF_3			271.0	60.3	279.5	54.2	277.2	53.1
3,5-Cl_2					278.6	58.8		
p-CF_3					281.5	56.3		

[a] Chemical shifts are ±0.1 ppm from Me_4Si (capillary). Complete sets of NMR data for these cations are available as supplementary material. [b] Data for these cations have been reported by Coxon et al.[10]

Ionization of the cyclopentyl carbinols **13** (Z = p-OCH_3 to p-H) in the same superacid medium proceeded smoothly to give the corresponding cations **8**, although when Z = m-CH_3 and p-H, the cations slowly rearranged to cations **14**, the identities of which were confirmed by ionization of the 1-aryl-2-methylcyclohexan-1-ols **15**. For substituents more electron demanding than p-H, the solutions generated from **13** exhibited ^{13}C signals corresponding only to **14** and unidentified impurities.

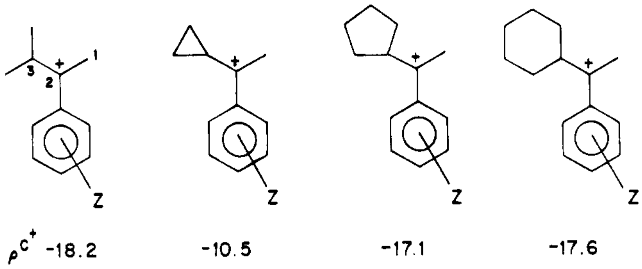


n = 2 — 6
n = 3 10 — 7 — 11 — 12
n = 4 13 — 8 — 14 — 15
n = 5 16 — 9

Ring expansions have been identified previously for 1-alkyl-1-cycloalkyl cations where a cascade occurs from both lower cyclic homologues (by ring expansion) and higher cyclic homologues (by ring contraction) to yield 1-alkyl-1-cyclohexyl cations.[8]

Ionization of the cyclohexyl carbinols **16** proceeded smoothly in the case of Z = p-OCH_3 to m-CF_3 to give solutions of **9** devoid of impurities or other species (Table I). However, attempts to generate the cations with more electron-withdrawing groups met with failure, the solutions exhibiting peaks of unidentified decomposition products. Similar difficulties have been observed in the case of 4-tert-butyl-1-aryl-1-cyclohexyl cations[9] and cations **11** and **14**.[10]

Plots of the cationic carbon substituent chemical shifts $\Delta\delta C^+$ against σ^{C+} for these cations give good correlations, **8**, $\rho^{C+} = -17.1$, $r = 0.999$, **9**, $\rho^{C+} = -17.6$, $r = 0.999$, although some upward deviation is observed at the more electron-demanding end of the plot (see below). Comparison of these ρ^{C+} values with ρ^+ from solvolysis of p-nitrobenzoates (above) is now possible. The values clearly parallel one another and provide further confirmation of the concept that information obtained on fully formed cationic intermediates in superacid media can be correlated with that obtained on transition states from solvolyses in nucleophilic media. Indeed, Arnett and co-workers have recently provided quantitative information to enable correlation of stability data from solvolysis, super acids, and the gas phase.[11]



The superior electron-donating ability of the cyclopropyl group is evidenced by the less negative ρ values. The differences between the stabilizing abilities of the other three groups is less dramatic but still allow us to conclude that the order is cyclopropyl > cyclopentyl > cyclohexyl > isopropyl,[12] with the cyclopentyl group providing slightly better hyperconjugative stabilization from the strained C–C bonds.

When the α-(cycloalkyl) carbon substituent shifts ($\Delta\delta C_3$ of **9**) are plotted against $\sigma^{\alpha C+}$ constants[13] ($\rho^{\alpha C+} = -5.0$, $r = 0.995$ for electron donors only) the points for the electron withdrawing substituents deviate downward to a small extent. When considered together with the slight upward deviation of a $\Delta\delta C^+$ vs. σ^{C+} plot for **9**, this observation suggests that equilibration **9** $\rightleftharpoons$ **17** may be involved for Z = m-F, m-Cl, m-CF_3.[14]

1-Aryl-2-methyl-1-cycloalkyl Cations. The cations **11** and **14** were prepared directly by ionization of the corresponding alcohols **12** and **15**, in turn prepared by addition of the corresponding bromo or iodo Grignard reagent to 2-methylcyclopentanone and 2-methylcyclohexanone, respectively, in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C. Selected ^{13}C NMR data recorded at −80 °C are reported in Table I. Although **11** Z = p-CF_3 was obtained, attempts to generate **11** Z = 3,5-$(CF_3)_2$ and **14** Z = p-CF_3, 3,5-$(CF_3)_2$ were unsuccessful. Coxon and co-workers reported similar difficulties in their study which described the formation of neutral arylcycloalkanes from the alcohols in FSO_3H/SO_2ClF.[10]

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[9] Kelly, D. P.; Jenkins, M. J., unpublished observations.

[10] Coxon, J. M.; Schuyt, H. A.; Steel, P. J. *Aust. J. Chem.* **1980**, *33*, 1863–1867.

[11] Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889–2895.

[12] For discussion on relative stabilizing ability of various alkyl and cycloalkyl groups see: Olah, G. A.; Surya Prakash, G. K.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666–2671. Olah, G. A.; Berrier, A. L.; Surya Prakash, G. K. *Proc. Natl. Acad. Sci. USA* **1981**, *78*, 1998–2002.

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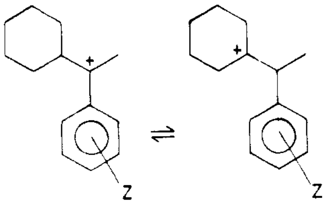
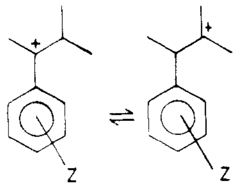
[14] Brown, H. C.; Periasamy, M. *J. Am. Chem. Soc.* **1983**, *105*, 529–533.

Plots of $\Delta\delta C^+$ vs. σ^{C+} for these two cations showed small upward deviations (**11**, $\rho^{C+} = -17.0$, $r = 0.999$; **14**, $\rho^{C+} = -18.7$, $r = 0.999$ for electron donors only) similar to that observed for **9**. Plots of the cycloalkyl α-carbon shifts ($\Delta\delta C_2$) against $\sigma^{\alpha C+}$ show major downward deviations for substituents less electron donating than m-CF_3 (**11**, $\rho^{\alpha C+} = -4.2$, $r = 0.998$; **14**, $\rho^{\alpha C+} = -4.9$, $r = 0.9997$ for electron donors only).

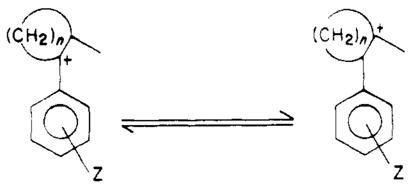
Similar observations of upward ($\Delta\delta C^+$) and downward ($\Delta\delta C^\alpha$) deviations in these plots have been observed for 2-aryl-3-methylbut-2-yl cations **18** carrying highly electron-withdrawing substituents.[13] These phenomena were rationalized by the equilibration **18** $\rightleftharpoons$ **19**, the incursion of a 1,2-hydride shift causing relative shielding of the cationic carbon, and deshielding of the α-carbon. The similarities of the plots with those for **11** and **9** indicate that equilibrations **11** $\rightleftharpoons$ **20**, **14** $\rightleftharpoons$ **21**, and **9** $\rightleftharpoons$ **17** occur here also.



9 17



18 19



$n = 3$ 11
$n = 4$ 14
20
21

The fact that the plot of the α-carbon ($\Delta\delta C_1$) against $\sigma^{\alpha C+}$ for 2-arylnorbornyl cations shows no such deviation suggests that equilibration is not the reason for the deviation in the plot of $\Delta\delta C^+$ vs. σ^{C+} for that system.[5]

Experimental Section

NMR Spectra. ^{13}C NMR spectra were recorded at -80 °C on a Varian CFT-20 spectrometer with 8-mm tubes containing a concentric 3-mm (o.d.) capillary tube of acetone-d_6 and Me_4Si, 8192 data points, a spectral width of 6500 Hz, and a pulse angle of 45°. Chemical shifts are ±0.1 ppm from external Me_4Si.

Precursors. 1-Aryl-1-cyclobutyl-1-ethanols (**10**), 1-aryl-1-cyclopentyl-1-ethanols (**13**), 1-aryl-1-cyclohexyl-1-ethanols (**16**), 1-aryl-2-methyl-1-cyclopentanols (**12**), and 1-aryl-2-methyl-1-cyclohexanols (**15**) were prepared by the addition of the corresponding ketone to the Grignard reagent prepared from the corresponding substituted bromo- or iodobenzenes. The physical constant data (bp) for these precursors are available as supplementary material. All of these compounds gave ^1H NMR and ^{13}C NMR data in accordance with the assigned structures. Satisfactory elemental analyses (C, H, F, Cl, ±0.3%) were obtained for all of the new compounds.

Carbocations. The ions were prepared by slow addition of the appropriate precursor as a solution in SO_2ClF at -78 °C to a solution of FSO_3H/SbF_5 (1:1 M), SO_2ClF cooled to -78 °C with rapid vortex mixing. The "magic acid", SbF_5/FSO_3H (1:1 M), concentration in the solution was 3 M. The concentration of the ion based on the alcohol added was 0.5 M. Transfer of the solution under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe as described previously.[15]

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Registry No. 8 (Z = p-OCH_3), 97703-71-4; 8 (Z = p-CH_3), 97703-72-5; 8 (Z = p-F), 97703-73-6; 8 (Z = p-Cl), 97703-74-7; 8 (Z = m-CH_3), 97703-75-8; 8 (Z = H), 97703-76-9; **9** (Z = p-OCH_3), 97703-77-0; **9** (Z = p-CH_3), 97703-78-1; **9** (Z = p-F), 97703-79-2; **9** (Z = p-Cl), 97703-80-5; **9** (Z = m-CH_3), 97703-81-6; **9** (Z = H), 97703-82-7; **9** (Z = m-F), 97703-83-8; **9** (Z = m-Cl), 97703-84-9; **9** (Z = m-CF_3), 97703-85-0; **10** (Z = p-OCH_3), 62861-32-9; **10** (Z = p-CH_3), 97704-07-9; **10** (Z = p-F), 97704-08-0; **10** (Z = p-Cl), 97704-09-1; **10** (Z = m-CH_3), 97704-10-4; **10** (Z = H), 62861-33-0; **10** (Z = m-F), 97704-11-5; **10** (Z = m-Cl), 97704-12-6; **10** (Z = m-CF_3), 97704-13-7; **10** (Z = 3,5-Cl_2), 97704-14-8; **10** (Z = p-CF_3), 62861-34-1; **11** (Z = p-OCH_3), 75968-54-6; **11** (Z = p-CH_3), 75968-52-4; **11** (Z = p-F), 51804-46-7; **11** (Z = p-Cl), 75968-56-8; **11** (Z = m-CH_3), 97703-86-1; **11** (Z = H), 75968-50-2; **11** (Z = m-F), 97703-87-2; **11** (Z = m-Cl), 97703-88-3; **11** (Z = m-CF_3), 97703-89-4; **11** (Z = 3,5-Cl_2), 97703-90-7; **11** (Z = p-CF_3), 75968-76-2; **12** (Z = p-OCH_3), 97704-15-9; **12** (Z = p-CH_3), 97704-16-0; **12** (Z = p-F), 97704-17-1; **12** (Z = p-Cl), 97704-18-2; **12** (Z = m-CH_3), 97704-19-3; **12** (Z = H), 19960-95-3; **12** (Z = m-F), 97704-20-6; **12** (Z = m-Cl), 97704-21-7; **12** (Z = m-CF_3), 97704-22-8; **12** (Z = 3,5-Cl_2), 97704-23-9; **12** (Z = p-CF_3), 97704-24-0; **13** (Z = p-OCH_3), 97703-95-2; **13** (Z = p-CH_3), 97719-81-8; **13** (Z = p-F), 97703-96-3; **13** (Z = p-Cl), 97703-97-4; **13** (Z = m-CH_3), 97703-98-5; **13** (Z = H), 97703-99-6; **14** (Z = p-OCH_3), 75968-62-6; **14** (Z = p-CH_3), 75968-60-4; **14** (Z = p-F), 51804-47-8; **14** (Z = p-Cl), 75968-64-8; **14** (Z = m-CH_3), 97703-91-8; **14** (Z = H), 75968-58-0; **14** (Z = m-F), 97703-92-9; **14** (Z = m-Cl), 97703-93-0; **14** (Z = m-CF_3), 97703-94-1; **15** (Z = p-OCH_3), 97704-25-1; **15** (Z = p-CH_3), 97704-26-2; **15** (Z = p-F), 72968-83-3; **15** (Z = p-Cl), 97704-27-3; **15** (Z = m-CH_3), 97704-28-4; **15** (Z = H), 15036-22-3; **15** (Z = m-F), 97704-29-5; **15** (Z = m-Cl), 97704-30-8; **15** (Z = m-CF_3), 97704-31-9; **16** (Z = p-OCH_3), 97704-00-2; **16** (Z = p-CH_3), 97719-82-9; **16** (Z = p-F), 97704-01-3; **16** (Z = p-Cl), 97704-02-4; **16** (Z = m-CH_3), 97704-03-5; **16** (Z = H), 4352-39-0; **16** (Z = m-F), 97704-04-6; **16** (Z = m-Cl), 97704-05-7; **16** (Z = m-CF_3), 97704-06-8.

Supplementary Material Available: Complete tables of ^{13}C chemical shifts (and ^{13}C–^{19}F coupling constants where appropriate) for cations **8**, **9**, **11**, **14**, Table of physical constants (bp) for precursor alcohols **10**, **12**, **13**, **15**, **16** (5 pages). Ordering information is given on any current masthead page.

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(15) Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* **1976**, *29*, 957-965.