mately 1 mL. The product (86% by GLC) was purified by preparative GLC on the 15-ft Tween-80 column: $[\alpha]^{21}_D$ -11.3° (c 1.19, $CHCl_3$); IR (neat) 2930, 2900, 2850, 1460, 1380, and 1360 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.76–1.97 (m).

Formic Acid Catalyzed Rearrangement of 16. Into a 10-mL vial fitted with a cap and magnetic stirring bar were placed 1 mL of formic acid (Mallinckrodt, 88%) and epoxide **16**. The mixture was stirred at room temperature for 20 min and transferred to a separatory funnel containing 10 mL of water. The contents were extracted with pentane (4 × 2 mL), washed with water (1 × 2 mL) and saturated sodium bicarbonate solution (1 × 2 mL), dried over anhydrous magnesium sulfate, and concentrated to 0.5 mL in vacuo. GLC (38-ft Tween-80, 100 °C) shows one major component (>95%). This material was isolated by preparative GLC on the 15-ft Tween-80 column and proved to be (+)-artemiseole (**15**): $[\alpha]^{26}_D$ +17.0° (c 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$, 60 MHz) δ 1.15–1.23 (10 H, m), 1.52 (1 H, dd), 3.66 (2 H, dd), 4.88–5.18 (2 H, m), 5.35–5.75 (1 H, m).

Structural Effects in Solvolytic Reactions. 47. Effects of *p*-Alkyl and *p*-Cycloalkyl Groups on the Carbon-13 NMR Shifts of the Cationic Carbon Center in *p*-Alkyl-*tert*-cumyl Cations

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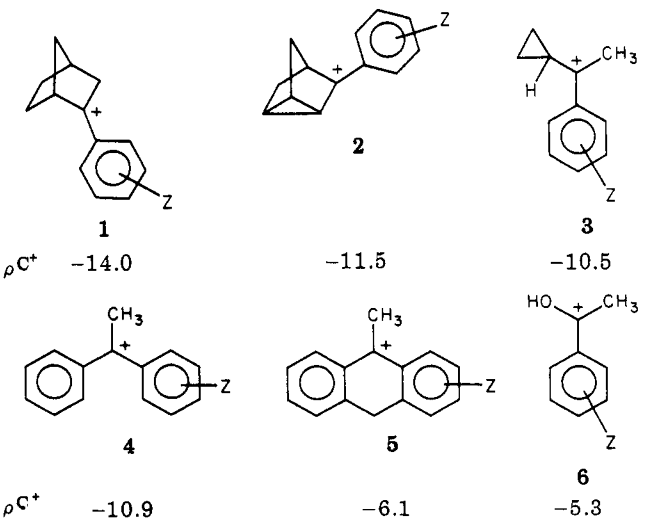
A series of *p*-alkyl- and *p*-cycloalkyl-*tert*-cumyl cations were prepared in $SbF_5/FSO_3H/SO_2ClF$ at -78 °C, and their ^{13}C NMR shifts were measured at -80 °C. The C^+ carbon in the *p*-alkyl derivatives is increasingly deshielded from *p*-methyl through *p*-*tert*-butyl. This observation is in accord with the Baker–Nathan order of stabilization (methyl > ethyl > isopropyl > *tert*-butyl) and in agreement with the rate data for the solvolysis of *p*-alkyl-*tert*-cumyl chlorides but in contrast to the gas-phase stability order for the para-protonated alkylbenzenes ($RC_6H_6^+$). Possible reasons for this difference in the apparent effects of these four alkyl groups are discussed. The stability order achieved by cycloalkyl groups based on the C^+ shifts is *p*-cyclopropyl ≫ *p*-cyclobutyl ≃ *p*-cyclopentyl > *p*-cyclohexyl. In the case of *p*-cyclopropyl-*tert*-cumyl cation, the C^+ signal appears relatively shielded (231.6 ppm) compared to the C^+ shift (244.0 ppm) for the *p*-isopropyl-*tert*-cumyl cation. This observation supports the ability of the cyclopropyl group to supply electrons (through C–C hyperconjugation) to the electron-deficient center without the intervention of σ-bridging through space. For other cycloalkyl derivatives, the C^+ signals of the *p*-cyclobutyl and *p*-cyclopentyl derivatives appear slightly upfield relative to the *p*-cyclohexyl derivatives. This may again be attributed to the greater hyperconjugating (CH and CC) ability of the strained cyclobutyl and cyclopentyl bonds, as compared with the nonstrained cyclohexyl bonds. For the *p*-norbornyl-*tert*-cumyl derivatives examined (*exo*-2- and *endo*-2-norbornyl and *exo*-5,6-trimethylene-*exo*- and -*endo*-2-norbornyl), the C^+ for the exo derivatives is relatively shielded compared to the C^+ of the endo derivatives. Although it may be attractive to interpret this observation in terms of a greater electron supply by the exo derivatives, the small effects may very well arise from the steric factors in the endo derivatives. Accordingly, the apparent stabilizing ability of the norbornyl moiety, as indicated by the relatively less negative ρ^{C^+} value (-14.0) observed in the $\Delta\delta C^+/\sigma^{C^+}$ plot of the 2-aryl-2-norbornyl cations, cannot be confirmed by this direct examination of the comparative electron-releasing characteristics of these two *exo*- and *endo*-norbornyl substituents.

Chart I



Recently we studied the possibility of achieving linear correlations for the ^{13}C NMR shifts of many aryldialkyl carbocations.[1-6] We have observed that the $\sigma^{C^+}/\Delta\delta C^+$ plots of a number of these cations are linear and give ρ^{C^+} values in the range of -16 to -18, with the exception of the 4-aryl-4-heptyl system, which yielded a ρ^{C^+} value of -14.6.[6] We have also observed that in several other systems (Chart I), the $\sigma^{C^+}/\Delta\delta C^+$ plots are linear only for electron-donating substituents.[7-10] The ρ^{C^+} values observed in these cations are relatively less negative (Chart I). Further, in these systems (**1**–**6**), the data points for the electron-withdrawing substituents deviate upward from the correlation line defined by the electron-donating substituents.[7-10]

We considered the possibility that the low ρ^{C^+} values and the deviation in the $\rho^{C^+}/\Delta\delta C^+$ plots might arise from the greater conjugating (or hyperconjugating) ability of these

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[1] Postdoctoral research associates on a grant provided by the Exxon Research and Engineering Company.

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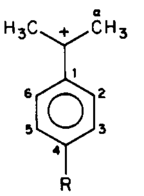
Table I. ^{13}C NMR Shifts[a] of *p*-Alkyl-*tert*-cumyl Cations 7A–L in $SbF_5/FSO_3H/SO_2ClF$ at −80 °C

cation[b]	chemical shift																	
	aromatic carbon atoms								alkyl carbon atoms									
	C^+	C_α (CH_3)	C_1	C_2	C_3	C_4	C_5	C_6										
7A,[c]	243.6	31.9	138.7	142.4	134.7	175.2	134.7	142.4	25.1									
7B	243.7	31.8	138.8	142.5	133.0	180.1	133.0	142.5	32.6	13.9								
7C	244.0	31.9	139.0	142.7	131.8	183.9	131.8	142.7	38.1	22.9								
7D	244.5	32.0	138.6	142.3	130.7	185.7	130.7	142.3	39.4	29.7								
7E[d]	231.6	30.2	137.7	142.3	129.2	184.7	129.2	142.3	23.7	21.1								
7F	241.6	31.5	138.7	142.4	131.3	181.6	131.3	142.4	43.8	30.0	18.9							
7G[e]	241.6	31.6	138.9	142.4	132.4	183.8	132.4	142.4	50.2	36.1	27.1							
7H	242.8	31.7	139.0	142.7	132.2	183.0	132.2	142.7	48.7	33.4	26.6	26.2						
7I	241.0	31.5	138.6	142.5	132.0	183.3	132.0	142.5	51.7	43.2	40.2	38.0	37.4	30.9	29.0			
7J[f]	241.8	31.6	138.7	141.7	133.2	181.9	133.2	141.7	51.5	45.4	41.8	38.7	34.8	30.2	24.2			
7K	240.8	31.4	138.5	142.3	132.1	183.8	132.1	142.3	51.5	49.6	48.1	46.9	42.3	39.3	32.9	32.5	31.4	27.9
7L[g]	241.3	31.5	138.7	141.5	133.2	182.2	133.2	141.5	50.8	49.4	49.0	42.7	42.7	35.4	34.1	33.1	32.9	27.5

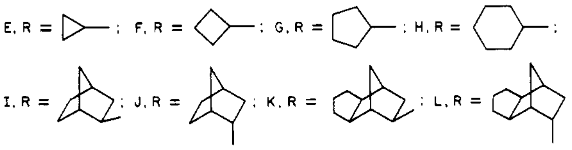
[a] The chemical shifts are ±0.1 ppm downfield from external tetramethylsilane. [b] The ions can also be prepared in FSO_3H/SO_2ClF except in a few cases (see below). [c] Data taken from ref 2. [d] This ion was prepared in FSO_3H/SO_2ClF. This ion gives an unidentified rearranged product in $SbF_5/FSO_3H/SO_2ClF$. [e] This ion rearranges to the 1-(*p*-isopropylphenyl)-1-cyclopentyl cation when the preparation was attempted in FSO_3H/SO_2ClF. [f] This ion rearranges to the 2-(*p*-isopropylphenyl)-2-norbornyl cation in the probe when the ion was prepared in FSO_3H/SO_2ClF. [g] This ion rearranges to 2-(*p*-isopropylphenyl)-5,6-*exo*-trimethylene-2-norbornyl cation in the probe when the ion was prepared in FSO_3H/SO_2ClF.

groups.[7-10] Accordingly, it appeared desirable to place some of these alkyl groups at the para position of the *tert*-cumyl cation 7 and to monitor the change in the C^+ chemical shifts. In addition, the data would also allow comparison of the stabilizing order of the alkyl groups in the superacid media with the corresponding order of stabilization achieved by these groups in the solvolytic transition states.



7

A, R = Me; B, R = Et;
C, R = *i*-Pr; D, R = *t*-Bu;



Results and Discussion

^{13}C NMR Shifts of *p*-Alkyl-*tert*-cumyl Cations. The alcohol precursors for the cations 7 were prepared following standard procedures previously used in our laboratories.[11] The carbocations 7 were prepared by slow addition of these alcohols as a solution in SO_2ClF at −78 °C or as a powder into a solution of $SbF_5/FSO_3H/SO_2ClF$ at −78 °C. The ^{13}C NMR spectra were recorded at −80 °C. The data are summarized in Table I.

Effect of Para Me, Et, *i*-Pr, and *t*-Bu Groups on the C^+ Shift of *tert*-Cumyl Cation. There has long been difficulty in interpreting the effect of alkyl groups in the para position on the stabilization of cationic species. We originally observed that the rates of solvolysis of *p*-alkyl-*tert*-cumyl chlorides in 90% aqueous acetone yielded the Baker–Nathan order: Me > Et > *i*-Pr > *t*-Bu.[12] The relative rates of solvolysis at 25 °C were Me:Et:*i*-Pr:*t*-Bu = 1.00:0.85:0.72:0.55. That order was attributed to decreased C^+ hyperconjugative contributions as the C–H bonds of alkyl groups were replaced by C–C bonds. However, Schubert and co-workers proposed an alternative explanation. They suggested that the Baker–Nathan order of stabilization results from greater steric hindrance to the solvation of the aryl moiety with increasing bulk of the alkyl group.[13,14] In apparent contradiction to this proposal was our observation that the above order was not significantly influenced by carrying out the solvolysis of the *p*-alkyl-*tert*-cumyl chlorides in methanol, ethanol, and 2-propanol.[15] Apparently the differences in the steric requirements of these solvent molecules do not affect the solvation sufficiently so as to influence the observed order.

On the other hand, in the closely related electrophilic substitutions, the Baker–Nathan order of stabilization by alkyl groups is not always followed.[16] For example, of some 15 reactions, 11 exhibit the Baker–Nathan trend, with the partial rate factor decreasing from p_f^{Me} to $p_f^{t\text{-}Bu}$. In two cases, nitration by acetyl nitrate in acetic anhydride and mercuridesilylation, the opposite order is exhibited: $p_f^{Me} < p_f^{Et} < p_f^{i\text{-}Pr} < p_f^{t\text{-}Bu}$. In the bromination reaction in trifluoroacetic acid, a reversal at an intervening stage is observed: $p_f^{Me} < p_f^{Et} < p_f^{i\text{-}Pr} > p_f^{t\text{-}Bu}$.

These results were accounted for on the basis of simultaneous operation of two factors, one which decreases regularly from methyl to *tert*-butyl (C–H hyperconjugation), the other (differences in the π-complexing ability of the aromatic rings arising from the inductive effects of the alkyl groups) which increases regularly in that order.[16] It was suggested that the variation in the solvent can produce a variation in the blend of these two factors, causing the observed trends.[16]

Arnett and Larsen, in their calorimetric studies, observed that the stability order of the para-protonated al-

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(14) Recently Taylor and co-workers have also suggested that in the solvolysis in aqueous acetone, the Baker–Nathan order is observed because solvation of the cations in nucleophilic solvents would be in that order because of steric difficulties for solvation (ref 20).

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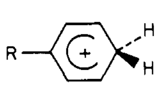
kylbenzenes 8 follows the Baker–Nathan trend (Me > Et > *i*-Pr > Bu).[17] However, Schleyer and co-workers calculated the reverse order for these cations in the gas phase.[18] It has been suggested that the difference between the gas-phase and solution trends could arise from differences in the solvation of the cations in solution, even in the very poorly solvating superacid medium.[18,19]



8

Recently, Taylor and co-workers suggested that in poorly solvating media, such as trifluoroacetic acid, the *p-tert*-butyl group becomes more electron releasing than the *p*-methyl group because of greater importance of C–C hyperconjugation over C–H hyperconjugation.[20] Obviously, this observation is in conflict with the realization of the Baker–Nathan order (Me > *t*-Bu) in the very poorly solvating superacid medium.[17]

In order to understand the possible role of solvent in modifying the stabilizing influence of *p*-alkyl groups on the remote cationic center, we measured the ^{13}C NMR shifts of the *p*-alkyl-*tert*-cumyl cations in $SbF_5/FSO_3H/SO_2ClF$, a very poor solvating medium for cations. A comparison of ^{13}C shift trend with that of solvolysis in 90% acetone should be able to reveal the role of solvent, if any, on this phenomenon.

The data observed for these derivatives (**9**–**12**) (Chart II) show that the C$^+$ center becomes modestly shielded (upfield shift) from *p*-Me to *p*-*t*-Bu, indicating a greater stabilizing ability of the *p*-Me group in accordance with the Baker–Nathan order, similar to the order indicated by the solvolytic data.[12]

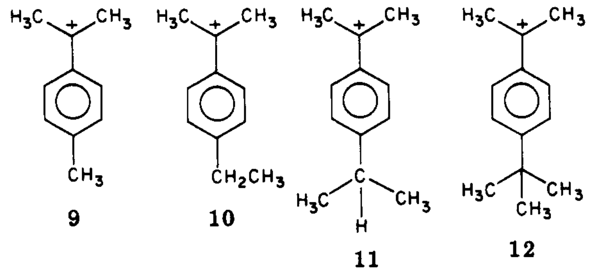
The identical trends observed in the ^{13}C shifts in poorly solvating media and in the rates of solvolysis in basic solvents clearly indicate that the solvent does not play any significant role in modifying the order of electronic influences of the alkyl groups on the remote cationic center.

An alternative to Taylor's proposal that C–C hyperconjugation is more important than C–H hyperconjugation in the gas phase must be considered.[21] The electronic effect of such alkyl groups must be a blend of hyperconjugative and inductive contributions. In the gas phase, in the absence of solvent, the inductive contribution would be more important. This could cause a reversal from the hyperconjugative order: Me > Et > *i*-Pr > *t*-Bu to the inductive order, Me < Et < *i*-Pr < *t*-Bu.

In solution the situation is further complicated. In addition to the hyperconjugative and inductive effects, other factors have been proposed. The electronic contributions can be influenced by the π-complexing ability of the aromatic group and its interaction with protonic solvents.[16] Alternatively, steric hindrance to solvation can be a significant factor.[13]

Thus, many factors have been proposed to influence the electronic contributions of alkyl groups in such electrophilic reactions: (a) hyperconjugative contributions, (b) inductive effects, (c) π-complexing of the aryl group with solvent, and (d) steric inhibition to solvation. With so many factors to call upon, it is easy to rationalize the individual orders observed in a given situation. However, it becomes difficult to predict the order to be anticipated in a new situation.

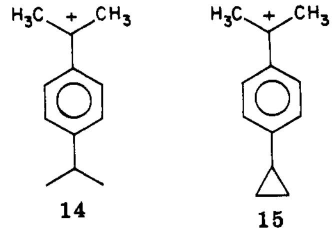
Chart II



	9	10	11	12
rel rate[12]	1.00	0.85	0.72	0.55
δC^+	243.6	243.7	244.0	244.5

(solvolysis of tertiary chlorides in 90% aqueous acetone at 25 °C)

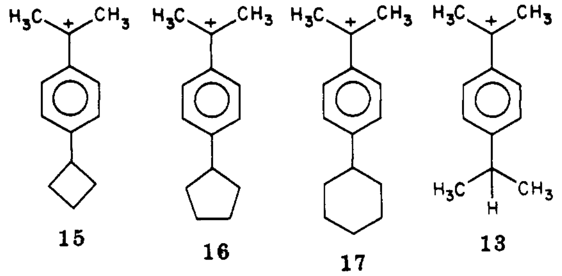
Chart III



	14	15
rel rate	1.00	6.7
δC^+	244.0	231.6

(solvolysis of tertiary chlorides in 90% acetone at 25 °C)

Chart IV



	15	16	17	13
rel rate[22]	1.10	1.3	1.00	1.00
δC^+	241.6	241.6	242.8	244.0

(solvolysis of tertiary chlorides in 90% aqueous acetone at 25 °C)

Variation of the C$^+$ Shifts and Stabilizing Abilities of *p*-Cycloalkyl Groups. The ability of the cyclopropyl group to release electron density to the electron-deficient center is well established. For example, the *p*-cyclopropyl-*tert*-cumyl chloride undergoes faster solvolysis than the corresponding *p*-isopropyl derivative[22] (Chart III).

The same trend is also observed in the C$^+$ shift data. The relatively shielded C$^+$ in the *p*-cyclopropyl derivative clearly indicates the greater electron-donating ability of the *p*-cyclopropyl group, even when the group is located at a position far removed from the C$^+$ center.

On the other hand, a *p*-cyclobutyl (**15**) group does not cause any unusual rate acceleration compared to *p*-cyclo-

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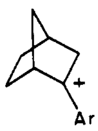
Chart V



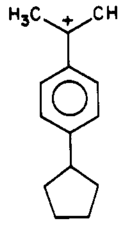
18

19

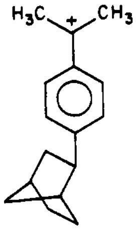
		18	19
ρ^{C^+}		−14.0	−17.1
ρ^{+} [25]	exo	−3.82	−3.92
	endo	−3.72	

(solvolysis of OPNB in 80% aqueous acetone at 25 °C)

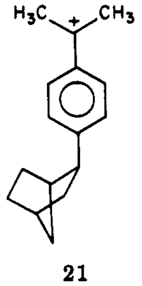
Chart VI



16



20



21

	16	20	21
rel rate[11]	1.00	1.1	0.9

(solvolysis of tertiary chloride in 90% aqueous acetone at 25 °C)

	16	20	21
δ^{C^+}	241.6	241.0	241.8

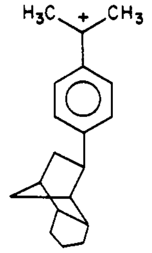
pentyl (**16**), *p*-cyclohexyl (**17**), or *p*-isopropyl (**13**)[22] (Chart IV).

The variation in the C^+ shifts is also small. Although no safe conclusion can be drawn from this variation, the relatively shielded (upfield) C^+ shifts observed for the cycloalkyl derivatives may indicate a greater electron-releasing ability for these groups as compared to the *p*-isopropyl group.

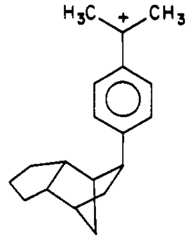
Variation in the C^+ Shifts and Stabilizing Abilities of *p*-2-Norbornyl and *p*-5,6-*exo*-Trimethylene-2-norbornyl Derivatives. The 2-aryl-2-norbornyl cations containing electron-donating substituents are accepted to be classical species even in magic acid medium.[23,24] A ρ^{C^+} value of −14.0 has been observed in the $\rho^{\mathrm{C}^+}/\Delta\delta\mathrm{C}^+$ plot of these derivatives.[7] This value is relatively less negative compared to the value of −17.1 observed for the 1-aryl-1-cyclopentyl cations.[6] This may indicate a greater electron-releasing ability for the norbornyl moiety. However, in solvolysis the ρ^+ values for the norbornyl derivatives **18** and the cyclopentyl derivatives **19** (Chart V) are almost the same.[25] Possibly, in the fully formed cations in superacid, the electron-releasing ability of the norbornyl derivative is enhanced over that possible in the transition state for a solvolytic process.

It was of interest to examine the electron-supplying properties of *exo*- and *endo*-norbornyl groups by placing these moieties at the para position of the *tert*-cumyl cation.

Chart VII



22



23

	22	23
δ^{C^+}	240.8	241.3

The solvolytic studies had shown that the exo derivative exhibits a slightly faster solvolysis rate than does the corresponding endo.[11] The rate for the *p*-cyclopentyl derivative **16** lies in between the exo and endo norbornyl derivatives **20** and **21** (Chart VI).

The C^+ in the *endo*-2-norbornyl **21** derivative is deshielded in comparison with C^+ in the *exo*-2-norbornyl derivative **20**. A similar trend is also observed in the case of the 5,6-*exo*-trimethylene-2-norbornyl derivatives **22** and **23** (Chart VII).

The question arises as to whether it is possible to account for these differences between the exo and endo derivatives on the basis of increased electron supply by the exo moieties.

Recently Taylor and co-workers suggested that such differences may arise from the steric difficulties in the endo derivatives which resist achieving maximum hyperconjugative interactions.[20] Accordingly, the slightly greater stabilizing ability of the exo derivative, as indicated by the above data, may arise from destabilization in the endo derivative because of steric difficulties. In any case, since the differences are very small, no definite conclusion can be drawn.

We continue to encounter difficulties in establishing enhanced electron release from the exo position of 2-norbornyl as compared to electron release from the endo position.

Experimental Section

Carbocations. The para-substituted *tert*-cumyl alcohols used for the preparation of the carbocations were synthesized following procedures reported from our laboratories.[11,12] The carbocations were prepared by slow addition of the alcohol precursor in SO_2ClF at −78 °C to a solution of $SbF_5/FSO_3H/SO_2ClF$ at −78 °C with rapid vortex mixing. The alcohols which are solids at room temperature would not dissolve in SO_2ClF at −78 °C. In these cases the ions were prepared by slow addition of the powdered alcohol into a solution of $SbF_5/FSO_3H/SO_2ClF$ at −78 °C. The acid (SbF_5/FSO_3H, 1:1 M) concentration in the solution was 3 M. The concentration of the ion based on the precursor added was ~0.5 M. Transfer of the solution under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended needle, as described previously.[26]

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 6000 Hz, and a pulse angle of 45°; Chemical shifts (±0.1 ppm) are in parts per million downfield from external Me_4Si.

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