The Onset of σ Delocalization in Substituted 2-Phenyl-2-norbornyl Cations as Studied by ^{13}C Nuclear Magnetic Resonance Spectroscopy. The Application of the "Tool of Increasing Electron Demand" to the 2-Norbornyl System[1a,b]

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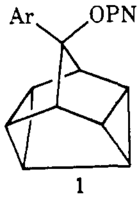
Abstract: Brown's recently accepted criterion for nonclassical ions, "the tool of increasing electron demand", has been applied to substituted 2-phenyl-2-norbornyl cations. ^{13}C NMR spectroscopic study of these ions with electron withdrawing substituents on the phenyl ring (such as p-CF$_3$, p-N$^+$H(CH$_3$)$_2$, and 3,5-(CF$_3$)$_2$) compared with electron donating substituents (p-OCH$_3$, p-CH$_3$) gives unambiguous evidence for the onset of nonclassical σ delocalization. The results have been compared with other 2-substituted norbornyl cations. Data obtained fully reinforce our previous conclusions on the nonclassical nature of the parent 2-norbornyl cation.

After a long and well documented controversy,[2] Brown has finally accepted the existence of nonclassical ions by using what he calls "the tool of increasing electron demand" in the solvolytic rate studies of 9-aryl-9-pentacyclo[4.3.0.^{2,4}.0.^{3,8}0^{5,7}]nonyl p-nitrobenzoates[3] (**1**) (Coates' previously studied cations[4] **2**). He concluded that the very low methyl/hydrogen and phenyl/methyl rate ratios observed in these systems are indicative of a transition state stabilized by major σ-p participation resulting in little demand by the developing carbonium ion center for further stabilization by the aryl substituents. He, however, also stated "... it should be pointed out that the application of the same criteria to 2-norbornyl cation **3** fails to reveal such a participation *under solvolytic conditions.*"[3] The latter statement is based on his preceding solvolytic rate studies of exo- and endo-substituted 2-phenyl-2-norbornyl esters where no significant differences of the exo/endo rate ratios were found from those in the parent systems.[5] Battiste[6] has, however, pointed out some of the reasons as to why such a rate study is not expected to show significant differences in spite of σ participation. Wilcox et al.[7] recently argued that the low alkyl vs. H and aryl vs. H rate ratio observed by Brown in the solvolysis of *exo-* and *endo-*2-norbornyl derivatives is not indicating the absence of σ participation in these systems, but possibly is providing a diagnostic test for its intervention. Kochi[8] also has reported that the electrophilic cleavage of *exo-* and *endo-*2-norbornylmethylmercury is consistent with enhanced σ participation in the exo epimer, whereas steric effects are unimportant for the endo epimer.

We regard the so-called "tool of increasing electron demand" as only one of the possible measurements of the electron demand in a system. Whereas the "tool" is a sensitive probe into structural changes in arylcarbenium ions, its effectiveness to similar changes in nonclassical ions is, however, drastically attenuated by the resonance stabilization of the aryl groups. It is thus not expected in the case of the 2-phenyl-2-norbornyl system, at least as far as exo/endo rate ratios are concerned, to be able to detect small degrees of assistance. Gassman[9] reported first that the introduction of a p-methoxy substituent into the 7-phenyl-7-norbornenyl system causes a significant break in the slope of the solvolytic rates as compared to other substituents, indicating that the p-methoxy substituted 2-phenyl-2-norbornyl cation is classical. Farnum[10] using ^{1}H NMR spectroscopy was able to show, in a series of stable 2-aryl-2-norbornyl cations, the onset of nonclassical stabilization by varying the substituents on the phenyl ring from electron donating to increasingly electron withdrawing ones. By necessity, ^{1}H NMR shift changes in this type of study were relatively small. However, in view of Brown's choice of the "tool of increasing electron demand" as the conclusive proof of nonclassicality, we wish to report that the application of this method by ^{13}C NMR spectroscopic study of a series of ring-substituted 2-phenyl-2-norbornyl cations **4** gives unambiguous evidence for the onset of σ delocalization, particularly in those ions bearing electron withdrawing substituents.



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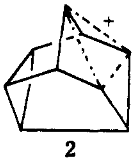

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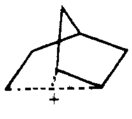

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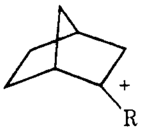

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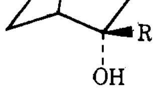
Results

Most of the precursor alcohols **5**-R were prepared by reported methods.[10,11a] The precursors **5**-C$_3$H$_5$, **5**-C$_6$F$_5$, and **5**-p-(N(CH$_3$)$_2$)C$_6$H$_4$ were prepared by the reaction of the



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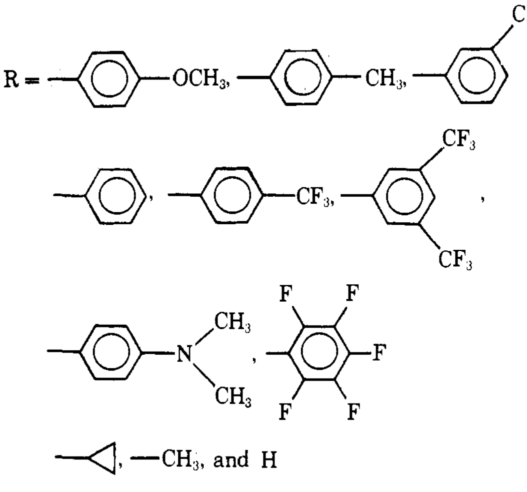
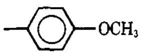
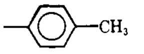
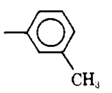
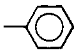
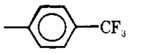
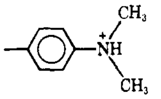
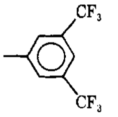
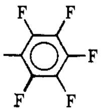
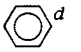


Table I. Carbon-13 NMR Parameters of 2-Aryl-2-Norbornyl Cations[a]

R	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	R[b,c]
	52.0	238.3	45.6	37.3	25.6	30.4	40.1	C_i: 127.7; C_o: 145.0; C_m: 118.0; C_p: 180.2; CH_3: 58.5
	56.3	252.3	48.6	38.4	25.1	32.4	40.6	C_i: 131.3; C_o: 141.3, 140.7; C_m: 133.0, 132.9; C_p: 169.8; CH_3: 23.9
	58.3	258.8 258.9	49.8	39.0	25.0	33.4	40.9	C_i: 142.8, 143.1; C_o: 140.8, 140.3; 138.8, 138.2; C_m: 133.2, 131.7; C_p: 153.1; CH_3: 19.9
	59.8	257.3	51.0	40.1	25.8	34.6	41.8	C_i: 133.9; C_o: 142.0, 141.2; C_m: 132.8; C_p: 152.7
	63.6	264.5	51.9	40.6	24.6	36.3	41.2	C_i: 133.8; C_o: 139.6, 140.5; C_m: 128.0; C_p: 155.9 (q, 33.8 Hz); CF_3: 122.5 (q, 282 Hz)
	65.5	264.6	53.2	48.6	25.7	37.8	48.6	C_i: 133.7; C_o: 142.3, 143.3; C_m: 124.5; C_p: 155.9; CH_3: 42.3
	66.23	262.84	52.40	41.55	24.55	38.01	41.55	C_p: 139.7; C_o: 138.28; C_m: 134.76 (q, 35.3 Hz); C_i: 131.92; CF_3: 122.40 (q, 272.7 Hz)

[a] Carbon-13 NMR shifts are in parts per million from the external Me_4Si (capillary) signal. [b] i = ipso, m = meta, o = ortho, and p = para. [c] Multiplicities, q = quartet.

Table II. Carbon-13 NMR Parameters of 2-Substituted-2-Norbornyl Cations for Comparison[a]

R	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	Other shifts
	67.2	255.8	57.1	40.0	23.6	24.5	41.7	
[d]	59.8	257.3	51.0	40.1	25.8	34.6	41.8	C_i: 133.9; C_o: 142.0, 141.2; C_m: 132.8; C_p: 152.7
[b]	55.0	288.1 (289.4)	49.4	38.2	23.9	30.1	39.5	CH: 65.3; CH_2: 43.0, 56.0
–F[e]	64.0	263.1 (d, 424.1 Hz)	48.6	42.5	23.0	38.9	39.5	
$-CH_3$	80.3	271.1	55.6	42.8	23.6	35.8	40.2	CH_3: 28.3
–H[c]	125.3	125.3	36.7	33.4	28.0	22.4	36.7	

[a] Carbon-13 NMR shifts are in parts per million from the external Me_4Si (capillary) signal. [b] At −90 °C. [c] At −150 °C in SO_2F_2/SO_2ClF. [d] i = ipso, m = meta, o = ortho, and p = para. [e] Multiplicities, d = doublet.

corresponding aryl/alkyl magnesium halides with 2-norbornanone. The corresponding 2-norbornyl ions **4**-R were generated from the precursors **5**-R with FSO_3H-SbF_5 (4:1) in SO_2ClF solution at −78 or −120 °C. The 2-fluoro substituted ion **4**-F[11b] was generated from 2,2-difluoronorbornane in SbF_5-SO_2ClF solution at −78 °C. The ^{13}C NMR spectral data of ions **4** are listed in Tables I and II. Table I summarizes ^{13}C NMR data relevant to the application of "tool of increasing electron demand". The shift assignments were based on proton decoupled, as well as coupled experiments. A plot of C(1) vs. C(3) shifts for the ions studied from the data of Table I is shown in Figure 1. A distinct break in the slope is found going from electron donating substituents such as the *p*-OCH_3 group to electron withdrawing substituents such as *p*-CF_3, *p*-dimethylamino (protonated form), or 3,5-$(CF_3)_2$. A similar plot of C(1) shifts (from Table I) vs. the Brown σ^+ substituent constants[12] also indicates a clear break in the slope (Figure 2). The σ^+ values were those reported[12] with the exception of the σ^+ value for the *p*-$N^+H(CH_3)_2$ group, which was estimated as 0.85 based on the σ^+ value for the *p*-$N(CH_3)_3$ group. For further comparison we have also prepared the 2-pentafluorophenyl-2-norbornyl cation **4**-C_6F_5 and the 2-cyclopropyl-2-norbornyl cation **4**-C_3H_5. Table II shows the ^{13}C NMR data of these ions along with those of the 2-methyl-2-norbornyl cation **4**-CH_3 and the parent norbornyl cation **3**.

Discussion

The "tool of increasing electron demand" as a measure of electron demand of a system has been previously utilized in both solvolytic[13] as well as stable ion studies.[9,10,14] Farnum et al.,[14] in a ^{13}C NMR study of a series of substituted 2-aryl-2-norbornenyl cations, were able to show the onset of σ delocalization, which was also observed by Brown in his solvolytic studies.[13] These results suggest that carbocations in nonnucleophilic media indeed provide reasonable models for the intermediate ion-like transition states in solvolysis, provided one takes into account the greater electron demand in carbocations.

The structure of the long lived parent secondary 2-norbornyl cation has now been firmly established as the σ-bridged nonclassical ion **3** based on a variety of spectroscopic studies, including ^1H NMR, ^{13}C NMR, Raman, IR, and ESCA spectroscopy, which have been well reviewed.[2a] From his extensive solvolytic studies of both *exo*- and *endo*-2-norbornyl esters, Brown, on the other hand, has concluded that high exo/endo rate and product ratios *do not necessitate σ participation* as

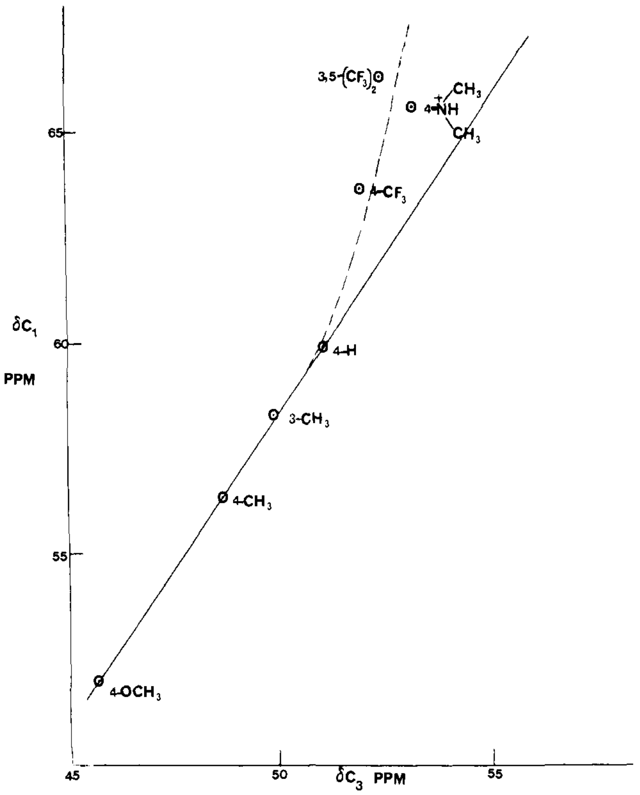


Figure 1. A plot of $\delta C(1)$ vs. $\delta C(3)$ chemical shifts of 2-aryl-2-norbornyl cations **4**.

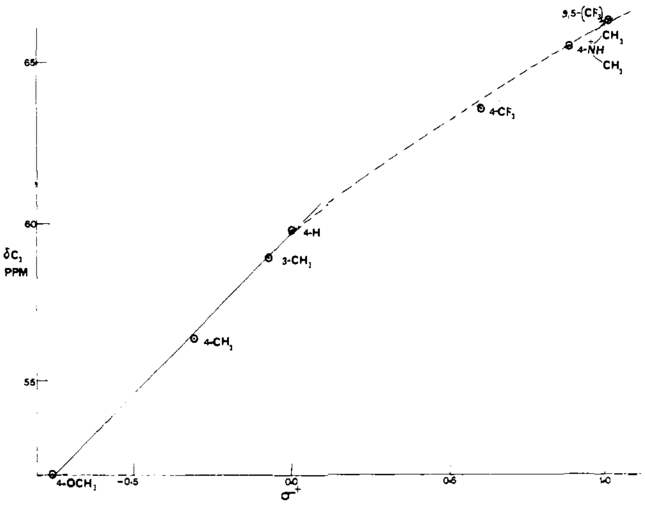


Figure 2. A plot of $\delta C(1)$ chemical shifts of 2-aryl-2-norbornyl ions **4** vs. σ^+ constants.

the explanation of the data. However, *none of his studies*[2b,c,15] *ever showed that σ participation cannot be involved.* High exo/endo rates indeed do not per se prove σ bridging in the 2-norbornyl system, but they are entirely consistent with it and no experimental evidence to the contrary was ever provided. In a critical evalution of all available evidence from solvolytic studies and related investigations, Schleyer[16] has also concluded that ion **3** has the bridged structure. Our objective in the present work was to probe the "onset" of σ delocalization in 2-phenyl-2-norbornyl cations by varying the nature of substituents on the phenyl ring, correlating the observed C(1) ^{13}C NMR shift vs. C(3) carbon shift of the norbornyl skeleton and the C(1) ^{13}C NMR shift vs. σ^+ substituent constants.

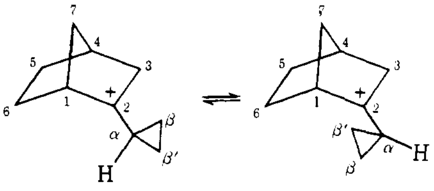
The "Tool of Increasing Electron Demand". Electron releasing substituents such as $-OCH_3$, $-CH_3$ at the para position cause a certain degree of leveling-off effect at C(1) (less shielded than in the parent ion **4**-C_6H_5) due to delocalization of the positive charge away from the C(2) position into the phenyl ring. This is also indicated by the deshielding of the ortho carbons. Strong electron withdrawing groups such as p-CF_3, p-$N^+H(CH_3)_2$, and 3,5-$(CF_3)_2$, however, show the opposite effect, and the C(1) carbon in these latter ions is deshielded by 11.6, 13.5, and 14.2 ppm, respectively, as compared to the p-methoxy substituted ion **4**-p-$CH_3OC_6H_4$. The p-CH_3 group causes C(1) to experience a lesser degree of deshielding. In **4**-m-$CH_3C_6H_4$ and the parent **4**-C_6H_5 ion both C(1) and C(2) carbons show similar shifts. The C(2) carbon shift in 2-aryl-2-norbornyl cations thus shows increase of deshielding going from electron releasing substituents in the attached phenyl ring to electron withdrawing ones; the range of such a change is approximately *25 ppm.*

^{13}C NMR shifts cannot be directly equated with charge densities and such charge-shift comparisons have been criticized.[17] It has been demonstrated,[18] however, 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 the chemical shift. If one plots the C(1) vs. C(3) ^{13}C NMR shifts for studied 2-aryl-2-norbornyl cations **4**-R of Table I as shown in Figure 1, there is a distinct break in the curve between electron releasing and electron withdrawing substituents. In Figure 1 the deviation for electron releasing and electron withdrawing substituents ranges from 2.5 to 4.1 ppm. This indicates that when the aryl group becomes less effective in delocalizing positive charge generated at the C(2) position, the neighboring C(1)-C(6)σ bond begins to interact with the empty p orbital (electron-deficient center), i.e., the "onset" of "σ delocalization." When one plots C(1) shift vs. σ^+ (Figure 2) a break in the slope is again found on going from electron donating substituents, such as the p-OCH_3 group, to electron withdrawing substituents such as p-CF_3, p-dimethylammonium or 3,5-$(CF_3)_2$. Such breaks clearly demonstrate the onset of σ participation. The "tool of increasing electron demand" is, however, not expected to show large effects in the case of 2-phenyl-2-norbornyl cations.[18] It must be remembered that any phenyl group, even bis(trifluoromethyl) substituted 3,5-$(CF_3)_2C_6H_3$-, is a π donor and can stabilize an adjacent carbocationic center. Electron withdrawing groups decrease the delocalization by the phenyl ring (but do not eliminate it) and thus enhance contribution by the norbornyl σ_1-σ_6 bond. Electron donating groups have the opposite effect, enhancing the "classical" nature of the ion. However, in the present system expected change due to substituent effects is obviously small.

Neighboring σ-bond participation in 2-aryl-2-norbornyl cations bearing strong electron withdrawing substituents on the phenyl ring is expected, since going from the tertiary 2-aryl- to 2-alkyl-2-norbornyl cations, charge delocalization into the neighboring σ bond becomes evident. The 2-methyl-2-norbornyl cation **4**-CH_3 has been shown to be a partially σ-delocalized ion which undergoes 1,2-Wagner-Meerwein shift at much higher temperature than **3**-H.[19] The C(1) carbon in **4**-CH_3 is surprisingly more deshielded than in other tertiary analogues. Thus besides hyperconjugative stabilization by the methyl C-H bonds, the positive charge seems also to be partially delocalized into the norbornyl framework through the neighboring C(1)-C(6) σ bond. The significantly deshielded C(6) carbon also indicates the same. A similar C(1)-C(6) σ-bond interaction with the p orbital of the electron deficient center at C(2) is observed in the case of ion **4**-C_6F_5, where the pentafluorophenyl group becomes a poor charge stabilizer due to the presence of five strongly electron withdrawing fluorine atoms. Hence one sees significant deshielding of C(1) over

C(3) (10.1 ppm). The deshielding of the C(1) and C_3 carbons may also be due to a small degree of steric effect by fluorine substituents of the 2 and 6 position of the phenyl ring, which would slightly decrease p-π delocalization.

The 2-cyclopropyl-2-norbornyl cation **4-C_3H_5** is not only instructive in its comparison with the related 2-phenyl- and 2-methyl-2-norbornyl cations, but also exhibits further characteristic properties. The ^{13}C NMR spectrum of **5-C_3H_5** in FSO_3H/SbF_5-SO_2ClF solution at −90 °C indicates the formation of two closely related ions with the carbenium centers at δ ^{13}C 289.4 and δ ^{13}C 288.1, respectively. The signal intensities indicate that one of the ions is predominant. The ^{13}C NMR shifts of the major species are listed in Table II. The data indicate that the 2-cyclopropyl-2-norbornyl cation is present as two isomers **4-C_3H_5(a,b)** due to the different orientation of the cyclopropyl ring. One of the conformations predominates at −90 °C. It is difficult to assign the orientation of the cyclopropane ring in the predominating species and we were also unable to observe the free rotation of the cyclopropane ring, as the ions immediately decompose above −70 °C. In ion **4-C_3H_5** (major species) the positive charge is delocalized into the cyclopropyl ring and thus shows a considerably less deshielded C(1) shift (Table I). The α-methine and one of the β-methylene groups are largely deshielded (65.3 and 56.0 ppm, respectively). This indicates that one of the bent cyclopropyl bonds is strongly interacting with the carbenium center in delocalizing the charge. The other β'-methylene group resonates at δ ^{13}C 43.0 ppm. Thus, the C(1)-C(6) σ bond interacts with the neighboring empty p orbital in a much more limited way in **4-C_3H_5** than in **4-CH_3**. This is also evident in the case of 2-fluoro-2-norbornyl cation **4-F**, wherein the positive charge at C(2) is significantly delocalized by the fluorine atom via p-p conjugation.[11b] For comparison the ^{13}C NMR shifts of the fully σ-delocalized parent ion **3** are also listed in Table II.



4-C_3H_5(a) 4-C_3H_5(b)

Conclusions

The application of what Brown calls the "tool of increasing electron demand" to a series of substituted 2-phenyl-2-norbornyl cations by ^{13}C NMR spectroscopic study of the long-lived ions clearly shows the "onset" of σ delocalization depending upon the electronic effects of the substituents. Carbocations (observable as stable species in superacidic media) are reasonable models for the intermediate ion like transition states of solvolytic reactions, if one takes into account the greater electron demand of carbocations. On the other hand, if the transition states lie earlier on the reaction coordinate, resembling starting materials more than the intermediate ions, then the knowledge of the structure of the ions does not necessarily indicate the nature of the transition state. In other words, if secondary norbornyl systems solvolyze not by a limiting S_N1 mechanism, the transition state can lie earlier on the reaction coordinate and thus not necessarily possesses carbocation-like structure (i.e., the solvolysis could show increasing S_N2 characteristics). The data obtained in our present study, however, fully support our previous conclusions[2a] reached on the nonclassical nature of the parent norbornyl cation **3**. Neither the application of Brown's tool of increasing electron demand nor any other experimental data we know contradict our conclusion. Dewar's recent preference for the classical structure was based on MINDO/3 calculations,[20] where minima were found corresponding to both classical and nonclassical structures, differing by only about 2 kcal mol^{-1} or less. Even when considering that these calculations relate only to the idealized gas phase and refinements may somewhat change values, the energy differences are small, not unlike in the case of the $C_3H_7^+$ system. As, however, similar MINDO/3 calculations by Dewar himself (not mentioned in his paper) of the heat of formation of the parent neutral hydrocarbon, i.e., norbornane, gave an error in excess of 20 kcal mol^{-1} compared with the experimentally measured value,[20b] it must be concluded that the limitations of his MINDO/3 calculations at the present time vastly exceed the energy differences involved.[20c]

Our view in this regard and also concerning the validity of our reported ESCA spectral studies were recently fully justified by Allen and Goetz,[21] who carried out an extensive nonempirical LCAO MO SCF investigation at the STO-3G and STO-4.31G level on the electronic structures of the classical and nonclassical norbornyl cation. Clark, Cromarty, and Colling[22] using these parameters were able to carry out a detailed interpretation of the experimental ESCA data for the core-hole spectra at the SCF STO 4.31G level and calculated equivalent cores at the STO-3G level. Agreement between experimental spectra and those calculated for the nonclassical ion are good, but dramatically different from those calculated for the classical ion. As we concluded previously, the so-called "classical-nonclassical ion controversy" should be considered closed, even when considering Brown's own criterion of the tool of increasing electron demand.

Experimental Section

2-Aryl-2-norbornyl alcohols **5-*p*-$CH_3OC_6H_4$**, **5-*p*-$CH_3C_6H_4$**, **5-*m*-$CH_3C_6H_4$**, **5-*p*-$CF_3C_6H_4$**, **5-C_6H_5**, **5-3,5(CF_3)$_2C_6H_3$**, and **5-CH_3** were prepared by the reported methods.[10,11] Alcohols **5-C_3H_5**, **5-*p*-[N(CH_3)$_2$]C_6H_4**, and **5-C_6F_5** were prepared by the reaction of the corresponding cyclopropylmagnesium bromide, *p*-dimethylaminophenylmagnesium bromide, and pentafluorophenylmagnesium bromide, respectively,[23] with 2-norbornanone in THF or ether.

***exo*-2-Cyclopropyl-2-norbornyl alcohol (5-C_3H_5):** bp 59 °C (1 mm); colorless liquid. The infrared spectrum (neat, cm^{-1}) showed ν_{OH} at 3520 cm^{-1} (b). The ^1H NMR spectrum (60 MHz, $CDCl_3$, from external capillary Me_4Si, 37 °C) showed absorptions at δ 2.8–1.2 (m, 12 H, norbornyl protons, OH and CH of Cpr) and 0.95–0.7 (m, 4 H, CH_2 of Cpr).

***exo*-2-p-Dimethylaminophenyl-2-norbornyl alcohol, (5-*p*-[N(CH_3)$_2$]C_6H_4):** mp 102–103 °C; pale yellow solid. The infrared spectrum (CCl_4, cm^{-1}) showed ν_{OH} at 3530 (s). The ^1H NMR spectrum (60 MHz, $CDCl_3$, from external capillary Me_4Si, 37 °C) showed absorptions at δ 7.3 (AB pattern, 4 H, aromatic protons), 3.3 (s, 3 H, CH_3 groups), 2.9 (b, 1 H, bridgehead proton at C(1)), 2.6 (b, 3 H, methylene at C(3) and bridgehead proton at C(4), 2.1 (1 H, OH), and 2.0–1.4 (b, 6 H, methylene protons at C(5), C(6), and C(7)).

***exo*-2-Pentafluorophenyl-2-norbornyl alcohol (5-C_6F_5):** mp 72–73 °C; white crystalline solid. The infrared spectrum (CCl_4, cm^{-1}) showed ν_{OH} at 3560 (s). The ^1H NMR spectrum (60 MHz, $CDCl_3$, from external capillary Me_4Si, 60 °C) showed absorptions at δ 3.5 (b, 1 H, proton at C(1)) and 3.1–1.4 (br multiplet, 10 H, 9 norbornyl protons and -OH). ^{19}F spectrum (from external capillary CCl_3F, 37 °C), broad peaks centered at −138.9. All new compounds had satisfactory elementary analyses.

Preparation of Carbocations. Freshly prepared magic acid (4:1) from twice distilled FSO_3H and SbF_5 was dissolved in twofold amount of SO_2ClF at dry ice–acetone temperature (ca. −78 °C) or ethanol/liquid nitrogen temperature (ca. −120 °C) in 12- or 5-mm (diameter) NMR tubes. To this solution was slowly added with vigorous stirring a cooled slurry of the appropriate precursor in SO_2ClF, to give an approximately 10–15% solution of the ion.

^1H NMR and ^{19}F NMR spectra were obtained on a Varian Model A56/60A NMR spectrometer. External capillary Me_4Si and CCl_3F were used as the reference.

^{13}C NMR spectra were obtained using a Varian Model XL-100 NMR spectrometer equipped with FT accessory with variable temperature probe as previously described.[24]

The *infrared spectra* were obtained on a Beckman IR-10 spectrometer and *melting points* (uncorrected) were measured on a Mettler FP-1 melting point apparatus.

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The Nature of the Electrical Effect of Alkyl Groups.
1. The Validity of the σ^* Constants

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Abstract: σ^* values for alkyl groups are defined from rate constants for the acid- and base-catalyzed hydrolysis of amides, $XCONH_2$. These σ^* values show no relationship with those defined by Taft from ester hydrolysis. They also do not show any systematic dependence on alkyl group structure. These results support the conclusion that the Taft σ^* constants for alkyl groups *do not* measure the electrical effects of alkyl groups.

In a recent communication, Macphee and Dubois[1] have presented arguments which they claim refute our conclusions[2] that the electrical effects of alkyl groups are essentially constant and that the σ^* values for alkyl groups are artifacts. These authors very correctly note that if our conclusions are indeed justified, it is necessary to reexamine a large body of published results in which the relative importance of steric and electrical effects of alkyl groups was studied. In this work we present new results which we feel strongly support our view that σ^* values for alkyl groups do not measure the electrical effects of those groups. The question of the significance of the Taft σ^* values for alkyl groups has long been a controversial one. Earlier work in this area has been thoroughly examined in an excellent critical review by Shorter.[3]

To apply the Taft method for separating polar and steric effects we require rate data for substituted compounds undergoing one reaction in which both steric and electrical effects occur and another reaction in which only steric effects occur. It is further necessary that the magnitude of the steric effects be the same in both reactions. We have recently shown[4] that acid-catalyzed hydrolysis of amides is a function only of steric effects, while the base-catalyzed hydrolysis is a function of both steric and electrical effects. Evidence for this statement is provided by the successful correlation of rate constants for acid hydrolysis of amides $XCONH_2$ with the modified Taft equation

$$\log k_X = \psi \upsilon_X + h \qquad (1)$$

whereas rate constants for basic hydrolysis required the LDS equation

$$\log k_X = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h \qquad (2)$$

Thus, the acid hydrolyses could be accounted for by a steric term whereas the basic hydrolyses require electrical effect terms as well. It should be noted that the sets studied included groups with a range of electrical effect in both the acid- and base-catalyzed hydrolyses. The data used in the correlations are tabulated in our earlier work.[4] The υ_X values used as steric parameters in eq 2 have been shown to be a linear function of the van der Waals radii in the case of spherically symmetric groups and are independent of electrical effects. Sets of rate constants for basic hydrolysis of amides which contained only alkyl substituents were then shown to be correlated well by the