Structural Effects in Solvolytic Reactions. 39. Examination of the Ability of the ^{13}C NMR Shift-σ^{C^+} Correlation for Substituted Benzylic Cations To Accommodate the Highly Electron Donating 5-Coumaranyl Moiety. Evaluation of the Significance of the ρ^{C^+} Values Observed for the Simple Aryldialkyl Carbocations

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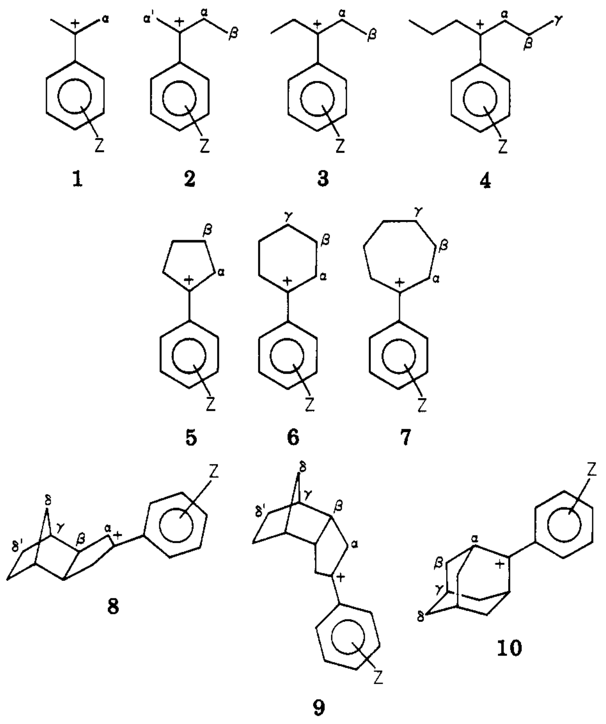
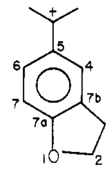
Six 5-coumaranyldialkyl carbocations were prepared from the corresponding alcohols in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C and the ^{13}C NMR shifts for the resulting carbocations were measured at −70 °C. The 5-coumaranyl moiety, with a σ^{C^+} value of −2.40, serves as a strong electron donor, even stronger than *p*-methoxyphenyl, to test the proposed linear relationship between the C^+ NMR shifts and the σ^{C^+} constants for representative aryldialkyl carbocations. Excellent linear correlations including the 5-coumaranyl moiety were observed. The trends in the variation of the ρ^{C^+} values observed for these systems are discussed.

Recently we introduced new σ^{C^+} constants to correlate the C^+ shifts in substituted aryldialkyl carbocations.[1] These constants, derived from the *tert*-cumyl cations, **1**, revealed excellent correlations against the C^+ shifts for nine representative aryldialkyl carbocations (**2–10**, Chart I).[2-5] However, a referee of one of these papers pointed out that these correlations depend heavily on the *p*-methoxy point. This referee suggested that another strong electron donor in the *p*-methoxy region would provide desirable confirmation for the soundness of the proposed correlation.

Chart I



We had encountered this problem earlier in correlating our solvolytic data against σ^+. At that time we selected the 5-substituted-2,3-dihydrobenzofuran (5-coumaranyl) moiety (Z = *p*-OCH_2CH_2-*m*) and the para methylthio (Z = *p*-SCH_3) substituent to fill the void. We established that these two groups possess σ^+ values of −0.984 and −0.54, respectively, compared with the previously determined σ^+ value of −0.778 for the *p*-methoxy group.[6,7] Accordingly, it would be anticipated that the 5-coumaranyl moiety and the *p*-methylthio substituent might provide σ^{C^+} values on either side of the *p*-methoxy group. On the basis of these considerations, Kelly and co-workers recently studied the ^{13}C NMR shifts for the corresponding *tert*-cumyl cations (**11** and **12**).[8] They reported that the ion **11** was prepared cleanly in the superacid medium from the corresponding alcohol and gave a σ^{C^+} value of −2.4. On the other hand, the *p*-methylthio group undergoes protonation on sulfur in superacid media. Consequently, it acts as an electron-withdrawing not as an electron-donating substituent in benzylic carbocations. Accordingly, we decided to test the 5-coumaranyl moiety against the C^+ shifts for our representative systems. In addition, it was of interest to examine the variation in the ρ^{C^+} values for these simple dialkyl carbocations.



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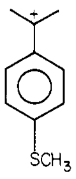

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Results and Discussion

The 5-coumaranyl alcohols (**13–18**) were synthesized by addition of the corresponding ketones to 5-lithiocoumaran, prepared from 5-bromocoumaran and *n*-butyllithium, as reported earlier from our laboratories.[7]

The corresponding cations, **2**, **4**, and **6–9** (Z = *p*-OCH_2CH_2-*m*), were prepared in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C and the carbon-13 NMR shifts were measured at −70 °C. The data for these cations are summarized in Table I. In order to provide a complete summary, we also

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

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

(3) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3161.

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

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

(6) Brown, H. C.; Inukai, T. *J. Am. Chem. Soc.* **1961**, *83*, 4825.

(7) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 7663.

(8) Ginsiracusa, J. J.; Jenkins, M. J.; Kelly, D. P. *Aust. J. Chem.*, in press.

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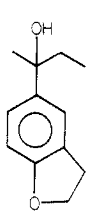

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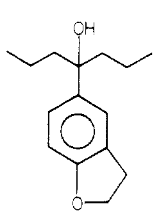

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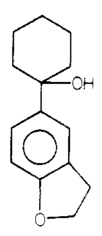

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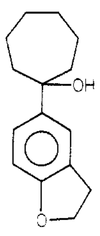

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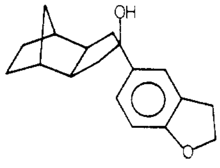

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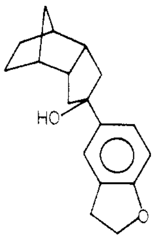

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included the data for cations **1**, **3**, **5**, and **10** (Z = *p*-OCH_2CH_2-*m*), examined by Kelly and co-workers,[8] in Table I.

Correlation of the $\Delta\delta C^+$ Shifts. The σ^{C^+}–$\Delta\delta C^+$ plots for these systems are presented in Figures 1–3. For convenience, the corresponding correlation parameters are summarized in Table II. It is evident from Figures 1–3 and Table II that the C^+ shifts in these simple dialkyl carbocations are nicely correlated, giving excellent correlations (r = 0.998–0.999) irrespective of whether the correlation excludes or includes the strongly electron-donating 5-coumaranyl moiety.

ρ^{C^+} Values. Recently, Olah and co-workers plotted the C^+ shifts for some arylbicyclic cations against the corresponding shifts for the arylcyclopentyl cations.[9] They observed that the values of the slopes do not change significantly in different systems. They suggested that ths may be due to similar anisotropy situations in the various bicyclic systems.

Unfortunately, they did not indicate the specific influence that such anisotropy effects might have on the ^{13}C shifts of the benzylic cations in different systems. Consequently, it is not possible to consider what part such anisotropy effects might have on the observed ^{13}C shifts.

However, it may be of interest to compare the ρ^{C^+} values for systems having similar structural features (**1**–**10**) and to examine whether we can find any trend based upon electronic or steric interactions in these and similar cations.

For example, ρ^{C^+} values of −18.2 and −18.0 are observed for systems **1** and **2**, respectively. These are comparable. The ρ^{C^+} value of −17.0 observed for the system **3** is significantly less negative. The corresponding ρ^+ values observed in the solvolyses of the corresponding para nitrobenzoates are −4.72 for system **1** and −4.52 for system **3**.[10] Both ρ^{C^+} and ρ^+ for system **3** are less negative than for system **1**. This change is in accordance with the predicted effect of an increase in the inductive contributions of ethyl vs. methyl groups (Et > Me).

The ρ^{C^+} value of −14.6 observed for the 4-aryl-4-heptyl system (**4**) is considerably less negative than the ρ^{C^+} values for systems **1**–**3**. It is difficult to account for this less negative ρ^{C^+} value on the basis of the inductive effect alone because the inductive effect would be expected to fall off sharply as the distance between the C^+ center and the alkyl substitution increases.

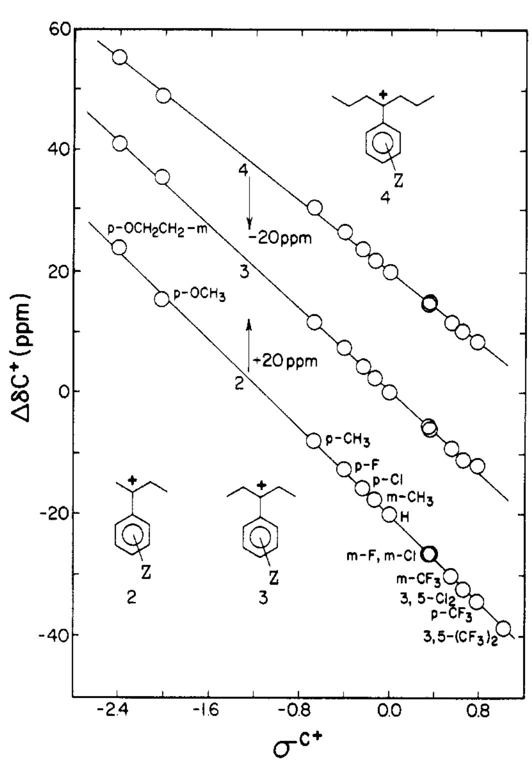

Figure 1. Plots of $\Delta\delta C^+$ against σ^{C^+} values for the 2-aryl-2-butyl **2**, 3-aryl-3-pentyl **3**, and 4-aryl-4-heptyl **4** carbocations.

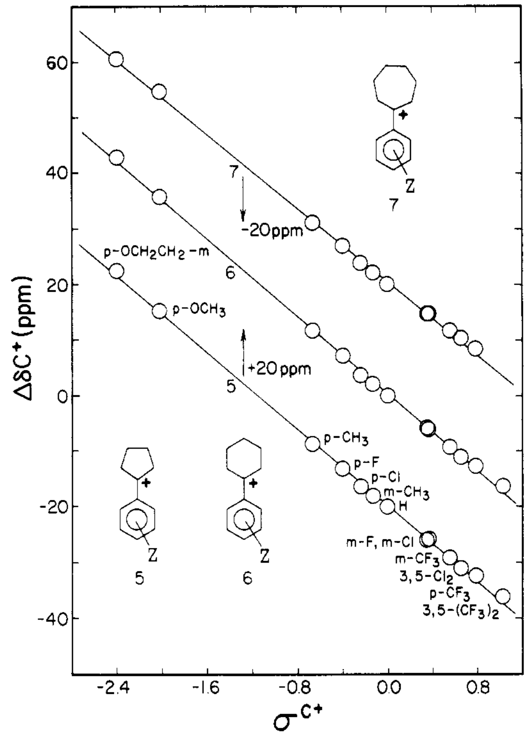

Figure 2. Plots of $\Delta\delta C^+$ against σ^{C^+} values for the 1-aryl-1-cyclopentyl **5**, 1-aryl-1-cyclohexyl **6**, and 1-aryl-1-cycloheptyl **7** carbocations.

Although a definite conclusion cannot be reached at this stage, the observed variations in the β-carbon shifts in systems **3** and **4** appear to provide a possible clue. The β-carbon in **3** undergoes a downfield shift by 2.5 ppm from Z = *p*-OCH_3 to *p*-CF_3.[5] The corresponding downfield shift in **4** is 4.2 ppm.[2] The increase in the downfield shift for the β-carbons in system **4** may be attributed to increased hyperconjugative interactions of the β-carbon atom with the C^+ center, interactions which are favored by certain

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[9] Olah, G. A.; Berrier, Al. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998.

[10] Brown, H. C.; Ravindranathan, M.; Peters, E. N.; Rao, C. G.; Rho, M. M. *J. Am. Chem. Soc.* **1977**, *99*, 5373.

Table I. ^{13}C NMR Shifts for the Coumaranyl (Z = *p*-OCH_2CH_2-*m* 1-10) Dialkyl Carbocations in $SbF_5/FSO_3H/SO_2ClF$ at -70 °C

	chemical shift^a													
cation	C^+	C^{α}	C^{β}	C^{γ}	C^{δ}	$C^{\delta'}$	C_2	C_3	C_4	C_5	C_6	C_7	C_{7a}	C_{7b}
$1^{b,c}$	212.0	28.1					27.1	80.5	138.0	136.1	148.0	115.9	184.8	134.9
2	216.5	34.9 (α-CH_2), 26.2 (α'-CH_3)	15.9				26.9	80.4	138.1, 137.2	136.5	148.3, 147.3	116.0	184.8	134.0
3^b	222.5	33.4	16.8				27.1	80.9	137.9	136.7	147.9	116.4	184.1	133.5
4	222.1	43.1	28.3	15.2			27.1	81.5	137.9	136.3	147.6	116.2	182.7	134.6
5^b	227.6	40.7	26.4				27.1	80.2	138.8	136.1	148.7	115.8	184.3	132.0
6	219.7	39.1, 39.0	34.6	26.7			27.0	80.2	136.8	136.8	146.6	116.1	185.1	132.1
7	223.1	39.8, 39.7	28.7	28, 27.4			27.1	80.4	136.2	137.2	146.9	115.8	183.4	134.5
8	229.7	45.7	47.7	44.0	32.8	28.8	27.0	80.3	135.7	138.6	148.3	115.6	183.2	130.8
9	227.6	41.0	43.9	42.0	40.0	23.3	27.0	80.4	136.2	138.7	148.4	115.9	183.7	131.1
10^b	230.3	43.7	44.5	28.7	36.3		27.1	79.8	135.4	136.5	145.0	116.0	184.7	130.7

[a] In parts per million downfield from external Me_4Si. [b] Data from ref 8. [c] The numbering of the coumaranyl moiety carbon atoms is shown in 11.

Table II. Correlation Parameters

	excluding coumaranyl^a				including coumaranyl			
system	ρ^{C^+}	*r*	SD(ρ^{C^+})	SD($\Delta\delta C^+$)	ρ^{C^+}	*r*	SD(ρ^{C^+})	SD($\Delta\delta C^+$)
2	−17.8	0.999	0.11	0.27	−18.0	0.999	0.12	0.39
3	−17.2	0.999	0.15	0.11	-17.0^b	0.999	0.13	0.41
4	−14.6	0.999	0.17	0.39	−14.6	0.999	0.12	0.38
5	−16.8	0.999	0.21	0.53	-17.1^b	0.999	0.19	0.62
6	−17.2	0.999	0.18	0.46	−17.4	0.999	0.15	0.50
7	−16.4	0.999	0.26	0.60	−16.5	0.999	0.19	0.58
8	−16.3	0.999	0.20	0.50	−16.3	0.999	0.14	0.45
9	−15.9	0.999	0.10	0.20	−16.0	0.999	0.08	0.23
10	−16.1	0.998	0.28	0.22	-16.5^b	0.998	0.25	0.81

[a] Data from ref 1-5. [b] Data from ref 8.

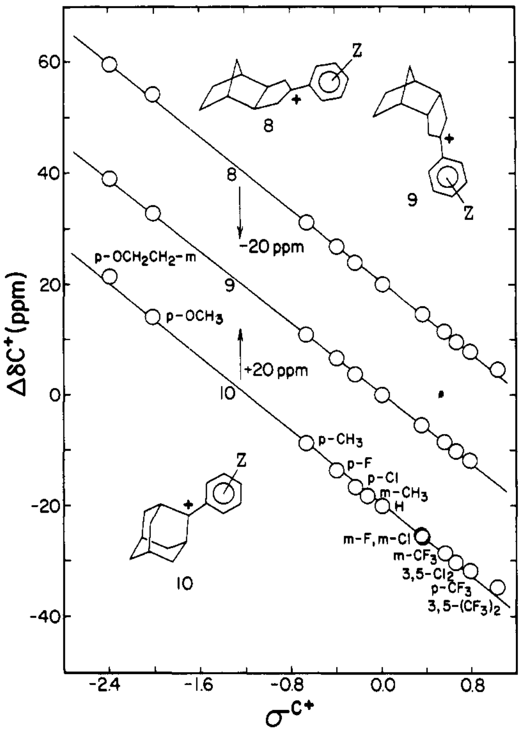
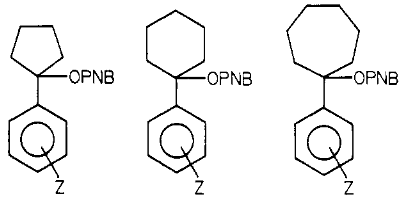


Figure 3. Plots of $\Delta\delta C^+$ against σ^{C^+} values for the 9-aryl-*exo*-5,6-trimethylene-9-norbornyl 8, 9-aryl-*endo*-5,6-trimethylene-9-norbornyl 9, and 2-aryl-2-adamantyl 10 carbocations.

rotamers. Dreiding models show that the number of possible rotamers with low energies may be more limited in the system 4 because of the strains introduced in accomodating the ends of the longer chain. Therefore, this system may favor desirable rotamers which can interact strongly with the cationic center, leading both to the increase in the magnitude of the β-carbon shifts and the magnitude of the decrease in the negative value of ρ^{C^+}.

Another possible factor in the observed change in ρ^{C^+} for 4 is the effect of the long side chains in hindering coplanarity. Such hindrance would arise from van der Waal's repulsion between the ortho hydrogens of the aryl ring and the alkyl side chains, probably coiled up in the polar superacid medium. Tanida and Matsumura reported that such interactions in sterically crowded systems yielded much less negative ρ^+ values.[11]

Although the variation in the ρ^{C^+} values with ring size is small for the cyclic systems 5–7, the cyclohexyl ρ^{C^+} value is more negative compared to the ρ^{C^+} values observed for the cyclopentyl 5 and cycloheptyl 7 systems. This trend is somewhat similar to the trend in the ρ^+ values observed in the solvolysis of the para nitrobenzoates (18–20).[10] The



18 19 20

ρ^+ (80% aqueous acetone, 25 °C) −3.82, −4.60, −3.87

variations in the ρ^+ values have been attributed to bond opposition forces which facilitate the rates of solvolyses of cyclopentyl and cycloheptyl derivatives and give less

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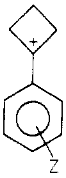
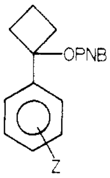
[11] Tanida, H.; Matsumura, H. *J. Am. Chem. Soc.* **1973**, *95*, 1586.

negative ρ^+ values. The C^+ shift data do not involve any bond making or bond breaking. Therefore, the bond opposition forces do not play any role in the NMR data, resulting in smaller changes in the ρ^{C^+} values compared to the ρ^+ values.

The ρ^{C^+} value for the 1-aryl-1-cyclobutyl cations (**21**) can be estimated to be −18.1 from the data reported by Olah and co-workers.[12] This is relatively more negative compared to the ρ^{C^+} values for the five–, six–, and seven-membered rings. Interestingly, the ρ^+ value observed for the solvolysis of the 1-aryl-1-cyclobutyl para nitrobenzoates (**22**) is also more negative than the ρ^+ values observed for the five-, six-, and seven-membered ring systems.[10] This relatively large negative ρ^+ value for the cyclobutyl system was attributed to the difficulty of incorporating an sp^2 atom into the ring, which makes the developing cationic center more electron demanding, resulting in relatively large electron supply from the aryl group and relatively large negative ρ^+ value.[10] The relatively large negative ρ^{C^+} value can also be accounted for on the basis of similar considerations.



21
ρ^{C^+} −18.1



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ρ^+ −4.9

The ρ^{C^+} values of −16.3 and −16.0 for systems **8** and **9**, respectively, compare with the value of −17.0 observed for the arylcyclopentyl system, **5**. Although a safe conclusion for the differences in the ρ^{C^+} values for the systems **8** and **9** and the cyclopentyl system **5** cannot be reached because of the suggested anisotropy effects in bicyclic systems, the relatively less negative ρ^{C^+} values for the systems **8** and **9** may be attributed to additional C–C hyperconjugative and inductive stabilizations provided by the norbornyl moiety fused onto the cyclopentyl ring in the systems **8** and **9**.

Table III. Physical Constant Data for the Coumaranyl Alcohols 13-18

alcohol	mp or bp (mm), °C	alcohol	mp or bp (mm), °C
13	106-108 (0.1)[a]	16	77
14	126-128 (0.1)[a]	17	113-114
15	74	18	125

[a] The distillate was found to contain the corresponding olefins along with the alcohol (^1H NMR and ^{13}C NMR) and was used for the ion preparation without further purification. Satisfactory analytical data (C ± 0.37 and H ± 0.2%) were obtained for all the other compounds.

Experimental Section

Precursors. The tertiary alcohols **13–18** were synthesized by the reaction of the corresponding ketone with 5-lithiocoumaran (prepared from 5-bromocoumaran and *n*-butyllithium) as reported from our laboratories.[7] The physical constant data for these alcohols are summarized in Table III. The alcohols **13** and **14** were found to contain considerable amounts of the corresponding olefins (^1H NMR and ^{13}C NMR) after distillation. These alcohols were used for ionization to the corresponding cations without further purification. Satisfactory analytical data (C ± 0.3% and H ± 0.2%) were obtained for the alcohols **15–18**.

Carbocations. The ions were prepared by slow addition of the appropriate alcohol as a solution in SO_2ClF (alcohols **13** and **14**) or as a powder (alcohols **15–18**) to a solution of FSO_3H/SbF_5(1:1, mol/mol)/SO_2ClF cooled to −78 °C with rapid vortex mixing. The "magic acid", SbF_5/FSO_3H (1:1, mol/mol), concentration in the solution was 3 M. The concentration of the ion based on the alcohol added was ~0.5 M. Transfer of the solutions under nitrogen to 8-mm NMR tubes was achieved via a cooled double-ended syringe, as previously described.[13]

NMR Spectra. The ^{13}C NMR spectra were recorded at −70 °C on a Varian CFT-20 spectrometer, using 8-mm tubes containing a concentric 3-mm (outside diameter) capillary tube of completely deuterated acetone and tetramethylsilane, and using 8192 data points, a spectral width of 6500 Hz, and a pulse angle of 45°. Chemical shifts are reported in parts per million downfield from external tetramethylsilane.

Registry No. **2** (Z = *p*-OCH_2CH_2-*m*), 79816-06-1; **4** (Z = *p*-OCH_2CH_2-*m*), 79816-07-2; **6** (Z = *p*-OCH_2CH_2-*m*), 79816-08-3; **7** (Z = *p*-OCH_2CH_2-*m*), 79816-09-4; **8** (Z = *p*-OCH_2CH_2-*m*), 79827-17-1; **9** (Z = *p*-OCH_2CH_2-*m*), 79827-18-2; **13**, 79816-10-7; **14**, 79816-11-8; **15**, 79816-12-9; **16**, 79816-13-0; **17**, 79839-02-4; **18**, 79839-03-5.

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

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

Hyperconjugation as a Parameter in Correlation Analysis

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Many years ago, Kreevoy and Taft suggested that hyperconjugation was an important factor in chemical reactivity and that a parameter which characterized hyperconjugation could be used together with other parameters to correlate log *k* values. A number of other groups of workers have extended this approach. A reexamination of the data shows that in all of the cases studied equally good results can be obtained by considering only electrical, steric, and polarizability effects. There is no need to involve hyperconjugation in order to satisfactorily account for the data. As all chemical reactivity data, including those studied here, can be described in terms of electrical and/or steric and/or polarizability parameters and as, at best, some data can be described in terms of hyperconjugation parameters, it is best to abandon the use of the unnecessary hyperconjugation parameters.

Kreevoy and Taft[1] proposed eq 1 for the correlation of

$$(Q_X/Q^\circ) = \rho^*\sigma^*_X + h(\Delta n_H) \qquad (1)$$

rate constants for the acid hydrolysis of substituted ethyl acetals and ketals, ΔG°_{333} values for the reaction of aldehydes and ketones with 2-propanol in toluene catalyzed

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(1) Kreevoy, M. M.; Taft, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 5590; **1957**, *79*, 4011.

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