interaction (**2** and **3**), the susceptibilities $\rho_R{}^6$ are drastically reduced. $\rho_I{}^5$ and $\rho_R{}^5$ reproduce largely the inductive effects of the substituent X.

If the deuteron behaves like a common substituent, compounds **1a**, **2a**, and **3a** (X = D) will show all the features pertinent to systems **1**, **2**, and **3**[8,9] at least on a qualitative level. This expectation is fully borne out by the experimental data given in the table. As compared to the hydrogen atom the deuteron performs like a polar donor substituent, $\sigma_{I,D} < 0$, whose absolute value is obviously much larger than $\sigma_{R,D}$. The polarization of the vinyl side chains is in the direction predicted. The extent of polarization is clearly dependent on the angle between the phenyl ring and the side chain lending further support to the concept of extended and local π-polarization in unsaturated systems. An additional test for these ideas is provided by compounds where a rigid aliphatic spacer is placed between the substituent and the π-system, e.g., 1-X-4-phenylbicyclo[2.2.2]octanes **4**. In **4a** (X = D) C–5 displays an isotope effect of sign and order of magnitude expected from its known $\rho_{I,R}$ values.

This qualitative correspondence between long-range deuterium isotope and substituent effects on ^{13}C chemical shifts calls for an inverse DSP correlation between the isotope-induced shifts $^n\Delta\delta_{C(D)}$ and the $\rho_I{}^i$ and $\rho_R{}^i$ parameters in order to deduce the substituent constants $\sigma_{I,D}$ and $\sigma_{R,D}$ for the deuteron spectroscopically. However, such a quantitative statistical analysis faces major obstacles. First, there exists an appreciable difference in the degree of accuracy of the $\rho_I{}^i$ and $\rho_R{}^i$ parameters and the long-range deuterium isotope effects as commonly determined. Second, a $\sigma_{R,D}$ value derived by this analysis will be a hybrid out of the different $\sigma_{I,R}$ scales currently used to establish highest fit correlations between substituents and SCS data, changing the scale even for different carbon atoms in a single compound.[8,9] Third, the numerical results for values of deuterium are expected to be at least 1 order of magnitude smaller than the σ values for common substituents.

Given these provisos a correlation based on 19 individual carbon atoms that predicts isotope-induced shifts with a standard deviation of 2.8 ppb and $\sigma_{I,D} = -0.0021$ and $\sigma_{R,D} = -0.0003$ with a multiple correlation coefficient of $R = 0.919$ is quite satisfactory.[11] The most important result, however, is that the spectroscopically derived $\sigma_{I,D}$ value for the deuteron compares well with the σ_m deduced by Streitwieser and Klein from their studies of deuterium isotope effects on ionization equilibria.[12] Good agreement is found between the isotope effect on the pK_a values for ring deuterated benzoic acids by using the known $\rho_{I,R}$ values for substituted benzoic acids.[7] Similar calculations for anilinium ions corroborate these results.[13,14]

The ratio $\sigma_{I,D}/\sigma_{R,D}$ is 7 and the resonance contribution for the DSP correlation as defined by Swain and Lupton[11] is only 12%; therefore a simple linear correlation between $\sigma_{I,D}$ and the isotope induced shifts is of similar quality, questioning the physical relevance of a $\sigma_{R,D}$ value different from zero. This important problem has to be clarified by further study of compounds where blends $\lambda_i = \rho_R{}^i/\rho_I{}^i$ largely favor mesomeric susceptibility.[15]

(11) The program of Swain and Lupton was used for the dual parameter correlations: Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968,** *90,* 4328–4337.

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(13) Bernasconi, C.; Koch, W.; Zollinger, H. *Helv. Chim. Acta* **1963,** *46,* 1184–1190.

(14) Using the $\sigma_{I,R}$ values given above for deuterium, $\rho_I = 0.997$, and $\rho_R = 1.003$[7] eq 1 yields a log K_H/K_D value of –0.0024, comparing well with one-fifth of the experimental value for C$_6$D$_5$COOH of –0.002.[12] For anilinium ions we used $\rho_I = 3.088$ and $\rho_R = 3.476$,[7] giving a log K_H/K_D ratio of –0.0075 which may be compared with one-fifth of the experimental value of –0.0046[13] for C$_6$D$_5$NH$_2$.

(15) If one allows for an additional offset in eq 1,[8,9] the estimated resonance contribution[11] amounts to 33% with $\sigma_{I,D} = -0.0016$, $\sigma_{R,D} = -0.0009$, a standard deviation of 2.3 ppb, and a correlation coefficient of 0.947.

(16) Ewing, D. F.; Toyne, K. J. *J. Chem. Soc., Perkin Trans. 2* **1979,** 243–248. Adcock, W.; Khar, T. C. *J. Am. Chem. Soc.* **1978,** *100,* 7799–7810.

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One referee has argued that deuterium as an ordinary polar substituent should cause isotope effects at the carbon atoms para to the deuterium substitution in biphenyl[6] and benzene.[20] The correlation presented here is solely based on carbon atoms outside the deuterated benzene ring, to exclude all possible vibrational effects which are unlikely effective over more than four bonds, whereas the situation within the deuterated benzene ring is more complex.

Nevertheless the substituent constants derived here for the deuteron describe the chemical behavior of isotopically-labeled molecules[21] pointing to the fact that long-range interaction of a substituent or of the deuterium isotope with a given reaction center is based on the same principles.

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(20) Günther, H.; Seel, H.; Günther, M. E. *Org. Magn. Reson.* **1978,** *11,* 97–102.

(21) One referee argued against the use of $\rho_{I,R}$ values derived from para-substituted benzoic acids and anilinium ions in the comparison with pK_a measurements in C$_6$D$_5$COOH and C$_6$D$_5$NH$_2$ since deuterium at the ortho and meta positions would have different effects. However, as given in ref 7, only the $\rho_{I,R}$ values of the ortho series are significantly deviating due to steric interaction between the substituent and the reaction center. Since the steric influence of the deuterium atom is minor we feel that our approach is acceptable for the order of magnitude comparison as given above.

The Role of Lithium Salts in Controlling the Regiochemistry of the Alkylation of a Lithium Enolate in a Weakly Polar Aprotic Solvent

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The enolate salt lithioisobutyrophenone (LiE) in dioxolane exists predominately as a cubic tetramer.[1] We now show that, although methylation by methyl *p*-toluenesulfonate (CH$_3$OTs) initially involves this species and the corresponding dimer, the production of LiOTs during the reaction gives rise to mixed aggregates, the reactions of which largely control the product orientation (C/O; C- vs. O-methylation) of the *overall* reaction.

Figure 1 shows that C/O falls sharply in the first 10% of the reaction. This is evidently due to LiOTs produced during the reaction since initially added LiClO$_4$ similarly affects C/O. The limiting value (0.79) of C/O reached at [LiClO$_4$] $\sim$ 0.3 M must be characteristic of a new reactant species. The initial rates of both C- and O-methylation, however, continue to increase with increasing [LiClO$_4$] (Table I, runs 8, 9) due to either increasing concentrations of this new species, electrophilic catalysis by Li$^+$, or both. That electrophilic catalysis can occur is clearly demonstrated by the dramatic effect of lithium tetraphenylborate on the initial rates of methylation (runs 10, 11).

The new reactant species is not a free or solvent-separated ion pair. This can be seen from the effects of Bu$_4$N$^+$OTs$^-$ and Bu$_4$N$^+$ClO$_4^-$ on initial rates (runs 12–17). The anions of these salts evidently compete (OTs$^-$ $\gg$ ClO$_4^-$) with E$^-$ for Li$^+$ in the aggregate and the reaction of the "free" E$^-$ is characterized by a very low C/O (run 12). These experiments indicate the probability that LiOTs and LiClO$_4$, like LiCl,[1] can form mixed aggregates with LiE.

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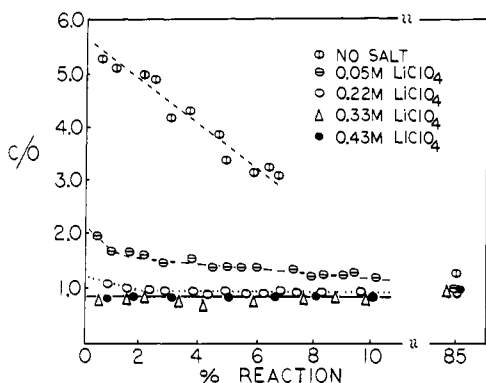
Figure 1. C/O for methylation of lithioisobutyrophenone (0.2 M) by methyl p-toluenesulfonate (0.24 M) in dioxolane at 30 °C.

Table I. Initial Rates (mol L^{-1} s^{-1}) for C- and O-Methylation of Lithioisobutyrophenone (0.2 M) by Methyl p-Toluenesulfonate (0.24 M) in Dioxolane at 30 °C

run	salt	[salt]	10^{6}d[C]/dt^a	10^{6}d[O]/dt^b	C/O^a
1			1.48 ± 0.09	0.26 ± 0.02	5.69 ± 0.15
2	LiClO$_4$	0.005	1.14 ± 0.03	0.24 ± 0.03	4.67 ± 0.08
3	LiClO$_4$	0.027	1.12 ± 0.07	0.53 ± 0.08	2.10 ± 0.03
4	LiClO$_4$	0.05	1.07 ± 0.04	0.57 ± 0.03	1.88 ± 0.05
5	LiClO$_4$	0.081	1.32 ± 0.05	1.04 ± 0.09	1.27 ± 0.03
6	LiClO$_4$	0.11	1.52 ± 0.07	1.54 ± 0.08	0.99 ± 0.02
7	LiClO$_4$	0.22	2.17 ± 0.09	2.11 ± 0.11	1.03 ± 0.03
8	LiClO$_4$	0.33	2.82 ± 0.19	3.92 ± 0.31	0.72 ± 0.03
9	LiClO$_4$	0.43	4.46 ± 0.37	5.72 ± 0.56	0.78 ± 0.04
10	LiBPh$_4$	0.007	2.99 ± 0.16	1.85 ± 0.17	1.62 ± 0.17
11	LiBPh$_4$	0.10	c	c	1.42^d
12	Bu$_4$NOTs	0.10	c	c	0.26^d
13	Bu$_4$NOTs	0.20	c	c	0.42^e
14	Bu$_4$NClO$_4$	0.10	1.54 ± 0.08	0.39 ± 0.02	3.97 ± 0.02
15	Bu$_4$NClO$_4$	0.20	1.81 ± 0.12	0.82 ± 0.06	2.21 ± 0.09
16	Bu$_4$NClO$_4$	0.50	1.83 ± 0.06	1.63 ± 0.06	1.12 ± 0.02
17	Bu$_4$NClO$_4$	0.75	2.86 ± 0.04	2.55 ± 0.6	1.12 ± 0.02

^{a} Calculated by fitting data for the first 10% of the reaction to a second-order polynomial. ^{b} Calculated from d[C]/dt and C/O. ^{c} Too fast to measure. ^{d} Value at 8% reaction. ^{e} Value at 60% reaction.

Table II. Initial Rates (mol L^{-1} s^{-1}) for C- and O-Methylation of Lithioisobutyrophenone by Methyl p-Toluenesulfonate (0.4 M) in Dioxolane at 30 °C

[LiE]	10^{6}d[C]/dt^a	10^{6}d[O]/dt	C/O^a
0.05	1.10 ± 0.04	0.31 ± 0.01	3.52 ± 0.05
0.10	1.40 ± 0.11	0.26 ± 0.02	5.49 ± 0.05
0.20	2.19 ± 0.16	0.37 ± 0.03	5.89 ± 0.26
0.40	2.51 ± 0.31	0.35 ± 0.04	7.16 ± 0.09

^{a} See footnotes a and b for Table I.

The data in Table II can be interpreted in terms of Li$_4$E$_4$ ⇌ 2Li$_2$E$_2$. Although the tetramer is the major species (at 0.5 M^1), the dimer is expected to be substantially more reactive.^{2} Runs 1–6 in Table I also show a manifestation of this equilibrium. Low concentrations of LiClO$_4$ actually retard C-methylation presumably by converting the dimer to Li$_4$E$_3$ClO$_4$, analogous to the reported interaction of Li$_2$E$_2$ with LiCl in dimethoxyethane.^{1} We postulate that this mixed aggregate is the new reactant species and that it undergoes C-methylation less rapidly than the dimer. At higher [LiClO$_4$] electrophilic catalysis prevails.

Evidence for the formation of species of the type Li$_4$E$_{4-n}$(ClO$_4$)$_n$ is provided by NMR studies of lithium 3,5-dimethylphenolate, which is also known^3 to be tetrameric in dioxolane. The addition of such solutions to solutions of LiClO$_4$ results in substantial increases in the line width of both ^{7}Li and ^{35}Cl while leaving unchanged the ipso and para ^{13}C chemical shifts which are highly characteristic of the state of aggregation^3 (see Table III). These observations are thus consistent with the formation of mixed

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Table III. Line Widths at Half-Height ($\Delta\nu$) for ^{7}Li and ^{35}Cl, C(4) Spin Lattice Relaxation Times, and C(1) and C(4) ^{13}C Chemical Shifts (δ) for Mixtures of Lithium 3,5-Dimethylphenolate and LiClO$_4$ in Dioxolane at 28 °C

[LiDMP], M	[LiClO$_4$], M	^{7}Li $\Delta\nu$, Hz	^{35}Cl $\Delta\nu$, Hz	C(4) T_1, s	$\delta_{C(1)}$, ppm	$\delta_{C(4)}$, ppm
0.2		1.3		0.41	167.5	117.2
0.2	0.4	5.5	130	0.46	167.4	117.5
0.4	0.4	5.5	165	0.46		
	0.4	0.9	63			

aggregates in which the local environment of the phenolate oxygen atom is the same as in the pure tetramer.

At this stage it is not possible to exclude the intervention of mixed tetramers with n > 1 nor is it yet clear why mixed species should undergo O-methylation more readily than the pure tetramer. Possibly the mixed aggregates can more readily open at one edge or face without actually dissociating, thereby exposing the enolate oxygen to attack by the electrophile.

Are Carbenium Ions Stabilized or Destabilized by α-Silyl Substitution? The Solvolysis of 2-(Trimethylsilyl)-2-adamantyl p-Nitrobenzoate

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There is considerable current interest in silicon chemistry.^{1} Surprisingly, the effect of silicon substitution on the stability of carbenium ions remains virtually unknown and poorly understood,^{1} in contrast to the plethora of analogous data for alkyl substitution.^{2} Such data are mechanistically interesting and important practically, because carbenium ions substituted by silyl groups at the α or β positions are believed to be intermediates when organosilicon reagents are used in synthesis.^{1} The biomimetic-type cyclization that yields D-homosteroids is one example.^{3} β-Silyl substituents stabilize carbenium ions, but this effect has yet to be quantitatively elucidated.^{1,4} The effect of α-silyl substitution is even qualitatively unclear.^{5} Older studies suggest, largely by implication, that α-silyl substituents destabilize carbenium ions even as compared to hydrogen.^{5a} Recently, Stang, Schiavelli, Apeloig, et al. failed to measure the α-effect directly because (CH$_3$)$_3$SiCH$_2$X (1, X = OSO$_2$C$_6$H$_4$CH$_3$-p) solvolyses by an S$_N$2 mechanism, so that carbenium ions are not formed.^{6} Similar studies of α-silyl vinyl cations were also inconclusive.^{7} We report here that tertiary esters

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