

The observation that k_a for enone **4** is greater than that for the monocyclic enones (Table I) is consistent with the earlier proposal¹⁷ that the energy of the reactive π, π^* triplet of these enones decreases as the ability of the triplet to relax by twisting about the C₂-C₃ bond increases. Furthermore, the low-energy (E_T ca. 50 kcal/mol) long-lived (ca. 10 μ s) triplet state of steroidal dienone **7** is not quenched by DABCO, since electron transfer in this case would be highly endothermic.¹⁸

We conclude from this study that amines react with relaxed enone π, π^* triplet states by the transfer of an electron and formation of solvated enone radical anions and amine radical cations. In the case of DABCO, the exclusive fate of the radical ion pair appears to be decay to the ground state since no enone-DABCO adducts have as yet been detected, although enone-amine adducts and reduced enone are formed when other tertiary amines are utilized.^{19,20}

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Spectroscopic Determination of σ_I and σ_R Substituent Constants for the Deuterium Atom

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Deuterium-induced differences $\Delta\delta$ in the chemical shifts of carbon atoms of isotopomeric molecules have been investigated by ¹³C NMR spectroscopy for a number of reasons.^{1,2} As a consequence of the Born-Oppenheimer approximation their origin should always be attributed to the difference in vibrational motion of the two isotopes. Yet, the interpretation of the observed isotope-induced shifts is often given in terms of electronic substituent effects. Thus, for example, shifts to lower field of carbon atoms in ortho and para position in side-chain deuterated alkyl derivatives of benzenes³ as well as the dependence of the shifts of both ortho positions of several trideuteriomethylated aromatic systems on π -bond order⁴ have been taken as a manifestation of isotopic perturbation of hyperconjugation. In extension of our earlier work⁵ we have recently discussed isotope-induced π -polarization to account for the experimental results in a series of deuterated derivatives of biphenyl.⁶

The behavior of the carbon atoms in the unsaturated side chain of the styrene derivatives **1a**, **2a**, and **3a** (X = D), which constitutes

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Table I. Long-Range Deuterium Isotope Effects $\Delta\delta$ on ¹³C Chemical Shifts^a and Substituent Susceptibilities $\rho_{I,R}$ from DSP Analysis^b

compd		C-5	C-6	C-7	C-8	C-9	ref
	$\Delta\delta$	-8	12				
	ρ_{I}^i	-2.39	4.97				10
	ρ_{R}^i	-0.36	8.99				
	$\Delta\delta$	-8	9				
	ρ_{I}^i	-1.83	4.03				10
	ρ_{R}^i	0.15	6.97				
	$\Delta\delta$	-9	0				
	ρ_{I}^i	-1.99	1.91				10
	ρ_{R}^i	-0.36	0.99				
	$\Delta\delta$	-6	0	0	0		
	ρ_{I}^i	-5.3	-0.73	0.26	1.15		16
	ρ_{R}^i	1.23	0.21	0.17	0.12		
	$\Delta\delta$	-10	0	0	4		
	ρ_{I}^i	-3.17	0.41	0.49	2.00		17
	ρ_{R}^i	-1.14	1.11	0.26	2.09		
	$\Delta\delta$	-5	-4			0	
	ρ_{I}^i	-2.31	-1.63			1.35	18
	ρ_{R}^i	0.52	-1.83			1.28	
	$\Delta\delta$	-8	15				
	ρ_{I}^i	-2.9	5.1				19
	ρ_{R}^i	-1.8	6.1				

^a Data given in ppb, spectra recorded at 100.6 MHz on a Bruker WH-400 spectrometer in acetone-*d*₆ solutions. All solutions contained unequal amounts of deuterated and parent compounds, errors amount to 0.75 ppb. The sign of the isotope effects follows the convention given by Hansen² and is, unfortunately, opposite to the convention used for substituent effects ($\text{SCS}^i = \delta_{RX}^i - \delta_{RH}^i$ and $\Delta\delta = \delta_{RH}^i - \delta_{RD}^i$).

a definitive experimental test of our proposal, is reported here along with an attempt to correlate a number of long-range deuterium isotope effects with data from studies of common substituent effects.

The para-substituent-induced chemical shift (SCS) of the carbon atoms of the vinyl sidechain in **1-3** has been analyzed by the DSP method⁷⁻⁹ by Reynolds and co-workers.¹⁰ The effect of substituents X on the chemical shifts of the vinyl carbon atoms is given by eq 1. The parameters ρ_I^i and ρ_R^i measure the sus-

$$\text{SCS}^i = \rho_I^i \sigma_{I,X} + \rho_R^i \sigma_{R,X} \quad (1)$$

ceptibility of the *i*th carbon atom on the polar ($\sigma_{I,X}$) and mesomeric ($\sigma_{R,X}$) nature of the substituent X. ρ_I^i and ρ_R^i values obtained from statistical analysis are included in Table I for compounds **1-7**. All C-6 atoms of **1-3** show a pronounced susceptibility to the mesomeric influence of substituents X. As the conjugation between the phenyl ring and the vinyl group is diminished by steric

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interaction (2 and 3), the susceptibilities ρ_R^6 are drastically reduced. ρ_I^5 and ρ_R^5 reproduce largely the inductive effects of the substituent X.

If the deuterium 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 deuterium 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 ¹³C chemical shifts calls for an inverse DSP correlation between the isotope-induced shifts $^n\Delta\delta_{C(D)}$ and the ρ_I^i and ρ_R^i parameters in order to deduce the substituent constants $\sigma_{I,D}$ and $\sigma_{R,D}$ for the deuterium spectroscopically. However, such a quantitative statistical analysis faces major obstacles. First, there exists an appreciable difference in the degree of accuracy of the ρ_I^i and ρ_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 deuterium 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 Lupton¹¹ 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

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(14) Using the $\sigma_{I,R}$ values given above for deuterium, $\rho_I = 0.997$, and $\rho_R = 1.0037$ eq 1 yields a $\log K_H/K_D$ value of -0.0024 , comparing well with one-fifth of the experimental value for C_6D_5COOH of -0.002 .¹² For anilinium ions we used $\rho_I = 3.088$ and $\rho_R = 3.476$, 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 $C_6D_5NH_2$.

(15) If one allows for an additional offset in eq 1,^{8,9} the estimated resonance contribution¹¹ 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.

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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 biphenyl⁶ 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 deuterium describe the chemical behavior of isotopically-labeled molecules²¹ 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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(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_6D_5COOH and $C_6D_5NH_2$ 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_3OTs) 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 $Bu_4N^+OTs^-$ and $Bu_4N^+ClO_4^-$ 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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