part responsible for the net decrease in the magnitudes of most of the vinylic couplings observed between the dienes and the diene complexes (Table I).

The J values obtained for the iron complexes do allow meaningful discussion of the relative orientation of the vinyl C and H atoms, but only after several competing coupling mechanisms have been unraveled. It can be assumed that the effect of (a) above will be very large for the three-bond J's and minimal for the four- and five-bond J's.[14] The results of several semiempirical calculations of the relative σ and π contributions to vinylic coupling have been published.[15] There is reasonable agreement among these calculations and in conjunction with experimental data the following relationships have been identified: (i) σ and π contributions to long range J's and σ contributions to vicinal J's are sensitive to H–H orientation;[14,15f] (ii) ^3J is σ dominant with π coupling estimated to contribute *ca.* 8–14% for cis coupling;[15a,e,g] (iii) there is disagreement regarding the relative σ and π contributions to ^4J;[16] however, the π component of ^4J appears to be minimal for H–H atoms trans-coplanar ("W" arrangement) and it becomes dominant as coplanarity between H atoms is lost;[12b,15d–f] and (iv) the π contribution to ^5J is also sensitive to relative H–H orientation. In a cisoid diene ^5J is predominantly π in character, as opposed to the trans–trans ^5J in a transoid diene which has nearly equivalent π and σ character.[12b,15d–f] Information of the relative signs of the σ and π vinylic couplings is also important; both theory and experiment indicate that for a cisoid diene $^2J_\sigma$, $^3J_\sigma$, $^3J_\pi$, and $^5J_\pi$ are plus in sign while $^2J_\pi$, $^4J_\pi$ are minus and both $^4J_\sigma$ and $^5J_\sigma$ may vary in sign as a function of H–H orientation.

Attachment of $Fe(CO)_3$ to dienes **1**, **3**, and **4** results in a decrease in magnitude of the vicinal J's by ~30–40% (^3J's of **1** and **3** adjusted to reflect a planar conformation). The X-ray of **7** shows a stretching of the sp^2–sp^2 double bond for $\mathbf{4} \rightarrow \mathbf{7}$ of *ca.* 0.11 Å,[13] which according to Karplus would decrease $J_{1,2}$ by ~32%.[14] Assuming for complexes **5**–**7** that the π contribution to $J_{1,2}$ approaches 0, a maximum diminution of $J_{1,2} \approx 46\%$ can be estimated for conversion of a diene to a diene–$Fe(CO)_3$ complex in which the H_1–H_2 dihedral angle is held constant at 0°. Significant torsion about the C_1–C_2 bond in the complexes would further decrease J_{12}. Thus it would appear that the observed trends in the ^3J couplings (Table I) roughly favor a diene–Fe(CO)$_3$ complex structure wherein H_1 and H_2 are coplanar.

More substantial evidence in support of this conclusion is obtainable from inspection of the four-bond J's in the table. There is essentially no variation in $^4J_{1,3}$ between the planar olefin models as compared to the corresponding iron complexes: $^4J_{1,3}(\mathbf{2}) = 1.0$ *vs.* $^4J_{1,3}(\mathbf{5}) = 1.4$ Hz; $^4J_{1,3}(\mathbf{3})$ (cor) $= 1.1$ *vs.* $^4J_{1,3}(\mathbf{6}) = 1.2$ and $^4J_{1,3}(\mathbf{7}) = 1.1$. The close similarity of the $^4J_{1,3}$ couplings among these five compounds is in accord with the notion that a four-bond J between H atoms in a planar "W" orientation is primarily σ in character (iii above). By analogy to the angular dependency of ^4J noted by Manatt, *et al.*[7] (for couplings of type $^4J_{1,3}$ in **1**), as well as by Barfield and Garbisch (four-bond allylic J's)[12a,17] one can estimate that for the diene iron complexes the value of $^4J_{1,3}$ will approach 0 Hz at an H_1–H_3 twist angle of ~30°. Finally, the behavior of ^5J and ^2J upon diene complexation to $Fe(CO)_3$, decrease in $^5J_{1,4}$ by ~80% and increase in $^2J_{1,1'}$ by ~50%, are indicative of an extensive loss of π contribution to J_{net} upon complex formation.

Based upon the above considerations we feel that the best structural description of a diene–$Fe(CO)_3$ complex is provided by structure A in which all the C and H atoms are coplanar. In addition these π complexes seem to provide an excellent empirical test of pmr coupling theory.[18]

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(15) (a) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960), **50**, 3133 (1969); (b) M. Barfield and J. J. Reed, *ibid.*, **51**, 3039 (1969); (c) M. Barfield, *ibid.*, **48**, 4463 (1968); (d) M. Barfield and B. Chakrabarti, *J. Amer. Chem. Soc.*, **91**, 4346 (1969); (e) A. V. Cunliffe, R. Grintner, and R. K. Harris, *J. Magn. Resonance*, **3**, 299 (1970); (f) M. Bacon and G. E. Maciel, *Mol. Phys.*, **21**, 257 (1971); (g) W. J. Van Der Hart, *ibid.*, **20**, 399 (1971).

(16) See discussion in ref 7 *vs.* ref 15e,f.

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Phillip Crews
Division of Natural Sciences
University of California, Santa Cruz
Santa Cruz, California 95060

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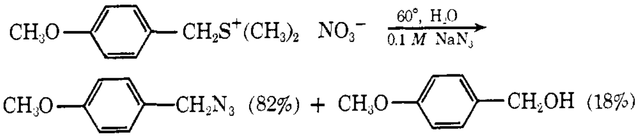
Evidence for a Unifying Mechanism of Nucleophilic Substitution into Sulfonium Ions[1]

Sir:

We wish to report that borderline behavior has now been observed in the competitive substitutions by solvent water and added nucleophile into benzyldimethylsulfonium ion (I^-, 140°, H_2O) and into *p*-methoxybenzyldimethylsulfonium ion (N_3^-, 60°, H_2O). Thus, for example, in the presence of 0.1 *M* NaN_3, an aqueous solution of *p*-methoxybenzyldimethylsulfonium nitrate (0.0066 *M*) at 60° furnishes 82% *p*-methoxybenzyl azide and 18% *p*-methoxybenzyl alcohol at a rate 1.82 times that observed in the absence of azide ion (Table I). It can readily be shown[2] that an SN2 model would predict a rate enhancement of a factor of (82/18) + 1 = 5.55 and that an SN1 model would predict a factor of 1.00.[3]



While kinetic behavior is obviously borderline, the ratio of products, $[ArCH_2N_3]/[ArCH_2OH]$, is a linear function of azide ion concentration from $[N_3^-] = 0.03$ to 0.12 *M*, with slope $m = 48.0 \pm 1.0$ (Table I).

These data are of course reminiscent of those which led us to propose[2] the ion-pair mechanism for substitution into alkyl halides and sulfonates and an analogous scheme, in which an ion-dipole assemblage, [ArC$^+$-

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(1) Supported in part by the National Science Foundation.

(2) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362, 6041 (1969).

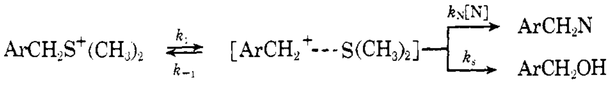
(3) Pertinent entries of Table I establish that salt effects are minimal at these concentrations and that solvolysis rates are independent of the concentration of sulfonium salt and of the nature of the nonnucleophilic anion. Rates and products were determined by titrating liberated acid as a function of time. The stoichiometry of acid production permits an evaluation of product distribution as alkyl azide formation is not accompanied by the liberation of acid.

Table I. Rate Constants and Product Distributions of Reactions of Sulfonium Salts with Solvent and Added Nucleophiles in Water

Substrate		$M \times 10^3$	Added salt, M	Temp, °C	10^4k, sec^{-1}	% RN	10^4k_{calcd}, sec^{-1}
p-$CH_3OC_6H_4CH_2S^+(CH_3)_2$	ClO_4^-	7.83		60	1.78 ± 0.01		
	NO_3^-	6.60	$KClO_4$, 0.10	60	1.80 ± 0.01		
	NO_3^-	15.0		60	1.79 ± 0.03		
	NO_3^-	15.2	NaN_3, 0.030	60		51.5	
	NO_3^-	15.2	NaN_3, 0.060	60		71.3	
	NO_3^-	11.0	NaN_3, 0.070	60	2.64 ± 0.17	76.5	3.06^b
	NO_3^-	15.2	NaN_3, 0.090	60		79.6	
	NO_3^-	6.60	NaN_3, 0.100	60	3.25 ± 0.30	82	3.23^b
	NO_3^-	15.2	NaN_3, 0.120	60		84.7	
	NO_3^-	11.0	NaN_3, 0.120	60	3,50 ± 0.23	84.4	3.30^b
$C_6H_5CH_2S^+(CH_3)_2$	ClO_4^-	7.82		150	3.36 ± 0.02		
	ClO_4^-	7.50		140	1.35 ± 0.01		
	NO_3^-	15.0		140	1.37 ± 0.03		
	ClO_4^-	15.0		140	1.35 ± 0.01		
	Br^-	7.50		140	2.25 ± 0.01		
	I^-	7.50		140	6.42 ± 0.07		6.09^c
	NO_3^-	7.50	I^-, 0.0075	140	6.31 ± 0.19		6.09^c
	I^-	7.50		140	6.43 ± 0.19		6.09^c
	I^-	7.50	I^-, 0.0072	140	8.95 ± 0.10		8.96^c
	I^-	15.0	I^-, 0.015	140	11.59 ± 0.11		12.3^c
	I^-	15.0	I^-, 0.015	140	13.0 ± 0.5		12.3^c
	I^-	15.0	I^-, 0.060	140	17.3 ± 0.8		16.2^c
	ClO_4^-			60	0.000135^a		
$(CH_3)_3CS^+(CH_3)_2$	ClO_4^-	7.5		75	2.32 ± 0.01		
	I^-	7.5		75	2.35 ± 0.01		
	N_3^-	7.5		75	2.35 ± 0.01	0	

[a] Extrapolated from data at higher temperatures. [b] Calculated assuming ion-dipole mechanism with $m = 48.0$ and $x = 1.19$. [c] Calculated assuming ion-dipole mechanism with $m = 655$ and $x = 14.3$.

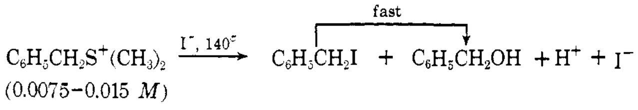
$H_2 \cdots S(CH_3)_2]$, replaces the ion pair is suggested for these reactions of sulfonium salts. For this scheme, one



$$ArCH_2S^+(CH_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ArCH_2{}^+\cdots S(CH_3)_2] \begin{cases} \xrightarrow{k_N[N]} ArCH_2N \\ \xrightarrow{k_s} ArCH_2OH \end{cases}$$

derives the relationship[2] $k_{\text{exptl}}/k_{\text{NS}} = (x + 1)(1 + m[\text{N}])/(x + 1 + m[\text{N}])$, (NS = no salt), where, for Ar = p-methoxyphenyl and $[N_3^-] = 0.10$ at 60° in water, $k_{\text{exptl}}/k_{\text{NS}} = 3.25/1.78 = 1.82$ and $m = k_N/k_s = 48.0$ (from product data); whence $x = k_{-1}/k_s = 1.19$ and $k_1 = 3.90 \times 10^{-4}$ sec^{-1} (see Table I).

While the available data obtained utilizing the p-methoxybenzyl substrate can also be rationalized, albeit with difficulty, in terms of a competitive SN1–SN2 scheme, the kinetic facts which emerge from our study of the competitive reactions of water and iodide ion with benzyldimethylsulfonium ion (140°) cannot. Under these conditions, the initial product of iodide attack, benzyl iodide, is solvolyzed almost instantaneously to solvolysis product.[4] Further, since HI is a strong acid in water, the concentration of iodide ion



$$\underset{(0.0075\text{–}0.015\ M)}{C_6H_5CH_2S^+(CH_3)_2} \xrightarrow{I^-,\ 140^\circ} C_6H_5CH_2I \overset{\text{fast}}{\longrightarrow} C_6H_5CH_2OH + H^+ + I^-$$

remains constant throughout a run. Of particular significance among the data is the observation that the (pseudo-first-order) rate of reaction is less than first order in added iodide ion. Thus, while the first 0.0075 M increment of iodide ion effects a rate enhancement of *ca.* 5×10^{-4} sec^{-1}, it requires approximately three additional increments of 0.0075 M iodide to enhance the rate an additional 5×10^{-4} sec^{-1}. It will be realized that a competitive SN1–SN2 mechanism predicts a linear increase in the rate constant with iodide concentration. The ion-dipole mechanism, with $m = k_N/k_s = 655$ and $x = k_{-1}/k_s = 14.3$, achieves an excellent correlation of the data (see Table I).

The nature of the ion-dipole assemblage is worthy of some consideration. We envisage it as a close analog of an ion pair, the dimethyl sulfide molecule interacting strongly with the carbonium ion center, $R^+ \cdots S(CH_3)_2$. Both because of its high nucleophilicity (relative to water) as well as because of its probably preferred orientation for return to sulfonium ion (microscopic reversibility), collapse should occur fairly readily. With increasingly stable carbonium ion centers (as, for example, p-methoxybenzyl), diffusion of the dimethyl sulfide into the bulk of the solvent should begin to compete more effectively with collapse, resulting in a decreasing value of $k_{-1}/k_s = x$, as is observed experimentally.

Richard A. Sneen,* G. Robert Felt, William C. Dickason
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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Ultraviolet-Visible Spectroscopic Evidence for Hydrogen-Bonded Alkali Carbanions in Protic Media

Sir:

Considerable information has become available in the last few years on the structure of alkali and alkaline earth carbanions and radical anions in aprotic media.[1] Much less is known in any detailed way about the solvation of these type ions and ion pairs in protic media. Extensive work on the stereochemistry of a variety of

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