that the fraction of dehydration occurring *via* seven-membered transition states is 28% in III and 38% in IV (Table II). The fact that these numbers are not identical must be attributed at least in part to the intervention of significant isotope effects.

Table II. Distribution of Water Elimination Processes

Compd	7-Center process, %	6-Center (or less) process, %
III	28 (−HDO)	19 (−HDO):53 (−H_2O)
IV	38 (−HDO)	15 (−H_2O):47 (−HDO)

Interestingly, less 1,5-hydrogen (deuterium) abstraction from C-22 was detected in the elimination of acetic acid from the corresponding acetate VI (Table I), accompanied by less H–D scrambling in the formation of *m/e* 315 (316) ions. This finding can be rationalized in the light of the known propensity of *n*-alkyl acetates to expel the elements of acetic acid by way of 1,2 (55%) and 1,3 (45%) H abstraction.[1] Structural features in II (that are not present in 1-hexanol,[1] for example) leading to the observed competition between C-22 and (presumably[1]) C-23 H abstraction by the ionized oxygen function in II–VI must include (i) the tertiary *vs.* secondary nature of the hydrogen atoms and (ii) the additional stabilization of the radical site at C-22 in b (Scheme II) by the adjacent tetrahydrofuran ring oxygen.[8] Thus our findings represent a further example of the modification of normal mass spectra by the influence of distant substituents.[11d]

In summary, all of the H–D exchange found in compounds III and IV (25% of *m/e* 315 ions) and a further 28% (III) and 38% (IV) of the dehydration reaction are characterized by the intervention of seven-center transition states. No conclusions can be drawn from our data concerning the possible stepwise *vs.* concerted nature of the seven-center C-22 to C-26 oxygen (1,6) H–D exchange process (arbitrarily depicted as stepwise in Scheme II).

However, the experimentally demonstrated lack of six-center H–D exchange between C-23 and C-26 oxygen (1,5) necessarily precludes the intervention of an intermediate such as b (Scheme II) (but with the radical site at C-23) of lifetime sufficient for C_{26}–O bond rotation and H (D) replacement at C-23 to compete effectively with stepwise loss of H_2O (HDO) by C–O bond cleavage. Thus this intermediate can play no role in the six-center (or less) dehydration reaction in this system, which must then proceed by an essentially concerted mechanism[22] on the mass spectrometer time scale.

For the seven-center dehydration reaction (*i.e.*, H abstraction from C-22) the mechanism could be concerted[22] and/or stepwise.[23]

The results reported here[24] are especially timely, in view of the very recent accounts of evidence against a stepwise McLafferty rearrangement (also a six-center hydrogen rearrangement) in butyric acid (M − C_2H_4),[25] but consistent with a stepwise rearrangement in 1-heptanal (M − C_2H_4).[26,27]

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[22] In this context, a "concerted" mechanism cannot have on its energy surface any intermediate or transition state such as b (Scheme II), where C–O bond rotation and deposition of an H (D) atom on carbon can compete efficiently with loss of H_2O (HDO) from the same species. In addition, both C–O and C–H (D) stretching will occur in the transition state for H_2O (HDO) loss.

[23] In contrast, a "stepwise" mechanism in this case must have on its energy surface at least one intermediate or transition state such as b (Scheme II), where C–O bond rotation and H deposition can compete efficiently with loss of H_2O (HDO) from the same species by C–O bond cleavage alone.

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A New Model for the Neighbor Anisotropy Nuclear Magnetic Resonance Solvent Effect. Nonpolar Solutes in Benzene

Sir:

Recently several attempts have been made[1−3] to find a quantitative understanding for the shielding factor σ_a due to neighboring solvent molecules having a large susceptibility anisotropy $\Delta\chi$ (such as benzene). The model presented here has the advantage of simplicity and apparent accuracy in spite of many gross simplifications. It is assumed (i) that the average "free" radius r_2 of a solvent (or solute) molecule can be obtained by considering the neat liquid close-packed,[4] resulting in

$$\bar{r}_2{}^3 = 0.297V_2 \qquad (1)$$

where V_2 is the molar volume of the neat liquid; (ii) that this average r_2 can be divided into components along the major axes of the molecule, leading for benzene at 30° to eq 2; and (iii) that the *ratio* of the "free" radius

$$\bar{r}_2 = 2.98\ \text{Å} = (r_{2\parallel} + 2r_{2\perp})/3 \qquad (2)$$

components is equal to that of the corresponding "hard" dimensions of the molecule. The latter can be estimated from the graphite interlayer distance (3.4 Å), C–C and C–H bond lengths, and the hydrogen van der Waals radius (1.0 Å), leading to eq 3. Combination of

$$r_{2\parallel}/r_{2\perp} = 1.70/3.15 = 0.54 \qquad (3)$$

eq 2 and 3 gives $r_{2\parallel} = 1.90$ Å and $r_{2\perp} = 3.52$ Å. It is next assumed (iv) that in the interaction between a globular solute and a benzene molecule only the extreme "flat-on" configuration (I) and the "edge-on" configuration (II) have to be taken into account, the latter (II) being twofold degenerate, and (v) that the appropriate

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intermolecular distance for I is given by $r_{\mathrm{I}} = r_1 + r_{2\parallel}$, which is shorter than the distance $r_{\mathrm{II}} = r_1 + r_{2\perp}$ for II. Stephen's formula[5] for the pair anisotropy shielding σ_a applied to the two configurations separately becomes

$$(\sigma_a)_{\mathrm{I}} = -2\Delta\chi/3r_{\mathrm{I}}^3 \qquad (\sigma_a)_{\mathrm{II}} = +\Delta\chi/3r_{\mathrm{II}}^3 \qquad (4)$$

In the *absence of preferred orientation* there will be at any time $Z/3$ solvent molecules in I and $2Z/3$ in II, Z being the coordination number of the first solvent shell which, following Bernstein,[4] can be obtained from $Z = \pi(r_1 + \bar{r}_2)^2/\bar{r}_2^2$. The total anisotropy shielding σ_a will therefore be

$$\sigma_a = \frac{-2\pi\Delta\chi(r_1 + \bar{r}_2)^2}{9\bar{r}_2^2}\left[\left(\frac{1}{r_{\mathrm{I}}}\right)^3 - \left(\frac{1}{r_{\mathrm{II}}}\right)^3\right] \qquad (5)$$

Equation 5 can be simplified by replacing algebraic by geometric means (permissible as long as the various radii are not too different). Substituting $r_1 + \bar{r}_2 \approx 2\sqrt{r_1\bar{r}_2}$, $r_1 + r_{2\parallel} \approx 2\sqrt{r_1 r_{2\parallel}}$, and $r_1 + r_{2\perp} \approx 2\sqrt{r_1 r_{2\perp}}$ then results in

$$\sigma_a = -\pi\Delta\chi(r_{2\parallel}^{-3/2} - r_{2\perp}^{-3/2})/9\bar{r}_2\sqrt{r_1} \qquad (6)$$

The main distinction of eq 6 is that it shows σ_a as a pure product of solvent and solute properties. Equations 5 and 6 were tested on gas-to-infinite dilution-in-benzene shifts, measured on methane, neopentane, tetraethylmethane, cyclohexane, and benzene. The results are given in Table I.

Table I. Proton Gas-to-Liquid Shieldings (ppm) of Nonpolar Solutes in Benzene (at 30°)

Solute	$-\sigma_{\mathrm{exptl}}$	$-\sigma_w$	$\sigma_{\mathrm{exptl}} - \sigma_b - \sigma_w$	σ_a Eq 5	σ_a Eq 6	σ_a Eq 7
CH_4	1.051	0.206	0.422	0.966	1.371	0.452
CEt_4	0.893 (CH_2)	0.105	0.479	1.049	1.383	0.456
	0.963 (CH_3)	0.150	0.454			
CMe_4	0.998	0.212	0.481	1.202	1.456	0.479
C_6H_{12}	0.962	0.186	0.491	1.270	1.488	0.490
C_6H_6	1.001	0.255	0.521	1.366	1.538	0.505

The experimental data were obtained on a Varian A-60A using techniques as described previously.[4] The van der Waals terms σ_w were calculated according to Rummens, *et al.*[4] The bulk susceptibility term σ_b was taken as −1.267 ppm (benzene at 30°), and a value of 9.91×10^{-29} emu was adopted for $\Delta\chi$ of benzene.[6] Table I shows that both eq 5 and 6 predict the correct trend, although the values are too large in both cases. The discrepancies can be taken care of by the introduction of an empirical correction factor (0.408 for eq 5 and 0.329 for eq 6). Recalculation of σ_a then gives a standard deviation $s = \pm 0.033$ ppm (±7%) for eq 5 and $s = \pm 0.017$ ppm (±3%) for eq 6. Although these small variances are probably fortuitous, the results can be termed highly encouraging. Combining the empirical constant of 0.329 with other numerical constants and benzene parameters eq 6 can be rewritten as

$$\sigma_a(\mathrm{ppm}) = +1.08/\sqrt[6]{\bar{V}_1} \qquad (7)$$

where $\bar{V}_1$ is the molar volume of the solute. Values of σ_a according to eq 7 have been given in the last column of Table I. Equation 7 is not only extremely simple and accurate, but shows also the small influence of the size of the solute molecule that has been noted before.[1,3] Of some special interest are the results on tetraethylmethane. Of the observed 0.070 ppm difference in gas-to-liquid shift for the CH_2 and CH_3 groups, 0.045 ppm can be explained in terms of a "site effect" on the van der Waals term.[4] The remaining 0.025 ppm constitutes only 5% of the σ_a shift. This is too low to be realistic and forms in fact the first experimental indication that the site factor for σ_a is unity as predicted before.[3,7]

Extensive further tests of the above model and variations thereof are under way and, together with full details of the present work, will be reported at a later date.

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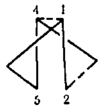
Stereochemical Course of the Thermally Induced Fragmentation of Bicyclo[2.2.0]hexanes to Diallyls. Pyrolysis of the Dimethyl Bicyclo[2.2.0]hexane-2,3-dicarboxylates

Sir:

When orbital symmetry considerations are applied to the thermal fragmentation of four-membered rings, the $(\sigma^2{}_s + \sigma^2{}_a)$ pathway, *i.e.*, A, is seen to be uniquely allowed.[1] This means that if such a process is concerted, a vicinal *cis* relationship of two groups in the cyclobutane must become *trans* in the olefinic product, and *vice versa.* Recent scrutiny of the pyrolytic cleavage of stereochemically labeled alkylcyclobutanes has disclosed that antarafacial motion by at least one of the developing olefinic moieties is not readily achieved.[2] As a result, little stereoselectivity has been observed. In contrast, the thermolysis of β-lactams[3] and β-lactones[4] proceeds with remarkably high stereospecificity *via* least-motion transition states (retention of configuration), thereby attesting to the ease with which the requisite rotational component can be provided by the carbonyl center.

A



B

We have now examined the stereochemistry of the thermal fragmentation of the three isomeric dimethyl

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