Table I. The Principal Values and Their Directions of the Hyperfine and g Tensors in Irradiated Maleic Acid-d_2 (DOOCCHCHCOOD)

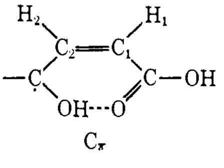
	Principal values, G[a]	Isotropic component	Direction cosines *a*	*b*	*c′*
O_σ	+6.4		+0.733	∓0.676	+0.078
A_H	+3.6	+3.9	+0.639	±0.723	+0.264
	+1.7		−0.234	∓0.144	+0.962
	2.0261		+0.676	±0.737	−0.014
g	2.0061	2.0119	−0.123	±0.131	+0.984
	2.0035		+0.727	∓0.663	+0.179
V_σ	+27.0		+0.573	±0.819	−0.025
$A_{H\alpha}$	+9.6	+13.5	+0.814	∓0.565	+0.133
	+3.9		−0.095	±0.096	+0.991
$A_{H\beta}$	58 ± 2 (nearly isotropic)				
	2.0032		−0.103	±0.120	+0.988
g	2.0026	2.0025	+0.915	∓0.378	+0.141
	2.0018		+0.390	±0.918	−0.071
C_π	−13.0		+0.984	∓0.129	+0.128
A_{H1}	−8.5	−8.2	−0.130	∓0.010	+0.992
	−3.2		+0.126	±0.992	+0.026
	−6.4		+0.807	±0.588	+0.047
A_{H2}	−5.2	−4.5	−0.050	∓0.011	+0.999
	−1.9		−0.588	±0.809	−0.020
	2.0043		−0.475	±0.880	+0.002
g	2.0040	2.0036	+0.877	±0.474	−0.085
	2.0024		+0.075	±0.039	+0.996

[a] The probable signs are determined from the hyperfine anisotropy.

potassium hydrogen maleate irradiated at room temperature.[6]

As for V_σ, it is evident that the anisotropic coupling having the isotropic component of 13.5 G and the nearly isotropic coupling of 58 G correspond to the α proton and the *trans* β proton, respectively, in the vinyl radical, as shown above. The g tensor also exhibits the characteristics of the σ radical of the vinyl type. From the principal directions of the hyperfine and g tensors, it was found that the radical carbon of V_σ is the one to which the -C(=O)—O· group of O_σ is attached. This strongly suggests that V_σ is produced by a loss of CO_2 from O_σ.

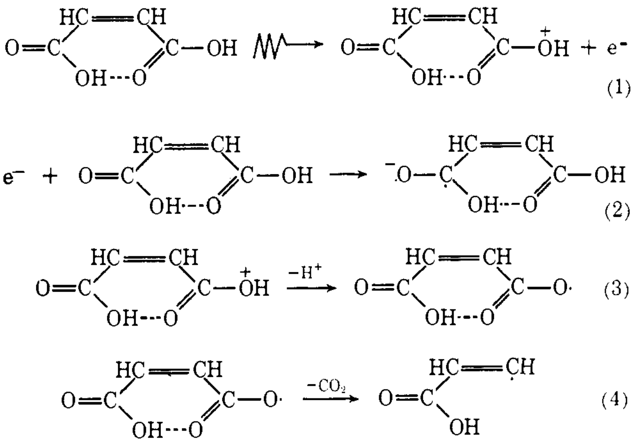
It is also concluded from the hyperfine and g tensors that the anion π radical (C_π) has the structure



C_π

where the unpaired electron is delocalized in the π system. From the hyperfine tensors characteristic of the α proton in π radicals, the spin densities on C_1 and C_2 are estimated to be 0.36 and 0.20, respectively.

From the formation of these radicals, the scheme shown in eq 1-4 may be proposed. In this scheme, O_σ is assumed to be produced from a cation by the ion-molecule reaction through the intermolecular hydrogen bond. Therefore, O_σ is considered to be a counterpart of the anion π radical formed by a capture of an ejected electron. The fact that O_σ is very unstable and converts into V_σ, accompanied by a loss of CO_2, suggests that the radical of type II found in saturated carboxylic acids might also have originated from the cation *via* O_σ-type radicals.



The existence of such an intermediate radical as O_σ has been also found in single crystals of potassium hydrogen maleate and fumarate irradiated at 77°K. Details will be given in subsequent papers.

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(6) (a) M. Iwasaki and K. Itoh, *Bull. Chem. Soc. Jap.*, **37**, 44 (1964); (b) H. C. Heller and T. Cole, *J. Amer. Chem. Soc.*, **84**, 448 (1962).

Structural Effects in Mass Spectrometry. Mechanistic Implications in the Dehydration of 26-Hydroxy-5α-furostan by Six- and Seven-Membered Cyclic Transition States

Sir:

It has been well established by deuterium-labeling studie sthat electron impact induced dehydration of acyclic alcohols ROH, where R = n-C_4H_9 or larger, proceeds preferentially (~90%) by 1,4-hydrogen abstraction *via* a six-membered cyclic transition state, with only approximately 5% each hydrogen abstraction by 1,3 and 1,5 processes.[1-4] The high degree of site specificity observed[1-4] for the hydrogen abstracted suggests that H-D scrambling in the alkyl chains[5] is not contributing significantly at least in 70-eV mass spectra.[1] Recently it has been shown[8,9] that loss of water can occur through much larger cyclic transitions states,[10]

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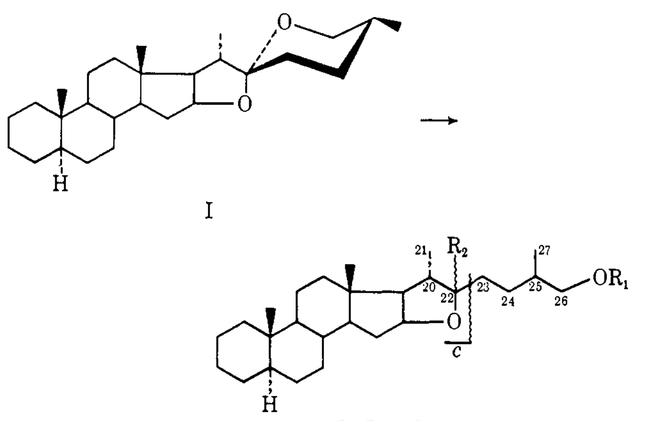
(1) W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 2375 (1964).
(2) S. Meyerson and L. C. Leitch, *ibid.*, **86**, 2555 (1964).
(3) W. H. McFadden, D. R. Black, and J. W. Corse, *J. Phys. Chem.*, **67**, 1517 (1963).
(4) C. G. MacDonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Lett.*, 807 (1963).
(5) H/D scrambling in the alkyl chains of aliphatic ketone molecular ions[6] and isopropyl n-butyl ether M − CH_3 ions[7] has been detected, especially in ions of lower internal energies (*e.g.*, metastable ions) and hence with longer lifetimes.
(6) A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 3582 (1969).
(7) G. A. Smith and D. H. Williams, *ibid.*, **91**, 5254 (1969).
(8) R. Brandt and C. Djerassi, *Helv. Chim. Acta*, **51**, 1750 (1968).
(9) M. M. Green, private communication.
(10) Reports of transfer of hydrogen[11] and other groups[12] *via* larger than six-membered transition states are accumulating.
(11) (a) M. Katoh and C. Djerassi, *Chem. Commun.*, 1385 (1969), and references cited therein: (b) A. N. H. Yeo and D. H. Williams, *Org. Mass Spectrom.*, **2**, 331 (1969); (c) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **88**, 56 (1966); (d) S. Meyerson, I. Puskas, and E. K. Fields, *Chem. Ind.* (London), 1845 (1968), and references cited therein.
(12) (a) R. G. Cooks, *Org. Mass Spectrom.*, **2**, 481 (1969); (b) J. Dieckmann, J. B. Thompson, and C. Djerassi, *J. Org. Chem.*, **33**, 2271 (1968); (c) G. Eglinton, D. H. Hunneman, and A. McCormick, *Org. Mass Spectrom.*, **1**, 593 (1968); (d) W. J. Richter and A. L. Burlingame, *Chem. Commun.*, 1158 (1968); (e) G. H. Draffen, R. N. Stillwell, and J. A. McCloskey, *Org. Mass Spectrom.*, **1**, 669 (1968).

particularly if the radical site resulting from hydrogen (deuterium) abstraction is appropriately stabilized, as exemplified by the documentation[8] of both M − H_2O and M − HDO processes in α-nonyl-α-d_1-α′-(5-hydroxypentyl)tetrahydrofuran.

The recent observation[13] of stereoselectivity[14] obtaining in the elimination of H_2O and HDO from diastereomeric *threo*- and *erythro*-1,2-diphenylethanols-2-d_1 (necessarily a 1,2 process) was taken[13] to indicate at least partial contribution by a concerted reaction mechanism (*i.e.*, C–O and C–H bond stretching in the transition state), or else stepwise with hydrogen radical transfer to ionized oxygen *preceding* C–O bond fission. We report here preliminary results of mechanistic studies on electron impact induced dehydration in another system, where evidence for a concerted elimination *via* a six-membered transition state has been uncovered.

Reduction of 3-deoxytigogenin (I, Scheme I) with $LiAlH_4$-$AlCl_3$ in ether[17] afforded 26-hydroxy-5α-furostan (II)[18] [M ($C_{27}H_{46}O_2$) = 402.3498, found[19] 402.3519; M − 87 (cleavage C, Scheme I, $C_{22}H_{35}O$), 315.2688, found 315.2734; M − 18, *m*/*e* 384, monoacetate V,[19] M = 444; M − 129 (cleavage C), *m*/*e* 315; M − 60, *m*/*e* 384; metastable ion peaks at *m*/*e* 246.8 (402 → 315) and 366.8 (402 → 384) were observed]. Reduction of I with $LiAlD_4$-$AlCl_3$ in ether[17] gave 26-hydroxy-5α-furostan-22-d_1 (III) [M = 403 (>97% isotopic purity)] which exhibited peaks in its mass spectrum at both M − 87 (*m*/*e* 316) and M − 88 (*m*/*e* 315) (cleavage C), as well as at M − H_2O and M − HDO (Table I),[19] the last of which *must involve a seven-center transition state.* Multiple pathways differing energetically and leading to M − 87 (*m*/*e* 316) and M − 88 (*m*/*e* 315) ions did not seem probable, in view of the almost negligible dependence observed of the peak ratio 315/316 on electron energy from 70 to 12 eV (Table I).

Scheme I



II, $R_1 = R_2 = H$
III, $R_1 = H$; $R_2 = D$
IV, $R_1 = D$; $R_2 = H$
V, $R_1 = Ac$; $R_2 = H$
VI, $R_1 = Ac$; $R_2 = D$

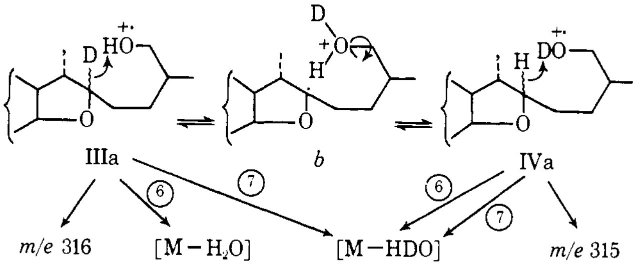
Table I. Peak Shifts due to Isotopic Substitution[a] (70-eV Spectra)

Compd	M *m*/*e*	M %	(M − R_1OD):(M − R_1OH) *m*/*e* 384	(M − R_1OD):(M − R_1OH) *m*/*e* 385	Cleavage C *m*/*e* 315	Cleavage C *m*/*e* 316
II	402	100	100	0	100	
III[b]	403	100	47[d]	53[d]	26[e]	74[e]
IV[c]	403	100	85	15	76	24
V	444	100	100	0	99	1
VI[b]	445	100	15	85	94	6

[a] Corrected for ^{13}C isotopic contributions; each peak group normalized to 100%; reproducibility ±1%. [b] >97% d_1. [c] Corrected to 100% O-d_1. [d] Ratio is 43:57 at 12 eV. [e] Ratio is 29:71 at 12 eV.

At this stage, a reciprocal H–D exchange was suspected (Scheme II), patterned after a similar exchange involving carboxyl and *o*-H atoms in benzoic acid.[20,21] The mass spectrum of 26-hydroxy-5α-furostan-O-d_1 (IV) confirmed this hypothesis by revealing (Table I) precisely reversed *m*/*e* 315/316 ratios compared with III (within experimental error). *This result also strongly implies that reciprocal H–D transfer is operating only between C-22 and the alcohol O atom.* Furthermore, a 1,5-hydrogen (deuterium) abstraction by ionized alcohol oxygen must be involved in all (~25%) of the isotope scrambling observed in the generation of (M − 87) and (M − 88) ions.

Scheme II



If it is assumed that M − 87 (88) and M − 18 (19) ions are produced by competing unimolecular reactions in the molecular ions, then it follows that H–D scrambling can occur in either IIIa or IVa (Scheme II), possibly *via* b, with competing cleavages to give *m*/*e* 316 and 315 ions, respectively, and with competing eliminations of H_2O and HDO. It should be noted that opposite proportions of IIIa and IVa are produced from III and IV upon ionization (75:25 in favor of initial structure) and that M − H_2O ions can only arise from IIIa by a six-membered[1] (or less) transition state, whereas M − HDO ions can come from IVa *via* both six- and seven-membered transition states and from IIIa by a seven-membered transition state (Scheme II). Ignoring isotope effects, it can readily be calculated

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(13) M. E. Munk, C. L. Kulkarni, C. L. Lee, and P. Brown, *Tetrahedron Lett.*, in press.

(14) Earlier pioneering studies of stereoselective elimination processes in aliphatic cyclic alcohols[15] and chlorides[15] and in acyclic chlorides[16] have been reported by Green.

(15) (a) M. M. Green and J. Schwab, *Tetrahedron Lett.*, 2955 (1968); (b) M. M. Green and R. J. Cook, *J. Amer. Chem. Soc.*, **91**, 2129 (1969).

(16) (a) M. M. Green, *ibid.*, **90**, 3872 (1968); (b) M. M. Green, *ibid.*, in press.

(17) G. R. Pettit and W. T. Bowyer, *J. Org. Chem.*, **25**, 84 (1960).

(18) G. R. Pettit, A. H. Albert, and P. Brown, to be published.

(19) Low-resolution mass spectra were taken on a Varian Atlas CH4B instrument, equipped with a molecular beam direct inlet system, under the following conditions: electron energy 70 eV, trap current 19 μA, source temperature 200°, probe temperature 70–75°, accelerating voltage 3 kV. Accurate mass measurements were made on a Varian Atlas SM1B double focussing instrument, using electron energy 70 eV, trap current 290 μA, source temperature 180°, probe temperature 70–75°, accelerating voltage 8 kV.

(20) J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Naturforsch. A*, *20*, 883 (1965).

(21) S. Meyerson and J. L. Corbin, *J. Amer. Chem. Soc.*, 87, 3045 (1965).

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.

[24] A preliminary account of this work has been given: A. H. Albert, 5th Western Regional Meeting, American Chemical Society, Anaheim, Calif., Oct 1969.

[25] R. B. Fairweather and F. W. McLafferty, *Org. Mass Spectrom.*, **2**, 755 (1969).

[26] C. Fenselau, J. L. Young, S. Meyerson, W. R. Landis, E. Selke, and L. C. Leitch, *J. Amer. Chem. Soc.*, **91**, 6847 (1969).

[27] R. J. Liedtke and C. Djerassi, *ibid.*, **91**, 6814 (1969).

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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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[1] J. C. Schug, *J. Phys. Chem.*, **70**, 1816 (1966).

[2] J. Homer, *Tetrahedron*, **23**, 4065 (1967).

[3] J. K. Becconsall, *Mol. Phys.*, **15**, 129 (1968).

[4] F. H. A. Rummens, W. T. Raynes, and H. J. Bernstein, *J. Phys. Chem.*, **72**, 2111 (1968).