mesh). The conversion percent was calculated from appearance of 3-hexene and disappearance of 2-pentene. Heptane was used as an internal standard.

Identification of Metathesis Products. A solution of 100 mg of bpyW(CO)$_4$ or 1.5 g of the corresponding polymer-bound catalyst in 20 mL of chlorobenzene was treated with 0.75 mL of ethylaluminum dichloride under an argon atmosphere and then 4 mL of 2-pentene was added. After 2 h, the reaction mixture was worked up with water, filtered, dried over MgSO$_4$, and then fractionally distilled. Identification of 3-hexene was made by comparing its IR, NMR, and mass spectra with those of the authentic material after fractional distillation (45–68 °C) of the product. Identification of 2-butene was made using a fraction (bp 25–40 °C) which also contained the starting 2-pentene.

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Hydrogen Rearrangements of Gaseous Butanoic Acid Cations

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Abstract: The principal pathways for the decomposition of butanoic acid ions (**1**) involve losses of C$_2$H$_4$ and CH$_3$. Approximately 5% of the C$_2$H$_4$ loss involves the α-CH$_2$ group, consistent with competitive isomerization to a cyclobutanediol intermediate. The loss of γ-CH$_3$ to form protonated acrylic acid occurs through two pathways; in addition to the one involving initial β-H rearrangement, a second path favored for metastable **1** ions proceeds through direct α-H transfer to the carbonyl group. In contrast to the C$_2$H$_4$ loss, this CH$_3$ loss is accompanied by little H/D scrambling, and appears to arise from an *isolated electronic state* of **1**; this could be the π-ionized state, with α-H transfer to the carbonyl oxygen occurring through a suprafacial [1,3] sigmatropic shift. Such metastable **1** ions also appear to form (M − CH$_3$)$^+$ ions through loss of (α-CH$_2$ + β-H). In the decompositions of higher energy **1** ions hydrogen transfers through five- and three-membered ring intermediates are competitive with the six-membered counterpart; this indicates for the classical γ-H rearrangement/olefin loss reaction that it is the β-cleavage step, not the γ-H transfer, whose favorability leads to the characteristically high abundance of such reaction products in mass spectra.

One of the first studies of mass spectral reactions utilizing isotopic labeling was that of butanoic acid by Happ and Stewart.[2a] Carbon-13 substitution showed that the unusual m/e 60 ion (**1**) from this compound had retained the carboxyl carbon; this ion is now understood to be formed by the ubiquitous reaction involving γ-hydrogen rearrangement and β-

cleavage,[2b] **1 → 3** (see Scheme I). Like its photochemical analogue, the Norrish type II rearrangement,[3] this reaction appears to be stepwise in nature; based on decompositions of metastable **1**-*O*-d_1 and **1**-γ-d_3 ions,[4] the exchange of β-, γ-, and O-hydrogen atoms prior to decomposition was postulated, **1 ⇌ 2 ⇌ 1a ⇌ 2a → 3a** and **1 ⇌ 4 ⇌ 1b ⇌ 2b → 3b**. Recent

Scheme I
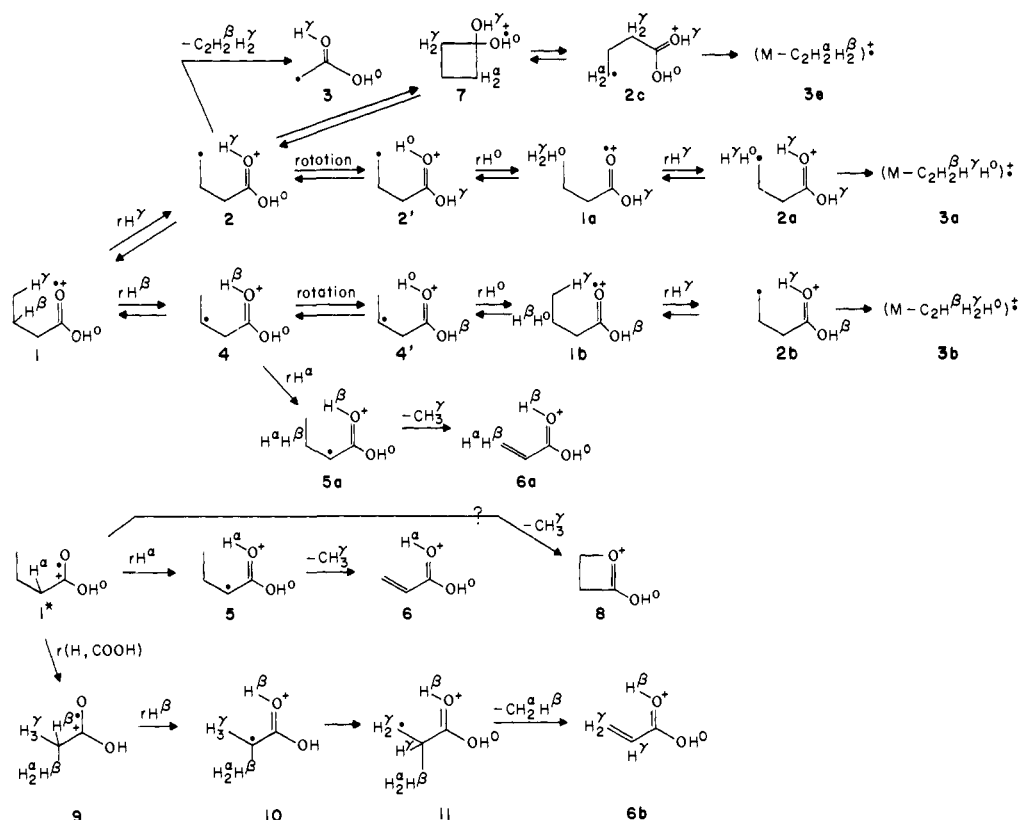
studies[5] showed that another major mass spectral product, protonated acrylic acid (**6**), is formed by initial β-hydrogen rearrangement and γ-cleavage (**1** → **4** → **5a** → **6a**). We report here further data on **1** decompositions, including evidence for rearrangement through a cyclobutanediol intermediate analogous to the well-known photochemical pathway. Another γ-methyl loss process apparently occurs from an isolated electronic state of **1**, which is unusual for an ion of this size.[6] A third CH_3 loss involves the α-CH_2 and a β hydrogen and also appears to originate from this isolated electronic state.

Experimental Section

Most spectra were measured on a Du Pont 21-491 mass spectrometer using 70-eV electrons and a source temperature of 230 °C. The data of Tables II and IV were measured on a reversed-geometry Hitachi RMU-7 double-focusing mass spectrometer having a special collision chamber in the field-free drift region after the magnetic analyzer and before the electrostatic analyzer.[7] Most compounds were obtained commercially or prepared as described earlier.[5] All were purified by gas chromatography. Isotopic purities: *n*-butanoic acid-*2*-[13]*C*, 91% [13]C; *-2,2-d₂*, 97% d_2, 3% d_1; *-3,3-d₂*, 95% d_2, 5% d_1; *-4,4,4-d₃*, 95% d_3, 4% d_2; *-O-d₁*, 87% d_1; *-2,2-d₂-O-d₁*, 85% d_3, 14% d_2; *-3,3-d₂-O-d₁*, 88% d_3, 12% d_2; *-4,4,4-d₃-O-d₁*, 77% d_4, 22% d_3; 2-methylbutanoic acid-*O-d₁*, 87% d_1; and 2,2-dimethylbutanoic acid-*O-d₁*, 90% d_1. 2-Methylpropanoic acid-*2-d₁* (99% d_1) was prepared by the reduction of acetone to 2-propanol-*2-d₁* with $LiAlD_4$, converting that alcohol to the bromide with 49% HBr, making the Grignard reagent of the bromide, and reacting the Grignard with solid CO_2.

Calculations. The origin and extent of hydrogen scrambling preceding ethylene loss was determined assuming the previously postulated[4] pathways for the formation of **3-3d** (Scheme I). Excluding the α-hydrogen atoms, five combinations of H atoms can be involved in the four H atoms lost as C_2H_4: $H_2{}^{\beta}H_2{}^{\gamma}$, $H_2{}^{\beta}H^{\gamma}H^O$, $H^{\beta}H_2{}^{\gamma}H^O$, $H^{\beta}H_3{}^{\gamma}$, and $H_3{}^{\gamma}H^O$. These correspond respectively to ions **3**, **3a**, **3b** (Scheme 1), **3c**, and **3d**. **3c** can be formed by **1a** → $CH_2{}^{\gamma}H^{O}\cdot$ $CH^{\beta}CH_2{}^{\alpha}C(OH^{\beta})OH^{\gamma}$ → $CH_2{}^{\gamma}H^{O}CH^{\beta}H^{\gamma}CH_2{}^{\alpha}COOH^{\beta}$ → $\cdot CH_2{}^{\gamma}CH^{\beta}H^{\gamma}CH_2{}^{\alpha}C(OH^{O})OH^{\beta}$ → **3c**, while **3d** can be formed similarly in six steps from **1b**. The relative contributions of these pathways for $C_2(H, D)_4$ loss can be estimated without correcting for isotope effects by comparing data for the two complementary pairs

of β-, γ-, and O-labeled compounds. For the pair **1-β,β-O-d₃** and **1-γ,γ,γ-d₃**, **3a** will be formed by the loss of C_2HD_3 (5%) and C_2H_3D (16%), respectively (product ion abundances shown in parentheses), while **3** + **3b** are formed by the loss of $C_2H_2D_2$ (44, 51%), and **3c** + **3d** by the loss of C_2H_3D (15%) and C_2HD_3 (6%), respectively. Thus approximately 15% of the C_2H_4 losses are **3a**, 70% **3** + **3b**, and 15% **3c** + **3d**. For the pair **1-β,β-d₂** and **1-γ,γ,γ-O-d₄**, **3** + **3a** will be formed by the loss of $C_2H_2D_2$ (37, 52%), **3b** + **3c** by the loss of C_2H_3D (31%) and C_2HD_3 (16%), respectively, and **3d** by the loss of C_2H_4 (<7%)[8] and C_2D_4 (0.7%), respectively. Thus approximately 64% of the C_2H_4 losses are **3** + **3a**, 33% **3b** + **3c**, and ~3% **3d**. Combining these results gives estimated values for these products of **3**, 49%; **3a**, 15%; **3b**, 21%; **3c**, 13%; and **3d**, 3 ± 2%. The C_2H_4 loss data for **1-O-d₁** are consistent with these figures if the same isotope effect, $k_H/k_D = 1.9$, is assumed for each H migration. The low abundance of **3d** indicates that pathways involving even more rearrangement steps are of minor importance under these conditions. The above calculations were based on the assumption that α-H scrambling is negligible; actually 5% of $C_2(H, D)_4$ lost from **1-α,α-d₂** is C_2H_3D.

Appearance Potentials (AP). The AP (value giving 0.1% of 70 eV abundance) for CH_3 loss [AP(**6**)] was found to be nearly the same as, but slightly *higher* than, that for C_2H_4 loss [AP(**3**)], both for **1** decompositions in the ion source and for metastable **1** decompositions in the second drift region of the RMU-7. Decreasing the ionizing electron energy to the lowest values (~12 eV) giving useful **3** and **6** measurements *decreased* the CH_3 loss relative to the C_2H_4 loss by 10-25% in several measurements for both normal and metastable ions, confirming that AP(**6**) ≥ AP(**3**).

Results and Discussion

γ-Hydrogen Rearrangement with β-Cleavage. The deuterium and C-13 incorporation (Table I) in the **3** ions formed by C_2H_4 loss from metastable **1** ions is generally consistent with the previously postulated mechanism of partial equilibration of the α-, γ-, and O-hydrogen atoms;[4] half of these **1** ions undergo such scrambling before decomposition. Additional pathways such as the 1,2 shifts **2** ⇌ **4** are not important for high-energy ion source reactions of **1**, being negligible in competition not only with the decomposition **2** → **3** but also with the 1,2 shift **4** → **5a** (vide infra); at lower energies reaction **4** → **2** forming a primary radical should be even less favored

Table I. Decompositions of Metastable $C_4(H,D)_8O_2^+$· Ions from Butanoic Acids[a]

ion	$\sum m^*/$ $[Pr]^b$	species lost							
		·CH₃	·CH₂D	·CHD₂	·CD₃	C₂H₄	C₂H₃D	C₂H₂D₂	C₂HD₃
$CH_3CH_2CH_2CO_2H$	0.037	100				51			
$CH_3CH_2CH_2CO_2D$		100	≤1^c			37	15		
$CH_3CH_2CD_2CO_2H$	0.047	100	≤0.5	21		71	4	3	
$CH_3CH_2CD_2CO_2D$	0.038	100	2^c	20	1^c	48	22	4	≤0.5
$CH_3CH_2{}^{13}CH_2CO_2H$		100		8^c(·$^{13}CH_3$)		79	3(C$^{13}CH_4$)		
$CH_3CD_2CH_2CO_2H$	0.026	100	8	4		7	31	37	
$CH_3CD_2CH_2CO_2D$	0.033	100	9^c	4	≤1	≤2	15	44	5
$CD_3CH_2CH_2CO_2H$	0.040	13	<1	<1.5	100	1	16	51	6
$CD_3CH_2CH_2CO_2D^d$	0.038	13	1.5^c	<1	100	1	2	52	16
$CH_3CH_2\dot{C}HC(OH)_2^e$	0.0097	100				1			
$CH_3CH_2\dot{C}HC(OH)OD^e$	0.010	100	<1^c			0.8	0.4		
$(CH_3)_2CHCO_2H$	0.12	100				1.8			
$(CH_3)_2CHCO_2D$	0.10	100	2.0 ± 1.7^c			0.9	0.7		
$(CH_3)_2CDCO_2H$	0.13	100	3.5			0.5	1.2		
$(CH_3)_2\dot{C}C(OH)_2^f$	0.016	100				0.9			
$(CH_3)_2\dot{C}C(OH)OD^f$	0.012	100	≤0.2^c			0.4	0.4		

[a] All intensities were normalized such that the value for the most abundant peak = 100. [b] The sum of the intensities of the peaks representing the metastable decompositions of a precursor ion divided by the intensity of that ion. These values varied sharply with the setting of the ion source repellers. [c] Values to which significant corrections were made as described in ref 29. The relative intensities greater than 10 were reproducible within ±5% between experiments. Corrected values of 1 or less varied as much as ±100%. [d] The value for the loss of C_2D_4 from this ion was 0.7. [e] Obtained from 2-ethylbutanoic acid-d_0 and -O-d_1. [f] Obtained from 2,2-dimethylbutanoic acid-d_0 and -O-d_1.

than **4 → 5a.** The CH_3 losses from metastable **1**-γ,γ,γ-d_3 and **1**-β,β-d_2 ions show little evidence for **2 ⇌ 4**, but it will be shown that most such products are formed from an isolated energy state.

The greater tendency to form **3b** than **3a** (21^9 vs. 15%) is interesting in light of previous assumptions of the overwhelming tendency for six-membered ring rearrangements in such compounds.[2b] For **3b** formation the initial H rearrangement **1 → 4** involves a secondary hydrogen, vs. a primary hydrogen in **1 → 2** for **3a** formation, thus favoring **1 → 4**; however, the higher abundance of **3b** also indicates that the reverse five-membered ring rearrangement **4′ → 1b** is competitive with the six-membered counterpart **2′ → 1a**. Thus it would appear that high tendency for the characteristic mass spectral reaction of unsaturated compounds involving γ-H rearrangement and β-bond cleavage[2b] is *not* due to any unusual steric or energetic favorability of the initial transfer of the hydrogen in the γ position (vs. the β or δ positions),[5] but rather to the favorability of the subsequent β-bond cleavage that this hydrogen rearrangement makes possible.

Cyclobutanediol (7) as a Possible Intermediate. Mass spectral analogies to the photochemical Norrish Type II formation of cyclobutanols from carbonyl compounds[3,10] have been postulated to explain particular olefin elimination data in the mass spectra of sample aldehydes[11] and ketene elimination from 1,3-diketones.[12] The **1**-α,α-d_2 and **1**-α-^{13}C derivatives show (Table I) that 4% of the C_2H_4 loss involves the α-CH_2 group; the pathway **1 ⇌ 2 ⇌ 7 ⇌ 2c → 3e** provides a rationale for these data. The appreciable abundance $(M - C_2H_3D)^+$· from **1**-α,α-d_2 suggests that before C_2H_4 loss the H atoms of **2c** undergo further scrambling of the type involved in the formation of **3a–d**.[13] A large effect of ion internal energy (and thus ion lifetime) would be expected for the relative rate of this rearrangement because of the stringent steric requirements for the attack of the -CH_2· group on the -$C(OH)_2^+$ group.

β-Hydrogen Rearrangement with γ-Cleavage. There appear to be three significant pathways for the formation of $(M - CH_3)^+$; two with substantially different energy requirements involve the loss of the γ-methyl group, while the third involves the loss of the α-methylene with a β hydrogen.

Stepwise rearrangement of a β-H and an α-H followed by γ-CH_3 loss, **1 → 4 → 5a → 6a**, provides a rationale for the abundant (22% of the base m/e 60) peak in the normal mass spectrum of butanoic acid.[5] The data of Table III support this;

for example, HDO and D_2O are the predominant forms of water lost by metastable decomposition of $C_3H_3D_2O_2^+$ and $C_3H_2D_3O_2^+$ ions from **1**-β,β-d_2 and **1**-β,β,O-d_3, respectively. Further, the longer lived $C_3H_3D_2O_2^+$ metastable ions from **1**-β,β-d_2 undergoing decomposition in the second field-free drift region show [-H_2O]:[-HDO] = 11, 12, and 32% when formed with 70, 13, and 11 eV, respectively, ionizing electrons, and 12% with collisional activation (CA)[15] of either 70 or 13 eV $C_3H_3D_2O_2^+$ ions. The product **6** should be stabilized by conjugation, a reason given for its formation in the δ- or ϵ-H rearrangement with γ-cleavage commonly found in aliphatic carbonyl compounds;[16] the mechanism for these reactions is the same as **1 → 4 → 5a → 6a** except for the origin of the first hydrogen atom rearranged, and all of these γ-cleavage reactions are important for hexanoic acid ions.[5] The ready tendency for methyl loss from **5** is also confirmed by the dominant fragmentation of the metastable $(M - C_2H_4)^+$· ions (presumably[2b] **5**) from 2-ethylbutanoic acid (Table I);[17] the negligible CH_2D (as well as C_2H_4) loss from the corresponding ions of the O-d_1 derivative of this compound indicates that the loose complex reaction **5 → 6** is favored over **5 ⇌ 4** or **5 ⇌ 1** even at low energies.

Consistent with the mechanism **1 → 6**, the CA mass spectra[15] of the $(M - CH_3)^+$ ions from **1** formed at either high or low electron energies (Table IV) are identical within experimental error with that of protonated acrylic acid (**6**). Although the same CA spectrum was obtained from protonated β-propiolactone (**8**), the only other $C_3H_5O_2^+$ isomer examined, the **8** ion which should be formed from **1**-β,β-d_2 would probably lose H_2O, not HDO as observed.

Low-Energy γ-Methyl Loss. The loss of γ-CH_3 from metastable **1** ions differs in several ways from the higher energy γ-CH_3 loss **1 → 4 → 5a → 6a**. In most low-energy product **6** ions the β-H has not moved to oxygen; for the CA mass spectrum of the $C_3H_3D_2O_2^+$ ions formed from **1**-β,β-d_2 in the first field-free drift region[18] [-H_2O]:[-HDO] = 3 ± 1, compared (Table III) to 0.14 for such ions formed in the ion source using 70 eV electrons (0.32 for 11 eV). Secondly, the much higher ratio of [**6**]:[**3**] from metastable **1** decomposition than from **1** ions produced at 70 eV should indicate that **6** has the lower appearance potential; actually AP(**6**) ≥ AP(**3**). Finally, the metastable decomposition producing $(M - \gamma$-$CH_3)^+$ is accompanied by little scrambling between the γ- and O-hydrogen atoms, far less than that accompanying **3** formation (Table I);

Table II. Decompositions of Longer Lived Metastable C$_4$H$_6$D$_2$O$_2$ · Ions from Butanoic Acid-β,β-d_2[a]

electron energy, eV	species lost					
	·CH$_3$	·CH$_2$D	·CHD$_2$	C$_2$H$_4$	C$_2$H$_3$D	C$_2$H$_2$-D$_2$
70	100	16	9	20	53	15
14	100	23	12	22	66	22
13[b]	100	23	20	27	66	26
statistical	67	100	20	25	66	25

[a] Measured with a reversed-geometry instrument in which ion lifetimes are substantially longer than those yielding data of Table I; see Experimental Section. [b] Values measured at 12.5 eV were the same as these within the larger error limits.

Table III. Losses of Water from Metastable C$_3$(H,D)$_5$O$_2^+$ Ions

compd	ion	species lost		
		$-$H$_2$O	$-$HDO	$-$D$_2$O
CH$_3$CH$_2$CH$_2$CO$_2$H	C$_3$H$_5$O$_2^+$	100		
CH$_3$CH$_2$CH$_2$CO$_2$D	C$_3$H$_4$DO$_2^+$	4[a]	100	
CH$_3$CH$_2$CD$_2$CO$_2$H	C$_3$H$_3$D$_2$O$_2^+$	100	3[a]	
CH$_3$CH$_2$CD$_2$CO$_2$D	C$_3$H$_2$D$_3$O$_2^+$	3[a]	100	4[a]
CH$_3$CD$_2$CH$_2$CO$_2$H	C$_3$H$_3$D$_2$O$_2^+$	14	100	<1[a]
CH$_3$CD$_2$CH$_2$CO$_2$D	C$_3$H$_2$D$_3$O$_2^+$	≤1	15	100
CD$_3$CH$_2$CH$_2$CO$_2$D[c]	C$_3$H$_4$DO$_2^+$	≤3[a]	100	b
(CH$_3$CH$_2$)$_2$CHCO$_2$D	C$_3$H$_4$DO$_2^+$	14	100	
(CH$_3$)$_2$CHCO$_2$D	C$_3$H$_4$DO$_2^+$	≤3[a]	100	
(CH$_3$)$_2$CDCO$_2$H	C$_3$H$_4$DO$_2^+$	100	≤2[a]	
C$_2$H$_5$C(CH$_3$)$_2$CO$_2$D	C$_3$H$_4$DO$_2^+$	45	100	

[a] Corrected for interference from overlapping peaks. None of the corrections for which results other than "less than" values are reported exceeded 30% of the measured intensities. [b] Impossible to determine. [c] All the possible C$_3$(H,D)$_5$O$_2^+$ ions from butanoic acid-γ-d_3 showed >90% loss of H$_2$O (82% for C$_3$H$_2$D$_3$O$_2^+$ ions decomposing in the second field-free (FF) region of the Hitachi RMU-7; those formed by 1-d_3 decomposition in the first FF region give [-H$_2$O] > [-HDO] with poor signal/noise by CA in the second FF region).[18]

reactions forming **1a–f** presumably originate from a quasi-equilibrium[20] population of energy levels of the ground electronic state, which should have an electron vacancy in a nonbonding n$_0$ orbital on the carbonyl. Those nonisomerized metastable **1** ions forming **6** could originate from the electronic state in which the electron is missing from the π orbital, whose energy should only be a little higher than the ground state.[21] The fact that this γ-CH$_3$ loss is only important for metastable ion decompositions indicates that intersystem crossing from this isolated state to the ground state is slow only for ions of very low internal energies.

For this γ-CH$_3$ loss from metastable **1** ions the previously postulated[22] displacement mechanism **1 → 8** forming protonated β-propiolactone is an attractive possibility; unfortunately, the CA spectrum of these ions[18] cannot test this, as **6** and **8** ions yield the same CA spectra (Table IV). The **8** ions should be less stable than **6** ions,[23] so rapid isomerization **8 → 6** could explain these data. However, the abundance of the γ-CH$_3$ loss by metastable **1** decomposition, relative to the CH$_3$ loss involving the α-CH$_2$ group (discussed below), is lowest for **1**-α,α-d_2, and it is not apparent why **1 → 8** should be slowed by such an isotope effect. An alternative pathway whose rate should be reduced in this way could involve initial α-H transfer, **1 → 5 → 6** (Scheme I); **6** ions produced from **1**-β, β-d_2 by **1 → 5 → 6** (or **1 → 8 → 6**) should give the observed H$_2$O loss. The path **1 → 5 → 6** should be energetically favorable; the radical site in **5** is resonance stabilized, while **6** should be more stable than **8**.[23] This path would involve a four-membered ring transition state, as would **1 → 8**, but formation of a bond from the oxygen to an α-H for **1 → 5** could be more favorable sterically than to the substituted β-carbon atom for **1 → 8** by reasoning analogous to that for **2 → 7** above.

State-Specific Reactions. The rearrangement of an α-H to a carbonyl oxygen is unimportant for ground-state molecular ions.[2b,24] A possible rationalization for **1 → 5 → 6** can be based on orbital symmetry arguments[25] and photochemical analogies. The γ-hydrogen rearrangement **1 → 2 → 3** should involve in-plane hydrogen transfer from a γ carbon to the lone pair n$_0$ orbital on carbonyl oxygen.[26] The transition state for such a process is accessible only upon removal of an electron from the n$_0$ orbital; similarly, in the photochemical Norrish type II process[3] the electron is removed by promotion to the n–π^* excited state of the neutral molecule. Although in principle out of plane transfer to a half-vacant π_{CO} orbital should also be possible, usually π–π^* states are unreactive toward Norrish type II photodecompositions,[3,27] presumably owing to poor mixing between π_{CO} orbitals and those of the same symmetry on γ-methylene groups. That such mixing is poor is evident from the inability of saturated chains to transmit π effects. From a similar argument it would follow that γ- and β-hydrogen transfers with bonding to the π_{CO} orbital would also be unfavorable for ionic species.

The transfer of an α hydrogen with bonding to the n$_0$ orbital on the carbonyl oxygen should have a prohibitive steric re-

this is also evident for the long-lived metastable ions decomposing in the second drift region (Table II). Under the latter conditions the (M − C$_2$H$_4$)$^+$ products are formed from metastable **1** ions that have had time to become equilibrated between the possible isotopic isomers of **1**, while the majority of (M − γ-CH$_3$)$^+$ ions arise from **1** ions in which the β hydrogen has not undergone prior rearrangement to either the γ or the O position; this is despite the fact that these metastable **1** ions leading to **3** and **6** must have approximately the same internal energies [AP(6) ∼ AP(3)] and decompose in the same time period (∼10^8 vibrations). The only explanation appears to be that **3** and **6** originate from isolated electronic states of the precursor metastable **1** ions.[19] Those **1** ions undergoing the

Table IV. Collisional Activation Mass Spectra of C$_3$H$_5$O$_2^+$ Ions[a]

precursor	m/e of daughter ion										
	26	27	29	31	43	45	46	53	55	71	72
CH$_3$CH$_2$CH$_2$CO-OH, 70 eV[b]	11	26	13	1.6	(6.7)	(36)	9.3	11	(170	6.4	22
14 eV	10	26	11	1.8	(3.9)	(32)	8.8	11	(110)	6.6	25
CH$_2$=CHCOOH + H$^+$[c]	11	24	10	1.8	(2.6)	(29)	9.0	10	(80)	5.9	28
[structure] + H$^+$[c]	11	22	13	2.1	(8.2)	(34)	8.5	9.1	(60)	6.2	28

[a] Abundances relative to the total ion abundance = 100 excluding those from metastable ion decompositions at m/e 43, 45, and 55. [b] Ionizing electron energy. [c] Protonation with isobutane.

quirement.[26] However, transfer to the π_{CO} orbital would be a suprafacial [1,3] sigmatropic shift.[25] When four electrons are involved (two in the C–H$^\alpha$ bond, two in π_{CO}) the reaction is symmetry forbidden, but when one electron is removed by ionization the process should be much more favorable, especially in comparison to β- and γ-hydrogen rearrangement.

Methyl Loss Involving the α-Methylene Group. The metastable ion data of Table I for **1-α**, α-d_2, **1-α-^{13}C**, and **1-β,β-d_2** indicate that yet a third pathway for methyl loss involves the $C^\alpha H_2^\alpha H^\beta$ group. These ions appear to have the structure $C_2H_3^\gamma C(OH^\beta)OH^O$ (**6b**), as $C_3H_2D_3O_2^+$ ions formed from **1-γ,γ,γ-d_3** lose mainly H_2O (Table III).[28] The absence of CH_2D and CHD_2 losses from metastable **1-γ,γ,γ-d_3** ions shows that the precursor **1** ions have not undergone **H/D** scrambling. This and the dramatic isotope effect increasing this pathway for **1-α,α-d_2** thus suggest that these $(M - CH_3)^+$ ions originate from the same isolated electronic state **1** ions postulated above as precursors to the low energy γ-CH_3 loss, and not from the diol ions **2** and **4** formed from the ground state of **1**.[28] A possible pathway is **1*** → **9** → **10** → **11** → **6b**; this, like **1*** → **5**, would involve an α-H rearrangement of the π-ionized state, **9** → **10**. However, the concerted rearrangement involved in **1*** → **9** must be regarded as speculative, at best, until more definitive evidence is obtained.

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(9) that 3 ± 2% of this 7% represented **3d** ions.
(9) The indirect formation of **4** from metastable **1** ions by the 1,2-hydride shift **2** → **4** cannot account for an important portion of the [**3b**] observed. The major path for **3b** formation would be **2** → $CH^\beta H_2^\gamma \dot{C}H^\beta CH_2^\alpha C(OH^\gamma)OH^O$ → $CH^\beta H_2^\gamma CH^\beta H^O CH_2^\alpha CO_2 H^\gamma$, the latter undergoing the **1** → **3** decomposition to produce [**3a**]/[**3b**] = 2. This proportion should be much larger, however, as additional **3a** would be produced directly from **2** (Scheme I).
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