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The Stepwise Nature of the γ-Hydrogen Rearrangement in Unsaturated Ions

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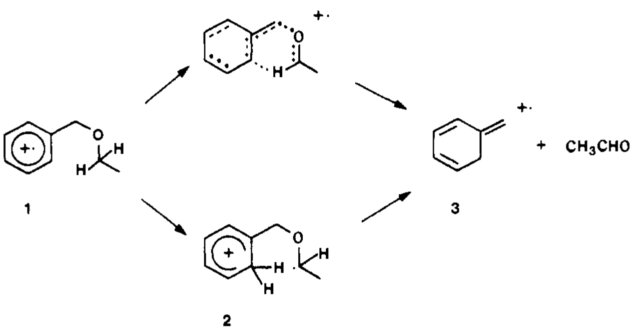
Abstract: The mechanism of acetaldehyde elimination from the benzyl ethyl ether cation radical (**1**) yielding $C_7H_8^{\bullet+}$ ions is re-examined. A distonic ion intermediate (**2**) pertinent to a stepwise route is generated independently by dissociative ionization of 3-methyl-2,4-dioxaspiro[5.5]undeca-8,10-diene and by reaction of the methylenecyclohexa-2,4-diene cation radical with acetaldehyde. Metastable **1** and **2** differ in the kinetic energy released upon dissociation (T_{av} = 7.0 and 1.1 kJ mol^{-1}, respectively), indicating an energy barrier to the isomerization **1** → **2**. During low-energy dissociation of **2** another $C_7H_8^{\bullet+}$ isomer, probably the more stable toluene cation radical, is also formed. This apparently takes place in an ion–molecule complex with acetaldehyde via reversible hydrogen transfer involving the acetaldehyde oxygen atom and represents an entropy bottleneck of the elimination. These competing second steps should produce D/H and the $^{18}O/^{16}O$ isotope effects in addition to the D/H effect of the first step **1** → **2**, accounting for the observations by Bowie, Derrick, et al. attributed to a concerted mechanism; we believe this to be the first case involving this mechanism for a double isotope effect in a stepwise reaction. The kinetic energy release data, intermediate preparation and dissociation, and product characterization by collisionally activated dissociation spectra support a stepwise mechanism.

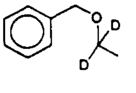
Of the unimolecular dissociations of gaseous positive ions, probably the most extensively studied is the specific rearrangement of a γ-hydrogen to an unsaturated site,[1] such as the loss of acetaldehyde from ionized benzyl ethyl ether (**1**, Scheme I). However, the stepwise or concerted nature of the reaction has been controversial for many years. Of early theoretical studies, one found that the rearrangement is stepwise,[2] but another concluded that it is concerted.[3] Recent theoretical evidence for a concerted transition state[4] has just been rebutted.[5] On the other hand, exceptions have now been cited[5a] to the general proposal[6] that multibond reactions cannot normally be synchronous. Experimental evidence seems conclusive for the stepwise nature of some rearrangements,[7] but there has been strong conflicting evidence, both experimental and theoretical, on the special case of benzyl ethyl ether (**1**, Scheme I). In an elegant labeling study[8] the bis-derivative $C_2H_5\text{-}OCH_2\text{-}C_6H_4\text{-}CH_2O\text{-}CD_2CH_3$ and its ^{18}O counterpart showed D/H and $^{18}O/^{16}O$ isotope effects, which was interpreted to result from near-simultaneous bond breaking demanded by the concerted reaction (Scheme I). An observation from our laboratory[9] of H/D exchange allowing C_2H_4O loss from $C_6H_5CH_2OCD_2CH_3$, giving evidence for the reversibility of the first of two steps (Scheme I), has recently been refuted[10] on both experimental and theoretical grounds, suggesting instead that a minor loss of C_2H_2DO accompanies the C_2H_3DO loss. However, experiments described here provide further mechanistic details consistent with a stepwise reaction. Although we now find no evidence for either H/D scrambling or C_2H_3O loss accompanying C_2H_4O loss, the intermediate **2** in Scheme I has been prepared by two independent methods. Further, at low energies the reaction **2** → **3** is in competition with one forming another $C_7H_8^{\bullet+}$ isomer through an ion–molecule complex that can account for the observed double isotope effect.

Scheme I

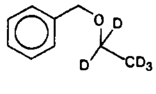


Results and Discussion

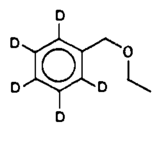
Hydrogen/Deuterium Exchange. The previous evidence[9] for the stepwise mechanism of Scheme I was based on the metastable ion (MI) spectra of the d_2 derivative **1a**. Reversible hydrogen/deuterium exchange **1** ⇄ **2** was inferred from an appreciable value of $[M^{\bullet+} - C_2H_4O]/[M^{\bullet+} - C_2H_3DO]$, increasing from 2% for a precursor ion lifetime of ~24 μs to 10% for ~47 μs. Loss of C_2H_4O from metastable **1** gives a Gaussian-like (n = 1.6 ± 0.1) $C_7H_8^{\bullet+}$ peak (Figure 1) in the mass-analyzed ion kinetic energy spectrum with kinetic energy release $T(0.5)$ = 2.2 kJ mol^{-1} and T_{av} = 7 kJ mol^{-1}. For the 24 μs ions (9.9 keV precursor ions) the energy resolution ($E/\Delta E$ > 1000) yields a peak width (half-height) of 0.4 mass units, so that adjacent peaks (e.g., 92, 93) are just resolved. At the lower energies, the mass resolution decreases (e.g., peak width 0.8 m.u. for 47 μs, 2.5 keV),[9] so that the relative abundances of the overlapping peaks were obtained by deconvolution.[9,10]



1a



1b



1c

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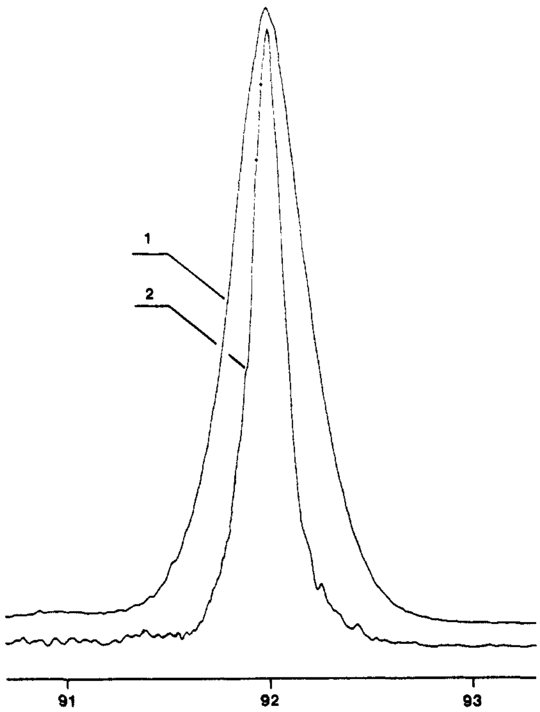


Figure 1. Peak profiles for $C_7H_8^{\cdot+}$ from metastable **1** and **2** by ESA-II separation.

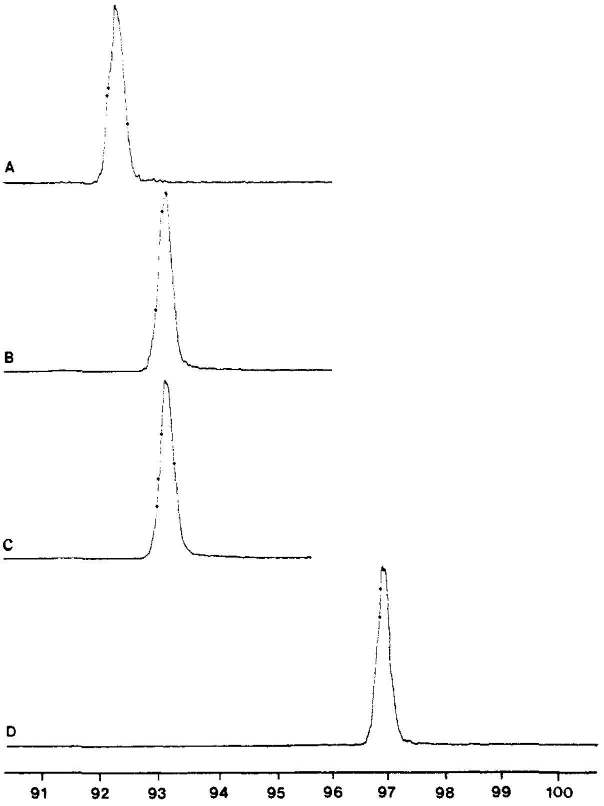


Figure 2. The *m/z* 90–100 ions from metastable **1** (A), **1a** (B), **1b** (C), and **1c** (D) by Magnet-II separation.

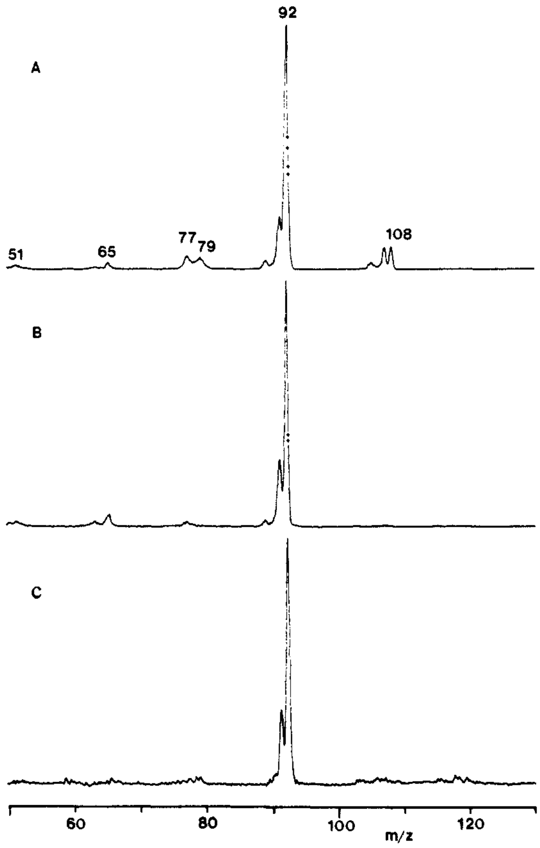
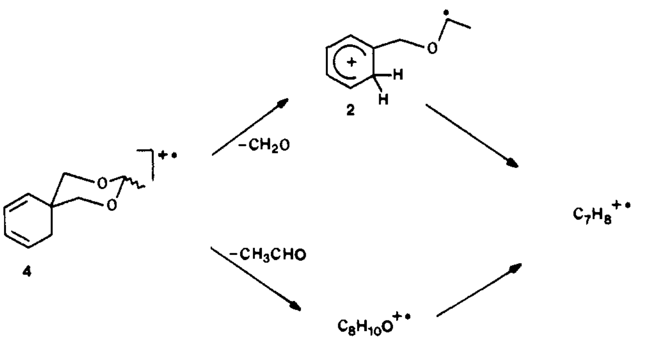


Figure 3. CAD spectra of $C_9H_{12}O^{\cdot+}$ from **1** (A), from **4** (B), and from the ion-molecule reaction of **3** with acetaldehyde (C).

Scheme II



To avoid this ambiguity, the H/D exchange was remeasured with the longer flight distance of the four-sector mass spectrometer and the higher resolution of its second magnet,[11] using computer integration of peak intensities.[12] Metastable **1**, **1a**, **1b**, and **1c** ions (9.9 keV) decomposing in the 4th field-free region (lifetimes 35–42 μs) gave spectra with 0.3 m.u. peak widths (Figure 2). However, in contrast to both of the previous reports,[9,10] this higher resolution shows *no* evidence for adjacent peaks. That expected to arise only from hydrogen/deuterium exchange[9] at *m/z* 96 (**1c**) shows an integrated intensity of 0.4% of that of the corresponding main peak, while those expected only for loss of $C_2(H,D)_3O$[10] at *m/z* 93 (**1**) and 98 (**1c**) show 1.6 and 1.2%, respectively, and those arising from both at *m/z* 94 (**1a**, **1b**) show 2.0 and 1.8%, respectively. These values, which can also arise from tailing of the main component and from experimental error, thus provide no evidence for the stepwise mechanism.

Generation of the Reaction Intermediate 2. The stepwise mechanism for the elimination in question relies on the existence of the pivotal distonic[13] intermediate **2** (Scheme I).[9,10] MNDO calculations[14] of Bowie, Derrick, et al.[10] and our previous thermochemical estimates[9] suggested **2** to be slightly more stable than

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Table I. Partial CAD Spectra of $C_7H_8^{\bullet +}$ [a]

preparation	$[C_6H_6^{\bullet +}]/[C_6H_5^{+}]$ [b]	preparation	$[C_6H_6^{\bullet +}]/[C_6H_5^{+}]$ [b]
1, ion source	0.67	**7**, CAD 3rd FFR	0.94
metastable **1**, 3rd FFR	0.66	**7** + CH_3CHO (70 mTorr)[d]	0.50
4, ion source	0.43	**7** + C_2H_4 (70 mTorr)	0.73
metastable **2**, 3rd FFR	0.47	**5**, ion source	0.72
7, ion source	0.73	**5** + CH_3CHO (70 mTorr)	0.46
metastable **7**, 1st FFR[c]	1.14	**6**, ion source	0.19

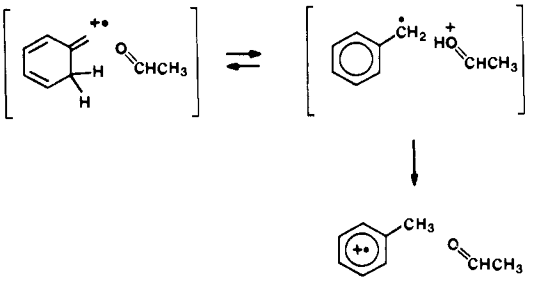
[a] 70-eV electron ionization; peak areas from base-line mass-resolved Magnet II scans; ion kinetic energies were 6.7 keV for $C_7H_8^{\bullet +}$ formed in the ion source, corresponding to those from MI and CAD dissociations of 9.9 keV **1** and **2** (6.8 keV from **7**). [b] CAD intensities for $C_7H_8^{\bullet +}$ produced by ion source decompositions were corrected for weighted contributions from decompositions of $^{13}CC_6H_7^{+}$. [c] CAD of **3** from metastable **7** decomposing in the 3rd FFR showed the same value. [d] Calculated from the pressure read with an ionization gauge (1×10^{-4} Torr) located outside the ion source near the inlet of the diffusion pump, the pumping speed, and the estimated vacuum conductance of the ionization chamber.

1. After several unsuccessful attempts to find an alternative precursor for **2**, 3-methyl-2,4-dioxaspiro[5.5]undeca-8,10-diene was synthesized. On electron ionization its $M^{\bullet +}$ ion (**4**) yields $C_9H_{12}O^{\bullet +}$ (presumably **2**, *m/z* 136), $C_8H_{10}O^{\bullet +}$ (*m/z* 122), $C_8H_9^{+}$ (*m/z* 105), and $C_7H_8^{\bullet +}$ (*m/z* 92) as the base peak of the spectrum (Scheme II). The MI spectrum of **2** shows a dominant Gaussian-like ($n = 1.7 \pm 0.1$) $C_7H_8^{\bullet +}$ peak (Figure 1) whose kinetic energy release values of $T(0.5) = 0.4$ kJ mol^{-1} and $T_{av} = 1.1$ kJ mol^{-1} are markedly lower than those of **1**. The spectra from collisionally activated dissociation (CAD)[15] of **1** and **2** (Figure 3) are dominated by $C_7H_8^{\bullet +}$ at *m/z* 92, but otherwise they show clear differences. Especially striking in the CAD spectrum of **2** are the very low relative intensities of the C_7-group ions at *m/z* 105, 107, 108 and of $C_6H_7^{+}$ (*m/z* 79). This is in keeping with the assumed structure **2** for which a very facile cleavage of the CH_2–O bond can be expected.

According to the principle of microscopic reversibility, ion **3** should react with acetaldehyde to give **2**. Since this reverse reaction is exothermic by ~30 kJ mol^{-1},[10] **2** so formed needs to be stabilized by collisional energy transfer to prevent decomposition back to its components. Ion **3** was generated by dissociative ionization of isopentylbenzene (**5**) and allowed to react with excess acetaldehyde in the ion source at ca. 0.07 Torr, yielding an ion at *m/z* 136 (0.1% of $C_7H_8^{\bullet +}$). The *m/z* 136 signal fell to background level (0.001% of $C_7H_8^{\bullet +}$) upon stopping the influx of either **5** or acetaldehyde, demonstrating that its formation requires both these components. The CAD spectrum (Figure 3) is closely similar to that of **2**; noteworthy is the absence of the peak at *m/z* 79 and the low relative intensity of the C_7 fragments at *m/z* 105, 107 and 108 typical of **1**. This provides strong evidence that **2** is formed by the ion-molecule reaction of **3** with acetaldehyde.[16,17]

Identification of $C_7H_8^{\bullet +}$ Products. Both the concerted and the stepwise mechanism for the acetaldehyde elimination should presumably produce the methylenecyclohexadiene ion **3**.[8-10] This is the second most stable $C_7H_8^{\bullet +}$ isomer,[18,19] $\Delta H_f = 934–959$ kJ mol^{-1}, with the toluene ion (**6**) being the most stable ($\Delta H_f = 901$ kJ mol^{-1}). Ions **3** and **6** can be distinguished through their CAD spectra, but these were found to depend on the mode of ion formation.[19] With low-energy **3**, formed from metastable *n*-butylbenzene (**7**) or 2-phenylethanol, the $[C_6H_6^{\bullet +}]/[C_6H_5^{+}]$ ratio (1.10–1.15) was significantly greater than with ions produced in the ion source (0.4–0.63). This was attributed to partial isomerization of the latter, presumably to the more stable **6** for which $[C_6H_6^{\bullet +}]/[C_6H_5^{+}] = 0.18$, although ionized cycloheptatriene and norbornadiene gave values of 0.33 and 0.28.[19]

Scheme III



Our data (Table I) agree well with those of Burgers et al.[19] with $[C_6H_6^{\bullet +}]/[C_6H_5^{+}] = 1.14$ for **3** and a decreasing proportion of **3** formed at higher excitation energies, e.g., ions prepared by CAD of **7** or ion source decompositions of **5** and **7**. In contrast, the CAD spectra of $C_7H_8^{\bullet +}$ from **1** are *insensitive* to the mode of ion formation, showing intermediate $[C_6H_6^{\bullet +}]/[C_6H_5^{+}]$ values (Table I). The same holds for the $C_7H_8^{\bullet +}$ ions from **2** which, surprisingly, show a lower proportion of **3**. The extremely low kinetic energy release in the decomposition of metastable **2** indicates a negligible reverse activation energy[20] and a low nonfixed energy,[21] which should minimize isomerization of the *newly formed* **3** to **6**. Prior studies[22] suggest that such a thermodynamically favorable isomerization can be possible in an ion–molecule complex,[22] such as a reversible proton transfer between **3** and acetaldehyde (Scheme III). Consistent with this, the CAD spectra of $C_7H_8^{\bullet +}$ produced in the ion source from alkylbenzenes in the presence of a large excess of acetaldehyde show a significant decrease of the $[C_6H_6^{\bullet +}]/[C_6H_5^{+}]$ ratios (Table I). To check the possibility that acetaldehyde has instead induced charge-transfer ionization of the alkylbenzenes ($\Delta E = 1.54$ eV),[23] the CAD spectrum of $C_7H_8^{\bullet +}$ formed from **7** was measured in the presence of an excess of ethylene ($\Delta E = 1.83$ eV),[23] showing (Table I) an unchanged value.

The catalytic effect of acetaldehyde is compatible with the energetics of the proton-transfer isomerization in Scheme III. Proton transfer from acid **3** to acetaldehyde forming the benzyl radical and $^{+}HO{=}CHCH_3$ is nearly thermoneutral ($\Delta H = -10 - +15$ kJ mol^{-1})[24] and can be further favored by hydrogen bonding

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(16) No decompositions of metastable **2** formed by this ion-molecule reaction could be detected; similar resistence toward unimolecular decompositions of collisionally stabilized ions has been observed: Groenewold, G. S.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6569–6575.

(17) A reviewer has made the cogent suggestion that the $C_9H_{12}O^{\bullet +}$ intermediate could be an ion–molecule complex of **3** and CH_3CHO, instead of the structure **2**. Such a complex could arise from the charge-dipole interaction of the positive methylene group and the negative oxygen, $^{\bullet +}C_6H_6CH_2{-}{-}{-}O{=}CHCH_3$; this complex should be less stable than **2**, as breaking this C–O bond is endothermic. However, our data do not distinguish between such possible structures.

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(19) Burgers, P. C.; Terlouw, J. K.; Levsen, K. *Org. Mass Spectrom.* **1982**, *17*, 295–298.

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(23) Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements, 1971–1981*; NSRDS-NBS 71, U.S. Department of Commerce: Washington, DC, 1982.

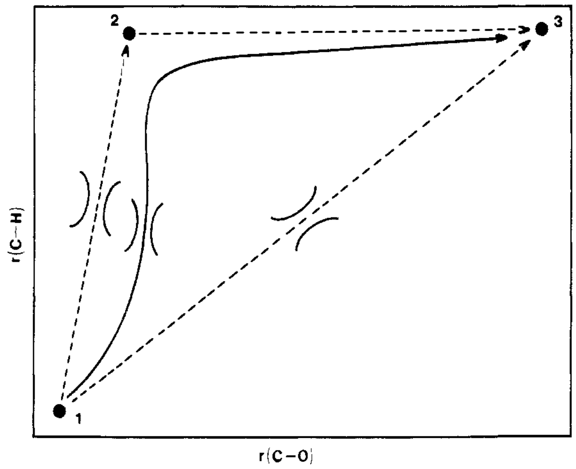

Figure 4. Reaction coordinates and pathways for dissociations of **1** and **2**.

of $^{+}HO{=}CHCH_3$ to the aromatic π-system.[28] The subsequent hydrogen transfer forming **6** and acetaldehyde is exothermic[24] and provides the driving force for the overall isomerization. According to MNDO calculations, the positive charge in **3** is delocalized over the exocyclic methylene group (+0.113) and the perimeter ring hydrogen atoms (ca. +0.100 each). The $C^{+}{=}O^{-}$ dipole of the acetaldehyde molecule thus can wander around the ring on a flat potential energy surface and reach the acidic ring methylene group without an appreciable energy barrier. On the other hand, due to a variety of accessible states, attaining the transition state for the proton transfer should represent an entropy bottleneck.[29] The absence of **3** → **6** isomerization in the decompositions of metastable **7** (loss of propene) and 2-phenylethanol (loss of formaldehyde) or in the interaction of **3** with ethylene is understandable, for the corresponding neutral molecules are too weakly basic to be protonated by the ion.[27]

Stepwise vs Concerted Mechanism. The existence of the distonic ion **2** and its formation by the ion–molecule reaction of **3** with acetaldehyde bear relevance to the mechanism of the forward elimination reaction (Scheme I). Allison et al.[10] used MNDO to approximate the energy barriers in the stepwise route; their RRKM calculations[30] of rate constants for **1** ⇄ **2** indicated that hydrogen/deuterium exchange should occur in **1a** on the time scale of dissociation. However, they assumed an energy barrier for **2** → **1** 15 kJ greater than that for **2** → **3**, while our energy release data (Figure 1) show that the latter should be substantially more favored. Further, RRKM calculations are known to be very sensitive to the reaction potential energy surface,[31] so even small variations in the height of the isomerization barrier would substantially affect the product distribution.

Consistent with our experimental data showing a higher energy barrier for **3** formation starting from **1** than from **2**, the ion–molecule reaction of **3** with acetaldehyde yields **2** and not **1**; ion–molecule reactions are severely hampered by potential energy barriers.[32] Since the calculations of Allison et al.[10] found a true transition state for the isomerization **1** ⇄ **2**, the existence of a concerted mechanism would require two independent pathways for the decomposition of **1**. This is, however, very unlikely as can be seen from a simple two-dimensional energy diagram (Figure 4). The hypothetical decomposition paths for a concerted and a stepwise elimination (broken lines) should be separated by a region of high potential energy to meet the obvious dynamic criteria. A preference for the concerted path (diagonal) would necessitate a high-lying saddle point along the isomerization barrier. Further, the branching between the two paths should occur before the system reaches the transition state of decomposition, since otherwise it would prefer following the more exoergic pathway to **2**.

The existence of the barrier separating the two dissociation paths would imply that as the C–O bond is stretched, the barrier for the C-1′ hydrogen atom to jump to the aromatic ring becomes impossibly high. The existence of such a barrier is without precedence;[5] qualitatively, there are no orbital-symmetry restrictions to this hydrogen migration. To account for the experimental data we suggest a curved reaction path that is close to the stepwise mechanism (full line in Figure 4). Stretching the C–O bond activates one of the C-1′ methylene hydrogens which jumps to the aromatic ring after passing the highest saddle point on the potential energy surface. Since the barrier is relatively narrow (C–H bond), tunneling is not excluded. This would account for the very low appearance energy of $C_7H_8^{\bullet+}$ from **1** measured by a very sensitive photoionization method.[33] Due to the barrier, **2** is formed in a non-equilibrium geometry and the system can cut the corner on the way to products (Figure 4).

The problem remains that isotope effects indicate that both C–H and C–O bond cleavages are involved in the rate-determining step(s); $^{16}O/^{18}O = 1.15$ for $C_2H_5{}^{16}OCH_2C_6H_4CH_2{}^{18}OC_2H_5$, although this was not measured for **1**.[8] CAD analysis of the $C_7H_8^{\bullet+}$ product from **1** (Table I) indicates that 35% does not represent isomer **3**. Since the Scheme III isomerization via proton transfer involves the oxygen atom, $^{18}O/^{16}O$ (as well as D/H) isotope effects can be expected for this fraction of the $C_7H_8^{\bullet+}$ product. This postulate could be tested by measuring $^{18}O/^{16}O$ for **1** dissociations yielding the **3** isomer separately from those yielding **6**.

Conclusions

The present experimental data support the stepwise elimination of acetaldehyde from the molecular ion of benzyl ethyl ether, in keeping with other γ-hydrogen transfer reactions[2,5,7] and general conclusions,[6] but in contradiction to the interpretation of Bowie, Derrick, et al.[8,10] The elusive distonic intermediate was generated independently and found to be identical with the product of the ion–molecule reaction of methylenecyclohexadiene ion with acetaldehyde. Both D/H and $^{18}O/^{16}O$ isotope effects[8,10] would be expected in the hydrogen migrations of the acetaldehyde-mediated isomerization of **3** to **6**, which represents an entropy bottleneck of the overall elimination. It has already been demonstrated that such double isotope effects can arise from similar barrier heights in a stepwise mechanism,[34] rather than a concerted one. This represents a somewhat different case of two competing second steps producing an isotope effect in addition to that caused by the higher energy first step.

Experimental Section

Measurements were made with a tandem mass spectrometer described previously,[11] consisting of a Hitachi Perkin-Elmer RMH-2 double-focusing mass spectrometer as MS-I, a special collision chamber with helium (30% transmittance), an electrostatic sector (ESA II), and a

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(24) The energy data are as follows: $\Delta H_f(3) = 934–959$ kJ mol^{-1};[18,19] $\Delta H_f(CH_3CHO) = -166$ kJ mol^{-1};[25] $\Delta H_f(C_6H_5CH_2^{\bullet}) = 200$ kJ mol^{-1};[26] $\Delta H_f(CH_3CH{=}OH^{+}) = 583$ kJ mol^{-1};[18,27] $\Delta H_f(6) = 901$ kJ mol^{-1}.[18]

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magnetic sector (Magnet II).[11] MI and CAD spectra were obtained as ion-kinetic-energy scans of MS-I selected ions decomposing in the 3rd field-free region (between MS-I and ESA II) or as mass scans of ions decomposing in the 4th field-free region (between ESA II and Magnet II). The reported spectra are averages of 15–100 repetitive scans.

Compounds **1**, **1a**, and **1b** were prepared by benzylation[35] (benzyl bromide, 1.2 eq, silver oxide, 2.5 eq, dimethyl formamide, 20 °C, 8 h) of ethanol, ethanol-*1,1-d*$_2$, and ethanol-*1,1,2,2,2-d*$_5$, respectively. To prepare **1c**, benzoic-*d*$_5$ acid (Aldrich) was reduced to benzyl-*2,3,4,5,6-d*$_5$ alcohol which was ethylated[35] with ethyl iodide. Ethers **1** and **1a–1c** were purified by vacuum distillation and their mass spectra revealed no impurities.

3-Methyl-2,4-dioxaspiro[5.5]undeca-8,10-diene. To a stirred solution of 3-methyl-2,4-dioxaspiro[5.5]undec-8-ene[36] (1.68 g, 10 mmol, mixture of diastereoisomers) in dichloromethane (30 mL) at -50 °C was added a solution of bromine (1.65 g, 10.3 mmol) in dichloromethane (20 mL). After 15 min the solvent was evaporated in vacuo to give a light yellow oil that solidified upon standing at 0 °C overnight. The dibromo derivative (3.2 g) was dissolved in dimethyl formamide (8 mL) and treated with 1,8-diazabicyclo[5.4.0]undec-7-ene[37] (6 g) at 140 °C under argon for 6 h. The cooled mixture was diluted with water (30 mL) and pentane (30 mL), the water layer was extracted twice with pentane (10 mL), the pentane layers were washed with ice-cold 5% HCl (2 × 100 mL) and water and dried with potassium carbonate, and pentane was distilled off through a 20 cm Vigreaux column. The residue was distilled (short path, 100 °C/10 Torr) to yield 825 mg (50%) of product as a mixture of diastereoisomers. MS (*m/z*, rel intensity): 166 ($M^{\bullet+}$, 1.1), 136 (0.2), 122 (1), 105 (5.3), 92 (100), 91 (81), 90 (16), 79 (4), 77 (7), 73 (2.5), 65 (14), 52 (4), 51 (9), 43 (15), 39 (19). ^{1}H NMR ($CDCl_3$, 200 MHz): 1.32 d, 1.34 d (CH_3), 1.84 m (CH_2), 2.62 m (CH_2), 3.40, 3.44 ddd (J = 11.0, 1.2, 1.1 Hz, CH_2O), 3.90, 3.98 dd (J = 11.0, 1.2 Hz, CH_2O), 4.62, 5.10 m (OCHO), 5.60, 5.80, 6.00, 6.22 m (CH=).

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Gas-Phase Chemistry of the Silaformyl Anion, $HSiO^-$

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Abstract: The silaformyl anion, $HSiO^-$, has been prepared by collisionally induced dissociation (CID) of H_3SiO^- in a tandem flowing afterglow selected ion flow tube (FA-SIFT). The chemistry of the silaformyl anion has been studied in detail. Reactions with CO_2, COS, CS_2, SO_2, O_2, acetic acid, nitromethane, and hexafluorobenzene reveal a rich chemistry. For example, the silaformyl anion reacts with CO_2 by both an oxidative pathway giving $HSiO_2^-$ and CO and a reductive path giving SiO and HCO_2^-. Typically, the silaformyl anion, which could have several sites of reactivity, behaves both as an oxygen nucleophile and as a hydride donor. Detailed mechanistic studies have been carried out on many of these reactions with isotopically labeled $H^{29}SiO^-$ and $HSi^{18}O^-$. In addition to its reaction chemistry, the heat of formation of the silaformyl anion, its basicity, and the heat of formation of its parent compound have been estimated. Ab initio computations on the silaformyl anion have been carried out and demonstrate that $HSiO^-$ is more than 40 kcal/mol more stable than $HOSi^-$.

Silicon analogues of alkanes and cycloalkanes, including those of some highly strained molecules, are generally stable compounds whose chemistry can readily be investigated.[1] Silicon analogues of unsaturated organic compounds, on the other hand, are with few exceptions highly reactive transient species that dimerize or polymerize readily and react rapidly with polar solvents or other components of their environment.[2] Despite the difficulties involved, a number of workers have made important contributions to our understanding of the chemistry of, for example, the silicon–carbon and silicon–oxygen double bond by examining gas-phase reactions of silenes (Si=C) and silanones (Si=O), by studying such species in matrices at low temperature, and by preparing highly substituted derivatives in which normal chemical reactions are inhibited by steric or electronic interactions.[3] Nevertheless, it is no exaggeration to say that our understanding of the chemistry of such species is extremely limited.

Our approach to this problem involves the study of the reactions of organosilicon anions in the gas phase using the flowing afterglow apparatus. This approach has a number of advantages. In the first place, we can easily prepare a large number of silicon-containing anions, ions that would likely be too reactive to study in solution.[4-8] Thus we can examine the chemical reactions of simple

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