concentrations were also corrected for water formed by acetal formation, both in water determinations and in kinetic measurements.

Rate Measurements. The two-electrode electrochemical system used for the kinetic measurements was described previously.[2,9,31] Argon was passed over the solution and then interrupted to avoid evaporation of bromine during the reaction. Bromine was produced by bromide ion electrolysis (constant current and measurement of the electrolysis time). It was observed that in the absence of added ketone, bromine concentration (ca. 10^{-6} M) decreased fairly rapidly (see Figure 1) with a roughly zeroth-order rate which depended on acid and water concentrations. The lower the water concentration and the higher the HBr concentration, the faster the blank reaction was; consequently, kinetic studies were restricted to narrow ranges of acid concentrations such that the largest water concentration effects could be examined. Another restriction on the choice of acid concentrations also came from the necessity to make the ketone-to-acetal equilibrium sufficiently fast. The ratios between $[Br_2]_{st}$ and i_{amp} (ca. 10^{-7} M/μA) were determined by jumps in bromine concentration due to successive electrolyses and i_{amp} measurements. In most cases, since i_{amp} was not strictly linear with concentration, corrections were introduced for rate constant determinations [this was due to the fact that the fixed electrode (anode) did not stay at a rigorously constant potential, contrary to what is required by the amperometric method]. Aliquots of the methanolic HBr solutions were transferred to the UV–vis spectrophotometry cell for water determination just before the kinetic measurements or just before water addition. Solutions of **1a**–**h** (15–50 μL) in chlorobenzene were introduced into the cell containing 20–40 mL of the acidic solution of bromine by using a weighed microsyringe. For measurements on equilibrated ketone–acetal systems, the mixture was allowed to equilibrate for some minutes (this time lag was calculated from kinetic data on ketone–acetal equilibration),[10] bromine was produced by electrolysis, and the i_{amp}–time curve was recorded (Esterline Angus, 1101S model). The zeroth-order rate constant was calculated from the slope and corrected for the blank reaction. The first-order rate constant was obtained by dividing the corrected slope by the overall ketone concentration. For most experiments, the fraction of overall ketone which reacted before the kinetic run itself was small, but in some cases it was necessary to correct the concentration. It was assumed that the α-bromo ketone dimethyl acetal formed was much less reactive than the starting materials, as expected from the polar effects of the bromine atom. Usually several successive runs could be performed in the same reaction mixture, after successive electrolyses, without significant changes in the first-order rate constants being observed.

Registry No. **1a**, 121-89-1; **1b**, 349-76-8; **1c**, 99-02-5; **1d**, 99-91-2; **1e**, 403-42-9; **1f**, 98-86-2; **1g**, 122-00-9; **1h**, 100-06-1; **2a**, 73585-54-3; **2b**, 73589-85-2; **2c**, 73585-53-2; **2d**, 72360-69-1; **2e**, 73585-52-1; **2f**, 4316-35-2; **2g**, 53578-01-1; **2h**, 27150-99-8; CH_3OH, 67-56-1; H_2O, 7732-18-5; 4-$CH_3OC_6H_4C(OCH_3){=}CH_2$, 51440-56-3; 4-$CH_3C_6H_4C(OCH_3){=}CH_2$, 51440-57-4; $C_6H_5C(OCH_3){=}CH_2$, 4747-13-1; 4-$FC_6H_4C(OCH_3){=}CH_2$, 67471-38-9; 4-$ClC_6H_4C(OCH_3){=}CH_2$, 67471-39-0; 3-$ClC_6H_4C(OCH_3){=}CH_2$, 89726-07-8; 3-$O_2NC_6H_4C(OCH_3){=}CH_2$, 89726-05-6.

Supplementary Material Available: Tables of primary kinetic results (Tables S1–S3) (8 pages). Ordering information is given on any current masthead page.

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(*E*)- and (*Z*)-1-Hydroxy-1,3-butadiene: New Kinetically Unstable C_4H_6O Isomers

František Tureček*

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Máchova 7, 121 38 Praha 2, Czechoslovakia

Zdeněk Havlas

Institute of Organic Chemistry and Biochemistry, 166 10 Praha 6, Czechoslovakia

Francis Maquin,[†] Nicholas Hill, and Tino Gäumann

Institute of Physical Chemistry, Swiss Federal School of Technology, CH-1015 Lausanne, Switzerland

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(*E*)- and (*Z*)-1-hydroxy-1,3-butadiene were prepared by the retro-Diels–Alder decomposition of the corresponding 3-*exo*-vinylbicyclo[2.2.1]hept-5-en-2-ols at 750 °C (10^{-6} torr). The ionization energies of the *E* and *Z* isomers were determined as 8.51 ± 0.03 and 8.47 ± 0.03 eV, respectively. The ionized (*E*)- and (*Z*)-dienols were generated from the same precursors by dissociative ionization, and their appearance energies were measured as 9.00 ± 0.05 and 8.95 ± 0.06 eV, respectively. The heats of formation of the ionic and neutral dienols were assessed as $\Delta H_f{}^\circ{}_{298}$ $[(E)\text{-}CH_2{=}CHCH{=}CHOH]^{\bullet+})$ = 733 ± 5 kJ·mol^{-1}, $\Delta H_f{}^\circ{}_{298}$ $((E)\text{-}CH_2{=}CHCH{=}CHOH)$ = −88 ± 5 kJ·mol^{-1}, $\Delta H_f{}^\circ{}_{298}$ $([(Z)\text{-}CH_2{=}CHCH{=}CHOH]^{\bullet+})$ = 728 ± 6 kJ·mol^{-1}, and $\Delta H_f{}^\circ{}_{298}$ $((Z)\text{-}CH_2{=}CHCH{=}CHOH)$ = −89 ± 9 kJ·mol^{-1}, in good agreement with semiempirical MNDO calculations. The neutral dienols are less stable than (*E*)-2-butenal ($\Delta\Delta H_f{}^\circ{}_{298}$ = 17–19 kJ·mol^{-1}), but *more stable* than 3-butenal ($\Delta\Delta H_f{}^\circ{}_{298}$ = −8 to −10 kJ·mol^{-1}). The transition state for the unimolecular 1,5-sigmatropic isomerization of (*Z*)-1-hydroxy-1,3-butadiene to (*Z*)-2-butenal was located by MNDO calculations at 236 kJ·mol^{-1} above the dienol. The corresponding barrier to isomerization in the cation radical was assessed as being lower than 187 kJ·mol^{-1}. The mass and collision-induced decomposition spectra are briefly discussed.

Prototropic isomerization of enols is thought to begin with proton attack at the electron-rich terminus of the enol system.[1] In dienols containing a terminal hydroxy group there are, in principle, two possibilities for the enol–keto conversion (Scheme I). Protonation of the dienol system at C-4, followed by hydroxyl hydrogen abstraction would yield an α,β-unsaturated aldehyde (e.g., 2-butenal, **2**, R = H), while protonation of the enol subsystem at C-2 would

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[†] Present address: Societé Roussel-Uclaf, Département des études physico-chimiques et structurales, 93230 Romainville, France.

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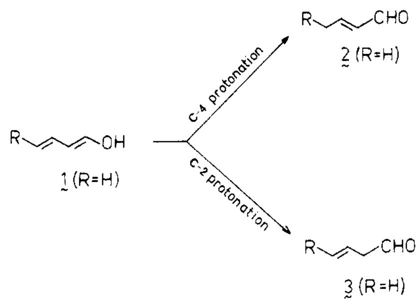
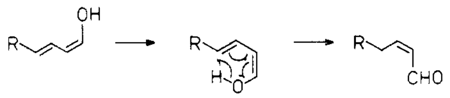
0022-3263/86/1951-4061$01.50/0

Scheme I



Scheme II



analogously give a β,γ-unsaturated aldehyde (e.g., 3-butenal, **3**, R = H). The composition of the reaction mixture in equilibrium would depend on the pertinent $\Delta G°$ values.

In addition to the prototropic isomerization initiated with a Brønsted acid, (*Z*)-1-hydroxy-1,3-dienes may undergo a unimolecular sigmatropic 1,5-hydrogen shift, yielding (*Z*)-α,β-unsaturated aldehydes (Scheme II). The reverse reaction, photoenolization of α,β-unsaturated aldehydes,[2] has been investigated theoretically for the simplest system, (*Z*)-2-butenal → (*Z*)-1-hydroxy-1,3-butadiene. The relative energies of the reactants, products, and transition states have been evaluated at different though not highly sophisticated levels of theory (STO-3G/CI,[3a] 4-31G,[3b] and INDO[3b]), and widely differing values have been arrived at. Nevertheless, the calculations agreed in that the energy barrier separating the ground-state (*Z*)-dienol and (*Z*)-enal was substantially higher than that between the excited triplet states.[3] The high barrier to isomerization suggests that (*Z*)-dienols may exist as thermally stable species.

In order to be able to study the dienol–enal interconversions, it is necessary to know or estimate thermochemical quantities (e.g., heats of formation) that characterize the relative stability of the isomeric species. While standard heats of formation of unsaturated aldehydes can be estimated with good accuracy from Benson's additivity rules,[4] there are only few thermochemical data on unstable enols[5] which do not allow for reliable determination of the $\Delta H_f°$ of a dienol system of a different type.

1-Hydroxy-1,3-butadiene (**1**) was generated as an extremely unstable iron–tricarbonyl complex[6] whereas the free dienol has been unknown. The goal of the present paper was (i) to prepare (*E*)- and (*Z*)-1-hydroxy-1,3-butadiene in the gas phase, (ii) to determine their standard heats of formation by critical energy measurements, and (iii) to compare the experimental data with those obtained by semiempirical MNDO quantum chemical calculations.

Scheme III

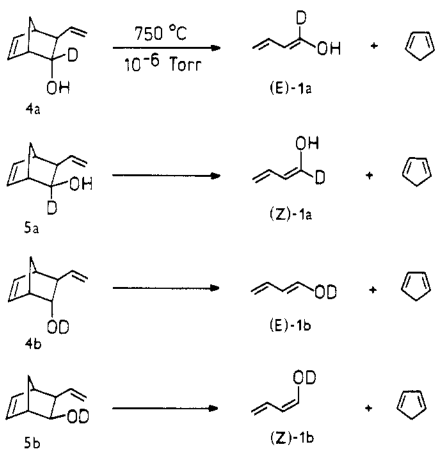


Table I. The 75-eV Electron-Impact Mass Spectral Data of (*E*)-1 and (*Z*)-1 and the CID Spectral Data of [(*E*)- and (*Z*)-1]$^{\bullet+}$

	relative abundance					
	electron impact		CID [(*E*)- and (*Z*)-1]$^{\bullet+}$			
			b,*d*		*c*,*d*	
m/*z*	(*E*)-1[a]	(*Z*)-1[a]	PA	PH	PA	PH
71	5	5				
70	92	93				
69	46	35	(137)	(435)	(105)	(308)
68	4	2	13	24	10	20
67			3	4	2	4
66			2	3	2	3
55	7	2	27	48	18	22
54	2	7	1	2	1.5	3
53	6	2	5	6	4	6
52	4	9	4.5	7	4	7
51	9	4	20	22	17	21
50	8	4	24	22	23	22
49	1	0.5	7	8	8	10
44	2		4.5	8.5	4.5	8.5
43	20	12	12	16	10	14
42	37	21	(59)	(66)	(58)	(67)
41	100	100	66	87	59	76
40	6	4	15	20	13	18
39	59	62	100	100	100	100
38	10	6	25	27	26	30
37	4	3	26	26	26	24
36	1	1	2	2	3	4
31	4	5	6	8	6	9
30	2	2	2	2.5	2	3
29	21	15	24	29	22	26
28	6	7	1.5	2.5	2	4
27	28	22	22	27	19	24
26	7	5	14	15	13	15
25	1	1	2	3	4	5
15	7	3	3	5	3.5	5
14	2	1	2	3	2	3.5

[a] The ion intensities at *m*/*z* 52–49, 41–36, 31, 27–25, 15, and 14 were corrected for contributions from cyclopentadiene. [b] Ions prepared by electron-impact ionization of (*E*)-1 or (*Z*)-1. PA = peak areas; PH = peak heights. [c] Ions prepared by dissociative ionization of **4** or **5**. Columns as in footnote *b*. [d] Values in parentheses contain contributions from unimolecular decompositions.

Results

Preparation. Dienols (*E*)-**1** and (*Z*)-**1** were generated from stereoisomeric 3-*exo*-vinylbicyclo[2.2.1]hept-5-en-2-ols **4** and **5**, respectively,[7] by high-vacuum flash pyrolysis.[8,9]

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1-^{2}H and O-^{2}H derivatives (E)-**1a**, (Z)-**1a**, (E)-**1b**, and (Z)-**1b** were prepared analogously from the corresponding labeled precursors (Scheme III). The experimental arrangement used[5c] allows us to analyze the decomposition products by mass spectrometry in a few milliseconds after the formation, which generally makes it possible to handle compounds which are extremely sensitive to catalyzed prototropic isomerization.[5d,9] Dienols (E)-**1** and (Z)-**1** were characterized by their 75-eV electron-impact mass spectra and by collision-induced decomposition (CID) spectra[10] of stable molecular ions $[(E)\text{-}\mathbf{1}]^{\cdot+}$ and $[(Z)\text{-}\mathbf{1}]^{\cdot+}$ (Table I).

The EI mass spectra of (E)-**1** and (Z)-**1** are closely similar, although minor but reproducible differences in the relative abundance of $[M - H]^+$, $[M - H_2O]^{\cdot+}$, ($C_2H_5^+$ + CHO^+), $C_2H_3^+$, and CH_3^+ are observed. These differences are, however, insufficient to safely distinguish the geometrical isomers. Our assignment of the molecular geometry is therefore based on the known stereospecificity of the retro-Diels–Alder reaction[11] and on the estimate that a thermal E–Z isomerization of the products would require additional 200–250 kJ·mol^{-1} to proceed,[12] which is beyond the energy transfer limits of the pyrolyzer.

Low-level ab initio calculations[3] predict even a higher barrier (482–577 kJ·mol^{-1}) for the unimolecular E–Z isomerization. The EI mass spectra of (E)-**1** and (Z)-**1** bear some similarity with that of (E)-2-butenal but not that of (Z)-2-butenal.[13]

The CID spectra of $[(E)\text{-}\mathbf{1}]^{\cdot+}$ and $[(Z)\text{-}\mathbf{1}]^{\cdot+}$ are identical within the reproducibility limits, and closely correspond to the CID spectrum of $[C_4H_6O]^{\cdot+}$ prepared from 6,6-dimethylcyclohex-2-en-1-ol, to which a structure of $[\mathbf{1}]^{\cdot+}$ (geometry unspecified) was assigned by Holmes and coworkers.[14] We prepared alternatively the cation radicals $[(E)\text{-}\mathbf{1}]^{\cdot+}$ and $[(Z)\text{-}\mathbf{1}]^{\cdot+}$ by dissociative ionization of the norbornene precursors **4** and **5**, respectively, and characterized them through CID spectra which again corresponded to that of the standard.[14] It should be noted that the CID spectra of the dienols prepared either way differed significantly from that of $[(E)\text{-}\mathbf{2}]^{\cdot+}$.[14] Nevertheless, since the differences were only quantitative, a small fraction of aldehyde ions accompanying the dienols cannot be excluded on the basis of the CID spectra alone. The CID spectra of $[(E)\text{-}\mathbf{1}]^{\cdot+}$ generated from **4** at 70, 20, and 15 eV showed no change in the relative intensities of structurally significant fragments at m/z 68, 55, 51, 50, 37, 27, and 26, implying that the dienol ion did not contain a large amount of another isomer.

The purity of the neutral dienols (E)-**1** and (Z)-**1** was further checked by examining the deconvoluted ionization efficiency curves[15] of the molecular ions (vide infra). There is a detectable break at ca. 9.7 eV on the curves of both isomers, which indicates the presence of **2** (IE = 9.75 eV),[16] coformed by pyrolysis or surface-catalyzed isomerization of the dienols. From the change of the slope of the ionization efficiency curves after the break and from the CID spectra, we estimate that the content of **2** in (E)-**1** and (Z)-**1** does not exceed 10–15%.

Thermochemistry. Thermochemical data of unstable enols can be determined from the threshold ionization energies (IE) of the neutral compounds and the heats of formation of the corresponding cation radicals.[17] The latter values can be obtained from the appearance energies (AE) of ionized enols, prepared by dissociative ionization of suitable stable precursors.[18] For (E)-**1** eq 1 holds, where

$$\Delta H_f^\circ((E)\text{-}\mathbf{1}) = \Delta H_f^\circ[(E)\text{-}\mathbf{1}]^{\cdot+} - \mathrm{IE}((E)\text{-}\mathbf{1})$$

$$\Delta H_f^\circ([(E)\text{-}\mathbf{1}]^{\cdot+}) = \Delta H_f^\circ(\mathbf{4}) + \mathrm{AE}([(E)\text{-}\mathbf{1}]^{\cdot+}) - \Delta H_f^\circ(C_5H_6) - E_{\mathrm{exc}} - E_{\mathrm{rev}} \quad (1)$$

E_{exc} is the "nonfixed" energy in the transition state[19] and E_{rev} is the activation energy of the reverse reaction that determines the inherent energy excess above the thermochemical threshold given by the ΔH_f° of the products. These terms are small for the retro-Diels–Alder fragmentation of $[\mathbf{4}]^{\cdot+}$ and $[\mathbf{5}]^{\cdot+}$, as discussed previously.[7]

The AE($[(E)\text{-}\mathbf{1}]^{\cdot+}$) from **4** was measured as 9.00 ± 0.05 eV,[7] while the formation of $[(Z)\text{-}\mathbf{1}]^{\cdot+}$ from **5** required 8.95 ± 0.06 eV. The ionization energies of the neutral dienols were measured as IE((E)-**1**) = 8.51 ± 0.03 eV and IE((Z)-**1**) = 8.47 ± 0.03 eV. The heat of formation of **4** and **5** was estimated as +1 kJ·mol^{-1} on the basis of Benson's rules, after having made correction for the ring strain, based on the revised ΔH_f° of norbornene.[20] Implementing $\Delta H_f^\circ(C_5H_6)$ = 136 kJ·mol^{-1},[5] we obtain $\Delta H_f^\circ{}_{298}([(E)\text{-}\mathbf{1}]^{\cdot+})$ = 733 ± 5 kJ·mol^{-1} and $\Delta H_f^\circ{}_{298}([(Z)\text{-}\mathbf{1}]^{\cdot+})$ = 728 ± 6 kJ·mol^{-1}, in good agreement with the value estimated by Holmes et al. (736 kJ·mol^{-1})[14] from group increments. For the heats of formation of the neutral dienols it follows $\Delta H_f^\circ{}_{298}((E)\text{-}\mathbf{1})$ = −88 ± 8 kJ·mol^{-1} and $\Delta H_f^\circ{}_{298}((Z)\text{-}\mathbf{1})$ = −90 ± 9 kJ·mol^{-1}. This shows that both dienols are less stable than (E)-**2** ($\Delta H_f^\circ{}_{298}$ = −107 kJ·mol^{-1}).[4] Hence the destabilization of the dienol system against the conjugated aldehyde (17–19 kJ·mol^{-1}) is comparable to that in a nonconjugated system prop-1-en-1-ol–propanal (17–22 kJ·mol^{-1}).[5e]

Although 3-butenal (**3**) is unknown owing to its facile isomerization to the more stable isomer **2**, its heat of formation can be estimated from standard group equivalents[4] as $\Delta H_f^\circ{}_{298}$ = −80 kJ·mol^{-1}. This probably represents a lower limit, since the additivity scheme tends to slightly overstabilize aliphatic aldehydes.[4] Dienols (E)-**1** and (Z)-**1** are therefore found to be more stable than the nonconjugated aldehyde **3**.

MNDO Calculations. The experimental ΔH_f° of (E)-**1** and (Z)-**1** were further compared with the values calculated by the MNDO method[21] for the corresponding anti,anti rotamers. The calculated $\Delta H_f^\circ{}_{298}((E)\text{-}\mathbf{1})$ = −89 kJ·mol^{-1} is lower than that of the Z isomer (−87 kJ·mol^{-1}), while both values are in excellent though perhaps fortuitous agreement with the experimental ones. It should be noted, however, that MNDO gives generally ΔH_f° values for simple enols that are in good agreement with the experimental data, the standard deviation being less than 6 kJ·mol^{-1}.[22] Substantially poorer results have been ob-

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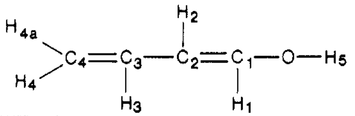
Table II. Bond Lengths and Angles in (*E*)-1 and (*Z*)-1



bond	(*E*)-1	(*Z*)-1
	Bond Lengths, nm	
C-1–O	0.136	0.136
C-1–C-2	0.136	0.136
C-2–C-3	0.146	0.146
C-3–C-4	0.135	0.135
C-1–H-1	0.110	0.110
C-2–H-2	0.109	0.109
C-3–H-3	0.109	0.109
C-4–H-4	0.109	0.109
C-4–H-4a	0.109	0.109
O–H-5	0.095	0.095
	Bond Angles, deg	
O–C-1–C-2	120.3	122.9
C-1–C-2–C-3	123.9	128.3
C-2–C-3–C-4	125.3	125.5
H-5–O–C-1	111.6	111.5
H-4–C-4–C-3	122.2	122.1
H-4a–C-4–C-3	124.4	124.5
H-3–C-3–C-2	118.6	118.1
H-2–C-2–C-1	116.0	115.8
H-1–C-1–C-2	123.1	120.6

tained by using INDO or ab initio methods of STO-3G or 4-31G quality.[3]

Neither the experimental nor the theoretical data give a definite answer as to the relative thermochemical stability of (*E*)- and (*Z*)-1, though they indicate that the isomers do not differ much in their $\Delta H_f°$. The optimized geometrical parameters and charge distribution in (*E*)- and (*E*)-1 are given in Tables II and III. The MNDO bond lengths slightly differ from those calculated by INDO in that the former method gives longer C–C and C–O bonds and a shorter O–H bond. The charge distribution shows that the dienol system is much less polarized than calculated for simple enols.[23] The frontier molecular orbitals in (*E*)- and (*Z*)-1 are very much "butadiene-like", while the interaction between the diene π-system and the p_z orbital at oxygen is antibonding in the two highest occupied MO's and in LUMO.

Unimolecular Isomerization of (*Z*)-1 to (*Z*)-2. We have also addressed the question of thermal (singlet energy hypersurface) isomerization of (*Z*)-1 to (*Z*)-2. The corresponding saddle point on the reaction energy hypersurface was located by MNDO[24] at 236 kJ·mol^{-1} above *anti,-anti*-(*Z*)-1, i.e., 258 kJ·mol^{-1} above (*Z*)-2. The latter barrier compares well with the previous ab initio calculations.[3] The geometry of the transition state is depicted in Figure 1. The most striking feature is the asymmetrical twist of the terminal methylene group out of the plane defined by C-4–C-3–C-2, ϑ(C-4,H-4) = +56°, ϑ(C-4,H-4a) = −24°. The torsional angles about the C-2–C-3, C-1–C-2, and C-1–O bonds are smaller (−17, −7, and −11°, respectively). The migrating hydrogen atom approaches C-4 at almost right angle to the C-3–C-4 bond, φ(H···C-4–C-3) = 99° and closer to the more twisted endo hydrogen atom, H-4.

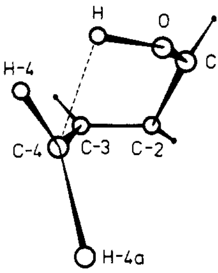


Figure 1. Stereoview of the transition state for the isomerization of (*Z*)-1 to (*Z*)-2.

The calculated activation energy for the conversion of (*Z*)-1 to (*Z*)-2 indicates that the unimolecular isomerization would require a very high temperature to proceed efficiently on the time scale of our experiment (ca. 10^{-3} s). Even under the most favorable conditions, e.g., complete thermalization of (*Z*)-1 in the oven, acceleration of the hydrogen transfer by tunneling (κ = 1.65 at 1023 K for the calculated imaginary vibrational frequency, $|\nu|$ = 2723 cm^{-1}), and neglect of the entropy decrease in the more ordered transition state, the calculated conversion of (*Z*)-1 to (*Z*)-2 is less than 3%. The unimolecular isomerization of (*E*)-1 is excluded because of the molecular geometry. It follows that the observed fraction of **2** (or **3**) arises by surface-catalyzed processes.

Fragmentation of [(*E*)- and (*Z*)-1]$^{•+}$. Following electron impact the molecular ions [(*E*)- and (*Z*)-1]$^{•+}$ decompose unimolecularly via several primary reactions, e.g., loss of a hydrogen atom, methyl radical, methane, water, and carbon monoxide. In the following we shall discuss the loss of hydrogen as the most abundant process for which a largest amount of data is available from labeling, product analysis, and energy measurements.

The loss of hydrogen dominates in the decompositions of metastable (lifetime ca. 10^{-5} s) cation radicals [1]$^{•+}$ that take place in the field-free regions of a mass spectrometer.[19] The fragmentation gives rise to a flat-top peak of large kinetic energy release, $T_{0.5}$ = 22.5 ± 0.8 kJ·mol^{-1}, which suggests a rearrangement preceding the hydrogen loss.[25] Deuterium labeling (compounds (*E*)- and (*Z*)-**1a**, (*E*)- and (*Z*)-**1b**) shows that the hydrogen atom eliminated comes primarily from C-1 (Table IV), with the regiospecificity decreasing at higher internal energies of [1]$^{•+}$. [The electron impact and CID spectra of the labeled compounds are available from the authors upon request.] The loss of the hydroxyl hydrogen atom from metastable [1]$^{•+}$ is negligible, while the ions decomposing in the ion source (lifetime less than 10^{-6} s) eliminate a significant fraction of the hydroxyl hydrogen. There is a small fraction of metastable [1]$^{•+}$ that eliminates hydrogen from C-2 through C-4 (Table IV), with the same $T_{0.5}$ (24.1 kJ·mol^{-1}) as for the loss of H-1 (vide supra). We assume that the loss of other skeletal hydrogen atoms does not proceed via a distinct mechanism but is the result of hydrogen migration in the diene subsystem that precedes the fragmentation. By comparison, ionized 1,3-butadiene undergoes complete scrambling of hydrogen atoms before decomposition.[26]

The $C_4H_5O^+$ ions, prepared by hydrogen loss from [1]$^{•+}$ or deuterium loss from [(*E*)- and (*Z*)-**1a**]$^{•+}$ were characterized through their CID spectra. The spectra (the CID spectra data of $C_4H_5O^+$ are available as supplementary material) were closely similar to those of $CH_3CH{=}CHCO^+$ generated from crotonyl precursors.[27] The kinetic energy release in the loss of carbon monoxide from metastable $C_4H_5O^+$ from [(*E*)- and (*Z*)-1]$^{•+}$ and [(*E*)- and (*Z*)-**1a**]$^{•+}$, $T_{0.5}$ = 2.4 kJ·mol^{-1}, agrees with that reported for metastable $CH_3CH{=}CHCO^+$ ($T_{0.5}$ = 2.8 kJ·mol^{-1}).[27]

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Table III. Charge Distribution in (*E*)-1 and (*Z*)-1[a]

	C-1	C-2	C-3	C-4	O	H-1	H-2	H-3	H-4	H-4a	H-5
(*E*)-1	0.069	−0.119	−0.064	−0.061	−0.257	0.054	0.068	0.042	0.036	0.042	0.190
(*Z*)-1	0.069	−0.116	−0.050	−0.071	−0.254	0.051	0.051	0.056	0.037	0.037	0.190

[a] MNDO net populations.

Table IV. Fractions of Loss of Hydrogen and Deuterium from [(*E*)- and (*Z*)-1a]$^{\bullet+}$ and [(*E*)- and (*Z*)-1b]$^{\bullet+}$[a]

	1a		1b	
spectrum	$(M - H)^+$	$(M - D)^+$	$(M - H)^+$	$(M - D)^+$
75-eV EI	31[a]	69	82	18
12–20-eV EI	19	81	91	9
metastables	16	84	99	1
CID	13	87	99	1

[a] Corrected for ^{13}C contributions (EI mass spectra) and normalized to the total intensity of $(M - (H,D))^+$.

The formation of $CH_3CH{=}CHCO^+$ from [(*E*)- and (*Z*)-**1a**]$^{\bullet+}$ necessitates a 1,5-sigmatropic shift of the hydroxyl hydrogen to form $[CH_3CH{=}CHCDO]^{\bullet+}$ as an intermediate. The overall barrier to the hydrogen loss was assessed from the appearance energy of $(M - D)^+$ ions from (*E*)-**1a**, AE = 10.45 ± 0.05 eV, which gives the energy of the transition state (E_{TS}) as being equal to or lower than 920 kJ·mol^{-1}, on the $\Delta H_f°$ scale and referred to the $\Delta H_f°$ of (*E*)-**1**. Since the fragmentation is accompanied by large kinetic energy release (vide supra), the transition state can be assumed to lie more than 23 kJ·mol^{-1} above the thermochemical threshold defined by $\Delta H_f°(CH_3CH{=}CHCO^+) + \Delta H_f°(D^\bullet)$. This gives 897 kJ·mol^{-1} for the latter, in reasonable agreement with the previously reported data, 909 kJ·mol^{-1} (from experiment)[27] and 912 kJ·mol^{-1} (from MNDO calculations).[28] The critical energy of the hydrogen loss, $E_c = E_{TS} - \Delta H_f°([(E)\text{-}\mathbf{1a}]^{\bullet+}) \leq 187$ kJ·mol^{-1}, can be ascribed unambiguously neither to the isomerization step nor to the final C–H bond cleavage, since both processes can exert nonthreshold barriers.[29,30] As the hydroxyl hydrogen atom is unaffected by the hydrogen scrambling within the diene system (vide supra), it appears probable that the 1,5-hydrogen shift is followed by rapid fragmentation, so the former step is rate-determining. The critical energy of the hydrogen loss from [(*E*)- and (*Z*)-**1**]$^{\bullet+}$ sets the upper limit for the barrier to the unimolecular 1,5-isomerization. Comparison of the thermal,[3] photochemical,[3] and electron-impact-induced reactions shows that the energy barrier to the 1,5-hydrogen shift in the 1-hydroxy-1,3-diene system is much lower in the open-shell species (cation radicals and triplet excited states) than in the closed-shell molecule.

Experimental Section

Electron-impact mass spectra were measured on a Jeol D-100 spectrometer (75 eV, 300 μA, 3 kV) furnished with a microoven located in the vicinity of the ionization chamber.[5c] The ionization and appearance energy measurements were carried out with 50 μA emission current and the repeller voltage set to 0.00 ± 0.01 V. Ion intensities were measured at slow scan rate (60 min/decade) with a data system in 50-meV steps from ca. 0.5 eV below the threshold up to 2–3 eV above it. The raw data were treated with the inverse convolution procedure,[15] and the resulting data were fitted with least-squares lines (IE) or polynoms (AE). The reported values are averages of at least three independent measurements which were reproducible over a period of several months. The CID spectra and the decompositions of metastable ions were monitored in the second field-free region of a VG Analytical ZAB-2F mass spectrometer. The CID spectra were measured with helium as collision gas at 40% attenuation of the primary ion beam. The metastable spectra were measured at background pressure lower than 10^{-8} torr. The $T_{0.5}$ values were obtained at medium-to-good energy resolution ($E/\Delta E$ = 2000–4000). The experimental peak half-widths were corrected for the energy spread of the main beam. ^1H NMR spectra were measured on a Varian XL-200 spectrometer (200.058 MHz, FT mode) in deuteriochloroform at 22 °C. The chemical shifts are given in the δ (ppm) scale.

Compounds **4** and **5** were described previously.[7] The labeled compounds (**4a**, **5a**) were prepared from 3-*exo*-vinylbicyclo[2.2.1]hept-5-en-2-one[7] by reduction with lithium aluminum deuteride in ether, separated by column chromatography (silica gel, elution with 3:1 pentane–ether), and purified by distillation in vacuo. **4a**: (yield 66%) ^1H NMR 6.16 (dddd, J = 5.7, 2.9, 0.6, 0.6 Hz, 1 H), 6.52 (dddd, J = 5.7, 3.2, 0.7, 0.4 Hz, 1 H), 5.88 (ddd, J = 17.2, 10.2, 7.8 Hz, 1 H), 5.11 (ddd, J = 17.2, 1.8, 1.1 Hz, 1 H), 5.04 (ddd, J = 10.2, 1.8, 1.0 Hz, 1 H), 2.97 (m, W = 8 Hz, 1 H), 2.65 (m, W = 8 Hz, 1 H), 1.72 (dm, J_d = 7.8 Hz, W_m = 5 Hz, 1 H), 1.57, 1.50 (AB(m), J_{AB} = 9.2 Hz, 2 H), 1.32 (br s, OH). **5a**: (yield 16%) ^1H NMR 6.25 (dddd, J = 6.0, 3.0, 0.7, 0.4 Hz, 1 H), 6.04 (dddd, J = 6.0, 3.2, 0.6, 0.4 Hz, 1 H), 5.77 (ddd, J = 17.0, 10.4, 8.8 Hz, 1 H), 5.22 (ddd, J = 17.0, 2.2, 1.0 Hz, 1 H), 5.15 (ddd, J = 10.4, 2.2, 0.7 Hz, 1 H), 2.79 (m, W = 8 Hz, 1 H), 2.63 (m, W = 8 Hz, 1 H), 2.31 (br d, J_d = 8.8 Hz, 1 H), 1.90 (dm, J_d = 8.9 Hz, 1 H), 1.63 (br s, OH), 1.55 (ddd, J = 8.9, 3.4, 1.8 Hz, 1 H).

Compounds **4b** and **5b** were prepared by hydrogen–deuterium exchange with methanol-*O*-*d* directly in the inlet system of the pyrolyzer. The ion source and the pyrolyzer were conditioned with deuterium oxide at 10^{-5} torr for 2 h before sampling **4b** and **5b**.

Registry No. (*E*)-1, 70411-98-2; (*Z*)-1, 70415-58-6; (*E*)-1$^{\bullet+}$, 104013-06-1; (*Z*)-1$^{\bullet+}$, 104013-07-2; **4**, 104013-08-3; **5**, 104013-09-4.

Supplementary Material Available: Table of electron impact mass spectral data of (*E*)- and (*Z*)-**1a** and (*E*)- and (*Z*)-**1b** and CID spectral data of [(*E*,*Z*)-**1a**]$^{\bullet+}$ and [(*E*,*Z*)-**1b**]$^{\bullet+}$ and table of CID spectral data of $C_4H_5O^+$ (3 pages). Ordering information is given on any current masthead page.

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