Chem. Biochem., **27**, 227 (1972).
(13) See, e.g., (a) M. Christl, H. J. Reich, and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 3463 (1971); (b) A. S. Perlin, N. Cyr, H. J. Koch, and B. Korsch, *Ann. N.Y. Acad. Sci.*, **222**, 935 (1973); (c) T. Usui, S. Tsushima, N. Yamaoka, K. Matsuda, K. Tuzimura, H. Sugiyama, S. Seto, K. Fujieda, and G. Miyajima, *Agric. Biol. Chem.*, **38**, 1409 (1974); (d) H. Sugiyama, N. Yamaoka, B. Shimizu, Y. Ishido, and S. Seto, *Bull. Chem. Soc. Jpn.*, **47**, 1815 (1974).
(14) See, e.g., (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972.
(15) P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **115**, 731 (1936).
(16) The NMR spectrum of **6b** showed it to contain 90% of the β isomer since, in Me$_2$SO-d_6, C$_1$H appeared as a doublet at 5.14 ppm which collapsed to a singlet upon adding D$_2$O.
(17) A. W. Johnson in "Ylid Chemistry", Academic Press, New York, N.Y., 1966, p 66.
(18) O. T. Schmidt, *Methods Carbohydr. Chem.*, **2**, 318 (1963).
(19) (a) J. D. Stevens and H. G. Fletcher, *J. Org. Chem.*, **33**, 1799 (1968); (b) R. L. Tolman, R. K. Robins, and L. B. Townsend, *J. Heterocycl. Chem.*, **4**, 230 (1967).
(20) J. M. Ballard and B. E. Stacey, *Carbohydr. Res.*, **12**, 37 (1970).
(21) We have discussed this matter with Dr. J. J. Fox of the Sloan-Kettering Institute for Cancer Research, who has examined our data and is in agreement with our conclusions. We are most thankful to Dr. Fox for his gracious cooperation.
(22) (a) L. M. Lerner and P. Kohn, *J. Org. Chem.*, **31**, 339 (1966); (b) J. B. Lee and T. J. Nolan, *Tetrahedron*, **23**, 2789 (1967).
(23) N. A. Hughes and P. R. H. Speakman, *J. Chem. Soc. C*, 1182 (1967).
(24) L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy for Organic Chemistry", 2nd ed, Pergamon Press, New York, N.Y., 1969, p 302.
(25) For useful references, see J. F. Stoddart, "Stereochemistry of Carbohydrates", Wiley-Interscience, New York, N.Y., 1971, Chapter 5.
(26) A. S. Perlin, *Can. J. Chem.*, **44**, 539 (1966).
(27) S. J. Angyal, *Angew. Chem., Int. Ed. Engl.*, **8**, 157 (1969).
(28) W. N. Haworth, L. N. Owen, and F. Smith, *J. Chem. Soc.*, 88 (1941).
(29) G. R. Barker, T. M. Noone, D. C. C. Smith, and J. W. Spoors, *J. Chem. Soc.*, 1327 (1955).
(30) R. S. Ranganathan, G. H. Jones, and J. G. Moffatt, *J. Org. Chem.*, **39**, 290 (1974).
(31) J. Kovár and H. H. Baer, *Can. J. Chem.*, **49**, 3203 (1971).
(32) (a) J. M. J. Tronchet and J. M. Bourgeois, *Helv. Chim. Acta*, **53**, 1463 (1970); (b) *Carbohydr. Res.*, **29**, 373 (1973).
(33) D. M. Brown and G. H. Jones, *J. Chem. Soc. C*, 249 (1967).
(34) (a) J. L. Imbach, J. L. Barascut, B. L. Kam, and C. Tapiero, *Tetrahedron Lett.*, 129 (1974); (b) B. Rayner, C. Tapiero, and J. L. Imbach, *J. Heterocycl. Chem.*, **10**, 417 (1973).
(35) For references, see L. B. Townsend, *Synth. Proced. Nucleic Acid Chem.*, **2**, 333 (1973).
(36) C. S. Hudson, *J. Chem. Educ.*, **18**, 353 (1941).
(37) T. B. Grindley and W. A. Szarek, *Carbohydr. Res.*, **25**, 187 (1972).
(38) S. J. Angyal, V. A. Pickles, and R. Ahluwalia, *Carbohydr. Res.*, **3**, 300 (1967).
(39) N. J. Cusack, B. J. Hildick, D. H. Robinson, P. W. Rugg, and G. Shaw, *J. Chem. Soc., Perkin Trans. 1*, 1720 (1973).
(40) M. Kawana and S. Emoto, *Bull. Chem. Soc., Jpn.*, **42**, 3539 (1969).
(41) P. Kohn, L. M. Lerner, and B. D. Kohn, *J. Org. Chem.*, **32**, 4076 (1967).
(42) See, e.g., (a) J. A. Mills, *Adv. Carbohydr. Chem.*, **10**, 1 (1955); (b) R. J. Ferrier and W. G. Overend, *Q. Rev., Chem. Soc.*, **13**, 265 (1959).
(43) W. E. Willy, G. Binsch, and E. L. Eliel, *J. Am. Chem. Soc.*, **92**, 5394 (1970).
(44) See, e.g., ref 25, Chapter 3, and references therein.
(45) Abstracts of the VII International Symposium on Carbohydrate Chemistry, Bratislava, Czechoslovakia, August 1974, pp 38, 73.
(46) D. Cromer and J. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

The Structure and Formation of Stable $C_2H_4O\cdot^+$ Ions[1]

C. C. Van de Sande[2] and F. W. McLafferty*

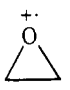
Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received September 10, 1974*

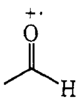
Abstract: The $C_2H_4O\cdot^+$ isomeric ions $\overline{CH_2CH_2O}\cdot^+$ (a), $CH_3CH{=}O\cdot^+$ (b), and $CH_2{=}CHOH\cdot^+$ (c) are stable, with lifetimes of $>10^{-5}$ sec, and can be identified from their collisional activation (CA) spectra. The earlier assignments of structure c for $C_2H_4O\cdot^+$ ions generated from cyclic alcohols, alkyl vinyl ethers, and aliphatic epoxides are confirmed. Surprisingly, 2-haloethanols yield c through 1,2 elimination of HX. Ions c are also produced from glycerol and 1,4-butanediol. Both ions b and c are produced from 1,3-butanediol, and a and c are generated from 1,3-dioxolane.

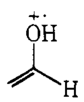
Our knowledge of the formation and unimolecular decompositions of gaseous positive ions has been greatly enhanced by the development of new techniques for ion structure determination such as ion cyclotron resonance,[3] unimolecular metastable ion (MI),[4] and collisional activation (CA)[5] spectra. The latter appear to be especially advantageous, because they are insensitive to differences in ion internal energy, and because the substantial number of peaks in their spectra provide specificity for ion characterization.

Studies on $C_2H_5O^+$,[4a,5b] $C_3H_7O^+$,[5c] $C_2H_6N^+$, and $C_3H_8N^+$ [5d] ions indicate that structural inferences are particularly straightforward for even-electron ions containing a heteroatom; the isomers found to be stable (lifetimes $\geq 10^{-5}$ sec) are generally those predicted from physical organic principles. This observation prompted us to extend our investigations to odd-electron species; although these would be expected to be of lower stability,[6] the odd-electron $C_3H_6O\cdot^+$ ions corresponding to the keto and enol forms of acetone have been shown to be stable.[3b,7] In the present paper, the results of a CA study on $C_2H_4O\cdot^+$ ions (*m/e* 44) are presented. These ions are of considerable interest as they are important rearrangement products in the mass spectra of aliphatic aldehydes, cyclic alcohols, alkyl vinyl ethers, aliphatic epoxides, functionalized alcohols, and cyclic ethers.[6]

Based on ground-state chemistry, structures a, b, and c can be visualized for $C_2H_4O\cdot^+$ ions. In a recent independent


a


b


c

study of the molecular ions a and b, Pritchard[8] reviews the inconclusive nature of the previous structural investigations of these ions and reports MI spectral data that "reveal no reason to suppose" that a isomerizes to b, in contrast to previous postulates based on the similarity of their mass spectra. The reported[8] facile tautomerization b $\rightleftarrows$ c also is in contrast to the conclusions concerning the analogous $C_3H_6O\cdot^+$ ions.[3b,7]

Results and Discussion

Reference Ions. The CA spectra of $C_2H_4O\cdot^+$ ions from a variety of sources are given in Table I. Ions of structures a and b have been generated through ionization of ethylene

Table I. Collisional Activation Spectra of $C_2H_4O\cdot^+$ Ions

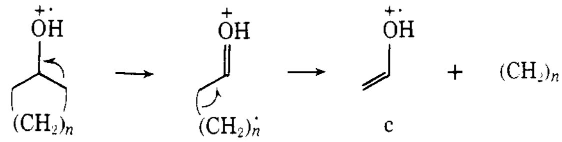
Compd	Electron energy, eV	13	14	15	16	25	26	27	28	29	30	31	40	41	42	43	Ion structure
		m/e of daughter ion[a]															
CH_2CH_2O	70	3.0	15	25	(9.3)	1.3	2.4	2.7	(11)	(242)	9.7	2.6	1.0	4.1	33	(137)	
	15	4.7	16	25	(6.4)	1.1	2.3	4.4	(11)	(282)	8.8	1.1	0.8	2.7	33	(104)	a
CH_3CHO	70	2.7	9.3	22	(3.1)	3.5	9.0	5.6	(16)	(119)	<0.2	<0.2	2.4	11	35	(516)	
	20	3.1	8.8	24	(2.8)	2.4	9.4	5.7	(13)	(110)	<0.2	<0.2	1.9	11	33	(631)	b
$CH_3(CH_2)_2CHO$	70	0.7	3.9	11	(0.3)	2.8	9.6	13	(2.8)	(22)	4.7	<0.5	1.8	5.6	47	(223)	
	20	1.6	5.2	14	(0.7)	3.1	11	13	(3.1)	(24)	3.9	<0.5	2.2	4.4	42	(207)	c
$CH_3(CH_2)_3CHO$	70	1.3	4.7	13	(0.6)	3.3	12	14	(2.3)	(26)	4.0	<0.5	1.2	6.3	41	(172)	c
$(CH_3)_2CHCH_2CHO$	70	0.9	4.2	12	(0.9)	3.0	11	13	(3.0)	(24)	4.5	<0.5	1.8	5.4	44	(236)	c
$CH_3(CH_2)_6CHO$[b]	70	1.1	4.3	12	(0.8)	3.0	10	13	(5.8)	(23)	4.0	<0.5	3.1	5.9	43	(159)	c
Cyclobutanol	70	0.9	4.4	13	(0.6)	3.3	10	12	(1.8)	(25)	4.2	0.5	0.6	5.3	46	(244)	c
Cyclopentanol	70	1.1	4.1	13	(0.6)	3.4	10	13	(2.3)	(25)	4.0	0.5	1.1	5.3	45	(199)	c
Cyclohexanol	70	1.0	5.0	11	(0.3)	3.7	9.7	13	(3.2)	(23)	4.2	0.5	1.5	5.0	46	(238)	c
Ethyl vinyl ether	70	1.2	4.3	13	(0.6)	2.8	11	12	(2.2)	(26)	3.7	0.5	0.9	6.8	45	(322)	c
Isopropyl vinyl ether	70	1.0	4.1	11	(0.4)	2.1	8.4	13	(3.0)	(22)	2.9	0.5	3.1	5.5	49	(228)	c
n-Butyl vinyl ether	70	1.3	5.6	12	(0.7)	4.1	10	13	(2.9)	(24)	4.9	0.5	1.2	5.4	42	(252)	c
Isobutyl vinyl ether	70	1.1	4.9	11	(0.6)	2.0	9.8	12	(3.1)	(27)	4.2	0.5	3.0	5.7	46	(306)	c
2-Chloroethyl vinyl ether	70	1.3	5.2	14	(0.7)	3.5	12	14	(2.3)	(26)	3.7	0.5	1.0	6.4	40	(247)	c
2-Methoxyethyl vinyl ether	70	2.0	5.8	12	(3.4)	2.9	9.7	11	(6.8)	(57)	2.2	0.5	1.1	7.6	45	(441)	c
1,2-Epoxybutane	70	1.0	5.1	12	(3.3)	2.0	8.4	11	(9.0)	(58)	2.1	0.5	3.2	7.8	47	(192)	c
1,2-Epoxypentane	70	1.5	6.3	12	(2.1)	2.7	8.4	11	(5.5)	(55)	4.4	0.5	3.0	5.5	44	(224)	c
1,2-Epoxyhexane	70	1.3	3.9	13	(5.8)	2.4	9.5	14	(36)	(39)	3.4	0.5	3.5	6.1	43	(172)	c
1,2-Epoxyoctane	70	1.1	3.8	11	(3.7)	2.9	9.4	13	(26)	(33)	4.8	0.5	1.2	5.5	47	(168)	c
2,3-Epoxybutane	70	1.2	4.7	14	(0.8)	2.8	10	14	(1.7)	(29)	3.3	0.5	1.1	5.3	44	(262)	c
2-Chloroethanol	70	1.2	4.6	12	(0.8)	3.4	12	14	(2.6)	(26)	4.1	0.5	1.0	6.3	42	(174)	c
2-Bromoethanol	70	1.3	3.6	11	(0.7)	4.0	11	13	(2.7)	(25)	5.1	0.5	1.1	6.7	44	(155)	c
2-Iodoethanol	70	1.3	4.2	12	(1.8)	2.5	9.7	12	(3.0)	(25)	4.1	0.5	0.9	6.8	46	(264)	c
Glycerol	70	1.2	4.0	13	(1.2)	3.4	10	13	(2.7)	(24)	4.9	0.5	0.6	5.2	45	(215)	c
1,4-Butanediol	70	1.1	4.4	13	(0.7)	2.2	11	13	(1.7)	(27)	5.1	0.5	0.9	6.0	43	(415)	c
1,3-Butanediol	70	1.7	5.7	15	(1.8)	3.2	8.3	9.2	(7.1)	(64)	2.0	0.5	2.2	7.3	45	(572)	1b:1c
	20	1.4	6.2	14	(1.2)	2.8	7.4	8.5	(6.4)	(81)	2.5	0.2	1.5	7.4	48	(917)	1b:3c
1,3-Dioxolane	70	2.1	15	19	(7.1)	1.0	3.2	4.8	(11)	(190)	9.6	2.3	1.2	3.4	39	(147)	5a:1c
	20	3.1	13	21	(4.6)	1.4	4.3	5.4	(7.7)	(178)	6.6	0.9	0.6	4.0	39		2a:1c

[a] Abundances relative to the total ion abundance = 100 excluding *m/e* 29 and 43 (MI contributions in some compounds) and *m/e* 16 and 28 (interference from $CO_2\cdot^+$background). [b] The spectra of *n*-hexanal and *n*-heptanal are identical with this spectrum within experimental error, except that *m/e* 43 is 208 and 199, respectively.

oxide and acetaldehyde, respectively. In both instances, a single species is produced as evidenced by the identity of the 70 eV and low electron energy CA spectra. The CA spectra are significantly different and consistent with the structures of the precursors: a, which contains a $-CH_2O-$ structural unit, gives a larger *m/e* 30 peak; b, which contains a labile hydrogen atom, gives a larger *m/e* 43 peak. Although the CA data thus support the indications from MI spectra[8] concerning a and b, this is not true of c. These ions should be generated through rearrangement from aliphatic aldehydes without α branching.[6,9] The six aldehydes studied do indeed yield the same CA spectrum, which is different than those from a and b. The enolic structure of c is reflected in the enhanced formation of *m/e* 27 (loss of a hydroxyl radical) and the lower intensity of *m/e* 15 (double bond to CH_2 in contrast to a and b). Thus these three isomers of the odd-electron ion have lifetimes $>10^{-5}$ sec and should be distinguishable on the basis of their CA spectra.

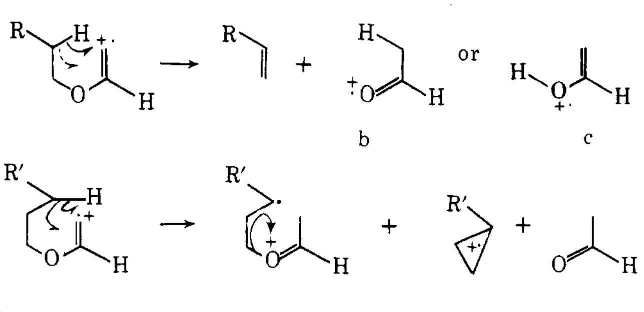
Cyclic Alcohols. Abundant $C_2H_4O\cdot^+$ ions are a useful characteristic of the mass spectra of lower cyclic alcohols.[10,11] Studies on labeled cycloalkanols[11] showed that the $C_2H_4O\cdot^+$ ion contains the hydroxyl carbon and one of the adjacent carbon atoms with retention of the original hydrogens; the postulated formation of the vinyl alcohol structure c (Scheme I) is confirmed by the CA data on the lower cycloalkanols.

Scheme I

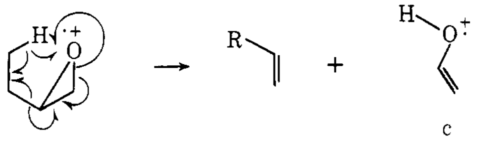


Alkyl Vinyl Ethers. For the structure of the $C_2H_4O\cdot^+$ ions in the mass spectra of these compounds, alternative mechanisms involving the formation of b through a six-membered ring intermediate,[12] and c through a four-membered ring,[13] have been proposed (Scheme II). Although both ostensibly require the migration of a β-hydrogen atom, labeling experiments show that the position of the hydrogen transferred in butyl vinyl ether is 10% α, 28% β, 41% γ, and 8% δ.[14] The CA spectrum[15] of the $C_4H_8\cdot^+$ base peak, the complementary ion product, indicates that a substantial

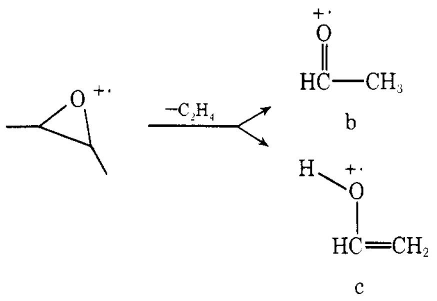
Scheme II



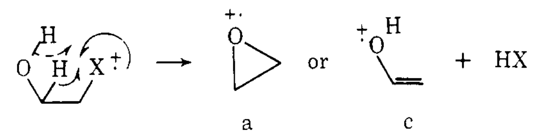
Scheme III



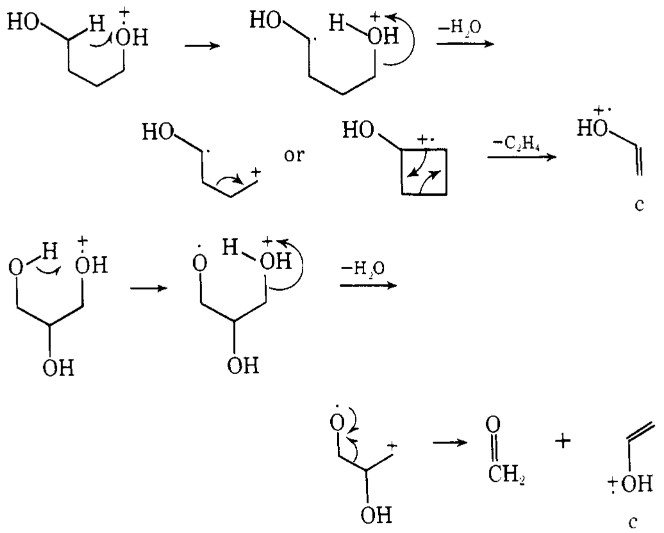
Scheme IV



Scheme V



Scheme VI



proportion of these ions have the methylcyclopropane structure, suggesting a γ-hydrogen transfer; a mechanism involving a seven-membered ring intermediate with acetaldehyde formation (Scheme II) is consistent with the γ-H transfer found to be involved in the major pathway for methyl loss.[14] The CA data show that the $C_2H_4O\cdot^+$ ions from six vinyl alkyl ethers have the vinyl alcohol structure c, even those for which γ-H transfer is possible. It appears that the low stability of b (ionization potential for the formation of b, 10.2 eV; c, 9.5 eV) minimizes its formation even in competition with ionized methylcyclopropane (ionization potential 10.1 eV).[16]

Aliphatic Epoxides. An extensive study[17] of the mass spectral behavior of these compounds utilizing deuterium labeling led to the proposal that $C_2H_4O\cdot^+$ ions are formed from unbranched terminal epoxides through the mechanism of Scheme III. The CA spectra of the four terminal epoxides are consistent only with the vinyl alcohol structure c, clearly confirming this postulate.

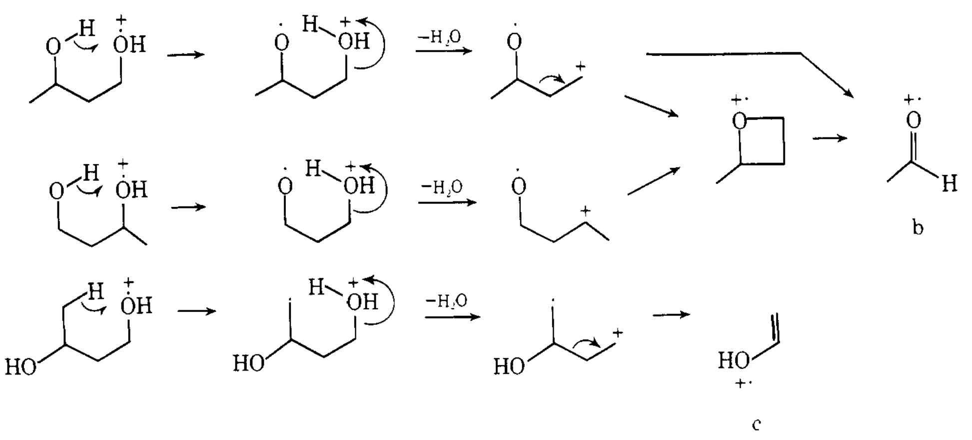
Epoxides also exhibit transannular cleavages[17] for which product structures have not previously been defined. On a simplistic basis (Scheme IV), a less extensive rearrangement is required to form the aldehyde structure b. However, in the case of 2,3-epoxybutane, the enolic ions c are the sole reaction product. Labeling evidence is obviously required to elucidate the mechanism more fully.

2-Haloethanols. In an attempt to find a decomposition yielding the ethylene oxide ion (a), the compounds XCH_2CH_2OH (X = Cl, Br, I) were included in our study. The observations that alkyl halides expel HX through a 1,3 mechanism and that the transfer of a hydroxylic hydrogen atom is generally favored in rearrangements[6] would favor the formation of a (Scheme V).[18] However, the CA spectra of the $C_2H_4\cdot^+$ ions from all three precursors show that only c ions are formed. The stability of ethylene oxide ions demonstrated above rules out the possibility that a major portion of the c ions are generated by isomerization of initially formed a ions. A 1,2 elimination of HX appears[19] to be the only plausible alternative. Perhaps the critical difference in the pathways for formation of a and c is that the former should have a tight activated complex involving fused three- and four-membered rings.

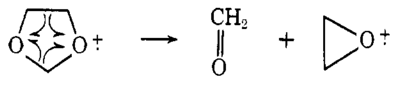
Aliphatic Polyols. Neither 1,2 nor 1,3 elimination is appreciable for 1,2-ethanediol (Scheme V, X = OH); $C_2H_4O\cdot^+$ is of <1% abundance in its mass spectrum. However, relatively intense *m/e* 44 peaks occur in the mass spectra of 1,4-butanediol and glycerol, and CA spectra demonstrate the enolic nature of these $C_2H_4O\cdot^+$ ions. Expulsion of water from alcohol molecular ions predominantly occurs by a 1,4 mechanism.[6] This can provide a rationale for the first step in $C_2H_4O\cdot^+$ formation in these compounds (Scheme VI), but the proposed fragmentation pathways are obviously speculative in the absence of labeling evidence.

Formation of a and b Ions. However, c ions are not com-

Scheme VII



Scheme VIII



a

pletely ubiquitous as mass spectral products; the CA spectrum of $C_2H_4O\cdot^+$ ions produced from a similar compound, 1,3-butanediol, shows the presence of a second isomer. The intensity of the CA peak at *m/e* 30 indicates that approximately half of the ions have the acetaldehyde structure b, this proportion decreasing at lower electron energies. Both species could be generated through 1,4 elimination of water (Scheme VII) between the two hydroxyl functions for b, and between the terminal hydroxyl function and the methyl group for c. However, the latter process can only give rise to part of the c ions, as 1,3-butanediol-*O,O*-d_2 largely (85%) loses D_2O; isomerization of b is a possible alternative pathway. Unfortunately, homologs such as 2,4-pentanediol give very small *m/e* 44 peaks.

Finally, it was found that the decomposition of 1,3-dioxolane yields the ethylene oxide ion (a) along with a minor amount of the c ions, although again the proportion of c increases at low electron energies. The mechanism of Scheme VIII involving elimination of formaldehyde is supported by the observation that 2- and 4-methyl-1,3-dioxolane produce $C_3H_6O\cdot^+$ ions in only the propylene oxide structure.[20]

Experimental Section

Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer in which the positions of ion source and electron multiplier were interchanged as described previously.[21] An ion accelerating potential of 3.9 kV, ionizing electrons of 100 μA and 70 eV (or lower where noted), and a sample reservoir and source temperature of 150° were used. MI spectra of the precursor ions selected by the magnetic field decomposing in the field-free drift region between the magnetic and electrostatic (ESA) analyzers are measured by scanning the ESA potential. The pressure in the field-free drift region between the magnet and ESA is then increased with helium until the precursor ion intensity is reduced to 10% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan.[5] The data are the computer-averaged composites of at least 16 separate scans. The contributions from MI products (corrected as described[5]) are subtracted from these values to obtain the CA spectrum.

Samples. Deuteriated 1,3-butanediol (78% d_2, 17.5% d_1) was prepared by exchange with D_2O in the spectrometer inlet system. All other compounds were obtained from commercial sources, checked for purity by mass spectrometry, and purified by gas chromatography where necessary.

Acknowledgment. We are grateful to the Army Research Office, Durham, and to the National Institutes of Health for generous financial support.

References and Notes

(1) Metastable Ion Characteristics. XXXV. Part XXXIV: N. M. M. Nibbering, C. C. Van de Sande, T. Nishishita, and F. W. McLafferty, *Org. Mass Spectrom.*, **9**, 1059 (1974).

(2) Postdoctoral Fellow, 1974; on leave from the NFWO, Belgium.

(3) (a) J. L. Beauchamp and R. C. Dunbar, *J. Am. Chem. Soc.*, **92**, 1477 (1970); (b) G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **92**, 6205 (1970); (c) D. J. McAdoo, F. W. McLafferty, and P. F. Bente, III, *ibid.*, **94**, 2027 (1972).
(4) (a) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966); (b) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.
(5) (a) F. W. McLafferty, P. F. Bente, III, R. Kornfeld, S.-C. Tsai, and I. Howe, *J. Am. Chem. Soc.*, **95**, 2120 (1973); (b) F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente, III, S.-C. Tsai, and H. D. R. Schuddemage, *ibid.*, **95**, 3886 (1973); (c) F. W. McLafferty and I. Sakai, *Org. Mass Spectrom.*, **7**, 971 (1973); (d) K. Levsen and F. W. McLafferty, *J. Am. Chem. Soc.*, **96**, 139 (1974).
(6) F. W. McLafferty, "Interpretation of Mass Spectra", 2nd ed, W. A. Benjamin, Reading, Mass., 1973.
(7) F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfeld, *J. Am. Chem. Soc.*, **93**, 3720 (1971).
(8) J. G. Pritchard, *Org. Mass Spectrom.*, **8**, 103 (1974).
(9) J. A. Gilpin and F. W. McLafferty, *Anal. Chem.*, **29**, 990 (1957); R. J. Liedtke and C. Djerassi, *J. Am. Chem. Soc.*, **91**, 6814 (1969).
(10) P. Natalis, *Bull. Soc. R. Sci. Liege*, **31**, 790 (1962).
(11) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967, p 110.
(12) F. W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959).
(13) S. Meyerson and J. D. McCollum, *Adv. Anal. Chem. Instrum.*, **2**, 211 (1963); H. Audier, *Org. Mass Spectrom.*, **2**, 283 (1969).
(14) M. Katoh, D. A. Jaeger, and C. Djerassi, *J. Am. Chem. Soc.*, **94**, 3107 (1972).
(15) T. Nishishita and F. W. McLafferty, submitted for publication.
(16) H. E. Audier, *Org. Mass Spectrom.*, **2**, 283 (1969); G. G. Meisels, J. Y. Park, and B. G. Giessner, *J. Am. Chem. Soc.*, **92**, 254 (1974).
(17) P. Brown, J. Kossanyi, and C. Djerassi, *Tetrahedron, Suppl. 8*, Part I, 241 (1966).

(18) However, very recent work employing ion kinetic energy measurements indicates that the formation of $(M - HCl)\cdot^+$ from $CH_3CH_2CH_2Cl\cdot^+$ involves a 1,2 elimination, although the formation from 1- and 2-$C_4H_9Cl\cdot^+$ involves a 1,3 elimination: K. C. Kim, J. H. Beynon, and R. G. Cooks, *J. Chem. Phys.*, **61**, 1305 (1974).

(19) The mass spectra of $ClCH_2CH_2OD$ and $BrCH_2CH_2OD$ also rule out the 1,3 elimination of HX: C. C. Van de Sande and F. W. McLafferty, submitted for publication.

(20) C. C. Van de Sande and F. W. McLafferty, *J. Am. Chem. Soc.*, the following paper in this issue.
(21) T. Wachs, P. F. Bente, III, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 333 (1972).