# The Structure and Formation of Stable $C_3H_6O\cdot^+$ Ions[1]

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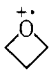
**Abstract:** The $C_3H_6O\cdot^+$ isomeric ions $\overline{CH_2CH(CH_3)O}\cdot^+$ (a), $\overline{CH_2CH_2CH_2O}\cdot^+$ (b), $CH_2{=}CHOCH_3\cdot^+$ (c), $C_2H_5CHO\cdot^+$ (d), $CH_3CH{=}CHOH\cdot^+$ (e), $CH_3COCH_3\cdot^+$ (f), and $CH_2{=}CH(OH)CH_3\cdot^+$ (g) are stable, with lifetimes $>10^{-5}$ sec, and can be identified from their collisional activation (CA) spectra. The molecular ion of allyl alcohol does not retain its original structure $CH_2{=}CHCH_2OH\cdot^+$ (h) but rearranges completely to ion e within $10^{-5}$ sec. Contrary to previous conclusions, aliphatic terminal epoxides give a mixture of ions a and c, suggesting that the rearrangements involved are stepwise, not concerted. The $C_3H_6O\cdot^+$ ions formed by the loss of $CH_2O$ from the 2-methyl- and 4-methyl-1,3-dioxolane molecular ions have the propylene oxide structure a; in a similar manner, 1,4-dioxane yields the cyclic ion b. The expected ion c is generated from compounds $CH_3OCH_2CH_2Y$ if Y = $OCH{=}CH_2$, OAc or $OCOCH{=}CH_2$; for Y = OH, however, both 1,2 and 1,4 elimination of water occur, giving rise to a mixture of ions b and c. Ions e are produced from 2-methyl-1,4-butanediol, ethyl propenyl ether, allyl ethers, and allyl acetate. Compounds $HOCH_2CH_2CH_2Y$ produce a mixture of ions b and e through loss of HY if Y = Cl, Br, or OH; for Y = $OCH_3$, however, only e was found. The results show that the size of the cyclic transition state in hydrogen rearrangements is sensitive to a number of competing factors.

In a previous study,[3] the structures of $C_2H_4O\cdot^+$ ions ($m/e$ 44) with lifetimes $>10^{-5}$ sec were investigated through use of collisional activation (CA) spectra.[4] Three possible isomers (ionized acetaldehyde, ethylene oxide, and vinyl alcohol) were shown to be stable within these lifetime requirements. Because of the applicability to unimolecular ion reaction mechanisms and molecular structure determination, we have extended these studies to the next higher homologs, ions of the composition $C_3H_6O\cdot^+$ ($m/e$ 58).

Based on ground-state chemistry, structures a–j should be among the most probable for $C_3H_6O\cdot^+$ ions; possible resonance forms, such as $\cdot CH_2{-}CH{=}O^+CH_3$ for c, are not shown. Two of these species, the acetone ion f and its enolic form g, have been the subject of extensive studies involving ion cyclotron resonance spectrometry,[5] isotopic labeling,[6] and kinetic energy released in metastable decompositions.[7] These studies provide definitive evidence that the $C_3H_6O\cdot^+$ ions generated from alkanones by both single and double $\gamma$-hydrogen rearrangement have the enolic structure g, and that the latter path does not yield ion j. The possible formation of other isomers in which three atoms are bonded to oxygen is discussed below. Ion i was not investigated in the present study because of lack of suitable precursors.


a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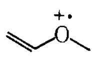
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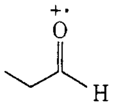
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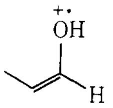
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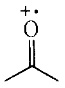
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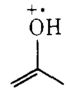
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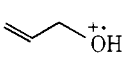
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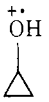
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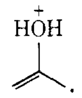

j

## Results and Discussion

**Reference Ions.** The CA spectra of $C_3H_6O\cdot^+$ ions from a variety of sources are given in Table I. To generate ions of structures a–d, f, and h, the corresponding molecules were ionized. Previous studies[5-10] have established precursors for generation of the enolic ions e and g, e by $\gamma$-hydrogen rearrangement from $\alpha$-methylvaleraldehyde,[9] and g by single and double hydrogen rearrangements from 2-hexanone and 4-octanone, respectively,[5-8] and from 1-methylcyclobutanol.[5,10] In each case the CA spectrum obtained from the ions formed using low (15–20 eV) electron energies was identical within experimental error (data not included in Table I), indicating that a single ion species is produced.[11] With one exception the CA spectra of the reference ions a–h are significantly different; for each spectrum at least one mass has the largest relative abundance of all the isomers. Thus most of the $C_3H_6O\cdot^+$ ions produced in each case must be due to a unique structure. The exception involves the ions e and h; these spectra are the same within experimental error, indicating that e and/or h have isomerized to a common structure. The enolic ion e should be stable as it is resonance stabilized, and its homolog $CH_2{=}CHOH\cdot^+$ was found to be the most common form of the $C_2H_4O\cdot^+$ ion giving abundant peaks in a variety of mass spectra.[3] On the other hand, deuterium labeling has shown[12] that H atom loss from ionized allyl alcohol molecules occurs from all three carbon atoms on a nearly statistical basis, showing that more energetic h ions undergo extensive scrambling. Thus the common ion structure probably is not h; we will assume that it is the enol e, although other structures such as i are conceivable.

The CA spectra of the reference ions are qualitatively consistent with the remaining structures a–g. The largest $m/e$ 43 (loss of $CH_3\cdot$) peaks, due in part to unimolecular decompositions of metastable ions, are found for ions a, f, and g which contain methyl groups which can be lost by $\alpha$ cleavage. The largest $m/e$ 39 peaks, which correspond to the loss of OH + $H_2$, are found for the hydroxylic ions e and g, while the isomers containing ether oxygen atoms have the least important $m/e$ 39 peaks. The $m/e$ 27 ($C_2H_3$) and 31 ($CH_3O$) peaks are largest in the methoxy-containing ion c, while $m/e$ 31 is smallest in the carbonyl ions d and f. Abundant ions at $m/e$ 30 and 28 from the trimethylene oxide ion c are consistent with its structural units $-CH_2O-$ and $-CH_2CH_2-$. The $m/e$ 29 peak is largest for the ethyl-containing ion d, and $m/e$ 15 for ions a, c, and f which contain methyl groups which are not attached to vinylic carbon atoms. Because of these spectra-structure consistencies, and because no other stable isomers appear to be plausible, we will assume that a–g are the actual structures of the corresponding ions reaching the collision region.

**Aliphatic Epoxides.** An extensive study[13] of the mass spectral behavior of unbranched terminal epoxides utilizing deuterium labeling led to the proposal that their abundant $C_3H_6O\cdot^+$ ions are formed as structure h through the concerted mechanism of Scheme I; an alternative stepwise pathway forming ion a′ has also been suggested.[14] However, the CA spectra of the epoxides R = H, $CH_3$ and $C_3H_7$ indi-

Table I. Collisional Activation Spectra of $C_3H_6O$ Ions

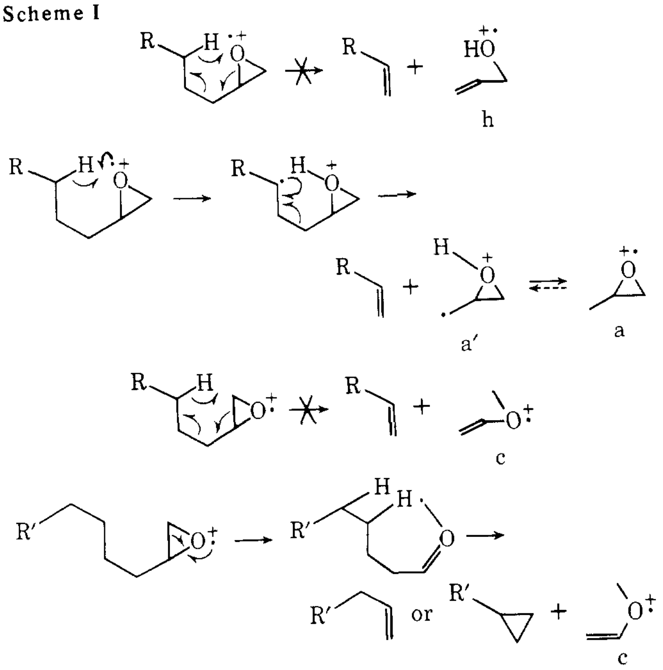
| Compd | Electron energy eV[b] | *m/e* of daughter ion[a] | | | | | | | | | | | | | | | Ion structure |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 15 | 26 | 27 | 28 | 29 | 30 | 31 | 39 | 40 | 41 | 42 | 43 | 55 | 56 | 57 | |
| Propene oxide | 70 | 6.8 | 6.6 | 17 | 33 | 19 | (8.4) | 12 | 0.5 | 0.5 | 1.4 | (16) | (51) | 0.4 | 0.3 | (35) | a |
| Trimethylene | 70 | 0.6 | 4.5 | 9.2 | 53 | 23 | (37) | 4.7 | 0.9 | 0.4 | 0.3 | (1.0) | (0.9) | 1.4 | 0.7 | (298) | b |
| Methyl vinyl ether | 70 | 8.8 | 6.3 | 22 | 21 | 18 | (3.7) | 11 | 0.4 | 0.5 | 2.1 | (21) | (31) | 1.0 | 1.3 | (18) | c |
| Propanal | 70 | 1.2 | 3.8 | 11 | 16 | 37 | (13) | 4.5 | 5.3 | 2.2 | 2.4 | (3.2) | (2.2) | 6.1 | 4.6 | (648) | d |
| 2-Methylpentanal | 70 | 1.1 | 4.8 | 9.2 | 7.3 | 25 | (11) | 13 | 11 | 3.4 | 2.3 | (3.3) | (3.4) | 9.3 | 4.7 | (197) | e |
| Acetone | 70 | 15 | 6.0 | 15 | 4.2 | 13 | (0.8) | 0.9 | 9.9 | 4.2 | 13 | (105) | (861) | 1.0 | 0.2 | (13) | f |
| 2-Hexanone | 70 | 4.2 | 2.8 | 8.5 | 3.1 | 16 | (2.7) | 13 | 20 | 5.5 | 8.6 | (21) | (109) | 4.6 | 0.3 | (35) | g |
| 4-Octanone | 70 | 3.6 | 2.9 | 7.1 | 3.3 | 16 | (3.5) | 11 | 21 | 5.7 | 9.6 | (22) | (67) | 4.4 | 1.6 | (30) | g |
| 1-Methylcyclobutanol | 70 | 3.2 | 2.4 | 7.2 | 3.2 | 15 | (2.9) | 13 | 20 | 5.9 | 9.1 | (21) | (166) | 5.6 | 0.9 | (47) | g |
| Allyl alcohol[c] | 70 | 1.0 | 4.8 | 10 | 8.4 | 23 | (17) | 12 | 9.9 | 5.7 | 1.9 | (4.0) | (2.8) | 8.0 | 6.3 | (890) | e |
| 1,2-Epoxypentane | 70 | 7.5 | 6.2 | 19 | 27 | 19 | (7.4) | 14 | 0.3 | 0.6 | 1.7 | (18) | (42) | 0.9 | 1.5 | (41) | a + c (1 : 1) |
| | 20 | 7.2 | 7.2 | 20 | 21 | 19 | (6.2) | 14 | 1.0 | 1.1 | 1.9 | (19) | (40) | 1.7 | 1.6 | (44) | c |
| 1,2-Epoxyhexane | 70 | 7.7 | 6.4 | 21 | 25 | 18 | (5.2) | 14 | 0.6 | 0.8 | 2.7 | (23) | (41) | 0.4 | 0.7 | (29) | a + c (1 : 3) |
| 1,2-Epoxyoctane | 70 | 8.0 | 6.2 | 21 | 24 | 19 | (6.0) | 15 | 1.0 | 0.8 | 2.5 | (21) | (38) | 0.8 | 0.6 | (30) | a + c (1 : 4) |
| | 20 | 8.6 | 7.1 | 23 | 23 | 18 | (5.4) | 12 | 1.2 | 0.8 | 2.6 | (23) | (35) | 0.9 | 0.8 | (15) | c |
| 2-Methyl-1,3-dioxolane | 70 | 3.9 | 9.9 | 16 | 36 | 17 | (7.0) | 12 | 0.3 | 0.4 | 1.3 | (12) | (57) | 0.7 | 1.2 | (133) | a |
| 4-Methyl-1,3-dioxolane | 70 | 3.4 | 7.7 | 18 | 31 | 20 | (5.7) | 14 | 0.4 | 0.5 | 0.9 | (8.7) | (34) | 0.6 | 1.0 | (24) | a |
| 1,4-Dioxane | 70 | 0.7 | 6.0 | 10 | 53 | 18 | (37) | 5.4 | 0.1 | 0.1 | 0.3 | (1.3) | (3.1) | 0.2 | 0.3 | (175) | b |
| 2-Methoxyethyl vinyl ether | 70 | 9.6 | 6.2 | 22 | 22 | 18 | (5.0) | 16 | 0.2 | 0.4 | 1.8 | (23) | (32) | 0.5 | 0.8 | (23) | c |
| 2-Methoxyethyl acetate | 70 | 8.4 | 6.5 | 21 | 22 | 18 | (4.5) | 15 | 1.8 | 0.8 | 2.5 | (24) | (40) | 0.8 | 0.3 | (18) | c |
| 2-Methoxyethyl acrylate | 70 | 8.4 | 6.1 | 22 | 23 | 17 | (5.0) | 16 | 0.8 | 0.8 | 2.5 | (25) | (36) | 0.7 | 0.1 | (16) | c |
| 2-Methoxyethanol | 70 | 1.6 | 6.2 | 12 | 49 | 19 | (33) | 7.1 | 0.2 | 0.2 | 0.7 | (3.8) | (6.7) | 1.0 | 0.5 | (152) | b + c (5 : 1) |
| | 20 | 1.7 | 6.5 | 12 | 44 | 19 | (28) | 8.7 | 0.2 | 1.1 | 1.3 | (3.1) | (4.1) | 1.1 | 0.5 | (162) | b + c (7 : 3) |
| Acetylacetone | 70 | 4.1 | 2.6 | 9.2 | 3.1 | 15 | (4.4) | 12 | 20 | 3.8 | 6.4 | (19) | (153) | 6.3 | 0.3 | (41) | g |
| 2-Methyl-1,4-butanediol | 70 | 1.0 | 3.8 | 8.2 | 7.3 | 26 | (12) | 14 | 10 | 4.1 | 3.0 | (3.8) | (5.1) | 11 | 4.5 | (15) | e |
| Ethyl propenyl ether[c] | 70 | 1.0 | 4.5 | 9.7 | 7.8 | 24 | (16) | 13 | 11 | 4.8 | 1.8 | (3.7) | (2.6) | 9.2 | 6.0 | (675) | e |
| Allyl ethyl ether[c] | 70 | 1.0 | 4.4 | 9.8 | 7.6 | 24 | (13) | 13 | 11 | 4.0 | 2.1 | (3.5) | (2.5) | 9.5 | 5.1 | (412) | e |
| Allyl pentyl ether | 70 | 0.9 | 4.3 | 10 | 7.4 | 25 | (11) | 13 | 11 | 3.8 | 2.2 | (4.0) | (2.5) | 9.6 | 4.8 | (225) | e |
| Allyl hexyl ether | 70 | 1.2 | 4.5 | 10 | 7.6 | 23 | (9.8) | 12 | 12 | 4.2 | 2.6 | (4.1) | (3.0) | 9.5 | 3.8 | (179) | e |
| Allyl acetate | 70 | 1.3 | 5.1 | 9.6 | 7.4 | 25 | (8.9) | 13 | 10 | 3.5 | 2.6 | (4.0) | (5.4) | 8.1 | 4.4 | (149) | e |
| 3-Methoxy-1-propanol | 70 | 1.0 | 4.5 | 11 | 9.4 | 22 | (18) | 12 | 11 | 4.5 | 2.6 | (4.4) | (7.6) | 10 | 5.2 | (795) | e |
| 3-Chloro-1-propanol | 70 | 0.8 | 4.1 | 9.3 | 36 | 20 | (47) | 9.0 | 4.7 | 2.7 | 1.3 | (2.3) | (1.9) | 5.1 | 2.3 | (300) | b + e (3 : 2) |
| | 15 | 0.6 | 4.3 | 8.0 | 35 | 22 | (46) | 8.6 | 4.9 | 3.1 | 1.1 | (2.6) | (1.9) | 4.4 | 2.8 | (457) | b + e (3 : 2) |
| 3-Bromo-1-propanol | 70 | 0.8 | 4.1 | 8.6 | 23 | 20 | (32) | 11 | 7.6 | 3.9 | 1.0 | (3.6) | (2.3) | 8.7 | 3.8 | (430) | b + e (1 : 2) |
| | 15 | 0.9 | 4.3 | 8.9 | 17 | 23 | (30) | 11 | 7.6 | 4.9 | 1.6 | (3.2) | (2.1) | 8.9 | 4.6 | (496) | b + e (1 : 4) |
| 1,3-Propanediol | 70 | 0.6 | 4.3 | 9.2 | 30 | 22 | (39) | 10 | 6.3 | 3.4 | 1.1 | (2.9) | (2.0) | 5.6 | 2.3 | (142) | b + e (1 : 1) |
| | 15 | 0.8 | 5.0 | 9.7 | 29 | 23 | (34) | 8.9 | 5.3 | 2.2 | 1.7 | (2.9) | (2.7) | 6.4 | 2.8 | (503) | b + e (1 : 1) |

[a] Abundances relative to the total ion abundance = 100, excluding *m/e* 30, 42, 43, and 57 which contain contributions from unimolecular decompositions of metastable ions in some or all compounds. Minor CA peaks at *m/e* 13, 14, 25, 36, 37, 38, 53, and 54 have not been included in the table. [b] Measurements were performed at 20 eV for systems which had unsuitably low ion intensities at 15 eV. [c] The CA spectrum was corrected for interfering decompositions of $^{13}CC_2H_5O^+$ (*m/e* 58) because of the presence of a large peak at *m/e* 57 in the mass spectrum. For these corrections the elemental compositions of all peaks in the CA spectrum of these $C_3H_5O^+$ ions (*m/e* 57) are obvious except for *m/e* 29 ($CHO^+$ and/or $C_2H_5^+$). Because previous work[d] established that the loss of CO from $C_3H_5O^+$ ions generated from allyl ethyl ether is strongly enhanced for ions of longer lifetimes, it was assumed that the collisionally decomposed $C_3H_5O^+$ ion yielded $C_2H_5^+$ ions only. [d] T. J. Mead and D. Williams, *J. Chem. Soc. B*, 1654 (1971).

cate that structures a and c are the dominant products. The mechanism forming h is unlikely as no e ions are observed, although it is conceivable the h ions of internal energies not attainable by ionization of allyl alcohol could isomerize to a or c. Formation of ion a by direct H rearrangement to carbon-3 appears less likely than by isomerization of a′ (Scheme I), altough it is also conceivable that the reference ion a isomerizes to a′. Similar H rearrangement reactions have been shown[15] to be stepwise, not concerted. Formation of c increases with lowered electron energy; again a concerted mechanism (Scheme I) not involving the radical site cannot produce the majority of this product, as only 55% of the transferred hydrogen originates from carbon-5.[13] This lack of specificity[13] suggests hydrogen rearrangement to a radical site on a *saturated* functionality;[14] possible pathways involve initial opening of the epoxide ring followed by H transfer through both seven- and eight-membered ring transition states (Scheme I).

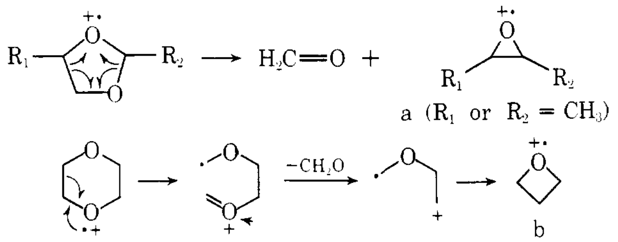
**Cyclic Ethers.** The CA spectra of the relatively abundant $C_3H_6O\cdot^+$ ions produced from 2-methyl-1,3-dioxolane and 4-methyl-1,3-dioxolane through loss of formaldehyde from the molecular ions show these to be of structure a. This is consistent with a mechanism (Scheme II) similar to that proposed[3] for the formation of ethylene oxide ions from

Scheme I



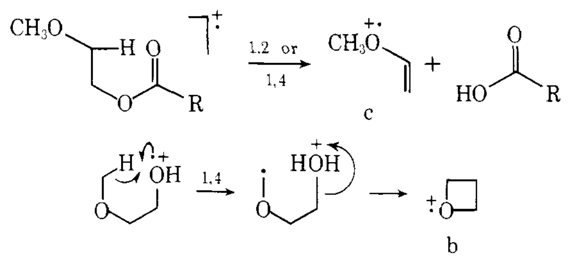
1,3-dioxolane. In a similar manner, 1,4-dioxane would be expected to yield the oxetane ion b (Scheme II), as confirmed by the data of Table I.

Scheme II



**$CH_3OCH_2CH_2Y$ Compounds.** For three of these compounds (Y = $OCH{=}CH_2$, OAc, $OCOCH{=}CH_2$), the CA spectra show that the loss of HY generates methyl vinyl ether ions c, presumably (Scheme III) through transfer of

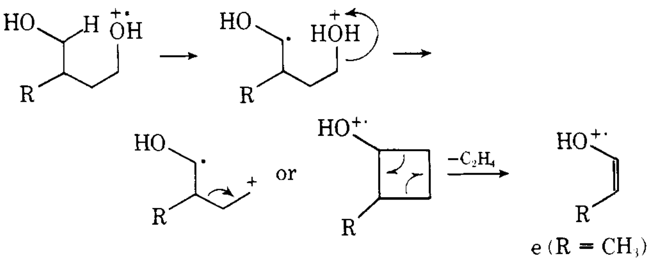
Scheme III



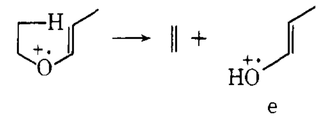
the methylene H adjacent to the methoxy group. This is consistent with the earlier finding of exclusive 1,2 elimination of HX from the molecular ions of haloethanols $XCH_2CH_2OH$,[3] although a 1,4 transfer to the unsaturated functionality cannot be ruled out in the present cases. However, for $CH_3OCH_2CH_2OH\cdot^+$ the elimination of $H_2O$ gives a mixture of ions b and c (Table I), with b formation most probably involving transfer of a methyl hydrogen (Scheme III). The expulsion of water from 1-alkanol molecular ions predominantly occurs by a 1,4 mechanism.[16]

**Enolic Ions (e, g).** Loss of ketene from acetylacetone yields $C_3H_6O\cdot^+$ ions of the acetone enol structure g (Table I), as expected.[17] The propionaldehyde enol ion e is formed from 2-methyl-1,4-butanediol; this is consistent with the mechanism (Scheme IV) proposed[3] for the formation of vinyl alcohol ions from 1,4-butanediol. Ions of structure e are also formed from ethyl propenyl ether, consistent (Scheme V) with hydrogen rearrangement to the oxygen atom[18] as found for vinyl ethers.[3]

Scheme IV



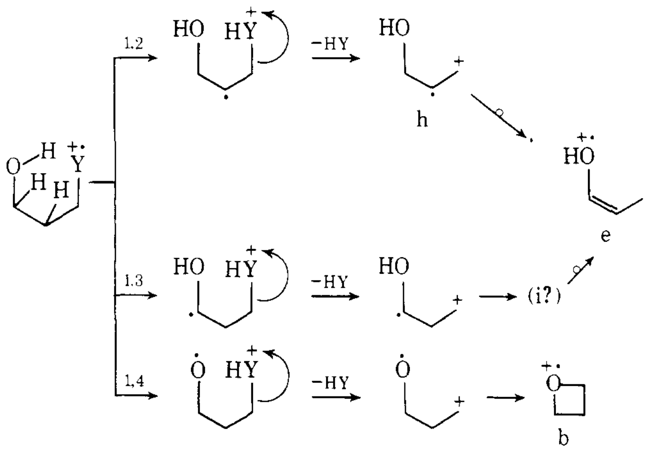
Scheme V



**Allyl Derivatives.** From ionization potential data Meyerson and McCollum[18] proposed that the abundant $C_3H_6O\cdot^+$ ions from allyl ethers had the ionized allyl alcohol structure h. Extensive deuterium labeling[19] showed that this process involves a nonspecific hydrogen transfer, again consistent with H transfer to the saturated oxygen atom to form h. The CA data for three allyl ethers and allyl acetate (Table I) are consistent with the initial formation of allylalcohol ions h, although these presumably have rearranged to e ions in the $10^{-5}$ sec delay before measurement of their CA spectra (vide supra).

**$HOCH_2CH_2CH_2Y$ Compounds.** Several of these compounds yield abundant $C_3H_6O\cdot^+$ ions through loss of HY. 3-Methoxy-1-propanol produces only the enolic ion e, which could be generated through 1,2 elimination producing h (shown in an alternate resonance form) which rearranges to e (Scheme VI), or 1,3 elimination producing an ion such as i which would rearrange to e. For $HOCH_2CH_2CH_2Y$ compounds in which Y = Cl, Br, and OH, the trimethylene oxide ion b is formed in addition to ion e, and the proportions of these are surprisingly insensitive to the ionizing electron energy. Formation of b can be rationalized as a 1,4-hydrogen transfer (Scheme VI), similar to the formation of this ion from 2-methoxyethanol (Scheme III). Confirming the 1,4 transfer, the normal mass spectrum of $DOCH_2CH_2CH_2Cl$ shows $[(M - DCl)\cdot^+]/[(M - HCl)\cdot^+] = 1.5$.[20]

Scheme VI



Neither of the carbonyl-containing $C_3H_6O\cdot^+$ ions, d or f, was observed as fragment ions in any of the compounds studied here. (By analogy to the formation of $CH_3CHO\cdot^+$,[3] the formation of f from $HOC(CH_3)_2CH_2CH_2OH$ might be expected, but unfortunately this compound was not available to us.) Note, however, that at least five of the seven stable $C_3H_6O\cdot^+$ isomers a–g should be common fragment ions, and the identification of their structures from CA spectra should thus be a valuable aid in elucidating the structures of complex molecules whose mass spectra contain an appreciable $C_3H_6O\cdot^+$ peak.

## 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 $\mu$A and 70 eV (or lower where noted), and a sample reservoir and source temperature of 150° were used. Metastable ion 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 35% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan.[4] The data are the computer-averaged composites of at least 16 separate scans. The contributions from MI products (corrected as described[4]) are subtracted from these values to obtain the CA spectrum.

**Samples.** Deuterated 3-chloro-1-propanol 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.

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## References and Notes

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# Carbanions. XVI. Reactions of 4-Chloro-1-*p*-biphenylylbutane with Alkali Metals. Formation of a Spiro Anion[1]

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**Abstract:** 4-Chloro-1-*p*-biphenylylbutane reacts with lithium in THF at −70° to give a mixture of 4-*p*-biphenylylbutyllithium and 8-phenylspiro[4.5]-6,8-decadienyllithium (**7**). With potassium, cesium, and Cs–K–Na alloy chiefly the spiro anion (**7**) and a little 1-*p*-biphenylylbutyl anion (**6**) are formed. Experiments with sodium and potassium, in which dioxane or tertiary alcohols were used as a proton source to "trap" intermediate anions, indicate that 4-*p*-biphenylylbutyl anion (**5**, M = K or Cs) is a precursor of **7**. From labeling experiments no evidence was found for the spiro anion **7** reverting back to the open anion **5**. The 4,4-diphenyl groups of 4-*p*-biphenylyl-4,4-diphenylbutyl anion facilitate both spiro cyclization and ring opening.

In a previous work,[2] it was shown that 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane reacts with potassium or cesium in tetrahydrofuran (THF) to give 4-*p*-biphenylyl-1,1-diphenylbutyl anion. Evidence was presented that this reaction proceeds according to Scheme I. Attempts, however, to detect the intermediate spiro anion **2** were unsuccessful even from a reaction of Cs–K–Na with the chloride at −75° for some 2 min, whereupon only the rearranged anion **3** was present, according to the products of carbonation or protonation. Since the anion **3** is stabilized by the two phenyl groups on carbon-1 which serve to delocalize the negative charge, it was thought possible that if these phenyls were