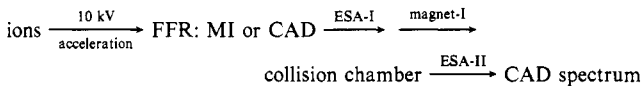enolic precursor; correcting for these shows that the proportion of non-ergodic dissociations increases with increasing precursor energy, as expected. Such behavior is also expected from the lifetime of $<10^{-12}$ s calculated[11] for the intermediate acetone ions b containing >49 kcal mol^{-1} excess internal energy, directly analogous to the behavior observed for non-ergodic neutral systems.[3,4]

Experimental Section

A tandem mass spectrometer[34] consisting of a Hitachi RMH-2 double-focusing mass spectrometer as MS-I, a molecular beam collision region, and an electrostatic analyzer as MS-II was used to obtain the CAD spectra. The temperatures of the all-glass sample inlet system and ion source were <130 °C. The collision gas pressure was adjusted to give 33% transmittance of the precursor ions. To measure the normal CAD spectra 7-keV ions were selected by the first MS at a resolution of $\sim$ 20 000 to ensure the purity of the precursor ions. For example, precursor $C_2H_3O^+$ ions sampled at m/z 43.0175, 43.0184, and 43.0193 gave identical CAD spectra, demonstrating the exclusion of other precursors such as C_2HDO^+. In addition, precursor ions formed by metastable ion decompositions in the field-free region (FFR) before the electrostatic analyzer were selected by increasing the accelerating voltage from 7

$$\text{ions} \xrightarrow[\text{acceleration}]{10 \text{ kV}} \text{FFR: MI or CAD} \xrightarrow{\text{ESA-I}} \xrightarrow{\text{magnet-I}}$$

$$\text{collision chamber} \xrightarrow{\text{ESA-II}} \text{CAD spectrum}$$

(34) McLafferty, F. W.; Todd, P. J.; McGilvery, D. C.; Baldwin, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 3360. Todd, P. J.; McGilvery, D. C.; Baldwin, M. A.; McLafferty, F. W. In "Tandem Mass Spectrometry"; McLafferty, F. W., Ed.; John Wiley: New York, 1983; Chapter 13.

to $\sim$10 kV while maintaining the electrostatic and magnetic analyzers of MS-I at the same nominal values. For CAD formation of precursor ions the pressure in FFR was increased with helium to 2×10^{-5} torr (gauge), reducing precursor ion transmission in this region by 50%. Metastable ion spectra (Table II) correspond to ion decompositions within the collision chamber (pressure 4×10^{-7} torr) following MS-I, with ion lifetimes of $\sim$22 μs for 7 keV ions, m/z 61. CAD spectra of doubly charged ions were measured separately with 9.9 keV ions at 33% transmittance of the precursor main beam.

1 was kindly supplied by Professor Chava Lifshitz. **2** was prepared from cyclobutanone-$2,2,4,4$-d_4[2] and methyl magnesium iodide, and **2** was converted to **3** with D_2O/CH_3OD, after conditioning the ion source and the inlet system with D_2O for 2 h before each measurement. Bromoacetaldehyde was prepared according to ref 35 and distilled immediately before use. 1-Isopropylcyclobutanol was prepared from cyclobutanone (Aldrich) and isopropyl magnesium bromide.

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Rearrangement and Methyl Loss from Ionized Propene Oxide and Methyl Vinyl Ether

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Abstract: Molecular cations of propene oxide (a) and methyl vinyl ether (b), despite a large difference (35 kcal mol^{-1}) in their heats of formation, undergo two very similar metastable methyl loss dissociations; for both of these dissociations a and b exhibit the same kinetic energy release values and produce acetyl ions. Deuterium labeling shows that a ions undergo little direct methyl loss, but instead isomerize by ring opening and 1,4-H transfer to b. The latter reversible reaction causes hydrogen exchange in metastable b ions prior to methyl loss by b $\rightarrow$ CH$_3$C=OCH$_3^+ \cdot \rightarrow$ CH$_3$CO$^+$. For long-lived a ions of energies below the decomposition threshold, nearly complete hydrogen exchange occurs between the methyl and methylene groups. Low-energy a ions also lose a methyl incorporating the ring methylene group and the methine hydrogen, consistent with the symmetry-allowed rearrangement to acetone ions in their first electronically excited state postulated recently by Bombach, Stadelmann, and Vogt. High-energy a ions also lose the methylene plus methine H, possibly through a non-ergodic process.

The gaseous $C_3H_6O^+ \cdot$ isomers have been the subject of a variety of investigations,[1–13] including a recent comprehensive ab initio

molecular orbital study.[8] Ionized propene oxide $CH_3\overline{CHCH_2O}^+ \cdot$ (a) appears to be unique among these isomers in several aspects. It is stable,[6,8,10] in contrast to ionized ethene oxide, which spontaneously ring opens.[14] Its heat of formation, 214 kcal mol^{-1},

(1) Diekman, J.; MacLeod, J. K.; Djerassi, C.; Baldeschwieler, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2069.

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Scheme I

$$\underset{a}{\text{CH}_3\text{CH}\!-\!\text{CH}_2} \; \rightleftharpoons \; \underset{d}{\text{CH}_3\text{CH}\!=\!\overset{+\cdot}{\text{O}}\text{CH}_2} \; \rightleftharpoons \; \underset{b}{\text{CH}_2\!=\!\text{CHOCH}_3^{+\cdot}} \; \longrightarrow \; \underset{c}{\text{CH}_3\overset{\cdot}{\text{C}}\!=\!\overset{+}{\text{O}}\text{CH}_3} \; \longrightarrow \; \text{CH}_3\text{CO}^+ + \cdot\text{CH}_3$$

ΔH_{f}, kcal/mol[14,17]   214[10]   221[10]   185[8]   (~210)   179[7a]   217[7b]   ~190[8]   191
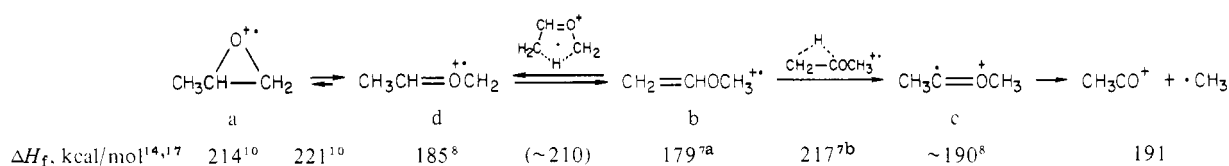
Table I. Formation of Methyl Loss Products from $C_3(H,D)_6O^{+\cdot}$ Ions[a]

precursor	method[b]	loss of			
		CH$_3$	CH$_2$D	CHD$_2$	CD$_3$
CH$_3$CDCH$_2$O (aa)	70 eV	81	19		
	CAD	83	17		
	15 eV	97	3		
	MI[c]	98	2		
CH$_3$CHCD$_2$O (ab)	70 eV	15	31	54	
	CAD	11	55	34	
	15 eV	10	44	46	
	MI	12	57	31	
CH$_3$CDCD$_2$O (ac)	70 eV	14	28	43	15
	CAD	8	48	38	7
	15 eV	14	47	39	<1
	MI	11	58	29	2
CD$_3$CHCH$_2$O (ad)	70 eV	18	40	32	10
	CAD	5	33	55	7
	15 eV	3	44	46	8
	MI	3	27	58	12
CH$_2$=CHOCD$_3$ (ba)	70 eV	2	7	26	65
	CAD	5	7	26	62
	15 eV	2	15	46	36
	MI[c]	2	22	50	26
CD$_2$=CHOCH$_3$ (bb)	70 eV	54	39	7	
	CAD	53	42	5[d]	
	15 eV	47	42	11	
	MI	26	59	15	
statistical	H$_3$D$_2$	10	60	30	
	H$_2$D$_3$		30	60	10
	H$_4$D$_2$	20	60	20	
	H$_3$D$_3$	5	45	45	5

[a] Normalized to the sum of intensities for loss of $C(H,D)_3$ corrected for loss of $C(H,D)_4$. [b] Figures are nominal values of ionizing electron energies. [c] Total yield for loss of $C(H,D)_3$ by metastable decomposition of b is ~20% that of a. [d] High experimental error in correction for loss of CH$_3$D.

Table II. Kinetic Energy Release Accompanying Metastable Decomposition

precursor	reaction	$T_r(0.5)$, kcal mol^{-1}
a	$C_3H_6O^{+\cdot} \rightarrow C_2H_3O^+ + CH_3$	17.4 ± 0.6
aa	$C_3H_5DO^{+\cdot} \rightarrow C_2H_2DO^+ + CH_3$	16.8 ± 0.7
ad	$C_3H_3D_3O^{+\cdot} \rightarrow C_2D_3O^+ + CH_3$	3 ± 2
b	$C_3H_6O^{+\cdot} \rightarrow C_2H_3O^+ + CH_3$	17.4 ± 0.8
ba	$C_3H_3D_3O^{+\cdot} \rightarrow C_2HD_2O^+ + CH_2D$	16.5 ± 0.6

Table III. Partial CAD Spectra of $C_2H_3O^+$ Ions

compound	ion formation[a]	[29]/[28]	[21]/[21.5]
CH$_3$COCH$_3$ [b]	70 eV	0.68	14
CH$_3$COOCH$_3$ [b]	70 eV	0.67	
	74$^+$ → 43$^+$	0.50	
a	70 eV	0.68	14
	58$^+$ → 43$^+$ [c]	0.55	
	58$^+$ → 43$^+$ [d]	0.57	
ab	70 eV	0.68	12
b	70 eV	0.68	12
ba	70 eV	0.67	12

[a] Nominal ionizing electron energy or metastable decomposition used. [b] Reference 12. [c] For ions from the center of the metastable peak ($T_r = 0$). [d] For ions from the wing of the metastable peak ($T_r = 12$-15 kcal mol^{-1}).

ion (b), ΔH_f = 179 kcal mol^{-1}.[7a] The present investigation utilizes deuterium-labeled derivatives of a and b to provide a more detailed picture of their isomerization and dissociation pathways.

Results and Discussion

The electron ionization (EI), metastable ion (MI), and collisionally activated dissociation (CAD)[4,18] data of Tables I–III show striking similarities for the threshold energy decomposition of ionized propene oxide (a) and methyl vinyl ether (b). Both yield only (≥95%) the acetyl isomer, as shown by CAD spectra (Table III); the detailed justification, including CAD spectra of their isomers, is presented in recent papers.[9,11,12] Also the major metastable dissociation of both a and b shows (Table II) the same kinetic energy release, $T_r(0.5)$ = 17 kcal mol^{-1}, consistent with a common transition state. Because the large difference (35 kcal mol^{-1}) in their heats of formation would require that any a $\rightleftharpoons$ b isomerization would greatly favor formation of b, its behavior will be considered first.

Major Pathway for Methyl Loss from CH_2=$CHOCH_3^{+\cdot}$ (b). The formation of acetyl ions from b almost surely does not involve an initial dissociation to CH_2=CHO^+ + $\cdot CH_3$ followed by ionic isomerization, as for these products $\sum\Delta H_f$ = 270 kcal mol^{-1} is predicted[8] (and is consistent with experiment),[9,12] while a threshold energy of 217 kcal mol^{-1} is observed.[7b] However, it is the original methyl that is lost; the spectra (Table I) of CH_2=$CHOCD_3^{+\cdot}$ (ba) show mainly CD$_3$ loss at higher energies.[19] Even for the MI spectrum this is true for ions that are not scrambled (vide infra). The most logical product of the initial isomerization appears to be CH_3C=$OCH_3^{+\cdot}$ (c), predicted[8] ΔH_f = ~190 kcal mol^{-1}, formed by a 1,2-H shift (Scheme I). An analogous mechanism has been proposed for the loss of D from CH_2=$CHOD^{+\cdot}$ to form CH_3CO^+,[9] for which metastable decompositions exhibit[20] a similar energy release (15 kcal mol^{-1}). For methyl loss from b the

is substantially higher than the values of 158–205 kcal mol^{-1} measured[7,13,15] or predicted[8] for 14 other $C_3H_6O^{+\cdot}$ isomers. Further, loss of methyl, its dominant low-energy decomposition, has been considered a simple reaction forming $\overline{CH_2CH}$=O^+, analogous to the α-cleavage decompositions occurring in ionized acyclic ethers.[5,16,17] However, recent evidence[9] shows that only acetyl ions are formed by the 70-eV electron ionization of propene oxide. Bombach, Stadelman, and Vogt very recently[10] have reported evidence from photoelectron–photoion coincidence (PEPICO) studies for two distinct low-energy isomerization channels for a leading to methyl loss. The first channel is proposed to yield $CH_3C(OH)CH_2^{+\cdot}$ and/or CH_3CH=$CHOH^{+\cdot}$ and the second to yield acetone ions (e) in their first electronically excited state.[10] These three are the most stable $C_3H_6O^{+\cdot}$ isomers, ΔH_f(ground state) = 158, 159, and 172 kcal mol^{-1}, respectively.[7,10,13]

We find, however, that the energy release values in two dissociations of metastable propene oxide ions (a) instead are nearly identical to those for such dissociations of the methyl vinyl ether

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threshold energy[7b] of 217 kcal mol^{-1} is consistent with the large amount (17 kcal mol^{-1}) of energy released in the metastable decomposition forming CH_3CO^+ + $\cdot CH_3$ ($\sum \Delta H_f$ = 191 kcal mol^{-1}).

Isomerization of CH_2=$CHOCH_3^+\cdot$ (b). At lower energies another isomerization pathway is competitive, as shown by the labeling data of Table I. In the metastable decomposition of b the scrambled hydrogens involve the methyl and methylene, but not the methine, hydrogens; to fit the data, metastable CH_2=$CHOCD_3$ (ba) ions losing 19% CD_3 before scrambling these hydrogens would yield CH_3:CH_2D:CHD_2:CD_3 losses of 0:24:48:27, compared to the observed values 2:22:50:26. Such a 1,4-H shift (Scheme I) would produce CH_3CH=$OCH_2^+\cdot$ (d), the ring-opened form of a;, the stability of d is predicted[8] to be comparable to that of b: $\Delta H_f(d)$ = 185 kcal mol^{-1}. The hydrogen scrambling shows that the energy barrier for b → d cannot be appreciably greater than that for b → c → CH_3CO^+ of 217 kcal mol^{-1}.[7b] However, mass-analyzed stable CH_2=$CHOCD_3^+\cdot$ and CD_2=$CHOCH_3^+\cdot$ ions which then undergo CAD lose $C(H,D)_3\cdot$ in nearly the same ratio as when formed by 70-eV electron ionization, indicating that an insignificant portion of these stable ions is formed with energies between that required for b → d and b → c → CH_3CO^+. Increasing the internal energy of b reduces the 1,4-H isomerization b → d relative to the 1,2-H rearrangement b → c, consistent with a tighter activated complex and lower ($\sim$210 kcal mol^{-1}) energy threshold for b → d.[21]

Major Pathway for Methyl Loss from $\overline{CH_3CHCH_2O}^+\cdot$ (a). The ring opening of a to form the more stable[8] CH_3CH=$OCH_2^+\cdot$ (d) should lead to methyl loss through isomers b and c (Scheme I). This mechanism also rationizes the similar energy release values (17 kcal mol^{-1}, Table II) for metastable dissociation of a and b and similar threshold energy values for a (221 kcal mol^{-1})[10] and b (217)[7b] dissociation. It is mainly the original methylene, not the methyl, group of a that is lost in forming CH_3CO^+ at higher energies. In the 70-eV spectrum (Table I) of $CH_3\overline{CHCD_2O}$ (ab) the loss of CHD_2 is dominant, while in that of $CD_3\overline{CHCH_2O}^+\cdot$ (ad) CD_3 loss is minor. These data are also consistent with the intermediacy of b (Scheme I), but not $CH_3C(OH)$=$CH_2^+\cdot$ or CH_3CH=$CHOH^+\cdot$.[10]

Facile Isomerization of $CH_3\overline{CHCH_2O}^+\cdot$ (a). Although non-decomposing a ions undergo little isomerization to CH_3CH=$OCH_2^+\cdot$ (d) or CH_2=$CHOCH_3^+\cdot$ (b),[6,8] the MI and CAD spectra of a ions show extensive hydrogen scrambling, much more than that shown by b (Table I). Stable $CH_3\overline{CHCD_2O}$ (ab) and $CD_3\overline{CHCH_2O}$ (ad) ions which are made to lose $C(H,D)_3\cdot$ by CAD show almost as extensive H/D scrambling as the slightly higher energy ab and ad ions which undergo metastable decomposition. As found for the H/D scrambling of b, this isomerization of a does not involve the methine hydrogen; the MI spectrum of $CH_3\overline{CDCH_2O}$ (aa) shows that only $\sim$2% of this hydrogen is transferred, during transit through the mass spectrometer, to the methyl ultimately lost. Exchange of the other hydrogens is nearly complete. Scrambling of all but the methine H would yield CH_3:CH_2D:CHD_2:CD_3 losses for ab of 10:60:30:0 and for ad of 0:30:60:10; the observed MI (CAD in parentheses) values are 12:57:31:0 (11:55:34:0) and 3:27:58:12 (5:33:55:7), respectively. However, ion cyclotron resonance experiments[8] show that for non-decomposing a ions (such as those producing the CAD data), this isomerization does *not* involve ring opening to CH_3CH=$OCH_2^+\cdot$ (d). This isomer transfers $CH_2^+\cdot$ to CH_3CN, while there

Scheme II
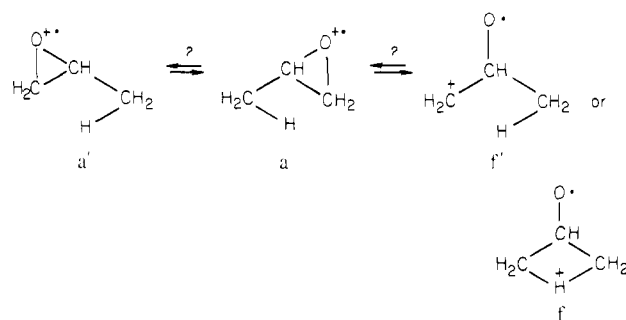
is no measurable transfer from ionized propene oxide. Scheme II shows speculative alternative mechanisms for this low-energy isomerization. Simultaneous bond forming and bond breaking yielding a' would involve an unusually tight activated complex. There would be less steric restriction for the formation of f' by concerted C–O bond cleavage and H transfer. This would require, however, that isomers f and a be of comparable stability. Unfortunately, a structure such as f was not considered in the extensive theoretical study of $C_3H_6O^+\cdot$ isomers.[8]

Minor Low-Energy Pathway for Methyl Loss from a and b. The PEPICO studies[10] gave evidence for a second methyl-loss pathway, in which the first step is the orbital symmetry allowed isomerization (1,2-H) to acetone ions [e($\tilde{A}$)] in their first excited state (ΔH_f = 220 kcal mol^{-1}). This could account for an additional decomposition pathway of metastable a and b ions which involves a much smaller energy release, producing a small ($\sim$2% of total area) hump in the center of the broad dished peak resulting from the 17 kcal mol^{-1} energy release.[22] For a this is confirmed by the relatively narrow peak for CH_3 loss by metastable decomposition of $CD_3\overline{CHCH_2O}$ (ad),[23] showing that for a this pathway involves the loss of the methine and methylene hydrogens. The methyl hydrogens also appear to be involved; there is small center hump in the broad metastable peak for CH_3 loss from $CH_3\overline{C}$-$\overline{DCD_2O}$ (ac).[23] The CAD spectra (Table III) of $C_2H_3O^+$ ions from this central portion of the metastable peaks from a, of which possibly 10–30% are formed by this reaction, show these to be >97% for the acetyl isomer, based on the CAD spectra of the other known $C_2H_3O^+$ isomers.[9,12] The same low-energy-release reaction observed for b could then occur by b → a → e($\tilde{A}$).

High-Energy Pathway for Methyl Loss from $CH_3\overline{CHCH_2O}^+\cdot$ (a). Ionization with 70-eV electrons produces a substantial increase in the proportion of the loss of methyl incorporating the methine and methylene hydrogens from a (but not from b), as shown by the 19% CH_2D loss from $CH_3\overline{CDCH_2O}$ (aa), 15% CD_3 loss from $CH_3\overline{CDCD_2O}$ (ac), and 18% CH_3 loss from $CD_3\overline{C}$-$\overline{HCH_2}$ (ad). However, this increase is not accompanied by the equivalent loss of the original methyl expected for the isomerization a → e($\tilde{A}$); ac and ad lose 14% CH_3 and 10% CD_3, respectively, and CAD studies[9] indicate that a substantial part of this is due to direct CH_3 loss to form $\overline{CH_2CH}$=O^+, whose heat of formation is $\sim$58 kcal mol^{-1} higher than that of CH_3CO^+.[8,9,12,24] A concerted loss of the methylene group and the methine hydrogen from a (or d) is a possible explanation for this, but would involve a very

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(19) The average internal energy of molecular ions after collisional activation is generally somewhat less than that after formation by 70-eV electron ionization: Kim, M. S.; McLafferty, F. W. *J. Am. Chem. Soc.* **1978**, *100*, 3279.

(20) Holmes, J. L.; Terlouw, J. K. *Can. J. Chem.* **1975**, *53*, 2076.

(21) 1,2-H rearrangement also appears to be entropically more favorable than 1,4-H rearrangement for CH_3C(=O^+H)CH_2CHCH_3: McAdoo, D. J.; McLafferty, F. W.; Hudson, C. E.; Parks, T. E. *Org. Mass Spectrom.*, accepted for publication.

(22) Confirming the original report,[9] we do not find such a center hump in the broad metastable produced by CH_2=$CHOD^+\cdot$ → CH_3CO^+ + $\cdot D$.

(23) Conclusions concerning the peak shape of $C_2H_3O^+$ ions formed by metastable decomposition of ad or ac are ambiguous because of overlap with the C_2HDO^+ peak.

(24) Because the methine-labeled isomer of b was not prepared, the proportion of higher-energy methyl losses incorporating this hydrogen cannot be quantitated. The CH_2=$CHOCD_3$ (ba) data show this to be ≪26% for 70-eV electron ionization, representing the CHD_2 loss from CH_2DCH=$OCD_2^+\cdot$; however, this can also isomerize to $\cdot CHDCH$=O^+CHD_2 which loses CHD_2 directly or through c. The data for ba and bb (Table I) also show that isomerization to a followed by direct methyl loss is negligible (≪7%).
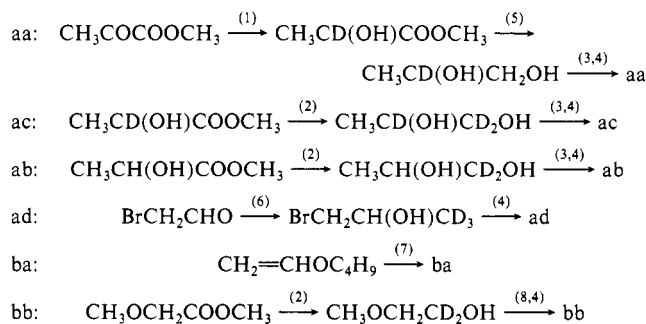
tight activated complex. Alternatively, it is conceivable that the 1,2-H isomerization a → e(Ã) at these higher energies produces $CH_3COCH_3^+\cdot$ with sufficient excess vibrational energy in the newly formed methyl to result in its favored loss in a non-ergodic process. This mechanism is demonstrated in the preceding paper[11] for excited $CH_3COCH_3^+\cdot$ ions formed by 1,3-H isomerization from $CH_3C(OH)CH_2^+\cdot$.

Experimental Section

The tandem mass spectrometer[25] and experimental conditions are described in the preceding article.[11] Propene oxide was obtained from Aldrich and ad from Merck, and methyl vinyl ether was prepared according to ref 26. Synthetic conditions for the labeled compounds were the following: (1) NaBD₄, methanol; (2) LiAlD₄, ether; (3) HBr (gas); (4) KOH; (5) LiAlH₄, ether; (6) CD₃MgI, ether; (7) CD₃OH, Hg(OCOCH₃)₂; (8) PBr₃, pentane.

(25) McLafferty, F. W.; Todd, P. F.; McGilvery, D. C.; Baldwin, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 3360.
(26) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828.

aa: $CH_3COCOOCH_3 \xrightarrow{(1)} CH_3CD(OH)COOCH_3 \xrightarrow{(5)}$
$CH_3CD(OH)CH_2OH \xrightarrow{(3,4)}$ aa

ac: $CH_3CD(OH)COOCH_3 \xrightarrow{(2)} CH_3CD(OH)CD_2OH \xrightarrow{(3,4)}$ ac

ab: $CH_3CH(OH)COOCH_3 \xrightarrow{(2)} CH_3CH(OH)CD_2OH \xrightarrow{(3,4)}$ ab

ad: $BrCH_2CHO \xrightarrow{(6)} BrCH_2CH(OH)CD_3 \xrightarrow{(4)}$ ad

ba: $CH_2{=}CHOC_4H_9 \xrightarrow{(7)}$ ba

bb: $CH_3OCH_2COOCH_3 \xrightarrow{(2)} CH_3OCH_2CD_2OH \xrightarrow{(8,4)}$ bb

He I and He II Photoelectron Spectra and CNDO/S and MNDO MO Calculations of Some Bridged [10]Annulenes

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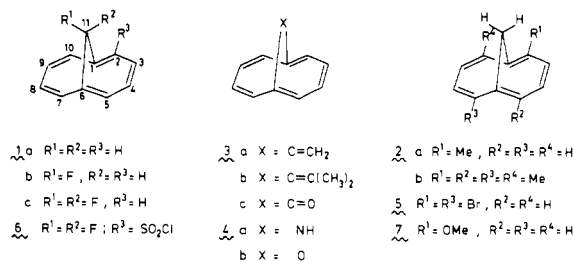
Abstract: He I and He II PE spectra of a series of 13 bridged [10]annulenes are reported. For all compounds the order of the observed π MO's of the peripheral ring from high to low energy is 7a₂, 13a₁, 9b₁, and 9b₂ (based on C_{2v} symmetry). For 1,6-methano[10]annulene (**1a**) and 11,11-difluoro-1,6-methano[10]annulene (**1c**), the ionization energies of the π MO's have been calculated by CNDO/S and MNDO calculations. With **1b**, **1c**, **2a**, **2b**, **3a**, and **3b** the observed perturbation on the π system as a result of the introduction of substituents on the bridge and in the peripheral ring appears to be distributed roughly to the same degree over the π MO's. Calculations for **2a** in which the methyl substituent is taken as a first-order perturbation on the perimeter π MO's leads to essentially the same conclusion. Computer plots of the upper four π MO's of **1a**, constructed from the eigenvectors calculated by CNDO/S and MNDO, show that the ring π system is locally not orthogonal to the σ framework. The observed relatively large stabilization of the 9b₂ as compared to the other π MO's of **3a** and **3b** may be explained by a *through-space* interaction of this MO with the carbon p_π orbital of the bridge.

1,6-Methano[10]annulene (**1a**), synthesized elegantly by Vogel,[1] is classified to be a Hückel aromatic hydrocarbon.[2] It formally results upon replacing in [10]annulene the hydrogens at C^1 and C^6 by a methylene group.

The nonplanar perimeter of **1a**[3] and its derivatives shows a high reactivity[4–6] and a very high positional selectivity toward electrophilic substitution.[4–8] Sulfonation with the dioxan–SO₃ complex,[4] bromination with Br₂ and with *N*-bromosuccinimide,[6–8] and isocyanosulfonylation[7] all yield exclusively the 2-substituted product. Also sulfonation of, e.g., 11-methylene- (**3a**),[5] 11-oxido- (**4b**),[9] and 11,11-difluoro-1,6-methano[10]annulene (**1c**)[9] with 1 equiv of dioxane–SO₃ yields exclusively the 2-sulfonic acid.

To obtain a better insight into the electronic structure of the bridged [10]annulenes, we have made a UV photoelectron spectroscopy (PES) study of **1–7** and have performed CNDO/S and MNDO MO calculations on **1a** and **1c**.

A decade ago Boschi, Schmidt, and Gfeller observed that in the He I spectrum of **1a**[10] the degeneracy of the $1e_{1g}$ and $1e_{2u}$ π

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1a R¹=R²=R³=H
b R¹=F, R²=R³=H
c R¹=R²=F, R³=H
6 R¹=R²=F; R³=SO₂Cl

3a X = C=CH₂
b X = C=C(CH₃)₂
c X = C=O
4a X = NH
b X = O

2a R¹=Me, R²=R³=R⁴=H
b R¹=R²=R³=R⁴=Me
5 R¹=R³=Br, R²=R⁴=H
7 R¹=OMe, R²=R³=R⁴=H

MO levels of the [10]annulene with D_{2h} symmetry is removed. This lifting of the degeneracy may a priori be explained in terms

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