determinations and the predictable substituent influence apparent in the data strongly suggest that crystallographically observed conformers seldom deviate from minimum energy positions regardless of hypothetical broad energy minima, metastable states, and small barriers to rotation.

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Supplementary Material Available: A listing of IUPAC names and complete references to the X-ray crystal structure determinations (5 pages). Ordering information is given on any current masthead page.

Stereoelectronic Control in the Gas-Phase Ionization of Cyclic Ortho Esters

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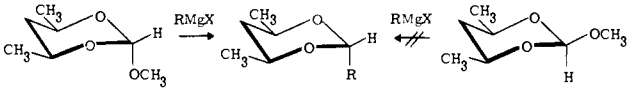
Abstract: As a test of stereoelectronic control in the gas phase, the rates of ionic cleavage of the exocyclic methoxyl group of 2-methoxy-*cis*-4,6-dimethyl-1,3-dioxane diastereomers have been measured by ion cyclotron resonance techniques. The reactant ions were isopropyl and (methylthio)methyl cations derived from electron-impact cleavage of 2-methylpropane and 2-(methylthio)ethanol, respectively. Within experimental error, the rates of cleavage of the equatorial methoxyl were the same as those of the axial methoxyl with a given reactant ion. With use of mixtures of deuterium-labeled and unlabeled diastereomers and reactant ions derived from isopropyl ether and acetylacetone, a slight (10%) preference was seen for cleavage of the axial methoxyl group. The significance of these results in terms of stereoelectronic and conformational effects is discussed.

Many reactions in organic and bioorganic chemistry are remarkably dependent on conformational effects. In fact, stereoselectivity in reactions under kinetic control arises when the transition state requires that the substrate assume a particular conformation. If, for reasons of conformational inflexibility, a given compound cannot achieve a "reactive" conformation, that compound will be unreactive. Also, steric demands of the transition state often dictate that only one of several possible stereoisomeric products will be formed.

The most obvious factor in the manifestation of stereoselectivity is the physical "size" of the reactants in the vicinity of the reaction site. The concept of bulk effects (steric hindrance) implies that a reactive conformation and hence the transition state can be achieved only with the expenditure of "strain" energy. In contrast, steric acceleration implies that repulsive steric effects are reduced in the transition state. However, reactions are known in which the observed selectivity is contrary to that expected if "best fit" or "size" criteria were controlling. Not infrequently, the reactive conformations are the least stable conformations—which means that factors other than simple size effects must be important. These factors have been ascribed to *stereoelectronic effects*, implying that a reaction has an optimal spatial arrangement of interacting bonding and nonbonding orbitals.[1] More explicitly, stereoelectronic control is the influence of lone-pair orbitals and polar bonds on the stability and reactivity of an intermediate (or transition state). There is a growing recognition that catalytic effects, especially in enzyme catalysis, may operate to impose (on the substrate) conformations which are reactive (but not necessarily the most stable) by virtue of an optimum overlap arrangement of participating orbitals.[2]

In general, our understanding of stereoelectronic control is derived from reactions of cyclic compounds possessing biased or fixed conformations. Stereoselectivity is normally observed as a difference in reactivity of closely related stereoisomeric substrates or as the preferential formation of one stereoisomeric product over another. In most cases, the critical step is one in which there is a hybridization change at carbon from sp^2 to sp^3 or the reverse.

Recent experimental studies have revealed many examples of stereoselectivity in carbonyl addition reactions and in the cleavage of tetrahedral intermediates,[3-5] and, to some extent, the experimental results are supported by theoretical studies.[2,6] The influence of stereoelectronic control in bond cleavage at a tetrahedral carbon was recognised initially by Eliel and Nader,[5] who observed that cyclic ortho esters of the 1,3-dioxane ring system show a striking preference for cleavage of an axial exocyclic C–O bond compared to an equatorial C–O bond. As an example, the conformationally biased 2-methoxy-1,3-dioxane **1** reacts smoothly



1 **4** **2**

with Grignard reagents to give the corresponding axially substituted 2-alkyl-1,3-dioxane **4**. The equatorial isomer **2** is unreactive under these conditions. To explain both the difference in reactivity between **1** and **2** and the fact that substitution occurs with retention of configuration, Eliel and Nader suggested that the entering and leaving groups are constrained to a direction that is antiparallel (antiperiplanar) to lone-pair orbitals on *both* ring oxygens. Antiparallel C–O bond cleavage maximizes π-orbital overlap in the resulting dioxacarbocation **3**, while antiparallel C–C

(1) Stereoelectronic control is defined by: E. L. Eliel in "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, pp 139, 227; E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, in "Conformational Analysis", Wiley, New York, 1965, pp 81, 92, 307.

(2) J. M. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **96**, 4048 (1974).

(3) For reviews on stereoelectronic control in the cleavage of tetrahedral intermediates see: P. Deslongchamps, *Tetrahedron*, **31**, 2463 (1975); *Heterocycles*, **7**, 1271 (1977).

(4) P. Deslongchamps, U. O. Cheriyan, A. Guida, and R. J. Taillefer, *Nouv. J. Chim.*, **1**, 235 (1977).

(5) E. L. Eliel and F. W. Nader, *J. Am. Chem. Soc.*, **92**, 584 (1970); **92**, 3045 (1970).

(6) J. M. Lehn and G. Wipff, *J. Am. Chem. Soc.* **98**, 7498 (1976); **102**, 1347 (1980).

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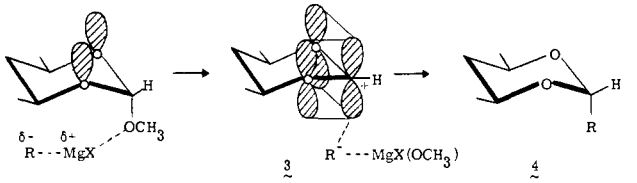
bond formation leads to the product **4** in a stable chair conformation, and only attack in the axial direction satisfies these conditions.



The subsequent extensive studies of Deslongchamps and coworkers have provided strong support for the importance of an antiperiplanar alignment of a polar bond and adjacent lone-pair orbitals in the oxidation of acetals and in the hydrolysis of estes and amides.[3,4] The phenomenon is apparently related to the so-called *anomeric* effect that pertains to the relative stabilities of carbohydrate anomers[7] and to the *gauche* effect regarding the relative stabilities of conformations having polar bonds and lone-pair orbitals.[8] The explanation of the observed stereoselectivity, whether it be manifested in chemical reactivity or conformational stability, is electronic in origin. Therefore, if the explanation is correct, the effect is an intrinsic molecular property. Theoretical calculations do indeed support the orbital electronic nature of stereoelectronic effects.[2,6,9] It is to be expected therefore that related stereoelectronic effects should exist in gas-phase organic reactions wherein the moderating influence of solvent and counterions are entirely absent and where reaction "conditions" more closely relate to the reactions of theory than to reactions in condensed phase. In fact, calculations indicate that the magnitude of stereoelectronic effects should be greater in the gas phase than in condensed phase.[6]

Gas-phase ionic reactions can be studied conveniently by the techniques of ion cyclotron resonance spectrometry (ICR),[10] chemical ionization mass spectrometry,[11a] high-pressure mass spectrometry,[11c] and flowing afterglow techniques.[11b] Recent work of this kind has provided fundamental information on the intrinsic (solvent-free) properties of organic ions and has made it possible to obtain thermochemical data (heats of formation of ions,[12] equilibria in proton-transfer reactions,[13] association energies[14]), reactivity data,[15] and information of reaction mechanisms.[16,17] There have been relatively few studies that focus on the stereochemistry of gaseous ion–molecule reactions,[18] and, in earlier work in collaboration with Beauchamp on the ionic reactions of alcohols in the gas phase, we observed no selectivity in the dehydration of diastereomers of 2-butanol-3-d_1.[19] The experiments described in this paper deal with the selectivity for C–O bond cleavage in the gas-phase ionic reactions of axial and equatorial isomers of 2-methoxy-*cis*-4,6-dimethyl-1,3-dioxane **1** and **2**. The objective of these experiments was to test for stereoelectronic control in gaseous ionic reactions for which a measure of stereoelectronic control has been demonstrated in comparable reactions in solution.

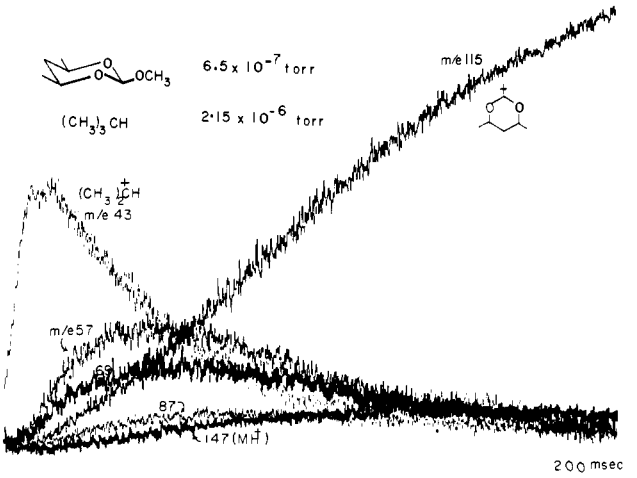


Figure 1. Time plot showing change in ion abundance with time for ions m/e 43, 57, 69, 87, 115, and 147 in the reaction of 2-methylpropane at 2.15×10^{-6} torr with 2*r*-methoxy-4-*cis*, 6-*cis*-dimethyl-1,3-dioxane **2** at 6.5×10^{-7} torr. Essentially the same time dependence of ion abundance was obtained in the comparable reaction of 2-methylpropane with the axial isomer **1**.

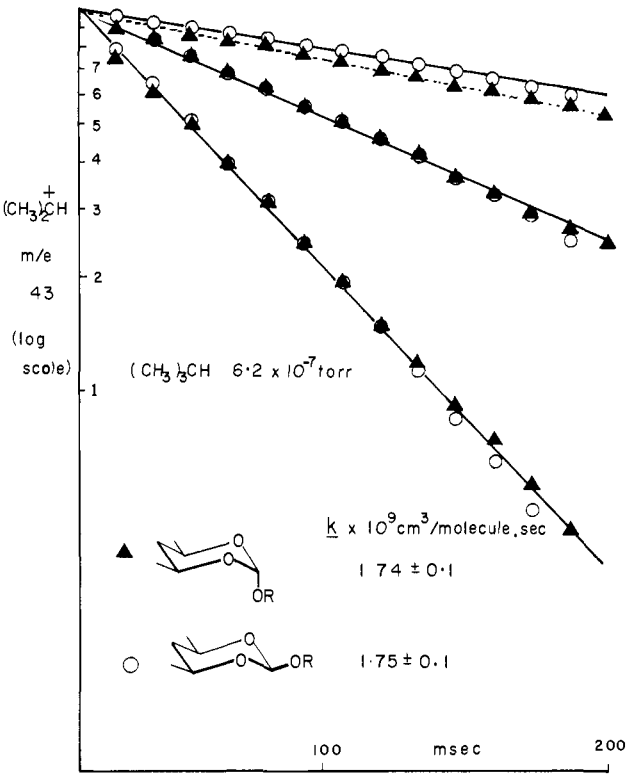


Figure 2. Plot of ion intensity of $CH_3C^+HCH_3$ m/e 43 with time (ms) in the reaction of 2-methylpropane at 6.2×10^{-7} torr with 2*r*-methoxy-4-*trans*,6-*trans*-dimethyl-1,3-dioxane **1** (full circles) and with the equatorial isomer **2** (open circles) at various pressures as indicated.

Experimental Section

Instrumentation. The gaseous ion–molecule chemistry of cyclic ortho esters **1** and **2** and mixtures thereof with other reactants was investigated by pulsed ICR techniques using a trapped-ion analyzer cell.[24] Samples

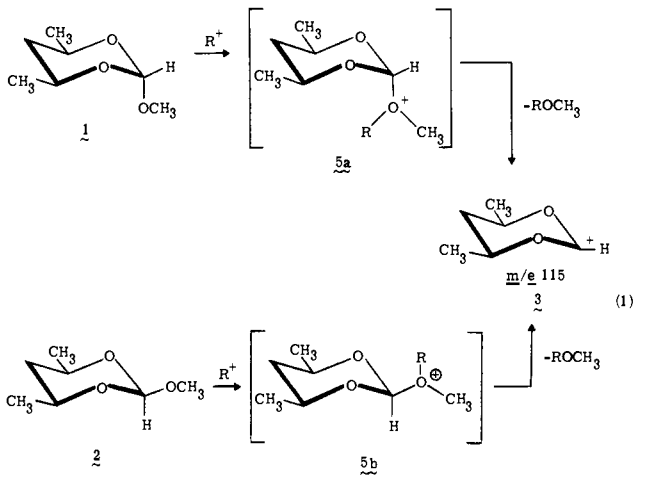
(7) See R. U. Lemieux, *Pure Appl. Chem.*, **25**, 527 (1971). For a description of the generalized anomeric effect see E. L. Eliel, *Angew. Chem., Int. Ed. Engl.*, **11**, 739 (1972).
(8) S. Wolfe, *Acc. Chem. Res.* **5**, 102 (1972).
(9) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc., B*, 136 (1971); S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 3806 (1973); C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1969).
(10) J. D. Baldeschwieler, *Science (Washington, D.C.)*, **159**, 263 (1968); C. J. Diewery, G. C. Goode, and K. R. Jennings, *MTP Int. Rev. Sci. Phys. Chem., Ser. One*, **5**, 259 (1972); J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(11) (a) F. H. Field, *Acc. Chem. Res.*, **1**, 42 (1968); (b) D. K. Bohme, E. Lee-Ruff, and L. B. Young, *J. Am. chem. Soc.*, **94**, 5153 (1972); B. M. Bierbaum, C. H. DePuy, R. H. Shapiro, and J. H. Stewart, *ibid.* **98**, 4229 (1976); (c) K. Hiraoka, E. P. Grimsrud, and P. Kebarle, *J. Am. Chem. Soc.*, **96**, 3359 (1974); A. J. Cunningham, J. D. Payzant, and P. Kebarle, *ibid.*, **94**, 7627 (1972).
(12) See J. E. Bartmess and R. T. McIver, Jr., in "Gas Phase Ion Chemistry", M. T. Bowers, Ed., Academic Press, New York, **1978**. See also T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 3399 (1976).
(13) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).
(14) P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977).
(15) W. N. Olmstead and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 4219 (1977).
(16) J. L. Beauchamp in "Interactions between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, 1975, pp 418–436.
(17) J. K. Pau, J. K. Kim, and M. C. Caserio, *J. Am. Chem. Soc.*, *100*, 3831, 3838 4242 (1978).
(18) C. A. Lieder and J. I. Brauman, *J. Am. Chem. Soc.*, **96**, 4028 (1974); *Int. J. Mass. Spectrom. Ion. Phys.*, **16**, 307 (1975).
(19) J. L. Beauchamp and M. C. Caserio, *J. Am. Chem. Soc.*, **94**, 2638 (1972).

pressures were on the order of 5×10^{-6} torr, and reaction times were varied from 10 to 200 ms. The precursor ions for each observed product ion were identified by double-resonance techniques and by measuring the change in ion intensities with time.

Synthesis of the isomeric cyclic ortho esters **1** and **2** was achieved by the condensation of *meso*-2,4-dimethylpentane-1,5-diol with methyl orthoformate according to the method of Eliel and Nader.[5] The reaction gave a 5:3 mixture of **1**–**2** which was separated into its pure components by GPC. The deuterium-labeled analogues **1**-*2-d* and **2**-*2-d* were prepared similarly by using deuterium-labeled orthoformate obtained from chloroform-d_1, methanol-d_1, and sodium metal.[20]

Results and Discussion

The gaseous ion chemistry of *both* cyclic ortho esters **1** and **2** was dominated by cleavage of the exocyclic C–O bond to give *m/e* 115 as the product ion, which is presumably the dioxacyclohexyl cation **3** (eq 1). In the absence of other neutral substrates the



precursor ions to *m/e* 115 were fragment ions *m/e* 57, 69, and 87. When 2-methylpropane was added as a reactant gas to provide a source of $(CH_3)_2CH^+$ *m/e* 43, then *m/e* 115 was formed at the expense of *m/e* 43 (Figure 1). By monitoring the rate of disappearance of *m/e* 43 at different partial pressures of **1** or **2**, we determined the rate of formation of *m/e* 115 from **1** or **2** (Figure 2). The reaction is expressed by eq 1 where the reactant ion R^+ is $(CH_3)_2CH^+$ formed by the fragmentation of 2-methylpropane on electron impact. The ion may react with the cyclic esters as shown in eq 1 by alkylation followed by dissociation of 2-methoxypropane, or it may transfer a proton to give **5** (R = H) which then dissociates by loss of methanol. Either way, the only observable product ion is *m/e* 115. The important point is that the rate of cleavage of the axial methoxyl group of **1** was found to be essentially equal to the rate of cleavage of the equatorial methoxyl of **2** or $(1.74 \pm 0.07) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

In a similar experiment, the production of *m/e* 115 by reaction of the ion $CH_3SCH_2^+$ *m/e* 61 with **1** and **2** was studied. The neutral source of *m/e* 61 was $CH_3SCH_2CH_2OH$ and the reaction is expressed by eq 1 where $R^+ = CH_3SCH_2^+$. The change in ion intensity of *m/e* 61 with time at different pressures of **1** and **2** was monitored, and, although the reactions were 1 order of magnitude slower than for the reactant ion $R^+ = CH_3CH^+CH_3$, the axial isomer **1** reacted at a rate ($k = (7.34 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) that was within experimental error the same as that of the equatorial isomer **2** ($(7.63 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). These results are shown in Figure 3.

The absence of any discernible difference in the rates of axial vs. equatorial C–O bond cleavage in **1** and **2** raises some doubt as to the validity of stereoelectronic control in the gas phase. However, unlike in solution-phase reactions, it is not appropriate to equate relative rates with relative transition-state energies in gas-phase ion–molecule reactions if the rates are determined solely by long-range effects of attraction between the gaseous ion and the dipolar (or induced-dipolar) neutral molecule.[21] Moreover,

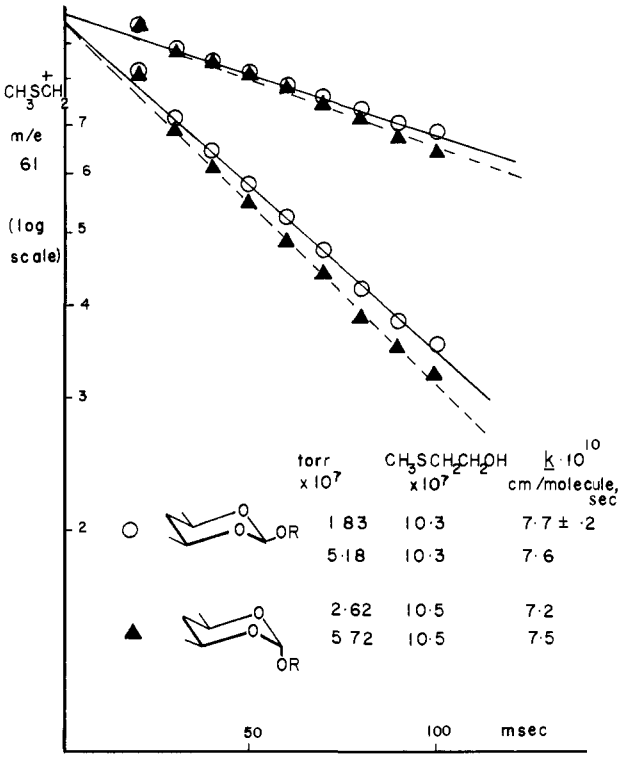


Figure 3. Plot of ion intensity of $CH_3SCH_2^+$ *m/e* 61 with time (ms) in the reaction of 2-(methylthio)ethanol at 1.04×10^{-6} torr with 2*r*-methoxy-4-*trans*,6-*trans*-dimethyl-1,3-dioxane **1** (triangles) and with the equatorial isomer **2** (open circles) at various pressures as indicated.

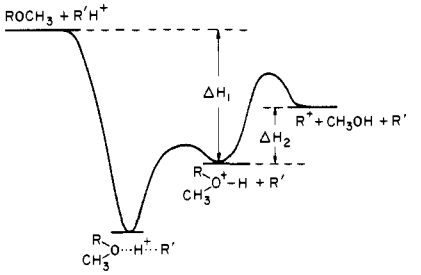
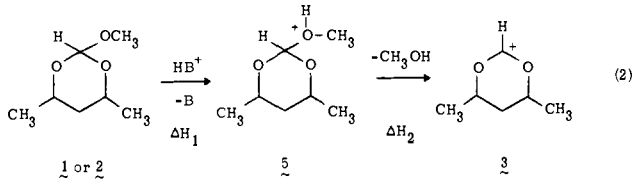


Figure 4. Energy profile for the reaction $ROCH_3 + R'H^+ \rightarrow R^+ + CH_3OH + R'$. The association complex $ROCH_3 \cdots H^+ \cdots R'$ represents an energy minimum but cannot be collision stabilized at low pressures before dissociating to reactants or products $(ROCH_3)H^+ + R'$ if ΔH_1 is exothermic. Dissociation of $(ROCH_3)H^+$ to R^+ and methanol requires about 20 kcal of energy based on $\Delta H_f(CH_3OH) = -48.05$ kcal mol^{-1}, $\Delta H_f(HC(OCH_3)_3) = -121.3$ kcal mol^{-1}, $\Delta H_f(H^+) = 366$ kcal mol^{-1}, and $\Delta H_f(HC^+(OCH_3)_2) = 118$ kcal mol^{-1} and an estimated PA($HC(OCH_3)_3$) of 195 kcal mol^{-1}.

the low pressure ICR conditions (10^{-6} torr) preclude reaction through thermal activation. Hence, when the ion and the neutral become associated during the initial (rate-controlling) stage, the complex will not dissociate to products if the net reaction is endothermic. The reaction profile of Figure 4 describes the situation.[22] Thus, the indistinguishable rates of reaction of **1** and **2** with $(CH_3)_2CH^+$ *m/e* 43 may mean that we are measuring only the effects of long-range association of the ion and the neutral, which not surprisingly are the same for both isomers. Also, the internal energy of either complex is more than enough to cause dissociation to *m/e* 115 without the intervention of an observable intermediate, **5a** or **5b**.

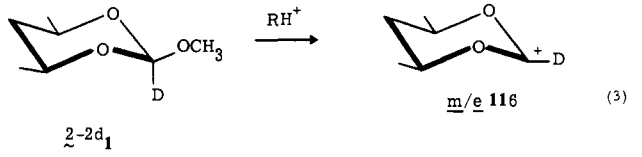
(20) P. P. T. Sah and T. S. Ma, *J. Am. Chem. Soc.*, **54**, 2964 (1932).
(21) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).
(22) For a discussion of reaction profiles in gaseous low-pressure ion–molecule reactions see ref 19 and 20. See also W. E. Farneth and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 7891 (1976).
(23) For a scale of proton affinities of neutral bases see ref 13. See also R. H. Staley, M. Taagepera, W. G. Henderson, I. Koppel, J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 326 (1977).
(24) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **49**, 111 (1977); **41**, 555 (1970).

A preference for elimination of axial over equatorial methoxyl (eq 1) is expected to be discernible by kinetic methods if the exothermicity ΔH_1 of the first step in Figure 4 (proton transfer or alkylation) is comparable to the endothermicity ΔH_2 of the second step. We therefore studied the reactions of **1** and **2** with reference acids of proton affinity (PA) comparable to that of **1** or **2** to keep the energy of proton transfer to a minimum. The acids of choice were the M + 1 ions derived from disopropyl ether (PA = 203 kcal mol^{-1}) and acetylacetone (PA = 205 kcal mol^{-1}). Using these reference acids, we were able to observe the protonated parent ions **5** as well as the dissociation product **3** (eq 2)



(2)

Relative rates of dioxacarbocation formation **3** from axial and equatorial ortho esters **1** and **2** can be obtained in principle from the relative intensities of product ions from the two sources. Such an experiment requires that one be able to distinguish the dioxacarbocation derived from **1** from that derived from **2**. In principle, this can be done by using isotopically labeled substrates. We therefore synthesized deuterium-labeled analogues **1**-*2*-d_1 and **2**-*2*-d_1. The gas-phase ion chemistry was then determined by using *mixtures* of labeled and unlabeled **1** and **2** at known partial pressures. The major product ions obtained from a mixture of **1**-d_0 and **2**-*2*-d_1 were *m/e* 115 and *m/e* 116, respectively (eq 3 and 4). At equal partial pressures of neutrals, we assume that



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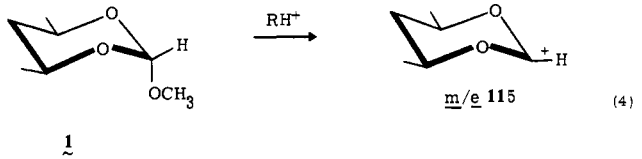
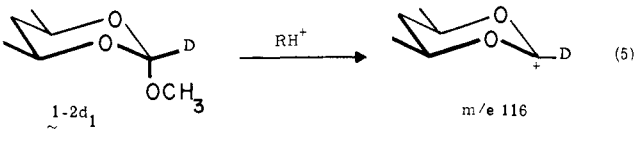


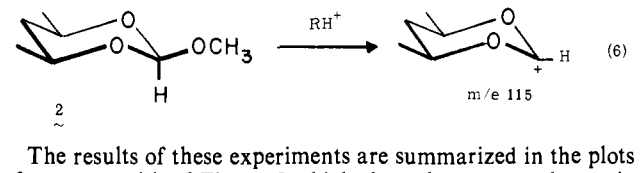
(4)

inequality in the intensities of *m/e* 115 and *m/e* 116 reflects stereoselectivity in the formation of one ion over the other.

As a necessary check on the validity of the experiment, it was repeated with the comparable mixture of **1**-*2*-d_1 and **2** which gave *m/e* 116 and *m/e* 115, respectively (eq 5 and 6).



(5)



(6)

The results of these experiments are summarized in the plots of parts a and b of Figure 5 which show the percent change in the ion intensity of *m/e* 115:*m/e* 116 (or 116:115) of mixtures of unlabeled **1** and labeled **2** (or labeled **1** and unlabeled **2**) as the pressure of the reactant gas (isopropyl ether or acetyl acetone) is increased. It must be remembered that ions *m/e* 115 and 116 are formed from the neutrals **1** and **2** without the agency of added

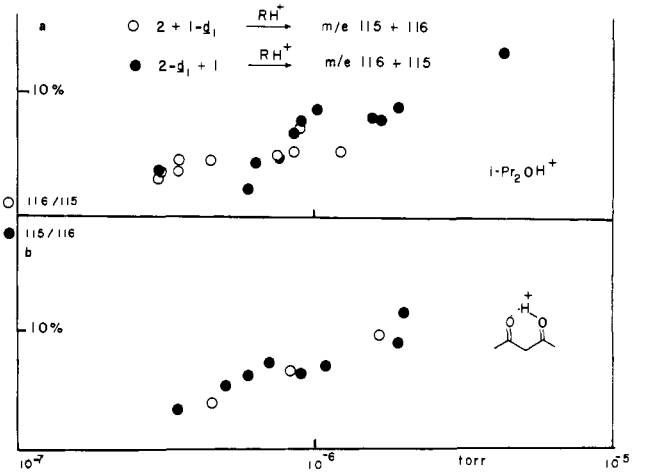
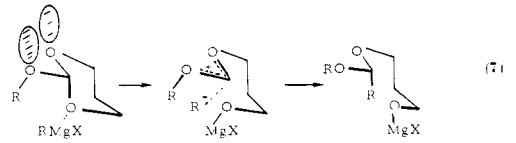


Figure 5. a. Plot of percent change in ion abundance ratio *m/e* 116:*m/e* 115 (open circles) for a 1:1 mixture of **1**-d_1 and **2** as a function of partial pressure of isopropyl ether added as a reagent gas. The percent change in *m/e* 115:*m/e* 116 (closed circles) is for the comparable reaction with **1** and **2**-d_1. b. Plot of percent change in the ratio *m/e* 116:*m/e* 115 (open circles) for a 1:1 mixture of **1**-d_1 and **2** with partial pressure of acetylacetone added as a reagent gas. The ratio *m/e* 115:*m/e* 116 (closed circles) is for a comparable reaction of **1** and **2**-d_1.

reactants at about equal rates. Thus, we are simply monitoring the *increase* in the relative abundance of *m/e* 115 and 116 in the presence of *added* reactants. As can be seen from the parts a and b of Figure 5, there is a small but significant change in the ion ratio 115:116 that is in the direction of preferential cleavage of the axial C–OCH_3 bond. The results are reproducible and internally consistent. Thus, the ratio 115:116 from (**1** + **2**-*d*) increases with the pressure of the reactant gas, showing that axial elimination from **1** is slightly faster than equatorial elimination from **2**-*d* (eq 3 and 4). Likewise, the ratio 116:115 from (**1**-*d* +**2**) increases with the pressure of reactant gas, again showing the axial elimination from **1** is slightly faster than equatorial elimination from **2** (eq 5 and 6). The observed increase in *m/e* 115:116 (or 116:115) is not dramatic and corresponds to a 10% increase for a 10–15-fold increase in pressure.

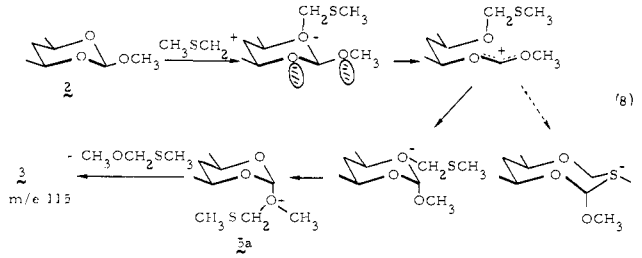
The observed selectivity for axial bond cleavage is consistent with the concept of stereoelectronic control. However, it is perhaps surprising that the effect of stereoelectronic control is less pronounced in the gas phase than it appears to be in solution. As previously mentioned, Grignard cleavage of **1** in solution is rapid whereas **2** fails to react under the same conditions.[5] However, Croteau and Bailey recently reported that the reactions of cyclic ortho esters with organometallic reagents are solvent dependent and, in the case of 2-methoxy-1,3-dioxane, give mainly ring-opened product (eq 7).[25] Although their results do not negate the concept



(7)

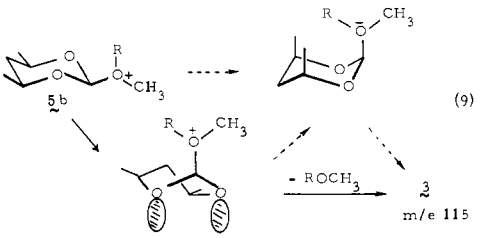
of stereoelectronic control, they emphasize that cleavage of a polar C–O bond in ortho esters is solvent dependent. If the dioxane ring is flexible and biased toward an equatorial orientation of the exocyclic OCH_3 group when complexed with RMgX, ring opening is consistent with stereoelectronic control (eq 7). It is possible, therefore, that in our gas-phase experiments the product ion *m/e* 115 could be formed from the equatorial isomer **2** by initial cleavage of a ring C–O bond followed by rapid ring closure to **5a** and elimination of $ROCH_3$ (eq 8). However, we discount this possibility because the intramolecular 1,3 migration of R^+ ($R \neq H$) from the ring oxygen to the exocyclic oxygen is unprecedented

(25) A. Croteau and W. F. Bailey, 178th National Meeting of the American Chemical Society, Washington, D. C., Sept 1979, Org. 105.



and, in the case of R = CH_3SCH_2, a more likely process would be cyclization by C-S bond formation to give a sulfonium ion, contrary to observation.

A further point to consider is whether the energy of ion-molecule association in the initial encounter (i.e., the well depth of the first minimum in Figure 4) is sufficient to fuel ring inversion to higher energy conformations. The association energy may be substantial (~20 kcal mol^{-1}).[26] If ring inversion occurs, the axial C-O bond would almost certainly dissociate spontaneously. However, it is not necessary for **5b** to convert to the all-axial chair conformation in order to lose the exocyclic methoxyl group. Conversion to a boat form would also situate the interacting orbitals on the ring oxygens antiperiplanar to the exocyclic C-O bond, and this would presumably lead to facile dissociation (eq 9).



The present system of conformationally biased 1,3-dioxanes **1** and **2** cannot then provide a definitive test of stereoelectronic control in the gas phase because of potentially accessible twist-boat forms. In the continuation of this work, it will be necessary to employ systems that have fixed conformations that exclude even boat-chair interconversions. Regardless of interpretation, the interesting fact remains that the greater propensity for ionic cleavage of the axial methoxyl in **1** relative to the equatorial methoxyl in **2** in condensed phase is not evident in the gas phase.

Acknowledgment. We gratefully acknowledge the support of this work through Grant no. CHE 7807993 awarded by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(26) J. L. Beauchamp in "Interactions Between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, 1975.

Alkyl Group Stabilization of Monoolefin Radical Cations. An ESR, ENDOR, and Cyclic Voltammetry Study

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Abstract: The ESR spectrum of the radical cation of adamantylideneadamantane (**1**) exhibits proton coupling constants of 0.605 (4, δ-H), 0.327 (8 equatorial, γ-H), 0.058 (4 H), 0.047 (8 axial, γ-H), and 0.012 mT (4 H). The indicated assignment was secured by the studies of the δ-d_2 (**2a/2b**) and equatorial-γ-d_1 (**3**) species. For the radical cation of bis(bicyclo-[3.3.1]non-9-ylidene) (**4**), the proton coupling constants determined from its ESR spectrum are 0.370 (8, γ-H), 0.320 (4 H), 0.105 (4 H), and 0.055 mT (8, γ-H), while the ENDOR measurements on the radical cation of 9,9′-bis(9-azabicyclo[3.3.1]nonane) (**5**) yield 0.160 (4 H), 0.128 (8, γ-H), 0.099 (4 H), 0.059 (8, γ-H), and 0.027 mT (4 H). Cyclic voltammetry (CV) gives $E^{o\prime}$ values (vs. SCE; solvent CH_3CN) of 1.45 V for **1**, 1.49 V for **4**, 1.61 V for 4(e)-chloroadamantylideneadamantane (**8**), and 1.35 V for bis(homoadamantane) (**9**). The implication of these hyperfine and CV data on the electronic structure and physicochemical properties of the pertinent compounds and their radical cations is discussed.

The lability of C-H bonds at carbon atoms directly attached to a π center bearing a high spin population leads to a short lifetime of the radical and makes the study of such a radical difficult. It has been shown that alkyl groups which force the pertinent C-H bonds to lie perpendicular to the axis of the spin-bearing $2p_z$ AO confer substantial kinetic stability (persistence) on a radical. Paramagnetic species exhibiting this structural feature have been called "Bredt's rule protected". Relevant examples are secondary nitroxides[2] and hydrazine radical cations,[3] both of which may be isolated, as well as the long-lived hydrazyl and α-amino radicals,[3,4] and some trialkylamine and dialkylchloroamine radical cations.[3] It has recently been found that Bredt's rule protection also contributes to the persistence of the adamantylideneadamantane (**1**) radical cation.[5]

This paper deals with ESR studies on the radical cations of **1** and its deuterio derivatives **2a/2b** and **3**, together with those of the bicyclo[3.3.1]nonane analogue **4** and the structurally related hydrazine **5** and its diketo derivative **6**. In the case of **5**, use of ENDOR spectroscopy was essential for the determination of the proton hyperfine data. The notation employed for the protons is specified in the formulas by indicating one hydrogen atom for each set of equivalent protons; the numbering scheme of the carbon

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(2) Dupeyre, R.M.; Rassat, A. *J. Am. Chem. Soc.* **1966**, *88*, 3180.
(3) (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 2392. (b) Nelsen, S. F.; Kessel, C. R. *J. Chem. Soc., Chem. Commun.* **1977**, 490. (c) Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.
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(5) Nelsen, S. F.;, Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503.

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