in MeCN were determined as described previously.[2] The products were benzonitrile, benzaldoxime, aryloxides, and *N*-arylamines.

Control Experiment. The stabilities of **1** and **2** in MeCN were demonstrated as described previously.[2]

Acknowledgment. This investigation was supported by grants from KOSEF and KOSEF-OCRC.

Registry No. **1**, 75735-29-4; **2**, 115828-60-9; pyrrolidine, 123-75-1; piperidine, 110-89-4; tetrahydroisoquinoline, 91-21-4; morpholine, 110-91-8; *N*-(2,4-dinitrophenyl)pyrrolidine, 14552-00-2; *N*-(2,4-dinitrophenyl)piperidine, 839-93-0; *N*-(2,4-dinitrophenyl)tetrahydroisoquinoline, 135226-10-7; *N*-(2,4-dinitrophenyl)morpholine, 39242-76-7; *N*-picrylpyrrolidine, 77379-02-3; *N*-picrylpiperidine, 67263-27-8; *N*-picryltetrahydroisoquinoline, 135226-11-8; *N*-picrylmorpholine, 77379-03-4.

Supplementary Material Available: Listing of rate constants for E2 and S_NAr reactions of (*E*)-*O*-(2,4-dinitrophenyl)-benzaldoxime (**1**) and (*E*)-*O*-picrylbenzaldoxime (**2**) with R_2NH in MeCN at 25.0 °C (3 pages). Ordering information is given on any current masthead page.

Stereoelectronic Effects in Ionization Reactions of Cyclic Ortho Thioesters

Marjorie C. Caserio,*,† Phoebe Shih, and Cindy L. Fisher

Department of Chemistry, University of California—Irvine, Irvine, California 92717

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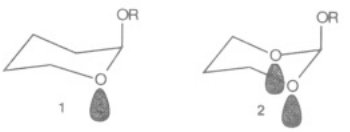
The objective of this work was to determine whether stereoselectivity observed in certain condensed-phase ionic reactions of ortho thioesters was also evident in related gas-phase reactions. Ionization of the C-2 epimers of *cis*-4,6-dimethyl-2-(methylthio)-1,3-dithianes **6** and **7** under FT-ICR conditions produced gaseous ions of m/z 147 corresponding to the *cis*-4,6-dimethyl-1,3-dithian-2-yl cation. Kinetics of ionization were followed by using mixtures of each epimer with 2-methylpropane or with 2-(ethylthio)ethanol. Kinetic parameters were calculated from the rates of decay of the precursor ions (m/z 43 from 2-methylpropane and m/z 75 from 2-(ethylthio)ethanol) at different pressures of reactants. Within experimental error, the specific rates of reaction of each epimer with m/z 43 and with m/z 75 were equal. Ionization is not therefore sensitive to stereochemical configuration at the C-2 reaction site in the gas phase. Solution-phase methylthiolation and methylation of the equatorial epimer (4*c*,6*c*-dimethyl-2*r*-(methylthio)-1,3-dithiane, **7**) led to reversible cleavage at C-2 to produce the *cis*-4,6-dimethyl-1,3-dithian-2-yl cation. Addition of sodium methanethiolate quenched the equilibrium and led irreversibly to a mixture of epimers **6** and **7** in which the axial epimer **6** was in modest excess. The control of reaction stereoselectivity in the formation and trapping of 1,3-dithian-2-yl cations from ortho thioesters is discussed.

Introduction

The reported selectivity for dissociation of *axial* substituents in polar displacement reactions of cyclic acetals **1** and ortho esters **2** has been attributed to stereoelectronic effects whereby reaction stereochemistry is controlled by the orientation of the reacting bond with nonbonding electron pairs on neighboring heteroatoms. The comprehensive studies of Deslongchamps reveal that the effect is operative only when the orbitals in question are antiparallel, which allows for their maximum interaction.[1,2] For example, the antiparallel orientation of the axial OR substituent of **1** and **2** with lone pair orbitals on the ring heteroatoms is believed to enhance the reactivity of the axial bond (over that of the equatorial epimer) through n $\rightarrow \sigma^*$ delocalization.[3] An alternative interpretation attributes a kinetic preference for axial cleavage to the principle of least nuclear motion, which is to say that the amount of reorganization at the reaction site is minimized (and the rate maximized) when the reacting bond is axial.[4,5] In addition, medium effects (due to solvent and counterions) and differences in leaving-group abilities undoubtedly influence reactivity. Because the relative importance of each effect in a given situation is not well understood and is difficult to determine,[3,6] any conclusion that reaction selectivities are due primarily to stereoelectronic effects would seem tenuous at best.



In an earlier paper we described an attempt to test for stereoelectronic effects in the gas-phase ionic dissociation of epimeric ortho esters **3** and **4** under conditions that eliminated solvent and counterions and hence ion-pairing effects.[7] The experiment used electron-impact ion cyclotron resonance (ICR) techniques for the generation of organic ions and the observation of their ensuing ion–molecule reactions at low pressure. We anticipated that, if stereoelectronic effects were significant factors in controlling ionic cleavage of ortho esters **3** and **4**, the cyclic ion **8** (m/z 115) would be produced more rapidly from the axial isomer **3** than from the equatorial isomer **4** (eq 1). The study showed that m/z 115 was indeed the major product ion of reaction of both esters with a variety of

* To whom correspondence should be addressed.
† Current address: University of California—San Diego, La Jolla, CA 92093.

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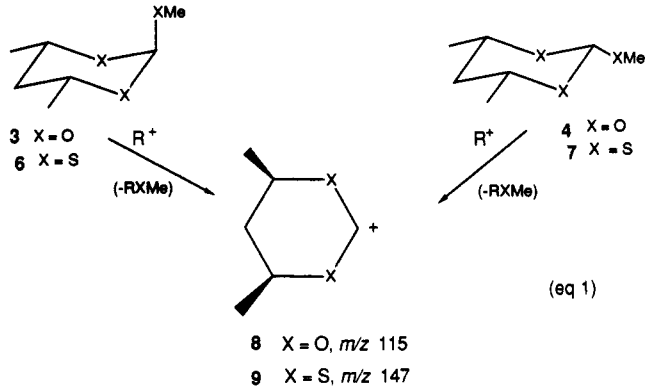
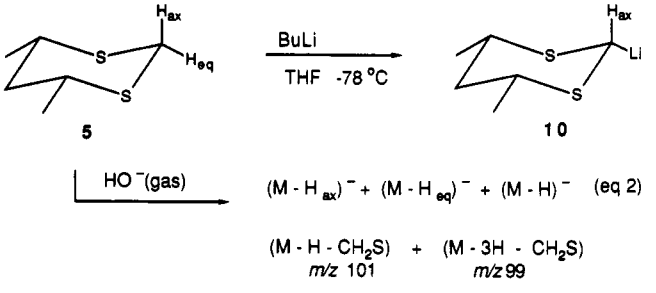


cations ($CH_3CH^+CH_3$, $CH_2{=}S^+CH_3$, R_2OH^+) but, contrary to expectation, m/z 115 was formed from either isomer at the *same* rate. These results are open to several interpretations. It is possible that conformational changes or rate-limiting ion–molecule association in the gas phase obscure the influence of stereoelectronic effects in the reactions of **3** and **4** under ICR conditions.[7] Alternatively, stereoelectronic effects may be less significant than anticipated.

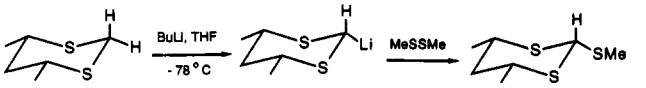
We reported recently another case where the stereoselectivity observed in solution could not be reproduced in the gas phase.[8] Reactions of the 1,3-dithiane system **5** with strong bases in aprotic solvents are highly selective for the equatorial C-2 proton,[9] but in the gas phase under ICR conditions reactions of **5** with basic anions (such as HO^-) are more selective for the *axial* C-2 proton and are accompanied by extensive proton loss from other CH sites and successive elimination (eq 2).[8] As before, our attempts to isolate possible stereoelectronic effects by eliminating solvent and counterion effects led to unexpected results.



The present paper describes further experiments that are pertinent to the stereoselectivities of related gaseous and condensed-phase ionic reactions. The compounds chosen for study were the C-2 epimers of *cis*-4,6-dimethyl-2-(methylthio)-1,3-dithiane (**6** and **7**) since they are related to the corresponding ortho esters **3** and **4** and to the 1,3-dithiane system **5** studied previously. Also, the conformational studies of Juaristi and co-workers[10,11] indicate a significant stereoelectronic effect of the ring heteroatoms in substituted 1,3-dithianes, including **6** and **7**, which stimulated our interest in the possibility that the effect would be also manifest in their reaction selectivities. Accordingly, the experiments here reported were designed initially to test for a Deslongchamp effect in the stereocontrol of gaseous reactions of 1,3-dithianes, but, as will be described, the ionic reactions of both **6** and **7** at the C-2 position to produce the cyclic ion **9** did not reveal any notable reactivity differences or stereocontrol in the gas phase.

Results and Discussion

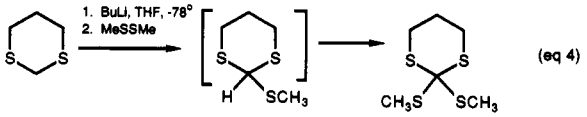
Solution Studies. Preparation of the equatorial ortho thioester **7** can be achieved with complete stereoselectivity by established procedures in which the corresponding 1,3-dithiane **5** is lithiated at low temperature in an aprotic solvent and then quenched with methyl disulfide (i.e., **5** → **10** → **7**, eq 3).[12] Under these conditions, lithiation



(eq 3)

replaces the C-2 equatorial proton exclusively.[8,9] The subsequent displacement step is equally selective for placing the entering methylthio group at the equatorial site provided low temperatures (−78 °C) are maintained. As noted earlier, comparable equatorial selectivity was not observed in gas-phase deprotonation of **5**.[8] It seems likely, therefore, that the selectivity observed in both steps of eq 3 is due to complexation and/or ion-pairing involving lithium such that the entering group approaches from the equatorial direction.[3]

As a point of possible interest, methylthiolation of the unsubstituted 1,3-dithiane **11** using the same conditions as in the methylthiolation of **5** gave the disubstituted product 2,2-bis(methylthio)-1,3-dithiane (**13**) (eq 4). The



(eq 4)

monomethylthio derivative **12** can be obtained only under conditions of inverse addition in which the lithiated dithiane is added to excess disulfide.

Synthesis of the axial ortho thioester **6** proved to be a challenge. The dominant reactivity in solution of the C-2 equatorial site of **5** made it unfeasible to prepare **6** by direct displacement involving dithianyl carbanions. Although equilibration of **6** and **7** can be achieved with base ($\Delta G_{173\,K}$ = 0.64 kcal mol^{-1} (CD_2CCl_2) in favor of the axial epimer **6**),[10] epimerization of **7** to **6** was attempted by a displacement sequence with sulfur electrophiles (eq 5). It was anticipated from previous work[13] that the C–SMe bond in the ortho thioester **7** would be activated on treatment with dimethyl(methylthio)sulfonium tetrafluoroborate **14**, giving **16** that would likely dissociate to give the dithianyl cation **9**, which, on subsequent reaction with sodium methanethiolate, would give the *axial* product **6** (eq 5). Thus, the significant feature of this reaction sequence is the anticipated trapping of an intermediate

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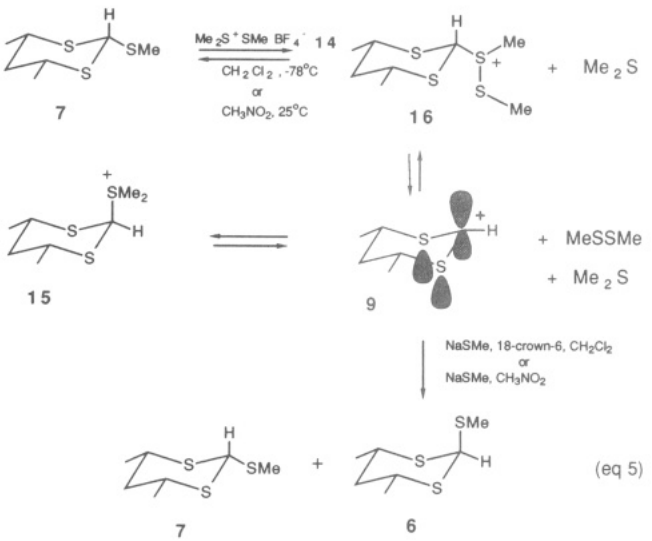
cation **9** by *axial* attack. Stereoelectronic arguments based on a considerable body of evidence lead to the expectation that an attacking nucleophile will enter preferably from the axial direction.

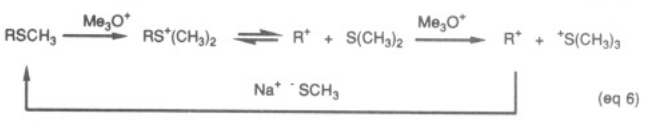
Based primarily on ^1H NMR evidence, the intermediate cation **9** was shown to be generated from **7** by the addition of the methylthiolating agent **14** in CD_3NO_2. When **14** was added, the solution turned bright yellow and the proton resonances of the starting ortho thioester **7** were replaced instantly by a complex set of broadened resonances that shifted downfield progressively as the amount of methylthiolating agent increased. Sharp singlets attributable to methyl sulfide (2.1 ppm) and disulfide (2.4 ppm) were also evident while the singlet at 2.34 ppm due to the methylthio group of **7** broadened and disappeared. Upon quenching the mixture by adding excess sodium methiolate at 25 °C, the solution became colorless and the signals of the starting ester **7** all reappeared along with those of the epimer **6** in the ratio of **7**:**6** = 3:4. These observations suggest the occurrence of a dynamic equilibrium in which the cation **9** is formed reversibly upon methylthiolation of **7** and is captured *irreversibly* by the methanethiolate nucleophile (eq 5). Higher selectivity for the formation



(eq 5)

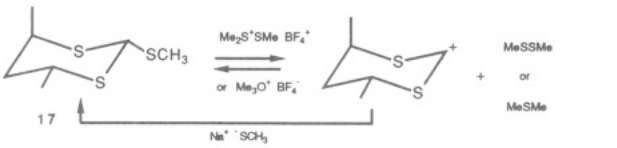
of the axial epimer was obtained at lower temperatures (−78 °C) in dry dichloromethane and with 18-crown-6 to solubilize the sodium methanethiolate whereby **6** was obtained as a 4:1 mixture with **7** from which **6** was separated chromatographically.

Similar results were observed in the reaction of **7** with trimethyloxonium tetrafluoroborate in nitromethane. Addition of the methylating agent produced an immediate color change (yellow) and a downfield shift and line-broadening of the proton resonances of **7**. When excess sodium methanethiolate was added, the starting ester **7** reappeared along with the axial epimer **6**. The main by-product was trimethylsulfonium tetrafluoroborate (eq 6).



(eq 6)

Reactions of the *racemic* ortho thioester **17** on methylthiolation and methylation were very similar to those observed for the meso isomer **7**. Immediately upon addition of the electrophile to a solution of **17** in nitromethane, there was a color change (red) and the proton resonances of **17** broadened and shifted downfield progressively as more of the electrophilic reagent was added. At the point of equivalence no further change occurred, but on adding excess sodium methanethiolate the color disappeared and the signals of **17** reappeared (eq 7).

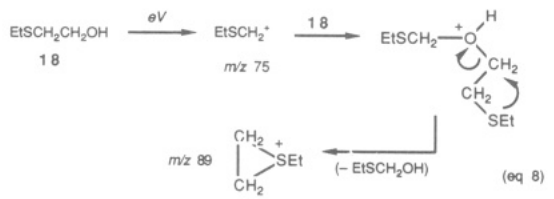


(eq 7)

It is tempting to conclude from these results that the step in which the cation (either **9** or its racemic counterpart) is captured irreversibly by methanethiolate anion produces a modest preference for axial attack. However, this conclusion is based on the assumption that methanethiolate reacts with the cation **9** and not with its precursors, particularly **15** and **16** or their respective C-2 epimers (eq 5), which are presumed to be in equilibrium with **9**. It is not possible to say how much of the reaction with MeS^- involves S_N2-type conversions of **15** and **16** to **6** and **7**. Analogous remarks apply to the regeneration of **17** in eq 7.

Gas-Phase Studies. The ion–molecule chemistry of each of the ortho thioesters **6** and **7** was investigated separately using Fourier Transform Ion Cyclotron Resonance techniques (FT-ICR) at sample pressures near 10^{-7} Torr and reaction times of up to 500 ms. The major primary fragment ion from each ester had m/z 69 corresponding in composition to $C_5H_9^+$. (This ion was also observed in the EI fragmentation of the oxygen analogues **3** and **4**.[7]) The major product ion had m/z 147, the ionic precursor of which was m/z 69. This remarkably simple ion chemistry is consistent with the reactions of eq 1 where the product ion m/z 147 corresponds to the cation **9** (X = S, R = $C_5H_9^+$). It is significant that m/z 147 is formed from *both* isomers, yet time plots do not reveal any striking difference in the rates of formation of m/z 147 from either one. A more quantitative assessment of this point was made from the reactions of **6** and **7** with other neutral reactants (2-(ethylthio)ethanol and 2-methylpropane) as the source of reactant ions, as described below.

The FT-ICR mass spectrum of 2-(ethylthio)ethanol showed two major peaks m/z 75, corresponding to the primary fragment ion $EtSCH_2^+$, and m/z 89, corresponding to the reaction product of m/z 75 with the parent neutral, for which a possible route is suggested in eq 8.



(eq 8)

The FT-ICR spectrum of a *mixture* of 2-(ethylthio)ethanol with either **6** or **7** showed the formation of m/z 147 from m/z 75, as expected of the reaction in eq 1 where R = $EtSCH_2^+$. This can be seen in the plot of ion intensity with time for the major ions produced from **7** and 2-(ethylthio)ethanol (Figure 1), which confirms that m/z 147 is formed at the expense of m/z 75 and that the competing reaction to produce m/z 89 is almost suppressed in the presence of the ortho thioester. Similar results were observed with **6** and 2-(ethylthio)ethanol. The logarithmic dependence of ion intensity of m/z 75 with time is shown in Figure 2 at different pressures of each thioester, **6** and **7**. The plots are reasonably linear, consistent with a first-order rate of decay of the reactant ion. The dependence of the slopes of the first-order plots in Figure 2 with

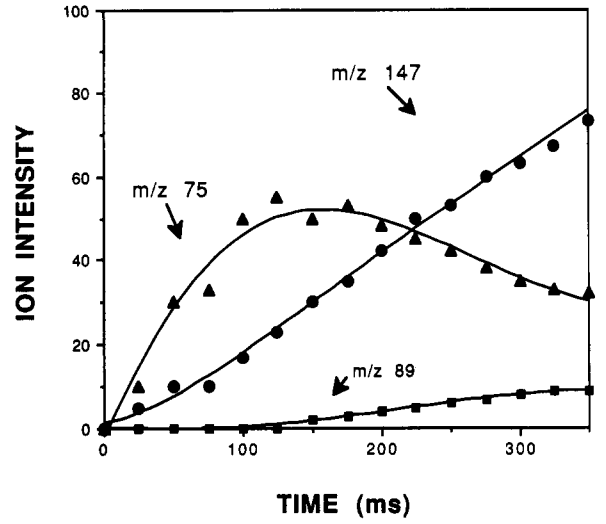


Figure 1. Plots of ion intensity with time in the reaction of a mixture of 2-(ethylthio)ethanol (5.7×10^{-7} Torr) with 7 (5.7×10^{-8} Torr) over 350 ms. The plots show the decay of the primary ion m/z 75 ($EtSCH_2^+$) and appearance of the major product ion m/z 147 (9) and m/z 89.

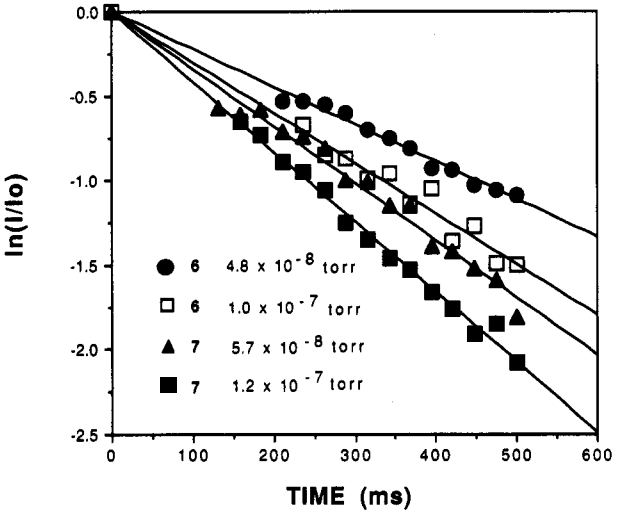


Figure 2. Logarithmic plot of ion intensity of m/z 75 with time (ms) for mixtures of 2-(ethylthio)ethanol (5.7×10^{-7} Torr) with meso epimers of 4,6-dimethyl-2-(methylthio)-1,3-dithianes 6 and 7 at different pressures: (●) 6 at 4.8×10^{-8} Torr; (□) 6 at 1×10^{-7} Torr; (▲) 7 at 5.7×10^{-8} Torr; (■) 7 at 1.2×10^{-7} Torr. The lines are extrapolated to zero time for purposes of comparison.

pressure of the corresponding ortho thioester, 6 or 7, provides an estimate of the second-order specific reaction rate of m/z 75 with 6 or 7. The values obtained were $k = (4.6 \pm 1.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the axial epimer 6 and $k = (3.7 \pm 1.0) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for the equatorial epimer 7. Thus, within the limits of error in the data, the rates of the two epimers are the same.

Similar results were obtained from mixtures of each ortho thioester with 2-methylpropane. The FT-ICR spectrum of 2-methylpropane by itself showed two major ions, m/z 43 ($C_3H_7^+$) and m/z 57 ($C_4H_9^+$). It was apparent from time plots and double resonance experiments that m/z 43 is the precursor to m/z 57 (eq 9). The FT-ICR

$$Me_3CH \xrightarrow{eV} \underset{m/z\ 43}{Me_2CH^+} + Me^\bullet$$

$$\underset{m/z\ 43}{Me_2CH^+} + Me_3CH \rightarrow \underset{m/z\ 57}{Me_3C^+} + Me_2CH_2 \qquad (9)$$

spectrum of a *mixture* of 2-methylpropane with either 6 or 7 gave m/z 147 at the expense of m/z 43, as expected of the reaction of eq 1 where $R = C_3H_7^+$. Logarithmic plots of ion intensity of m/z 43 with time at different pressures of 6 or 7 were reasonably linear. The dependence of the slopes of these plots with pressure of the corresponding neutral ortho thioesters gave the specific rate of reaction of m/z 43 with ortho thioester 6 as $k = (6.0 \pm 1.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and with 7 as $k = (6.2 \pm 2.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. As can be seen from this data, the rates are the same for each epimer within experimental error.

Conclusions. The collective results of the gas-phase reactions described here are similar in kind to the previously reported gas-phase ionization of ortho esters 3 and 4.[7] To the extent allowed by the precision of the experiment, both epimers 6 and 7 are similarly reactive toward m/z 75 ($C_2H_5SCH_2^+$) and toward m/z 43 ($C_3H_7^+$). It may be concluded that, under the conditions of the FT-ICR experiment, the reactivity of 6 and 7 in ionic cleavage of the exocyclic methylthio group is not significantly dependent on stereochemical configuration. There are several possible explanations for this apparent insensitivity, one of which is that formation of the product ion 9 is not kinetically significant. This would be the case if the rate-determining step is association rather than dissociation. The Langevin model of ion–molecule association relates the ion "capture" rate to forces of attraction between the ion and the induced dipole (polarizability) of the neutral molecule.[14] Since the polarizability of 6 and 7 should be very similar, the Langevin rates of association should also be similar, all other things being equal. If, in fact, polarizability of the neutral rather than activation energy of dissociation of the ion–molecule complex determines the rate of reaction, significant reactivity differences between stereoisomers would seem unlikely. However, Langevin limiting rates are more commonly observed in proton transfer and charge exchange reactions than with slower complex ion–molecule reactions of the type described here.[15]

Alternatively, the extent to which stereocontrol is evident in condensed phase reactions may actually be the result of medium effects. If so, similar control would not be apparent in the low-pressure gas-phase environment of the FT-ICR experiment where medium effects are absent. A Deslongchamps effect that would favor axial cleavage in the generation of the cation 9 would not then be seen. Our results, therefore, seem to have chased an elusive effect, and further studies of a more definitive nature are needed to unravel the relative importance of medium and stereoelectronic effects.

Experimental Section

The Fourier transform ICR experiments were performed on an Ion Spec Corporation FT-MS 2000 system based on FT-ICR principles first developed by Comisarow and Marshall[16] and later by Hunter and McIver.[17] Sample pressures were maintained

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(16) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282–283.

(17) (a) Hunter, R. L.; McIver, R. T., Jr. *Chem. Phys. Lett.* **1977**, *49*, 577–582. (b) Hunter, R. L.; McIver, R. T., Jr. *Am. Lab.* **1977**, *9*, 13–14, 18, 21–4, 26.

within the range of 10^{-8} to 10^{-6} Torr and electron energy at 19 eV.

Dimethyl(methylthio)sulfonium tetrafluoroborate (14) was prepared by previously published procedures.[18] Commercial samples of 2-methylpropane and 2-(ethylthio)ethanol were purified by distillation before use, and sodium methanethiolate was freshly prepared before use by a procedure adapted from Plieuinger.[19] Both the meso and racemic diastereomers of 4,6-dimethyl-1,3-dithiane, 5 and 19, respectively, were obtained by conversion of a mixture of meso and racemic 2,4-pentanediol to the corresponding dithiol followed by condensation with dimethoxymethane catalyzed by BF_3 etherate in chloroform.[8] The meso isomer 5 separated as a white crystalline solid on recrystallization of the product mixture in methanol, leaving the racemic form in solution.

4*c*,6*c*-Dimethyl-2*r*-(methylthio)-1,2-dithiane (7) was prepared following the procedure of Ellison, Woessner, and Williams.[12] To a solution of 5 (0.715 g, 4.82 mmol) in 10 mL of dry THF at −78 °C under dry nitrogen was added 3.47 mL (7.25 mmol) of 2.09 M butyllithium in hexane over a period of 45 min. Stirring was continued for 2 h at −78 °C following which the mixture was cannulated into 0.541 g (5.76 mmol) of dimethyl disulfide in 5 mL of THF (also at −78 °C). After 20 min the mixture was allowed to warm to room temperature, poured into 50 mL of 0.05 M hydrochloric acid, and concentrated by rotary evaporation to remove the THF. The residue was twice extracted with 50-mL portions of 1:1 pentane/dichloromethane, and the organic extracts were washed first with 10% aqueous sodium bicarbonate, then water, and with saturated aqueous NaCl, then dried over sodium sulfate, and concentrated by rotary evaporation. The solid that crystallized out was removed by filtration and recrystallized from methanol to give 0.567 g (60%) of white crystals, mp 50.5–50.7 °C: ^{1}H NMR δ (ppm, $CDCl_3$) 1.198 (CH_{axial} of C-5, part of ABX_2 system, J = 13.9, 11.5 Hz, 1 H), 1.255 (CH_3 on C-4,6, d, J = 6.9 Hz, 6 H), 2.061 ($CH_{equatorial}$ of C-5, part of ABX_2 system, J = 13.9, 2.3 Hz, 1 H), 2.342 (SCH_3, s, 3 H), 2.933–3.070 (CH of C-4,6, m, J = 6.9, 11.5, 2.3 Hz, 2 H), 4.939 (CH of C-2, s, 1 H); ^{13}C NMR δ (ppm, $CDCl_3$) 13.14 (SCH_3), 21.16 (CH_3 on C-4,6), 41.31 (CH_2 of C-5), 42.40 (CH of C-4,6), 49.83 (CH of C-2); MS m/z (rel intensity) EI, 194 (2.03), 147 (100.00), 105 (5.66), 92 (9.07), 69 (37.71); CI, 195 (38.12), 147 (100.00).

Anal. Calcd for $C_7H_{14}S_3$: C, 43.26; H, 7.26. Found: C, 43.48; H, 7.40.

4*c*,6*t*-Dimethyl-2*r*-(methylthio)-1,2-dithiane (17) was prepared by the methylthiolation of racemic *trans*-4,6-dimethyl-1,3-dithiane (19) by using the same procedure described for the meso isomer 7. The product had the following: ^{1}H NMR δ (ppm, $CDCl_3$) 1.35, 1.41 (CH_3 on C-4 or C-6, d, 3 H, and on C-6 or C-4, d, 3 H), 1.79–1.96 (CH_2 of C-5, m, 2 H), 2.30 (SCH_3, s, 3 H), 3.24–3.42 (CH of C-4, and C-6, m, 2 H), 5.08 (CH of C-2, s, 1 H); high resolution MS, calcd for $C_7H_{14}S_3$ (M^+) 194.02576, found 194.0254.

4*t*,6*c*-Dimethyl-2*r*-(methylthio)-1,3-dithiane (6). A solution of 7 (0.156 g, 0.801 mmol) in 20 mL of CH_2Cl_2 at −78 °C was treated with 0.0826 g (0.756 mmol) of dimethyl(methylthio)-sulfonium tetrafluoroborate[18] and stirred for 5 h. Sodium methiolate (0.670 g; 3.44 mmol) and 18-crown-6 (0.0212 g, 0.0802 mmol) were added under nitrogen. After 3 days of stirring at −78 °C, the mixture was warmed to room temperature, washed with water, dried over potassium carbonate, and reduced to half volume on a rotary evaporator. The mixture was chromatographed on Activity I alumina using 90:10 hexane/dichloromethane. Further separation by gas chromatography (10% OV-17 on Chromasorb W) and recrystallization from methanol gave 96% pure 6, mp 45.5–47.0 °C in 30% yield overall: ^{1}H NMR δ (ppm, $CDCl_3$) 1.232 (CH_3 on C-4,6, J = 6.9 Hz, 6 H), 1.369 (CH_{axial} of C-5, part of ABX_2 system, J = 14.1, 12.0 Hz, 1 H), 2.107 ($CH_{equatorial}$ of C-5, part of ABX_2 system, J = 14.1 Hz, 0.9 Hz, 1 H), 2.193 (SCH_3, s, 3 H), 3.31–3.45 (CH of C-4,6, m, J = 6.9, 12.0, 0.9 Hz, 2 H), 4.934 (CH of C-2, s, 1 H); ^{13}C NMR δ (ppm, $CDCl_3$) 18.86 (SCH_3), 21.33 (CH_3 on C-4,6), 34.30 (CH_2 of C-5), 44.30 (CH of C-4,6), 51.27 (CH of C-2); MS m/z (rel intensity) EI, 194 (3.05), 147 (100.00), 105 (6.72), 92 (4.91), 69 (40.14); CI, 195 (37.01), 147 (100.00); high resolution MS calcd for $C_7H_{14}S_3$ (M^+) 194.02576, found 194.0244; calcd for $C_6H_{11}S_2$ ($M - SCH_3^+$) 147.0302, found 147.0304.

Kinetics. The pseudo-first-order rate constants k_{obs} for the reactions of m/z 43 from 2-methylpropane and m/z 75 from 2-(ethylthio)ethanol with 6 and 7 were determined from the slopes of the first-order logarithmic plots of ion intensity data versus time, as displayed in Figure 2. The k_{obs} values are related to the second-order rate constants k by eq 10, where r is the number

$$k = \frac{k_{obs}}{r} \tag{10}$$

density of the reacting compound (6 or 7) in molecules cm^{-3}. The number density r was calculated from the ideal gas law, assuming a temperature of 298 K. The conversion factor to obtain the density from the pressure of the sample is thus 3.2405×10^{16} molecules cm^{-3} Torr. The dependence of k_{obs} on the number density r is linear for a second-order process and gives a slope equal to the specific rate $k = (6.0 \pm 1.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for 6 with m/z 43, $k = (6.2 \pm 2.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for 7 with m/z 43, $k = (4.6 \pm 1.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for 6 with m/z 75, and $k = (3.7 \pm 1.0) \times 10^{10}$ cm^3 molecule^{-1} s^{-1} for 7 with m/z 75. (The lines in Figure 2 are extrapolated to a common point at zero time. The errors in k represent the average deviation from the mean value.)

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