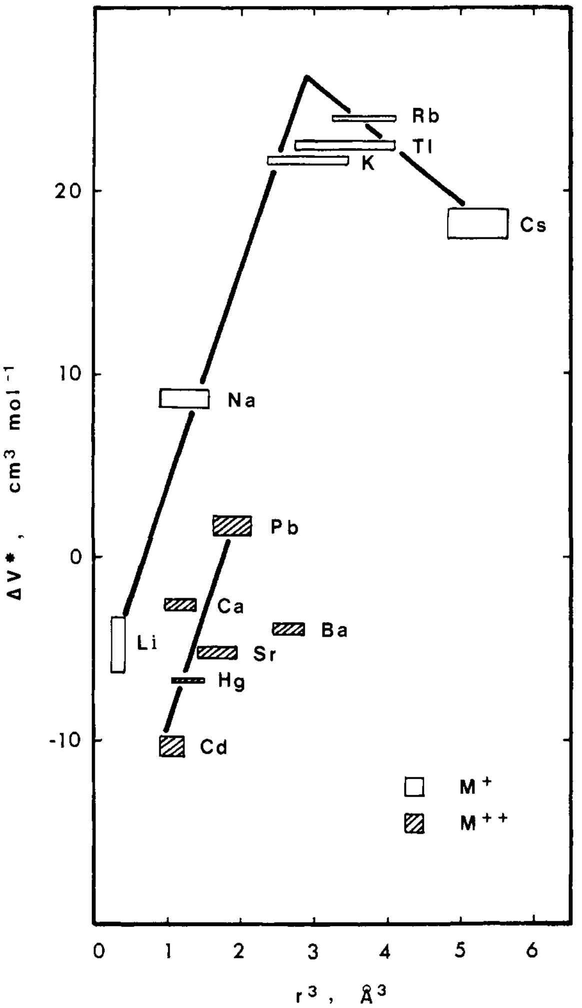

Figure 3. ΔV^* of 2.2.2 with various monovalent[5] and divalent cations in water vs. the cation's radius.

of complexation decreases by about 13 cm^3 mol^{-1}; this decrease, which is almost independent of the radius of the cation, thus seems to be due to a negative contribution to the volume of interaction related to the charge increase. The case of Ba^{2+}-cryptate is interesting: this cation is of the size of K$^+$ which is almost of the size of the internal cavity of 2.2.2. Thus we would normally expect Ba^{2+} to fill completely the cavity of the ligand without distorting the bonds. The solid-state structure of barium-cryptate shows, however, that the ligand takes the shape of a distorted trigonal prism, the trapped cation being still partially hydrated and in interaction with the anion.[27] These cation-solvent interactions may explain why our ΔV^* result for barium is much lower than what was estimated from the extrapolation of the straight line of Figure 3. In some measure, the behavior of Ca^{2+}- and Sr^{2+}-cryptates is also peculiar. Of course, the interactions involved with the alkaline-earth cations are very different from those involved with Pb^{2+}, Hg^{2+}, and Cd^{2+}, and it may not be surprising that both sets of divalent cryptates behave slightly differently. Our results are too close together, however, and the uncertainties too important to give, at present, a clearer description of the situation.

It would have been interesting to complete this study of the charge effect by adding some results for trivalent cryptates. Unfortunately, it has been shown that the 2.2.2-cryptate of Eu^{3+} (which is of the size of Na$^+$ and Ca^{2+}) has a formation constant 10^7 smaller than for the corresponding divalent cryptate and that, in addition, it has a strong tendency to complex small anions.[28]

Conclusion

From the volumes of complexation of 2.2.2, 2.2.1, and 2.1.1 with alkali-metal and divalent cations in water and in methanol, we can draw the following conclusions.

The cryptate–solvent interactions show some discontinuity when the radius of the complexed cation is equal to the radius of the internal cavity of the ligand. This modification of the nature of the interactions is likely to be due to a greater accessibility of the solvent to the large cations.

The transfer effect from water to methanol as well as the charge effect in water shows that the cryptates behave like charged species. Thus, we cannot consider that the cation in the cavity of the ligand is totally shielded from the environment.

Acknowledgment. We are indebted to Professor J. M. Lehn for inciting suggestions and helpful discussions.

Supplementary Material Available: Tables of measured densities and calculated apparent molar volumes (5 pages). Ordering information is given on any current masthead page.

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Elimination, Fragmentation, and Proton Transfer in 1,3-Dithianes and 1,3-Dithiolanes in the Gas Phase

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Received September 25, 1980. Revised Manuscript Received March 9, 1981

Abstract: The gas-phase negative ion-molecule chemistry of 1,3-dithianes and 1,3-dithiolanes differs considerably from that in solution. When treated with anionic bases, 1,3-dithiane undergoes successive elimination reactions giving thiolates, in competition with deprotonation at the 2 carbon, which is the sole solution phase reaction channel. The appearance of the various product ions with changing base strength agrees with their calculated thermochemical onset. The gas-phase acidity of 1,3-dithiane is measurable if the elimination reaction is blocked by *gem*-dimethyl substitution at the 5 carbon. For 1,3-dithiolane, no deprotonation product is observed; even at thermochemical threshold, cycloreversion to RCS_2^- and ethylene occurs. This competes with successive eliminations to thiolates, as with the six-membered ring. The differences between the gas phase and solution reactivities are rationalized in terms of counterion effects.

The use of 2-lithio-1,3-dithianes **2** as acyl anion equivalents has since its inception[2] become an important technique in synthetic organic chemistry.[3] These species are equally intriguing to physical organic chemists, due to the considerable stabilization

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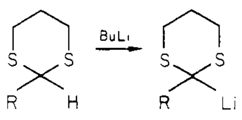
of the anion without formal π resonance delocalization[4,5] and the kinetic and thermodynamic preference of the lithium for the equatorial position.[6] Although overlap of the carbanion with the d orbitals on sulfur has been invoked as an explanation for the considerable stabilization of the anion,[3,4] recent MO calculations[7-9] indicate that such as effect is negligible. The stabilization is explicable in terms of sulfur's polarizability,[7-9] while the stereoelectronic preference is due to p–σ^* overlap of the anion or C–Li orbitals with the C–S MO's.[8] The production of such metalated dithianes with butyllithium is clean and quantitative. In contrast,



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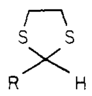

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the homologous five-membered ring, 1,3-dithiolane (3), is reported to undergo a variety of reactions upon treatment with strong base, including deprotonation,[10] cycloreversion,[11] elimination,[12,13] and no reaction,[12] depending on conditions.

As part of a general program of investigating structural effects on anion stability in the gas phase, we were interested in the acidities of various 2-substituted dithianes. It has been claimed that sp^2 carbanions are destabilized by substituents with α lone pairs, while pyramidal carbanions are stabilized.[14] The dithianes, at least those without strong resonance withdrawing substituents on the acidic carbon, should give pyramidal anions, which can be compared to the same substituents on other carbon acids such as esters and nitriles. Preliminary investigation has revealed, however, that the anionic chemistry of dithianes in the gas phase is nowhere near as clean as in solution. In order to further the acidity work and investigate the reasons for the conflicting reports on 1,3-dithiolane chemistry, the present study was undertaken.

Experimental Section

Instrumentation. The ICR instrumentation used is similar to that reported in the literature,[15] save that it is equipped with a capacitance bridge detector[16] currently utilizing field sweep mode for mass scans. An MKS Baratron Type 146 capacitance manometer was used in the 10^{-6}–10^{-5}-torr range to calibrate the Granville-Phillips Type 270 ionization gauge controller with a Huntington Mechanical Labs Bayard–Alpert gauge. Mass scans were normally done at 153.56 kHz, except when masses beyond the 14-kG range of the magnet required a lower (typically 100 or 75 kHz) frequency. Rate constants were obtained at as high a magnetic field as practical to minimize collisional ion loss from the cell. We obtain a rate constant for the reaction $CH_4^{+\cdot} + CH_4 \rightarrow CH_5^+ + CH_3\cdot$ of $(1.06 \pm 0.11)10^{-9}$ cm^3 molecule^{-1} s^{-1}, in good agreement with the average literature value[17] of $(1.11 \pm 0.04)10^{-9}$ cm^3 molecule^{-1} s^{-1}.

Scheme I

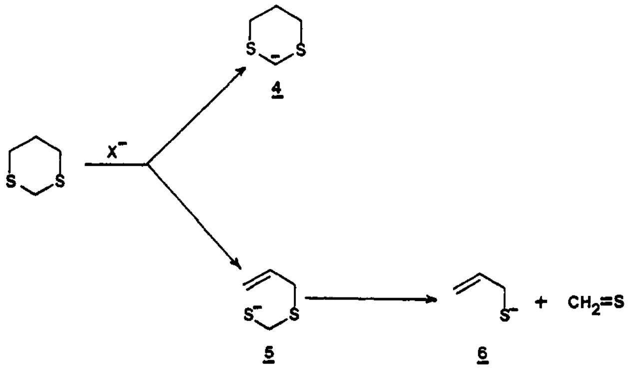

Table I. Products from Reaction of 1,3-Dithiane-*5,5*-d_2 with Anioic Bases[a]

base	deprotonation[b]	elimination[c]	fragmentation[d]	$k_{ADO} \times 10^{10}$ cm^3 molecule^{-1} s^{-1}
NH_2^-	0.40 (0.22)	0.31 (0.18)	0.29	33.5
HO^-	0.30 (0.14)	0.42 (0.20)	0.23	32.6
MeO^-	0.36 (0.13)	0.64 (0.17)	0.0	25.4
n-PrO^-	0.12 (0.03)	0.88 (0.35)	0.0	20.0
t-$BuCH_2O^-$	0.02	0.98 (0.42)	0.0	17.7
$PhCH_2O^-$	0.0	1.0	0.0	16.7
MeS^-	0.0	0.0	0.0	21.7
HS^-	0.0	0.0	0.0	24.8

[a] Fraction of total ions, unquenched mode, constant field. Numbers in parentheses are reaction efficiencies.[41] [b] To ion 4. [c] To ion 5. [d] To ion 6.

Materials. Most of the chemicals used in this work were obtained commercially and purified before use by distillation, sublimation, or preparative GC. All compounds had appropriate NMR and positive electron impact mass spectra. Neopentyl and benzyl nitrites were prepared from the corresponding alcohols by the general literature method for butyl nitrite.[18] We thank Drs. Michal W. Majchrzak and Joseph L. Lambert for the 1,3-dithiane-*5,5*-d_2 and Dr. E. L. Eliel for a sample of 5,5-dimethyl-1,3-dithiane. The procedure of Fuhrer and Günthard[19] was followed for the preparation of 1,3-dithiolane and its 2-methyl and 2,2-dimethyl derivatives. The 1,3-dithiane-*2,2*-d_2 was prepared by exchange with Me_2SO-d_6.

1,3-Dithiolane-*2,2*-d_2. A suspension of 410 mg (4.27 mmol) of paraformaldehyde-d_6, 1.1 mL (25 mmol) of 1,2-ethanedithiol, and 50 mg of *p*-toluenesulfonic acid monohydrate in 20 mL of CH_2Cl_2 was refluxed under a Dean–Stark trap for 20 h. The reaction mixture was cooled, washed with H_2O, 1 N aqueous NaOH, and H_2O, dried ($MgSO_4$), concentrated, and distilled by evaporation [oven temperature 50–70 °C (1 mm)] to afford 1.04 g (76%) of product as a clear liquid: NMR ($CDCl_3$) δ 3.17 (s), mass spectrum, *m/e* (relative intensity) 108 (M^+, 100), 106 (7), 80 (37), 75 (7), 62 (19), 60 (33), 59 (20).

2,2-Dimethyl-1,3-thioxolane. This was prepared from acetone and 2-mercaptoethanol in 45% yield as for 1,3-dithiolane-*2,2*-d_2, save that benzene was used as solvent. The product was a clear oil: NMR (CD-

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Table II. Products from Reaction of 1,3-Dithiolane-*2,2-d*$_2$ with Anionic Bases[a]

base	cycloreversion[b]	elimination[c]	fragmentation[d]	$k_{ADO} \times 10^{10}$ cm^3 molecule^{-1} s^{-1}
NH_2^-	0.48	0.0	0.52	29.7
HO^-	0.44 (0.50)	0.0	0.56	29.0
MeO^-	0.41	0.25 (0.09)	0.34	22.6
n-PrO^-	0.20	0.58 (0.09)	0.22	18.0
t-$BuCH_2O^-$	0.12	0.76 (0.14)	0.12	16.0
$PhCH_2O^-$	0.0	1.0	0.0	15.2
MeS^-	0.0	0.0	0.0	19.4
HS^-	0.0	0.0	0.0	22.1

[a] Fraction of total ions, unquenched mode, constant field. Numbers in parentheses are reaction efficiencies.[41] [b] To ion 8. [c] To ion 9. [d] To ion 10.

Cl_3) δ 1.63 (s, 6 H), 3.10 (t, *J* = 6 Hz, 2 H), 4.15 (t, *J* = 6 Hz, 2 H).

5,5-Dimethyl-1,3-dioxane. This was prepared from 2,2-dimethyl-1,3-propanediol and paraformaldehyde as for the thioxolane, with a 24-h reflux. A clear liquid, bp 121-123 °C (755 mm) [lit. 121-125 °C (740 mm)] was obtained in 50% yield.

Results

Under conditions in the ICR appropriate for measuring equilibrium acidities,[20] the parent 1,3-dithiane (**1**), R = H, is not observed to equilibrate by proton transfer with any of a variety of acids tried. An M − 1 anion at 119^- is formed by deprotonation with a wide variety of anions, but 119^- does not fully react with the conjugate acid of those same anions as measured by double resonance. In addition, a small amount of 73^-, corresponding to allyl thiolate, is observed from reaction with hydroxide. These facts are consistent with the reactions shown in Scheme I, where two different M − 1 anions are produced by deprotonation and elimination. The elimination product **5**, if it possesses enough excess energy, can fragment unimolecularly to **6** and thioformaldehyde. As evidence for this scheme, 1,3-dithiane-*5,5-d*$_2$ upon reaction with hydroxide gives both 121^-, via proton loss at the 2 carbon, and 120^- from from deuteron loss at C-5 and elimination. The allyl thiolate peak also shifts to 74^- as expected. Reaction of the undeuterated dithiane with DO^-/D_2O[21] gives some 120^- as well as 119^-, just as 1,3-dithiane-*2,2-d*$_2$ and hydroxide gives 121^- (elimination), 120^- (deprotonation), and 119^- (deprotonation with exchange).

From Table I, the reaction efficiency for deprotonation appears to decrease somewhat with decreasing base strength, while for elimination it remains fairly constant. Double resonance indicates that neither **5** nor **6** act as bases to give **4**; such reactions are expected to be endothermic. Likewise **4** does not give **5** via elimination, even though it is comparable in basicity to neopentoxide, which is fairly efficient in that process.

The reactions of 1,3-dithiolane follow a similar pattern of successive eliminations competing with deprotonation, as shown in Table II. For this compound, however, the deprotonation product **7** in Scheme II appears not to be stable with respect to a retro [2 + 4] cycloreversion reaction and therefore gives **8** and ethylene. None of the anionic bases tried gave any **7**, even when deprotonation of the dithiolane should be virtually thermoneutral, as with neopentoxide. Otherwise, the pattern is much the same as for dithiane: decreasing amounts of deprotonation and fragmentation with decreasing base strength. The cutoff for fragmentation occurs at least 8 kcal/mol lower base strength than for the dithiane.

For the dithiolanes methylated at the 2 position, elimination by deprotonation on the methyl substituent can also give an M − 1 anion, $CH_2{=}CRSCH_2CH_2S^-$. Such an ion should not be

Scheme II

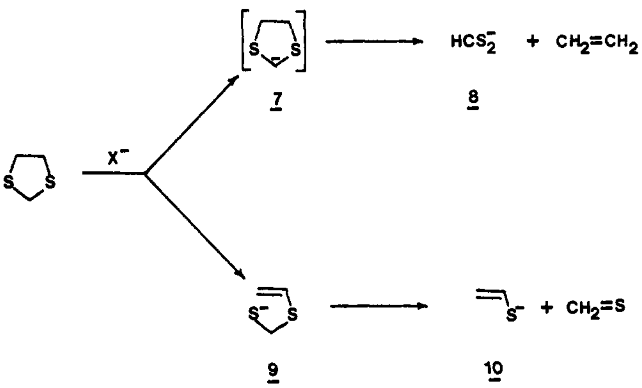


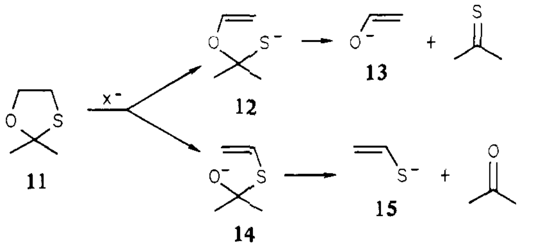
Table III. Products from Reaction of Various Methylated Sulfur Heterocycles with Anionic Bases[a]

compd	products	NH_2^-	MeO^-	*t*-$BuCH_2O^-$
2-methyl-1,3-dithiolane	$(M - 1)^-$	0.0		0.67
	$CH_2{=}CHS^-$	0.62		0.33
	$MeCS_2^-$	0.38		0.0
2,2-dimethyl-1,3-dithiolane	$(M - 1)^-$	0.0	0.0	0.0
	$CH_2{=}CHS^-$	0.62	0.76	0.95
	$CH_2{=}CMeS^-$	0.38	0.14	0.05
2,2-dimethyl-1,3-thioxolane	$(M - 1)^-$		0.0	0.0
	$CH_2{=}CHS^-$		0.90	0.84
	$CH_2{=}CMeO^-$		0.10	0.16

[a] Fraction of ions, unquenched mode, constant field.

susceptible to further fragmentation at the energies available in these reactions. For 2-methyl-1,3-dithiolane, the reactivity pattern seen in Table III is very similar to the parent compound, so that the exo elimination is probably only a minor pathway, if present at all. For the 2,2-dimethyl compound, much more extensive fragmentation of the first elimination product is seen than for the less substituted systems. The M − 1 of the thioacetone arises from proton transfer between $CH_2{=}CHS^-$ and $(CH_3)_2C{=}S$ formed in the fragmentation step before the cluster complex breaks up. If the thiocarbonyls are like their oxygen analogues, the ketone should be less acidic than the aldehyde by a few kcal/mol.[20] This is consistent with the predominance of 59^- over 73^- in all cases. The increase of the $73^-/59^-$ ratio with increasing primary base strength can be attributed to driving of the endothermic proton transfer by increasing excess energy. Double resonance indicates that 73^- does not arise from 59^-, consistent with internal proton transfer in the cluster ion.

For 2,2-dimethylthioxolane (**11**) there are two possible ring eliminations, corresponding to removal of the protons next to sulfur or next to oxygen. We observe fragmentation product **15** arising



exclusively from loss of a proton next to the sulfur. This results in the *less* stable anion from the first elimination, but the more stable from the second. As with the disulfur analogue, a small amount of acetone enolate is formed from endothermic proton transfer in the chemically activated cluster ion.

In order to accurately measure the equilibrium acidity of 1,3-dithiane, the elimination reaction must be blocked. Replacement of the hydrogens at C-5 with methyls accomplishes this. For 5,5-dimethyl-1,3-dithiane (**16**) reacting with hydroxide, no 73^- is seen, and the equilibria established with *tert*-butyl alcohol and neopentyl alcohol are clean, show proper double resonance

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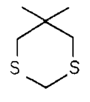

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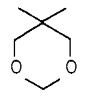

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both ways,[20] and have equilibrium constants independent of the ratio of neutral pressures. We find $\Delta G_{\text{acid}}°$ for **16** is 365.6 ± 2 kcal/mol. The uncertainty reflects the absolute value; relative to other gas-phase acids, the acidity is probably good to ±0.2 kcal/mol. This makes it comparable to Me_2SO, acetonitrile, and HF in gas-phase acidity. If we assume that the anion is localized, but freezes out the chair–chair flipping of the ring due to p-σ* overlap[8] and preference of the carbanion for the equatorial position,[6] then $\Delta S_{\text{acid}}° = 24.6 \pm 0.5$ eu, and $\Delta H_{\text{acid}}° = 372.9 \pm 2.1$ kcal/mol. Considering the distance of the methyl groups from the acidic site, polar and polarizability effects should be small so that the parent 1,3-dithiane should have acidity comparable to that of the methylated form.

The reactions of the oxygen analogues to these sulfur compounds with methoxide have also been investigated. For 1,3-dioxolane, both an M − 1 anion, presumably from elimination, and 43^- are observed. Only an M − 1 is seen for 1,3-dioxane. If the elimination reaction is blocked, as in **17**, no reaction is seen with methoxide. A small amount of M − 1 anion is seen for reaction with NH_2^-, although the major product is 85^-.[22] Hydroxide gives M − 1 of **17** only under double resonance excitation conditions, placing **17** between NH_3 and H_2O in acidity.

Discussion

Acidities. The only equilibrium acidity value in solution for 1,3-dithiane is the ion-pair pK_a in cyclohexylamine (CHA) of Streitwieser and co-workers.[14b] Since the extent of ion pairing, and therefore the pK_a, is dependent on the nature of the carbanion in CHA solvent,[23] for a proper comparison we must look at relative pK_a's for acids giving localized carbanions. Phenylacetylene, *tert*-butylacetylene, and benzene have approximately the same acidities relative to each other in the gas phase and CHA.[20,24] The dithiane, however, is 8 kcal/mol less acidic than *tert*-butylacetylene in CHA but 3 kcal/mol more acidic in the gas phase. This puts the dithiane in the direction of delocalized acids in CHA, less acidic than those with localized anions, compared to the gas phase. Due to the different hybridization at carbon and the presence of large polarizable groups, we cannot ascribe this shift in relative pK_a's to resonance effects.

In Me_2SO solvent, where ion pairing of carbanions is negligible, 1,3-dithiane is too weakly acidic to be measured ($pK_a \geq 35$).[25] This is not surprising, since in the gas-phase Me_2SO and 1,3-dithiane have virtually the same acidity, and the lack of good hydrogen bond donation by the solvent should disfavor the localized dithianyl anion more than the delocalized dimsyl anion.[20b] The acidity of 1,3-dithiane in Me_2SO may also be arrived at by extrapolation from the pK_a of 2-phenyl-1,3-dithiane of 30.7 and known phenyl stabilizing effects on pyramidal carbanions.[25] We estimate the pK_a for 1,3-dithiane in Me_2SO as 39 this way, consistent with the above arguments.

Molecular orbital calculations[8] indicate that $(HS)_2CH^-$ should be less basic by 43 kcal/mol than the 1-propyl anion. While the acidity of propane in the gas phase has not been experimentally determined, $\Delta H_{\text{acid}}°$ for CH_4 is 416.6 ± 1.0 kcal/mol from a thermochemical cycle,[20a] and both known substituent effects[20b,27,28] and molecular orbital calculations[26] indicate that propane should be only a few kilocalories per mole more acidic than methane, at most. The difference in $\Delta H_{\text{acid}}°$ for methane and 1,3-dithiane is 43.5 ± 4 kcal/mol, in remarkable agreement with the calculations. These same MO calculations[8] predict $(HO)_2CH_2$ to be 12 kcal/mol less acidic at carbon than $(HS)_2CH_2$, which would put it at a $\Delta H_{\text{acid}}°$ of 385 kcal/mol, on the basis of our dithiane acidity, or 6 kcal/mol more acidic than water. This contrasts with our experimental findings that put **17** at least 2 kcal/mol less acidic than water. Other MO calculations do predict a larger oxygen–sulfur difference, however.[7] There is considerable other experimental evidence, both in gas phase[20,27,28] and solution,[14a,14d,25,29] which indicates that an oxygen next to a carbanion is only weakly stabilizing at best, and often destabilizing, relative to a methylene group. This is presumably a balance of stabilizing polar and polarizability effects and destabilizing p–p electron repulsion.

An equilibrium acidity could not be determined for 1,3-dithiolane, since blocking the elimination reaction would require 4,4,5,5-tetra-*tert*-butyl or tetraphenyl substitution. This would sufficiently alter the acidity by polar and polarizability effects, as well as reducing volatility, that a comparison of the five- and six-membered rings would not afford useful information. From the onset of deprotonation products with increasing base strength shown in Tables I and II and the correlation of this with the measured equilibrium acidity of **16**, we believe that 1,3-dithiolane may be 1–2 kcal/mol more acidic than the dithiane. This parallels the isotope exchange rates in solution: **3** (R = H) exchanges 139 times as fast as **1**.[30]

Thermochemical Calculations. Analysis of the reactions seen here requires some knowledge of the potential energy (or, more conveniently, enthalpy) surface on which the reactions occur. This is complicated by a general lack of thermochemical information for the cyclic sulfides and thiocarbonyl structures involved. We estimate $\Delta H_f°$ for 1,3-dithiane and 1,3-dithiolane as −0.8 ± 4 and +4.1 ± 4 kcal/mol, respectively, based on group additivity methods.[32,33] These values include no ring strain correction, since the long C–S bonds should reduce this to less than the already small values for the corresponding cyclic ethers.[32] The $\Delta H_f°$ for thiolates **5**, **6**, **9**, and **10** can be obtained from $\Delta H_f°$ and ΔH_{acid} for the conjugate thiol acid.[20a] The former is obtained from group additivity,[32] the latter from known acidities and estimates based on linear free energy relationships.[20] This is not straightforward for **5** and **9**, since the presence of second row atoms β to an anion can stabilize it by up to 14 kcal/mol over that expected from a $\sigma_I\rho_I$ correlation,[34] presumably by polarizability interactions.[35] The occurrence of **5** from reaction with $PhCH_2O^-$ but not from CH_3S^- indicates a $\Delta H_f°$ for **5** of −3 ± 7 kcal/mol. This corresponds to an acidity of $CH_2{=}CHCH_2SCH_2SH$ of 346 kcal/mol or 10 kcal/mol more so than expected for an *n*-alkanethiol.

No values for the enthalpy of formation of thiocarbonyl compounds appear to be known. For diisopropyl thioketone in the liquid state, however, the keto–enol tautomers exist approximately in a 1:1 mixture.[36] Assuming equal heats of vaporization of the

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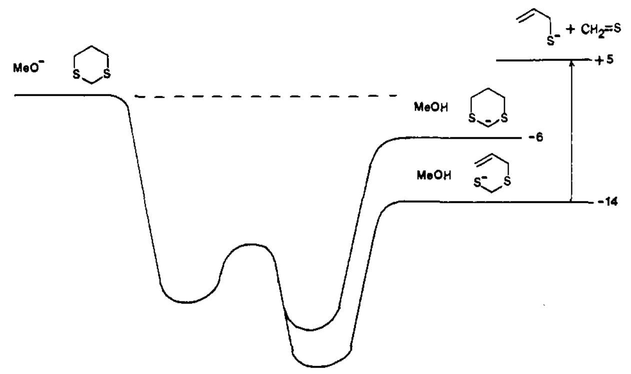

Figure 1.

Table IV. Thermochemistry for Production of Products from 1,3-Dithiane and Anionic Bases[a]

base	deproton-ation,[b] kcal/mol	elimin-ation,[c] kcal/mol	fragmen-ation,[d] kcal/mol
NH_2^-	−30	−38	−20
HO^-	−17	−26	−7
MeO^-	−6	−14	+5
n-PrO^-	−1.5	−10	+9
t-$BuCH_2O^-$	+1.5	−7	+12
$PhCH_2O^-$	+4	−5	+14
MeS^-	+14	+6	+25
HS^-	+20	+11	+30

[a] $\Delta H_r°$, kcal/mol, relative to dithiane plus base = 0. [b] To give **4** plus conjugate acid of the base. [c] To give **5** plus conjugate acid of the base. [d] To give **6** plus conjugate acid of the base.

tautomers, since thiols are only weakly hydrogen bonded,[37] $\Delta H_f°(i\text{-}Pr_2C{=}S) \sim \Delta H_f°[Me_2C{=}C(SH)i\text{-}Pr]$ in the gas phase. The $\Delta H_f°$ for the enethiol can be estimated from group additivity.[32] On the basis of heats of formation for the homologous series of ketone, aldehyde, formaldehyde,[38] plus the above thiocarbonyl data, we extrapolate $\Delta H_f°(CH_2{=}S)$ as 15 ± 10 kcal/mol. Estimates for the heat of dehydrogenation of CH_3SH give a similar value. As will be seen below, this value is consistent with the reactions observed in the gas phase.

From group additivity $\Delta H_f°(CH_2{=}CHSH)$ can be estimated as 20.9 kcal/mol. This enethiol is undoubtedly more acidic than ethanethiol for both polar and resonance reasons, but the increase is probably less than that for vinyl alcohol vs. ethanol, due to resonance saturation effects.[31] We arbitrarily take half the difference for the acidities of the two oxygen acids[20a,39] as that for the sulfur compounds, giving $\Delta H_{acid}°(CH_2{=}CHSH) = 349 \pm 8$ kcal/mol and $\Delta H_f°(CH_2{=}CHS^-) = 2.7 \pm 10$ kcal/mol.

Reaction Coordinates. The above thermochemical data allows us to construct reaction coordinates such as that shown in Figure 1 using the data in Table IV. The relative levels of the products on the right-hand side of the figure do not change as the base is changed, only the level of the reactants compared to the various products. The depth of the central well for the cluster ion in the figure can be estimated from eq 1 based on the data of Kebarle

$$A^-\cdots HB \rightarrow A^- + HB \qquad (1)$$

$$\Delta H°(2) = 0.2\ \Delta H_{acid}°(AH) - 0.134 \Delta H_{acid}°(BH) \qquad (2)$$

and co-workers.[40] Knowledge of the *exact* well depth is not critical to any of the energy-reactivity arguments here, since it is the energy levels of the maxima on the coordinate, relative to the reactants' energy level, that determines reaction efficiency.[41]

Figure 1 represents the cluster-ion well between reactants and the various products as a double minimum. Such a coordinate with an intermediate barrier has been used to explain the fact that many exothermic ion-molecule reactions proceed at less than collision rate.[34,43] The barrier at the bottom of the well can appreciably decrease the efficiency[41] of a reaction, even if its top is many kilocalories per mole below the energy of reactants of products.[34] Since most of the efficiencies reported in Tables I and II are less than unity even though the reactions are exothermic, such a barrier probably exists for both deprotonation and elimination steps. The occurrence or nonoccurrence of a given reaction with changing base strength is explicable in terms of product and reactant energies alone, however, so that knowledge of the exact height of this barrier is not necessary to explain the observed reactivities.

For both dithiane and dithiolane, the deprotonation products **4** and **7** are not seen when the proton affinity of the attacking base is less than 371 kcal/mol. This is consistent with the equilibrium acidity of the dithiane and the fact that, on the time scale of the ICR experiment, reactions more than 3–4 kcal/mol endothermic are not observed to proceed.[44] In terms of Figure 1 and its analogues for other anionic bases, if the level of the reactants falls below the level of the deprotonation products, the reaction slows greatly and no **4** or **7** are seen. Similarly, when the base's proton affinity falls below 365 ± 7 kcal/mol, the elimination reaction becomes endothermic and ceases. The observed cutoff agrees with that expected from the thermochemical estimates above. The cutoff is rather uncertain, due to a lack of sources for electron impact generated anions in this region of the acidity scale.

The cutoffs for the appearance of fragmentation products **6** and **10** with changing base strength differ considerably. Only the strongest bases give **6** from 1,3-dithiane, while **10** appears in the reaction of 1,3-dithiolane with anions at least 10 kcal/mol less basic than for **6**. If we assume that these ions arise from unimolecular fragmentation of **5** and **9**, respectively, when the precursor ions are chemically activated by exothermic elimination, then the cutoffs are consistent with the thermochemistry derived above. The fragmentation of **5** to allyl thiolate and thioformaldehyde should be endothermic by ca. 19 kcal/mol by our thermochemical estimates; the elimination to yield **5** must be exothermic by at least this amount in order to drive the fragmentation. In terms of Figure 1, the energy of the reactants must be above that of the fragmentation products. This requires a base of proton affinity greater than 384 kcal/mol, falling nicely between the experimental limits of hydroxide at 390.7 and methoxide at 379.2. This provides further confirmation, though admittedly with considerable uncertainty, for our estimate of $\Delta H_f°$ for $CH_2{=}S$. For the five-membered ring, the fragmentation is estimated to be 8.5 kcal/mol uphill from **9**; a base with a proton affinity of at least 380 kcal/mol should be needed to activate the fragmentation. The considerably lower onset at 371 kcal/mol is within the large error limits for the uncertainties in the fragmentation products' heats of formation.

For all cases where the reactants' energy is above threshold for both elimination and deprotonation, there are appreciable amounts

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(41) The reaction efficiency (RE) is the fraction of ion–molecule collisions which proceed on to products and is commonly taken as k_{obsd}/k_{ADO}. The ADO rate constant was evaluated by the method of Su and Bowers.[42] We use the empirical equation $c = 0.3886(\mu_D/\sqrt{\alpha})^{1/2} - 0.1379(\mu_D/\sqrt{\alpha}) - 0.0081$ to evaluate the locking constant. This fits the discrete points in ref 42c to a standard deviation of 0.0027. The polarizabilities are obtained by the method of: Miller, K. J.; Savchick, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206–7213. The dipole moment of dithiane is from: Kalff, H. T.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 467–484. That of the dithiolane is estimated from oxygen and sulfur analogues: McClelland, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman; San Francisco, CA, 1963.

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of both products formed, with some preference for elimination. This preference is reasonable in terms of **5** and **9** being lower in energy than **4** and **7**, respectively, and thus the number of states up to the reactants' energy being greater.[34] The elimination is also favored entropically (higher density of states), since the elimination reaction opens up the ring, while the deprotonation should freeze out the chair flipping, due to the equatorial preference of the anion.[6,8] The increasing preference for elimination over deprotonation with decreasing base strength qualitatively follows the prediction of RRK theory.[45]

For anionic eliminations such as reaction 3 which are exothermic, only Y^- is seen. If the elimination of Y^- is endothermic,

$$X^- + RCH_2CH_2Y \rightarrow XH + RCH{=}CH_2 + Y^- \qquad (3)$$

$$X^- + RCH_2CH_2Y \rightarrow XH\cdots Y^- + RCH{=}CH_2 \qquad (4)$$

but less so than the cluster strength of $XH\cdots Y^-$, then the clustering of XH to the leaving group allows the reaction to proceed. This has been observed for alkoxides reacting with fluoroalkanes,[46] NH_2^-, HO^-, and F^- with ethers,[47] and for fluoro alcohols.[48] In the present work, no such cluster ion was seen for bases MeS^-, HS^-, and AcO^- reacting with dithiane, even though the clustering enthalpy of these to **5** should change the elimination from endothermic to between 7 and 20 kcal/mol exothermic. These eliminations differ from those where clustering is observed in several respects. Thiols are known to be weak hydrogen bonding species in solution,[37] so eq 2 may overestimate the effect of clustering; no quantitative data on $RSH\cdots X^-$ strengths is available. We are currently developing a clustering scale for such data in our laboratories but do not have pertinent data for thiols at this time. The base and leaving group in the present systems have an enforced orientation such that the leaving group is distant from the attacking base, possibly reducing the chances for cluster ion formation. Most importantly, reaction 4 produces a neutral alkene, which can carry away part of the excess energy, as well as the cluster ion. For the dithiane, the net reaction corresponding to reaction 4 is an addition, since the alkene is tied to the leaving group. Such addition ions, when produced exothermically, are not usually stable in low pressures of the ICR, fragmenting to more stable species or reverting to reactants.[49] Thermochemical analysis of the reaction here using eq 2 reveal that all reasonable products other than the addition ion are endothermic, so the excited cluster ion can only revert to reactants.

For the thioxolane **11**, the exclusive elimination from loss of the proton next to sulfur is similar to the reactivity observed in solution.[12] This represents E_1cb-type reactivity and is unlike most of the other reactions seen here, where reactivity is explicable in terms of the overall thermochemistry. In this case, elimination to give the alkoxide **14** is near thermoneutral, while elimination to the thiolate **12** is 10-15 kcal/mol downhill. In such a case, the branching ratio must be controlled by the barrier in the double minima well. The proton transfer adjacent to sulfur involves a more stable incipient carbanion than that next to oxygen and so should involve a lower barrier. The lack of any **14** in the spectrum (100% fragmentation to **15** and acetone) is explicable by thermochemistry also: unlike the other fragmentations here, this one is *exothermic* by 9 kcal/mol.

Solvation and Counterion Effects. The lack of any elimination for butyllithium reacting with 1,3-dithiane in solution,[2,3] as compared to the competing elimination and deprotonation reactions seen in the gas phase for most bases, must be attributable to solvation, the counterion, or some mixture of these effects. In the gas phase, elimination is the thermodynamically favored process by ca. 8 kcal/mol. To determine which reaction is favored in solution, we must examine the energetics of solvation and ion pairing of **4** and **5**. The relative heats of solvation of anions can be obtained from a thermochemical cycle involving gas-phase acidities, the heat of solution of the acid in some solvent, $\Delta H_s°$ (AH), and the heat of proton transfer in solution, ΔH_i (AH).[50] For thiols in Me_2SO, such data is available.[51] For the dithiane, $\Delta H_i°$ can be obtained from pK_a in Me_2SO of 39 estimated above, and the known correlation of Me_2SO pK_as with $\Delta H_i°$ for a wide variety of acids.[52] We make a reasonable assumption that $\Delta H_s°$ (dithiane) is about +4 kcal/mol, comparable to other alkane-like structures.[51] From this approach, we find that **5** should be 20 ± 10 kcal/mol better solvated than **4** in Me_2SO, ignoring ion pairing effects.[51] This makes the thermodynamic preference for elimination even larger in Me_2SO. On going to the ethereal solvents where these reactions are commonly run,[2,3] both **4** and **5** should be extensively ion paired, considering their localized nature. While there is data indicating that localized ions are more stabilized by ion pairing than delocalized ones,[23] there does not seem to be data on enough localized ion–lithium pairs to make a quantitative estimate of the relative stabilizations of **4** and **5**. The carbanion, being much less stable than the thiolate, probably pairs more tightly, but whether this is sufficient to reverse the intrinsic stabilities of **4** and **5** under solution phase conditions is unsure. We note that MO calculations show such reversals: ethane is more acidic than methane when going to a free anion[26] but less acidic upon going to the lithiocarbon.[53] Likewise, the difference between oxygen and sulfur stabilized carbanions decreases upon lithiation.[8]

If the course of the solvated reaction is thus dictated by kinetic control, we speculate that it is the ion pairing of the counterion of the base to the sulfurs which causes this. In such a position, molecular models indicate that the base is properly oriented to remove either the equatorial hydrogen on C-2, as observed, or the axial C-5 hydrogen. The latter, however, involves a syn-clinal elimination which is usually disfavored with respect to an antiperiplanar elimination.[54] The preferred elimination involves the C-5 equatorial hydrogen, which should not be accessible to the base if counterion sulfur ion pairing occurs. In the gas phase, there is no counterion, and thus no special preference for orientation in the long-lived orbiting complex. The hydrogen leading to elimination is thus not sterically disfavored, unlike solution, allowing the reaction products to form on the basis of thermochemical control.

Acknowledgment. This research was supported by grants from the Research Corporation and the National Science Foundation (CHE 79-19528).

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