The Thio-Wittig Rearrangement of Deprotonated Allyl Methyl Sulfide. A Gas-Phase Unimolecular Isomerization Probed with a Variable Temperature Flowing Afterglow-Triple Quadrupole Device

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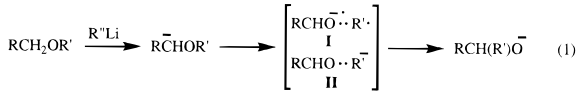
Abstract: The thio-Wittig rearrangement of deprotonated allyl methyl sulfide has been examined in the gas phase with a variable temperature flowing afterglow-triple quadrupole device. Collision-induced dissociation studies of a series of thiolate anions (RS^-) reveal that methyl deprotonation leads to 3-butene-1-thiolate (**2a**), the [2,3]-Wittig product, while 1-thiomethylallyl anion (**1a**) isomerizes to 1-butenyl thiolate (**4a**), the [1,4]-Wittig product, at elevated temperatures. Activation energies for these processes have been estimated using the Arrhenius equation and are compared to high-level (G2) calculations for the homolytic and heterolytic bond dissociation energies. Stepwise and concerted [1,4] pathways are found to have similar energy requirements, which accounts for some of the mechanistic controversy regarding these transformations in solution. The observed selectivity, [1,2] vs [1,4], is most easily accommodated by a concerted process but can be explained in terms of a stepwise mechanism by considering the spin density and charge location in a radical anion intermediate (**6a**). Frontier molecular orbital theory, however, leads to the wrong prediction. The [2,3]-Wittig rearrangement appears to proceed via a concerted pathway in the gas phase as has been invoked in the liquid phase. Heats of formation for acrolein ($\Delta H°_{f298} = -15.6$ kcal mol^{-1}), thioacrolein ($\Delta H°_{f298} = 37.9$ kcal mol^{-1}), and their radical anions ($\Delta H°_{f298} = -17.3$ kcal mol^{-1} and $\Delta H°_{f298} = 16.3$ kcal mol^{-1}, respectively) are also provided.

In 1924 Schörigen[1] and in 1928 Schlenk and Bergmann[2] reported an isomerization which subsequently was developed and elaborated upon by Wittig and his co-workers.[3] This transformation, which involves the conversion of an ether to an alkoxide upon reaction with a strong base, has come to be known as the Wittig or [1,2]-Wittig rearrangement (eq 1). Variants of this process involving [1,4] and [2,3] migrations



have also been reported and are referred to as Wittig rearrangements as well. Taken together, these reactions represent an extremely powerful synthetic tool which has been extensively exploited.[4] Numerous mechanistic studies indicate that the formally forbidden [1,2] pathway typically takes place by a stepwise dissociation−recombination mechanism involving the intermediacy of a radical pair (**I**), although a carbanion intermediate (**II**) has been invoked for some substrates.[5] The [2,3] isomerization has been found to be stereospecific and is widely believed to proceed via a concerted process,[6] whereas the mechanism for the thermally allowed [1,4] sigmatropic shift is controversial; it appears that both stepwise and concerted pathways are possible.[5,7]

The Wittig rearrangement of deprotonated allylic ethers and thioethers can involve competing pathways.[8] Both [1,2] and [1,4] migrations are often observed in these systems. For example, the room temperature reaction of *n*-butyllithium with allyl alkyl ethers in tetrahydrofuran affords both isomerization products upon workup (eq 2).[7a,8b,j] This transformation is sensitive to the reaction conditions, and if the solvent is changed to hexane neither of the Wittig products are formed. Instead an enol ether, an alcohol, and 1-heptene are produced (eq 3).[8a]

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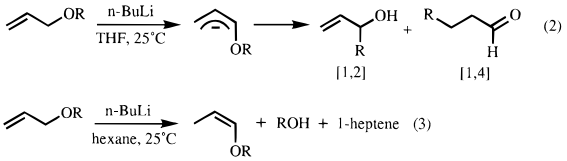
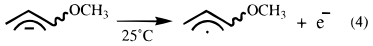
The latter two compounds arise from an S_N2 or S_N2' reaction, and their formation represents a striking solvent dependence. Consequently, it is of interest to examine this rearrangement in a solvent-free environment without complicating aggregation and counterion effects (i.e., the gas phase).



Unimolecular rearrangements of ionic species are inherently difficult processes to follow in the gas phase because mass spectrometry, the most common technique for probing charged particles, is essentially blind to these transformations. That is, the mass-to-charge ratio does not change during the course of these reactions. Conventional mass spectrometry has been used, nevertheless, to study unimolecular isomerizations.[9−11] For example, Bowie and co-workers have reported the occurrence of a number of rearrangements in the ion source of a double sector mass spectrometer by using collisional activation as a structural tool.[9] These transformations, however, do not necessarily correspond to thermal processes, and different techniques are needed in order to study thermal rearrangements. Radiolysis is one such approach and has been used to examine the temperature dependence of carbonium ion isomerizations.[10] Carbanions cannot be probed in the same manner, but we have previously shown that a variable temperature flowing afterglow device can be used in this regard.[11]

We have previously generated the conjugate base of allyl methyl ether in the gas phase at subambient temperatures.[12] It readily decomposes at room temperature by facile loss of an electron (eq 4) so it is not a suitable substrate for studying the Wittig rearrangement. The corresponding thioether was also



prepared, and it is a much more robust anion. This is equally true in the liquid phase, and as a result the thio anion does not isomerize at 25 °C in solution.[8i,13] At elevated temperatures 1-thiomethylallyl anion rearranges in the gas phase to an unreactive isomer, but we were unable to deduce its structure via a wide variety of ion−molecule reactions. More recently, our variable temperature flowing afterglow was outfitted with a triple quadrupole mass filter enabling us to characterize ion structures by collision-induced dissociation (CID). In this well-established technique,[14] ions of a given mass-to-charge ratio are selected (mass separated) with the first quadrupole (Q1), broken apart in Q2 by adding a collision gas, and the resulting fragment ions are analyzed with Q3. In this way a potentially unique mass spectrum of an ion with a given *m*/*z* ratio can be obtained. With this new added capability, we now report on the unimolecular rearrangement of deprotonated allyl methyl sulfide and the identification of its isomerization products.

Experimental Section

The collision-induced dissociation (CID) spectra and all of the gas-phase experiments reported herein were carried out with a variable temperature flowing afterglow apparatus[15] which has not been described since it was modified. A brief description of the new instrument (Figure 1) is therefore provided.

Precursor ions are generated by electron ionization of appropriate neutral reagents, as done previously, and are swept down a meter long flow tube by a constant flow of rapidly moving helium. System pressures of 0.35−0.45 Torr are maintained with a Kinney MBD1600 roots blower (1600 cfm, 755 l s^{-1}) and a T150 (150 cfm, 71 l s^{-1}) booster pump, which have a combined pumping speed for air of 1160 cfm (547 l s^{-1}) at 0.4 Torr. Multistep reactions are carried out by adding neutral reagents through fixed inlets along the flow tube. A fraction of the ions is sampled through a 0.5 mm orifice and focused into an EXTREL Corporation triple quadrupole mass analyzer (5/8″ diameter rods). The mass filtered ions are detected with a conversion dynode electron multiplier using standard pulse counting techniques. The detection region is differentially pumped with two 6″ Varian oil diffusion pumps, an M-6 (1800 L s^{-1} for He) and a recently installed VHS-6 (3000 L s^{-1} for He), and is maintained at a pressure between 10^{-6} and 10^{-7} Torr. This background pressure is low enough that collision-induced dissociation does not take place, except in rare instances, without adding a target gas. Some experiments were carried out by raising the temperature of the flow tube from 25 to 375 °C with tubular heaters, while subambient temperatures were achieved with a Neslab Co. Cryocool CC-100 refrigeration system. In both cases the temperature was monitored with four type J thermocouples and held constant with an Omega CN5001 temperature controller.

A triple quadrupole assembly consists of three coaxially aligned quadrupole mass filters: Q1, Q2, and Q3. The first (Q1) and the third (Q3) are rf/dc units, while the middle one (Q2) is an rf-only quadrupole with a gas-tight sheath so that it can function as a collision chamber for CID experiments. Both Q1 and Q3 are operated in mass resolving mode during CID studies. The desired ion is mass-selected with Q1, injected into Q2 where an added target gas induces fragmentation, and the resulting ions are mass-separated with Q3 and then detected. In our experiments, collision-induced dissociation was carried out over a pressure range of 8.0×10^{-6}−2.0×10^{-5} Torr as measured by an ion gauge located in the front chamber of the detection region; the actual pressure in Q2 undoubtedly is higher. Ion translational energies in Q2 can be varied from 0−200 eV, but values of less than 10 eV were typically employed.

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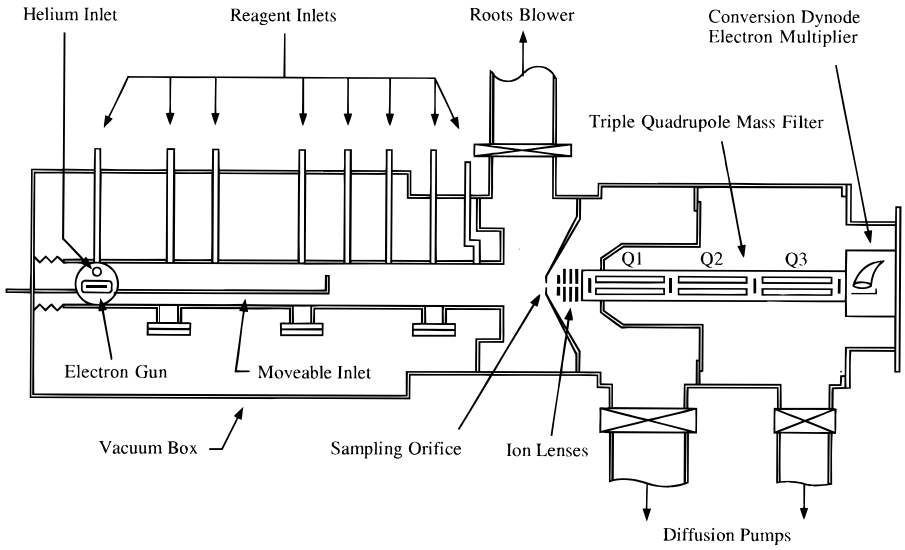


Figure 1. Schematic of our variable temperature flowing afterglow-triple quadrupole device.

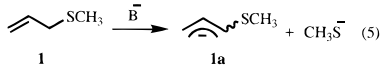
In this work F^-, *t*-BuO^-, MeO^-, OH^-, and NH_2^- were produced by electron impact on NF_3, (*t*-BuO)$_2$, MeONO (generated *in situ*), N_2O/CH_4 (∼1:2), and NH_3, respectively. All liquid samples were subjected to at least one freeze−pump−thaw cycle before use to remove volatile impurities and trapped gases. The conjugate base of allyl methyl sulfide and all of the other $C_4H_7S^-$ isomers we studied were generated by proton abstraction or base-catalyzed elimination using F^- or *t*-BuO^-, unless otherwise noted, and an appropriate neutral precursor. Deprotonation is selective for the most acidic site with these two relatively weak bases, whereas labeling studies, showed that stronger bases such as OH^- and NH_2^- lead to mixtures.

Materials. Allyl methyl sulfide (**1**) and tetrahydrothiophene (**2**) were obtained from commercial sources and used without further purification. Additional isomers of these compounds were prepared using literature procedures. (*E*)- and (*Z*)-1-Butenyl ethyl sulfide (**4**) was synthesized as a 1:1 mixture following the method of Brandsma and Boelens.[16] The isomers were not separated but were distilled through a Vigreaux column at reduced pressure (bp 40−43 °C at 12 mm) before being used. 3-Butene-2-thiol (**3**) was generated by modifying the procedure of Cope.[17] In particular, a substitution reaction in ethanol between sodium hydrogen sulfide (NaSH) and 3-chloro-1-butene afforded the desired 3-butene-2-thiol along with 2-butene-1-thiol in a 1:1 ratio. Both compounds were individually isolated by preparative gas−liquid chromatography (SE-30 on Chrom W, column temperature 75 °C). (*E*)-2-Butene-1-thiol (**5**) was conveniently made and purified in large quantity using (*E*)-crotyl alcohol and thiourea as described by Lee et al.[18] Allyl methyl-d_3 sulfide (**1**-d_3) was synthesized from allyl mercaptan and iodomethane-d_3 by the method of Ono et al.,[19] and the proton NMR indicated ≥99% deuterium incorporation.

Calculations. *Ab initio* molecular orbital calculations were carried out using Gaussian 92[20] and SPARTAN[21] on an IBM RS/6000, a SGI R4000, and a Cray X-MP at the Minnesota Supercomputer Institute. Geometry optimizations of all closed-shell neutral sulfur compounds and their corresponding anions were carried out at the restricted Hartree−Fock (RHF) level of theory with the 6-31+G(d) basis set.[22] Open-shell systems were optimized using the same basis set but with the unrestricted Hartree−Fock (UHF) procedure. In both cases symmetry was exploited, and each structure was checked by calculating its analytical harmonic vibrational frequencies. Minima on the potential energy surface only have positive force constants, while transition structures have one imaginary frequency. In the latter instances the structures were reoptimized without constraint and several additional conformations were examined. In every case the energy differences between the conformers were small (i.e., less than 4 kcal mol^{-1}). Electron correlation was accounted for by carrying out single-point energy calculations using second-order Møller−Plesset perturbation theory (MP2(fc)/6-31+G(d)//HF/6-31+G(d)).[23] The lowest energy structures (supporting information), as determined by their MP2 energies, were also computed using quadratic configuration interaction and the 6-311++G(d,p) basis set (i.e., QCISD(T)/6-311++G(d,p)//HF/6-31+G(d), supporting information).[24] In addition, some G2 calculations[25] (Tables 1−3) were carried out to obtain thermochemical data. This well-established protocol corresponds effectively to a QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) calculation and typically provides energies within ± 2 kcal mol^{-1} of experimental values.

Results

1-Thiomethylallyl Anion (1a). Fluoride and *tert*-butoxide selectively deprotonate allyl methyl sulfide (**1**) at the allylic position to afford 1-thiomethylallyl anion (**1a**, *m*/*z* 87) along with some methanethiolate (*m*/*z* 47, eq 5). The former process is inefficient at room temperature with fluoride (<2%) because



it is slightly endothermic.[26] In fact, the major product is a cluster ion (CH_2=$CHCH_2SCH_3$·F^-, *m*/*z* 107), but a sufficient amount of the M − 1 ion is produced to obtain its CID spectrum. At elevated temperatures the importance of the adduct diminishes, and **1a** is readily generated. The reactivity of 1-thiomethylallyl anion has previously been reported, and its proton affinity (375 ± 3 kcal mol^{-1}) and electron binding energy (1.00 ± 0.22 eV)

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Table 1. Calculated G2 Energies and Experimental Heats of Formation[a]

compd	$G2_0$	$G2_{298}$	$\Delta H°_{f\ 288}$ [b]	compd	$G2_0$	$G2_{298}$	$\Delta H°_{f\ 298}$ [b]
C	−37.784 32[c]	−37.781 96	171.3	CH_2CH_2	−78.415 93[c]	−78.411 92[d]	12.5
H	−0.500 00[c]	−0.497 64	52.1	H_2S	−398.930 73[c]	−398.926 93[d]	−4.9
S	−397.654 95[c]	−397.652 59	66.2	CH_3SH	−438.148 47[c]	−438.143 92[d]	−5.5
O	−74.982 03[c]	−74.979 67	59.6	*t*-CH_2=CHCH=CH_2	−155.664 27	−155.658 72	26.11
CH_2O	−114.338 88[c]	−114.335 07[d]	−26.0	*t*-CH_2=CHCHO	−191.592 65	−191.587 42	−15.6[f][−18]
CH_2S	−436.933 69[c]	−436.929 80[d]	27.96[e][25]	*t*-CH_2=CHCHS	−514.187 89	−514.182 48	37.9[f][32]
H_2O	−76.332 05[c]	−76.328 27[d]	−57.80	$CH_2S^{\bullet-}$	−436.948 53	−436.944 19	17.52[e,g]
CH_4	−40.410 88[c]	−40.407 07[d]	−17.8	*t*-CH_2=CHCHS$^{\bullet-}$ (**6a**)	−514.221 51	−514.215 73	16.3[f]
CH_3OH	−115.534 89[c]	−115.530 58[d]	−48.2	*t*-CH_2=CHCHO$^{\bullet-}$	−191.594 81	−191.589 01	−17.3[f]

[a] G2 energies are in hartrees and heats of formation are in kcal mol^{-1}. [b] Experimental values, including those in brackets, come from ref 28. [c] See ref 25. [d] Temperature corrections were made using scaled (0.89) 6-31+G(d) frequencies (in the other instances 6-31G(d) frequencies were used). Low frequency modes were replaced by $^1/_2RT$ when their contribution to the temperature correction was greater than 1/2*RT*. [e] See ref 48. [f] This work, see Table 2 and/or 3. [g] See ref 46.

Table 2. Calculated G2 Reaction Enthalpies (ΔH_{298}) and Derived Heats of Formation ($\Delta H_f°_{298}$) for Acrolein and Thioacrolein (**6**)[a]

reaction	ΔH_{298}	$\Delta H_f°_{298}$(**6**)
CH_2=CHCHO → 3C + 4H + O	797.8	−15.9
CH_2=CHCHO + C_2H_4 → CH_2=CHCH=CH_2 + CH_2O	3.5	−15.9
CH_2=CHCHO + 2H_2O + 2CH_4 → 3CH_3OH + C_2H_4	34.2	−15.1
		av = −15.6
CH_2=CHCHS (**6**) + H_2 → CH_2=CHCH_2SH	−24.7[b]	37.7[b]
6 + 2H_2S + 2CH_4 → 3CH_3SH + C_2H_4	4.3	37.1
6 + 2CH_4 → CH_3SH + 2C_2H_4	18.1	37.0
6 + C_2H_4 → CH_2S + CH_2=CHCH=CH_2	3.7	37.9[c]
6 + CH_2O → CH_2S + CH_2=CHCHO	0.21	38.2[c,d]
6 → 3C + 4H + S	748.9	39.6
		av = 37.9

[a] All values are in kcal mol^{-1}. [b] QCISD(T)/6-311++G(d,p)//HF/6-31+G(d) + ZPE energies corrected to 298 K were used ($E_{\mathbf{6}}$ = −514.005 85, E_{H_2} = −1.155 53, and $E_{CH_2=CHCH_2SH}$ = −515.200 73 hartrees) along with an estimate (Benson's group equivalents, ref 39) for the heat of formation of allyl thiol (13.0 kcal mol^{-1}). [c] A recently recommended G2 value for the heat of formation of thioformaldehyde (27.96 kcal mol^{-1}, ref 46) was used. [d] Our value for the heat of formation of acrolein was employed since an experimentally determined energy does not appear to be available.

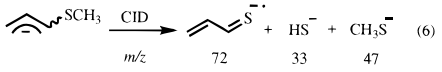
Table 3. Calculated G2 Reaction Enthalpies (ΔH_0) and Derived Electron Affinities for Thioformaldehyde, Thioacrolein (**6**), and Acrolein[a]

reaction	ΔH_0	EA
$CH_2S^{\bullet-}$ → CH_2=S + e^-	9.31	9.31 (0.40 eV) [expt = 10.72 (0.46 eV)][b]
6 + $CH_2S^{\bullet-}$ CH_2=CHCHS$^{\bullet-}$(**6a**) + CH_2=S	11.79	22.5 (0.98 eV)
6a → **6** + e^-	21.10	21.1 (0.91 eV)
		av = 21.8 (0.95 eV)
CH_2=CHCHO$^{\bullet-}$ → CH_2=CHCHO + e^-	1.36	1.36 (0.059 eV)
CH_2=CHCHO$^{\bullet-}$ + CH_2S → CH_2=S$^{\bullet-}$ + CH_2=CHCHO	−7.95	2.77 (0.12 eV)
		av = 2.07 (0.09 eV)

[a] All values are in kcal mol^{-1} unless otherwise indicated. [b] See ref 46 for the experimental data.

were assigned via the bracketing technique and a thermochemical cycle, respectively.[12] Stabilization by the sulfur heteroatom is responsible for the thermodynamic stability and the relative lack of reactivity of **1a** compared to other allylic anions. In this work, the reactions of **1a** with methanol-OD, pyrrole, and *tert*-butyl mercaptan are particularly important because they can be used to readily distinguish between **1a** and its rearranged isomers. The allylic anion undergoes three hydrogen−deuterium (H−D) exchanges with MeOD ($\Delta H°_{acid}$ = 382.5 kcal mol^{-1})[27,28] and very efficiently abstracts a proton from pyrrole and *tert*-butyl mercaptan ($\Delta H°_{acid}$ = 358.7 and 352.5 kcal mol^{-1}, respectively), whereas isomeric thiolates do not react with these reagents.

Collision-induced dissociation of **1a** was carried out under a variety of conditions with several target gases (He, Ar, and Kr). Thioacrolein radical anion (*m*/*z* 72, M − CH_3, 93%) is the major fragment ion (eq 6, Figure 2), but a minor amount of HS^- (*m*/*z* 33, M − C_4H_6, 7%) and, depending upon the collision gas, a



(6)

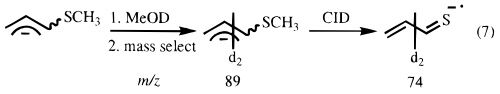
trace of methanethiolate (*m*/*z* 47, M − C_3H_4 <1%) are also observed.[29] Our normal CID conditions (voltages and the collision gas pressure are set as low as practical for obtaining efficient CID) readily lead to the fragmentation of **1a** at pressures below 1 × 10^{-5} Torr indicating that it has a relatively large dissociation cross-section. Direct homolytic cleavage of the CH_3−S bond in **1a** leads to the predominant fragment, whereas the formation of HS^- requires either a skeletal reorganization during the CID process or further fragmentation of the thioacrolein radical anion. The former pathway (CH_3−S cleavage) is consistent with the fact that **1a**-d_3, the d_3-methyl analog of **1a**, affords an *m*/*z* 72 (M − CD_3) ion along with traces of HS^- and DS^-, and the d_2-species, generated by reacting **1a** with MeOD, leads to a *m*/*z* 74 (M − CH_3) ion (eq 7).

Thio Carbanion 1b. Deprotonation of allyl methyl-d_3 sulfide (**1**-d_3) by hydroxide or amide affords both M − H (*m*/*z* 90) and

(27) It is possible to convert all of the *m*/*z* 87 ion to *m*/*z* 90 with this reagent.

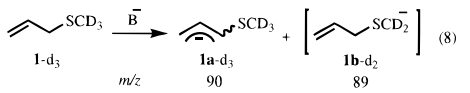
(28) All acidities and other thermodynamic data, unless otherwise noted, come from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phy. Chem. Ref. Data* **1988**, *17*, Supplement 1 or the slightly updated form available on a personal computer, *NIST Negative Ion Energetics Database* (Version 3.00, 1993); NIST Standard Reference Database 19B.

(29) Methyl thiolate is observed when kyrpton is used as the target gas but not when argon or helium is employed.



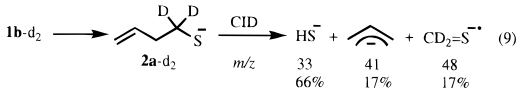
(7)

M − D (*m*/*z* 89) ions in approximately 5−10:1 ratio over a wide temperature range (i.e., −40 to 300 °C, eq 8). Weaker bases such as F^- and *t*-BuO^-, however, selectively form **1a**-d_3 (M − H) even at temperatures up to 300 °C. The M − D ions are quite unreactive and do not undergo acid−base chemistry



(8)

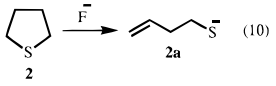
with MeOD or lead to any new products with N_2O. This is inconsistent with the previously reported behavior of α-thio carbanions (i.e., $^-CH_2SH$ and $^-CH_2SCH_3$) which react readily with these reagents.[15,30] Therefore, it appears that the *m*/*z* 89 ion rearranges and has a different structure than **1b**-d_2. The unlabeled version of the M − D ion was generated by deprotonating allyl methyl sulfide with hydroxide and reacting away the allylic anion with pyrrole. The residual signal at *m*/*z* 87 corresponds to an anion derived from deprotonation at the methyl group. Collision-induced dissociation of this species with argon gave three fragments: HS^- (*m*/*z* 33, M − C_4H_6), allyl anion (*m*/*z* 41, M − CH_2S), and thioformaldehyde radical anion (*m*/*z* 46, M − C_3H_5) in approximately a 4:1:1 ratio. This spectrum is identical to that of 3-butene-1-thiolate (**2a**) and is in accord with the CID data from the labeled substrate. More specifically, fragmentation of the M − D ion (*m*/*z* 89) gave HS^- (*m*/*z* 33), allyl anion (*m*/*z* 41), and $CD_2{=}S^{\bullet -}$ (*m*/*z* 48) in a 4:1:1 ratio (eq 9). These results clearly indicate that deprotonation of allyl methyl sulfide at the methyl position affords a rearranged product, namely **2a**.



(9)

Mechanistically, 3-butene-1-thiolate (**2a**) could arise from **1b** via a concerted [2,3] rearrangement or a dissociation−recombination pathway (i.e., a stepwise [2,3] process) involving an initial allyl anion-thioformaldehyde or allyl radical-thioformaldehyde radical anion complex, which upon recombining would afford the observed product. A direct elimination reaction bypassing the formation of **1b** and leading to the same intermediate as in the stepwise pathway also is a possibility.[31] In an attempt to distinguish between these pathways we tried to generate **1b** as a stable species by deprotonating allyl methyl sulfide with hydroxide at ca. −40 °C; methyl deprotonation does occur at this temperature as indicated with the d_3-labeled substrate. The resulting M − 1 ion does not react with N_2O or MeOD, except for some clustering. This indicates that if **1b** is formed it still rearranges rapidly at −40 °C. An analogous attempt to generate the conjugate base of dimethyldisulfide was equally unsuccessful.

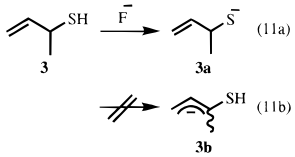
3-Butene-1-thiolate (2a). This ion (**2a**) was generated efficiently by a base-induced ring opening elimination reaction of tetrahydrothiophene as previously described by de Koning and Nibbering (eq 10).[32] Repeated collision-induced dissociation experiments using helium, argon, and krypton under a



(10)

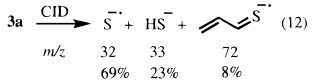
variety of conditions gave spectra which are indistinguishable from each other. Three fragment ions, HS^- (*m*/*z* 33), allyl anion (*m*/*z* 41), and thioformaldehyde radical anion (*m*/*z* 46), are formed in approximately a 4:1:1 ratio (Figure 2). The fragment ions presumably arise by (1) elimination of 1,3-butadiene to give HS^- (*m*/*z* 33), (2) heterolytic cleavage of the C_1-C_2 bond to afford allyl anion (*m*/*z* 41) and thioformaldehyde, and (3) homolytic C_1-C_2 bond cleavage to form thioformaldehyde radical anion (*m*/*z* 46) and allyl radical. Formation of S^- (*m*/*z* 32) and an accompanying unconjugated primary radical via homolytic cleavage of the CH_2-S^- bond in **2a** was never observed. In addition, the parent ion does not fragment as readily as **1a** and only has a moderate dissociation cross-section.

3-Butene-2-thiolate (3a). Deprotonation of 3-butene-2-thiol by F^- or *t*-BuO^- selectively affords the desired thiolate (**3a**, eq 11a). This result was anticipated because experiments and computations indicate that a thiolate such as **3a** is about 20 kcal mol^{-1} more stable than a 1-substituted thioallyl anion (**3b**).[12,28] In addition, the formation of the latter ion (eq 11b) is likely to



(11a)
(11b)

be inefficient and slightly endothermic. Nevertheless, the selectivity was confirmed by examining the reactivity of the resulting anion with a variety of reagents including O_2, SO_2, CS_2, MeOD, and pyrrole. No reactions were observed, except for cluster formation, in accord with **3a** but in contrast to the expected behavior of **3b**. Inert gas CID of **3a** using helium, argon, or krypton (Figure 2) gives S^- (*m*/*z* 32) and HS^- (*m*/*z* 33) in approximately a 3:1 ratio, along with small amounts of thioacrolein radical anion (*m*/*z* 72, eq 12). Standard conditions at relatively low pressures result in extensive fragmentation of



(12)

the parent ion (**3a**) and a significant reduction in its intensity. The observed products presumably arise by (1) elimination of 1,3-butadiene or methylallene to afford HS^- (*m*/*z* 33), (2) homolytic cleavage of the $C-S^-$ bond to yield S^- (*m*/*z* 32) and 1-methylallyl radical, and (3) homolytic CH_3-C bond cleavage to form thioacrolein radical anion (*m*/*z* 72) and methyl radical.

(*E*)- and (*Z*)-1-Butenyl Thiolate (4a). A 1:1 mixture of *cis*- and *trans*-1-butenyl ethyl sulfide (**4**) undergoes an elimination reaction with F^- and *t*-BuO^- (eq 13a) to give (*E*)- and (*Z*)-1-butenyl thiolate (**4a**). An alternative product, 2-butenyl thiolate (**5a**), can be envisioned to arise via proton abstraction at the allylic position followed by an intramolecular elimination reaction (eq 13b). This latter type of pathway is known[32,33] but could be ruled out by independently preparing **5a** (*vide infra*) and showing that it has a unique CID spectrum. The fragmentation products of **4a** are S^- (*m*/*z* 32), HS^- (*m*/*z* 33), and thioacrolein radical anion (*m*/*z* 72) and are formed in roughly equal amounts. On occasion a trace of a *m*/*z* 57 ion is also observed; this fragment probably is ethynyl thiolate (eq 14,

(30) Ingemann, S.; Nibbering, N. M. M. *Can. J. Chem.* **1984**, *62*, 2273.
(31) For a similar proposal, see: Grabowski, J. J.; Zhang, L. *J. Am. Chem. Soc.* **1989**, *111*, 1193.
(32) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1988**, *110*, 2066.
(33) van Berkel, W. W.; de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 7602.

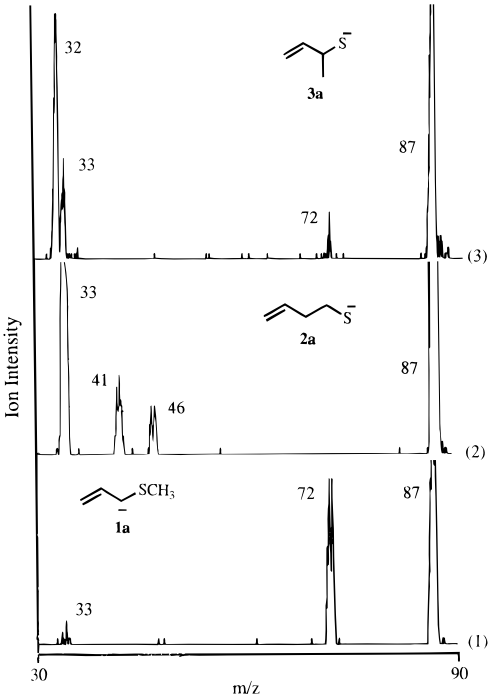


Figure 2. Collision-induced dissociation spectra of mass-resolved (*m*/*z*) 1-thiomethylallyl anion (**1a**, (1)), 3-butene-1-thiolate (**2a**, (2)), and 3-butene-2-thiolate (**3a**, (3)) with argon as the collision gas. Note, the tops of the *m*/*z* 87 ions have been clipped as has the very top of the *m*/*z* 33 fragment in spectrum 2.

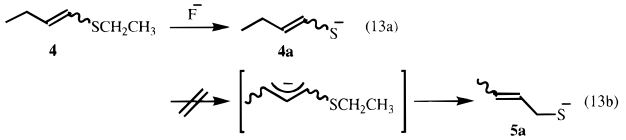
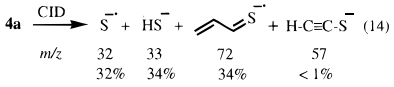
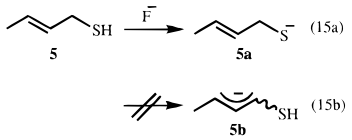


Figure 3). Unlike any of the other $C_4H_7S^-$ isomers that we studied **4a** is difficult to break apart, and our standard conditions



resulted in a large residual signal. This is a unique feature of **4a**, in addition to its characteristic CID spectrum. A reasonable explanation for the observed fragments is (1) homolytic C−S$^-$ bond cleavage to form S$^-$ (*m*/*z* 32) and 1-butenyl radical, (2) elimination of 1-butyne to form HS$^-$ (*m*/*z* 33), (3) homolytic cleavage of the CH_3−C bond to afford thioacrolein radical anion (*m*/*z* 72) and methyl radical, and (4) elimination of ethane to form ethynyl thiolate (*m*/*z* 57).

(*E*)-2-Butene-1-thiolate (5a). Fluoride and *tert*-butoxide react with (*E*)-2-butene-1-thiol (**5**) to give (*E*)-2-butene-1-thiolate (**5a**) and a trace of HS$^-$ (eq 15). The deprotonation is selective



for the same reason that it is with 3-butene-2-thiol (**3**). This was borne out by examining the reactivity of the M − 1 ion with N_2O, MeOD, and pyrrole. No new reaction products were observed, except for a little clustering, in accord with the known behavior of thiolates and in contrast to the reactivity of a 1-substituted thioallyl anion. Collision-induced dissociation of

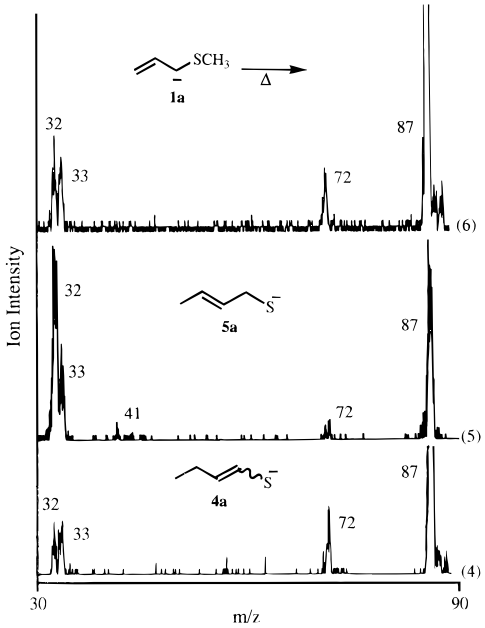
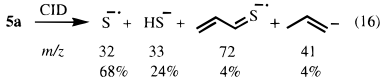


Figure 3. Collision-induced dissociation spectra of (*E*)- and (*Z*)-1-butenyl thiolate (**4a**, (4)), (*E*)-2-butene-1-thiolate (**5a**, (5)), and the rearranged isomer of deprotonated allyl methyl sulfide at 310 °C (6) with argon as the collision gas. The tops of the *m*/*z* 87 ions in spectra 4 and 6 have been truncated for visual purposes.

5a (eq 16) yields S$^-$ (*m*/*z* 32) and HS$^-$ (*m*/*z* 33) in approximately a 3:1 ratio.. Minor amounts of what we presume are 1-propenyl



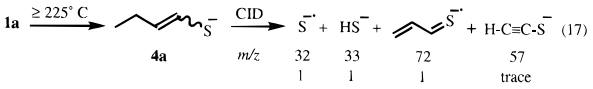
anion (*m*/*z* 41) and thioacrolein radical anion (*m*/*z* 72) were also detected (Figure 3). In several ways this spectrum is similar to the one obtained from **3a**. Both allylic thiolates readily generate S$^-$ and HS$^-$, and under our standard conditions there is a significant reduction in the intensity of the selected M − 1 (*m*/*z* 87) ions.

Thermolysis of Deprotonated Allyl Methyl Sulfide (1a). Allylic anion **1a** was generated by deprotonating allyl methyl sulfide with F$^-$ and *t*-BuO$^-$ over a temperature range of 25 to 375 °C. The structure of the resulting anion was probed chemically with pyrrole since it readily protonates **1a** but does not react with thiolate ions. At low temperatures pyrrole completely quenches **1a**, but at elevated temperatures the ion signal at *m*/*z* 87 does not disappear entirely indicating the presence of a rearranged isomer(s). The residual intensity increases with temperature as expected for a unimolecular process. The onset temperature for the rearrangement (i.e., the lowest temperature which leads to detectable isomerization) was found to be 225 °C regardless of whether fluoride or *tert*-butoxide was used to generate **1a**. Similar results were also obtained when MeOD and *tert*-butyl mercaptan were used as the chemical probe reagents. These test procedures are not applicable, however, when strong bases such as OH$^-$ or NH_2^- are used because methyl deprotonation takes place and an unreactive thiolate is produced. It is interesting to note that the residual M − 1 signal increases with temperature upon heating above 25 °C when strong bases are used. In this case it is unclear whether this result is due to a change in the proportion of methyl deprotonation or if the heat liberated upon forming **1a** ($\Delta H° = -16$ and -29 kcal mol^{-1} for OH$^-$ and

NH_2^-, respectively) facilitates the isomerization.[34] In either case, this is not a problem when fluoride or *tert*-butoxide is used since proton abstraction is slightly endothermic or thermonetrual ($\Delta H° = +4$ and 0 kcal mol^{-1}, respectively), and deprotonation only occurs at the allylic position.

A new product, thioacrolein radical anion (CH_2═$CHCHS^{\bullet -}$, *m*/*z* 72), is observed when allyl methyl sulfide reacts with F^- or *t*-BuO^- at about 225 °C. The relative ratio of this species to the M − 1 ion at *m*/*z* 87 increases with temperature, but it is always a small contributor.[35] The formation of this radical anion presumably results from a facile homolytic cleavage of the S−CH_3 bond in **1a** and coincides with the start of the unimolecular rearrangement of the latter ion. Consequently, it seems natural to relate these two pathways mechanistically, although this need not be the case.

In order to identify the structure of the rearranged ion, a large excess of pyrrole or *tert*-butyl mercaptan was added to the flow tube in order to remove all of the unrearranged ion (**1a**). The remaining *m*/*z* 87 signal was mass-selected and collisionally dissociated. Once efficient fragmentation conditions such as pressure, ion translational energy, lens settings, etc. were achieved, all of the authentic $C_4H_7S^-$ isomers were generated and fragmented using the same settings. The rearranged ion generated the following fragments: *m*/*z* 32, 33, and 72 in a 1:1:1 ratio (eq 17). Occasionally, a trace of *m*/*z* 57 was also observed (Figure 3). Furthermore, this ion undergoes only a little fragmentation using our standard operating conditions. Since the CID spectra of **2a**, **3a**, **4a**, and **5a** are unchanged at elevated temperatures and are distinct, *these results clearly indicate that the rearranged isomer is predominantly, if not exclusively, 1-butenyl thiolate (**4a**)*. Furthermore, the rearranged isomer of **1a** has the same CID spectrum over the entire temperature range we examined.

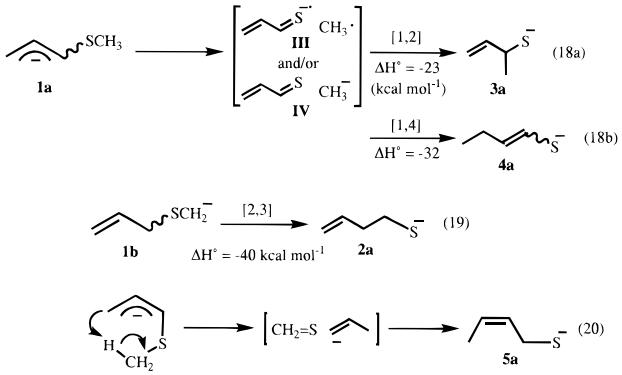


(17)

Discussion

We have considered four transformations of 1-thiomethylallyl anion (**1a**) and its thioallylmethyl anion isomer (**1b**): [1,2]-, [1,4]-, and [2,3]-Wittig rearrangements as well as an elimination−addition pathway (eqs 18−20). These isomerizations lead to 3-butenyl-2-thiolate (**3a**), 1-butenyl thiolate (**4a**), 4-butenyl-1-thiolate (**2a**), and 2-butenyl-1-thiolate (**5a**), respectively. All four isomeric thiolates have similar basicities and are relatively unreactive, consequently, we were unable to distinguish between them using chemical probe reagents. Their collision-induced dissociation spectra, however, are distinct (Figures 2 and 3) and can be used to unambiguously identify each of these species. In this way, we found that the thermolysis of **1a** leads predominantly, if not exclusively, to **4a** and that deprotonation of a methyl proton from allyl methyl sulfide yields 3-butene-1-thiolate (**2a**) even at subambient temperatures. In order to gain a better understanding of these results the energetics and mechanisms of the isomerizations will be considered in turn.

Thermochemistry. Deprotonation of allyl methyl sulfide (**1**) can occur at the methyl group or the allylic site. The latter position is more acidic and has an experimental acidity ($\Delta H°_{acid}$) of 375 ± 3 kcal mol^{-1}.[12] This result is in good accord with our calculated MP2/6-31+G(d)//HF/6-31+G(d) value of 373.6



kcal mol^{-1} for the allylic position in allyl mercaptan (CH_2═C-HCH_2SH).[36] The acidity of the methyl site has not been measured but should be similar to the known values for dimethyl sulfide ($\Delta H°_{acid}$ = 393 ± 3 kcal mol^{-1})[30] and methanethiol ($\Delta H°_{acid}$(CH_3SH) = 394 ± 3 kcal mol^{-1}).[15,37] Our observation that hydroxide ($\Delta H°_{acid}$(H_2O) = 391 kcal mol^{-1}) and amide ($\Delta H°_{acid}$(NH_3) = 404 kcal mol^{-1}) abstract a methyl proton from **1** but methoxide ($\Delta H°_{acid}$(MeOH) = 381 kcal mol^{-1}) does not is in accord with this expectation. Consequently, there is a 15−20 kcal mol^{-1} thermodynamic preference for the formation of **1a** which explains why weak bases selectively form this ion and strong bases preferentially afford it.

The [1,2]- and [1,4]-Wittig rearrangement of 1-thiomethylallyl anion is calculated to be exothermic by 23 and 32 kcal mol^{-1} (eq 18 and supporting information),[38] respectively, at a high level of theory (QCISD(T)/6-311++G(d,p)//HF/6-31+G(d)). The former value can also be evaluated using experimental data and Benson's group equivalents for the conjugate acids of **1a** and **3a**; the reaction enthalpy is −25 ± 6 kcal mol^{-1} which is in good agreement with the computed result.[39] Both pathways are thermodynamically accessible, but the [1,4] rearrangement is favored. The energy difference between the two reaction channels (eq 18a vs 18b), 9 kcal mol^{-1}, is considerably less than for the analogous oxygen containing species (i.e., $\Delta H°_f$(CH_2═$CHCH_2O^-$) − $\Delta H°_f$(CH_3CH═CHO^-) = 23 kcal mol^{-1}).[28] This 14 kcal mol^{-1} difference can be accounted for by the greater stability of a carbonyl compared to a thiocarbonyl (eq 21)[40] and the smaller resonance stabilization of a thioenolate

(34) Deprotonation of **1**-d_3 with hydroxide results in a M−H:M−D ratio which seems to be somewhat dependent on the temperature.

(35) The radical anion of thioacrolein presumably undergoes some electron detachment at elevated temperatures. It never amounts to more than approximately 25% of **1a**.

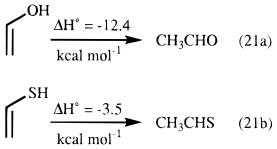
(36) A bigger basis set and further accounting of electron correlation (supporting information) leads to similar results: 375.3 (MP2), 381.3 (MP3), 378.6 (MP4), and 379.7 kcal mol^{-1} (QCISD(T)) where all of the energies were obtained with HF/6-31+G(d) optimized geometries and the 6-311++G-(d,p) basis set. A reasonable value for the S−H acidity of CH_2═$CHCH_2$-SH was also obtained using the same level of theory: 354.2 (MP2), 357.8 (MP3), 356.4 (MP4), and 356.8 kcal mol^{-1} (QCISD(T)), given that $\Delta H°_{acid}$-(*n*-PrSH) = 354 kcal mol^{-1} (ref 29). The usually reliable MP2/6-31+G-(d)//HF/6-31+G(d) result (346.7 kcal mol^{-1}), however, appears to be significantly too low.

(37) For calculations on the thiomethyl anion, see: Downard, K. M.; Sheldon, J. C.; Bowie, J. H.; Lewis, D. E.; Hayes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 8112.

(38) In our calculations on **1a**, **3a**, and **4a** the methyl group was replaced by a hydrogen atom. This substitution should have little impact on the computed results.

(39) The heats of formation of **1a** (19.1 ± 4 kcal mol^{-1}) and **3a** (−6.1 ± 4 kcal mol^{-1}) can be derived using the following thermodynamic relationship: $\Delta H°_f(A^-) = \Delta H°_{acid}$ (A−H) − $\Delta H°_f$ (H^+) + $\Delta H°_f$(A−H), where $\Delta H°_f(H^+)$ = 365.7 kcal mol^{-1}, $\Delta H°_{acid}$ (**1**) = 375 ± 3 (ref 12), $\Delta H°_{acid}$ (**3**) = 353 ± 3 (estimate based on the known acidities of several alkyl thiols), $\Delta H°_f$ (**1**) = 9.8 kcal mol^{-1} (Benson's group equivalents), and $\Delta H°_f$ (**3**) = 6.6 kcal mol^{-1} (Benson's group equivalents, where C−$(C)_2$-(H)(S) was substituted for C−(C_d)(C)(H)(S)). Note, uncertainties of ±3 kcal mol^{-1} were ascribed to the heats of formation of **1** and **3** and were derived using the following reference: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976.

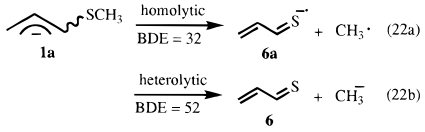
(40) The cited energies are based on QCISD(T)/6-311++G(d,p)//HF/6-31+G(d) calculations. For further details and the effect of correlation on the energies, see the supporting information.



ion.[41] The third Wittig pathway, the [2,3] rearrangement (eq 19), is exothermic by 40 kcal mol^{-1}, which makes it energetically the most favorable transformation.[42]

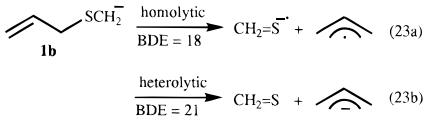
Activation energies for unimolecular isomerizations can readily be obtained with our apparatus by using the Arrhenius equation, an estimated pre-exponential factor (A), and the observed onset temperature for rearrangement.[11] The unimolecular rate constant at the lowest temperature which leads to an observable isomerization (i.e., the onset temperature) is 10 s^{-1}. This was determined from the known reaction time (7 ms)[43] and by setting $[A^-]/[A^-]_0 = 0.95$ at the onset temperature; we assume that a 5% conversion is needed in order to reliably detect isomerization. By combining this minimum reaction rate with a typical frequency factor of 10^{13} and the measured onset temperature of 225 °C leads to an activation energy of 27 kcal mol^{-1} for the rearrangement of **1a**. This value is similar to a calculated barrier for the suprafacial $\sigma_{2s} + \pi_{4s}$ [1,4] hydrogen shift in 1-methylallyl anion (30 kcal mol^{-1}, MP2/6-31G(d)//HF/6-31G(d)) and is in accord with typical activation energies for concerted processes.[44] In a similar manner, an upper limit of 13 kcal mol^{-1} can be obtained for the [2,3]-Wittig process given that methyl deprotonation of allyl methyl sulfide affords **2a** even at −40 °C.[45]

Homolytic and heterolytic stepwise mechanisms always provide an alternative to a concerted transformation. Distinguishing between these possibilities is often difficult and sometimes contentious, in part, because the requisite thermochemical data for the postulated reactive intermediates is typically unavailable. In this instance the bond dissociation energies of 1-thiomethylallyl anion are needed, and this requires a knowledge of the heat of formation and electron affinity of thioacrolein (**6**). These quantities have not been measured so we have computed them using the G2 procedure; this corresponds effectively to a QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) calculation.[25] This level of theory has been targeted to give energies which are accurate to within ±2 kcal mol^{-1} of experimental values. Our results (Table 1), $\Delta H_f°$(**6**) = 37.9 kcal mol^{-1} and EA(**6**) = 21.8 kcal mol^{-1} (0.95 eV), are in reasonable accord with an estimate of the former quantity by Lias et al.[28] and expectation for the latter quantity given the measured electron affinities for thioformaldehyde (0.465 eV, 10.72 kcal mol^{-1}),[46] formaldehyde (−0.86 eV, −19.8 kcal mol^{-1}),[47] and acrolein (>0 eV (expt); 0.09 eV, 2.1 kcal mol^{-1} (calc)). The resulting data were used to derive the homolytic and heterolytic bond dissociation energies of **1a** (eq 22).[28,39] It is interesting to note that these values are similar to the analogous bond dissociation energies of the conjugate base of dimethyl sulfide ($CH_3SCH_2^-$); experimental data affords BDEs

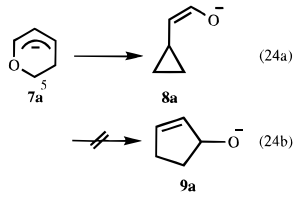


of 34 and 43 kcal mol^{-1}, respectively.[48] The carbon-sulfur bond strength in neutral dimethyl sulfide is 77 kcal mol^{-1},[49] and thus deprotonation of **1** or Me_2S activates the C−S bond by about 45 kcal mol^{-1}.

The bond dissociation energies of **1b** can be derived from experimental data and are considerably smaller than for the allylic isomer (eq 23).[28,42,48] This is expected because allyl radical and allyl anion are more stable than methyl radical and methyl anion.



Mechanism. Allyl ethers typically undergo the Wittig rearrangement in solution to afford alcohols ([1,2] product) and aldehydes or ketones ([1,4] product).[7a,8b,j,k] Numerous studies have led to the general conclusion that the [1,2] rearrangement involves a cleavage−recombination mechanism in which a radical−radical anion complex plays an important part.[5] The [1,4] isomerization is mechanistically less clear; both stepwise and concerted pathways have been suggested.[5,7] For example, the dihydropyranyl anion **7a** rearranges exclusively to (*Z*)-cyclopropyl enolate **8a** (eq 24).[50] In this case, the ring structure enforces a *cis* orientation of the allylic anion which ensures that the two interacting ends are in close proximity as required for a concerted [1,4] suprafacial bond migration. If a stepwise mechanism were operative one might expect the less strained cyclopentenyl ring (**9a**) to dominate (eq 24b). The complete absence of this product, even though frontier molecular orbital



theory favors [1,4] addition,[51] has been taken as evidence for a concerted pathway. Resonance stabilizing groups located at C5, however, facilitate the isomerization and are required for analogous thioether rearrangements.[7b,d] These latter observations suggest a stepwise mechanism rather than a concerted one. In either case, it is clear that cyclic ethers which cannot adopt a *cis* configuration must isomerize via a stepwise route and other

(41) The sulfur 3p orbitals are higher in energy than oxygen's 2p orbitals so the interaction with the olefinic π bond in the thioenolate is less.

(42) The following values were used to derive the heats of formation of **1b** (37.1 kcal mol^{-1}) and **2a** (−2.6 kcal mol^{-1}): $\Delta H°_f$(3-butene-1-thiol) = 9.1 kcal mol^{-1} (Benson's group equivalents), $\Delta H°_f$(**1**) = 9.8 kcal mol^{-1} (ref 39), PA(**2a**) ≈ PA(*n*-PrS$^-$) = 354 kcal mol^{-1}, and PA(**1b**) = 393 kcal mol^{-1}.

(43) The reaction time follows directly from the known ion velocity (1.6 $\bar{v}_{He}$ or ≈14 400 cm s^{-1}) and the reaction distance (100 cm).

(44) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682.

(45) An alternative elimination−addition mechanism cannot be excluded, but we think this pathway is less likely based upon thermodynamic grounds. See the text for additional details.

(46) Moran, S.; Ellison, G. B. *Int. J. Mass. Spectrom. Ion Processes* **1987**, *80*, 83.

(47) For the electron affinity of formaldehyde and acrolein, see: Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

(48) The following heats of formation (in kcal mol^{-1}) were used: $\Delta H°_f(CH_3SCH_2^-)$ = 18.3, $\Delta H°_f(CH_2S)$ = 27.96, $\Delta H°_f(CH_2S^{\bullet-})$ = 17.2, $\Delta H°_f(CH_3^-)$ = 33.2, and $\Delta H°_f(CH_3^{\bullet})$ = 35.1. These energies come from or can be derived from data in refs 29, 46, and Nobes, R. H.; Radom, L. *Chem. Phys. Lett.* **1992**, *189*, 554.

(49) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(50) Rautenstrauch, V. *Helv, Chim. Acta* **1972**, *55*, 594.

(51) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley and Sons: New York, 1976.

species, such as some 2-alkoxypyridine oxides, proceed by a concerted pathway.[52]

In the gas phase, the isomerization of 1-thiomethylallyl anion (**1a**) occurs at elevated temperatures (≥225 °C), and the sole product, 1-butenyl thiolate (**4a**), results from a [1,4] migration. The activation energy for this process is 27 kcal mol^{-1} which is in the predicted range for similar concerted transformations.[44] Consequently, it is tempting to attribute the observed selectivity in this conformationally flexible substrate to a suprafacial $\sigma_{2s} + \pi_{4s}$ process.[53,54] However, the homolytic bond dissociation energy is virtually the same as the reaction barrier, and a fragmentation product, thioacrolein radical anion (**6a**), resulting from the scission of the S−CH_3 bond is observed. The formation of **6a** need not be related to the isomerization pathway, but this seems an unlikely coincidence. It therefore appears that both pathways have similar energy requirements and probably are involved in the rearrangement of **1a**. Such a conclusion is consistent with liquid-phase results and accounts for some of the controversy regarding the mechanism of [1,4] migrations. That is, a small change in the substrate can lead to a change in the reaction pathway.

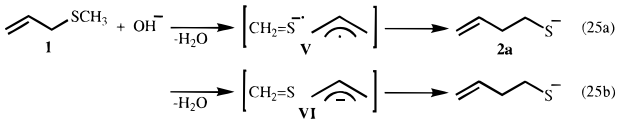
In terms of selectivity, the observed rearrangement product **4a** is thermodynamically favored over **3a** and can readily be explained in terms of a concerted pathway; the [1,4] migration leading to **4a** is an allowed process, whereas the [1,2] shift affording **3a** is forbidden by orbital symmetry. The product distribution also can be explained by a stepwise mechanism. Two limiting pathways involving homolytic and heterolytic cleavage (eq 18a) need to be considered, but the bond dissociation energy for the former process is 20 kcal mol^{-1} less than for the latter one (eq 22). This energy difference is somewhat misleading in that the intermediates (**III** and **IV**, eq 18) do not fully dissociate during the isomerization and the interaction energy between thioacrolein and methyl anion (**IV**) is larger than between thioacrolein radical anion and methyl radical (**III**).[55] Nevertheless, the homolytic pathway most readily accounts for the observed selectivity. In particular, in this process the key interaction involves the coupling of the two radical centers. Since the spin density, and the charge, is greatest on the remote carbon (C3, Table 4), [1,4] addition should be favored.[56] Frontier molecular orbital (FMO) theory, on the other hand, does not appear to be useful for predicting the selectivity in [1,2]- and [1,4]-Wittig rearrangements. Regardless of whether one uses the singly occupied molecular orbital (SOMO) of **6a** or the lowest unoccupied molecular orbital (LUMO) of **6** the incorrect conclusion (i.e., [1,2] > [1,4]) is reached. Similarly, 1-methoxyallyl anion is predicted to rearrange in the opposite sense [1,4] > [1,2], which is inconsistent with the observed behavior of most ethers in solution.[4e,8k,57]

Table 4. Calculated Spin Densities and Charges for the Radical Anion of Thioacrolein (**6a**)[a]

	spin density		charge		
site	Mulliken	NPA[b]	Mulliken	NPA[b]	EP[c]
S	0.15	0.13	−0.88	−0.60	−0.89
C_1	0.78	0.66	−0.24	−0.38	0.02
C_2	−0.79	−0.44	−0.05	−0.29	0.06
C_3	1.03	0.74	−0.51	−0.47	−0.63

[a] A UHF/6-31+G(d) optimized structure and wave function was used. The results (not shown) are essentially the same for the *cis* conformer and if the hydrogen contributions are summed into the carbon atoms. [b] Natural population analysis (see ref 56). [c] Electrostatic potential.

The formation of 4-butenyl-1-thiolate (**2a**) upon reaction of allyl methyl sulfide (**1**) with strong bases can occur via a [2,3] Wittig rearrangement or an elimination−addition pathway (eq 25). The latter channel, however, is unlikely based upon thermodynamic grounds. The elimination reaction to afford all



three separate constituents water, thioformaldehyde, and allyl anion or water, thioformaldehyde radical anion, and allyl radical is endothermic by 23 and 20 kcal mol^{-1}, respectively.[58] As a result, formation of complexes **V** and **VI** are apt to be endothermic or thermoneutral at best, and thus a significant barrier should retard the formation of **2a**. On the other hand, the methyl position is somewhat acidic so that **1b** is a reasonable intermediate when strong bases such as hydroxide and amide are used. Its homolytic and heterolytic bond dissociation energies (eq 23) are greater than the 13 kcal mol^{-1} upper limit established for this isomerization, so it appears that a concerted mechanism is operative. This conclusion is in accord with solution results and accounts for why thiomethyl methyl anion ($CH_3SCH_2^-$) and thiomethyl anion ($HSCH_2^-$) can be generated, they cannot rearrange via an orbital symmetry allowed process, whereas **1b** is not observed even at −40 °C.[59]

Conclusions

Deprotonation of allyl methyl sulfide (**1**) with weak bases selectively affords 1-thiomethylallyl anion (**1a**), and this ion undergoes a unimolecular rearrangement at elevated temperatures. The rearranged product is 1-butenyl thiolate (**4a**), which was distinguished from several other isomers by collision-induced dissociation. The activation barrier for this [1,4] shift is 27 kcal mol^{-1}, which is similar to the activation energies for several related pericyclic reactions. A concerted pathway for the formation of **4a** is allowed by orbital symmetry, but a stepwise route also appears to be energetically accessible for this transformation. The latter pathway accounts for the

(52) It has been concluded that many 2-alkoxypyridine oxides rearrange via a concerted mechanism based upon their activation parameters (small enthalpies and large negative entropies of activation) and the observed stereochemistry of the migrating group (i.e., complete retention of configuration). When a radical stabilizing substituent such as diphenylmethyl (Ph_2CH) is employed, however, very different activation parameters (bigger enthalpies and much less negative entropies) are obtained, and a CIDNP signal can be detected. In these cases, a stepwise mechanism seems to be operative. For further details, see ref 7c.

(53) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: Germany, 1971.

(54) The allylic anion (**1a**) can adopt a *cis* orientation and the *trans* species should be able to readily convert to it. In this regard, it is interesting to note that Wiberg et al. calculated a 19.4 kcal mol^{-1} (MP3/6-311++G(d,p)//6-31G(d)) barrier for rotation about allyl anion. Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61.

(55) Thioacrolein, undoubtedly, has a larger dipole moment and is considerably more polarizable than methyl radical so the interaction energy in **IV** is larger than in **III**.

(56) For details regarding natural atomic populations, see: Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(57) It is interesting to note that in both the sulfur and oxygen cases the interaction of methyl radical with the second highest π-type orbital leads to the correct prediction. For example, the SOMO-2 of thioacrolein radical anion (*cis* or *trans*) has a much larger coefficient at C3 than C1. Moreover, the energy match between this MO and the SOMO of methyl radical is much better than between the two SOMOs.

(58) The following heats of formation (in kcal mol^{-1}) were used: $\Delta H°_f$(**1**) = 9.8, $\Delta H°_f(CH_2S)$ = 27.96, $\Delta H°_f(CH_2S^{\bullet-})$ = 17.2, $\Delta H°_f(CH_2{=}CHCH_2^-)$ = 29.9, and $\Delta H°_f(CH_2{=}CHCH_2{\bullet})$ = 38.1, $\Delta H°_f(H_2O)$ = −57.8, and $\Delta H°_f(OH^-)$ = −32.7. These energies come from refs 28, 39, 47, and 48.

(59) The homolytic and heterolytic BDEs for $CH_3SCH_2^-$ (34 and 43 kcal mol^{-1}, respectively) and $HSCH_2^-$ (48 and 41 kcal mol^{-1}, respectively) are also larger, and this too explains their stability. Note, this energetic data was obtained using refs 28 and 48.

observed fragmentation product, thioacrolein radical anion, at the rearrangement onset temperature and can explain the observed selectivity: the unpaired electron in thioacrolein radical anion largely resides on the remote carbon (C3) which should lead to the [1,4] product upon reaction with methyl radical. Frontier molecular orbital theory, on the other hand, leads to the wrong prediction in this instance. The thioallyl methyl anion **1b** undergoes an extremely facile [2,3] Wittig rearrangement even at −40 °C. The mechanism for this reaction appears to be a concerted process just as in solution.

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Supporting Information Available: Calculated structures (HF/6-31+G(d)), absolute energies (HF to QCISD(T)), and relative energies for, $CH_2{=}CHCH_2SH$, $^{-}CH_2CH{=}CHSH$, $CH_2{=}CHCH_2S^{-}$, (*Z*)-$CH_3CH{=}CHS^{-}$, CH_3CHS, and $CH_2{=}CH$-SH (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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