

Figure 2. Structure of the Fe_4O_6 core of $[\text{Fe}_4\text{L}_2\text{O}_2(\text{OH})_2]^+$ showing 50% probability ellipsoids and atom labeling scheme. The tetrahedral iron core is cumulatively bridged on each edge by two phenolates (Fe1–O12, 2.074 (3) Å; Fe2–O12, 2.084 (3) Å), two hydroxides (Fe1–O11 and Fe2–O22, both 1.989 (2) Å), and two oxo ligands (Fe1–O21, 1.792 (3) Å; Fe2–O21, 1.790 (3) Å). The iron–iron separations across the phenolate, the hydroxo, and the oxo bridges are 3.631 (1), 3.442 (1), and 3.469 (1) Å, respectively, with Fe–O–Fe angles of 121.65 (13)°, 119.24 (24)°, and 151.23 (19)°, respectively. The iron–carboxylates range from 2.095 (3) Å for Fe2–O5 to 2.127 (3) Å for Fe1–O3.

solution of the binuclear complex with an excess of pyrrolidine. An ORTEP plot of the Fe_4O_6 core is shown in Figure 2. Two binuclear pieces have fused into a distorted tetrahedron of iron bridged by six oxygens in a structure similar to that of $(\text{tacn})_4\text{Mn}_4\text{O}_4$.¹³ In the process of fusion, two water ligands are displaced. The four iron atoms are coordinated in distorted octahedra and cumulatively bridged by two phenolates, two hydroxides, and two oxo ligands. The oxo bridges undoubtedly provide the pathway for the strong antiferromagnetic coupling observed for this cluster.

Comparison of the iron–ligand bond lengths for the two structures reveals substantial weakening of the bonds to the binucleating ligand in the tetranuclear complex. The iron–phenolate bond lengths have increased by about 0.07 Å and the iron–carboxylate bond lengths by at least 0.12 Å. Correspondingly, short Fe–oxo bonds (1.79 Å) in the tetranuclear complex replace the Fe–OH₂ bonds (2.01 Å) in the binuclear complex. Although phenolates are unlikely to be involved in the coordination of iron in ferritin,¹⁴ these observations may be relevant to the formation of the iron core of ferritin. Various studies have suggested the importance of binuclear complex formation in initiating core nucleation in ferritin.^{2,15,16} The protein shell, probably via its carboxylates, plays an important role in this process.^{2,16–18} The conversion of the binuclear complex to the tetranuclear form that we observe suggests the next stage in the process, where the core–protein shell interactions weaken and the continuation of core growth occurs on the core itself without the aid of the protein shell.

Acknowledgment. This work has been supported by the National Institutes of Health (GM-33162). L.Q. is grateful for an

(13) Wieghardt, K.; Bossek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328–329.

(14) Thiel, E. C. *Adv. Inorg. Biochem.* **1983**, *5*, 1–38.

(15) Chasteen, N. D.; Antanaitis, B. C.; Aisen, P. *J. Biol. Chem.* **1985**, *260*, 2926–2929.

(16) Sayers, D. E.; Thiel, E. C.; Rennick, F. J. *J. Biol. Chem.* **1983**, *258*, 14076–14079.

(17) Rice, D. W.; Ford, G. C.; White, J. L.; Smith, J. M. A.; Harrison, P. M. *Adv. Inorg. Biochem.* **1983**, *5*, 39–50.

(18) Weitz, K.; Crichton, R. R. *Eur. J. Biochem.* **1976**, *61*, 545–550.

NIH Research Career Development Award (1982–1987) and an Alfred P. Sloan Research Fellowship (1982–1986).

Supplementary Material Available: Tables of atomic positional and thermal parameters for $[\text{Fe}_2\text{L}(\text{OH})(\text{H}_2\text{O})_2] \cdot 3.8\text{H}_2\text{O}$ and $(\text{C}_4\text{H}_{10}\text{N})_4[\text{Fe}_4\text{L}_2(\text{O})_2(\text{OH})_2] \cdot 2\text{CH}_3\text{OH} \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{H}_2\text{O}$ (11 pages). Ordering information is given on any current masthead page.

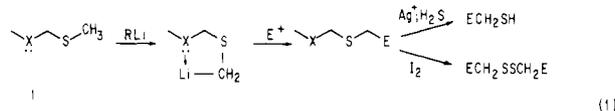
(2-Tetrahydrofuranyl)- and (2-Tetrahydropyranyl)(thiomethyl)lithium: Methanethiol Carbanion Equivalents

Eric Block*† and Mohammad Aslam

Department of Chemistry
State University of New York at Albany
Albany, New York 12222

Received May 29, 1985

Alkanethiols are of considerable importance as starting materials for preparation of a vast array of sulfur-containing structures. It is therefore surprising that synthetic approaches to these key compounds are quite limited.¹ We sought a fundamentally new approach to alkanethiol synthesis based on a methanethiol carbanion (HSCH_2^-) synthon which would permit carbon functionalization with the wide range of reagents employed in carbanion chemistry.^{2,4} A reagent **1** containing carbon geminally substituted with a thiomethyl group and an oxygen or nitrogen substituent seemed suitable for our purposes since the latter group could assist deprotonation of the thiomethyl group by metal coordination⁷ and could subsequently facilitate hydrolytic release of thiol along with water-soluble carbonyl byproducts (eq 1).⁸ We further envisioned that cleavage of the protected thiols



under oxidative conditions could lead directly to disulfides.⁸ Thus the initial reagent could also serve as a $^-\text{CH}_2\text{SSCH}_2^-$ synthon. Of the several reagents examined, 2-(methylthio)tetrahydrofuran (**2**) and 2-(methylthio)tetrahydropyran (**3**) seemed ideal. We describe herein the generation and electrophilic substitution of (2-tetrahydrofuranyl)(thiomethyl)lithium (**4**) and (2-tetra-

* Fellow of the John Simon Guggenheim Memorial Foundation, 1984–1985.

(1) (a) Standard syntheses of alkanethiols involve interaction of sulfur-free substrates with nucleophilic, electrophilic, or radical (or radical accepting) sulfur agents: Wardell, J. L. In "The Chemistry of the Thiol Group"; Patai, S., Ed.; Wiley: New York, 1974; Chapter 4. (b) Ohno, A.; Oae, S. In "Organic Chemistry of Sulfur"; Oae, S., Ed.; Plenum: New York, 1976. (c) Barrett, G. C. In "Comprehensive Organic Chemistry"; Jones, D. N., Ed.; Pergamon Press: New York, 1979; Vol. 3, Chapter 11.1.

(2) (a) α -Carbanion formation in alkanethiols is unfavorable^{1c} except in the case of prop-2-enethiol and α -toluenethiol which have been shown to yield dianions.³ (b) For a multistep approach to "mercaptomethylation", see: Ogura, K.; Furukawa, S.; Tsuchihashi, G. *Synthesis* **1976**, 202–204 (this approach is unsuitable for synthesis of silicon compounds because of side reactions). (c) For doubly metalated methanol reagents, see: Seebach, D.; Meyer, N. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 438. Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290–1303. Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201–1202.

(3) Geiss, K.; Seuring, B.; Pieter, R.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 479–480. Seebach, D.; Geiss, K. H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 202–203.

(4) After the initiation of this work we became aware of the alkylation of the THP derivative of diphenylmethanethiol;⁵ dianions of the latter thiol can be readily prepared by alkali-metal reduction of thiobenzophenone.⁶

(5) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917–925.

(6) Minoura, Y.; Tsuboi, S. *J. Org. Chem.* **1972**, *37*, 2064–2069.

(7) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1–360.

(8) Greene, T. W. "Protective Groups in Organic Synthesis"; Wiley-Interscience: New York, 1981. Wolman, Y. In "The Chemistry of the Thiol Group"; Patai, S., Ed.; Wiley: New York, 1974; Chapter 14.

Table I. Thiol and Disulfide Synthesis Using (2-Tetrahydrofuranyl)(thiomethyl)lithium (**4**) and (2-Tetrahydropyryl)(thiomethyl)lithium (**5**)

| reagents ^a | adduct ^m (yield, %) | thiol or disulfide ^m (yield, %) ^d |
|---|---|--|
| PhCHO, 5 | $\text{CH}_2(\text{CH}_2)_3\text{CHSCH}_2\text{CHOHPh}$ (81) | PhCHOHCH ₂ SH ^f (100) |
| <i>n</i> -C ₇ H ₁₅ I, 5 | $\text{CH}_2(\text{CH}_2)_3\text{CHSCH}_2\text{-}n\text{-C}_7\text{H}_{15}$ (90) | <i>n</i> -C ₈ H ₁₇ SH ^g (60) |
| Br(CH ₂) ₆ Br, 5 | $[\text{CH}_2(\text{CH}_2)_3\text{CHS}(\text{CH}_2)_4\text{-}]_2$ (98) | HS(CH ₂) ₈ SH ^h (76) |
| PhCH ₂ Br, 5 | $\text{CH}_2(\text{CH}_2)_3\text{CHSCH}_2\text{CH}_2\text{Ph}$ (49) | PhCH ₂ CH ₂ SH ^g (93) |
| <i>t</i> -BuMe ₂ SiCl, 5 | $\text{CH}_2(\text{CH}_2)_3\text{CHSCH}_2\text{SiMe}_2\text{-}t\text{-Bu}$ (87) | <i>t</i> -BuSiMe ₂ CH ₂ SH or (<i>t</i> -BuSiMe ₂ CH ₂ S) ₂ (77) |
| <i>t</i> -BuMe ₂ SiCl, 5 ^b | $\text{CH}_2(\text{CH}_2)_3\text{CHSCH}(\text{SiMe}_2\text{-}t\text{-Bu})_2$ (78) | (<i>t</i> -BuSiMe ₂) ₂ CHSH (89) |
| <i>t</i> -BuMe ₂ SiCl, 4 ^b | $\text{CH}_2(\text{CH}_2)_2\text{CHSCH}(\text{SiMe}_2\text{-}t\text{-Bu})_2$ (44) | (<i>t</i> -BuSiMe ₂) ₂ CHSH (91) |
| Me ₃ SiCl, 9 ^{b,c} | $\text{CH}_2(\text{CH}_2)_3\text{CHSC}(\text{SiMe}_3)_3$ (83) ⁱ | (Me ₃ Si) ₃ CSH ^j (80) |
| EtI, 9 ^c | $\text{CH}_2(\text{CH}_2)_3\text{CHSCH}(\text{Et})\text{SiMe}_3$ (90) | Me ₃ SiCH(Et)SH ^k (71) |
| PhCHO, 9 ^c | $\text{CH}_2(\text{CH}_2)_3\text{CHSCH}=\text{CHPh}$ ^l (74) | PhCH=CHSH ^l (55) |
| Me ₂ SiCl ₂ , 5 ^c | $[\text{CH}_2(\text{CH}_2)_3\text{CHSCH}_2]_2\text{SiMe}_2$ (74) | Me ₂ Si(CH ₂ SH) ₂ (22) |

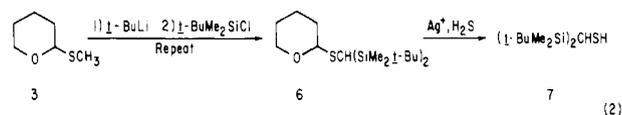
^a **4** = (2-Tetrahydrofuranyl)(thiomethyl)lithium; **5** = (2-tetrahydropyryl)(thiomethyl)lithium; **9** = lithio derivative of 2-[[trimethylsilyl]methyl]thio]tetrahydropyran. ^b Addition of base and electrophile is repeated a second time. ^c Base is *n*-butyllithium. ^d Distilled product. ^e Fourfold excess of **5** used. ^f Alcedia, F.; Farina, F.; Ruano, J. L. G.; Sanchez, F. *J. Chem. Soc., Perkin Trans. 2* **1978**, 412–416. ^g Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Company: New York, 1958; Vol. 1. ^h Whittaker, V. P. *Biochem. J.* **1947**, *41*, 56–62. ⁱ Contains 10% of bis(trimethylsilyl) derivative. ^j Reference 14. ^k Block, E.; Wall, A. *Tetrahedron Lett.* **1985**, *26*, 1425–1428. ^l Reference 11d. ^m All new compounds gave satisfactory spectroscopic and analytical data.

hydropyryl)(thiomethyl)lithium (**5**) and the conversion of their reaction products to thiols and disulfides.

Reagent **2** can be prepared in two steps in 46% yield from tetrahydrofuran by light-initiated α -chlorination with sulfuryl chloride⁹ at -30°C followed by reaction with methanethiol/triethylamine at -78°C while reagent **3** can be easily prepared on a large scale in 84% yield by pyridinium *p*-toluenesulfonate¹⁰ catalyzed addition of methanethiol to 2,3-dihydrofuran.¹¹ Both **2** and **3** undergo clean deprotonation at the methyl position with *tert*-butyllithium in 10:1 THF/HMPA at -90°C giving **4** and **5**, respectively. As summarized in Table I, **4** and **5** react smoothly with a variety of electrophiles including aldehydes, alkyl halides and dihalides, and silyl chlorides and dichlorides, giving adducts that can be converted in good yield to the thiols with silver nitrate or mercuric chloride followed by hydrogen sulfide or hydrogen chloride or to disulfides with iodine.^{8,12} While thioacetals such as 1,3-oxathiane and methoxymethyl phenyl thioether¹³ can be readily deprotonated on the central methylene position, there was no evidence of deprotonation at the 2-position in **2** and **3** with

tert-butyllithium. We attribute this to steric hindrance, favorable oxygen–lithium coordination effects, and reduced acidity of the methine position.¹³

Multiple electrophilic substitution with the same or different electrophiles can be effected if acidifying groups, such as trialkylsilyl groups, are used (see Table I), allowing preparation of bis- and tris(trialkylsilyl)methanethiols^{14,15} (eq 2) as well as silyl



dithiols, compounds of interest as hindered ligands.¹⁶ Anion **9**, formed by deprotonation of 2-[[trimethylsilyl]methyl]thio]tetrahydropyran **8** with *n*-butyllithium, undergoes the Peterson reaction¹⁷ with aldehydes or ketones permitting synthesis of 1-alkenyl thiols or bis(1-alkenyl) disulfides. Compound **8** could be prepared by silylation of **3** or via pyridinium *p*-toluenesulfonate catalyzed addition of (trimethylsilyl)methanethiol¹⁸ to dihydrofuran. We shall describe elsewhere other applications of tetrahydropyryl and tetrahydrofuranyl α -mercapto carbanion reagents.

Acknowledgment. We gratefully acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Soci t  Nationale Elf Aquitaine, and the Northeastern New York Chapter of the American Heart Association. Support from

(9) Vilsmaier, E.; Westernacher, R. *Justus Liebigs Ann. Chem.* **1972**, *757*, 170–180. Kruse, C. G.; Broekhof, N. L. J. M.; van der Gen, A. *Tetrahedron Lett.* **1976**, 1725–1728.

(10) Miyashita, N.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772–3774.

(11) (a) Parham, W. E.; DeLaitch, D. M.; *J. Am. Chem. Soc.* **1954**, *76*, 4962–4965. (b) Hiskey, R. G.; Tucker, W. P. *J. Am. Chem. Soc.* **1962**, *84*, 4789–4794. (c) Kipnis, F.; Ornfelt, J. *J. Am. Chem. Soc.* **1951**, *73*, 822. (d) Missakain, M. G.; Ketcham, R.; Martin, A. R. *J. Org. Chem.* **1974**, *39*, 2010–2012.

(12) Typical procedure: A solution of **3** (11.3 mmol) in 30 mL of dry THF and 4 mL of dry HMPA is treated at -95°C with 1.4 equiv of *t*-BuLi followed by *n*-heptyl iodide (7.5 mmol) in 3 mL of THF. The product was warmed to -10°C and after workup (H₂O; ether; drying; concentration) distilled at 100°C (0.01 mm), giving 2-(octylthio)tetrahydropyran in 90% yield (Anal. (C₁₃H₂₆OS) C, H). The oil was dissolved in MeOH and treated with aqueous AgNO₃ or HgCl₂ in aqueous acetonitrile and the precipitate collected, suspended in CHCl₃, and treated with H₂S for 10 min. Workup of the organic layer afforded pure octanethiol in 60% yield.

(13) Eliel, E. L.; Koskimes, J. K.; Lohri, B.; *J. Am. Chem. Soc.* **1978**, *100*, 1614–1616. Fujii, K.; Ueda, M.; Sumi, K.; Kajiwara, K.; Fujita, E.; Iwashita, T.; Miura, I. *J. Org. Chem.* **1985**, *50*, 657–661. Fujii, K.; Ueda, M.; Sumi, K.; Fujita, E. *J. Org. Chem.* **1985**, *50*, 662–666. Trost, B. M.; Miller, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 7182–7183. Mandai, T.; Moriyama, T.; Nakayama, Y.; Sugino, K.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1984**, *25*, 5913–5916. Vatele, J.-M. *Tetrahedron Lett.* **1984**, 5997–6000. Hackett, S.; Livinghouse, T. *Tetrahedron Lett.* **1984**, *25*, 3539–3542. Juaristi, E.; Gordillo, B.; Aparicio, D. M.; Bailey, W. F.; Patricia, J. *J. Tetrahedron Lett.* **1985**, *26*, 1927–1930.

(14) Block, E.; Aslam, M. *Tetrahedron Lett.* **1985**, *26*, 2259–2262.

(15) Alkylation procedure (eq 2): A solution of **3** (10 mmol) in 25 mL of dry THF and 3 mL of dry HMPA is treated at -95°C with 1.2 equiv of *t*-BuLi followed by *t*-BuMe₂SiCl (1.2 equiv) in 5 mL of THF. The mixture is warmed briefly to -78°C , cooled to -95°C , and treated a second time with 1.2 equiv of base and silyl chloride as above. Workup as above gave a crystalline adduct **6** (mp 44–45 $^\circ\text{C}$; from ethanol) in 65% yield (Anal. (C₁₈H₄₀OSSi₂) C, H). Treatment of this adduct with AgNO₃ at 100°C for 0.5 h followed by treatment with H₂S and workup as above gave thiol **7** in 89% yield: IR 1465 (s), 1390 (m), 1362 (m), 1255 (s), 820 cm⁻¹ (vs); ¹H NMR (CDCl₃) δ 1.34 (d, *J* = 7 Hz, 1 H), 1.5 (d, *J* = 7 Hz, 1 H), 0.99 (s, 18 H), 0.13 (s, 6 H), 0.10 (s, 6 H); ¹³C NMR (CDCl₃) δ 27.90, 18.96, 3.05, -2.33, -5.12.

(16) Aslam, M.; Bartlett, R. A.; Block, E.; Olmstead, M. M.; Power, P. P.; Sigel, G. E. *J. Chem. Soc., Chem. Commun.*, in press. Zubieta, J.; Block, E.; Aslam, M.; Gebreyes, K., unpublished results.

(17) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780–784.

(18) Block, E.; Aslam, M. *Tetrahedron Lett.* **1982**, *23*, 4203–4206.

the National Science Foundation for the purchase of a Varian XL-300 NMR spectrometer is acknowledged.

Registry No. 2, 98194-87-7; 3, 31053-11-9; 4, 98194-88-8; 4-*t*-BuMe₂SiCl adduct, 98194-97-9; 5, 98194-89-9; 5-PhCHO adduct, 98194-92-4; 5-*n*-C₇H₁₅I adduct, 98194-93-5; 5-Br(CH₂)₆Br adduct, 98194-94-6; 5-PhCH₂Br adduct, 51380-98-4; 5-*t*-BuMe₂SiCl adduct, 98194-95-7; 5-*t*-BuMe₂SiCl adduct, 98194-96-8; 5-Me₂SiCl₂ adduct, 98217-00-6; 8, 98194-90-2; 9, 98194-91-3; 9-Me₂SiCl adduct, 98194-98-0; 9-EtI adduct, 98194-99-1; 9-PhCHO adduct, 98195-00-7; PhCHOHCH₂SH, 28713-50-0; *n*-C₈H₁₇SH, 111-88-6; *t*-BuSiMe₂CH₂SH, 38225-24-0; (*t*-BuSiMe₂CH₂S)₂, 98195-01-8; (*t*-BuSiMe₂)₂CHSH, 98195-02-9; (Me₂Si)₂CSH, 98195-03-0; Me₂SiCH(Et)SH, 97203-60-6; Me₂Si(CH₂SH)₂, 10605-38-6; HSCH₂⁺, 51422-57-2; PhCHO, 100-52-7; *n*-C₇H₁₅I, 4282-40-0; Br(CH₂)₆Br, 629-03-8; PhCH₂Br, 100-39-0; *t*-BuMe₂SiCl, 18162-48-6; Me₂SiCl, 75-77-4; EtI, 75-03-6; Me₂SiCl₂, 75-78-5; HS(CH₂)₆SH, 1191-62-4; PhCH₂CH₂SH, 4410-99-5; PhCH=CHSH, 4363-47-7; (trimethylsilyl)methonethiol, 18165-76-9; tetrahydrofuran, 109-99-9; 2,3-dihydropyran, 110-87-2.

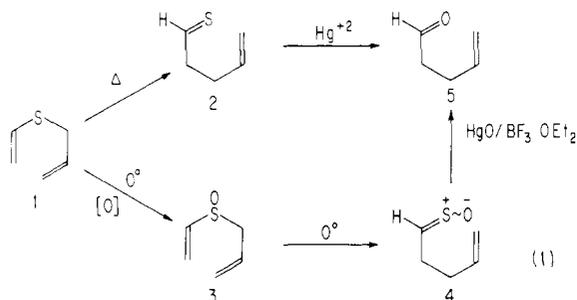
Unusually Facile Thio-Claisen Rearrangement of 1-Alkenyl 2-Alkenyl Sulfoxides: A New Sulfine Synthesis¹

Eric Block*† and Saleem Ahmad

Department of Chemistry
State University of New York at Albany
Albany, New York 12222

Received August 6, 1985

While the thio-Claisen rearrangement of 1-alkenyl 2-alkenyl sulfides (e.g., 1, eq 1) is of considerable mechanistic interest, its



synthetic utility is limited by the elevated temperature required together with the need to conduct the rearrangement in the presence of mercuric salts to trap and desulfurize the reactive thiocarbonyl intermediates (e.g., 2).² We have discovered that oxidation of 1-alkenyl 2-alkenyl sulfides to the corresponding sulfoxides leads to a remarkable acceleration in the rate of the [3,3]-sigmatropic process,³ which now occurs below 0 °C in some cases, affording isolable sulfines (thiocarbonyl *S*-oxides), which

Table I. Conversion of 1-Alkenyl 2-Alkenyl Sulfides into 4-Pentenethial *S*-Oxides and 4-Pentenals via 1-Alkenyl 2-Alkenyl Sulfoxides

| sulfide | yield of sulfoxide 8, % | yield of sulfine 9, % (<i>E/Z</i> , temp, °C) | yield of aldehyde 10, % |
|--|-------------------------|--|----------------------------------|
| 7a, R = R' = R'' = H | <i>a</i> | 81 ^b (5:95, 0) | 90 ^c |
| 7b, R = CH ₂ Cl; R' = R'' = H | <i>a</i> | 90 ^b (2:98, 0) | 94, ^d 63 ^e |
| 7c, R = CH ₃ ; R' = R'' = H | <i>a</i> | 76 ^f (2:98, 0) | 92 ^c |
| 7d, R = Ph; R' = R'' = H | <i>a</i> | 98 ^b (2:98, 0) | 74 ^f |
| 7e, R = R' = H; R'' = CH ₃ | <i>a</i> | 96 ^b (33:66, 0) | |
| 7f, R = R' = CH ₃ ; R'' = H | 92 | 100 (70:30, 25) | 80 ^f |
| 7g, R-R' = -(CH ₂) ₅ -; R'' = H | 94 | 100 (83:17, 25) | 78 ^f |
| 7h, R-C-R' = 2-adamantylidene; R'' = H | 98 ^h | 100 (65:35, 90) | 77 ^f |

^aNot isolated. ^bYield from sulfide. ^cGC yield. ^dCrude yield; some 2-methylene-4-pentenal present. ^eYield of 2-methylene-4-pentenal from 10, R = CH₂Cl, R' = R'' = H. ^fYield by preparative TLC. ^gOverall yield from 6 (LiEt₃BH then CH₃CO₃H). ^hMp 56-57 °C. Anal. C, H.

can be converted into carbonyl compounds under mild conditions or further transformed.^{1b} Also notable is our observation that the stereochemistry of the sulfines varies with the substitution pattern of the 1-alkenyl 2-alkenyl sulfoxides in a manner reflecting the preference of sulfoxide oxygen for pseudoequatorial or pseudoaxial orientation in the chairlike transition state for rearrangement.

In a typical case, allyl vinyl sulfide (1) is oxidized at -20 °C to allyl vinyl sulfoxide (3), which can be characterized by NMR spectroscopy at -10 °C. At -7 °C 3 rearranges in 81% yield with a half-life of 159 min to a 95:5 mixture of (*Z*)- and (*E*)-4-pentenethial *S*-oxide (4). Lacrymatory 4 has spectral properties similar to those of propanethial *S*-oxide, the onion lacrymatory factor,⁴ and can be converted by treatment with boron trifluoride-mercuric oxide⁵ at room temperature for 30 min to 4-pentenal (5) in 90% yield (Table I). While the activation enthalpy for the thio-Claisen reaction is typically greater than that for the Claisen,^{6a} we find the activation enthalpy for the sulfoxide thio-Claisen reaction of allyl vinyl sulfoxide ($\Delta H^\ddagger = 19.32 \pm 0.50$ kcal/mol by NMR methods; $\Delta S^\ddagger = -4.30 \pm 1.60$ cal/(mol K)^{3a}) to be lower than that for the Claisen rearrangement of allyl vinyl ether ($\Delta H^\ddagger = 25.40$ kcal/mol; $\Delta S^\ddagger = -15.9$ cal/(mol K)).^{6b,7}

The synthetic utility of the sulfoxide thio-Claisen rearrangement is indicated by the data in Table I. The conversion of diallyl sulfide to 2-methylene-5-pentenal by way of 2-(chloromethyl)-5-pentenethial *S*-oxide in 53% overall yield (eq 2) is noteworthy.⁸

* Fellow of the John Simon Guggenheim Memorial Foundation, 1984-1985.

(1) (a) The Chemistry of Sulfines. 12. (b) Part 11: Block, E.; Wall, A.; Zubieta, J. J. *Am. Chem. Soc.* **1985**, *107*, 1783-1784.

(2) (a) Corey, E. J.; Shulman, J. I. *J. Am. Chem. Soc.* **1970**, *92*, 5522-5523. (b) Oshima, K.; Takahashi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 2693-2694. (c) Morin, L.; Lebaud, J.; Paquer, D.; Chaussin, R.; Barillier, D. *Phosphorus Sulfur* **1979**, *7*, 69-80. (d) Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978. (e) Tamaru, Y.; Furukawa, Y.; Mizutani, M.; Kitao, O.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 3631-3639.

(3) For related examples, see: (a) Makisumi, Y.; Takada, S.; Matsukura, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 850. Rearrangement of 1-(allyl-sulfinyl)naphthalene shows $\Delta H^\ddagger = 21.6$ kcal mol⁻¹ and $\Delta S^\ddagger = -26.1$ cal K⁻¹ mol⁻¹ at 130 °C. (b) Bell, R.; Cottam, P. D.; Davies, J.; Jones, D. N.; Meanwell, N. A. *Tetrahedron Lett.* **1980**, *21*, 4379-4382. (c) Bycroft, B. W.; Landon, W. *J. Chem. Soc., Chem. Commun.* **1970**, 967-968. (d) Following submission of this work we have learned that sulfoxide thio-Claisen rearrangements leading to sulfines were also observed by L. Brandsma (unpublished observation).

(4) Block, E.; Revelle, L. K.; Bazzi, A. A. *Tetrahedron Lett.* **1980**, 1277-1280.

(5) Vedejs, E.; Fuchs, P. L. *J. Org. Chem.* **1971**, *36*, 366-367.

(6) (a) Kwart, H.; Schwartz, J. L. *J. Org. Chem.* **1974**, *39*, 1575-1583. (b) Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6983-6984.

(7) The low ΔH^\ddagger for the sulfoxide thio-Claisen rearrangement can be attributed to the low C-S(O) bond strength (ca. 55 kcal/mol),^{2d} e.g., compared to the C-S, C-SO₂, or C-O bond strengths. Thio-Claisen rearrangement of allyl vinyl sulfone is unfavorable (King, J. F.; Harding, D. R. K. *J. Am. Chem. Soc.* **1976**, *98*, 3312-3316). The negatively charged sulfoxide oxygen may make the sulfoxide thio-Claisen analogous to the alkoxide or anion-facilitated Cope or Claisen rearrangements, known to be accelerated compared to their unassisted counterparts. Furthermore, in the thio-Claisen process stabilizing conjugation between the lone pairs on sulfur and the 1-alkenyl double bond may be lost in the non-planar chair-like transition state; no such loss of conjugation energy occurs in the sulfoxide thio-Claisen (suggestion of Professor B. Carpenter).