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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)₃CSH, 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)₈SH, 1191-62-4; PhCH₂CH₂SH, 4410-99-5; PhCH=CHSH, 4363-47-7; (trimethylsilyl)methionethiol, 18165-76-9; tetrahydrofuran, 109-99-9; 2,3-dihydropyran, 110-87-2.

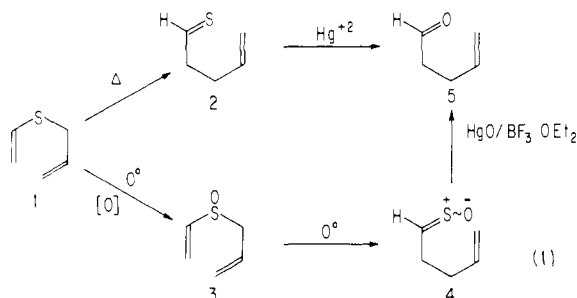
Unusually Facile Thio-Claisen Rearrangement of 1-Alkenyl 2-Alkenyl Sulfoxides: A New Sulfine Synthesis¹

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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

7 sulfide	8 yield of sulfoxide %, %	9 yield of sulfine 9, % (<i>E/Z</i> , temp, °C)	10 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 ^b	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

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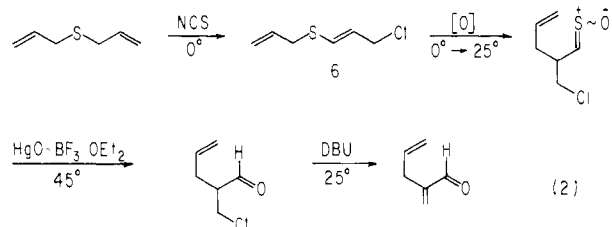
(3) For related examples, see: (a) Makisumi, Y.; Takada, S.; Matsukura, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 850. Rearrangement of 1-(allyl-sulfinyl)naphthalene shows $\Delta H^\ddagger = 21.6$ kcal mol⁻¹ and $\Delta S^\ddagger = -26.1$ cal K⁻¹ mol⁻¹ at 130 °C. (b) Bell, R.; Coutam, P. D.; Davies, 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).

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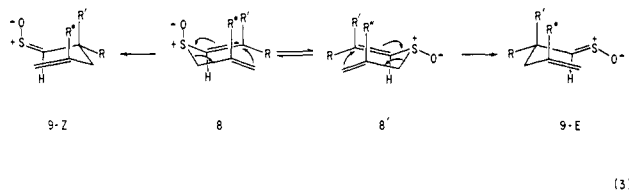
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(7) The low ΔH^\ddagger for the sulfoxide thio-Claisen rearrangement can be attributed to the low C-S(O) bond strength (ca. 55 kcal/mol),^{2d} e.g., compared to the C-S, C-SO₂, or C-O bond strengths. Thio-Claisen rearrangement of allyl vinyl sulfone 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).



Attempts to achieve this same transformation by way of sulfide **6** were unsuccessful due to the instability of this compound and its transformation products under the conditions required for the normal thio-Claisen reaction. An important consequence of the mild conditions used for the sulfoxide thio-Claisen and sulfine hydrolysis is that overall yields are in general superior to those obtained by the thio-Claisen route.^{2a}

Examination of the sulfines formed from variously substituted 1-alkenyl 2-alkenyl sulfides **7** (Table I)¹⁰ reveals an interesting stereochemical effect. Thus for **7a-e** *Z* stereochemistry is favored, as it is for alkanethial *S*-oxides prepared by other routes;^{4,11} while for **7f-h** (e.g., where $R' \neq H$) *E* stereochemistry is favored. We find that the (*E*)-sulfines, which in some cases can be obtained in stereochemically pure form by chromatography,¹² rearrange thermally and photochemically to the thermodynamically more stable (*Z*)-sulfines.^{11,12} If it is assumed that rearrangement of sulfoxides **8** to sulfines **9** involves a chairlike transition state then pseudoaxial or pseudoequatorial orientations are possible for the sulfoxide oxygen. For thiane *S*-oxides an axial oxygen orientation is favored *except* when there are substituents at the 3- or 5-positions cis to sulfoxide oxygen, such as 3,3-dimethylthiane *S*-oxide where the equatorial/axial oxygen ratio is >95:5.¹³ We suggest that similar effects prevail in the sulfoxide thio-Claisen favoring **8'** over **8** when $R, R' \neq H$ (eq 3). The decreased ability



of the C-R'' bond compared to the C-R' bond to shift the sulfoxide oxygen from its normally favored pseudoaxial orientation may

(8) 2-Propenyl 3-chloro-1-propenyl sulfide, prepared in 100% yield by treatment of diallyl sulfide with NCS/CCl₄ at 0 °C,⁹ was oxidized with CH₃CO₃H (0 °C), warmed to 25 °C (1 h), washed (NaHCO₃), dried, and concentrated in vacuo giving (*Z*)-2-(chloromethyl)-4-pentenethial *S*-oxide (90%): ¹H NMR (CDCl₃) δ 8.11 (d, 1 H, *J* = 7 Hz), 5.74 (m, 1 H), 5.12 (m, 2 H), 3.85 (m, 3 H), 2.42 (m, 2 H); ¹³C NMR δ 176.4, 133.3, 118.7, 45.6, 38.1, 35.5; ca. 5% of the (*E*)-sulfine was also present. The sulfine in THF was added to HgO and BF₃-Et₂O (1:1) in THF-H₂O (85:15) at 25-45 °C for 2.5 h. Workup (ether-brine washing, drying, concentration in vacuo) gave 2-(chloromethyl)-4-pentalen (94% yield). This unstable compound was treated with an equimolar amount of DBU at 25 °C (15 min), diluted with pentane, water washed, dried, concentrated (Vigreux column), and distilled giving 2-methylene-4-pentalen (63%): IR 1690, 1640 cm⁻¹; ¹H NMR δ 9.67 (s, 1 H), 6.24 (br s, 1 H), 6.03 (br s, 1 H), 5.79 (m, 1 H), 5.09 (m, 2 H), 2.96 (m, 2 H).

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(12) 2-Allyl 2-adamantanethiocarbonyl sulfide *S*-oxide (**9h**) was separated by preparative TLC into *E* and *Z* isomers whose configurational assignments follow past work.⁴ The *E* isomer had mp 35-36 °C. Anal. C, H. IR 1093 (s) cm⁻¹; ¹H NMR δ 8.82 (s, 1 H, CH=SO) in CDCl₃ and 8.50 in C₆D₆; ¹³C NMR δ 192.5 (C=SO, *J*_{C-H} = 163.2 Hz), 131.7, 119.7 (C=C). The *Z* isomer had mp 50-51 °C. Anal. C, H; IR 1115 (s) cm⁻¹; ¹H NMR δ 7.42 (s, 1 H, CH=SO) in CDCl₃ and 6.83 in C₆D₆; ¹³C NMR δ 182.3 (C=SO, *J*_{C-H} = 157.1 Hz), 133.4, 118.1 (C=C). After 36 h at 90 °C, conversion of (*E*)-**9h** to (*Z*)-**9h** was complete.

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be due to the greater distance of the C-R'' bond from the S-O bond compared to the C-R' bond in the rearrangement transition state.¹⁴

In addition to the stereoselectivity seen at sulfur in the sulfoxide thio-Claisen rearrangement, possibilities exist for intramolecular chirality transfer from sulfur to carbon in the case of *chiral* 1-alkenyl 2-alkenyl sulfoxides. Efforts to prepare these compounds are in progress.

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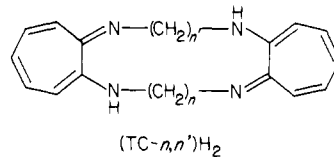
(14) The S-O bond is separated from the C-R' bond by an sp² C-sulfoxide bond and a C-C double bond (which in the transition state becomes a sulfine thiocarbonyl bond and an sp³-sp² C-C bond, respectively) and from the C-R'' bond by an sp²-sp³ C-C bond and an sp² C-sulfoxide bond (the latter is broken in the transition state).

Dicopper(I) Tropocoronands: Synthesis, X-ray Crystal Structure, and Spectral Properties of Neutral Binuclear Copper(I) Complexes Bridged by Symmetrically Substituted Alkynes

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We have been exploring the coordination chemistry of the tropocoronands, H₂(TC-*n,n'*), a new class of macrocycles¹ which



(TC-*n,n'*)H₂

n,n' = 3,3; 4,4; 4,5; 5,5; 6,6

bind divalent metal ions with loss of two enamine protons to form stable neutral mononuclear complexes.^{2,3} Binuclear species form in the reaction of cupric acetate monohydrate with H₂(TC-6,6) in methanol, which yields the doubly bridged μ -acetato- μ -methoxo derivative [Cu₂(OAc)(OMe)(TC-6,6)] (**1**).⁴ Because of the great current interest in the chemistry of binuclear cuprous sites,⁵ we have recently turned our attention to the synthesis and characterization of discrete binuclear copper(I) species using tropoco-

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