A CONVENIENT SYNTHESIS OF VINYL SULFIDES

ABIMAEL D. RODRIGUEZ AND ALEX NICKON*

Department of Chemistry, The Johns Hopkins University Baltimore, Maryland 21218 U.S.A.

(Received in USA 11 June 1985)

Abstract - Dithioketals are converted in good yields to vinyl sulfides by action of diethylzinc and methylene iodide. The reaction has been successfully applied to dialkyl and diaryl dithioketals, to spirocyclic analogs, and to a dithioacetal. A monothioketal produced a vinyl ether (enol ether) with the same reagent.

Vinyl sulfides (i.e. thioenol ethers) have become increasingly useful and versatile synthons.¹ Among other things, they expand chemists' ability to manipulate carbonyl groups.² Therefore, easy access to molecules having the C=C-S- structural unit is highly desirable. Thioalcohols in the presence of strong acids (P_2O_5 ; p-TsOH; AlCl₃) can sometimes convert ketones directly to their corresponding vinyl sulfides,³ but the limitations of this method have prompted searches for alternative routes.⁴

Dithioketals are appealing starting points because they are readily obtained from ketones or from alkylation of dithioacetals.^{1,2} In one approach, diphenyl dithioketals have been oxidized to monosulfoxides and then thermolyzed to produce vinyl phenyl sulfides.^{2,5} A more straightforward route to a C=C-SAr unit focuses on direct elimination^{6a} of a thiophenol from a diaryl dithioketal by reagents such as mercuric triflate/Li₂CO₃ or copper(I) triflate.^{6b} For dithioacetal substrates, Cu(II) salts in the presence of tertiary amines have been used.^{6c} We now wish to report what appears to be a fairly general one-step procedure that converts dialkyl dithioketals as well as diaryl dithioketals to vinyl sulfides in good yields.

The method involves treatment of a dithioketal with diethylzinc and methylene iodide. These two chemicals are presumed to generate organometallic carbenoid precursors like $EtZnCH_2I$ and/or $Zn(CH_2I)_2$ probably akin to those involved in Simmons-Smith reactions.⁷ Fast capture of the "CH₂" carbenoid by a sulfur in the dithioketal is expected to produce a transient sulfonium ylide⁸ capable of undergoing a syn α ', β -elimination through a five-membered cyclic transition state (see equation).⁹ Similar α ', β -eliminations are well known for amine oxides, sulfoxides,



	CONVERS	SION OF 1	DITHIO	KETALS TO VINYL	SULFIDES ^{a,I}	A
PRE	PARATION OF SU	BSTRATES	REAC	TION WITH DIETHYLZIN	C-METHYLENE	IODIDE
	COMPOUND	M.P. YIELD (FROM C=0)	TEMP. TIME	PRODUCT	E-Z ISOMERS ^C RELATIVE %	TOTAL
-	SCH ₃	72-73°C 85 %	80°C 2 h	ScH3	1 a 55% 1 b 45%	%12
2	ASPh SPh	67-68°C ^d 85 %	70°C 1 h	HdS-	2a 73% 2b 27%	92%
3	⟨S S	81-82°C 89 %ei	25°C 4 h	Sch3	30^e 51 % 3b^e 49 %	67%
4	⟨s ⟨s ⟨s	107-107.5°C 9	25°C 2.5 h	Straight Sch3	4 a e,9,h	% 2 2
S	H ^{3C} XS H ^{3C} H	i 98 %	25°C 2 h	∕S	50	
9	\$ S	37-38°C 94 %	25°C 8 h	SCH3	6a ^h	70%

,

Footnotes to Table

- a. New compounds were characterized spectrally and by elemental analyses (see Experimental).
- b. All compounds are liquids at room temperature except where noted. Melting points are those of analytically pure samples.
- c. One isomer is E and the other is Z, but we don't know which is which.
- d. Reported earlier, mp 64.5-66°C but without elemental analyses (ref. 2).
- e. Its preparation and characterization are described in the Ph.D. dissertation of A.D. Rodriguez, The Johns Hopkins University, 1983.
- f. Nickon, A.; Rodriguez, A.D.; Shirhatti, V.; Ganguly, R. J. Org. Chem. in press.
- g. Nickon, A.; Rodriguez, A.D.; Ganguly, R.; Shirhatti, V. <u>Tetrahedron Lett</u>. 1984, <u>25</u>, 3555-3558. Full paper <u>J. Org. Chem</u>. 1985, <u>50</u>, in press.
- h. Only one geometric isomer was obtained. We do not know whether it is E or Z.
- Prepared from 1,3-dithiane (Corey, E.J.; Seebach, D. <u>Angew. Chem. Int. Ed. Engl.</u> 1965, <u>4</u>, 1075-1077).
- j. Yield of this volatile olefin not available because of losses during <u>in vacuo</u> evaporation of solvent. However, prior to workup, TLC showed complete conversion of starting material to this product.

and selenoxides, and for ylides derived from sulfonium, hydrazonium, and quaternary ammonium salts.⁹ We applied this modified Simmons-Smith type reagent¹⁰ to substrates representing six different structural classes; the conditions and results are collected in the adjoining Table.

The first compound (1) typifies a normal dialkyl dithioketal, and we prepared it readily from cyclododecanone. With Et_2Zn/CH_2I_2 , substrate 1 gave the corresponding vinyl methyl sulfide (71%) as a 55:45 mixture of E-Z isomers 1a and 1b. The expected by-product, CH_3SCH_3 , was not isolated but was evident from its distinctive odor. And, typically, a small amount of insoluble polymer formed but was readily separated.^{7,10} Because vinyl sulfides themselves can react with carbenoids to produce sulfur ylides, we routinely quenched our reactions with acetaldehyde prior to workup. This technique has been used by others to regenerate vinyl sulfides from their ylides (presumably through formation of propene oxide^{10,12}) and it improved our yields markedly.

The second substrate, a typical diaryl dithioketal (2) was made conventionally and gave the corresponding E-Z vinyl phenyl sulfides (2a + 2b) in 92% yield. In this case we also isolated the co-product methyl phenyl sulfide and identified it by ¹H NMR and TLC comparison with an authentic sample.

Substrate 3 illustrates a spirocyclic dithioketal, which affords a vinyl sulfide still chained to the SCH₃ unit. In this case the E-Z isomers (3a + 3b) were obtained in virtually equal proportions. The Et₂Zn/CH₂I₂ reaction was likewise successful with a spirocyclic dithioketal having an adjacent olefinic link (compound 4). At 25°C, this allylic-type precursor led to vinyl sulfide 4a with conjugated double bonds. Diene 4a (77% yield) was stereochemically homogeneous and, therefore, is entirely Z or E. Of special interest in connection with substrate 4 was the possibility that the transient ylide might have undergone competitive [2,3] signatropic rearrangement. Such competition was not observed at 25°C, but at higher temperature (70° and 110°C) products of [2,3] rearrangement accompanied the diene.¹³ Therefore, with allylic substrates like 4 temperature appears to be an important variable that influences yield.

We also examined 2-methyl-1,3-dithiane (5) as a substrate. The reaction gave the known 1-(ethenylthio)-3-(methylthio)-propane $(5a)^{14}$ as the only product and indicates that our method is applicable to dithioacetals as well as to dithioketals.

Our final test compound 1,4-oxathiaspiro[4.11]hexadecane (6) is a monothicketal and was included in our study because it differs functionally from the other substrates. The product was identified as vinyl ether 6a (70%), produced as a single geometric isomer. This result

demonstrates that the carbenoid generated <u>in situ</u> prefers to combine with sulfur (as expected) rather than with oxygen. This formation of an enol ether from a 1,3-oxathiolane (6) is specially noteworthy in view of recent findings by Nakayama and co-workers.¹⁵ They demonstrated that the action of benzyne on 1,3-oxathiolanes effects net cleavage to produce vinyl phenyl sulfides. Thus, from the standpoint of synthetic methodology the Et_2Zn/CH_2I_2 reagent and the benzyne reagent complement each other by allowing selective ways to produce either a vinyl ether or a vinyl sulfide from a 1,3-oxathiolane.

EXPERIMENTAL

General - Melting points are uncorrected and were determined in open Pyrex capillaries. Infrared (IR) spectra were obtained with a Perkin-Elmer Model 457A or Model 5998 spectrophotometer; polystyrene was the calibration standard. The letters s, m, w refer to strong, medium, and weak IR bands, respectively. H NMR refer to CDCl₃ solutions at 60 MHz on a Varian Model T-60; or at 80 MHz on a Varian Model CFT-20. UV were obtained on a Cary Model 219 double beam spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. THF and DMF refer to tetrahydrofuran and dimethylformamide, respectively.

1,1-Bis(methylthio)cyclododecanone (1). Cyclododecanone (6.42 g, 35.2 mmol) was dissolved in 3:1 glacial acetic acid-THF (80 mL) and the solution was cooled to 0°C. Methylmercaptan (Matheson Gas Products) was slowly bubbled through as freshly distilled BF₃-etherate (10 g, 70.4 mmol) was added. After 1.5 h at 0°C, the solution was poured into ice and was extracted with ether (3 × 80 mL). The organic phase was washed with water and with saturated aqueous NAHCO₃ and dried (Na₂SO₄). Evaporation left white crystals. Recrystallization from hot ethanol gave 7.55 g, 85%; mp 72-73°C. ¹H NMR (60 MHz) 6 2.0 (s, 6H), 1.9-1.2 (m, 22H). IR (CHCl₃) 2950, 2850, 1470, 1440 cm⁻¹. UV (hexane) λ 238, 214 nm. <u>Anal</u>. Calcd for C₁₄H₂₈S₂: C, 64.55; H, 10.83. Found: C, 64.73; H, 11.09.

1,1-Bis(phenylthio)cyclododecanone (2). Gaseous HCl was bubbled through a solution of cyclododecanone (4.0 g, 0.02 mol) in thiophenol (5.20 g, 0.047 mol) for 2-5 min, and the solution was stirred at 25°C for ca. 24 h. The mixture was dissolved in CH₂Cl₂ (70 mL) and washed with 5% aqueous NaOH (3×40 mL) and saturated aqueous sodium chloride (1×40 mL). The dried (Na₂SO₄) organic solution was concentrated <u>in vacuo</u> and the crude material was recrystallized from ethanol; off-white crystals (7.17 g, 85%); mp 67-68°C (lit. 64.5-66°C). ¹H NMR (60 MHz) s 7.6(m, 4H), 7.2 (m, 6H), 1.6-1.4 (m, 22H). IR (CHCl₃) 2950, 2850, 1580, 1470, 1440 cm⁻¹. <u>Anal</u>. Calcd for C₂₄H₃₂S₂: C, 74.94; H, 8.38. Found: C, 74.96; H, 8.57.

1,5-Dithiaspiro[5.11]heptadecane (3). A 0°C solution of cyclododecanone (3.0 g, 16.4 mmol) in 3:1 acetic acid-THF (40 mL) and 1,3-propanedithiol (1.8 g, 17 mmol) was treated with BF₃-etherate (4.3 g, 30 mmol) and stirred vigorously for I h. The temperature was increased to 25°C and stirring was continued for another 48 h, during which a white, thick slurry formed. The mixture was cooled to 0°C and the white solid was collected and rinsed repeatedly with cold THF and was recrystallized twice from EtOH; mp 81-82°C (4.01 g, 89.4%). IR (CCl₄) 2940 (s), 2860 (s), 2850 (s), 1470 (m), 1445 (m), 1345 (w), 1275 (w), 1240 (w), 915 (w) cm⁻¹. ¹H NMR (80 MHz) δ 2.8 (m, 4H, -SCH₂), 2.0 (m, 6H), 1.36 (broad s, 18H). Anal. Calcd for C₁₅H₂₈S₂: C, 66.11; H, 10.35. Found: C, 66.36; H, 10.55.

7-Methylene-1,5-dithiaspiro[5.11]heptadecane (4). For experimental procedure, see footnote "g" of the Table.

2-Methyl-1,3-dithiane (5). A stirred solution of 1,3-dithiane (4.0 g, 33 mmol) in dry THF (80 mL) at -30°C under argon was treated slowly (5-8 min) with 1.26 M n-butyllithium in hexane (26.6 mL). After 1.5 h at -30°C, the solution was brought to 0°C and iodomethane (5.11 g, 36 mmol) was added. After 10 h at 0°C, water was added and the mixture was worked up with ether. The derived GLC-pure liquid 5 (4.38 g, 98%) was used without further purification (see footnote "1" of the Table). ¹H NMR (60 MHz) δ 4.2 (q, 1H), 2.8 (m, 4H), 2.1 (m, 2H), 1.5 (d, 3H).

1,4-Oxathiaspiro[4.11]hexadecane (6). A mixture of cyclododecanone (4.0 g, 22 mmol), 2-mercaptoethanol (1.72 g, 22 mmol) and BF₃-etherate (6.54 g, 46 mmol) in a 3:1 mixture glacial acetic acid-THF (80 mL) was stirred at room temperature overnight for 12 h. The mixture was poured in ice-cold water and was extracted with ether. The organic phase was washed with water, 5% aqueous NaOH, water, and brine. Concentration of the dried solution (Na₂SO₄) left a colorless oil, which solidified after a few hours under refrigeration. Recrystallization from ethanol-water gave white crystals (5.06 g, 94.5%); mp 37-38°C. ¹H NMR (60 MHz) § 4.1 (t, 2H), 3.0 (t, 2H), 2.4-1.7 (m, 4H), 1.4 (m, 18H). IR (CHCl₃) 2925, 2850, 1440, 1050 cm⁻¹; UV (EtOH) λ 206 nm. Anal. Calcd for $C_{14}H_{26}OS$: C, 69.36; H, 10.81. Found: C, 69.59; H, 11.04.

1-(Methylthio)cyclododecene (E,Z) (1a and 1b). To a 25° C toluene solution of diethylzinc¹⁶ (1.6 mmol) in dry freshly distilled benzene (10 mL) was added quickly a solution of dithioketal 1 (0.30 g, 1.15 mmol) in dry benzene (10 mL). Diiodomethane (0.3 mL, 0.99 g, 3.72 mmol) was then added and the flask was lowered into a preheated oil bath (80°C). After 2 h the content

4446

was allowed to cool slowly to room temperature then was quenched with acetaldehyde (3 mL) and stirred at 25°C for 10-15 min. The mixture was poured into aqueous NH₄Cl and was extracted with benzene. The organic phase was washed with brine and was dried over Na₂SO₄. Evaporation first with a water aspirator and then under vacuum (to remove toluene and excess CH₂I₂) left a liquid residue which was triturated with pentane. After filtration of insoluble polymeric material and evaporation, an oily residue (171 mg, 71%) was obtained. Separation by chromatography on silica gel (hexane) gave isomer 1a (94.2 mg, 39.2%) as a colorless oil. ¹H NMR (60 MHz) & 5.6 (t, 1H), 2.3 (m, 4H), 2.1 (s, 3H), 1.7-1.2 (m, 16H). IR (neat) 2925, 2850, 1620, 1460, 1420 cm⁻¹. UV (EtOH) λ 249, 228, 206 nm. Anal. Calcd for C₁₃H₂₄S: C, 73.51; H, 11.39. Found: C, 73.85; H, 11.66. Further elution gave isomer 1b (76.4 mg, 31.8%) also as a colorless oil. ¹H NMR (60 MHz) & 2.95, 2850, 1620, 1460, 1420 cm⁻¹. UV (EtOH) λ 228 nm. Anal. Calcd for C₁₃H₂₄S: C, 73.51; H, 11.39. Found: C, 73.85; H, 11470, 1420 cm⁻¹. UV (EtOH) λ 228 nm. Anal. Calcd for C₁₃H₂₄S: C, 73.51; H, 11.39. Found: C, 73.69; H, 11.75.

1-(Phenylthio)cyclododecene (E,Z) (2a and 2b). To a solution of diethylzinc (1.02 mmol) in dry benzene (10 mL) under argon at room temperature was added a solution of dithioketal 2 (0.30 g, 0.78 mmol) in benzene (10 mL). Diiodomethane (0.665 g, 2.48 mmol) was added by syringe and the solution was immersed in an oil bath at 70°C. After 1 h the mixture was allowed to cool slowly to room temperature, was quenched with acetaldehyde (3 mL) and was stirred at 25°C for 10-15 min. The mixture was partitioned between benzene and aqueous NH₄Cl. The combined benzene phase was washed with brine and was dried over Na₂SO₄. Concentration at 30°C left a liquid. After precipitation of the polymer (with pentane) and filtration, the solvent was removed to leave a liquid, which was chromatographed on silica gel. The first product eluted was 2a (0.14 g, 66.5%); colorless liquid. ¹H NMR (60 MHz) & 7.1 (s, 5H), 6.0 (t, 1H), 2.4 (m, 4H), 1.4 (m, 16H). IR (neat) 3050, 2950, 2850, 1580, 1480, 1460, 1440 cm⁻¹. UV (EtOH) λ 265, 248, 205 nm. Anal. Calcd for $C_{18}H_{26}$ S: C, 78.78; H, 9.55. Found: C, 79.02; H, 9.78. The second isomer 2b (0.054 g, 25.4%) was also eluted as a colorless liquid. ¹H NMR (60 MHz) & 7.15 (s, 5H), 5.8 (t, 1H), 2.2 (m, 4H), 1.3 (m, 16H). IR (neat) 3075, 2950, 2850, 1580, 1470, 1440 cm⁻¹. UV (EtOH) λ 265, 248, 205 nm. Anal. Calcd for $C_{18}H_{26}$ S: C, 78.78; H, 9.55. Found: C, 79.18; H, 9.82. The third product eluted (19 mg, 20%) was a fetid liquid, which proved to be thioanisole by ¹H NMR and TLC comparisons with a commercial sample.

(3-Methylthio)propyl cyclododecenyl sulfide (E,Z) (3a and 3b). A solution of diethylzinc (2.86 mmol), spirodithioketal 3 (0.60 g, 2.2 mmol) and diiodomethane (1.18 g, 4.4 mmol) in dry benzene (10 mL) under argon was stirred at 25°C for 4 h. The stirred mixture was quenched with acetaldehyde (3 mL) and after 10 min was poured into saturated aqueous NH₄Cl (40 mL) and was worked up with benzene. After precipitation of polymer with petroleum ether as in previous runs, we obtained a GLC-pure liquid residue (0.420 g, 67%). Separation of the two isomers by chromatography on silica gel (40:1 petroleum ether-ether) gave the first olefin 3a (0.214 g, 34%) as a colorless oil. ¹H NMR (80 MHz) δ 5.5 (t, 1H), 2.9-2.15 (m, 8H), 2.05 (s, 3H), 1.8 (m, 2H), 1.3 (broad s, 16H). IR (neat) 2920, 2860, 1460, 1440, 1255, 1245 cm⁻¹. Anal. Calcd for C16H30S2: C, 67.06; H, 10.55. Found: C, 67.23; H, 10.61. Further elution gave the second isomer 3b (0.206 g, 33%) as a colorless oil. ¹H NMR (80 MHz) δ 5.9 (t, 1H), 2.9-2.15 (m, 8H), 2.9-2.15 (m, 8H), 2.05 (s, 3H), 1.8 (m, 2H), 1.3 (broad s, 16H). IR (neat) 2920, 2860, 1460, 1440, 1255, 1245 cm⁻¹. Anal. Calcd for C16H30S2: C, 67.06; H, 10.55. Found: C, 67.23; H, 10.61. Further elution gave the second isomer 3b (0.206 g, 33%) as a colorless oil. ¹H NMR (80 MHz) δ 5.9 (t, 1H), 2.9-2.15 (m, 8H), 2.05 (s, 3H), 1.8 (m, 2H), 1.3 (broad s, 16H). IR (neat) 2920, 2860, 1460, 1440, 1255, 1245 cm⁻¹. Anal. Calcd for C16H30S2: C, 67.07; H, 10.55. Found: C, 67.23; H, 10.56.

3-Methylene-2-[(3-methylthio)propyl]-cyclododecenyl sulfide (E or Z) (4a). A solution of diethylzinc (0.85 mmol), spirodithioketal 4 (0.20 g, 0.70 mmol) and diiodomethane (0.50 g, 1.86 mmol) in dry benzene (15 mL) under argon was stirred at 25°C for 2.5 h. The reaction was quenched with acetaldehyde (3 mL), was stirred for 15 min, was poured into saturated aqueous NH₄Cl solution (40 mL), and was extracted with ether (3 × 30 mL). The ether was processed as in other runs. The polymer-free 4a (0.16 g, 7%) was a colorless oil. ¹H NMR (80 MHz) δ 5.75 (t, 1H), 4.95 (m, 2H), 2.5 (m, 8H), 2.05 (s, 3H), 1.25 (broad s, 16H). IR (neat) 3070, 2920, 2860, 1620, 1465, 1445, 1260, 1250, 905 cm⁻¹. UV (EtOH) λ 260 nm. Anal. Calcd for $C_{17}H_{30}S_2$: C, 68.39; H, 10.13. Found: C, 68.59; H, 10.27.

1-(Ethenylthio)-3-(methylthio)-propane (5a). 2-Methyl-1,3-dithiane (5, 0.39 g, 2.9 mmol) in dry benzene (15 mL) was added to a solution of diethylzinc (3.76 mmol) in dry benzene (15 mL) under argon at 25°C. Diiodomethane (2.47 g, 9.2 mmol) was added, and the content was stirred for 2 h. The reaction was treated with acetaldehyde (3 mL) and stirred for another 10-15 min. TLC analysis at this point revealed complete conversion of the starting thioacetal into the product. The mixture was poured into aqueous NH₄Cl and was worked up with benzene. Removal of the solvent at 45°C in vacuo led to indvertent evaporation of most of the volatile product. The remainder was chromatographed on silica gel (4:1 hexane-benzene) to give (after careful handling) the pure 5a (22.1 mg, 5.3%) as a colorless liquid (STENCHI) ¹H NHR (60 MHz) δ 6.2 (m, 1H), 5.0 (m, 2H), 2.6 (m, 4H), 2.05 (s, 3H), 1.8 (m, 2H). IR (neat) 3100, 2920, 1580, 1430, 1260 cm⁻¹. UV (EtOH) λ 228, 205 nm. Compound 5a has been prepared before by other means.

(2-Methylthio)ethyl cyclododecenyl ether (E or Z) (6a). To a 25°C solution of diethylzinc (1.6 mmol) in dry benzene (10 mL) under argon was added a solution of spirooxathiolane 6 (0.30 g, 1.23 mmol) in dry benzene (15 mL) followed by diiodomethane (1.05 g, 3.9 mmol). After being stirred at 25°C for 8 h, the solution was quenched with acetaldehyde (3 mL), was stirred for 15 min, was poured into water, and was extracted with ether. Workup as described earlier gave the polymer-free oily product, which was passed quickly through a short column of silica gel (4:1 hexane-benzene). A total of 0.22 g (70%) of the pure liquid vinyl ether 6a was recovered. ¹NNR (60 MHz) δ 4.2 (t, 1H), 3.7 (t, 2H), 2.6 (t, 2H), 2.1 (m, 7H), 1.3 (m, 16H). IR (neat) 2950, 2850, 1660, 1470, 1440 cm⁻¹; UV (EtOH) λ 209 nm. Anal. Calcd for C₁₅H₂₈OS: C, 70.25; H, 11.00. Found: C, 70.51; H, 11.33.

Acknowledgements - This research was supported by the National Institutes of Health (GO1ESO2300) and by the National Science Foundation (CHE-81008022). A.D.R. held an NSF Minority Graduate Fellowship and a Vernon K. Krieble Fellowship.

REFERENCES AND FOOTNOTES

- 1. Organic Compounds of Sulphur, Selenium, and Tellurium, Vol. 1-5, The Chemical Society, Burlington House, London, 1970-79.
- 2. Trost, B. M.; Lavoie, A. C. J. Am. Chem. Soc. 1983, 105, 5075-5090; and references cited.
- (a) Kakimoto, M.; Yamamoto, T.; Okawara, M. <u>Tetrahedron Lett.</u> 1979, 623-624. (b) Akiyama, F. J. Chem. Soc., Chem. Commun. 1976, 208. (c) Akiyama, F. <u>Bull. Chem. Soc. Jpn</u>. 1977, <u>50</u>, 936-938.
- 930-938.
 4. For indirect routes to vinyl sulfides having specialized structures, see reference 2 and also: (a) Miller, R. D.; Hassig, R. Tetrahedron Lett. 1985, 26, 2395-2398. (b) Vermeer, P.; DeGraaf, C.; Meijer, J. Rec. Trav. Chim. 1974, 93, 24-25. (c) Naidu, M. S. R.; Peeran, S. G. Tetrahedron 1975, 31, 465-468. (d) Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. J. Chem. Soc., Chem. Commun. 1975, 248-249. (e) Roedig, A.; Zaby, G. Tetrahedron Lett. 1977, 1771-1772. (f) Carey, F. A.; Court, A. S. J. Org. Chem. 1972, 37, 939-943. (g) Gotthardt, H. Tetrahedron Lett. 1971, 2343-2344; 2345-2348. (h) Schaumann, E.; Walter, W. Chem. Ber. 1974, 107, 3562-3573. (i) Kumamoto, T.; Hosoi, K.; Mukaiyama, T. Bull. Chem. Soc. Jpn. 1968, 41, 2742-2745. (j) Trost, B. M.; Keeley, D. L. J. Am. Chem. Soc. 1976, 98, 248-250. (k) Jensen, L.; Thomsen, I.; Lawesson, S. O. Bull. Soc. Chim. Belges 1977, B6, 309-311. (l) Morin, L.; Paquer, D.; Smadja, S. Rec. Trav. Chim. 1976, 95, 179-182. (m) Verny, M.; Vessiere, R. Bull. Soc. Chim. Fr. 1970, 746-750. (n) Atavin, A. S.; Gusarova, N. K.; Amosova, S. V.; Troïfmov, B. A.; Kalabin, G. A. Zhur. Org. Khim. 1970, 288-2392. (o) Gusarova, N. K.; Trofimov, B. A.; Atavin, A. S.; Amosova, S. V.; Gusarov, A. V. Zhur. Org. Khim. 1971, 7, 1780-1783. (p) Prilezhaeva, E. N.; Vasilev, G. S.; Mikhelashvili, I. L.; Bogdanov, V. S. Zhur. Org. Khim. 1971, 7, 1349-1355. (q) Trofimov, B. A.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A. S.; Amosova, S. V.; Gusarova, N. K.; Atavin, A.
- (a) Trost. B. M.; Bridges, A. J. Org. Chem. 1975, 40, 2014-2016. (b) Balenovic, K.; Deljac, A. <u>Rec. Trav. Chim</u>. 1973, <u>92</u>, 117-122.
- (a) Cohen, T.; Mura, A. J.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. J. Org. <u>Chem</u>. 1976, 41, 3218-3219. (b) Cohen, T.; Herman, G.; Falk, J. R.; Mura, A. J. Jr. <u>J. Org.</u> <u>Chem</u>. 1975, 40, 812-813. (c) Olda, T.; Tanimoto, S.; Ikehira, H.; Okano, M. <u>Bull. Chem.</u> <u>Soc. Jpn</u>. 1983, <u>56</u>, 959-960.
- (a) Furukawa, J.; Kawabata, N.; Kitayama, M. Tetrahedron 1971, <u>27</u>, 1799-1806. (b) Furukawa, J.; Kawabata, N.; Nishimura, J. <u>Tetrahedron</u> 1968, <u>24</u>, 53-58.
- 8. For analogies, see a review by Ando, W. Acc. Chem. Res. 1977, 10, 179-185.
- 9. (a) Biellmann, J. F.; D'Orchymont, H.; Schmitt, J. L. J. Am. Chem. Soc. 1979, 101, 3283-3288. (b) Saunders, W. H., Bonadies, S. D.; Braunstein, M.; Borchardt, J. K.; Hargreaves, R. T. Tetrahedron 1977, 33, 1577-1580. (c) Borchardt, J. K.; Hargreaves, R.; Saunders, W. H. Tetrahedron Lett. 1972, 2307-2308.
- 10. The Et₂Zn/CH₂I₂ reagent has been used elegantly to convert allyl phenyl thioethers to homoallyl phenyl thioethers, presumably via transient sulfur ylides that rearrange by a [2,3] sigmatropic path. Cohen, T.; Kosarych, A. <u>Tetrahedron Lett</u>. 1982, <u>23</u>, 3019-3022.
- 11. All E-Z isomers were separated by column chromatography and were individually characterized.
- 12. Trost, B. M.; Melvin, L. S. Jr. "Sulfur Ylides"; Academic Press:New York, 1975, p. 52.
- 13. In these cases, the diene component 4a consisted of an E-Z mixture. The details of these high temperature runs are described elsewhere (see footnote "g" of the Table).
- 14. (a) Hase, T. A.; Kivikari, R. <u>Synth. Commun.</u> 1979, 9, 107-112. (b) Ponticello, I. S.; Perry, E. J.; Tuites, R. C. U.S. Patent 3,860,428 [Chem. Abstr. 1975, <u>83</u>, 18931c].
- Nakayama, J.; Sugiura, H.; Shiotsuki, A.; Hoshino, M. <u>Tetrahedron Lett</u>. 1985, <u>26</u>, 2195-2198.
- 16. Diethylzinc was obtained from Aldrich Chemical Co. as a 15% solution (1.6 M) in toluene and was always used as such.

4448