Reactions of Sulfoxides with Magnesium Amides. Transformation of Sulfoxides into Sulfides, Dithioacetals, and Vinyl Sulfides

Kazuhiro Kobayashi,* Masataka Kawakita, Kouichi Yokota, Tohru Mannami, Koji Yamamoto, Osamu Morikawa, and Hisatoshi Konishi

Department of Materials Science, Faculty of Engineering, Tottori University, Koyama-minami, Tottori 680

(Received October 27, 1994)

The reactions of sulfoxides with magnesium amides generated in situ from the reaction of ethylmagnesium bromide and secondary amines, such as diisopropylamine (DIPA) or 2,2,6,6-tetramethylpiperidine (TMP) in diethyl ether, were examined. Diaryl sulfoxides were heated with the diisopropylaminomagnesium reagent in diethyl ether to give the corresponding diaryl sulfides in 42—52% yields. Sulfoxides bearing hydrogens at the α-positon only ($RSOCH_2R^1$) reacted with the tetramethylpiperidinomagnesium reagent at room temperature to produce the corresponding dithioacetals ($RSCHR^1SR$) in 47—86% yields. The treatment of sulfoxides bearing hydrogens both at the α- and β-positions ($RSOCHR^1CHR^2R^3$) with the magnesium amides at room temperature afforded the corresponding vinyl sulfides ($RSCR^1{=}CR^2R^3$) in 52—72% yields accompanying 2.3—27% yields of the corresponding dithioacetals. The pathways leading to the products involving the formation of the sulfur-stabilized carbonium ion intermediates are discussed.

The deoxygenation of sulfoxides is of importance from a synthetic viewpoint in organic chemistry. A survey of the literature has revealed that a variety of reducing agents have been employed for the transformation of sulfoxides into the corresponding sulfides.[1] We examined the reactions of various sulfoxides **1**, **3**, and **9** with magnesium amides,[2] generated in situ by the treatment of ethylmagnesium bromide with secondary amines, such as diisopropylamine (DIPA) or 2,2,6,6-tetramethylpiperidine (TMP), and found that the reactions give the corresponding sulfides **2**, dithioacetals **4**, and(or) vinyl sulfides **10**, depending on the structure of the starting sulfoxides. In the present publication we wish to report on the details of these reactions.[3]

Diaryl sulfoxides **1** are reduced with the diisopropylaminomagnesium reagent to give the corresponding diaryl sulfides **2**, indicating that the reagent is a new reducing agent for the transformation of sulfoxides into sulfides.

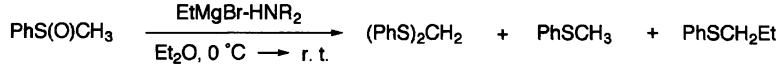
Sulfoxides bearing α-hydrogens **3** react with the magnesium amides to afford the corresponding dithioacetals **4**. Dithioacetals have been utilized in C–C bond formations,[4] and generally prepared by the acid-catalyzed condensation of carbonyl compounds with thiols.[5] The reaction offers a new entry to this class of compounds.

The reaction of sulfoxides bearing both of α- and β-hydrogens **9** with the reagents affords the corresponding vinyl sulfides **10**. The reaction provides an efficient method for the preparation of vinyl sulfides, which are convenient intermediates in organic synthesis.[6] There have been reported a number of methods for the preparation of these derivatives: for instance, 1) condensation of carbonyl compounds with thiols,[7] 2) interaction of α-sulfenyl carbanions with carbonyl compounds,[8] 3) the addition of thiols to acetylenes,[9] 4) transition metal-catalyzed coupling between alkenyl halides and thiolates and the related reactions,[10] 5) elimination of thiols from dithioacetals,[11] and so on.[12] Miller and McKean have also reported on the eliminative deoxygenation of sulfoxides bearing both α- and β-hydrogens to vinyl sulfides with trimethylsilyl iodide.[13] The magnesium amides are illustrated to be useful reagents for the eliminative deoxygenation of sulfoxides.

Results and Discussion

Reduction of Diaryl Sulfoxides 1 with the Magnesium Amides. Sulfoxides **1a** and **b** were treated with the diisopropylaminomagnesium reagent to give the corresponding sulfides **2a** and **b** in moderate yields (Eq. 1). For example, a mixture of **1a** (1 mmol) and the magnesium amide, generated from ethylmagnesium bromide (2 mmol) and DIPA (4 mmol) in 10 ml of diethyl ether at 0 °C for 1 h, was heated under reflux for 6 h. After the usual work-up of the resulting reaction mixture, purification of the crude product by preparative TLC on silica gel gave **2a** in 42% yield. Similarly, **1b** was converted to **2b** in 54% yield. The reduction of **1** with the 2,2,6,6-tetramethylpiperidinomagnesium reagent was very sluggish, and

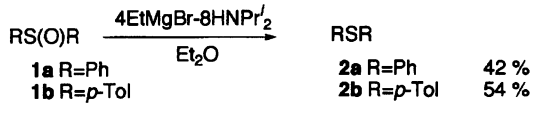
Table 1. Reactions of Methyl Phenyl Sulfoxide (**3a**) with Magnesium Amides Generated from Various Combinations of Ethylmagnesium Bromide and Secondary Amines



Entry	EtMgBr equiv	HNR_2	equiv	Yield[a]/% 4a	6	7
1	1	TMP	1	5	4	8
2	2	TMP	2	19	5	31
3	2	TMP	4	47	2	0
4	2	DIPA	4	40	3	0
5	4	TMP	8	86	0	0

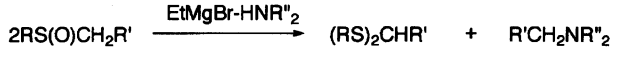
a) Isolated yields determined by preparative TLC on SiO_2.

the starting compound was recovered almost quantitatively in each case.



(1)

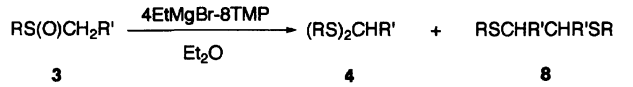
Formation of Dithioacetals 4 by Treatment of Sulfoxides Bearing α-Hydrogens 3 with the Magnesium Amides. It has been found that sulfoxides **3** react with the magnesium amides to afford dithioacetals **4** in moderate to good yields (Eq. 2). Methyl phenyl sulfoxide (**3a**) was chosen as a model substrate, and reactions of **3a** with magnesium amides, generated from various ratios of ethylmagnesium bromide to secondary amines, such as TMP or DIPA, were initially examined (Table 1). The magnesium amides were prepared by the treatment of ethylmagnesium bromide with DIPA, as mentioned above, or TMP at reflux for 5 h in diethyl ether. All reactions of **3a** and magnesium amides were carried out at room temperature. As can be seen from Table 1, phenyl methyl sulfide (**6**) was obtained by using 1 or 2 equiv of ethylmagnesium bromide, and unchanged sulfoxide was recovered (Entries 1, 2, 3 and 4). Phenyl propyl sulfide (**7**) was formed by the 1:1 uses of ethylmagnesium bromide and TMP (Entries 1 and 2). The use of 4 equiv of ethylmagnesium bromide and 8 equiv of TMP was found to be most effective for the reaction, and dithioacetal **4a** was obtained in 86% yield without any detectable formation of **6** and **7** and the recovery of unreacted sulfoxide (Entry 5).



(2)

Next, under the optimum conditions described above, various sulfoxides **3** was successfully employed in the formation of dithioacetals **4** in isolating yields ranging from 47 to 86%, as listed in Table 2. Aliphatic sulfoxides, such as dimethyl sulfoxide (**3d**) and *t*-butyl methyl sulfoxide (**3e**), worked well to give the corresponding dithioacetals **4d** and **4e** in good yields (Entries 4 and 5, respectively). The conversion of dibenzyl sulfoxide (**3f**) to dithioacetal **4f** was accompanied by the formation of 1,2-bis(benzylthio)-1,2-diphenylethane (**8**) (Entry 6).

Table 2. Thioacetals **4** from Sulfoxides **3**



Entry	3 R	R'		Yield/%[a] 4	8
1	Ph	H	(**3a**)	86 (**4a**)	—
2	*p*-ClPh	H	(**3b**)	68 (**4b**)	—
3	*p*-Tol	H	(**3c**)	47 (**4c**)	—
4	Me	H	(**3d**)	68 (**4d**)	—
5	*t*-Bu	H	(**3e**)	63 (**4e**)	—
6	Bn	Ph	(**3f**)	71 (**4f**)	15

a) Isolated yields by preparative TLC on SiO_2 or distillation.

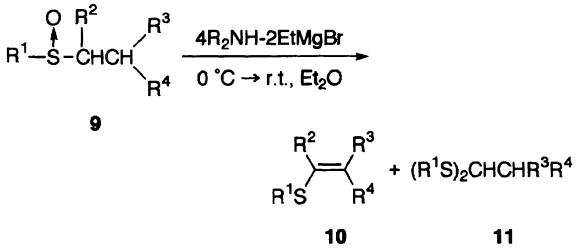
Eliminative Deoxygenation of Sulfoxides Bearing both α- and β-Hydrogens 9 Yielding Vinyl Sulfides 10. Sulfoxides **9** have proven to give vinyl sulfides **10** upon treatment with the magnesium amides (Eq. 3). The results are summarized in Table 3. The dehydration reactions of **9a**, **b**, **c**, **d**, and **e** were carried out using TMP as a secondary amine, affording **10a**, **b**, **c**, **d**, and **e** (53—72%) together with the corresponding dithioacetals **11a**, **b**, **c**, **d**, and **e** (2.3—27%) (Entries 1, 2, 3, 4, and 5). The proper choice of a secondary amine was important in these reactions. The transformation of **9a**, **b**, **c**, **d**, and **e** with DIPA in the place of TMP proved not to be effective. Considerably diminished yields of **10a b**, **c**, **d**, and **e** were realized. On the other hand, the reactions of **9f** and **g** were effected with DIPA to give **10f** and **g** in 65 and 71% yields, respectively, without any detectable formation of the corresponding dithioacetals (Entries 6 and 7). The dehydration of an aliphatic sulfoxide could be performed using TMP (Entry 8). The *E*/*Z* ratios of **10c**, **f**, and **g**

Table 3. Formation of Vinyl Sulfides **10** and Dithioacetals **11** by the Treatment of Sulfoxides **9** with Magnesium Amides

Entry	9					R_2NH	**10** (Yield/%)[a]		**11** (Yield/%)[a]	
	R^1	R^2	R^3	R^4						
1	Ph	H	H	H	(**9a**)	TMP	**10a**[b]	(72)	**11a**	(10)
2	*p*-Tol	H	H	H	(**9b**)	TMP	**10b**	(62)	**11b**	(17)
3	Ph	H	Me	H	(**9c**)	TMP	**10c**[c]	(59)	**11c**	(15)
4	Ph	H	Me	Me	(**9d**)	TMP	**10d**	(53)	**11d**	(27)
5	Ph	H	Ph	H	(**9e**)	TMP	**10e**	(59)	**11e**	(2.3)
6	Ph	Me	H	H	(**9f**)	DIPA	**10f**	(71)	—	
7	Ph	Ph	H	H	(**9g**)	DIPA	**10g**	(65)	—	
8	Bu	H	Et	H	(**9h**)	TMP	**10h**[d]	(55)	—	

a) Isolated yields. b) A mixture of stereoisomers (E: Z=1 : 1). c) A mixture of stereoisomers (E: Z=8 : 5). d) A mixture of stereoisomers (E: Z=1 : 1).

were confirmed by ^{1}H NMR spectra.



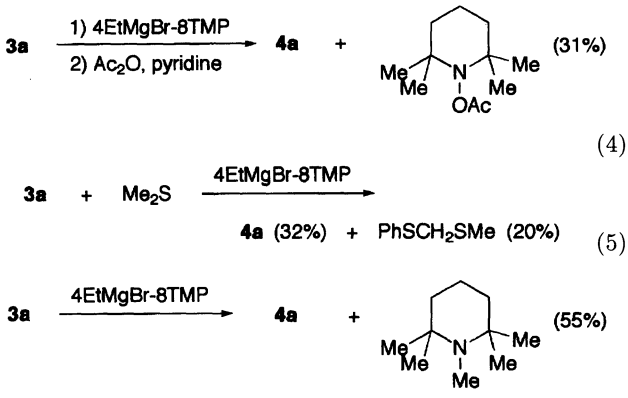
9 **10** **11** (3)

Probable Pathways Leading to the Products.[14] The probable mechanism for the reduction of sulfoxide **1** to sulfide **2** is outlined in Scheme 1. First, the addition of the magnesium amide **12** to **1** generates the tetracovalent sulfur intermediate **13**.[14b] Disproportionation of **13** gives rise to **2** and a hydroxylamine.

The pathway shown in Scheme 2 may be assumed for the transformation of sulfoxides **3** into dithioacetals **4**. Deprotonation of α-hydrogen of **3** by **12** generates the ylide **14**,[14c] which then gives the stabilized carbonium ion **15**. A preferential attack of the sulfide **16**, produced by the reduction of **3** (as mentioned above) to **15** gives the sulfonium ion intermediate **17**. Phenyl propyl sulfide (**7**) aries from a combination of **15** (R=Ph, R′=H) and an excess of ethylmagnesium bromide. Compound **8** results from a reaction of **15** (R=Bn, R′=Ph) with **14** (R=Bn, R′=Ph) followed by a reduction of the resulting intermediate **18**; the formation of **8** is attributable to the stability of **14** (R=Bn, R′=Ph). The addition of the amide to **15** does not proceed. Most probably, this is due to a steric hindrance of the amide base. The sulfonium ion **17** is cloven by an attack of the amide to produce **4**.[15]

Scheme 3 outlines a reaction path for the formation of vinyl sulfides **10** from sulfoxides **9**. This reaction is also considered to proceed through the stabilized cationic intermediate **19**, which is deprotonated to afford **10**.

The disproportionation process in the reduction of sulfoxides to sulfides has been verified by the isolation of rather unstable 1-hydroxy-2,2,6,6-tetramethylpiperidine as its *O*-acetylated form in the reaction of **3a** with the tetramethylpiperidinomagnesium reagent followed by a treatment with acetic anhydride (Eq. 4). The participation of **16** in the reaction pathway has been confirmed by the finding that the reaction of **3a** with the magnesium amide in the presence of dimethyl sulfide affords methylthio(phenylthio)methane (Eq. 5). Moreover, the isolation of 1,2,2,6,6-pentamethylpiperidine (**5**: R′=H, NR''_2=2,2,6,6-tetramethylpiperidino) in the reaction of **3a** with the magnesium amide gives further support to our mechanism (Eq. 6).



(4)

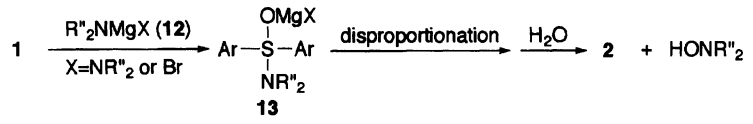
(5)

(6)

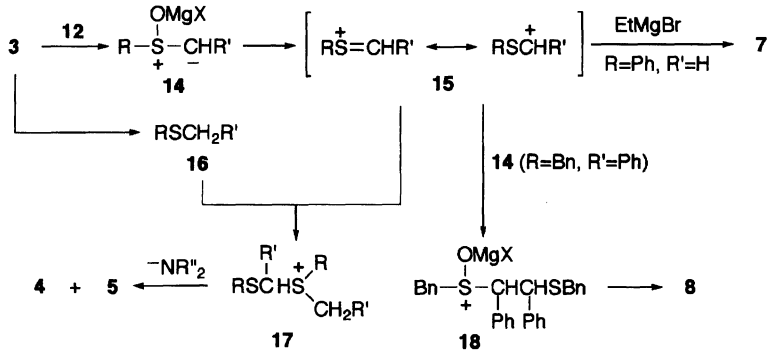
Experimental

General. The mps were recorded with a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were determined with a Perkin–Elmer 1600 Series FT IR spectrometer. The ^{1}H NMR spectra were determined using $SiMe_4$ as an internal reference with either a Hitachi R-90 FT NMR spectrometer operating at 90 MHz or a JEOL JNM-GX270 NMR spectrometer operating at 270 MHz. High- and low-resolution mass spectra were recorded with a JEOL JMS-DX 303 spectrometer. Column chromatography was carried out on Merck Kieselgel 60 F_{254}. TLC was carried out on a Merck Kieselgel 60 PF_{254}. All of the solvents used were dried over appropriate drying agents and distilled under argon prior to use. All of the reactions were carried out under argon.

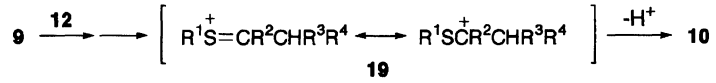
Starting Materials. Sulfoxides **1a**, **b**, **3a**, **d**, and **f**



Scheme 1.



Scheme 2.



Scheme 3.

were commercially available. Sulfoxides **3b**,[16] **c**,[17] and **e**[18] were prepared by the $NaIO_4$ oxidation of the corresponding sulfides obtained commercially. Sulfoxides **9a**,[19] **b**,[20] **c**,[21] **d**,[22] **e**,[23] **f**,[22] and **g**[14f] were prepared by the standard method (alkylation of the corresponding sodium thiolates followed by the $NaIO_4$ oxidation of the resulting sulfides).

Diphenyl Sulfide (2a). To a turbid solution of magnesium amide, which was generated by a treatment of EtMgBr (2.0 mmol) with diisopropylamine (0.41 g, 4.0 mmol) in Et_2O (6 ml) at 0 °C for 1 h, was added a solution of diphenyl sulfoxide (**1a**) (0.10 g, 0.50 mmol). The resulting mixture was refluxed for 6 h. After the resulting mixture was allowed to cool to room temperature, it was quenched by adding aq NH_4Cl and extracted with Et_2O. The extract was washed with brine, dried over anhyd $MgSO_4$, and evaporated. The residue was subjected to purification by preparative TLC (3 : 1 hexane–EtOAc) to afford **2a** (39 mg, 42%).

Bis(4-methylphenyl) Sulfide (2b): Mp 55—57 °C (EtOH) (lit,[24] 56—57 °C). This compound was obtained from bis(4-methylphenyl) sulfoxide (**1b**) in 54% yield in a similar manner as above.

Reaction of Methyl Phenyl Sulfoxide (3a) with Magnesium Amides Generated from Various Combinations of EtMgBr and Secondary Amines. Methyl phenyl sulfoxide (**3a**) (0.14 g, 1.0 mmol) was added dropwise to a turbid solution of magnesium amides generated from various combinations of EtMgBr and secondary amines, such as TMP (reflux, 5 h) or DIPA (0 °C, 1 h) in Et_2O (12 mL), at 0 °C. After the resulting mixture had been stirred overnight at room temperature, it was quenched with aq NH_4Cl and extracted with Et_2O. The extract was washed with brine and dried over anhyd $MgSO_4$. Upon evaporation of the dried extract a yellow oil remained, which was purified by preparative TLC (EtOAc–hexane = 1 : 10) to afford products **4a**, **6** and (or) **7** in the yields listed in Table 1.

Bis(phenylthio)methane (4a): Identified by a direct comparison with an authentic sample obtained commercially.

Methyl Phenyl Sulfide (6): Identified by a direct comparison with an authentic sample obtained commercially.

Phenyl Propyl Sulfide (7): Identified by a comparison of its ^1H NMR spectrum with that reported by Kremer and Helquist.[25]

Reactions of Sulfoxides 3 with the Magnesium Amide Generated from 4 equiv of EtMgBr and 8 equiv of TMP. Following the procedure described above, products **4b**, **c**, **d**, **e**, **f**, and **8** were obtained. The spectral and/or analytical data of these compounds are as follows.

Bis(4-chlorophenylthio)methane (4b):[26] R_f 0.52 (1 : 10 EtOAc–hexane); IR (neat) 1476, 1093, 1012, and 814 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ = 4.27 (2H, s) and 7.31 (8H, s); MS *m/z* (%) 302 (11), 300 (M^+, 15), and 157 (100).

Bis(4-methylphenylthio)methane (4c):[26] Identified by a comparison of its ^1H NMR spectrum with that reported by Kakimoto, Seri, and Imai.[5b]

Bis(methylthio)methane (4d): Identified by a direct comparison with an authentic sample obtained commercially.

Bis(*t*-buthylthio)methane (4e):[27] Identified by a comparison of its ^1H NMR spectrum with that reported by Bannister.[27b]

Phenyl[bis(phenylthio)]methane (4f): Mp 59—60 °C (hexane) (lit,[28] 61 °C).

1,2-Bis(benzylthio)-1,2-diphenylethane (8): A mixture of diastereomers (ca. 1 : 1) R_f 0.44 (EtOAc–hexane = 1 : 10); IR (neat) 1492, 1452, 714, and 697 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ = 3.13 (1H, d, J = 16.9 Hz), 3.31 (1H, d, J = 13.1 Hz), 3.33 (1H, d, J = 16.9 Hz), 3.48 (1H, d, J = 13.1 Hz), 3.97 (1H, s), 4.07 (1H, s), and 6.9—7.3 (20H, m); MS *m/z* (%) 426 (M^+, 0.68), 213 (80), and 91 (100). Found: *m/z* 426.1477. Calcd for $C_{28}H_{26}S_2$: M, 426.1476.

Isolation of 1- Acetoxy- 2, 2, 6, 6- tetramethylpiperidine in the Reaction of Methyl Phenyl Sulfoxide (3a) with the Magnesium Amide Generated from EtMgBr and TMP Followed by Treatment with Acetic Anhydride. A reaction mixture of **3a** (1 mmol) with the magnesium amide generated from EtMgBr (4 mmol) and TMP (8 mmol) was worked up as usual. After evaporation of the dried Et_2O solution, pyridine (1.5 ml) and acetic anhydride (1.1 ml) were added to the residue at 0 °C. The resulting mixture was stirred overnight at room temperature and then diluted with Et_2O. The Et_2O solution was successively washed with water, 0.1% aq HCl, and sat. $NaHCO_3$, dried over anhyd $MgSO_4$, and evaporated. Dry-column chromatography (1 : 3 EtOAc–hexane) of the residue gave a crude product (78 mg, R_f 0.5—0.7), which was recrystallized from light petroleum to give pure 1-acetoxy-2,2,6,6-tetramethylpiperidine (31 mg, 31%): Mp 63—65 °C (lit,[29] 63.5—65 °C).

Reaction of 3a with the Magnesium Amide in the Presence of Dimethyl Sulfide. To a stirred solution of the magnesium amide generated from 4 mmol of EtMgBr and 8 mmol of TMP was added successively **3a** (0.14 g, 1.0 mmol) and dimethyl sulfide (31 mg, 0.5 mmol) at 0 °C. The reaction mixture was stirred overnight and worked up in a similar manner as mentioned above. Purification of the crude product by preparative TLC gave **4a** (37 mg, 32%) and methylthio(phenylthio)methane[30] (34 mg, 20%): R_f 0.18 (EtOAc–hexane=1 : 10); IR (neat) 1583, 1480, 1438, 1200, 1088, 1068, 1025, 738, and 689 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ=2.17 (3H, s), 3.91 (2H, s), and 7.05—7.45 (5H, m).

Isolation of 1,2,2,6,6-Pentamethylpiperidine in the Reaction of 3a with the Magnesium Amide. The resulting mixture of the reaction of **3a** (1 mmol) and the tetramethylpiperidinomagnesium reagent was filtered, and the filtrate was extracted with 10% aq HCl. The aqueous extract was made alkaline by adding 10% aq NaOH and extracted with Et_2O. Kugelrohr distillation (bath temp; 120 °C/267 Pa) of the dried Et_2O solution gave a mixture of 1,2,2,6,6-pentamethylpiperidine and TMP (ca. 1 : 5, 0.24 g; the former, 43 mg, 55%), which were identified by a direct comparison with authentic samples obtained commercially.

Phenyl Vinyl Sulfide (10a) and 1,1-Bis(phenylthio)ethane (11a). Typical Procedure for the Reaction of Sulfoxide 9 with Magnesium Amides. A solution of EtMgBr (1.3 mmol) and TMP (0.29 g, 2.6 mmol) in Et_2O (4 ml) was refluxed for 5 h. To the turbid mixture was added ethyl phenyl sulfoxide (**9a**) (0.10 g, 0.65 mmol) at room temperature under stirring; the resultant mixture was stirred for an additional 3 h at room temperature. It was then quenched by adding aq NH_4Cl, and the organic phase was separated. After the aqueous phase had been extracted with diethyl ether, the combined extract was washed with brine, dried over anhyd $MgSO_4$, and evaporated to give a residue, which was purified by preparative TLC (1 : 10 EtOAc–hexane). The isolated products were **10a** (75 mg, 72%) and **11a**[31] (8.0 mg, 10%).

The reactions of **9b**, **c**, **d**, **e**, and **h** were conducted under the above-mentioned conditions. The reactions **9f** and **g** were carried out using the magnesium amide generated from EtMgBr and DIPA in place of TMP.

4-Methylphenyl Vinyl Sulfide (10b).[20] The spectral data (IR and ^1H NMR) of this product were identical with those reported by Magnus et al.[12f]

1,1-Bis[(4-methylphenyl)thio]ethane (11b): R_f 0.41; IR (neat) 1492, 1443, 1178, 1091, 1046, 1018 and 809 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.48 (3H, d, J=7.0 Hz 2-H), 2.26 (6H, s, ArMe), 4.34 (1H, q, J=7.0 Hz, 1-H), 7.03 (4H, d, J=8.1 Hz, ArH), and 7.30 (4H, d, J=8.1 Hz, ArH); MS m/z (%) 274 (M^+, 10) 246 (18), and 151 (100). Found: m/z 274.0875. Calcd for $C_{16}H_{18}S_2$: M, 274.0851.

Phenyl (*E*)- and (*Z*)-1-Propenyl Sulfide (10c):[32] (ca. 1 : 1); R_f 0.68; IR (neat) 1615, 1586, 1480, 1439, 1091, 1025, 738, and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ=1.83 and 1.84 (3H, 2d J=6.6 Hz each, Me), 5.7—6.3 (2H, m, vinylic H), and 7.1—7.35 (5H, m, ArH).

1,1-Bis(phenylthio)propane (11c):[33] The spectral data (IR and ^1H NMR) of this product were identical with those reported by Blatcher and Warren.[33b]

2-Methyl-1-propenyl Phenyl Sulfide (10d): The spectral data (IR and ^1H NMR) of this product were identical with those reported by Carey and Court.[8]

2-Methyl-1,1-bis(phenylthio)propane (11d): The spectral data (IR and ^1H NMR) of this product were identical with those reported by Blatcher and Warren.[33b]

Phenyl (*E*)- and (*Z*)- 2- Phenylethenyl Sulfide (10e):[35] (ca. 8 : 5) The spectral data (IR and ^1H NMR) of this product were identical with those reported by Ogawa, Hayami, and Suzuki.[35b]

2-Phenyl-1,1-bis(phenylthio)ethane (11e):[33] The spectral data (IR and ^1H NMR) of this product were identical with those reported by Blatcher and Warren.[33b]

1-Methylethenyl Phenyl Sulfide (10f):[34] The spectral data (IR and ^1H NMR) of this product were identical with those reported by Groen et al.[32a]

Phenyl 1-Phenylethenyl Sulfide (10g):[33a] The spectra data (IR and ^1H NMR) of this product were identical with those reported by Deljac et al.[33a]

(*E*)- and (*Z*)-1-Butenyl Butyl Sulfide (10h):[13] (ca. 1 : 1); R_f 0.58 (hexane); IR (neat) 1607, 1463, 1378, 1298, 1274, 940, 744, and 668 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ=0.92 [3H, t, J=7.3 Hz, $(CH_2)_3C\underline{H}_3$], 1.00 (3H, J=6.6 Hz, $=CHCH_2C\underline{H}_3$), 1.35—1.45 [2H, m, $-(CH_2)_2C\underline{H}_2CH_3$], 1.55—1.65 (2H, m, $CH_3C\underline{H}_2C_2H_5$), 2.05—2.15 (2H, m, $=CHC\underline{H}_2CH_3$), 2.6—2.7 (2H, m, SCH_2), 5.52 (0.5H, dt, J=9.2 and 6.9 Hz, SCH=C$\underline{H}$ of *Z* form), 5.65 (0.5H, dt J=15.2 and 6.3 Hz, SCH=C$\underline{H}$ of *E* form), and 5.85—5.95 (1H, m, SC$\underline{H}$=CH).

References

1) For reviews: H. Togo, M. Mikolajczyk, and S. Oae, *Org. Prep. Proced. Int.*, **16**, 171 (1984); M. Madesclaire, *Tetrahedron*, **44**, 6537 (1988); see also: Y. Guindon, J. K. Atkinson, and H. E. Morton, *J. Org. Chem.*, **49**, 4538 (1984); R. A. Amos, *J. Org. Chem.*, **50**, 1311 (1985); H. Suzuki, H. Manabe, R. Enokiya, and Y. Hanazaki, *Chem. Lett.*, **1986**, 1339; Y. Handa, J. Inanaga, and M. Yamaguchi, *J. Chem. Soc., Chem. Commun.*, **1989**, 298; H. Bartsch and T. Ercker, *Tetrahedron Lett.*, **33**, 191 (1992); F. Mohanazadeh, A. R. Momeni, and Y. Ranjbat, *Tetrahedron Lett.*, **35**, 6127 (1994), and references cited therein.

2) For recent synthetic reactions using magnesium amides: K. Kobayashi and H. Suginome, *Bull. Chem. Soc.*

Jpn., **59**, 2635 (1986); T. Hiyama, K. Kobayashi, and K. Nishide, *Bull. Chem. Soc. Jpn.*, **60**, 2127 (1987); R. Sanchez and W. Scott, *Tetrahedron Lett.*, **29**, 139 (1988); M. C. Carreno, J. L. Garcia Ruano, C. Pedregal, and A. Rubio, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1335; R. Sanchez, G. Vest, and W. Scott, *J. Org. Chem.*, **54**, 4026 (1989); R. E. Eaton, C.-H. Lee, and Y. Xion, *J. Am. Chem. Soc.*, **111**, 8016 (1989); K. Kobayashi, Y. Kanno, S. Seko, and H. Suginome, *J. Chem. Soc., Chem. Commun.*, **1992**, 780.

3) Preliminary communication: K. Kobayashi, M. Kawakita, T. Mannami, O. Morikawa, and H. Konishi, *Chem. Lett.*, **1994**, 1551.

4) For recent reports: M. Oshima, M. Murakami, and T. Mukaiyama, *Chem. Lett.*, **1985**, 1871; I. Mori, P. A. Bartlett, and C. H. Heathcock, *J. Am. Chem. Soc.*, **109**, 7199 (1987); K. Saigo, Y. Hashimoto, N. Kihara, K. Hara, and M. Hasegawa, *Chem. Lett.*, **1990**, 1097.

5) a) T. W. Greene, "Protective Groups in Organic Synthesis," John Willey, New York (1974), pp. 20, 60, 145, 182, 192, and 260; see also: b) M. Kakimoto, T. Seri, and Y. Imai, *Synthesis*, **1987**, 164, and references cite therein.

6) K. Oshima, K. Shimoji, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **95**, 2695 (1973); R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, **1978**, 821; H. Okamura, M. Miura, and H. Takei, *Tetrahedron Lett.*, **1979**, 43; M. Kakimoto, T. Yamamoto, and M. Okawara, *Tetrahedron Lett.*, **1979**, 623; B. M. Trost and Y. Tanigawa, *J. Am. Chem. Soc.*, **101**, 4743 (1979); A. Matsumoto, K. Suda, and C. Yijima, *J. Chem. Soc., Chem. Commun.*, **1981**, 263; V. Fiandanese, G. Marchese, F. Naso, and L. Ronzini, *J. Chem. Soc., Perkin. Trans. 1*, **1985**, 1115.

7) E. Campaign and J. R. Leal, *J. Am. Chem. Soc.*, **76**, 1272 (1954); T. Mukaiyama and K. Saigo, *Chem. Lett.*, **1973**, 479; B. M. Trost and A. C. Lavoie, *J. Am. Chem. Soc.*, **105**, 5075 (1983), and references cited therein.

8) a) F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 939 (1972); b) J. I. Grayson and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 2263; c) B. M. Trost, M. J. Crimmin, and D. Butler, *J. Org. Chem.*, **43**, 4549 (1978); d) K. Ogura, K. Arai, and G. Takahashi, *Bull. Chem. Soc. Jpn.*, **55**, 3669 (1982); e) K. Takai, Y. Kataoka, T. Okazoe, and K. Utimoto, *Tetrahedron Lett.*, **28**, 1443 (1987).

9) Y. Ichinose, K. Wakamatsu, K. Nozaki, J.-L. Birbaum, K. Oshima, and K. Utimoto, *Chem. Lett.*, **1987**, 1647; H. Kuniyasu, A. Ogawa, K. Sato, I. Ryu, N. Kambe, and N. Sonoda, *J. Am. Chem. Soc.*, **114**, 5902 (1992); I. D. Gridnev, N. Miyaura, and A. Suzuki, *J. Org. Chem.*, **58**, 5354 (1993), and references cited therein.

10) a) G. H. Posner and P.-W. Tang, *J. Org. Chem.*, **43**, 4131 (1978); b) S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, *J. Org. Chem.*, **44**, 2408 (1979); c) M. Hoshi, Y. Masuda, and A. Arase, *J. Chem. Soc., Chem. Commun.*, **1985**, 1068; d) H. J. Cristau, B. Chabaud, R. Labaudinere, and H. Christol, *J. Org. Chem.*, **51**, 875 (1986); e) Y. Hoshino, T. Ishiyama, N. Miyaura, and A. Suzuki, *Tetrahedron Lett.*, **29**, 3983 (1988); f) T. Yoshimura, E. Tsukurimichi, Y. Iizuka, H. Mizuno, H. Isaji, and C. Shimasaki, *Bull. Chem. Soc. Jpn.*, **62**, 1891 (1989).

11) T. Mukaiyama, M. Shiono, and T. Sato, *Chem. Lett.*, **1974**, 37; T. Cohen, G. Herman, J. R. Falck, and A. J. Mura, Jr., *J. Org. Chem.*, **40**, 812 (1975); T. Oida, S. Tanimoto, H. Ikehira, and M. Okano, *Bull. Chem. Soc. Jpn.*, **56**, 959 (1983); B. Bartels, R. Hunter, C. D. Simon, and G. O. Tomlinson, *Tetrahedron Lett.*, **28**, 2985 (1987).

12) a) T. Kumamoto, K. Hosoi, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **41**, 2742 (1968); b) T. Yamamoto, M. Kakimoto, and M. Okawara, *Tetrahedron Lett.*, **1977**, 1695; c) L. Narashimhan, R. Sanitra, and J. Swenton, *J. Chem. Soc., Chem. Commun.*, **1978**, 719; d) T. Kojima and T. Fujisawa, *Chem. Lett.*, **1978**, 1425; e) W. Dumont and A. Krief, *J. Chem. Soc., Chem. Commun.*, **1980**, 673; f) F. Cooke, R. Moerck, J. Schwindeman, and P. Magnus, *J. Org. Chem.*, **45**, 1046 (1980); g) H. Takei, H. Sugimura, M. Miura, and H. Okamura, *Chem. Lett.*, **1980**, 1209; h) T. Aida, D. N. Harpp, and T. H. Chan, *Tetrahedron Lett.*, **21**, 3247 (1980); i) G. A. Russell and J. Hershberger, *J. Am. Chem. Soc.*, **102**, 7603 (1980); j) V. Reutrakul and P. Poochairatananon, *Tetrahedron Lett.*, **24**, 531 (1983).

13) R. D. Miller and D. R. McKean, *Tetrahedron Lett.*, **24**, 2619 (1983).

14) Cf. a) T. Durst, *Adv. Org. Chem.*, **6**, 285 (1969); b) A. Sekera, J. E. Fauvet, and P. Rumpf, *Ann. Chim. (Paris)*, **10**, 413 (1965); c) P. Manya, A. Sekera, and P. Rumpf, *C. R. Acad. Sci., Paris, Ser. C*, **264**, 1196 (1967).

15) H. Alper and G. Wall, *J. Chem. Soc, Chem. Commun.*, **1976**, 263.

16) A. Cerniani and G. Modena, *Gazz. Chim. Ital.*, **89**, 843 (1959).

17) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 283 (1962).

18) H. B. Henbest, J. A. W. Reid, and C. J. M. Sterling, *J. Chem. Soc.*, **1964**, 1220.

19) C. R. Johnson and J. E. Keiser, *Org. Synth.*, Coll. Vol. V, 791 (1973).

20) R. Brown and R. C. G. Moggeridge, *J. Chem. Soc.*, **1946**, 816.

21) S. Oae, T. Masuda, K. Tsujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **45**, 3586 (1972).

22) A. Ceruniani, G. Modena, and P. E. Todesca, *Gazz. Chim. Ital.*, **90**, 9 (1960).

23) F. Gasparrini, M. Giovannoli, D. Misiti, G. Natile, and G. Palmieri, *Tetrahedron*, **39**, 3181 (1983).

24) K. W. Rosenmundt and H. Harms, *Ber.*, **53**, 2235 (1920).

25) K. A. M. Kremer and P. Helquist, *J. Organomet. Chem.*, **285**, 231 (1985).

26) K. Schank and H. -G. Schmitt, *Chem. Ber.*, **111**, 3497 (1978).

27) a) H. J. Backer and P. L. Stedehouder, *Recl. Trav. Chim. Pays-Bas*, **52**, 437 (1933); b) B. Bannister, *J. Chem. Soc., Perkin. Trans. 1*, **1980**, 540.

28) D. Shah and J. P. Trivedi, *J. Indian Chem. Soc.*, **41**, 223 (1964).

29) T. Kurumada, H. Ohsawa, O. Oda, T. Fujita, T. Toda, and T. Yoshioka, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1477 (1985); J. E. Anderson and J. E. T. Corrie, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 1027.

30) H. Boehme and P. Heller, *Chem. Ber.*, **86**, 765 (1953).

31) a) E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966); b) D. J. Ager, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1131.

32) a) S. H. Groen, R. M. Kelly, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1967); b) D. S. Tarbell

and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).
33) a) A. Deljac, Z. Stefanac, and K. Balenovic, *Tetrahedron, Suppl.*, **8**, 33 (1966); b) P. Blatcher and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 1074.
34) N. K. Kulbovskaya, E. P. Graheva, and M. F. Shostakovskii, *Zh, Obschch. Khim.*, **30**, 81 (1960).
35) a) W. A. Truce, H. E. Hill, and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2760 (1956); b) T. Ogawa, K. Hayami, and H. Suzuki, *Chem. Lett.*, **1989**, 773.