

# The First Example of $\alpha$ -Thiomagnesiums Generated from Dithioacetal Monoxides with Grignard Reagent; Their Properties and Some Synthetic Applications

Tsuyoshi SATOH\* and Kiyoshi AKITA

Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162–8601, Japan. Received November 5, 2002; accepted December 4, 2002

Dithioacetal monoxides were synthesized from aldehydes and cyclohexanone, and reaction of the dithioacetal monoxides with Grignard reagents was investigated. The dithioacetal monoxide synthesized from alkylaldehyde and 4-chlorobenzenethiol reacted with *i*-PrMgCl to afford the desired  $\alpha$ -thiomagnesium in high yield. The generated  $\alpha$ -thiomagnesium was found to be stable at room temperature and to be useful in organic synthesis. In contrast to this, the dithioacetal monoxides derived from benzaldehyde and cyclohexanone did not give satisfactory results.

**Key words**  $\alpha$ -thiomagnesium; dithioacetal monoxide; sulfoxide-magnesium exchange; Grignard reagent

The hydrogen on the carbon bearing an alkylthio or an arylthio group is known to be acidic (for example: **1**; R=Ph, R'=H;  $pK_a=48$ )<sup>1</sup> and lithium  $\alpha$ -sulfenyl carbanion **2** can be generated from the sulfide **1** with butyllithium. However, such generation is not an easy task except when R' is a carbanion stabilizing group. For example, Corey and Seebach reported quantitative generation of phenylthiomethyl lithium (**2**: R=Ph, R'=H) from thioanisole with *n*-BuLi in the presence of Dabco.<sup>2</sup> In the absence of Dabco, the yield of the phenylthiomethyl lithium was less than 35%.<sup>3,4</sup> Methylthiomethyl lithium (**2**: R=CH<sub>3</sub>, R'=H) was also generated from dimethyl sulfide with *n*-BuLi in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA).<sup>5</sup> On the other hand, no example of the magnesium  $\alpha$ -sulfenyl carbanion ( $\alpha$ -thio Grignard reagent) has been reported.<sup>6–8</sup>

Recently, we have extensively studied the generation of alkylmetals having a heteroatom on their  $\alpha$ -position **4** from sulfoxide **3**<sup>9–18</sup> by the sulfoxide-metal exchange reaction.<sup>19</sup> In continuation of our interest in the generation of carbanions having a heteroatom on their  $\alpha$ -position, we investigated the reaction of dithioacetal monoxides **5** with Grignard reagents and we were able to generate, for the first time,  $\alpha$ -thiomagnesiums **6a**. In this paper the generation of the  $\alpha$ -thiomagnesiums from dithioacetal monoxides and the properties and synthetic application of the generated  $\alpha$ -thiomagnesiums **6a** are described.

## Results and Discussion

**Synthesis of Dithioacetal Monoxides from Aldehydes and Cyclohexanone** The dithioacetal monoxides used in this study (**8–10**) were synthesized from 3-phenylpropanal, benzaldehyde, and cyclohexanone, respectively, as shown in Chart 3. For example, 3-phenylpropanal was treated with an equimolar amount of arenethiol in chloroform with BF<sub>3</sub>·OEt<sub>2</sub> at 0 °C to give dithioacetal **7** in high yield. Mono-oxidation

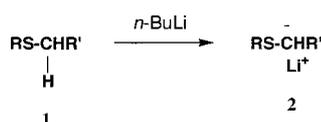
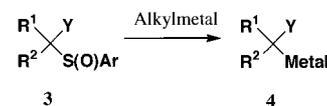


Chart 1

of the dithioacetal was carried out with an equimolar amount of *m*-chloroperbenzoic acid (MCPBA) in a mixture of saturated aqueous NaHCO<sub>3</sub> and chloroform at 0 °C to afford the desired dithioacetal monoxide **8** in over 70% yield as a mixture of two diastereomers.

The dithioacetal monoxides **8** are somewhat unstable under acidic conditions, and the oxidation must be carried out in the presence of a weak base such as NaHCO<sub>3</sub>. These



Alkylmetal=RLi or RMgX  
Y=O, N, Halogen

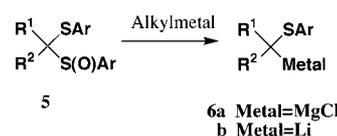


Chart 2

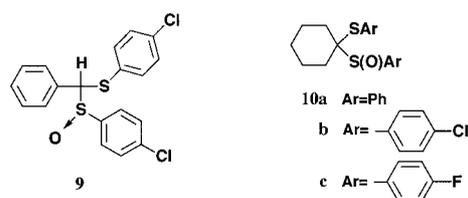
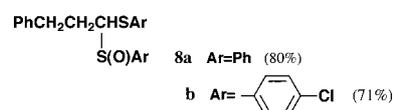
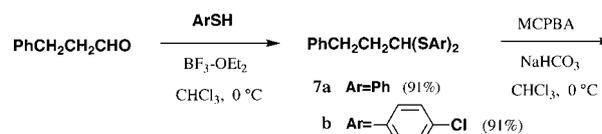


Chart 3

\* To whom correspondence should be addressed. e-mail: tsatoh@ch.kagu.tus.ac.jp

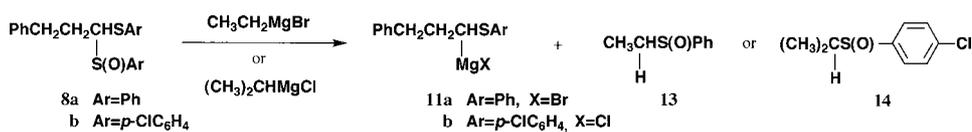
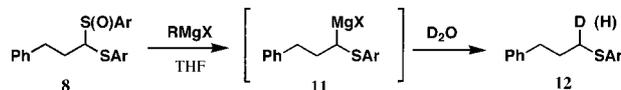


Chart 4

Table 1. Generation of  $\alpha$ -Thiomagnesiums **11** from **8** with Three Equivalents of Grignard Reagent and Trapping with Deuterium Oxide

Entry	<b>8</b>		Temp (°C)	Reaction time (min)	<b>12</b>	
	Ar	RMgX			Yield/% (D content/%)	
1	Ph	EtMgBr	-78	15	<b>12a</b> 74 <sup>a)</sup>	
2	Ph	EtMgBr	-78—r.t.	20	<b>12b</b> 87 (87)	
3	Ph	EtMgBr	-78—r.t.	60	<b>12b</b> 90 (73)	
4	Ph	EtMgBr	-78—r.t.	360	<b>12b</b> 90 (57)	
5	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	PhMgBr	r.t.	30	0 <sup>b)</sup>	
6	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>i</i> -PrMgCl	-78—r.t.	15	<b>12c</b> 85 (94) <sup>c)</sup>	
7	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>i</i> -PrMgCl	-78—r.t.	60	<b>12c</b> 94 (89) <sup>c)</sup>	
8	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>i</i> -PrMgCl	-78—r.t.	360	<b>12c</b> 90 (71) <sup>c)</sup>	

a) The reaction was quenched with H<sub>2</sub>O. b) Starting material and di(4-chlorophenyl) disulfide were obtained. c) Before the reaction with *i*-PrMgCl, *t*-BuMgCl (0.5 eq) was added to the reaction mixture in order to remove a trace of moisture in the reaction mixture (see text).

dithioacetal monoxides **8a** and **8b** could be purified by silica gel column chromatography; however, in the case of **8b** recrystallization was found to be more convenient.

**Reaction of the Synthesized Dithioacetal Monoxides with Grignard Reagents** Reaction of the synthesized dithioacetal monoxides **8**–**10** with Grignard reagents was investigated. First, dithioacetal monoxide **8a** was added dropwise to a solution of EtMgBr (3 eq) in THF at -78 °C and after 15 min, the reaction was quenched with water (Chart 4 and Table 1, entry 1). The starting material **8a** disappeared and the desired phenyl 3-phenylpropyl sulfide **12a** was isolated in 74% yield. This result indicates that the desired sulfoxide-magnesium exchange takes place and  $\alpha$ -thiomagnesium **11a** must be formed.

Next, this reaction was conducted at -78 °C and after the addition of **8a**, the cooling bath was removed and the reaction mixture was stirred at room temperature and finally the reaction was quenched with deuterium oxide (entries 2–4). As shown in entries 2–4, yield of the isolated deuterated sulfide **12b** was about 90%; however, deuterium incorporation was not satisfactory (87%) even right after the sulfoxide-metal exchange reaction was carried out (entry 2) and was slowly decreased from 87% to 57% after 6 h at room temperature. One reason why this problem arises was supposed to be the trace moisture in the reaction medium. Another reason was supposed to be the generated ethyl phenyl sulfoxide **13** (see Chart 4) which has a rather acidic hydrogen on the carbon bearing the sulfinyl group.

In view of these results, we came up with some modification of the reaction conditions. First, we synthesized a dithioacetal monoxide having an electron-withdrawing group on the aromatic ring. The selected aromatic ring was *p*-chlorophenyl group **8b**. We anticipated that the carbanion of **11b** is stabilized and the basicity of **11b** could be lowered by the electron-withdrawing nature of the chlorine atom. Sec-

ond, we investigated other Grignard reagents such as PhMgBr and *i*-PrMgCl. Third, before the sulfoxide-magnesium exchange reaction, *t*-BuMgCl (0.5 eq) was added to the reaction mixture to remove the trace of moisture in the reaction medium. Note that *t*-BuMgCl has been found to be inert to the sulfoxides.

To overcome the above-mentioned problem, first of all, we investigated the reaction of **8b** with PhMgBr, because we thought that if the reaction worked, the produced by-product, *p*-chlorophenyl phenyl sulfoxide, would have no acidic hydrogen. However, the sulfoxide-magnesium exchange reaction did not take place even at room temperature (entry 5).

Next, **8b** was treated with *t*-BuMgCl (0.5 eq) followed by *i*-PrMgCl at -78 °C, then at room temperature for 15 min (entry 6). The reaction worked quite good to give a high yield of the sulfide **12c** with high deuterium content (94%). The generated  $\alpha$ -thiomagnesium **11b** was found to be stable at room temperature within 1 h (entry 7). However, **11b** was slowly protonated at room temperature (entry 8). As mentioned above, the proton source of this reaction was thought to be the generated sulfoxide **14**. We separated the sulfoxide from the reaction mixture and investigated by <sup>1</sup>H-NMR if the deuterium incorporation took place and we found that no deuterium was incorporated in the sulfoxide **14**. In any event, we found that the  $\alpha$ -thiomagnesium **11b** could be generated and it could be used at room temperature for at least 1 h.

Before the study to apply the generated  $\alpha$ -thiomagnesium **11b** in organic synthesis, we investigated the sulfoxide-magnesium exchange reaction with the dithioacetal monoxide derived from benzaldehyde and cyclohexanone, **9** and **10**, respectively.

The results for the sulfoxide-magnesium exchange reaction of **9** with Grignard reagents are summarized in Chart 5. The sulfoxide **9** was treated with EtMgBr, *i*-PrMgCl, and PhMgBr. The sulfoxide-magnesium exchange reaction took

place even with PhMgBr at  $-78\text{ }^{\circ}\text{C}$ ; however, these reactions were not always completed and a considerable amount of the starting material **9** remained in the reaction mixture even with a large excess amount of the Grignard reagent added. The yield of sulfide **15** was less than 67%.

When this reaction was quenched with  $\text{D}_2\text{O}$ , we found that the remained starting material was not **9** but deuterated sulfoxide **16** (deuterium incorporation was over 99%). These results implied that when the reaction of **9** with the Grignard reagent was carried out, both the sulfoxide-magnesium exchange reaction (gave **17**) and hydrogen abstraction (gave **18**) took place competitively, because the hydrogen on the carbon bearing the sulfoxide is highly acidic.

The results for the reaction of dithioacetal monoxide **10** with Grignard reagents are summarized in Table 2. The sulfoxide **10a** did not react at all with EtMgBr at room temperature (entry 1). Quite interestingly, the reaction took place in the presence of HMPA to give **19a**; however, the deuterium content was very low (entry 2). The sulfoxide-magnesium exchange reaction of **10b** proceeded with EtMgBr without

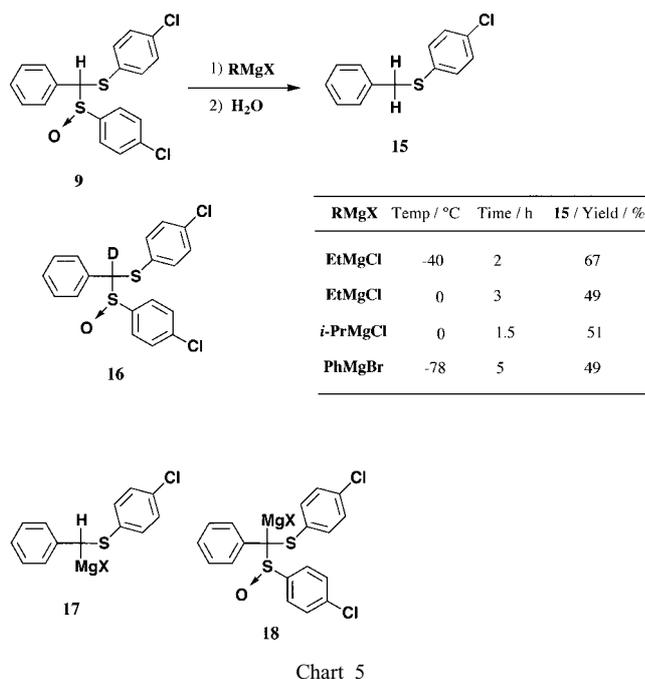


Chart 5

Table 2. Reaction of the Dithioacetal Monoxide **10** with Grignard Reagent

Entry	Ar	RMgX	Temp ( $^{\circ}\text{C}$ )	Reaction time (min)	<b>19</b>	
					Yield/%	(D content/%) <sup>a)</sup>
1	Ph	EtMgBr	r.t.	60		0 <sup>b)</sup>
2	Ph	EtMgBr <sup>c)</sup>	r.t.	30	<b>19a</b>	65 (9)
3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	EtMgBr	r.t.	8	<b>19b</b>	90 (60)
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	EtMgBr <sup>c)</sup>	r.t.	8	<b>19b</b>	93 (0)
5	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>i</i> -PrMgCl	0—r.t.	8	<b>19b</b>	96 (58)
6	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	EtMgBr	0—r.t.	8	<b>19c</b>	74 (64)
7	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>i</i> -PrMgCl	r.t.	6	<b>19c</b>	74 (63)

a) Deuterium incorporation was measured by  $^1\text{H-NMR}$ . b) No reaction. c) The reaction was carried out in the presence of HMPA.

HMPA to afford **19b** and the deuterium incorporation was 60% (entry 3). In the presence of HMPA, the deuterium content was found to be 0% (entry 4). This reaction took place with *i*-PrMgCl with slightly better results; however, the deuterium content was still less than 60% (entry 5).

Entries 6 and 7 show the results with **10c**. As shown in Table 2, the deuterium content was found to be slightly better, but the chemical yield of **19c** could not be improved. The sulfoxide-magnesium exchange reaction of **9** and **10**, on the whole, was found to be unsuccessful for the generation of  $\alpha$ -thiomagnesiums in significant yield.

**An Application of the Generated  $\alpha$ -Thiomagnesium **11b** in Organic Synthesis** Next, we investigated the reactivity of the  $\alpha$ -thiomagnesium **11b** derived from **8b** by the sulfoxide-magnesium exchange reaction with some electrophiles (Chart 6, Table 3). In a solution of **11b**, generated from **8b** under the conditions shown in Table 1 (entry 6), 5 equivalents of ethyl chloroformate was added and the reaction mixture was stirred at room temperature for 30 min to give the ester **20** in 51% yield (Chart 6). Reductive desulfurization of the *p*-chlorophenylthio group was easily carried out with  $\text{Bu}_3\text{SnH}$  to afford ethyl 4-phenylbutyrate **21** in almost quantitative yield.<sup>20–24</sup> Oxidation of the sulfur in **20** with MCPBA followed by thermal elimination of the resulting sulfoxide afforded the  $\alpha,\beta$ -unsaturated ester **22** in 84% overall yield.

Reactions of the  $\alpha$ -thiomagnesium **11b** with several electrophiles other than ethyl chloroformate are summarized in Table 3. As shown in Table 3, the  $\alpha$ -thiomagnesium **11b** was found to have relatively low reactivity compared to that of other simple Grignard reagents. Alkylation of **11b** with several halogenoalkanes gave the alkylated products **23–26** in low to moderate yields (entry 1–4). Excellent yield was obtained with benzaldehyde (entry 5); however, **11b** did not add to 3-phenylpropanal. Addition of **11b** to 2,2-dimethylpropanal gave the adduct **28** in only 26% yield (entry 6). Benzoyl chloride and phenyl isocyanate reacted to give the desired products **29** and **30**; however, the yields were only up to 34%.

In conclusion, we were able to generate, for the first time,  $\alpha$ -thiomagnesiums from dithioacetal monoxides by the sulfoxide-magnesium exchange reaction. The generated  $\alpha$ -thiomagnesiums were found to be stable at room temperature; however, the reactivity toward several electrophiles was

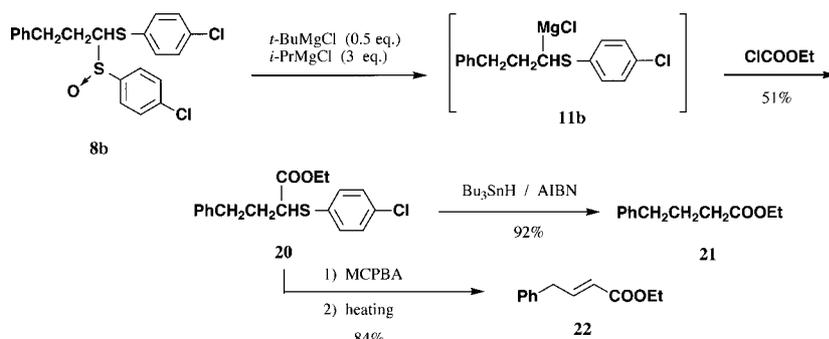


Chart 6

Table 3. Reaction of the Generated  $\alpha$ -Thiomagnesium **11b** with Electrophiles

Entry	Electrophile	Reaction time (min)	Product (yield/%)
1	CH <sub>3</sub> I (4 eq.)	60	(51) <sup>a)</sup>
2	Ph(CH <sub>2</sub> ) <sub>2</sub> I (4 eq.)	210	(27)
3	PhCH <sub>2</sub> Br (4 eq.)	90	(23)
4	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl (4 eq.)	60	(25)
5	PhCHO (5 eq.)	40	(92)
6	(CH <sub>3</sub> ) <sub>3</sub> CCHO (5 eq.)	50	(26)
7	PhCOCl (4 eq.) <sup>b)</sup>	10	(25)
8	PhNCO (4 eq.)	20	(34)

a) The product of this reaction was a mixture of **23** (51%) and **12a** (25%). The yield was calculated by <sup>1</sup>H-NMR. b) The reaction was carried out at  $-78^{\circ}\text{C}$ .

found to be low.

### Experimental

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. <sup>1</sup>H-NMR spectra were measured in a CDCl<sub>3</sub> solution with JEOL JNM-LA 400 and 500 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel 60 (MERCK) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent, THF was distilled from benzophenone ketyl; HMPA and diisopropylamine were distilled from CaH<sub>2</sub>. The molecular sieves 4A used in this study was flame-dried under Ar atmosphere before use.

**1,1-Bis(phenylthio)-3-phenylpropane (7a)** To a solution of 3-phenylpropanal (4.27 g, 32.6 mmol) and benzenethiol (7.4 ml, 71.7 mmol) in 40 ml of CHCl<sub>3</sub> at 0 °C was added dropwise BF<sub>3</sub>·Et<sub>2</sub>O (9.9 ml, 78.9 mmol). The reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched by sat. aq. NaHCO<sub>3</sub> and the whole was extracted with *n*-hexane. The organic solution was washed with 5% NaOH followed by water. The solution was dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated. The product was purified by silica gel column chromatography to give **7a** (9.99 g, 91%) as colorless oil. IR (neat) 3059, 2921, 1582, 1479, 1438, 1024, 739, 691 cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta$  2.14 (2H, q, *J*=7.3 Hz), 2.92 (2H, t, *J*=7.5 Hz), 4.35 (1H, t, *J*=6.7 Hz), 7.11 (2H, d, *J*=8.0 Hz), 7.17–7.20 (1H, m), 7.24–7.30 (8H, m),

7.39–7.41 (4H, m). MS *m/z* (%) 336 (M<sup>+</sup>, 10), 227 (22), 149 (7), 117 (100), 91 (83). Calcd for C<sub>21</sub>H<sub>20</sub>S<sub>2</sub>: M, 336.1007. Found: *m/z* 336.1009.

**1,1-Bis(*p*-chlorophenylthio)-3-phenylpropane (7b)**: Colorless oil. IR (neat) 3025, 2923, 1475, 1093, 1013, 821, 746, 700 cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta$  2.10 (2H, q, *J*=7.2 Hz), 2.90 (2H, t, *J*=7.5 Hz), 4.24 (1H, t, *J*=6.9 Hz), 7.11–7.14 (2H, m), 7.19–7.31 (11H, m). MS *m/z* (%) 404 (M<sup>+</sup>, 5), 261 (14), 149 (13), 117 (100), 91 (78). Calcd for C<sub>21</sub>H<sub>18</sub>Cl<sub>2</sub>S<sub>2</sub>: M, 404.0226. Found: *m/z* 404.0219.

**1-(Phenylsulfinyl)-1-(phenylthio)-3-phenylpropane (8a)** To a suspension of dithioacetal **7a** (1.94 g, 5.7 mmol) in sat. aq. NaHCO<sub>3</sub> (23 ml) and CHCl<sub>3</sub> (11.4 ml) at 0 °C was added MCPBA (1.48 g, 5.99 mmol) with stirring. The reaction mixture was stirred for 30 min. The reaction was quenched with sat. aq. Na<sub>2</sub>SO<sub>3</sub> and the whole was extracted with *n*-hexane and AcOEt. The organic solution was washed with water and dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated and the residue was purified by silica gel column chromatography to give **8a** (diastereomeric mixture) (1.62 g, 80%) as colorless viscous oil. IR (neat) 3060, 1476, 1442, 1086, 1047 (SO), 748, 691 cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta$  1.34–1.42 (0.4H, m), 1.92–2.00 (0.6H, m), 2.38–2.45 (0.6H, m), 2.49–2.56 (0.4H, m), 2.74–2.83 (1H, m), 3.00–3.07 (1H, m), 3.81 (0.6H, dd, *J*=10.7, 3.1 Hz), 4.07 (0.4H, dd, *J*=11.0, 3.4 Hz), 7.03–7.75 (15H, m); MS *m/z* (%) 353 ([M+H]<sup>+</sup>, trace), 352 (M<sup>+</sup>, trace), 226 (41), 117 (100), 91 (44). Calcd for C<sub>21</sub>H<sub>21</sub>OS<sub>2</sub>: [M+H], 353.1034. Found: *m/z* 353.1014.

**1-(*p*-Chlorophenylsulfinyl)-1-(*p*-chlorophenylthio)-3-phenylpropane (8b)**:

Colorless crystals (diastereomeric mixture). mp 76.8–77.5 °C (AcOEt-hexane); IR (KBr) 3026, 2923, 1475, 1093, 1050 (SO), 1012, 820, 743, 700 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.36–1.59 (0.4H, m), 1.85–1.95 (0.6H, m), 2.33–2.42 (0.6H, m), 2.45–2.54 (0.4H, m), 2.75–2.85 (1H, m), 3.00–3.08 (1H, m), 3.75 (0.6H, dd, *J* = 13.9, 3.8 Hz), 3.98 (0.4H, dd, *J* = 13.7, 4.3 Hz), 7.05–7.64 (13H, m). MS *m/z* (%) 260 (39), 160 (17), 143 (12), 117 (100), 91 (23). *Anal.* Calcd: C, 59.85; H, 4.31; Cl, 16.83; S, 15.22. Found: C, 59.54; H, 4.81; Cl, 16.59; S, 15.21.

(*p*-Chlorophenylsulfanyl)(*p*-chlorophenylthio)phenylmethane (**9**): Colorless crystals (diastereomeric mixture). mp 130.5–132.0 °C (benzene); IR (KBr) 1482, 1095, 1050 (SO), 1010, 818, 698 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 4.96 (0.3H, s), 5.01 (0.7H, s), 7.04–7.53 (13H, m). MS *m/z* (%) 286 (94), 233 (6), 143 (100), 108 (49).

1-(Phenylsulfanyl)-1-(phenylthio)cyclohexane (**10a**): Colorless crystals. mp 105–106 °C (AcOEt); IR (KBr) 2931, 1439, 1079, 1046 (SO), 748, 686 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 0.96–0.99 (1H, m), 1.15–1.24 (1H, m), 1.53–1.78 (6H, m), 1.89–1.95 (1H, m), 2.04–2.10 (1H, m), 7.35–7.42 (3H, m), 7.48–7.54 (3H, m), 7.72–7.74 (2H, m), 7.91–7.93 (2H, m). MS *m/z* (%) 218 (100), 185 (7), 154 (10), 140 (3), 109 (66).

1-(*p*-Chlorophenylsulfanyl)-1-(*p*-chlorophenylthio)cyclohexane (**10b**): Colorless crystals. mp 105–106 °C (AcOEt); IR (KBr) 2935, 1476, 1093, 1040 (SO), 1012, 816 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 0.99–1.01 (1H, m), 1.15–1.25 (1H, m), 1.55–1.73 (6H, m), 1.84–1.90 (1H, m), 2.00–2.06 (1H, m), 7.34–7.36 (2H, m), 7.47–7.50 (2H, m), 7.65–7.68 (2H, m), 7.81–7.84 (2H, m). MS *m/z* (%) 286 (13), 224 (98), 160 (36), 143 (34), 112 (46), 108 (37), 81 (100). *Anal.* Calcd: C, 56.10; H, 4.71; Cl, 18.40; S, 16.64. Found: C, 55.89; H, 4.55; Cl, 18.44; S, 16.79.

1-(*p*-Fluorophenylsulfanyl)-1-(*p*-fluorophenylthio)cyclohexane (**10c**): Colorless crystals. mp 108–109 °C (AcOEt); IR (KBr) 2931, 1489, 1235, 1047 (SO), 835 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 0.96–0.99 (1H, m), 1.15–1.26 (1H, m), 1.54–1.76 (6H, m), 1.83–1.91 (1H, m), 2.00–2.07 (1H, m), 7.04–7.10 (2H, m), 7.18–7.24 (2H, m), 7.69–7.74 (2H, m), 7.87–7.92 (2H, m). MS *m/z* (%) 254 (95), 208 (27), 127 (100), 83 (41), 81 (22).

1-(Phenylthio)-3-phenylpropane (**12a**) To a solution of EtMgBr (0.6 ml, 0.6 mmol) in 2 ml of THF at –78 °C was added dropwise with stirring a solution of dithioacetal monoxide **8a** (70.5 mg, 0.2 mmol) in THF. The reaction mixture was stirred for 15 min. The reaction was quenched by sat. aq. NH<sub>4</sub>Cl and the whole was extracted with *n*-hexane. The solution was dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated. The product was purified by silica gel column chromatography to give **12a** (40.2 mg, 87%) as colorless oil. IR (neat) 2916, 1583, 1480, 1438, 1091, 1025, 737, 690 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.97 (2H, quin, *J* = 7.4 Hz), 2.75 (2H, t, *J* = 7.5 Hz), 2.92 (2H, t, *J* = 7.2 Hz), 7.14–7.20 (4H, m), 7.25–7.31 (6H, m). MS *m/z* (%) 228 (M<sup>+</sup>, 92), 137 (14), 118 (100), 110 (37), 91 (63), 77 (17). Calcd for C<sub>15</sub>H<sub>16</sub>S: M, 228.0971. Found: *m/z* 228.0967.

1-Deuterio-1-(phenylthio)-3-phenylpropane (**12b**) Above-mentioned reaction was quenched with D<sub>2</sub>O. The product was purified by silica gel column chromatography to give **12b** (87%). MS *m/z* (%) 229 (M<sup>+</sup>, 90), 138 (14), 119 (100), 110 (45), 91 (62), 77 (15). Calcd for C<sub>15</sub>H<sub>15</sub>DS: M, 229.1034. Found: *m/z* 229.1043.

1-Deuterio-1-(*p*-chlorophenylthio)-3-phenylpropane (**12c**) To a solution of *t*-BuMgCl (0.1 ml, 0.1 mmol) in 2 ml of THF at –78 °C was added dropwise with stirring a solution of dithioacetal monoxide **8b** (84.2 mg, 0.2 mmol) in THF. After 5 min, to the reaction mixture was added dropwise *i*-PrMgCl (0.3 ml, 0.6 mmol) and warmed to room temperature. After 15 min, the reaction was quenched by D<sub>2</sub>O and the whole was extracted with *n*-hexane. The solution was dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated. The product was purified by silica gel column chromatography to give **12c** (40.2 mg, 87%). Protonation (H) product: colorless oil. IR (neat) 3025, 2933, 1476, 1096, 1011, 811, 746, 699 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.95 (2H, quin, *J* = 7.4 Hz), 2.74 (2H, t, *J* = 7.5 Hz), 2.89 (2H, t, *J* = 7.3 Hz), 7.12–7.31 (8H, m). <sup>13</sup>C-NMR δ 30.46, 33.03, 34.57, 126.03, 128.41, 128.45, 128.99, 130.38, 131.74, 135.05, 141.07. MS *m/z* (%) 262 (M<sup>+</sup>, 68), 171 (8), 144 (29), 118 (100), 108 (15), 91 (75), 77 (8). Calcd for C<sub>15</sub>H<sub>15</sub>ClS: M, 262.0582. Found: *m/z* 262.0583. Deuteration (D) product: MS *m/z* (%) 263 (M<sup>+</sup>, 62), 172 (7), 144 (33), 119 (100), 108 (16), 91 (72), 77 (8). Calcd for C<sub>15</sub>H<sub>14</sub>DCIS: M, 263.0645. Found: *m/z* 263.0652.

(*p*-Chlorophenylthio)phenylmethane (**15**) To a solution of EtMgCl (0.5 ml, 0.5 mmol) in 1.6 ml of THF at –40 °C was added dropwise with stirring a solution of dithioacetal monoxide **9** (39.3 mg, 0.1 mmol) in THF. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by sat. aq. NH<sub>4</sub>Cl and the whole was extracted with *n*-hexane. The solution was dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated. The product was purified by silica gel column

chromatography to give **15** (15.7 mg, 67%) as a low-melting solid. IR (KBr) 1477, 1100, 813, 712, 695 cm<sup>-1</sup>; <sup>1</sup>H-NMR (solvent CDCl<sub>3</sub>) δ 4.08 (2H, s), 7.21 (4H, s), 7.23–7.31 (5H, m), <sup>1</sup>H-NMR (solvent CD<sub>3</sub>OD) δ 4.12 (2H, s), 7.17–7.28 (9H, m). MS *m/z* (%) 234 (M<sup>+</sup>, 25), 143 (5), 108 (6), 91 (100). Calcd for C<sub>13</sub>H<sub>11</sub>ClS: M, 234.0269. Found: *m/z* 234.0279.

Phenylthiocyclohexane (**19a**) To a solution of EtMgBr (0.6 ml, 0.6 mmol) and HMPA (0.32 ml, 1.8 mmol) in 2 ml of THF at room temperature was added dropwise with stirring a solution of dithioacetal monoxide **10a** (64.0 mg, 0.2 mmol) in THF. The reaction mixture was stirred for 30 min. The reaction was quenched by sat. aq. NH<sub>4</sub>Cl and the whole was extracted with *n*-hexane. The solution was dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated. The product was purified by silica gel column chromatography to give **19a** (25.1 mg, 65%) as colorless oil. IR (neat) 2929, 2852, 1478, 1438, 1262, 1025, 750, 691 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.21–1.41 (5H, m), 1.59–1.63 (1H, m), 1.75–1.79 (2H, m), 1.97–2.00 (2H, m), 3.07–3.13 (1H, m), 7.19–7.40 (5H, m). MS *m/z* (%) 192 (M<sup>+</sup>, 36), 110 (100), 83 (11). Calcd for C<sub>12</sub>H<sub>16</sub>S: M, 192.0971. Found: *m/z* 192.0967.

*p*-Chlorophenylthiocyclohexane (**19b**): Colorless oil. IR (neat) 2931, 2853, 1472, 1095, 1013, 820 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.23–1.39 (5H, m), 1.60–1.63 (1H, m), 1.76–1.78 (2H, m), 1.95–1.97 (2H, m), 3.03–3.08 (1H, m), 7.23–7.33 (4H, m). MS *m/z* (%) 226 (M<sup>+</sup>, 31), 144 (100), 108 (15), 83 (22). Calcd for C<sub>12</sub>H<sub>15</sub>ClS: M, 226.0581. Found: *m/z* 225.0580.

*p*-Fluorophenylthiocyclohexane (**19c**): Colorless oil. IR (neat) 2931, 2853, 1589, 1490, 1448, 1227, 1155, 831 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.19–1.37 (5H, m), 1.58–1.62 (1H, m), 1.75–1.77 (2H, m), 1.92–1.95 (2H, m), 2.94–3.00 (1H, m), 6.96–7.02 (2H, m), 7.38–7.46 (2H, m). MS *m/z* (%) 210 (M<sup>+</sup>, 35), 128 (100), 83 (25). Calcd for C<sub>12</sub>H<sub>15</sub>FS: M, 210.0878. Found: *m/z* 210.0879.

Ethyl 2-(*p*-Chlorophenylthio)-4-phenylbutanoate (**20**) To a solution of *t*-BuMgCl (0.1 ml, 0.1 mmol) in 2 ml of THF at –78 °C was added dropwise with stirring a solution of dithioacetal monoxide **8b** (84.2 mg, 0.2 mmol) in THF. After 5 min, to the reaction mixture was added dropwise *i*-PrMgCl (0.3 ml, 0.6 mmol) and the reaction mixture was warmed to room temperature. After 10 min, ethyl chloroformate (0.10 ml, 1.00 mmol) was added to the flask. The reaction mixture was stirred for 60 min. The reaction was quenched by sat. aq. NH<sub>4</sub>Cl and the whole was extracted with *n*-hexane and AcOEt. The solution was dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated. The product was purified by silica gel column chromatography to give **20** (34.0 mg, 51%) as colorless oil. IR (neat) 2929, 1732 (CO), 1476, 1259, 1095, 746, 700 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.20 (1H, t, *J* = 7.2 Hz), 1.99–2.08 (1H, m), 2.15–2.25 (1H, m), 2.75 (2H, t, *J* = 7.6 Hz), 3.57 (1H, t, *J* = 7.4 Hz), 4.08–4.16 (2H, m), 7.15–7.37 (9H, m). MS *m/z* (%) 334 (M<sup>+</sup>, 57), 230 (20), 191 (19), 157 (27), 144 (16), 117 (65), 91 (100). Calcd for C<sub>18</sub>H<sub>19</sub>ClO<sub>2</sub>S: M, 334.0792. Found: *m/z* 334.0790.

Ethyl 4-Phenylbutanoate (**21**) To a solution of **20** (63 mg, 0.19 mmol) in benzene (5 ml) at room temperature were added Bu<sub>3</sub>SnH (0.22 ml, 0.8 mmol) and AIBN (33.9 mg, 0.2 mmol) with stirring. The reaction mixture was refluxed for 4 h and then the whole was extracted with *n*-hexane and AcOEt. The organic solution was washed with water, then dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated and the residue was purified by silica gel column chromatography to give **21** (33.3 g, 92%) as colorless oil. IR (neat) 2935, 1735 (CO), 1201, 1031, 745, 700 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.25 (3H, t, *J* = 7.2 Hz), 1.96 (2H, quin, *J* = 7.6 Hz), 2.32 (2H, t, *J* = 7.5 Hz), 2.65 (2H, t, *J* = 7.6 Hz), 4.12 (2H, q, *J* = 7.1 Hz), 7.17–7.20 (3H, m), 7.26–7.30 (2H, m). MS *m/z* (%) 192 (M<sup>+</sup>, 32), 147 (40), 104 (57), 91 (60), 84 (72), 49 (100). Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: M, 192.1148. Found: *m/z* 192.1142.

Ethyl (*E*)-4-Phenyl-2-butenolate (**22**) To a solution of **20** (80 mg, 0.24 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2.4 ml) at –40 °C was added MCPBA (65.1 mg, 0.26 mmol) with stirring. The reaction mixture was stirred for 2 h. The reaction was quenched by sat. aq. Na<sub>2</sub>SO<sub>3</sub> and the whole was extracted with *n*-hexane and AcOEt. The organic solution was washed with water and dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated and the residue was purified by silica gel column chromatography to give ethyl 2-(*p*-chlorophenylsulfanyl)-4-phenylbutanoate (diastereomeric mixture; colorless oil. IR (neat) 2981, 1730 (CO), 1475, 1148, 1091, 1057 (SO), 1012, 825, 742, 701 cm<sup>-1</sup>; <sup>1</sup>H-NMR δ 1.12–1.18 (3H, m), 2.08–2.21 (1H, m), 2.30–2.44 (1H, m), 2.62–2.67 (1H, m), 2.74–2.82 (1H, m), 3.42 (0.5H, dd, *J* = 10.4, 4.0 Hz), 3.58 (0.5H, dd, *J* = 10.1, 4.6 Hz), 3.95–4.13 (2H, m), 7.10–7.29 (5H, m), 7.46–7.55 (4H, m). MS *m/z* (%) 350 (M<sup>+</sup>, trace), 191 (82), 190 (33), 160 (25), 145 (54), 117 (80), 91 (100). Calcd for C<sub>18</sub>H<sub>19</sub>ClO<sub>3</sub>S: M, 350.0744. Found: *m/z* 350.0749). The sulfoxide was refluxed for 3.5 h in toluene and then the whole was extracted with *n*-hexane and AcOEt. The organic solution was washed with water, then dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated and the residue was purified by silica gel column chromatog-

raphy to give **22** (32.0 g, 84%, 2 steps) as colorless oil. IR (neat) 2982, 1720 (CO), 1653 (C=C), 1271, 1161, 699  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$   $\delta$  1.27 (3H, t,  $J=7.2$  Hz), 3.52 (2H, dd,  $J=6.7, 1.4$  Hz), 4.18 (2H, q,  $J=7.1$  Hz), 5.81 (1H, dt,  $J=17.1, 1.5$  Hz), 7.10 (1H, dt,  $J=15.6, 6.9$  Hz), 7.17—7.33 (5H, m). MS  $m/z$  (%) 190 ( $\text{M}^+$ , 60), 162 (8), 145 (41), 117 (100), 91 (31), 28 (51). Calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2$ : M, 190.0993. Found:  $m/z$  190.0989.

**2-(*p*-Chlorophenylthio)-4-phenylbutane (23)** To a solution of *t*-BuMgCl (0.1 ml, 0.1 mmol) in 2 ml of THF at  $-78^\circ\text{C}$  was added dropwise with stirring a solution of dithioacetal monoxide **8b** (84.2 mg, 0.2 mmol) in THF. After 5 min, to the reaction solution was added dropwise *i*-PrMgCl (0.3 ml, 0.6 mmol) and the reaction mixture was warmed to room temperature. After 10 min, CuI (3.8 mg, 10  $\text{mol}\%$ )<sup>25</sup> and  $\text{CH}_3\text{I}$  (0.06 ml, 0.88 mmol) were added to the flask. The reaction mixture was stirred for 60 min. The reaction was quenched by sat. aq.  $\text{NH}_4\text{Cl}$  and the whole was extracted with *n*-hexane. The solution was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated. The product was a mixture of **23** (28.4 mg, 51%) and **12a** (13.1 mg, 25%). IR (neat) 2925, 1475, 1095, 1013, 819, 746, 699  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$   $\delta$  1.30 (3H, d,  $J=6.7$  Hz), 1.77—1.85 (1H, m), 1.87—1.94 (1H, m), 2.72—2.83 (2H, m), 3.15 (1H, sex,  $J=6.7$  Hz), 7.1—7.3 (9H, m).  $^{13}\text{C-NMR}$   $\delta$  21.05 (1C, q), 33.10 (1C, t), 38.08 (1C, t), 42.74 (1C, t), 125.97 (1C, d), 128.43 (4C, d), 128.93 (2C, d), 132.82 (1C, d), 133.29 (2C, d), 133.58 (1C, s), 141.45 (1C, s). MS  $m/z$  (%) 276 ( $\text{M}^+$ , 34), 262 (10), 144 (16), 132 (33), 117 (24), 91 (100). Calcd for  $\text{C}_{16}\text{H}_{17}\text{ClS}$ : M, 276.0739. Found:  $m/z$  276.0741.

**3-(*p*-Chlorophenylthio)-1,5-diphenylpentane (24)**: Colorless oil. IR (neat) 2926, 1496, 1475, 1454, 1095, 1013, 820, 746, 699  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$   $\delta$  1.83—1.97 (4H, m), 2.77 (4H, t,  $J=7.0$  Hz), 3.01 (1H, quin,  $J=6.5$  Hz), 7.04—7.33 (14H, m). MS  $m/z$  (%) 366 ( $\text{M}^+$ , 47), 145 (20), 131 (46), 117 (14), 91 (100). Calcd for  $\text{C}_{23}\text{H}_{23}\text{ClS}$ : M, 366.1207. Found:  $m/z$  366.1200.

**2-(*p*-Chlorophenylthio)-1,4-diphenylbutane (25)**: Colorless oil. IR (neat) 3026, 2925, 1496, 1475, 1454, 1095, 1013, 745, 699  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$   $\delta$  1.75—1.82 (1H, m), 1.90—1.97 (1H, m), 2.71—2.77 (1H, m), 2.80—2.97 (3H, m), 3.24—3.29 (1H, m), 7.07—7.31 (14H, m). MS  $m/z$  (%) 352 ( $\text{M}^+$ , 32), 262 (3), 149 (11), 131 (20), 117 (92), 91 (100). Calcd for  $\text{C}_{22}\text{H}_{21}\text{ClS}$ : M, 352.1052. Found:  $m/z$  352.1061.

**2-(*p*-Chlorophenylthio)-1-(*p*-methoxyphenyl)-4-phenylbutane (26)**: Colorless oil. IR (neat) 2919, 1509, 1475, 1245, 1094  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$   $\delta$  1.72—1.82 (1H, m), 1.88—1.97 (1H, m), 2.70—2.91 (1H, m), 3.20—3.26 (1H, m), 3.78 (3H, s), 6.77—6.82 (2H, m), 7.01—7.05 (2H, m), 7.07—7.10 (2H, m), 7.16—7.27 (7H, m). MS  $m/z$  (%) 382 ( $\text{M}^+$ , 47), 149 (15), 131 (32), 121 (83), 117 (100), 91 (93). Calcd for  $\text{C}_{23}\text{H}_{23}\text{ClOS}$ : M, 382.1156. Found:  $m/z$  382.1148.

**2-(*p*-Chlorophenylthio)-1,4-diphenyl-1-butanol (27)**: Diastereomeric mixture; colorless oil. IR (neat) 3445 (OH), 3027, 2926, 1475, 1095, 1013, 746, 699  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (more polar product)  $\delta$  1.60—1.67 (1H, m), 1.76—1.83 (1H, m), 2.66 (1H, dt,  $J=13.8, 8.2$  Hz), 2.89—2.94 (1H, m), 3.11—3.15 (1H, m), 3.17 (1H, d,  $J=2.5$  Hz), 4.51 (1H, dd,  $J=7.9, 2.5$  Hz), 6.97 (2H, d,  $J=7.0$  Hz), 7.14—7.35 (12H, m),  $^1\text{H-NMR}$  (less polar product)  $\delta$  1.70—1.78 (1H, m), 1.92—1.99 (1H, m), 2.61 (1H, dt,  $J=13.8, 8.4$  Hz), 2.66 (1H, d,  $J=2.8$  Hz), 2.86—2.92 (1H, m), 3.27 (1H, dt,  $J=10.1, 3.4$  Hz), 4.76 (1H, s), 6.99—7.01 (2H, m), 7.14—7.32 (12H, m). MS  $m/z$  (%) 368 ( $\text{M}^+$ , 6), 262 (74), 117 (98), 91 (100). Calcd for  $\text{C}_{22}\text{H}_{21}\text{ClOS}$ : M, 368.1002. Found:  $m/z$  368.1009.

**4-(*p*-Chlorophenylthio)-2,2-dimethyl-6-phenyl-3-hexanol (28)**: Diastereomeric mixture; colorless oil. IR (neat) 3480 (OH), 2956, 1475, 1096, 1013, 821, 746, 700  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (less polar product)  $\delta$  0.78 (9H, s), 1.76—1.84 (1H, m), 2.03 (1H, d,  $J=4.6$  Hz), 2.16—2.23 (1H, m), 2.79 (1H, dt,  $J=13.75, 8.5$  Hz), 3.01—3.06 (1H, m), 3.23 (1H, dt,  $J=10.6, 2.5$  Hz), 3.37 (1H, d,  $J=2.4$  Hz), 7.26—7.31 (9H, m). MS  $m/z$  (%) 348 ( $\text{M}^+$ , 25), 262 (71), 144 (24), 118 (67), 117 (57), 91 (100). Calcd for  $\text{C}_{20}\text{H}_{25}\text{ClOS}$ : M, 348.1314. Found:  $m/z$  348.1316.

**2-(*p*-Chlorophenylthio)-1,4-diphenyl-1-butanone (29)**: Colorless oil. IR (neat) 2925, 1682 (CO), 1475, 1448, 1095, 1014, 746, 699  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$   $\delta$  2.07—2.15 (1H, m), 2.29—2.36 (1H, m), 2.71—2.84 (2H, m), 4.37 (1H, t,

$J=7.2$  Hz), 7.13—7.29 (9H, m), 7.40—7.46 (2H, m), 7.54—7.57 (1H, m), 7.82—7.84 (2H, m). MS  $m/z$  (%) 366 ( $\text{M}^+$ , 4), 262 (42), 117 (91), 105 (71), 91 (100), 77 (39). Calcd for  $\text{C}_{22}\text{H}_{19}\text{ClOS}$ : M, 366.0844. Found:  $m/z$  366.0843.

***N*-Phenyl-3-(*p*-chlorophenylthio)-4-phenylbutanamide (30)**: Colorless oil. IR (neat) 3274 (NH), 2923, 1659 (CO), 1532, 1096, 752  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$   $\delta$  2.09—2.16 (1H, m), 2.36—2.43 (1H, m), 2.83—2.94 (2H, m), 3.68 (1H, t,  $J=7.2$  Hz), 7.04—7.56 (14H, m), 8.21 (1H, s). MS  $m/z$  (%) 381 ( $\text{M}^+$ , 23), 277 (99), 158 (42), 117 (41), 91 (100). Calcd for  $\text{C}_{22}\text{H}_{20}\text{ClNOS}$ : M, 381.0955. Found:  $m/z$  381.0963.

**Acknowledgments** We thank Mr. Shinya Kikuchi for his technical assistance. This work was supported by a Grant-in-Aid for Scientific Research No. 11640545 from the Ministry of Education, Culture, Sports, Science and Technology, Japan, which is gratefully acknowledged.

## References and Notes

- Block E., "Reactions of Organosulfur Compounds," Academic Press, New York, 1978, p. 47.
- Corey E. J., Seebach D. J., *J. Org. Chem.*, **31**, 4097—4099 (1966).
- Gilman H., Webb F. J., *J. Am. Chem. Soc.*, **62**, 987—988 (1940).
- Gilman H., Webb F. J., *J. Am. Chem. Soc.*, **71**, 4062—4066 (1949).
- Peterson D. J., *J. Org. Chem.*, **32**, 1717—1720 (1967).
- Wakefield B. J., "Organomagnesium Methods in Organic Synthesis," Academic Press, London, 1995.
- Richey H. G., Jr., "Grignard Reagents New Developments," John Wiley, Chichester, 2000.
- Generation of 1-(methylthio)ethenylmagnesium chlorides ( $\alpha$ -thioalkenylmagnesium chloride) from the corresponding ketenedithioacetal monoxides by ethylmagnesium chloride was known: Ogura K., Arai K., Tsuchihashi G., *Bull. Chem. Soc. Jpn.*, **55**, 3669—3670 (1982).
- Generation of the carbanion having oxygen (4: Y=O): Satoh T., Horiguchi K., *Tetrahedron Lett.*, **36**, 8235—8238 (1995).
- Satoh T., Kobayashi S., Nakanishi S., Horiguchi K., Irisa S., *Tetrahedron*, **55**, 2515—2528 (1999).
- Generation of the carbanion having nitrogen (4: Y=N): Satoh T., Ozawa M., Takano K., Kudo M., *Tetrahedron Lett.*, **39**, 2345—2348 (1998).
- Satoh T., Ozawa M., Takano K., Chyouma T., Okawa A., *Tetrahedron*, **56**, 4415—4425 (2000).
- Satoh T., Matsue R., Fujii T., Morikawa S., *Tetrahedron Lett.*, **41**, 6495—6499 (2000).
- Satoh T., Matsue R., Fujii T., Morikawa S., *Tetrahedron*, **57**, 3891—3898 (2001).
- Generation of the carbanion having a halogen (4: X=halogen): Satoh T., Takano K., *Tetrahedron*, **52**, 2349—2358 (1996).
- Satoh T., Takano K., Ota H., Someya H., Matsuda K., Koyama M., *Tetrahedron*, **54**, 5557—5574 (1998).
- Satoh T., Kurihara T., Fujita K., *Tetrahedron*, **57**, 5369—5375 (2001).
- Satoh T., Sakamoto T., Watanabe M., *Tetrahedron Lett.*, **43**, 2043—2046 (2001).
- A review for the chemistry of the sulfoxide-metal exchange reaction: Satoh T., *J. Syn. Org. Chem. Jpn.*, **54**, 481—489 (1996).
- Gutierrez C. G., Stringham R. A., Nitasaka T., Glasscock K. G., *J. Org. Chem.*, **45**, 3393—3395 (1980).
- Gutierrez C. G., Summerhays L. R., *J. Org. Chem.*, **49**, 5206—5213 (1984).
- Watanabe Y., Araki T., Ueno Y., Endo T., *Tetrahedron Lett.*, **72**, 5385—5388 (1986).
- Satoh T., Kubota K., *Tetrahedron Lett.*, **41**, 2121—2124 (2000).
- Satoh T., Sugiyama S., Ota H., *Tetrahedron Lett.*, **43**, 3033—3036 (2002).
- Wakefield B. J., "Organomagnesium Methods in Organic Synthesis," Academic Press, London, 1995, pp. 153—154.