

## Phosphinidenes and Related Intermediates. IV.<sup>1)</sup> Reactions of Phosphinothiolydenes with *cis*- and *trans*-Stilbene Oxides

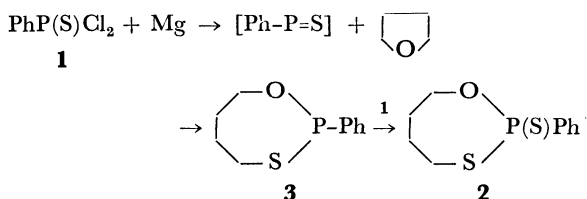
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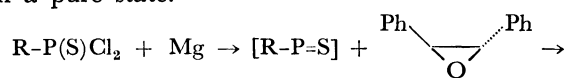
Phosphinothiolydenes were generated by the reaction of phosphonothioic dichlorides with magnesium. Reactions of phosphinothiolydenes with *cis*- and *trans*-stilbene oxides gave 1,3,2-oxathiaphospholane 2-sulfide derivatives (**6**, **7**, **9**, and **11**) stereospecifically, except for the reaction of phenylphosphinothiolydene with *trans*-stilbene oxide, along with *cis*- and/or *trans*-stilbenes. The formation mechanisms, which involve phenylphosphinothiolydene coordinated by the ethereal oxygen atom, and the conformation of 1,3,2-oxathiaphospholane 2-sulfides were discussed.

There is no report on reactions of phosphinidenes, phosphinylidenes, and phosphinothiolydenes with cyclic ethers, but reaction of phenylphosphinylidene with ketene acetal<sup>2)</sup> and reaction of phenylphosphinidene with allyl ethyl sulfide<sup>3)</sup> have been reported. In the previous paper,<sup>1)</sup> it has been reported that phenylphosphinothiolydene generated by the reaction of phenylphosphonothioic dichloride (**1**) with magnesium reacted with tetrahydrofuran (THF) to give 2-phenyl-1,3,2-oxathiaphospholane 2-sulfide (**2**), but phenylphosphinylidene generated from phenylphosphonic dichloride and magnesium gave no identified product with THF.



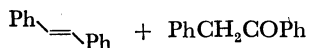
This paper describes the reactions of phosphinothiolydenes with *cis*- and *trans*-stilbene oxides, which are more reactive than THF, to afford insertion products into the C-O bond of the epoxides and deoxygenation products of the epoxides.

Phenylphosphinothiolydene generated from **1** and magnesium reacted with *trans*-stilbene oxide to give *trans*-stilbene (**4**), benzyl phenyl ketone (**5**), 2, *trans*-4,5-triphenyl- (**6**), and 2, *cis*-4,5-triphenyl-1,3,2-oxathiaphospholane 2-sulfides (**7**) in 65, 9, 8, and 17% yields, respectively, based on *trans*-stilbene oxide consumed. Among the isomers of **6** and **7**, 2, *c*-4, *t*-5- (**6a**), 2, *t*-4, *t*-5- (**7a**), and 2, *c*-4, *c*-5-triphenyl-1,3,2-oxathiaphospholane *r*-2-sulfides could be isolated in a pure state.



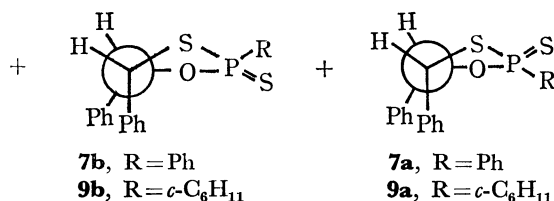
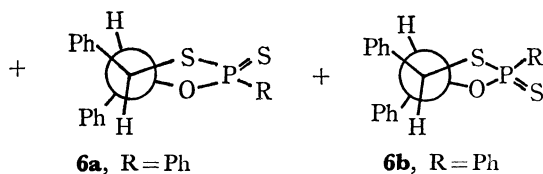
**1**, R = Ph

**8**, R = *c*-C<sub>6</sub>H<sub>11</sub>



**4**

**5**

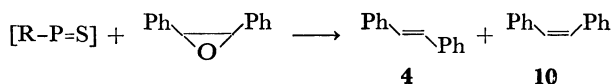


Cyclohexylphosphonothioic dichloride (**8**) reacted similarly with *trans*-stilbene oxide in the presence of magnesium to give **4**, 2-cyclohexyl-*t*-4, *t*-5-diphenyl- (**9a**), and 2-cyclohexyl-*c*-4, *c*-5-diphenyl-1,3,2-oxathiaphospholane *r*-2-sulfides (**9b**) in 34, 6, and 9% yields, respectively.

The structures of **6**, **7**, and **9** were confirmed by elemental analyses and spectral data. The assignment of *cis* or *trans* configuration between 4- and 5-phenyl groups in **6** and **7** was done by comparison of their spectral data with those of authentic samples synthesized by unequivocal routes. In the case of **9**, the assignment was done based on the similarity of the coupling constants of the methine protons to those of **7**.

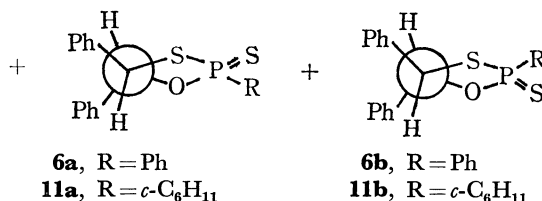
A mixture of **6a** and **6b** was synthesized from *threo*-2-mercapto-1,2-diphenylethan-1-ol<sup>4)</sup> and **1** using triethylamine as a base. Reaction of the *erythro* derivative<sup>4)</sup> and **1** gave a mixture of **7a** and **7b** by use of pyridine as a base, but the use of triethylamine afforded only **7b**.

The assignment of *cis* or *trans* between 2- and 4-substituents in **6**, **7**, and **9** was done based on chemical shifts and coupling constants of the methine protons by use of molecular models as will be discussed later.



**4**

**10**



*cis*-Stilbene oxide reacted with **1** in the presence of magnesium to afford *trans*- (**4**), *cis*-stilbenes (**10**), and **6** in 28, 2, and 31% yields, respectively. Similarly the reaction of *cis*-stilbene oxide with **8** in the presence of magnesium gave **4**, **10**, and 2-cyclohexyl-*trans*-4,5-diphenyl-1,3,2-oxathiaphospholane 2-sulfides (**11**) in 16, 14, and 32% yields, respectively, based on *cis*-

stilbene oxide consumed. In these reactions, **7** and **9** could not be detected by NMR.

In the presence of magnesium(II) chloride, the reaction of **1** with magnesium and *trans*-stilbene oxide gave **4**, **5**, **6**, and **7** in 39, 5, 18, and 1% yields, respectively, based on *trans*-stilbene oxide consumed. The product ratio of **6** and **7** in this reaction is remarkably different from that in the absence of magnesium(II) chloride.

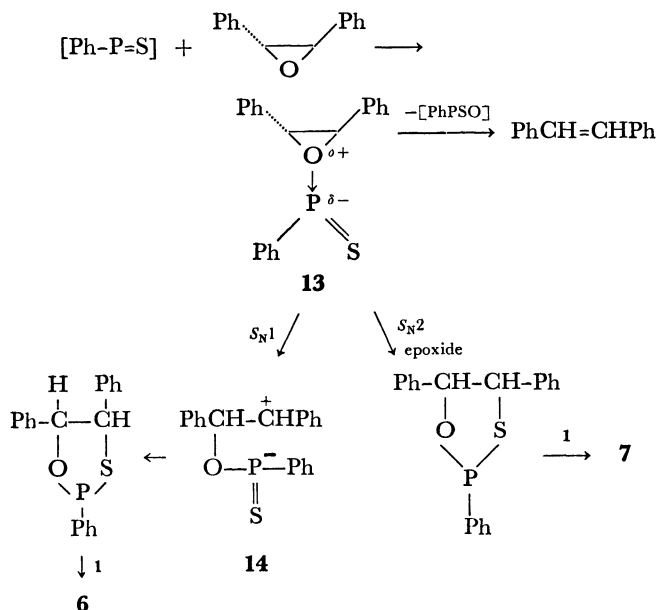
Reaction of *trans*-stilbene oxide with magnesium and magnesium(II) chloride gave no stilbenes but benzyl phenyl ketone (**5**) and *erythro*-2-chloro-1,2-diphenylethan-1-ol (**12**) in 53 and 43% yields, respectively, based on *trans*-stilbene oxide consumed. It is known that **5** is formed in the reaction of stilbene oxide with magnesium chloride.<sup>5)</sup>

Reactions of phosphinylidenes with stilbene oxides gave different and complicated products, except for the formation of stilbenes. These results will be reported in near future.

**Reaction Mechanism.** Only the reaction of **1** with *trans*-stilbene oxide and magnesium gave **5** and a mixture of inverted and retained 1,3,2-oxathiaphospholane 2-sulfide derivatives, indicating a contribution of  $S_N1$  pathway, but the other reactions gave only the inverted derivatives stereospecifically, suggesting the  $S_N2$  character. Moreover, in the reaction of **1** with magnesium and *trans*-stilbene oxide, the presence of magnesium(II) chloride increased the formation of retention products (**6**) and decreased that of inversion products (**7**), supporting an increase of a contribution of  $S_N1$  pathway by the epoxide coordinating to magnesium(II) chloride, because **6** is more thermodynamically stable than **7**.

Mechanism for the formation of **6** and **7** is considered as follows, though participation of Grignard type species,  $[\text{PhClPS}]^- + \text{MgCl}$ , could not be ruled out completely.

The mechanism involves phenylphosphinothioylidene coordinated by the oxygen atom of *trans*-stilbene oxide (**13**) as an intermediate.



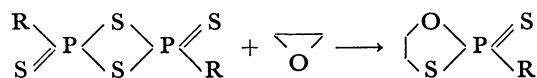
Stilbenes are considered to be produced by the decomposition of the intermediate (**13**), but isolation of the expected phosphonothioic acid was not tried.

The intermediate (**13**) attacks *trans*-stilbene oxide as sulfide anion in a  $S_N2$  fashion or cleavages in a  $S_N1$  manner to give **14**. Since the  $S_N2$  attack suffers a steric hindrance by the phenyl groups in the *trans* relation and the anionic center of the zwitterion (**14**) is stabilized by the *P*-phenyl group, the  $S_N1$  pathway becomes possible.

In the reaction with **8**, the  $S_N2$  attack suffers a similar steric hindrance by the phenyl groups, but the cyclohexyl group does not stabilize the zwitterion analogous to **14**. Thus, the  $S_N1$  pathway does not occur and the reaction becomes stereospecific.

In the case of *cis*-stilbene oxide, the reactions are stereospecific in the reactions with both **1** and **8**, because of almost no steric hindrance for the  $S_N2$  attack.

The formation of **2** in the reaction of THF with phenylphosphinothioylidene<sup>1)</sup> is explained by a similar mechanism. The following reaction has been reported to afford an analogous compound.<sup>6)</sup>



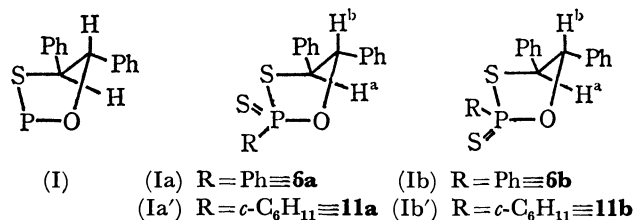
**Conformation of 6, 7, 9, and 11.** Their conformations were determined by consideration of NMR data and molecular models. The NMR data of the methine protons of **6**, **7**, **9**, and **11** are summarized in Table 1.

In the following discussion, it was assumed that protons in a 1,3-*cis* relation to a  $\text{P}=\text{S}$  group are deshielded, because protons in a 1,3-*cis* relation to a  $\text{P}=\text{O}$  group are deshielded in a five-membered ring<sup>7)</sup> and it has been reported that  $\text{P}=\text{O}$  and  $\text{P}=\text{S}$  groups show a similar tendency in the case of six-membered rings.<sup>8,9)</sup>

At first, the conformations of **6** and **11** are discussed.

The values of  $J_{\text{HCCH}}$ ,  $J_{\text{PSCH}}$ , and  $J_{\text{POCH}}$  for all possible conformations were estimated using dihedral angles obtained from the molecular models. For  $J_{\text{POCH}}$ , a relationship proposed by Bergesen and Albriktsen<sup>10)</sup> was used, but, for  $J_{\text{PSCH}}$ , a similar relationship was assumed considering that  $J_{\text{PSCH}}$  is usually larger than the corresponding  $J_{\text{POCH}}$ .<sup>11)</sup>

From these considerations, the most plausible conformation is that such as (I), in which four atoms of C-S-P-O bonds form one plane. To determine the full conformation, the chemical shifts of two methine protons were taken into account.



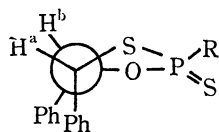
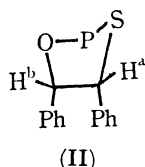
In the case of (Ia'),  $\text{H}^b$  should be deshielded by the  $\text{P}=\text{S}$  group, whereas, in the case of (Ib'),  $\text{H}^a$  should be deshielded. Thus, the  $\delta_{\text{H}^b} - \delta_{\text{H}^a}$  value in (Ia') becomes larger than that in (Ib'). Therefore, it is

TABLE 1. NMR DATA OF METHINE PROTONS OF **6**, **7**, **9**, AND **11** (IN CDCl<sub>3</sub>)

		<b>6a</b>	<b>6b</b>	<b>7a</b>	<b>7b</b>	<b>9a</b>	<b>9b</b>	<b>11a</b>	<b>11b</b>
$\delta$	SCH<	5.08	5.17	5.3	5.07	5.2	5.00	4.77	4.93
(ppm)	OCH<	5.83	5.52	6.38	5.72	6.23	5.77	5.62	5.32
$J_{\text{HCCH}}$ (Hz)		10.6	10.6	5	5	5	5.3	10.6	10.0
$J_{\text{PSCH}}$		0	0	14	12	12	12	0	0
$J_{\text{POCH}}$		1.5	2	5	8	5	7.3	1.6	0

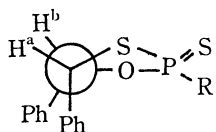
reasonable to consider that **11a** and **11b** have the conformations such as (Ia') and (Ib'), respectively. Since it has been known that the effects on H<sup>a</sup> and H<sup>b</sup> are analogous, even though an alkyl group on the phosphorus atom is substituted by a phenyl group,<sup>7,8</sup>) it may be reasonable to consider that **6a** and **6b** have the conformations such as (Ia) and (Ib), respectively.

Next, the conformations of **7** and **9** are discussed. On the basis of a similar consideration, the partial conformation (II) is the most reasonable for these compounds.



(IIa) R = Ph  $\equiv$  **7b**

(IIa') R = *c*-C<sub>6</sub>H<sub>11</sub>  $\equiv$  **9b**



(IIb) R = Ph  $\equiv$  **7a**

(IIb') R = *c*-C<sub>6</sub>H<sub>11</sub>  $\equiv$  **9a**

In the case of (IIa'), H<sup>a</sup> and H<sup>b</sup> should be shielded by the P=S group. In the case of (IIb'), H<sup>a</sup> and H<sup>b</sup> should be deshielded. Thus, it may be reasonable to consider that **9a** and **9b** have the full conformations such as (IIb') and (IIa'), respectively. In the cases of (IIa) and (IIb), it may be reasonable to consider that **7a** and **7b** have the full conformation such as (IIb) and (IIa), respectively.

## Experimental

All melting and boiling points are uncorrected. The instruments used for spectral measurements were the same as those described in the previous paper.<sup>1)</sup> All reactions were carried out under nitrogen.

**Materials.** The following compounds were prepared by the methods reported in the literature: phenylphosphonothioic (**1**)<sup>12)</sup> (bp 134–138 °C/14 mmHg), cyclohexylphosphonothioic dichlorides (**8**)<sup>13)</sup> (bp 96–97 °C/0.95 mmHg), *cis*-<sup>14)</sup> (mp 37.3–37.6 °C), and *trans*-stilbene oxides<sup>15)</sup> (mp 69.5–71 °C).

**Reaction of 1 in the Presence of trans-Stilbene Oxide.** a) *With Magnesium.* A solution of **1** (5.32 g, 25.2 mmol) in THF (7 ml) was added dropwise to a stirred mixture of magnesium (0.66 g, 27.5 mg-atom) and *trans*-stilbene oxide (2.47 g, 12.6 mmol) in THF (43 ml) under cooling with water occasionally, initiating by addition of a small amount of iodine. After the exothermal reaction ceased (about

1 hr), the mixture was refluxed with stirring for additional 2 hr. The solvent was removed *in vacuo*, and the residue was extracted with chloroform. The extract was washed with water, and dried with anhydrous magnesium sulfate. After evaporation, the residue was chromatographed using a silica gel dry column to give 0.45 g (2.3 mmol) of unchanged *trans*-stilbene oxide, 1.21 g (6.7 mmol) of **4**, 0.17 g (0.9 mmol) of **5**, mp 56–57 °C (from *n*-hexane) (lit.<sup>16)</sup> 57 °C), 0.29 g (0.8 mmol) of a mixture of **6a** and **6b** (18 : 1 by NMR), and 0.62 g (1.7 mmol) of a mixture of **7a** and **7b** (1.1 : 1 by NMR). The yields of **4**, **5**, **6**, and **7** were 65, 9, 8, and 17%, respectively, based on *trans*-stilbene oxide consumed.

Recrystallization of the mixture of **6a** and **6b** from methanol gave pure **6a**, mp 112.5–113.5 °C. IR (KBr): 1107 (P-Ph) and 975 cm<sup>-1</sup> (P-O-C); NMR (CDCl<sub>3</sub>):  $\delta$  5.08 (d,  $J_{\text{HCCH}}$  10.6 Hz, 1H, S-CH<), 5.83 (dd,  $J_{\text{HCCH}}$  10.6,  $J_{\text{POCH}}$  1.5 Hz, 1H, O-CH<), 7.0–7.4 (m, 10 H, 2Ph), 7.4–7.9 (m, 3H, 2H<sup>m</sup> and H<sup>p</sup> of P-Ph), and 7.9–8.45 (m,  $J_{\text{PH}}$  16 Hz, 2H, 2H<sup>o</sup> of P-Ph); Mass: *m/e* 368 (M<sup>+</sup>).

Found: C, 65.36; H, 4.43; S, 17.12%. Calcd for C<sub>20</sub>H<sub>17</sub>OPS<sub>2</sub>: C, 65.20; H, 4.65; S, 17.40%.

Compound **6b** could not be isolated from the mixture in the pure state. NMR (CDCl<sub>3</sub>):  $\delta$  5.17 (d,  $J_{\text{HCCH}}$  10.6 Hz, 1H, S-CH<) and 5.52 (dd,  $J_{\text{POCH}}$  2,  $J_{\text{HCCH}}$  10.6 Hz, 1H, O-CH<). The signal of the three phenyl groups were not clearly distinguished from those of **6a**.

Recrystallization of the mixture of **7a** and **7b** from methanol gave pure **7a** and **7b**.

**7a**: mp 154–155 °C; IR (KBr): 1115 (P-Ph) and 955 cm<sup>-1</sup> (P-O-C); NMR (CDCl<sub>3</sub>):  $\delta$  5.3 (dd,  $J_{\text{HCCH}}$  5,  $J_{\text{PSCH}}$  14 Hz, 1H, S-CH<), 6.38 (t,  $J_{\text{HCCH}} = J_{\text{POCH}}$  5 Hz, 1H, O-CH<), 6.85–7.45 (m, 10 H, 2Ph), 7.45–7.8 (m, 3H, 2H<sup>m</sup> and H<sup>p</sup> of P-Ph), and 7.95–8.4 (m,  $J_{\text{PH}}$  16 Hz, 2H, 2H<sup>o</sup> of P-Ph); Mass: *m/e* 368 (M<sup>+</sup>).

**7b**: mp 129–131 °C; IR (KBr): 1102 (P-Ph) and 950 cm<sup>-1</sup> (P-O-C); NMR (CDCl<sub>3</sub>):  $\delta$  5.07 (dd,  $J_{\text{HCCH}}$  5,  $J_{\text{PSCH}}$  12 Hz, 1H, S-CH<), 5.72 (dd,  $J_{\text{HCCH}}$  5,  $J_{\text{POCH}}$  8 Hz, 1H, O-CH<), 7.0–7.3 (m, 10 H, 2Ph), 7.3–7.65 (m, 3H, 2H<sup>m</sup> and H<sup>p</sup> of P-Ph), and 7.9–8.4 (m,  $J_{\text{PH}}$  16 Hz, 2H, 2H<sup>o</sup> of P-Ph); Mass: *m/e* 368 (M<sup>+</sup>).

Found: C, 65.17; H, 4.66; S, 17.35%. Calcd for C<sub>20</sub>H<sub>17</sub>OPS<sub>2</sub>: C, 65.20; H, 4.65; S, 17.40%.

b) *With Magnesium-Magnesium(II) Chloride.* A suspended mixture of magnesium (0.66 g, 27.5 mg-atom), magnesium(II) chloride (2.61 g, 27.5 mmol), and *trans*-stilbene oxide (2.47 g, 12.6 mmol) in THF (45 ml) was stirred under reflux until magnesium(II) chloride had almost dissolved. At room temperature, a solution of **1** (5.30 g, 25.1 mmol) in THF (5 ml) was added drop by drop with stirring to the above mixture. A small amount of iodine was added to start the reaction. The reaction was so exothermic that the mixture was cooled with water occasionally. The reaction mixture was stirred until the exothermal reaction had ceased (about 1 hr), and then further stirred under reflux for 2 hr. After a similar work-up, the residue was chromatographed using

a silica gel dry column to give 0.17 g (0.9 mmol) of unchanged oxide, 0.82 g (4.6 mmol) of **4**, 0.11 g (0.6 mmol) of **5**, 0.76 g (2.1 mmol) of a mixture of **6a** and **6b**, and 0.04 g (0.1 mmol) of a mixture of **7a** and **7b**. They yields of **4**, **5**, **6**, and **7** were 39, 5, 18 and 1%, respectively, based on *trans*-stilbene oxide consumed.

**Reaction of 8 with Magnesium and trans-Stilbene Oxide.** A solution of **8** (4.34 g, 20.0 mmol) in THF (5 ml) was added drop by drop to a stirred suspension containing magnesium (0.53 g, 21.8 mg-atom), *trans*-stilbene oxide (2.00 g, 10.3 mmol), and THF (40 ml). When a small amount of iodine was added, an exothermal reaction occurred, and ended in about 1 hr. The mixture was stirred at room temperature for 14 hr. After a similar work-up, the residue was chromatographed using a silica gel dry column to give 0.63 g (3.5 mmol) of **4**, 0.23 g (0.6 mmol) of **9a**, and 0.33 g (0.9 mmol) of **9b**. The yields of **4**, **9a**, and **9b** were 34, 6, and 9%, respectively, based on *trans*-stilbene oxide used.

**9a:** mp 162.3–163.3 °C (from hexane); NMR (CDCl<sub>3</sub>):  $\delta$  1.0–3.0 (m, 11H, *c*-C<sub>6</sub>H<sub>11</sub>), 5.2 (dd,  $J_{\text{HCH}}$  5,  $J_{\text{PSCH}}$  12 Hz, 1H, S-CH), 6.23 (t,  $J_{\text{HCH}}=J_{\text{POCH}}$  5 Hz, 1H, O-CH), and 7.08 (m, 10 H, 2Ph); Mass:  $m/e$  374 (M<sup>+</sup>).

Found: C, 64.28; H, 6.24; S, 17.13%. Calcd for C<sub>20</sub>-H<sub>23</sub>OPS<sub>2</sub>: C, 64.14; H, 6.19; S, 17.12%.

**9b:** mp 167–168 °C (from hexane); NMR (CDCl<sub>3</sub>):  $\delta$  1.0–2.6 (m, 11H, *c*-C<sub>6</sub>H<sub>11</sub>), 5.00 (dd,  $J_{\text{HCH}}$  5.3,  $J_{\text{PSCH}}$  12 Hz, 1H, S-CH), 5.77 (dd,  $J_{\text{HCH}}$  5.3,  $J_{\text{POCH}}$  7.3 Hz, 1H, O-CH), and 7.12 (s, 10 H, 2Ph); Mass:  $m/e$  374 (M<sup>+</sup>).

Found: C, 64.37; H, 6.30; S, 17.04%. Calcd for C<sub>20</sub>-H<sub>23</sub>OPS<sub>2</sub>: C, 64.14; H, 6.19; S, 17.12%.

**Reaction of 1 with Magnesium and cis-Stilbene Oxide.** A solution of **1** (2.49 g, 11.8 mmol) in THF (5 ml) was added dropwise to a stirring mixture containing magnesium (0.30 g, 12.5 mg-atom), *cis*-stilbene oxide (1.15 g, 5.9 mmol), and THF (20 ml). To activate magnesium was added a small amount of iodine. After the exothermal reaction ceased, the mixture was further stirred under reflux for 2 hr. After a similar treatment, the residue was chromatographed using a silica gel dry column to give 0.10 g (0.5 mmol) of unchanged oxide, 0.27 g (1.5 mmol) of **4**, 0.02 g (0.1 mmol) of **10**, and 0.62 g (1.7 mmol) of a mixture of **6a** and **6b** (1.8 : 1 by NMR), but **7a** and **7b** were not detected by tlc and NMR. The yields of **4**, **10**, and **6** were 28, 2, and 31%, respectively, based on the *cis*-stilbene oxide consumed.

**Reaction of 8 with Magnesium and cis-Stilbene Oxide.** A solution of **8** (1.95 g, 9.0 mmol) in THF (5 ml) was added dropwise with stirring to a mixture of magnesium (0.23 g, 9.5 mg-atom) and *cis*-stilbene oxide (0.89 g, 4.5 mmol) in THF (18 ml). A small amount of iodine was added to start the reaction. After exothermal reaction ended, the mixture was refluxed for 2 hr. After a similar treatment, the residue was chromatographed using a silica gel dry column to give 0.02 g (0.1 mmol) of unchanged oxide, 0.12 g (0.7 mmol) of **4**, 0.11 g (0.6 mmol) of **10**, and 0.54 g (1.4 mmol) of a mixture of **11a** and **11b** (1.7 : 1 by NMR). However, **9a** and **9b** were not detected by NMR. The yields of **4**, **10**, and **11** were 16, 14, and 32%, respectively, based on *cis*-stilbene oxide consumed. The mixture of **11a** and **11b** could not be separated by tlc and fractional recrystallization. The following data are those of the mixture, mp 139–160 °C (from methanol or hexane); NMR (CDCl<sub>3</sub>):  $\delta$  1.0–2.8 (m, *c*-C<sub>6</sub>H<sub>11</sub>), 4.77 (d,  $J_{\text{HCH}}$  10.6 Hz, S-CH of **11a**), 4.93 (d,  $J_{\text{HCH}}$  10 Hz, S-CH of **11b**), 5.32 (d,  $J_{\text{HCH}}$  10 Hz, O-CH of **11b**), 5.62 (dd,  $J_{\text{HCH}}$  10.6,  $J_{\text{POCH}}$  1.6 Hz, O-CH of **11a**), and 7.25 (s, Ph); Mass:  $m/e$  374 (M<sup>+</sup>).

Found: C, 64.44; H, 6.21; S, 16.98%. Calcd for C<sub>20</sub>-H<sub>23</sub>OPS<sub>2</sub>: C, 64.14; H, 6.19; S, 17.12%.

#### Preparation of **7a** and **7b**. a) Using Pyridine as Base.

A solution of *erythro*-2-mercapto-1,2-diphenylethan-1-ol<sup>4)</sup> (0.23 g, 1 mmol) and pyridine (0.4 ml) in dry benzene (10 ml) was added with stirring to a solution of **1** (0.23 g, 1.1 mmol) in dry benzene (40 ml) over 6 hr. Stirring was continued at room temperature for 17 hr and then under reflux for 9 hr. After filtration of pyridinium chloride and similar work-up, the residue was chromatographed using a silica gel dry column to give 0.07 g (0.19 mmol, 19%) of a mixture of **7a** and **7b** (1 : 1).

b) Using Triethylamine as Base. A solution of *erythro*-diphenylethane derivative (0.42 g, 1.8 mmol) and triethylamine (1.2 ml) in dry benzene (10 ml) was added to a stirring solution of **1** (0.38 g, 1.8 mmol) in dry benzene (40 ml) over 9 hr. The mixture was further stirred at room temperature for 15 hr. Similar treatment gave 0.12 g (0.32 mmol, 18%) of **7b**, mp 129–131 °C (from methanol), but **7a** could not be detected by NMR.

**Preparation of 6a and 6b.** A solution of *threo*-2-mercapto-1,2-diphenylethan-1-ol<sup>4)</sup> (0.55 g, 2.4 mmol) and triethylamine (1.6 ml) in dry benzene (10 ml) was added to a stirring solution of **1** (0.51 g, 2.4 mmol) in dry benzene (40 ml) over 8 hr, and the mixture was further stirred at room temperature for 16 hr. Similar treatment gave 0.05 g (0.15 mmol) of a mixture of **6a** and **6b**, and 0.24 g (1.0 mmol) of the starting ethane. The yield was 12% based on the diphenylethane derivative consumed.

**Reaction of trans-Stilbene Oxide with Magnesium–Magnesium(II) Chloride.** A mixture of magnesium (0.22 g, 9.3 mg-atom) and magnesium(II) chloride (0.86 g, 9.1 mmol) in THF (40 ml) was stirred under reflux for 2 hr until magnesium(II) chloride had dissolved. A few drops of carbon tetrachloride were added to activate magnesium, and the mixture was stirred under reflux. A solution of *trans*-stilbene oxide (1.57 g, 8.0 mmol) in THF (10 ml) was added dropwise to the above mixture, and the mixture was further stirred under reflux for 96 hr. Similar treatment gave 0.98 g (5.0 mmol) of unchanged oxide, 0.32 g (1.6 mmol) of **5**, 0.31 g (1.3 mmol) of *erythro*-2-chloro-1,2-diphenylethan-1-ol (**12**), mp 81–82 °C (from hexane) (lit.<sup>17)</sup> 76–77 °C); Mass:  $m/e$  196 (M<sup>+</sup>–HCl). The yields of **5** and **12** were 53 and 43%, respectively, based on *trans*-stilbene oxide consumed.

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