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A series of new types of sulfur-bridged Lewis acids were synthesized. The ligands that contained the sulfoxide or sulfone as the joint moieties of two phenols were found to quantitatively give Lewis acids. These obtained Lewis acids also have good discrimination properties of some epoxides. The reaction properties of the Lewis acids were studied using the rearrangement of the epoxides to carbonyl compounds.

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### Introduction.

A bulky oxygenophilic organoaluminum reagent has been recognized as a highly useful Lewis acid in selective organic synthesis and has also been used in other areas of chemistry [1-8]. Recently, Schaverien [9] and Okuda [10] reported titanium alkoxide complexes that contain a bidentate bis(phenoxy) ligand [11-15] as catalysis for olefin oligo-polymerization. These studies also showed the usefulness of this new type of Lewis acid which contains two phenols that are connected with a linker moiety. In a previous study, the authors developed a new type of trisulfide ligand for Lewis acids that contained the linked bisphenol moiety [16]. In spite of any effort to obtain a pure Lewis acid, the reaction of all the sulfides (**1a**, **2a**, **3a**, and **4a**) and the disulfides (**1b**, **2b**, **3b**, and **4b**) with trimethylaluminum gave a mixture of Lewis acids. On the other hand, we determined the usefulness of sulfoxide-bridged bisphenol type ligands (**7**, **8**, **9**, **10**, and **11**) and sulfone-bridged bisphenol type ligands (**12**, **13**, **14**, and **15**) to give new types of Lewis acids. In this study, the authors discuss the synthesis and properties of methyl[2,2'-sulfoxidebis(phenoxy)]aluminum (**17**, **18**, **19**, **20**, and **21**) and methyl[2,2'-sulfonebis(phenoxy)]aluminum (**22**, **23**, **24**, and **25**).

### Results and Discussion.

#### Preparation.

The syntheses of the sulfides (**1a**, **2a**, **3a**, **4a**) were carried out using our known method [16]. Bis(3-bromo-5-*t*-butyl-2-hydroxyphenyl)sulfide (**6**) was obtained by bromination of the sulfide (**5**) [17] in 68% yield. The sulfoxide-type ligands and sulfone-type ligands were synthesized by the oxidation of the corresponding sulfide (**1a**, **2a**, **3a**, **4a** and **6**). The oxidation of the sulfide (**1a**, **2a**, **3a**, **4a** and **6**) with *m*-chloroperbenzoic acid gave the sulfoxides (**7**, **8**, **9**, **10**, and **11**) in 76%, 81%, 33%, 47%, and 53% yields respectively. The treatment of the sulfides (**1a**, **2a**, **3a**, **4a** and **6**) with hydrogen peroxide gave the sulfones (**12**, **13**, **14**, **15**, and **16**) in 66%, 91%, 68%, 77%, and 81% yields respectively. The syntheses of the new type of

Lewis acids incorporating bisphenols linked by a sulfoxide or sulfone were carried out by the reaction of the obtained nine ligands and trimethylaluminum at room temperature. However, the synthesis of **25** was done at 0° due to the instability of **25** at room temperature [18].

#### <sup>1</sup>H NMR of New Type Lewis Acids.

The <sup>1</sup>H nmr analyses of the new type Lewis acids are summarized in Table 5. In the case of the sulfoxide-type Lewis acid, the chemical shifts of the methyl groups that are connected to the aluminum of the Lewis acids were observed at -0.51 ~ -0.40 ppm. In the case of the sulfone-type Lewis acids, the chemical shifts were seen at -0.39 ~ -0.31 ppm. The chemical shift of the methyl group connected to the aluminum of the trisulfide-type Lewis acids was at -0.34 ~ -0.25 ppm [16]. In addition, the <sup>1</sup>H nmr showed clean signals of the aromatic protons and no phenolic OH signals. These results also support the formation of the cyclic Lewis acids. We confirmed the formation of these cyclic Lewis acids, based on cryoscopy measurements. The obtained molecular weight of **17** (MW 510) closely corresponded with the value (MW 498) calculated for a cyclic and monomeric species. Also, that of **22** (MW 490) also corresponded with the calculated value (MW 514).

#### Reactivities of Lewis Acids.

The acid catalyzed rearrangement of epoxides to carbonyl compounds is a useful transformation, but only a few reagents can be employed with respect to the efficiency of the reaction [19]. This rearrangement was used as a typical reaction to evaluate the effectiveness of the Lewis acids [20]. Table 2 shows the results for the transformation of *trans*-stilbene oxides in dichloromethane with the Lewis acids under various conditions, which gave only the diphenylacetaldehyde. The sulfoxide-type Lewis acids (**17-21**) showed no reactivity with the *trans*-stilbene oxides. On the other hand, the *p*-chloro or *p*-bromo or *o*-bromo substituted sulfone type Lewis acids (**24**, **25**, **26**) were found to have a good propensity to convert the *trans*-stilbene oxides to diphenylacetaldehydes at room temperature. Interestingly, even at -30°, the alde-

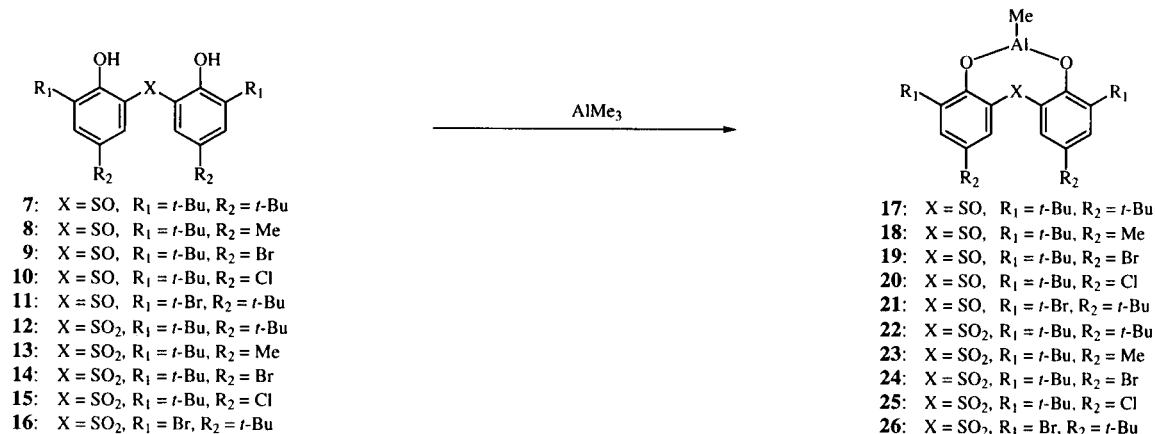
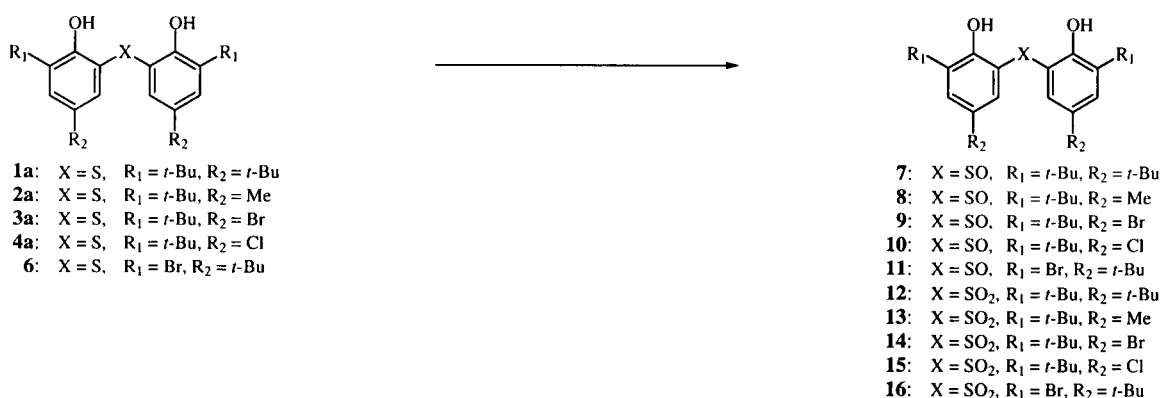
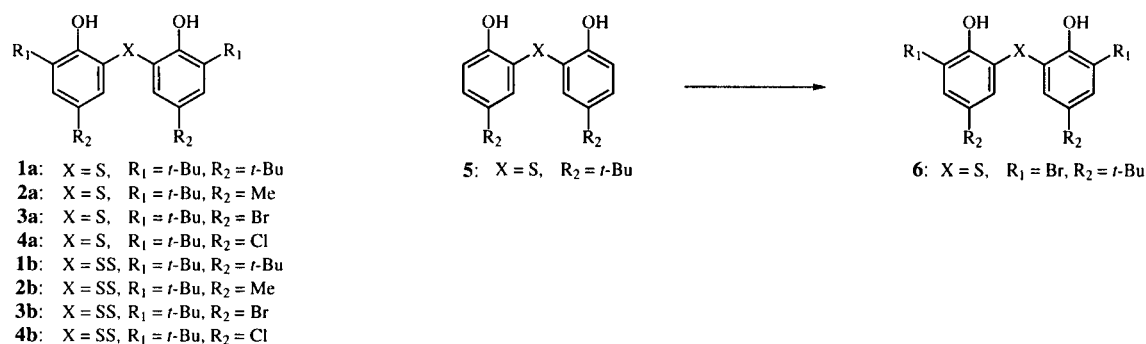


Table 1

<sup>1</sup>H NMR Data of Lewis Acids

Lewis Acid	δ (AlMe)/ppm	δ (Ar-H)/ppm	
<b>17</b>	-0.51	7.05	7.44
<b>18</b>	-0.51	6.87	7.17
<b>19</b>	-0.47	7.19	7.46
<b>20</b>	-0.46	7.06	7.34
<b>21</b>	-0.40	7.11	7.72
<b>22</b>	-0.39	7.47	7.52
<b>23</b>	-0.39	7.25	7.30
<b>24</b>	-0.35	7.53	7.61
<b>25</b>	-0.35	7.41	7.48
<b>26</b>	-0.31	7.52	7.79

hyde was obtained in 98% yield with the *o*-brominated sulfone-type Lewis acid (**26**). Table 3 shows the results of the transformation of the styrene oxides with the Lewis acids under various conditions. In this case, some sulfoxide-type Lewis acids were found to be able to convert the epoxide to an aldehyde (entry 4 and 7). Comparing these results with that of the *trans*-stilbene oxide, with the less bulky epoxide (styrene oxide) seems to be able to easily coordinate to the Lewis acids and then convert to the aldehyde with excellent yield.

The yields of the aldehyde were not good in some cases (entries 11, 13, 14, 15, 16, and 18). This result may be explained by the polymerization of the obtained aldehyde in the presence of the Lewis acids [21]. The result shown

Table 2  
Reactivities of *trans*-Stilbene Oxide with Sulfoxide- or Sulfone-bridged Lewis Acids

Entry	Lewis Acid	Amount of Lewis Acid (mole %)	Conditions (°)	Aldehyde % Yield [a]	Recovered Epoxide % [a]
1	<b>17</b>	10	room temperature	0	100
2	<b>18</b>	10	room temperature	0	100
3	<b>19</b>	10	room temperature	0	100
4	<b>20</b>	10	room temperature	0	100
5	<b>21</b>	10	room temperature	0	100
6	<b>22</b>	10	room temperature	2	98
7	<b>22</b>	100	-30	0	100
8	<b>23</b>	10	room temperature	0	100
9	<b>23</b>	100	-30	0	100
10	<b>24</b>	10	room temperature	91	5
11	<b>24</b>	100	-30	31	69
12	<b>25</b>	10	room temperature	94	6
13	<b>25</b>	100	-30	34	66
14	<b>26</b>	10	0	<99	trace
15	<b>26</b>	100	-30	98	trace

[a] Yields were determined by <sup>1</sup>H nmr spectra.

Table 3  
Reactivities of Styrene Oxide with Sulfoxide- or Sulfone-bridged Lewis Acids

Entry	Lewis Acid	Amount of Lewis Acid (mole %)	Conditions (°) (Minutes)	Aldehyde % Yield [a]	Recovered Epoxide % [a]
1	<b>17</b>	10	room temperature, 60	0	100
2	<b>18</b>	10	room temperature, 60	0	100
3	<b>19</b>	10	room temperature, 60	7	90
4	<b>19</b>	100	room temperature, 60	88	0
5	<b>19</b>	100	-80, 60	5	92
6	<b>20</b>	10	room temperature, 60	8	88
7	<b>20</b>	100	room temperature, 60	90	0
8	<b>20</b>	100	-80, 60	6	90
9	<b>21</b>	10	0, 60	6	92
10	<b>22</b>	10	0, 60	25	68
11	<b>22</b>	100	-80, 60	53	0
12	<b>23</b>	10	room temperature, 60	45	46
13	<b>23</b>	100	-80, 60	52	0
14	<b>24</b>	10	room temperature, 60	76	0
15	<b>24</b>	100	-80, 60	53	0
16	<b>25</b>	10	room temperature, 60	45	0
17	<b>25</b>	100	-80, 10	80	0
18	<b>25</b>	100	-80, 60	48	0

[a] Yields were determined by <sup>1</sup>H nmr spectra.

in Table 4 exhibit the highly selective conversion of the less steric epoxide to an aldehyde. Lewis acids (**22-25**) were found to be useful to provide excellent and selective conversion of styrene oxide to 2-phenylacetaldehyde. On the other hand, the trisulfide-type Lewis acid (**27-30**) [16] converts both epoxides at -80° [22]. The reaction site of the Lewis acid (**22-25**), which were formed by two phenols and the bridge-sulfone moiety, are so small that they can not accommodate the  $\beta$ -methylstyrene oxide. Table 5 also shows the excellent and selective conversion of styrene oxide (entries 1-8).

Table 5 also shows the selective conversion of styrene oxide when we used the 1:1 mixture of styrene oxide and *trans*-stilbene oxide as the reaction substrate. Lewis acids (**19**), (**20**), (**22**), and (**23**) can exclusively convert styrene oxide at room temperature. These results must be useful for the selective synthesis from a less substituted epoxide to an aldehyde at room temperature without using any special protecting reagents.

In conclusion, we investigated the syntheses of sulfoxide- or sulfone-bridged Lewis acids and found high reactivity of the sulfone-bridged Lewis acids compared with

Table 4  
Selective Conversion of *trans*-Styrene Oxide and  $\beta$ -Methylstyrene Oxide with Lewis Acids





Entry	Lewis Acid	Conditions ( $^{\circ}$ , Minutes)	Epoxides	Conversion (%)
1	17	room temperature, 60		0/0
2	18	room temperature, 60		0/0
3	19	room temperature, 60		100/0
4	20	room temperature, 60		100/0
5	22	-80, 10		100/0
6	23	-80, 10		100/0
7	24	-80, 10		100/0
8	25	-80, 10		100/0
9	27	-80, 10		89/51
10	28	-80, 10		88/57
11	29	-80, 10		91/58
12	30	-80, 10		95/56

Table 5  
Selective Conversion of Styrene Oxide and *trans*-Stilbene Oxide with Lewis Acids

Entry	Lewis Acid	Conditions ( $^{\circ}$ , Minutes)	Epoxides	Conversion (%)
1	17	room temperature, 60		0/0
2	18	room temperature, 60		0/0
3	19	room temperature, 60		100/11
4	20	room temperature, 60		100/13
5	22	room temperature, 60		100/7
6	23	room temperature, 60		100/9
7	24	-80, 10		100/0
8	25	-80, 10		100/0
9	27	-80, 10		88/10
10	28	-80, 10		84/23
11	29	-80, 10		100/42
12	30	-80, 10		100/45

that of the sulfoxide-bridged type Lewis acids, and elucidated the selective conversion properties from styrene oxide to an aldehyde using some new Lewis acids.

## EXPERIMENTAL

All of the melting points are uncorrected. The  $^1\text{H}$  nmr spectra were recorded on a Varian Mercury 200 or a Varian INOVA 500 instrument at 500 MHz, using TMS as the internal reference. The ir (KBr disk) and mass spectra (70 eV) were recorded on Hitachi EPI-S2 and JEOL AX-350 spectrometers, respectively. Elemental analyses were performed using a Perkin-Elmer PE2400-II CHNS/O analyzer. Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385) without any pretreatment. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and chloroform were dried over tetraphosphorus decaoxide ( $\text{P}_4\text{O}_{10}$ ), and then freshly distilled before use. The trimethylaluminum in hexane was commercially available from the Kanto Chemical Co., Inc. Cryoscopy was carried out using a SANSYO Beckmann thermometer. The syntheses of **1a**, **2a**, **3a**, **4a**, **1b**, **2b**, **3b**, and **4b** have been reported in our previous paper [16].

General Procedure for the Synthesis of Sulfoxides **7**, **8**, **9**, and **10**.

Bis(3,5-di-*t*-butyl-2-hydroxyphenyl)sulfoxide (**7**).

To a solution of sulfide **1a** (0.5 g, 1.1 mmoles) in chloroform (30 ml) was added a solution of *m*-chloroperbenzoic acid (0.195 g, 1.1 mmoles) in chloroform (100 ml) over a period of 5 hours at  $0^{\circ}$  and the reaction mixture was stirred for 8 hours at room temperature. The obtained colorless needles of *m*-chlorobenzoic acid were removed by filtration, the filtrate was washed with two 100 ml portions of saturated sodium hydrogen sulfite, with three 100 ml portions of saturated sodium hydrogen carbonate, and with three 100 ml portions of water. After the dichloromethane was removed, the residue was chromatographed (silica gel/hexane-ethyl acetate = 40/1) to give bis(3,5-di-*t*-butyl-2-hydroxyphenyl)sulfoxide (**7**) (0.39 g, 76%), pale yellow crystals, mp  $130\text{--}132^{\circ}$  (from hexane);  $^1\text{H}$  nmr (200 MHz, deuteriochloroform):  $\delta$  1.21 (s, 18H), 1.41 (s, 18H), 6.72 (d,  $J = 2.1$  Hz, 2H), 7.45 (d,  $J = 2.1$  Hz, 2H), 9.38 (s, 2H, -OH);  $^{13}\text{C}$  nmr (50.3 MHz, deuteriochloroform):  $\delta$  29.5, 31.3, 34.4, 35.4, 120.8, 121.6, 128.1, 139.4, 142.0, 155.6; ir:  $3259\text{ cm}^{-1}$ ,  $\nu$  O-H; ei-ms:  $m/z$  (%) 458 ( $\text{M}^+$ , 32).

Anal. Calcd. for  $\text{C}_{28}\text{H}_{42}\text{O}_3\text{S}$ : C, 73.32; H, 9.23. Found: C, 73.21; H, 9.30.

Bis(3-*t*-butyl-5-methyl-2-hydroxyphenyl)sulfoxide (**8**).

The sulfoxide (**8**) was obtained by the reaction of the sulfide **2a** in 81% yield as colorless plates, mp 157-159° (from hexane); <sup>1</sup>H nmr (200 MHz, deuteriochloroform): δ 1.39 (s, 18H), 2.23 (s, 6H), 6.63 (d, J = 1.5 Hz, 2H), 7.19 (d, J = 1.5 Hz, 2H), 9.34 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 20.80, 29.42, 35.14, 122.01, 124.22, 128.71, 131.96, 139.87, 155.44; ir: 3201 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 374 (M<sup>+</sup>, 100).

*Anal.* Calcd. for C<sub>22</sub>H<sub>30</sub>O<sub>3</sub>S: C, 70.55; H, 8.07. Found: C, 70.45; H, 7.99.

Bis(5-bromo-3-*t*-butyl-2-hydroxyphenyl)sulfoxide (**9**).

The sulfoxide (**9**) was obtained by the reaction of the sulfide **3** in 85% yield as yellow crystals, mp 170-172° (from hexane); <sup>1</sup>H nmr (200 MHz, deuteriochloroform): δ 1.39 (s, 18H), 7.02 (d, J = 2.2 Hz, 2H), 7.50 (d, J = 2.2 Hz, 2H), 9.34 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 20.80, 29.42, 35.14, 122.01, 124.22, 128.71, 131.96, 139.87, 155.44; ir: 3214 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 504 (M<sup>+</sup>, 12).

*Anal.* Calcd. for C<sub>20</sub>H<sub>24</sub>Br<sub>2</sub>O<sub>3</sub>S: C, 47.64; H, 4.80. Found: C, 47.38; H, 4.60.

Bis(3-*t*-butyl-5-chloro-2-hydroxyphenyl)sulfoxide (**10**).

The sulfoxide (**10**) was obtained by the reaction of the sulfide **4a** in 47% yield as colorless powder, mp 157-159° (from hexane); <sup>1</sup>H nmr (200 MHz, deuteriochloroform): δ 1.30 (s, 18H), 7.58 (d, J = 2.2 Hz, 2H), 7.62 (d, J = 2.2 Hz, 2H), 8.28 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 29.2, 35.5, 123.2, 123.4, 125.0, 131.5, 142.4, 156.0; ir: 3158 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 414 (M<sup>+</sup>, 70).

*Anal.* Calcd. for C<sub>20</sub>H<sub>24</sub>Cl<sub>2</sub>O<sub>3</sub>S: C, 57.83; H, 5.82. Found: C, 57.58; H, 5.60.

General Procedure for the Synthesis of Sulfone **12**, **13**, **14**, and **15**.Bis(3,5-di-*t*-butyl-2-hydroxyphenyl)sulfone (**12**).

To a solution of the sulfide **1a** (0.5 g, 1.1 mmoles) in acetic acid (35 ml) was added 30% hydrogen peroxide (2.5 ml, 22 mmoles) and the reaction mixture was heated at 100° with stirring for 1 hour, then cooled to room temperature. The reaction mixture was poured into ice water (10 ml). The precipitate was collected by filtration, and dissolved into chloroform (30 ml). The solution was washed with water (50 ml, five times) and brine (50 ml) and the dried over anhydrous sodium sulfate and concentrated. Recrystallization from hexane gave **12** as colorless crystals (0.35 g, 66%), mp 174-176° (from ethylacetate-hexane); <sup>1</sup>H nmr (200 MHz, deuteriochloroform): δ 1.24 (s, 18H), 1.39 (s, 18H), 7.50 (d, J = 2.4 Hz, 2H), 7.52 (d, J = 2.4 Hz, 2H), 9.41 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 29.4, 31.2, 35.6, 121.8, 123.8, 130.9, 139.0, 142.6, 151.9; ir: 3437 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 474 (M<sup>+</sup>, 100).

*Anal.* Calcd. for C<sub>28</sub>H<sub>42</sub>O<sub>4</sub>S: C, 70.85; H, 8.92. Found: C, 71.03; H, 9.17.

Bis(3-*t*-butyl-2-hydroxy-5-methylphenyl)sulfone (**13**).

Compound **13** was obtained by the reaction of **2a** with hydrogen peroxide in 91% yield as a colorless powder, mp 174-176° (from ethyl acetate-hexane); <sup>1</sup>H nmr (200 MHz, deuterio-

chloroform): δ 1.40 (s, 18H), 2.18 (s, 6H), 7.26 (s, 4H), 9.51 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 20.7, 29.4, 35.4, 123.7, 125.3, 129.3, 134.6, 139.5, 152.3; ir: 3319 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 390 (M<sup>+</sup>, 100).

*Anal.* Calcd. for C<sub>22</sub>H<sub>30</sub>O<sub>4</sub>S: C, 67.66; H, 7.74. Found: C, 67.45; H, 7.50.

Bis(5-bromo-3-*t*-butyl-2-hydroxyphenyl)sulfone (**14**).

Compound **14** was obtained by the reaction of **3a** with hydrogen peroxide in 68% yield as a colorless powder, mp 171-172° (from ethyl acetate-hexane); <sup>1</sup>H nmr (200 MHz, deuteriochloroform): δ 1.40 (s, 18H), 7.56 (d, J = 2.3 Hz, 2H), 7.58 (d, J = 2.3 Hz, 2H), 9.50 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 20.1, 35.8, 112.3, 125.0, 127.8, 137.0, 142.7, 153.7; ir: 3330 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 520 (M<sup>+</sup>, 67).

*Anal.* Calcd. for C<sub>20</sub>H<sub>24</sub>Br<sub>2</sub>O<sub>4</sub>S: C, 46.17; H, 4.65. Found: C, 46.06; H, 4.79.

Bis(3-*t*-butyl-5-chloro-2-hydroxyphenyl)sulfone (**15**).

Compound **15** was obtained by the reaction of **4a** with hydrogen peroxide in 77% yield as a colorless powder, mp 151-153° (from ethyl acetate-hexane); <sup>1</sup>H nmr (200 MHz, deuteriochloroform): δ 1.40 (s, 18H), 7.44 (s, 4H), 9.50 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 29.1, 35.8, 114.4, 124.8, 125.3, 134.3, 142.4, 153.2; ir: 3331 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 430 (M<sup>+</sup>, 46).

*Anal.* Calcd. for C<sub>20</sub>H<sub>24</sub>Cl<sub>2</sub>O<sub>4</sub>S: C, 55.69; H, 5.61. Found: C, 55.58; H, 5.40.

Bis(3-bromo-5-*t*-butyl-2-hydroxyphenyl)sulfide (**6**).

To a solution of bis(5-*t*-butyl-2-hydroxyphenyl)sulfide (**5**) (15 g, 45.5 mmoles) in chloroform (150 ml) was added bromine (16 g, 100 mmoles) in chloroform (30 ml) at 0° over a period of 30 minutes, and this was stirred for 1 hour at the same temperature. This reaction mixture was then poured into 20 g of ice and the organic layer was separated. The organic layer was washed with water and brine and then dried over anhydrous sodium sulfate and concentrated. The yellow residue was recrystallized to give **6** (14 g, 64%), mp 110-112° (from ethyl acetate-hexane); <sup>1</sup>H nmr (200 MHz, deuteriochloroform): δ 1.23 (s, 18H), 7.30 (d, J = 2.2 Hz, 2H), 7.45 (d, J = 2.2 Hz, 2H), 9.38 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 31.2, 34.3, 109.5, 119.8, 130.6, 130.7, 145.3, 150.0; ir: 3259 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 488 (M<sup>+</sup>, 100).

*Anal.* Calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>Br<sub>2</sub>S: C, 49.20; H, 4.95. Found: C, 48.96; H, 5.05.

Bis(3-bromo-5-*t*-butyl-2-hydroxyphenyl)sulfone (**16**).

Compound **16** was obtained by the reaction of bis(3-bromo-5-*t*-butyl-2-hydroxyphenyl)sulfide (**6**) with hydrogen peroxide in 81% yield as a pale yellow powder, mp 218-220° (from ethyl acetate-hexane); <sup>1</sup>H nmr (200 MHz, deuteriochloroform): δ 1.29 (s, 18H), 7.74 (s, 4H), 8.20 (s, 2H, -OH); <sup>13</sup>C nmr (50.3 MHz, deuteriochloroform): δ 31.1, 34.6, 112.3, 124.8, 136.5, 145.0, 149.6; ir: 3361 cm<sup>-1</sup>, ν O-H; ei-ms: m/z (%) 520 (M<sup>+</sup>, 56).

*Anal.* Calcd. for C<sub>20</sub>H<sub>24</sub>Br<sub>2</sub>O<sub>4</sub>S: C, 46.17; H, 4.65. Found: C, 46.06; H, 4.70.

General Procedure for the Preparation of the Lewis Acids **17-26**.Methyl[2,2'-sulfinylbis(4,6-di-*t*-butylphenolato)]aluminum (**17**).

Bis(3,5-di-*t*-butyl-2-hydroxyphenyl)sulfoxide (**7**) (45.8 mg, 1 mmole) was placed into a 50 ml flask under reduced pressure

(133.322 Pa) and purged with argon gas. To remove moisture, the reaction flask was evacuated and purged with argon three times, then heated at 90° for 1 hour and cooled to room temperature. To this flask air-free dichloromethane (5 ml) was added and 1.0 M hexane solution of trimethylaluminum (0.1 ml, 0.1 mmole) was added to this dichloromethane solution and the reaction mixture was stirred for 1 hour at room temperature. To confirm the purity of the Lewis acid **17**, the solvent of **17** was replaced from dichloromethane to deuteriochloroform. The obtained <sup>1</sup>H nmr of the Lewis acids were as follows: (**17**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.51 (s, 3H), 1.27 (s, 18H), 1.39 (s, 18H), 7.05 (d, 2H, J = 2.6 Hz), 7.44 (d, 2H, J = 2.6 Hz); (**18**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.51 (s, 3H), 1.36 (s, 18H), 2.23 (s, 6H), 6.87 (d, 2H, J = 2.5 Hz), 7.17 (d, 2H, J = 2.5 Hz); (**19**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.47 (s, 3H), 1.35 (s, 18H), 7.19 (d, 2H, J = 2.4 Hz), 7.46 (d, 2H, J = 2.4 Hz); (**20**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.46 (s, 3H), 1.36 (s, 18H), 7.06 (d, 2H, J = 2.6 Hz), 7.34 (d, 2H, J = 2.6 Hz); (**21**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.40 (s, 3H), 1.25 (s, 18H), 7.11 (d, 2H, J = 2.4 Hz), 7.72 (d, 2H, J = 2.4 Hz); (**22**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.39 (s, 3H), 1.28 (s, 18H), 1.38 (s, 18H), 7.47 (d, 2H, J = 2.5 Hz), 7.52 (d, 2H, J = 2.5 Hz); (**23**); <sup>1</sup>H nmr (deuteriochloroform): δ -0.39 (s, 3H), 1.35 (s, 18H), 2.25 (s, 6H), 7.25 (d, 2H, J = 2.1 Hz), 7.30 (d, 2H, J = 2.1 Hz); (**24**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.35 (s, 3H), 1.34 (s, 18H), 7.35 (d, 2H, J = 2.7 Hz), 7.61 (d, 2H, J = 2.7 Hz); (**25**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.35 (s, 3H), 1.35 (s, 18H), 7.41 (d, 2H, J = 2.7 Hz), 7.48 (d, 2H, J = 2.7 Hz); (**26**) <sup>1</sup>H nmr (deuteriochloroform): δ -0.31 (s, 3H), 1.27 (s, 18H), 7.52 (d, 2H, J = 2.4 Hz), 7.79 (d, 2H, J = 2.4 Hz).

#### General Procedure for the Reaction of Lewis Acid with Stilbene Oxides.

A solution of trimethylaluminum (0.1 ml, 0.1 mmole) in hexane was added to a solution of bis(3,5-di-*t*-butyl-2-hydroxyphenyl)sulfoxide (**14**) (52 mg, 0.1 mmole) in dichloromethane (5 ml) at room temperature under an argon atmosphere. This solution was stirred for 1 hour and then *trans*-stilbene oxide (196 mg, 1 mmole) in absolute dichloromethane (5 ml) was added by a syringe to this flask at room temperature. The mixture was stirred for 1 hour at room temperature and treated with powdered sodium fluoride (NaF) (17 mg, 0.4 mmole) followed by water (0.2 ml) at the same temperature. The solution was stirred vigorously at room temperature for 1 hour and filtered. The filtrate was concentrated and the residue obtained was purified by column chromatography on silica gel (Wako C-200; hexane-ethyl acetate 10:1) to give diphenylacetaldehyde (178 mg, 91%) and *trans*-stilbene oxide (9 mg, 5%).

#### General Procedure for the Competitive Conversion of Styrene Oxide and β-Methylstyrene Oxide.

A solution of trimethylaluminum (0.2 ml, 0.2 mmole) in hexane was added to a solution of bis(3,5-di-*t*-butyl-2-hydroxyphenyl)sulfoxide (**12**) (95 mg, 0.2 mmole) in dichloromethane (10 ml) at room temperature under an argon atmosphere. This solution was stirred for 1 hour and then styrene oxide (24 mg, 0.2 mmole) and β-methylstyrene oxide (27 mg, 0.2 mmole) in absolute dichloromethane (5 ml) was added by a syringe to this flask at -80°. The mixture was stirred for 1 hour at -80° and

treated with powdered sodium fluoride (NaF) (17 mg, 0.4 mmole) followed by water (0.2 ml) at the same temperature. The solution was stirred vigorously at room temperature for 1 hour and filtered. The filtrate was concentrated and the residue obtained was purified by column chromatography on silica gel (Wako C-200; hexane-ethyl acetate 10:1) to give a mixture (51 mg) of 2-phenylacetaldehyde and β-methylstyrene oxide. The <sup>1</sup>H nmr (deuteriochloroform) showed that 100% of styrene oxide converted to 2-phenylacetaldehyde and β-methylstyrene oxide (100%) was recovered.

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