SYNTHESIS OF MONO- AND POLYSULFUR-BRIDGED BISPHENOLS AND THEIR APPLICATION TO NEW TYPE LEWIS ACIDS

Yoshihiro Ohba*, Kazuaki Ito, and Tomomi Nagasawa
Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa 992-8510, Japan

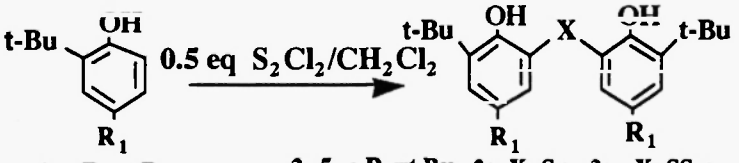
Abstract: Several bisphenoles which contain sulfur (s) as bridge moiety were synthesized by the reaction of sulfur monochloride with phenols and the reaction of the trisulfur-bridged bisphenols with trimethylalumininum quantitatively gave new type of Lewis acids.

Introduction

Various Lewis acids have been used to control the selectivity of carbon-carbon bond-forming reactions (1). The bulky oxygenophilic organoaluminum reagents have been recognized as a highly useful Lewis acid and usually they are the methylaluminum bisphenoxide type molecules (2). We reported a new type of Lewis acids that contain carbon chain-bridged bisphenol moiety (3). We found out that sulfur-bridge of acyclic and cyclic phenol-formaldehyde oligomers improved inclusion properties of these compounds (4). And some reports showed that sulfur-bridged Lewis acids have high activity for olefin polymerization (5). These works prompted us to synthesize several ligands containing sulfur (s) to bridge the moiety of two phenols. We also report the syntheses of new type Lewis acids by the reaction of these ligands and trimethylaluminum and their properties.

The bishpenols (**2**~**4**) were prepared by the reaction of 2,4-di-*t*-butylphenol with sulfur monochloride (S_2Cl_2) at 0 °C in yields of 19% (**2**), 19% (**3**), 11% (**4**) and 9% (**5**) respectively. On the other hand, when this reaction was carried at room temperature in CH_2Cl_2, **2** (9%),**3** (9%),**4** (15%), and **5** (3%) were obtained respectively. The yields of sulfide (**2**) and disulfide (**3**) were decreased by the reaction at room temperature. The results of the reaction of 2-*t*-butyl-4-methylphenol with sulfur monochloride at various temperature were also shown in Table 1.

Scheme 1



1 : R_1=*t*-Bu
6 : R_1=Me
11 : R_1=Br
16 : R_1=Cl

2~**5** : R_1=*t*-Bu, **2**: X=S ; **3**: X=SS ; **4**: X=SSS ; **5**: X=SSSS
7~**10** : R_1=Me, **7**: X=S ; **8**: X=SS ; **9**: X=SSS ; **10**: X=SSSS
12~**15** : R_1=Br, **12**: X=S ; **13**: X=SS ; **14**: X=SSS ; **15**: X=SSSS
17~**20** : R_1=Cl, **17**: X=S ; **18**: X=SS ; **19**: X=SSS ; **20**: X=SSSS

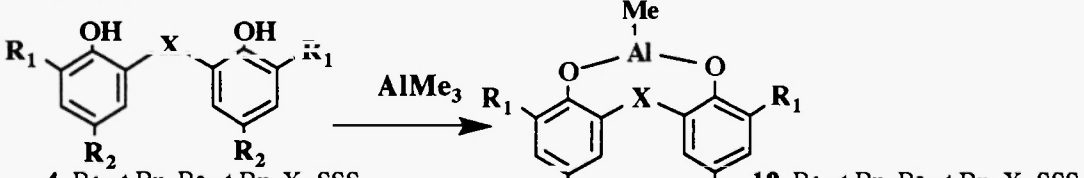
To increase the activity of Lewis acid, bromine and chlorine were introduced at *p*-position of phenol as electron-withdrawing group(2). The reaction of **11** with S_2Cl_2 in CH_2Cl_2 at room temperature

Table 1. Reaction of 2,4-Disubstituted Phenols with Sulfurmonochloride.

entry	Phenol	Reaction Temperature	Isolate Yield of Sulfide (%)	Isolate Yield of Disulfide (%)	Isolate Yield of Trisulfide (%)	Isolate Yield of Tetrasulfide (%)
1	**1**	0 °C	19	19	11	9
2	**1**	R.T.	9	9	15	3
3	**1**	40 °C	9	9	14	2
4	**6**	0 °C	31	13	7	3
5	**6**	R.T.	28	11	11	4
6	**6**	40 °C	16	10	16	2

gave **12** (4%), **13** (13%), **14** (4%), and the recovery of **11** (53%). In order to decrease the starting material **11**, we changed the reaction temperature as follows. The reaction of **11** with S_2Cl_2 under CH_2Cl_2 reflux (40 °C) gave **12** (13%), **13** (11%), **14** (7%), and **15** (1%). Compound **16** when treated with S_2Cl_2 at 40 °C gave **17** (15%), **18** (18 %), **19** (2%), **20** (1%), and **16** (25%).

Syntheses of the new types of sulfur-chain containing bisphenoxide type Lewis acids were tried using the reaction of the obtained twelve ligands and trimethylaluminum. In spite of any effort to obtain a pure Lewis acid, the reaction of all of the sulfides (**2**, **7**, **12**, and **17**) and the disulfides (**3**, **8**, **13**, and **18**) with trimethylaluminum gave a mixture of Lewis acids. However, the reaction of the trisulfide (**4**, **9**, **14**, and **19**) and tetrasulfide (**5**) with trimethylaluminum gave new type Lewis acids as a single and pure product.



4 R1=*t*-Bu, R2=*t*-Bu, X=SSS
8 R1=*t*-Bu, R2=CH3, X=SSS
14 R1=*t*-Bu, R2=Br, X=SSS
19 R1=*t*-Bu, R2=Cl, X=SSS

19 R1=*t*-Bu, R2=*t*-Bu, X=SSS
20 R1=*t*-Bu, R2=CH3, X=SSS
21 R1=*t*-Bu, R2=Br, X=SSS
22 R1=*t*-Bu, R2=Cl, X=SSS

Scheme 2

^{1}H NMR also showed the clean signals of the aromatic protons at 7.20~7.55 ppm and no resonances for the phenolic OH groups which is consistent with the formation of the desired cyclic Lewis acid (**21**). Other Lewis acids (**22**, **23**, and **24**) were also synthesized by this same procedure, and the structure of these Lewis acids were confirmed by the ^{1}H NMR spectra. The ^{1}H NMR signal of the methyl group connected aluminum of other Lewis acids showed a sharp singlet at a high magnetic field(–0.34~–0.25ppm). In addition, the molecular weight of **21** was measured by means of cryoscopy in benzene in order to confirm its structure. The obtained molecular weight (MW 539.4) closely corresponded to the value (MW 546.8) calculated for a monomeric species. The authors could not examine the formation of Lewis acid from the reaction of **10**, **15**, and **20** and trimethylaluminum because of the low yield of the tetrasulfide-bridge ligands (**10**, **15**, and **20**). The properties of these new Lewis acids are now under investigation.

We studied the rearrangement of *trans*-stilbene oxide to carbonyl compounds to analyze the

properties of these new type of Lewis acids. Table 2 shows the results under various conditions. The reaction of *trans*-stilbene oxide with these new Lewis acids gave diphenylacetaldehyde in

Table 2. Lewis Acid-Catalyzed Rearrangements of trans-Stilbene Oxide

entry	Lewis acid	Amount of Lewis acid mol amt. x 100	Conditions °C	Diphenylacet-aldehyde (%)	Recovered epoxide (%)
1	**19**	10	R.T.	96	0
2	**19**	100	-80	98	trace
3	**20**	10	R.T.	97	0
4	**20**	100	-80	95	trace
5	**21**	10	R.T.	98	0
6	**21**	100	-80	94	trace
7	**22**	10	R.T.	97	0
8	**22**	100	-80	93	trace

quantitative yield at room temperature and at -80 °C. Comparing with the result obtained by using hydrocarbon-bridged Lewis acids, it is very interesting that these new trisulfur-bridged Lewis acids gave no benzophenone which was obtained as by-product by using hydrocarbon-bridged Lewis acids.(3)

Experimental

The melting points are uncorrected. NMR spectra were recorded at 500 MHz on a Varian INOVA 500 instrument. Signals were expressed as ppm downfield from tetramethylsilane used as the internal standard (δ value in $CDCl_3$) unless otherwise described. IR(KBr disk) and mass spectra(70eV) were obtained on Hitachi EPI-S2 and on 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) with any pretreatment. Dichloromethane (CH_2Cl_2) and chloroform were dried over P_4O_{10}, and were freshly distilled before use. The trimethylaluminum in hexane was of commercial grade. Cryoscopy was carried out using a Sansyo Beckmann thermometer.

General procedure for the preparation of sulfur-bridged bisphenol

To an absolute dichloromethane solution (40 ml) of 2,4-di-*t*-butylphenol (1)(5 g, 24 mmol) in three-necked round bottom flask equipped with a magnetic stirrer, a dropping funnel, and a thermometer, the S_2Cl_2 (1.7 g, 12 mmol) in absolute CH_2Cl_2 (7 ml) was added over a period of 1.5 h at 25 °C, and stirred for 3 more hours at the same temperature. Dichloromethane was removed by distillation, and then obtained residue was dissolved by adding chloroform (50 ml), washed with water (40 ml x 6), and dried over Na_2SO_4, and then evaporated to dryness. The obtained residue was chromatographed on silica gel (Wako C-200; hexane/$CHCl_3$=7/1) and the obtained products were recrystallized from hexane to give **2** (0.5 g, 9%), **3** (0.5 g, 9%), **4** (0.9 g, 15%) and **5** (0.2 g, 3%).

***Bis(3,5-di-t-butyl-2-hydroxyphenyl)sulfide* 2** : yellow powder (hexane), mp 105-107 °C; IR (KBr) 3406, 2962, 2870, 1466, 1390, 871, 818, and 756 cm^{-1}; ^1H NMR δ=1.21 (18H, s), 1.41 (18H, s), 6.48 (2H, s, -OH), 7.16 (2H, d, J=2.1 Hz), and 7.26 (2H, d , J=2.1 Hz); ^{13}C δ=151.76, 143.02, 135.99, 127.78, 125.15, 118.95,

35.24, 34.33, 31.39, and 29.53; MS *m/z* 442 (M^+, 100%). Found: C, 76.11; H, 9.61%. Calcd for $C_{28}H_{42}O_2S$: C, 75.97; H, 9.56%.

Bis(3,5-di-t-butyl-2-hydroxyphenyl)disulfide **3** : yellow prisms (hexane), mp 112-113 °C; IR (KBr) 3426, 2960, 2913, 2868, 1457, 1242, 876, 819 and 756 cm^{-1}; ^1H NMR δ=1.21 (18H, s), 1.37 (18H, s), 6.57 (2H, s, -OH), 7.18 (2H, d, J=2.1 Hz), and 7.33 (2H, d , J=2.1 Hz); ^{13}C NMR δ=153.27, 142.48, 135.77, 130.35, 127.73, 119.40, 35.32, 34.29, 31.43, and 29.47; MS *m/z* 474 (M^+, 100%). Found: C, 71.05; H, 9.11%. Calcd for $C_{28}H_{42}O_2S2$: C, 70.84; H, 8.92%.

Bis(3,5-di-t-butyl-2-hydroxyphenyl)trisulfide **4** : yellow powder (hexane), mp 145-147°C; IR (KBr) 3427, 2960, 2868,1439, 1241, 871, 818 and 756 cm^{-1}; ^1H NMR δ=1.32 (18H, s), 1.43 (18H, s), 6.55 (2H, s, -OH), 7.41 (2H, d, J=2.3 Hz), and 7.49 (2H, d , J=2.3 Hz); ^{13}C NMR δ=152.89, 142.77, 136.22, 129.70, 127.88, 120.16, 35.39, 34.35, 31.46, and 29.49; MS *m/z* 506 (M^+, 8%). Found: C, 66.24; H, 8.46%. Calcd for $C_{28}H_{42}O_2S_3$: C, 66.35; H, 8.35%.

Bis(3,5-di-t-butyl-2-hydroxyphenyl)tetrasulfide **5** : yellow oil ; IR (KBr) 3448, 2960, 2910, 2870, 1468, 1242, 879, 820 and 756 cm^{-1}; ^1H NMR δ=1.28 (18H, s), 1.40 (18H, s), 6.58 (2H, s, -OH), 7.39 (2H, d, J=2.6 Hz), and 7.41 (2H, d , J=2.6 Hz); ^{13}C NMR δ=153.27, 142.86, 136.20, 130.51, 128.08, 119.47, 35.43, 34.42, 31.46, and 29.44; MS *m/z* 538 (M^+, 11%). Found: C, 62.64; H, 8.06%. Calcd for $C_{28}H_{42}O_2S_4$: C, 62.41; H, 7.86%.

The mixture of sulfide **7**, disulfide **8** , trisulfide **9**, and tetrasulfide **10** was obtained by the reaction of 2-*t*-butyl-4-methylphenol **6** with S_2Cl_2 at 25 °C under the same condition used for the reaction of 2,4-di-*t*-butylphenol (**1**). Isolation by means of chromatography and recrystallization from hexane gave the sulfide **7** (28%), disulfide **8** (11%), trisulfide **9** (11%) and tetrasulfide **10** (4%).

Bis(3-t-butyl-2-hydroxy-5-methylphenyl)sulfide **7** : colorless prisms (hexane), mp 83-84 °C; IR (KBr) 3493, 2960, 2866, 1439, 1234, 860, 777 and 754 cm^{-1}; ^1H NMR δ=1.40 (18H, s), 2.19 (6H, s), 6.56 (2H, s, -OH), 6.98 (2H, d, J=2.2 Hz), and 7.02 (2H, d, J=2.2 Hz); ^{13}C δ=152.07, 136.56, 131.43, 129.65, 129.08, 119.32, 34.96, 29.47, and 20.73. ; MS *m/z* 358 (M^+, 100%). Found: C, 73.95; H, 8.55%. Calcd for $C_{22}H_{30}O_2S$: C, 73.70; H, 8.43%.

Bis(3-t-butyl-2-hydroxy-5-methylphenyl)disulfide **8**: yellow prism (hexane), mp 114-115 °C; IR(KBr) 3440, 2998, 2958, 2914, 2872,1483, 1234, 864, 777 and 756 cm^{-1}; ^1H NMR δ=1.37 (18H, s), 2.19 (6H, s), 6.54 (2H, s, -OH), 7.00 (2H, d, J=2.2 Hz), and 7.12 (2H, d , J=2.2 Hz); ^{13}C NMR δ=153.19, 136.32, 133.92, 131.40, 129.09, 120.63, 35.04, 29.38, and 20.51; MS *m/z* 390 (M^+, 15%). Found: C, 67.86; H, 7.74%. Calcd for $C_{22}H_{30}O_2S_2$: C, 67.65; H, 7.74%.

Bis(3-t-butyl-2-hydroxy-5-methylphenyl)trisulfide **9** : yellow powder (hexane), mp 132-134 °C; IR (KBr) 3454, 2953, 2914, 2870,1439, 1234, 1157, 858, 777 and 752 cm^{-1}; ^1H NMR δ=1.39 (18H, s), 2.25 (18H, s), 6.50 (2H, s, -OH), 7.14 (2H, d, J=2.2 Hz), 7.21 (2H, d , J=2.2 Hz); ^{13}C NMR δ=152.92, 136.67, 133.04, 131.43, 129.36, 120.57, 35.06, 29.42, and 20.62; MS *m/z* 422 (M^+, 84%). Found: C, 62.75; H, 7.33%. Calcd for $C_{22}H_{30}O_2S_3$: C, 62.52; H, 7.15%.

Bis(3-t-butyl-2-hydroxy-5-methylphenyl)tetrasulfide **10** : yellow viscous oil; IR (KBr) 3454, 2953, 2914, 2870, 1439, 1234, 1157, 858, 777 and 752 cm^{-1}; ^1H NMR δ=1.39 (18H, s), 2.25 (6H, s), 6.54 (2H, s, -OH), 7.15 (2H, d, J=2.2 Hz), 7.190 (1H, d , J=2.2 Hz), and 7.193 (1H, d , J=2.2 Hz); ^{13}C NMR δ=153.43, 136.70, 133.79, 131.61, 129.47, 119.87, 35.13, 29.38, and 20.56; MS *m/z* 454 (M^+, 35%). Found: C, 57.85; H, 6.73%. Calcd for $C_{22}H_{30}O_2S_4$: C, 58.11; H, 6.65%.

To an absolute dichloromethane solution (100 ml) of 2-*t*-butyl-4-bromophenol (6a)(9 g, 39 mmol) in three-necked round bottom flask with a magnetic stirrer, a dropping funnel, and a thermometer, the disulfur dichloride (5 g, 37 mmol) in absolute CH_2Cl_2 (30 ml) was added over a period of 1.5 h at 20 °C , and then heated to reflux for 11 h. The CH_2Cl_2 was removed by distillation, and the obtained residue was dissolved by adding $CHCl_3$ (200 ml) then washed with water (100 ml x 6) and dried over Na_2SO_4, followed by evaporating to dryness. The obtained residue was chromatographed on silica gel (Wako C-200; hexane/$CHCl_3$=7/1) and the obtained products were recrystallized from hexane to give **11** (4.6 g, 15%), **12** (3.6 g, 11%), **13** (3.2 g, 9%) and **14** (3.2 g, 9%). The mixture of sulfide **11**, disulfide **12** , and trisulfide **13** and tetrasulfide **14** was obtained by the reaction of 2-*t*-butyl-4-bromophenol **11** (10) with disulfur dichloride at 20°C. Isolation by means of chromatography and recrystallization from hexane gave sulfide **12** (4%), disulfide **13** (13%), trisulfide **14** (4%) and tetrasulfide **15** (0.5%).

***Bis(3-t-butyl-5-bromo-2-hydroxyphenyl)sulfide* 12** : colorless prisms (hexane), mp 123-124 °C; IR (KBr) 3452, 2964, 2871, 1560, 1430, 1230, 866, 752 and 690 cm^{-1}; ^1H NMR δ=1.40 (18H, s), 6.55 (2H, s, -OH), 7.24 (2H, d, J=2.4 Hz), and 7.34 (2H, d , J=2.4 Hz); ^{13}C NMR δ=153.33, 139.35, 133.08, 131.68, 120.69, 112.69, 35.33, and 29.22; MS *m/z* 488 (M^+, 100%). Found: C, 49.37; H, 5.16%. Calcd for $C_{20}H_{24}O_2Br_2S$: C, 49.20; H, 4.95%.

***Bis(3-t-butyl-5-bromo-2-hydroxyphenyl)disulfide* 13** : yellow prisms (hexane), mp132-134 °C; IR (KBr) 3434, 2952, 2910, 2872, 1429, 1389, 1228, 868, 754 and 690 cm^{-1}; ^1H NMR δ=1.37 (18H, s), 6.64 (2H, s, -OH), 7.28 (2H, d, J=2.3 Hz), and 7.42 (2H, d , J=2.3 Hz); ^{13}C δ=154.56, 139.11, 135.55, 133.80, 121.76, 111.89, 35.43, and 29.12; MS *m/z* 520 (M^+, 31%). Found: C, 46.36; H, 4.81%. Calcd for $C_{20}H_{24}O_2Br_2S_2$: C, 46.17; H, 4.65%.

***Bis(3-t-butyl-5-bromo-2-hydroxyphenyl)trisulfide* 14** : yellow powder (hexane), mp 134-135 °C; IR (KBr) 3448, 2954, 2915, 2871, 1430, 1386, 1226, 1153, 860, 754 and 692 cm^{-1}; ^1H NMR δ=1.38 (18H, s), 6.54 (2H, s, -OH), 7.44 (2H, d, J=2.3 Hz), and 7.48 (2H, d , J=2.3 Hz); ^{13}C NMR δ=154.15, 139.32, 134.53, 133.71, 122.18, 112.15, 35.44, and 29.16; MS *m/z* 552 (M^+, 12%). Found: C, 43.60; H, 4.38%. Calcd for $C_{20}H_{24}O_2Br_2S_3$: C, 43.49; H, 4.38%.

***Bis(3-t-butyl-5-bromo-2-hydroxyphenyl)tetrasulfide* 15** : yellow needles (hexane), mp 134-135 °C; IR (KBr) 3448, 2954, 2915, 2871, 1430, 1386, 1226, 1153, 860, 754 and 692 cm^{-1}; ^1H NMR δ=1.38(18H, s), 6.65 (2H, s, -OH), 7.45 (2H, d, J=2.3 Hz), and 7.52 (2H, d, J=2.3 Hz); ^{13}C NMR δ=154.15, 139.32, 134.53, 133.71, 122.18, 112.15, 35.44, and 29.16; MS *m/z* 584 (M^+, 12%). Found: C, 44.18; H, 4.38%. Calcd for $C_{20}H_{24}O_2Br_2S_4$: C, 41.10; H, 4.14%.

The mixture of sulfide **17**, disulfide **18** , trisulfide **19** and tetrasulfide **20** was obtained by the reaction of 2-*t*-butyl-4-chlorophenol **16** (6b) with S_2Cl_2 under the same conditions used for the reaction of 2-*t*-butyl-4-bromophenol with S_2Cl_2 as already described. Isolation by means of chromatography and recrystallization from hexane gave the sulfide **17** (15%), disulfide **18** (18%), trisulfide **19** (2%), and tetrasulfide **20** (1%).

***Bis(3-t-butyl-5-chloro-2-hydroxyphenyl)sulfide* 17** : colorless prism (hexane), mp 113-114 °C; IR (KBr) 3460, 2966, 2912, 2873,1577, 1433, 1230, 866, 752 and 690 cm^{-1}; ^1H NMR δ=1.40 (18H, s), 6.50 (2H, s, -OH), 7.10 (2H, d, J=2.3 Hz), and 7.21 (2H, d , J=2.3 Hz); ^{13}C δ=152.85, 138.92, 130.16, 128.84, 125.37, 120.21, 35.33, and 29.20; MS *m/z* 398 (M^+, 11%). Found: C, 60.29; H, 6.13%. Calcd for $C_{20}H_{24}O_2Cl_2S$: C, 60.15; H, 6.06%.

Bis(3-t-butyl-5-chloro-2-hydroxyphenyl)disulfide 18: yellow prisms (hexane), mp 123-125 °C; IR (KBr) 3435, 2999, 2960, 2912, 2873, 1570, 1433, 1390, 1228, 870, 756 and 721 cm^{-1}; ^1H NMR δ=1.36 (18H, s), 6.60 (2H, s, -OH), 7.14 (2H, d, J=2.5 Hz), and 7.29 (2H, d , J=2.5 Hz); ^{13}C NMR δ=154.12, 138.73, 132.62, 131.00, 124.69, 121.28, 35.45, and 29.09; MS *m/z* 430 (M^+, 50%). Found: C, 55.90; H, 5.85%. Calcd for $C_{20}H_{24}O_2Cl_2S_2$: C, 55.68; H, 5.61%.

Bis(3-t-butyl-5-chloro-2-hydroxyphenyl)trisulfide 19 : yellow powder (hexane), mp 134-136 °C; IR (KBr) 3450, 2954, 2914, 2872, 1433, 1380, 1227, 1153, 862, 754 and 721 cm^{-1}; ^1H NMR δ=1.38(18H, s), 6.54 (2H, s, -OH), 7.31 (2H, d, J=2.6 Hz), and 7.36 (2H, d , J=2.6 Hz); ^{13}C NMR δ=153.68, 138.91, 131.62, 130.86, 124.85, 121.69, 35.43, and 29.13; MS *m/z* 462 (M^+, 17%). Found: C, 51.70; H, 5.29%. Calcd for $C_{20}H_{24}O_2Cl_2S_3$: C, 51.83; H, 5.22%.

Bis(3-t-butyl-5-chloro-2-hydroxyphenyl)tetrasulfide 20 : yellow oil; IR (KBr) 3444, 2960, 2912, 2873, 1571, 1432, 1398, 1228, 1170, 868, 754 and 721 cm^{-1}; ^1H NMR δ=1.39 (18H, s), 6.64 (2H, s, -OH), 7.32 (2H, d, J=2.6 Hz), and 7.38 (2H, d , J=2.6 Hz); ^{13}C NMR δ=154.18, 138.88, 132.52, 130.98, 124.82, 121.14, 35.50, and 29.12; MS *m/z* 494 (M^+, 20%). Found: C, 48.22; H, 4.96%. Calcd for $C_{20}H_{24}O_2Cl_2S_4$: C, 48.47; H, 4.88%.

Preparation of Lewis Acid (general procedure)

Bis(3,5-di-*t*-butyl-2-hydroxyphenyl)trisulfide 4 (44.2 mg, 0.1 mmol) was placed in two-necked flask and air was removed under reduced pressure (1 mmHg) and purged with argon gas. Removing the gas and purging by argon was repeated three times, then this reaction flask was heated at 80 °C for 1 h to completely remove the moisture and cooled to room temperature. To this flask air free CH_2Cl_2 (5ml) was added in by using syringe. A 1.0 M solution of trimethylaluminum (0.1 cm^3, 0.1 mmol) was added to this solution and stirred for 1h at room temperature. After removing the solvents under reduced pressure (1 mmHg), oxygen-free absolute chloroform-d_1 was added and the ^1H NMR spectrum was obtained. 21 : ^1H NMR δ=-0.34 (3H, s, Al-CH_3), 1.30 (18H, s), 1.44 (18H, s), 7.30 (2H, d, J=2.6 Hz), and 7.43 (2H, d , J=2.6 Hz). 22 : ^1H NMR δ=-0.34 (3H, s, Al-CH_3), 1.41 (18H, s), 2.25 (6H, s), 7.13 (2H, d, J=2.1 Hz), and 7.17 (2H, d , J=2.1Hz). 23 : ^1H NMR δ=-0.29 (3H, s, Al-CH_3), 1.40 (18H, s), 7.44 (2H, d, J=2.5 Hz), and 7.46 (2H, d, J=2.5 Hz). 24 : ^1H NMR δ=-0.30 (3H, s, Al-CH_3), 1.40 (18H, s), and 7.32 (4H, br s). 25 : ^1H NMR δ=-0.25 (3H. s. Al-CH_3), 1.29 (9H, s), 1.40 (9H, s), 7.42 (2H, d, J=2.4 Hz), and 7.43-7.47 (2H, br s).

The activity of Lewis acids was investigated by the established method.(3)

Acknowledgement: We would like to thank Dr. Tyo Sone for his kind advice.

References

1) T. Bach, *Angew. Chem. Int. Ed. Engl.* 33, 417 (1994).
2) (a) Review: H. Yamamoto, K. Maruoka, and K. Ishihara, *J. Synth. Org. Chem.,Jpn.*, **52**, 40 (1994). (b) K. Maruoka, Y. Araki, and H. Yamamoto, *J. Am. Chem. Soc.*, **110**, 2650 (1988).
3) Y. Ohba, K. Ito, H. Maeda, H. Ebara, S. Takaki, and T. Nagasawa, *Bull. Chem. Soc. Jpn.*, (1998). in press.
4) (a) Y. Ohba, K. Moriya, and T. Sone, *Bull. Chem. Soc. Jpn.*,**64**, 576(1991). (b) T. Sone Y. Ohba, K. Moriya, H. Kumada, and K. Ito, *Tetrahedron*, **53**, 10689 (1997).
5) T. Miyatake, K. Mizunuma, and M. Kakugo, *Macromol. Chem., Macromol. Symp.*, **66**, 203 (1993).
6) (a) H. Hart, *J. Am. Chem. Soc.*, **71**, 1966 (1949). (b) J. C. Carlton and W. C. Bradbury, *J. Am. Chem. Soc.*, **78**, 1069 (1956). (b) G. Stork and W. N. White, *J. Am. Chem. Soc.*, **78**, 4604 (1956).

Received on July 31, 1998