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# SYNTHESIS OF NEW TYPES OF LEWIS ACIDS REARRANGEMENT OF STILBENE OXIDES

Yoshihiro Ohba [a] , Kazuaki Ito [a] & Tomomi Nagasawa [a]

[a] Department of Materials Science and Engineering Faculty of Engineering , Yamagata University , Yonezawa, 992-8510, Japan

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# SYNTHESIS OF NEW TYPES OF LEWIS ACIDS REARRANGEMENT OF STILBENE OXIDES

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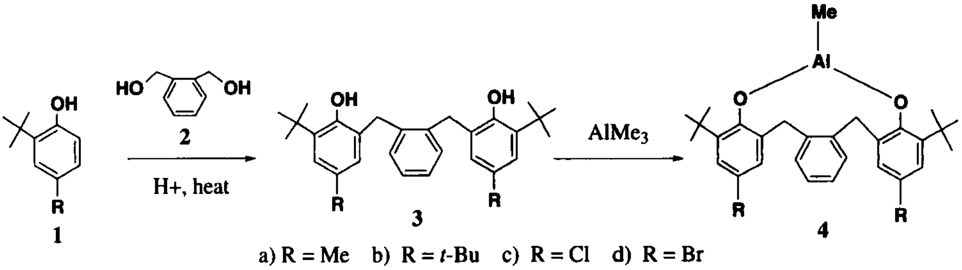
Yoshihiro Ohba*, Kazuaki Ito and Tomomi Nagasawa

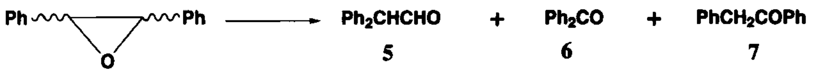
*Department of Materials Science and Engineering*
*Faculty of Engineering, Yamagata University*
*Yonezawa 992-8510, JAPAN*

Lewis acids have been used as promoters of carbon-carbon bond-forming reactions such as the Friedel-Crafts reaction[1] and oxygenophilic organoaluminum reagents Lewis acids which usually include methylaluminum bisphenoxide type molecules are highly useful for selective carbon-carbon coupling and selective Diels-Alder reaction.[2] A previous described new type of Lewis acid that contains a linked bisphenol moiety[3,4] and that methyl [2,2'-*m*-xylene-α,α'-diyl*bis*(4,6-di-*t*-butylphenoxide)]aluminum and its derivatives also are useful in the protection of some ketones from selective reductions.[3] However, the properties of methyl [2,2'-*o*-xylene-α,α'-diylbis(4,6-di-*t*-butylphenoxide)]aluminum (**4**) were not reported. We now describe four new Lewis acids, which incorporate bisphenols linked by an *o*-xylene-α,α-diyl moiety.

The reaction of 1,2-*bis*(hydroxymethyl)benzene (**2**) with *p*-substituted 2-*t*-butylphenol (**1a-d**) gave ligands **3a-3d** in 36%, 39%,[3] 49%, and 44% yields respectively; upon treatment with trimethylaluminum, **3a-3d** gave **4a-4d** as single pure products. Although **4a-4d** are very unstable toward oxygen and moisture (thus no elemental analyses could be obtained), their structures were confirmed by $^1H$ and $^{13}C$ NMR spectra.The $^1H$ NMR showed signals of aromatic protons at δ 7.20~7.55 and no



resonance ascribable to phenolic OH; the methyl group bound to aluminum of **4a-d** showed sharp singlets at high magnetic field (δ -1.58 and -1.57). In addition, the molecular weight (531.5) of **4b** determined cryoscopically in benzene corresponds closely with the calculated value (MW 554.8) for a monomeric species.



The rearrangement of epoxides to carbonyl compounds was used as a typical reaction[2] to evaluate the effectiveness of these new Lewis acids. Table 1 shows the results for the transformation of *cis*- and *trans*-stilbene oxides in dichloromethane under various conditions, to give diphenylacetaldehyde (**5**), benzophenone (**6**), and benzylphenyl ketone (**7**). While diphenylacetaldehyde (**5**) is the major product (66-90%) with (**4a**) as the catalyst at room temperature, at -80° benzophenone was the unexpected major product, albeit in somewhat lower yields (36-71%); the mechanism of the formation of benzophenone is under investigation. Interestingly, even at -80° the aldehyde was also the major product with the halogenated acids **4c** and **4d**. Comparing with usual Lewis acids ($AlMe_3$, $AlCl_3$, and $TiCl_4$), the conversion reaction of stilbene oxides with these Lewis acids (**4c-4d**) gave **5** or benzophenone in good yield. The halogenated acids **4c** and **4d** also catalyzed Claisen rearrangement of aryl phenyl ether to *o*-arrylphenole at room temperature in 92% and 90% yields. This result also suggests the usefulness of these new Lewis acids.

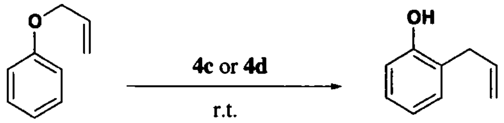
## EXPERIMENTAL SECTION

Mps are uncorrected. The NMR spectra were recorded at 500 MHz on a Varian INOVA 500 instrument. Signals are expressed as δ downfield from TMS used as the internal standard. IR (KBr disk) and mass spectra (70eV) were obtained using 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) with no pretreatment. Dichloromethane ($CH_2Cl_2$) and chloroform were dried over $P_4O_{10}$, and were freshly distilled before use. The trimethylaluminum (**Caution**: flamable!) in hexane is commercially available from Kanto Chemical Co., Inc. Cryoscopy was carried out using a Sansyo Beckmann thermometer. The synthesis of **3b** has been reported in our previous paper.[3]

**TABLE 1.** Rearrangements of *cis*- and *trans*-Stilbene Oxide with Acids **4**

| Lewis Acid | Amount (mol%) | Conditions (°C, h) | Yield (%)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | (**5**) | | (**6**) | | (**7**) | | Epoxides[b] | |
| | | | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* | *trans* |
| **4a** | 10 | rt, 1 h | 66 | 90 | 5 | 7 | 21 | 3 | 0 | 0 |
| **4a** | 100 | -80, 1 h | trace | 11 | 58 | 36 | 13 | 0 | 22 | 13 |
| **4a** | 100 | -80, 3 h | trace | 12 | 71 | 40 | 16 | 0 | trace | trace |
| **4b** | 10 | rt, 1 h | 54 | 92 | 0 | 0 | 31 | 0 | 0 | 0 |
| **4b** | 100 | -80, 1 h | 0 | 22 | 30 | 24 | 24 | 0 | 42 | 20 |
| **4b** | 100 | -80, 3 h | 0 | 30 | 45 | 36 | 0 | 0 | 12 | 4 |
| **4c** | 10 | rt, 1 h | 75 | 95 | 4 | 2 | 13 | 2 | 0 | 0 |
| **4c** | 100 | -80, 1 h | 74 | 64 | 13 | 11 | 8 | 0 | 0 | 0 |
| **4d** | 10 | rt, 1 h | 76 | 93 | 4 | 4 | 13 | 2 | 0 | 0 |
| **4d** | 100 | -80, 1 h | 64 | 65 | 24 | 11 | 8 | 0 | 0 | 0 |
| $Me_3Al$ | 10 | rt,1 h | 27 | 31 | 0 | 0 | 20 | 0 | 46 | 56 |
| $Me_3Al$ | 100 | -80, 1 h | 0 | 0 | 0 | 0 | 0 | 0 | 100 | 100 |
| $AlCl_3$ | 10 | rt,1 h | 18 | 48 | 0 | 0 | 0 | 0 | 0[c] | 0[c] |
| $TiCl_4$ | 10 | rt,1 h | 18 | 10 | 0 | trace | 11 | 0 | 32 | 88 |

a) Isolated yield. b) Recovered epoxide. c) Polymer of aldehyde was mainly obtained.



**1,2-*bis*(3-*t*-Butyl-2-hydroxy-5-methylbenzyl)benzene (3a). Typical Procedure.**- A mixture of 1,2-*bis*(hydroxymethyl)benzene (**2**, 1.6 g, 11.6 mmol), 2-*t*-butyl-4-methylphenol (**1a**, 19 g, 116 mmol), and p-toluenesulfonic acid (0.25 g) was heated at 95° for 5 h under a nitrogen atmosphere. After being cooled to room temperature, the reaction mixture was steam-distilled to remove any unreacted 2-*t*-butyl-4-methylphenol. The obtained residue was chromatographed on silica gel (Wako C-200; 15:1 hexane-ethyl acetate) to give **3a** (1.8 g, 36%) as a colorless powder (hexane), mp. 83-85°.

IR (KBr): 3550, 2957, 2914, 1601, 1475, 1446, 1361, 1222, 1170, 862, and 750 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.39 (18H, s), 2.23 (6H, s), 3.92 (4H, s, $-CH_2-$), 4.58 (2H, s, -OH), 6.66 (2H, d, $J$ = 1.6 Hz), 7.00 (2H, dd, $J$ = 1.6 Hz), 7.10 (2H, m), and 7.21 (2H, m). $^{13}C$ NMR ($CDCl_3$): 150.50, 137.59, 136.39, 129.53, 129.29, 128.72, 127.37, 126.21, 125.77, 34.44, 34.03, 34.26, 29.91, and 20.87. MS *m/z* 430 ($M^+$, 100%).

*Anal.* Calcd for $C_{30}H_{38}O_2$: C, 83.67; H, 8.89. Found: C, 83.88; H, 8.87

Bisphenol **3c** was obtained by the reaction of 2-*t*-butyl-4-chlorophenol (**1c**) with **2** in 49% yield as a colorless powder (hexane), mp. 144-145° (hexane).

IR (KBr): 3590, 3469, 2962, 2912, 2870, 1600, 1437, 1433, 1321, 1209, 1178, 871, and 746 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 1.38 (18H, s), 3.89 (4H, s, $-CH_2-$), 4.76(2H, s, -OH), 6.78 (2H, d, *J* = 2.5 Hz), 7.11 (2H, dd, *J* = 5.1 and 3.3 Hz), 7.15 (2H, d, *J* = 2.5 Hz), and 7.26 (2H, *J* = 5.1 and 3.3 Hz). $^{13}$C NMR ($CDCl_3$): δ 151.25, 138.34, 136.70, 129.87, 127.87, 127.62, 127.59, 125.74, 125.34, 34.69, 33.83, and 29.66. MS *m/z* 470 ($M^+$, 100%).

*Anal.* Calcd for $C_{28}H_{32}Cl_2O_2$: C, 71.33; H, 6.84. Found: C, 71.37; H, 7.04

Bisphenol **3d** was obtained by the reaction of 2-*t*-butyl-4-bromolphenol (**1d**) with **2** in 44% yield as a colorless powder (hexane), mp. 132-133° (hexane).

IR (KBr): 3589, 3467, 2960, 2908, 2870, 1597, 1432, 1300, 1207, 1176, 870, and 746 cm$^{-1}$. $^1$H NMR ($CDCl_3$): δ 1.38 (18H, s), 3.89 (4H, s, $-CH_2-$), 4.77(2H, s, -OH), 6.93 (2H, d, *J* = 2.4 Hz), 7.10 (2H, dd, *J* = 5.6 and 3.8 Hz), 7.24 (2H, dd, *J* = 5.6 and 3.8 Hz), and 7.29 (2H, *J* = 2.4 Hz). $^{13}$C NMR ($CDCl_3$): δ 151.81, 138.79, 136.65, 130.59, 129.83, 128.67, 128.12, 127.89, 113.03, 34.68, 33.77, and 29.69. MS *m/z* 560 ($M^+$, 34%), 57 (100%).

*Anal.* Calcd for $C_{28}H_{32}Br_2O_2$: C, 60.02; H, 5.76. Found: C, 60.04; H, 5.87

**Preparation of Lewis Acids (4a-4d). Typical Procedure.**- 1,2-*bis*(3-*t*-Butyl-2-hydroxy-5-methylbenzyl)benzene (**3a**, 43.0 mg, 0.1 mmol) was placed in a two-necked flask, air was removed under reduced pressure (1 mmHg), and the system was then purged with argon gas. Evacuation and purging with argon were repeated three times. The reaction flask was heated at 80° for 1 h to completely remove moisture and then cooled to room temperature. To this flask, deaerated dichloromethane (5 mL) (by the same procedure described above) was added using a syringe. Then a 1.0 M solution of trimethylaluminum (0.1 mL, 0.1 mmol) was added by a syringe to this stirred solution over 1 h at room temperature. After removal of the solvents under reduced pressure (1 mmHg), oxygen-free chloroform-$d_1$ was added and the $^1$H NMR spectrum was obtained.

**4a**: $^1$H NMR ($CDCl_3$): δ -1.58 (3H, s, Al-$\underline{CH_3}$), 1.34 (18H, s), 2.33 (6H, s), 3.54 (2H, br s), 4.76 (2H, br s), 6.99 (2H, d, *J* = 2 Hz), 7.07 (2H, d, *J* = 2 Hz), 7.36 ( 2H, dd, *J* = 6.0 and 3.5 Hz), and 7.46 (2H, dd , *J* = 6.0 and 3.5 Hz). $^{13}$C NMR ($CDCl_3$): δ 152.90, 138.80, 138.05, 133.17, 132.09, 129.40, 128.02, 127.20, 126.91, 34.68, 34.60, 30.12, and 20.90, and -10.32.

**4c**: $^1$H NMR ($CDCl_3$): δ -1.57 (3H, s, Al-$\underline{CH_3}$), 1.32 (18H, s), 3.55 (2H, d, *J* = 12.4 Hz), 4.72 (2H, d, *J* = 12.4 Hz), 7.17 (2H, d, *J* = 2.7 Hz), 7.23 (2H, d, *J* = 2.7 Hz), 7.42-7.49 (4H, m). $^{13}$C NMR ($CDCl_3$): δ 153.75, 141.03, 137.23, 133.29, 132.75, 129.41, 128.17, 126.53, 123.18, 34.89, 34.39, 29.81, and -10.30.

**4d**: $^1$H NMR ($CDCl_3$): δ -1.57 (3H, s, Al-$\underline{CH_3}$), 1.32 (18H, s), 3.55 (2H, d, *J* = 12.4 Hz), 4.72 (2H, d, *J* = 12.4 Hz), 7.17 (2H, d, *J* = 2.7 Hz), 7.23 (2H, d, *J* = 2.7 Hz), 7.42-7.49 ( 4H, m). $^{13}$C NMR ($CDCl_3$): δ 154.30, 141.60, 137.21, 133.32, 132.79, 131.11, 130.00, 129.45, 110.83, 34.91, 34.31, 29.83, and -10.29.

**Typical Procedure for the Reaction of Lewis Acid with Stilbene Oxides.**- An 1.0 M solution of hexane solution of trimethylaluminum (1 mL, 1 mmol) was added to a solution of 1,2-*bis*(3-*t*-butyl-2-hydroxy-5-methylbenzyl)benzene (**3a**, 430 mg, 1 mmol) in dichloromethane (50 mL) at room temperature under an argon atmosphere and this solution was stirred for 1 h and then *trans*-stilbene oxide (196 mg, 1 mmol) in absolute dichloromethane (5 mL) was added by a syringe this flask at -80° (using Cryocool cc-100, Neslab Instruments, Inc.). The mixture was stirred for 1 h at -80° and treated with powdered NaF (85 mg, 2.0 mmol) followed by water (0.2 mL) at the same temperature. The solution was stirred vigorously at -80° for 1 h 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 (22mg, 11%), benzophenone (66 mg, 36%), and *trans*-stilbene oxide (25 mg, 13%). The identity of these products was checked by mp, $^1$H NMR, infrared and mass spectral comparison with those of standard samples.

**Typical Procedure for the Rearrangement of Allyl Phenyl Ether**.- To a solution of 1,2-*bis*(3-chloro-2-hydroxy-5-methylbenzyl)benzene (**3c**, 470 mg, 1 mmol) in dichloromethane (50 mL) was added allyl phenyl ether (134 mg, 1 mmol) in absolute dichloromethane (5 mL) by means of a syringe this flask at room temperature. After the usual work-up, the residue obtained was purified by column chromatography on silica gel (Wako C-200; hexane-ethyl acetate 20:1) to give 2-allylphenol (123mg, 92%). The identity of these products was checked by $^1$H NMR, infrared and mass spectral comparison with those of standard samples.

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