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A Stereoselective Approach to Optically Active Bifunctional 1,3-Dimethyl-1,3-diphenyldisiloxanes

Motoi Oishi and Yusuke Kawakami*

Graduate School of Materials Science, Japan Advanced Institute of Science & Technology [JAIST], 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292 Japan

kawakami@jaist.ac.jp

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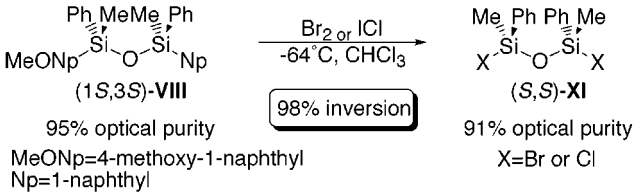
ABSTRACT



Functionalized disiloxanes have attracted much attention as versatile synthetic intermediates in the preparation of disiloxane-containing polymers. In this report, a highly stereoselective (98% inversion) halogenating cleavage reaction of the silicon–naphthyl bond to obtain optically active (*S*,*S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol ((*S*,*S*):(*R*,*S*):(*R*,*R*) = 86:14:0) was demonstrated.

Functionalized disiloxanes[1] have attracted much attention as versatile synthetic intermediates in the preparation of disiloxane-containing polymers which exhibit good permeability properties[2] and liquid crystalline properties.[3] Optically active functionalized disiloxanes will act as key intermediates in the synthesis of new optically active and/or stereoregular polysiloxanes, which are expected to exhibit novel unique properties different from those of ordinary polysiloxanes without stereoregularity. We reported a synthesis of enantiomerically pure vinyl and hydrosilyl functionalized disiloxane. The polymerization afforded optically active and stereoregular polycarbosiloxane.[4]

However, functionalized disiloxanes with controlled stereochemistry have been insufficiently studied. To our knowledge, there is only one report on an optically active disiloxane containing two asymmetric silicon centers, i.e., 1,3-dimethyl-1,3-di(1-naphthyl)-1,3-diphenyldisiloxane prepared from optically active methyl(1-naphthyl)phenylchlorosilane and optically active potassium methyl(1-naphthyl)phenylsilanolate.[5] However, this method requires multistep reactions.

To establish a more convenient route to optically active disiloxanes containing two asymmetric silicon centers, reaction of optically active chlorosilane with metal oxide was studied. We also investigated the functionalization of newly designed optically active 4-methoxy-1-naphthyl-substituted disiloxane.

Metal oxides can act as an anhydrous oxygen source,[6] but the stereochemical aspect of the formation of disiloxane linkage was not reported. The coupling reaction of (*S*)-

(1) For some references on functionalized disiloxanes, see: (a) Mori, A.; Hishida, T.; Soga, Y.; Kawakami, Y. *Chem Lett.* **1995**, 107. (b) Mori, A.; Sato, H.; Mizuno, K.; Hiyama, T.; Shintani, K.; Kawakami, Y. *Chem Lett.* **1996**, 517.

(2) (a) Kawakami, Y.; Aoki, T.; Hisada, H.; Yamamura, Y.; Yamashita, Y. *Polym. Commun.* **1985**, *26*, 133. (b) Kawakami, Y.; Karasawa, H.; Kamiya, H.; Yamashita, Y. *Polym. J.* **1986**, *18*, 237. (c) Kawakami, Y.; Sugisaka, T. *J. Member. Sci.* **1990**, *50*, 189. (d) Kawakami, Y.; Kishimoto, N.; Takeshita, K.; Watanabe, T. *Design Monom. Polym.* **1999**, *2*, 93.

(3) (a) Kawakami, Y.; Ito, Y.; Toida, K. *Macromoleclues* **1993**, *26*, 1177. (b) Kawakami, Y.; Toida, K. *Macromolecules* **1995**, *28*, 816. (c) Kawakami, Y.; Ichitani, M.; Kunisada, H.; Yuki, Y. *Polym. J.* **1996**, *28*, 513. (d) Komuro, K.; Kawakami, Y. *Polym. Bull.* In press.

(4) (a) Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31*, 5592. (b) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 548.

(5) Sommer, L. H.; Frye, C. L. *J. Am. Chem. Soc.* **1960**, *82*, 3796.

(6) Takiguchi, T.; Sakurai, M.; Ichimura, J.; Iizuka, Y. *J. Org. Chem.* **1960**, *25*, 310.

(7) Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271.

(8) Since (*S*)-methyl(1-naphthyl)phenylchlorosilane **1** is unstable to the moisture, the ee was determined on (*R*)-methyl(1-naphthyl)phenylsilane after the reduction of (*S*)-**1**.

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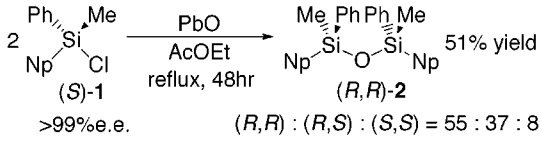
methyl(1-naphthyl)phenylchlorosilane **1** (>99% enantiomer excess (ee))[7,8] was carried out in the presence of various metal oxides (ZnO, Ag_2O, Li_2O, CuO, PbO, and MnO_2). The absolute configuration of **2** was determined on the reduced product by $LiAlH_4$. The reduction was reported to proceed with retention of configuration.[4,9] Among the above metal oxides, the highest stereoselectivity ((*R*,*R*):(*R*,*S*):(*S*,*S*) = 55:37:8 determined by HPLC analysis)[10] was observed in ethyl acetate at refluxing temperature with PbO (Scheme 1), although the reaction itself was slow. However, it was noticed that considerable racemization of (*S*)-**1** occurred under the reaction condition to result in no stereoselectivity in many cases.

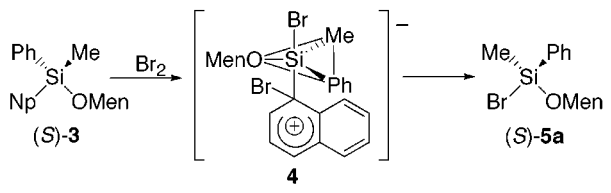
Scheme 1



One of the typical ways to functionalize organosilicon compounds is to introduce a reactive functional group such as Br, Cl, and OTf by the cleavage of the silicon−naphthyl bond. We reported that the stereoselectivity of the cleavage of the silicon−naphthyl bond of (*R*)-(+)-[(+)-menthyloxy]-methyl(1-naphthyl)phenylsilane (>99% ee) by bromine was significantly influenced by the reaction conditions, and the best result (84.5% diastereomer excess (de), 92% inversion)[11] was obtained by using $CHCl_3$ as the solvent at −64 °C. Thus, the development of a more stereoselective cleavage reaction of the silicon−naphthyl bond by bromine is required to prepare optically pure functionalized disiloxanes. However, it was very difficult to carry out such reactions with high stereoselectivity.[12]

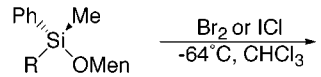
It was reported that the brominating cleavage reaction of the silicon−naphthyl bond proceeded with preference in inversion of configuration of the silicon atom (Scheme 2).[13] If the naphthyl group is modified so as to stabilize the trigonal bipyramidal transition state **4**, higher stereoselectivity could be expected.

Scheme 2



An optically active silicon compound having a methoxy group as an electron-donating group at the 4-position of the naphthyl group, (*S*)-(−)-[(−)-menthyloxy](4-methoxy-1-naphthyl)methylphenylsilane **6**, was designed, synthesized, and purified by fractional recrystallization from pentane at −78 °C. The de of (*S*)-**6** was found to be >99% as determined by ^1H NMR and HPLC.[10] The halogenating cleavage reaction of (*S*)-**6** was carried out at −64 °C in $CHCl_3$ to give (*S*)-**5a**[14] or (*S*)-**5b** (Table 1). As expected, the optical yield of (*S*)-**5a** increased from 84.5% de (92% inversion) to 91.3% de (96% inversion) (entries 1 and 3) and that of (*S*)-**5b** from 73.2% de (87% inversion) to 90.5% de (95% inversion) (entries 2 and 4) by the introduction of a methoxy substituent.

Table 1. Halogenating Cleavage Reaction of (*S*)-**3** and (*S*)-**6**



(*S*)-**3** R=1-naphthyl
(*S*)-**6** R=4-methoxy-1-naphthyl
(*S*)-**5a** X=Br
(*S*)-**5b** X=Cl

entry	substrate	reagent	product (d.e.)[a]	stereospecificity
1	(*S*)-**3**	Br_2	(*S*)-**5a** (84.5)	92% inversion
2	(*S*)-**3**	ICl	(*S*)-**5b** (73.2)	87% inversion
3	(*S*)-**6**	Br_2	(*S*)-**5a** (91.3)	96% inversion
4	(*S*)-**6**	ICl	(*S*)-**5b** (90.5)	95% inversion

[a] The diastereomer excess (d.e.) was determined by ^1H NMR.

Thus, optically active (*S*,*S*)-1,3-di(4-methoxy-1-naphthyl)-1,3-dimethyl-1,3-diphenyldisiloxane seems to be a suitable starting material to functionalized disiloxanes. However, (*S*)-(4-methoxy-1-naphthyl)methylphenylchlorosilane could not be obtained by chlorination of easily accessible (*R*)-(4-methoxy-1-naphthyl)methylphenylsilane[15] because of some side reactions. Therefore, (1*S*,3*S*)-1-(4-methoxy-1-naphthyl)-1,3-dimethyl-3-(1-naphthyl)-1,3-diphenyldisiloxane **8**, which could be obtained similarly with compound **2** according to the ref 5, was used as the starting material (Scheme 3). The stereoisomer ratio and absolute configuration of (1*S*,3*S*)-**8** were determined similarly with (*R*,*R*)-**2**. Since the ee[10] of (*R*)-(4-methoxy-1-naphthyl)methylphenylsilane **9** and (*R*)-methyl(1-naphthyl)phenylsilane **10** were >99% and 90.4%, respectively, the stereoisomer ratio of (1*S*,3*S*)-**8** could be determined as (1*S*,3*S*):(1*S*,3*R*):(1*R*,3*S*):(1*R*,3*R*) = 95:5:0:0.

(9) Sommer, L. H.; Frye, C. L.; Parker, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 3276

(10) HPLC analysis: Daicel Chem. Ind., CHIRALCEL OD, *n*-hexane as an eluent, 0.4 mL/min, 254 nm.

(11) Kawakami, Y.; Takahashi, T.; Yada, Y.; Imae, I. *Polym. J.* **1998**, *30*, 1001.

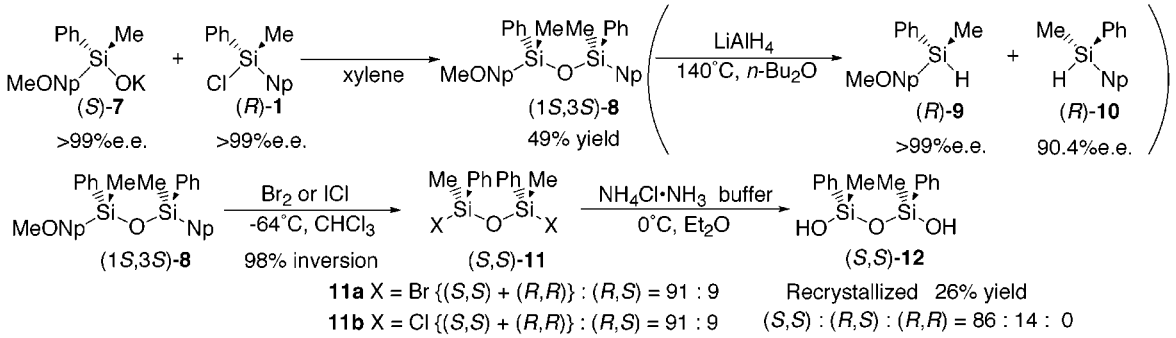
(12) Sommer, L. H.; Michael, K. W.; Korte, W. D. *J. Am. Chem. Soc.* **1967**, *89*, 868.

(13) Earbon, C.; Steward, O. W. *Proc. Chem. Soc.* **1963**, 59.

(14) To a mixture of (*S*)-**6** (0.4328 g, 1.0 mmol) in $CHCl_3$ (8.0 mL) was added a solution of bromine in $CHCl_3$ (0.5 mol/L, 2.0 mL, 1.0 mmol) dropwise during 30 min at −64 °C. The reaction mixture was stirred at the same temperature for 45 min. The de of (*S*)-**5a** was determined to be 91.3% by the integral ratio of the signals at 0.62 ppm and 0.79 ppm in ^1H NMR.

(15) ^1H NMR (300 MHz, $CDCl_3$) δ 0.64 (d, *J*=3.8 Hz, 3H), 3.92 (s, 3H), 5.21 (q, *J*=3.8 Hz, 1H), 6.73 (d, *J*=7.7 Hz, 1H), 7.23−7.38 (m, 2H), 7.39−7.40 (m, 2H), 7.46−7.49 (m, 2H), 7.56 (d, *J*=7.7 Hz, 1H), 7.89 (d, *J*=8.7 Hz, 1H), 8.23 (d, *J*=7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.45, 55.4, 103.6, 122.7, 124.1, 125.2, 125.9, 126.1, 126.8, 127.9, 128.1, 129.5, 135.0, 136.1, 138.3, 157.7; IR (KBr, cm^{-1}) 3067, 3049, 3014, 2958, 2935, 2124, 1586, 1417, 1130, 1088; EI-MS (*m*/*e*) 278 (M^+), 263 ([M − Me]$^+$), 247 ([M − OMe]$^+$), 185 ([M − Me − Ph]$^+$), 121 ([M − NpOMe]$^+$).

Scheme 3



The halogenating cleavage reaction of the silicon−naphthyl bond of (1*S*,3*S*)-**8** was carried out under optimal reaction conditions for (*S*)-**6**. The stereoisomer ratio of 1,3-dibromo-1,3-dimethyl-1,3-diphenyldisiloxane **11a** was determined to be {(*S*,*S*) + (*R*,*R*)}:(*R*,*S*) = 91:9 (98% inversion) by ^{1}H NMR. When iodine monochloride was used as a halogenating agent, 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane **11b** with {(*S*,*S*) + (*R*,*R*)}:(*R*,*S*) = 91:9 (98% inversion) was obtained, but hydrolysis of (*S*,*S*)-**11b** with NH_4Cl·NH_3 buffer did not give 1,3-dimethyl-1,3-diphenyldisiloxanediol **12** with high optical yield ({(*S*,*S*) + (*R*,*R*)}:(*R*,*S*) = 63:37). On the other hand, the hydrolysis of dibromodisiloxane (*S*,*S*)-**11a** gave the optically active 1,3-dimethyl-1,3-diphenyldisiloxanediol **12**[16] in 83% yield with higher stereoselectivity ({(*S*,*S*) + (*R*,*R*)}:(*R*,*S*) = 78:22 determined by ^{1}H NMR). Further recrystallization from a minimal amount of 1:1 petroleum ether:CCl_4 at 0 °C gave (*S*,*S*)-**12** with (*S*,*S*):(*R*,*S*):(*R*,*R*) = 86:14:0 as determined by ^{1}H NMR and HPLC.

In conclusion, we have developed a highly stereoselective halogenating cleavage reaction of the silicon−(4-methoxy-1-naphthyl) bond. We also demonstrated the first example of the synthesis of highly optically active bifunctional 1,3-dimethyl-1,3-diphenyldisiloxane derivatives such as 1,3-dibromo-1,3-dimethyl-1,3-diphenyldisiloxane **11a**, 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane **11b**, and 1,3-dimethyl-1,3-diphenyldisiloxanediol **12**, which are not only useful compounds but also the most important synthetic intermediates for preparing optically active and/or stereoregular polysiloxanes. Further studies of the synthesis of optically active and/or stereoregular polysiloxanes are now in progress.

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Supporting Information Available: Experimental procedure for compounds (*S*)-**6** and (1*S*,3*S*)-**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) **1,3-Dimethyl-1,3-diphenyldisiloxanediol (**(1*S*, 3*S*)-**8**, 1.6484 g, 3.0 mmol) was converted to (*S*,*S*)-**11a** via a brominating cleavage reaction at −64 °C in $CHCl_3$. A solution of (*S*,*S*)-**11a** (3.0 mmol) was added to a mixture of aqueous NH_4Cl·NH_3 buffer (120 mL) and Et_2O (120 mL) at 0 °C under stirring. The organic phase was separated and dried over anhydrous Na_2SO_4. Removal of the solvent afforded a crude product, which was purified by recrystallization from a minimal amount (16 mL) of petroleum ether at −30 °C (0.7230 g, 83% yield, {(*S*,*S*) + (*R*,*R*)}:(*R*,*S*) = 78:22). Further recrystallization from a minimal amount (20 mL) of 1:1 petroleum ether:CCl_4 at 0 °C gave (*S*,*S*)-**12** (0.2305 g, 26% yield) with (*S*,*S*):(*R*,*S*):(*R*,*R*) = 86:14:0 as determined by ^{1}H NMR and HPLC (Daicel Chem. Ind., CHIRALPAK AD, 10:1 *n*-hexane:2-propanol as an eluent, 0.4 mL/min, 254 nm): mp 96.0−97.4 °C; $[\alpha]^{25}_D = +3.3$ (*c* = 1.045, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.42 (major) and 0.43 (minor) (2s, 6H), 2.58 (br s, 2H), 7.36−7.42 (m, 6H), 7.64 and 7.65 (2d, *J* = 6.5 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.11 (major) and −1.07 (minor), 128.1, 130.3, 133.5, 136.7; IR (KBr, cm^{-1}) 3225, 3071, 1592, 1429, 1126, 1066; EI-MS (*m*/*e*) 290 (M^+), 197 ([M − Me − Ph]$^+$).