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Stereospecific formation of optically active trialkylsilyllithiums and their configurational stability

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Abstract

Optically active trialkylsilyllithiums, (*R*)-(*n*-butyl)methylphenylsilyllithium (63% ee) and (*S*)-methyl(1-naphthyl)phenylsilyllithium (96% ee), were prepared by cleavage of the silicon–silicon bond of (*R*)-1-(*n*-butyl)-1-methyl-1-phenyl-2,2-diphenyl-2-methyldisilane with lithium metal, or the silicon–tin bond of (*S*)-methyl(1-naphthyl)phenylsilyltrimethylstannane with methyllithium, respectively. Optical purity of the silyllithiums was evaluated as corresponding silanes by HPLC on optically active stationary phase after hydrolysis. The formation of silyllithium was found to be highly stereospecific (>94, $>99\%$ retention, respectively). (*S*)-Methyl(1-naphthyl)phenylsilyllithium is configurationally stable for at least 1 h at $-78°C$ in tetrahydrofuran.

Keywords: Inter-element linkage; Chlorosilane; Disilane; Silylstannane; Optically active silyllithium; Stereospecificity; Configuration

1. Introduction

We have been interested in the stereospecific reactions of optically active silicon compounds and their application in the synthesis of stereoregular and/or optically active polymers, such as poly(carbosilane) [1–3], poly(carbosiloxane) [4–6] and poly(siloxane) [7,8]. The stereoregularity of these polymers reflected the optical purity of the starting monomers. Optically active silicon compounds are important synthetic intermediates in organic chemistry as well as in polymer chemistry.

Optically active silyllithium derivatives can be versatile synthetic intermediates in obtaining various optically active silicon compounds, if optically active silyllithium derivatives can be generated stereospecifically, and the configuration of the formed silyllithium is stable in the reaction media. Such optically active silyllithium derivatives will make it possible to synthesize silicon–carbon bonds in which asymmetry is introduced at both silicon and carbon centers, which can not be achieved by the substitution reaction by a carbanion at the asymmetric silicon center. Optically active silyllithium derivatives should also give optically active disilane derivatives having two asymmetric centers by the reaction with optically active chlorosilanes. Such optically active compounds will find versatile utility in the synthesis of various optically active silicon compounds and polymers.

Silyllithium derivatives are reported to form by a cleavage reaction of silicon-containing inter-element linkages by lithium metal or alkyllithium [9–15]. For example, the reaction of lithium metal with chlorosilanes or disilanes can give silyllithium derivatives [9,11,12]. It is also reported that the silicon–silicon bond of hexamethyldisilane can be cleaved by methyllithium to give trimethylsilyllithium in the presence of hexamethylphosphoric triamide (HMPA) [13,14], although the silicon–silicon bond of other substituted disilanes was hardly cleaved by the treatment with methyllithium. The reaction of alkyllithium with silylstannane derivatives is another typical method to obtain silyllithium derivatives [15]. Ikenaga pointed out

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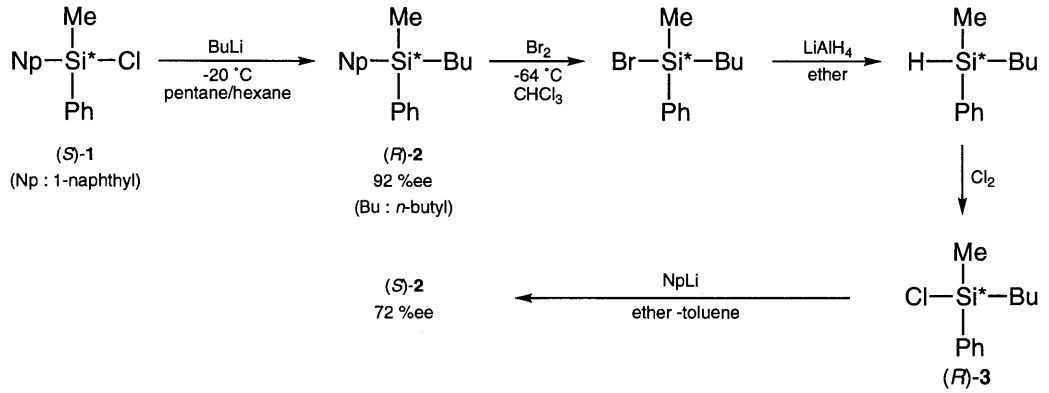


Scheme 1. Synthesis of optically active (*R*)-**3**.

the formation of disilane derivatives by the addition of alkyllithium to silylstannane derivatives [16]. The order of the addition of the reagent is important to form silyllithium selectively. Sommer [17] and Corriu [18,19] reported the formation of optically active silyllithium derivatives from optically active disilane and silylcobalt derivatives, respectively, but the stereospecificity of the reaction and the stereochemistry of the formed silyllithium has not been well established. In this report, methods for the formation of silyllithium were studied paying special attention to the stereospecificity of the formation reaction and the configurational stability of the formed silyllithium derivatives.

2. Results and discussion

2.1. Opticall active chlorosilane, disilane, and silylstannane derivatives as starting materials

To obtain starting materials to prepare silyllithium, new optically active chlorosilane, disilane, and silylstannane derivatives were synthesized.

(*R*)-(*n*-Butyl)methylphenylchlorosilane (*R*)-**3** was obtained according to Scheme 1.

Alkylation of (*S*)-methyl(1-naphthyl)phenylchlorosilane (*S*)-**1** by *n*-butyllithium proceeded with 92% stereoselectivity at −20°C in pentane–hexane mixed solvent to give (*R*)-(*n*-butyl)methyl(1-naphthyl)phenylsilane, (*R*)-**2**. Bromination and reduction of (*R*)-**2** gave (*S*)-(*n*-butyl)methylphenylsilane, which was further converted into (*R*)-(*n*-butyl)methylphenylchlorosilane, (*R*)-**3**. The optical purity of (*R*)-**3** was estimated to be 72% enantiomer excess (ee) by HPLC analysis of **2** obtained by the reaction with 1-naphthyllithium (Fig. 1).

The disilane and silylstannane derivatives were obtained by the reaction of chlorosilane with silyllithium or stannyllithium derivatives as shown in Scheme 2.

Diphenylmethylsilyllithium, which can be easily formed from lithium metal and diphenylmethylchlorosilane [9] was used to synthesize optically active disilanes, (*R*)-1-methyl-1-(1-naphthyl)-1-phenyl-2,2-diphenyl-2-

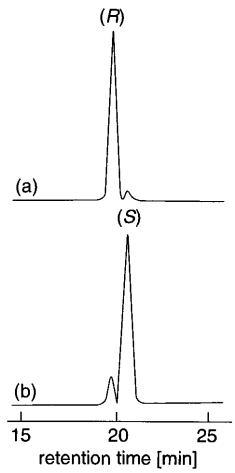
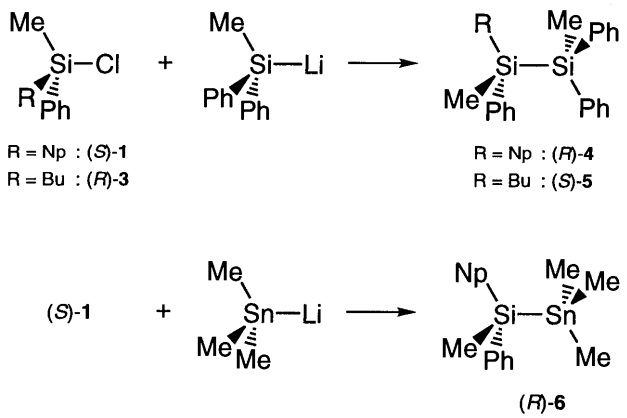


Fig. 1. HPLC of (a) (*R*)-**2** from (*S*)-**1**, and (b) (*S*)-**2** from (*R*)-**3** in Scheme 1.



Scheme 2. Synthesis of optically active (*R*)-**4**, (*S*)-**5**, and (*R*)-**6**.

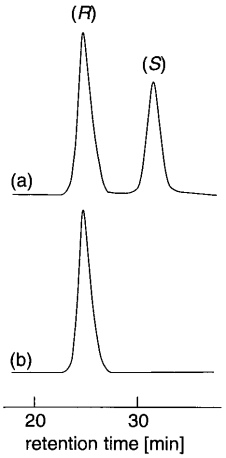


Fig. 2. HPLC of (*S*)-**5** obtained in (a) run 2 and (b) run 3 in Table 1.

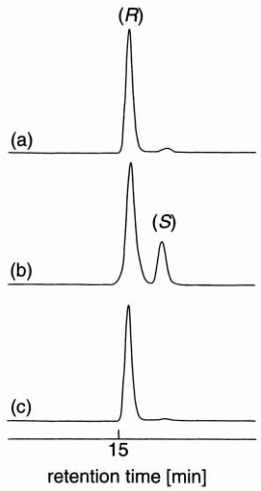


Fig. 3. HPLC of (*R*)-**6** obtained in (a) run 4, (b) run 5, and (c) run 6 in Table 1.

methyldisilane, (*R*)-**4**, and (*S*)-1-(*n*-butyl)-1-methyl-1-phenyl-2,2-diphenyl-2-methyldisilane, (*S*)-**5**. The stereospecificity of the reactions was analyzed by HPLC, and the results are shown in Fig. 2 and Table 1.

The substitution reaction to give (*R*)-**4** proceeded with almost complete inversion stereospecificity at the asymmetric silicon center when the diphenylmethylsilyllithium, generated in THF, was added dropwise to the pentane solution of (*S*)-**1** at −8°C (run 3). The optical purity of (*S*)-**5** could not be estimated because of poor separation on HPLC. However, stereoselectivity of the reaction to obtain (*S*)-**5** is considered to be similarly high as in the synthesis of (*R*)-**4**.

Optically active (*S*)-**1** was converted into optically active silylstannane derivatives by the reaction with trimethyl- or tri(*n*-butyl)stannyllithium [20]. Stereoselectivity of the nucleophilic displacement was evaluated by the direct analysis of ee of the formed silylstannanes by HPLC. The results are shown in Fig. 3 and Table 1.

The reaction of tri(*n*-butyl)stannyllithium in THF at −20°C gave racemized methyl(1-naphthyl)phenylsilyltri(*n*-butyl)stannane. Addition of tri(*n*-butyl)stannyllithium in THF dropwise to (*S*)-**1** dissolved in ether at −20°C gave the best selectivity (>85%). Trimethylstannyllithium gave better results, as shown in Table 1 (run 4) and Fig. 3. Lowering of the temperature resulted in poor stereoselectivity, probably because of the racemization of (*S*)-**1** over a long reaction period in THF (run 5). Addition of trimethylstannyllithium dropwise into a 1:1 pentane–ether (v/v) solution of (*S*)-**1** gave (*R*)-methyl(1-naphthyl)phenylsilyltrimethylstannane, (*R*)-**6**, of 97% ee (run 6).

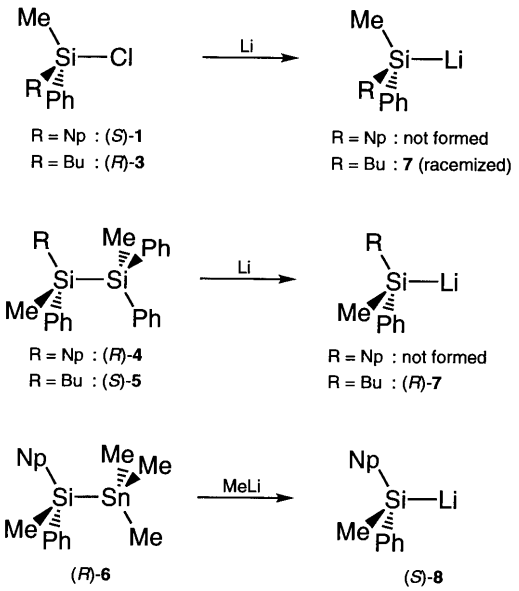
2.2. Optically active silyllithiums

Optically active silyllithium derivatives were synthesized starting from optically pure (*S*)-**1** as a mother compound according to the following reactions: (1) reaction of lithium metal with chlorosilanes (*S*)-**1** or (*R*)-**3** or disilane derivatives (*R*)-**4** or (*S*)-**5**, and (2)

Table 1
Synthesis of optically active disilane and silylstannane derivatives
(*S*)-**1** in solvent $\xrightarrow[\text{Temp. 15 min}]{\text{MLi in THF}}$ (*R*)-**4**, (*R*)-**6**

Run	M	Solvent	Temperature (°C)	Product	
				Compound (yield %)	ee (%)
1	$SiMe(Ph)_2$	THF	−8	(*R*)-**4** (–)	20
2		Et_2O	−8	(*R*)-**4** (–)	30
3		Pentane	−8	(*R*)-**4** (74)	99
4	$Sn(Me)_3$	Ether	−20	(*R*)-**6** (54)	90
5 [a]		Ether	−78	(*R*)-**6** (–)	50
6		Ether/pentane [b]	−20	(*R*)-**6** (48)	97

[a] Reaction time: 60 min.
[b] Volume ratio = 1/1.



Scheme 3. Formation of optically active silyllithiums.

reaction of methyllithium with (*R*)-**6** as shown in Scheme 3.

By taking further transformation of the obtained silicon compound into consideration, naphthyl-substituted silyllithium was attempted to form from (*S*)-**1**. However, complex reaction products were formed, probably because of an electron transfer reaction from the lithium metal to the naphthyl group.

Although the reaction between (*R*)-**3** with lithium metal gave (*n*-butyl)methylphenylsilyllithium **7**, the reaction was slow at a temperature lower than −10°C even in THF. Stereochemistry of the formed silyllithium **7** was studied by analyzing the stereochemistry of **2** obtained according to Scheme 1 from **7**, after **7** was converted into (*n*-butyl)methylphenylsilane by hydrolysis.

It was found that silyllithium **7** from (*R*)-**3** in THF at −8°C is racemic. Relatively high temperatures and lengthy reaction times in THF may cause racemization of the starting (*R*)-**3** before the formation of silyllithium.

Since the presence of HMPA is considered not to be desirable to obtain optically active silyllithium, cleavage of the silicon–silicon bond of (*R*)-**4** and (*S*)-**5** by the lithium metal was attempted. Naphthyl-substituted (*R*)-**4** also gave complex products, as in the case of (*S*)-**1**. (*S*)-**5** gave (*R*)-**7** in reasonable yield. The optical purity (63% ee) of (*S*)-**2** obtained by hydrolysis indicates that (*R*)-**7** was formed from (*S*)-**5** (72% ee) and lithium metal with 94% stereoselectivity, and that the formation of silyllithium is a retention process.

The results are shown in Table 2.

In order to avoid the formation of disilane, (*R*)-**6** was added dropwise to the diluted solution of alkyllithium. The results are also included in Table 2. Presence of the naphthyl group on the silicon atom did not cause interferene in the reaction, and gave a clean product in reasonable yield. The stereospecificity of the reaction increased with decreasing reaction temperature (runs 4–6 in Table 2). Treatment of (*R*)-**6** with methyllithium in 1:1 THF–pentane (v/v) produced the silyllithium (*S*)-**8** with the highest stereospecificity (run 7 in Table 2). Tri(*n*-butyl)stannane derivative (run 3 in Table 2) gave lower stereoselectivity.

2.3. Configurational stability

The configurational stability of the formed silyllithium is very important if it is to be used as an intermediate. The change in ee with time and tempera-

Table 2
Formation of optically active silyllithiums [a]

(*R*)-**3**, (*S*)-**5**, (*R*)-**6** $\xrightarrow[\text{THF, temp., time}]{\text{Li or MeLi}}$ **7**, (*R*)-**7**, (*S*)-**8**

Run	Starting materials		Product	Time (h)	Temperature (°C)	Silane [b]		
		ee (%)				Yield (%)	ee (%)	Stereospecificity (%)
1	(*R*)-**3**	72	**7**	36	−8		0 [c]	
2	(*S*)-**5**	72	(*R*)-**7**	36	−8	71	64 [c]	94
3	SiMeNpPh–$SnBu_3$	>85	(*S*)-**8**	2	−78	14	67	90
4	(*R*)-**6**	90		2	0	54	67	88
5		90		2	−20	52	79	94
6		90		2	−78	63	88	99
7 [d]		97		2	−78	46	96	~100

[a] Li for runs 1 and 2, MeLi for runs 3–7 were used, respectively.
[b] After hydrolysis of silyllithium.
[c] Converted into **2**.
[d] 1:1 THF–pentane (v/v) was used as a solvent.

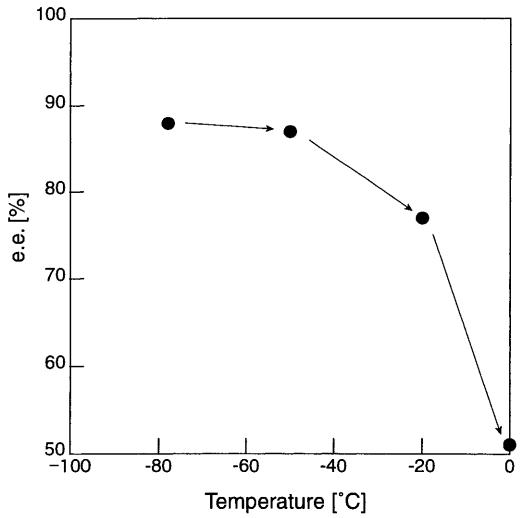


Fig. 4. Change of optical purity of (*S*)-**8** with the temperature in THF.

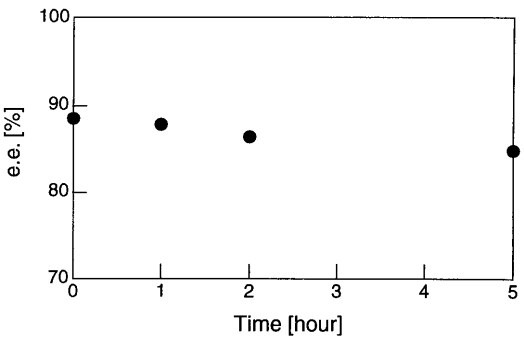


Fig. 5. Stability of optical purity of (*S*)-**8** with time in THF at −78°C.

ture are shown in Figs. 4 and 5. As the silyllithium solution was kept as −50, −20, and 0°C for 1 h, the optical purity was remakably decreased to 50% ee by elevating the temperature. However, the optical purity was kept higher than 85% ee at −78°C even after 5 h. Enantiomer excess virtually did not change in 1 h at −78°C. Thus, it was found that the optically active silyllithium is stable enough (at least for 1 h in THF at −78°C) to be used as a synthetic intermediate.

3. Conclusions

Optically active (*S*)-methyl(1-naphthyl)phenylsilyllithium (96% ee), was prepared by the cleavage of the silicon–tin bond of (*S*)-methyl(1-naphthyl)phenylsilyltrimethylstannane with methyllithium. The configuration of the silyllithium is stable for at least 1 h at −78°C in tetrahydrofuran. Naphthyl-substituted optically active silyllithium will find wide applicability to obtain a variety of optically active silicon compounds.

4. Experimental

4.1. Analysis

^{1}H-NMR spectra were obtained in $CDCl_3$ on a Varian 500 MHz spectrometer model Unity INOVA. Chemical shifts are reported in ppm, relative to $CHCl_3$ (δ 7.26). Mass spectra were taken on a Shimadzu QP-5000 mass spectrometer. High-resolution mass spectra were taken on a Bruker DALTONICS Bio-Apex 70 E. Optical purity of the compounds was evaluated by HPLC on a Daicel CHIRALCEL® OD column (cellulose triscarbamate derivative) with *n*-hexane as an eluent at a flow rate of 0.4 ml min^{-1} at 35°C.

4.2. Materials

4.2.1. (R)-(n-Butyl)methylphenylchlorosilane [(R)-3]

Alkylation of (*S*)-**1** with *n*-butyllithium in hexane gave (*R*)-(*n*-butyl)methyl(1-naphthyl)phenylsilane, (*R*)-**2**, (92% ee, 74% yield). Bromination of (*R*)-**2** (2.17 g, 7.0 mmol) in $CHCl_3$ (10 ml) by Br_2 in $CHCl_3$ (0.5 M, 7.0 mmol) at −64°C for 0.5 h, and following reduction by the addition of an Et_2O (10 ml) solution of $LiAlH_4$ (0.27 g, 7.0 mmol) at the temperature gave (*S*)-(*n*-butyl)methylphenylsilane (53% yield) after purification by silica-gel column chromatography (hexane). ^{1}H-NMR: δ 0.33 (d, 3H, $J = 3.6$ Hz, SiCH_3), 0.88 (t, 3H, $J = 3.2$ Hz, $SiCH_2CH_2CH_2CH_3$), 1.18–1.39 (m, 6H, $SiCH_2CH_2CH_2CH_3$), 4.30–4.37 (m, 1H, Si*H*), 7.30–7.86 (m, 5H, Ar*H*).

Passing chlorine gas to the silane (0.53 g, 3.0 mmol) in CCl_4 (10 ml) gave (*R*)-**3** (0.64 g, 99% yield).

^{1}H-NMR: δ 0.66 (s, 3H, SiCH_3), 0.91 (t, 3H, $J = 4.2$ Hz, $SiCH_2CH_2CH_2CH_3$), 1.25–1.50 (m, 6H, $SiCH_2CH_2CH_2CH_3$), 7.30–7.85 (m, 5H, Ar*H*).

4.2.2. (R)-1-Methyl-1-(1-naphthyl)-1-phenyl-2,2-diphenyl-2-methyldisilane [(R)-4] and (S)-1-(n-butyl)-1-methyl-1-phenyl-2,2-diphenyl-2-methyldisilane [(S)-5]

In a flask was placed a solution (10 ml) of (*S*)-**1** or (*R*)-**3** (3.0 mmol), and diphenylmethylsilyllithium in THF (0.4 M solution, 4.0 mmol) was added dropwise for 30 min at −8°C. Phosphate buffer solution (pH 6.8) was added, and the organic compounds were extracted with Et_2O (3 × 30 ml). Purification by silica-gel column chromatography (hexane) afforded (*R*)-**4** (0.99 g, 74% yield) and (*S*)-**5** (0.30 g, 27% yield).

(*R*)-**4**: ^{1}H-NMR: δ 0.68 (s, 3H, $Si(Ph)_2CH_3$), 0.80 (s, 3H, Si (Np)(Ph)CH_3), 7.06–8.16 (m, 22H, Ar*H*). MS (*m*/*z*): 444 [M^+ (weak)], 247 (SiMeNpPh), 197 ($SiMe(Ph)_2$). Found: *m*/*z* 444.1753. Calc. for $C_{30}H_{28}Si_2$: M, 444.1730.

(*S*)-**5**: ^{1}H-NMR: δ 0.40 (s, 3H, $SiCH_2CH_2CH_2CH_3$), 0.59 (s, 3H, $Si(Ph)_2CH_3$), 0.89 (t, 3H, $J = 6.6$ Hz, Si(*n*-Bu)(Ph)CH_3), 1.21–1.33 (m, 6H, $SiCH_2CH_2CH_2$

CH_3), 7.24–7.53 (m, 15H, Ar*H*). MS (*m*/*z*): 374 [M^+ (weak)], 197 ($SiMe(Ph)_2$), 177 (SiBuMePh), 121 (SiMePh). Found: *m*/*z* 374.1906. Calc. for $C_{24}H_{30}Si_2$: M, 374.1886.

4.2.3. (R)-Methyl(1-naphthyl)phenylsilyltrimethylstannane [(R)-6]

In a flask (*S*)-**1** (1.13 g, 4.0 mmol) was dissolved in 5 ml of Et_2O and 5 ml of pentane. To the solution, trimethylstannyllithium in THF (0.5 M solution, 5.0 mmol) was added dropwise for 1 h at −20°C under stirring. After decomposition by a phosphate buffer solution, the products were extracted with Et_2O (3 × 30 ml) and purified by silica-gel column chromatography (10:1 hexane–toluene) to afford (*R*)-**6** (0.88 g, 54% yield).

^{1}H-NMR: δ 0.10 (s, 9H, $SnCH_3$), 0.88 (s, 3H, $SiCH_3$), 7.32–7.90 (m, 12H, Ar*H*). MS (*m*/*z*): 412, 410, 408 [M^+ (weak)], 397, 395, 393 [M-15(Me)], 247 (SiMeNpPh), 135, 133, 131 (SnMe). Found: *m*/*z* 412.0667. Calc. for $C_{20}H_{24}SiSn$: M, 412.0669.

The tri(*n*-butyl) analogue was obtained similarly (2.29 g, 50% yield).

^{1}H-NMR: δ 0.74 (t, 3H, $J = 7.1$ Hz, $SnC_3H_6CH_3$), 0.87 (t, 2H, $J = 7.3$ Hz, $SnCH_2C_3H_7$), 0.89 (s, 3H, $SiCH_3$), 1.15 (seq, 2H, $J = 7.3$ Hz, $SnC_2H_4CH_2CH_3$), 1.32 (quin, 2H, $J = 7.3$ Hz, $SnCH_2CH_2C_2H_5$), 7.29–7.91 (m, 12H, Ar*H*). MS (*m*/*z*): 481, 479, 477 [M-57(Bu) (weak)], 425, 423, 421 ([M + H]-113 (Bu_2) [weak]), 369, 367, 365 ([M + H_2]-171 (Bu_3) [weak]), 247 (SiMeNpPh), 121, 119, 117 (Sn + H).

4.2.4. (n-Butyl)methylphenylsilyllithium (7)

In a flask were placed finely cut lithium (0.11 g, 15 mmol), dry THF (10 ml) under argon. (*R*)-**3** (0.26 g, 0.7 mmol) was added and the reaction system was stirred at −8°C for 36 h. The extent of the formation of **7** was evaluated as (*n*-butyl)methylphenylsilane after hydrolysis with 1 N HCl. The stereochemistry was studied by HPLC after conversion of the silane into **2** via chlorination and alkylation by 1-naphthyllithium.

4.2.5. (R)-methyl(1-naphthyl)phenylsilyllithium [(S)-8]

To methyllithium (1.5 mmol) in THF (20 ml) kept at −78°C under argon atmosphere, (*R*)-**6** (412 mg, 1 mmol) in a solvent (20 ml) was added dropwise for 2 h. The extent of the formation and the stereochemistry of (*S*)-**8** were evaluated as methyl(1-naphthyl)phenylsilane after hydrolysis.

Methyl(1-naphthyl)phenylsilane: Found: *m*/*z* 248.1026. Calc. for $C_{17}H_{16}Si$: M, 248.1021.

Acknowledgements

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