

REACTION OF 2-SILATETRALINS WITH ALKYL HALIDES AND KETONES UNDER BASIC CONDITIONS¶

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Abstract ---The reaction of 2-silatetralins with alkyl halides (methyl iodide, benzyl chloride) and ketones (acetone, cyclohexanone) in *sec*-butyllithium (BuLi)-, *sec*-BuLi-tetramethylenediamine- or *sec*-BuLi-hexamethylphosphoramide-tetrahydrofuran media at lower temperature is described. The reaction gave rise to 1-alkylated 2-silatetralins in fair to good yield, serving a method for synthesis of a potent intermediate leading to novel silicon-containing compounds.

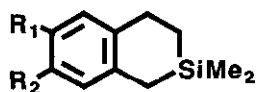
Although nucleophilic substitution¹ of 2-silatetralins has been investigated extensively, there are few reports on electrophilic reaction. Unlike tetralins, the reaction of 2-silatetralin (**1**)² with electrophiles under basic conditions seems to take place at 1 position rather than 4 position, because the former position is more activated than the latter position by the effect where silicon will stabilize an adjacent carbon-metal bond, so-called carbanions. Therefore, alkylation of 2-silatetralins would lead to a key compound for synthesis of novel silicon-containing compound (*e.g.* **2**³ or **3**). The present paper deals with the reaction of 2-silatetralins with alkyl halides and ketones under basic conditions.

RESULT AND DISCUSSION

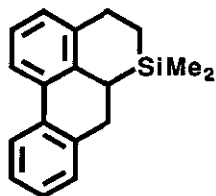
Reaction of 2-Silatetralin (**1**) with Alkyl Halides and Ketones under Basic Conditions

At first, lithiation of **1** with lithium diisopropylamide, *n*-butyllithium (BuLi), *sec*-BuLi or *tert*-BuLi in THF or

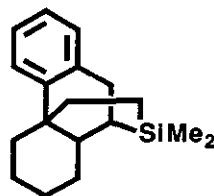
¶ This paper is dedicated to Professor Rolf Huisgen on the occasion of his 75th birthday.



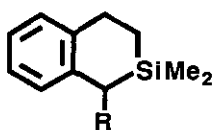
- 1 $R_1 = R_2 = H$
 5 $R_1 = H, R_2 = OMe$
 6 $R_1 = OMe, R_2 = H$
 14 $R_1 = H, R_2 = OH$

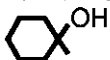
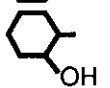


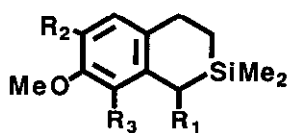
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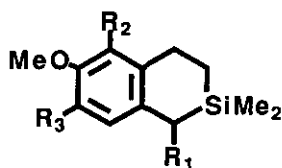
3



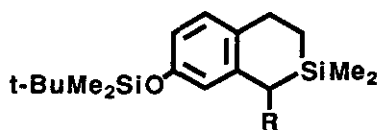
- 4a $R = Me$
 4b $R = CH_2Ph$
 4c $R = C(OH)Me_2$
 4d $R =$ 
 4e $R =$ 



- 7 $R_1 = R_3 = H, R_2 = Me$
 8 $R_1 = R_2 = H, R_3 = Me$
 9 $R_1 = Me, R_2 = R_3 = H$
 10 $R_1 = CH_2Ph, R_2 = R_3 = H$



- 11 $R_1 = R_2 = H, R_3 = Me$
 12 $R_1 = R_3 = H, R_2 = Me$
 13 $R_1 = CH_2Ph, R_2 = R_3 = H$



- 15 $R = H$
 16 $R = CH_2Ph$
 17 $R = CH_2C_6H_4OMe-4$

Et₂O followed by treatment with methyl iodide (MeI) in THF under a variety of conditions (reaction temperature, reaction time etc) was examined. Consequently, among the lithium reagents employed, *sec*-BuLi gave the most satisfactory results. Namely, the reaction of **1** with *sec*-BuLi in THF at -30 °C followed by treatment with MeI gave 1-methyl-2-silatetralin (**4a**) in 57% yield. The reaction with benzyl chloride under conditions similar to those noted for **4a** produced **4b** in 73% yield. Furthermore, the reaction with acetone and cyclohexanone took place smoothly to give **4c** and **4d** in acceptable yields. Yields and boiling points for **4a-d** are listed in Table 1. Expectedly, the reaction was proved exclusively to occur at 1 position. The reaction with cyclohexene oxide afforded also 1-(2-hydroxycyclohexyl)-2-silatetralin (**4e**) in 79% yield. However, with benzaldehyde the reaction showed poor reproducible results.⁴

Table 1 Yields and boiling points for **4a-d**

Entry	Electrophile		Product		bp °C / mmHg of 4
	Alkyl Halide	Ketone	4	Yield (%)	
1	Methyl Iodide		4a	57	80-82 / 2
2	Benzyl Chloride		4b	73	146-148 / 1
3		Acetone	4c	51	120-122 / 3
4		Cyclohexanone	4d	44	136-137 / 0.6

Next, in order to obtain a potent intermediate for synthesis of novel silicon-containing compound (*e.g.* **3**), the reaction of 7- and 6-methoxy-2-silatetralins (**5** and **6**)⁵ with alkyl halides was performed. In the reaction, *sec*-BuLi was also effective. With MeI, **5** gave a mixture of 6- and 8-methyl products (**7** and **8**)(42% yield) in a product ratio of 5 : 4 along with a mixture of 1-methylated product (**9**) and **5**, whereas **6** afforded exclusively a mixture of 5- and 7-methyl products (**11** and **12**)(34% yield) in a product ratio of 3 : 7. However, all attempts to separate each product chromatographically were unfruitful. On the other hand, although the reaction of **5** with benzyl chloride gave 1-benzylated product (**10**) in 32% yield, the reaction of **6** did not proceed. The unsuccessful alkylation of **6** at 1 position would be attributable to the lower acidity of methylene group at 1 position due to electron-donating effect of the methoxyl group at 6-position. After exploration of the base

effective for formation of carbanion at 1 position, the reaction of **6** with benzyl chloride in *sec*-BuLi-tetramethylenediamine (TMEDA) medium was found to give a 1-benzylated product (**13**), although in low yield. Finally, to obtain 1-arylmethyl-7-hydroxy-2-silatetralins, arylmethylation of 7-(*tert*-butyldimethylsilyloxy)-2-silatetralin (**15**), which was prepared from 7-hydroxy-2,2-dimethyl-2-silatetralin⁵ (**14**), in *sec*-BuLi-hexamethylphosphoramide (HMPA) medium was carried out to produce **16** and **17** in fair to good yield. Deprotection of **16** and **17** to obtain 1-arylmethyl-7-hydroxy-2-silatetralins is now in progress.

In conclusion, the reaction of 2-silatetralins with alkyl halides (for **1**, **5**, **6**, and **15**) and ketones (for **1**) under basic conditions was proved to give 1-alkylated 2-silatetralins (**4**, **9**, **10**, **13**, **16**, and **17**), although the reaction conditions were not always optimized. Application of the methodology to synthesis of novel silicon-containing compounds is reported elsewhere.³

ACKNOWLEDGEMENTS

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EXPERIMENTAL

General----All boiling points are uncorrected. Ir spectra were taken with a Hitachi model 260-10 spectrophotometer in CHCl₃ solution. ¹H-Nmr spectra were recorded on a JEOL model FX-100 spectrometer in CDCl₃ solution using Me₄Si or CHCl₃ as an internal standard, unless otherwise noted. Ms were measured on a Hitachi M-80 or M-80A spectrometer. HRms were measured on a Hitachi M-80 spectrometer. The preparative tlc was carried out on Kieselgel 60F₂₅₄ (Merck).

Materials----THF was distilled from sodium wire and benzophenone prior to use. *sec*-BuLi-cyclohexane solution was purchased from Kanto Chemical Co. Inc., and titrated before use.

General Procedure for Preparation of 1-Alkyl-2,2-dimethyl-2-silatetralins (4)---- *sec*-BuLi-cyclohexane solution was added dropwise to a stirred solution of 2-silatetralin (**1**)² in THF at -30 °C under Ar and stirring was continued for 80 min at the same temperature. To the stirred reaction mixture was added a solution of alkyl halide or ketone in THF, and the whole was stirred at the same temperature for 50 min. The reaction mixture was poured onto ice-water and the product was taken up in CH₂Cl₂. The CH₂Cl₂ extract was

washed with water and dried over MgSO_4 . The oily residue obtained on removal of the solvent *in vacuo* was distilled under reduced pressure to give oily product (4).

1,2,2-Trimethyl-2-silatetralin (4a) --- **1** (1.5 g, 8.5 mmol)-THF (15 ml), *sec*-BuLi-cyclohexane (9.2 ml, 9.4 mmol), and MeI (1.5 ml, 9.4 mmol)-THF (15 ml) were used. **4a** (oil, 0.92 g, 57 %, bp 80-82 °C / 2 mmHg). $^1\text{H-Nmr}$ δ : -0.25, 0.17 (each 3H, s, SiMe_2), 0.53-1.10 (2H, m, 3- H_2), 1.37 (3H, d, $J = 7.1$ Hz, *CHMe*), 2.02 (1H, q, $J = 7.1$ Hz, *CHMe*), 2.46-3.03 (2H, m, 4- H_2), 6.88-7.21 (4H, m, Ar-H x 4). Ir : 1250 (SiCH_2) cm^{-1} . HRms m/z calcd for $\text{C}_{12}\text{H}_{18}\text{Si}$ (M^+) : 190.1176, found : 190.1176; ms m/z : 190 (M^+).

1-Benzyl-2,2-dimethyl-2-silatetralin (4b) --- **1** (1.5 g, 8.5 mmol)-THF (15 ml), *sec*-BuLi-cyclohexane (9.2 ml, 9.4 mmol), and PhCH_2Cl (1.2 g, 9.4 mmol)-THF (15 ml) were used. **4b** (oil, 1.65 g, 73 %, bp 146-148 °C / 1 mmHg). $^1\text{H-Nmr}$ δ : -0.22, -0.10 (each 3H, s, SiMe_2), 0.53-1.05 (2H, m, 3- H_2), 2.63-2.97 (2H, m, Ar CH_2CH), 2.97-3.32 (2H, m, 4- H_2), 3.58 (1H, t, $J = 8.3$ Hz, 1-H), 6.80-7.36 (9H, m, Ar-H x 9). Ir : 1250 (SiCH_2) cm^{-1} . HRms m/z calcd for $\text{C}_{18}\text{H}_{22}\text{Si}$ (M^+) : 266.1490, found : 266.1502; ms m/z : 266 (M^+).

1-(1-Hydroxy-1-methyl)-ethyl-2,2-dimethyl-2-silatetralin (4c) --- **1** (1.5 g, 8.5 mmol)-THF (15 ml), *sec*-BuLi-cyclohexane (12.5 ml, 12.8 mmol), and acetone (0.5 g, 8.5 mmol)-THF (15 ml) were used. **4c** (oil, 1.0 g, 51%, bp 120-122 °C / 3 mmHg). $^1\text{H-Nmr}$ δ : 0.12 (6H, s, SiMe_2), 0.77-0.97 (2H, m, 3- H_2), 1.69 [4H, d, $J = 2$ Hz, 1-H, C(OH)(*Me*)*Me*], 1.90 [3H, d, $J = 2$ Hz, C(OH)(*Me*)*Me*], 3.51-3.71 (2H, m, 4- H_2), 6.24 (1H, bs, OH), 6.92-7.19 (4H, m, Ar-H x 4). Ir : 3700-3200 (OH) cm^{-1} . HRms m/z calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$ (M^+) : 234.1439, found : 234.1450; ms m/z : 234 (M^+).

1-(1-Hydroxycyclohexyl)-2,2-dimethyl-2-silatetralin (4d) --- **1** (1.0 g, 5.7 mmol)-THF (15 ml), *sec*-BuLi-cyclohexane (6.1 ml, 6.2 mmol), and cyclohexanone (0.612 g, 6.2 mmol)-THF (15 ml) were used. **4d** (oil, 0.68 g, 44 %, bp 136-137 °C / 0.6 mmHg). $^1\text{H-Nmr}$ δ : 0.38 (6H, s, SiMe_2), 0.87-1.27 (2H, m, 3- H_2), 1.70-2.53 (12H, m, 1-hydroxycyclohexyl, 1-H), 2.72-3.13 (2H, m, 4- H_2), 6.80-7.17 (4H, m, Ar-H x 4). Ir : 3700-3200 (OH) cm^{-1} . HRms m/z calcd for $\text{C}_{12}\text{H}_{18}\text{Si}$ (M^+) : 274.1751, found : 274.1746; ms m/z : 274 (M^+).

1-(2-Hydroxycyclohexyl)-2,2-dimethyl-2-silatetralin (4e) --- **1** (0.3 g, 1.7 mmol)-THF (5 ml), *sec*-BuLi-cyclohexane (2.0 ml, 2.0 mmol), and cyclohexene oxide (0.268 g, 2.7 mmol)-THF (5 ml) were used. **4e** [oil, 0.37 g, 79 %, bp 250 °C / 0.6 mmHg (bath temperature)]. $^1\text{H-Nmr}$ δ : -0.04, 0.80 (each 3H, s, SiMe_2), 0.60-0.97 (2H, m, 3- H_2), 0.97-2.09 (11H, m, 2-hydroxycyclohexyl), 2.52-2.92 (2H, m, 4- H_2), 3.24-3.57 (1H, m, 1-H), 6.88-7.21 (4H, m, Ar-H x 4). Ir : 3700-3200 (OH) cm^{-1} ; ms m/z : 274 (M^+).

General Procedure for Reaction of 7- and 6-Methoxy-2,2-dimethyl-2-silatetralins (5 and 6) --

-- *sec*-BuLi-cyclohexane solution was added dropwise to a stirred solution of 7- and 6-methoxy-2-silatetralins (**5** and **6**)⁵ in THF at -70 ~ -60 °C under Ar and stirring was continued for 10-25 min at the same temperature. To the stirred reaction mixture was added dropwise a solution of alkyl halide in THF at the same temperature and the whole was stirred under reaction conditions described below. The reaction was quenched with water and the product was taken up in CHCl₃. The CHCl₃ extract was washed with water and dried over MgSO₄. The oily residue obtained on removal of the solvent *in vacuo* was purified by preparative tlc to give **7** - **13**.

With **5**: (a) **5** (130 mg, 0.63 mmol)-THF (2 ml), *sec*-BuLi-cyclohexane (0.76 ml, 0.76 mmol), and MeI (108 mg, 0.76 mmol)-THF (1 ml) were used. The reaction was carried out for 220 min at -40 ~ -10 °C. After preparative tlc (developing solvent; hexane-EtOAc = 100 : 1; two developments), products (**7** + **8**)[oil, 37.4 mg, 27%; a product ratio of **5** : **4**; ms *m/z* : 220 (M⁺)] and (**9** + **5**)[oil, 97 mg, a product ratio of **3** : **2**; ms *m/z* : 220 (M⁺); ms *m/z* : 206 (M⁺)] were obtained. As each product could not be separated, a product ratio was estimated by comparison of each peak due to 1-H₂ and ArMe in the ¹H-nmr spectrum. *7-Methoxy-2,2,6-trimethyl-2-silatetralin* (**7**): ¹H-Nmr δ : 0.04 (6H, s, SiMe₂), 1.91 (2H, s, 1-H₂), 2.16 (3H, s, Ar-Me), 3.89 (3H, s, OMe), 6.56 (1H, s, 8-H), 6.81(1H, s, 5-H); *7-Methoxy-2,2,8-trimethyl-2-silatetralin* (**8**): ¹H-Nmr δ : 0.02 (6H, s, SiMe₂), 1.90 (2H, s, 1-H₂), 2.18 (3H, s, Ar-Me), 3.88 (3H, s, OMe), 6.55 (1H, d, *J* = 7.5 Hz, 8-H), 6.84(1H, d, *J* = 7.5 Hz, 5-H); *7-Methoxy-1,2,2-trimethyl-2-silatetralin* (**9**)⁶: ¹H-Nmr⁷ δ : -0.02, 0.22 (each 3H, s, SiMe₂), 0.65-1.16 (2H, m, 3-H₂), 1.40 (1H, d, *J* = 7 Hz, 1-Me), 2.57-2.90 (3H, m, 1-H, 4-H₂), 3.82 (3H, s, OMe), 6.50-7.20 (3H, m, Ar-H x 3).

(b) **5** (30 mg, 0.145 mmol)-THF (1ml), *sec*-BuLi-cyclohexane (0.17 ml, 0.17 mmol), and PhCH₂Cl (22 mg, 0.17 mmol)-THF (1 ml) were used. The reaction was carried out 90 min at -60 ~ -50 °C. *1-Benzyl-7-methoxy-2,2-dimethyl-2-silatetralin* (**10**)(oil, 15 mg, 35%)[after preparative tlc (developing solvent; hexane EtOAc = 50 : 1; two developments)]: ¹H-Nmr δ : -0.21, -0.12 (each 3H, s, SiMe₂), 0.66-0.94 (2H, m, 3-H₂), 2.28-2.48 (1H, t, *J* = 8.6 Hz, 1-H), 2.76 (2H, d, *J* = 8.6 Hz, ArCH₂), 2.97-3.22 (2H, m, 4-H₂), 3.66 (3H, s, OMe), 6.46-7.24 (8H, m, Ar-H x 8); ms *m/z* : 296 (M⁺).

With **6**: (a) **6** (54.7 mg, 0.27 mmol)-THF (1 ml), *sec*-BuLi-cyclohexane (0.27 ml, 0.29 mmol), and MeI (41.6 mg, 0.29 mmol)-THF (1 ml) were used. The reaction was carried out for 150 min at -50 to -10 °C. After preparative tlc (developing solvent ; hexane-EtOAc = 50 : 1), products (**11** + **12**)(oil, 19.7 mg, 34%; a product ratio of **7** : **3**). As each product could not be separated, a product ratio was estimated by comparison of each

peak due to 1-H₂ and ArMe in ¹H-nmr spectrum. HRms *m/z* calcd for C₁₃H₂₀OSi (M⁺) : 220.1283, found : 220.1283; ms *m/z* : 220 (M⁺). **6-Methoxy-2,2,7-trimethyl-2-silatetralin (11)**: ¹H-Nmr δ : 0.04 (6H, s, SiMe₂), 1.84 (2H, s, 1-H₂), 2.16 (3H, s, Ar-Me), 3.78 (3H, s, OMe), 6.57 (1H, s, 5-H), 6.81 (1H, s, 8-H). **6-Methoxy-2,2,5-trimethyl-2-silatetralin (12)**: ¹H-Nmr δ : 0.01 (6H, s, SiMe₂), 1.88 (2H, s, 1-H₂), 2.20 (3H, s, Ar-Me), 3.78 (3H, s, OMe), 6.60 (1H, d, *J* = 7.5 Hz, 5-H), 6.85 (1H, d, *J* = 7.5 Hz, 8-H).

(b) **6** (49 mg, 0.24 mmol)-HMPA (85 mg, 0.48 mmol)-THF (3 ml), *sec*-BuLi-cyclohexane (0.44 ml, 0.48 mmol), and PhCH₂Cl (36.2 mg, 0.29 mmol)-THF (3 ml) were used. The reaction was carried out for 80 min at -78 °C. **1-Benzyl-6-methoxy-2,2-dimethyl-2-silatetralin (13)**(oil, 9.3 mg, 13%)[after preparative tlc (developing solvent; hexane-EtOAc = 30 : 1; two developments)]: ¹H-Nmr δ : -0.22, -0.11 (each 3H, s, SiMe₂), 0.64-0.90 (2H, m, 3-H₂), 2.32 (1H, t, *J* = 7.9 Hz, 1-H), 2.97-3.22 (2H, m, 4-H₂), 3.03 (2H, d, *J* = 7.9 Hz, ArCH₂), 3.74 (3H, s, OMe), 6.50-7.24 (8H, m, Ar-H x 8). HRms *m/z* calcd for C₁₉H₂₄OSi (M⁺) : 296.1594, found : 296.1586; ms *m/z* : 296 (M⁺).

7-(tert-Butyldimethylsilyloxy)-2,2-dimethyl-2-silatetralin (15) ---A solution of *tert*-BuMe₂SiCl (347 mg, 2.3 mmol) and DBU (382 mg, 2.5 ml) in CH₂Cl₂ (4 ml) was added to a stirred solution of 7-hydroxy-2-silatetralin (**14**)⁵ (401 mg, 2.1 mmol) in CH₂Cl₂ (4 ml) at room temperature and the whole was stirred at the same temperature for 12 h. The reaction mixture was washed with 0.1N HCl and saturated NaHCO₃ solution, and water, and dried over MgSO₄. The oily residue (540 mg) obtained by usual work-up was purified on preparative tlc (developing solvent; hexane - AcOEt = 50 : 1) to afford **15** (440 mg, 69%) as a colorless oil. ¹H-Nmr δ : 0.00 (6H, s, 2-SiMe₂), 0.20 (6H, s, OSiMe₂), 0.60-0.90 (2H, m, 3-H₂), 1.00 (9H, s, SiBu^t), 1.90 (2H, s, 1-H₂), 2.60-2.90 (2H, m, 4-H₂), 6.50-7.00 (3H, m, Ar-H x 3). HRms *m/z* calcd for C₁₇H₃₀OSi₂ (M⁺) : 306.1834, found : 306.1835; ms *m/z* : 306 (M⁺).

General Procedure for Reaction of 15 with Aralkyl Chlorides--- *sec*-BuLi-cyclohexane solution was added dropwise to a stirred solution of **15** in THF and HMPA at -78 °C under Ar and stirring was continued for 70 min at the same temperature. To the stirred reaction mixture was added dropwise a solution of aralkyl halide in THF at the same temperature and the whole was stirred for 18 h at -78 °C to room temperature. The reaction was quenched with water and the product was taken up in CHCl₃. The CHCl₃ extract was washed with water and dried over MgSO₄. The oily residue obtained on removal of the solvent *in vacuo* was purified by preparative tlc (developing solvent: hexane - AcOEt = 50 : 1) to lead to **16**, **17**.

1-Benzyl-7-(tert-butyldimethylsilyloxy)-2,2-dimethyl-2-silatetralin (16): **15** (1.0 g, 3.27 mmol)-HMPA (0.63 g, 3.60 mmol)-THF (6 ml), *sec*-BuLi-cyclohexane (3.27 ml, 3.60 mmol), and PhCH₂Cl (0.45 g, 3.6 mmol)-THF (3 ml) were used. **16** (oil, 690.7 mg, 53%): ¹H-Nmr δ : -0.13, -0.08 (each 3H, s, 2-SiMe₂), 0.07 (6H, s, OSiMe₂), 0.95 (9H, s, SiBu^t), 0.79-1.01 (2H, m, 3-H₂), 2.28-3.16 (5H, m, 1-H, 4-H₂, ArCH₂), 6.40-7.18 (3H, m, Ar-H x 3). HRms *m/z* calcd for C₂₄H₃₆OSi₂ (M⁺) : 396.2303, found : 396.2305; *ms m/z* : 396 (M⁺).

7-(tert-Butyldimethylsilyloxy)-1-(3-methoxybenzyl)-2,2-dimethyl-2-silatetralin (17): **15** (1.05 g, 3.3 mmol)-HMPA (0.65 g, 3.60 mmol)-THF (6 ml), *sec*-BuLi-cyclohexane (3.3 ml, 3.60 mmol), and 3-MeOC₆H₄CH₂Cl (0.56 g, 3.6 mmol)-THF (3 ml) were used. **17** (oil, 816 mg, 58%): ¹H-Nmr δ : -0.14, -0.12 (each 3H, s, 2-SiMe₂), 0.03 (6H, s, OSiMe₂), 0.95 (9H, s, SiBu^t), 0.84-1.01 (2H, m, 3-H₂), 2.24-3.12 (5H, m, 1-H, 4-H₂, ArCH₂), 3.72 (3H, s, ArOMe), 6.40-7.12 (3H, m, Ar-H x 3). HRms *m/z* calcd for C₂₅H₃₈O₂Si₂ (M⁺) : 426.2408, found : 426.2402; *ms m/z* : 426 (M⁺).

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3. A. Hirokawa, A. Tatsuno, and O. Hoshino, *Heterocycles.*, 1994, **38**, 1103.
4. The reaction of **1** with benzaldehyde under conditions similar to those noted for **4** afforded 1-(α -hydroxybenzyl)-2,2-dimethyl-2-silatetralin (13%) along with **1** (67%). On the other hand, lithiation (-78 °C, 90 min) of **1** with *sec*-BuLi-hexane in THF followed by treatment (-78 °C, 60 min) with benzaldehyde led to 1-(α -hydroxybenzyl)-2,2-dimethyl-2-silatetralin (8%) and ring opening product, 2-(3-hydroxy-3,3-dimethyl-3-silapropyl)stilbene (25%) together with **1** (61%).
5. O. Hoshino, A. Hirokawa, T. Taguchi, and K. Miyauchi, *Heterocycles.*, 1994, **38**, 883.
6. ¹H-Nmr spectral data were obtained by cancellation of peaks in ¹H-nmr spectrum for **5** from those in ¹H-nmr spectrum for a mixture of **9** and **5**.
7. The spectrum was measured on a Hitachi R-24B (60 MHz) instrument in CDCl₃ solution using CHCl₃ as an internal standard.

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