RADICAL REACTION OF 1-(2-BROMOARYLMETHYL)-2-SILATETRALINS : FORMATION OF POLYCYCLIC ORGANOSILICON COMPOUNDS

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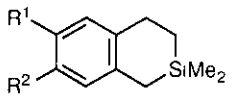
Abstract ----Radical reaction of 1-(2-bromoarylmethyl)-2-silatetralins (**4a-f**) with Bu_3SnH in boiling benzene containing AIBN was found to give novel tetracyclic (**5a-f**) and tricyclic (**6a-f**) organosilicon compounds, and 9-silylphenanthrenes (**7a-c**), respectively.

Introduction

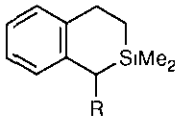
Recently,[1] we have reported that 2-silatetralins (**1**) having oxygen functional groups are readily synthesized by intramolecular Friedel-Crafts reaction coupled with the Grignard reaction. Furthermore, alkylation[2] of 2-silatetralins (**1a**) with alkyl halides under basic conditions was found to give rise to the corresponding 1-alkyl-2-silatetralins (**2**) in fair to good yields. In connection of our studies on synthesis and reaction of organosilicon compounds, the 1-alkyl-2-silatetralins thus obtained attracted our attention on synthesis of polycyclic silicon-containing compounds from them, because they might have a promise of biologically active silicon-containing compounds.

Numerous methods for construction of polycyclic ring systems have been reported ; photochemical cyclization,[3] phenolic[4] and non-phenolic[5] oxidative coupling reaction, the Pschorr reaction,[6] the intramolecular benzyne reaction,[7] radical reaction[8] and so on. Among them, at the present time, we tried synthesis of polycyclic silicon-containing compounds by radical reaction, because the

reaction is known to proceed under mild conditions [9] The present paper deals with synthesis of polycyclic silicon-containing compounds by radical reaction.



1 R^1=H, OMe
R^2=H, OMe



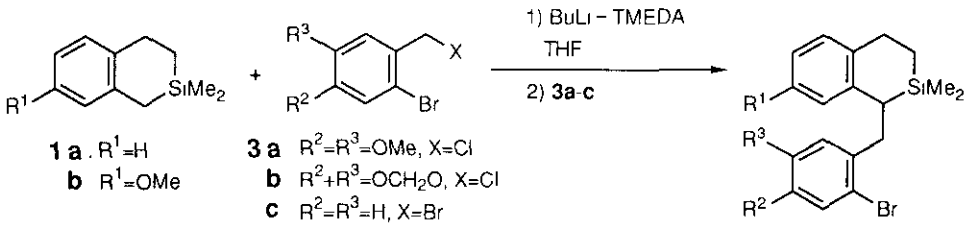
2 R=Me, CH_2Ph

RESULT AND DISCUSSION

Synthesis of 1-(2-Bromoarylmethyl)-2-silatetralins (4a-f)

Alkylation[2] of 2-silatetralin (**1a**) with alkyl halide under basic conditions readily proceeded at 1-position to give 1-alkyl-2-silatetralins (**2**) in fair to good yields. Therefore, the method was applied to synthesis of the 1-(2-bromoarylmethyl)-2-silatetralins (**4a-f**) as the starting material for radical cyclization.

Lithiation of 2-silatetralin (**1a**) with butyllithium (BuLi) (1 2 eq.) in tetrahydrofuran (THF) containing tetramethylethylenediamine (TMEDA) (1.2 eq.) at 0-5 °C for 1 5 h followed by treatment with 2-bromoveratryl chloride[10] gave in 67 % yield 1-(2-bromoveratryl)-2-silatetralin (**4a**) as colorless oil. Structure of **4a** was determined on the basis of proton nuclear magnetic resonance and mass spectra (^{1}H-nmr and ms). Analogously, 1-(2-bromoarylmethyl)-2-silatetralins (**4b-f**) were obtained in moderate yields The results are listed in Table 1.



1a . R^1=H
b R^1=OMe

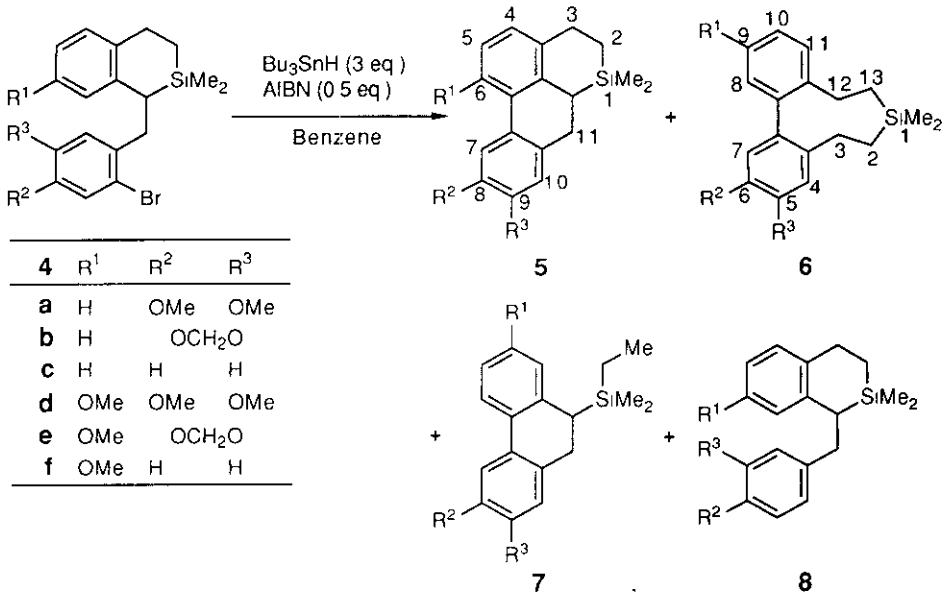
3a R^2=R^3=OMe, X=Cl
b R^2+R^3=OCH_2O, X=Cl
c R^2=R^3=H, X=Br

4a-f

Table 1 Yields and ^{1}H-Nmr Spectra for 1-(2-Bromoarylmethyl)-2-silatetralins (**4a-f**)

	Compound **4**			Yield (%)	^{1}H-Nmr δ (*J*, Hz)				
	R^1	R^2	R^3		$SiMe_2$	3-H	1-H	OMe	OCH_2O
a	H	OMe	OMe	67	-0.06, 0.11 (each s)	0.84 (t, 7.1)	2.41 (dd, 7.1, 8.6)	3.59, 3.84 (each s)	—
b	H	OCH_2O		16	-0.02, 0.01 (each s)	0.59-0.95 (m)	2.46 (t, 7.1)	—	5.89 (s)
c	H	H	H	24	-0.05, 0 04 (each s)	0 68-0.95 (m)	2.56 (t, 8.6)	—	—
d	OMe	OMe	OMe	48	-0.06, 0.09 (each s)	0 82 (t, 7.1)	2.41 (dd, 7.1, 8 6)	3.64, 3.65, 3.84 (each s)	—
e	OMe	OCH_2O		36	-0.02, -0.01 (each s)	0.64-0 94 (m)	2.44 (t, 7.1)	3.69 (s)	5.89 (s)
f	OMe	H	H	36	-0.06, 0 04 (each s)	0 59-0.99 (m)	2.52 (t, 7.1)	3 64 (s)	—

Radical Reaction of 4 leading to Cyclized Products (5, 6, and 7)



4	R^1	R^2	R^3
a	H	OMe	OMe
b	H	OCH_2O	
c	H	H	H
d	OMe	OMe	OMe
e	OMe	OCH_2O	
f	OMe	H	H

The reaction of **4a** with tributyltin hydride (Bu_3SnH) (2.0 eq) in boiling benzene (0.01 M) containing azobisisobutyronitrile (AIBN ; 0.5 eq.) for 2 h did not take place completely. Therefore, the reaction was carried out with 3 eq. of Bu_3SnH in the same concentration. After usual work-up, the reaction mixture was separated by silica gel column chromatography followed by medium pressure liquid and then preparative thin layer chromatographies (mplc and prep. tlc) to give tetracyclic (**5a**) and tricyclic silicon compounds (**6a** and **7a**) together with debrominated product (**8a**) (14 %) in 32, 19, and 3 % yields, respectively. ^{1}H-Nmr spectrum of **5a** showed one proton due to aromatic proton at 7-position at δ 7.21 (s) and one proton due to aromatic proton at 6-position at δ 7.59 (dd, J = 1.4, 7.1 Hz) and in the ms a molecular peak (M^+) was measured at *m/z* 324. On the other hand, ms of **6a**, **7a**, and **8a** showed the same molecular peaks (M^+) at *m/z* 326. ^{1}H-Nmr spectrum of **6a** indicated a pair of two methylene protons at δ 0.60-0.89 (4H) and 2.17-2.84 (4H) as each multiplet, while that of **7a** showed peaks due to an ethyl group at δ 0.31 (q, J = 7.1 Hz) and 0.79 (t, J = 7.1 Hz). From these spectral data structures of **5a**, **6a**, and **7a** were proved to be 8,9-dimethoxydibenzo[*de,g*]-1-siladecalin, 5,6-dimethoxydibenzo[*d,f*]-1,1-dimethyl-1-silacyclononane, and 9-ethyldimethylsilyl-2,3-dimethoxy-9,10-dihydrophenanthrene, respectively. Compound (**8a**) was also determined to be 1-veratryl-2,2-dimethyl-2-silatetralin on the basis of ^{1}H-nmr. Moreover, in order to examine effect of the solvent and the concentration on yield of **5a**, the reaction of **4a** in toluene (0.01 M) or *o*-xylene (0.01 M) was carried out under conditions similar to those noted for the reaction of **4a** in benzene However, no remarkable improvement[11] in the reaction was observed. The reaction in benzene (0 01 M) using syringe pump or in low concentration (0.002 M) did not proceed completely Thus, the reaction of **4b** and **4c** was performed under the conditions similar to those noted for the reaction of **4a** in benzene to provide **5b** (23 %), **6b** (24 %), and **7b** (3 %) and **5c**,[12] **6c** (19 %), and **7c** (4 %) along with **8b** (8 %) and **8c**,[2, 12] respectively. Carbon nuclear magnetic resonance (^{13}C-nmr) spectrum for **6c** supported also the structure.

Next, radical reaction of **4d** was investigated, because the presence of a methoxyl group at 7-position might decrease formation of a phenanthrene such as **7** (see Scheme 1). Thus, the reaction of **4d** was performed under the conditions similar to those noted for **4a**. However, the reaction did not proceed completely and the starting material (**4d**) was recovered in 35 % yield.

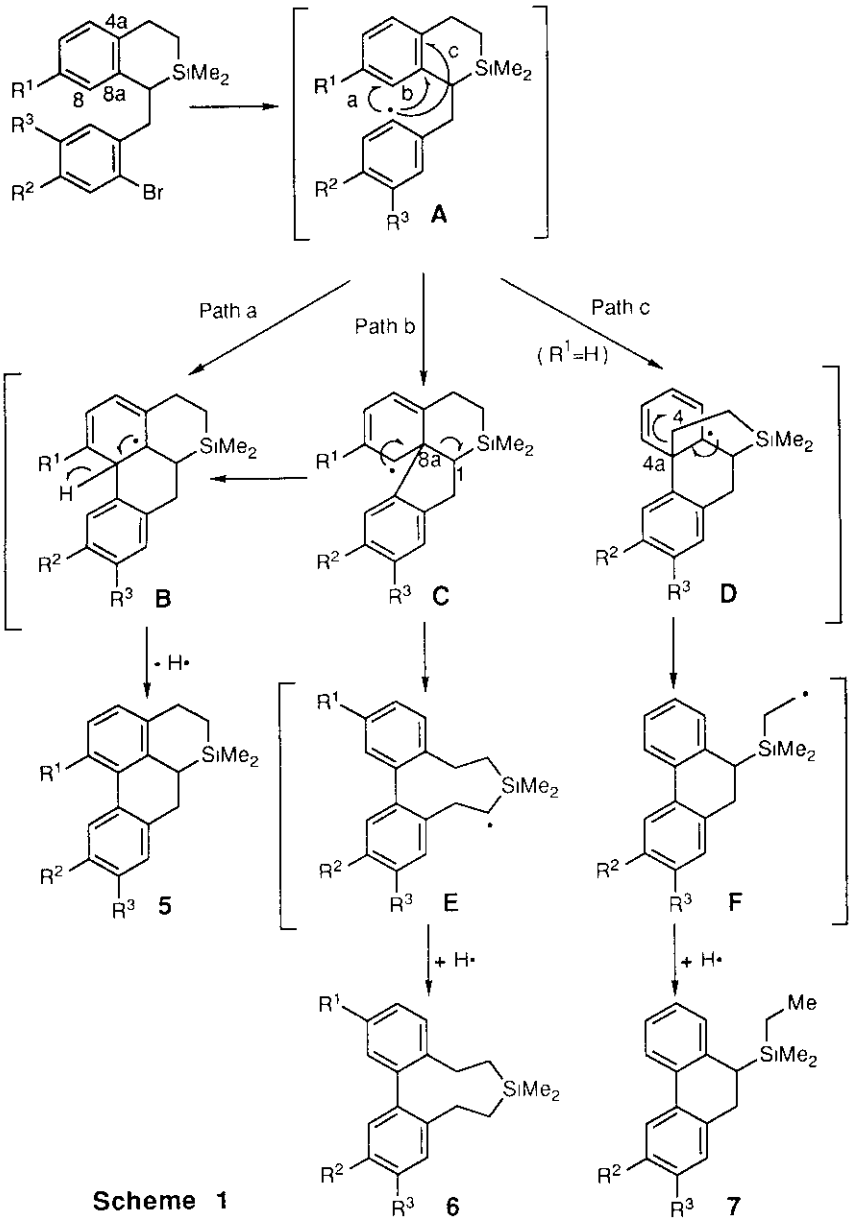
After several attempts to examine reaction conditions, 12 molar eq. of Bu_3SnH were required for disappearance of the starting material on tlc. Purification of the reaction mixture by the methods similar to those noted for **4a** gave **5d**, **6d**, and **8d** together with **3d** (4 %) in 11, 12, and 14 % yields, respectively. No phenanthrene derivative (**7d**) was detected. Structures of **5d**, **6d**, and **8d** were characterized on the spectral data. Similarly, **4e**, **f** gave **5e**, **f**, **6e**, **f**, and **8e**, **f**,[2] respectively. The results are listed in Table 2.

Table 2 Yields of Cyclized Products (**5**, **6**) and Debrominated Compounds (**8**)

Starting Materials **4** (R^1=OMe)	Bu_3SnH (eq.)	Yield (%) [a] 5	6	8
d : R^2=R^3=OMe	3[b]	23	6	5
	12[c]	11	12	14
e : R^2+R^3=OCH_2O	3	21	8	_ [d]
	12[e]	24	14	22
f : R^2=R^3=H	3	22	7	_ [f]
	12	23	8	_ [g]

a) Isolated yield b) **4d** was recovered in 35 % yield c) **4d** was recovered in 4 % yield.
d) Product ratio (**8e** : **4e** = 2.0 : 1) was estimated by glc analysis.
e) **4e** was not isolated. f) Product ratio (**8f** : **4f** = 1.6 : 1) was estimated by glc analysis.
g) Product ratio (**8f** : **4f** = 5.1 : 1) was estimated by glc analysis.

The reaction pathway on formation of **5**, **6**, and **7** was deduced as follows. A radical intermediate (**A**) generated from **4** would be able to attack on 8- (path a), 8a- (path b), or 4a-position (path c) to produce further radical intermediate (**B**, **C** or **D**) as depicted in Scheme 1. Elimination of hydrogen radical from intermediate (**B**) provided **5**, which might be also formed from intermediate (**C**) by rearrangement and elimination of hydrogen radical (paths a and b). Compound (**6**) would be produced through intermediate (**E**) by cleavage of a carbon-carbon bond between 8a- and 1-positions in intermediate (**C**) (path b). On the other hand, intermediate (**D**) would provide radical (**F**) by ß-effect of a silicon atom to give **7**. With **4d-f**, however, generation of radical intermediate **D** might be prevented by a methoxyl group at 7-position, although the reason remains uncertain.



Scheme 1

In conclusion, radical reaction of 1-(2-bromoarylmethyl)-2-silatetralins was proved to give tetracyclic (**5**) and tricyclic (**6**) organosilicon compounds, and 9-silylphenanthrenes (**7a-c**), respectively The present results suggested the possibility on synthesis of polycyclic organosilicon

compounds Evaluation on biological activity of the polycyclic organosilicon compounds is now under way.

ACKNOWLEDGEMENT

This work was supported in part by Grants-in-Aid for Scientific Research (No 04671313) from the Ministry of Education, Sciences and Culture of Japan. The authors are indebted to Miss N. Sawabe, Mrs. F. Hasegawa, and Mr. H. Igarashi of this faculty for ^{1}H-nmr and mass spectral measurements and elemental analyses.

EXPERIMENTAL

General.—— All melting points were measured on Büchi or Yanagimoto (hot plate) melting point apparatus and are uncorrected. Ir spectra were taken with a Hitachi model 260-10 spectrophotometer in $CHCl_3$ solution, unless otherwise noted. ^{1}H-Nmr and ^{13}C-nmr spectra were recorded on a JEOL model FX-100 spectrometer in $CDCl_3$ solution using $CHCl_3$ as 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. Ball-to-ball distillation was carried out by means of a Sibata glass tube oven model GTO-250RS. Mplc was carried out by a Kusano kagakukikai KP-6H or KPW-20 micro pump. Prep tlc was performed with Kieselgel $60F_{254}$ Art. 5744 (Merck) or Kieselgel $60GF_{254}$ Art 7730 (Merck) For column chromatography, silica gel (Wako gel C-200) was used.

Materials.—— THF was distilled from sodium wire and benzophenone prior to use. Benzene, toluene or *o*-xylene was distilled from CaH_2 or $LiAlH_4$ prior to use. Bu_3SnH was purchased from Aldrich Chemical Company, Inc.

General Procedure for Preparation of 1-(2-Bromoarylmethyl)-2,2-dimethyl-2-silatetralins (4a-f) —— A solution of BuLi (BuLi-hexane) was added dropwise to an ice-cold, stirred solution of 2-silatetralin (**1a**) and TMEDA in THF under Ar stream and the whole was stirred at 0-5 °C for 1.5 h. A solution of 2-bromoarylmethyl bromide or chloride in THF was added dropwise to the mixture and stirring was continued at the same temperature for 1 h. The reaction was quenched with addition of water The organic layer was separated and the aqueous layer was

extracted with CH_2Cl_2. The combined organic layers were washed with 10 % HCl and brine, and dried ($MgSO_4$). Removal of the solvent *in vacuo* followed by ball-to-ball distillation under reduced pressure gave an oily residue, which was purified by column chromatography combined with prep. tlc.

4a : A mixture of **1a** (529 mg, 3.0 mmol), TMEDA (0 54 ml, 3.6 mmol) and 1.18 M BuLi-hexane (3.1 ml, 3.6 mmol) in THF (30 ml) was allowed to react with **3a**[10] (956 mg, 3.6 mmol) in THF (6 ml) to give a brown oil (967 mg). Column chromatography (twice) of the oil with hexane-AcOEt (30 : 1) and (40 . 1), successively, furnished **4a** (811 mg, 67 %), which was purified by ball-to-ball distillation to give **4a** [679 mg, 56 %, bp 156-187 °C / (5.0-6.0)x10^{-3} Torr.] as a colorless oil. ^{1}H-Nmr δ : -0.06, 0.11 (6H, each s, $SiMe_2$), 0.84 (2H, t, J = 7.1 Hz, C_3-H), 2.41 (1H, dd, J = 7.1, 8.6 Hz, C_1-H), 2.65-3.34 (4H, m, C_4-H, CH_2Ph), 3.59, 3.84 (6H, each s, 2xOMe), 6 28 (1H, s, Ar-H), 6.61-6.81 (1H, m, Ar-H), 6.85-7.21 (4H, m, 4xAr-H). Ir : 1260 (SiMe) cm^{-1}. Ms *m/z* (rel. int., %) : 406 (M^++2, 22), 404 (M^+, 21), 229 (100) ; HRms *m/z* calcd for $C_{20}H_{25}O_2BrSi$ (M^+) : 404.0806, found : 404.0800.

4b : A mixture of **1a** (529 mg, 3.0 mmol), TMEDA (0.54 ml, 3 6 mmol) and 1.55 M BuLi-hexane (2.3 ml, 3.6 mmol) in THF (30 ml) was allowed to react with **3b**[13] (898 mg, 3.6 mmol) in THF (7 ml) to give a brown oil (450 mg). Column chromatography of the oil with hexane and hexane-AcOEt (100 : 1) followed by that with hexane afforded **4b** (192 mg, 16 %), purification of which by ball-to-ball distillation gave a pale yellow oil (161 mg, 14 %, bp 170-185 °C / 7.8x10^{-3} Torr.). ^{1}H-Nmr δ : -0.02, 0.01 (6H, each s, $SiMe_2$), 0.59-0.95 (2H, m, C_3-H), 2.46 (1H, t, J = 7.1 Hz, C_1-H), 2.65-2.99 (2H, m, C_4-H), 3.12 (2H, d, J = 7.1 Hz, CH_2Ph), 5.89 (2H, s, OCH_2O), 6.48 (1H, s, Ar-H), 6.64-7.15 (5H, m, 5xAr-H). Ir : 1245 (SiMe) cm^{-1}. Ms *m/z* (rel int., %) : 390 (M^++2, 22), 388 (M^+, 21), 59 (100) ; HRms *m/z* calcd for $C_{19}H_{21}O_2BrSi$ (M^+) : 388 0492, found : 388.0490.

4c · A mixture of **1a** (529 mg, 3.0 mmol), TMEDA (0.54 ml, 3 6 mmol) and 1.59 M BuLi-hexane (2.3 ml, 3.6 mmol) in THF (30 ml) was allowed to react with **3c**[14] (900 mg, 3.6 mmol) in THF (6 ml) to give a brown oil (777 mg). Repeated (four times) column chromatography of the oil with hexane gave **4c** (251 mg, 24 %) as a colorless oil, which was crystallized by trituration in MeOH to give a solid. Analytical sample had mp 70-70.5 °C (MeOH). Anal. Calcd for $C_{18}H_{21}BrSi$: C, 62.60; H, 6.13 Found : C, 62.53; H, 6.12. ^{1}H-Nmr δ -0 05, 0 04 (6H, each s, $SiMe_2$), 0.68-0.95 (2H, m, C_3-

H), 2.56 (1H, t, J = 8.6 Hz, C_1-H), 2.76-3.02 (2H, m, C_4-H), 3.21 (2H, d, J = 8.6 Hz, CH_2Ph), 6 68-7.21 (7H, m, 7xAr-H), 7.44-7.64 (1H, m, Ar-H). Ir (KBr) : 1270 (SiMe) cm^{-1}, ms *m/z* (rel. int., %) : 346 (M^++2, 5), 344 (M^+, 6), 59 (100).

4d : A *mixture* of **1b**[1] (516 mg, 2 5 mmol), TMEDA (0.45 ml, 3.0 mmol) and 1.48 M BuLi-hexane (2.0 ml, 3.0 mmol) in THF (25 ml) was allowed to react with **3a** (730 mg, 2.75 mmol) in THF (7.5 ml) to give an orange red oil (1.03 g). Column chromatography of the oil with hexane-AcOEt (70 : 1 and 50 : 1) produced fractions A (165 mg) and B (500 mg). The fraction A was separated by prep. tlc (three developments with hexane AcOEt = 20 · 1) to give fraction C (140 mg). Combined fractions B and C were twice chromatographed with hexane-AcOEt (70 : 1, 50 : 1) to afford **4d** (552 mg, 48 %), purification of which by ball-to-ball distillation furnished **4d** [497 mg, 46 %, bp 190-210 °C / (5 0-6 6)x10^{-3} Torr.] as a pale yellow oil ^{1}H-Nmr δ -0 06, 0.09 (6H, each s, $SiMe_2$), 0.82 (2H, t, J = 7.1 Hz, C_3-H), 2.41 (1H, dd, J = 7.1, 8.6 Hz, C_1-H), 2.68-3 21 (4H, m, C_4-H, CH_2Ph), 3.64, 3.65, 3.84 (9H, each s, 3xOMe), 6.36 (2H, s, C_8-H, Ar-H), 6.56 (1H, dd, J = 2.9, 8.6 Hz, C_6-H), 6.99 (1H, s, Ar-H), 7.02 (1H, d, J = 8.6 Hz, C_5-H). Ir 1260 (SiMe) cm^{-1}. Ms *m/z* (rel. int., %) : 436 (M^++2, 8), 434 (M^+, 7), 231 (100) ; HRms *m/z* calcd for $C_{21}H_{27}O_3BrSi$ (M^+) : 434 0912, found : 434.0911.

4e · A mixture of **1b** (516 mg, 2.5 mmol), TMEDA (0 45 ml, 3.0 mmol) and 1.21 M BuLi-hexane (2.5 ml, 3 0 mmol) in THF (25 ml) was allowed to react with **3b** (748 mg, 3 0 mmol) in THF (7.5 ml) to give a brownish oily crystals (598 mg). Column chromatography with hexane : AcOEt = 150 : 1 followed by flash chromatography wiht hexane . AcOEt = 20 : 1 gave fractions A (173 mg) and B (269 mg). Prep. tlc of the fraction A (five developments with AcOEt = 40 : 1) gave fraction C (157 mg) Combined fractions B and C were crystallized by trituration to give **4e** (381 mg, 36 %, mp 84.5-91 °C) as pale yellow crystals. Colorless prisms of mp 97-99 °C (hexane) were used as analytical sample. Anal. Calcd for $C_{20}H_{23}O_3BrSi$ C, 57.28; H, 5.53. Found · C, 57.30; H, 5.63. ^{1}H-Nmr δ : -0.02, -0.01 (6H, each s, $SiMe_2$), 0.64-0 94 (2H, m, C_3-H), 2.44 (1H, t, J = 7.1 Hz, C_1-H), 2.68-2.94 (2H, m, C_4-H), 3.09 (2H, d, J = 7.1 Hz, CH_2Ph), 3.69 (3H, s, OMe), 5.89 (2H, s, OCH_2O), 6.42 (1H, d, J = 2 9 Hz, C_8-H), 6.51 (1H, s, Ar-H), 6.58 (1H, dd, J = 2 9, 8.6 Hz, C_6-H), 6.99 (1H, s, Ar-H), 7.01 (1H, d, J = 8.6 Hz, C_5-H) Ir (KBr) . 1240 (SiMe) cm^{-1}; ms *m/z* (rel. int., %) : 420 (M^++2, 5), 418 (M^+, 5), 59 (100).

4f : A mixture of **1b** (516 mg, 2.5 mmol), TMEDA (0 45 ml, 3 0 mmol) and 1.48 M BuLi-hexane (2.0 ml, 3.0 mmol) in THF (25 ml) was allowed to react with **3c** (687 mg, 2.75 mmol) in THF (7.5 ml) to give a brownish oil (665 mg). Twice column chromatography with hexane gave **4f** (334 mg, 36 %), purification of which by ball-to-ball distillation gave **4f** [317 mg, 34 %, bp 130-170 °C / (5.5-6.0)x 10^{-3} Torr.]. ^{1}H-Nmr δ : -0.06, 0.04 (6H, each s, $SiMe_2$), 0.59-0.99 (2H, m, C_3-H), 2.52 (1H, t, J = 7.1 Hz, C_1-H), 2.66-2.99 (2H, m, C_4-H), 3.19 (2H, d, J = 7.1 Hz, CH_2Ph), 3.64 (3H, s, OMe), 6.38 (1H, d, J = 2.9 Hz, C_8-H), 6.58 (1H, dd, J = 2 9, 7.1 Hz, C_6-H), 6.85-7 19 (4H, m, 4xAr-H), 7.44-7.61 (1H, m, Ar-H). Ir : 1250 (SiMe) cm^{-1}. Ms *m/z* (rel. int., %) : 376 (M^++2, 23), 374 (M^+, 22), 205 (100) ; HRms *m/z* calcd for $C_{19}H_{23}OBrSi$ (M^+) : 374.0700, found : 374 0697

Radical Reaction of 1-(2-Bromoarylmethyl)-2,2-dimethyl-2-silatetralins (4a-f) —— With **4a** : **4a** (203 mg, 0.5 mmol), AIBN (41 mg, 0.25 mmol), Bu_3SnH (437 mg, 1 5 mmol), and benzene (50 ml) were used. After refluxing for 2 h, a residue (684 mg) obtained on removal of the solvent was purified by column chromatography with hexane and AcOEt to give a yellow oil (234 mg). The oil was purified by further column chromatography with hexane-AcOEt (30 : 1) to furnish a pale yellow oil (207 mg), which was subjected to mplc [petroleum ether (bp 47-64 °C) : AcOEt = 400 : 1, 200 : 1, 100 : 1, and 10 : 1] to be separated into fractions A (40 mg), B (8 mg), C (27 mg), and D (66 mg), respectively. Fraction A . **6a** (31 mg, 19 %) as a colorless oil was obtained by further prep. tlc [twice developments with petroleum ether : AcOEt = 10 : 1]. **6a** : ^{1}H-Nmr (CD_3OD) δ : -0.41, -0 39 (6H, each s, $SiMe_2$), 0 60-0.89 [4H, m, $(CH_2)_2Si$], 2.17-2.84 [4H, m, $(CH_2CH_2)_2Si$], 3 73, 3.84 (6H, each s, 2xOMe), 6 56, 6.84 (2H, each s, 2xAr-H), 6.90-7 33 (4H, m, 4xAr-H). Ir : 1240 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{20}H_{26}O_2Si$ (M^+) . 326.1701, found : 326.1710; ms *m/z* (rel. int., %) : 326 (M^+, 75), 255 (100). Fraction B : **7a** (5 mg, 3 %) as a colorless oil was obtained by further prep. tlc similar to that noted for **6a**. **7a** : ^{1}H-Nmr δ -0.29, -0.28 (6H, each s, $SiMe_2$), 0.31 (2H, q, J = 7.1 Hz, $SiCH_2Me$), 0 79 (3H, t, J = 7.1 Hz, $SiCH_2Me$), 2.45 (1H, dd, J = 1.4, 7.1 Hz, CHSi), 2.76 [1H, dd, J = 1.4, 14.3 Hz, CH(H)CHSi], 3.25 [1H, dd, J = 7.1, 14.3 Hz, CH(H)CHSi], 3.91, 3.95 (6H, each s, 2xOMe), 6 69 (1H, s, Ar-H), 6.96-7 22 (4H, m, 4xAr-H), 7.52-7.71 (1H, m, Ar-H). Ir : 1265 (SiMe) cm^{-1} HRms *m/z* calcd for $C_{20}H_{26}O_2Si$ (M^+) : 326 1700, found : 326.1689; ms *m/z* (rel. int., %) : 326 (M^+, 52), 311 (100), 238 (M^+-$SiHMe_2Et$, 58). Fraction C : **8a** (22 mg, 14 %, mp 62-64 °C) was obtained by further prep. tlc similar to that noted for **6a**. Colorless prisms of mp

68-69 °C (MeOH-H_2O) was used as analytical sample **8a** Anal Calcd for $C_{20}H_{26}O_2Si$: C, 73.57; H, 8 03. Found : C, 73.62, H, 7.99. ^{1}H-Nmr δ : -0.15, -0.06 (6H, each s, $SiMe_2$), 0.59-0.99 (2H, m, C_3-H), 2 36 (1H, dd, *J* = 7.1, 8.6 Hz, C_1-H), 2.64-3 28 (4H, m, C_4-H, SiCHC*H*$_2$), 3 79, 3.85 (6H, each s, 2xOMe), 6.64 (1H, s, Ar-H), 6.74 (2H, s, 2xAr-H), 6.85-7 16 (4H, m, 4xAr-H). Ir (KBr) : 1255 (SiMe) cm^{-1}; ms *m/z* (rel. int., %) : 326 (M$^+$, 10), 151 (100). Fraction D : **5a** (52 mg, 32 %) was obtained by further prep. tlc similar to that noted for **6a** (four developments). Analytical sample had mp 106 °C (hexane) as colorless plates. **5a** · Anal. Calcd for $C_{20}H_{24}O_2Si$. C, 74.03; H, 7 45. Found C, 73.70; H, 7.49. ^{1}H-Nmr δ : 0.04, 0.25 (6H, each s, $SiMe_2$), 0 64-1.21 (2H, m, C_2-H), 2.09 (1H, dd, *J* = 8 6, 11.4 Hz, CHSi), 2.56-3.16 (4H, m, C_3-H, C_{11}-H), 3 92, 3.95 (6H, each s, 2xOMe), 6.74 (1H, s, Ar_{10}-H), 7.02 (1H, dd, *J* = 1 4, 7 1 Hz, Ar_4-H), 7.15 (1H, t, *J* = 7.1 Hz, Ar_5-H), 7 21 (1H, s, Ar_7-H), 7.59 (1H, dd, *J* = 1.4, 7 1 Hz, Ar_6-H) Ir (KBr) : 1260 (SiMe) cm^{-1}; ms *m/z* (rel. int , %) : 324 (M$^+$, 100).

With **4b** · **4b** (195 mg, 0 5 mmol), AIBN (41 mg, 0 25 mmol) Bu_3SnH (437 mg, 1.5 mmol), and benzene (50 ml) were used. After refluxing for 2 h, a residue (656 mg) obtained on removal of the solvent *in vacuo* was subjected to column chromatography with hexane and hexane-AcOEt (20 . 1) to give a pale yellow oil (182 mg). The oil was purified by further column chromatography with hexane-AcOEt (40 : 1) to furnish a pale yellow oil (160 mg), mplc of which with hexane-AcOEt (400 : 1) afforded fractions A (40 mg) and B (73 mg), respectively. From fraction A, **6b** (37 mg, 24 %, colorless oil) and **7b** (5 mg, 3 %, colorless oil) were obtained by further prep. tlc (five developments with hexane : AcOEt = 50 1) **6b** ^{1}H-Nmr (CD_3OD) δ : -0.41, -0.36 (6H, each s, $SiMe_2$), 0.57-0 93 [4H, m, $(CH_2)_2Si$], 2.13-2.86 [4H, m, $(CH_2CH_2)_2Si$], 5.90 (2H, s, OCH_2O), 6.44, 6 74 (2H, each s, 2xAr-H), 6.87-7.33 (4H, m, 4xAr-H). Ir : 1245 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{22}O_2Si$ (M$^+$) : 310.1387, found 310 1387; ms *m/z* (rel int , %) : 310 (M$^+$, 68), 239 (100). **7b** : ^{1}H-Nmr δ · -0.26, -0.25 (6H, each s, $SiMe_2$), 0 34 (2H, q, *J* = 7.1 Hz, SiC*H*$_2$Me), 0.81 (3H, t, *J* = 7.1 Hz, $SiCH_2$*Me*), 2.42 (1H, dd, *J* = 1 4, 7 1 Hz, CHSi), 2.76 [1H, dd, *J* = 1.4, 14 3 Hz, C*H*(H)CHSi], 3.22 [1H, dd, *J* = 7.1, 14.3 Hz, CH(*H*)CHSi], 5 95, 5 98 (2H, each d, *J* = 1 4 Hz, OCH_2O), 6.66 (1H, s, Ar-H), 6 92-7.24 (4H, m, 4xAr-H), 7 45-7.76 (1H, m, Ar-H). Ir : 1275 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{22}O_2Si$ (M$^+$) : 310.1388, found 310 1396; ms *m/z* (rel. int , %) : 310 (M$^+$, 27), 222 (M$^+$-$SiHMe_2Et$, 59), 59 (100) Mplc of fraction B with hexane-AcOEt (400 : 1) produced an oil (67 mg),

prep. tlc of which [developing solvents; hexane : AcOEt = 30 : 1 (two developments), 20 : 1 and 30 : 1 and, petroleum ether : AcOEt = 30 : 1 and 10 : 1 (two developments)] afforded fractions C (13 mg) and D (39 mg). Fraction D gave fraction E (5 mg) and **5b** (35 mg, 23 %, colorless oil) by further prep. tlc (three developments with petroleum ether : AcOEt = 10 : 1). **5b** ^{1}H-Nmr δ : 0.04, 0.25 (6H, each s, $SiMe_2$), 0.62-1.06 (2H, m, C_2-H), 2.05 (1H, dd, J = 8.6, 11.4 Hz, CHSi), 2.59-3.19 (4H, m, C_3-H, C_{11}-H), 5.95 (2H, s, OCH_2O), 6.69 (1H, s, Ar_{10}-H), 7.02 (1H, dd, J = 1.4, 7.1 Hz, Ar_4-H), 7.14 (1H, t, J = 7.1 Hz, Ar_5-H), 7.18 (1H, s, Ar_7-H), 7.52 (1H, dd, J = 1.4, 7.1 Hz, Ar_6-H). Ir : 1245 (SiMe) cm^{-1} HRms *m/z* calcd for $C_{19}H_{20}O_2Si$ (M^+) : 308.1231, found : 308.1231; ms *m/z* (rel. int., %) : 308 (M^+, 100). Combined fractions C and E were further separated by prep. tlc (two developments with the same developing solvent as noted for fraction D) to give **8b** (13 mg, 8 %, colorless oil). **8b** : ^{1}H-Nmr δ : -0.12, -0.09 (6H, each s, $SiMe_2$), 0.56-1.06 (2H, m, C_3-H), 2.36 (1H, dd, J = 7.1, 8.6 Hz, C_1-H), 2.62-3.35 (4H, m, C_4-H, SiCHCH_2), 5.91 (2H, s, OCH_2O), 6.68 (3H, s, 3xAr-H), 6.85-7.16 (4H, m, 4xAr-H). Ir : 1250 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{22}O_2Si$ (M^+) : 310.1388, found : 310.1391; ms *m/z* (rel. int., %) : 310 (M^+, 18), 135 (100).

With **4c** : **4c** (207 mg, 0.6 mmol), AIBN (49 mg, 0.3 mmol), Bu_3SnH (524 mg, 1.8 mmol), and benzene (60 ml) were used. After refluxing for 2 h, removal of the solvent *in vacuo* gave a pale yellow oily solid (788 mg), which was chromatographed with hexane to give a yellow oil (534 mg). Further column chromatography of the oil with hexane gave a colorless oil (485 mg), mplc of which with cyclohexane was separated into fractions A (110 mg) and B (104 mg). Each fraction was purified by prep. tlc (twice developments with hexane). From fraction A, **6c** (31 mg, 19 %) were obtained. **6c** : ^{1}H-Nmr δ : -0.42 (6H, s, $SiMe_2$), 0.64-0.88 [4H, m, $(CH_2)_2Si$], 2.19-2.84 [4H, m, $(CH_2CH_2)_2Si$], 6.85-7.34 (8H, m, 8xAr-H). ^{13}C-Nmr δ : -1.468 (q, SiMe), 17.545 (t, CH_2Si), 27.605 (t, ArCH_2), 125.483, 127.472, 129.286, 129.637 (each d, Ar-C), 141.162, 142.683 (each s, Ar-C). Ir : 1250 (SiMe) cm^{-1} HRms *m/z* calcd for $C_{18}H_{22}Si$ (M^+) : 266.1490, found : 266.1496; ms *m/z* (rel. int., %) : 266 (M^+, 16), 195 (100). The mixture (90 mg) combined with a component obtained from fractions A and B was purified by prep. tlc (three developments with the same developing solvent) to produce **7c** (6 mg, 4 %) and a mixture (71 mg), respectively. **7c** : ^{1}H-Nmr δ : -0.29 (6H, s, $SiMe_2$), 0.31 (2H, q, J = 7.1 Hz, SiCH_2Me), 0.79 (3H, t, J = 7.1 Hz, $SiCH_2Me$), 2.48 (1H, dd, J = 1.4, 7.1 Hz, CHSi), 2.88 [1H, dd, J = 1.4, 14.3 Hz, CH(H)CHSi], 3.31 [1H, dd, J = 7.1, 14.3 Hz,

CH(*H*)CHSi], 6.96-7.41 (6H, m, 6xAr-H), 7 49-7.81 (2H, m, 2xAr-H). Ir 1270 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{18}H_{22}Si$ (M^+) : 266.1489, found : 266 1485; ms *m/z* (rel. int., %) : 266 (M^+, 10), 178 (M^+-$SiHMe_2Et$, 100) The mixture (71 mg) was further purified by prep. tlc (five developments with petroleum ether) to afford an inseparable mixture of **5c** and **8c** in 2.4 : 1 product ratio, which was estimated by glc analysis (column : 1 % OV-1, column temperature, 230 °C, Rt 27.5 min for **5c** ; Rt 13.5 min for **8c**). **5c** : ^{1}H-Nmr δ : 0.05, 0.26 (6H, each s, $SiMe_2$), 2 14 (1H, dd, *J* = 7.1, 11.4 Hz, CHSi), 7.56-7.81 (2H, m, 2xAr-H); ms *m/z* (rel. int., %) · 264 (M^+, 100). **8c**[2] : ^{1}H-Nmr δ : -0.16, -0.06 (6H, each s, $SiMe_2$), 2 45 (1H, dd, *J* = 7 1, 8.6 Hz, C_1-H), ms *m/z* (rel. int., %) : 266 (M^+, 16), 59 (100)

With **4d** : **4d** (218 mg, 0 5 mmol), AIBN (41 mg, 0 25 mmol), Bu_3SnH (1.75 g, 6.0 mmol), and benzene (50 ml) were used After refluxing for 2 h, work-up similar to noted for **4a** gave an oily solid (2.0g), which was subjected to column chromatography with hexane and hexane-AcOEt (10 : 1 and 5 : 1) to produce an oily solid (244 mg) Mplc of the oily solid with hexane-AcOEt (100 : 1, 70 · 1, 50 : 1, 30 1, 20 : 1, and 5 : 1) gave **6d** (21 mg, 12 %, mp 78-80 °C), **4d** (8 mg, 4 %), and fraction A (70 mg). Analytical sample for **6d** had mp 80-80.5 °C (hexane) as colorless prisms. **6d** : Anal. Calcd for $C_{21}H_{28}O_3Si$: C, 70.74; H, 7.91. Found C, 70.82; H, 7.91. ^{1}H-Nmr δ : -0.36, -0.35 (6H, each s, $SiMe_2$), 0.62-0.91 [4H, m, $(CH_2)_2Si$], 2.19-2.79 [4H, m, $(CH_2CH_2)_2Si$], 3.79, 3.82, 3.92 (9H, each s, 3xOMe), 6 58 (1H, s, Ar_4-H), 6.62 (1H, d, *J* = 2.9 Hz, Ar_8-H), 6.76 (1H, s, Ar_7-H), 6.85 (1H, dd, *J* = 2.9, 8 6 Hz, Ar_{10}-H), 7.18 (1H, d, *J* = 8 6 Hz, Ar_{11}-H). Ir (KBr) : 1260 (SiMe) cm^{-1}; ms *m/z* (rel int., %) : 356 (M^+, 82), 285 (100) Prep. tlc (four developments with hexane : AcOEt = 5 : 1) of fraction A gave fractions B (36 mg) and C (26 mg). Further purification of fraction B by prep. tlc (three developments with hexane · AcOEt = 5 : 1) led to fractions D (26 mg, mp 141-144.5 °C) and E (3 mg). Prep. tlc (three developments with hexane : AcOEt = 10 : 1) of combined fractions C and E furnished **8d** (24 mg, 14 %, colorless oil) **8d** · ^{1}H-Nmr δ : -0.15, -0.06 (6H, each s, $SiMe_2$), 0.51-0 99 (2H, m, C_3-H), 2.34 (1H, t, *J* = 8 6 Hz, C_1-H), 2.64-3.19 (4H, m, C_4-H, CH_2Ph), 3.69, 3.81, 3.85 (9H, each s, 3xOMe), 6.42-6.76 (5H, m, 5xAr-H), 7 01 (1H, d, *J* = 8.6 Hz, Ar_5-H). Ir : 1260 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{21}H_{28}O_3Si$ (M^+) : 356.1806, found : 356.1813; ms *m/z* (rel. int., %) : 356 (M^+, 10), 151 (100). Fraction D gave after prep. tlc (four developments with hexane : AcOEt = 5 : 1) **5d** (20 mg, 11 %, mp 142-146 °C). Analytical sample had mp 151 5-153 °C (hexane) as colorless

prisms. **5d** : Anal. Calcd for $C_{21}H_{26}O_3Si$: C, 71.44, H, 7.39. Found : C, 71.05; H, 7.30. ^{1}H-Nmr δ : -0.04, 0.21 (6H, each s, $SiMe_2$), 0 62-1 02 (2H, m, C_2-H), 1.96 (1H, dd, *J* = 7 1, 11.4 Hz, CHSi), 2.42-2.99 (4H, m, C_3-H, C_{11}-H), 3.88, 3.89, 3.91 (9H, each s, 3xOMe), 6 72 (1H, s, Ar_{10}-H), 6.76 (1H, d, *J* = 7.1 Hz, Ar_5-H), 6.98 (1H, d, *J* = 7.1 Hz, Ar_4-H), 7 89 (1H, s, Ar_7-H) Ir (KBr) : 1255 (SiMe) cm^{-1}; ms *m/z* (rel. int., %) · 354 (M^+, 100).

With **4e** : **4e** (210 mg, 0 5 mmol), AIBN (41 mg, 0.25 mmol), Bu_3SnH (1 75 g, 6.0 mmol), and benzene (50 ml) were used. After refluxing for 2 h, a residue (2.0 g) obtained in a way similar to that noted for **4a** was subjected to column chromatography with hexane and hexane-AcOEt (20 : 1) to afford a pale yellow oil (246 mg), mplc of which with hexane-AcOEt (100 : 1 and 5 : 1) gave fractions A (67 mg), B (49 mg), and C (45 mg), respectively. Prep. tlc (three developments with hexane · AcOEt = 50 : 1 and three developments with hexane . AcOEt = 40 : 1) of fraction A gave **6e** (23 mg, 14 %, colorless oil). **6e** : ^{1}H-Nmr δ -0.36, -0.34 (6H, each s, $SiMe_2$), 0.62-0.85 [4H, m, $(CH_2)_2Si$], 2.19-2 75 [4H, m, $(CH_2CH_2)_2Si$], 3 78 (3H, s, OMe), 5.95 (2H, s, OCH_2O), 6.56 (1H, s, Ar_4-H), 6.59 (1H, d, *J* = 2.9 Hz, Ar_8-H), 6.75 (1H, s, Ar_7-H), 6 84 (1H, dd, *J* = 2.9, 8.6 Hz, Ar_{10}-H), 7.16 (1H, d, *J* = 8.6 Hz, Ar_{11}-H) Ir 1235 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{20}H_{24}O_3Si$ (M^+) · 340.1493, found : 340.1495; ms *m/z* (rel int , %) · 340 (M^+, 69), 269 (100). Fraction B afford **5e** (40 mg, 24 %, pale yellow oil) by prep tlc (four developments with hexane · AcOEt = 100 : 1). **5e** : ^{1}H-Nmr δ . -0.02, 0.21 (6H, each s, $SiMe_2$), 0.46-1.15 (2H, m, C_2-H), 1 92 (1H, dd, *J* = 7.1, 11.4 Hz, CHSi), 2.38-3.06 (4H, m, C_3-H, C_{11}-H), 3.86 (3H, s, OMe), 5.94 (2H, s, OCH_2O), 6.71 (1H, s, Ar_{10}-H), 6.75 (1H, d, *J* = 7.1 Hz, Ar_5-H), 6.98 (1H, d, *J* = 7 1 Hz, Ar_4-H), 7.76 (1H, s, Ar_7-H). Ir : 1270 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{20}H_{22}O_3Si$ (M^+) : 338.1336, found : 338 1333; ms *m/z* (rel int., %) : 338 (M^+, 100). Prep. tlc (development with hexane and four developments with hexane · AcOEt = 100 : 1) of fraction C gave **8e** (38 mg, 22 %, mp 89-92 °C). Analytical sample had mp 93-94 °C (hexane) as colorless prisms **8e** Anal Calcd for $C_{20}H_{24}O_3Si$: C, 70.55; H, 7.10. Found : C, 70 65; H, 7.12 ^{1}H-Nmr δ : -0.14, -0.11 (6H, each s, $SiMe_2$), 0.46-1.02 (2H, m, C_3-H), 2.34 (1H, t, *J* = 7.1 Hz, C_1-H), 2.58-3.31 (4H, m, C_4-H, CH_2Ph), 3.71 (3H, s, OMe), 5 89 (2H, s, OCH_2O), 6 48-6 78 (5H, m, 5xAr-H), 6.99 (1H, d, *J* = 8.6 Hz, Ar_5-H). Ir (KBr) . 1245 (SiMe) cm^{-1} , ms *m/z* (rel. int., %) : 340 (M^+, 19), 135 (100).

With **4f** : **4f** (225 mg, 0.6 mmol), AIBN (49 mg, 0.3 mmol), Bu_3SnH (2.1 g, 7 2 mmol), and benzene (60 ml) were used. After refluxing for 2 h, a residue (2.45 g) obtained on removal of the solvent *in vacuo* was subjected to column chromatography with hexane and hexane-AcOEt (30 : 1) to afford a pale yellow oil (283 mg), which was further separated by mplc with hexane-AcOEt (200 : 1 and 5 : 1) to produce fractions A (186 mg, colorless oil) and B (24 mg, colorless oil). Prep. tlc of fraction A (three developments with hexane : AcOEt = 100 · 1) gave fractions C (17 mg, colorless oil), D (57 mg, pale yellow solid), and E (21 mg, pale yellow oil), respectively Fractions B [by prep. tlc (three developments with hexane : AcOEt = 50 : 1)] and C [by prep. tlc (four developments with hexane AcOEt = 100 1)] gave an inseparable mixture (32 mg) of **4f** and **8f** in 1 5 1 of product ratio, which was estimated by glc analysis (column : 1 % OV-1, column temperature, 255 °C, Rt 23.1 min for **4f** ; Rt 13.7 min for **8f**). **8f**[2] . ^{1}H-Nmr δ : -0.18, -0.08 (6H, each s, $SiMe_2$), 0.48-0.99 (2H, m, C_3-H), 2.41 (1H, t, J = 7.1 Hz, C_1-H), 2 59-3.39 (4H, m, C_4-H, CH_2Ph), 3 69 (3H, s, OMe), 6.48-6.64 (2H, m, 2xAr-H), 6.88-7.24 (6H, m, 6xAr-H); ms *m/z* (rel. int , %) 296 (M^+, 36), 205 (100). Prep. tlc (five developments with hexane AcOEt = 100 : 1) of fraction D gave a solid (47 mg, mp 75-77 °C), which was further purified by prep. tlc (three developments with the same developing solvent as noted for fraction D) to produce **5f** (41 mg, 23 %, mp 74 5-77 °C). Analytical sample had mp 82-83 °C (hexane) as colorless needles **5f** : Anal. Calcd for $C_{19}H_{22}OSi$ C, 77.50; H, 7.53. Found . C, 77.86, H, 7 40. ^{1}H-Nmr δ . -0 04, 0.21 (6H, each s, $SiMe_2$), 0.49-1.14 (2H, m, C_2-H), 1.95 (1H, dd, J = 7 1, 11.4 Hz, CHSi), 2 46-3.06 (4H, m, C_3-H, C_{11}-H), 3.88 (3H, s, OMe), 6.75 (1H, d, J = 7.1 Hz, Ar_5-H), 6.99 (1H, d, J = 7 1 Hz, Ar_4-H), 7.02-7.22 (3H, m, 3xAr-H), 8.09-8.29 (1H, m, Ar_7-H). Ir (KBr) 1270 (SiMe) cm^{-1}; ms *m/z* (rel int., %) . 294 (M^+, 100). Repeated (twice) prep. tlc (three developments with hexane : AcOEt = 100 : 1) of fraction E gave **6f** (15 mg, 8 %) as a pale yellow oil. **6f** · ^{1}H-Nmr δ : -0.38, -0.35 (6H, each s, $SiMe_2$), 0.59-0.91 [4H, m, $(CH_2CH_2)_2Si$], 2.24-2.84 [4H, m, $(CH_2CH_2)_2Si$], 3.78 (3H, s, OMe), 6.62 (1H, d, J = 2.9 Hz, Ar_8-H), 6.85 (1H, dd, J = 2.9, 8.6 Hz, Ar_{10}-H), 6.99-7.35 (5H, m, 5xAr-H) Ir · 1260 (SiMe) cm^{-1}. HRms *m/z* calcd for $C_{19}H_{24}OSi$ (M^+) 296 1594, found · 296.1586; ms *m/z* (rel int., %) 296 (M^+, 61), 225 (100).

REFERENCES AND NOTES

1 O. Hoshino, A. Hirokawa, T. Taguchi, and K. Miyauchi, *Heterocycles*, in press.

2. O. Hoshino, T. Taguchi, K. Miyauchi, and A. Tatsuno, unpublished results.

3. *Cf.* R. K. Sharma and N. Kharasch, *Angew Chem. Int. Ed. Engl.*, 1968, **7**, 36 ; T. Kametani and K. Fukumoto, *Acc. Chem. Res.*, 1972, **5**, 212 ; F. B Mallory and C. W. Mallory, 'Organic Reactions, ' Vol 30, ed, by W. G. Dauben, John Wiley & Sons, New York, 1984, Chapter 1.

4. *Cf* A. R. Battersby, 'Oxidative Coupling of Phenols, ' eds, by W. I Taylor and A. R. Battersby, Marcel Dekker, New York, 1967 ; T. Kametani and K. Fukumoto, *Synthesis*, **1972**, 657.

5. *Cf.* A. Mckillop, A. G. Turrell, D. W Young, and E. C. Taylor, *J. Am. Chem. Soc.*, 1980, **102**, 6504 ; E C Taylor, J. G. Andrade, G. J. H. Rall, and A. Mckillop, *ibid.*, 1980, **102**, 6513.

6 *Cf.* D. F. DeTar, 'Organic Reactions, ' Vol 9, ed, by R Adams, John Wiley & Sons, 1957, Chapter 7.

7. *Cf.* M. S. Gibson and J. M. Walthrew, *Chem. Ind.*, **1965**, 185 ; S. V. Kessar, S. Batra, and S. S. Gandhi, *Indian J. Chem.*, 1970, **8**, 468 ; T. Kametani, S Shibuya, K. Kigasawa, M. Hiiragi, and O. Kusama, *J. Chem. Soc. (C)*, **1971**, 2712 ; T. Kametani, K. Fukumoto, and T. Nakano, *J. Heterocyclic Chem.*, 1972, **9**, 1363.

8. *Cf.* B. Giese, 'Radicals in Organic Synthesis : Formation of Carbon-Carbon Bonds, ' Pergamon Press, Oxford, 1986.

9. *Cf.* C. P. Jasperse, D. P. Curran, and T. L. Fevig, *Chem Rev.*, 1991, **91**, 1237.

10. K. Ito and H. Tanaka, *Chem. Pharm Bull*, 1974, **22**, 2108

11. The product ratios were estimated to be 7 : 1 · 1 4 : 1 (toluene) or 8 · 1 : 3 : 2 (*o*-xylene) for **5a** : **6a** : **7a** : **8a** by hplc analysis. When the boiling point of the solvent became high, the product ratio for **7a** increased slightly.

12. Compounds **5c** and **8c** were inseparable. Therefore, the product ratio was estimated to be 2.4 : 1 for **5c** : **8c** by hplc analysis.

13. F. Dallacker, K.-W. Glombitza, and M. Lipp, *Liebigs Ann. Chem.*, 1961, **643**, 91.

14. D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, 1956, **78**, 475 ; H. L. Yale, F. A. Sowinski, and J. Bernstein, U S. Patent 3069432 (1962) (*Chem Abstr.*, 1963, **58**, p11386c).

Received, 7th January, 1994