SYNTHESIS OF 2-SILATETRALIN DERIVATIVES BEARING OXYGEN FUNCTIONAL GROUPS

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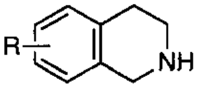
Abstract ---The Grignard reagents of methoxy- or methylenedioxyphenylmethyl chlorides (**12a**-**e**) were treated with trichlorovinylsilane in THF or ether to give methoxy- or methylenedioxybenzyldichlorovinylsilanes (**13a**-**e**). The reaction of **13a**-**d** in the presence of $AlCl_3$ in CS_2 or CH_2Cl_2 followed by treatment with MeOH and cyclohexylamine or Et_3N afforded methoxy-2-silatetralins (**16a**-**d**). Treatment of **16a**-**d** with MeMgI or EtMgBr in ether gave the corresponding 2,2-dimethyl- or 2,2-diethyl-2-silatetralins (**17a**-**d** or **18**). Demethylation of **17a**, **17b** or **18** with BBr_3 in CH_2Cl_2 furnished hydroxy-2-silatetralins (**19a**, **19b** or **20**).

Introduction

Numerous synthetic studies on compounds (**1**-**8**) containing a heteroatom for exploring new materials and biologically active compounds have been carried out so far. For instances, compounds (**3**,[1] **4**,[2] **5**,[3] **6**,[4] **7**,[5] and **8**[6]), in which one carbon atom in dihydro- or tetrahydronaphthalene moiety is replaced with a heteroatom such as silicon, sulfur, selenium, phosphorus, boron or arsenic, have been synthesized and their properties and reactivities have been examined. On the other hand, among heteroatom-containing compounds, organosilicon compounds (cf. **9**,[7] **10**,[8] and **11**[9]) have been known to have biological activities similar to those of the carbon analogues[10] (the carbon analogues of **11** do not exist). Therefore, we have been interested in cyclic silicon-containing compounds and planned to synthesize derivatives of the 2-silatetralin (**3**), which are silicon analogues of tetralin, because they would have the different reactivities and biological activities from those of the tetralins and might be converted into novel organosilicon compounds. In this paper, we describe synthesis of 2-silatetralins having oxygen functional groups.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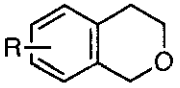
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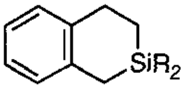
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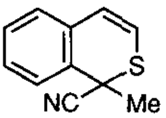
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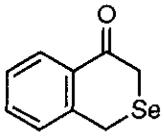
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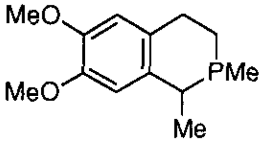
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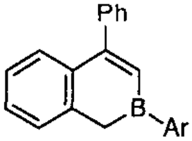
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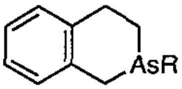
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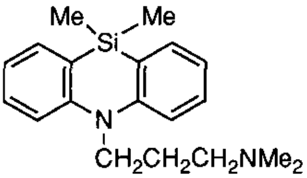
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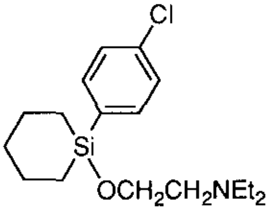
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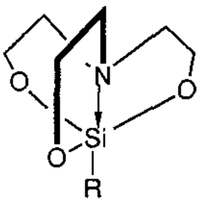
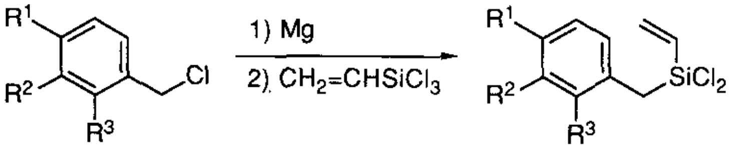

11 silatranes

RESULT AND DISCUSSION

Synthesis of Arylmethyldichlorovinylsilanes (13a-e)

In general, synthesis of 2-silatetralins has been performed by reaction[11] of the Grignard reagent derived from dihalide with dichlorosilane or by intramolecular Friedel-Crafts reaction[11] of benzyldichlorovinylsilane. Therefore, in order to prepare the oxygenated 2-silatetralins the intramolecular Friedel-Crafts reaction was investigated, because the starting materials were readily available.

In preparation of the Grignard reagents from arylmethyl chlorides (**12b**,[12] **12c**,[13] **12d**,[14] and **12e**[15]) having the electron-donating group at para or ortho position, more than ten equivalent atoms[16] of magnesium (Mg) were required. However, the reaction of **12b**, **12c**, and **12e** under ultrasonication[17] proceeded with 2.0-2.2 equivalent atoms of Mg to give the corresponding Grignard reagents. The Grignard reagents thus prepared from **12a-e** reacted with trichlorovinylsilane in ether or THF to lead to arylmethyldichlorovinylsilanes (**13a-e**) in a usual manner in fair to good yields. The results are shown in Table 1.



12a-e **13a-e**

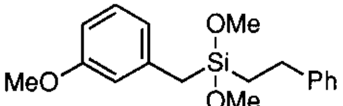
Table 1 Reaction Conditions, Yields and Bp of Arylmethyldichlorovinylsilanes (**13a-e**)

Arylmethyl Chlorides				Reaction conditions		Yield (%) of **13**	Bp °C / Torr.
	R^1	R^2	R^3	Mg (eq.)	Solvent		
12a	H	OMe	H	1.3	Et_2O	**13a** (68)	123-128 / 4
12b	OMe	H	H	10	THF	**13b** (44)	120-124 / 2
12b	OMe	H	H	2.0	THF a)	**13b** (55)	
12c	OMe	OMe	H	10	THF	**13c** (37)	127-129 / 3
12c	OMe	OMe	H	2.0	THF a)	**13c** (16)	
12d	H	OMe	OMe	10	THF	**13d** (39)	126-128 / 1
12e	OCH_2O		H	10	THF	**13e** (52)	125-128 / 2.5
12e	OCH_2O		H	2.2	THF a)	**13e** (41)	

a) Reaction was carried out under ultrasonication.

Synthesis of Methoxy-2,2-dimethyl- or 2,2-diethyl-2-silatetralins (17a-d or 18)

Cyclization of benzyldichlorovinylsilane was carried out according to Corriu's method.[11] The reaction of **13a** in the presence of $AlCl_3$ (2.0 eq.) in benzene gave an unstable dichlorosilane, treatment of which, without purification, with a mixture of MeOH and cyclohexylamine gave an uncyclized product **14** in 63 % yield. The similar reaction of **13a** in CS_2 instead of benzene gave a desired product **16a** in 53 % yield. In order to examine molar equivalent of $AlCl_3$, the reaction of **13b** in CS_2 or CH_2Cl_2 was carried out. The reaction of **13b** in the presence of 1 eq. of $AlCl_3$ in CH_2Cl_2 gave only **15** in 60 % yield, whereas that with 1.5 eq. of $AlCl_3$ afforded a cyclized product (**16b**) in 62 % yield. These finding suggested that molar equivalent of $AlCl_3$, which is more than that corresponding to number(s) of the methoxyl group(s) present in the starting material, should be used. The results are listed in Table 2.



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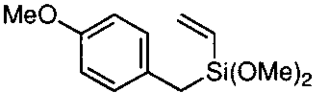

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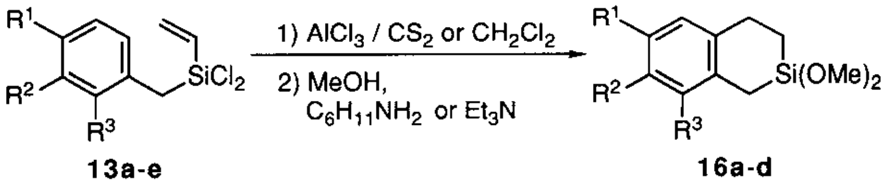
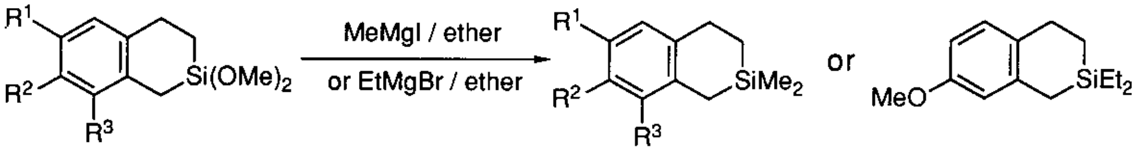


Table 2 Reaction Conditions, Yields and Bp of Methoxy-2-silatetralins (**16a-d**) and Uncyclized Product (**15**)

Starting Materials				Reaction Conditions		Yield (%) of **15** and **16**	Bp °C / Torr.
	R^1	R^2	R^3	$AlCl_3$ (eq.)	Solvent		
13a	H	OMe	H	2.0	CS_2 [a]	**16a** (53)	108-109 / 3
13b	OMe	H	H	1.0	CH_2Cl_2 [b]	**15** (60)	117 / 2
13b	OMe	H	H	1.5	CH_2Cl_2 [b]	**16b** (62)	
13b	OMe	H	H	2.0	CS_2 [a]	**16b** (48)	114-117 / 2
13b	OMe	H	H	2.0	CH_2Cl_2 [b, c]	**16b** (53)	
13c	OMe	OMe	H	3.0	CS_2 [a]	**16c** (12)	127-131 / 2
13d	H	OMe	OMe	2.5	CH_2Cl_2 [b, c]	**16d** (20)	
13d	H	OMe	OMe	3.0	CH_2Cl_2 [b]	**16d** (11)	145-152 / 1.5
13e	OCH_2O		H	2.5	CH_2Cl_2 [b, c]	__ [d]	

a) A mixture of MeOH and cyclohexylamine was used. b) A mixture of MeOH and Et_3N was used. c) Reaction was carried out without addition of NaCl. d) Reaction gave an inseparable mixture.

As methoxyl group on silicon atom was reactive, 2,2-dimethoxy-2-silatetralins (**16a-d**) thus obtained was converted to stable 2,2-dimethyl-2-silatetralins (**17a-d**) by treatment with MeMgI in ether. The reaction of **16a** with EtMgBr in ether gave stable 2,2-diethyl-2-silatetralin (**18**) in 81 % yield. The results are shown in Table 3.



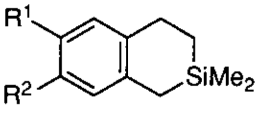
16a-d **17a-d** **18**

Table 3 Yields and Bp of 2,2-Dimethyl-2-silatetralins (**17a-d**) and 2,2-Diethyl-2-silatetralin (**18**)

	Starting Materials R^1	 R^2	 R^3	Grignard Reagent [a)]	Yield (%) of **17** and **18**	Bp °C / Torr.
16a	H	OMe	H	A	**17a** (71)	80-83 / 3
16a	H	OMe	H	B	**18** (81)	108-111 / 2
16b	OMe	H	H	A	**17b** (73)	87-90 / 2
16c	OMe	OMe	H	A	**17c** (53)	103-105 / 2
16d	H	OMe	OMe	A	**17d** (46)	111-120 / 2

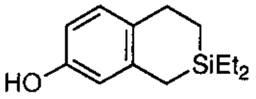
a) Four molar equivalents of the Grignard reagents were used in all reactions; A: MeMgI ; B: EtMgBr.

Synthesis of 7- or 6-Hydroxy-2,2-dimethyl-2-silatetralins (19a, 19b) and 7-Hydroxy-2,2-diethyl-2-silatetralin (20)



19a, b

19	R^1	R^2
a	H	OH
b	OH	H



20

As phenolic 2-silatetralins attracted our attention on their biological activity, demethylation of methoxy-2-silatetralins was investigated. Many methods[18] for ether cleavage have been reported. However, demethylation of methoxy-2-silatetralin seemed to be limited, because ring-opening of silacyclohexene might occur in a usual way. After unsuccessful attempts[19] to cleave methoxyl group, the reaction with boron tribromide[20] in CH_2Cl_2 at ambient temperature readily proceeded to afford a phenolic product. In this way, **17a**, **17b**, and **18** produced the corresponding phenolic 2-silatetralins (**19a**, **19b**, and **20**) in 57, 89, and 64 % yields.

Biological evaluation of the 2-silatetralins thus synthesized is now under way.

ACKNOWLEDGEMENTS

This work was supported in part by Grants-in-Aid for Scientific Research (No. 63571008) from the Ministry of Education, Sciences and Culture of Japan. The authors are indebted to Miss N. Sawabe and Mrs. F. Hasegawa of this faculty for ^{1}H-nmr and mass spectral measurements and to Sankyo Co., Ltd. for elemental analysis.

EXPERIMENTAL

General.—— All melting points were measured on a Büchi 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 spectra were recorded on a JEOL model FX-100 *spectrometer in* $CDCl_3$ *solution using* Me_4Si *or* $CHCl_3$ *as internal standard.* Ms were measured on a Hitachi M-80 or M-80A spectrometer. HRms were measured on a Hitachi M-80 spectrometer. Reactions under ultrasonication were carried out with an Iuchi ultrasonic cleaner VS-100 instrument. Ball-to-ball distillation was carried out by use of a Sibata glass tube oven model GTO-250RS.

Materials.—— THF or ether was distilled from sodium wire and benzophenone or from $LiAlH_4$ prior to use. CH_2Cl_2 was distilled from CaH_2 prior to use, after treatment in a usual manner.

General Procedure for Preparation of Arylmethyldichlorovinylsilanes (13a-e) —— A solution of arylmethyl chlorides (**12a**-**e**) in ether or THF was added dropwise to a stirred mixture of magnesium (Mg) turnings in a small volume of ether or THF at room temperature during 0.5-1.5 h under Ar and the mixture was refluxed for 0.5-3 h. The Grignard reagent thus prepared was added dropwise to a stirred solution of trichlorovinylsilane in ether or THF and the mixture was refluxed. The residue obtained on removal of the solvent *in vacuo* was dissolved in dry ether (except **13a**).

A precipitate was removed by filtration. The filtrate was condensed *in vacuo* to give an oily residue, which was fractionally distilled under reduced pressure.

13a : The Grignard reagent was prepared by the reaction of **12a**[12] (37 g, 0.24 mol) with Mg (7.5 g, 0.31 g atom) in ether (510 ml). The reaction of trichlorovinylsilane (31 ml, 0.24 mol) in ether (530 ml) with the Grignard reagent (addition during 1 h and refluxing for 2 h) gave **13a** (40.3 g, 68 %, bp 123-128 °C / 4 Torr.) as a colorless oil. ^{1}H-Nmr δ : 2.66 (2H, s, SiCH_2Ph), 3.74 (3H, s, ArOMe), 5.92-6.28 (3H, m, CH_2=CH), 6.56-6.76 (3H, m, 3xAr-H), 7.04-7.42 (1H, m, Ar-H). Ir : 1270 ($SiCH_2$) cm^{-1}. HRms *m/z* calcd for $C_{10}H_{12}OCl_2Si$ (M^+) : 246.0033, found : 246.0029; ms *m/z* : 246 (M^+).

13b : The Grignard reagent was prepared by the reaction of **12b**[12] (10.7 g, 0.068 mol) with Mg (16.6 g, 0.68 g atom) in THF (100 ml) containing a few pieces of I_2. The reaction of trichlorovinylsilane (10.4 ml, 0.082 mol) in THF (120 ml) with the Grignard reagent (addition during 40 min and refluxing for 2 h) gave **13b** (7.5 g, 44 %, bp 120-124 °C / 2 Torr.) as a colorless oil. ^{1}H-Nmr δ : 2.64 (2H, s, SiCH_2Ph), 3.77 (3H, s, ArOMe), 5.96-6.29 (3H, m, CH_2=CH), 6.80, 7.06 (4H, each d, J = 8.6 Hz, 4xAr-H). Ir (neat) : 1255 ($SiCH_2$) cm^{-1}. HRms *m/z* calcd for $C_{10}H_{12}OCl_2Si$ (M^+) : 246.0033, found : 246.0043; ms *m/z* : 246 (M^+).

13c : The Grignard reagent was prepared by the reaction of **12c**[13] (9.3 g, 0.05 mol) with Mg (12.2 g, 0.5 g atom) in THF (90 ml) containing a few pieces of I_2. The reaction of trichlorovinylsilane (6.4 ml, 0.05 mol) in THF (50 ml) with the Grignard reagent (refluxing for 3 h) gave **13c** (5.2 g, 37 %, bp 127-129 °C / 3 Torr.) as a colorless oil. ^{1}H-Nmr δ : 2.64 (2H, s, SiCH_2Ph), 3.84 [6H, s, $Ar(OMe)_2$], 5.74-6.30 (3H, m, CH_2=CH), 6.44-6.82 (3H, m, 3xAr-H). Ir : 1240 ($SiCH_2$) cm^{-1}. HRms *m/z* calcd for $C_{11}H_{14}O_2Cl_2Si$ (M^+) : 276.0139, found : 276.0142; ms *m/z* : 276 (M^+).

13d : The Grignard reagent was prepared by the reaction of **12d**[14] (22.4 g, 0.12 mol) with Mg (29.2 g, 1.2 g atom) in THF (230 ml) containing a few pieces of I_2. The reaction of trichlorovinylsilane (18.3 ml, 0.144 mol) in THF (210 ml) with the Grignard reagent (addition during 1 h and refluxing for 2 h) gave **13d** (13.1 g, 39 %, bp 126-128 °C / 1 Torr.) as a colorless oil. ^{1}H-Nmr δ : 2.76 (2H, s, SiCH_2Ph), 3.81, 3.84 [6H, each s, $Ar(OMe)_2$], 6.04-6.27 (3H, m, CH_2=CH), 6.77-7.01 (3H, m, 3xAr-H). Ir (neat) : 1220 ($SiCH_2$) cm^{-1}. HRms *m/z* calcd for $C_{11}H_{14}O_2Cl_2Si$ (M^+) : 276.0139, found : 276.0144; ms *m/z* : 276 (M^+).

13e : The Grignard reagent was prepared by the reaction of **12e**[15] (11.9 g, 0.07 mol) with Mg (17.0 g, 0.7 g atom) in THF (140 ml) containing a few pieces of I_2. The reaction of trichlorovinylsilane (10.7 ml, 0.084 mol) in THF (130 ml) with the Grignard reagent (addition during 40 min and refluxing for 3 h) gave **13e** (9.6 g, 52 %, bp 125-128 °C / 2.5 Torr.) as a colorless oil. ^{1}H-Nmr δ : 2.62 (2H, s, $SiCH_2Ph$), 5.90.(2H, s, OCH_2O), 6.00-6.20 (3H, m, CH_2=CH), 6.48-6.76 (3H, m, 3xAr-H). Ir : 1240 ($SiCH_2$) cm^{-1}. HRms *m/z* calcd for $C_{10}H_{10}O_2Cl_2Si$ (M^+) : 259.9826, found : 259.9833; ms *m/z* : 260 (M^+).

General Procedure for Preparation of Arylmethyldichlorovinylsilanes (13b, c, e) under Ultrasonication —— A solution of arylmethyl chlorides (**12b**, **c**, **e**) in THF was added dropwise to a stirred mixture of Mg turnings in a small volume of THF containing a few pieces of I_2 at 60-70 °C in stream of Ar under ultrasonication and the mixture was refluxed at 50-65 °C under the same conditions. The Grignard reagent thus prepared was added dropwise to a solution of trichlorovinylsilane in THF at reflux under Ar and the mixture was refluxed. The residue obtained on removal of the solvent *in vacuo* was dissolved in dry ether. A precipitate was removed by filtration. The filtrate was condensed *in vacuo* to give an oily residue, which was fractionally distilled under reduced pressure.

13b : The Grignard reagent was prepared by the reaction of **12b** (5.0 g, 0.032 mol) with Mg (1.6 g, 0.064 g atom) in THF (30 ml) (addition at 65 °C and refluxing at 50-60 °C for 80 min). The reaction of trichlorovinylsilane (4.9 ml, 0.038 mol) in THF (40 ml) with the Grignard reagent (refluxing for 1.3 h) gave **13b** (4.4 g, 55 %) as a colorless oil.

13c : The Grignard reagent was prepared by the reaction of **12c** (6.0 g, 0.032 mol) with Mg (1.6 g, 0.064 g atom) in THF (40 ml) (addition at 68-70 °C and refluxing at 60-65 °C for 30 min). The reaction of trichlorovinylsilane (4.9 ml, 0.039 mol) in THF (40 ml) with the Grignard reagent (refluxing for 3 h) gave **13c** (1.4 g, 16 %) as a colorless oil.

13e : The Grignard reagent was prepared by the reaction of **12e** (7.0 g, 0.041 mol) with Mg (2.2 g, 0.092 g atom) in THF (60 ml) (addition at 60-63 °C and refluxing at 60-63 °C for 40 min). The reaction of trichlorovinylsilane (7.0 ml, 0.055 mol) in THF (60 ml) with the Grignard reagent (refluxing for 3 h) gave **13e** (4.4 g, 41 %) as a colorless oil.

General Procedure for Preparation of 2,2-Dimethoxy-2-silatetralins (16a-d) —— a) A mixture of arylmethyldichlorovinylsilanes (**13a**-**d**) and $AlCl_3$ in CS_2 was stirred at room temperature. Dry NaCl was added to the reaction mixture and stirring was continued at the same temperature for 1 h. A precipitate was removed by filtration. The filtrate was condensed *in vacuo* to give a dark brown oil, to which were added the organic solvent (benzene or ether) and a mixture of MeOH and cyclohexylamine. The mixture was stirred at room temperature for 1 h. A precipitate was removed by filtration and the filtrate was washed with 10 % HCl, saturated $NaHCO_3$ and brine or with brine alone, and dried ($MgSO_4$). Removal of the solvent *in vacuo* gave an oil, which was fractionally distilled under reduced pressure.

b) The reaction was carried out in CH_2Cl_2 instead of CS_2 in a manner similar to that noted in **a)**. A precipitate was removed by filtration and washed with CH_2Cl_2. To an ice-cooled combined filtrate was added a mixture of MeOH and Et_3N and stirring was continued at room temperature for 1 h. A precipitate was filtered off and the filtrate was diluted with ether. The organic layer was washed with brine and dried ($MgSO_4$). Usual work-up gave an oil, which was fractionally distilled under reduced pressure.

16a : The reaction was carried out in a manner similar to that noted in **a)**. **13a** (7.95 g, 0.032 mol), $AlCl_3$ (8.6 g, 0.064 mol), CS_2 (110 ml) (stirring for 2 h) and NaCl (15.2 g, 0.26 mol) were used. A benzene (110 ml) solution of the dark brown residue was treated with a mixture of MeOH (9.1 ml, 0.22 mol) and cyclohexylamine (26 ml, 0.23 mol) in benzene (170 ml). **16a** (4.1 g, 53 %, bp 108-109 °C / 3 Torr.) was obtained as a colorless oil. ^{1}H-Nmr δ : 0.84 (2H, t, J = 7.1 Hz, C_3-H), 2.09 (2H, s, C_1-H), 2.79 (2H, t, J = 7.1 Hz, C_4-H), 3.48 [6H, s, $Si(OMe)_2$], 3.75 (3H, s, ArOMe), 6.56 (1H, dd, J = 2.6, 8.6 Hz, C_6-H), 6.66 (1H, d, J = 2.6 Hz, C_8-H), 6.96 (1H, d, J = 8.6 Hz, C_5-H). Ir : 1070 (SiO) cm^{-1}. HRms *m/z* calcd for $C_{12}H_{18}O_3Si$ (M^+) : 238.1023, found : 238.1019; ms *m/z* : 238 (M^+).

16b : **i)** With 2.0 eq. of $AlCl_3$: The reaction was carried out in a manner similar to that noted in **a)**. **13b** (10 g, 0.041 mol), $AlCl_3$ (10.8 g, 0.081 mol), CS_2 (145 ml) (stirring for 6 h) and NaCl (18.9 g, 0.32 mol) were used. An ether (145 ml) solution of the dark brown residue was treated with a mixture of MeOH (13.1 ml, 0.32 mol) and cyclohexylamine (37.2 ml, 0.32 mol) in ether (250 ml). **16b** (4.6 g, 48 %, bp 114-117 °C / 2 Torr.) was obtained as a colorless oil. ^{1}H-Nmr δ : 0.86 (2H, t, J

= 7.1 Hz, C_3-H), 2.04 (2H, s, C_1-H), 2.80 (2H, t, J = 7.1 Hz, C_4-H), 3.48 [6H, s, $Si(OMe)_2$], 3.73 (3H, s, ArOMe), 6.62 (1H, dd, J = 2.6, 8.6 Hz, C_7-H), 6.68 (1H, d, J = 2.6 Hz, C_5-H), 7.00 (1H, d, J = 8.6 Hz, C_8-H). Ir : 1080 (SiO) cm^{-1}. HRms *m/z* calcd for $C_{12}H_{18}O_3Si$ (M^+) : 238.1024, found : 238.1028; ms *m/z* : 238 (M^+).

ii) With 2.0 eq. of $AlCl_3$: The reaction was carried out in a manner similar to that noted in **b)** except NaCl. **13b** (0.74 g, 3 mmol), $AlCl_3$ (0.80 g, 6 mmol), CH_2Cl_2 (17 ml) (stirring for 4.5 h). The reaction mixture was treated with a mixture of MeOH (1.5 ml, 36 mmol) and Et_3N (5.0 ml, 36 mmol) in CH_2Cl_2 (22 ml). **16b** (0.38 g, 53 %) was obtained as a pale yellow oil.

iii) With 1.5 eq. of $AlCl_3$: The reaction was carried out in a manner similar to that noted in **b)**. **13b** (1.48 g, 6 mmol), $AlCl_3$ (1.2 g, 9 mmol), CH_2Cl_2 (34 ml) (stirring for 4.5 h) and NaCl (2.1 g, 36 mmol) were used. The precipitate was washed with CH_2Cl_2 (45 ml). The combined filtrates were treated with a mixture of MeOH (2.2 ml, 54 mmol) and Et_3N (7.5 ml, 54 mmol) in CH_2Cl_2 (43 ml). **16b** (0.89 g, 62 %) was obtained as a pale yellow oil.

16c : The reaction was carried out in a manner similar to that noted in **a)**. **13c** (3.7 g, 0.013 mol), $AlCl_3$ (5.35 g, 0.040 mol), CS_2 (48 ml) (stirring for 2.25 h) and NaCl (9.4 g, 0.161 mol) were used. An ether (48 ml) solution of the dark brown residue was treated with a mixture of MeOH (8 ml, 0.2 mol) and cyclohexylamine (23 ml, 0.2 mol) in ether (155 ml). **16c** (416 mg, 12 %, bp 127-131 °C / 2 Torr.) was obtained as a pale yellow oil. ^1H-Nmr δ : 0.86 (2H, t, J = 7.1 Hz, C_3-H), 2.03 (2H, s, C_1-H), 2.79 (2H, t, J = 7.1 Hz, C_4-H), 3.49 [6H, s, $Si(OMe)_2$], 3.82, 3.83 [6H, each s, $Ar(OMe)_2$], 6.62, 6.63 (2H, each s, 2xAr-H). Ir : 1070 (SiO) cm^{-1}. HRms *m/z* calcd for $C_{13}H_{20}O_4Si$ (M^+) : 268.1130, found : 268.1132; ms *m/z* : 268 (M^+).

16d : **i)** With 3.0 eq. of $AlCl_3$: The reaction was carried out in a manner similar to that noted in **b)**. **13d** (10.8 g, 0.04 mol), $AlCl_3$ (15.6 g, 0.117 mol), CH_2Cl_2 (140 ml) (stirring for 2.5 h) and NaCl (27.4 g, 0.468 mol) were used. The precipitate was washed with CH_2Cl_2 (320 ml). The combined filtrates were treated with a mixture of MeOH (19 ml, 0.468 mol) and Et_3N (65.3 ml, 0.468 mol) in CH_2Cl_2 (555 ml). **16d** (1.1 g, 11 %, bp 145-152 °C / 1.5 Torr.) was obtained as a pale yellow oil. ^1H-Nmr δ : 0.83 (2H, t, J = 7.1 Hz, C_3-H), 2.17 (2H, s, C_1-H), 2.80 (2H, t, J = 7.1 Hz, C_4-H), 3.51 [6H, s, $Si(OMe)_2$], 3.79, 3.83 [6H, each s, $Ar(OMe)_2$], 6.60, 6.80 (2H, each d J = 8.6 Hz, 2xAr-H). Ir :

1080 (SiO) cm^{-1}. HRms *m/z* calcd for $C_{13}H_{20}O_4Si$ (M+) : 268.1130, found : 268.1133; ms *m/z* : 268 (M+).

ii) With 2.5 eq. of $AlCl_3$: The reaction was carried out in a manner similar to that noted in **b)** except NaCl. **13d** (1.11 g, 4 mmol), $AlCl_3$ (1.33 g, 10 mmol), CH_2Cl_2 (14 ml) (stirring for 4.5 h). The reaction mixture was treated with a mixture of MeOH (2.3 ml, 57 mmol) and Et_3N (8.0 ml, 57 mmol) in CH_2Cl_2 (86 ml). **16d** (0.21 g, 20 %) was obtained as a colorless oil.

Formation of (Dimethoxy)(3-methoxybenzyl)(phenethyl)silane (14) —— The reaction was carried out in a manner similar to that noted in **a)** except solvent. **13a** (346 mg, 1.4 mmol), $AlCl_3$ (373 mg, 2.8 mmol), benzene (5 ml) (stirring for 25 min) and NaCl (656 mg, 11.2 mmol) were used. A benzene (5 ml) solution of the residue was treated with a mixture of MeOH (0.45 ml, 11.0 mmol) and cyclohexylamine (1.28 ml, 11.2 mmol) in benzene (8.6 ml) for 1 h. The reaction mixture was quenched with water and the mixture was extracted with ether, and dried ($MgSO_4$). The solvent was evaporated to give a residue (354 mg), which was purified by silica gel column chromatography with hexane-AcOEt (5 : 1, v / v) to give **14** (279 mg, 63 %) as a colorless oil. ^{1}H-Nmr δ : 0.80-1.04 (2H, m, $SiCH_2CH_2Ph$), 2.20 (2H, s, $SiCH_2Ar$), 2.44-2.68 (2H, m, $SiCH_2CH_2Ph$), 3.50 [6H, s, $Si(OMe)_2$], 3.74 (3H, s, ArOMe), 6.53-6.74 (3H, m, 3xAr-H), 6.91-7.31 (6H, m, 6xAr-H). HRms *m/z* calcd for $C_{18}H_{24}O_3Si$ (M+) : 316.1494, found : 316.1504; ms *m/z* : 316 (M+).

Formation of (Dimethoxy)(4-methoxybenzyl)vinylsilane (15) —— The reaction was carried out in a manner similar to that noted in **b)**. **13b** (1.48 g, 6 mmol), $AlCl_3$ (0.80 g, 6 mmol), CH_2Cl_2 (34 ml) (stirring for 4.5 h) and NaCl (1.40 g, 24 mmol) were used. The precipitate was washed with CH_2Cl_2 (30 ml). The combined filtrates were treated with a mixture of MeOH (1.5 ml, 36 mmol) and Et_3N (5.0 ml, 36 mmol) in CH_2Cl_2 (43 ml) for 1 h. **15** (0.86 g, 60 %, bp 117 °C / 2 Torr.) was obtained as a pale yellow oil. ^{1}H-Nmr δ : 2.19 (2H, s, $SiCH_2Ph$), 3.49 [6H, s, $Si(OMe)_2$], 3.76 (3H, s, ArOMe), 5.76-6.23 (3H, m, CH_2=CH), 6.74, 7.03 (4H, each d, *J* = 8.6 Hz, 4xAr-H).Ir : 1090 (SiO) cm^{-1}. HRms *m/z* calcd for $C_{12}H_{18}O_3Si$ (M+) : 238.1024, found : 238.1026; ms *m/z* : 238 (M+).

General Procedure for Preparation of 2,2-Dimethyl-2-silatetralins (17a-d) and 2,2-Diethyl-2-silatetralin (18) —— A mixture of Mg turnings and MeI or EtBr in ether was refluxed for 0.5 h under Ar. A solution of 2,2-dimethoxy-2-silatetralins (**16a-d**) in ether was added to the

Grignard reagent prepared above at room temperature and the mixture was stirred at the same temperature for 19-70 h. 10 % Aqueous HCl was added carefully under ice-cooling and the product was taken up in ether or AcOEt. The extract was washed with water and dried ($MgSO_4$). Removal of the solvent gave an oil, which was fractionally distilled under reduced pressure.

17a : **16a** (3.0 g, 0.013 mol), ether (12 ml), and the Grignard reagent [Mg (1.2 g, 0.05 g atom), MeI (3.1 ml, 0.05 mol), and ether (38 ml)] were used. **17a** (1.85 g, 71 %, bp 80-83 °C / 3 Torr.) as a colorless oil. ^{1}H-Nmr δ : 0.09 (6H, s, $SiMe_2$), 0.75 (2H, t, J = 7.1 Hz, C_3-H), 1.97 (2H, s, C_1-H), 2.72 (2H, t, J = 7.1 Hz, C_4-H), 3.81 (3H, s, ArOMe), 6.61 (1H, dd, J = 2.6, 8.6 Hz, C_6-H), 6.69 (1H, d, J = 2.6 Hz, C_8-H), 7.01 (1H, d, J = 8.6 Hz, C_5-H). Ir : 1240 (SiMe) cm^{-1}. HRms m/z calcd for $C_{12}H_{18}OSi$ (M^+) : 206.1125, found : 206.1119; ms m/z : 206 (M^+).

17b : **16b** (4.6 g, 0.019 mol), ether (19 ml), and the Grignard reagent [Mg (1.88 g, 0.077 g atom), MeI (4.8 ml, 0.077 mol), and ether (76 ml)] were used. **17b** (2.9 g, 73 %, bp 87-90 °C / 2 Torr.) as a colorless oil. ^{1}H-Nmr δ : 0.02 (6H, s, $SiMe_2$), 0.75 (2H, t, J = 7.1 Hz, C_3-H), 1.86 (2H, s, C_1-H), 2.72 (2H, t, J = 7.1 Hz, C_4-H), 3.75 (3H, s, ArOMe), 6.54-6.70 (2H, m, 2xAr-H), 6.98 (1H, d, J = 8.6 Hz, C_8-H). Ir : 1250 (SiMe) cm^{-1}. HRms m/z calcd for $C_{12}H_{18}OSi$ (M^+) : 206.1126, found : 206.1130; ms m/z : 206 (M^+).

17c : **16c** (0.88 g, 0.0033 mol), ether (3 ml), and the Grignard reagent [Mg (0.32 g, 0.013 g atom), MeI (0.8 ml, 0.013 mol),and ether (13 ml)] were used. **17c** (0.42 g, 53 %, bp 103-105 °C / 2 Torr.) as a colorless oil. ^{1}H-Nmr δ : 0.02 (6H, s, $SiMe_2$), 0.74 (2H, t, J = 7.1 Hz, C_3-H), 1.84 (2H, s, C_1-H), 2.68 (2H, t, J = 7.1 Hz, C_4-H), 3.82 [6H, s, $Ar(OMe)_2$], 6.64, 6.65 (2H, each s, 2xAr-H). Ir : 1250 (SiMe) cm^{-1}. HRms m/z calcd for $C_{13}H_{20}O_2Si$ (M^+) : 236.1230, found : 236.1228; ms m/z : 236 (M^+).

17d : **16d** (1.0 g, 0.004 mol), ether (9 ml), and the Grignard reagent [Mg (0.44 g, 0.018 g atom), MeI (0.93 ml, 0.015 mol), and ether (16 ml)] were used. **17d** (0.41 g, 46 %, bp 111-120 °C / 2 Torr.) as a colorless oil [after purification by silica gel column chromatography with hexane-AcOEt (50 : 1, v / v)]. ^{1}H-Nmr δ : 0.05 (6H, s, $SiMe_2$), 0.71 (2H, t, J = 7.1 Hz, C_3-H), 2.02 (2H, s, C_1-H), 2.68 (2H, t, J = 7.1 Hz, C_4-H), 3.75, 3.82 [6H, each s, $Ar(OMe)_2$], 6.59, 6.81 (2H, each d, J = 8.6 Hz, 2xAr-H). Ir : 1265 (SiMe) cm^{-1}. HRms m/z calcd for $C_{13}H_{20}O_2Si$ (M^+) : 236.1230, found : 236.1224; ms m/z : 236 (M^+).

18 : **16a** (3.83 g, 0.016 mol), ether (16 ml), and the Grignard reagent [Mg (1.56 g, 0.064 g atom), EtBr (4.8 ml, 0.064 mol), and ether (40 ml)] were used. **18** (3.05 g, 81 %, bp 108-111 °C / 2 Torr.) as an oil. ^{1}H-Nmr δ : 0.39-1.08 (12H, m, $SiEt_2$, C_3-H), 1.96 (2H, s, C_1-H), 2.71 (2H, t, J = 7.1 Hz, C_4-H), 3.79 (3H, s, ArOMe), 6.58 (1H, dd, J = 2.9, 8.6 Hz, C_6-H), 6.68 (1H, d, J = 2.9 Hz, C_8-H), 6.98 (1H, d, J = 8.6 Hz, C_5-H). HRms *m/z* calcd for $C_{14}H_{22}OSi$ (M^+) : 234.1438, found : 234.1446; ms *m/z* : 234 (M^+).

General Procedure for Demethylation of 17a, b and 18 —— A mixture of methoxy-2-silatetralins (**17a, b, 18**) and BBr_3 in CH_2Cl_2 was stirred at room temperature for 10-20 min. Water was added to the mixture and the product was taken up in CH_2Cl_2. The CH_2Cl_2 extract was washed with saturated $NaHCO_3$ and brine, and dried ($MgSO_4$). Removal of the solvent gave a residue, which was recrystallized or fractionally distilled under reduced pressure.

19a : **17a** (1.0 g, 5 mmol), BBr_3 (0.5 ml 5 mmol), and CH_2Cl_2 (10 ml) were used. **19a** [0.53 g, 57 %, mp 83-84 °C (petroleum ether)]. An analytical sample had mp 89-90 °C (petroleum ether). Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39. Found : C, 68.41; H, 8.32. ^{1}H-Nmr δ : 0.08 (6H, s, $SiMe_2$), 0.74 (2H, t, J = 7.1 Hz, C_3-H), 1.94 (2H, s, C_1-H), 2 68 (2H, t, J = 7.1 Hz, C_4-H), 4.44-5.01 (1H, br, OH), 6.51 (1H, dd, J = 2.9, 7.1 Hz, C_6-H), 6.59 (1H, d, J = 2.9 Hz, C_8-H), 6.94 (1H, d, J = 7.1 Hz, C_5-H). Ir : 3610 (OH) cm^{-1}; ms *m/z* : 192 (M^+).

19b : **17b** (1.0 g, 5 mmol), BBr_3 (0.5 ml 5 mmol), and CH_2Cl_2 (10 ml) were used. **19b** (0.83 g, 89 %) [after purification by silica gel column chromatography with hexane-AcOEt (3 : 1, v / v)]. An analytical sample had mp 74.5-75 °C (petroleum ether). Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39. Found : C, 68.72; H, 8.53. ^{1}H-Nmr δ : 0.06 (6H, s, $SiMe_2$), 0.74 (2H, t, J = 7.1 Hz, C_3-H), 1.88 (2H, s, C_1-H), 2.68 (2H, t, J = 7.1 Hz, C_4-H), 4.44-4.71 (1H, brs, OH), 6.48-6.64 (2H, m, C_5-H, C_7-H), 6.92 (1H, d, J = 7.1 Hz, C_8-H). Ir : 3600 (OH) cm^{-1}; ms *m/z* : 192 (M^+).

20 : **18** (1.0 g, 4 mmol), BBr_3 (0.4 ml 4 mmol), and CH_2Cl_2 (10 ml) were used. **20** (0.60 g, 64 %, bp 123-126 °C / 5 Torr.) as a colorless oil [after purification by silica gel column chromatography with hexane-AcOEt (2 : 1, v / v)]. ^{1}H-Nmr δ : 0.36-1.04 (12H, m, $SiEt_2$, C_3-H), 1.90 (2H, s, C_1-H), 2.66 (2H, t, J = 7.1 Hz, C_4-H), 4.40-4.73 (1H, br, OH), 6.46 (1H, dd, J = 2.9, 8.6 Hz, C_6-H), 6.56 (1H, d, J = 2.9 Hz, C_8-H), 6.89 (1H, d, J = 8.6 Hz, C_5-H). Ir : 3610 (OH) cm^{-1}. HRms *m/z* calcd for $C_{13}H_{20}OSi$ (M^+) : 220.1281, found : 220.1278; ms *m/z* : 220 (M^+).

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Received, 20th December, 1993