Preparation of (α,α-Dichlorobenzyl)silanes and (α-Halobenzyl)silanes

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Two general methods for the preparation of (α-halobenzyl)silanes are the metalation of α,α-dichlorotoluene followed by reaction with chlorosilanes and subsequent reduction with tributyltin hydride and the insertion of halophenylcarbenes generated from halophenyldiazirenes into Si–H bonds. The former process involves Si–C bond formation with inversion and the latter with retention of stereochemistry at silicon. The diazirene insertion route permits the preparation of α-bromo and α-fluoro silanes as well as the α-chloro silanes.

Introduction

α-Halo silanes have a diverse reaction chemistry, including considerable synthetic potential, such as the generation of silyllithium and silylmagnesium reagents. We have been particularly interested in rearrangements of α-halo silanes that result in C–C bond formation and that take place under a variety of conditions: Lewis acid catalyzed, thermal, nucleophilic attack at silicon, and nucleophilic displacement at the α-silyl carbon.[4] Despite the versatile chemistry of this class of compounds, the widespread use of α-halo silanes in organic and organosilicon chemistry has been limited by a lack of convenient methods of preparation.[5-7]

Synthesis of (α-Halobenzyl)silanes. Brook et al.[8] reported clean thermal rearrangements of (α-halobenzyl)silanes. We explored similar chemistry with (α-chloroalkyl)silanes but encountered problems with byproducts formed at the high temperatures necessary for the thermal rearrangement. For that reason, we decided to study the catalyzed and uncatalyzed rearrangements of (α-halobenzyl)silanes in more detail. As a prelude to that study, we explored a number of synthetic routes to this class of compounds with the object of preparing (α-halobenzyl)silanes with different halogens at the benzylic position and different aryl groups attached to silicon. Brook et al.[9] utilized a four-step route that involved the generation of silyldiazoalkanes and subsequent reaction with a hydrogen halide. This procedure gave overall yields of approximately 20% starting from the silane and utilized conditions incompatible with the presence of various substituents in the aromatic ring attached to the silicon.

The direct halogenation of benzylsilanes[10] affords low yields and also gives undesired double halogenation products. Moreover, halogenation/desilylation products were observed when electron donors were attached to an aromatic ring bonded to silicon (eq 1).

$$RC_6H_4SiMe_2CH_2Ph \xrightarrow{SO_2Cl_2/Bz_2O_2} RC_6H_4Cl + ClSiMe_2CH_2Ph \quad (1)$$

$$R = OMe, {}^tBu$$

The dependence on the nature of the substituent in the aromatic ring for a successful α-halogenation was further tested by monitoring the reaction of both α-$NpSiMe_2CH_2Ph$ and 4-Cl-α-$NpSiMe_2CH_2Ph$ with *N*-bromosuccinimide (NBS). The deactivated chloronaphthyl derivative was successfully brominated; whereas, naphthylsilane underwent halogenation/desilylation.[11] Kumada et al.[12] have reported a similar dependence of reactivity on electronic effects in the NBS cleavage of C–Si bonds in aryl hexacoordinated silicon compounds.

An alternative route to (α-chlorobenzyl)silanes, which involved reacting aryl Grignard reagents with (α-chlorobenzyl)dimethylchlorosilane ($ClSiMe_2CHClC_6H_5$) afforded low yields of the desired (α-chlorobenzyl)silanes.[13] The reaction of an (aryldimethylsilyl)lithium reagent with aryl aldehydes followed by conversion of the hydroxy group to a halide[14] resulted in only moderate yields of the desired (α-chlorobenzyl)silane.

In a recent paper, Andringa et al.[15] reported a synthesis of (α-chlorobenzyl)trimethylsilane by the trimethylsilylation of the carbenoids obtained by α-metalation of benzyl chloride and benzyl bromide with lithium diisopropylamide. In another recent publication, Fry et al.[16] reported the electrochemical synthesis of (α-chlorobenzyl)trimethylsilanes and (α-bromobenzyl)trimethylsilane from a benzal halide and excess chlorotrimethylsilane.

We wish to report two general routes to (α-halobenzyl)silanes which allow for the synthesis of (α-chlorobenzyl)-, (α-bromobenzyl)-, and (α-fluorobenzyl)silanes. A variety of (α-chlorobenzyl)silanes has been prepared

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Table I. Properties of the (α,α-Dichlorobenzyl)- and (α-Halobenzyl)silanes

product	% yield	method[a]	bp (mp), °C/press, Torr	anal. calc (found)	^{1}H NMR δ	^{13}C NMR δ	^{29}Si NMR δ	MS[d]
Me_3SiCCl_2Ph	65	A	60/0.02	known[33]	7.71–7.16 (b m, 5 H), 0.17 (s, 9 H)	141.2, 127.9, 126.9, 85.4, −3.5	14.81	232 (1), 126 (38), 124 (100), 113 (18), 89 (19), 73 (46)
Et_3SiCCl_2Ph	78	A	112/0.02	C, 56.72; H, 7.32 (C, 56.79; H, 7.34)	7.0–7.8 (b m, 5 H), 0.4–1.5 (b m, 15 H)	142.0, 127.8, 127.7, 126.9, 85.7, 7.44, 2.35	15.19	159 (3), 124 (53), 115 (69), 87 (100), 53 (59)
$PhMe_2SiCCl_2Ph$	69	A	(67–8)	C, 61.01; H, 5.46 (C, 60.90; H, 5.48)	7.41–7.16 (b m, 10 H), 0.50 (s, 6 H)	140.7, 135.2, 132.9, 130.2, 127.8, 127.4, 127.3, 84.8, −5.2		229 (4), 208 (6), 166 (62), 165 (41), 135 (100), 89 (11)
$Ph_2MeSiCCl_2Ph$	37	A	*b*	C, 67.22; H, 5.08 (C, 67.31; H, 5.13)	7.65–7.08 (b m, 15 H), 0.79 (s, 3 H)	140.8, 136.0, 131.9, 130.2, 128.0, 127.8, 127.7, 127.5, 83.7, −5.1	−4.36	217 (13), 197 (19), 166 (23), 165 (21), 159 (2)
1-$NpPhMeSiCCl_2Ph$	47	A	(95–6)	C, 70.75; H, 4.95 (C, 70.81; H, 4.97)	8.08–7.0 (b m, 17 H), 0.92 (s, 3 H)	141.0, 137.5, 137.0, 135.7, 133.6, 133.5, 131.2, 130.0, 128.8, 128.7, 128.0, 127.7, 125.4, 125.2, 124.6, 83.8, −2.4	−2.6	
1-$NpPhMeSiCCl_2C_6H_4$-4-^{t}Bu	40	A	(168.9)	C, 72.55; H, 6.09 (C, 72.43; H, 6.16)	8.05–7.44 (m, 16 H), 1.26 (s, 9 H), 0.94 (s, 3 H)	151.2, 138.1, 137.7, 137.1, 135.8, 133.9, 133.4, 131.1, 129.9, 129.5, 128.8, 127.7, 125.3, 125.1, 124.5, 84.1, 34.4, 31.2, −2.0	−2.7	
$Me_3SiCHClPh$	64	B	45/0.02	known[10a,34]	7.16 (m, 5 H), 4.24 (s, 1 H), 0.00 (s, 9 H)	140.2, 127.8, 126.9, 126.5, 52.9, −3.6	5.70	198 (3), 155 (8), 105 (5), 90 (8), 89 (9), 73 (100)
$Et_3SiCHClPh$	40	B	*c*	C, 64.83; H, 8.79 (C, 65.01; H, 8.93)	7.3 (s, 5 H), 4.5 (s, 1 H), 0.4–1.5 (m, 15 H)	140.6, 128.2, 127.0, 126.5, 50.7, 7.2, 1.97	8.47	240 (3), 118 (32), 115 (100), 93 (36), 91 (43), 87 (95), 59 (48)
$PhMe_2SiCHClPh$	62	B	*c*	C, 69.07; H, 6.57	7.48–6.98 (m, 10 H), 4.44 (s 1 H),	139.6, 134.9, 134.4, 129.6, 128.6,		260 (1), 167 (9), 165 (5),
	72	C	*c*	(C, 69.28; H, 6.71)	0.41 (s, 3 H), 0.31 (s, 3 H)	127.9, 127.6, 127.2, 126.2, 52.2, −5.2		136 (13), 135 (100), 107 (5), 105 (8), 93 (7), 89 (5), 63 (5)
$Ph_2MeSiCHClPh$	42	B	ca. 170/0.1	C, 74.39; H, 5.93	7.9–6.8 (b m, 15 H), 4.9 (s, 1 H),	139.1, 135.4, 135.1, 133.9, 133.6,	−8.17	199 (3), 197 (100), 165 (11),
	65	C		(C, 74.18; H, 5.97)	0.65 (s, 3 H)	133.0, 129.9, 129.7, 127.9, 127.8, 127.7, 126.8, 50.6, −6.03		125 (24), 105 (29), 89 (20), 53 (15)
1-$NpPhMeSiCHClC_6H_4$-4-^{t}Bu mixture of diastereomers	64	B	*c*		7.80–6.92 (m, 32 H), 5.15 (s, 1 H), 5.06 (s, 1 H), 1.27 (s, 9 H), 1.19 (s, 9 H), 0.84 (s, 3 H), 0.73 (s, 3 H)	149.9, 149.7, 137.1, 137.0, 136.2, 136.0, 135.8, 135.5, 135.1 134.7, 133.6, 133.4, 131.9, 131.3, 131.0, 130.7, 129.8, 129.6, 129.1, 129.0, 128.8, 128.4, 127.8, 127.5, 127.2 125.7, 125.4, 125.3, 125.1, 124.9, 50.9, 50.4, 34.4, 34.3, 31.4, 31.3, −4.2, −4.5	−6.8, −7.0	
1-$NpPhMeSiCHClPh$	61	B	*c*	C, 77.29; H, 5.68	7.97–6.93 (b m, 34 H), 5.17 (s, 1 H),	139.1, 137.0, 136.9, 135.9, 135.7,	−6.36, −6.75	
mixture of diastereomers	72	C	*c*	(C, 77.42; H, 5.60)	5.08 (s, 1 H), 0.82 (s, 3 H), 0.68 (s, 3 H)	135.5, 135.0, 133.3, 131.6, 131.1, 131.0, 130.8, 129.8, 129.6, 128.6, 128.3, 127.8, 127.6, 127.4, 126.6, 125.7, 125.3, 124.9, 50.9, 50.5, −4.5, −4.8		
4-^{t}Bu$C_6H_4Me_2SiCHClPh$	70	C	*c*	C,72.00; H, 7.95 (C, 71.98; H, 8.11)	7.35–7.09 (m, 9 H), 4.46 (s, 1 H), 1.31 (s, 9 H), 0.41 (s, 3 H), 0.26 (s, 3 H)	152.8, 134.3, 131.5, 128.0, 127.3, 126.6, 124.6, 52.4, 34.7, 31.3, −4.9, −5.2		316 (1), 193 (6), 191 (100), 176 (9), 161 (9), 125 (5)
4-$F_3CC_6H_4Me_2SiCHClPh$	75	C	*c*	C,58.44; H, 4.90 (C, 58.07; H, 4.92)	7.56–7.07 (m, 9 H), 4.51 (s, 1 H), 0.49 (s, 3 H), 0.41 (s, 3 H)	136.6, 130.8, 129.3, 129.1, 126.2, 53.8, −3.0, −3.1		328 (2), 205 (5), 203 (100), 89 (5)
4-$MeOC_6H_4Me_2SiCHClPh$	72	C	*c*		7.35–6.82 (m, 9 H), 4.43 (s, 1 H), 3.91 (s, 3 H), 0.40 (s, 3 H), 0.31 (s, 3 H)	136.0, 128.0, 127.3, 126.6, 113.6, 55.8, 52.7, −4.9		290 (1), 167 (6), 166 (14), 165 (100), 135 (6), 91 (5), 89 (7), 63 (6), 59 (5)
4-$ClC_6H_4Me_2SiCHClPh$	70	C	*c*	C, 61.01; H, 5.47 (C, 60.66; H, 5.40)	7.29–7.08 (m, 9 H), 4.44 (s, 1 H), 0.42 (s, 3 H), 0.34 (s, 3 H)	139.5, 136.0, 133.5, 128.3, 128.2, 127.3, 127.0, 52.2, −5.0		294 (1), 171 (36), 169 (100), 165 (6), 125 (5), 63 (16)
1-$NpMe_2SiCHClPh$	70	C	*c*	C,73.40; H, 6.16 (C, 73.12; H, 5.97)	8.07–6.97 (m, 12 H), 4.87 (s, 1 H), 0.67 (s, 3 H), 0.45 (s, 3 H)	134.9, 130.6, 129.2, 128.6, 128.0, 127.9, 126.9, 126.5, 125.9, 125.4, 124.9, 52.3, −2.7, −3.7		

$PhMe_2SiCHBrPh$	70	C	c	C, 59.01; H, 5.61 (C, 59.09; H, 5.71)	7.50–7.10 (m, 10 H), 4.41 (s, 1 H), 0.47 (s, 3 H), 0.37 (s, 3 H)	134.3, 129.6, 128.4, 128.0, 127.6, 126.7, 42.6, −4.3, −4.5	306 (1), 304 (1), 210 (5), 181 (10), 165 (8), 135 (100) 105 (14)
$Ph_2MeSiCHBrPh$	60	C	c	C, 65.39; H, 5.21 (C, 65.43; H, 5.34)	7.55–7.14 (m, 15 H), 4.76 (s, 1 H), 0.71 (s, 3 H)	135.4, 135.2, 134.0, 129.9, 129.7, 128.8, 128.1, 127.8, 127.7, 127.0, 40.5, −5.1	366 (0.4), 199 (6), 198 (23), 197 (100), 181 (7), 165 (13), 105 (30)
$PhMe_2SiCHFPh$	55	C	c		7.44–6.98 (m, 10 H), 5.62 (d, 1 H, J = 44.5 Hz), 0.36 (s, 3 H), 0.29 (s, 3 H)	134.3, 129.6, 128.0, 127.8, 126.5, 124.3, 93.6 (d, J = 170 Hz), −5.9, −6.0	244 (1), 168 (8), 167 (49), 135 (100), 105 (16), 90 (36), 77 (30)
$Ph_2MeSiCHFPh$	50	C	c	C, 78.39; H, 6.25 (C, 78.01; H, 5.98)	7.59–6.95 (m, 15 H), 5.97 (d, 1 H, J = 44.4 Hz), 0.53 (s, 3 H)	135.2, 134.1, 131.9, 129.8, 128.5, 128.4, 128.2, 127.9, 127.4, 92.8 (d, J = 171.3 Hz), −7.0	306 (1) 197 (100), 165 (16), 139 (63), 119 (11), 105 (35)

[a] Method A: Reaction of a chlorosilane with (α,α-dichlorobenzyl)lithium. Method B: Reduction of the (α,α-dichlorobenzyl)silane to the (α-chlorobenzyl)silane. Method C: Reaction of a silane with the 3-aryl-3-halodiazirine. [b] Literature[33] bp 84–5 °C/1.5. [c] Purified by silica gel chromatography. [d] Mass spectra reported as m/e (relative intensity).

from the reaction of (α,α-dichlorobenzyl)lithium with a chlorosilane followed by reduction of one of the chlorines.[17] Alternatively, (α-bromobenzyl)-, (α-chlorobenzyl)-, and (α-fluorobenzyl)silanes have been prepared by the insertion of the appropriate arylhalocarbene, generated from 3-aryl-3-halodiazirines,[18] into a Si–H bond. Two examples of the latter process, not optimized for preparative purposes, have been recently reported by Doyle et al.[19]

Results and Discussion

Reaction of (α,α-Dichlorobenzyl)lithium with Chlorosilanes. Although the preparation of (α,α-dichlorobenzyl)lithium from α,α,α-trichlorotoluene has been reported,[20] we felt that a better route might be the deprotonation of α,α-dichlorotoluene (benzal chloride) utilizing the general method of Villieras et al.[21] This proved to be the case. Thus, reacting benzal chloride with lithium diisopropylamide in a mixture of THF/ether/hexane at −100 °C for 30 min followed by the addition of trimethylchlorosilane at that temperature and warming to 25 °C resulted in the isolation of a 65% yield of the desired trimethyl(α,α-dichlorobenzyl)silane. In a like manner, other (α,α-dichlorobenzyl)silanes were prepared according to eq 2. The preparation of the lithium reagent in

$$PhCHCl_2 + iPr_2NLi \xrightarrow{THF/ether/hexane} PhCCl_2Li$$

$$R_3SiCl + PhCCl_2Li \rightarrow R_3SiCCl_2Ph \qquad (2)$$

THF/hexane resulted in lower yields and more rapid decomposition of the lithium reagent. A rather rapid decomposition of the lithium reagent was also observed at the higher temperature of −78 °C. The systems synthesized and their key physical and spectral properties are given in Table I.

In order to ascertain the stereochemistry of the reaction of (α,α-dichlorobenzyl)lithium at silicon, (*R*)-(+)-1-naphthylphenylmethylchlorosilane was reacted with this reagent and the resulting dextrorotatory product reduced to the known (*R*)-(−)-1-naphthylphenylmethylbenzylsilane[22] (Scheme I), whose optical rotation compares favorably with that of the same product obtained from the reaction of benzylsodium and 1-naphthylphenylmethylchlorosilane.[22] The result illustrates that the reaction of this reagent with a chlorosilane occurs with a high degree of inversion of configuration at silicon, unlike benzyllithium itself, which gives a low stereoselectivity in its reactions with chlorosilanes.

Scheme I

(*R*)-(+)-1-NpPhMeSiCl + $PhCCl_2Li$ →
(*S*)-(+)-1-NpPhMeSiCCl_2Ph

(*S*)-(+)-1-NpPhMeSiCCl_2Ph $\xrightarrow[AIBN]{2Bu_3SnH}$
(*R*)-(−)-1-NpPhMeSiCH_2Ph

Reduction of (α,α-Dichlorobenzyl)silanes to (α-Chlorobenzyl)silanes. Based on our successful monoreduction of (α,α-dichloroethyl)silanes to (α-chloroethyl)silanes[17] we applied the same tributyltin hydride procedure to the reduction of the (α,α-dichlorobenzyl)silanes according to eq 3. These reactions occurred with

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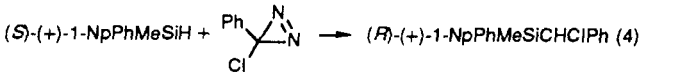
$$R_3SiCCl_2Ph \xrightarrow[AIBN]{Bu_3SnH} R_3SiCHClPh \quad (3)$$

very little overreduction under the conditions employed. As anticipated, the reduction of (α,α-dichlorobenzyl)-naphthylphenylmethylsilane gave an inseparable equimolar mixture of diastereomers, as evidenced by ^1H NMR analysis. The yields, boiling points, and key spectral properties for these materials are also given in Table I.

In an attempt to prepare an (α-chlorobenzyl)silane in pure diastereomeric form, (α-chloro-*p*-*tert*-butylbenzyl)-naphthylphenylmethylsilane was prepared in the hope that it would have greater crystallinity and therefore would separate into the pure diastereomers. Thus, *p*-*tert*-butylbenzaldehyde was treated with thionyl chloride in dimethylformamide[23] to give the corresponding benzal chloride. Deprotonation of the benzal chloride and reaction of the resulting lithium reagent with (*R*)-(+)-1-naphthylphenylmethylchlorosilane gave the desired (α,α-dichlorobenzyl)silane in 40% yield. Treatment of this with 1 equiv of tributyltin hydride gave (α-chlorobenzyl)silane as an equimolar mixture of diastereomers, which, unfortunately, proved inseparable as well.

Reaction of Arylhalodiazirines with Trisubstituted Silanes. It is well-known that carbenes insert into the Si–H bond.[24] We therefore felt that arylhalocarbenes, available by the thermolysis or photolysis of arylhalodiazirines, would insert into the Si–H bond to generate the (α-halobenzyl)silanes in a single step directly from readily available silanes. The 3-aryl-3-halodiazirines were synthesized from arylamidine hydrochlorides by using Graham's reaction.[18] Arylamidine hydrochlorides are commercially available or can be prepared from arenenitriles.[25] For simplicity the arylhalocarbenes were generated by the thermal decomposition of the 3-aryl-3-halodiazirines. The reaction was carried out in the absence of a solvent and with an excess of the diazirine. This reaction nicely overcomes the halogenation/desilylation problem stated above and affords the (α-halobenzyl)silanes in good yields. (α-Fluorobenzyl)silanes can be made available by using 3-aryl-3-fluorodiazirines generated by substitution of 3-aryl-3-bromodiazirine with tetrabutylammonium fluoride.[26] This is a particularly valuable addition to the synthetic capabilities, since the formation of the thermodynamically favored Si–F bond ordinarily prevents the use of fluorinating agents to perform a selective benzylic fluorination. Since the temperature required to decompose the 3-aryl-3-fluorodiazirines is between 80 and 100 °C, and the α-fluoro silanes, especially those with a phenyl group attached to silicon, show a high tendency to rearrange,[8] some rearrangement of the desired (α-fluorobenzyl)silanes took place during the thermal insertion of the arylfluorocarbenes. This problem was overcome by photochemically generating the arylfluorocarbenes from the 3-aryl-3-fluorodiazirines.

The chiral silane, (*S*)-(+)-1-naphthylphenylmethylsilane, was heated with 3-phenyl-3-chlorodiazirine to afford an equimolar diastereomeric mixture of chiral (α-chlorobenzyl)silanes (eq 4), which we were not successful in



separating by chromatographic means. As predicted, this diastereomeric mixture showed an opposite rotation to that obtained from the (α,α-dichlorobenzyl)lithium route, indicating retention stereochemistry in the insertion step. Sommer et al.[27] found similar results in studying the insertion reaction of dichlorocarbene and dibromocarbene with a chiral silane.

The methodology described here compares favorably with that employing other available phenylchlorocarbene sources.[28,29] Treating phenyldichloromethane with potassium *tert*-butoxide[29] entails severely basic conditions which may either modify the silicon–hydrogen bond of the silane before the insertion takes place or produce a rearrangement by nucleophilic attack on the (α-halobenzyl)-silane just formed. The recently developed system of phenylchlorocarbene transfer reported by Cunico and Chu[30] by treatment of (α,α-dichlorobenzyl)trimethylsilane with anhydrous potassium fluoride in the presence of 18-crown-6 was tested with triethylsilane and afforded (α-chlorobenzyl)triethylsilane in 44% yield (detected by GC). The low yield could be attributed to attack of the fluoride source on the triethylsilane substrate present in a 4-fold excess. Moreover, this methodology does not seem appropriate for treatment of chiral substrates due to potential isomerization at the silicon center after the insertion reaction had occurred.[31] This isomerization occurs more rapidly in the presence of a phase-transfer agent such as the crown ether which is used under these mild reaction conditions.

At the time this paper was in preparation, Doyle et al.,[19] when studying the reactivity and selectivity in intermolecular insertion reactions of chlorophenylcarbene, reported a diazirine-generated carbene insertion reaction into the silicon–hydrogen bond of triethylsilane and diphenylsilane. The thermal decomposition of 3-chloro-3-phenyldiazirine under refluxing benzene for 3 h generated phenylchlorocarbene. Under Doyle's conditions, the carbene reacted with a more than 3-fold excess of silane, whereas, in our conditions the silane is the limiting reagent, and the reaction is performed without solvent. In all of our runs, we have used no more than 5 g of diazirene. We do not recommend large scale-ups of the procedure due to the possibility for explosive decomposition of the reagent.

Experimental Section

^1H, ^{13}C, and ^{29}Si NMR spectra were recorded as solutions in deuteriochloroform on Bruker AC 100, AC/WP 200, and Jeol FX90Q spectrometers. Mass spectra were obtained on a Hewlett-Packard 5985 GC/MS system operating at 70 eV using a 30 m × 0.25 mm i.d., 0.2-mm OV-1-BP fused-silica capillary column. For new compounds, MS patterns and C and H elemental analyses were in agreement with expected values (Table I). The starting silanes were synthesized either by standard routes in our laboratories or were obtained from commercial sources. 3-Aryl-3-fluoro-,[26] 3-aryl-3-chloro-,[32] and 3-aryl-3-bromodiazirene[18,26] were prepared by published procedures.

Reaction of 3-Chloro-3-phenyldiazirine with Dimethylphenylsilane. Representative Procedure. A 10-mL round-bottomed flask equipped with a condenser, Ar inlet system, and a small magnetic stirrer was charged with 1.5 g (0.011 mol) of phenyldimethylsilane and 2.5 g (0.0165 mol) of 3-chloro-3-

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phenyldiazirine. After heating above 80 °C with an oil bath, some bubbles started to evolve (N_2); at the end of 4 h the reaction mixture appeared darker, and the reaction was stopped. The reaction was monitored by the disappearance of the Si–H ^{1}H NMR signal and the appearance of the new benzylic ^{1}H NMR signal. Separation of the reaction mixture by silica gel column chromatography using hexane as eluent provided 2 g (0.0077 mol, 70% yield) of the title product, whose spectral properties are given in Table I.

Preparation of Trimethyl(α,α-dichlorobenzyl)silane. Representative Procedure. Following the procedure of Villieras et al., a 250-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, dropping funnel, and a no-air stopper was charged with 40 mL of THF, 40 mL of ether, and 5.2 mL of diisopropylamine. The mixture was cooled to −78 °C, 25 mL (40 mmol) of 1.56 M butyllithium was added, and the reaction mixture was stirred for an additional 30 min. The reaction mixture was then cooled to −100 °C, and 5.1 mL (6.44 g, 40 mmol) of α,α-dichlorotoluene in 20 mL of THF was added followed by stirring for 1 h. To this was added 2.53 mL (2.17 g, 20 mmol) of chlorotrimethylsilane in 20 mL of THF and the resulting reaction mixture stirred at −100 °C for 1 h, after which time it was allowed to slowly warm to 25 °C. After cooling to 0 °C, the reaction mixture was hydrolyzed with a cold solution of 1.5 M hydrochloric acid (50 mL). The aqueous layer was extracted with pentane (2 × 20 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The solvents were removed at reduced pressure, and the product was distilled to give 3.03 g (65%) of the title product, whose spectral properties are given in Table I. In some instances the products were purified by silica gel chromatography eluting with hexane.

Preparation of Trimethyl(α-chlorobenzyl)silane. Representative Procedure. A two-necked, round-bottomed flask of 25-mL capacity equipped with magnetic stirring and a nitrogen inlet was charged with 10 mL of anhydrous benzene (or hexane), 2.87 g (12.3 mmol) of trimethyl(α,α-dichlorobenzyl)silane, and then 3.58 g (3.31 mmol) of tributyltin hydride and a small amount of 2,2′-azobis(2-methylpropanenitrile) (AIBN). The solution was heated to reflux for 6 h, the hexane was removed at reduced pressure, and the product was distilled to give 1.57 g (64%) of the title compound, whose spectral properties are given in Table I.

Preparation of (+)-1-Naphthylphenylmethyl(α,α-dichlorobenzyl)silane. Following the general procedure above, 20 mmol of (−)-1-naphthylphenylmethylchlorosilane provided 3.8 g (47%) of the title compound: $[\alpha]^{20}_D$ = +8.96° (*c* 6.92, cyclohexane).

Preparation of (−)-1-Naphthylphenylmethyl(α-chlorobenzyl)silane. Following the general reduction procedure above, 6.2 mmol of (+)-1-naphthylphenylmethyl(α,α-dichlorobenzyl)-silane provided 1.35 g (61%) of the title compound as a 1:1 mixture of diastereomers: $[\alpha]^{28}_D$ = −20.7° (*c* 5.9, chloroform). All attempts to separate the diastereomers failed.

Preparation of (−)-1-Naphthylphenylmethylbenzylsilane. A 25-mL flask was charged with 0.82 g (2 mmol) of (+)-1-naphthylphenylmethyl(α-chlorobenzyl)silane, 1.75 g (6 mmol) of tributyltin hydride, 0.1 g of AIBN, and 8 mL of benzene. The reaction mixture was heated to reflux for 6 h, and the solvent and tributyltin chloride were removed by distillation at reduced pressure. This provided 0.54 g (80%) of the title compound $[\alpha]^{28}_D$ = −6.76° (*c* 6.66, cyclohexane) (lit.[22] $[\alpha]^{25}_D$ = −6.8°).

Preparation of (+)-1-Naphthylphenylmethyl[α,α-dichloro(4-*tert*-butylphenyl)methyl]silane. Following the above procedure, 60 mmol of [α,α-dichloro(4-*tert*-butyl)benzyl]lithium was reacted with (−)-naphthylphenylmethylchlorosilane to give 5.6 g (40%) of the title compound, which was purified by silica gel chromatography eluting with hexane–ethyl acetate (9:1 v/v) and then crystallization from hexane: $[\alpha]^{28}_D$ = +9.78° (*c* 3.72, chloroform).

Preparation of (−)-1-Naphthylphenylmethyl[α-chloro(4-*tert*-butylbenzyl)]silane. Following the general reduction procedure above, 0.42 g (0.9 mmol) of (+)-1-naphthylphenylmethyl[α,α-dichloro(4-*tert*-butylphenyl)methyl]silane produced, after flash chromatography eluting with hexane to remove the tributyltin chloride and then hexane–ethyl acetate (5:95 v/v), the title compound in 65% yield: $[\alpha]^{28}_D$ = −17.2° (*c* 5.8, chloroform).

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