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ASYMMETRIC INDUCTION BY CHIRAL SILICON GROUPS

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Summary

The reduction of racemic $RPhMeSiCCl_2CH_3$ systems (R = cyclohexyl, isopropyl, t-butyl and 2-mesityl) to the diastereomeric $RPhMeSiCHClCH_3$ with tributyltin hydride was used as a probe into the potential of the RPhMeSi group to induce asymmetry at an α position. Favorable results were obtained for R = mesityl.

Introduction

As a part of our overall interest in the use of organosilicons in organic synthesis we have embarked on a study of organosilicons optically active at silicon as potential reagents for the synthesis of optically active, silicon-free systems. We envision the chiral silicon moiety as being able to perform either or both of two functions, namely asymmetric induction and/or the separation of the diastereomers formed. Stereoselective removal for substitution of the silyl group would then provide the silicon-free optically active product. This is presented in general form for an α-functionalized organosilicon in Scheme 1.

Although considerable work has been done with optically active silicon, the majority of these studies have centered on the mechanisms of reaction at silicon [1] with only two studies aimed at possible chiral synthesis [2,3]. In addition to these studies the 1-naphthylphenylmethylsilyl group was employed in the resolution of cyclophosphamides. [4] Brook and coworkers have generated diastereomeric mixtures from 1-naphthylphenylmethylbenzoylsilane [5,6,7] and (1-naphthylphenylmethylsilyl)phenylmethyllithium [8] and we have reported the tributyltin hydride reduction of (α,α-dichloro)- (VIa) and (α,α-dibromoethyl)-1-naphthylphenylmethylsilane (VIb) to give the corresponding α-haloethylsilanes (VIIa, VIIb) with no asymmetric induction on the part of the 1-naphthylphenylmethylsilyl group (eq. 1) [9].

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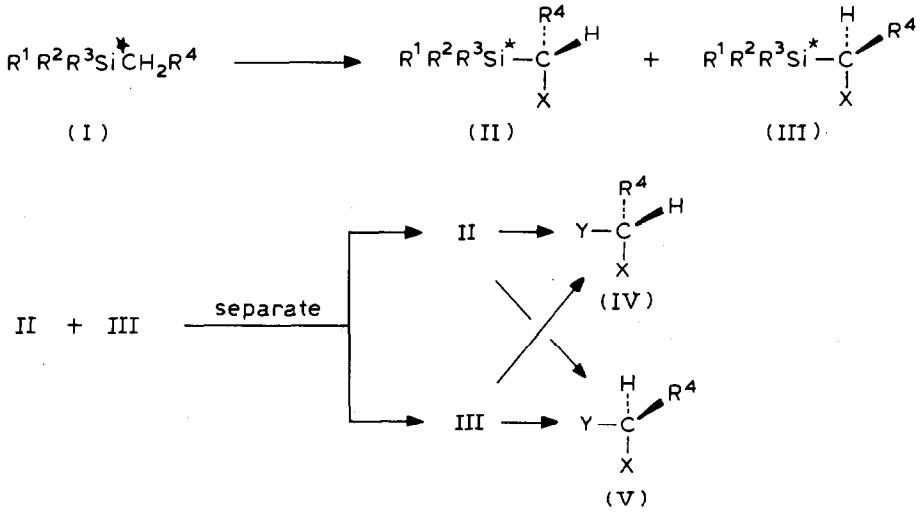
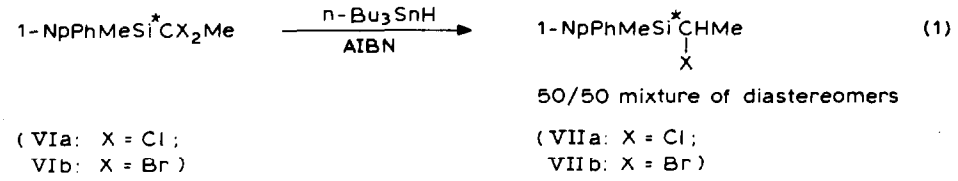


SCHEME 1

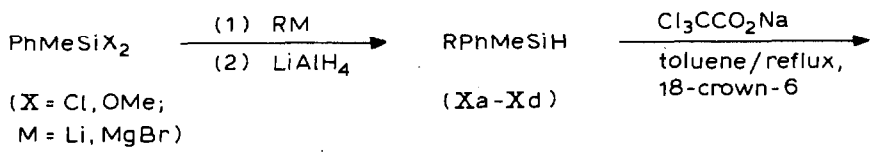


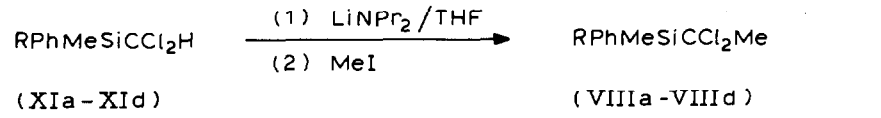
The interest in and tendency towards the use of the 1-naphthylphenylmethylsilyl group stems from the pioneering work of Sommer and coworkers, who prepared, resolved and studied this system. [10] Owing to the considerable work with this particular system it lends itself well to the use of Walden cycles of stereochemical assignments at silicon. One other, though scarcely employed, property of this group is that it often provides crystalline products, which can lead to facile separation of created diastereomers [4,9] (See Scheme 1).

Results and dicussion

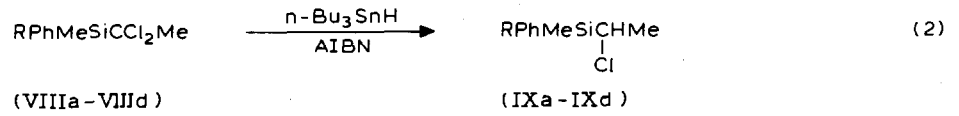
General

Based on the disappointing results of asymmetric induction of the 1-naphthylphenylmethylsilyl group in the reduction (eq. 1) and the mixed results on the asymmetric induction of this group reported in the literature [3,5–8] coupled with the fact that studies of models implied to us that at least part of the problem could be that the effective sizes of the naphthyl and phenyl groups are very similar, we decided to replace the naphthyl group with the cyclohexyl (VIIIa), isopropyl (VIIIb), t-butyl (VIIIc) and mesityl (VIIId) groups and study the asymmetric induction in the reduction of these systems (eq. 2). This series was attractive because Sommer and coworkers had shown that it is possible to prepare the RPhMeSi system stereoselectively from the 1-NpPhMeSi system. [11]. The reduction shown in eq. 1 was chosen to study the asymmetric induction because it provided the worst possible results (R = 1-Np) and because we felt that we could use ^{1}H NMR to determine the diastereomeric ratio by integration of the diastereotopic methyl groups on silicon.





SCHEME 2



(R = cyclo-C_6H_{11} (a), i-Pr (b), t-Bu (c), 2-mesityl (d))

Synthesis of reactants

The required α,α-dichloroethylsilanes (VIIIa–VIIId) were prepared according to Scheme 2. The results are shown in Table 1. The silanes were prepared in a two-step, single-flask operation. Preformed cyclohexylmagnesium bromide in THF was reacted with dimethoxyphenylmethylsilane and the resulting product reduced directly to give Xa in 6.3% yield. Since this provided sufficient material for our needs no further effort was invested in this reaction. A different approach was employed for Xb in which 2-bromopropane was added to a THF solution of dimethoxyphenylmethylsilane and magnesium turnings with ultrasound activation. Direct reduction of this reaction mixture gave Xb in 17% yield. The t-butyl (Xc) and mesityl (Xd) systems were prepared in 69 and 51% yield, respectively, by treating phenylmethyldichlorosilane with t-butyllithium in pentane and mesitylmagnesium bromide in THF and direct reduction of the reaction mixtures.

The sodium trichloroacetate generated dichlorocarbene insertion into the silicon–hydrogen bond according to our procedure [12] proceeded well as did the deprotonation-methylation [13].

Reduction and product analysis

The monoreduction of the α,α-dichloroethylsilanes (VIIIa–VIIId) was accom-

TABLE 1

PREPARATION OF THE COMPOUNDS IN SCHEME 2: X, XI, AND VIII

Series	X (%)	XI (%)	VIII (%)
a	6.3	40.4	69
b	17	71	81
c	68.5	46	66
d	51	38	96

TABLE 2

RATIO OF DIASTEREOMERS OF IX FROM eq. 2

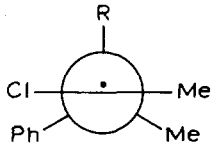
R	Ratio[a]	% *d*
Cyclo-C_6H_{11} (IXa)	47/53	6
i-Pr (IXb)	51/49	2
t-Bu (IXc)	52/48	4
Mesityl (IXd)	40/60	20

[a] Ratio of low field silicon methyl singlet to higher field silicon methyl singlet at about 0.3 ppm, except for the mesityl case where the carbon methyl doublets were used (see text).

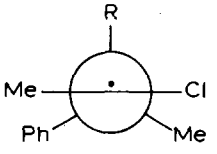
plished with tributyltin hydride in benzene in the presence of a catalytic amount of azoisobutyronitrile (AIBN). The 90 MHz ^{1}H NMR spectrum of the crude reaction product showed two peaks at ca. 0.3 ppm for the diastereotopic silicon methyl groups, except in the case of IXa, which showed no separation of these peaks. Integration of the silicon methyls with qualitative corroboration by observation of the overlapping quartets at ca. 4 ppm gave the results shown in Table 2. This procedure permitted analysis of the reaction prior to purification and thus avoided possible inadvertent separation of diastereomers prior to analysis.

Purification of the mesityl system VIIId prior to analysis was necessary because the silicon methyl groups were not distinguishable in the ^{1}H NMR spectrum. Although analysis of the overlapping quartets at 4.16 ppm indicated that asymmetric induction had occurred, integration of this resonance was not considered precise enough. Chromatographic purification of IXd gave materials that showed an identical resonance centered at 4.16 ppm to that of the crude sample indicating that no separation of diastereomers had occurred during the purification. Integration of the methyl doublets at 1.16 and 1.50 ppm, now clearly visible with the absence of the tributyltin chloride, showed a ratio of diastereomers of 40/60.

The tributyltin hydride reduction of α-halosilanes has been shown to be a radical process [14]. Therefore, asymmetric induction in the VIII to IX step would come from a preference of conformation XIIa over XIIb, assuming the R group to be larger than the phenyl group.



(XIIa)

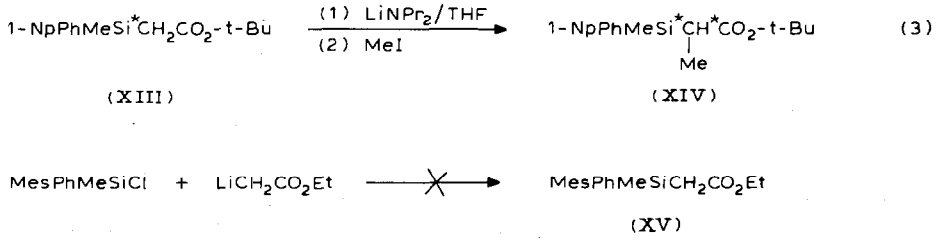


(XIIb)

As can be seen from the results shown in Table 2, only the mesityl group demonstrates asymmetric induction (20% *d*) and that the cyclohexyl, isopropyl and t-butyl groups, all of which looked promising from studies of models, give no induction.

Further studies of the mesitylphenylmethylsilyl group, which has been prepared in optically active form [15] are now underway. We wish to report one experiment, however, that demonstrates the problem of a sterically congested silicon group. We had shown that the α-silyl ester XIII, prepared by silylation of lithium t-butyl acetate [16,17], could be deprotonated and methylated to give XIV in 81% yield and

80% *d* (eq. 3). Attempts to prepare the corresponding α-silyl ester (XV) have failed, presumably due to steric reasons. Thus reaction of an excess of ethyl lithioacetate with chloromesitylmethylphenylsilane in THF and in THF/HMPA gave only mesitylmethylphenylsilanol upon aqueous workup.



Conclusions

Properly substituted chiral organosilicon groups can lead to asymmetric induction, but the required bulky nature of the ligands on silicon preclude chemistry at the silicon or in some cases at the α position. This coupled with the fact that optically active organosilicons with small ligands are readily racemized under a variety of conditions bodes ill for clean asymmetric induction by a silicon moiety. It does not, however, rule out the possibility of utilizing optically active silicon in a combination of asymmetric induction-separation.

Experimental

General

All reagents were used as received from the suppliers. Solvents were dried by accepted procedures. All reactions were run in a standard apparatus under an atmosphere of prepurified nitrogen. NMR spectra were recorded on a Jeol FX90Q spectrophotometer as $CDCl_3$ solutions and are reported in δ units from internal TMS. GC-MS analyses were carried out on a Hewlett–Packard 5995A spectrometer with an SE-30 GC column.

Cyclohexylphenylmethylsilane (Xa)

A 2-liter, three-necked, round-bottomed flask was charged with 19.4 g (0.80 g-at) of magnesium turnings and the apparatus flame-dried under a stream of nitrogen. The apparatus was cooled to room temperature and 400 ml of THF added. The Grignard formation was initiated by the addition of 6 ml of bromocyclohexane. This was followed by the addition of 61.5 ml of bromocyclohexane (0.50 mol total) in 100 ml of THF at such a rate as to maintain a gentle reflux. After the addition was complete the mixture was heated to reflux for 16 h after which time 91.8 ml (91.2 g; 0.50 mol) of phenylmethyldimethoxysilane in 100 ml of THF added dropwise. The resulting reaction mixture was refluxed for 9 h and 10 g (1.26 mol) of lithium aluminum hydride slowly added with ice-bath cooling. This was followed by a 20 h reflux. The excess hydride was decomposed by the cautious, dropwise addition of ethyl acetate. The reaction mixture was transferred to a 2-liter separatory funnel half-filled with crushed ice and 250 ml of concentrated hydrochloric acid. The

aqueous phase was removed and extracted with ether (2 × 100 ml). The organic layers were combined and washed with water until the aqueous phase was neutral to litmus and dried (Na_2SO_4). Concentration and distillation gave 6.4 g (6.3%) of the desired product of approximately 95% purity: b.p. 106–10°C/2.2 mmHg; IR (neat): 2100 cm^{-1}; ^1H NMR: δ 7.5 (m, 5H), 4.2 (m, 1H), 1.7 and 1.2 (two multiplets, 14H), 0.3 ppm (d, 3H, *J* 3.9 Hz); ^{13}C NMR: δ 135.88, 134.70, 129.10, 127.73, 28.22, 27.88, 26.81, 24.27, −7.75 ppm; ^{29}Si NMR: δ −8.98 ppm; MS 204(12), 121(100).

Isopropylphenylmethylsilane (Xb)

A 500 ml, three-necked, round-bottomed flask was charged with 12 g (0.50 g-at) of magnesium turnings, flame dried, cooled and 106 g (0.50 mol) of phenylmethyldimethoxysilane and 200 ml of THF were added. The reaction vessel was then immersed in a sonicator. A dropping funnel was charged with 56.4 g (0.5 mol) of 2-bromopropane. Approximately 5 g of the bromide was added to the reaction vessel with sonication. After the reaction had initiated the remainder of the bromide was diluted with 20 ml of THF and this solution added dropwise. The reaction mixture was refluxed for 16 h, cooled to 0°C and 6 g (0.158 mol) of lithium aluminum hydride added and then refluxed an additional 10 h. Workup as above and distillation gave 14 g (17%) of the title silane, which was ultimately purified by preparative GLC (5% SE-30 column): b.p. 40°C/0.4 mmHg; IR (neat): 2007 cm^{-1}; ^1H NMR: δ 7.36 (m, 5H), 4.21 (m, 1H), 1.3 (m, 1H), 1.01 (bs, 6H), 0.31 ppm (d, 3H, *J* 3.66 Hz); ^{13}C NMR: (wrt $CDCl_3$) δ 135.80, 134.63, 129.17, 127.76, 18.20, 17.91, 12.50, −7.89 ppm; ^{29}Si NMR: δ −6.30 ppm; MS 164 (7), 121 (100); Anal. Found: C, 72.90; H, 9.84. $C_{10}H_{16}Si$ calcd.: C, 73.09; H, 9.82%.

t-Butylphenylmethylsilane (Xc)

A 250 ml, three-necked, round-bottomed flask was flame dried, cooled and charged with 70 ml of dry pentane and 9.6 g (50 mmol) of phenylmethyldichlorosilane. A dropping funnel was then charged via syringe with 54.5 ml (100 mmol) of a 1.84 *M* solution of t-butyllithium in pentane and this solution added dropwise to the reaction mixture. The resulting mixture was refluxed for 72 h, cooled and 2.4 g (63 mmol) of lithium aluminum hydride added followed by a 12 h reflux. Workup as above and silica gel chromatography (hexane) gave 6.1 g (68.5%) of the title silane about 90% pure; IR (neat): 2052 cm^{-1}; ^1H NMR: δ 7.4 (m, 5H), 4.14 (m, 1H), 0.94 (s, 9H), 0.33 ppm (d, 3H, *J* 3.67 Hz); ^{13}C NMR: δ 135.05, 129.20, 127.63, 26.87, 16.63, −8.45 ppm; ^{29}Si NMR: δ −1.34; MS 178 (10), 121 (100).

Mesitylphenylmethylsilane (Xd)

A 500 ml standard apparatus was charged with 5.8 g (0.24 g-at) of magnesium turnings and 150 ml of THF and 23.0 g (0.15 mol) of 1-bromomesitylene in THF added dropwise. The reaction mixture was refluxed for 1 h and 25.6 g (0.15 mol) of phenylmethyldichlorosilane in 50 ml of THF added at 0°C. The reaction mixture was refluxed for 18 h and 3.8 g (0.10 mol) of lithium aluminum hydride added and the new reaction mixture refluxed for 18 h. Workup as before and fractional distillation gave 18.4 g (51%) of the title silane: b.p. 126–131°C/0.6 mmHg; IR (neat): 2245 cm^{-1}; ^1H NMR: δ 7.54–7.24 (m, 5H), 6.83 (bs, 2H), 5.22 (q, 1H, *J* 4 Hz), 2.35 (s, 6H), 2.25 (s, 3H), 0.65 (d, 3H, *J* 4 Hz); ^{13}C NMR: δ 144.96, 139.49, 136.30, 134.35, 129.04, 128.66, 127.90, 24.10, 21.12, −4.12 ppm. MS: 240(28), 162(100), 147(91), 119(26).

Dichloromethylcyclohexylmethylphenylsilane (XIa)

According to our published procedure [12] a 100 ml standard apparatus was charged with 12.4 g (66.9 mmol) of sodium trichloroacetate, 0.6 g (2.2 mmol) of 18-crown-6 and 42 ml of dry toluene and finally 4.6 g (22.5 mmol) of cyclohexylmethylphenylsilane. The reaction mixture was refluxed for 18 h, and filtered through a pad of celite. The organic phase was washed with 1.5 *N* HCl (2 × 50 ml) dried over $MgSO_4$. Distillation of the solvent and then the residue gave 2.60 g (40.4%) of the title compound: b.p. 155–160°C/2.4 mmHg; ^{1}H NMR: δ 7.4 (m, 5H), 5.5 (s, 1H), 1.7–1.2 (two m, 11H), 0.49 ppm (s, 3H); ^{13}C NMR: δ 134.85, 131.83, 130.08, 127.88, 61.48, 27.79, 27.15, 26.63, 23.25, −9.46 ppm; ^{29}Si NMR: δ −2.34 ppm; MS: 286 (not observed) 121 (100).

Dichloromethylisopropylmethylphenylsilane (XIb)

The reaction of sodium trichloroacetate (150 mmol) with isopropylmethylphenylsilane (50 mmol) as above gave 8.3 g (71%) of the title compound contaminated with a small amount of *sym*-diphenyltetramethyldisiloxane: b.p. 119–22°C/2.2 mmHg; ^{1}H NMR: δ 7.5 (m, 5H), 5.60 (s, 1H), 1.55 (m, 1H), 1.11 (d, 3H), 1.02 (d, 3H), 0.49 ppm (s, 3H); ^{13}C NMR: δ 134.94, 131.75, 130.18, 127.90, 61.48, 17.54, 17.33, 11.43, 1.02 ppm; MS: Parent ion (not observed), 163 (100).

Dichloromethyl-t-butylmethylphenylsilane (XIc)

Following the procedure above 60 mmol of sodium trichloroacetate was reacted with 20 mmol of t-butylmethylphenylsilane to give 2.4 g (46%) of the title compound: b.p. 96–98°C/1.5 mmHg; ^{1}H NMR: δ 7.6–7.3 (m, 5H), 5.69 (s, 1H), 1.03 (s, 9H), 0.54 ppm (s, 3H); ^{13}C NMR (with reference to $CDCl_3$) δ 134.75, 133.94, 132.31, 129.87, 127.82, 60.97, 27.43, 18.33, −9.95 ppm; MS: Parent ion (not observed) 57 (100).

Dichloromethylmethylmesitylphenylsilane (XId)

Following the procedure above 72 mmol of sodium trichloroacetate was treated with 24 mmol of mesitylmethylphenylsilane for 18 h. An aliquot taken and analyzed by ^{1}H NMR indicated that the reaction was incomplete and another 20 mmol of sodium trichloroacetate was added followed by refluxing for 18 h. In this way 2.97 g (38%) of the title compound was obtained: b.p. 175–210°C/0.6 mmHg ^{1}H NMR: δ 7.6–7.2 (m, 5H), 6.85 (s, 2H), 5.98 (s, 1H), 2.34 (s, 6H), 2.27 (s, 3H), 0.94 ppm (s, 3H); ^{13}C NMR: δ 145.13, 140.20, 135.27, 134.68, 129.85, 124.58, 127.97, 63.98, 24.97, 21.02, −1.41 ppm; ^{29}Si NMR: −5.8 ppm; MS: Parent ion (not observed) 239 (100).

(1,1-Dichloroethyl)cyclohexylmethylphenylsilane (VIIIa)

A 50 ml standard apparatus was charged with 0.7 g (7 mmol) of diisopropylamine and 16 ml of THF, cooled to −78°C and 5.2 ml (6.97 mmol) of 1.34 *M* n-butyllithium in hexane added. The reaction mixture was allowed to reach room temperature for 15 min, recooled to −78°C and 1.0 g (3.5 mmol) of XIa in 6 ml of THF added. The lithium reagent was allowed to form for 2 h at −78°C and 2.4 g (17.5 mmol) of iodomethane added. The reaction mixture was stirred for 1.5 h at −78°C, warmed to room temperature and worked with 1.5 *N* HCl (15 ml). The aqueous layer was extracted with ether (3 × 7 ml) and the combined organic layers dried over

$MgSO_4$. After solvent removal at reduced pressure the residue was subjected to silica gel chromatography eluting with hexane to give 0.73 g (69%) of the title compound: ^{1}H NMR: δ 7.45 (m, 5H), 2.01 (s, 3H), 1.9–1.1 (m, 11H), 0.52 ppm (s, 3H); ^{13}C NMR: δ 135.18, 132.67, 129.94, 127.82, 81.31, 34.89, 27.96, 26.70, 23.45–8.92 ppm; ^{29}Si NMR: δ 2.96; MS Parent ion (not observed) 203 (17), 121 (100).

(1,1-Dichloroethyl)isopropylmethylphenylsilane (VIIIb)

Following the procedure above on a 4.3 mmol scale 0.89 g (81%) of the title compound was obtained: ^{1}H NMR: 7.7–7.2 (m, 5H), 2.01 (s, 3H), 1.66 (septet, 1H), 1.24 (d, 3H, *J* 7.2 Hz), 1.02 (d, 3H, *J* 7.2 Hz), 0.52 ppm (s, 3H); ^{13}C NMR: δ 135.16, 132.67, 130.02, 127.80, 81.21, 18.53, 18.42, 11.54, −9.59 ppm; ^{29}Si NMR: δ 5.60 ppm; MS: Parent ion (not observed) 121 (100).

(1,1-Dichloroethyl)t-butylmethylphenylsilane (VIIIc)

Following the procedure above 6 mmol of XIc gave 1.05 g (66%) of the title compound: ^{1}H NMR: δ 7.9–7.3 (m, 5H), 2.07 (s, 3H), 1.13 (s, 9H), 0.55 ppm (s, 3H); ^{13}C NMR: (with reference to $CDCl_3$) δ 135.35, 134.58, 129.82, 127.71, 81.44, 35.99, 28.51, 19.58, −7.83 ppm; MS: Parent ion (not observed) 177 (17), 135 (26), 105 (22), 73 (42), 57 (100).

(1,1-Dichloroethyl)mesitylmethylphenylsilane (VIIId)

Following the procedure above 1.5 mmol of XId gave 0.48 g (96%) of the title compound: ^{1}H NMR: δ 7.75–7.16 (m, 5H), 6.82 (s, 2H), 2.33 (s, 3H), 2.28 (s, 6H), 2.24 (s, 3H), 0.88 ppm (s, 3H); ^{13}C NMR: δ 146.49, 140.21, 138.42, 133.54, 123.91, 128.94, 128.07, 126.01, 82.24, 35.76, 26.00, 20.96, 4.01 ppm; ^{29}Si NMR: δ −4.80 ppm; MS: Parent ion (not observed), 239 (100).

(1-Chloroethyl)cyclohexylmethylphenylsilane (IXa)

A 25 ml standard apparatus was charged with 3 ml of dry benzene and 0.68 g (2.3 mmol) of VIIIa. To this was added 0.76 g (2.6 mmol) of tri-n-butyltin hydride. The reaction was followed by ^{1}H NMR and stopped after 16 h. The ^{1}H NMR spectrum of the crude sample showed two singlets for the silicon methyl groups of each diastereomer at 0.38 and 0.33 ppm in a ratio of 47/53. A sample purified by thick-layer silica gel chromatography eluting with hexane showed: ^{1}H NMR: δ 7.44 (m, 5H), 3.70 (two overlapped quartets, 1H, *J* 7.5 Hz) 1.60–0.70 (m, 14H), 1.54 (d of one diastereomer, *J* 7.5 Hz), 1.48 (d of other diastereomer, *J* 7.5 Hz), 0.07 (s of one diastereomer), 0.00 ppm (s of other diastereomer); ^{13}C NMR: δ 134.89, 134.62, 129.42, 127.80, 127.69, 42.90, 27.95, 27.52, 26.81, 20.47, 20.31, 1.03 ppm.

(1-Chloroethyl)isopropylmethylphenylsilane (IXb)

Following the general procedure above yielded a crude reaction product that showed a diastereomeric ratio of 51/49 based on an integration of the silicon methyls at 0.38 and 0.33 ppm. A sample purified by silica gel chromatography with hexane showed ^{1}H NMR: δ 7.7–7.2 (m, 5H), 3.71 (two overlapping quartets, *J* 7.7 Hz), 1.54 (d of one diastereomer, *J* 7.5 Hz), 1.49 (d of other diastereomer, *J* 7.7 Hz), 1.48 (m, 1H), 1.09 (d, *J* 6.2 Hz), 0.95 (d, *J* 6.8 Hz) (these two doublets appear as a quartet), 0.38 (s), 0.33 (s) ppm.

(1-Chloroethyl)-t-butylmethylphenylsilane (IXc)

The reduction carried out as above gave a crude product that showed the two diastereomeric silicon methyls at 0.35 and 0.30 ppm in a ratio of 52/48. A sample purified by silica gel chromatography showed: ^{1}H NMR: δ 7.7–7.2 (m, 5H), 3.86 (doublet of quartets, J 7.5 Hz), 1.61 (d for one diastereomer, J 7.6 Hz), 1.42 (d for other diastereomer, J 7.6 Hz), 1.01 (s for one diastereomer), 0.99 (s for other diastereomer), 0.43 (s), 0.37 (s) ppm.

(1-Chloroethyl)mesitylmethylphenylsilane (IXd)

The reduction carried out as above gave a crude reaction product that did not lend itself to a direct determination of the diastereomeric ratio since both silicon methyls had the same chemical shift. A sample was purified by preparative TLC and this sample showed 7.7–7.2 (m, 5H), 6.8 (s, 2H), 4.16 (two quartets, J 7.6 Hz), 2.33 (s, 3H), 2.27 (s, 6H), 1.66 (d, J 7.5 Hz), 1.50 (d, J 7.6 Hz), 0.76 ppm (s, 3H). Integration of the two doublets at 1.66 and 1.50 ppm showed the ratio to be 40/60. This material showed the same overlapped quartets at 4.16 ppm as the crude sample so that no separation of the diastereomers occurred.

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