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Silylcuprate Routes to Cyclohex-2-enylsilanes

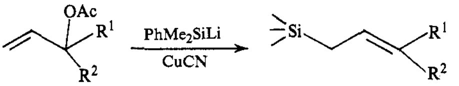
Bronwyn Laycock,[A] *Ian Maynard,*[A] *Geoffrey Wickham*[A] *and*
William Kitching[A, B]

[A] Department of Chemistry, University of Queensland,
St. Lucia, Qld. 4067.
[B] To whom correspondence should be addressed.

Abstract

The efficacy of the dimethyl(phenyl)silylcuprate and (to a lesser extent) the methyldiphenylsilylcuprate reagents in converting cyclohex-2-enyl chlorides into the corresponding allylsilanes has been investigated. The presence of copper(I) greatly suppresses formation of the coupled hydrocarbon, and promotes stereo- and regio-selective carbon–silicon bond formation, in a predominantly *anti*-S_N2' manner. Spectroscopic characterization of the diastereomeric silanes is presented. Grignard routes to some of these silanes are described.

Procedures that exhibit a high level of regio- and stereo-chemical control in the formation of allylsilanes are necessary for the exploitation of these silanes in synthesis and mechanistic studies. In recent years a number of attractive approaches based on copper(I) mediation of organosilyllithium reactions have been developed, particularly by Fleming and his group.[1–4] Our studies of stereochemical aspects of the S_E2' process encompassed cyclohex-2-enylsilanes,[5] and we sought methods for their formation that might incorporate high levels of stereocontrol. When we commenced this work, Fleming had demonstrated that tertiary-allylic acetates[3] were converted into allylsilanes with silylcuprate reagents, providing the isomer with the silyl group at the less substituted end of the allyl fragment (Scheme 1).



Scheme 1

We attempted (unsuccessfully) to extend this approach to secondary-allylic acetates, but, in the meantime, Fleming has reported[4] that a solvent mixture (tetrahydrofuran/ether/pentane, rather than tetrahydrofuran alone) and triphenylphosphine result in useful yields of silanes. Our earlier failure led to studies of allylsilane formation from secondary chlorides, available with moderate stereocontrol from the alcohols with chlorinating agents, such as thionyl chloride or

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[1] Ager, D. J., Fleming, I., and Patel, S. K., *J. Chem. Soc., Perkin Trans. 1*, 1981, 2520.
[2] Fleming, I., Newton, T. W., and Roessler, F., *J. Chem. Soc., Perkin Trans. 1*, 1981, 2527.
[3] Fleming, I., and Marchi, D., *Synthesis*, 1981, 560.
[4] Fleming, I., and Thomas, A. P., *J. Chem. Soc., Chem. Commun.*, 1985, 411.
[5] Wickham, G., and Kitching, W., *J. Org. Chem.*, 1983, **48**, 612.

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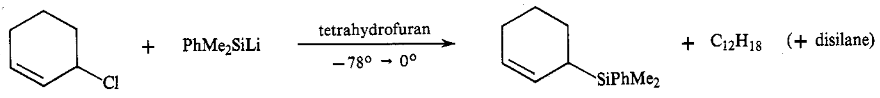
N-chlorosuccinimide/dimethyl sulfide.[6] In this report, we describe fully our studies of silylcuprate reactions with cyclohex-2-enyl chlorides.[7] In this general area, it should be noted that Fleming[8] has developed newer procedures permitting stereospecific formation of allylsilanes from secondary acetates and urethanes, whereas Trost[9] has reported systems based on transition metal catalysis of tris(trimethylsilyl)aluminium reagents, which exhibit useful stereocontrol.

Results and Discussion

Displacement of halo or oxyfunctions from carbon by organometal anion reagents (e.g. R_3MM'; M = Si, Ge, Sn; M′ = Li, Na, K) will exhibit stereocontrol if the nucleophilic capability of the reagent is ascendant, rather than some other, e.g. electron transfer. From our experiences with R_3MM' reagents,[6] particularly where M = Sn, Ge, and M′ = Li, it seemed likely that the reactions of most R_3SiLi reagents with allylchlorides would be stereochemically poorly disciplined. To promote genuinely nucleophilic transfer of the silyl group, we relied on silylcuprate chemistry, of the type being developed by Fleming.[1–4] Our studies utilized $PhMe_2SiLi$ and to a lesser extent $Ph_2MeSiLi$, both of which are easily prepared in tetrahydrofuran directly from the silyl chloride and lithium metal.[10] On the other hand, Me_3SiLi does not form directly from Me_3SiCl and lithium in tetrahydrofuran,[1] and hexamethylphosphoric triamide is employed as solvent in the simplest method for generating Me_3SiLi.[11]

Cyclohex-2-enyl chloride, on reaction with $PhMe_2SiLi$ (50% excess; tetrahydrofuran; $-78° \rightarrow 0°$), in the *absence* of CuI, yielded the allylsilane and coupled hydrocarbon ($C_{12}H_{18}$) (70 : 30), together with the disilane (g.l.c.–m.s. analysis). Purification was effected by Kugelrohr distillation, column chromatography (neutral alumina, hexane) and then preparative gas chromatography. The target silane (M^+, *m/z* 216, $C_{14}H_{20}Si^+$, 1·5%) showed inequivalent Si–CH_3 in the ^1H (0·27, 0·20 ppm) and ^{13}C n.m.r. spectra (−4·68, −4·81 ppm) as expected. The vinyl ^1H absorption was extremely narrow at δ 5·63 with >CHSi at δ 1·66 ($W_{h/2} \approx 18$ Hz). Addition of CuI (0·5 mole equiv.) to the $PhMe_2SiLi$ solution (−78°; stirring for 30 min), prior to addition of cyclohex-2-enyl chloride, strongly suppressed hydrocarbon formation, now 7 : 93 with respect to the silane (75% isolated yield). Disilane production was also markedly decreased. These observations are summarized in Scheme 2.



no CuI 70 : 30

Scheme 2

0·5 mole equiv. CuI 93 : 7

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[6] Wickham, G., Young, D., and Kitching, W., *J. Org. Chem.*, 1982, **47**, 4884.

[7] For preliminary communication, see Laycock, B., Kitching, W., and Wickham, G., *Tetrahedron Lett.*, 1983, **24**, 5785.

[8] Fleming, I., and Thomas, A. P., *J. Chem. Soc., Chem. Commun.*, 1986, 1456.

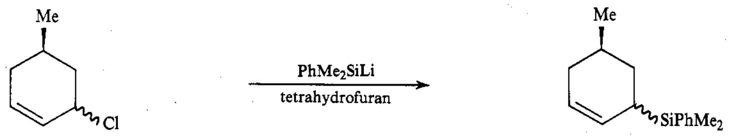
[9] Trost, B. M., Yoshida, J., and Lautens, M., *J. Am. Chem. Soc.*, 1983, **105**, 4494.

[10] George, M. V., Peterson, D. J., and Gilman, H., *J. Am. Chem. Soc.*, 1960, **82**, 403.

[11] Still, W. C., *J. Org. Chem.*, 1976, **41**, 3063.

This pattern of results resembles that reported by Smith,[12] who found that reaction of simple allyl halides with Me_3SiLi (hexamethylphosphoric triamide solvent) afforded almost none of the desired silane, but that CuI (1 equiv.) resulted in good to excellent yields. (Compared with $PhMe_2SiLi$ or $Ph_2MeSiLi$, Me_3SiLi is probably a more efficient electron-transfer or halogen–metal exchange reagent[6]).

This encouraging result led to an examination of the stereochemistry of silane formation in the cyclohex-2-enyl case, and we utilized the symmetrical 5-methylcyclohex-2-enyl system.[6] Predominantly *cis* 5-methylcyclohex-2-enyl chloride (*cis/trans* 81 : 19) (from the alcohol and thionyl chloride in ether) when treated with $PhMe_2SiLi$ afforded mixtures of the diastereomeric silanes whose composition was a function of added CuI. Similar observations apply to the reactions of the predominantly *trans* 5-methylcyclohex-2-enyl chloride (87 : 13). If, for the moment, the correctness of the configurational assignments for the product silanes is accepted, the results may be summarized as shown in Scheme 3.

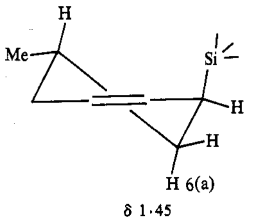


system	*cis/trans*	*cis/trans*	
(a)	81 : 19	54 : 46	20 : 80
(b)	13 : 87	72 : 28	85 : 15
		no CuI	added CuI

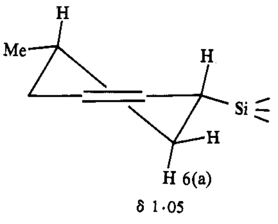
Scheme 3

In the absence of CuI, the stereochemical outcome is of no obvious attraction, but added CuI improves the situation to the extent of apparent stereospecific inversion.

The configurations of the isomeric *cis*- and *trans*-5-methylcyclohex-2-enyl(phenyldimethyl)silanes were established in the following way, the very likely predominant conformations (A) and (B) being used.



(A)
trans



(B)
cis

The 400-MHz ^1H n.m.r. spectrum of the silane product from the predominantly *cis* chloride [use of CuI; system (a), Scheme 3] showed $>$CHSi at δ 1·84 ($W_{h/2} \approx$ 18 Hz), and irradiation of this signal removed a small coupling (*c.* 3 Hz) from the signal at δ 1·45, thus locating H 6(a), now a doublet of doublets ($2 \times J \approx$ 11 Hz), appropriate for axial–axial and geminal interactions. Thus the magnitude of $J_{H6(a)-H1}$ confirms H 6(a) and the silyl group as *trans*. The predominant silane from system

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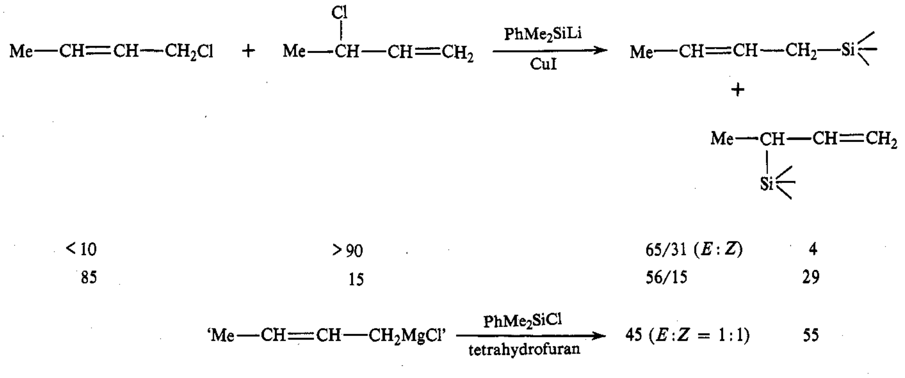
[12] Smith, J. G., Drozda, S. E., Petraglia, S. P., Quinn, N. R., Rice, E. M., Taylor, B. S. and Viswanathan, M., *J. Org. Chem.*, 1984, **49**, 4112.

(b) showed >CHSi at δ 1·85 ($W_{h/2} \approx 22$ Hz), and H 6(a) (δ 1·05) was a broadened 'quartet', indicative of three roughly equal (*c.* 11 Hz) couplings, as expected for H 6(a) in the *cis* conformation shown. The broader nature of the >CHSi signal (now predominantly quasi-axial) is consistent with this analysis. The ^{13}C n.m.r. shifts confirm these conclusions. In particular, the higher field shift of C 5 (24·91 ppm) for the major isomer in system (a) compared with that for the major isomer in system (b) (29·44 ppm) reflects the γ-shielding effect of the *quasi-axial* silyl group in the *trans* isomer. General trends within these series of silanes, germanes and stannanes are observed. The ^{29}Si n.m.r. shifts for various compounds have been obtained and listed in Table 1, but we are reluctant to use them diagnostically, as the range of shifts is small.

The observation of apparent stereospecific inversion accompanying substitution of the silyl group for chloride in this symmetrical cyclohexenyl system could be the result of an uncomplicated S_N2 reaction, or S_N2' replacement proceeding stereospecifically *anti*. Previous observations on allylic alkylation, with copper(I)-based reagents, lend credibility to the latter suggestion.[13] Distinction between them was achieved as follows. Regioselectively ^{2}H-labelled, predominantly *trans*, 5-methylcyclohex-2-enyl chloride (C) is accessible by *N*-chlorosuccinimide/dimethyl sulfide chlorination of the ^{2}H-labelled *cis*-5-methylcyclohex-2-enol, resulting from reduction ($LiAlD_4$) of the enone as outlined previously.[6] Reaction of this chloride with $PhMe_2SiLi/CuI$ proceeded with stereospecific formation of silane (*cis/trans* 85 : 15) but with extensive allylic relocation of ^{2}H, so that now allyl ^{2}H/vinyl ^{2}H = 30/70 (δ 1·83 and 5·69), based on direct ^{2}H n.m.r. observations. This result is consistent with substantial, even exclusive *anti*–S_N2' displacement of chloride by the silyl cuprate reagent. (Any isomerization of the chloride prior to reaction would reduce the apparent stereospecificity.) This result is analogous to the observations of Goering on copper(I)-mediated allylic alkylation,[13] and by Fleming on *syn* and *anti* introduction of silyl groups with urethanes and benzoates respectively.[8]

Our examination of the reactions of α-methylallyl and but-2-enyl chlorides with $PhMe_2SiLi/CuI$ is in line with Smith's generalization[12] as summarized in Scheme 4. In contrast, silylation of the butenyl Grignard reagent affords marginally more of the α-methylallylsilane.[14]



Scheme 4

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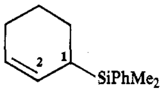
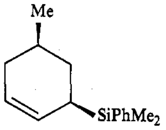
[13] Goering, H. L., and Singleton, V. D., *J. Org. Chem.*, 1983, **48**, 1531, and references therein.

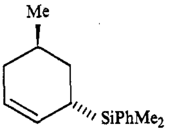
[14] Hosomi, A., Iguchi, H., and Sakurai, H., *Chem. Lett.*, 1982, 223.



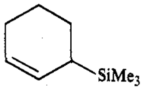
(1)



(2)



(3)



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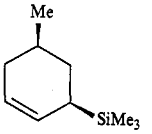
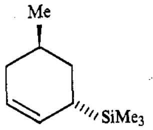
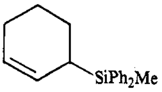


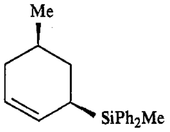
(5)



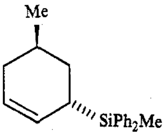
(6)



(7)



(8)



(9)

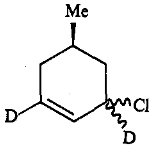
Table 1. ^{13}C and ^{29}Si n.m.r. chemical shifts of some cyclohex-2-enylsilanes

Compound	^{13}C chemical shifts (see Experimental) C 1	C 2	C 3	C 4	C 5	C 6	Other^A	^{29}Si shift^B
(1)	25·61	127·47	125·88	25·02	22·54	23·84	−4·68, −4·81	−2·54
(2)	26·46	128·88	126·03	32·65	29·55	33·99	22·42, −4·95, −5·29	−2·48
(3)	26·22	127·74	125·25	31·19	24·90	32·99	21·18, −4·07, −4·11	−2·52
(4)	26·12	127·88	125·33	25·05	22·61	23·73	−3·22	+2·66
(5)	27·00	127·49	125·49	34·06	29·43	32·65	22·51, −3·56	+2·59
(6)	26·41	127·49	123·64	33·09	25·48	31·24	21·29, −2·54	+2·68
(7)	24·27	127·27	126·42	24·97	22·61	23·95	−6·12	−7·80
(8)	25·24	C	C	33·87	29·43	32·57	22·27, −6·63	−7·70
(9)	25·97	C	C	32·75	22·97	31·02	20·83, −5·44	−7·92

^{A} Methyl carbons. Aromatic carbon signals are not listed; typical shifts are 138·48, 133·85, 127·84 and 128·83 for compound (5).

^{B} Relative to internal Me$_4$Si.

^{C} Not distinguishable from resonances of inequivalent phenyl groups.



cis/trans
15 : 85

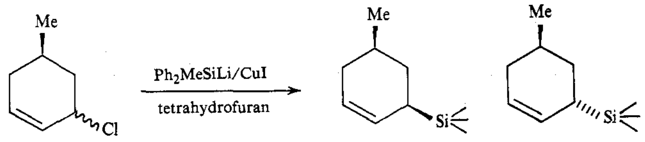
$$\frac{\text{allyl } ^2\text{H } (\delta\ 4\cdot60)}{\text{vinyl } ^2\text{H } (\delta\ 5\cdot87)} = \frac{80}{20}$$

(C)

In related studies, Smith[12] has observed that the formation of 3-(trimethylsilyl)alkenes from (E)-1-haloalk-2-enes from Me_3SiLi/CuI is favoured by the use of allyl chlorides, low temperatures and an ether/hexamethylphosphoric triamide solvent.

[The α-methylallylsilane in Scheme 4 shows dual Si–CH_3 signals at $-5\cdot49$ and $-5\cdot05$ ppm, with the (E)-but-2-enylsilane at $-3\cdot42$ ppm and the (Z)-isomer at $-3\cdot32$ ppm. ^{29}Si shifts are $-2\cdot13$, $-4\cdot57$ and $-3\cdot76$ ppm respectively.]

Less extensive studies with the methyldiphenylsilyllithium/copper iodide reagent were conducted. The parent silane, cyclohex-2-enyl(methyldiphenyl)silane, was separated from other products by column chromatography (neutral alumina, pentane) and Kugelrohr distillation, and characterized by its ^{13}C n.m.r. spectrum (Si–CH_3 at $-6\cdot1$ ppm; inequivalent phenyl groups) and ^{29}Si shift ($-7\cdot80$ ppm). Stereochemical studies utilized both heavily 'lopsided' ratios of the *cis*- and *trans*-5-methylcyclohex-2-enyl chlorides, and configuration assignments of products were based largely on ^{13}C shifts, and analogies with other cyclohex-2-enylmetallics. These results are summarized in Scheme 5.



cis/trans		
15:85	83	17
75:25	23	77

Scheme 5

Again, it is clear that stereospecific formation of the allylsilane has occurred, and if the ^2H labelling results alluded to above apply for these $Ph_2MeSiLi$ reactions, as seems very likely, *anti*-S_N2' displacement has been operative.

Grignard formation of cyclohex-2-enylsilanes.—Refluxing a tetrahydrofuran solution of the cyclohex-2-enyl chloride, magnesium turnings and the appropriate triorganosilyl chloride (and also trimethylbromogermane) led to acceptable yields (40–50%) of the corresponding allylic silane or germane. In this way, cyclohex-2-enyltrimethyl- and dimethylphenyl-silanes were acquired, whereas use of 5-methylcyclohex-2-enyl chloride led to predominantly *cis* trimethylsilane (88% *cis*), dimethylphenylsilane (81% *cis*) or germane (65% *cis*). The configurational assignments for the trimethylsilyl derivatives were based on trends in ^{13}C and ^1H n.m.r. spectra, and on comparisons with the trimethylgermanes, which were additionally characterized by hydrogenation (rhodium/carbon) to the *cis*- and *trans*-3-methylcyclohexyltrimethylgermanes, whose ^{13}C n.m.r. shifts were unambiguously diagnostic.[15,16] A general observation in the 5-methylcyclohexenyl system is that the vinylic H 2,3 resonance is quite narrow in *cis* isomers, but separated in the *trans* isomer.

With methods available for synthesis of a variety of cyclohex-2-enyl silanes, germanes and stannanes, their substitution reactions have been investigated and will be reported in full subsequently.

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[15] Kitching, W., Harvey, K., and Olszowy, H. A., *J. Org. Chem.*, 1982, **47**, 1893, and references therein; Wickham, G., Ph.D. Thesis, University of Queensland, 1983.

[16] Okuda, Y., Sato, M., Oshima, K., and Nozaki, H., *Tetrahedron Lett.*, 1983, **24**, 2015.

Experimental

Reagents

Cyclohex-2-enyl chloride and *cis*- and *trans*-5-methylcyclohex-2-enyl chlorides were obtained as described previously.[6] Dimethyl(phenyl)silyl chloride and methyldiphenylsilyl chloride were commercial samples, and were carefully distilled before use.

Silylcuprate Reactions

The following description of the synthesis of predominantly *trans* dimethyl(5-methylcyclohex-2-enyl)phenylsilane is illustrative.

Lithium (0·8 g, 0·11 mol, fourfold excess) was chipped into deoxygenated anhydrous tetrahydrofuran (15 cm^3) under an argon atmosphere. Chlorodimethylphenylsilane (4·45 g, 26 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to the stirred lithium, and the solution stirred for *c.* 4 h at 20°C, during which time the white reaction mixture changed to a deep rust red. The mixture was filtered (gas pressure) through a frit from the first reaction bulb into a second attached bulb, and cooled to −78°. A suspension of cuprous iodide (2·7 g, 14 mmol) in tetrahydrofuran (25 cm^3) was added, and the solution stirred for *c.* 2 h. The *cis*/*trans* mixture of predominantly *cis* 5-methylcyclohex-2-enyl chloride (2·44 g, 9 mmol) in tetrahydrofuran (12 cm^3) was added dropwise to the stirred reaction mixture maintained at −78°. After 30 min at this temperature, during which time the colour changed from dark brown to green-brown, the reaction mixture warmed to room temperature, and after *c.* 3 h was quenched with ammonium chloride solution, and vigorously stirred. The organic phase (yellowish green) was separated from the blue aqueous phase, which was further extracted with ether (2×100 cm^3). The combined ethereal layers were dried ($MgSO_4$) and the solvent removed (Büchi evaporator). The crude mixture was distilled (Kugelrohr: oven 130–200°; 2 cm) to separate the oil from solid residue. Yields in the range 70–75% were obtained, and pure samples for spectroscopic measurements were obtained by preparative gas chromatography. Ratios of isomeric silanes were based on capillary gas chromatography and ^{13}C n.m.r. measurements.

Grignard Reactions

The appropriate cyclohex-2-enyl chloride (38·5 mmol) in anhydrous tetrahydrofuran (19 cm^3) was added dropwise to a mixture of chlorotrimethylsilane (4·18 g, 4·88 ml, 38·5 mmol), magnesium turnings (0·98 g, 40·4 mmol) and tetrahydrofuran (10 cm^3) under a nitrogen atmosphere. After addition was complete, the mixture was refluxed for *c.* 7 h, during which time a copious white precipitate formed. The mixture was cooled, saturated ammonium chloride solution added and extracted with ether. The combined ether extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to provide the crude silane, which was purified by fractional distillation or Kugelrohr distillation.

Specific Compounds

Cyclohex-2-enyl (methyldiphenyl) silane was obtained as a clear oil, b.p. 83–44°/3 mm. Mass spectrum: *m/z* 216 (M, 1·5%); 135 ($C_8H_{11}Si$, 100); 43 (C_3H_4, 22). ^1H n.m.r. δ 0·27, 0·26, both s, 6H; 1·35–2·1, m, 7H; 5·63, tight 'AB' system, 2H; 7·3–7·6, m, 5H. These data agree with those reported.[16]

Predominantly *cis* dimethyl(5-methylcyclohex-2-enyl)phenylsilane was obtained by the Grignard procedure and predominantly *trans* by the silylcuprate route, as discussed in the text. Mass spectrum (both isomers): *m/z* 230 (M, 2%); 135 [$C_6H_5(CH_3)_2Si$, 100]; 43 (C_3H_7, 15%). B.p. 130–200°/2 mm (Kugelrohr). Pure samples were obtained by preparative gas chromatography. ^1H n.m.r. for the *trans* isomer: δ 0·29; 0·30, s, $SiCH_3$; 0·89, d, J 8 Hz, CH_3CH; 1·42, ddd, J 11, 3 Hz, H 6(a); 1·5–1·7, m, 3H; 1·82, br s, $W_{h/2} \approx 18$ Hz, CHSi; 1·95–2·08, m, 1H; 5·7, broader 'AB' system, vinyl, 2H; 7·3–7·7, m, 5H. ^1H n.m.r. for the *cis* isomer: δ 0·26 0·27, s, $SiCH_3$; 0·92, d, J 8 Hz, CH_3CH; 1·05, br quartet, $J \approx 11$ Hz, H 6(a), 1·5–2·1, 5H, m, ring protons, with CHSi at 1·83; 5·62, narrower 'AB' system, vinyl, 2H; 7·3–7·6, m, 5H.

Cyclohex-2-enyltrimethylsilane was obtained (52% yield) by the Grignard route, b.p. 72°/23 mm, and had properties in agreement with those reported.[17] ^{1}H n.m.r.: δ 0·06, s, $(CH_3)_3Si$; 1·2–2·2, m, 7H; 5·62, br s, 2H, vinyl.

Trimethyl(5-methylcyclohex-2-enyl)silane was obtained as an 88:12 *cis/trans* mixture (44% yield) by the Grignard route, b.p. 86°/35 mm (Found: C, 71·2; H, 11·9. $C_{10}H_{20}Si$ requires C, 71·3; H, 11·5%). Mass spectrum: *m/z* 168 (M, 9%); 94 (20%); 73 [$(CH_3)_3Si$, 100%]. ^{1}H n.m.r.: δ −0·01, s, $(CH_3)_3Si$; 0·97, d, *J* 6 Hz, CCH_3; 1·3–2·3, 6H; 5·62, br s, vinyl, 2H.

The cyclohex-2-enyl(methyldiphenyl)silanes were characterized predominantly by their ^{13}C and ^{29}Si n.m.r. spectra, which are located in Table 1. In the mass spectrum, weak M molecular ions were observed, with the base peak at *m/z* 197 [$(C_6H_5)_2CH_3Si$].

N.M.R. Spectra

300-MHz ^{1}H n.m.r. spectra were obtained on the Bruker CXP-300 spectrometer of the Brisbane N.M.R. Centre. 100-MHz spectra were obtained with either a JEOL JNM-MH-100 or a JEOL JNM-FX-100 spectrometer. 25-MHz ^{13}C spectra were obtained with the latter instrument, whereas 75·446-MHz ^{13}C spectra were measured on the Bruker CXP-300 spectrometer, all for $CDCl_3$ solutions. Chemical shifts are referenced to the central peak of the $CDCl_3$ triplet at 77·00 ppm.

^{2}H n.m.r. spectra, under broad-band ^{1}H-decoupled conditions, were obtained at 15·29 MHz (JEOL JNM-FX-100) or 46·05 MHz (Bruker CXP-300). Chloroform was used as solvent, with $CDCl_3$ added as internal standard (7·24 ppm).

Broad-band ^{1}H-decoupled ^{29}Si n.m.r. spectra were recorded at 19·79 MHz on the JEOL JNM-FX-100 spectrometer, the INEPT polarization transfer pulse sequence being used to obtain signal enhancement. Chemical shifts were referenced to internal Me_4Si (0 ppm).

Combined Gas Chromatography–Mass Spectrometry

This was performed on a Hewlett–Packard 5992B instrument, fitted with an OV101 capillary column (operator Mr V. Alberts). Preparative gas chromatography was performed on a Shimadzu preparative gas chromatograph.

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