

References

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Stereochemical Induction in the Generation of 1-Chloro-1-phenyl-2-neopentylsilene

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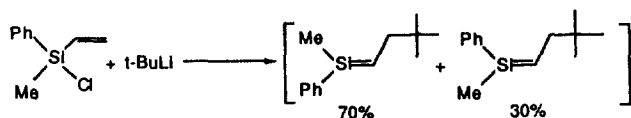
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The reaction of dichlorophenylvinylsilane with *tert*-butyllithium in hydrocarbon solvents at room temperature or below generated the *Z* and *E*-isomers of 1-chloro-1-phenyl-2-neopentylsilene. The intermediates were trapped by cyclopentadiene, anthracene and methoxytrimethylsilane to give a consistent 90/10 ratio for the *Z*-silene to *E*-silene adduct. This result was interpreted as an evidence for stereochemical induction in the silene generation reaction.

Introduction

The reaction of *tert*-butyllithium with chlorodimethylvinylsilane in hydrocarbon solvent at low temperatures gave rise to 1,1-dimethyl-2-neopentylsilene which dimerized to the typical 1,3-disilacyclobutane¹ and trapped to [4+2] adducts in the presence of dienes.² In extension of this work, the *E*- and *Z*-isomers of 1-methyl-1-phenyl-2-neopentylsilene were generated from the reaction of *tert*-butyllithium with chloromethylphenylvinylsilane.^{3,4} A consistent 70 to 30 ratio for the *E*- to *Z*-silene adducts trapped by dienes was interpreted as an evidence for stereochemical induction in the silene generation reaction.⁴

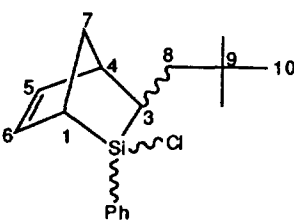


In this paper we report the generation of the *E*- and *Z*-isomers of 1-chloro-1-phenyl-2-neopentylsilene and the sub-

stituent effects on the stereochemical induction favoring the formation of the *Z*-isomer.

Results and Discussion

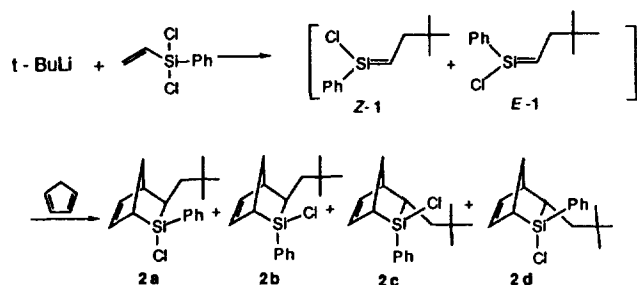
When *Z*- and *E*-1-chloro-1-phenyl-2-neopentylsilene, **1**, were generated by the reaction of *tert*-butyllithium with dichlorophenylvinylsilane in hexane at low temperature in the presence of cyclopentadiene, GLC analysis of the reaction mixture indicated four volatile components comprising 74% of the products. The fragmentation patterns of GC/MS spectra for the four components were identical to each other, which strongly suggested that the four components were considered to be the anticipated four isomeric 2-silanorbornenes, **2a-d**. The isotopic molecular ion [M⁺] and other major peaks of the isomers in mass spectra were observed at *m/e*, 292 (20%), 290 (58%), 169 (33%) and 167 (100%) respectively. These isomers were purified by a preparative gas chromatography and subsequent spectral analyses in comparison with the spectral data of the similar structures³ led to the assignments

Table 1. ^{13}C -NMR Data for the 2-Silanorbornene, **2a-d**


Carbons	2a	2b	2c	2d
1	34.06	32.06	34.15	34.66
3	20.60	20.66	25.09	24.14
4	50.04	49.54	47.22	47.31
7	42.14	42.25	42.55	43.44
8	44.27	44.48	44.48	43.57
9	31.55	31.55	31.55	31.42
10	29.35	29.64	29.35	29.76
aryl& vinyl	a	b	c	d

a, b and c: 127.73, 127.82, 128.03, 128.33, 130.34, 132.57, 133.78, 134.00, 134.24, 134.72, 135.45, 135.89, 136.04, 136.70, 137.35, 137.47; d: 128.13, 130.35, 133.54, 133.97, 134.23.

of the stereochemistry for the isomers as: **2a**, 2-chloro-2-*exo*-phenyl-3-*exo*-neopentyl-, 9%; **2b**, 2-chloro-2-*endo*-phenyl-3-*exo*-neopentyl-, 45%; **2c**, 2-chloro-2-*endo*-phenyl-3-*endo*-neopentyl-, 4%; and **2d**, 2-chloro-2-*exo*-phenyl-3-*endo*-neopentyl-2-silabicyclo[2.2.1]hept-5-ene, 42%.



According to both ^1H and ^{13}C -NMR data, protons and carbons of *tert*-butyl group are more shielded when it is *cis* to phenyl group, as in **2a** and **c**, than when it is *trans*, as in **2b** and **d**. The structure assignments were primarily based on ^{13}C -NMR chemical shift for **2a-c** which are given in Table 1. 2-Silanorbornene-carbon 7 is the most shielded when two bulky substituents are *exo*, as in the *exo*-neopentyl-*exo*-phenyl-, **2a**, and less shielded when the two bulky substituents are *endo*, as in *endo*-phenyl-*endo*-neopentyl-, **2c**. The carbon 7 in the *exo*-neopentyl-*endo*-phenyl-, **2b**, is more shielded than that in the *endo*-neopentyl-*exo*-phenyl-2-silanorbornene, **2d**.

In the reaction mixture the ratio of **2b** and **2d** in which the neopentyl and phenyl silene substituents have an *E*-stereochemistry, to **2a** and **2c** in which these bulky substituents have a *Z*-relationship, was 89 to 13.

Trapping reaction of **1** with anthracene was carried out at room temperature by using benzene as the solvent due to the low solubility of anthracene in hexane. Analysis of the product mixture indicated that the [4+2] cycloadducts, **Z-3a** and **E-3b**, were produced in 68% and 7% yields, respec-

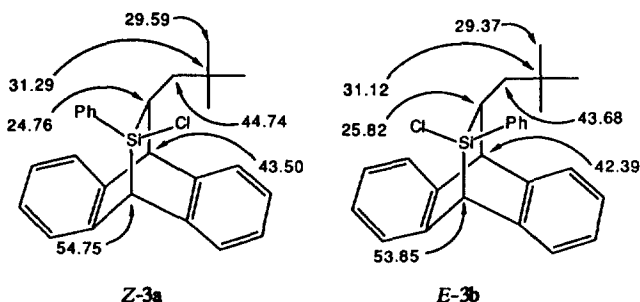
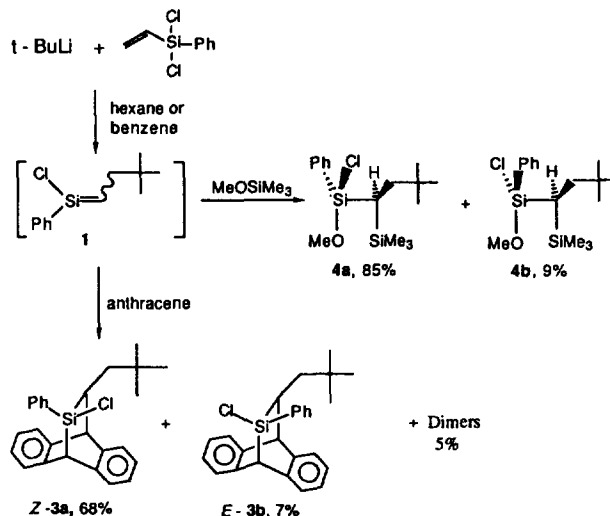


Figure 1. Carbon-13 chemical shifts for the isomers of 2-chloro-2-phenyl-3-neopentyl[5,6:7,8]dibenzo-2-silabicyclo[2.2.2]octane, **Z-3a** and **E-3b**. The aryl carbons which appeared in the region 124.73-143.05 ppm are omitted for clarity.

vely, along with a 5% yield of dimers.⁵



The structural assignments were again based primarily on the carbon-13 NMR chemical shifts for **Z-3a** and **E-3b** which are given in Figure 1.

The carbon-13 NMR chemical shifts for the isomers are consistent with the bulk shielding, *tert*-butyl and methylene-carbon of neopentyl group which have *E*-relation with respect to chlorine in **E-3b** are more shielded than **Z-3a**.

The 91/9 ratio of *Z*- to *E*-silene-anthracene cycloadducts is similar to the 87/13 of *Z*- to *E*-adducts obtained with the cyclopentadiene.

Attempt to trap the silene, **1**, was carried out in the presence of methoxytrimethylsilane, which has been known to be an efficient regiospecific⁶ and stereospecific⁷ silene trap. When silene, **1**, was generated in the presence of methoxytrimethylsilane, diastereomeric isomers, 1-chloro-4,4-dimethyl-1-methoxy-1-phenyl-2-trimethylsilyl-1-silapentanes, **4a** and **4b**, were obtained in 85% and 9% yield, respectively. Again, as with the cyclopentadiene and anthracene, the ratio of *Z*- to *E*-adducts, [(*R,R*), (*S,S*)-**4a** to (*R,S*), (*S,R*)-**4b**], was 90/10.

The results observed in trapping reactions indicated that the silene, **1**, can be efficiently trapped its adducts by trapping agents. Most striking was the consistent 90/10 ratio of *Z*- to *E*-cycloadducts which were obtained with dienes, and (*R,R*) (*S,S*)-**4a** to (*R,S*), (*S,R*)-**4b** which was obtained with

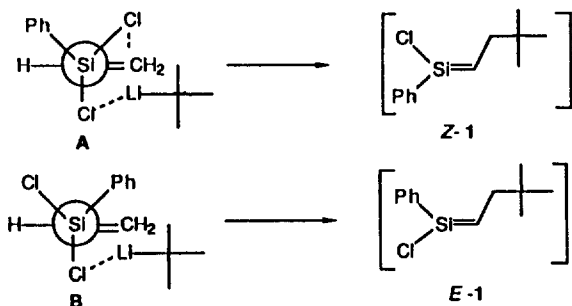


Figure 2. Hypothetical mechanism for stereochemical induction in the formation of silene.

methoxytrimethylsilane. It seems much more likely that the 90/10 ratio observed in the trapped products represents the ratio of *Z*-to-*E*-silence which was formed under our reaction conditions. Jones and Lee have observed the formation of the 1-methyl-1-phenyl-2-neopentylsilene intermediate which was trapped stereospecifically with methoxytrimethylsilane indicating that the silene is the configurationally stable up to 300°C.⁸

Therefore, it appears that the stereochemical induction in the reaction of *tert*-butyllithium with chloromethylphenylvinylsilane³⁴ or dichlorophenylvinylsilane occurs favoring the formation of *trans* form between neopentyl and phenyl group. The 90/10 ratio of both geometric silene isomers observed from the reaction of dichlorophenylvinylsilane is larger than the 70/30 ratio³⁴ from using chloromethylphenylvinylsilane. This different ratio could be rationalized in terms of the mechanistic point of view for the silene formation. As shown in Figure 2, the initial interaction between the lithium reagent and vinylsilane almost certainly involves some sort of bridge association between lithium reagent and dichlorine of the dichlorophenylvinylsilane, which is expected to be more favorable to form the complex than the association between monochlorine and lithium reagent in the reaction of chloromethylphenylvinylsilane.^{4,9} Based on the reported similar system, the conformation, **A**, which would tend to minimize the steric interaction between the phenyl group on silicon and the very bulky butyllithium aggregate, could be drawn as shown in Figure 2. Such a complex could lead directly to the *Z*-silene **1** as a major by lithium chloride elimination reaction. *E*-Silene **1**, was also generated from the conformation **B**, which is expected to have more steric interaction between the bulky groups than that of the conformation **A**.

Experimental

The solvents, *n*-hexane, benzene, and tetrahydrofuran were dried by distillation from lithium aluminium hydride and sodium ketyl of benzophenone, respectively, prior to use. Dichlorophenylvinylsilane was obtained from Petrarch Systems. All reaction were carried out in flame-dried glassware under an atmosphere of dry nitrogen. All air-sensitive liquids, and the dried solvents, were transferred by a standard syringe or double tipped needle techniques. The samples for characterization were purified by a preparative GLC using a Varian aerograph series 1400 gas chromatograph with thermal conductivity detector and a 4 m by 1/8 inch stainless steel column packed with 15% SE-30 or SE-54 with a Varian 3300

gas chromatograph, flame ionization detector, and a Varian 4290 integrator. Product yields were determined by GLC using *n*-docosane as the internal standard. Proton, carbon and 2D (proton-proton correlation) NMR spectra were obtained on a Bruker AM 200-SY or a Varian Gem 300-spectrometer in chloroform-*d* solvent and chemical shifts are reported in parts per million down-field from the internal standard tetramethylsilane. Mass spectra were obtained using a Hewlett Packard 5980 GC/MS. Elemental analyses were performed by the Chemical Analysis Laboratory of Korea Institute of Science and Technology. In this experimental section compounds are reported in the order that they eluted under these chromatographic conditions.

Trapping Reaction with Cyclopentadiene. To a solution of 4 g (19.7 mmole) of dichlorophenylvinylsilane (Petrarch), 13 g (200 mmol) of cyclopentadiene, and 100 ml of dry hexane cooled to -78°C was slowly added 11.6 ml (19.7 mmol) of a solution of 1.7 M *tert*-butyllithium. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. The white precipitate which had formed filtered off. After the reaction mixture was concentrated by the evaporation of solvent, viscous yellow oil was obtained which GLC analysis indicated to be 74% silene adducts. GLC analysis of the mixture gave in order of elution 2-chloro-2-*exo*-phenyl-3-*exo*-neopentyl-, **2a**, 2-chloro-2-*endo*-phenyl-3-*exo*-neopentyl-, **2b**, 2-chloro-2-*endo*-phenyl-3-*endo*-neopentyl-, **2c**, 2-chloro-2-*exo*-phenyl-2-*endo*-neopentyl-2-silanorbornene, **2d**, in 9, 45, 4 and 42% yields, respectively. The samples for the characterization were purified by a preparative GLC.

2a: ¹H-NMR δ 0.79 (s, 9H, C(CH₃)₃), 1.02-1.50 (m, 4H, overlapping protons with those of **2b** and **2c**) (norbornene-CH₂ and neopentyl-CH₂), 2.00 (m, 1H, SiCH), 2.45-2.51 (br. s, 1H) and 2.93-2.98 (br. s, 1H) (CH), 613-616 (br. d, 2H, vinyl-H), 7.35-7.72 (m, 5H, aryl-H)

2b: ¹H-NMR δ 0.89 (s, 9H, C(CH₃)₃), 1.07-1.19 (br., 1H) (one proton of norbornene-CH₂), 1.94 (dd, $J=7$, 14 Hz, 1H) (neopentyl-CH₂), 1.99-2.08 (m, 2H, SiCH and other proton of norbornene-CH₂), 2.38 (br. t, $J=3$ Hz, 1H, CH), 2.79 (br. s, 1H, CH), 5.83 (dd, $J=3$, 6 Hz, 1H) and 6.10 (dd, $J=3$, 6 Hz, 1H) (vinyl-H), 7.35-7.72 (m, 5H, aryl-H)

2c: ¹H-NMR δ 0.78 (s, 9H, C(CH₃)₃), 1.23-1.41 (m, 2H, neopentyl-CH₂), 1.93 (m, 1H, overlapping proton with those of **2a**), 2.45-2.51 (br. s, 1H) and 2.99-3.03 (br. s, 1H) (CH), 6.08 (dd, $J=4$, 6 Hz, 1H) and 6.31 (dd, $J=3$, 6 Hz, 1H) (vinyl-H), 7.35-7.72 (m, 5H, aryl-H)

2d: ¹H-NMR δ 0.90 (s, 9H, C(CH₃)₃), 1.24 (dd, $J=4$, 13 Hz, 1H) and 1.38 (dd, $J=4$, 7 Hz, 1H) (norbornene-CH₂), 1.43 (dd, $J=7$, 13 Hz, 1H) and 1.69 (br. d, $J=11$ Hz, 1H) (neopentyl-CH₂), 1.99 (dt, $J=4$, 11 Hz, 1H, CH), 2.49 and 3.00 (br. s, 1H) (CH), 6.14 (br. s, 2H, vinyl-H), 7.40-7.79 (m, 5H, aryl-H)

The mass spectra for all four of the 2-silanorbornene isomers, **2a-e**, were very similar; *m/e* (relative intensity) 290 (20) and 290 (58) (M⁺), 233 (17), 225 (16), 224 (11), 206 (12), 169 (33) and 167 (100) (PhClSiVi)⁺, 168 (13), 141 (23), 63 (13); Anal. Calcd. for SiC₁₇H₂₃Cl: C, 70.19; H, 7.97. Found for a mixture of the 2-silanorbornene isomers, **2a-d**; C, 70.48; H, 7.98.

Trapping Reaction with Anthracene. To a mixture of 4 g (20 mmol) of dichlorophenylvinylsilane and 8 g (46 mmol) of anthracene in 700 ml of dry benzene at room tem-

perature was slowly added 12 ml (20 mmol) of a solution of 1.7 M *tert*-butyllithium in pentane. The mixture was allowed to room temperature and stirred overnight and benzene solvent was evaporated off. Then the reaction mixture was dissolved in hexane, lithium chloride and anthracene were filtered off. Procedure as described above was followed by GLC analysis which gave 75% yield of *Z*-, **3a**, and *E*-2-chloro-2-phenyl-3-neopentyl[5,6:7,8]dibenzo-2-silabicyclo[2.2.2]octanes, **3b**. The ratio 91/9 of *Z*-**3a** to *E*-**3b** was determined by ¹H-NMR analysis for the sample which was purified by a preparative GLC. *Cis*-configurational adduct, **3a** was precipitated out from the reaction mixture in hexane at low temperature (*ca.* 0°C). Recrystallization of this crude precipitate in hexane afforded the pure *cis*-adducts (mp. 151-2°C, colorless crystal)

For *Z*-**3a**; ¹H-NMR δ 0.81 (s, 9H, (C(CH₃)₃), 1.28-1.45 (m, 3H, CH and CH₂), 4.13 (s, 1H), 4.32 (d, *J*=2.1 Hz, 1H) (benzyl-H), 6.97-7.39 (m, 13H, aryl-H)

For *E*-**3b**; ¹H-NMR δ 0.74 (s, 9H, (C(CH₃)₃), 1.14-1.41 (m, 3H, CH and CH₂), 4.13 (s, 1H), and 4.27 (d, *J*=2.5 Hz, 1H) (benzyl-H), 7.11-7.59 (m, 13H, aryl-H); MS: *m/e* (relative intensity) 404 (3) and 402 (10) (M⁺), 179 (14), 178 (96) (anthracene⁺), 169 (34) and 167 (100) (PhClSiVi)⁺, 143 (10), 141 (27), 63 (14); Anal. Calcd. for SiC₂₆H₂₇Cl: C, 77.48; H, 6.75. Found for a mixture of *E*-**3a** and *Z*-**3b**; C, 77.40 H, 6.78

Trapping Reaction with Methoxytrimethylsilane.

To a solution of 2.4 g (11.8 mmol) of dichlorophenylvinylsilane and 4.2 g (40 mmol) of methoxytrimethylsilane in 80 ml of dry *n*-hexane cooled to -78°C was slowly added 7 ml (11.8 mmol) of 1.7 M *tert*-butyllithium in pentane. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. Lithium chloride which had formed removed by using centrifuge. After the reaction mixture was concentrated by the evaporation of solvent, colorless liquid was obtained which analysis indicated to be 94% silene adducts. The samples for the characterization were purified by a preparative GLC and the ratio 90/10 of **4a/4b** was determined by ¹H-NMR.

For **4a(4b)**; ¹H-NMR δ 0.10 (0.06) (s, 9H, Si(CH₃)₃), 0.38 (0.43) (dd, *J*=2.8, 15.7 Hz (2.5, 6.1 Hz), (1H, SiCH), 0.70 (0.75) (s, 9H, C(CH₃)₃), 1.44 (1.41) (dd, *J*=2.8, 14.4 Hz (2.5, 14.3 Hz), 1H) and 1.77 (1.70) (dd, *J*=5.7, 14.4 Hz (6.1, 14.3 Hz), 1H) (CH₂), 3.50 (3.46) (s, 3H, OCH₃), 7.38-7.70 (m, 5H, aryl-H); ¹³C-NMR δ 0.14 (-0.02) (Si(CH₃)₃), 10.57 (11.48) (CH), 29.31 (29.31) (C(CH₃)₃), 31.56 (31.67) (C(CH₃)₃), 36.49 (31.67) (CH₂), 51.10 (50.82) (OCH₃), 127.49, 127.90, 128.18, 130.37, 133.87, 134.25, 134.57 (aryl-carbons); MS: *m/e* (relative intensity) 313 (20) and 315 (7) (M-15)⁺, 171 (10), 164 (14), 163 (100), 141 (15), 137 (11), 121 (17), 107 (11), 91 (24), 73 (91), 63 (13), 59 (56), 57 (45); Anal. Calcd. for Si₂C₁₆H₂₉OCl; C, 58.41; H, 8.88. Found for a mixture of **4a** and **4b**: C, 58.63; H, 8.90.

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Stainless Steel Surface Oxidized in Strong Oxidizing Solution

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Stainless steel 304 2B and BA are oxidized in 2.5 M CrO₃/5.0 M H₂SO₄ solution, and elemental composition and oxidized state of the surface region is analyzed as a function of the surface depth using X-ray photoelectron spectroscopy. It is found that Fe and Cr are preferentially oxidized and diffuse outward following the oxidation. Element Ni, the third major component of the steel is not oxidized and remains deep under the surface. It is also found that the oxidized Fe dissolves considerably into the solution thereby enriching the gas-oxide interface with Cr.

Introduction

Stainless steels are multi-component alloys, and their sur-

face layers have a different elemental composition as a consequence of surface treatment given in the course of rolling the steel. The surface layer so formed protects the bulk from