Silene Intermediates. The Reaction of Chlorodiphenylvinylsilane with *tert*-Butyllithium

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The reaction of *t*-butyllithium with chlorodiphenylvinylsilane at low temperatures in hexane gave a 52% yield of the two isomeric 1,1,3,4-tetraphenyl-2,4-dineopenty-1,3-disilacyclobutanes mixture, formed by a head-to-tail dimerization of 1,1-diphenyl-2-neopentylsilene intermediate. In the presence of the trapping agents such as trimethylmethoxysilane and anthracene, the expected trapped adducts, 1-methoxy-1,1-diphenyl-2-trimethylsilyl-4,4-dimethyl-1-silapentane and 2,2-diphenyl-3-neopentyl-(5,6 : 7,8)-dibenzo-2-silabicyclo-(2.2.2)-octane, were obtained in 74% and 46% yields, respectively. These products were separated and their stereochemistry were assigned on the basis of ^{1}H- and ^{13}C-NMR data.

Introduction

The chemistry of species containing a silicon-carbon double bond, silenes, is an area of much current activity.[1] Of special interest is the chemistry of α-metallosilanes with functionality on silicon, which can eliminate M-X to provide low temperature silene sources.[2,3]
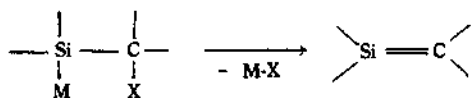
The reaction of *tert*-butyllithium with chlorodimethylvinylsilane in hydrocarbon solvents at low temperature gives rise to 1,1-dimethyl-2-neopentylsilene which dimerizes to give *cis*- and *trans*-1,3-disilacyclobutanes.[2] Extention of this reaction to methylphenylvinylchlorosilane produces the *E*-and *Z*-isomers of 1-methyl-1-phenyl-2-neopentylsilene, which dimerize to give the five isomeric 1,3-disilacyclobutanes.[4] Silenes produced from α-lithiochlorosilanes can be trapped by conjugated dienes.[2,3,5] With use of these techniques, we have carried out the reaction of *tert*-butyllithium with chlorodiphenylvinylsilane to examine the effects of the substituents on silicon. Here we wish to report the generation of new silene, 1,1-diphenyl-2-neopentylsilene, and its dimerization reaction including its reactions with trimethylmetoxysilane and anthracene.

Results and Discussion

The reaction of *tert*-butyllithium with chlorodiphenylvinylsilane in hexane at −78°C gave a 52% yield of an anticipated mixture of the *trans*- and *cis*-isomers of 1,1,3,3-tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutane, 4. Crystals of pure isomers were separated and purified by recrystalization from diethylether.


eq. 1
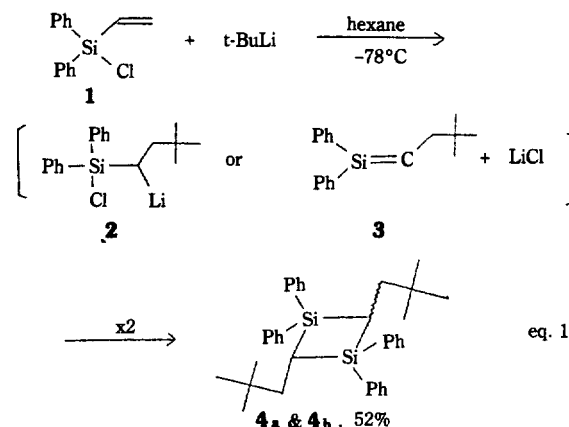
On the basis of the reasoning described below the isomers were assigned as: 1,1,3,3-tetraphenyl-*trans*-2,4-dineopentyl-

1,3-disilacyclobutane, 4a, 65%, and 1,1,3,3-tetraphenyl-*cis*-2,4-dineopentyl-1,3-disilacyclobutane, 4b, 35%. The ¹H-NMR spectral data of the isomers given in experimental section provided little help in the stereochemical characterization of the isomers, but the ¹³C-NMR spectra for the isomers shown in Table 1 provided the key to differentiate the structure of each isomer. Based on the symmetric point of view, one can predict the number of chemically distinct carbons for each of the isomers. The isomer 4a has four chemically equivalent phenyl groups, while the 4b has chemically non-equivalent phenyl groups, *i.e.*, two of them have a Z-relationship to neopentyl groups and the other two have a E-relationship to neopentyl group. By comparison with the spectral data given in Table 1, unambiguous assignments of *trans*-isomer, 4a, with 8 different chemical shifts and *cis*-isomer, 4b, with 12-different ones were made.

4a, 65%   4b, 35%
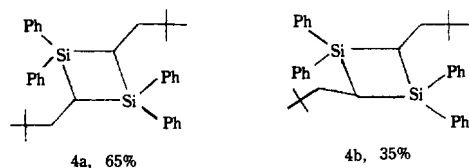
The carbon-13 NMR chemical shifts for the isomers are consistent with the bulk shielding and γ effects.[6,7] In 4b, the carbons of phenyl groups which have a Z-relation with respect to two neopentyl groups are more shielded than those without shielding by neopentyl group. A larger effects are observed for the *ipso-* and *ortho*-carbon of silicon-phenyl group giving 4.6 and 3.4 ppm up-field shift for both Z-interaction with neopentyl groups. In addition, the carbons of phenyl groups in 4a shielded by only one neopentyl group

**Table 1.** ¹³C-NMR Data for the Isomeric 1,1,3,3-Tetraphenyl-2,4-dineopentyl-1,3- disilacyclobutane[a]
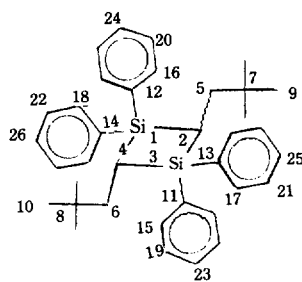
carbons	4a	4b
C (11,12,13,14)	135.2	139.1
		134.5
C (15,16,17,18)	135.8	137.0
		133.6
C (19,20,21,22)	127.8	127.9
		127.3
C (23,24,25,26)	129.3	129.2
		127.8
C (5,6)	39.4	39.9
C (7,8)	31.9	31.7
C (9,10)	29.3	29.3
C (2,4)	10.1	15.1

[a]In ppm downfield from TMS using external CDCl₃ lock as the reference. [b]Assigned by analogy with known 1,3-disilacyclobutane

have chemical shifts intermediate between those observed for shielding by two neopentyl groups and no neopentyl group. The chemical shift of ring carbons (methine carbon) in 4a occur further up-field, 5.0 ppm, when compared with that in 4b, consistent with their shielding by the bulky ring substituents. The fragmentation patterns of GC-MS spectra for the isomers were identical to each other. The weak [M⁺] and base peak, [(Ph)₂SiH⁺] were observed at *m/z* 532 (1%) and 183 (100%), respectively.

Attempt to trap the silene, 3, carried out in the presence of trimethylmethoxysilane, which has been shown to be an efficient, regiospecific silene trap,[8] gave the corresponding trapped adduct. When 1,1-diphenyl-2-neopentylsilene, 3, was generated by the reaction of *tert*-butyllithium with chlorodiphenylvinylsilane in hexane at low temperature in the presence of trimethylmethoxysilane, there was obtained a 74% yield of the 1-methoxy-1,1-diphenyl-2-trimethylsilyl-4,4-dimethyl-1-silapentane, 5, and no dimers were obtained. Trapping reaction of silene, 3, with anthracene was carried out at room temperature using benzene as the solvent due to the low solubility of anthracene in hexane. From this reaction the 2,2-diphenyl-3-neopentyl-(5,6: 7,8)-dibenzo-2-silabicyclo-(2.2.2)-octane, 6, and dimers, 4, were produced in 46% and 21% yield, respectively. The structural identifications for the

5, 74%

6, 46%   4, 21%
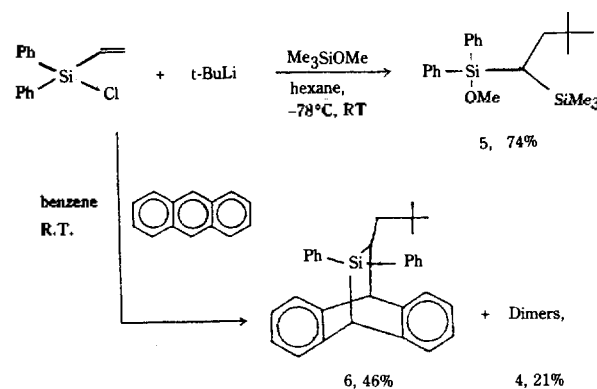
trapped products, 5 and 6, were made on the basis of the ¹H-and ¹³C-NMR spectra. The chemical shifts and assignments are summarized in experimental section.

The results, which were observed in trapping reactions, indicate that the silene, 3, was generated and subsequently trapped as its trapped adducts. It is of interest to note the yields of dimers in each trapping experiment. As shown in Table 2, only the trapped adduct was obtained with a high

Table 2. Comparison of the Yields of Dimers in the Trapping Reactons

	Trap	%-yield of adducts	%-yield of dimers	Remark (ref.)
R = R′ = Me	Anthracene	70		5 (a)
R = Me,R′ = Ph	Anthracene	77	5	4
R = R′ = Ph	Anthracene	46	21	this work
R = R′ = Ph	Me₃SiOMe	74	0	this work
R = R′ = Ph	none		52	this work

Silene Intermediates

Bull. Korean Chem. Soc., Vol. 8, No. 5, 1987 357

yield, 74%, in the trapping reaction by trimethylmethoxysilane, but interestingly much higher yield of the dimers, 21% was observed with 46% yield of [2 + 4]cycloadduct in the trapping reaction by anthracene. This results might be rationalized in terms of the change of polarity of silene intermediate. The dipolar character of the silene can be enhanced due to the inductive and resonance effects of two phenyl groups.

That is why the concerted [2 + 4]cycloaddition reaction[5(b)] with anthracene was surpressed and a silene dimerization, which has been reported to be a dipolar-stepwise mechanism,[4] was increased.[1(c)] In addition, 0% yield of dimers in the presence of trimethylmethoxysilane, polar compound, strongly supports the suggestion mentioned above. As far as steric factors are concerned, their influence is clear. The bulkier the substituents, the more shielded the system and, hence, the less reactive silene.

It is of considerable interest to note that the *trans/cis* ratio of dimers is varied with the change of substituents on silicon. The trans/cis ratio for the dimers, 4, 1.9 is much

Table 3. Distribution Ratio of Dimers

	% yield of dimers	distribution		Remark (ref.)
		trans	cis	
R = R′ = Me	46	47	53	2
R = Me, R = Ph	43	53	47[a]	4
R = R′ = Ph	52	65	35	this work

[a]Only the position of two neopentyl groups are considered.

higher than the ratio for 1,1-dimethyl-2-neopentylsilene dimers, 0.9, and the ratio for 1-methyl-1-phenyl-2-neopentylsilene dimers, 1.1, is about intermediate between two ratios. These results suggest that the substituents effects might involve to form the dimers from the reaction of *tert*-butyllithium with chlorovinylsilane in hexane at low temperature.
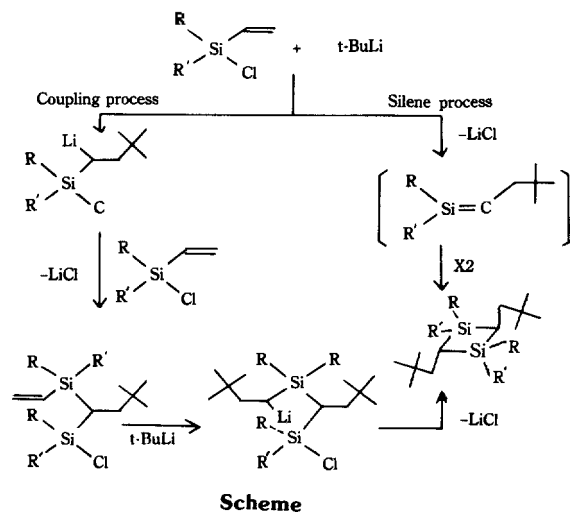
Scheme

It has been reported that the dimerization mechanism is either a [2s + 2s] dipolar stepwise pathway or coupling process which allows to favour the formation of *cis* configurational dimer.[2,5,9] The mechanisms are illustrated in Scheme.

The dimethyl groups with less steric hindrance allow to be proceeded in both way, leading to the lowest *trans/cis* ratio, while the diphenyl groups with more steric hindrance allow to be proceeded in only silene dimerization pathway. The silene dimerization would be occured in fashion to minimize the steric interaction between the phenyl groups on silicon and the bulky neopentyl group, leading to a higher *trans/cis* ratio. The intermediate ratio for the 1-methyl-1-phenyl-silene dimers could be explained on the basis of the same arguments above.

Experimental

All experiments were carried out under dry nitrogen atmosphere in apparatus that was flame-dried or assembled hot from the drying oven. Solvents were distilled from sodium prior to use. Reagents and solvents were transferred by standard syringe or double ended needle techniques. Product mixture analyses were performed on a Hitachi model 163 FID gas chromatograph using a 1 m SE-30 column, programmed at 1°C/min. from 200 to 250°C. Carbon NMR were obtained using a Bruker FT-80SY 80 MHz spectrometer with an internal standard CDCl₃ lock. Proton NMR were obtained on a Varian EM-360L 60 MHz spectrometer in CCl₄ or CDCl₃ solution using TMS as an internal standard. Percent yields of all products were determined by GC using a hexadecane as an internal standard. Elemental Analyses were performed by Galbraith Laboratories, Knoxville, TN, U.S.A.

Reaction of t-butyllithium with chlorodiphenylvinylsilane. To a stirred solution of 4.9 g (20 mmol) of chlorodiphenylvinylsilane,[10] synthesized from the reaction of trichlorovinylsilane with phenylmagnesiumbromide, in 100 m*l* of dried hexane cooled to -78°C was added dropwise 10 m*l* (20 mmol) of 2.0M *t*-butyllithium in pentane (Aldrich). The reaction mixture was allowed to warm slowly to room temperature, and was stirred overnight. The white precipitate was dissolved when the reaction mixture was quenched with saturated ammonium chloride solution. After quenching, the organic layer was separated, combined with hexane extract of the aqueous layer and dried with anhydrous sodium sulfate. After evaporaticn of the solvents using a rotary evaporater, viscous yellow oil was obtained which GC analysis indicated to be 52% silene dimers. *Trans*-configurational dimer was precipitated out from the reaction mixture in diethylether at low temperature (ca. 0°C). Recrystalization of this crude precipitate in diethylether afforded the pure *trans*-dimer. (mp 208-209°C, colorless crytal). The remaining solution which was rich in *cis*-dimer was applied to a liquid chromatograph column to get the pure *cis*-isomer.

1,1,3,3-Tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutane, 4; colorless single crystal; ¹H-NMR, 4a; δ 0.65(s, 9H, -C(CH₃)₃); 1.30-1.57(m, 2H, -CH₂-); 1.70-2.05(m, 1H, -CH=); 7.30-7.85 (m, 5H, -C₆H₅). 4b; δ 0.71(s, 9H, -C(CH₃)₃); 1.53-1.82(m, 2H, -CH₂-); 1.16-1.43(m, 1H, -CH=); 7.25-7.80 (m, 5H, -C₆H₅). MS; The mass spectra for the isomers, 4a and 4b were identical. m/z(relative intensity), [M⁺] 532(1), 475(24), 266(15), 265(61), 260(19), 259(83), 215(19), 219(17), 209(76), 184(19), 183(100), 181(27), 105(30), 57(24). Anal.; Calcd. for Si₂C₃₆H₄₄; C, 81.12; H, 8.34 Found; C, 81.59; H, 8.28 ¹³C-NMR data for the isomers were given in Table 1.

Trapping reaction using trimethylmethoxysilane. To a solution of 7.35 g(30.0 mmol) of chlorodiphenylvinylsilane and 5.0 m*l*(36 mmol) of trimethylmethoxysilane in 130 m*l* of

dry hexane cooled to −78°C was slowly added 15 m*l* (30 mmol) of 2.0M *t*-buthyllithium in pentane. The mixture was allowed to warm slowly to room temperature and was stirred overnight. Work-up as described above was followed by GC analysis which gave 74% yield of 1-methoxy-1,1-diphenyl-2-trimethylsily-4,4-dimethyl-1-silapentane. This product was isolated by column chromatography as colorless liquid.

1-Methoxy-1,1-diphenyl-2-trimethylsilyl-4,4-dimethyl-1-sila-pentane 5; colorless liquid; ^{1}H-NMR; δ −0.09(s, 9H, -Si (CH₃)₃), −0.03-0.45(m, 1H, Si-CH-Si), 0.75(s, 9H -C(CH₃)₃), 1.2-1.6 (m, 2H, -CH₂-), 3.55(s, 3H, -OCH₃), 7.2-7.8(m, 10H, Si-aryl); ^{13}C-NMR; δ 0.60, -Si(CH₃)₃; 8.11, Si-CH-Si-; 29.62, -C(CH₃)₃; 31.77, -C(CH₃)₃, 37.35, -CH₂-; 51.45, -OCH₃; 127.71, 127.99, 129.49, 135.29, 135.34, 135.86; 136.44, Si-aryl; MS; m/z(relative intensity), [M$^+$-15] 355(82), 313(34), 213(100), 209(8), 106(5), 73(22), 59(20), 57(7).

Trapping reaction with anthracene. To a mixture of 4.9 g(20 mmol) of chlorodiphenylvinylsilane and 6.41 g (36 mmol) of anthracene in 700 m*l* of dry benzene at room temperature was slowly added 10 m*l* (20 mmol) of 2.0 M *t*-butyllithium in pentane. The mixture was allowed to stir overnight and then subjected to the usual work-up. GC analysis showed the mixture of dimers in 21% and the expected trapped adduct, 2,2-diphenyl-3-neopentyl-(5,6: 7,8)-dibenzo-2-silabicyclo-(2.2.2)-octane, in 46%. The dimeric isomers were precipitated out from the product mixture in hexane at low temperature (ca. 0°C). The remaining solution was applied to a liquid chromatographic column to get the pure anthracene adduct (mp 165-166°C, colorless crystal).

2,2-Diphenyl-3-neopentyl-(5,6: 7,8)-dibenzo-2-silabicyclo-(2.2.2)-octane, 6; colorless crystal; ^{1}H-NMR, δ 0.86(s, 9H, -C(CH₃)₃), 1.23(d, 2H, -CH₂-), 1.42-1.80(m, 1H, Si-CH-NP), 4.31(s, 1H, Si-CH≡), 4.45(d, 1H, -CH≡), 6.68-7.56(m, 18H, aryl); ^{13}C-NMR, δ 23.80, Si-CH-NP; 29.90, -C(CH₃)₃; 32.32, -C(CH₃)₃; 40.21, Si-CH≡; 43.15, -CH₂-; 53.20, -CH≡; 124.27, 124.93, 125.07, 125.57, 125.58, 126.07, 126.19, 126.89, 127.22, 127.53, 129.16, 129.24, 133.15, 134.16, 135.06, 136.55, 139.81, 140.07, 141.24, 142.71, phenyl car-

bons. MS; m/z (relative intensity), [M$^+$] 444(3), 266(21), 210 (20), 209(100), 184(5), 183(30), 178(13), 105(10), Anal.; Calcd. for SiC₃₂H₃₂; C, 86.42; H, 7.27 Found; C, 86.62; H,7.35

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XPS Studies of Oxygen Adsorption on Polycrystalline Nickel Surface

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The interaction of oxygen with polycrystalline nickel surface has been studied by investigating the X-ray photoelectron spectra of 0 ls, Ni 2p$_{3/2}$, and their valence band electrons. By comparing the oxygen exposure of this work with the reported results of LEED, AES, and work function measurements, it is found that the atomic oxygen, adsorbed dissociatively in the initial stage of exposure, is responsible for a p(2 × 2) structure and a subsequent c(2 × 2) structure on the Ni(100) surface. This dissociatively adsorbed oxygen species forms surface NiO layer subsequently on further oxygen exposure. The NiO layer is more easily formed with the increasing temperature. Non-stoichiometric oxygen species is also found to accompany the NiO layer. It appears prior to the formation of bulk NiO at all of the temperatures of this work except at 523K.

Introduction

There have been up to now quite a number of investiga-

tions of the oxygen adsorption on nickel surface[1-11], as the subject is very crucial in understanding such surface processes, as oxidation, heterogeneous catalysis, and adsorption