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THE SYNTHESIS AND STEREOCHEMICAL CHARACTERIZATION OF THE FIVE ISOMERIC 1,3-DIPHENYL-1,3-DIMETHYL-2,4-DINEOPENTYL-1,3-DISILACYCLOBUTANES

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Summary

The reaction of t-butyllithium with phenylmethylvinylchlorosilane at low temperature in hexane solvent gave a 48% yield of a mixture of the five isomers of the 1,3-diphenyl-1,3-dimethyl-2,4-dineopentyl-1,3-disilacyclobutanes, along with an acyclic isomer. The separation and determination of the stereochemistry of the diasteromeric 1,3-disilacyclobutanes by means of carbon-13 NMR is described.

Introduction

We recently reported that the reaction of t-butyllithium with vinyldimethylchlorosilane provides a high-yield route to *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutane [1]. Subsequent studies provided evidence that, at low temperatures in hydrocarbon solvents, the initial reaction of t-butyllithium and the vinylchlorosilane gives rise to 1,1-dimethyl-2-neopentylsilene as an intermediate. In the absence of trapping agents this intermediate dimerizes to give the observed products [2,3]. As a prelude to the study of the stereochemistry of silene reactions it was necessary to prepare, separate and characterize the stereoisomers of the dimers of a silene which could exhibit *cis—trans* isomerism. We chose for this endeavor the silene produced by the reaction of t-butyllithium with phenylmethylvinylchlorosilane.

Results and discussion

Based on our earlier work, the reaction of t-butyllithium with phenylmethylvinylchlorosilane would be expected to give rise to both the *E*- and *Z*-isomers of 1-methyl-2-neopentyl-1-phenylsilene (I). Head-to-tail dimerization of these silenes could produce five isomeric 1,3-disilacyclobutanes. To our surprise,

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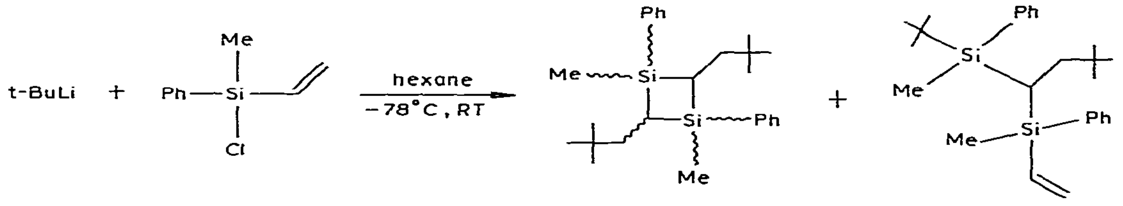
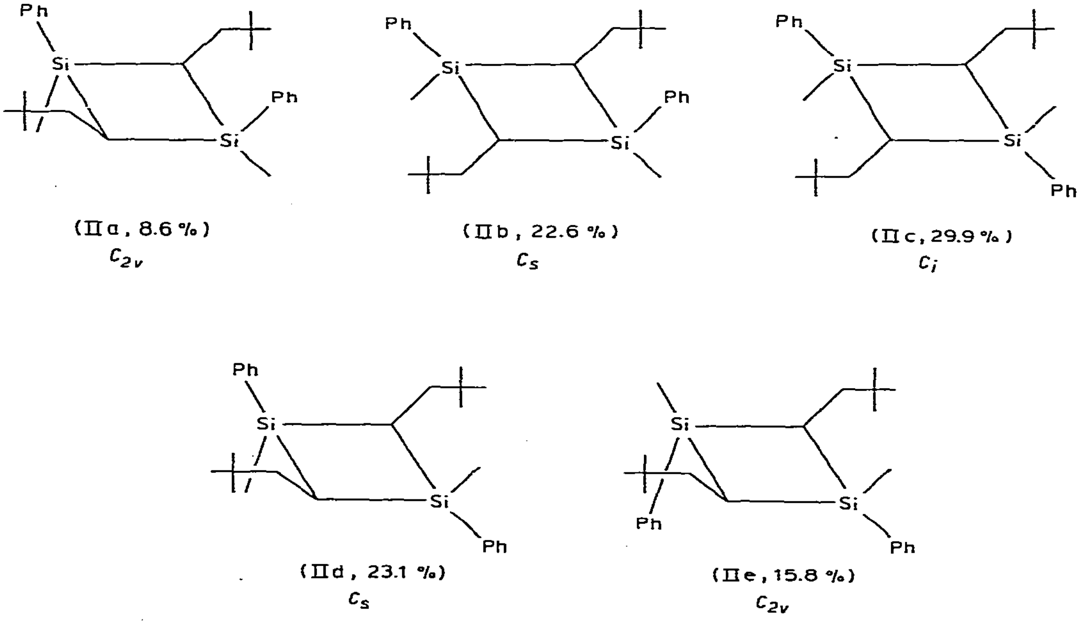
when the reaction was carried out by warming a hexane solution of the reactants from −78°C to room temperature, chromatographic analysis of the reaction mixture indicated six volatile components comprising 48% of the products. Based on analytical data, all six of these products were isomers corresponding to the formula $C_{26}H_{40}Si_2$, the anticipated formula for the dimers. Separation of these isomers by preparative gas chromatography and subsequent spectral analysis indicated that the first isomer to elute was the acyclic compound, III. The remaining five peaks corresponded to the anticipated isomeric 1,3-disilacyclobutanes, IIa—IIe.



(IIa–IIe, 43%) (III, 5%)

Based on the reasoning described below we have assigned the isomers of II as *syn*-(*cis*-1,3-diphenyl-*cis*-2,4-dineopentyl)-1,3-dimethyl- (IIa, 8.6%), *cis*-1,3-diphenyl-*trans*-2,4-dineopentyl-1,3-dimethyl- (IIb, 22.6%), *trans*-1,3-diphenyl-*trans*-2,4-dineopentyl-1,3-dimethyl- (IIc, 29.9%), *trans*-1,3-diphenyl-*cis*-2,4-dineopentyl-1,3-dimethyl- (IId, 23.1%) and *anti*-(*cis*-1,3-diphenyl-*cis*-2,4-dineopentyl)-1,3-dimethyl-1,3-disilacyclobutanes (IIe, 15.8%). We are using *syn* and *anti* to designate those isomers in which *cis*-phenyl groups and *cis*-neopentyl



(IIa, 8.6%) C_{2v}

(IIb, 22.6%) C_s

(IIc, 29.9%) C_i

(IId, 23.1%) C_s

(IIe, 15.8%) C_{2v}

Fig. 1. Structures, product distribution, and symmetries of the five isomeric 1,3-disilacyclobutanes (II).

TABLE 1

PROTON-NMR DATA FOR THE ISOMERIC 1,3-DIMETHYL-2,4-DINEOPENTYL-1,3-DIPHENYL-1,3-DISILACYCLOBUTANES [a]

Protons	IIa	IIb	IIc	IId	IIe
$SiCH_3$	0.76(s)	0.78(s)	0.87(s)	0.78(s) 0.87(s)	0.78(s)
$C(CH_3)_3$	0.90(s)	0.73(s) 0.99(s)	0.98(s)	0.91(s)	0.94(s)
CH_2 [b]	1.62(d)	1.70(m)	1.61(d)	1.68(d)	1.72(d)
C_6H_5	7.25(m)	7.37(m)	7.46(m)	7.40(m)	7.42(m)

[a] Chemical shifts (multiplicities) in ppm downfield from tetramethylsilane measured using methylene chloride as an external standard. The ring methine protons appeared as broad multiplets in the region 0.45—1.2 ppm. [b] The methylene protons of the neopentyl groups with the exception of those for IIb appeared as broadened doublets.

groups are on the same and opposite sides of the disilacyclobutane ring, respectively. The structures of these five isomers, are illustrated in Fig. 1.

The stereochemical characterization of the five disilacyclobutane isomers was a non-trivial problem. The ^1H NMR spectra of the isomers, Table 1, provided little help in the resolution of this problem. Based on the symmetry of the isomers, IIb is the only isomer which should have chemically non-equivalent neopentyl groups and IId is the only isomer which should have chemically distinct silicon-methyl groups. On this basis, IIb and IId could be tentatively assigned.

The ^{13}C spectra for the isomers provide the key to the problem. Based on the symmetry of the isomers, one can predict the number of chemically distinct carbons for each of the isomers, Table 2. By comparison with the experimental results given in Table 3, unambiguous assignment of isomers IIb with 13 lines, and IId, with 14 lines can be made. This assignment is consistent with the tentative assignment made on the basis of the ^1H NMR spectra for these isomers. Symmetry arguments alone do not permit the differentiation of IIa, IIc, or IIe, all of which are predicted to have 9 distinct carbon resonances. Consideration of bulk shielding and γ effects [4] permitted the identification of these isomers.

In IId, one of the silicon-methyls has a Z relationship to both neopentyl

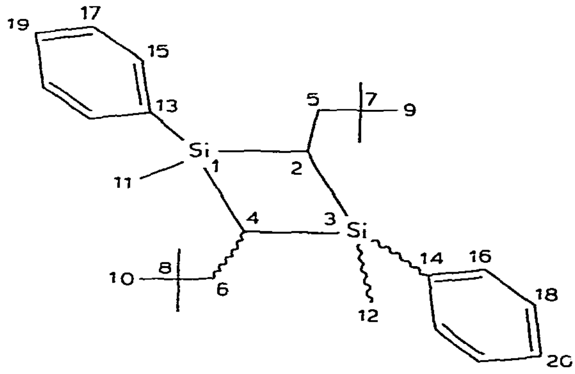
TABLE 2

PREDICTED NUMBER OF CHEMICALLY DISTINCT CARBONS FOR THE ISOMERS OF II

Structure element	IIb	IId	IIa, IIc, IIe
$(CH_3)_3C$	2	1	1
$(CH_3)_3C$	2	1	1
(CH_2)	2	1	1
CH	2	1	1
$Si\text{-}CH_3$	1	2	1
Si-aryl	4	8	4
Total	13	14	9

TABLE 3

^{13}C NMR DATA FOR THE ISOMERIC 1,3-DIMETHYL-2,4-DINEOPENTYL-1,3-DIPHENYL-1,3-DISILACYCLOBUTANES [a]



Carbons	IIa	IIb	IIc	IId	IIe
C(13, 14)	136.3(s)	137.3(s)	137.4(s)	140.5 135.9	140.1(s)
C(15,16) [b]	135.9(d)	134.3(d)	134.0(d)	135.1 133.0	134.3(d)
C(17,18) [b]	127.5(d)	127.9(d)	127.7(d)	127.9 127.7	128.0(d)
C(19,20)	129.1(d)	129.2(d)	129.0(d)	132.6 129.0	129.1(d)
C(5,6)	39.9(t)	40.0(t) 39.4(t)	39.7(t)	40.0	40.0(t)
C(7,8)	31.7(s)	31.7(s) 31.5(s)	31.5(s)	31.5	31.5(s)
C(9,10)	29.4(q)	29.5(q) 29.2(q)	29.3(q)	29.4	29.4(q)
C(2,4)	15.0(d)	13.4(d) 10.2(d)	11.3(d)	13.3	12.7(d)
C(11,12)	2.9(q)	—2.3(q)	—2.4(q)	1.8 —6.6	—6.8(q)

[a] In ppm downfield from tetramethylsilane using external D_2O lock and $DCCl_3$ as the reference. Letters in parentheses indicate the multiplicity for the off-resonance proton decoupled spectra. [b] Assigned by analogy with known phenylsilanes [10].

groups and is therefore the most shielded, δ —6.6 ppm. Only one other isomer, IIe, has the silicon-methyls in a similar *Z* orientation to both neopentyl groups. The chemical shift for these methyl groups, —6.8 ppm, is in accord with the shielding effects of the two neopentyl groups. In addition; the chemical shift of the *ipso* carbons for the phenyl groups in IIe, 140.1 ppm; is consistent with the absence of the shielding of these carbons by the other ring substituents; and with the chemical shift of the similarly oriented phenyl group in isomer IId.

The assignment of the structure of IIc is based on the similarity of the chemical shift of the silicon-methyl carbon, —2.3 ppm, to that for the silicon-methyls in IIb. In both of these isomers the methyl groups have a *Z* orientation with respect to one neopentyl group. In addition, the *ipso* carbons of the phenyl groups in these isomers, shielded by only one neopentyl group, have chemical shifts intermediate between those observed for shielding by two neopentyl groups and no neopentyl groups, as is the case in IId.

The ^{13}C NMR chemical shifts of the remaining isomer, IIa, are consistent with the bulk shielding effects discussed above. The silicon-methyls, with minimal shielding by the other substituents occur furthest downfield. The shielding of the *ipso* carbons of the phenyl groups by both neopentyl groups results in a chemical shift nearly the same as that for the correspondingly oriented *ipso* carbon of IId. In addition, the ring carbons for IIa occur furthest downfield for the series of isomers, consistent with their minimum shielding by the bulky ring substituents.

In the ^{13}C NMR spectra of the *E* and *Z* isomers of 1,2-dimethylsilacyclobutane, the steric interaction of the two methyl groups in the *Z* isomer resulted in an upfield shift for its silicon-methyl resonance of 4.7 ppm when compared with the *E* isomer [5]. Based on our assignment of the structures of the isomers of II, it appears that each additional *Z* interaction between a silicon-methyl group and the bulky neopentyl group in the 1,3-disilacyclobutane rings results in an upfield shift of 4 to 5 ppm for the silicon-methyl. A similar but smaller effect is observed for the *ipso* carbons of the silicon-phenyl groups giving about a 1 to 2 ppm upfield shift for each *Z* interaction with the neopentyl group. These steric shielding effects are apparently much smaller for the methylene carbons of the neopentyl groups, which show very little variation. This insensitivity might be attributed to the dominant shielding effect of the t-butyl groups on the methylene carbons.

It is of interest to consider the isomer distribution obtained from the dimerization of I in light of possible mechanistic information which might be obtained. The relative amounts of the isomers obtained are indicated in Fig. 1. Evidence has been presented that the Si=Si bond in 2,3-diphenyl-2,3-disila-2-butene is configurationally stable at temperatures up to 350°C [6]. If silenes possess similar configurational stability, a point which has not yet been established [7], then the isomer distribution which we observe is quite close to that which would be predicted for a [2*s* +2*s*], perhaps dipolar or stepwise, dimerization. Such a dimerization occurring in a reaction where equal amounts of *E*- and *Z*-1-methyl-2-neopentyl-1-phenylsilene were reacting with similar activation energies [8] to give the dimers would be predicted to give 12.5% each of IIa and IIe, and 25% each of IIb, IIc, and IId. The variation from this isomer distribution which we observe seems to be consistent with differences in the activation energy for dimerization which might arise from steric requirements.

On the other hand, a [2*s* + 2*a*] concerted dimerization pathway would require the production of 50% of IIa + IIe and 50% of IIb + IIc + IId. Experimentally, we observe that the relative amount of (IIa + IIe)/(IIb + IIc + IId) is approximately 24/76.

Experimental

Reactions were carried out in flame-dried glassware under an atmosphere of dry nitrogen. The hexane solvent was distilled from sodium/potassium alloy prior to use. Product mixture analyses and the determination of the purity of samples collected from the preparative GC were performed on a Perkin—Elmer Sigma-3 FID gas chromatograph using a 25 m fused silica capillary column with methylsilicone fluid stationary phase, programed from 200 to 250°C at 2°/min. Under these conditions base-line resolution of the six isomeric products could be obtained. The order of elution was III, IIa, IIb, IIc, IId, and IIe. Preparative GC samples were collected from a Varian Series 1800 TCD gas chromatograph using a 20′ by 3/8″ stainless steel, 10% OV 17 on 80-100 mesh Supelcoport, programed from 200 to 300°C at 10°/min.

Mass spectra of the isomers were obtained using a Finnegan Automated 9500 GC/MS system with chromatographic conditions to those described for the analytical work. Proton NMR were obtained on a Hitachi Perkin—Elmer R 24B 60 MHz spectrometer in CCl_4 solution using CH_2Cl_2 as an external standard. Carbon NMR were obtained using a JEOL FX 90Q, Fourier Transform 90 MHz spectrometer with an external D_2O lock.

Reaction of t-butyllithium with phenylmethylvinylchlorosilane

To a stirred solution of 39.6 mmol of phenylmethylvinylchlorosilane (Petrarch) in 100 ml of dry hexane cooled to —78°C was added dropwise 39.6 mmol of t-butyllithium (Aldrich) diluted to 1.2 *M* in pentane. The reaction mixture was allowed to warm slowly to room temperature. A mildly exothermic reaction accompanied by the formation of a white precipitate occurred. After quenching with saturated ammonium chloride solution, the organic layer was separated, combined with hexane extractions of the aqueous layer and dried with anhydrous sodium sulfate. After evaporation of the solvents using a rotary evaporator, 8.3 g of a viscous yellow oil was obtained which GC analysis indicated to be 43% silene dimers, II, 5% of the acyclic isomer, II, and 52% of higher boiling by-products, which have yet to be characterized. The volatile products were separated from the by-products by bulb to bulb vacuum distillation at 200°C, 0.05 Torr.

The individual components were separated by preparative GC, using capillary tubes for collection of the ^{13}C and ^{1}H NMR samples. Spectra were determined by inserting the capillary tubes in ordinary NMR tubes containing CH_2Cl_2 or D_2O for the ^{1}H or ^{13}C spectra, respectively.

3,5,6,6-Tetramethyl-4-neopentyl-3,5-diphenyl-3,5-disila-1-heptene (III)

^{1}H NMR: δ 0.51, s(3H), CH_3Si; 0.59, s(3H), CH_3Si; 1.00, s(9H), $(CH_3)_3C$; 1.20, s(9H), $(CH_3)_3C$; 0.80, t(1H), methine proton; ca. 1.40, m(2H), methylene protons; 5.8—6.3, m(3H), vinyl protons; 7.20—7.40 ppm, m(10H), aryl protons. ^{13}C NMR, proton decoupled: δ 134.6, 134.4, 134.3, 134.2, 133.6, 133.3, 129.2, 128.4, 128.0, and 127.7, aryl and vinyl carbons; 38.4, methylene carbon; 31.1, quaternary carbon of the neopentyl group; 28.8, t-butyl methyls; 7.8, methine carbon; —4.7 and —5.8 ppm, silicon methyls. The quaternary carbon of the silicon t-butyl group was not observed.

Mass spec; *M/e* (relative intensity): 408(<1), 204(16), 198(11), 190(23), 158(19), 156(54), 136(27), 127(31), 121(100), 105(22), 73(18), 57(20). The Raman spectrum of III showed a distinctive band at 1590 cm^{-1} for the C—C stretch of the terminal olefin.

,3-Dimethyl-2,4-dineopentyl-1,3-diphenyl-1,3-disilacyclobutanes (IIa—IIe)

The proton and carbon NMR data for these compounds are given in Tables 1 nd 3, respectively. All five of the isomers showed very similar mass spectral agmentation patterns; *M/e* (relative intensity): 408(<1), 351(27), 215(15), 10(14), 204(56), 198(48), 154(17), 148(59), 136(52), 121(100), 104(23), 3(21), 59(20), 57(22), 42(20). Analysis: Found: C, 76.34; H, 10.18. $C_{26}H_{40}Si_2$ alcd.: C, 76.39; H, 9.86%.

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