Silene Stereochemistry. 5. Stereospecific Syntheses Using Silene Precursors[1]

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Received July 31, 1984

The diastereomers produced by the stereospecific trapping of (*E*)- or (*Z*)-1-methyl-1-phenyl-2-neopentylsilene with methoxytrimethylsilane can be converted by stereospecific reactions to diastereomeric methoxy-, hydrido-, chloro-, or fluorosilanes of known relative stereochemistry. Evidence that the addition of methoxytrimethylsilane to silenes proceeds by stereospecific syn pathway is presented, and the relative stereochemistry of the diastereomers is tentatively assigned on this basis.

Introduction

The *E* and *Z* isomers of 1-phenyl-1-methyl-2-neopentylsilene, **1**, generated by the low-temperature reaction of *tert*-butyllithium with vinylphenylmethylchlorosilane in hydrocarbon solvents, can be stereospecifically trapped as their [4 + 2] cycloadducts with dienes.[2] We recently reported that (*E*)- and (*Z*)-**1** are configurationally stable up to approximately 300 °C and that they can be trapped stereospecifically by methoxytrimethylsilane to give diastereomeric adducts.[3] While other workers have observed asymmetric induction in the reaction of prochiral silenes with chiral alcohols,[4] our results represent the first demonstration of a stereospecific silene addition reaction. This discovery led us to probe the possibility of using the methoxy–trimethylsilyl adducts to (*E*)- or (*Z*)-**1** as precursors to diastereomeric organosilanes of known relative stereochemistry by means of reactions which have been shown to be stereospecific at silicon.[5]

Results and Discussion

D1-OMe and D2-OMe. When (*Z*)- and (*E*)-**1**, generated by the reaction of *tert*-butyllithium with vinylphenylmethylchlorosilane at −78 °C, are trapped with methoxytrimethylsilane,[6] a 33:67 mixture of their methoxy–trimethylsilyl adducts, D1-OMe and D2-OMe, is obtained. The enantiomeric pairs of these diastereomeric adducts, as well as all of the other diastereomeric mixtures discussed in this paper, can be separated for analytical purposes using capillary column GLC methods. After isolation and purification the ratio of D1-OMe:D2-OMe in the mixture used for subsequent reactions was 35:65.

Scheme I

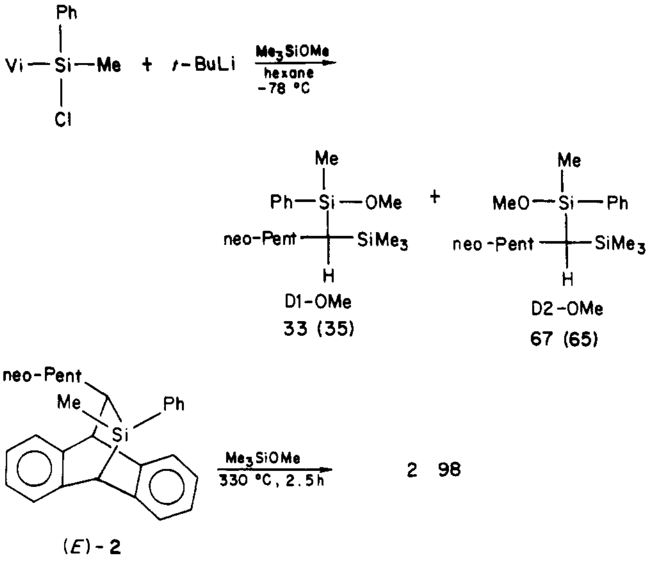

Table I. Chlorination Reactions of D1-OMe and D2-OMe

reagent	D1-OMe: D2-OMe	temp, °C	time, h	yield, %	D1-Cl: D2-Cl
PhCOCl	0:100	100	12	85	54:46
	35:65	95	16	90	50:50
	19:81	95	16	90	49:51
PCl_3	35:65	25	2	93	50:50
	19:81	25	2	93	51:49
$SOCl_2$	35:65	115	2	80	52:48

Nearly diastereomerically pure D2-OMe was prepared by the sealed tube thermolysis of pure (*E*)-**2**, the [4 + 2] cycloadduct of (*E*)-**1** with anthracene,[2] under nonisomerizing conditions in the presence of a tenfold excess of methoxytrimethylsilane. A variety of experimental conditions were tried for these sealed tube thermolyses. Those reported represent the optimum that we were able to obtain for conversion of (*E*)-**2** to D2-OMe with minimum formation of 5,5-dimethyl-2-methoxy-2-phenyl-2-silahexane, **3**, a secondary product arising from the reaction of D1- or D2-OMe with methoxytrimethylsilane.[3]

Stereospecific Transformations of D1-OMe and D2-OMe. The conversion of the methoxy diastereomers to their corresponding chloro compounds was carried out by using benzoyl chloride,[7] PCl_3,[8] or $SOCl_2$.[9] As the data given in Table I show, although good yields of mixtures of D1-Cl and D2-Cl were obtained, the ratio of D1-Cl to D2-Cl produced in these reactions was close to 50:50. These results are consistent with the rapid racemization of optically active chlorosilanes which occurs in the pres-

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[2] Jones, P. R.; Lee, M. E.; Lin, L. T. *Organometallics* **1983**, *2*, 1039–1042.

[3] Jones, P. R.; Lee, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 6725–6726.

[4] Bertrand, G.; Dubac, J.; Mazerolles, P.; Ancelle, J. *J. Chem. Soc., Chem. Commun.* **1980**, 382–383.

[5] For a recent review see: Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43–198.

[6] It is, of course, critical that the methoxytrimethylsilane be free of methanol. Because we were unable to obtain methanol-free methoxytrimethylsilane from commercial sources all of the reagent used in these studies was prepared by the reaction of methanol with excess hexamethyldisilazane and was more than 99% pure. Me_3SiOMe and MeOH form a binary azeotrope containing 14–16% MeOH, bp 50 °C. Sauer, R. O. *J. Am. Chem. Soc.* **1944**, *66*, 1706–1708.

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[9] Sommer, L. H.; Blankman, H. D.; Miller, P. C. *J. Am. Chem. Soc.* **1951**, *73*, 3542.

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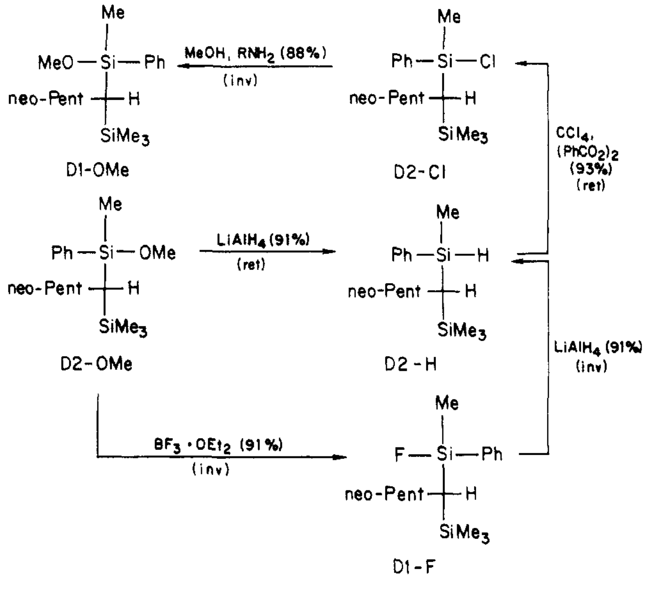
Scheme II



neo-Pent = neopentyl

ence of nucleophiles or in solvents of high nucleophilicity.[10]

Reductions of optically active alkoxysilanes with $LiAlH_4$ have been shown to occur with predominant retention of configuration at silicon.[11] When a 35:65 or a 2:98 mixture of D1-OMe:D2-OMe was reduced with $LiAlH_4$ in ether, a mixture of D1-H:D2-H in ratios of 38:62 or 5:95, respectively, was obtained in better than 90% yield. These results correspond to greater than 98% stereospecific retention for the reduction.

The treatment of either a 35:65 or a 5:95 mixture of D1-OMe and D2-OMe with $BF_3{\cdot}OEt_2$ in ether gave a mixture of D1-F and D2-F with ratios of 66:34 or 93:7, respectively. This is consistent with predominant inversion of configuration at silicon which has been observed for this reaction with optically active silicon compounds in ether.[11]

The free radical chlorination of mixtures of D1-H and D2-H with ratios of 38:62 or 5:95 using benzoyl peroxide as the initiator in CCl_4 solvent[12] gave mixtures of D1-Cl and C2-Cl in ratios of 38:62 or 5:95, respectively; corresponding to complete retention of configuration for the reaction. The methanolysis of these chlorides in the presence of cyclohexylamine, a reaction known to occur with predominant inversion of configuration at silicon,[10] gave mixtures of D1-OMe and D2-OMe with ratios of 62:38 or 93:7, respectively.

The $LiAlH_4$ reduction of 66:34 or 93:7 mixtures of D1-F and D2-F gave mixtures of D1-H and D2-H with ratios of 30:70 or 8:92, respectively. The stereochemical outcome for reduction of fluorosilanes is known to be highly sensitive to solvent and salt effects.[13] Comparison of the ratio of D1-H and D2-H obtained in this reaction with those obtained for the methoxysilanes D1-OMe and D2-OMe indicates predominant inversion for the reduction of the fluorosilanes under our experimental conditions.

Scheme II summarizes the stereochemical results of the transformations which we carried out and indicates typical yields for the reactions. Although the present work did involve the preliminary separation of isomerically pure (*E*)-**2** for use as a silene source,[14] the viability of using silenes of known stereochemistry as precursors to diastereomeric silanes with known relative stereochemistry has been demonstrated for the first time. A concrete example illustrated is the use of D2-OMe, which can be prepared in large quantities from the easily crystallized (*E*)-**2**, to prepare D1-OMe in high diastereomeric purity. The alternate route to D1-OMe, trapping the silene produced by the thermolysis of (*Z*)-**2** with methoxytrimethylsilane, is much less satisfactory because (*Z*)-**2** is produced in smaller quantities in the low-temperature silene-trapping reactions with anthracene[2] and can only be obtained free of its *E* isomer with great difficulty.[14]

Table II. Carbon-13 Chemical Shifts for the Diastereomers[a]

	D1-OMe[b]	D1-OMe	D1-H	D1-Cl	D1-F
$XSiCH_3$	−2.92	−2.59	−4.70	2.60	−1.46
$Si(CH_3)_3$	0.01	−0.26	−0.35	0.92	−0.16
$CHSiMe_3$	9.24	9.14	5.67	10.07	9.42
$(CH_3)_3C$-	29.59	29.45	29.80	29.73	29.33
-$C(CH_3)_3$	31.61	31.34	31.89	31.34	31.41
-CH_2-	36.94	36.96	38.56	36.92	36.81
OCH_3	50.40	50.28			
aryl	127.59	127.39	127.83	127.65	127.52
	129.09	128.96	129.08	129.67	129.67
	134.42	134.02	134.69	133.50	133.37
ipso	137.98	137.47	137.90	137.08	136.04
	D2-OMe[b]	D2-OMe	D2-H	D2-Cl	D2-F
$XSiCH_3$	−3.64	−3.97	−4.52	3.12	−1.46
$Si(CH_3)_3$	0.40	−0.26	−0.01	0.92	−0.16
$CHSiMe_3$	8.85	8.71	5.67	10.47	9.74
$(CH_3)_3C$-	29.59	29.46	29.80	29.73	29.33
-$C(CH_3)_3$	31.61	31.34	31.89	31.34	31.41
-CH_2-	36.94	36.81	38.86	36.92	36.81
OCH_3	50.60	50.07			
aryl	127.59	127.39	127.83	127.65	127.52
	129.09	128.95	129.08	129.67	129.67
	134.10	133.70	134.86	133.50	133.50
ipso	138.78	138.19	137.40	137.08	136.82

[a] ppm downfield from tetramethylsilane: neat with D_2O lock. [b] $CDCl_3$ solvent and lock.

Relative Stereochemistry of the Diastereomers. We have noted previously that when 1-methyl-1-phenyl-2-neopentylsilene is generated at low temperatures with the *tert*-butyllithium method the ratio of (*E*)- to (*Z*)-silene [4 + 2] cycloadducts with dienes obtained is consistently 70:30.[2] As reported above, when the same silene, generated under the same conditions, is trapped with methoxytrimethylsilane the ratio of D2-OMe to D1-OMe obtained is 67:33 (Scheme I). Furthermore, under nonisomerizing conditions, D2-OMe is the diastereomer obtained when the silene generated by cycloreversion of an *E* [4 + 2] cycloadduct is trapped with methoxytrimethylsilane, and D1-OMe is obtained from the *Z* cycloadduct.[3] Taken together these results demonstrate that the [4 + 2] cycloaddition/cycloreversion reactions of silenes and the reaction of silenes with methoxytrimethylsilane *must* have the same relative stereochemistry. If the cycloaddition/cycloreversion reactions are [4s + 2s], as seems likely,[2] our results indicate that the reaction of methoxytrimethylsilane with silenes is a stereospecific syn addition.

If this conclusion is correct, we can then tentatively assign the relative stereochemistries of the diastereomers as (*R*,*R*)(*S*,*S*) for the D1 isomers and (*R*,*S*)(*S*,*R*) for the

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[10] (a) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1–28. (b) Sommer, L. H. "Stereochemistry, Mechanism and Silicon"; McGraw Hill: New York, 1965; pp 84–87.

[11] Corriu, R. J. P.; Ould-Kada, S.; Lanneau, G. *J. Organomet. Chem.* **1983**, *248*, 23–37; ref 10b, pp 51–52.

[12] Franke, F.; Wells, P. R. *J. Org. Chem.* **1979**, *44*, 4055–4060.

[13] Corriu, R. J. P.; Fernandez, J. M.; Guerin, C. *Tetrahedron Lett.* **1978**, 3391. Corriu, R. J. P.; Masse, J. *Bull. Soc. Chim. Fr.* **1969**, 3491.

[14] Lee, M. E. Doctoral Dissertation, North Texas State University, Aug 1984. Details of our present method for purifying (*E*)- and (*Z*)-**2** are given in the Experimental Section.

isomers designated D2 in this paper. The ^{13}C chemical shifts for the diastereomers are given in Table II. Although there are distinct chemical shift differences for several of the carbons in related D1 and D2 diastereomeric pairs, there is no obvious correlation with our tentative stereochemical assignment. A similar result has been recently reported for other silicon-containing diastereomeric pairs.[15] It seems likely that varying conformational populations for different diastereomeric pairs preclude the use of chemical shifts alone to establish stereochemistry. Experiments aimed at the definitive determination of the stereochemistry of the reaction between silenes and alkoxysilanes and the relative stereochemistry of the resulting diastereomers are currently in progress.

Experimental Section

Solvents were dried by distillation from lithium aluminum hydride or sodium–potassium alloy prior to use. Glassware was dried by flaming the assembled apparatus while flushing with dry nitrogen or argon. Reactions were carried out under atmospheres of dry nitrogen or argon, and reagents and solvents were transferred by using standard syringe techniques. GLC analyses of reaction mixtures were performed using a Perkin-Elmer Sigma-3 gas chromatograph equipped with a 25 m SE-54 fused silica capillary column or a 3 mm × 5 m stainless-steel column packed with 3% OV-17 on 100–120 mesh Supelcoport, an FID detector, and a Hewlett-Packard 3390A reporting integrator. GLC yields were calculated by using response factors of the various compounds determined relative to hexadecane as the internal standard. Samples were purified by preparative GLC using a Varian series 1800 gas chromatograph equipped with thermal conductivity detection and a 8 mm × 5 m glass column packed with 15% OV-17 on 60–80 mesh Supelcoport.

NMR spectra were determined on a Perkin-Elmer R24B 60-MHz or a JEOL FX-90Q 90-MHz spectrometer with D_2O or $CDCl_3$ as the lock solvents. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained by using a Hewlett-Packard 5970A MSD mass spectrometer and data system. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Methanol-free methoxytrimethylsilane was prepared by the reaction of dry methanol with excess hexamethyldisilazane (Petrarch), bp 56–58 °C (lit.[6] bp 57 °C).

(*E*)- and (*Z*)-2-Methyl-2-phenyl-3-neopentyl[5,6:7,8]dibenzo-2-silabicyclo[2.2.2]octadiene, (*E*)- and (*Z*)-2. Since our original report of these compounds,[2] we have developed the following method for the synthesis and purification of these stereoisomers. To a solution of 8.8 mL (50 mmol) of vinylphenylmethylchlorosilane and 26.7 g (150 mmol) of anthracene in 700 mL of dry benzene at room temperature was slowly added 26.3 mL of a 1.90 M solution of *tert*-butyllithium (50.0 mmol) in pentane. After being stirred overnight, the mixture was hydrolyzed with saturated ammonium chloride solution, the organic layer was separated, combined with hexane extracts of the aqueous layer, and dried with anhydrous magnesium sulfate. GLC analysis of the resulting solution showed a 5% yield of the silene dimers[2] and (*E*)-2 and (*Z*)-2 in 55 and 22% yields, respectively. The solvents were removed under reduced pressure. The portion of the residue that was soluble in hexane was separated from the precipitated anthracene by filtration. Column chromatography of the hexane solution using a 1 cm × 60 cm 100–200 mesh silica gel with hexanes as the eluent was used to separate the anthracene adducts (*E*)- and (*Z*)-2, which elute last, from the residual anthracene and silene dimers. When the hexane solution of the adducts is concentrated and held at 0 °C, a solid which is about 90% pure (*E*)-2 crystallizes slowly from the solution. Successive recrystallizations using hexane permits isolation of pure (*E*)-2 as white crystals, mp 106–107 °C. Column chromatography (silica gel, petroleum ether) of the residual solution which is rich in the *Z* isomer permits isolation of nearly pure (*Z*)-2 as white crystals, mp 94–95 °C. For normal-phase thin-layer chromatography on silica gel (Eastman 13181 with fluorescent indicator) using hexane the R_f factors for (*E*)-2 and (*Z*)-2 are 0.50 and 0.55, respectively. Reverse-phase TLC (Whatman Partisil-40 ODS-3) using 20% ethyl acetate in hexane gives better separation and R_f factors of 0.45 for (*E*)-2 and 0.40 for (*Z*)-2.

2-Methoxy-2-phenyl-5,5-dimethyl-3-(trimethylsilyl)-2-silahexane, D1- and D2-OMe. Method A. To a solution of 1.83 g (10.0 mmol) of methylphenylvinylchlorosilane (Petrarch) in 110 mL of dry hexanes cooled to −78 °C for 1 h was added 5.6 mL of a 1.78 M solution of *tert*-butyllithium (10 mmol) in pentane (Aldrich). After the reaction mixture was stirred for an additional hour at −78 °C, 2.0 mL (14 mmol) of trimethylmethoxysilane was added. The mixture was allowed to warm slowly to room temperature and stirred for an additional 16 h, prior to hydrolysis with saturated ammonium chloride solution. The organic layer was separated, combined with hexane extractions of the aqueous layer, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue vacuum distilled to give 2.08 g (68%) of a 35:65 mixture of D1-OMe and D2-OMe as a colorless liquid, bp 95 °C (0.5 torr).[3] Anal. Calcd for $C_{17}H_{32}Si_2O$: C, 66.16; H, 10.45. Found: C, 65.90; H, 10.57.

Method B. In a typical preparation 1.5 g of more than 99% pure ((*E*)-2)[2] in 2 mL of cyclohexane was combined with a 10-fold excess of methanol-free methoxytrimethylsilane, placed in a Pyrex heavy-walled tube, degassed, and sealed under vacuum. The entire tube was placed in a vertical pyrolysis oven preheated to 330 ± 3 °C and held at this temperature for 2.5 h. GLC analysis of the reaction mixture showed 48% conversion to a 2:98 mixture of D1-OMe and D2-OMe. The diastereomers for subsequent reactions were purified by preparative GLC. Under these conditions the sealed tube thermolyses typically gave less than 2% of 5,5-dimethyl-2-methoxy-2-phenyl-2-silahexane, 3.[3] Anal. Calcd for $C_{14}H_{24}SiO$: C, 71.12; H, 10.23. Found: C, 70.95; H, 10.50.

2-Phenyl-5,5-dimethyl-3-(trimethylsilyl)-2-silahexane, D1- and D2-H. To a stirred mixture of 0.10 g (2.7 mmol) of lithium aluminum hydride (Alfa) in 15 mL of dry ether was added 2 mL (7 mmol) of a 35:65 mixture of D1-OMe and D2-OMe. GLC analysis of the reaction mixture indicated that the reduction was complete after 3 h. The ether was evaporated under vacuum, and hexanes were added to the mixture. After filtration the precipitate was washed with three additional 10-mL portions of hexanes. The combined hexane solutions were evaporated under reduced pressure to give a 90% yield of a 38:62 mixture of D1-H and D2-H as a colorless liquid: ^1H NMR (neat, D_2O lock) δ −0.35 (br s, 12 H), 0.05 (m, 1 H), 0.46 (s, 9 H), 1.00–1.34 (m, 2 H), 4.24 (m, 1 H), 6.84–7.21 (br m, 5 H); MS, *m/z* (relative intensity), 263 (6, P − 15), 221 (18), 204 (14), 200 (12), 147 (100), 135 (62), 121 (45), 105 (12), 85 (16), 73 (85), 59 (23). Anal. Calcd for $C_{16}H_{30}Si_2$: C, 68.98; H, 10.85. Found: C, 69.03; H, 11.07.

When the same reaction was carried out by using a 2:98 mixture of D1-OMe and D2-OMe, a 5:95 mixture of D1-H and D2-H was obtained in 92% yield.

2-Chloro-5,5-dimethyl-2-phenyl-3-(trimethylsilyl)-2-silahexane, D1- and D2-Cl, from D1- and D2-OMe. A. Benzoyl Chloride.[7] To 0.32 mL (7.1 mmol) of benzoyl chloride was added 1.0 mL (3.5 mmol) of a mixture of D1-OMe and D2-OMe. The reaction was heated by using an oil bath to 90–100 °C. GLC analysis of the reaction mixture showed ratios of D1-Cl to D2-Cl given in Table I.

B. Phosphorus Trichloride.[8] Treatment of 2 mL (7 mmol) of mixtures of D1-OMe and D2-OMe with 0.65 mL (7.5 mmol) of phosphorus trichloride at room temperature gave complete reaction within 2 h. GLC analysis of the reaction mixtures indicated a greater than 90% yields of mixtures of D1-Cl and D2-Cl. The results are summarized in Table I.

C. Thionyl Chloride.[9] A mixture of 0.28 mL (3.8 mmol) of $SOCl_2$ and 1 mL of quinoline was heated to 115 °C for 15 min. A 35:65 mixture of D1-OMe and D2-OMe (500 μL, 1.75 mmol) was added, and the reaction was held at 115 °C for 2 h. GLC analysis of the reaction mixture gave an 80% yield of a 52:48 mixture of D1-Cl and D2-Cl.

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(15) Larson, G. L.; Sandoval, S.; Cartledge, F.; Fronczek, F. R. *Organometallics* 1983, *2*, 810–815.

(16) It should be noted that under our preparative GLC conditions it was found that attempted collection of 95% pure D2-Cl gave a 50:50 mixture of D1-Cl and D2-Cl, presumably through racemization at silicon in either the column or the thermal conductivity detector. This racemization was not a problem in our analytical method employing capillary GLC with flame ionization detection.

Samples of the 50:50 mixtures of D1-Cl and D2-Cl were purified as colorless liquids by preparative GLC for characterization:[16] ^{1}H NMR (neat, D_2O lock) δ −0.20 (br s, 12 H), 0.42 (m, 1 H), 0.52 (s, 9 H), 1.26 (m, 2 H), 6.96–7.02 (br m, 5 H); MS, m/z (relative intensity) 297 (12, P − 15), 298 (4), 299 (5), 300 (1), 147 (100), 141 (10), 121 (16), 73 (31), 45 (15). Anal. Calcd for $C_{16}H_{29}Si_2Cl$: C, 61.39; H, 9.34. Found: C, 61.14; H, 9.37.

Free Radical Chlorination of D1-H and D2-H. To a solution of 1.0 mL (3.5 mmol) of a 38:62 mixture of D1-H and D2-H in 25 mL of carbon tetrachloride was added 6.8 mg of benzoyl peroxide, and the resulting solution was refluxed for 12 h. GLC analysis of the reaction mixture indicated the formation of a 38:62 mixture of D1-Cl and D2-Cl in 90% yield. When the same reaction was carried out by using a 5:95 mixture of D1-H and D2-H, there was obtained a 93% yield of a 5:95 mixture of D1-Cl and D2-Cl.

Methanolysis of D1-Cl and D2-Cl. To a solution of 1 mL of dry methanol and 2 mL of cyclohexylamine in 30 mL of pentane cooled to 0 °C was added dropwise a solution of 0.92 g (2.9 mmol) of a 38:62 mixture of D1-Cl and D2-Cl in 15 mL of pentane. The reaction mixture was stirred for 4 h after the formation of the amine hydrochloride precipitate was observed. After hydrolytic workup and solvent evaporation under reduced pressure GLC analysis showed a 90% yield of a 62:38 mixture of D1-OMe and D2-OMe. A similar experiment using a 5:95 mixture of D1-Cl and D2-Cl gave a 93:7 mixture of D1-OMe and D2-OMe in 88% yield.

2-Fluoro-2-phenyl-5,5-dimethyl-3-(trimethylsilyl)-2-silahexane, D1- and D2-F. To a solution of 0.43 mL (3.5 mmol) of boron trifluoride etherate in 5 mL of ether was added 1.0 mL (3.5 mmol) of a 35:65 mixture of D1-OMe and D2-OMe. After the mixture was stirred for 12 h, GLC analysis of the mixture showed the formation of a 66:34 mixture of D1-F and D2-F in 90% yield. A similar reaction starting with a 5:95 mixture of D1-OMe and D2-OMe gave a 91% yield of a 93:7 mixture of D1-F and D2-F. Pure mixtures of the diastereomers were isolated by preparative GLC for characterization as colorless liquids: ^{1}H NMR (neat, D_2O lock) δ −0.30 (s, 9 H), 0.28 (d, J_{H-F} = 2.86 Hz, 3 H), 0.13 (m, 1 H), 0.49 (s, 9 H), 1.26 (m, 2 H), 6.89–7.20 (br, 5 H); MS, m/z (relative intensity) 281 (9, P − 15), 204 (13), 147 (100), 141 (14), 121 (19), 73 (39), 59 (10), 45 (12). Anal. Calcd for $C_{16}H_{29}Si_2F$: C, 64.80; H, 9.86. Found: C, 64.94; H, 9.84.

Lithium Aluminum Hydride Reduction of D1- and D2-F to D1- and D2-H. To a stirred mixture of 50 mg (1.4 mmol) of lithium aluminum hydride in 3 mL of ether was added 0.90 g (3.0 mmol) of a 66:34 mixture of D1-F and D2-F. After the mixture was stirred at room temperature for 12 h, GLC analysis showed the formation of a 90% yield of a 30:70 mixture of D1-H and D2-H. When the reduction was carried out by using a 93:7 mixture of D1-F and D2-F, there was obtained an 8:92 mixture of D1-H and D2-H in 91% yield.

Acknowledgment. This work was supported by the National Science Foundation, Grant CHE 8100668, the Robert A. Welch Foundation, and the North Texas State Faculty Research Fund.

Registry No. (*E*)-**2**, 85803-40-3; (*Z*)-**2**, 85803-41-4; **3**, 94597-07-6; D1-OMe, 94597-05-4; D1-H, 94597-08-7; D1-Cl, 94597-10-1; D1-F, 94597-12-3; D2-OMe, 94597-06-5; D2-H, 94597-09-8; D2-Cl, 94597-11-2; D2-F, 94597-13-4; *t*-BuLi, 594-19-4; Me_3SiOMe, 1825-61-2; PhCOCl, 98-88-4; PCl_3, 7719-12-2; $SOCl_2$, 7719-09-7; CCl_4, 56-23-5; $(PhCO_2)_2$, 94-36-0; vinylphenylmethylchlorosilane, 17306-05-7; anthracene, 120-12-7.

Silabenzene and Silafulvene by Ring Contraction and Expansion of Cyclic Silylcarbenes

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Received July 24, 1984

Thermolysis of diazo-2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-diene resulted in the formation of 1,2,3,4-tetraphenyl-6,6-dimethyl-6-silafulvene by the ring contraction of 2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-dienylidene. Silacyclopentadienylmethylene generated from thermolysis and photolysis of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazomethane and (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazirine rearranged to 2,3,4,5-tetraphenyl-1-silatoluene by the ring expansion and to 1,2,3,4-tetraphenyl-6-methyl-5-silafulvene by 1,2 migration of a methyl group. These sp^2-hybridized silicon species were successfully trapped by alcohols, ketone, and diene. However, photolysis of 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)diazoethane gave normal carbene products. The reactions of cyclic silyl diazo compounds diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene and 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene are also described.

Introduction

In recent years, interest in the chemistry of α-silylcarbenes has remarkably increased,[1] and detailed studies of α-silylcarbenes; silylcarboalkoxycarbenes,[2] silylketocarbenes,[3] silylphenylcarbenes,[4] (trimethylsilyl)carbene,[5] disilylcarbenes,[6] and their derivatives have been reported.

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0276-7333/85/2304-0584$01.50/0