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Lewis Base Induced Reversal of Diastereoselectivity in the Addition of Alcohols to Chiral Silylenes

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Summary: The steric course of the addition of alcohol to photochemically generated chiral silylenes, (1-phenylethyl)methylsilylene and (1-(2-methoxyphenyl)ethyl)methylsilylene, is reversed in the presence of Lewis bases. The reversal in the stereoselectivity results when the Lewis base coordinates inter-/intramolecularly to the silylene from the less hindered face, after which the addition of alcohol to the silylene takes place.

Silylenes are an important class of highly reactive organosilicon compounds.[1] In striking contrast to carbenes, silylenes prefer to possess singlet ground states, with a vacant p orbital and a lone pair in an sp^2 hybrid orbital. Lewis bases can coordinate to silicon through the vacant orbital to form a base-coordinated silylene.[2] Matrix isolation of complexes of photochemically generated silylenes with various Lewis bases, such as ethers, alcohols, or amines, has been reported.[3,4]

Silylenes with two different substituents, R^1R^2Si:, are prochiral, and addition of alcohol (or insertion of silylenes into an alcoholic RO−H bond) should create chirality on the silicon. In particular, if one of the two substituents is chiral, a diastereotopic face can be defined and diastereoselective addition of alcohol would be expected.[5] Indeed, we reported recently the successful diastereoselective addition of alcohol to silylenes.[6] Because the selectivity in this procedure is governed essentially by the steric demand of the substituent on the silylene and/or alcohol, it is not easy to control the selectivity for a given combination of silylene and alcohol. We report in this paper that Lewis bases are powerful tools for controlling the diastereoselective addition of alcohol to silylenes, resulting in the reversal of the steric course.[7−9]

Results and Discussion

A prochiral silylene was generated by photoirradiation with 254 nm light of a trisilane[10] with the chiral substituent **1** in the presence of *t*-BuOH as a trapping reagent and Lewis bases, as shown in eq 1. Addition of alcohol to the silylene gave the expected adducts **2**. In this reaction, four diastereomers, or two pairs of enantiomers were obtained, where 1*R*,2*R*/1*S*,2*S* and 1*R*,2*S*/1*S*,2*R* were defined as the A and B isomers, respectively. The ratio of diastereomers was determined by GC with a capillary column. The results are summarized in Table 1. Addition of alcohol to the silylene proceeded in a diastereoselective manner. For example, the photoreaction of **1** with *t*-BuOH in the absence of Lewis bases at −75 °C gave a 1:1.99 mixture of A and B isomers (entry 1), which could be interpreted as reported before:[6] i.e., the selective addition of alcohol to the silylene takes place from the less hindered face and results in formation of **2B** as the major product (1*R*,2*S*/1*S*,2*R*), as shown in path a of Scheme 1, where one of the stereoisomers is illustrated.[11] However, in the photoreaction of **1** with *t*-BuOH in the presence of a large excess of Me_2S as a Lewis base at −78 °C, the ratio of the diastereomers decreased to 1.43 (entry 2). In the presence of a large excess of 2-MeTHF, a slight

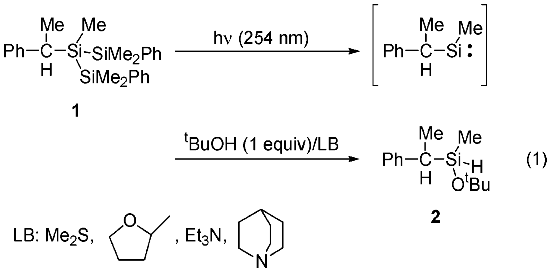

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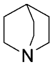
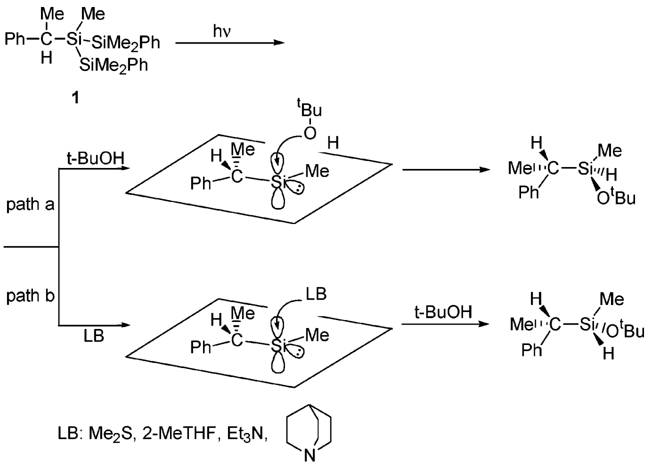
Table 1. Addition of *tert*-Butyl Alcohol to Silylenes Generated in the Photolysis of 1 and 3 in Hexane

entry	precursor	ROH (amt, equiv)	additive (amt, equiv)	*T* (°C)	[B]/[A][a]
1	**1**	*t*-BuOH (1)	*b*	−75	1.99
2			Me_2S (20)	−78	1.43
3			2-MeTHF (20)	−78	0.91
4			Et_3N (20)	−78	0.65
5			 (20)	20[c]	0.56
6	**3**	*t*-BuOH (0.5)	*b*	−78	0.49
7		(4)	*b*	−78	0.49
8		(20)	*b*	−78	0.51
9		(4)	*b*	18	0.49

[a] The isomer ratio was determined by GLC. [b] No additive. [c] The low solubility of quinuclidine in hexane hampered a reaction run at −78 °C.

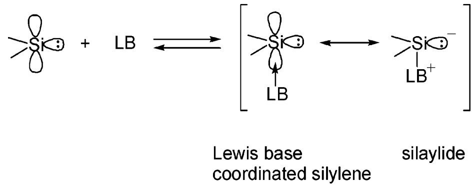
Scheme 1



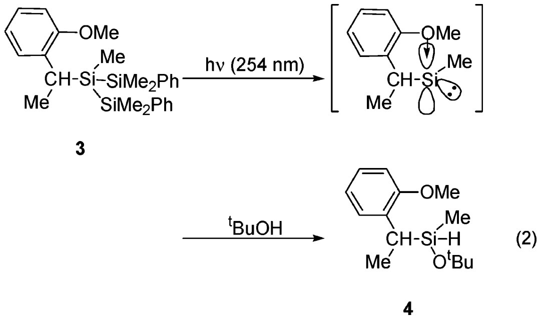
predominance of **2A** over **2B** was observed; the [B]/[A] ratio was 0.91 (entry 3).[12] Furthermore, in the presence of amines such as triethylamine and quinuclidine as Lewis bases, the reaction also proceeded in a diastereoselective manner and then the [B]/[A] ratios were found to be 0.65 and 0.56 under the given conditions, respectively (entries 4 and 5). The reversal in selectivity of about 1:2 obtained at −78 °C is approximately 0.6 kcal/mol, because the selectivity of 2:1 corresponds to a ΔG value of 0.3 kcal/mol at −78 °C, based on the previous study.[6] The trend of the selectivity was in good agreement with the strength of the interaction between silylenes and Lewis bases (amines > ethers > sulfides).[3,13]

The tentative reaction pathway for the addition reaction of alcohols to silylenes in the presence of Lewis bases is shown in path b of Scheme 1. Most probably, the reversal in the stereoselectivity results when the Lewis base coordinates intermolecularly to the silylene from the less hindered face, after which the addition of alcohol to the silylene takes place, although the silylene has many available conformations, each of which could be reactive. The stereochemistry of the major isomer should be 1*R*,2*R*/1*S*,2*S*. A detailed description of the mechanism based on, for example, theoretical calculation requires further study.

In the addition reaction of alcohols to silylenes in the presence of Lewis bases, a large excess of the Lewis base was used and then the Lewis base easily coordinated intermolecularly to the silylene. The Lewis base−silylene complexes could be described as silaylides, in which the silicon center has a nucleophilic character rather than an electrophilic character. In practice, however, examples of nucleophilic silylenes are limited,[14,15] and the electronic character of silylenes appears to dominate their reactivity in the reaction.



Next, we designed another silylene precursor, **3**, where the oxygen atom on the phenyl group could serve as a Lewis base to coordinate intramolecularly to the silylene.[16] The photoreaction of **3** with *t*-BuOH at −78 °C proceeded smoothly to give a mixture of trapping products **4** (eq 2), and a clear diastereoselectivity was observed. Isomer **4A** was formed as a major adduct in the reaction, and the ratio of [B] to [A] was found to be 0.49 (entry 6 in Table 1),[17] where the pair 1*R*,2*R*/1*S*,2*S* and 1*R*,2*S*/1*S*,2*R* could also be defined as isomers A and B. The diastereoselectivity was somewhat high compared with that observed for the foregoing intermolecular counterparts, where the diastereoselectivity was almost independent of the concentration of alcohol (entries 6−8). The reaction, even at room temperature, also gave **4A** with a diastereomer ratio of 0.49 (entry 9). These results are suggestive of intramolecular coordination of the Lewis base to the silylene.[18]



In summary, we have demonstrated diastereoselective alcohol addition to silylenes where inter- or intramolecular coordination

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(11) The stereostructure of the major isomer was definitely determined by NOE spectra and X-ray crystallographic analysis of the related compounds, and details of the stereochemical course of the reaction were discussed.[6]

(12) The photolysis of precursor **1** in hexane with *t*-BuOH in the presence of 2-MeTHF gave **2** with a ratio of [B]/[A] = 1.16 at 21% conversion and [B]/[A] = 1.15 at 75% conversion at room temperature. This indicates that no secondary photochemical reaction occurred at all under these conditions. **2** was obtained in 7% yield at 48% conversion.

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(17) The diastereoselectivity of alcohol addition to the silylenes was independent of the conversion of **3**, indicating that no secondary photochemical reaction occurred at all under these conditions. The trapping product **4** was obtained in 24% yield at 21% conversion.

(18) An attempt to isolate the silylene−base complex in a 3-methylpentane matrix failed.

of Lewis bases plays a crucial role in controlling the steric course. We believe that the present finding will provide a useful tool in the reaction chemistry of silylenes. Further extension in this area is in progress in our laboratories.

Experimental Section

General Procedure. All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon or nitrogen. All solvents were distilled over appropriate drying agents prior to use. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{29}Si NMR (59.6 MHz) spectra were recorded on a Bruker DPX300 spectrometer at ambient temperature. ^{1}H and ^{13}C chemical shifts were referenced to solvent residues (^{1}H at δ 7.24 ppm and ^{13}Ca t δ 77.0 ppm for $CDCl_3$). ^{29}Si NMR chemical shifts were reported in ppm relative to internal Me_4Si (0 ppm). GC was carried out on a Shimadzu GC 17A instrument (HP-5 5% phenylmethysilicone, SUS column 0.32 mm i.d. × 30 m). GC-MS was carried out on a Shimazu GC-MS 17A/QP-5000 mass spectrometer. High-resolution mass spectra were obtained with a JEOL JMS-700 mass spectrometer at an ionization potential of 70 eV. IR spectra were recorded on a HORIBA FT/IR 730 spectrometer.

All solvents and reagents were of reagent quality, purchased from commercial sources and used without further purification, unless otherwise noted below. THF was dried and distilled from sodium/benzophenone just before use. Hexane was distilled from calcium hydride. **1** and **2** were prepared according to the previously reported procedures.[6]

Synthesis of the Photochemical Precursor 1,1,2,3,3-Pentamethyl-1,3-diphenyl-2-(1-(2-methoxyphenyl)ethyl)trisilane (3). To methyltrichlorosilane (3.0 g, 20 mmol) in hexane was added a THF solution of (1-(2-methoxyphenyl)ethyl)lithium[19] (9.3 mmol) at 0 °C. After 10 min the solvent and excess methyltrichlorosilane were removed in vacuo. To the residue was added a THF solution of (phenyldimethylsilyl)lithium (38 mmol), and the mixture was stirred for 10 min at room temperature. After the usual workup, the resulting mixture was subjected to column chromatography on silica gel (3/1 hexane/toluene) gave **3** as a colorless oil (84 mg, 20%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.07 (s, 3H, $SiSiCH_3Si$), 0.13 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.21 (s, 3H, $SiCH_3$), 0.25 (s, 3H, $SiCH_3$), 1.21 (d, $J = 7.8$ Hz, 3H, $CHCH_3$), 2.90 (q, $J = 7.8$ Hz, 1H, CH_3CH), 3.61 (s, 3H, $O-CH_3$), 6.50−7.30 (m, 4H, MeO*Ph*), 7.25−7.37 (m, 12H, Si*Ph*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −8.5, −2.7, −2.6, −2.2, −2.0, 17.6, 17.7, 54.6, 109.5, 120.4, 125.0, 127.3, 127.5, 127.6, 128.2, 128.3, 133.9, 134.0, 135.4, 140.1, 140.3, 155.5. ^{29}Si NMR ($CDCl_3$, 59 MHz): δ −36.3, −18.5, −18.1. MS (20 eV): *m/z* (%) 316 ($M^+ - 132$, 10), 315 (28), 314 (100), 298 (3.5), 283 (3.5), 268 (2), 255 (10), 193 (13), 178 (6), 135 (26). Anal. Calcd for $C_{26}H_{36}OSi_3$: C, 69.58; H, 8.08. Found: C, 69.81; H, 8.07.

Synthesis of an Authentic Sample of (1-(2-Methoxyphenyl)-ethyl)methyl-*tert*-butoxysilane (4). **4** was independently prepared and then confirmed by comparing the spectroscopic data and the retention time on the GC with a capillary column. A mixture of (1-(2-methoxyphenyl)ethyl)methylchlorosilane (1.02 g, 4.75 mmol), *t*-BuOH (1.27 g, 17.2 mmol), and triethylamine (0.60 g, 5.98 mmol) in hexane (20 mL) was stirred for 2 h at room temperature. After the mixture was filtered and evaporated, Kugelrohr distillation gave **4** as a colorless oil (420 mg, 40%). Bp: 120−135 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.03 (s, 3H, $SiCH_3$), 1.23 (s, 9H, $O-C(CH_3)_3$), 1.30−1.45 (m, 3H, $CHCH_3$), 2.62−2.82 (m, 1H, Si*H*), 3.80 (s, 3H, OCH_3), 4.45−4.55 (m, 1H, CH_3CH), 6.75−7.15 (m, 4H, Ar *H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −3.62, −1.85, 13.5, 14.6, 21.5, 21.7, 31.2, 31.3, 55.0, 55.1, 72.2, 72.3, 109.6, 109.7, 120.4, 120.5, 125.2, 125.3, 127.1, 127.4, 133.1, 133.4, 156.3, 156.4. ^{29}Si NMR ($CDCl_3$, 59 MHz): δ −6.65, −4.15. MS (20 eV): *m/e* (%) 252 (M^+, 18), 181 (100), 163 (74), 149 (13), 135 (16), 105 (11), 91 (20), 61 (68). High-resolution MS: calcd for $C_{14}H_{24}O_2Si$, *m/e* 252.1552; found, *m/e* 252.1555.

Photoreaction. A typical photolysis of **1** is as follows. A solution of **1** (18.4 mg, 4.40×10^{-5} mmol), *t*-BuOH (3.26 mg, 4.40×10^{-5} mmol), and 2-methyltetrahydrofuran (75.5 mg, 9.46×10^{-4} mmol) in hexane (2 mL) in a quartz tube (7 mm i.d.) was bubbled with nitrogen gas and then irradiated with a low-pressure Hg arc lamp (125 W) at −78 °C. After irradiation, tetracosane (1 mg) as a standard was added to the mixture. Then the reaction mixture was analyzed by GLC with a capillary column.

A typical photolysis of **3** is as follows. A solution of **3** (20.0 mg, 4.45×10^{-5} mmol) and *t*-BuOH (65.1 mg, 8.90×10^{-4} mmol) in hexane (2 mL) in a quartz tube (10 mm i.d.) was bubbled with nitrogen gas and then irradiated with a low-pressure Hg arc lamp (125 W) at −78 °C. After irradiation, tetracosane (1 mg) as a standard was added to the mixture. Then the reaction mixture was analyzed by GLC with a capillary column.

Acknowledgment. We thank the Ministry of Education, Culture, Sports, Science, and Technology of Japan for financial support.

Supporting Information Available: Figures giving spectroscopic details for **3** and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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