

Diastereoselective Addition of Alcohol to Diastereotopic Silylenes

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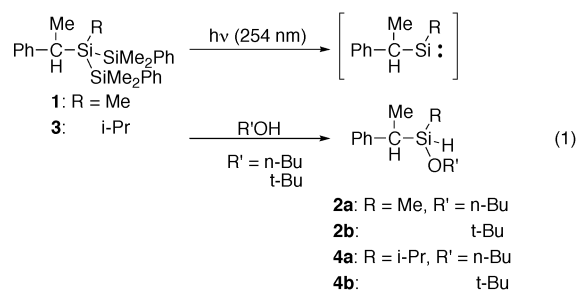
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Silylenes with two different substituents, R¹R²Si:, are prochiral, and addition of alcohol (or insertion of silylenes into an alcoholic RO–H bond) should create chirality on the silicon.¹ In particular, if one of the two substituents is chiral, a diastereotopic face could be defined, and diastereoselective addition of alcohol could be expected. However, no such example has been reported either for silylenes or for carbenes and germynes.^{1,2} We report herein the successful example of diastereoselective addition of alcohol to diastereotopic silylenes.

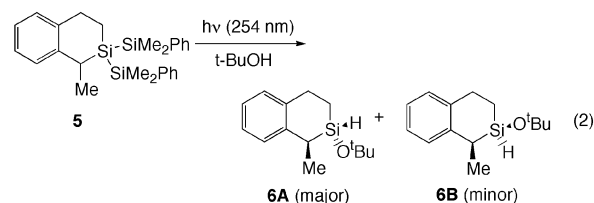
To generate the requisite silylenes, trisilanes with a chiral substituent, **1** and **3**, were synthesized as the photochemical precursors.³ A series of diastereotopic silylenes was generated by photoirradiation of the trisilanes with 254 nm light in the presence of *t*-BuOH or *n*-BuOH as a trapping reagent, as shown in eq 1. Addition of alcohol to these silylenes gave the expected products.⁴ In this reaction, four diastereoisomers or two pairs of enantiomers were obtained, because the silylene precursors were racemic.⁵ The ratio of these two isomers was determined by GC with a capillary column. For example, the photolysis of precursor **1** in hexane with *t*-BuOH gave **2b** with diastereoisomer excess (de) of 19% at 28.5% conversion and 18% at 49.2% conversion at room temperature.⁶ This indicates that no secondary photochemical reaction occurred at all under these conditions. The diastereoselectivity of alcohol addition to the silylenes is also not dependent on the concentration of alcohol (see Supporting Information). This suggests that the stereochemistry of the products is determined by the primary diastereofacial selection of the alcohol, because an intra- and intermolecular transfer of the proton⁷ gave the same products. It is rather surprising to find such a highly biased value for the diastereoselectivity.

The results are summarized in Table 1. Interestingly, alcohol addition to the silylene proceeded in the diastereoselective manner with a high value, where the ratio of diastereomers is found to depend on the substituent groups on the silylene and/or alcohol. For example, for *n*-BuOH addition to the *i*-Pr-substituted silylene at room temperature, the de of **4a** was estimated to be 9%, but the de of **4b** was 26% for *t*-BuOH. However, in the photoreaction of **1** with *n*-BuOH, almost no selectivity was observed. The temperature dependence of the isomer ratio, as well as effects of the steric demand of alcohol, were also examined. Indeed, fairly high diastereoselection was observed, and the stereoselectivity gradually increased with a decrease in temperature, especially for **4b**, the largest de being 52% at –76 °C.

To elucidate the reaction pathway, analysis of the configuration of the trapping products was required. However, the stereochemical structure for the diastereoisomers of **2** and **4** is difficult to determine at the present stage because no crystals were obtained for these isomers. Next, we designed a cyclic silylene with asymmetric chiral



carbon, **5**, which could give a cyclic trapping adduct **6**, as shown in eq 2. The de was found to be 24% at room temperature under similar photochemical reaction conditions. Each cyclic trapping product **6** could be separated, and the stereochemistry was analyzed by NOE spectra (see Supporting Information). The stereochemistry of the major isomer was found to be **6A**, where the H– and the *t*-BuO– group on the silicon atom are located on the same side of the ring structure. This indicates that the alcohol addition to the cyclic silylene occurred on the less hindered side to produce the **6A** isomer predominantly in the reaction.



Finally, the stereostructure of the trapping products could be definitely determined by X-ray crystallographic analysis of **8A**, which was obtained by photolysis of **7** with 2,6-dimethylphenol as a major product, as shown in eq 3. Figure 1 shows the ORTEP drawing of **8A**.⁹ Thus, the stereochemistry was determined to be 1*R*2*R*/1*S*2*S*.¹⁰

Table 1. Addition of Alcohol to Diastereotopic Silylenes Generated in the Photolysis of **1** and **3**

entry	R	R'OH	T/°C	de/% ^{a,b}
1	Me	<i>n</i> -BuOH	20	0
2		<i>t</i> -BuOH	20	19
3			–75	33
4	<i>i</i> -Pr	<i>n</i> -BuOH	20	9
5		<i>t</i> -BuOH	20	26
6			–14	32
7			–30	35
8			–45	39
9			–62	46
10			–76	52

^a Determined by GLC. ^b Each isomer is not assigned for stereostructures.

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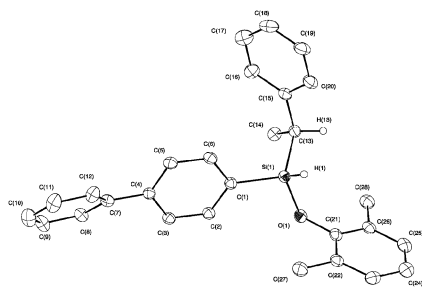
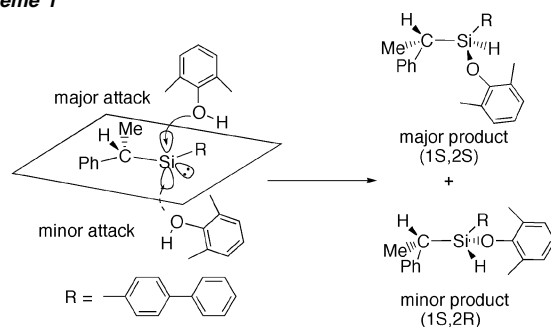
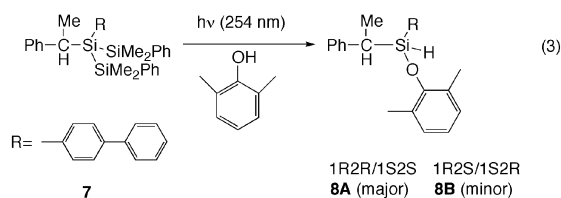


Figure 1. ORTEP drawing of **8A**.

Scheme 1

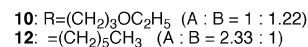
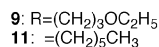
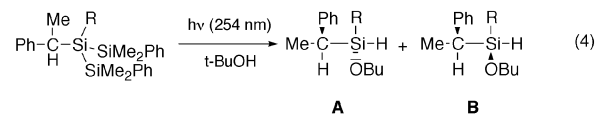


The diastereoselectivities could be rationalized by reference to the mechanism shown in Scheme 1. The selective addition of alcohol to the silylene takes place from the less hindered face.



Next, the diastereoselective addition of alcohol to a silylene with an etheral substituent was examined, where the oxygen atom can coordinate intermolecularly to the silylene. The photoreaction of **9** with *t*-BuOH at $-60\text{ }^{\circ}\text{C}$ proceeded smoothly to give a mixture of trapping products (eq 4). Interestingly, a slight predominance of **10B** over **10A** was observed; the ratio of **A**:**B** was 1:1.22. However, the photoreaction of **11** with *t*-BuOH at $-60\text{ }^{\circ}\text{C}$ gave a 2.33:1 mixture of **A** and **B** isomers, which could be interpreted in the same way as that described above. Most probably, the antistereoselectivity in the reaction of **9** results when the oxygen atom on the ether group coordinates to the silylene from the less hindered face, after which the addition of alcohol to the silylene takes place.

Thus, we have demonstrated the clear example of diastereoselectivity in the reaction of group 14 divalent reactive intermediates. Details of the mechanism will be reported in due course. Further work is in progress.



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Supporting Information Available: Experimental details, spectroscopic and analytical data for **1–11**, dependence of de on concentration of alcohol, Arrhenius plots of the diastereomers of **2b** and **4b**, ^1H NMR NOE difference spectra of **6**, ^1H – ^{13}C COSY spectra of **6**, crystal packing of **8A** (PDF), and crystallographic file of **8A** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) The inversion process of the anionic silicon after the attack of alcohols may be impossible, because the barrier to inversion of the silyl anions is normally high, see: Lambert, J. B.; Urdaneta-Pérez, M. *J. Am. Chem. Soc.* **1978**, *100*, 157.
- (9) Crystal data for the major isomer at 120 K: MF = $\text{C}_{28}\text{H}_{28}\text{OSi}$, MW = 408.59, monoclinic, $P2_1/n$, $a = 9.4120(6)\text{ \AA}$, $b = 19.5450(12)\text{ \AA}$, $c = 12.8760(7)\text{ \AA}$, $\beta = 105.840(4)^\circ$, $V = 2278.7(2)\text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.191\text{ g/cm}^3$. The final R factor was 0.0600 for 5455 reflections with $I_0 > 2\sigma(I_0)$ ($R_w = 0.0845$ for all data).
- (10) The stereochemistry of the major isomer of **2** and **4** is 1R2S/1S2R, because the Me and *i*-Pr groups on the silylene have sterically lower priority than the phenylethyl group.

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