Communications to the Editor

Stereo- and Regiochemistry of Aldehyde Insertions into the C−Si Bonds of Siliranes

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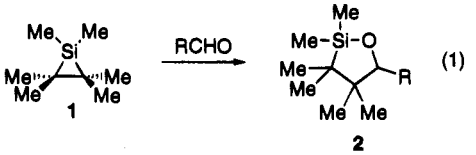
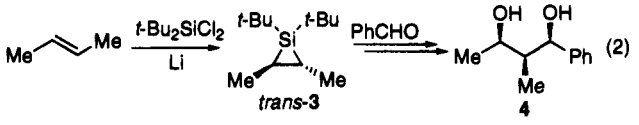
During investigations of the basic reactivity of siliranes, Seyferth observed that hexamethylsilirane (**1**) undergoes insertion of aldehydes to afford oxasilacyclopentane **2** (eq 1).[1,2] Since this silirane was the only one examined, the stereochemistry and regiochemistry of this carbon−carbon bond-forming process have not been investigated, although this information would provide vital clues about the reaction mechanism. In fact, little is known about the scope of silirane chemistry.[2−8] We have discovered that siliranes undergo stereochemically and regiochemically defined insertions of aldehydes, and the outcome is determined by the reaction conditions. Furthermore, siliranes were used for the synthesis of diols such as **4** in two steps (aldehyde insertion and oxidation) from the silirane *trans*-**3**, which can be obtained by silacyclopropanation of (*E*)-2-butene (eq 2).[9]

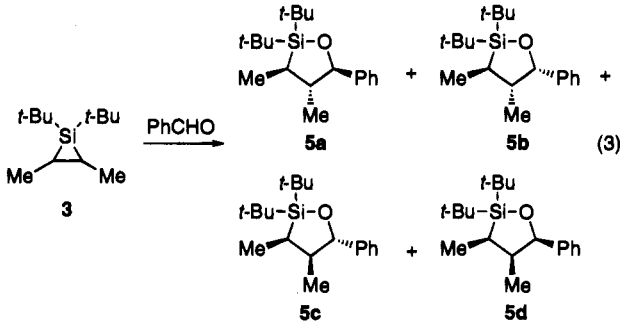




The observations of Seyferth *et al.* suggest that the reactions of silirane **1** with aldehydes proceed via diradical intermediates.[10] However, siliranes **3** may react by different pathways. The reaction of *trans*-**3** with benzaldehyde at 100 °C proceeded predominately with retention of configuration, affording a mixture of oxasilacyclopentanes **5a−d** as a 75:7:8:10 mixture in 52% yield after chromatography (eq 3, Table 1).[11] The major product, **5a**, possesses anti−anti stereochemistry. The reaction of *cis*-**3**[9] with benzaldehyde afforded the same major product, but oxasilacyclopentanes **5a−d** were obtained as a 48:6:32:14 mixture. Although the thermal reaction is not stereospecific, *cis*- and *trans*-**3** afford different product distributions, suggesting that if the reaction proceeds by carbanion or radical pathways, severe constraints must be placed on the lifetimes of reactive intermediates.

Table 1. Stereoselectivity of Insertion of PhCHO into Siliranes (Eq 3)

silirane	conditions	5a	5b	5c	5d
trans-**3**	100 °C	75	7	8	10
cis-**3**	100 °C	48	6	32	14
trans-**3**	25% KO*t*-Bu/18-crown-6	3	1	13	83
cis-**3**	10% KO*t*-Bu/18-crown-6	69	30	<1	<1



Because of the forcing conditions necessary for the thermal aldehyde insertion, various catalysts were investigated to facilitate this process. When a catalyst such as *tert*-BuOK/18-crown-6 (10−25 mol %) was added to a solution of *trans*-**3** and benzaldehyde in THF at 22 °C,[12] *inversion* of stereochemistry was observed: the products **5a−d** were obtained as a 3:1:13:83 mixture of diastereomers, favoring the syn−syn diastereomer **5d** (54% yield after chromatography). Under similar conditions, *cis*-**3** also underwent inversion, affording a 69:30:<1:<1 mixture of diastereomers of oxasilacyclopentanes **5a−d** (73% yield, eq 3, Table 1), with the anti-anti isomer **5a** dominating. Therefore, in the catalyzed reaction, 96% and 99% inversion of stereochemistry was observed for the *trans*- and *cis*-siliranes, respectively, which contrasts dramatically with the stereochemical outcome of the thermal reactions.[13,14] It should be noted that no isomerization of silirane was observed during either the thermal or catalyzed insertions.

Since C−Si bonds can be oxidized to C−O bonds with retention of configuration,[15] the conversion of oxasilacyclopentanes **5a−d** to the corresponding 1,3-diols would reveal the

(1) Seyferth, D.; Duncan, D. P.; Shannon, M. L. *Organometallics* **1984**, *3*, 579−583 and references cited therein.

(2) Similar reactions have been observed for alkylidenesiliranes: Saso, H.; Ando, W.; Ueno, K. *Tetrahedron* **1989**, *45*, 1929−1940.

(3) Seyferth, D.; Annarelli, D. C.; Shannon, M. L.; Escudie, J.; Duncan, D. P. *J. Organomet. Chem.* **1982**, *225*, 177−191.

(4) Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281−1288.

(5) Boudjouk, P.; Black, E.; Kumarathasan, R. *Organometallics* **1991**, *10*, 2095−2096.

(6) Boudjouk, P.; Black, E.; Kumarathasan, R.; Samaraweera, U.; Castellino, S.; Oliver, J. P.; Kampf, J. W. *Organometallics* **1994**, *13*, 3715−3727.

(7) Belzner, J.; Ihmels, H.; Kneisel, B. O.; Gould, R. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 305−311.

(8) Recently, there has been interest in the use of silacyclobutanes in synthesis: Myers, A. G.; Kephart, S. E.; Chen, H. *J. Am. Chem. Soc.* **1992**, *114*, 7922−7923. Denmark, S. E.; Griedel, B. D.; Coe, D. M.; Schnute, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 7026−7043 and references cited therein.

(9) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355−1356. The synthesis of siliranes **3** is operationally simple and efficient.

(10) Seyferth noted that silirane **1** reacted with aryl aldehydes under thermal conditions, but irradiation was needed for insertion into alkyl aldehydes (ref 1). This observation supported the viability of radical pathways.

(11) The stereochemical course of these reactions has been determined unambiguously. Each oxasilacyclopentane **5** was oxidized to the corresponding diol, the derived acetonides were analyzed (Evans, D. A.; Rieger, D. L.; Gage, J. R. *Tetrahedron Lett.* **1990**, *31*, 7099−7100. Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, *58*, 3511−3515), reference diols were prepared for comparison, and X-ray crystallography was employed. Full details are provided as supporting information.

(12) These conditions were inspired by insertions of aldehydes into silacyclobutanes: Takeyama, Y.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6059−6062.

(13) We have also determined that protonolysis of siliranes **3** occurs stereospecifically. Although they provided no evidence for siliranes, Jones *et al.* invoked them as reactive intermediates in the stereospecific conversion of alkenes, $(Me_2Si)_6$, and methanol into (*sec*-butyl)methoxysilanes: Tortorelli, V. J.; Jones, M., Jr.; Wu, S.-h.; Li, Z.-h. *Organometallics* **1983**, *2*, 759−764.

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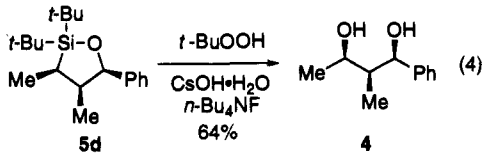
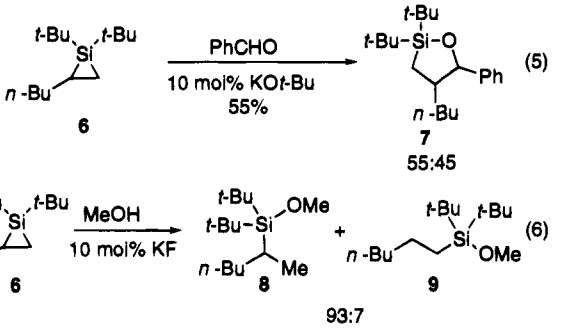
stereochemistry of the insertion as well as demonstrate a synthetic application of siliranes.[16] Although exposure of oxasilacyclopentanes such as **5d** to previously reported oxidation conditions (e.g., aqueous H_2O_2, KF, $KHCO_3$)[15] afforded only recovered starting material, treatment with *tert*-BuOOH, $CsOH{\cdot}H_2O$, and *n*-Bu_4NF in DMF at 75 °C afforded the corresponding 1,3-diol **4** stereospecifically in 64% yield (eq 4).[11,17] The successful oxidation demonstrates that both C–Si bonds of siliranes can be functionalized to form new carbon-carbon and carbon–oxygen bonds with stereochemical control.



(4)

Siliranes which are unsymmetrically substituted were also examined, since these compounds are more representative of what would be expected in synthetic applications. The catalyzed insertion of benzaldehyde into butylsilirane **6** (eq 5) shows high regioselectivity (85:15) for formation of the new bond at the more hindered carbon atom.[18] The product **7** was obtained as a 55:45 mixture of cis and trans isomers. It must be noted, however, that this regioselectivity is not exhibited for protonation of the silirane: fluoride-catalyzed[19] methanolysis of the silirane **6** cleaves the ring at the less substituted carbon (eq 6).[20]

At this stage, the origin of the selectivities of aldehyde insertion is not clear. Since the stereochemistry of the silirane is transferred to the product, particularly in the catalyzed reaction, it is likely that C–C bond formation and C–Si bond cleavage occur simultaneously. For the catalyzed reactions, our working mechanism involves alkoxide attack at the silicon atom,



affording a pentacoordinate siliconate.[21] Subsequent electrophilic attack of the aldehyde occurs with inversion.[22] The seemingly contrasteric regioselectivity observed for the unsymmetrical silirane insertion of benzaldehyde cannot be readily rationalized since methanolysis proceeds with opposite selectivity. Future experiments will probe the origin of these selectivities.

In conclusion, we have demonstrated that the aldehyde insertion reactions of siliranes proceed with stereo- and regiochemical control, the exact course depending on reaction conditions. Furthermore, the oxasilacyclopentane products can be oxidized to afford 1,3-diols, suggesting that siliranes may be synthetic as well as reactive intermediates. With this basic knowledge of the stereo- and regiochemistry of silirane chemistry and its dependence on reaction conditions, we are exploring new reactions of siliranes in order to probe their mechanisms and applications in organic synthesis.

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Supporting Information Available: Listing of full spectral and experimental details for all new compounds as well as X-ray crystallographic data for **5d** and a derivative of **4** (33 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) Siliranes **3** insert other nonenolizable aldehydes with stereoselectivity. Significant amounts of products arising from hydride transfer from the silirane to the aldehyde were also produced. With enolizable aldehydes such as isobutyraldehyde, silyl enol ethers were obtained instead of oxasilacyclopentanes; similar enolizations were observed for **1** and ketones (ref 1).

(15) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694–1696.

(16) For a review covering the stereoselective synthesis of 1,3-polyols, see: Oishi, T.; Nakata, T. *Synthesis* **1990**, 635–645.

(17) These conditions are much less sterically sensitive than the standard protocols. Details will be presented shortly.

(18) Similar regioselectivity was observed when fluoride was used as a catalyst, but the isolated yield of oxasilacyclopentane was significantly lower.

(19) Kumarathasan, R.; Boudjouk, P. *Tetrahedron Lett.* **1990**, *31*, 3987–3990.

(20) Boudjouk observed that thermolysis of methyl-substituted di-*tert*-butylsilirane in methanol afforded an approximately equimolar mixture of isomeric propylsilanes (ref 5).

(21) For a review covering penta- and hexacoordinate silicon compounds, see: Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448.

(22) Inversion of configuration has been observed for bromination of organopentafluorosiliconates with NBS: Tamao, K.; Yoshida, J.-i.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics* **1982**, *1*, 355–368.