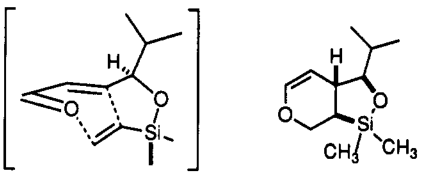


26

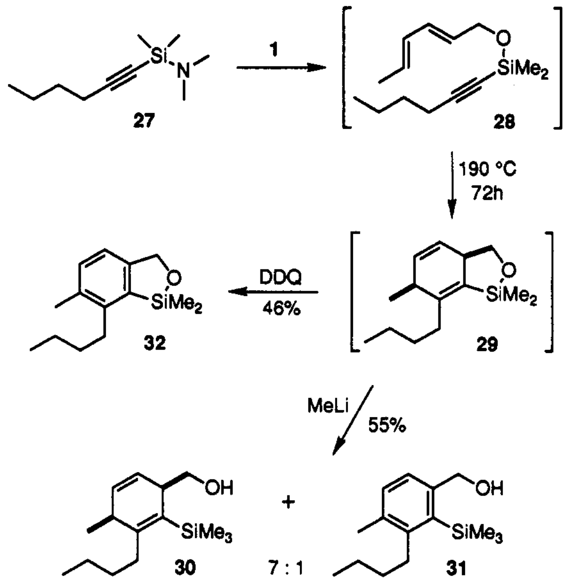
Figure 1.

products, and the di-*tert*-butylsilyl group results in largely the exo-derived product with an isomer ratio of 1:4.[18] In contrast, cycloaddition of the dimethylvinylsilyl ether of dienol **17** yields a predominantly exo product, and increasing the size of the silicon substituent progressively increases the selectivity of the cycloaddition. Changing methyl to phenyl changes the ratio of isomers from 1:4 to 1:10, while a di-*tert*-butylsilyl group results in the formation of a single isomer.[19]

Entries 8 and 9 illustrate the use of a heterodiene[20] and the effect of a stereogenic center. Dioxene alcohol **20**, prepared by the method of Funk,[21] was subjected to our standard conditions with both dimethyl and diphenylvinylsilanes. In both cases the expected retro-DA-DA-Tamao oxidation sequence proceeded smoothly and only a single isomer could be detected for compound **26** or the final product **21**. The relative configurations were confirmed by X-ray crystallography.[22] This isomer presumably results from a transition state that minimizes nonbonding interactions (Figure 1).

Initial evaluation of alkynyl silanes[23] as dienophiles in this reaction sequence has found these to be similarly useful. The rate of cycloaddition for **28** is slower than for the vinylsilanes, requiring 72 h at 190 °C for complete reaction. The cyclohexadiene product **29** (Scheme III) is also more labile, suffering significantly from aromatization under the reaction conditions. Addition of BHT (5 mol %) to the solution largely eliminates this problem. Thermolysis followed by treatment with methyllithium yields cyclohexadiene **30** (55%), contaminated with 15% of the aromatized **31**. Compound **31** is not observed in the crude reaction mixture but appears to have formed during isolation. Treatment of the crude thermolysis product with DDQ serves to aromatize cyclohexadiene **29**, and **32** is isolated in 46% yield. The heterocyclic ring of **32** is surprisingly stable to chromatography, in view of our experience with **4**, and does not suffer from hydrolysis of the silyl ether during silica gel chromatography.

Scheme III



We have demonstrated the efficiency of an intramolecular Diels–Alder reaction of vinylsilyl ethers for assemble of uniquely functionalized intermediates. Several key features of the reaction have been elucidated, including the effect of tether length, the control of stereogenesis by alkyl substituents on silicon, as well as by a stereogenic center on the tether. Alkynyl silyl ethers appear to be similarly useful.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research through grants 22739-G1 and 25375-AC1. The authors would like to thank Dr. Kenneth J. O'Connor for helpful discussions. Assistance with X-ray analysis was provided by Professor Stephen Koch and Michael Rickenbach. The Bruker AC-250 NMR was obtained with instrumentation grants from the NIH (RR05547A) and the NSF (CHE 8911350) and with support of the Center for Biotechnology and from SUNY Stony Brook. The X-ray diffractometers were purchased with a grant from the NIH (RR05859).

Supplementary Material Available: Detailed experimental procedures for the preparation of **6–9** and physical data for compounds **6–9**, **11–14**, **16**, **18**, **19**, **21**, and **30–32** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(18) The assignment of cis and trans ring fusion is based on the expected effect of steric interactions and a striking resemblance of the NMR spectra of cycloaddition products **4** with the DA products derived from allyl 2,4-hexadienyl ether. We thank Dr. Kenneth J. O'Connor for providing copies of these spectra: O'Connor, K. J. Ph.D. Thesis, University of Rochester, 1989.

(19) Compounds **22c**, **23c**, **24c** and **25c** have proven resistant to oxidation of the silicon–carbon bond. The effect of the steric environment on the oxidation of silicon–carbon bonds is currently under investigation.

(20) For examples see: Martin, S. F.; Benage, B.; Geraci, L. S.; Hunter, J. E.; Mortimore, M. *J. Am. Chem. Soc.* **1991**, *113*, 6161 and references cited therein. For a review of the thermal cycloaddition chemistry of unsaturated carbonyl compounds see: Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651.

(21) Funk, R. L.; Bolton, G. L. *J. Am. Chem. Soc.* **1988**, *110*, 1290.

(22) The authors have deposited atomic coordinates for compounds **18** and **21** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

(23) Prepared by the method of Stork and Keitz: Stork, G.; Keitz, P. F. *Tetrahedron Lett.* **1989**, *30*, 6981.

Addition of Germylenes to α,β-Unsaturated Acetals: A Net [2,3] Sigmatropic Rearrangement

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Received June 19, 1992

Summary: Addition of germanium dichloride dioxane complex to α,β-unsaturated acetals gives β-dichloroalkoxygermane enol ethers via a net [2,3]-sigmatropic rearrangement.

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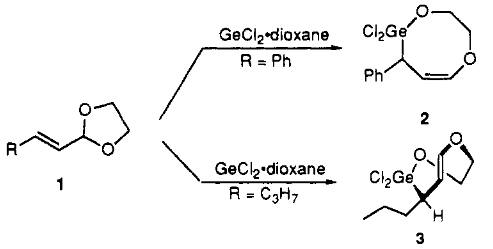
We previously reported that tin(II) chloride dihydrate efficiently converts α,β-unsaturated acetals to the corresponding aldehydes.[1] Subsequent studies have shown that reaction of germanium(II) chloride with α,β-unsaturated acetals leads to dichloroalkoxygermanes via a net [2,3] sigmatropic rearrangement.

Germanium(II) compounds are useful reagents in organometallic synthesis.[2] They display reactivity similar to carbenes and silylenes and can insert into hydrogen–halogen,[3] carbon–halogen,[4] metal–halogen,[5] metal–hydride,[6] and metal–metal bonds.[7] Due to its ease of preparation, germanium(II) chloride is one of the most commonly used germylenes. It reacts with olefins, alkynes, and other unsaturated organic molecules to give organogermanium polymers.[8] In some cases, germanium(II) chloride promotes self-condensation reactions between carbonyl compounds or imines.[9]

We have observed that germanium(II) chloride dioxane complex[10] may behave like a Lewis acid. In the presence of germanium(II) chloride, for example, citronellal cyclizes to isopulegol in quantitative yield.[11] Similarly, addition of ethyl diazoacetate to a mixture of an aldehyde and germanium(II) chloride yields a β-keto ester.[12] Germanium(II) chloride proved too reactive toward α,β-unsaturated aldehydes, however, yielding polymerization products.

We discovered that α,β-unsaturated acetals behave quite differently in the presence of germanium(II) chloride than their aldehyde precursors. When germanium(II) chloride dioxane complex was added to 2-(2(*E*)-phenethylenyl)-1,3-dioxolane (1), germacycle 2 was obtained stereoselectively and in high yield (eq 1, Table I).[13] The cis stereochemistry, in this case, was assigned based on the coupling constant of the enol protons (J = 5.0 Hz). In contrast, addition of germanium(II) chloride to the 1,3-dioxolane of *trans*-2-hexenal yielded enol 3 (J = 12.4 Hz) in a trans–cis ratio of 10:1 after 4 h, along with some minor decomposition products (eq 2). The stereochemical results in these two cases remained the same even when the reaction time was extended to 17 h.[14]

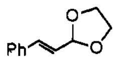
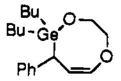
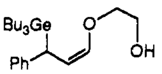
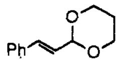
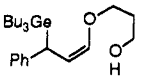
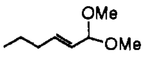
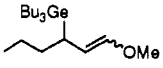
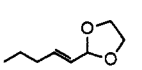
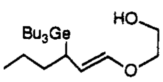
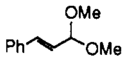
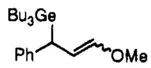
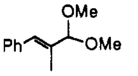
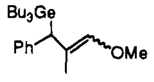


1

2 (1)

3 (2)

Table I. Di- and Tributyl Derivatives of Dichloroalkoxygermanes

acetal	product		cis:trans
		95%	>25:1[e]
		40%[a,c]	>25:1
		20%[a,d]	6:1[e]
		62%[b,g]	1:9[f]
		26%[b]	1:10[e]
		37%[b,h]	1:1[e]
		35%[b]	1:1[e]

[a] Procedure A. [b] Procedure B. [c] A 5:1 bis:trans ratio in 34% yield via procedure B. [d] A 3:2 cis:trans ratio via procedure B. [e] Derivatized after 4 h. [f] Derivatized after 30 min. [g] 70% 1:40, when reaction was run in Et_2O. [h] 52%, 1:5, when reaction was run in Et_2O.

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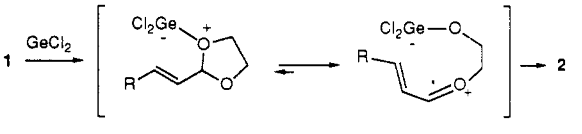
(13) Ph_3P–$GeCl_2$ and Et_3N–$GeCl_2$ did not react with 2-(2(*E*)-phenylethylenyl)-1,3-dioxolane.

(14) The trans enol 3 ether slowly decomposes under these conditions.

Reaction of germanium(II) chloride with α,β-unsaturated dimethoxy and diethoxy acetals yields acyclic dichloroalkoxygermanes. The stereoselectivity in these reactions is not as high, however, as that obtained with the corresponding dioxolanes. The dimethoxy acetal of cinnamaldehyde, for example, yielded a mixture of cis and trans enol ethers in a 4:1 ratio after 30 min; after a reaction time of 4 h the ratio was 1:1. Reaction of the dimethoxy acetal of *trans*-2-hexenal with germanium(II) chloride gave a mixture of cis–trans enol ethers in a ratio of 1:9. Once again, the ratio of enol ethers was 1:1 when the reaction time was increased to 4 h.

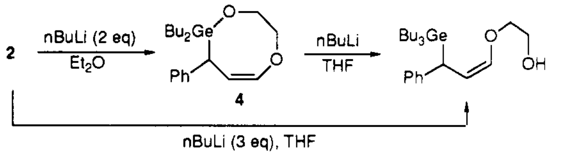
The mechanism of the rearrangement is thought to begin with coordination of the Lewis acidic germanium to an acetal oxygen forming an ylide (eq 3).[15,16] Stereochemical and equilibrium results suggest that the next step involves opening of the acetal to an oxocarbenium ion intermediate. Finally, conjugate addition of germanium to the α,β-unsaturated oxocarbenium ion yields the enol ether. Trans enol ethers predominate in reactions where the intermediate is stabilized by an n-aliphatic group. In contrast, cis enol ethers are formed in reactions when the intermediate is stabilized by an aryl group.



(3)

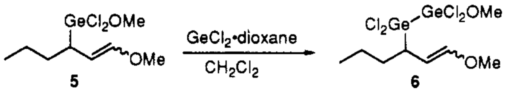
If an aldehyde is added to germacycle **2**, an acetal exchange reaction occurs. For example, addition of benzaldehyde to compound **2** yielded 2-phenyldioxolane along with a cinnamaldehyde–$GeCl_2$ polymer.[17] In addition, we observed partial conversion of **2** to the starting dioxolane, 2-(2(*E*)-phenethylenyl)-1,3-dioxolane, when the germacycle was dissolved in THF. Thus, these germacycles are relatively unstable and appear to exist in equilibrium with their α,β-unsaturated acetals.

Both the cyclic and acyclic dichloroalkoxygermanes produced in this reaction are labile. To provide additional support for our structure assignments, these compounds were converted to either a dibutyl or tributyl derivative.[18] For example, reaction of germacycle **2** with 2 equiv of *n*-BuLi in *diethyl ether* at −78 °C for 1 h gave **4** in good yield (eq 4). Preparation of the tributyl derivative could be done in one of two ways: (1) by adding 1 equiv of *n*-BuLi to **4** in *tetrahydrofuran* (procedure A) or (2) by adding 3 equiv of *n*-BuLi to **2** in *tetrahydrofuran* (procedure B).[19]



(4)

We have also observed that the enol ethers produced in this addition reaction will undergo further insertion chemistry with germanium(II) chloride. More specifically, a second equivalent of germanium(II) chloride can be inserted into the Ge–alkoxy bond of the first product (eq 5).



(5)

Furthermore, the insertion product can be obtained in a single step by reaction of the α,β-unsaturated acetal with 2 equivalents of germanium(II) chloride. Cyclic enol ethers, such as **2**, also give insertion products upon addition of a second equivalent of germanium(II) chloride.

Acknowledgment. We wish to thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (GM42732) for support of this research.

Supplementary Material Available: Representative procedures and compound characterization data (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[17] Control experiments show that germanium dichloride forms an oligomer with 2-phenyldioxolane. We conclude, therefore, that there is no germanium dichloride remaining in solution.

[18] Particularly in the acyclic acetal cases, it proved more helpful to prepare the tributyl derivatives. Mironov, V. F.; Berliner, E. M.; Gar, T. K. *Zh. Obshch. Khim.* **1969**, 2701; **1970**, 109. Lappert, M. F.; Sanger, A. R.; Power, P. P.; Srivastava, R. C. *Metal and Metalloid amides*, Wiley: Chichester, 1980.

[19] The alkoxide substituent on germanium can be displaced efficiently when the reaction is run in THF. However, THF allows **2** to equilibrate with starting material during the addition of butyllithium, thus decreasing the cis–trans ratio of the enol ethers. Rearrangement products that have an aliphatic substituent at the β-position, **3**, are less prone to isomerization in THF and can be derivatized with butyllithium without change in enol ether ratio.

Reactivity of *o*-Styryl Oxazolines with Nucleophiles

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Summary: The reaction of *o*-styryl oxazolines with organolithium reagents leads to conjugated addition to the exocyclic double bond in very good yields.

The oxazoline has proved to be an efficient auxiliary to achieve substitution in aromatic rings by displacement of an *o*-methoxy group with nucleophiles.[1] Oxazolines are also used to direct ortho metalation of aromatic rings in order to introduce electrophiles in this position.[1] Recently, Meyers and co-workers have been carrying out studies on the conjugated addition to naphthalene rings with an ox-

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[1] Reuman, M.; Meyers, A. I. *Tetrahedron* **1985**, *41*, 837.