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Novel Synthesis of Dienylsiloxanes. Stereoselective Synthesis of 3-Cyclohexene-1,2-diols by Intramolecular Diels−Alder Reactions of Siloxane-Tethered Bis-Dienes

Ruey-Min Chen, Wu-Wang Weng, and Tien-Yau Luh*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

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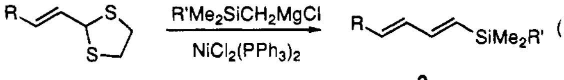
Organosiloxanes are unique due to their wide range of properties and variety of structural forms.[1] Indeed, the introduction of functional groups can facilitate modification of the polymer backbones such that the properties of these materials can be changed. Typically, organofunctional siloxanes have centered around a few selected groups of materials containing functionality such as halides, amines, alcohols, thiols, carboxylic acids, and vinyl groups.[1] To the best of our knowledge, no corresponding dienylsiloxane has been reported. As the silyl-substituted dienes can readily undergo regioselective hydrosilylation reactions to give 1,4-bis-silylbutadienes, further modification of these species would be versatile in organic synthesis. Intramolecular Diels−Alder cycloaddition has been shown to be extremely important for the construction of bicyclic skeletons.[2] The silyl ether or silylenedioxy bridges connecting a diene moiety with a dienophile group furnish a useful entry for the synthesis of functionalized cyclohexenes via the intramolecular cycloaddition followed by Tamao oxidation.[3] The corresponding siloxane-bridged substrates have not been previously reported. We recently reported a convenient synthesis of silyl-substituted conjugated dienes **2** from the corresponding allylic dithioacetals **1** (eq 1).[4] It is well documented that an alkyl silyl ether can be transformed into a siloxane under various conditions.[5] Accordingly, when the isopropoxy-substituted silylmethyl Grignard reagent[6] (R′ = ^{i}PrO, eq 1) is employed, the corresponding isopropoxysilyl-substituted dienes **2** (R′ = ^{i}PrO) can be further transformed into siloxane-tethered bis-dienes **3**. In continuation of our recent interest in the new synthetic application of silyl-sbustituted dienes,[7] we report an unprecedented stereoselective intramolecular Diels-Alder reactions of **3** followed by the Tamao oxidation to afford substituted cyclohexenediols **5**.



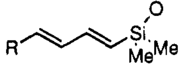
(1)

1 2

Table 1. Synthesis of 3-Cyclohexene-1,2-diols 5 from Allylic Dithioacetals 1

R	% yield 2[a]	3	4	5
Ph	88	64	62	75
4-MeOC$_6$H$_4$	80	60	50	74
2-MeOC$_6$H$_4$	88	60	45	70
trans-PhCH=CH	30	42	48	70

[a] R′ = OPr^i.



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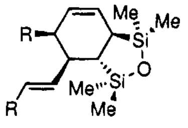

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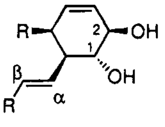
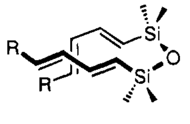
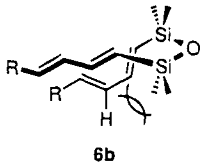


5

NiCl$_2$(PPh$_3$)$_2$-catalyzed reactions of **1** with (^{i}PrO)Me$_2$SiCH$_2$MgCl in THF under reflux for 16 h gave **2** (R′ = ^{i}PrO) in satisfactory yields. The corresponding trienes were prepared similarly. Treatment of **2** with 1 equiv of 0.5 M aqueous NaOH in THF under reflux for 4 h afforded **3** in moderate yield. It is noteworthy that an excess amount of the base resulted in poorer yield of siloxane **3**. A toluene solution of **3** was heated in a sealed tube (bath temperature 180 °C) for 48−60 h to give **4** in satisfactory yield. Bis-trienes also gave the corresponding cycloadduct. The results are summarized in Table 1. The stereochemical assignments for **4** were based on NOE experiments. It is noteworthy that the intramolecular cycloaddition is stereoselective, a single diastereomer being obtained. There are only limited examples in the literature on the intramolecular Diels−Alder reactions of acyclic bis-dienes.[8] Normally, the reaction leads to a mixture of regio- and stereoisomers. The high stereoselectivity for the reactions of **3** may arise from the relative stability of the transition state, conformer **6a** being more stable than conformer **6b**.



6a



6b

The reaction of **4** under conventional conditions[9] using a mixture of KF with H$_2$O$_2$ afforded the diol **5** in low yields. However, the sequence of the addition appeared to be important in this oxidation reaction. Thus, when the MeOH−THF solution of **4** was first allowed to react with 4 equiv of KHCO$_3$ and 20 equiv of 30% H$_2$O$_2$ followed

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by addition of 8 equiv of KF and the mixture was refluxed for 16 h, work up with 50% $Na_2S_2O_3$ afforded diol **5** in good yields. The results are also outlined in Table 1. The stereochemical assignments for **5** were based on NOE experiments. As expected, diols exhibited the same configuration as those in **4**.[9]

In summary, we have domonstrated an unprecedented approach for the convenient stereoselective synthesis of substituted 3-cyclohexene-1,2-diols. Further applications are in progress in our laboratory.

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Supplementary Material Available: Experimental procedures, compound characterization data, and ^1H NMR spectra of **5** (12 pages).

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