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Preparation of Polyenes with an Allylsilane Moiety Using 2-(Phenylsulfonylmethyl)-3-(trimethylsilyl)propene and Their Cyclization Reactions

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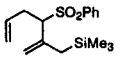
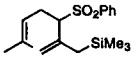
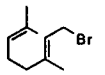
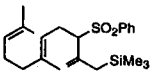
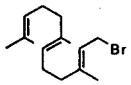
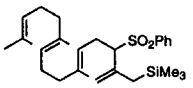
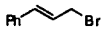
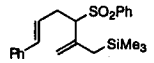
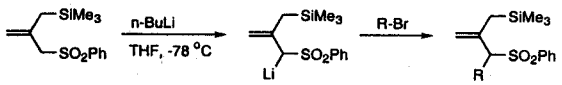
Lewis acid-induced intramolecular annulations of allylsilanes with an electrophilic terminus such as epoxide, aldehyde, ketone, enone, acetal, oxonium ion, and iminium ion were extensively applied for a regioselective formation of several ring systems.[1] However, the cyclization of allylsilane with simple alkene terminator is quite rare.[2] We describe herein the preparation of the polyenes with an allylsilane moiety **3** using 2-(phenylsulfonylmethyl)-3-(trimethylsilyl)propene (**1**) and their cyclizations to form methylenecycloalkanes. Compound **1** was readily prepared by the reaction of 2-(iodomethyl)-3-(trimethylsilyl)propene with sodium benzenesulfinate at 100 ℃ in N,N-dimethylformamide.[3] When the bifunctional reagent **1** was treated with *n*-butyllithium in THF at −78 ℃, α-lithiosulfone **2** was generated selectively and then treated with allylic bromides gave the correponding allylation products **3** in good yields (Table 1).

Table 1. Allylation of the bifuntional reagent **1**

Entry	Allylic bromide	Allylsilane **3**	Yield (%)
a			87
b			82
c			79
d			90
e			95

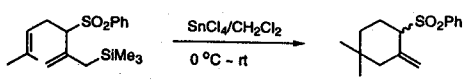
When the allylsilane **3b** was treated with stannic chloride (3 equivalents) in dichloromethane at 0 ℃ to room temperature, the methylenecyclohexane **4** was produced in 76% yield.[4] Due to complexation with the sulfone oxygens an excess of Lewis acid was required. The allylsilane cleanly cyclized to the cyclohexane having an exocyclic double bond. The regioselectivity in this reaction is controlled by the remarkable ability of silicon to stabilize a developing carbocation β to itself.[5] Stannic chloride appears to be the most promising Lewis acid for the cyclization of the allylsilanes **3**.



1 **2** **3**

In the ^{1}H NMR spectrum the two methyl protons of **4** appear at higher field (δ 0.82 and 1.02) than the methyl protons of **3b** (δ 1.54 and 1.62). This indicates that the methyl groups in **4** are bonded on sp^3 carbon atoms while the methyl groups in **3b** are attached to sp^2 carbon atoms.

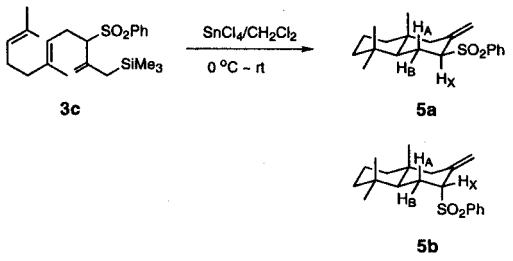
On the contrary, the reactions of the allylsilanes **3a** and **3e** with Lewis acid afforded only desilylated products.



3b **4**

Cyclization of **3c** under the same reaction conditions gave 8-methylenedecaline **5** in 75% yield.[6] Surprisingly, this reaction occurred stereoselectively, and only **5a** was formed between two possible epimers. The chemical shifts of the three methyls at δ 0.70, 0.78, and 0.86 in the ^{1}H NMR spectrum indicates that the methyl groups are no longer attached to olefinic carbon atoms. The stereochemistry at the C-7 pheny-

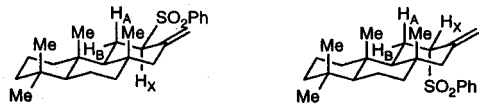
lsulfonyl group of the product **5a** clearly appears to be equatorial on the basis of the ^{1}H NMR data of the C-7 proton (δ 3.63, dd, J=12.2 and 3.8 Hz). The larger coupling constant (J=12.2 Hz) indicates that the proton Hx is located at the axial position. The shifts of the methyl protons to higher field in the cyclized product **5a** are also observed.



3c **5a**

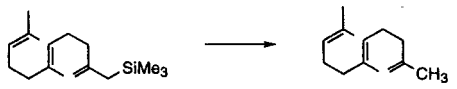
5b

The cyclization of **3d** was not stereospecific, and gave a diastereomeric mixture of 13-methyleneperhydrophenanthrenes **6** in 62% yield.[7] The epimers **6a** and **6b** were isolated by the repeated chromatography (silica gel, hexane : ether=1 : 1), and the ratio was 2 : 1. In the ^{1}H NMR spectrum of **6a** the four methyl protons appear at δ 0.79 (6H), 0.83 and 0.86, and the Hx proton appears at δ 3.59 as a double doublet (J=12.2 and 4.0 Hz). The ^{1}H NMR spectrum of **6b** has four peaks at δ 0.78, 0.80, 0.81, and 0.87 for the methyl protons, and a doublet at δ 3.73 (J=6.6 Hz) for the proton (Hx).



6a **6b**

To our surprise all attempts to cyclize the allylsilane **7** having no phenylsulfonyl group with stannic chloride or other Lewis acids failed. Only desilyation was occurred to produce **8** from **7**.[5] It is noteworthy that the phenylsulfonyl group play an important role in the cyclization process, however, the role is not clear at present time.



7 **8**

Acknowledgment. The present studies were supported by the Basic Science Research Institute Program, Ministry of Education, 1995, Project No. BSRI-95-3408 and LG Chem. Research Park.

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4. mp 97 ℃; ^{1}H NMR ($CDCl_3$) δ 0.08 (3H, s), 1.02 (3H, s), 1.78-1.98 (4H, m), 2.47-2.64 (2H, m), 3.63 (1H, d, J=5.6 Hz), 4.61 (1H, m), 4.88 (1H, s), 7.49-7.64 (3H, m), 7.82-7.87 (2H, m); ^{13}C NMR δ 22.15, 24.84, 29.15, 32.09, 34.61, 45.33, 67.84, 119.50, 129.17, 129.42, 133.87, 138.13, 139.23; MS m/e 264 (M^+, trace), 123 (100), 77 (38%).
5. For a comprehensive review, see: Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.
6. **5a**: mp 145-147 ℃; ^{1}H NMR ($CDCl_3$) δ 0.70 (3H, s), 0.78 (3H, s), 0.86 (3H, s), 0.99-1.96 (10H, m), 3.63 (1H, dd, J= 12.3, 3.8 Hz), 4.98 (1H, s), 5.53 (1H, s), 7.45-7.65 (3H, m), 7.91-7.95 (2H, m); ^{13}C NMR δ 18.88, 19.15, 21.55, 24.27, 32.76, 33.26, 36.11, 41.01, 42.13, 53.10, 55.46, 67.65, 113.08, 128.40, 129.00, 133.45, 136.90, 139.12; MS m/e 332 (M^+, trace), 191 (100), 77 (38%).
7. **6a**: mp 167 ℃; ^{1}H NMR ($CDCl_3$) δ 0.79 (6H, s), 0.83 (3H, s), 0.86 (3H, s), 0.87-1.95 (16H, m), 3.59 (1H, dd, J=12.2, 4.0 Hz), 4.97 (1H, s), 5.57 (1H, s), 7.52-7.65 (3H, m), 7.90-7.95 (2H, m); ^{13}C NMR δ 15.97, 18.41, 18.66, 20.41, 21.37, 23.20, 33.33, 36.53, 37.60, 39.48, 41.95, 42.35, 55.79, 56.90, 57.34, 67.50, 112.82, 128.39, 129.01, 133.44, 136.64, 139.10. **6b**: mp 165-167 ℃; ^{1}H NMR ($CDCl_3$) δ 0.78 (3H, s), 0.80 (3H, s), 0.81 (3H, s), 0.87 (3H, s), 0.97-1.87 (14H, m), 2.42-2.55 (2H, m), 3.73 (1H, d, J=6.1 Hz), 4.43 (1H, s), 4.89 (1H, s), 7.47-7.62 (3H, m), 7.82-7.87 (2H, m); ^{13}C NMR δ 15.16, 18.50, 18.69, 19.95, 21.82, 21.55, 33.33, 33.37, 35.58, 37.27, 39.36, 41.86, 42.65, 50.81, 50.99, 56.58, 68.55, 118.97, 128.64, 129.01, 133.33, 137.76, 137.89.
8. The allylsilane **7** was prepared from the palladium-catalyzed cross coupling reaction of 3-(tributylstannyl)-2-(trimethylsilylmethyl)propene with geranyl bromide. **7**: ^{1}H NMR δ 0.02 (9H, s), 1.54 (2H, s), 1.61 (6H, s), 1.69 (3H, s), 1.97-2.09 (8H, m), 4.53 (1H, s), 4.60 (1H, s), 5.01-5.16 (2H, m). **8**: ^{1}H NMR δ 1.55 (3H, s), 1.61 (6H, s), 1.68 (3H, s), 1.93-2.10 (8H, m), 5.04-5.20 (4H, m).

Rearrangement of 2,4-bisalkylpyrrole Unit to 2, 5-bisalkylpyrrole Unit in the Ligand-Modified Porphyrinogens

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The porphyrins and related macro cyclic systems are the most widely studied of all macro cyclic compounds.[1] The convenience of meso-substituents as sites for functionalization, controlling the substituents geometry and the wealth of available meso-substituents make meso-substituted porphyrins ideally suited for use in various model systems. Although porphyrin is easily obtainable from pyrroles and aldehydes, generic methods are still limited to symmetric porph-