Formation of Seven-Membered Oxacycles through Ring Expansion of Cyclopropanated Carbohydrates

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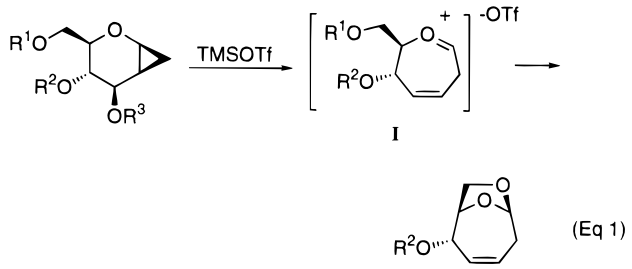
The cyclopropanation and ring expansion of 4,6-*O*-(di-*tert*-butylsilanediyl)-D-glucal (**1**) to produce oxepanes have been investigated. Using catalytic amounts of TMSOTf and an excess of a silylated nucleophile, a wide range of substituted oxepanes have been synthesized. Good to excellent yields are obtained; however, only modest diastereoselectivity resulted. This new methodology should provide convenient access into the synthesis of optically active oxepanes.

Introduction

Seven-membered oxacycles (oxepanes) are an important structural unit found in a variety of biologically active substances and natural products.[1] Due to their abundance and biological activity, efficient methods for their synthesis are becoming important. In view of this, a variety of racemic syntheses have been reported, including Cope rearrangement of 2,3-divinyl epoxides,[2] Claisen rearrangements of lactones,[3] cyclization of linear substrates,[4] and other novel methods.[5] However, methods for their enantioselective syntheses are few in comparison.[6] As part of a program to convert carbohydrates into higher-value materials,[7] we envisioned that transformation of cyclopropanated carbohydrates would provide a new route toward the synthesis of optically active oxepanes (eq 1). This strategy would take advantage of the naturally occurring optical activity in carbohydrates producing oxepanes containing multiple functionalities for use in further transformations. In a preliminary study, we recently reported the cyclopropanation of a series of glycals and our initial results on the Lewis acid-promoted ring expansion of cyclopropanated glycals.[8] We proposed that the reaction proceeded via Lewis acid-promoted removal of the OR^3 group to form oxonium ion **I**. Nucleophilic attack by the C-6 oxygen (OR^1) at the anomeric center produces the bicyclic oxepane. Herein we report on an extensive study of this ring expansion which provides a facile method for oxepane synthesis.



(Eq 1)

Our initial attempts at the ring expansion met with limited success. Although we achieved the desired ring expansion, a general method and a substrate suitable for trapping by a variety of nucleophiles were not found. Two major obstacles that we encountered were the instability of the protecting groups, R^1 and R^2, and the difficulty in introducing an activated leaving group at OR^3. The intramolecular attack, as depicted in eq 1, was the foremost difficulty since neither an acetonide (at R^1, R^2) nor a *tert*-butyldimethylsilyl group (at R^1) prevented the intramolecular attack. Therefore, only bicylic oxepanes were produced. The second difficulty resulted from the use of modest to poor leaving groups which we believe resulted in lower yields. We therefore felt that by increasing the leaving ability of OR^3, the formation of the intermediate oxonium ion would be enhanced and higher yields would be attained. Our recent efforts have therefore focused on finding a glycal with superior protection at R^1 and on using activated leaving groups such as alkyl and aryl sulfonates. The substrate and method we report here achieve both of these objectives and produce oxepanes in good to excellent yields without the intramolecular cycylization.

Results and Discussion

The choice for a protected glycal was our recently reported silyl-protected **1**, which displayed excellent

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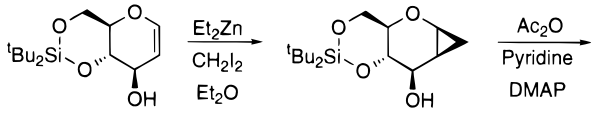
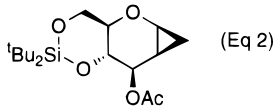
stability to Lewis acid-catalyzed reactions (eq 2).[9] This substrate not only provided robust protection at C-4 and C-6 but also furnished the hydroxy unit at C-3. Using Furukawa cyclopropanation conditions,[10] the oxygen-directed cyclopropanation[11] gave cyclopropane **2** in 96% yield with over 250:1 diastereoselectivity. The stereochemistry of the cyclopropane was determined by comparison to our previously synthesized 1,2-cyclopropanated glycals.[8]

The activation of the hydroxy moiety for ring expansion was examined using several different groups. Formation of the triflate of **2** was attempted under standard conditions with triflic anhydride in pyridine.[12] Although this produced a single product as seen by TLC, we were unable to isolate or use this in-situ. Our efforts at isolating this substrate produced a mixture of olefinic compounds. We therefore tried formation of a tosylate and a mesylate. Tosylate formation under a variety of conditions failed completely, perhaps due to steric interactions with the cyclopropane. Mesylate formation was achieved (indicated by TLC) using methanesulfonic anhydride in pyridine, but again the resulting substrate proved to be too reactive for isolation. We therefore introduced an acyl group using acetic anhydride in pyridine which provided the stable, isolable **3** in 97% yield.



1 **2**

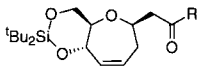
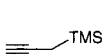
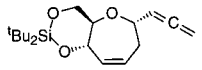
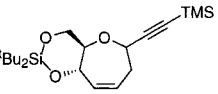


(Eq 2)

3

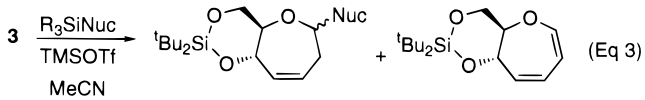
Ring expansion of **3** as shown in eq 3 proved to be successful as good to excellent yields were obtained with a variety of nucleophiles (Table 1). Entries 1−6 show the diverse range of nucleophiles which can be used. Using catalytic amounts of TMSOTf (20 mol %) and 5 equiv of a silylated nucleophile in acetonitrile, the preferential formation of **4** results with minor formation of diene **5**. The amount of **5** formed in each reaction was determined by GCMS and generally ranged from 0% to 12%. The separation of **4** and **5**, with the exception of entry 5, was accomplished by flash chromatography. The reactions in entries 7 and 9 however produced noticeable amounts of **5**. For entry 7, a 28% yield of **5** resulted while the (trimethylsilyl)thiazole in entry 9 gave exclusive formation of **5**. Although the formation of the thiazole oxepane in entry 9 was not accomplished, a facile method

Table 1. Ring Expansion of 3

Entry	Nucleophile	Product (% yield)[a]	Diastereoselectivity[b]
1	$TMSN_3$	**4a** (93)	2:1
2	$TMSCH_2CH{=}CH_2$	**4b** (92)	1:1
3	TMSSPh	**4c** (93)	2:1
4	TMSCN	**4d** (82)	2:1
5	Et_3SiH	**4e** (73)[c]	-
6			
	R = OEt	**4f** R = OEt (85)	2:1
	R = Ph	**4g** R = Ph (--)	
7			1:1
		4h (67)	
8			-
		4i (0)	
9		**5** (81)	-

[a] Isolated by flash chromatography. [b] Determined on the crude reaction mixture by fused silica gel capillary gas chromatography. [c] Calculated yield.

for the generation of this optically active diene has been achieved. The usefulness of dienes in organometallic chemistry is well documented,[13] and we are currently exploring the chemistry of compound **5**. The limitations of the ring expansion can be seen in entries 6 (R = Ph) and 8. For entry 6, only a 50% conversion was obtained using the phenyl enol ether. This produced a complicated mixture which was not pursued further. For entry 8, no reaction was observed under any conditions. The low reactivity of the bis(trimethylsilyl)acetylene nucleophile may be unable to compete with other acid-induced reactions.[14]



4 **5**

(Eq 3)

Finally, the stereochemistry of the ring expansion in entries 1−6 has been tentatively assigned as the syn isomer as shown in entry 6.[15] The assignments were made by comparison of ^{13}C NMR shifts to similar compounds.[16] However, the opposite stereochemistry was observed in entry 7; the reasons for this are unclear. The poor selectivity is thought to be due to a planar geometry in the intermediate oxonium ion. Molecular modeling studies of the intermediate oxonium ion supported this assumption. The intermediate geometry was modeled

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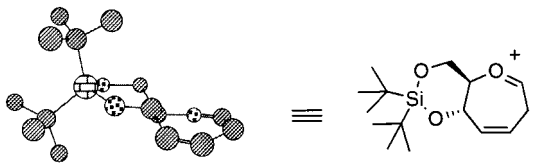

Figure 1. Oxonium intermediate (hydrogens omitted for clarity).

using a semiempirical AM1 calculation, and the result is shown in Figure 1.[17] As can be seen, with both *tert*-butyl groups connected to the silicon atom, each face of the oxepane ring is unhindered to nucleophilic attack. Studies are underway to improve the selectivity of the reaction.

Conclusion

We have developed a facile method for the synthesis of highly functionalized seven-membered ring systems that uses a readily available glycal as an enantiomerically pure, chiral template.[18] This ring expansion greatly enhances the available methodology for oxepane synthesis.[19] Furthermore, the chemistry demonstrated above offers access to the framework of naturally occurring seven-membered ring systems such as isolaurepinnacin and rogioloxepane A.[6c] Further research is underway to expand the scope of this system with increased functionalization at the cyclopropane methylene moiety.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz with chemical shifts reported relative to $CDCl_3$ (7.23 and 77.0, respectively). ^{1}H and ^{13}C NMR spectra are reported as mixtures of isomers unless otherwise noted. IR spectra were measured on a FT-IR spectrometer. Elemental analyses were obtained from Huffman Laboratories, Inc., Golden, CO, and HRMS was obtained from the University of Colorado, Boulder, CO. Semiempirical AM1 molecular orbital calculations were performed using the Spartan Semiempirical Program, IBM release 4.0.2b. TMSOTf and silyl nucleophiles were purchased from Aldrich and used as received; 1-[(*tert*-butyldimethylsilyl)oxy]-1-ethoxyethene was synthesized using literature procedures.[20] Acetonitrile and pyridine were distilled from CaH_2 prior to use, and ether was distilled from sodium/benzophenone. Standard syringe techniques were employed for handling air-sensitive reagents, and all reactions were carried out under argon.

1,5-Anhydro-2-deoxy-1,2-*C*-methylene-4,6-*O*-(di-*tert*-butylsilanediyl)-D-*glycero*-D-hexitol (2). To a solution of 1.771 g of **1** (6.182 mmol) in 20 mL of ether at 0 °C was added 18.6 mL of 1 M Et_2Zn in hexanes (18.6 mmol) followed by 1.50 mL of CH_2I_2 (18.6 mmol). The solution was stirred for 5 h at 0 °C, then poured into saturated NH_4Cl, and extracted twice with 75 mL of ether. The combined ether layers were washed with 50 mL of brine and 50 mL of water and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (2:1) gave 1.790 g (96% yield) of an oil which crystallized to a white solid under high vacuum. ^{1}H NMR: δ 4.15 (t, J = 6.4 Hz, 1H), 4.06 (dd, J = 10.2, 4.4 Hz, 1H), 3.74 (m, 1H), 3.67 (t, J = 10.9 Hz, 1H), 3.48 (t, J = 8.7 Hz, 1H), 3.35 (ddd, J = 10.4, 6.2, 4.4 Hz, 1H), 2.52 (brs, 1H), 1.41 (m, 1H), 1.02 (s, 9H), 0.96 (s, 9H), 0.72 (m, 2H). ^{13}C NMR: δ 78.7, 72.6, 72.1, 65.6, 54.1, 27.4, 27.0, 22.6, 19.8, 17.6, 11.9. IR ($CDCl_3$): 3597, 3456, 2931, 2864, 1137, 1043, 834 cm^{-1}. Anal. Calcd for $C_{15}H_{28}O_4Si$: C, 60.00; H, 9.39. Found: C, 60.02; H, 9.58.

3-Acetyl-1,5-anhydro-2-deoxy-1,2-*C*-methylene-4,6-*O*-(di-*tert*-butylsilanediyl)-D-*glycero*-D-hexitol (3). To a solution of 4.105 g of **2** (13.66 mmol) in 10 mL of pyridine at room temperature were added 2.6 mL of Ac_2O (27.3 mmol) and 84 mg of (dimethylamino)pyridine (0.68 mmol). The solution was stirred for 1 h, diluted with 200 mL of ether, washed twice with 75 mL of water, and then dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (5:1) gave 4.54 g (97% yield) of a colorless oil. ^{1}H NMR: δ 5.19 (t, J = 8.0 Hz, 1H), 4.09 (dd, J = 10.5, 4.9 Hz, 1H), 3.70 (m, 3H), 3.43 (dt, J = 9.9, 4.9 Hz, 1H), 2.13 (s, 3H), 1.58 (m, 1H), 1.00 (s, 9H), 0.96 (s, 9H), 0.72 (m, 2H). ^{13}C NMR: δ 171.1, 75.5, 74.6, 73.1, 65.7, 54.7, 27.3, 26.9, 22.6, 21.2, 19.8, 16.0, 12.5. IR (neat): 2933, 2866, 1739, 1127, 821 cm^{-1}. Anal. Calcd for $C_{17}H_{30}O_5Si$: C, 59.62; H, 8.83. Found: C, 59.60; H, 8.72.

(1*R*,7*S*)-3-Azido-9,9-di-*tert*-butyl-2,8,10-trioxa-9-silabicyclo[5.4.0]undec-5-ene (4a). To a solution of 242.4 mg of **3** (0.708 mmol) in 2.8 mL of MeCN at −40 °C was added 470 μL of $TMSN_3$ (3.54 mmol) followed by 27 μL of TMSOTf (0.142 mmol). The solution was allowed to warm to −20 ° C over 20 min and then stirred for an additional 1.5 h at −20 °C. The solution was poured into 20 mL of saturated $NaHCO_3$, extracted twice with 50 mL of ether, and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (15:1) gave 214 mg (93% yield) of a colorless oil. ^{1}H NMR: δ 5.82 (t, J = 12.0 Hz, 2H), 5.57 (m, 2H), 5.30 (dd, J = 6.8, 4.6 Hz, 1H), 4.77 (dd, J = 8.8, 2.4 Hz, 1H), 4.56 (m, 2H), 4.10 (m, 3H), 3.90 (m, 2H), 3.54 (dt, J = 9.5, 4.8 Hz, 1H), 2.40 (m, 4H), 1.04 (s, 18H), 0.99 (s, 18H). ^{13}C NMR: δ major isomer 139.5, 121.9, 90.6, 76.9, 76.8, 66.4, 35.8, 27.4, 27.0, 22.6, 19.9; minor isomer 136.7, 121.0, 88.9, 76.7, 68.7, 67.0, 32.6, 27.4, 27.0, 22.6, 19.9. IR (neat): 2940, 2866, 2112, 1119, 1067, 828, 657 cm^{-1}. Anal. Calcd for $C_{15}H_{27}N_3O_3Si$: C, 55.35; H, 8.36; N, 12.91. Found: C, 55.74; H, 8.56; N, 12.84.

(1*R*,7*S*)-3-Allyl-9,9-di-*tert*-butyl-2,8,10-trioxa-9-silabicyclo[5.4.0]undec-5-ene (4b). To a solution of 351.8 mg of **3** (1.027 mmol) in 4.1 mL of MeCN at −20 °C was added 816 μL of allyltrimethylsilane (5.14 mmol) followed by 40 μL of TMSOTf (0.205 mmol). The solution was stirred for 30 min, allowing to warm to 0 °C. After stirring for an additional 30 min at 0 °C, the solution was poured into 20 mL of saturated $NaHCO_3$, extracted twice with 50 mL of ether, and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (17:1) gave 309.0 mg (93% yield) of a colorless oil. ^{1}H NMR: δ 5.75 (m, 6H), 5.04 (m, 4H), 4.69 (d, J = 8.5 Hz, 1H), 4.53 (d, J = 8.5 Hz, 1H), 3.90 (m, 6H), 3.46 (m, 1H), 3.36 (m, 1H), 2.24 (m, 8H), 1.04 (s, 18H), 0.99 (s, 18H). ^{13}C NMR: δ 138.6, 136.1, 134.9, 134.5, 125.3, 124.9, 117.2, 116.8, 80.6, 78.5, 77.9, 76.3, 75.1, 71.5, 67.2, 66.9, 41.3, 39.3, 36.2, 33.4, 27.4, 27.1, 26.9, 22.5, 20.0. IR (neat): 2934, 2865, 1484, 1099, 828, 651 cm^{-1}. HRMS (M^+) *m/e* calcd for $C_{18}H_{32}O_3Si$, 324.2121; found, 324.2104.

(1*R*,7*S*)-3-(Phenylthio)-9,9-di-*tert*-butyl-2,8,10-trioxa-9-silabicyclo[5.4.0]undec-5-ene (4c). To a solution of 343.4 mg of **3** (1.003 mmol) in 4.0 mL of MeCN at 0 °C was added 950 μL of TMSSPh (5.02 mmol) followed by 39 μL of TMSOTf (0.200 mmol). The solution was stirred for 30 min at 0 °C and then for 5 h at room temperature. The solution was poured into 20 mL of saturated $NaHCO_3$, extracted twice with 50 mL of ether, and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (20:1) gave 366.1 mg (93% yield) of a colorless oil. ^{1}H NMR: δ 7.44 (m, 4H), 7.27 (m, 6H), 5.82 (t, J = 12.0 Hz, 2H), 5.68 (m, 2H), 5.44 (t, J = 5.2 Hz, 1H), 4.87 (dd, J = 9.3, 3.0 Hz, 1H), 4.62 (m, 2H), 4.37 (m, 1H), 3.86 (m, 4H), 3.36 (m, 1H), 2.86−2.54 (m, 4H), 1.04 (s, 18H), 1.00 (s, 18H). ^{13}C NMR: δ major isomer 138.5, 132.2, 128.6, 128.5, 127.4, 123.9, 87.7, 78.8, 76.8, 66.0, 36.4, 27.2, 26.7, 22.3, 19.6; minor isomer 137.8, 130.7, 128.7, 127.0, 126.7, 122.2, 85.8, 77.0, 67.3, 66.7, 34.5, 27.2, 26.7, 26.8, 19.7, 18.0. IR (neat):

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2934, 2858, 1477, 1105, 1067, 834, 657 cm^{-1}. HRMS *m/e* calcd for $C_{21}H_{32}O_3SSi$, (M^+) 392.1841; found, 392.1842.

(1*R*,7*S*)-3-Cyano-9,9-di-*tert*-butyl-2,8,10-trioxa-9-silabicyclo[5.4.0]undec-5-ene (4d). To a solution of 182.3 mg of **3** (0.532 mmol) in 2.1 mL of MeCN at −20 °C was added 355 μL of TMSCN (2.66 mmol) followed by 21 μL of TMSOTf (0.106 mmol). The solution was stirred for 20 min, allowing to warm to −10 °C. The solution was poured into 15 mL of saturated $NaHCO_3$, extracted twice with 25 mL of ether, and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (8:1) gave 135.1 mg (82% yield) of a colorless oil that solidified under high vacuum. ^{1}H NMR: δ 6.01 (d, J = 11.7 Hz, 1H), 5.89 (d, J = 12.5 Hz, 1H), 5.71 (m, 2H), 4.81 (t, J = 3.9 Hz, 1H), 4.61 (m, 2H), 4.38 (d, J = 10.8 Hz, 1H), 4.07 (dd, J = 10.8, 4.5 Hz, 1H), 4.02 (dd, J = 9.1, 2.8 Hz, 1H), 3.86 (t, J = 6.0 Hz, 3H), 3.42 (m, 1H), 2.72 (m, 2H), 2.49 (m, 2H), 1.05 (s, 18H), 1.01 (s, 9H), 0.98 (s, 9H). ^{13}C NMR: δ 141.8, 140.6, 122.6, 121.7, 117.6, 116.5, 78.9, 77.1, 72.9, 68.7, 66.3, 66.2, 65.9, 35.1, 33.3, 27.4, 27.0, 22.6, 20.1. IR (neat): 2940, 2858, 1478, 1119, 1067, 828 cm^{-1}. Anal. Calcd for $C_{16}H_{27}NO_3Si$: C, 62.10; H, 8.79; N, 4.53. Found: C, 62.32; H, 8.70; N, 4.44.

(1*R*,7*S*)-9,9-Di-*tert*-butyl-2,8,10-trioxa-9-silabicyclo[5.4.0]undec-5-ene (4e). To a solution of 245.0 mg of **3** (0.7153 mmol) in 2.9 mL of MeCN at 0 °C was added 571 μL of Et_3SiH (3.58 mmol) followed by 28 μL of TMSOTf (0.143 mmol). The solution was stirred for 30 min at 0 °C, poured into 20 mL of saturated $NaHCO_3$, extracted twice with 50 mL of ether, and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (15:1) gave 160.0 mg of a yellow oil. NMR integration revealed **4** and **5** in a 12:1 ratio, respectively (calcd 73% yield of **4**). ^{1}H NMR: δ 5.76 (s, 2H), 4.56 (d, J = 9.8 Hz, 1H), 4.02 (m, 2H), 3.80 (t, J = 10.2 Hz, 1H), 3.48 (t, J = 11.9 Hz, 1H), 3.32 (dt, J = 4.4, 9.6 Hz, 1H), 2.43 (m, 1H), 2.09 (m, 1H), 1.03 (s, 9H), 0.98 (s, 9H). ^{13}C NMR: δ 138.8, 126.3, 78.6, 78.2, 71.0, 66.9, 31.6, 27.7, 27.4, 27.1, 22.5, 19.9. IR (neat): 2935, 2857, 1119, 1064, 829, 649 cm^{-1}. HRMS *m/e* calcd for $C_{15}H_{28}O_3Si$, 284.1808; found, 284.1765.

(1*R*,7*S*)-3-(Ethoxy-2-propanoyl)-9,9-di-*tert*-butyl-2,8,10-trioxa-9-silabicyclo[5.4.0]undec-5-ene (4f). To a solution of 230.0 mg of **3** (0.6715 mmol) in 2.7 mL of MeCN at 0 °C was added 340.0 mg of 1-[(*tert*-butyldimethylsilyl)oxy]-1-ethoxyethene (1.68 mmol) followed by 26 μL of TMSOTf (0.134 mmol). The solution was allowed to warm to room temperature and stirred for 9 h. The solution was poured into 20 mL of saturated $NaHCO_3$, extracted twice with 50 mL of ether, and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate/CH_2Cl_2 (10:1:1) gave 211 mg (85% yield) of a colorless oil: ^{1}H NMR δ 5.70 (m, 4H), 4.74 (m, 1H), 4.51 (m, 1H), 4.39 (m, 1H), 4.11 (m, 4H), 3.92 (m, 4H), 3.78 (m, 2H), 3.40 (dt, J = 4.4, 9.5 Hz, 1H), 2.60−2.10 (m, 8H), 1.25 (t, J = 6.8 Hz, 6H), 1.01 (s, 18H), 0.96 (s, 18H). ^{13}C NMR: δ major isomer 169.8, 138.9, 124.6, 78.5, 77.7, 77.6, 66.8, 60.5, 42.0, 36.2, 27.4, 27.0, 22.5, 19.9, 14.3; minor isomer 171.0, 136.2, 124.3, 75.8, 72.2, 72.1, 67.1, 60.5, 40.4, 34.0, 27.4, 27.0, 22.5, 19.9, 14.3. IR (neat): 2931, 2868, 1741, 1102, 826, 654 cm^{-1}. HRMS *m/e* calcd for $C_{19}H_{34}O_5Si$, 370.2176; found, 370.2190.

(1*R*,7*S*)-3-Allene-9,9-di-*tert*-butyl-2,8,10-trioxa-9-silabicyclo[5.4.0]undec-5-ene (4h). To a solution of 293.6 mg of **3** (0.8572 mmol) in 3.4 mL of MeCN at −20 °C was added 640 μL of 1-propargyl-3-trimethylsilane (4.29 mmol) followed by 33 μL of TMSOTf (0.171 mmol). The solution was stirred at −20 °C for 1 h and then for 1 h at 0 °C. The solution was poured into 20 mL of saturated $NaHCO_3$, extracted twice with 50 mL of ether, and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (15:1) gave 185.6 mg (67% yield) of a yellow oil. ^{1}H NMR: δ 5.82−5.59 (m, 4H), 5.23 (q, J = 6.3 Hz, 1H), 4.81 (dd, J = 2.4, 6.2 Hz, 2H), 4.63 (m, 1H), 4.53 (m, 1H), 4.10−3.79 (m, 4H), 3.42 (dt, J = 5.0, 9.2 Hz, 1H), 2.50−2.23 (m, 4H), 1.03 (s, 18H), 0.98 (s, 18H). ^{13}C NMR: δ major isomer 208.3, 136.6, 124.4, 91.4, 77.0, 76.9, 73.7, 70.5, 67.2, 33.3, 27.4, 27.1, 22.5, 20.0; minor isomer 207.4, 138.9, 124.9, 93.2, 78.5, 78.0, 77.2, 77.0, 66.9, 36.1, 27.4, 27.1, 22.5, 20.0. IR (neat): 2938, 2855, 1479, 1127, 1095, 1070, 826, 654 cm^{-1}. HRMS *m/e* calcd for $C_{18}H_{30}O_3Si$, 322.1964; found, 322.1925.

(1*R*,7*S*)-9,9-Di-*tert*-butyl-2,8,10-trioxa-9-silabicyclo[5.4.0]undeca-3,5-diene (5). To a solution of 127.8 mg of **3** (0.3731 mmol) in 3.0 mL of MeCN at room temperature was added 72.0 μL of (trimethylsilyl)thiazole (0.448 mmol) followed by 15 μL of TMSOTf (0.075 mmol). The solution was heated to reflux, stirred for 1 h, and then allowed to cool to room temperature. The mixture was poured into 20 mL of saturated $NaHCO_3$, extracted twice with 50 mL of ether, and dried ($MgSO_4$). Flash chromatography on silica gel with hexanes/ethyl acetate (30:1) gave 85.4 mg of a colorless oil (81% yield). ^{1}H NMR: δ 6.33 (d, J = 7.3 Hz, 1H), 5.78 (d, J = 11.5 Hz, 1H), 5.63 (m, 1H), 4.91 (t, J = 7.3 Hz, 1H), 4.49 (d, J = 7.8 Hz, 1H), 4.23 (dd, J = 10.5, 4.9 Hz, 1H), 3.95 (t, J = 10.5 Hz, 1H), 3.66 (m, 1H). ^{13}C NMR: δ 147.1, 134.9, 119.1, 102.7, 75.9, 75.8, 65.7, 27.4, 26.9, 22.4, 20.0. IR (neat): 2931, 2861, 1127, 1119, 826, 656 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_3Si$: C, 63.79; H, 9.28. Found: C, 63.99; H, 9.11.

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Supporting Information Available: ^{1}H and ^{13}C NMR and FTIR spectra for all compounds (31 pages). This material is contained in 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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