Notes

Intramolecular 4 + 3 Cycloadditions. Further Studies of (Trimethylsilyl)methyl Allylic Sulfones

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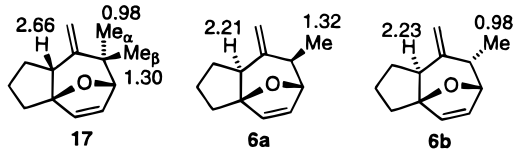
Received March 19, 1997

The intramolecular 4 + 3 cycloaddition reaction of allylic cations with dienes has been shown to be of promise in the preparation of organic compounds possessing seven-membered and larger rings.[1,2] As part of our program involving the study of this process, we are pursuing the application of (trimethylsilyl)methyl allylic sulfones to the reaction.[3] We have found that the reaction of such compounds affords a variety of products which depend on diene substitution in a predictable way. Further, we have uncovered an unusual case of relative stereocontrol in this reaction.

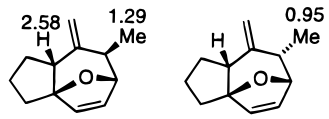
(Trimethylsilyl)methyl allylic sulfones were investigated as part of our plan to explore and expand the scope of the application of allylic sulfones in the 4 + 3 cycloaddition reaction. The preparation of (trimethylsilyl)methyl allylic sulfones is a simple process involving cuprate addition to the appropriate allenes.[4] Further elaboration via deprotonation and alkylation makes substrates for intramolecular 4 + 3 cycloadditions readily available.[3]

The results of the study are shown in Table 1. Treatment of a (trimethylsilyl)methyl allylic sulfone with 2 equiv of trimethylaluminum in CH_2Cl_2 at −78 °C followed by slow warming to and stirring at room temperature afforded the products indicated in reasonable yield. Unlike the corresponding furans, simple butadienes do not trap the intermediate allylic cation very efficiently (Table 1, entries 1, 2).[3] The inherently lower nucleophilicity of the butadiene relative to furan and problems with s-cis/s-trans equilibria may be responsible for this result. The cycloadducts **2** and **4** were obtained as mixtures. The ratio of isomers was determined by capillary GC analysis of the crude reaction mixture. While neither MPLC nor $AgNO_3$/silica gel could fully separate the isomers of **2** or **4**, we were able to obtain pure **4b** by MPLC. A NOESY experiment on this compound showed an interaction between the two angular hydrogens, and the compound was thus assigned the cis stereochemistry. This assignment is in agreement with findings by Giguere and coworkers.[5] They found that the minor product in an intramolecular 4 + 3 cycloaddition related to that of **1** gave a product which possesses a cis ring fusion.[5]

On the other hand, the conversion of **5** to **6** proceeds in good yield but with little stereocontrol. Four stereoisomers **6a-d** were obtained in a ratio of 2.9:3.7:3.7:1.6 The poor simple diastereoselection suggests that both sickle and W-shaped cations are intermediates and that exo and endo transition states are viable for both cation



17 **6a** **6b**



6c **6d**

geometries. Alternatively, a stepwise process with little inherent stereochemical bias might intervene and lead to the products observed. Our work with related cycloadducts suggests that they are kinetically formed: such cycloadducts are stable under the conditions of their formation.

The structures and stereochemistry of **6a**−**d** were established by ^1H and ^{13}C NMR spectroscopy. While shift reagent studies were inconclusive, NOESY experiments and comparisons of ^1H NMR spectra with other cycloadducts were useful in establishing stereochemical relationships. For example, a NOESY experiment was performed on compound **17**.[7] This established that the β-methyl group (1.30 ppm) was *syn* to the angular hydrogen and allowed us to assign the α-methyl as well (0.98 ppm). A NOESY experiment on **6b** confirmed its stereochemistry and allowed us to use chemical shifts to establish the stereochemistry of the methyl groups in the other cycloadducts. Ring fusion stereochemistry could be established in a similar fashion. The structures and selected proton chemical shift data are as shown.[8]

Unfortunately, with no additional alkyl substitution on the allylic sulfone portion of the cycloaddition substrate, no cycloaddition was observed. Thus, **7** could not be converted to **8** even with stronger Lewis acids such as $TiCl_4$ (Table 1, entry 4).

Substitution on the furan ring also proved to be detrimental with respect to the 4 + 3 cycloaddition process but was interesting in any event. For example, treatment of **9** with $AlMe_3$ gave no cycloadduct but afforded the spirocycle **18a** in 16% yield as a single stereoisomer. No optimization was performed on this reaction. The stereochemistry was assigned on the basis

(1) For reviews of 4 + 3 cycloadditions, see: (a) Hosomi, A.; Tominaga, Y. [4 + 3] cycloadditions. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds., Pergamon: Oxford, 1991; Vol. 5, Chapter 5.1, pp 593-615. (b) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1. (c) Mann, J. *Tetrahedron* **1986**, *42*, 4611. (d) Noyori, R. and Hayakawa, Y. *Org. React.* **1983**, *29*, 163−344. (e) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819.

(2) For a review of intramolecular 4 + 3 cycloadditions, see: (a) Harmata, M. *Tetrahedron* **1997**, *53*, 6235. (b) Harmata, M. In *Advances in Cycloaddition;* Lautens, M., Ed.; JAI: Greenwich, 1997; Vol. 4, pp 41−86.

(3) Harmata, M.; Herron B. F. *J. Org. Chem.* **1993**, *58*, 7393.

(4) Harmata, M.; Herron, B. F. *Synthesis* **1993**, 202.

(5) Giguere,R. J.; Duncan, S. M.; Bean, J. M.; Purvis, L. *Tetrahedron Lett.* **1988**, *29*, 6071.

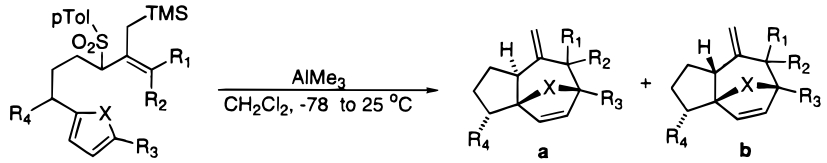
(6) The relative ratios were based on capilliary GC analysis of the crude reaction mixture.

(7) The ring fusion stereochemistry of this compound had been established by other means. See reference 5.

(8) It is presumed that the angular hydrogen of **6d** occurs as part of a two-proton multuplet at 2.60−2.41 ppm.

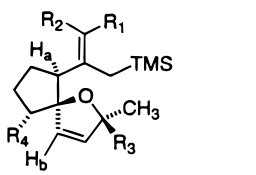
S0022-3263(97)00511-2 CCC: $14.00

Table 1. 4 + 3 Cycloadditions of (Trimethylsilyl)methyl Allylic Sulfones

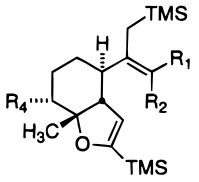


entry	substrate	R_1	R_2	R_3	R_4	X	cycloadduct	yield (%)[a]	ratio (**a**:**b**)
1	**1**	Me	Me	H	H	H_2	**2**	28	1.2:1
2	**3**	$-(CH_2)_5-$		H	H	H_2	**4**	31	1.3:1
3	**5**	H	Me	H	H	O	**6**	67	*b*
4	**7**	H	H	H	H	O	**8**	0	–
5	**9**	$-(CH_2)_5-$		Me	H	O	**10**	0[c]	–
6	**11**	$-(CH_2)_5-$		TMS	H	O	**12**	0[c]	–
7	**13**	Me	Me	H	Me	O	**14**	40	1.2:1
8	**15**	$-(CH_2)_5-$		H	Me	O	**16**	48	2:1

[a] Yield after chromatographic purification. [b] See text. [c] A side product was obtained. See text.

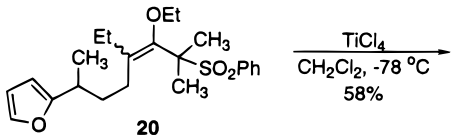


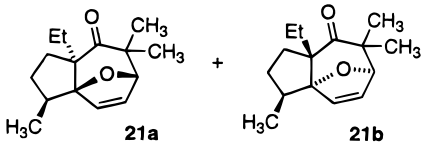
18a: R_1, R_2=-$(CH_2)_5$-; R_3=Me; R_4=H
18b: R_1, R_2=-$(CH_2)_5$-; R_3=H; R_4=Me



19a: R_1, R_2=-$(CH_2)_5$-; R_4=H
19b: R_1, R_2=-$(CH_2)_5$-; R_4=Me

of difference NOE experiments. Irradiation of the signal at 2.88 ppm (Ha in **18a**) resulted in a 4.3% enhancement of the signal at 5.47 ppm (Hb) and the stereochemistry was assigned accordingly. Similarly, **11** gave only **19a** with complete stereocontrol in 58% unoptimized yield. The structure and stereochemistry of this compound were assigned based on spectroscopic data in comparison with a related structure.[3] These results suggest that furan





From (Z)-**1** : 1.5:1
From (E)-**1** : 2.4:1

substitution can divert the 4 + 3 cycloaddition process toward simple, but stereoselective, Friedel–Crafts alkylation with subsequent trapping of the resultant σ complex.

Finally, we examined the question of relative stereocontrol in these reactions. We recently reported on the relative stereocontrol possible in the reactions of certain alkoxyallylic sulfones tethered to dienes. For example, treatment of **20** with $TiCl_4$ resulted in the formation of two cycloadducts in which simple diastereoselection was complete but relative stereocontrol was rather poor. The differences in product distribution as a function of the olefin geometry in **20** suggested that the reactive intermediates produced by Lewis acid treatment were stereochemically distinct, and that their stereochemical integrity was maintained through the course of the cycloaddition process.[9]

With this background of poor relative diastereoselection in the cycloaddition reaction of certain alkoxy allylic sulfones and poor simple diastereoselection in the cycloaddition of (trimethylsilyl)methyl allylic sulfones, we undertook the cycloadditions of **13** and **15** with no real expectation of any stereocontrol of any kind.

To our surprise, treatment of a dichloromethane solution of **13** with 2 equivalents of trimethylaluminum at −78 °C, followed by slow warming and stirring at room temperature, resulted in the formation of **14a** and **14b** in 40% yield in a ratio of 1.2:1. Similar treatment of **15** gave **16a** and **16b** in a ratio of 2:1 in 48% yield. The structures of **16a/b** were secured by X-ray diffraction.[10] The structures of **14a/b** were assigned by comparing their NMR data to those of **16a/b**.

In the cyclization of **15** several side products were also isolated. Though not rigorously characterized, a 1:1 mixture of an isomer of **18b** and **19b** were obtained in 12% yield. Their structures were assigned by comparison of the ^1H NMR of the mixture with that of more rigorously characterized products.[3] Also isolated in 9% yield was **18b**. Structural and stereochemical assignments of **18b** were based on ^1H and ^{13}C NMR as well as APT, DEPT, and NOESY experiments. The assignment of the methyl group on the dihydrofuran ring to the ostensibly more hindered position suggests that it may be delivered via a tight ion pair.[11]

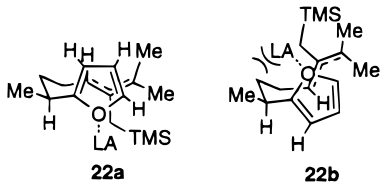
What is the origin of the high degree of relative stereocontrol in the formation of the 4 + 3 cycloadducts **14** and **16**? We hypothesize that coordination of the trimethylaluminum to the furan oxygen produces a conformational bias which forces the methyl group away from the oxygen bridge to avoid untoward steric interactions with the trimethylaluminum group. This induced conformational bias should be independent of mechanism and apparently has no effect on simple diastereoselection. For example, transition state **22a** should be preferred

(9) Harmata, M.; Gamlath, C. B.; Barnes, C. L.; Jones, D. E. *J. Org. Chem.* **1995**, *60*, 5077.

(10) The author has deposited atomic coordinates for this structure 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, UK.

(11) Presumably, the trimethylaluminum used to effect heterolysis of the phenylsulfonyl group also serves as the source of the methyl group present in the dihydrofuran ring of **11b**.

over **22b** due to the steric problems illustrated in **22b**.[12] This hypothesis remains to be critically examined. However, we have conducted a preliminary study of the ability of trimethylaluminum to coordinate to furan. Thus, treatment of a CD_2Cl_2 solution of furan with 1 equiv of trimethylaluminum in toluene resulted in changes in the chemical shift of carbons 2 and 3 of furan and the methyl groups of $AlMe_3$ by −0.005, +0.66, and −0.20 ppm, respectively. Some interaction is clearly taking place. Whether it is sufficient to account for the stereochemical



22a **22b**

results obtained with **13** and **15** remains to be established.[13,14] Further studies of stereochemistry in these reactions need to be performed. Mechanistic and synthetic studies in this area are in progress, and the results will be reported in due course.

Experimental Section[15,16]

General Procedure for the Synthesis of Cycloaddition Precursors. 2-Methyl-4-(4-methylbenzenesulfonyl)-3-[(trimethylsilyl)methyl]-2,8(*E*),10-undecatriene (1). A flame-dried, round-bottom flask equipped with a stir bar, septum, and N_2 balloon was charged with 2-methyl-4-(4-methylbenzenesulfonyl)-3-[(trimethylsilyl)methyl]-2-butene (0.99 mmol, 0.307 g, 1 equiv) and sufficient dry THF (10 mL) was added to give a 0.1 M solution. The flask was placed in a dry ice/acetone bath and allowed to cool. *n*-BuLi (1.29 mmol, 0.57 mL of a 2.26 M solution, 1.3 equiv) was added followed after 20 min by 7-iodo-1,3-heptadiene (1.59 mmol, 0.308 g, 1.4 equiv). The reaction mixture was allowed to warm slowly to rt. Upon completion (TLC), the reaction was quenched with water and extracted with ether. The organic phase was washed with water and brine. The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure. Flash chromatographic purification (FC) of the crude product (solvent system: 0% to 24% ethyl acetate gradient in hexane) gave **1** in 91% yield. An analytical sample was obtained by taking a center fraction of a flash chromatography purification (solvent system: 0% to 24% ethyl acetate gradient in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 6.28 (dt J = 17.0, 10.2 Hz, 1H), 6.03 (dd J = 10.4, 15.0 Hz, 1H), 5.64 (dt, J = 15.2, 7.0 Hz, 1H), 5.10 (d, J = 16.9 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.08 (dd, J = 8.9, 4.2 Hz, 1H), 2.45 (s, 3H), 2.11 (m, 3H), 1.78 (dd J = 9.2, 4.7 Hz, 2H), 1.42 (s, 3H), 1.45 (m, 2H), 1.27 (s, 3H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 137.0, 136.0, 133.9, 133.1, 131.7, 129.1, 128.6, 122.8, 115.2, 68.2, 53.4 (CH_2Cl_2), 32.2, 27.3, 25.3, 22.6, 21.6, 20.7, 18.1, 0.2; IR (CCl_4) 1315 s, 1145 s, 1118 s, 856 s, cm^{-1}. Anal. Calcd for $C_{23}H_{36}SiSO_2$: C, 68.28; H, 8.98. Found: C, 68.10; H, 8.94.

2-Cyclohexylidene-3-(4-methylbenzenesulfonyl)-1-(trimethylsilyl)-8,10-decadiene (3). FC (solvent system: hexanes/ethyl acetate, 20/1) gave **3** in 81% yield. An analytical sample was obtained by MPLC (solvent system: 0% to 100% ethyl acetate gradient in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.29 (dt, J = 17.0, 10.2 Hz, 1H), 6.03 (dd, J = 10.5, 15.2 Hz, 1H), 5.64 (dt, J = 15.2, 7.0 Hz, 1H), 5.10 (d, J = 17.0 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.18 (dd, J = 4.0, 9.0 Hz, 1H), 2.44 (s, 3H), 2.25−2.05 (m, 3H), 1.94−1.89 (m, 2H), 1.82 (dd, J = 165.0, 14.9 Hz, 2H), 1.78 (d septet, J = 9.4, 4.8 Hz, 1H), 1.67−1.60 (m, 1H), 1.55−1.21 (m, 8H), 0.98−0.86 (m, 1H), 0.08 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 144.0, 140.8, 137.0, 136.0, 133.9, 131.6, 129.2, 128.7, 119.7, 115.2, 67.3, 32.3, 32.1, 30.5, 27.3, 26.9, 26.3, 25.2, 21.5, 17.4, 0.3; IR (CCl_4) 2931s, 1314s, 1302s, 1248s, 1144s, 855s, 842s cm^{-1}. Anal. Calcd for $C_{26}H_{40}O_2SSi$: C, 70.22; H, 9.07. Found: C, 70.10; H, 8.92.

2-[4-Benzenesulfonyl-5-[(trimethylsilyl)methyl]-5(Z)-heptenyl]furan (5). FC (solvent system: hexanes/ethyl acetate, 17/1) gave a **5** in 77% yield. An analytical sample was obtained by HPLC (solvent system: 7% ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.28 (s, 1H), 6.27 (dd, J = 2.0, 2.9 Hz, 1H), 5.97 (d, J = 2.8 Hz, 1H), 5.44 (q, J = 6.8 Hz, 1H), 4.05−4.03 (m, 1H), 2.71−2.56 (m, 2H), 2.20−2.13 (m, 1H), 2.03−1.95 (m, 1H), 1.70−1.46 (m, 5H), 1.21 (d, J = 6.7 Hz, 3H), 0.07 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.0, 140.9, 138.6, 133.4, 129.1, 129.0, 128.8, 128.71, 110.1, 105.3, 66.2, 27.6, 25.6, 24.2, 19.0, 13.4, −0.6; IR (CCl_4) 2956m, 1447m, 1319m, 1307m, 1250m, 1149s cm^{-1}. Anal. Calcd for $C_{21}H_{30}SO_3Si$: C, 64.59; H, 7.75. Found: C, 64.64; H, 7.66.

2-[4-Benzenesulfonyl-5-[(trimethylsilyl)methyl]-5-hexenyl]furan (7). FC (solvent system: hexanes/ethyl acetate, 10/1) gave a **7** in 83% yield. An analytical sample was obtained by FC (solvent system: hexanes/ethyl acetate, 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 7.3 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.28−7.27 (m, 1H), 6.26 (dd, J = 1.9, 2.9 Hz, 1H), 5.95 (d, J = 2.6 Hz, 1H), 4.95 (s, 1H), 4.71 (s, 1H), 3.50 (dd, J = 4.3, 10.1 Hz, 1H), 2.63 (d septet, J = 9.9, 7.5 Hz, 2H), 2.14−2.05 (m, 1H), 1.87−1.66 (m, 3H), 1.63 (dd, J = 15.1, 27.6 Hz, 2H), 0.05 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.0, 140.9, 138.8, 137.2, 133.5, 129.4, 128.6, 116.4, 110.1, 105.2, 72.4, 27.7, 27.3, 26.5, 25.6, −1.1; IR (CCl_4) 2966s, 1247s, 856s, 839s cm^{-1}. Anal. Calcd for $C_{20}H_{34}O_3SSi$: C, 62.79; H, 8.97. Found: C, 63.00; H, 9.16.

2-[5-Cyclohexylidene-4-(4-methylbenzenesulfonyl)-6-(trimethylsilyl)hexyl]-5-methylfuran (9). FC (solvent system: hexanes/ethyl acetate, 17/1) gave **9** in 70% yield. An analytical sample was obtained by taking a center fraction of a MPLC purification (solvent system: 0% to 100% ethyl acetate gradient in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.83 (s, 2H), 4.21 (dd, J = 4.1, 9.0 Hz, 1H), 2.65−2.54 (m, 2H), 2.45 (s, 3H), 2.25 (s, 3H), 2.23−2.16 (m, 1H), 1.95−1.90 (m, 3H), 1.83 (d septet, J = 9.5, 9.5 Hz, 1H), 1.82 (dd, J = 14.9, 158.3 Hz, 2H), 1.73−1.59 (m, 2H), 1.45−1.39 (m, 2H), 1.36−1.33 (m, 2H), 1.31−1.23 (m, 2H), 0.94−0.89 (m, 1H), 0.08 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 153.2, 150.3, 143.9, 140.8, 136.0, 129.2, 128.7, 119.6, 105.8, 105.7, 67.4, 32.2, 30.4, 27.6, 27.2, 26.9, 26.4, 26.3, 25.1, 21.5, 17.4, 13.4, 0.3; IR (CCl_4) 2931s, 2928s, 1313s, 1302s, 1248s, 1144s, 1087s, 856s, 842s cm^{-1}. Anal. Calcd for $C_{27}H_{39}SO_3Si$: C, 68.75; H, 8.34. Found: C, 68.62; H, 8.59.

2-[5-Cyclohexylidene-4-(4-methylbenzenesulfonyl)-6-(trimethylsilyl)hexyl]-5-(trimethylsilyl)furan (11). FC (solvent system: hexane/ethyl acetate, 10/1) gave a **11** in 91% yield. An analytical sample was obtained by FC (solvent system: hexane/ethyl acetate, 10/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.50 (d, J = 3.0 Hz, 1H), 5.95 (d, J = 2.9 Hz, 1H), 4.22 (dd, J = 4.1, 9.1 Hz, 1H), 2.73−2.57 (m, 2H), 2.45 (s, 3H), 2.24−2.17 (m, 1H), 1.99−1.89 (m, 2H), 1.82 (dd, J = 161.9, 15.1 Hz, 2H), 1.84 (d septet, J = 9.4, 4.6 Hz, 1H), 1.79−1.71 (m, 1H), 1.69−1.60 (m, 1H), 1.42−1.22 (m, 7H), 0.89−0.93 (m, 1H), 0.25 (s, 9H), 0.08 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.4, 158.5, 144.0, 140.9, 136.1, 129.2, 128.8, 120.3, 119.6, 105.2, 67.2, 32.3, 30.5, 27.8, 27.3, 26.9, 26.3, 26.3, 25.2, 21.6, 17.4, 0.3, −1.6; IR (CCl_4) 2956s, 2932s, 1313s, 1302s, 1250s, 1144s, 1067s, 845s cm^{-1}. Anal. Calcd for $C_{29}H_{46}SO_3Si_2$: C, 65.61; H, 8.73. Found: C, 65.70; H, 8.54.

2-[1,6-Dimethyl-4-(4-methylbenzenesulfonyl)-5-[(trimethylsilyl)methyl]-5-heptenyl]furan (13). FC (solvent system: 0% to 100% ethyl acetate gradient in hexane) gave **13**

(12) The preference of **22a** over **22b** can be viewed as an avoidance of 1,3-allylic strain. See: Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841.

(13) We are unaware of any studies involving the coordination of furans to Lewis acids and the effect such coordination might have on the course of chemical reactions. However, the absence of metal binding by calixfurans has been noted. See: de Sousa Healy, M.; Rest, A. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 973.

(14) Stereocontrol via furan coordination of a metal cation in an intermolecular 4 + 3 cycloaddition has been proposed. See: Lautens, M.; Aspiotis, R.; Colucci, J. *J. Am. Chem. Soc.* **1996**, *118*, 10930.

(15) For general experimental information, see reference 3.

(16) The synthesis of the alkyl halide needed for the synthesis of **13** and **15** has been described. See: Harmata, M.; Gamlath, C. B.; Barnes, C. L.; Jones, D. E. *J. Org. Chem.* **1995**, *60*, 5077.

in 52% yield. An analytical sample was obtained by MPLC (solvent system: 0% to 100% ether gradient in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 0.5H), 7.68 (d, J = 8.2 Hz, 0.5H), 7.29−7.26 (m, 3H), 6.27 (dd, J = 2.7, 1.9 Hz, 0.5H), 6.25 (dd, J = 2.7, 1.9 Hz, 0.5H), 5.97 (d, J = 3.0 Hz, 0.5H), 5.95 (d, J = 3.0 Hz, 0.5H), 4.05 (dd, J = 7.5, 11.7 Hz, 1H), 2.80 (septet, J = 7.0 Hz, 1H), 2.45 (s, 3H), 2.20−2.09 (m, 1H), 1.90−1.58 (m, 6H), 1.47 (s, 1.5H), 1.46 (s, 1.5H), 1.29−1.23 (m, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.3, 143.9, 140.7, 140.7, 136.0, 133.1, 132.9, 129.1, 128.6, 123.0, 122.8, 109.8, 109.8, 104.0, 103.9, 68.3, 68.1, 34.1, 33.7, 33.0, 32.9, 24.0, 23.7, 22.6, 22.6, 21.6, 20.4, 19.1, 19.0, 18.0, 0.2, 0.2. Anal. Calcd for $C_{24}H_{36}SO_3Si$: C, 66.62; H, 8.39. Found: C, 66.75; H, 8.49.

2-[5-Cyclohexylidene-1-methyl-4-(4-methylbenzenesulfonyl)-6-(trimethylsilyl)hexyl]furan (15). FCP (solvent system: hexane/ethyl acetate, 10/1) gave a **15** in 74% yield. An analytical sample was obtained by MPLC (solvent system: 0% to 100% of ether in hexane (HPLC grade)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71−7.68 (m, 2H), 7.30−7.26 (m, 3H), 6.27 (dd, J = 2.9, 1.9 Hz, 0.5H), 6.25 (dd, J = 2.9, 1.9 Hz, 0.5H), 5.97 (d, J = 3.1 Hz, 0.5H), 5.94 (d, J = 3.1 Hz, 0.5H), 4.18-4.14 (m, 1H), 2.86−2.75 (m, 1H), 2.44 (s, 3H), 2.21−2.13 (m, 1H), 1.95−1.90 (m, 4H), 1.78−1.54 (m, 6H), 1.43−1.23 (m, 7H), 0.92−0.94 (m, 1H), 0.06 (s, 3.3H), (0.04, s, 5.7H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.4, 159.3, 143.9, 140.8, 140.7, 140.6, 136.1, 129.2, 128.8, 119.8, 119.7, 109.9, 109.8, 104.0, 103.9, 67.4, 67.2, 34.0, 33.6, 33.0, 32.8, 32.2, 30.5, 27.3, 26.9, 26.3, 23.9, 23.6, 21.5, 19.1, 19.0, 17.4, 0.3, 0.2; IR (CCl_4) 2967s, 2932s, 1313s, 1302s, 1248s, 1145s, 855s, 845s, cm^{-1}. Anal. Calcd for $C_{27}H_{40}O_3SSi$: C, 68.61; H, 68.80. Found: C, 8.54; H, 8.75.

General Cyclization Procedure. Preparation of 2. A flame-dried, round-bottom flask equipped with a stir bar, septum and N_2 balloon was charged with CH_2Cl_2 (131 mL) and trimethylaluminum (2.61 mmol, 1.31 mL of a 2 M solution in toluene, 2.0 equiv). The flask was placed in a dry ice/acetone bath and allowed to cool for 25 min. A solution of **1** (1.31 mmol, 0.528 g, 1.0 equiv) in CH_2Cl_2 (10 mL) was added. The reaction mixture was allowed to warm slowly to room temperature. The reaction was monitored by TLC. Upon completion (2−3 h) the reaction was quenched with water. The reaction mixture was filtered through Celite then extracted with CH_2Cl_2. The organic phase was washed with water and brine. The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The ratio of **2a** and **2b** was 1.2:1 as determined by capillary GC analysis of the crude reaction mixture. The crude products were purified by MPLC (solvent system: pentane) to give **2a/b** in 28% yield. Attempts to use $AgNO_3$/silica gel failed to separate the mixture. Cycloadduct **2a** was lost during purification. An analytical sample was obtained by MPLC (solvent system: pentane). **Data for 2b:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71−5.55 (m, 1H), 5.45 (d, J = 10.3 Hz, 1H, br), 4.90 (s, 1H), 4.70 (s, 1H), 3.11 (dt, J = 4.2, 8.3 Hz, 1H), 2.75−2.69 (m, 1H), 2.48 (dd, J = 6.5, 13.6 Hz, 1H), 1.91−1.77 (m, 3H), 1.73−1.62 (m, 2H), 1.56−1.37 (m, 2H), 1.13 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.3, 133.7, 126.2, 106.9, 44.6, 43.0, 41.8, 39.2, 31.9, 31.2, 30.6, 27.2, 23.2; IR (CCl_4) 2977s, 2963s, 2950s, 2928s, 2869s, 1120s cm^{-1}; MS (70 eV) m/e 177 (M + 1, 5), 176 (M$^+$, 35), 133 (88), 105 (50), 91 (100), 79 (57). Anal. Calcd for $C_{13}H_{20}$: C, 89.07; H, 10.93. Found: C, 88.89; H, 11.19.

Cycloadducts 4a/b. The ratio of **4a** to **4b** was 1.3:1 as determined by capillary GC analysis of the crude reaction mixture. Purification by MPLC (solvent system: pentane) gave **4a** and **4b** in 31% yield. Attempts to separate **4a** and **4b** by reverse phase (C18) chromotography failed. An analytical sample of the mixture was obtained by MPLC (solvent system: pentane). **Data for 4a/b:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76−5.74 (m, 1H), 5.64−5.59 (m, 1H), 5.53−5.44 (m, 2H), 4.93 (s, 2H), 4.84 (s, 1H), 4.75 (s, 1H), 3.10 (dt, J = 4.9, 8.3 Hz, 1H), 2.74−2.69 (m, 1H), 2.40−2.35 (m, 1H), 2.25 (dd, J = 3.4, 7.2 Hz, 1H), 2.22 (dd, J = 7.3, 1.7 Hz, 2H), 2.14−2.04 (m, 3H), 2.00−1.96 (m, 1H), 1.90−1.18 (m, 30H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 159.7, 136.7, 134.1, 126.9, 125.7, 106.9, 104.8, 47.9, 45.9, 45.4, 44.5, 41.9, 41.7, 38.9, 37.2, 35.3, 33.1, 32.9, 32.6, 32.1, 31.4, 26.6, 26.5, 23.5, 22.7, 22.5, 22.4, 22.4, 22.1; IR (CCl_4) 2935s, 2866m, 1452m, 908m, 894m cm^{-1}; MS (70 eV) m/e 217 (M + 1, 4), 216 (M$^+$, 20), 133 (52), 91 (100), 79 (67). Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.69; H, 10.98.

Cycloadducts 6a−d). The ratio of **6a**, **6b**, **6c** and **16** was 2.9:3.7:3.7:1 as determined by capillary GC analysis of the crude reaction mixture. The crude products were purified by MPLC (solvent system: pentane) to give **6a−d** in 67% yield. Analytical samples were obtained by tMPLC (solvent system: pentane). **Data for 6a:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (dd, J = 1.6, 5.9 Hz, 1H), 6.03 (d, J = 5.9 Hz, 1H), 4.88 (s, 1H), 4.85 (s, 1H), 4.47 (s, 1H), 2.23 (t, J = 9.7 Hz, 1H), 2.19 (q, J = 7.3 Hz, 1H), 2.0−1.84 (m, 5H), 1.71−1.63 (m, 1H), 1.32 (d, J = 7.3 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 149.7, 134.8, 133.4, 115.3, 93.0, 83.7, 50.3, 38.2, 32.5, 32.1, 23.2, 22.6; IR (CCl_4) 2970m, 2934m, 1617s, 1234s, 910m, cm^{-1}; MS (70 eV) m/e 177 (M + 1, 1), 176 (M$^+$, 10), 147 (71), 132 (100), 105 (88), 91 (100), 81 (98). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.64; H, 9.47. **Data for 6b:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (d, J = 6.0 Hz, 1H), 6.12 (dd, J = 6.1, 1.4 Hz, 1H), 4.87 (s, 2H, br), 4.50 (d, J = 3.4 Hz, 1H, br), 2.71−2.69 (m, 1H), 2.23 (dd, J = 7.6, 11.0 Hz, 1H), 1.97−1.68 (m, 6H), 0.98 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 149.7, 136.1, 130.9, 112.8, 93.9, 83.4, 50.6, 36.2, 31.8, 29.7, 22.2, 13.6; IR (CCl_4) 2969s, 2939s, 2871s, 1637m, 1090m, 1078m, 952m, 904m cm^{-1}; MS (70 eV) m/e 177 (M + 1, 1), 176 (M$^+$, 9), 132 (79), 105 (86), 91 (100), 81 (94). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.63; H, 9.31. **Data for 6c:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.22 (dd, J = 5.9, 1.6 Hz, 1H), 5.92 (d, J = 5.9 Hz, 1H), 4.72 (t, J = 1.5 Hz, 1H), 4.56 (t, J = 1.8 Hz, 1H), 4.54 (s, 1H, br), 2.58 (m, 1H), 2.06 (q, J = 7.1 Hz, 1H), 1.96−1.69 (m, 5H), 1.28 (d, J = 7.2 Hz, 3H), 1.26−1.21 (m, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 151.5, 134.5, 132.9, 109.4, 91.9, 85.0, 48.5, 38.2, 30.0, 23.2, 19.6, 18.7; IR (CCl_4) 2966m, 2875m, 1643m, 1617s, 1593m, 1511m, 1457m, 1234s, 1213m, 950m, 909s cm^{-1}; MS (70 eV) m/e 177 (M + 1, 2), 176 (M$^+$, 12), 147 (85), 133 (85), 132 (81), 105 (79), 91 (92), 81 (100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.63; H, 8.91. **Data for 6d:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.17 (dd, J = 1.4, 5.9 Hz, 1H), 6.00 (d, J = 6.0 Hz, 1H), 4.74 (m, 1H), 4.66 (s, 1H, br), 4.60 (dd, J = 1.8, 3.0 Hz, 1H), 2.61−2.40 (m, 2H), 1.99−1.67 (m, 5H), 1.32-1.20 (m, 1H), 0.95 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 150.7, 134.5, 131.6, 107.3, 92.2, 84.8, 51.0, 37.4, 30.2, 23.5, 20.1, 13.0; IR (CCl_4) 1617s, 1511m, 1346m, 1234s, 1213m, 1123m, 909s, cm^{-1}; MS (70 eV) m/e 177 (M$^+$ + 1, 12), 176 (M$^+$, 13), 147 (88), 133 (91), 132 (78), 105 (76), 91 (90), 81 (100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.29.

Formation of 18a. FC (solvent system: 0% to 100% ether gradient in pentane) gave **18a** in 16% yield. An analytical sample was obtained by MPLC (solvent system: 0% to 100% ether gradient in pentane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (d, J = 5.8 Hz, 1H), 5.47 (d, J = 5.8 Hz, 1H), 2.88 (dd, J = 7.3, 11.4 Hz, 1H), 2.28−2.15 (m, 1H), 2.09−2.04 (m, 1H), 1.99−1.84 (m, 3H), 1.81−1.33 (m, 13H), 1.28 (s, 3H), 1.19 (s, 3H), 0.02 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 133.8, 131.8, 131.2, 126.3, 101.2, 87.2, 50.0, 41.0, 32.1, 31.0, 30.1, 30.1, 28.6, 28.4, 27.8, 27.2, 23.1, 21.4, 0.2; IR (CCl_4) 2967s, 2926s, 1246 s, 1164m, 856s cm^{-1}; MS (70 eV) m/e 289 (M$^+$ − 43, 1), 136 (100), 73 (57). Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.85; H, 10.92. Found: C, 76.13; H, 10.61.

Formation of 19a. FC (solvent system: 0% to 100% ether gradient in pentane) gave **19a** in 58% yield. An analytical sample was obtained by MPLC (solvent system: pentane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.32 (d, J = 2.5 Hz, 1H), 2.35 (m, 1H, br), 2.29−2.24 (m, 1H), 2.15−2.08 (m, 4H), 2.00−1.96 (m, 1H), 1.61−1.41 (m, 11H), 1.35−1.33 (m, 1H), 1.20−1.15 (m, 1H), 1.16 (s, 3H), 0.14 (s, 9H), 0.06 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.9, 131.0, 129.2, 119.0, 85.5, 50.1, 45.2 (br), 33.7, 32.3, 28.7, 27.1, 28.0, 27.4, 27.2, 21.4, 0.3, −2.4; IR (CCl_4) 2955s, 2928s, 2853m, 1248s, 1096m, 870s cm^{-1}. Anal. Calcd for $C_{23}H_{42}OSi_2$: C, 70.72; H, 10.85. Found: C, 70.80; H, 10.65.

Cycloadducts 14a/b. The ratio of **14a** and **14b** was 1.2:1 as determined by capillary GC analysis of the crude reaction mixture. The crude products were purified by MPLC (solvent system: pentane/ether, 0% to 100% gradient ether in pentane) to give **14a** and **14b** in 40% yield. An analytical sample was obtained by MPLC (solvent system: pentane/ether, 0% to 100% gradient ether in pentane). **Data for 14a:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.22 (dd, J = 1.7, 6.1 Hz, 1H), 6.15 (d, J = 6.1 Hz, 1H), 4.97 (d, J = 0.9 Hz, 1H), 4.85 (s, 1H), 4.17 (d, J = 1.1 Hz, 1H), 2.32 (dd, J = 7.9, 11.8 Hz, 1H), 2.21−2.08 (m, 2H), 2.00−1.89 (m, 1H), 1.84−1.78 (m, 1H), 1.32 (s, 3H), 1.25−1.19 (m, 1H), 1.04 (d, J = 7.2 Hz, 3H), 0.98 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$)

δ 154.0, 133.6, 132.8, 113.4, 96.7, 87.4, 48.0, 39.4, 38.9, 32.8, 32.0, 31.3, 24.6, 19.4; IR (CCl_4) 2960s, 2930s, 1631m, 1470m, 1367m, 1264s, 1070s, 1044s, 942s,894s cm^{-1}; MS (70 eV) *m/e* 204 (M^+, 20), 189 (97), 161 (93), 119 (70), 95 (100), 91 (78). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.09; H, 10.06. **Data for 14b:** ^1H NMR (500 MHz, $CDCl_3$) δ 6.31 (d, J = 5.7 Hz, 1H), 5.95 (d, J = 6.1 Hz, 1H), 4.76 (dd, J = 1.0, 1.8 Hz, 1H), 4.57 (s, 1H), 4.23 (d, J = 1.5 Hz, 1H), 2.65 (ddt, J = 7.8, 11.7, 2.1 Hz, 1H), 2.26−2.11 (m, 2H), 1.79−1.72 (m, 1H), 1.39−1.28 (m, 1H), 1.27 (s, 3H), 0.98 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.3, 134.6, 130.7, 106.8, 95.0, 88.7, 47.8, 38.5, 36.7, 29.4, 26.8, 23.3, 22.1, 14.5; IR (CCl_4) 2960s, 2944s, 1640m, 1454m, 1379m, 1058s, 984s, 891s cm^{-1}; MS (70 eV) *m/e* 204 (M^+, 18), 189 (84), 161 (99), 147 (56), 95 (100), 91 (68). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.18; H, 10.04.

Cycloadducts 16a/b. The crude products were purified by MPLC (solvent system: 0% to 100% ether gradient in pentane) to give **16a** and **16b** in 48% yield, an isomer of **18b** and **19b** (not characterized) in 12% yield and **18b** in 9% yield. Analytical samples were obtained by MPLC (solvent system: 0% to 100% ether gradient in pentane). Compounds **16a** and **16b** were recrystallized from hexane/ether. **Data for 16a:** mp 58.5−60.0 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 6.23 (dd, J = 6.1, 1.8 Hz, 1H), 6.15 (d, J = 6.1 Hz, 1H), 5.03 (s, 1H), 4.92 (s, 1H), 4.86 (s, 1H), 2.34 (dd, J = 8.1, 11.6 Hz, 1H), 2.31−2.28 (m, 1H), 2.19−2.10 (m, 2H), 1.93−1.79 (m, 2H), 1.72−1.52 (m, 5H), 1.44 (tq, J = 3.4, 12.9 Hz, 1H), 1.33−1.15, (m, 4H), 1.04 (d, J = 7.1 Hz, 3H); 13C NMR (125.8 MHz, $CDCl_3$) δ 154.9, 133.6, 132.4, 113.7, 96.3, 80.4, 48.6, 42.6, 39.0, 38.7, 33.0, 32.7, 26.1, 21.9, 21.9, 19.4; IR (CCl_4) 2960s, 2933s, 2865s, 1626m, 1453m, 1072m, 1041m, 997m, 891m, cm^{-1}; MS (70 eV) *m/e* 245 (M + 1, 13), 244 (M^+, 71), 161 (67), 95 (100), 91 (98), 81 (58), 79 (71). Anal. Calcd for $C_{17}H_{24}O$: C, 83.54; H, 9.91. Found: C, 83.76; H, 9.79. **Data for 16b:** mp 113−115 °C; 1H NMR (500 MHz, $CDCl_3$) δ 6.28 (d, J = 5.9 Hz, 1H), 5.94 (d, J = 6.1 Hz, 1H), 4.84 (s, 1H), 4.83 (s, 1H), 4.56 (s, 1H), 2.68−2.64 (m, 1H), 2.26−2.10 (m, 3H), 1.75−1.60 (m, 5H), 1.57−1.47 (m, 2H), 1.42−1.10 (m, 5H), 0.98 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.5, 133.9, 130.8, 107.0, 95.0, 83.4, 47.7, 41.4, 36.6, 34.5, 31.8, 29.3, 26.5, 22.3, 21.8, 14.6; IR (CCl_4) 2958s, 2931s, 1454m, 987m, 890m cm^{-1}; MS (70 eV) *m/e* 245 (M + 1, 11), 244 (M^+, 59), 201 (86), 200 (79), 161 (81), 95 (100), 91 (94). Anal. Calcd for $C_{17}H_{24}O$: C, 83.54; H, 9.91. Found: C, 83.25; H, 9.77. **Data for 18b:** ^1H NMR (500 MHz, $CDCl_3$) δ 5.73 (dd, J = 6.0, 1.2 Hz, 1H), 5.43 (dd, J = 5.9, 2.0 Hz, 1H), 4.84 (q, J = 5.3 Hz, 1H, br), 3.15 (t, J = 9.5 Hz, 1H), 2.23−2.14 (m, 2H), 2.09−2.05 (m, 1H), 2.01−1.95 (m, 1H), 1.90−1.84 (m, 3H), 1.68−1.40 (m, 8H), 1.67 (dd, J = 54.2, 14.9 Hz, 2H), 1.16 (d, J = 6.3 Hz, 3H), 0.86 (d, J = 6.2 Hz, 3H), 0.02 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 131.8, 131.1, 131.0, 126.7, 104.1, 82.7, 49.2, 43.5, 32.2, 31.4, 31.2, 28.6, 28.0, 27.2, 27.2, 22.6, 21.6, 12.8, 0.2; IR (CCl_4) 2960s, 2933s, 2865s, 1453m, 1072m, 1041m, 891s, cm^{-1}; MS (70 eV) *m/e* 136 (100), 73 (91). Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.85; H, 10.92. Found: C, 76.01; H, 10.68.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8912190 and CHE-9220679) and by the Petroleum Research Fund, administered by the American Chemical Society, to whom we are grateful. We thank the National Science Foundation for partial support of the NMR (PCM−8115599) facility at the University of Missouri-Columbia and for partial funding for the purchase of a 500 MHz spectrometer (CHE-89-08304) and an X-ray diffractometer (CHE-90-11804).

JO970511C