Stereocontrolled Preparation of Spirocyclic Ethers by Intramolecular Trapping of Oxonium Ions with Allylsilanes

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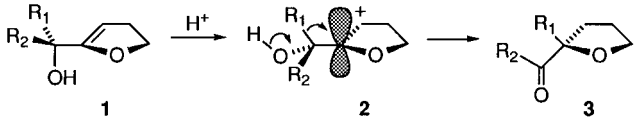
The stereoselectivity of the spontaneous intramolecular cyclization of 2-(benzenesulfonyl)-2-(4-((trimethylsilyl)methyl)-4-pentenyl)tetrahydropyrans substituted by alkyl groups at various ring positions has been examined. For the 4- and 6-methyl derivatives, formation of the spirocyclic center occurs exclusively anti to the methyl. The outcome in the 5-methyl example is a 3.7:1 syn/anti split. For the *trans*-4,6-dimethyl derivative, the substituents act in a reinforcing manner and direct cyclization uniquely in one direction. Both the cis and trans bicyclic ethers ring close on that π-surface of the intermediate oxonium ion syn to the angular hydrogen. The results are rationalized in terms of the predilection of the associated oxonium ions for nucleophilic capture via a chairlike or twist-boat transition state.

Oxonium ion intermediates are playing an ever-increasing role as important synthetic intermediates,[1,2] and the stereochemistry of their nucleophilic capture is of considerable interest.[3,4] Various methods have been developed for trapping the oxonium ion intramolecularly as a useful means for elaborating functionalized rings. Marko's silyl-modified Sakurai reaction,[5] Ley's α-alkoxy sulfone approach to methylenecyclohexane systems,[6] and the Marko−Krief spiro acetal synthesis[7] all rely on the nucleophilic responsiveness of the allylsilane functionality toward transient oxonium ion centers. This well-matched reactivity results in efficient C−C bond construction.

Earlier work from this laboratory has focused on the fate of oxonium ions substituted at C_α with a carbinol carbon.[8] The conversion of **1** to **2** was found to initiate a pinacol-like Wagner−Meerwein rearrangement. The

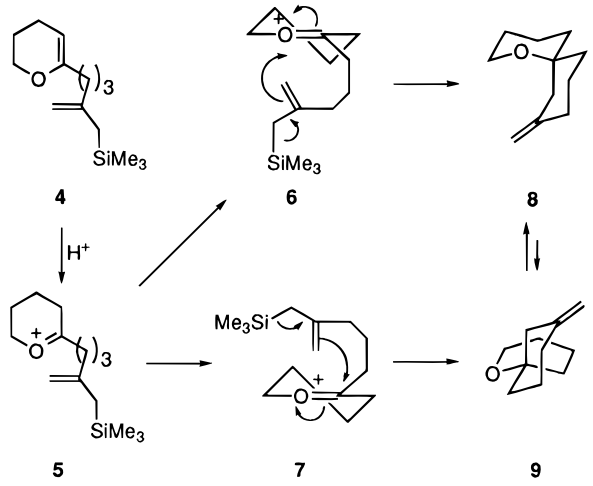


1 **2** **3**

steric and stereoelectronic factors involved in this isomerization have been investigated,[9] and the products have served as useful mechanistic probes in numerous contexts.[10] Several direct applications of this chemistry to total synthesis have also been achieved.[11,12]

A more expansive scrutiny of these reactive intermediates is undoubtedly warranted. A particularly informative case study involves the stereoselective synthesis of oxabicyclics that are typified by **8** (Scheme 1). The expectation was that protonation of **4** would trigger the formation of **5** and induce ring closure along two possible pathways. Rapid equilibration between two conformations of **5**, depicted as **6** and **7**, can be anticipated. Antiperiplanar intramolecular attack by the flanking allylsilane residue[13] should follow. In the case of **6**, direct conversion to the chairlike product **8** would materialize. Cyclization via **7** would lead first to the twist-boat conformer **9**[4a] and subsequently, for thermodynamic reasons, to the chair−chair geometry.

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

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(3) Hopkins, M. H.; Overman, L. E.; Rishton, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 5354.

(4) (a) Pothier, N.; Goldstein, S.; Deslongchamps, P. *Helv. Chim. Acta* **1992**, *75*, 604. (b) Deslongchamps, P.; Dory, Y. L.; Li, S. *Can. J. Chem.* **1994**, *72*, 2021. (c) Deslongchamps, P.; Dory, Y. L.; Li, S. *Helv. Chim. Acta* **1996**, *79*, 41.

(5) Marko, I. E.; Bayston, D. J. *Tetrahedron* **1994**, *50*, 7141.

(6) Ley, S. V.; Kouklovsky, C. *Tetrahedron* **1994**, *50*, 835.

(7) Marko, I. E.; Bailey, M.; Murphy, F.; Declercq, J.-P.; Tinant, B.; Feneau-Dupont, J.; Krief, A.; Dumont, W. *Synlett* **1995**, 123.

(8) (a) Paquette, L. A.; Lawhorn, D. E.; Teleha, C. A. *Heterocycles* **1990**, *30*, 765. (b) Negri, J. T.; Rogers, R. D.; Paquette, L. A. *J. Am. Chem. Soc.* **1991**, *113*, 5073. (c) Paquette, L. A.; Negri, J. T.; Rogers, R. D. *J. Org. Chem.* **1992**, *57*, 3947.

(9) (a) Paquette, L. A.; Andrews, J. F. P.; Vanucci, C.; Lawhorn, D. E.; Negri, J. T.; Rogers, R. D. *J. Org. Chem.* **1992**, *57*, 3956. (b) Paquette, L. A.; Lanter, J. C.; Johnston, J. N. Submitted for publication.

(10) (a) Paquette, L. A.; Branan, B. M.; Friedrich, D.; Edmondson, S. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1994**, *116*, 506. (b) Branan, B. M.; Paquette, L. A. *J. Am. Chem. Soc.* **1994**, *116*, 7658. (c) Paquette, L. A.; Branan, B. M. *Heterocycles* **1995**, *40*, 101. (d) Paquette, L. A.; Branan, B. M.; Rogers, R. D. *J. Org. Chem.* **1995**, *60*, 1852. (e) Paquette, L. A.; Branan, B. M.; Rogers, R. D.; Bond, A. H.; Lange, H.; Gleiter, R. *J. Am. Chem. Soc.* **1995**, *117*, 5992. (f) Paquette, L. A.; Branan, B. M.; Stepanian, M. *Tetrahedron Lett.* **1996**, *37*, 1721. (g) Paquette, L. A.; Stepanian, M.; Branan, B. M.; Edmondson, S. D.; Bauer, C. B.; Rogers, R. D. *J. Am. Chem. Soc.* **1996**, *118*, 4504.

(11) (a) Paquette, L. A.; Lord, M. D.; Negri, J. T. *Tetrahedron Lett.* **1993**, *34*, 5693. (b) Paquette, L. A.; Dullweber, U.; Cowgill, L. D. *Tetrahedron Lett.* **1993**, *34*, 8019. (c) Lord, M. D.; Negri, J. T.; Paquette, L. A. *J. Org. Chem.* **1995**, *60*, 191. (d) Paquette, L. A.; Wang, H.-L. *Tetrahedron Lett.* **1995**, *36*, 6005. (e) Paquette, L. A.; Wang, H.-L. *J. Org. Chem.* **1996**, *61*, 5352.

(12) Paquette, L. A.; Kinney, M. J.; Dullweber, U. Submitted for publication.

(13) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

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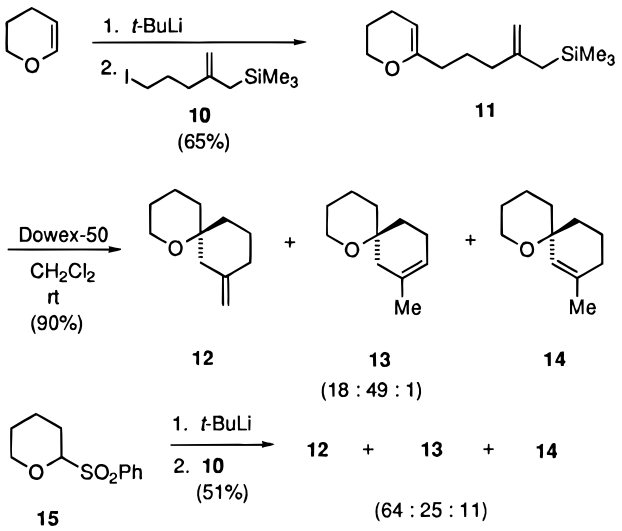
Scheme 2



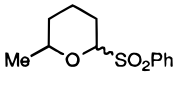
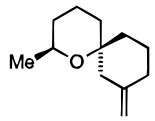
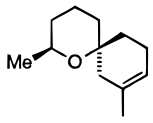
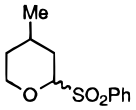
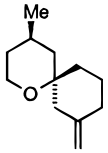
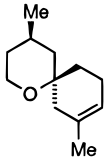
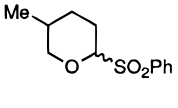
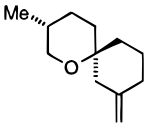
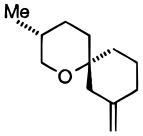
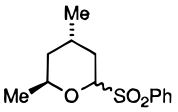
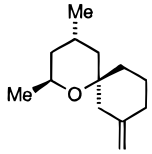
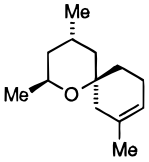
In the absence of additional stereochemical markers, these two pathways cannot be distinguished. The goals of the present undertaking were initially to determine feasibility in the parent system and subsequently to probe possible stereoelectronic bias by alkyl substitution resident at various positions on the pyran ring.

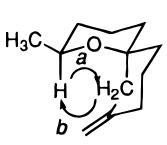
Results

The systematic investigation was initiated by metalation of dihydropyran with *tert*-butyllithium and alkylation with the known iodide **10**,[5] giving the sensitive product **11**. Exposure of **11** to Dowex-50 in CH_2Cl_2 for 5 h led efficiently to first-formed **12** and its postequilibrated isomers **13** and **14** (Scheme 2). In an alternative approach, sulfone **15**[14] was deprotonated and condensed with **10** at −78 °C. Slow warming of the reaction mixture to room temperature resulted in spontaneous generation of the oxonium ion[14] and direct generation of **12**−**14**. Since the overall yields of the two synthetic pathways are rather comparable, further work has relied on the sulfone approach because of its convenience and the readiness with which the starting substituted pyrans can be prepared. Also, the conditions do not require the coaddition of a strongly acidic catalyst such as Dowex-50. Spirocycle **12** is notably sensitive to acid and experiences a prototropic shift readily during chromatography, while standing in $CDCl_3$ solution, and the like. The varied product distributions recorded in Scheme 2 reflect the different reaction conditions and times and are intended to serve only as a reflection of the acid lability of **12**. The structural assignments to the olefinic isomers **13** and **14** are based reliably on 2D-COSY experiments. The distinctive nature of their vinyl proton chemical shifts in $CDCl_3$ (δ 5.35 for **13** and δ 5.54 for **14**) easily distinguishes these isomers from each other as well as from **12** (δ 4.71, 4.66).

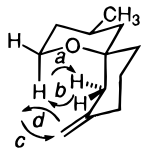
The known sulfones **16**[15] and **19**[16] were readily procurable in reasonable amounts as diastereomeric mixtures, which were used without separation. Alkylation of **16** with **10** led directly to a 98:2 mixture of **17** and **18** (Table 1). When **19** was subjected to the same protocol, a clear colorless oil consisting of **20** and **21** in an 81:19 ratio was produced. As in the case of **15**, the yields were modest because of the high volatility of the resulting spirocyclic ethers and the associated losses incurred during workup. The stereoselectivities of the two ring closures were exclusive and in the same direction. NOE enhancements observed for **17** and **20**, as revealed in **A** and **B**, confirm the proximity of the neopentyl allylic protons to the axial α-oxy protons shown. The ready isomerization of **17** to **18** and of **20** to **21** under acidic conditions demand that they be stereochemically related at the two stereogenic centers.

Table 1. Spontaneous Cyclization Reactions of Alkyl-Substituted 2-(Benzenesulfonyl)pyrans following Alkylation with 10

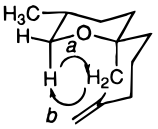
sulfone	yield, %	products (ratio)
 **16**	54	 **17** +  **18** (98 : 2)
 **19**	56	 **20** +  **21** (81 : 19)
 **22**	53	 **23** +  **24** (3.7 : 1)
 **25**	88	 **26** +  **27** (7.4 : 1)



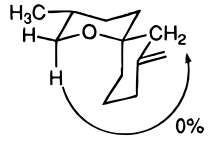
A
NOE; **a**: 6.8%
b: 11.0%



B
NOE; **a**: 1.8%; **b**: 1.9%
c: 3.4%; **d**: 3.6%



C
NOE; **a**: 6.2%
b: 3.8%

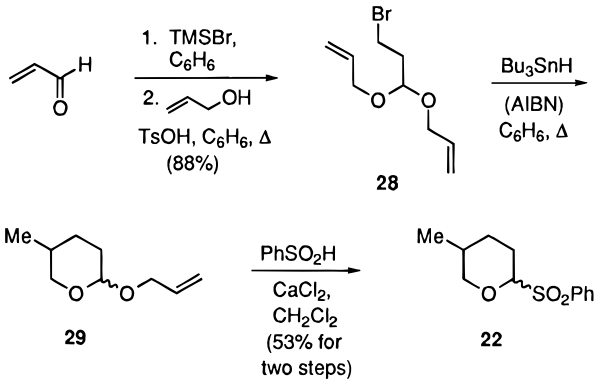


D

The 5-methyl substituted tetrahydropyranyl sulfone **22** was prepared according to Scheme 3. Conversion of

(14) Ley, S. V.; Lygo, B.; Sternfeld, F.; Wonnacott, A. *Tetrahedron* **1986**, *42*, 4333.
(15) Boons, G.-J.; Entwistle, D. A.; Ley, S. V.; Woods, M. *Tetrahedron Lett.* **1993**, *34*, 5649.
(16) Genicot, C.; Ley, S. V. *Synthesis* **1994**, 1275.

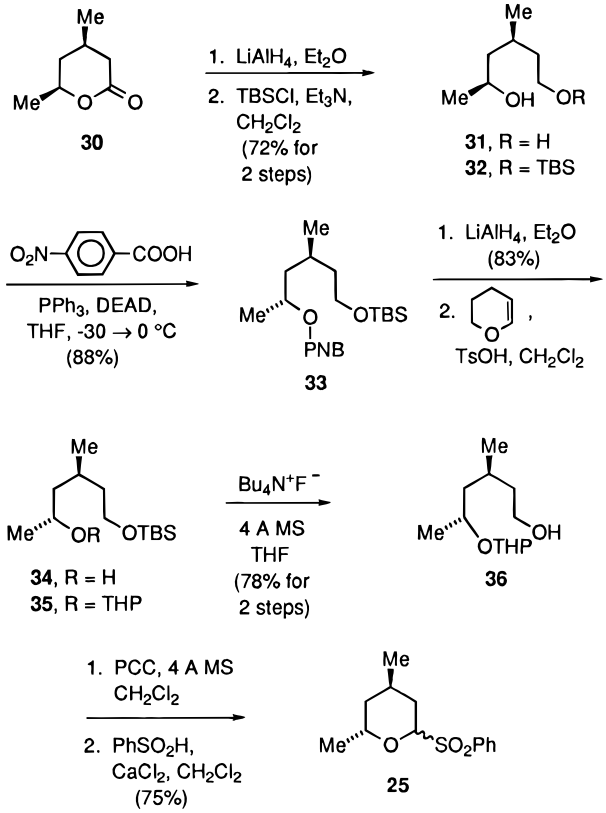
Scheme 3



acrolein to the bromine-substituted diallyl acetal **28**[17] set the stage for the free-radical cyclization[18] that involved heating with tributylstannane in benzene under AIBN catalysis. The direct conversion of **29** to **22** proceeded with good efficiency. A notable aspect of the alkylative spirocyclization of **22** is formation of the two diastereomeric ethers **23** and **24** (3.7:1, Table 1). Although it did not prove possible to effect isomer separation, the 300 MHz ^{1}H NMR spectrum of this mixture was sufficiently well-defined to allow acquisition of the NOE data depicted in **C** and **D**. Therefore, in contrast to **16** and **19**, the major pathway followed by **22** is to generate the new C−C bond syn to the methyl substituent.

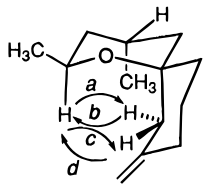
In order to probe whether the 4- or 6-methyl group is more controlling of the stereochemistry, attention was next directed to the *trans*-4,6-dimethyl example **25**. The starting point for this phase of the undertaking was the previously described lactone **30**.[19] Hydride reduction of **30** to diol **31** was followed by protection of the primary hydroxyl as the *tert*-butyldimethylsilyl derivative (Scheme 4). Subsequent Mitsunobu inversion[20] of the secondary

Scheme 4



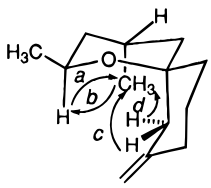
carbinol with *p*-nitrobenzoic acid[21] gave **33** from which the doubly protected **35** and the mono alcohol **36** were conventionally crafted. The final two steps consisted of oxidation to the aldehyde level with pyridinium chlorochromate in the presence of 4 Å molecular sieves and direct treatment of this penultimate intermediate with benzenesulfinic acid in the presence of $CaCl_2$. The assumption that complete inversion of configuration has materialized during the conversion of **32** into **33** was confirmed within experimental uncertainty by the high-yield conversion of **25** into **26** and **27** (7.4:1, Table 1).

As before, the isomer ratio and structural assignments were established using ^{1}H NMR and particularly NOE methods directly on the product mixture. The proximity of an axial proton and an axial methyl group to the neopentyl allylic methylene proton pair proved particularly diagnostic, as summarized in **E** and **F**. The post-isomerization of **26** to **27** parallels in its regioselectivity the formation of **18** and **21** and is taken to be a reflection of the greater thermodynamic stability of that internal olefin isomer carrying its double bond away from the pyran ring.



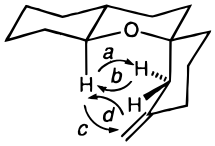
E

NOE; **a**: 2.2%; **b**: 3.1%
c: 1.9%; **d**: 5.1%



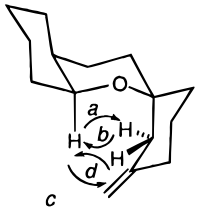
F

NOE; **a**: 1.0%; **b**: 2.8%
c: 1.4%; **d**: 1.0%



G

NOE; **a**: 1.8%; **b**: 1.9%
c: 3.4%; **d**: 3.6%



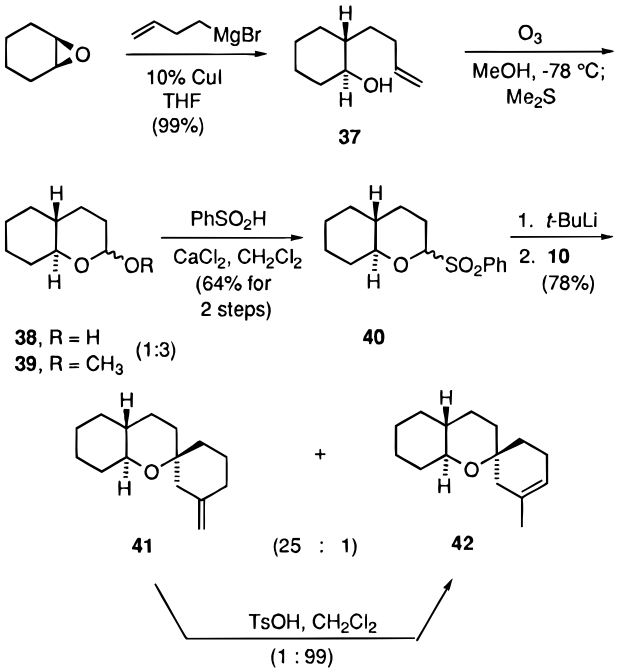
H

NOE; **a**: 3.5%; **b**: 4.3%
c: 5.3%; **d**: 7.6%

In order to assess the role of conformational rigidity during these cyclizations, the rigid trans-fused bicyclic sulfone **40** and its conformationally flexible cis isomer **47** were targeted for study. In the first instance, the efficiency with which cyclohexene oxide undergoes ring cleavage in the presence of 3-butenylmagnesium bromide and copper(I) iodide[22] was taken advantage of (Scheme 5). The formation of **37** in this way allowed for the subsequent ozonolysis in methanol. Following the work-up with methyl sulfide, a 1:3 mixture of cyclic lactol **38** and acetal **39** could be obtained and transformed directly into **40**. Low-temperature alkylation of the anion of **40**

(17) Hsung, R. P. *Synth. Commun.* **1990**, *20*, 1175.
(18) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741.
(19) McKelvey, R. D.; Kawada, Y.; Sugawara, T.; Iwamura, H. *J. Org. Chem.* **1981**, *46*, 4948.
(20) Hughes, D. L. *Org. React.* **1992**, *42*, 335.
(21) Martin, S. F.; Dodge, J. A. *Tetrahedron Lett.* **1991**, *32*, 3017.
(22) Bartlett, P. A.; Ting, P. C. *J. Org. Chem.* **1986**, *51*, 2230.

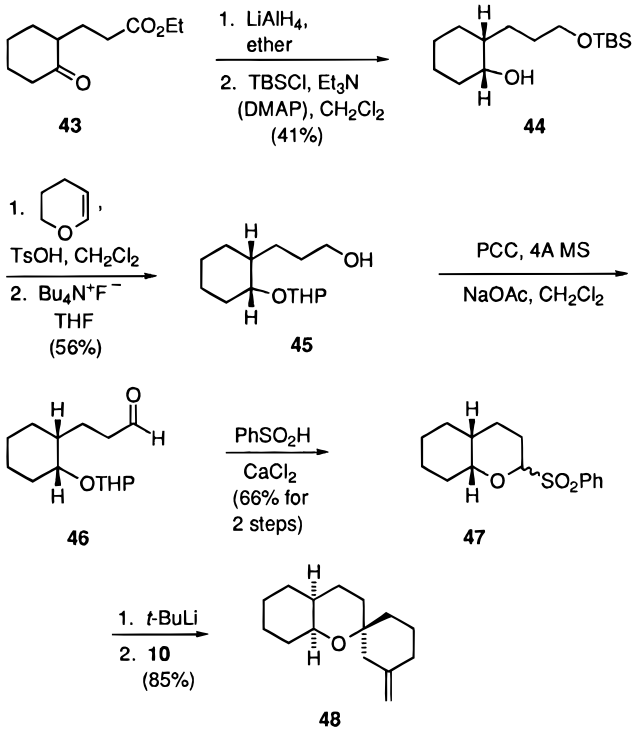
Scheme 5



with **10** followed by warming to room temperature delivered a 25:1 mixture of **41** and **42**. Under the aegis of *p*-toluenesulfonic acid, the isomerization of **41** to **42** was readily accomplished, to the point where **42** predominated heavily (99:1).

In order to avail ourselves of **47**, keto ester **43**[23] was transformed via **44** to the primary alcohol **45**, oxidation of which with pyridinium chlorochromate afforded the cis aldehyde **46** (Scheme 6). The conversion of **46** into sulfone **47** ensued. In this example, alkylation and desulfonylative cyclization was met with the exclusive formation of **48**. Remarkably, **48** is stable to *p*-toluenesulfonic acid in CH_2Cl_2. Evidently, the thermodynamics in the cis series differs significantly from that resident in the trans-fused counterpart.

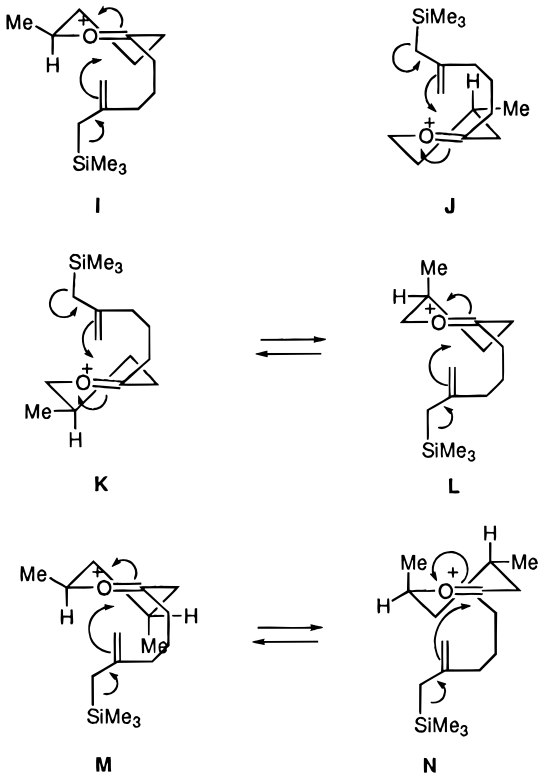
Scheme 6



The tricyclic exomethylene ethers **41** and **48** display diagnostic spectral characteristics similar to those of their lower analogues. In both of the examples, the axial α-oxy proton depicted in conformers **G** and **H** exhibited unmistakable NOE interactions with the proximal allylic methylene protons.

Discussion of Results

The stereoelectronic considerations central to a proper assessment of the above results are found in Scheme 1. Conformational analysis of the oxonium ion derived from **16** suggests that minimization of the nonbonded steric interactions would be best realized by projecting the methyl group pseudoequatorially as in **I**. Intramolecular



capture of the allylsilane likely proceeds under kinetic control without a necessary link to product stability. Since antiperiplanar attack, as shown in **I**, would lead via a chairlike transition state to the product, our expectation was that this pathway would be followed.[4,9b,12] Indeed, the conversion to **17** and **18** does indicate that C−C bond formation proceeds exclusively from that π-surface of the oxonium ion anti to the alkyl substituent on the tetrahydropyran ring.

In the case of **19**, the intervention of conformer **J** and the parallel stereoelectronic control during cyclization concisely rationalize the production of **20** and **21**.

Sulfone **22** represents the only example where two stereochemically distinctive pathways were found to operate. The favored formation of **23** suggests that cyclization of oxonium ion **K** via a chairlike transition state predominates over the second chairlike option **L**. While this bias is in line with the energetic advantage that should accrue to the equatorial methyl conformer, the dual operation of the two reaction channels implies that a 5-methyl substituent is less controlling of the

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conformational energies than one at either C-4 or C-6. A similar dropoff in the stereoselectivity has been noted by Mukaiyama for reductions of structurally related oxonium intermediates with triethylsilane.[24]

The *trans*-4,6-dimethyl example **25** is a particularly intriguing case study. The finding that cyclization operates cleanly cis to the 4-Me and trans to the 6-Me suggests that the substitution resident in the associated oxonium ion is reinforcing of stereocontrol rather than being mismatched. However, the configuration set at the spiro carbon can be reconciled only via the chairlike closure depicted in **M** or the boatlike alternative **N**. Although we are not in a position to distinguish between these alternatives, attention is called to the potential enthalpic disadvantage associated with the developing 1,3-diaxial interaction in **M**. This feature is not present in **N**, which instead must face the energetic costs of proceeding to a twist-boat product. This particular geometry may be more readily accommodated than what was initially assumed since the methylenecyclohexane ring encounters minimal steric compression against either methyl group in that arrangement.[12,25]

For the trans and cis bicyclic sulfones **40** and **47**, analysis of the stereochemical data leads one to conclude that stereoinduction is totally controlled by cyclization on that face of their oxonium ions syn to the angular α-oxy proton. By inspection of **G** and **H**, it can easily be gauged that chairlike transition states are adopted in both instances.

Although ground state torsional interactions can be complex in their origin, extrapolation of these data to transition structures is often done for estimation purposes. However, there is yet no way to estimate the torsional effects of the developing bonds in the developing transition states. Some of the difficulty lies in our lack of knowledge of the extent of rehybridization, which is dependent in turn on the earliness or lateness of the transition state. Notwithstanding, the present study provides a foundation upon which predictions involving the nucleophilic capture of cyclic oxonium ions may be more soundly based.

Experimental Section

General Considerations. Melting points are uncorrected. The column chromatographic separations were performed with Woelm silica gel (230−400 mesh). Solvents were reagent grade and in most cases dried prior to use. The purity of all of the compounds was shown to be >95% by TLC and high-field ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz). The high-resolution mass spectra were obtained at The Ohio State University Campus Chemical Instrumentation Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and at Atlantic Microlab, Inc., Norcross, GA.

Alkylation−Cyclization of Dihydropyran. A cold (−78 °C), magnetically stirred solution of dihydropyran (461 mg, 5.48 mmol) in dry THF (30 mL) was treated with *tert*-butyllithium (3.9 mL of 1.7 M in pentane), stirred for 10 min, warmed to 0 °C for 30 min, and returned to −78 °C, at which point iodide **10**[5] (506 mg, 1.79 mmol) was introduced. The reaction mixture was allowed to warm slowly to rt, stirred for 15 h, and quenched with water (20 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 × 30 mL). The combined organic solutions were dried over anhydrous K_2CO_3 and concentrated to leave a residue that was flash chromatographed on basic alumina (elution with 8:1 hexanes/ethyl acetate with 1% triethylamine). The product **11** was isolated as a colorless liquid (178 mg, 65%).

A CH_2Cl_2 solution (15 mL) of **11** (91 mg, 0.382 mmol) was stirred with Dowex-50 (30 mg) for 5 h, passed through a small pad of Celite, and concentrated. Chromatography of the crude product on silica gel (elution with 4:1 hexanes/ethyl acetate) gave 57 mg (90%) of an 18:49:1 mixture of **12**, **13**, and **14** as a colorless oil.

For **12**: IR (neat, cm^{-1}) 1660, 1500, 1095, 1060; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.71 (s, 1 H), 4.66 (s, 1 H), 3.40 (m, 2 H), 2.34 (d, J = 13.2 Hz, 1 H), 2.17 (d, J = 13.2 Hz, 1 H), 2.2−2.1 (m, 2 H), 1.85 (m, 1 H), 1.7−1.6 (m, 4 H), 1.6−1.4 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 146.2, 109.2, 73.4, 61.0, 44.0, 34.6, 34.43, 34.39, 26.0, 22.3, 19.0; MS m/z (M^+) calcd 116.1358, obsd 116.1353. Anal. Calcd for $C_{11}H_{18}O$: C, 79.45; H, 10.92. Found: C, 79.64; H, 10.96.

For **13**: ^{1}H NMR (300 MHz, $CDCl_3$) distinctive signals appear at δ 5.35 (br s, 1 H), 2.00 (s, 2 H), and 1.63 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm key absorptions at 131.2, 120.2, 71.4, 60.9, 23.7.

For **14**: ^{1}H NMR (300 MHz, $CDCl_3$) distinctive signals appear at δ 5.54 (s, 1 H) and 1.68 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm key absorptions at 137.9, 125.3, 70.6, 61.4, 23.8.

General Procedure for the Alkylation−Cyclization of the 2-(Benzene-sulfonyl)tetrahydropyrans. A. A cold (−78 °C), magnetically stirred solution of **15**[14] (620 mg, 2.74 mmol) in dry THF (10 mL) was treated dropwise with *tert*-butyllithium (1.9 mL of 1.7 M in hexanes, 3.23 mmol) under N_2. After 1 h, iodide **10** (773 mg, 2.74 mmol) was slowly introduced, and the reddish reaction mixture was stirred for 1 h at −78 °C and for 6 h at rt prior to being quenched with water (20 mL). The separated aqueous layer was extracted with ether (2 × 30 mL), and the combined organic layers were dried and carefully evaporated. Column chromatography of the residue on silica gel (elution with 20:1 hexanes/ether) gave 230 mg (51%) of a 64:25:11 mixture of **12**, **13**, and **14**.

B. The 6-Methyl Derivative. Comparable treatment of **16**[15] (890 mg, 3.70 mmol) furnished 362 mg (54%) of a 98:2 mixture of **17** and **18** as a colorless oil.

For **17**: IR (neat, cm^{-1}) 1655, 1450, 1250, 1080, 1055; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (s, 1 H), 4.60 (s, 1 H), 3.70 (ddt, J = 11.4, 2.2, 6.1 Hz, 1 H), 2.37 (s, 2 H), 2.11 (t, J = 6.2 Hz, 2 H), 1.8−1.4 (m, 10 H), 1.10 (d, J = 6.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 146.7, 108.8, 74.1, 65.4, 40.3, 39.9, 34.7, 33.6 (2 C), 32.7, 22.7, 19.3; MS m/z (M^+) calcd 180.1514, obsd 180.1504. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.84; H, 11.13.

For **18**: ^{1}H NMR (300 MHz, $CDCl_3$) distinctive signals appear at δ 5.33 (s, 1 H), 2.07 (s, 2 H), and 1.61 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm key absorptions at 131.4 and 120.9.

C. The 4-Methyl Derivative. Analogous processing of **19**[16] (247 g, 1.03 mmol) provided 104 mg (56%) of an 81:19 mixture of **20** and **21** as a colorless oil.

For **20**: IR (neat, cm^{-1}) 1652, 1445, 1374, 1325, 1162, 1086; ^{1}H NMR (300 MHz, C_6D_6) δ 4.79 (s, 1 H), 4.70 (s, 1 H), 3.63 (ddd, J = 1.6, 5.1, 11.8 Hz, 1 H), 3.48 (dt, J = 2.5, 12.2 Hz, 1 H), 2.46 (d, J = 13.3 Hz, 1 H), 2.03 (d, J = 13.3 Hz, 1 H), 2.20−1.80 (m, 3 H), 1.67 (m, 1 H), 1.60−1.35 (m, 4 H), 1.23 (m, 1 H), 1.05 (m, 1 H), 0.80 (m, 1 H), 0.76 (d, J = 6.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 146.3, 109.2, 74.0, 60.7, 42.9, 39.9, 39.6, 34.62, 34.57, 25.1, 22.7, 22.5; MS m/z (M^+) calcd 180.1514, obsd 180.1511. Anal. Calcd for $C_{12}H_{20}O$: 79.94; H, 11.18. Found: C, 79.66; H, 11.16.

For **21**: ^{1}H NMR (300 MHz, $CDCl_3$) distinctive signals appear at δ 5.38 (s, 1 H), 2.14 (s, 2 H), and 1.66 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm one of the olefnic carbons is evident at 120.3.

D. The 5-Methyl Derivative. From the alkylation of **22** (927 mg, 3.86 mmol), there was obtained 368 mg (53%) of a 3.7:1 mixture of **23** and **24** as a colorless oil: IR (neat, cm^{-1}) 1652, 1439, 1356, 1084; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.71 (s, 1 H), 4.64 (s, 1 H), 3.56 (m, 1 H), 3.24 (dd, J = 10.5, 11.5 Hz,

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0.78 H, major), 3.15 (dd, J = 10.3, 11.5 Hz, 0.22 H, minor), 2.42 (d, J = 13.3 Hz, 1 H), 2.23 (d, J = 12.9 Hz, 1 H), 2.20−1.95 (m, 2 H), 1.75−1.15 (series of m, 9 H), 0.82 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) (for **23**) ppm 146.2, 109.2, 73.1, 67.1, 39.5, 38.9, 34.6, 33.5, 30.8, 27.5, 22.6, 17.3; ^{13}C NMR (75 MHz, $CDCl_3$) (for **24**) ppm 146.2, 109.1, 73.1, 67.4, 48.1, 38.9, 34.3, 30.6, 29.4, 27.8, 22.2, 17.3; MS m/z (M^+) calcd 180.1514, obsd 180.1506. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.82; H, 11.10.

E. The *trans*-4,6-Dimethyl Derivative. Comparable treatment of **25** (931 mg, 3.66 mmol) gave rise to 625 mg (88%) of a 7.4:1 mixture of **26** and **27** as a colorless oil.

For **26**: IR (neat, cm^{-1}) 1650, 1450, 1380, 1075; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (s, 1 H), 4.61 (s, 1 H), 4.00−3.65 (m, 1 H), 2.29 (d, J = 13.0 Hz, 2 H), 2.30−1.80 (series of m, 3 H), 1.80−1.35 (series of m, 6 H), 1.35−1.10 (m, 2 H), 1.15 (d, J = 6.3 Hz, 3 H), 1.01 (d, J = 7.0 Hz, 3 H); ^{13}C (75 MHz, $CDCl_3$) ppm 146.8, 108.9, 74.6, 63.1, 45.9, 39.6, 39.5, 38.3, 34.5, 23.6, 23.1, 22.6, 21.8; MS m/z (M^+) calcd 194.1670, obsd 194.1656. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.20; H, 11.47.

For **27**: ^{1}H NMR (300 MHz, $CDCl_3$) distinctive signals seen at δ 5.40 (m, 1 H), 2.08 (d, J = 13.0 Hz, 2 H), and 1.63 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm key absorptions at 131.7, 120.1, 72.3, 63.8.

F. Starting from 40. Analogous processing of **40** (360 mg, 1.28 mmol) afforded 220 mg (78%) of a 25:1 mixture of **41** and **42**.

For **41**: colorless oil; IR (neat, cm^{-1}) 1651, 1449, 1365, 1105, 1074; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.68 (s, 1 H), 4.61 (s, 1 H), 3.20 (m, 1 H), 2.45 (d, J = 13.0 Hz, 1 H), 2.31 (d, J = 13.0 Hz, 1 H), 2.15 (m, 2 H), 1.80−0.0 (series of m, 17 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 148.8, 109.0, 74.2, 73.9, 42.5, 40.3, 40.2, 34.8, 33.6, 33.2, 31.8, 26.6, 26.0, 25.3, 22.8; MS m/z (M^+) calcd 220.1827, obsd 220.1823. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.89; H, 11.03.

A 50 mg (0.23 mmol) sample of **41** was stirred in CH_2Cl_2 (20 mL) containing a crystal of *p*-toluenesulfonic for 15 h resulting in isomerization to a 1:99 mixture of **41** and **42**.

For **42**: colorless oil; IR (neat, cm^{-1}) 1680, 1445, 1355, 1100, 1085; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (s, 1 H), 3.20 (m, 1 H), 2.33 (d, J = 17.0 Hz, 1 H), 2.15−1.90 (m, 3 H), 1.85−1.40 (m, 6 H), 1.66 (s, 3 H), 1.40−0.85 (series of m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 131.8, 120.2, 74.3, 72.5, 42.5, 37.1, 36.4, 33.3, 32.8, 31.8, 26.9, 26.0, 25.3, 23.9, 23.2; MS m/z (M^+) calcd 220.1827, obsd 220.1828.

G. Starting from 47. Comparable treatment of **47** (252 mg, 0.90 mmol) yielded 168 mg (85%) of **48** as a colorless oil: IR (neat, cm^{-1}) 1650, 1445, 1079, 1060, 1051, 1014; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 1 H), 4.59 (s, 1 H), 3.82 (m, 1 H), 2.48 (d, J = 12.9 Hz, 1 H), 2.26 (d, J = 12.9 Hz, 1 H), 2.10 (m, 2 H), 1.90−1.10 (series of m, 17 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 147.0, 108.8, 74.1, 66.4, 40.4, 40.1, 34.8, 34.7, 32.3, 27.3, 26.2, 25.2, 24.9, 22.7, 20.3; MS m/z (M^+) calcd 220.1827, obsd 220.1828. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.49; H, 10.79.

Tetrahydro-2-(benzenesulfonyl)-5-methyl-2*H*-pyran (22). A cold (0 °C) solution of acrolein (6.68 mL, 0.10 mol) in dry benzene (120 mL) was treated with trimethylsilyl bromide (15.8 mL, 0.12 mol), stirred for 30 min at 0 °C, allowed to warm to rt, and stirred for an additional hour prior to the addition of allyl alcohol (20 mL, 0.30 mol) and *p*-toluenesulfonic acid (500 mg). The mixture was refluxed under a Dean-Stark trap for 15 h, cooled, and evaporated. Chromatography of the residue on silica gel (elution with 4:1 hexanes/ethyl acetate) gave **28** as a colorless liquid (20.8 g, 88%): IR (neat, cm^{-1}) 1647, 1423, 1388, 1346, 1263, 1215, 1117, 1045; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (m, 2 H), 5.25 (m, 4 H), 4.77 (t, J = 5.5 Hz, 1 H), 4.10 (m, 4 H), 3.43 (t, J = 6.8 Hz, 2 H), 2.18 (dt, J = 5.6, 6.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 134.3, 116.9, 100.5, 67.2, 36.8, 28.5; MS m/z (M^+) calcd 234.0255, obsd 234.0271.

A refluxing benzene solution (100 mL) of **28** (20.8 g, 88.5 mmol) and AIBN (100 mg) was treated dropwise with tri-*n*-butyltin hydride (28.5 mL, 106 mmol) in benzene (22 mL) over 4 h. After an additional hour of heating, the reaction mixture was concentrated, and the residue was filtered through silica gel (elution with 10:1 hexanes/ethyl acetate) to give **29** which was stirred overnight at rt with benzenesulfinic acid (20.0 g, 107 mmol) and $CaCl_2$ (30.0 g) in CH_2Cl_2 (200 mL). The reaction mixture was filtered and evaporated, and the product was purified by chromatography on silica gel (elution with 8:1 hexanes/ethyl acetate) to give **22** as a colorless solid, mp 103−105 °C (10.8 g, 53% for 2 steps). IR (neat, cm^{-1}) 1447, 1307, 1148, 1081, 1022; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (m, 2 H), 7.65 (m, 1 H), 7.52 (m, 2 H), 4.28 (br d, J = 11.5 Hz, 1 H), 3.91 (br d, J = 11.3 Hz, 1 H), 2.95 (t, J = 11.1 Hz, 1 H), 2.15 (m, 1 H), 1.95 (m, 1 H), 1.65 (m, 2 H), 1.15 (m, 1 H), 0.73 (d, J = 6.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 136.2, 133.8, 129.4, 128.7, 91.3, 75.0, 30.4, 29.7, 23.8, 16.4; MS m/z ($M^+ - SO_2$-Ph) calcd 99.0809, obsd 99.0807. Anal. Calcd for $C_{12}H_{13}O_3S$: C, 59.98; H, 6.71. Found: C, 60.06; H, 6.68.

(1*R,3*S**)-5-(*tert*-Butyldimethylsiloxy)-1,3-dimethylpentyl *p*-Nitrobenzoate (33).** A solution of **30** (8.56 g, 66.8 mmol) in ether (200 mL) was stirred at 0 °C with lithium aluminum hydride (2.53 g, 66.8 mmol) for 1.5 h, quenched with saturated Na_2SO_4 solution at 0 °C, filtered, and concentrated. Chromatography of the residue on silica gel (elution with 1:1 hexanes/ethyl acetate) gave **31** as a colorless oil. The diol was dissolved in CH_2Cl_2 (150 mL) containing triethylamine (14.0 mL, 100 mmol), cooled to 0 °C, and treated with a solution of *tert*-butyldimethylsilyl chloride (10.1 g, 66.8 mmol) and 4-(dimethylamino)pyridine (50 mg) in CH_2Cl_2 (50 mL). After stirring overnight at rt, the reaction mixture was washed with 2 N HCl (100 mL) and brine (50 mL), dried, and concentrated. Chromatography of the residue on silica gel (elution with 4:1 hexanes/ethyl acetate) afforded 11.8 g (72%) of **32** as a colorless oil: IR (neat, cm^{-1}) 3360, 1463, 1378, 1255, 1096, 1005, 901; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (m, 1 H), 3.65 (m, 2 H), 1.72 (s, 1 H), 1.85−1.65 (m, 1 H), 1.60−1.30 (m, 3 H), 1.25−1.05 (m, 1 H), 1.17 (d, J = 6.1 Hz, 3 H), 0.91 (d, J = 6.8 Hz, 3 H), 0.88 (s, 9 H), 0.04 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 66.0, 61.3, 46.9, 40.3, 26.6, 26.0, 24.3, 19.9, 18.4, −5.2; MS (M^+ − OH) calcd 229.1988, obsd 229.1972.

To a mixture of triphenylphosphine (15.1 g, 57.5 mmol) and *p*-nitrobenzoic acid (9.61 g, 57.5 mmol) in THF (200 mL) was added **32** (11.8 g, 47.9 mmol) dissolved in THF (30 mL), and subsequently after cooling to -30 °C, a THF solution (70 mL) of diethyl azodicarboxylate (9.19 mL, 57.5 mmol) was added. The reaction mixture was warmed slowly to 0 °C and after 2.5 h was quenched with saturated $NaHCO_3$ solution (150 mL). The separated aqueous layer was extracted with ether (2 × 100 mL), and the combined organic solutions were dried and evaporated. Purification of the product by initial addition of 1:3 ether/hexanes to precipitate the triphenylphosphine oxide and subsequent chromatography on silica gel (elution with 8:1 hexanes/ethyl acetate) furnished 16.6 g (88%) of **33**, a colorless oil: IR (neat, cm^{-1}) 1723, 1608, 1471, 1349, 1276, 1101, 1015; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (m, 4 H), 5.29 (m, 1 H), 3.62 (m, 2 H), 1.80−1.55 (m, 4 H), 1.35 (m, 1 H), 1.35 (d, J = 6.2 Hz, 3 H), 0.95 (d, J = 6.4 Hz, 3 H), 0.83 (s, 9 H), 0.00 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 164.1, 150.4, 136.2, 130.6, 123.4, 71.6, 60.7, 43.2, 39.6, 26.4, 25.8, 20.1, 19.7, 18.2, −5.4; MS m/z (M^+) calcd 395.2128, obsd 395.2112. Anal. Calcd for $C_{20}H_{33}NO_5Si$: C, 60.73; H, 8.41. Found: C, 60.88; H, 8.47.

Tetrahydro-2-(benzenesulfonyl)-*trans*-4,5-dimethyl-2*H*-pyran (25). A solution of **33** (16.6 g, 42.0 mmol) in ether (200 mL) was treated with lithium aluminum hydride (3.20 g, 84.0 mmol) at 0 °C. After 1.5 h, saturated Na_2SO_4 solution was introduced with ice cooling, and the reaction mixture was filtered and concentrated. Chromatography of the residue on silica gel (elution with 4:1 hexanes/ethyl acetate) gave **34** (8.63 g, 83%) as a colorless oil: IR (neat, cm^{-1}) 3360, 1472, 1378, 1255, 1097, 1006, 981; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (m, 1 H), 3.65 (m, 2 H), 1.74 (s, 1 H), 1.80−1.55 (m, 2 H), 1.40−1.25 (m, 3 H), 1.17 (d, J = 6.1 Hz, 3 H), 0.91 (d, J = 6.6 Hz, 3 H), 0.89 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 65.9, 61.3, 46.8, 39.4, 26.6, 25.9, 23.6, 20.5, 18.3, −5.3; MS m/z (M^+ − OH) calcd 229.1988, obsd 229.1993.

A mixture of **34** (8.63 g, 35.0 mmol) and *p*-toluenesulfonic acid (50 mg) in CH_2Cl_2 (100 mL) was treated with dihydropyran (6.4 mL, 70 mmol), stirred for 2 h, concentrated in vacuo,

and subjected directly to chromatography on silica gel (elution with 10:1 hexanes/ethyl acetate). The resulting **35** was dissolved in THF (150 mL) and treated with 4 Å molecular sieves (20 g) and tetra-*n*-butylammonium fluoride hydrate (13.2 g, 50.4 mmol). After 3 h of stirring at rt, the reaction mixture was decanted, washed with water (100 mL) and brine (50 mL), dried, and concentrated. Column chromatography of the residue on silica gel (elution with 2:1 hexanes/ethyl acetate) gave **36** as a colorless oil (6.00 g, 78%): IR (neat, cm^{-1}) 3417, 1454, 1378, 1260, 1200, 1120, 1076, 1023; ^1H NMR (300 MHz, C_6D_6) δ 4.71 (m, 0.6 H), 4.58 (m, 0.4 H), 4.00−3.75 (m, 2 H), 3.75−3.45 (m, 2 H), 3.45−3.25 (m, 1 H), 2.80 (br s, 1 H), 1.95 (m, 1 H), 1.85−1.00 (m, 10 H), 1.27 (d, J = 6.2 Hz, 1.8 H), 1.01 (d, J = 6.0 Hz, 1.2 H), 0.90 (d, J = 6.7 Hz, 1.2 H), 0.85 (d, J = 6.6 Hz, 1.8 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 98.6, 96.6, 72.7, 69.6, 63.0, 62.1, 60.6, 60.4, 45.5, 44.9, 40.4, 40.0, 31.7, 31.6, 26.7, 26.3, 26.0, 25.8, 22.2, 20.8, 20.4, 20.3, 19.9, 19.7; MS m/z (M^+) calcd 216.1725, obsd 216.1706.

A mixture of **36** (2.88 g, 13.3 mmol), 4 Å molecular sieves (6.0 g), and sodium acetate (100 mg) in CH_2Cl_2 (100 mL) was treated with pyridinium chlorochromate (4.30 g, 20.0 mmol), stirred for 1.5 h, loaded directly atop a column of silica gel, and eluted with 10:1 hexanes/ethyl acetate to give the aldehyde as a colorless oil. This material was stirred overnight with benzenesulfinic acid (5.00 g, 26.9 mmol) and calcium chloride (10.0 g) in CH_2Cl_2 (150 mL). The reaction mixture was suction-filtered, the filtrate was evaporated, and the residue was purified by chromatography on silica gel (elution with 8:1 hexanes/ethyl acetate) to provide 2.53 g (75%) of **25** as a white solid, mp 67−69 °C: IR (neat, cm^{-1}) 1446, 1383, 1308, 1150, 1074; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (m, 2 H), 7.65 (m, 1 H), 7.55 (m, 2 H), 4.62 (dd, J = 3.4, 11.5 Hz, 0.4 H, minor), 4.57 (dd, J = 3.1, 11.4 Hz, 0.6 H, major), 4.30 (m, 0.4 H, minor), 3.60 (dqq, J = 2.6, 6.1, 11.8 Hz, 0.6 H, major), 2.25 (m, 0.4 H, minor), 2.10 (m, 0.6 H, major), 1.95−1.70 (m, 1.4 H), 1.50−1.25 (m, 2.6 H), 1.08 (d, J = 6.2 Hz, 2.4 H), 1.06 (d, J = 6.3 Hz, 1.8 H), 0.96 (d, J = 6.5 Hz, 1.8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm (major) 136.2, 133.6, 129.2, 128.5, 88.0, 69.8, 37.7, 28.6, 23.7, 21.4, 17.5; (minor) 136.4, 133.6, 129.6, 128.7, 86.8, 70.1, 37.4, 30.3, 25.0, 22.0, 17.9; MS m/z ($M^+ - SO_2C_6H_5$) calcd 113.0966, obsd 113.0945.

(4a*R,8a*S**)-Hexahydro-2-(phenylsulfonyl)chroman (40).** Into a methanol solution (100 mL) of **37** (1.50 g, 9.72 mmol) was passed ozone for 1.5 h at −78 °C. The reaction mixture was treated with dimethyl sulfide (2.00 mL, 27.2 mmol), allowed to warm to rt overnight, and freed of solvent. The residue was subjected to chromatography on silica gel (elution with 4:1 hexanes/ethyl acetate) and afforded a 1:3 mixture of **38** and **39** which was immediately dissolved in CH_2Cl_2 (100 mL) and stirred overnight with benzenesulfinic acid (3.00 g, 16.1 mmol) and $CaCl_2$ (6.00 g). Following the predescribed workup, 1.75 g (64%) of **40** was isolated as a colorless liquid: IR (neat, cm^{-1}) 1450, 1320, 1155, 1100, 1090; ^1H NMR (300 MHz, C_6D_6) δ 8.01 (m, 2 H), 7.00 (m, 3 H), 4.17 (dd, J = 2.4, 11.7 Hz, 1 H), 2.35 (m, 1 H), 2.10 (m, 1 H), 1.7−0.4 (series of m, 12 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 137.9, 133.3, 130.1, 128.6, 91.9, 82.9, 40.6, 32.2, 31.1, 29.3, 25.6, 24.8, 24.7; MS m/z ($M^+ - SO_2C_6H_5$) calcd 139.1122, obsd 139.1121.

(4a*R,8a*R**)-Hexahydro-2-(phenylsulfonyl)chroman (47).** A solution of **43** (21.3 g, 0.107 mmol) in anhydrous ether (200 mL) was treated with lithium aluminum hydride (8.15 g, 0.122 mol) at 0 °C, stirred for 1.5 h, quenched with saturated Na_2SO_4 solution at 0 °C, filtered, and concentrated. Chromatography of the product gave the diol, which was dissolved in CH_2Cl_2 (250 mL) containing triethylamine (22.0 mL, 0.161 mol), and treated with a solution of *tert*-butyldimethylsilyl chloride (16.0 g, 0.107 mmol) and 4-(dimethylamino)pyridine (50 mg) at 0 °C. After being stirred overnight, the reaction mixture was washed with 2 N HCl (100 mL) and brine (50 mL) and then dried and concentrated. Column chromatography of the residue on silica gel (elution with 4:1 hexanes/ethyl acetate) gave 12.0 g (41%) of **44** as a colorless oil: IR (neat, cm^{-1}) 3405, 1471, 1388, 1255, 1102, 974; ^1H NMR (300 MHz, $CDCl_3$) δ 3.87 (m, 1 H), 3.60 (t, J = 6.5 Hz, 2 H), 1.85−1.15 (series of m, 14 H), 0.90 (s, 3 H), 0.88 (s, 6 H), 0.08 (s, 2 H), 0.03 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 69.2, 63.5, 41.1, 33.0, 30.2, 28.0, 26.8, 25.9, 25.6, 25.2, 20.5, 18.3, −3.6, −5.3; MS m/z (M^+) calcd 272.2172, obsd 272.2179.

A solution of **44** (2.30 g, 8.44 mmol) and *p*-toluenesulfonic acid (50 mg) in CH_2Cl_2 (50 mL) was treated with dihydropyran (1.20 mL, 13.2 mmol), stirred for 2 h, and concentrated in vacuo. Chromatography of the residue on silica gel (elution with 10:1 hexanes/ethyl acetate) gave the diprotected diol as a colorless oil, which was directly dissolved in THF (100 mL) and treated with 4 Å molecular sieves (10 g) and tetra-*n*-butylammonium fluoride hydrate (4.40 g, 16.8 mmol). After 3 h of stirring at rt, the decanted reaction mixture was washed with water (100 mL) and brine (50 mL), dried, and concentrated. Purification of the residue by chromatography on silica gel (elution with 4:1 hexanes/ethyl acetate) gave 1.15 g (56%) of **45** as a colorless oil: IR (neat, cm^{-1}) 3388, 1453, 1354, 1260, 1199, 1076, 1021, 999; ^1H NMR (300 MHz, C_6D_6) δ 4.66 (t, J = 3.5 Hz, 0.45 H), 4.58 (t, J = 3.9 Hz, 0.55 H), 4.00−3.30 (m, 5 H), 2.30−2.00 (series of m, 20 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 100.2, 95.9, 77.5, 72.5, 62.9 (2 C), 62.3 (2 C), 41.4, 41.3, 32.3, 31.8, 31.5, 30.9, 30.8, 28.8, 28.3, 28.0, 27.9, 26.1, 25.9, 25.7, 25.3, 22.2, 21.2, 20.5, 20.4, 20.1; MS m/z (M^+) calcd 242.1882, obsd 242.1882.

Oxidation of **45** (1.15 g, 4.75 mmol) with pyridinium chlorochromate (1.53 g, 7.10 mmol) as before and exposure of the resulting aldehyde to benzenesulfinic acid (3.00 g, 16.1 mmol) and $CaCl_2$ (6.0 g) in the customary manner furnished **47** (878 mg, 66%) as a colorless oil: IR (neat, cm^{-1}) 1446, 1310, 1307, 1150, 1060; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (m, 2 H), 6.95 (m, 3 H), 4.19 (dd, J = 3.3, 11.4 Hz, 1 H), 3.00 (m, 1 H), 1.85−0.75 (series of m, 13 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 137.4, 133.3, 130.2, 128.5, 92.4, 76.7, 33.9, 31.6, 28.0, 25.9, 24.9, 20.5, 19.4; MS m/z ($M^+ - C_6H_5SO_2$) calcd 139.1122, obsd 139.1134.

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Supporting Information Available: Copies of the high field ^1H and ^{13}C NMR spectra for those compounds lacking combustion data (20 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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