Sequential Annulation Approach to Sterpuric Acid and Sterpurene-3,12,14-triol, Metabolites of the Silver Leaf Fungus *Stereum purpureum*

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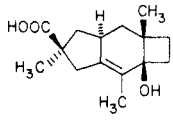
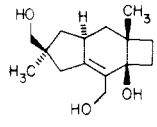
Abstract: Sterpuric acid (**1**) and sterpurene-3,12,14-triol (**2**), unusual oxygenated sesquiterpenes produced by the fungus *Stereum purpureum*, have been stereoselectively synthesized from the common precursor **5b**. Our approach begins with a Diels–Alder reaction involving diene **14**. Direct Jones oxidation of the product mixture delivers chiefly **13**, thereby setting the stage for [2 + 2] photocycloaddition to ethylene and the acquisition of **18**, an intermediate already possessing the complete carbocyclic skeleton of the target molecules. The *tert*-butyldimethylsilyl enol ether of **18** underwent peracid oxidation to afford principally **29**, reductive desulfonylation of which delivered **32**. Condensation of this ketone with methylenetriphenylphosphorane accomplished introduction of the final carbon atom. The resulting exo methylene derivative **33** proved to be the branching point in the two syntheses. To arrive at sterpuric acid, **33** was subjected to sequential ene reaction with *N*-sulfinylbenzenesulfonamide and Raney nickel desulfurization. Final deblocking of the silyl ether and ester saponification delivered **1** in 11 steps with 11% efficiency. To acquire **2**, it was necessary to avoid a strong proclivity of the system for framework isomerization to linear triquinane derivatives. The key step involved oxidation of **33** with selenium dioxide in the presence of *tert*-butyl hydroperoxide. The tertiary allylic alcohol so formed (**42**) could then be oxidatively rearranged in the presence of Cr(VI). Dibal reduction of aldehyde **43** and unmasking of the tertiary hydroxyl afforded **2**. The overall efficiency in this instance was 5.5%.

In 1981, Ayer reported that the fungus *Stereum purpureum*, when grown in liquid culture, produces as metabolites several unique sesquiterpenes known to be responsible for "silver leaf disease".[1] In nature, this particular fungus attacks various types of trees through open wounds and proceeds to kill the sapwood and bark. The infected trees are easily recognized by means of the metallic luster of their foliage.[2] Under laboratory conditions, the culture broth yields sterpuric acid (**1**) and sterpurene-3,12,14-triol (**2**)[3] as major constituents. Hydrocarbon **3**, known as l-sterpurene, has been isolated from the mycelium.[4]



1



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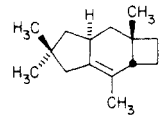
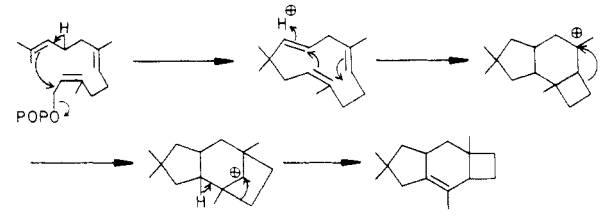


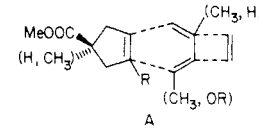
3

The sterpurenes, which are constructed of contiguously fused five-, six-, and four-membered carbocyclic rings, constitute natural products of a new structural type. Seemingly, their framework is assembled in vivo from farnesyl pyrophosphate via humulene and the protoilludyl cation (Scheme I).[5] In 1981, Murata and co-workers disclosed that **3** could, in fact, be derived chemically from humulene via a protocol analogous to the suggested biosynthesis.[6] More recently, l-sterpurene has also been prepared by an electroreductive cyclization route.[7]

Scheme I



Herein we detail a synthetic approach to the more highly oxygenated systems **1** and **2** that holds the prospect of being adaptable to yet other sterpurenes.[8] Our efforts have focused on the retrosynthetic concept of sequential annulation as summarized in A. The chemical issues requiring exploration were



A

(i) suitable activation of the cyclopentenyl double bond (note R) for its use as a dienophile, with proper allowance for its regiodirecting capabilities and for its eventual removal, (ii) direct elaboration of a bicyclic intermediate that would prove photoactivatable and therefore amenable to [2 + 2] photocycloaddition, (iii) appendage of the methyl or hydroxymethyl substituent on the central ring from a common precursor if possible, and (iv) introduction of the tertiary allylic hydroxyl onto the cyclobutane ring under conditions that would preclude allylic or more deep-seated rearrangement. The extent to which all of these tactics would lend themselves to stereochemical control was also of premier concern.

Discussion and Results

Cyclopentene Activation and Setting of the Tetrahydroindane Stereostructure. Advantage was first taken of a scheme recently developed in these laboratories[9] for the dienophilic activation of

(1) Ayer, W. A.; Saeedi-Ghomi, M. H.; Van Engen, D.; Tagle, B.; Clardy, J. *Tetrahedron* **1981**, *37*, Suppl. No. 1, 379.

(2) (a) Westcott, C. *Plant Disease Handbook*, 3rd ed.; van Nostrand Reinhold: Toronto, 1971; pp 354–355. (b) Hepting, G. H. *Diseases of Forest and Shade Trees of the United States*, Agriculture Handbook No. 386; U.S. Department of Agriculture Forest Service: Washington, DC, 1971; pp 61, 84, 90, 236, 400.

(3) Ayer, W. A.; Saeedi-Ghomi, M. H. *Can. J. Chem.* **1981**, *59*, 2536.

(4) Ayer, W. A.; Nakashima, T. T.; Saeedi-Ghomi, M. H. *Can. J. Chem.* **1984**, *62*, 531.

(5) (a) Ayer, W. A.; Browne, L. M. *Tetrahedron* **1981**, *37*, 2199. (b) Abell, C.; Leech, A. P. *Tetrahedron Lett.* **1987**, *28*, 4887.

(6) Murata, Y.; Ohtsuka, T.; Shirashama, H.; Matsumoto, T. *Tetrahedron Lett.* **1981**, *22*, 4313.

(7) Möens, L.; Baizer, M. M.; Little, R. D. *J. Org. Chem.* **1986**, *51*, 4497. **Note Added in Proof**: A short enantioselective synthesis of (+)-sterpurene has just been reported: Gibbs, R. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 4062.

(8) For a preliminary report dealing with a portion of this investigation, consult: Paquette, L. A.; Lin, H.-S.; Coghlan, M. J. *Tetrahedron Lett.* **1987**, *28*, 5017.

(9) (a) Paquette, L. A.; Crouse, G. D. *J. Org. Chem.* **1983**, *48*, 141. (b) Kinney, W. A.; Crouse, G. D.; Paquette, L. A. *Ibid.* **1983**, *48*, 4986.

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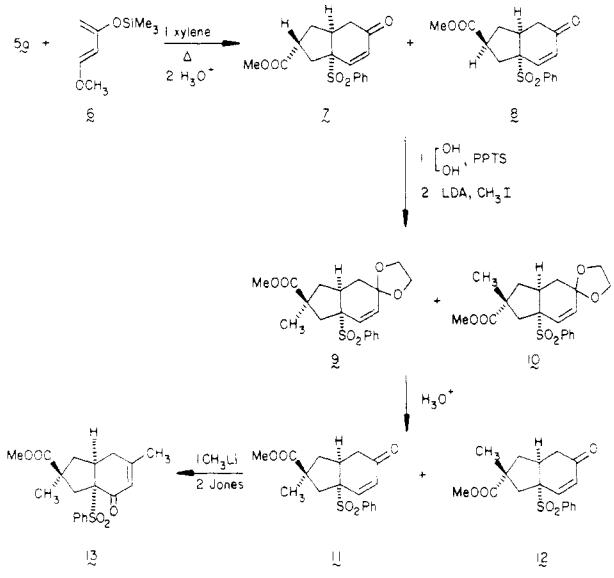
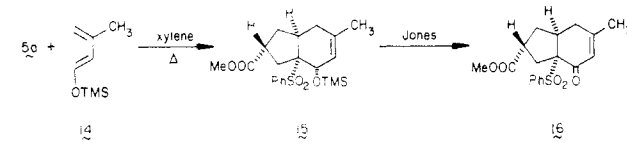
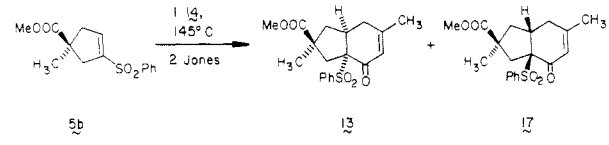
Scheme II



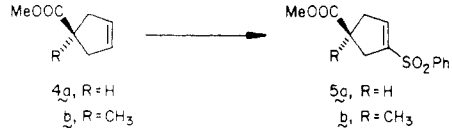
Scheme III



Scheme IV

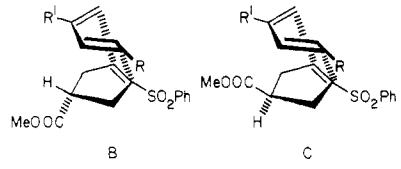


cyclic and acyclic olefins. Applied to the problem at hand, the method involved the photochemical[10] selenosulfonation[11] of **4a** and **4b**. 3-Cyclopentenecarboxylic acid, now simply and efficiently



available,[12,13] was esterified with diazomethane or under Fischer conditions to provide **4a**. Alkylation of the enolate anion of this ester with methyl iodide afforded **4b**. The conversions to **5a** and **5b**, respectively, proceeded efficiently. At a later point in this investigation, we became aware of a literature report[14] that described the addition of benzenesulfonyl bromide[15] across olefinic double bonds under free-radical conditions in the presence of zinc chloride. The potential economic advantage and convenience of this alternative led to its brief evaluation. Indeed, benzenesulfonyl bromide added readily to **4a** in the presence of a catalytic amount of benzoyl peroxide and zinc chloride in refluxing benzene during 36 h. Subsequent dehydrobromination with triethylamine in dichloromethane at room temperature afforded **5a** in 80% overall yield. Therefore, the latter option merits serious consideration in future activation schemes of this type.

The stage was now set for Diels–Alder coupling. However, the tactical demands surrounding **5a** differ from those associated with **5b**. In the first instance, application of the Alder rule and simple first-order consideration of steric effects lead one to conclude that transition state B should be kinetically more accessible than C.



Although the heavy predominance of one diastereomer is certainly attractive, definition of the important relative stereochemistry α to the carbomethoxy group is left to a subsequent enolate alkylation step, a process for which no reliable topological precedent was available. On the other hand, when beginning with **5b** the necessary stereochemical discrimination occurs during [4 + 2] cycloaddition and is subject to recognition by the diene partner of the steric differences between the methyl and carbomethoxy groups. Although some leveling of diastereoselectivity was anticipated in these circumstances, the issue had not been addressed previously. For these reasons, both avenues of investigation were pursued.

As seen in Scheme II, heating of **5a** with 1 equiv of Danishefsky's diene (**6**)[16] in xylene for 72 h delivered an 88:12 mixture of enones **7** and **8** following acid hydrolysis. Because these diastereomers proved not to be separable, the mixture was directly ketalized and methylated at −70 °C. Chromatography at this point made readily available in pure condition the functionalized bicyclic sulfones **9** and **10** in a ratio of 2:1. Following independent hydrolysis of these intermediates, enone **11** was treated in turn with methyllithium and the Jones reagent. The relative stereochemistries of **11** and **12** were established by 2D NOE studies carried out at 300 MHz.[17]

The response of **5a** to diene **14**[18] was more stereoselective (Scheme III), giving rise to **15** in 70% isolated yield following chromatography. Unfortunately, methylation of **15** α to its carbomethoxy group could not be effected without destruction of the material. However, its conversion to **16** by Jones oxidation proceeded well. The anticipated cis relationship of the benzenesulfonyl and carbomethoxy groups in **16** was confirmed by X-ray crystallographic analysis of its ethylene cycloadduct.[19]

The preceding experiments clarify two relevant issues, one stereochemical and one tactical. Since the **9**:**10** ratio is only 2:1, the differential steric shielding prevailing about the two faces of the ester enolate is clearly not very large, notwithstanding appearances given by Dreiding molecular models. Secondly, the use of **14** as diene makes available the properly substituted cyclohexenone subunit (see **13** and **16**) much more expediently than does the use of **6**. However, the utilization of **14** requires that the dienophile already be methylated as in **5b**.

Expectedly, **5b** was found to respond more sluggishly than **5a** to the same diene. Heating the methyl-substituted vinyl sulfone in the absence of solvent with 2.7 equiv of **14** at 145 °C for 5 days in the presence of a small amount of 2,6-di-*tert*-butylphenol, followed by direct Jones oxidation, provided **13** and **17** in a ratio of 2.1:1 (Scheme IV). When proper account is taken of the amount of unreacted **5b** (which is easily recovered and recycled) and the ease with which **13** and **17** are separated, this route to key intermediate **13** is seen to be highly expedient.

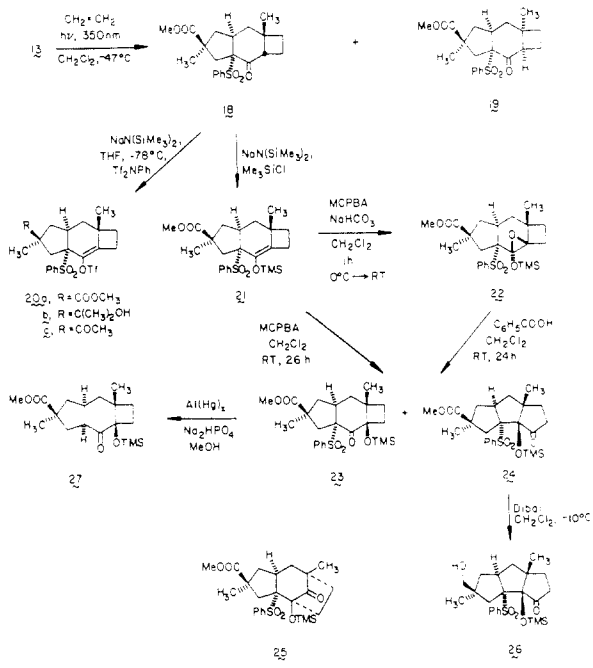
Consideration was also given to performing this cyclocondensation under high pressure. However, **14** is rapidly polymerized at room temperature under such conditions.

The predominance of **13** is fully consistent with the *A* values established for $COOCH_3$ (1.1 kcal mol^{-1}) and CH_3 groups (1.7 kcal mol^{-1}).[20]

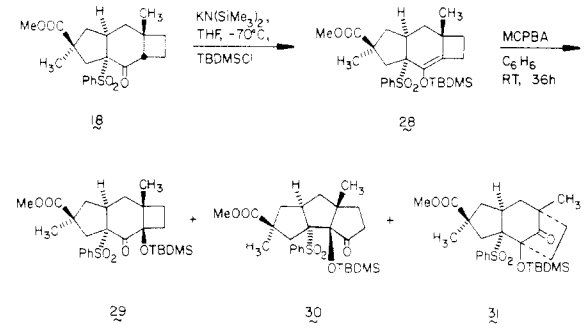
The [2 + 2] Photocycloaddition. Steric Congestion and the Proclivity for Skeletal Rearrangement. The original synthetic

(10) Gancarz, R.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899.
(11) Bock, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249.
(12) Depres, J.-P.; Greene, A. E. *J. Org. Chem.* **1984**, *49*, 928.
(13) Murdock, K. C.; Angier, R. B. *J. Org. Chem.* **1962**, *27*, 2395.
(14) Böll, W. *Liebigs Ann. Chem.* **1979**, 1665.
(15) Kakharkin, L. I.; Zhigareva, G. G. *Zh. Org. Khim.* **1973**, *9*, 891.
(16) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807.
(17) Gunn, B. P. MS Thesis, The Ohio State University, 1984.
(18) Rosner, A.; Tolkiehn, K.; Krohn, K. *J. Chem. Res., Miniprint* **1978**, 3831.
(19) We thank Dr. J. P. Springer (Merck Institute) for undertaking this study.
(20) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Interscience: New York, 1965; pp 435–442.

Scheme V



Scheme VI



model (A) contemplates a [2 + 2] photochemical cycloaddition between **13** and ethylene. Since the enone possesses a number of stereochemical centers somewhat remote from the double bond, product stereochemistry was expected to be dictated by the extent to which these pendant groups sterically shield the two avenues of approach.[21] At one extreme, there resides the angular benzenesulfonyl substituent. Although this group does possess substantial intrinsic steric bulk (A = 2.5 kcal mol^{-1}),[20] it alone was not considered adequate to override the blockade produced by the endo-oriented, cyclopentane-bound carbomethoxyl. Thus, while **18** was expected to be the major product, it remained to establish to what extent it would dominate over **19** in the product mixture.

Initial investigation of the photoaddition revealed that attempts to achieve consumption of all the starting enone caused appreciable diminution in yields because **18** and **19** were being degraded by the incident light. To circumvent this problem, cold (−47 °C) dichloromethane solutions of **13** were irradiated with 350-nm light only to ca. 50% conversion as denoted by TLC analysis (Scheme V). Under these circumstances, yields of **18** and **19** equal to 71 and 23%, respectively, could be routinely realized following chromatographic separation. The stereochemical assignment to **18** was established by X-ray crystallographic analysis.

Arrival at the target molecules from **18** minimally required (a) replacement of the cyclohexanone carbonyl by methyl and (b) insertion of an angular α-hydroxyl group. Access to a vinylic methyl intermediate could set the stage for subsequent epoxy sulfone formation and reductive desulfonylation–oxirane cleavage in the manner detailed by Kocienski.[22] The second option appeared more problematic and, therefore, attention was initially extended to enol triflate **20a**. It did not take long to discover, however, that the triflate functionality in **20a** and its associated π bond suffer from severe steric congestion. This intermediate proved totally unreactive to those protocols developed so successfully in other contexts by McMurry (Me_2CuLi, THF, 20 °C),[23] Stille (Me_4Sn, $Pd(PPh_3)_4$, LiCl, THF, reflux),[24] and Kumada (MeLi, $ZnBr_2$, $Ni(acac)_2$, THF, 20 °C).[25] Recourse to the more reactive higher order cuprate $Me_2Cu(CN)Li_2$[26] at −20 °C caused condensation to occur only at the ester group. The addition products **20b** (65%) and **20c** (18%) were formed efficiently while the enol triflate moiety remained intact.

In light of the above, the decision was made to introduce the angular α-hydroxyl substituent first. As with **20a**, it proved an easy matter to prepare silyl enol ether **21** without interference from the nearby oxygenated functional groups. Oxidation of **21** with MCPBA under buffered conditions at 0 °C for 1 h led exclusively to epoxide **22**. The remarkable kinetic stability of **22** and its exceptional crystallinity permitted structural analysis by X-ray techniques. At the time of this discovery, **22** represented the only documented example of a shelf-stable (trimethylsilyl)oxy epoxide.[27] In the interim, Davis and Sheppard have disclosed their independent discovery of an alternative, mild method for preparing structurally related molecules.[28]

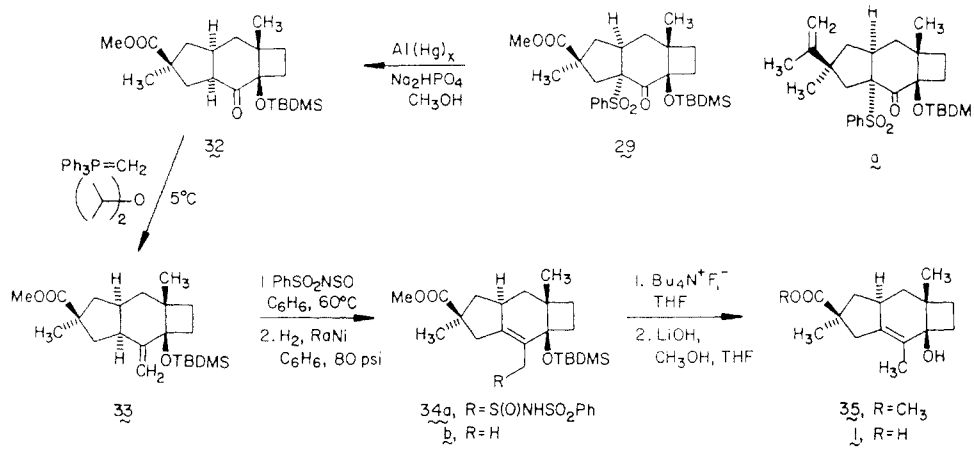
The susceptibility of **22** to acid[29] was made evident by its quantitative conversion to a 77:23 mixture of **23** and **24** when stirred with a catalytic quantity of benzoic acid in dichloromethane solution at room temperature for 24 h. Comparably, direct treatment of **21** with *unbuffered* MCPBA for a similar period of time gave rise directly to **23** in 76% yield alongside **24** (~10%).

Ketone **24** arises by 1,2-shift of the internal cyclobutane bond in tandem with translocation of the trimethylsilyl group. A priori, the possibility also exists for the formation of **25**, the consequence of involvement by the external four-membered σ bond.[30] However, this isomer was not seen. The structural assignment to **24** rests on its infrared carbonyl absorption (1745 cm^{-1}) characteristic of five-ring ketones and the experimental observation that exposure to Dibal resulted in exclusive reduction of the ester carbonyl and formation of **26**. In **24**, the cyclopentanone carbonyl finds itself in a severely crowded environment where hydride attack is disfavored. In contrast, one face of the ketone carbonyl group in **25** is sterically unencumbered.

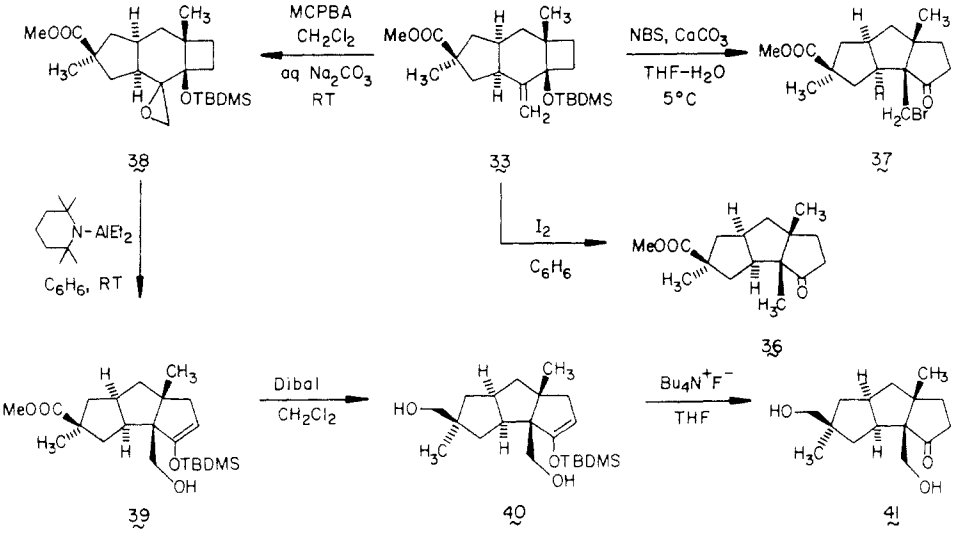
Pilot studies carried out on **18** showed this β-keto sulfone to undergo ready loss of its phenylsulfonyl group via electron transfer from such reagents as lithium dimethylcuprate and Lombardo's methylene titanium complex.[31] Since at this juncture it was necessary to remove the α-phenylsulfonyl group in **23**, its response to buffered aluminum amalgam[32] was probed. Although the conversion to **27** was shown to be feasible, the yield of this product never exceeded 34%. The source of the problem was traced to the lability of the TMSO group to the conditions of reduction. A change to a more stable blocking group was mandated, and the set of reactions outlined in Scheme VI was therefore performed.

(21) Baldwin, S. W. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, Chapter 2.
(22) Kocienski, P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 945, and relevant papers cited therein.
(23) McMurry, J. E.; Scott, W. J. *Tetrahdron Lett.* **1980**, *21*, 4313.
(24) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630.
(25) (a) Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915. (b) Hayashi, T.; Katsuro, Y.; Okamoto, Y.; Kumada, M. *Ibid.* **1981**, *22*, 4449.
(26) McMurry, J. E.; Mohanraj, S. *Tetrahedron Lett.* **1983**, *24*, 2723.
(27) Paquette, L. A.; Lin, H.-S.; Gallucci, J. C. *Tetrahedron Lett.* **1987**, *28*, 1363.
(28) Davis, F. A.; Sheppard, A. C. *J. Org. Chem.* **1987**, *52*, 954.
(29) All prior attempts to isolate a trimethylsilyl epoxide have led instead directly to α-silyloxy ketones, a clear reflection of the lability of such molecules: (a) Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, *15*, 4319. (b) Brook, A. G.; Macrae, D. M. *J. Organomet. Chem.* **1974**, *77*, C19. (c) Hassner, A.; Reuss, R. H.; Pinnick, H. W. *J. Org. Chem.* **1975**, *40*, 3427.
(30) Compare Sengupta, D.; Venkateswaran, R. V. *J. Chem. Soc., Chem. Commun.* **1986**, 1638.
(31) Lombardo, L. *Tetrahedron Lett.* **1982**, *23*, 4293.
(32) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, *17*, 3477.

Scheme VII



Scheme VIII



Elaboration of Sterpuric Acid. In the *tert*-butyldimethylsilyl series, the yield of **28** was maximized (95%) only when recourse was made to potassium hexamethyldisilazide as base. Direct treatment of **28** with MCPBA in benzene solution resulted in conversion to the desired tricyclic ketone **29** (72%) together with an inseparable mixture of **30** and **31** (28%, 2:1 ratio). As before, an intermediate silyloxy epoxide was discerned in this reaction (TLC analysis). Evidently, the slower migrating ability of *tert*-butyldimethylsilyl relative to trimethylsilyl allows external cyclobutane bond migration to become somewhat competitive.

Concordant with our rationale, chemospecific removal of the phenylsulfonyl group in **29** furnished **32** in 88% yield (Scheme VII). No tendency was exhibited for concurrent loss of the α-silyloxy substituent. Furthermore, whereas **29** reacted with the Wittig reagent to give **a**, **32** underwent smooth condensation with methylenetriphenylphosphorane in diisopropyl ether at 5 °C[33] to deliver **33**.

Our efforts now concentrated on migrating the external bond in **33** to the necessary internal site. To our dismay, all attempts to effect this transformation with such transition-metal reagnets as $RhCl_3 \cdot 3H_2O$, $(Ph_3P)_3RhCl$, and $Pd(C_6H_5CN)_2Cl_2$ either promoted no chemical change or afforded complex mixtures under more forcing conditions. This chemical behavior caused us to consider instead the more controlled response offered by ene reactions. In fact, the above complication was efficiently circumvented by admixing **33** with *N*-sulfinylbenzenesulfonamide[34] in benzene solution at 60 °C. Under these conditions, conversion to **34a** was complete after 7 h. Direct reductive desulfurization of this product with W-2 Raney nickel *in benzene solution*[35] furnished **34b** in 80% yield for the two steps.

With this simple solution to the final obstacle in the synthesis of sterpuric acid, the acquisition of **1** was completed by sequential exposure of **34b** to tetra-*n*-butylammonium fluoride and saponification. The synthetic sample of **1** was spectroscopically identical to the natural product.[36]

To sum up, sterpuric acid has been successfully elaborated in 11 steps from the vinyl sulfone **5b** in 11% overall yield.

The Challenge of Side-Chain Hydroxylation. Access to Sterpurene-3,12,14-triol. Application of the concerted mechanistic model often invoked for ene reactions[37] to the **33** → **34a** transformation provides a convenient conceptual framework for appreciating the fact that isomerization to a linear triquinane did not operate concurrently. At the other extreme, **33** undergoes skeletal rearrangement with exceptional facility. For example, exposure to a catalytic quantity of iodine in an inert solvent such as benzene suffices to induce efficient conversion to **36** (Scheme VIII). In like fashion, bromo ketone **37** was produced when **33** was reacted with *N*-bromosuccinimide in a reaction medium buffered with calcium carbonate.

(33) Schostarez, H.; Paquette, L. A. *Tetrahedron* **1981**, *37*, 4431.

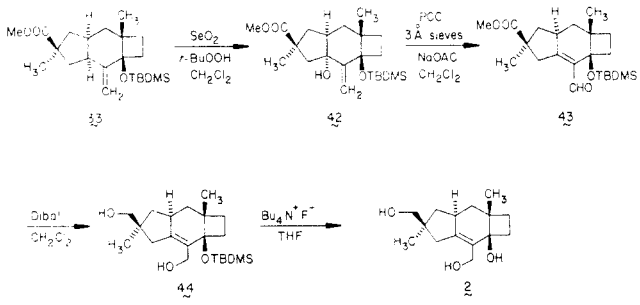
(34) (a) Deleris, G.; Kowalski, J.; Dunoguès, J.; Calas, R. *Tetrahedron Lett.* **1977**, *18*, 4211. (b) Deleris, G.; Dunoguès, J.; Calas, R. *Ibid.* **1979**, *20*, 4835. (c) Deleris, G.; Dunoguès, J.; Gadras, A. *Ibid.* **1984**, *25*, 2135.

(35) Use of the previously recommended[34] ethanol solvent furnished no **13b**.

(36) We thank Professor W. A. Ayer for graciously providing us with copies of the IR and ^1H NMR spectra.

(37) (a) Hoffman, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (b) Oppolzer, W.; Snieckus, V. *Ibid.* **1978**, *17*, 476. (c) Taber, D. F. *Intramolecular Diels–Alder and Alder Ene Reactions*; Springer-Verlag: Heidelberg, 1984; Chapter 3.

Scheme IX



When **33** was admixed with MCPBA under strongly buffered conditions and the epoxide so produced (**38**) treated directly with diethylaluminum 2,2,6,6-tetramethylpiperidide,[38] the richly functionalized triquinane **39** was isolated in 77% yield. The two-step conversion to **41** was subsequently undertaken in order to confirm that the silyl enol ether functionality in **39** was indeed contained within a five-membered ring. Later, an X-ray crystal structure analysis of **39** was secured.

The transformations collected in Scheme VIII signal unmistakably that **33** enters into Wagner–Meerwein bond relocation with much greater readiness than its ketone analogues **27** and **32**. To set the stage for regiospecific introduction of sterpurenetriol's primary hydroxyl substituent, it was necessary to reduce this proclivity to the zero level, or at least very close to this point. The reagent discovered to be optimal for our purposes was the combination of selenium dioxide and *tert*-butyl hydroperoxide.[39] Our intent was to take advantage of the recognized special ability of this oxidant to insert oxygen directly into an allylic carbon–hydrogen bond.[40] When performed in dichloromethane as solvent, this process furnished **42** in 47% yield (Scheme IX).

With this first-level oxidation accomplished, it proved most efficient to effect 1,3 oxidative rearrangement[41] within **42** by means of pyridinium chlorochromate. Since aldehyde **43** proved to be difficult to purify, this intermediate was immediately reduced to give **44**. The final deblocking step that delivered **2** was performed conventionally. The triol prepared in this manner was identified through spectral comparison with naturally derived sterpurene-3,12,14-triol.[36]

Thus, two of the more highly oxygenated sterpurane sesquiterpenes have been synthesized stereoselectively for the first time. It is expected that the basic approach developed here will prove useful for the synthesis of other members of this novel class of fungal metabolites.

Experimental Section

Methyl 1-(Phenylsulfonyl)cyclopentene-4-carboxylate (5a). A. By Selenosulfonation. A solution containing 2.3 g (18.25 mmol) of **4a**[42] and 5.1 g (17.1 mmol) of phenylselenenyl benzenesulfonate in 25 mL of carbon tetrachloride was irradiated for 2.5 h at 253.7 nm in a Rayonet reactor. The solvent was removed in vacuo, and the residue was diluted with 80 mL of dichloromethane. This solution was cooled to 0 °C, and 15 mL of 15% hydrogen peroxide was introduced with vigorous stirring. After 1 h at 0 °C, the reaction mixture was allowed to warm and stirred at room temperature for 1 h. The separated organic layer was washed with saturated sodium bicarbonate solution (2 × 75 mL) and brine (50 mL) prior to drying. The solvent was removed in vacuo to leave a solid, crystallization of which from ethyl acetate–hexane afforded 3.85 g (93%) of **5a**: colorless crystals, mp 63–64 °C; IR (CCl_4) 3060, 3000, 2950, 1740, 1620, 1580, 1445, 1350, 1310, 1205, 1150, 1090, 1015, 750, 715, 600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (m, 2 H), 7.62 (m, 3 H), 6.68 (br s, 1 H), 3.67 (s, 3 H), 3.28 (m, 1 H), 2.98 (d, J = 7.5 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.15, 143.29, 140.86, 139.33, 133.58, 129.24, 127.96, 52.13, 42.17, 36.22, 34.25; MS m/z (M^+) calcd 266.0613, obsd 266.0620. Anal. Calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30. Found: C, 58.55; H, 5.33.

B. Free-Radical Addition of Benzenesulfonyl Bromide. Ester **4a** (1.0 g, 7.9 mmol), benzene (10 mL), benzenesulfonyl bromide (1.75 g, 7.9 mL), zinc chloride (50 mg), and benzoyl peroxide (50 mg) were heated at reflux for 36 h. The reaction mixture was cooled and diluted with water (20 mL). The separated organic phase was dried and concentrated in vacuo. The crude bromo sulfone was directly taken up in dichloromethane (20 mL) to which triethylamine (1.20 g, 11.9 mmol) had been added. The resulting mixture was stirred at 25 °C for 36 h and washed successively with water (1 × 50 mL), 10% hydrochloric acid (1 × 50 mL), and water (1 × 50 mL). Following drying and solvent evaporation, the residue was subjected to MPLC purification on silica gel (30% ethyl acetate in petroleum ether) to afford 1.64 g (80%) of **5a** as a crystalline solid, mp 63–64 °C, which proved in all respects identical to the material prepared above.

Methyl 1-(Phenylsulfonyl)-4-methylcyclopentene-4-carboxylate (5b). A solution of ester **4b**[43] (2.00 g, 14.3 mmol) and phenylselenenyl benzenesulfonate (4.45 g, 15.0 mmol) in 100 mL of carbon tetrachloride was irradiated as described above and subsequently oxidized with 30% hydrogen peroxide in 80 mL of dichloromethane. The identical workup left an oil, which was purified by Kugelrohr distillation [bp 200–222 °C (1 Torr)]. There was isolated 2.80 g (70%) of **5b**: IR ($CDCl_3$) 3080, 2960, 1735, 1625, 1450, 1320, 1310, 1160, 1100, 990, 915 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85–7.48 (m, 5 H), 6.60 (br s, 1 H), 3.59 (s, 3 H), 3.01 (br t, J = 12 Hz, 2 H), 2.43 (br d, J = 12 Hz, 2 H), 1.23 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 142.2, 140.0, 139.0, 133.4, 129.0, 127.6, 52.0, 49.1, 43.8, 41.6, 25.3; MS m/z (M^+) calcd 280.0770, obsd 280.0787. Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75. Found: C, 59.95; H, 5.88.

Methyl (2*R,3a*S**,7a*R**)-3a,6,7,7a-Hexahydro-6-oxo-3a-(phenylsulfonyl)-2-indancarboxylate (7 and 8).** A solution of vinyl sulfone **5a** (3.5 g, 12.1 mmol) and Danishefsky's diene **6** (2.8 g, 13.8 mmol) in dry xylene (25 mL) was refluxed for 72 h in base-washed glassware. After the solution was cooled, concentrated hydrochloric acid (15 mL) and water (10 mL) were added, and the mixture was stirred at room temperature for 1 h. After extraction with dichloromethane (3 × 50 mL), the combined organic layers were dried and concentrated in vacuo to leave a dark oil, which was purified by MPLC on silica gel (35% ethyl acetate in petroleum ether) to return 1.1 g of **5a** and give 2.65 g (88% based on recovered starting material) of the cycloadducts **7** and **8** in an 88:12 ratio: IR (CCl_4) 3020, 2950, 1735, 1685, 1440, 1430, 1350, 1310, 1220, 1140, 1075 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (m, 2 H), 7.6 (m, 3 H), 6.45 (dd, J = 9, 2 Hz, 1 H), 6.18 (d, J = 9 Hz, 1 H), 3.62 (s, 3 H), 3.25 (m, 1 H), 2.78 (m, 2 H), 2.38 (m, 3 H), 1.75 (m, 2 H).

This material was directly ketalized.

Methyl (2′*R,3′a*R**,7′a*S**)-3′a,7′a-Dihydro-7′a-(phenylsulfonyl)spiro[1,3-dioxolane-2,5′(4′*H*)-indan]-2′-carboxylate.** A solution of the **7**/**8** mixture (2.65 g, 7.9 mmol), ethylene glycol (1.75 g, 28 mmol), and pyridinium tosylate (100 mg) in benzene was refluxed for 18 h with provision for azeotropic removal of water via a Dean–Stark trap. After being cooled, the solution was washed successively with saturated sodium bicarbonate solution (1 × 50 mL) and water (1 × 50 mL). The organic layer was dried, concentrated in vacuo, and purified by MPLC on silica gel (40% ethyl acetate in petroleum ether). There was obtained 3.0 g (100%) of the ketal mixture as a colorless crystalline solid: mp 142–144 °C (from ethyl acetate); IR (CCl_4) 3050, 2950, 2860, 1725, 1680, 1580, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (m, 2 H), 7.60 (m, 3 H), 5.85 (d, J = 9 Hz, 2 H), 3.90 (m, 4 H), 3.70 (s, 3 H), 2.95 (m, 3 H), 2.25 (m, 3 H), 1.60 (m, 2 H). Anal. Calcd for $C_{19}H_{22}SO_6S$: C, 60.30; H, 5.86. Found: C, 60.30; H, 5.88.

Methyl (2′*R,3′a*R**,7′a*S**)-3′a,7′a-Dihydro-2′-methyl-7′a-(phenylsulfonyl)spiro[1,3-dioxolane-2,5′(4′*H*)-indan]-2′-carboxylate (9 and 10).** A flame-dried flask equipped with a dropping funnel and magnetic stirrer was charged with tetrahydrofuran (2.5 mL) and diisopropylamine (0.11 mL, 0.78 mmol). After the mixture was cooled to −70 °C, *n*-butyllithium (0.47 mL of a 1.65 M solution, 0.78 mmol) was added dropwise over 2 min, and the resulting solution was stirred for 15 min at −70 °C. A tetrahydrofuran solution (2.5 mL) of the above ketal mixture (300 mg, 0.71 mmol) was added dropwise over 5 min. The resulting yellow solution was stirred for 15 min at −78 °C followed by the addition of methyl iodide (0.067 mL, 1.065 mmol). After 10 min, the reaction mixture was diluted with water (10 mL) and allowed to warm to room temperature. Extraction with diethyl ether (2 × 25 mL) followed by drying and concentration in vacuo yielded a yellow oil, which was purified by MPLC (35% ethyl acetate in petroleum ether) to afford 120 mg of **9** and 60 mg of **10** for a combined yield of 60%.

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For **9**: IR (CCl_4) 2945, 2890, 1730, 1445, 1301, 1140, 1081, 1051 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94–7.82 (m, 2 H), 7.71–7.62 (m, 1 H), 7.59–7.43 (m, 2 H), 5.82 (m, 2 H), 3.90 (m, 4 H), 3.74 (s, 3 H), 2.81–1.51 (m, 7 H), 1.30 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.46, 136.45, 131.86, 131.35, 128.47, 102.54, 70.72, 64.72, 63.95, 52.13, 47.41, 46.32, 44.40, 41.15, 36.99, 32.78, 25.62.

For **10**: IR (CCl_4) 2945, 2890, 1730, 1445, 1301, 1140, 1081, 1051 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.95–7.80 (m, 2 H), 7.71–7.60 (m, 1 H), 7.51–7.40 (m, 2 H), 5.80 (m, 2 H), 3.90–3.70 (m, 4 H), 3.64 (s, 3 H), 2.90–1.52 (m, 7 H), 1.40 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.99, 136.23, 133.89, 131.22, 130.12, 128.75, 102.42, 70.04, 64.64, 63.93, 52.29, 48.06, 46.18, 41.04, 37.40, 32.07, 26.09.

Methyl (2*R,3a*S**,7a*R**)-3a,6,7,7a-Tetrahydro-2-methyl-6-oxo-3a-(phenylsulfonyl)-2-indancarboxylate (11 and 12).** Stirring either **9** or **10** (100 mg, 0.26 mmol) in acetone (10 mL) and water (2 mL) at reflux with pyridinium tosylate (20 mg) for 6 h resulted in quantitative conversion to **11** and **12**, respectively.

For **11**: IR ($CDCl_3$) 2955, 1730, 1680, 1445, 1302, 1141, 1080 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90–7.86 (m, 2 H), 7.75–7.67 (m, 1 H), 7.64–7.55 (m, 2 H), 6.38 (dd, J = 10.2, 2 Hz, 1 H), 6.10 (d, J = 10.2 Hz, 1 H), 3.62 (s, 3 H), 2.67–1.94 (m, 7 H), 1.40 (s, 3 H).

For **12**: IR ($CDCl_3$) 2953, 1731, 1681, 1442, 1302, 1143, 1081 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91–7.85 (m, 2 H), 7.75–7.64 (m, 1 H), 7.62–7.54 (m, 2 H), 6.55 (dd, J = 10.2, 2 Hz, 1 H), 6.15 (d, J = 10.2 Hz, 1 H), 3.72 (s, 3 H), 2.66–1.83 (m, 7 H), 1.27 (s, 3 H). Anal. Calcd for $C_{18}H_{20}O_5S$: C, 62.05; H, 5.79. Found: C, 62.19; H, 5.99.

Methyl (2*R,3a*S**,7a*S**)-3a,4,7,7a-Tetrahydro-2,6-dimethyl-4-oxo-3a-(phenylsulfonyl)-2-indancarboxylate (13).** A solution of **11** (400 mg, 1.15 mmol) in diethyl ether (10 mL) was cooled to −78 °C, and methyllithium (1.14 mL, 1.72 mmol) was added over 1 min. After being stirred for 1 h at −78 °C, the reaction mixture was quenched with aqueous ammonium chloride solution at −78 °C. Ether extraction (3 × 25 mL), drying of the organic layers, and concentration in vacuo afforded a mixture of tertiary alcohols, which was submitted directly to oxidation by dissolution in dichloromethane (15 mL) and stirring at 25 °C for 18 h with pyridinium chlorochromate (0.50 g, 2.3 mmol) and dry Celite (1 g). After filtration of the reaction mixture through a Celite pad and successive washing of the filtrate with water (1 × 25 mL), 10% hydrochloric acid (1 × 25 mL), saturated sodium bicarbonate solution (1 × 25 mL), and water (1 × 25 mL), the solution was dried and concentrated in vacuo. The colorless oil so obtained was purified by MPLC on silica gel (36% ethyl acetate in petroleum ether) to give 70 mg (33%) of enone **13**, mp 134–135.5 °C (from diethyl ether–dichloromethane), and 65 mg of tertiary alcohol.

For **13**: IR (CH_2Cl_2) 2958, 1726, 1658, 1436, 1308, 1214, 1145, 1087 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (br d, J = 7.5 Hz, 2 H), 7.65 (br t, J = 7.5 Hz, 1 H), 7.51 (br d, J = 7.5 Hz, 2 H), 6.04 (br s, 1 H), 3.63–3.53 (m, 1 H), 3.55 (s, 3 H), 3.08 (br dd, J = 19.5, 6.3 Hz, 1 H), 2.82 (d, J = 14.2 Hz, 1 H), 2.27 (t, J = 13.0 Hz, 1 H), 2.26 (d, J = 19.5 Hz, 1 H), 2.08 (d, J = 14.2 Hz, 1 H), 2.01 (s, 3 H), 1.87 (dd, J = 13.0, 7.3 Hz, 1 H), 1.39 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.18, 176.76, 160.60, 136.90, 134.03, 130.07, 128.60, 125.34, 76.22, 52.26, 45.81, 43.83, 42.49, 37.76, 31.76, 26.77, 24.73; MS m/z ($M^+ - SO_2$) calcd 298.1569, obsd 298.1562. Anal. Calcd for $C_{19}H_{22}O_5S$: C, 62.96; H, 6.12. Found: C, 63.07; H, 6.19.

Diels–Alder Cycloaddition of 5a to 14. A solution of **5a** (5.00 g, 18.7 mmol), dienyl silyl ether **14** (8.00 g, 51.3 mmol), and 2,6-di-tert-*butyl*-4-methylphenol (200 mg) in 200 mL of dry xylene was stirred under nitrogen at the reflux temperature for 4 days. The cooled reaction mixture was poured into diethyl ether (300 mL) and washed with water and brine. Drying and solvent removal in vacuo gave 6.1 g of crude product, which was purified by MPLC on silica gel (10% ethyl acetate in petroleum ether). There was isolated 5.52 g (70%) of **15**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.9–7.5 (m, 5 H), 5.37 (br s, 1 H), 4.55 (br s, 1 H), 3.65 (s, 3 H), 2.85 (m, 2 H), 2.53–1.84 (series of m, 6 H), 1.69 (br s, 3 H), −0.03 (br s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 137.5, 134.5, 133.7, 130.2 (2 C), 128.9 (2 C), 121.9, 73.4, 64.9, 51.8, 41.0, 36.5, 36.2, 35.2, 30.3, 23.7, −0.06 (3 C).

A cold (0 °C) solution of **15** (478 mg, 1.13 mmol) in 5 mL of acetone was oxidized with Jones reagent in the manner described below. There was directly isolated a solid, recrystallization of which from ethyl acetate gave pure **16**: colorless crystals, mp 194–195 °C dec; IR ($CHCl_3$) 3020, 2980, 1740, 1665, 1640, 1450, 1410, 1310, 1195, 1080 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.7–7.2 (m, 5 H), 6.04 (br s, 1 H), 3.65 (s, 3 H), 3.47 (m, 1 H), 3.04 (dd, J = 4.8, 9.4 Hz, 1 H), 2.67–2.20 (series of m, 5 H), 2.00 (br s, 3 H), 1.75 (q, J = 11.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.4, 174.6, 161.5, 136.8, 133.9, 129.8 (2 C), 128.5 (2 C), 125.4, 75.8, 52.1, 38.9, 38.1, 36.5, 34.3, 32.1, 24.7; MS m/z (M + 1) calcd 349.1110, obsd 349.1136. Anal. Calcd for $C_{18}H_{20}O_5S$: C, 62.05; H, 5.79. Found: C, 61.73; H, 5.88.

Diels–Alder Cycloaddition of 5b to 14. A mixture of **5b** (8.37 g, 29.9 mmol), dienyl silyl ether **14** (12.53 g, 80.3 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (35 mg) was heated in an oil bath under nitrogen at 145 °C for 5 days. After having been cooled to room temperature, the mixture was purified by flash column chromatography on silica gel (5, 15, and 27% ethyl acetate in petroleum ether used sequentially) to give 7.53 g of **15** and its stereoisomers and 4.5 g (53% recovery) of unreacted **5b**.

The adduct mixture was dissolved in acetone (500 mL), the solution was cooled in an ice bath, and Jones reagent was added dropwise with vigorous stirring until a dark brown color developed. After 10 min at 0 °C, isopropyl alcohol was added dropwise to consume the excess oxidant. The solvent was evaporated under reduced pressure, and water was added to dissolve the salts. This solution was extracted with 2:1 diethyl ether–dichloromethane (3 × 200 mL), and the combined organic phases were washed with half-saturated brine (2 × 100 mL) and saturated sodium bicarbonate solution (100 mL) prior to drying. After concentration, the residue was purified by MPLC on silica gel (32% ethyl acetate in petroleum ether) to give 2.32 g (21%) of **13** and 1.11 g (45%) of **17**.

For **17**: colorless crystals, mp 112.5–113.0 °C (from diethyl ether–petroleum ether); IR (CH_2Cl_2) 2950, 1724, 1658, 1438, 1309, 1225, 1207, 1150, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (br d, J = 7.5 Hz, 2 H), 7.66 (br t, J = 7.5 Hz, 1 H), 7.52 (br t, J = 7.5 Hz, 2 H), 6.08 (br s, 1 H), 3.73 (s, 3 H), 3.55–3.44 (m, 1 H), 3.11–2.98 (m, 1 H), 2.79 (d, J = 14.0 Hz, 1 H), 2.59 (dd, J = 13.1, 7.4 Hz, 1 H), 2.26 (d, J = 19.6 Hz, 1 H), 2.24 (d, J = 14.0 Hz, 1 H), 2.02 (s, 3 H), 1.46 (t, J = 13.1 Hz, 1 H), 1.08 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.07, 177.18, 161.06, 136.79, 133.92, 129.92, 128.50, 125.18, 75.69, 52.43, 46.17, 43.32, 43.06, 39.13, 31.74, 26.37, 24.69; MS m/z ($M^+ - PhSO_2$) calcd 221.1178, obsd 221.1190.

Photocycloaddition of Ethylene to 13. A cold (−47 °C) solution of **13** (663 mg, 1.83 mmol) in dichloromethane (120 mL) was irradiated in a Rayonet reactor fitted with a bank of 350-nm lamps for 4 h while ethylene was bubbled through the solution. After concentration, the residue was purified by MPLC on silica gel (10% ethyl acetate in petroleum ether). In addition to the recovery of 344 mg (52%) of unreacted **13**, there were isolated 240 mg (71%) of **18** and 75 mg (23%) of **19**.

For **18**: colorless crystals, mp 125.5–127.0 °C (from diethyl ether); IR (CH_2Cl_2) 2958, 2878, 1725, 1688, 1448, 1308, 1220, 1147, 1087 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.86–7.81 (m, 2 H), 7.03–6.91 (m, 3 H), 3.74–3.64 (m, 1 H), 3.15 (s, 3 H), 2.99–2.86 (m, 1 H), 2.96 (d, J = 15.5 Hz, 1 H), 2.63–2.57 (m, 1 H), 2.34 (d, J = 1k.5 Hz, 1 H), 2.33–2.11 (m, 4 H), 1.97 (dd, J = 14.5, 4.7 Hz, 1 H), 1.53–1.46 (m, 1 H), 1.38 (s, 3 H), 1.23 (dd, J = 14.5, 8.5 Hz, 1 H), 0.90 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 207.89, 177.52, 137.55, 133.60, 131.09, 128.42, 81.23, 51.78, 50.67, 47.75, 45.66, 44.16, 40.28, 38.03, 37.02, 31.86, 30.80, 26.37, 19.45; MS m/z ($M^+ - C_2H_4$) calcd 362.1188, obsd 362.1205. Anal. Calcd for $C_{21}H_{26}O_5S$: C, 64.59; H, 6.71. Found: C, 64.74; H, 6.84.

For **19**: colorless crystals, mp 109.5–110.5 °C (from diethyl ether–petroleum ether); IR (CH_2Cl_2) 2950, 1724, 1702, 1448, 1310, 1222, 1197, 1165, 1142, 1087 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67–7.59 (m, 3 H), 7.49 (br t, J = 7.8 Hz, 2 H), 3.62–3.53 (m, 1 H), 3.60 (s, 3 H), 3.15 (t, J = 8.7 Hz, 1 H), 3.12 (dd, J = 14.9, 1.7 Hz, 1 H), 2.37–2.24 (m, 2 H), 2.18 (dd, J = 13.4, 8.5 Hz, 1 H), 2.12–1.98 (m, 1 H), 1.95 (d, J = 14.9 Hz, 1 H), 1.87–1.76 (m, 1 H), 1.65–1.55 (m, 2 He, 1.43 (s, 3 H), 1.42 (d, J = 13.4 Hz, 1 H), 1.35 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.48, 177.76, 135.21, 134.00, 130.15, 128.64, 83.01, 52.11, 49.60, 48.89, 45.26, 41.61, 41.52, 40.55, 39.17, 33.25, 26.33, 26.03, 19.98; MS m/z ($M^+ - C_2H_4$) calcd 362.1188, obsd 362.1164. Anal. Calcd for $C_{21}H_{26}O_5S$: C, 64.59; H, 6.71. Found: C, 64.70; H, 6.75.

Formation of Enol Triflate 20a. To a magnetically stirred solution of **18** (64.2 mg, 0.165 mmol) in 3 mL of dry tetrahydrofuran that had been cooled to −75 °C under argon was added sodium hexamethyldisilazide (0.247 mL of 1.0 M in THF, 0.247 mmol). The reaction mixture was stirred at −75 °C for 1 h before a solution of *N*-phenyltriflimide (118 mg, 0.330 mmol) in 1 mL of dry tetrahydrofuran was introduced. An hour later, the solution was allowed to warm to room temperature where 15 min later it was filtered through a small pad of neutral aluina (activity III) with 30% ethyl acetate in petroleum ether as eluant. The concentrated eluate was subjected to MPLC purification (silica gel, 1.5% ethyl acetate in benzene) to return 8 mg (12%) of **18** and furnish 71 mg (93%) of **20a**: colorless crystalline solid, mp 125.8–126.8 °C (from diethyl ether–petroleum ether); IR (film) 2980, 2950, 1732, 1450, 1410, 1310, 1287, 1250, 1215, 1150, 1087, 1070, 985, 938, 834, 770, 724, 698 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.84 (br d, J = 7.0 Hz, 2 H), 7.00–6.86 (m, 3 H), 3.38–3.27 (m, 1 H), 3.33 (s, 3 H), 2.95 (d, J = 15.1 Hz, 1 H), 2.77–2.66 (m, 1 H), 2.60 (d, J = 15.1 Hz, 1 H), 2.56 (d, J = 14.1 Hz, 1 H), 2.47 (d, J = 13.2 Hz, 1 H), 1.67 (br d, J = 14.1 Hz, 1 H), 1.46 (dd, J = 12.5, 6.5 Hz, 1 H), 1.40 (s, 3 H), 1.23 (td, J = 8.9, 2.5 Hz, 1

H), 1.16–1.04 (m, 2 H), 1.00 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 176.31, 140.86, 139.19, 134.28, 133.69, 130.31, 128.84, 118.94 (q), 74.55, 51.86, 47.07, 45.75, 42.68, 41.61, 40.55, 36.50, 32.98, 31.99, 25.79, 25.39; MS m/z ($M^+ - SO_2Ph$) calcd 381.0984, obsd 381.0938.

Reaction of 20a with a Higher Order Methyl Cuprate Reagent. A stirred slurry of copper(I) cyanide (31.3 mg, 0.349 mmol) in 1 mL of dry tetrahydrofuran at −78 °C under argon was treated dropwise with methyllithium (0.47 mL of 1.4 M in diethyl ether, 0.66 mmol), and the resulting mixture was allowed to warm to −20 °C. Enol triflate **20a** (52 mg, 0.10 mmol) in 1.5 mL of dry tetrahydrofuran was introduced dropwise, and the mixture was stirred at −20 °C for 3.5 h, quenched with 3 mL of 0.5 M aqueous ammonium acetate solution, and allowed to warm to room temperature. One hour later, the products were extracted into 2:1 diethyl ether–dichloromethane (2 × 20 mL) and processed as usual. MPLC on silica gel (20% ethyl acetate in petroleum ether) afforded 34 mg (65%) of **20b** and 9 mg (18%) of **20c**.

For **20b**: crystalline solid, mp 118.5–120.0 °C; IR (CH_2Cl_2) 3605, 2945, 1404, 1308, 1265, 1248, 1220, 1150, 1090, 983, 935, 837 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.89 (d, J = 6.8 Hz, 2 H), 6.98–6.88 (m, 3 H), 3.43–3.31 (m, 1 H), 2.73 (dt, J = 13.6, 9.1 Hz, 1 H), 2.60 (d, J = 14.9 Hz, 1 H), 2.60–2.42 (m, 2 H), 2.37 (d, J = 14.9 Hz, 1 H, 1.45–1.26 (m, 2 H), 1.19 (td, J = 9.1, 2.3 Hz, 1 H), 1.14–1.01 (m, 2 H), 1.12 (s, 3 H), 1.06 (s, 3 H), 0.96 (s, 3 H), 0.93 (s, 3 H), 0.88–0.75 (m, 1 H); ^{13}C NMR (75 MHz, C_6D_6) δ 140.19, 139.24, 134.66, 133.50, 130.30, 128.73, 119.05 (q), 74.65, 72.97, 48.87, 45.70, 43.19, 38.99, 37.91, 36.65, 33.23, 31.73, 26.35, 26.32, 25.74, 25.59, 23.98; MS m/z [$M^+ - (SO_2Ph + H_2O)$] calcd 363.1241, obsd 363.1291.

For **20c**: crystalline solid, mp 117.0–118.0 °C; IR (CH_2Cl_2) 2945, 1704, 1448, 1405, 1360, 1309, 1218, 1148, 1087, 1070, 982, 935, 865, 830 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.89–7.82 (m, 2 H), 6.96–6.82 (m, 3 H), 3.36–3.24 (m, 1 H), 2.76 (d, J = 15.2 Hz, 1 H), 2.68 (dt, J = 13.7, 9.1 Hz, 1 H)e, 2.60–2.49 (m, 1 H), 2.50 (d, J = 15.2 Hz, 1 H), 2.25 (dd, J = 14.7, 13.7 Hz, 1 H), 1.76 (s, 3 H), 1.46 (dd, J = 14.7, 5.5 Hz, 1 H), 1.28–1.11 (m, 1 H), 1.19 (s, 3 H), 1.01 (dd, J = 14.3, 2.0 Hz, 1 H), 0.98–0.84 (m, 1 H), 0.95 (s, 3 H), 0.52–0.42 (m, 1 H); MS m/z ($M^+ - SO_2Ph$) calcd 365.1035, obsd 365.1038.

O-Silylation of 18. A magnetically stirred solution of **18** (135 mg, 0.346 mmol) in 3 mL of dry tetrahydrofuran cooled to −78 °C under argon was treated dropwise with sodium hexamethyldisilazide (0.52 mL of 1.0 M in THF, 0.52 mmol), and the resultant mixture was stirred at −78 °C for 1 h prior to the addition of chlorotrimethylsilane (88 μL, 0.69 mmol). The reaction mixture was allowed to warm slowly to room temperature during 1 h and filtered through a short pad of neutral alumina (activity III, 25% ethyl acetate in petroleum ether as eluant). After concentration, the residue was purified by MPLC on silica gel (20% ethyl acetate in petroleum ether) to give 146 mg (91%) of **21**: colorless solid, mp 107.5–108.5 °C; IR (film) 2960, 2938, 1727, 1688, 1448, 1303, 1290, 1255, 1231, 1205, 1160, 1137, 1087, 1030, 865, 851, 760, 721, 695 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 8.01 (br d, J = 7.5 Hz, 2 H), 7.04–6.92 (m, 3 H), 3.57–3.48 (m, 1 H), 3.25 (s, 3 H), 2.73 (d, J = 14.7 Hz, 1 H), 2.61–2.38 (m, 3 H), 2.48 (d, J = 14.7 Hz, 1 H), 2.14 (dd, J = 13.9, 4.7 Hz, 1 H), 1.60–1.44 (m, 3 H), 1.46 (s, 3 H), 1.30 (dd, J = 13.9, 2.1 Hz, 1 H), 1.17 (s, 3 H), 0.00 (m, 9 H); ^{13}C NMR (75 MHz, C_6D_6) δ 177.31, 141.73, 137.14, 132.66, 130.90, 128.00, 124.27, 75.88, 51.59, 47.21, 44.26, 42.61, 41.43, 41.33, 37.84, 33.73, 31.16, 25.80, 25.55, 0.28; MS m/z ($M^+ - OCH_3$) calcd 431.1713, obsd 431.1665.

Epoxidation of 21. To a cold (0 °C), magnetically stirred solution of **21** (146 mg, 0.315 mmol) in dry dichloromethane (4 mL) was added sodium bicarbonate (53 mg, 0.63 mmol) followed by *m*-chloroperbenzoic acid (75 mg of 80–85% purity, 0.35 mmol) in small portions. The resulting mixture was allowed to warm to room temperature during 1 h and filtered through a small pad of neutral alumina (activity III, 10% ethyl acetate in petroleum ether). The concentrated filtrate was purified by MPLC on silica gel (10% ethyl acetate in petroleum ether) to give 130 mg (86%) of **22**: colorless crystalline solid, mp 102–104 °C (from petroleum ether); IR (film) 2955, 1730, 1448, 1305, 1255, 1230, 1207, 1140, 1102, 1085, 870, 850, 761, 723, 695 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 8.04–8.00 (m, 2 H), 7.03–6.90 (m, 3 H), 3.52–3.41 (m, 1 H), 3.31 (s, 3 H), 3.18 (d, J = 14.9 Hz, 1 H), 2.59 (dd, J = 14.0, 12.3 Hz, 1 H), 2.51 (d, J = 14.9 Hz, 1 H), 2.31–2.14 (m, 3 H), 1.58 (q, J = 9.4 Hz, 1 H), 1.48–1.32 (m, 2 H), 1.43 (s, 3 H), 1.14 (dd, J = 14.6, 2.2 Hz, 1 H), 1.10 (s, 3 H), 0.03 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) δ 176.88, 141.54, 132.74, 131.10, 128.42, 84.98, 74.46, 70.58, 51.62, 47.42, 41.47, 40.47, 40.43, 40.05, 32.68, 30.53, 27.21, 25.90, 24.33, 1.92; MS m/z ($M^+ - OCH_3$) calcd 447.1662, obsd 447.1710. Anal. Calcd for $C_{24}H_{34}O_6SiS$: C, 60.22; H, 7.16. Found: C, 60.01; H, 7.22.

Acid-Catalyzed Isomerization of 22. A magnetically stirred solution of **22** (55 mg, 0.114 mmol) in 1.5 mL of dry dichloromethane was treated with 1 mg of benzoic acid, and the resultant mixture was maintained at room temperature for 24 h. After concentration, the residue was subjected to MPLC on silica gel (10% ethyl acetate in petroleum ether). There were isolated 42 mg (77%) of **23** and 13 mg (23%) of **24**.

For **23**: colorless solid, mp 86–87 °C; IR (film) 2960, 1729, 1701, 1450, 1312, 1255, 1218, 1149, 1085, 932, 850, 762, 728, 697 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.85–7.78 (m, 2 H), 7.03–6.92 (m, 3 H), 3.72–3.61 (m, 1 H), 3.18 (s, 3 H), 3.18–3.10 (m, 1 H), 3.09 (d, J = 16.1 Hz, 1 H), 2.55 (dd, J = 13.3, 7.5 Hz, 1 H), 2.47 (d, J = 16.1 Hz, 1 H), 2.38 (dd, J = 13.3, 2.3 Hz, 1 H), 2.22–2.02 (m, 2 H), 1.56–1.38 (m, 2 H), 1.43 (s, 3 H), 1.22 (dd, J = 14.2, 12.0 Hz, 1 H), 1.05 (s, 3 H), 0.20 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) δ 207.76, 177.71, 136.92, 133.73, 131.27, 128.42, 83.36, 80.92, 51.79, 48.84, 45.97, 45.35, 44.77, 39.58, 38.46, 30.49, 26.75, 25.03, 24.88, 2.15; MS m/z ($M^+ - SO_2Ph$) calcd 337.1835, obsd 337.1814.

For **24**: oil; IR (neat) 2960, 1752–1725, 1465, 1450, 1308, 1269, 1255, 1230, 1195, 1150, 1130, 1115, 1088, 888, 852, 770, 752, 700 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.92–7.84 (m, 2 H), 7.00–6.91 (m, 3 H), 3.83 (d, J = 16.8 Hz, 1 H), 3.50–3.39 (m, 1 H), 3.34 (s, 3 H), 2.94–2.82 (m, 1 H), 2.43 (d, J = 13.5 Hz, 1 H), 2.26–2.14 (m, 1 H), 2.21 (d, J = 16.8 Hz, 1 H), 2.00–1.85 (m, 1 H), 1.63 (dd, J = 13.5, 7.6 Hz, 1 H), 1.55–1.36 (m, 2 H), 1.27–1.16 (m, 1 H), 1.20 (s, 3 H), 0.73 (s, 3 H), 0.23 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) δ 216.83, 178.17, 138.91, 133.38, 131.51, 128.58, 95.33, 94.68, 53.69, 51.88, 51.25, 49.53, 42.45, 41.96, 41.00, 36.29, 28.85, 28.25, 21.52, 2.16; MS m/z ($M^+ - PhSO$) calcd 353.1784, obsd 353.1792.

Oxidative Rearrangement of 21. A magnetically stirred solution of **21** (44 mg, 0.095 mmol) in 3 mL of dry dichloromethane was treated with *m*-chloroperbenzoic acid (18 mg of 80–85% purity, 0.10 mmol) in small portions and stirred at room temperature under argon for 26 h. Workup in the manner described above gave 34 mg (76%) of **23** and 4.5 mg (10%) of **24**.

Dibal Reduction of 24. To a cold (−78 °C), magnetically stirred solution of **24** (13 mg, 0.027 mmol) in 1 mL of dry dichloromethane under argon was added Dibal (0.274 mL of 1 M in hexane, 0.274 mmol), and reaction was allowed to proceed for 30 min at −78 °C and for an equal time at −10 °C. Half-saturated Rochelle's salt solution (3 mL) was introduced, stirring was continued for 40 min, and the product was extracted into diethyl ether (3 × 5 mL). The combined organic layers were dried and concentrated. Purification of the residue by MPLC on silica gel (7% ethyl acetate in petroleum ether) gave 5.2 mg (42%) of **26**: colorless solid, mp 177.5–177.8 °C (from diethyl ether–petroleum ether); IR ($CHCl_3$) 3630, 3480, 2960, 1745, 1305, 1255, 1143, 1118, 1083, 882, 850 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.94–7.83 (m, 2 H), 7.00–6.85 (m, 3 H), 3.62–3.50 (distorted q, 1 H), 3.26 (dd, J = 10.3, 4.7 Hz, 1 H), 3.13 (dd, J = 10.3, 5.3 Hz, 1 H), 2.92 (ddd, J = 18.9, 8.8, 0.9 Hz, 1 H), 2.66 (d, J = 16.3 Hz, 1 H), 2.45–2.30 (m, 1 H), 2.04 (d, J = 16.3 Hz, 1 H), 2.01–1.85 (m, 1 H), 1.68–1.47 (m, 3 H), 1.40 (dd, J = 13.5, 8.5 Hz, 1 H), 1.30–1.18 (m, 1 H), 0.93 (s, 3 H), 0.92–0.77 (m, 1 H), 0.76 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) δ 217.14, 138.98, 133.18, 131.51, 128.43, 96.31, 95.22, 70.83, 54.45, 49.45, 47.04, 44.61, 42.10, 40.50, 36.56, 29.15, 26.76, 21.61, 2.23; MS m/z (M^+) calcd 450.1896, obsd 450.1921.

Reductive Desulfurization of 23. Aluminum foil (24 mg, 0.88 mmol) was dipped into 4 N sodium hydroxide until hydrogen evolution became vigorous. The metal was washed with water and placed in a 1% mercuric chloride solution for 30 s. Following a second water rinse and washing with dry methanol, the foil was immediately added to a magnetically stirred solution of **23** (14 mg, 0.029 mmol) and disodium hydrogen phosphate (16.6 mg, 0.117 mmol) in 2 mL of dry methanol at room temperature. The mixture was stirred for 36 h, filtered through a short pad of neutral alumina (activity III), and concentrated. The residue was purified by MPLC on silica gel (5% ethyl acetate in petroleum ether) to give 3.4 mg (34%) of **27**: colorless oil; IR (neat) 2960, 1728, 1708, 1452, 1283, 1264, 1251, 1209, 1170, 1140, 1118, 927, 872, 850 cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 3.34 (s, 3 H), 2.88–2.68 (m, 2 H), 2.53–2.33 (m, 1 H), 2.05–1.90 (m, 2 H), 1.81–1.68 (m, 1 H), 1.68–1.54 (m, 3 H), 1.54–1.40 (m, 1 H), 1.22 (dd, J = 13.8, 5.9 Hz, 1 H), 1.10 (s, 3 H), 1.08 (s, 3 H), 0.81 (dd, J = 13.8, 12.3 Hz, 1 H), 0.35 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) δ 212.29, 176.82, 82.40, 51.43, 48.69, 48.39, 45.95, 44.60, 40.30, 37.55, 37.28, 30.31, 24.40, 24.25, 23.59, 2.51; MS m/z (M^+) calcd 338.1914, obsd 338.1899.

***tert*-Butyldimethylsilylation of 18.** A magnetically stirred solution of **18** (507 mg, 1.30 mmol) in 10 mL of dry tetrahydrofuran under argon at −70 °C was treated with potassium hexamethyldisilazide (3.12 mL of 0.5 M in toluene, 1.56 mmol). The greenish-yellow reaction mixture was stirred at −70 °C for 40 min before being added to a benzene solution of *tert*-butyldimethylsilyl chloride (1.57 mL of 1.49 M, 2.34 mmol), allowed to warm to 5 °C, and stirred for 40 min. Magnesium sulfate decahydrate (ca. 400 mg) was introduced, and after 10 min, the mixture was filtered through a small pad of neutral alumina (activity III) and concentrated. MPLC purification of the residue on silica gel (10% ethyl

acetate in petroleum ether) afforded 623 mg (95%) of **28**: colorless crystals, mp 129.2–131.0 °C (from petroleum ether); IR ($CHCl_3$) 2960, 2936, 2832, 1725, 1449, 1300, 1288, 1257, 1143, 1088, 842 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 8.08–7.95 (m, 2 H), 7.12–6.95 (m, 3 H), 3.40–3.24 (m, 1 H), 3.31 (s, 3 H), 2.94 (d, J = 15.4 Hz, 1 H), 2.71 (d, J = 15.4 Hz, 1 H), 2.54–2.31 (m, 2 H), 2.21 (ddd, J = 12.5, 8.1, 1.7 Hz, 1 H), 1.53 (dd, J = 12.0, 6.0 Hz, 1 H), 1.46 (s, 3 H), 1.35 (dd, J = 14.0, 5.3 Hz, 1 H), 1.30–1.16 (m, 1 H), 1.15–1.03 (m, 1 H), 1.08 (s, 3 H), 1.07 (s, 9 H), 0.56 (q, J = 8.7 Hz, 1 H), 0.16 (s, 3 H), 0.14 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 177.25, 140.08, 137.05, 133.06, 130.45, 128.31, 124.87, 75.58, 51.61, 46.69, 43.77, 43.10, 42.39, 40.58, 37.26, 33.12, 31.31, 26.25, 26.11, 24.89, 18.92, −3.14, −5.09; MS m/z (M^+ − C_4H_9) calcd 447.1662, obsd 447.1621. Anal. Calcd for $C_{27}H_{40}O_5SSi$: C, 64.25; H, 7.99. Found: C, 64.38; H, 8.06.

Oxidative Rearrangement of 28. A solution of **28** (157 mg, 0.311 mmol) in 3 mL of anhydrous benzene was treated with *m*-chloroperbenzoic acid (70 mg of 85% purity, 0.34 mmol), and the mixture was stirred at room temperature under an inert atmosphere for 36 h. After filtration through a small pad of neutral alumina (activity III, diethyl ether as eluant), the filtrate was concentrated and the product mixture purified by MPLC on silica gel (10% ethyl acetate in petroleum ether). There were isolated 117 mg (72%) of **29** and 46 mg (28%) of a 2:1 mixture of **30** and **31**.

For **29**: colorless crystals, mp 121.5–122.0 °C (from petroleum ether); IR ($CHCl_3$) 2960, 2938, 1725, 1702, 1450, 1310, 1255, 1145, 838 cm^{-1}; ^{13}C NMR (300 MHz, C_6D_6) δ 7.86–7.74 (m, 2 H), 7.04–6.90 (m, 3 H), 3.71–3.58 (m, 1 H), 3.23–3.06 (m, 1 H), 3.18 (s, 3 H), 3.09 (d, J = 15.8 Hz, 1 H), 2.57 (dd, J = 13.3, 7.4 Hz, 1 H), 2.45 (d, J = 16.0 Hz, 1 H), 2.32 (d, J = 13.3 Hz, 1 H), 2.28–2.04 (m, 2 H), 1.63–1.47 (m, 1 H), 1.45–1.32 (m, 1 H), 1.41 (s, 3 H), 1.26–1.14 (m, 1 H), 1.08 (s, 3 H), 0.99 (s, 9 H), 0.21 (s, 3 H), 0.21 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 207.84, 177.69, 136.80, 133.76, 131.26, 128.42, 83.49, 80.83, 51.80, 48.84, 45.90, 45.51, 45.19, 39.52, 38.62, 30.81, 26.76, 26.34, 25.14, 24.97, 19.08, −2.84, −2.92; MS m/z (M^+ − $PhSO_2$) calcd 379.2305, obsd 379.2325. Anal. Calcd for $C_{27}H_{40}O_6SSi$: C, 62.27; H, 7.74. Found: C, 62.44; H, 7.90.

Reductive Desulfonylation of 29. Reduction of **29** (145 mg, 0.279 mmol) with aluminum foil (113 mg, 4.18 mmol) in dry methanol (15 mL) for 12 h as described above gave after MPLC purification (7.5% ethyl acetate in petroleum ether) 94 mg (88%) of **32** and 7.7 mg (5%) of recovered **29**. For **32**: colorless crystals, mp 96.5–97.0 °C (from petroleum ether); IR ($CHCl_3$) 2960, 2940, 2862, 1723, 1708, 1276, 1253, 1135, 834 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 3.36 (s, 3 H), 2.85–2.67 (m, 2 H), 2.58–2.37 (m, 1 H), 2.10–1.93 (m, 2 H), 1.80–1.43 (m, 5 H), 1.23 (dd, J = 13.8, 5.8 Hz, 1 H), 1.10 (s, 3 H), 1.09 (s, 3 H), 1.07 (s, 9 H), 0.81 (dd, J = 13.4, 12.8 Hz, 1 H), 0.47 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (75 MHz, C_6H_6) δ 212.20, 176.79, 82.05, 51.44, 48.70 (2 C), 46.19, 44.60, 40.32, 37.48, 37.40, 30.27, 26.59, 24.69, 24.48, 23.66, 19.20, −2.31, −3.20; MS m/z (M^+ − C_4H_9) calcd 323.1679, obsd 323.1683. Anal. Calcd for $C_{21}H_{36}O_4Si$: C, 66.27; H, 9.53. Found: C, 66.19; H, 9.46.

Wittig Methylenation of 32. To a stirred suspension of methyltriphenylphosphonium bromide (2.60 g, 7.28 mmol) in 20 mL of dry diisopropyl ether at 5 °C under argon was added potassium hexamethyldisilazide (12.5 mL of 0.5 M, 6.24 mmol). The resulting bright yellow solution was stirred at 5 °C for 15 min prior to the dropwise addition of **32** (395 mg, 1.04 mmol) in 15 mL of the same solvent. After 24 h at 5 °C, the reaction mixture was quenched with 5 mL of anhydrous acetone and allowed to warm to room temperature. After 20 min, the solution was filtered through a short pad of silica gel (10% ethyl acetate in petroleum ether) and concentrated. Purification of the residue by MPLC on silica gel (2.5% ethyl acetate in petroleum ether) gave 350 mg (89%) of **33**: colorless solid, mp 70.0–70.6 °C (from methanol); IR ($CHCl_3$) 2960, 2940, 2900, 2865, 1720, 1462, 1435, 1250, 1158, 1138, 1028, 920, 900, 840 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 5.34 (br s, 1 H), 4.89 (br s, 1 H), 3.37 (s, 3 H), 2.84–2.71 (m, 1 H), 2.41 (t, J = 12.1 Hz, 1 H), 2.32–2.16 (m, 2 H), 2.16–2.02 (m, 1 H), 1.93–1.68 (m, 3 H), 1.58 (t, J = 8.1 Hz, 2 H), 1.27–1.04 (m, 2 H), 1.21 (s, 3 H), 1.09 (s, 3 H), 1.06 (s, 9 H), 0.22 (s, 3 H), 0.15 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 177.69, 153.23, 109.44, 79.14, 51.41, 48.58, 46.26, 44.86, 43.28, 41.59, 40.39, 35.47, 31.16, 26.44, 25.85, 24.67, 24.29, 19.03, −2.13, −2.30; MS m/z (M^+) calcd 378.2590, obsd 378.2571. Anal. Calcd for $C_{22}H_{38}O_3Si$: C, 69.79; H, 10.12. Found: C, 69.75; H, 10.15.

Ene Reaction–Desulfurization of 33. A solution of **33** (20 mg, 0.053 mmol) and *N*-sulfinylbenzenesulfonamide (161 mg, 0.794 mmol) in 2 mL of dry benzene was heated in an oil bath at 60 °C for 7 h under argon. After being cooled, the reaction mixture was treated with excess Raney nickel in 1 mL of dry benzene and stirred vigorously under 80 psi of hydrogen for 8 h. The catalyst was removed by filtration, the filtrate concentrated, and the residue purified by MPLC on silica gel (2.5% ethyl acetate in petroleum ether). There was isolated 16 mg (86%) of **34b**: colorless oil; IR (neat) 2960, 2935, 2900, 2860, 1732, 1462, 1258, 1242, 1225, 1145, 1118, 1098, 840, 778 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 3.34 (s, 3 H), 2.98 and 2.16 (AB system, J = 17.2 Hz, 2 H), 2.42–2.22 (m, 2 H), 2.00–1.91 (m, 1 H), 1.78–1.56 (m, 5 H), 1.50–1.05 (series of m, 4 H), 1.25 (s, 3 H), 1.24 (s, 3 H), 0.98 (s, 9 H), 0.19 (s, 3 H), 0.13 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 177.74, 137.42, 128.92, 76.05, 51.39, 47.13, 45.09, 44.17, 41.48, 37.11, 34.94, 34.86, 26.40, 25.65, 24.93, 22.88, 18.93, 14.30, −1.22, −1.34; MS m/z (M^+) calcd 378.2590, obsd 378.2576.

Methyl Sterpurate (35). A solution of **34b** (23 mg, 0.061 mmol) in 1.5 mL of dry tetrahydrofuran was treated with tetra-*n*-butylammonium fluoride (0.912 mmol of 1.0 M in THF, 0.912 mol) and magnetically stirred for 14 h. The reaction mixture was filtered through a small pad of neutral alumina (50% tetrahydrofuran in diethyl ether), the filtrate was concentrated, and the residue was purified by MPLC on silica gel (20% ethyl acetate in petroleum ether). There was obtained 12.5 mg (78%) of **35**: colorless oil; IR (neat) 3400, 2955, 1730, 1245, 1225, 1148, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3 H), 2.84 and 2.25 (AB system, J = 17.5 Hz, 2 H), 2.65–2.50 (m, 1 H), 2.14 (dd, J = 20.8, 10.2 Hz, 1 H), 2.05–1.97 (m, 1 H), 1.85 (dd, J = 12.0, 6.7 Hz, 1 H), 1.75–1.44 (m, 4 H), 1.65 (br s, 3 H), 1.34 (s, 3 H), 1.29–1.20 (m, 1 H), 1.21 (s, 3 H), 0.89 (dd, J = 13.1, 11.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.59, 138.25, 127.59, 73.31, 51.89, 46.94, 44.12, 43.78, 41.17, 36.67, 34.75, 34.38, 25.34, 23.39, 22.00, 12.80; MS m/z (M^+) calcd 264.1726, obsd 264.1729.

Sterpuric Acid (1). Ester **35** (12.5 mg, 0.047 mmol) was dissolved in 3 mL of tetrahydrofuran–methanol (1:1), 0.47 mL of 1.0 M aqueous lithium hydroxide was introduced, and stirring was maintained at room temperature for 24 h. The mixture was cooled to 0 °C and treated with 0.5 mL of 4 N hydrochloric acid. After dilution with half-saturated brine (10 mL), the product was extracted into dichloromethane–diethyl ether (1:2, 4 × 20 mL), and the combined organic phases were washed with brine (10 mL), dried, and concentrated. There was isolated 12 mg (100%) of a colorless solid, mp 200.0–200.5 °C (from ethyl acetate; lit.[1] mp 203–207 °C), which was pure **1** on the basis of its spectral properties: IR (KBr) 3400, 2980, 2965, 2945, 2930, 2915, 3200–2500, 1698, 1287, 1247 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 2.82 (d, J = 17.3 Hz, 1 H), 2.57 (m, 1 H), 2.20 (d, J = 17.3 Hz, 1 H), 2.15 (dd, J = 20.7, 10.1 Hz, 1 H), 1.93–1.85 (m, 1 H), 1.82 (dd, J = 11.8, 6.6 Hz, 1 H), 1.66–1.47 (m, 3 H), 1.61 (s, 3 H), 1.31 (s, 3 H), 1.24–1.15 (m, 1 H), 1.16 (s, 3 H), 0.86 (dd, J = 12.9, 11.3 Hz, 1 H); ^{13}C NMR (75 MHz, CD_3OD) δ 182.05, 139.04, 129.36, 73.99, 47.95, 45.56, 44.77, 42.23, 38.00, 36.11, 34.05, 25.75, 24.16, 22.89, 13.09; MS m/z (M^+) calcd 250.1569, obsd 250.1564.

Rearrangement of 33 Induced by *N*-Bromosuccinimide. A magnetically stirred solution of **33** (5.3 mg, 0.014 mmol) in 3 mL of cold (5 °C) tetrahydrofuran–water (9:1) was treated sequentially with calcium carbonate (8.4 mg, 0.084 mmol) and *N*-bromosuccinimide (5.5 mg, 0.030 mmol). The mixture was stirred at 5 °C for 1 h before excess 2-methyl-2-butene was introduced and allowed to warm to room temperature. Following dilution with half-saturated brine (3 mL), the product was extracted with diethyl ether (3 × 5 mL) and the combined organic layers were dried and concentrated. The residue was purified by MPLC on silica gel (7% ethyl acetate in petroleum ether) to give 3.5 mg (73%) of **37**: colorless oil; IR (neat) 2960, 2882, 1740, 1730, 1252, 1140 cm^{-1}; ^{13}C NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3 H), 3.56 and 3.38 (AB system, J = 10.4 Hz, 2 H), 2.90 (dt, J = 11.9, 8.3 Hz, 1 H), 2.52–2.40 (m, 2 H), 2.29 (dd, J = 19.4, 9.6 Hz, 1 H), 2.05 (t, J = 12.2 Hz, 1 H), 1.97–1.65 (m, 6 H), 1.40 (s, 3 H), 1.35–1.15 (m, 1 H), 1.19 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 221.24, 177.97, 63.40, 52.68, 51.98, 50.90, 50.81, 48.49, 44.81, 40.42, 38.45, 35.79, 34.53, 30.73, 25.02, 23.54; MS m/z (M^+ − COOMe) calcd 283.0697, obsd 283.0694.

Iodine-Promoted Isomerization of 33. A small crystal of iodine was added to a magnetically stirred solution of **33** (1.3 mg, 0.0034 mmol) in 0.5 mL of dry benzene. The mixture was stirred at room temperature under argon for 16 h and applied directly to a short silica gel column (7% ethyl acetate in petroleum ether) to give 0.8 mg (88%) of **36**: colorless oil; IR (neat) 2960, 2940, 2875, 1730, 1255 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3 H), 2.86 (q, J = 9.8 Hz, 1 H)e, 2.62–2.48 (m, 1 H), 2.38–2.24 (m, 2 H), 2.02 (t, J = 11.8 Hz, 1 H), 1.94–1.72 (m, 3 H), 1.69–1.40 (m, 4 H), 1.20 (s, 3 H), 1.17 (s, 3 H), 0.89 (s, 3 H); MS m/z (M^+) calcd 264.1725, obsd 264.1728.

Sequential Epoxidation and Rearrangement of 33. To a magnetically stirred solution of **33** (76 mg, 0.20 mmol) in 4 mL of dichloromethane were added dropwise and sequentially a solution of sodium carbonate (64 mg, 0.60 mmol) in 3 mL of water and a solution of *m*-chloroperbenzoic acid (106 mg of 85% purity, 0.522 mmol) in 3 mL of dichloromethane. The mixture was stirred at room temperature for 3 h prior to quenching with 2-methyl-2-butene. After 10 min, 50 mL of 1:1 diethyl ether–pe-

troleum ether was added, and the organic phase was washed with half-saturated brine (10 mL), dried, and concentrated to give 86 mg of the epoxide as a colorless solid.

To a magnetically stirred solution of 2,2,6,6-tetramethylpiperidine (170 μL, 1.01 mmol) in 3 mL of dry benzene under argon at room temperature was added *n*-butyllithium (631 μL of 1.6 M in hexane, 1.01 mmol). After 5 min, the resulting solution was treated dropwise with diethylaluminum chloride (561 μL of 1.8 M in toluene, 1.01 mmol) to be followed 5 min later with a solution of **38** in 6 mL of dry benzene. This reaction mixture was stirred at room temperature for 2 h before being quenched with 10 mL of cold (0 °C) half-saturated Rochelle's salt solution. One hour later, the product was taken up in 1:1 diethyl ether–petroleum ether (4 × 30 mL). Subsequent MPLC purification on silica gel (15% ethyl acetate in petroleum ether) gave 61 mg (77%) of **39**: colorless solid, mp 85.0–85.5 °C (from methanol); IR (film) 3562, 2960, 2935, 2862, 1730, 1255, 1240, 1220, 1210, 845 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 4.52 (t, J = 2.3 Hz, 1 H), 3.80 and 3.74 (AB system, J = 10.8 Hz, 2 H), 3.36 (s, 3 H), 2.84 (dt, J = 12.4, 7.7 Hz, 1 H), 2.51–2.36 (m, 1 H), 2.25 (t, J = 12.5 Hz, 1 H), 2.12–1.95 (m, 3 H), 1.87–1.58 (m, 5 H), 1.24 (s, 3 H), 1.19 (s, 3 H), 0.91 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 178.02, 156.12, 101.02, 63.81, 63.05, 51.85, 51.45, 51.11, 49.65, 49.24, 45.09, 43.72, 41.78, 38.37, 25.77, 25.50, 25.01, 18.21, −4.52, −5.16; MS m/z (M^+) calcd 394.2540, obsd 394.2505.

Reduction of 39. A cold (−78 °C), magnetically stirred solution of **39** (60 mg, 0.15 mmol) in 4 mL of dry dichloromethane under argon was treated with Dibal (0.755 mL of 1.0 M in hexane, 0.755 mmol) and allowed to warm slowly to 5 °C during 1 h. Half-saturated Rochelle's salt solution (8 mL) was introduced, and the reaction mixture was stirred at room temperature for 1.5 h before extractive workup with 1:1 diethyl ether–petroleum ether (3 × 30 mL). After MPLC purification on silica gel (40% ethyl acetate in petroleum ether), 53 mg (95%) of **40** was obtained: colorless oil; IR (neat) 3400, 2940, 2860, 1645, 1467, 1315, 1250, 1210, 1045, 904, 844, 788 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 4.55 (t, J = 2.4 Hz, 1 H), 3.84 and 3.78 (AB system, J = 10.8 Hz, 2 H), 3.18 (s, 2 H), 2.91–2.81 (m, 1 H), 2.56–2.42 (m, 1 H), 2.12 (dd, J = 15.0, 2.1 Hz, 1 H), 2.04 (dd, J = 15.0, 2.6 Hz, 1 H), 1.85 (dd, J = 13.2, 9.0 Hz, 1 H), 1.57–1.30 (m, 5 H), 1.23 (s, 3 H), 1.09–0.78 (m, 2 H), 0.93 (s, 9 H), 0.91 (s, 3 H), 0.11 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 156.26, 101.03, 71.74, 63.83, 63.10, 52.45, 49.49, 49.25, 47.03, 45.12, 41.87, 41.62, 36.67, 25.79, 25.63, 24.50, 18.23, −4.48, −5.16; MS m/z (M^+) calcd 366.2590, obsd 366.2593.

Dihydroxy Triquinane Ketone 41. A magnetically stirred solution of **40** (50 mg, 0.14 mmol) in 2 mL of dry tetrahydrofuran under argon was treated with tetra-*n*-butylammonium fluoride (0.683 mL of 1.0 M in THF, 0.683 mmol), and the resultant mixture was stirred at room temperature for 3 h. After dilution with 40 mL of diethyl ether–dichloromethane (4:1), the mixture was washed with 30 mL of half-saturated brine and the aqueous phase was reextracted as above. The combined organic layers were dried and concentrated to leave a residue, which was purified by MPLC on silica gel (ethyl acetate as eluant). There was isolated 30 mg (87%) of **41**: colorless crystals, mp 119.0–119.5 °C (from diethyl ether); IR ($CHCl_3$) 3625, 3450, 2942, 2870, 1720, 1035, 1002 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.74 and 3.67 (AB system, J = 11.1 Hz, 2 H), 3.40 (s, 2 H), 2.85–2.74 (m, 1 H), 2.58–2.27 (m, 3 H), 2.41 (s, 2 H), 1.90–1.30 (m, 8 H), 1.23 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 226.29, 71.23, 64.27, 62.02, 51.06, 50.39, 47.93, 47.01, 42.78, 41.09, 36.80, 36.44, 34.42, 24.42, 23.12; MS m/z (M^+) calcd 252.1725, obsd 252.1781. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.59; H, 9.59.

Selenium Dioxide Oxidation of 33. A stirred suspension of selenium dioxide (4.2 mg, 0.038 mmol) in 3 mL of dry dichloromethane was treated with *tert*-butyl hydroperoxide (20.7 μL, 0.151 mmol), and the resultant mixture was stirred at room temperature for 30 min prior to the addition of solid **33** (28.5 mg, 0.0754 mmol). This mixture was stirred in the absence of moisture for 1 h, filtered through a small pad of silica gel (ether elution), and concentrated. Purification of the residue by MPLC on silica gel (7% ethyl acetate in petroleum ether) provided 14.0 mg (47%) of **42**: viscous oil; IR (neat) 3490, 2960, 2930, 2890, 2860, 1718, 1460, 1255, 1230, 1215, 1200, 1155, 1126, 952, 840, 778 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 5.47 (s, 1 H), 5.32 (s, 1 H), 3.38 (s, 3 H), 3.03 (d, J = 14.4 Hz, 1 H), 2.30–2.04 (m, 4 H), 1.78–1.69 (m, 1 H), 1.61 (dd, J = 14.3, 1.7 Hz, 1 H), 1.60 (s, 3 H), 1.40–1.08 (series of m, 4 H), 1.11 (s, 3 H), 1.01 (s, 9 H), 0.63 (br s, 1 H), 0.14 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) δ 179.18, 155.81, 122.87, 83.02, 76.55, 51.56, 48.37, 47.55, 46.55, 44.57, 43.83, 38.69, 34.12, 29.19, 26.04, 24.63, 23.75, 18.65, −2.49, −2.52; MS m/z ($M^+ - CH_3$) calcd 379.2305, obsd 379.2311.

Oxidative Rearrangement and Reduction of 42. A cold (5 °C) stirred suspension containing **42** (13.5 mg, 0.0343 mmol), sodium acetate (16.8 mg, 0.206 mmol), and powdered 3-Å molecular sieves (68.6 mg) in 2 mL of dry dichloromethane was treated with pyridinium chlorochromate (22.2 mg, 0.103 mmol). The mixture was stirred under argon at 5 °C for 4 h, diluted with dry diethyl ether (10 mL), and filtered through a small pad of silica gel (ether elution).

The concentrated filtrate was dissolved in dry dichloromethane (1.5 mL), and the resultant mixture was cooled to −20 °C and treated with Dibal (130 μL of 1.0 M in hexane, 0.130 mmol) while being stirred under argon. After 1 h at −20 °C, 10 mL of half-saturated Rochelle's salt solution was introduced and the mixture was stirred at room temperature for 1 h. Extractive workup with ethyl acetate (4 × 10 mL) followed by MPLC purification of the concentrated residue (40% ethyl acetate in petroleum ether) afforded 6.8 mg (54%) of **44**: colorless crystalline solid, mp 133.5–134.5 °C (from diethyl ether–petroleum ether); IR ($CHCl_3$) 3610, 3400, 2960, 2935, 2900, 2860, 1255, 1108, 1092, 1005, 905, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.16 and 4.05 (AB system, J = 11.4 Hz, 2 H), 3.39 (s, 2 H), 2.68–2.51 (m, 1 H), 2.54 (d, J = 16.7 Hz, 1 H), 2.43 (dd, J = 20.4, 10.0 Hz, 1 H), 2.16 (d, J = 16.7 Hz, 1 H), 2.12 (br s, 2 H), 2.10–2.00 (m, 1 H), 1.65 (dd, J = 12.1, 7.7 Hz, 1 H), 1.58–1.43 (m, 2 H), 1.28–1.15 (m, 2 H), 1.15 (s, 3 H), 1.10 (s, 3 H), 0.97–0.83 (m, 1 H), 0.87 (s, 9 H), 0.22 (s, 3 H), 0.16 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.84, 131.75, 76.10, 60.25, 45.03, 42.39, 42.27, 39.16, 36.73, 35.37, 34.57, 26.20, 24.74, 24.24, 22.33, 18.49, −1.11, −1.87; MS m/z ($M^+ - H_2O$) calcd 348.2484, obsd 348.2494. Anal. Calcd for $C_{21}H_{38}O_3Si$: C, 68.80; H, 10.45. Found: C, 68.82; H, 10.44.

When the three-step sequence from **33** (154 mg, 0.407 mmol) was carried out without isolation, there was isolated 44.4 mg (30% overall) of **44**.

Sterpurene-3,12,14-triol (2). A solution of **44** (34 mg, 0.093 mmol) in dry tetrahydrofuran (2 mL) under argon was treated with tetra-*n*-butylammonium fluoride (0.464 mL of 1.0 M in THF, 0.464 mmol), and the resultant mixture was stirred for 4 h and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate and 5% methanol in ethyl acetate as eluants) to give 20 mg (85%) of **2**: colorless solid, mp 157.5–159.5 °C (lit. for (+)-**2**,[3] mp 146–148 °C); IR (KBr) 3310, 2978, 2960, 2935, 2865, 2835, 1468, 1452, 1440, 1428, 1382, 1268, 1252, 1241, 1222, 1185, 1151, 1142, 1106, 1088, 1040, 1010, 988, 978, 820 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.28 and 4.20 (AB system, J = 11.6 Hz, 2 H), 3.41 (s, 2 H), 2.74 (br s, 1 H), 2.74–2.55 (m, 1 H), 2.55 (d, J = 16.6 Hz, 1 H), 2.23 (dd, J = 21.1, 10.2 Hz, 1 H), 2.13 (d, J = 16.6 Hz, 1 H), 2.09–2.02 (m, 1 H), 1.96 (br s, 1 H), 1.73–1.55 (m, 2 H), 1.58 (br s, 1 H), 1.51 (dd, J = 19.4, 10.0 Hz, 1 H), 1.35–1.23 (m, 2 H), 1.22 (s, 3 H), 1.11 (s, 3 H), 0.92 (dd, J = 13.2, 11.2 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.71, 129.55, 74.34, 71.59, 60.53, 44.23, 42.44, 42.41, 39.21, 36.65, 35.71, 35.30, 24.72, 22.89, 21.89; MS m/z (M^+) calcd 252.1725, obsd 252.1752.

Acknowledgment. We thank the National Institutes of Health (Grant GM 30827) for their financial support of this research effort.

Supplementary Material Available: ORTEP drawings for **16**, **18**, **22**, and **39**, experimental crystallographic data for **18**, **22**, and **39**, and tables of bond lengths, bond angles, and final positional and thermal parameters for **18**, **22**, and **39** (22 pages). Ordering information is given on any current masthead page.