added at 25 °C, and a visible reaction ensued. Two additional drops of 1,2-dibromoethane were added every 10 min until the reaction was judged complete (GLC, 4 h). The reaction was worked up in the usual fashion, and the solvent was removed under reduced pressure to give a yellow oil. Chromatography on silica gel gave the desired vinylic fluoride as a mixture of *E* and *Z* isomers.

(*E*)- and (*Z*)-3-Fluoro-1-phenyl-2-butene (4a). Reduction of **3a** afforded a 35:65 mixture of the *E* and *Z* isomers of 3-fluoro-1-phenyl-2-butene (**4a**) in yields of 60% (method 1), 64% (method 2), 58% (method 3), and 77% (method 4). **4a**: IR (ν_{max}^{film}) 3040, 2910, 1700, 1600, 1490, 1430, 1380, 1310, 1270, 1210, 1140, 1080, 1060, 1020, 985, 925, 850, 790, 730, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.87 (d of m, 3 H, $J[CH_3,F]$ = 18 Hz), 3.23/3.35 (d/d, 2 H, J = 8 Hz; *E* and *Z* isomers), 4.7–5.2 (1 H; *Z* isomer: d of t at δ 4.65, J_t = 8 Hz, J[H,F] = 37 Hz, *E* isomer: d of t at δ 5.17, J_t = 8 Hz, J[H,F] = 21 Hz), 7.23 (s, 5 H); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(E)$ −94.2 (d of q, $J[CH_3,F]$ = 18 Hz and J[H,F] = 24 Hz), $\delta(Z)$ −104.8 (d of q, $J[CH_3,F]$ = 18 Hz, and J[H,F] = 44 Hz); mass spectrum, *m/e* (relative intensity) 150 (M^+), 135 (100) 129, 115, 91, 78, 77. Anal. Calcd for $C_{10}H_{11}F$: C, 79.97; H, 7.38. Found: C, 80.12; H, 7.14.

(*E*)- and (*Z*)-Methyl 6-Fluoro-5-heptenoate (4b). Reduction of **3b** afforded a 55:45 mixture of the *E* and *Z* isomers of methyl 6-fluoro-5-heptenoate (**4b**) in yields of 20% (method 1), 48% (method 2), and 44% (method 3). The reduction of **3b** according to method 4 never proceeded to completion. **4b**: IR (ν_{max}^{film}) 3000, 1720, 1440, 1350, 1160, 1080, 1030, 990, 910, 850, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.5–2.5 (m, 9 H) including 1.83 (d, $J[CH_3,F]$ = 18 Hz), 3.63 (s, 3 H), 4.0–5.2 (1 H; *Z* isomer: d of t at δ 4.40, J_t = 7 Hz, J[H,F] = 39 Hz; *E* isomer: d of t at δ 4.90, J_t = 7 Hz, J[H,F] = 23 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(E)$ −99.5 (d of q, $J[CH_3,F]$ = 20 Hz and J[H,F] = 24 Hz), $\delta(Z)$ −107.9 (d of q, $J[CH_3,F]$ = 20 Hz and J[H,F] = 44 Hz); mass spectrum, *m/e* (relative intensity) 150 (M^+), 135 (100), 129, 115, 91, 78, 77. Anal. Calcd for $C_8H_{13}FO_2$: C, 59.98; H, 8.18. Found: C, 60.00; H, 8.01.

Ethyl 5-Fluoro-4-hexenoate (4c). Reduction of **3c** afforded a 57:43 mixture of the *E* and *Z* isomers of ethyl 5-fluoro-4-hexenoate (**4c**) in yields of 87% (method 1) and 40% (method 3). The reduction of **3c** according to method 4 never proceeded to completion. **4c**: IR (ν_{max}^{film}) 3000, 1740, 1700 (shoulder), 1450, 1390, 1375, 1350, 1300, 1250, 1190, 1140, 1100, 1040, 1020, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3 H, J = 7 Hz), 1.87 (d, $J[CH_3,F]$ = 18 Hz), 2.33 (s, 4 H), 4.13 (q, 2 H, J = 7 Hz), 4.3–5.2 (1 H; *Z* isomer: d of t at δ 4.50, J_t = 8 Hz, J[H,F] = 40 Hz; *E* isomer: d of t at δ 5.00, J_t = 8 Hz, J[H,F] = 20 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$) $\delta(E)$ −94 (d of q, $J[CH_3,F]$ = 18 Hz and J[H,F] = 22 Hz), $\delta(Z)$ −102 (d of q, $J[CH_3,F]$ = 18 Hz and J[H,F] = 38 Hz); mass spectrum, *m/e* (relative intensity) 160 (M^+), 115, 111, 89, 87, 86, 83, 73 (100). Anal. Calcd for $C_8H_{13}FO_2$: C, 59.98; H, 8.18. Found: C, 59.61; H, 7.81.

Methyl 5-Fluoro-4-hexenoate (4d). Reduction of **3d** afforded a 55:45 mixture of the *E* and *Z* isomers of methyl 5-fluoro-4-hexenoate (**4d**) in 44% yield (method 3). **4d**: IR (ν_{max}^{film}) 2900, 1740, 1710 (shoulder), 1440, 1390, 1365, 1320, 1200, 1180, 1140, 1100, 1035, 1000, 900, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.87 (d, 3 H, $J[CH_3,F]$ = 18 Hz), 2.36 (s, 4 H), 3.70 (s, 3 H), 4.2–5.3 (1 H; *Z* isomer: d of t at δ 4.53, J_t = 8 Hz, J[H,F] = 38 Hz; *E* isomer: d of t at δ 5.00, J_t = 8 Hz, J[H,F] = 20 Hz); ^{19}F NMR ($CDCl_3/CFCl_3$): $\delta(E)$ = −98.1 (d of q,$J[CH_3,F]$ = 20 Hz and J[H,F] = 24 Hz); and δ(Z) = −106.1 (d of q,$J[CH_3,F]$ = 20 Hz and J[H,F] = 44 Hz); mass spectrum, *m/e* (relative intensity) 146 (M^+), 115, 87, 86 (100), 85, 74, 73. Anal. Calcd for $C_7H_{11}FO_2$: C, 57.52; H, 7.59. Found: C, 57.74; H, 7.74.

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Registry No. **1a**, 2550-26-7; **1b**, 2046-21-1; **1c**, 13984-57-1; **1d**, 13984-50-4; **2a**, 20849-77-8; **2b**, 95739-61-0; **2c**, 95739-62-1; **2d**, 64037-75-8; **3a**, 95739-63-2; **3b**, 95739-64-3; **3c**, 95739-65-4; **3d**, 95739-66-5; (*E*)-**4a**, 95739-67-6; (*Z*)-**4a**, 95739-68-7; (*E*)-**4b**, 95739-69-8; (*Z*)-**4b**, 95739-70-1; (*E*)-**4c**, 95739-71-2; (*Z*)-**4c**, 95739-72-3; (*E*)-**4d**, 95739-73-4; (*Z*)-**4d**, 95739-74-5; **5a**, 95739-75-6; **5b**, 95739-76-7; **5c**, 95739-77-8; **5d**, 95739-78-9; (diethylamino)sulfur trifluoride, 38078-09-0.

Coupling of Allylic Alcohol Epoxides with Sulfur-Stabilized Allylic Anions

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A study of the coupling of epoxy alcohol **15** with sulfur-stabilized allylic anions was undertaken as a route to dienes **16** and **17**. The allylic sulfone **9a** upon deprotonation with *n*-butyllithium in THF–HMPA undergoes smooth coupling with the epoxy magnesio alkoxide **15c** at −78 °C to give the sulfone diol **17** in high yield. Sulfone **9a** is prepared via allylic oxidation of geranyl phenyl sulfone with selenium dioxide–*tert*-butyl hydroperoxide (TBHP). Epoxy alcohol **15a** is secured by addition of propargylmagnesium bromide to methacrolein followed by silylation and selective epoxidation with $VO(acac)_2$–TBHP. A facile reaction is also observed with the lithiated sulfide **5b** and epoxide **15c** to afford the diol **16**. In contrast, the lithium salt **15b** of epoxy alcohol **15a** is only slowly attacked by the lithiated sulfide **5b** and not at all by the lithiated sulfone **9b**. The coupling products **16** and **17** are intermediates in a projected cembranolide synthesis.

Important new developments in epoxidation methodology have enhanced the status of allylic alcohol epoxides as synthetic intermediates.[1] These substances can now be prepared in high stereochemical purity from readily available precursors. As a result, epoxy alcohols have played increasingly key roles in stereocontrolled syntheses of diverse natural products and drugs,[1] polyols,[2a] and most recently, carbohydrates.[2b] In work to date, major emphasis has been placed on the epoxide function as a latent diol or methylcarbinol moiety. The direct utilization of epoxy

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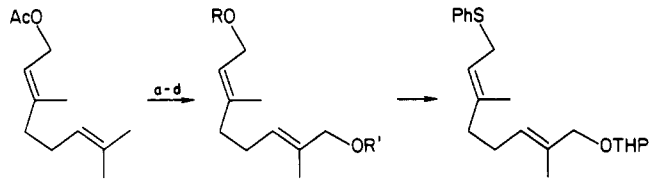
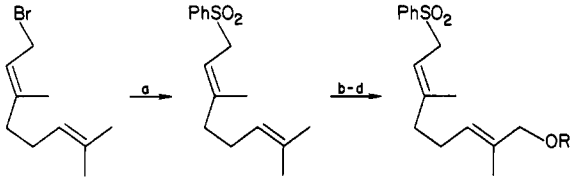
Scheme I[a]



1 2, R=Ac; R'=H 3, R=Ac; R'=THP 4, R=H; R'=THP 5a

[a] (a) SeO_2, *t*-BuOOH, CH_2Cl_2; (b) $NaBH_4$, EtOH; (c) DHP, C_5H_5NH, OTs; (d) K_2CO_3, MeOH; (e) PhSCN, *n*-Bu_3P, THF.

Scheme II[a]



6 7 8, R=H 9a, R=THP

[a] (a) $PhSO_2Na$, DMF; (b) SeO_2, *t*-BuOOH; (c) $NaBH_4$, EtOH; (d) DHP, C_5H_5NH, OTs.

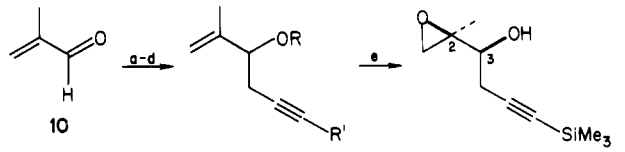
alcohols in chain-building processes is still relatively uncommon in complex systems.[3] Pursuant to synthetic work on cembranolides[4] we wished to homologate the epoxy alcohol **15a** with a geranyl chain by means of a sulfur-stabilized anion. Our studies of this reaction have led to an efficient process which, in view of the aforementioned developments, could find considerable application in natural product synthesis.

The dienyl segments **5a** and **9a** required for these studies were readily secured from geraniol. Allylic oxidation of the acetate **1** with selenium dioxide–*tert*-butyl hydroperoxide followed by reduction with sodium borohydride afforded the hydroxy acetate **2** in 55% yield (Scheme I).[5] Conversion to the tetrahydropyranyl ether **3** and subsequent basic methanolysis led to alcohol **4**. Phenylsulfenation using phenyl thiocyanate and tri-*n*-butylphosphine then gave sulfide **5a** in 92% yield.[6]

The dienyl sulfone **8** was most efficiently prepared (76% yield) via allylic oxidation of geranyl phenyl sulfone (**7**) with selenium dioxide and *tert*-butyl hydroperoxide (Scheme II). This oxidation is even more selective than the analogous oxidation of geranyl acetate (**1**).[5] Alcohol **8** was protected as its tetrahydropyranyl ether **9a**.

The preparation of epoxy alcohol **15a** commenced with alcohol **11**, the adduct of methacrolein and propargylmagnesium bromide (Scheme III).[7] Protection as the ethoxyethyl ether followed by lithiation, silylation, and

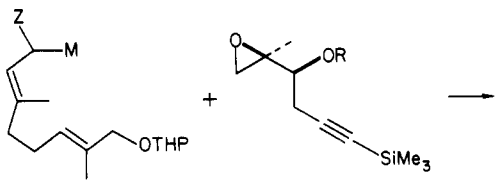
Scheme III[a]



10 11, R=R'=H 12, R=CH(CH3)OEt; R'=H 13, R=CH(CH3)OEt; R'=SiMe3 14, R=H; R'=SiMe3 15a

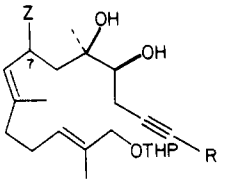
[a] (a) $HC{\equiv}CCH_2MgBr$, ether; (b) vinyl ethyl ether; C_5H_5NH, OTs; CH_2Cl_2; (c) *n*-BuLi, THF; Me_3SiCl; (d) H_2O, HCl; (e) $VO(acac)_2$, *t*-BuOOH, CH_2Cl_2 or *t*-BuOOH, (+)-diisopropyl tartrate, Ti(O-*i*-Pr)$_4$.

Scheme IV



5a, Z=SPh; M=H b, Z=SPh; M=Li 9a, Z=SO_2Ph; M=H b, Z=SO_2Ph; M=Li

15a, R=H b, R=Li c, R=MgBr d, R=$SiMe_3$ e, R=CH(CH3)OC_2H_5



16, Z=SPh; R=$SiMe_3$ 17, Z=SO_2Ph; R=$SiMe_3$ 18, Z=H; R=$SiMe_3$ 19, Z=SPh; R=H 20, Z=SO_2Ph; R=H 21, Z=R=H

acidic hydrolysis afforded alcohol **14**. Epoxidation using vanadyl acetylacetonate–*tert*-butyl hydroperoxide gave the racemic epoxy alcohol **15a**.[8] We also prepared the optically active 2*R*,3*S* enantiomer of epoxy alcohol **15a** via the Sharpless kinetic resolution methodology. However, for the current studies we employed the racemic material.

Additions of thiophenyl-stabilized allyllithiums to simple epoxides have been previously reported.[9] An intramolecular variant constitutes a pivitol step in Itô's synthesis of medium- and large-ring terpenoids.[10] For these additions prolonged reaction times and lithium-complexing amines such as Dabco are required for best results. Employing Itô's conditions (2 eq *n*-BuLi, THF, Dabco, 10 h, 0 °C),[10] we were able to prepare diol **16** in 60% yield via addition of sulfide **5b** to epoxy alkoxide **15b**. An extra equivalent of butyllithium was used to neutralize the acidic hydroxyl grouping of epoxy alcohol **15a** (Scheme IV). While this result was encouraging, it was clear that the prolonged exposure to base and the relatively high reaction temperature were causing degradation of the product. The

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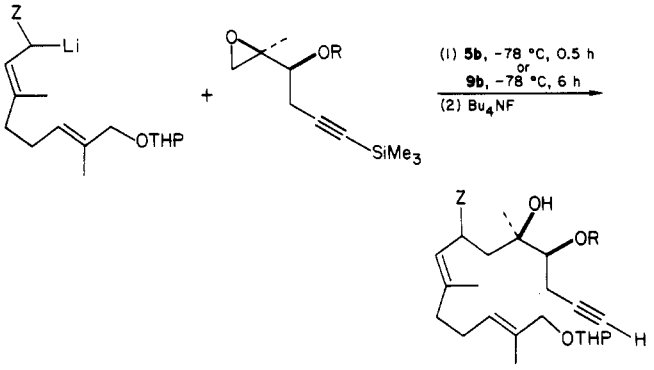
Table I. Coupling of Sulfur-Stabilized Anions with Epoxy Alcohol Derivatives



entry	Z	R	additive[a]	% yield[b]	% recovd
1	SPh (**5b**)	Li (**15b**)	Dabco		89 (**5a**)
2			TMEDA		80 (**5a**)
3			HMPA	15 (**19**)	60 (**5a**)
4		MgBr (**15c**)	Dabco	21 (**19**)	68 (**5a**)
5			TMEDA	15 (**19**)	59 (**5a**)
6			HMPA	77 (**19**)	
7	SO_2Ph (**9b**)	Li (**15b**)	HMPA	9 (**20**)	90 (**9a**)
8		MgBr (**15c**)	Dabco	64 (**20**)	
9			TMEDA	68 (**20**)	
10			HMPA	70 (**20**)	
11		Me_3Si (**15d**)	HMPA		43 (**9a**)
12		EE (**15e**)	HMPA		81 (**9a**)
13			HMPA–$MgBr_2$		90 (**9a**)

[a] Dabco = 1,4-diazabicyclo[2.2.2]octane; TMEDA = *N,N,N′,N′*-tetramethyl-1,2-ethylenediamine; HMPA = hexamethylphosphoric triamide. [b] The yield was determined after cleavage of the trimethylsilyl grouping.

use of HMPA in place of Dabco appeared to facilitate the addition and led to fewer byproducts, but long reaction times were still required. Hoping to accelerate the epoxide cleavage through intramolecular Lewis acid catalysis, we treated the epoxy alcohol **15a** with 1 equiv of ethylmagnesium bromide prior to addition of the lithium species **5b**. The effect was dramatic. Complete addition was observed in less than 1 h at −78 °C, and the diol **16** could be isolated in 77% yield. Unfortunately, we encountered difficulties in the hydrogenolysis of the phenyl sulfide grouping of **16** en route to the cembranolide precursor **21**. We therefore turned our attention to the sulfone derivative **9b** in anticipation of a more facile hydrogenolysis[11] of the coupling product **17**.

The alkylation of lithiated allylic sulfones with alkyl halides is a well-documented, synthetically useful process.[9,12] The reaction of such sulfones with epoxides is less established, a consequence no doubt of the lower nucleophilicity of a sulfone-stabilized carbanion.[13] In fact, the reaction of sulfone **9b** with the magnesio epoxide **15c** in THF–HMPA was significantly slower than the corresponding reaction of sulfide **5b** under identical conditions. Even so, the desired diol **17** was produced cleanly in 70% yield free of byproducts. HMPA was the preferred cosolvent, but Dabco and TMEDA were nearly equally effective. In contrast, the lithio alkoxide **15b** reacted negligibly with sulfone **9b** in THF under any of the aforementioned conditions. Furthermore, the Me_3Si ether **15d** and the ethoxyethyl ether **15e** gave no coupling product at all with the lithio sulfone **9b**, even in the presence of added magnesium bromide. Table I summarizes results of a comparative study in which various derivatives of epoxy alcohol **15** were treated with the lithio sulfide **5b** and the sulfone **9b** under controlled conditions. While the effect of HMPA is noteworthy, clearly the neighboring magnesium alkoxide is the critical element, particularly in the case of the less reactive sulfone anion. The ability of this element to facilitate the regioselective addition of sulfones to allylic alcohol epoxides significantly enhances the potential application of the reaction to complex synthesis.[14]

As an aside it should be noted that the coupling of sulfide **5** or sulfone **9** with epoxide **15** introduces a new chiral center in the product **16** or **17**. In the case of sulfide **16** a 1:1 mixture of diastereomers was obtained.[15] Sulfone **17**, on the other hand, consisted of an 8:1 mixture of diastereomers. Evidently, the sulfone reaction proceeds via a more diastereoselective transition state, possibly owing to greater steric bulk or dipolar attraction. Regardless, the observation is of interest in the context of acyclic stereodirected carbon–carbon bond forming reactions.

We are currently examining sequences for the conversion of sulfone **20** into cembranoid natural products. These studies will be reported in due course.

Experimental Section

(2*E*,6*E*)-3,7-Dimethyl-8-[(2-tetrahydropyranyl)oxy]-2,6-octadienyl Acetate (3). A solution of 10.128 g (47.71 mmol) of the alcohol **2** in 10 mL of dichloromethane was stirred at room temperature under nitrogen as 100 mg (0.378 mmol) of pyridinium *p*-toluenesulfonate was added followed by dropwise addition of 4.35 mL (52.5 mmol) of dihydropyran. The mixture was stirred at ambient temperature for 13 h and was then diluted with 50 mL of ether. The organic layer was washed with two portions of half-saturated brine and one portion of brine. Drying of the organic solution followed by removal of solvent at reduced pressure afforded 13.827 g (98%) of the tetrahydropyranyl ether **3** as an oil: IR (film) ν 2910, 1740, 1445, 1375, 1230, 1025 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.60 (m, THP CH_2's), 1.66 (s, C3 vinyl CH_3), 1.70 (s, C7 vinyl CH_3), 2.04 (s, CH_3CO), 2.10 (br s, H_4, H_5), 3.53, 3.90 (m, THP carbinyl), 3.94 (AB q, J = 12 Hz, $\Delta\nu$ = 23 Hz, H8), 4.56 (d, J = 7 Hz, H1), 4.60 (s, THP acetal H), 5.34 (m, H2, H6); ^{13}C NMR ($CDCl_3$) δ 169.4, 140.4, 131.8, 125.8, 118.3, 96.2, 71.6, 60.8, 60.2, 38.3, 29.9, 25.1, 24.9, 19.8, 18.6, 15.5, 13.1. Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.26; H, 9.57.

(2*E*,6*E*)-3,7-Dimethyl-8-[(2-tetrahydropyranyl)oxy]-2,6-octadienol (4). A solution of 13.827 g (46.650 mmol) of acetate **3** was stirred in 25 mL of dry methanol as 1.30 g (9.42 mol) of anhydrous potassium carbonate was added. After it was stirred rapidly under nitrogen at ambient temperature for 45 min, the mixture was diluted with an equal volume of water and extracted with two 40-mL portions of ether. The combined ether layers were washed with water and brine and were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed on 20 g of silica gel (elution with 20% ethyl acetate/hexane) to give 11.539 g (95%) of the alcohol **4** as a colorless oil: IR (film) ν 3380, 2910, 1665, 1430, 1200, 1120, 1040, 1020 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.58 (m, THP CH_2 and C3 vinyl CH_3), 1.65 (s, C7 vinyl CH_3), 1.82 (br s, OH), 2.09 (br s, H4, H_5), 3.52, 3.78 (m, THP carbinyl), 3.95 (AB q, J = 11 Hz, $\Delta\nu$ = 21 Hz, H8), 4.12 (d, J =7 Hz, H1), 4.56 (br s, THP acetal H), 5.36 (br t, J = 7 Hz, H2, H6); ^{13}C NMR ($CDCl_3$) δ 137.6, 131.7, 127.1, 124.0, 96.7, 72.4, 61.5, 58.6, 38.7, 30.2,

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(14) Pronounced accelerations of related couplings have also been observed by J. D. Clark (unpublished results) in our laboratory.
(15) The ratios were established by high-field ^1H NMR and ^{13}C NMR of the THP-cleaved *tert*-butyldimethylsilyl derivatives.
(16) Meyers, A. I.; Comins, D. L.; Roland, D. M.; Henning, R.; Shimizu, K. *J. Am. Chem. Soc.* **1979**, *101*, 7104–7105. Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772–3774.

25.6, 25.1, 19.0, 15.7, 13.5. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.61; H, 10.34.

(2*E*,6*E*)-3,7-Dimethyl-8-[(2-tetrahydropyranyl)oxy]-2,6-octadienyl Phenyl Sulfide (5a). A stirred solution of 3.274 g (12.87 mmol) of alcohol **4** in 32 mL of dry tetrahydrofuran under an argon atmosphere was treated with 1.912 g (14.16 mmol) of phenyl thiocyanate[6] followed by dropwise addition of 3.53 mL (14.2 mmol) of tri-*n*-butylphosphine. After 18 h, the solvent was removed under reduced pressure, and the residue was chromatographed on 25 g of silica gel (elution with 5% ethyl acetate/hexane) to give 4.107 g (92%) of the sulfide **5a** as an oil: IR (film) ν 2920, 1582, 1425, 1125, 1082, 1035 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.55 (s, C3 vinyl CH_3), 1.60 (m, THP CH_2's), 1.63 (s, C7 vinyl CH_3), 2.03 (br s, H4, H5), 3.42 (m, THP carbinyl), 3.50 (d, J = 7 Hz, H1), 3.80 (m, THP carbinyl), 3.92 (AB q, J = 12 Hz, $\Delta\nu$ = 23 Hz, H8), 4.54 (s, THP acetal H), 5.27 (m, H2, H6), 7.20 (m, aromatic); ^{13}C NMR ($CDCl_3$) δ 138.8, 136.4, 131.9, 129.5, 128.2, 126.6, 125.5, 119.4, 119.3, 96.9, 72.3, 61.5, 38.7, 31.7, 30.3, 25.7, 25.2, 19.1, 15.5, 13.6. Anal. Calcd for $C_{21}H_{30}O_2S$: C, 72.79; H, 8.73. Found: C, 72.82; H, 8.74.

(2*E*,6*E*)-3,7-Dimethyl-8-hydroxy-2,6-octadienyl Phenyl Sulfone (8). A suspension of 6.95 g (62.6 mmol) of selenium dioxide was stirred in 120 mL of dichloromethane at 0 °C under nitrogen as 43.0 mL (314 mmol) of 70% aqueous *tert*-butyl hydroperoxide was added all at once.[5] The mixture was stirred at 0 °C for 15 min, and then 34.87 g (125.3 mmol) of the sulfone **7** in 20 mL of dichloromethane was added over a period of 40 min. After the mixture was stirred at 0 °C for 2 h and at room temperature for 8 h, it was diluted with 500 mL of water and was extracted with two 200-mL portions of ether. The combined organic layers were washed with water and brine and were dried over magnesium sulfate; solvent was removed at reduced pressure to provide a crude oil which was stirred in 160 mL of 95% ethanol at 0 °C under nitrogen as 2.30 g (60.8 mmol) of sodium borohydride was added in small portions. The mixture was stirred for 15 min at 0 °C and 50 mL of saturated ammonium chloride was added dropwise. The reaction mixture was then poured into water and was extracted with two 200-mL portions of ether. The combined organic layers were washed with water and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the residue was chromatographed on 250 g of silica gel (elution with 35% ethyl acetate/hexane followed by 70% ether/hexane) to provide 27.92 g (76%) of the hydroxy sulfone **8** as a viscous oil: IR (film) ν 3450, 2910, 1455, 1315, 1160, 1098 cm^{-1}; ^1H NMR (90 MHz $CDCl_3$) δ 1.37 (s, C3 vinyl CH_3), 1.64 (s, C7 vinyl CH_3), 1.73 (s, OH), 2.06 (s, H4, H5), 3.76 (d, J = 8 Hz, H1), 3.97 (s, H8), 5.18 (t, J = 8 Hz, H2), 5.30 (m, H6), 7.57 (m, meta and para aromatic), 7.88 (m, ortho aromatic); MS, calcd for $C_{16}H_{22}O_3S$ m/e 294.4, found (M^+) 294, (M^+ + 1) 295, (M^+ + 3) 297, (M^+ - $PhSO_2$) 153.

(2*E*,6*E*)-3,7-Dimethyl-8-[(2-tetrahydropyranyl)oxy]-2,6-octadienyl Phenyl Sulfone (9a). A solution of 21.15 g (71.84 mmol) of the sulfone **8** was stirred in 15 mL of dichloromethane under nitrogen as 902 mg (3.59 mmol) of pyridinium *p*-toluene sulfonate was added, followed by 7.20 mL (78.9 mmol) of dihydropyran. After the mixture was stirred at room temperature for 21 h, it was diluted with 150 mL of ether and was washed with three portions of half-saturated brine and one portion of brine. The organic solution was dried over magnesium sulfate, and solvent was removed at reduced pressure to provide 26.82 g (99%) of the sulfone **9a** as a liquid: IR (film) ν 2920, 1455, 1320, 1160, 1035 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.32 (s, C3 vinyl CH_3), 1.64 (br s, C7 vinyl CH_3 and THP CH_2's), 2.05 (s, H4, H5), 3.52 (m, THP carbinyl), 3.78 (d, J = 8 Hz, H1), 3.87 (m, H8 and THP carbinyl), 4.57 (br s, THP acetal), 5.17 (t, J = 8 Hz, H2), 5.33 (br s, H6), 7.54 (m, meta and para aromatic), 7.76 (m, ortho aromatic); ^{13}C NMR ($CDCl_3$) δ 145.8, 138.6, 133.3, 132.5, 128.8, 128.3, 126.4, 110.4, 97.4, 72.5, 62.0, 55.9, 39.0, 30.5, 25.7, 25.3, 19.4, 16.0, 13.8. Anal. Calcd for $C_{21}H_{30}O_4S$: C, 66.63; H, 7.99. Found: C, 66.55; H, 8.03.

2-Methyl-6-(trimethylsilyl)-1-hexen-5-yn-3-ol (14). A solution of 33.06 g (300.5 mmol) of alcohol **11**[7] was stirred in 35 mL of dichloromethane at 0 °C under nitrogen as 100 mg of pyridinium p-toluenesulfonate was added, followed by 31.6 mL (331 mmol) of ethyl vinyl ether.[15] After the mixture was stirred at 0 °C for 15 min and then at room temperature for 24 h, it was diluted with 150 mL of ether and was washed twice with half-saturated brine and once with brine. The organic solution was dried over magnesium sulfate, and solvents were removed under reduced pressure to afford the 2-ethoxyethyl ether **12** as a colorless oil. Crude **12** in 300 mL of tetrahydrofuran under nitrogen was cooled to -78 °C as 125 mL (338 mmol) of 2.70 M *n*-butyllithium was added over 18 min with stirring. The deep yellow mixture was stirred at -78 °C for 30 min, and then 45.0 mL (355 mmol) of chlorotrimethylsilane was added rapidly to the mixture. After 15 min the mixture was warmed to room temperature, acidified with 400 mL of 10% hydrochloric acid, and stirred rapidly at room temperature for 4 h. The organic layer was separated, and the aqueous layer was extracted with one 200-mL portion of ether. The combined organic solutions were washed with water, saturated aqueous sodium bicarbonate, and brine. The organic solution was dried over magnesium sulfate, and solvent was removed at reduced pressure to afford the crude alcohol. Kugelrohr distillation (122-137 °C, 1.2 mmHg) provided 47.14 g (86%) of the alcohol **14** as a liquid: IR (film) ν 3370, 3060, 2950, 2180, 1440, 1260, 1020, 855 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.12 (s, Me_3Si), 1.71 (s, C2 vinyl CH_3), 2.15 (br s, OH), 2.47 (d, J = 6 Hz, H4), 4.18 (t, J = 6 Hz, H3), 5.84 (br s, H1), 5.98 (br s, H1). Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95. Found: C, 65.60; H, 9.99.

***rel*-(2*R*,3*S*)-1,2-Epoxy-2-methyl-6-(trimethylsilyl)-5-hexyn-3-ol (15a).** A solution of 13.81 g (75.75 mmol) of alcohol **14** in 80 mL of dichloromethane was stirred at room temperature as 200 mg (0.754 mmol) of vanadyl bis(acetylacetonate) was added.[8] The blue-green solution was cooled to 0 °C under nitrogen as 19.50 mL (91.26 mmol) of 4.68 M *tert*-butyl hydroperoxide in 1,2-dichloroethane was added dropwise. The deep red mixture was stirred for 27 h at 0 °C, at which time it was poured into water and was extracted with two 80-mL portions of ether. The combined ether solutions were washed with saturated sodium sulfite, water, and brine and were dried over magnesium sulfate. The solvent was removed at reduced pressure, and the residue was chromatographed on 55 g of silica gel (elution with 10% ethyl acetate/hexane) to afford 14.11 g (94%) of epoxide **15a** as a colorless oil: IR (film) ν 3430, 3040, 2950, 2170, 1420, 1255, 845 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.10 (s, Me_3Si), 1.33 (s, C2 CH_3), 2.47 (d, J = 6 Hz, H4), 2.48 (br s, OH), 2.76 (AB q, J = 4 Hz, $\Delta\nu$ = 31 Hz, H1), 3.68 (d t, J = 6, 3 Hz, H3); ^{13}C NMR ($CDCl_3$) δ 102.6, 86.6, 70.3, 58.1, 50.7, 24.2, 17.5, -0.39. Anal. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15. Found: C, 60.64; H, 9.18.

***rel*-(2*R*,3*S*)-1,2-Epoxy-2-methyl-6-(trimethylsilyl)-5-hexyn-3-ol Trimethylsilyl Ether (15d).** To a solution of 1.887 g (9.516 mmol) of epoxide **15a** in 12 mL of dichloromethane at 0 °C under nitrogen was added 1.50 mL (11.8 mmol) of chlorotrimethylsilane. The mixture was stirred at 0 °C briefly, and then 1.60 mL (11.5 mmol) of triethylamine was added dropwise. After the mixture was allowed to warm to room temperature and stirred thusly for 0.5 h, it was poured into saturated aqueous sodium bicarbonate solution and was extracted with two 20-mL portions of ether. The combined ether layers were washed with water and brine and were dried over sodium sulfate. Solvent removal at reduced pressure followed by flash chromatography on 30 g of silica gel (elution with hexane and then with 5% ethyl acetate/hexane) afforded 2.326 g (90%) of the trimethylsilyl ether **15d** as a colorless oil: IR (film) ν 2950, 2180, 1123, 1085, 955, 860, 765 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.13 (s, Me_3Si), 1.26 (s, C2 CH_3), 2.33 (dd, J = 7, 4 Hz, H4), 2.62 (AB q, J = 6 Hz, $\Delta\nu$ = 15 Hz, H1), 3.52 (dd, J = 7, 4 Hz, H3). Anal. Calcd for $C_{13}H_{26}O_2Si_2$: C, 57.72; H, 9.70. Found: C, 57.80; H, 9.75.

***rel*-(2*R*,3*S*)-1,2-Epoxy-2-methyl-6-(trimethylsilyl)-5-hexyn-3-ol 2-Ethoxyethyl Ether (15e).** A solution of 1.140 g (5.749 mmol) of epoxide **15a** was stirred in 2.5 mL of dichloromethane at room temperature under nitrogen as 57 mg (0.23 mmol) of pyridinum *p*-toluenesulfonate was added. The solution was then treated with 2.20 mL (23.0 mmol) of ethyl vinyl ether and was allowed to stir at room temperature for 19.5 h.[15] The mixture was diluted with 30 mL of ether and was washed with three portions of half-saturated brine and one portion of brine. The solution was dried over magnesium sulfate followed by solvent removal at reduced pressure to afford 1.517 g (98%) of the 2-ethoxyethyl (EE) ether **15e** as a colorless liquid: IR (film) ν 2960, 2175, 1384, 1260, 1142, 1095, 958, 851, 762 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.11 (s, Me_3Si), 1.15 (t, J = 6 Hz, EE CH_3CH_2O), 1.28

(s, C2 CH_3), 1.30 (m, EE CH_3CH), 2.53 (m, H4), 2.70 (AB q, J = 5 Hz, $\Delta\nu$ = 19.4 Hz, H1), 3.37 (dd, J = 5, 6 Hz, H3), 3.52 (m, 2 H, EE CH_3CH_2O), 4.82 (br q, J = 5 Hz, EE acetal H). Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 62.18; H, 9.69. Found: C, 62.26; H, 9.73.

***rel*-(4*S*,5*R*)-(8*E*,12*E*)-5,9,13-Trimethyl-7-(phenythio)-14-[(2-tetrahydropyranyl)oxy]-8,12-tetradecadien-1-yne-4,5-diol (19).** A solution of 200 mg (0.577 mmol) of phenyl sulfide **5a** in 0.4 mL of tetrahydrofuran and 0.1 mL of HMPA was cooled to −78 °C under nitrogen. The mixture was stirred at −78 °C as 0.33 mL (0.59 mmol) of 1.79 M *n*-butyllithium was added dropwise. The red-orange mixture was stirred for 20 min at −78 °C. In a separate vessel, 113 mg (0.570 mmol) of epoxide **15a** was stirred in 0.4 mL of tetrahydrofuran and 0.1 mL of HMPA at −78 °C under nitrogen as 0.21 mL (0.59 mmol) of 2.82 M ethylmagnesium bromide in ether was added dropwise. The resulting slurry of magnesium salt was stirred for 10 min at −78 °C. The mixture was warmed rapidly to 0 °C and was taken up into a dry syringe, a 0.2-mL tetrahydrofuran rinse ensuring quantitative transfer. The magnesium salt was then added dropwise to the stirring, −78 °C solution of **5b**. After the mixture was stirred at −78 °C for 0.5 h, it was quenched by addition of 2 mL of methanol and 1 mL of saturated aqueous ammonium chloride, and then it was poured into water and was extracted with two 20-mL portions of ether. The combined organic layers were washed with water and brine and were dried over magnesium sulfate. The solvent was removed to afford the crude diol **16**.

This material was stirred in 1 mL of tetrahydrofuran under nitrogen at room temperature as 1.0 mL (1.0 mmol) of 1 M tetrabutylammonium fluoride in tetrahydrofuran was added. After 0.5 h, the mixture was poured into water and was extracted with two 20-mL portions of ether. The ether layers were washed with water and brine and were dried over anhydrous magnesium sulfate. Solvent was removed at reduced pressure to provide an oil, which was purified by chromatography on 10 g of silica gel (elution with 20% ethyl acetate/hexanes) to afford 208 mg (77%) of the sulfide diol **19** as 1:1 mixture of C7 epimers: IR (film) ν 3420, 3270, 2910, 1585, 1442, 1390, 1205, 1125, 1080, 1023, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, C5 CH_3), 1.23 (s, C9 vinyl CH_3), 1.48 (m, THP CH_2's), 1.53 (s, C13 vinyl CH_3), 1.73 (m, H6), 1.92, (m, H1, H10, H11), 2.29 (dd of AB q, J_{AB} = 16.4 Hz, $\Delta\nu$ = 55.6 Hz, J_1 = 3.2, 2.8 Hz, J_2 = 9.2, 3.2 Hz, H3), 2.50, 2.53 (two s, OH), 2.70, 2.73 (two d, J = 4.5 Hz, OH), 3.40 (m, THP carbinyl), 3.48 (ddd, J = 9.2, 4.5, 2.8 Hz, H4), 3.77 (m, THP carbinyl), 3.84 (AB q, J_{AB} = 11.6 Hz, $\Delta\nu$ = 107 Hz, H14), 4.00 (m, H7), 4.48 (t, J = 3.5 Hz, THP acetal), 5.03, 5.05 (two d, J = 6.0 Hz, H8), 5.23 (br t, J = 6.8 Hz, H12), 7.17 (m, meta and para aromatic), 7.32 (m, ortho aromatic); ^{13}C NMR ($CDCl_3$) δ 137.60, 137.57, 134.7, 134.5, 134.4, 134.3, 133.8, 132.4, 128.5, 127.8, 127.7, 127.0, 126.9, 126.8, 97.6, 97.5, 81.8, 75.7, 74.3, 72.8, 72.7, 70.3, 62.3, 62.2, 43.5, 42.3, 42.0, 39.0, 30.6, 25.8, 25.4, 23.0, 21.8, 21.7, 19.52, 19.47, 16.0, 14.0; MS, calcd for $C_{28}H_{40}O_4S$ m/e 472.7, found (M^+ − PhS) 363, (M^+ − PhS + 1) 364, (M^+) 473, (M^+ + 1) 474, (M^+ + 2) 476. Anal. Calcd for $C_{28}H_{40}O_4S$: C, 71.15; H, 8.53. Found: C, 70.38, H, 8.43.

***rel*-(4*S*,5*R*)-(8*E*,12*E*)-5,9,13-Trimethyl-7-(phenylsulfonyl)-14-[(2-tetrahydropyranyl)oxy]-8,12-tetradecadien-1-yne-4,5-diol (20).** A mixture of 324 mg (1.63 mmol) of epoxide **15a** and 676 mg (1.79 mmol) of phenyl sulfone **9a** in 2.4 mL of tetrahydrofuran and 0.6 mL of HMPA was stirred with cooling to −78 °C under argon. Then 0.58 mL (1.64 mmol) of 2.82 M ethylmagnesium bromide in ether was added. After 5 min, 1.00 mL (1.79 mmol) of 1.79 M *n*-butyllithium was added dropwise, giving a red-orange mixture which was stirred at −78 °C for 6.0 h and quenched with 2 mL of methanol and 2 mL of saturated ammonium chloride. The mixture was poured into water and extracted with two 20-mL portions of ether. The combined ether layers were washed with water and brine and were dried over magnesium sulfate. Solvent removal at reduced pressure provided a crude oil, which was subsequently stirred in 2 mL of tetrahydrofuran under nitrogen at room temperature as 2.0 mL (2.0 mmol) of 1 M tetrabutylammonium fluoride was added. After 2.0 h, 50 mL of ether was added, and the mixture was washed with three portions of water and one portion of brine and was dried over magnesium sulfate. Solvent removal afforded a viscous oil, which was purified by chromatography on 30 g of silica gel (elution with 25% ethyl acetate/hexane) to provide 511 mg of one sulfone epimer of diol **20** as a viscous oil: IR (film) ν 3450, 3290, 2920, 1455, 1390, 1310, 1155, 1090, 1035, 920, 740 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.18 (s, C5, C9 CH_3), 1.55 (m, THP CH_2's), 1.62 (s, C13 vinyl CH_3), 2.03 (br s, H1, H6, H10, H11), 2.39 (dd of AB q, J_{AB} = 4 Hz, $\Delta\nu$ = 11 Hz, J_1 = 1, 0 Hz, J_2 = 5, 1 Hz, H3), 2.67 (s, OH), 3.05 (m, OH), 3.52 (m, H4 and THP carbinyl), 3.78 (m, THP carbinyl), 3.92 (AB q, J_{AB} = 12 Hz, $\Delta\nu$ = 24 Hz, H14), 4.02 (m, H7), 4.54 (br s, THP acetal), 5.02 (d, J = 10 Hz, H8), 5.28 (m, H12), 7.52 (m, meta and para aromatic), 7.82 (m, ortho aromatic); ^{13}C NMR ($CDCl_3$) δ 143.9, 143.7, 143.5, 137.2, 137.1, 135.4, 133.2, 132.32, 132.27, 129.1, 128.5, 126.4, 126.2, 123.5, 119.1, 97.7, 97.3, 81.7, 75.1, 73.5, 73.2, 72.6, 72.3, 70.2, 70.1, 65.5, 62.2, 62.0, 61.9, 60.9, 38.8, 35.0, 34.9, 30.4, 25.1, 22.5, 21.7, 19.4, 19.2, 15.8, 14.9, 13.7, 13.4; MS, calcd for $C_{28}H_{40}O_6S$ m/e 504.7, found (M^+ − $PhSO_2$) 363, (M^+) 505. Anal. Calcd for $C_{28}H_{40}O_6S$: C, 66.64; H, 7.99. Found: C, 66.59; H, 8.04.

Continued elution afforded 63 mg of the other sulfone epimer of diol **20**, the combined yield being 70%: IR (film) ν 3450, 3290, 2930, 1460, 1395, 1310, 1160, 1090, 1040, 920, 740 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.16 (s, C5 and C9 CH_3), 1.52 (br s, C13 vinyl CH_3 and THP CH_2's), 2.06 (m, H1, H6, H10, H11), 2.33 (m, H3), 2.60 (m, OH), 3.51 (m, H4 and THP carbinyl), 3.80 (m, THP carbinyl), 3.98 (AB q, $J_{A,B}$ = 12 Hz, $\Delta\nu$ = 37 Hz, H14), 4.03 (m, H7), 4.56 (s, THP acetal), 5.04 (br d, J = 10 Hz, H8), 5.28, 5.52 (two br t, J = 7 Hz, H12), 7.53 (m, meta and para aromatic), 7.80 (m, ortho aromatic); ^{13}C NMR ($CDCl_3$) δ 144.2, 143.4, 143.3, 137.2, 133.3, 133.2, 132.4, 129.4, 129.2, 128.8, 128.6, 128.1, 127.4, 126.5, 119.3, 119.2, 97.5, 97.4, 81.7, 81.5, 75.2, 73.5, 73.3, 72.6, 70.5, 70.4, 70.3, 62.0, 61.0, 39.1, 38.9, 30.4, 25.3, 25.1, 22.8, 21.9, 21.7, 19.5, 19.3, 16.0, 15.9, 13.8; MS, calcd for $C_{28}H_{40}O_6S$ m/e 504.7, found (M^+ − $PhSO_2$) 363, (M^+) 505. Anal. Calcd for $C_{28}H_{40}O_6S$: C, 66.64; H, 7.99. Found: C, 66.56; H, 8.03.

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