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Intramolecular Diels-Alder Reaction of Vinylsulfonates Derived from Hydroxyalkyl Substituted 1,3-Dienes and Oxidative Desulfurization of the Resultant Sultones

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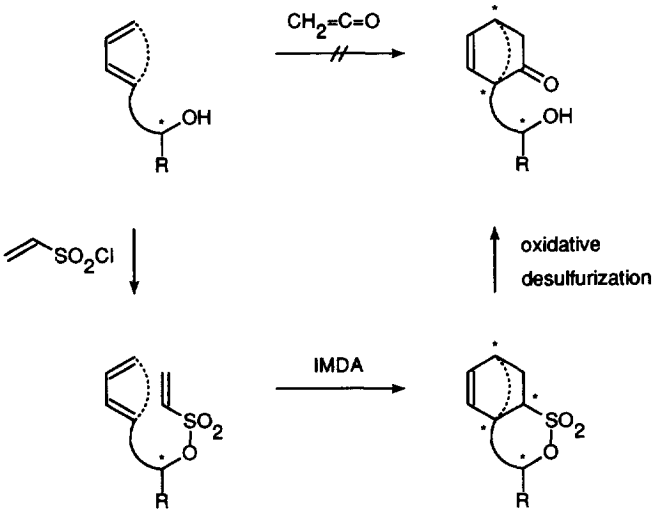
Abstract: Vinylsulfonates prepared from hydroxyalkyl substituted cycloalka-1,3-dienes and acyclic 1,3-dienes by esterification with vinylsulfonyl chloride cycloadd to δ-sultones at temperatures ranging from 0 °C to reflux in toluene. High diastereoselectivity is observed for substrates **2** featuring a cyclic 1,3-diene moiety, whereas a substituent R^2 larger than hydrogen is necessary to achieve good to excellent levels of stereocontrol for substrates **9** possessing an acyclic 1,3-diene unit. Oxidative desulfurization of the resultant sultones *via* borylation and subsequent peracid treatment yields hydroxy ketones, thus establishing vinylsulfonyl chloride as a regio- and stereoselectively reacting ketene equivalent for the intramolecular Diels-Alder cycloaddition.

INTRODUCTION

A common route to the synthetically valuable but not directly attainable [4+2] adducts of ketene involves intermolecular Diels-Alder reaction of dienophilic ketene equivalents followed by functional group manipulation of the derived products.[1] During our studies on intramolecular Diels-Alder cycloadditions of vinylsulfonates, initiated to eventually control side-chain chirality,[2] we investigated the feasibility of the reaction sequence shown in Scheme 1 which promised to give a regio- and diastereoselective access to formal [4+2] adducts of ketene with hydroxyalkyl substituted 1,3-dienes.[2b,c]

Intramolecular Diels-Alder reaction of a vinylsulfonate, readily available by esterification of the corresponding alcohol with vinylsulfonyl chloride,[2a] generates a sultone which is oxidatively cleaved to the desired hydroxy ketone in a subsequent operation. Complete regiocontrol is at hand through choosing an appropriate tether length which prevents formation of the isomeric bridged cycloadduct.[3] Moreover, a defined stereochemical relationship between acyclic and cyclic stereogenic moieties within the hydroxy ketone is established if the cycloaddition step proceeds diastereoselectively with respect to the chiral center in the tether linking diene and dienophile. Both selectivities can hardly be efficiently achieved through an intermolecular [4+2] addition strategy.[4]

Here, we give a full account of our studies on intramolecular Diels-Alder reactions of vinylsulfonates derived from carbocyclic and acyclic 1,3-dienes possessing a homoallylic hydroxy group and on the oxidative desulfurization of the resultant δ-sultones.



Scheme 1. Regio- and diastereoselective formal [4+2] cycloaddition of ketene to hydroxyalkyl substituted 1,3-dienes *via* intramolecular Diels-Alder (IMDA) reaction of vinylsulfonates/sultone cleavage

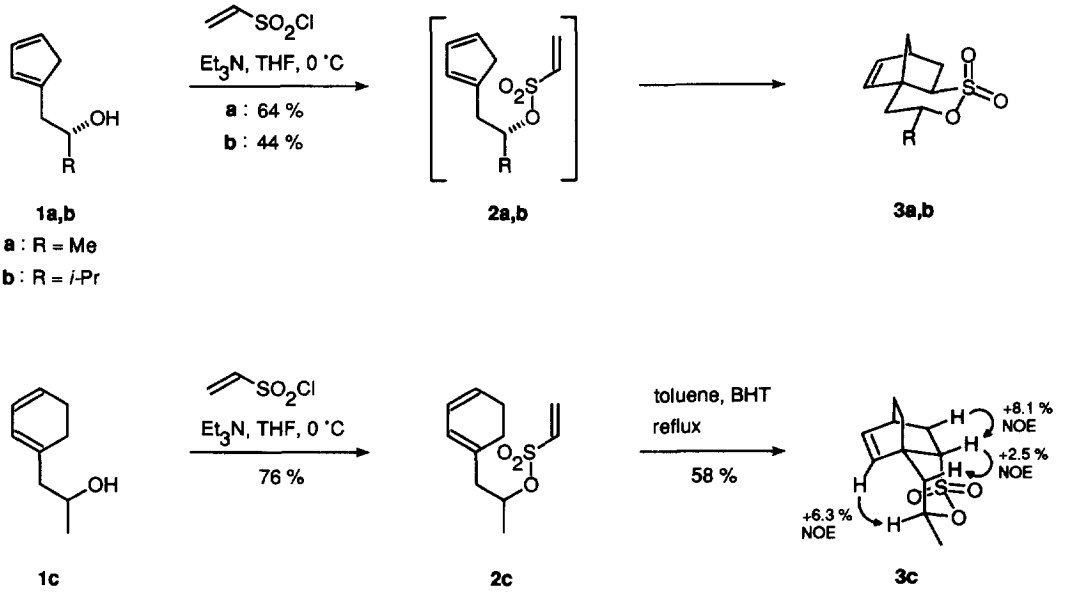
RESULTS AND DISCUSSION

Intramolecular Diels-Alder Reactions - Carbocyclic Dienes

Gratifyingly, the electron-withdrawing sulfur functionality of vinylsulfonates, unhampered by the unfavorable conformational preferences associated with acrylates,[5] allows for rather mild cycloaddition conditions. Thus, esterification of alcohols **1a,b** as equilibrium mixtures of diene isomers with vinylsulfonyl chloride[6] led after 2-3 h at 0°C directly to *exo* sultones **3a,b** with excellent diastereoselectivity (*ds* = 96 % by capillary GC analysis of the crude product) for both substrates (Scheme 2). Only the depicted C-1 substituted diene isomers **2a,b** cyclize, while the other isomers are presumably converted to **2a,b** by 1,5-H shift during the reaction course.[7] The cyclohexadiene homolog **2c** derived from alcohol **1c** required reflux in toluene for complete conversion within a few hours. To avoid side reactions of vinylsulfonate **2c** at this elevated temperature, a small amount of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added as a radical scavenger. Intramolecular Diels-Alder reaction of **2c** proceeded with high diastereoselectivity as well (*ds* = 93 % by capillary GC analysis of the crude product), but interestingly *endo* sultone **3c** was obtained predominantly.

The relative configuration of **3a-c** follows from diagnostic $^1H,^1H$ coupling constants and was unambiguously proven for **3a** by X-ray diffraction analysis (Figure 1), while the stereochemical assignment for **3c** is further supported by the NOE difference data listed in Scheme 2. Since the alkyl substituent at the inducing stereogenic center occupies an equatorial position of a chair δ-sultone for all major products, a chair-like folded tether with minimized nonbonding interactions is probably the favored geometry in the transition state of these cycloadditions.

The requisite alcohol **1a** was prepared in racemic form from sodium cyclopentadienide and 1,2-epoxypropane according to a published procedure.[10] In an analogous manner, enantiomerically pure **1b** was obtained through alkylation of sodium cyclopentadienide with (2*R*)-1,2-epoxy-3-methylbutane which in turn is available from (*S*)-valine by a known three step sequence.[11] Racemic alcohol **1c** was synthesized from sulfone **4** using a methodology developed by *Bäckvall* (Scheme 3).[12] Temporary blocking of the secondary alcohol (**5** → **6**) proved necessary to achieve a clean 1,4-elimination of benzenesulfinic acid without concomitant isomerization of the diene moiety.



Scheme 2. Intramolecular Diels-Alder reaction of vinylsulfonates **2** derived from alcohols **1**
(BHT = 2,6-di-*tert*-butyl-4-methylphenol)

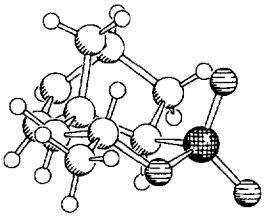
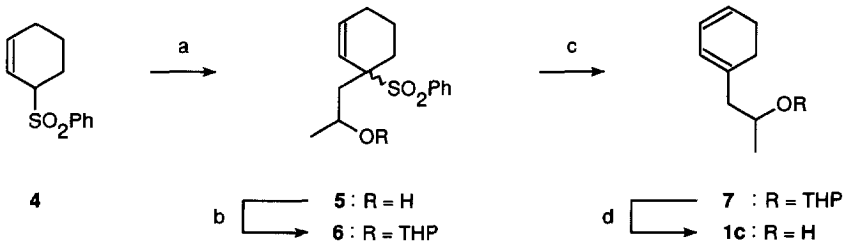


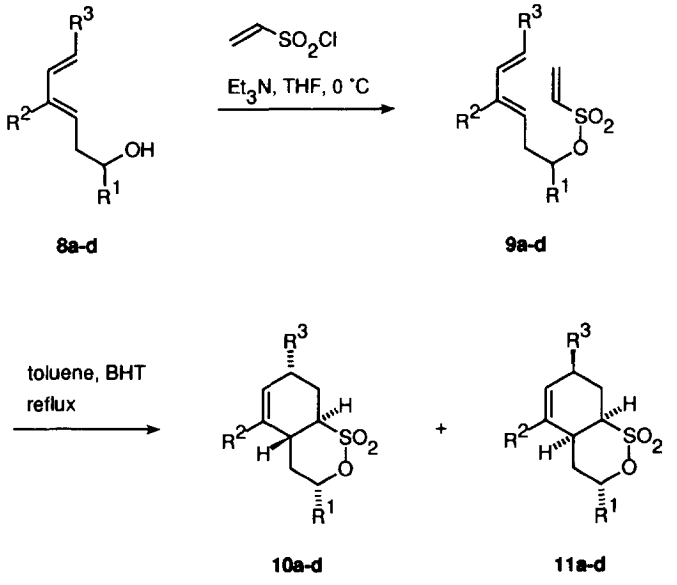
Figure 1. Crystal structure of sultone **3a**[8,9]



Scheme 3. Preparation of alcohol **1c**. a: (i) *n*-BuLi, THF, -30 °C, (ii) 1,2-epoxypropane, -30 °C to 20 °C, 81 %; b: 3,4-dihydro-2*H*-pyrane, pyridinium *p*-toluenesulfonate (PPTS), CH_2Cl_2, 20 °C, 98 %; c: *t*-BuOK, *t*-BuOH, reflux, 70 %; d: PPTS, EtOH, 60 °C, 83 %
(THP = tetrahydropyranyl)

Intramolecular Diels-Alder Reactions - Acyclic Dienes

Vinylsulfonates **9a-d** possessing an acyclic diene moiety were easily derived from the corresponding alcohols **8a-d** by esterification with vinylsulfonyl chloride. Attempts to trigger cyclization of **9a** at low temperature using different Lewis acids failed. Thus, no acceleration occurred in the presence of boron trifluoride, while aluminum trichloride or ethylaluminum dichloride caused decomposition of the substrate due to elimination of vinylsulfonic acid. But again, heating **9a-d** at reflux in toluene was effective, provided that a small amount of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was present (Scheme 4, Table 1). The high dienophilicity of the vinylsulfonate moiety is underlined by the finding that the intramolecular Diels-Alder cycloaddition of the acrylate of **8a** requires a reaction temperature of 210 °C.[13]



Scheme 4. Intramolecular Diels-Alder reaction of vinylsulfonates **9** derived from alcohols **8** (BHT = 2,6-di-*tert*-butyl-4-methylphenol)

Table 1. Preparation and Intramolecular Diels-Alder Reaction of Vinylsulfonates **9**.

8-11	R^1	R^2	R^3	Yield **9** [%][a]	**10** : **11**[b]	Yield **10+11** [%][c]
a	H	H	H	87	1 : 1	76
b	Me	H	Me	82	1.4 : 1	64
c	*t*-Bu	Me	H	78	4.7 : 1	61
d	Me	$SiMe_3$	H	86	> 99 : 1	39

[a] Yields of crude products. [b] Diastereomeric ratios determined by capillary GC analysis of the crude products. [c] Yields of pure products after flash chromatography.

Substrates **9a-d** were chosen to investigate both the simple as well as the substrate-induced diastereoselectivity of the [4+2] addition (Table 1). In contrast to the situation with cyclic 1,3-diene units,

there is no or only marginal discrimination between *trans* and *cis* fused sultones from **9a** and **9b**. On the other hand, a stereogenic center within the tether (**9b-d**) induces a highly selective formation of isomers **10** and **11** out of four possible product diastereomers. Only for **9c**, capillary GC/MS analysis of the crude cycloadducts suggested the presence of a minor third isomer **i** (**10c** : **11c** : **i** = 4.7 : 1 : 0.2). Configurational assignment for **10b-d** and **11b,c** rests on diagnostic ^{1}H, ^{1}H coupling constants and NOE difference spectra.

Sultones **10** and **11** presumably arise *via* chair-like transition states **A** and **B**, respectively, featuring an equatorial orientation of R^1 (Figure 2). A substituent R^2 larger than hydrogen additionally causes a notable preference for the formation of **10** relative to **11** for R^2 = Me (**9c**) already, while virtually complete diastereoselectivity in favor of sultone **10** is achieved for the bulky R^2 = $SiMe_3$ (**9d**) which may be viewed as a temporary control element.[14] The sterically unfavorable interaction between R^2 and the axial hydrogen at the carbinol center in **B** is likely to be responsible for this enhanced *trans* selectivity.[14,15]

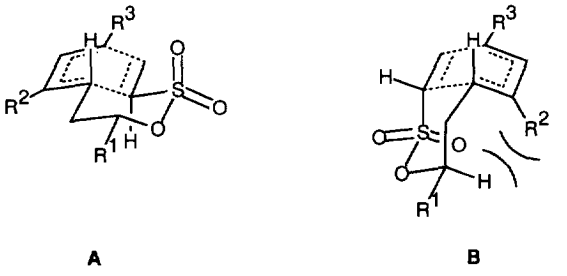
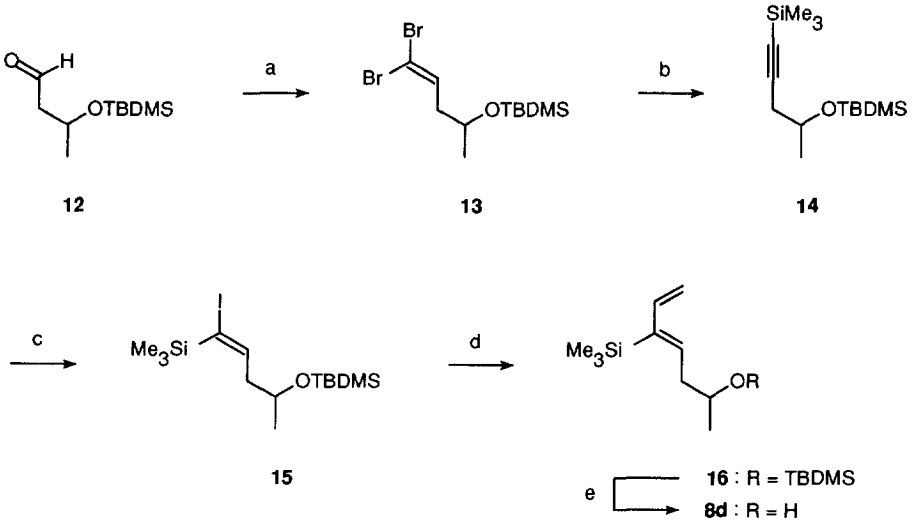


Figure 2. Transition states leading to sultones **10** (**A**) and **11** (**B**)

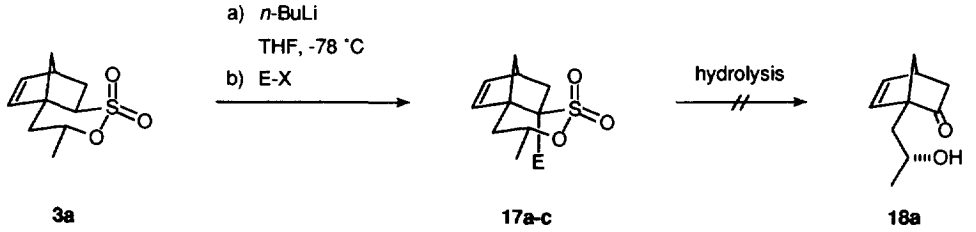


Scheme 5. Preparation of alcohol **8d**. a: Ph_3P, CBr_4, CH_2Cl_2, 0 °C, 82 - 91 %; b: (i) *n*-BuLi, THF, -78 °C to 20 °C, (ii) Me_3SiCl, -78 °C, 96 %; c: (i) *i*-$BuCp_2ZrCl$, ether, toluene, 60 °C, (ii) I_2, THF, -30 °C to 20 °C; d: CH_2=CHSn(*n*-Bu)$_3$, DMF, 2 mol % $PdCl_2(PhCN)_2$, 20 °C; e: *n*-Bu_4NF, THF, 20 °C, 9.4 % from **14**
(TBDMS = *tert*-butyldimethylsilyl)

Alcohols **8a**,[16] **8b**,[17] and **8c**[18] were prepared according to published procedures. The synthesis of dienol **8d** from aldehyde **12**[19] is illustrated in Scheme 5. Conversion of **12** to silylalkyne **14** *via* the Corey-Fuchs procedure[20] was followed by a non-optimized sequence consisting of hydrozirconation/iodination[21] of **14** to iodoalkene **15** and subsequent palladium-catalyzed cross-coupling[22] of **15** with tri(*n*-butyl)vinylstannane to diene **16** as the key steps.

Oxidative Desulfurization of Sultones

Sultone **3a** was chosen as a model substrate to elaborate suitable conditions for oxidative sultone cleavage.[23] In a first series of experiments, lithiation of **3a** with *n*-BuLi[24] was followed by treatment with a range of standard electrophilic hydroxylation agents to effect a direct conversion to sultone **17** with E = OH which in turn should decompose like a bisulfite adduct to hydroxy ketone **18a** (cf. Scheme 6). In contrast to corresponding oxidative desulfurizations of sulfones,[25] this method was not efficient for **3a**.[26] Next, we investigated the two-step process depicted in Scheme 6.



3a **17a-c** **18a**

Scheme 6. Attempted desulfurization of sultone **3a** to hydroxy ketone **18a** *via* hydrolysis of sultones **17**

Table 2. Preparation of Sultones **17** from Sultone **3a**.

E-X	E	**17**	Yield **17** [%]
Cl_3C-CCl_3	Cl	**a**	79[a]
$BrCl_2C$-CCl_2Br	Br	**b**	70[b] (**17b** : **17a** = 1.8 : 1)[b]
	Cl	**a**	
MeS-SMe	SMe	**c**	81[a]

[a] Yield of pure product after flash chromatography. [b] Determined by capillary GC analysis.

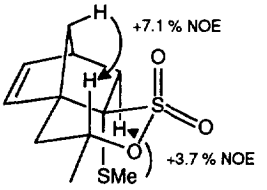
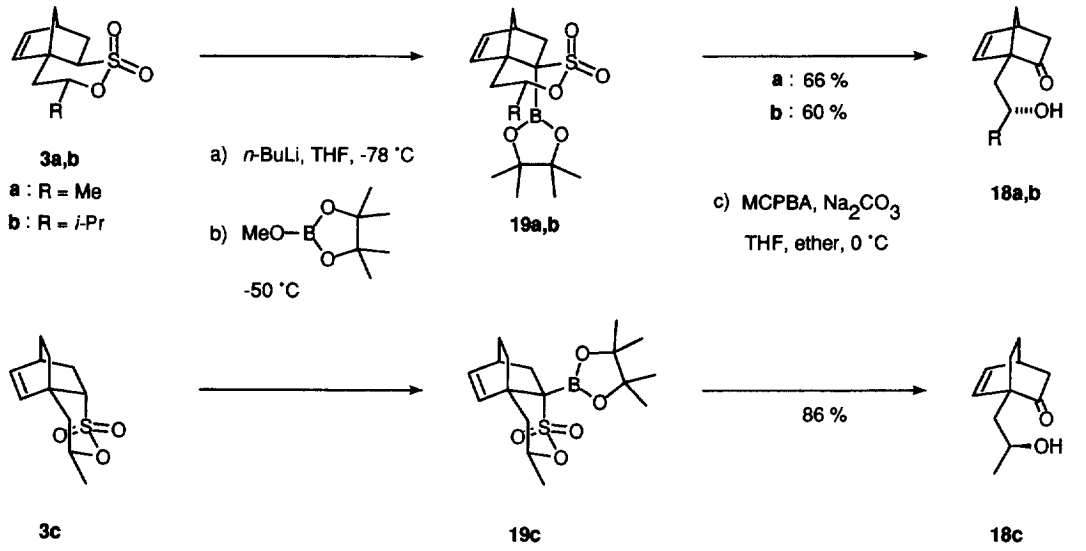


Figure 3. Selected NOE difference data for sultone **17c**

Sultones **17a-c** were readily available as single diastereomers from **3a** in high yield (Table 2).[28] NOE difference spectra of **17c** allowed for elucidation of both the relative configuration at the electrophilically substituted carbon atom and the conformation of the δ-sultone (Figure 3). However, attempted hydrolyses[28] of halogenated compounds **17a,b** or methylthio sultone **17c** to **18a** proceeded unsatisfactorily.[29]

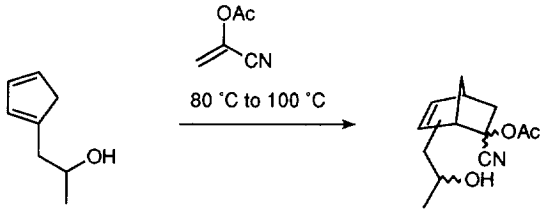
Eventually, an efficient oxidative desulfurization of **3a-c** to hydroxy ketones **18a-c** was accomplished by borylation of the α-lithiated sultones with 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[30] and subsequent chemoselective oxidation of the resulting boronates **19a-c** using *m*-chloroperbenzoic acid in the presence of sodium carbonate[31] (Scheme 7). Gratifyingly, GC/MS and ^{1}H NMR analysis of the crude product established, that the alkene moiety of **19** is completely unaffected by the peracid under these conditions. Only the boron atom is attacked to give an intermediate α-oxygenated sultone which, as anticipated, breaks down to the desired hydroxy ketone **18**. Though isolation of the intermediates **19** is easily achieved, and conversion to **18** can be performed in a separate operation, best results were obtained when borylation was immediately followed by cannulating the resultant solution of **19** to a suspension of the oxidizing agent at low temperature.

Since hydroxy ketones **18a-c** are formal [4+2] adducts of ketene to the hydroxyalkyl substituted dienes **1a-c** from which sultones **3a-c** were prepared, vinylsulfonyl chloride can be used as a ketene equivalent for the intramolecular Diels-Alder reaction both in a completely regioselective as well as highly diastereoselective fashion.



Scheme 7. Oxidative desulfurization of sultones **3**

The degree of regio- and stereocontrol gained by this intramolecular variant of a formal ketene [4+2] cycloaddition is highlighted by the result of the intermolecular Diels-Alder reaction of cyclopentadiene **1a** with the standard ketene equivalent 2-acetoxyacrylonitrile[32] (Scheme 8). Analysis of the crude product obtained after 2h at 80-100°C by capillary GC/MS revealed an unselective formation of at least eleven isomers of gross structure **20**, and subsequent basic hydrolysis yielded a mixture of **18a** with virtually all its regio- and stereoisomers.[33]



1a **20**

Scheme 8. Diels-Alder reaction of cyclopentadiene **1a** with 2-acetoxyacrylonitrile

EXPERIMENTAL

General Remarks

All reactions requiring exclusion of moisture were run under argon using flame-dried glassware. Solvents were dried by distillation from benzophenone ketyl (THF, ether) or else from CaH_2. Flash chromatography was performed on Merck silica gel 60 (40 - 63 μm). Capillary GC analyses were performed with a Shimadzu GC-14APFsc, a Shimadzu C-R6A integrator, a SE 54 CB column, 25 m length, 0.25 mm i. d., 0.25 μm film, and a HP1 CB column, 25 m length, 0.32 mm i. d., 0.25 μm film. Analytical HPLC separations were performed with a Knauer 64 pump, a Knauer 51.78 differential refractometer, a Knauer 42.00 recorder, a Rheodyne 7125 injector, and a Nucleosil 100 (3 μm) column, 250 mm length, 8 mm i. d.. Preparative HPLC separations were performed with a Waters Delta Prep 3000, a Waters R 404 differential refractometer, a Waters 740 data module, and a Porasil 125 (15-20 μm) column, 300 mm length, 50 mm i. d.. Melting points were determined on a Kofler microscope desk. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. ^1H NMR spectra (300 MHz, $CDCl_3$), NOE difference spectra (300 MHz, $CDCl_3$), and ^{13}C NMR spectra (75.47 MHz, $CDCl_3$) were obtained on a Bruker WM 300 - m_c = multiplet centered at, br. = broad. ^{13}C multiplicities were determined using INEPT or DEPT pulse sequences. IR spectra ($CHCl_3$) were obtained on a Shimadzu IR-408 and a Nicolet 5DXC FT-IR - s = strong, m = medium, w = weak, br. = broad. Mass spectra (70 eV) were recorded with a Varian Saturn 2 and a Finnigan MAT 8230 + data system Finnigan SS 300. Microanalyses were performed by the analytical laboratory of the Organisch-Chemisches Institut, Universität Münster, and by Mikroanalytisches Laboratorium M. Beller, Göttingen.

Esterification of Alcohol **1a** *with Vinylsulfonyl Chloride and Cyclization to Sultone* **3a**

Vinylsulfonyl chloride[6] (2.19 ml, 24.2 mmol) is added to a solution of **1a**[10] (3.00 g, 24.2 mmol) and triethylamine (6.75 ml, 48.4 mmol) in THF (100 ml) cooled to 0 °C. After stirring the mixture for additional 2 h at 0 °C, it is poured into ice-cold water (50 ml). The aqueous layer is saturated with NaCl and extracted with ether (3 x 100 ml). The combined organic layers are washed with 2 N HCl (25 ml), sat. aqueous $NaHCO_3$ (25 ml), and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the crude product is recrystallized from hexane, the colorless crystals are collected by filtration and washed with cold hexane (2.29 g **3a**). The filtrate is concentrated *in vacuo* to yield a brown oil which is purified by flash chromatography using petroleum ether/ethyl acetate 6 : 1 to give further **3a** (1.00 g). The total yield of pure **3a** is 3.29 g (64 %).

(1R,2R*,4S*,2'R*)-1-Propyl-5-norbornene-2,2'-sultone* (**3a**). mp 79 °C (hexane); R_f = 0.27 (petroleum ether/ethyl acetate 6 : 1); ^1H NMR δ 1.28 (ddd, 1 H, *J* = 1.7, 2.4, 8.6 Hz, 7-H_a), 1.47 (d, 3 H, *J* = 6.4 Hz, 3'-H), 1.66 (ddd, 1 H, *J* = 2.4, 8.5, 12.5 Hz, 3-H_a), 2.07 (dd, 1 H, *J* = 2.8, 14.9 Hz, 1'-H_a), 2.16 (dd, 1 H, *J* = 11.3 Hz, 14.9 Hz, 1'-H_b), 2.24 (d, 1 H, *J* = 8.6 Hz, 7-H_b), 2.28 (ddd, 1 H, *J* = 4.0, 4.2, 12.5 Hz, 3-H_b), 2.83 (ddd, 1 H, *J* = 1.6, 4.2, 8.5 Hz, 2-H), 3.04 (s, br., 1 H, 4-H), 4.83 (ddq, 1 H, J_d = 2.8, 11.3 Hz, J_q = 6.4 Hz, 2'-H), 5.80

(d, 1 H, J = 5.6 Hz, 6-H), 6.33 (dd, 1 H, J = 3.1, 5.6 Hz, 5-H); ^{13}C NMR δ 20.9 (q, C-3'), 28.4 (t, C-3), 35.3 (t, C-1'), 41.9 (d, C-4), 47.1 (t, C-7), 55.9 (s, C-1), 57.8 (d, C-2), 78.8 (d, C-2'), 138.2 (d), 140.2 (d); IR (KBr) 3130 (m, br.), 3060 (m), 2990 (m), 2930 (m), 2910 (w), 2860 (w), 1440 (m), 1390 (m), 1350 (s, SO_2OR), 1325 (s), 1310 (s), 1250 (m), 1160 (s, SO_2OR), 1140 (m), 1120 (m), 1065 (m), 1055 (m), 1000 (w), 920 (s), 875 (s), 860 (s) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 214 (M^+, 2), 135 ($CH_3CHOSO_2CHCH_2^+$, 2), 107 (11), 106 (M^+ - CH_2CHSO_3H, 100), 105 (8), 92 (5), 91 (M^+ - CH_2CHSO_3H - CH_3, $CH_2CHSO_2^+$, 51), 79 ($C_6H_7^+$, 22), 78 (10), 77 (9), 66 (6), 65 (3), 53 (2), 45 (2), 43 (5), 41 (2), 39 (3). Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59. Found: C, 56.11; H, 6.69.

Esterification of Alcohol **1b** *with Vinylsulfonyl Chloride and Cyclization to Sultone* **3b**

Cyclopentadienyl alcohol **1b** (2.314 g, 15.17 mmol) is dissolved in THF (60 ml) and converted to the corresponding vinylsulfonate according to the procedure described for **1a** (triethylamine: 4.21 ml, 30.4 mmol; vinylsulfonyl chloride: 1.38 ml, 15.2 mmol; 3 h 0 °C). Again, cyclization is complete after work-up. Hexane (150 ml) is added to the crude product, and the mixture is heated to reflux and filtered. The filtrate is concentrated *in vacuo*, and the residue is purified by flash chromatography using petroleum ether/ether 4 : 1. From a first product fraction, the pure major diastereomer **3b** was obtained as a colorless crystalline solid. A second fraction contained some alcohol **1b** which could not be separated even by HPLC. After acetylation of the alcohol using Ac_2O, pyridine, and 4-(dimethylamino)pyridine in dichloromethane,[34] flash chromatography afforded additional **3b** (total yield: 1.632 g, 44 %).

(-)-(1R,2R,4S,2'S)-1-(3-Methylbutyl)-5-norbornene-2,2'-sultone (**3b**). mp 85 °C; R_f = 0.27 (petroleum ether/ether 4 : 1); $[\alpha]_D^{20}$ = -24.0 (c = 1.0 in $CHCl_3$); ^{1}H NMR δ 1.02 (d, 3 H, J = 6.8 Hz, 3'-CH_3), 1.06 (d, 3 H, J = 6.7 Hz, 3'-CH_3), 1.26 (dd, 1 H, J = 2.5, 8.6 Hz, 7-H_a), 1.66 (ddd, 1 H, J = 2.5, 8.5, 12.6 Hz, 3-H_a), 1.95 (m_c, 1 H, 3'-H), 2.05 (dd, 1 H, J = 2.4, 14.7 Hz, 1'-H_a), 2.17 (dd, 1 H, J = 11.8, 14.7 Hz, 1'-H_b), 2.24 (d, 1 H, J = 8.6 Hz, 7-H_b), 2.29 (ddd, 1 H, J = 3.9, 4.2, 12.6 Hz, 3-H_b), 2.85 (ddd, 1 H, J = 1.5, 4.2, 8.5 Hz, 2-H), 3.04 (m_c, 1 H, 4-H), 4.43 (ddd, 1 H, J = 2.4, 6.1, 11.8 Hz, 2'-H), 5.81 (d, 1 H, J = 5.6 Hz, 6-H), 6.33 (dd, 1 H, J = 3.1, 5.6 Hz, 5-H); ^{13}C NMR δ 17.4 (q), 17.9 (q), 28.3 (t, C-3), 30.5 (t, C-1'), 32.1 (d, C-3'), 41.8 (d, C-4), 47.0 (t, C-7), 55.7 (s, C-1), 58.2 (d, C-2), 86.7 (d, C-2'), 138.3 (d), 140.1 (d); IR (KBr) 3046 (w), 2983 (s), 2961 (s), 2878 (m), 1469 (m), 1445 (m), 1429 (w), 1347 (s, SO_2OR), 1332 (s), 1302 (m), 1256 (m), 1169 (s, SO_2OR), 1147 (s), 1133 (m), 1056 (m), 1031 (m), 967 (m), 952 (s), 892 (s), 852 (m), 837 (s), 796 (m), 753 (m), 711 (s), 693 (m), 644 (w), 603 (s), 582 (m), 560 (m), 485 (m) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 163 (M^+ - C_6H_7, 2), 135 (14), 134 (M^+ - CH_2CHSO_3H, 100) 120 (4), 119 (M^+ - CH_2CHSO_3H - CH_3, 32), 117 (2), 107 (2), 106 (5), 105 (9), 92 (12), 91 (M^+ - CH_2CHSO_3H - C_3H_7, 22), 79 ($C_6H_7^+$, 32), 78 (38), 77 (11), 69 (6), 66 (8), 65 (5), 56 (4), 55 (20), 44 (11), 42 (11), 40 (6); Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.48; H, 7.49. Found: C, 59.58; H, 7.49.

Alkylation of Sulfone (**4**) *to Alcohol* **5**

A 2.0 M solution of *n*-BuLi in hexane (5.27 ml, 10.6 mmol) is added dropwise to a solution of sulfone **4** (2.132 g, 9.59 mmol) in THF (50 ml) at -30 °C. The resultant deep red solution is stirred for further 20 min at -30 °C, and then 1,2-epoxypropane (0.87 ml, 12.5 mmol) is added at the same temperature. After additional 30 min at -30 °C, the mixture is allowed to warm up to room temperature. Water (25 ml) is added, and the mixture is extracted with ether (4 x 25 ml). The combined organic layers are washed with brine (20 ml), dried over $MgSO_4$, and the residue obtained after evaporation of the solvent *in vacuo* is purified by flash chromatography using petroleum ether/ethyl acetate 1 : 1 to give **5** (2.182 g, 81 %) as a 1 : 1 mixture of two diastereomers.

1-[3-(Phenylsulfonyl)cyclohexen-3-yl]-2-propanol (**5**), *Diastereomeric Mixture*. R_f = 0.36 (petroleum ether/ethyl acetate 1 : 1); ^{1}H NMR δ 1.22 (d, 3 H, J = 6.2 Hz, 3-H), 1.23 (d, 3 H, J = 6.3 Hz, 3-H), 1.39 - 1.61 (m, 4 H), 1.61 - 1.86 (m, 4 H), 1.86 - 2.03 (m, 4 H), 2.08 (dd, 1 H, J = 2.6, 15.1 Hz), 2.18 (dd, 1 H, J = 9.5,

15.1 Hz), 2.29 (s, br., 1 H, OH), 2.95 (s, br., 1 H, OH), 4.16 (m_c, 1 H, 2-H), 5.78 (dd, 1 H, J = 2.0, 10.2 Hz, 2'-H), 5.91 (d, 1 H, J = 10.3 Hz, 2'-H), 6.13 (m_c, 4 H, 1'-H), 7.54 (m_c, 4 H), 7.64 (m_c, 2 H), 7.87 (m_c, 4 H); IR 3503 (s, br., O-H), 3087 (m), 3066 (m), 3027 (m), 2969 (s), 2919 (s), 2877 (m), 2834 (m), 1653 (w, C=C), 1646 (w, C=C), 1448 (s), 1401 (m), 1376 (m), 1324 (m), 1277 (s, br.), 1183 (m), 1140 (s, SO_2R), 1124 (s, br., SO_2R), 1081 (s, br., C-O), 1041 (m), 1000 (w), 938 (w), 894 (w), 847 (w), 785 (w), 763 (m), 740 (s), 719 (s), 645 (s), 640 (s), 598 (s), 557 (s) cm^{-1}; MS *m/e* (relative intensity): 281 (M^++1, 0.8), 236 (M^+ - C_2H_4O, 1.8), 223 (2), 187 (8), 149 (10), 139 (M^+ - $C_6H_5SO_2$, 18), 95 (100), 94 (46), 93 (33), 91 (33), 81 ($C_6H_9^+$, 16), 80 (24), 79 (64), 78 (33), 77 (46), 67 (40), 57 (18), 55 (28). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.38; H, 7.30.

Conversion of Alcohol **5** *to THP-Ether* **6** *and Elimination of Benzenesulfinic Acid to Diene* **7**

Alcohol **5** (868 mg, 3.10 mmol) is dissolved in dichloromethane (20 ml) and a solution of pyridinium-*p*-toluenesulfonate (85.5 mg, 0.328 mmol) in dichloromethane (5 ml) is added followed by 3,4-dihydro-2*H*-pyrane (0.445 ml, 4.93 mmol). The resultant mixture is stirred for 22 h at room temperature, diluted with ether (60 ml), and washed with brine (20 ml). After drying over $MgSO_4$ and evaporation of the solvent *in vacuo*, purification of the crude product by flash chromatography using petroleum ether/ether 1 : 1 affords 1-[3-(phenylsulfonyl)cyclohexen-3-yl]-propan-2-yl tetrahydropyran-2-yl ether (**6**; 1.105 g, 98 %) as a mixture of 4 diastereomers (detected by ^1H NMR).

A solution of THP-ether **6** (3.71 g, 10.2 mmol) in *tert*-butanol (14 ml; dried and distilled over CaO) is added to a solution of potassium *tert*-butoxide (2.54 g, 22.6 mmol) in *tert*-butanol (30 ml). The resultant mixture is heated to reflux for 9.5 h, additional potassium *tert*-butoxide (1.55 g, 13.8 mmol) dissolved in *tert*-butanol (10 ml) is added, and reflux is continued for further 3.5 h. Water (30 ml) is added, and the mixture is extracted with ether (4 x 30 ml). The combined organic layers are washed with water (2 x 15 ml), brine (15 ml), and dried over $MgSO_4$. After evaporation of the solvent *in vacuo*, flash chromatography using petroleum ether/ethyl acetate 4 : 1 as eluent affords diene **7** (1.59 g, 70 %) as a colorless oil.

1-(1,3-Cyclohexadienyl)propan-2-yl Tetrahydropyran-2-yl Ether (**7**)*, 1 : 1 Mixture of 2 Diastereomers.* R_f = 0.45 (petroleum ether/ether 6 : 1); ^1H NMR δ 1.11 (d, 3 H, J = 6.1 Hz), 1.23 (d, 3 H, J = 6.3 Hz), 1.48 - 1.60 (m, 8 H), 1.66 - 1.74 and 1.78 - 1.83 (m, 4 H), 2.07 - 2.21 (m, 10 H), 2.35 (dd, 1 H, J = 6.4, 13.7 Hz), 2.45 (dd, 1 H, J = 6.3, 13.5 Hz), 3.46 - 3.51 (m, 2 H), 3.86 - 3.99 (m, 4 H), 4.68 (dd, 1 H, J = 2.9, 2.9 Hz), 4.74 (dd, 1 H, J = 3.4, 3.4 Hz), 5.67 - 5.73 (m, 4 H), 5.85 - 5.89 (m, 2 H); IR 3038 (m), 2938 (s), 2871 (s), 2850 (m), 2825 (m), 1648 (w, C=C), 1590 (w, C=C), 1453 (m), 1440 (m), 1372 (m), 1352 (m), 1339 (m), 1322 (w), 1200 (s), 1122 (s), 1077 (s), 1032 (s), 1021 (s), 996 (s), 942 (w), 904 (w), 871 (m), 813 (m), 747 (w), 692 (m) cm^{-1}; MS (GC/MS, nearly identical spectra for both diastereomers) *m/e* (relative intensity): 222 (M^+, 1.3), 179 (2), 178 (12), 138 (M^+ - C_5H_8O, 8), 131 (6), 129 (M^+ - C_7H_9, 2), 121 (M^+ - $C_5H_9O_2$, 17), 120 (M^+ - $C_5H_{10}O_2$, 23), 105 (11), 101 ($C_5H_9O_2^+$, 11), 93 ($C_7H_9^+$, 21), 92 (18), 91 ($C_7H_7^+$, 55), 86 (15), 85 ($C_5H_9O^+$, 100), 84 (12), 79 ($C_6H_7^+$, 61), 78 (30), 77 (25), 67 (42), 57 (38), 55 (30), 45 (22), 43 (61), 41 (47), 39 (18). HRMS Calcd for $C_{14}H_{22}O_2$ (M^+): 222.1620. Found: 222.1616.

Deblocking of THP-Ether **7** *to 1-(1,3-Cyclohexadienyl)-2-propanol* (**1c**)

THP-ether **7** (5.12 g, 23.0 mmol) is dissolved in ethanol (185 ml), and a catalytic amount of pyridinium-*p*-toluenesulfonate (578 mg, 2.30 mmol) is added. After stirring the resultant solution at 55 °C to 60 °C for 7.5 h, the solvent is removed *in vacuo*. Flash chromatography using petroleum ether/ethyl acetate 3 : 1 gives **1c** (2.65 g, 83 %) as a colorless oil.

1-(1,3-Cyclohexadienyl)-2-propanol (**1c**). R_f = 0.36 (petroleum ether/ethyl acetate 3 : 1); ^1H NMR δ 1.23 (d, 3 H, J = 6.3 Hz, 3-H), 1.70 (s, 1 H, OH, removed by D_2O-exchange), 2.05 - 2.22 (m, 6 H, 1-H, 5'-H, 6'-H), 3.93 (m_c, 1 H, J = 6.3 Hz, 2-H), 5.74 (m_c, 2 H, 2'-H, 4'-H), 5.90 (m_c, 1 H, 3'-H); ^{13}C NMR δ 22.8 (q, C-3), 22.9 (t, C-5'), 26.4 (t, C-6'), 47.5 (t, C-1), 65.4 (d, C-2), 121.8 (d, C-4'), 124.3 (d), 124.5 (d), 136.0 (s,

C-1'); IR 3367 (s, br., O-H), 3038 (s), 2967 (s), 2928 (s), 2872 (s), 2825 (s), 1648 (w, C=C), 1590 (m, C=C), 1456 (m), 1435 (m), 1425 (s), 1396 (m), 1372 (s, O-H), 1240 (m), 1117 (s, C-O), 1078 (s), 1011 (m), 937 (s), 825 (m), 749 (m), 691 (s) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 139 (M^++1, 4), 138 (M^+, 37), 120 (M^+ - H_2O, 8), 105 (M^+ - H_2O - CH_3, 10), 95 (7), 94 (58), 93 (30), 92 (15), 91 ($C_7H_7^+$, 77), 80 (13), 79 ($C_6H_7^+$, 100), 78 (40), 77 (48), 66 (7), 65 ($C_5H_5^+$, 15), 51 (11), 45 (CH_3CHOH^+, 96), 43 (20), 41 (15), 39 (25). HRMS Calcd for $C_9H_{14}O$ (M^+): 138.1045. Found: 138.1042.

Esterification of Alcohol **1c** *with Vinylsulfonyl Chloride*

Dienol **1c** (2.29 g, 16.6 mmol) is dissolved in THF (125 ml) and converted to vinylsulfonate **2c** according to the procedure described for **1a** (triethylamine: 4.60 ml, 33.2 mmol; vinylsulfonyl chloride: 2.10 ml, 23.2 mmol; 6.5 h 0 °C). Because the crude product **2c** (2.88 g, 76 %) tends to polymerize quickly, it is immediately used for cyclization.

1-(1,3-Cyclohexadienyl)-propan-2-yl Vinylsulfonate (**2c**). R_f = 0.43 (petroleum ether/ethyl acetate 3 : 1); ^1H NMR δ 1.34 (d, 3 H, *J* = 6.4 Hz, 3'-H), 2.03 - 2.10 (m, 4 H, 5"-H, 6"-H), 2.31 (dd, 1 H, *J* = 6.3, 13.9 Hz, 1'-H_a), 2.41 (dd, 1 H, *J* = 7.2, 13.9 Hz, 1'-H_b), 4.67 (m_c, 1 H, 2'-H), 5.65 - 5.70 (m, 2 H, 2"-H, 4"-H), 5.78 - 5.85 (m, 1 H, 3"-H), 5.98 (d, 1 H, *J* = 9.7 Hz, 2-H_a), 6.31 (d, 1 H, *J* = 16.6 Hz, 2-H_b), 6.46 (dd, 1 H, *J* = 9.7, 16.6 Hz, 1-H).

Intramolecular Diels-Alder Reaction of Vinylsulfonate **2c**

Vinylsulfonate **2c** (2.88 g, 12.6 mmol) is dissolved in toluene (300 ml), and a catalytic amount (20 mg) of 2,5-di-*tert*-butyl-4-methylphenol (BHT) is added. After degassing the resultant mixture in an ultrasonic bath for 15 min while purging with helium, it is heated to reflux for 4 h 50 min. The solvent is evaporated *in vacuo*, and flash chromatography using petroleum ether/ethyl acetate 3 : 1 affords the main diastereomer **3c** (1.67 g, 58 %) as a colorless crystalline solid.

(1R,2S*,4S*,2'S*)-1-Propylbicyclo[2.2.2]oct-5-ene-2,2'-sultone* (**3c**). mp 138 °C - 139 °C; R_f = 0.39 (petroleum ether/ethyl acetate 3 : 1); ^1H NMR δ 1.24 - 1.46 (m, 3 H, 7-H, 8-H), 1.46 (d, 3 H, *J* = 6.3 Hz, 3'-H), 1.55 - 1.62 (m, 1 H), 1.65 (dd, 1 H, *J* = 11.7, 14.5 Hz, 1'-H_a), 1.76 (dddd, 1 H, *J* = 2.7, 2.7, 5.9, 13.4 Hz, 3-H_a), 1.93 (dd, 1 H, *J* = 1.8, 14.5 Hz, 1'-H_b), 2.08 (ddd, 1 H, *J* = 2.8, 9.8, 13.4 Hz, 3-H_b), 2.75 (m_c, 1 H, 4-H), 3.13 (dd, 1 H, *J* = 5.9, 9.8 Hz, 2-H), 4.93 (ddq, 1 H, J_d = 1.8, 11.7 Hz, J_q = 6.3 Hz, 2'-H), 6.06 (d, 1 H, *J* = 8.2 Hz, 6-H), 6.44 (dd, 1 H, *J* = 6.9, 8.2 Hz, 5-H); ^{13}C NMR δ 20.9 (q, C-3'), 23.9 (t), 27.8 (t), 29.2 (d, C-4), 33.8 (t), 38.2 (s, C-1), 41.3 (t, C-1'), 58.9 (d, C-2), 78.6 (d, C-2'), 131.8 (d), 134.4 (d); IR (KBr) 3052 (m), 2983 (m), 2947 (s), 2935 (s), 2914 (m), 2870 (m), 1650 (w, C=C), 1450 (m), 1440 (w), 1382 (m), 1354 (s, SO_2OR), 1338 (s), 1326 (s), 1296 (m), 1197 (m), 1172 (s, SO_2OR), 1139 (m), 1099 (m), 1051 (m), 943 (m), 915 (m), 899 (s), 891 (s), 871 (s), 801 (s), 736 (m), 711 (m), 593 (s), 573 (m), 549 (m), 466 (m) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 229 (M^++1, 2), 228 (M^+, 15), 200 (M^+ - C_2H_4, 12), 146 (M^+ - H_2SO_3, 5), 135 ($CH_3CHOSO_2CHCH_2^+$, 2), 131 (3), 121 (7), 120 (M^+ - CH_2CHSO_3H, 22), 119 (19), 118 (M^+ - C_2H_4 - H_2SO_3, 42), 117 (5), 105 (M^+ - CH_2CHSO_3H - CH_3, 11), 103 (4), 93 (12), 92 (88), 91 ($CH_2CHSO_2^+$, 100), 79 (13), 78 (15), 77 (11), 65 (8), 45 (14), 43 (11), 41 (12), 39 (9); Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06. Found: C, 57.75; H, 7.12.

Esterification of (4E,6E)-4,6-Octadien-2-ol (**8b**) *with Vinylsulfonyl Chloride*

Dienol **8b**[17] (687 mg, 5.44 mmol) is dissolved in THF (31 ml) and converted to vinylsulfonate **9b** according to the procedure described for **1a** (triethylamine: 1.52 ml, 11.0 mmol; vinylsulfonyl chloride: 0.49 ml, 5.44 mmol; 4.5 h 0 °C). In this case, the crude product (968 mg, 82 %) was purified by flash chromatography using petroleum ether/ethyl acetate 4 : 1. Pure **9b** (687 mg, 58 %) was obtained, but obviously some decomposition occurred during chromatography. For this reason, all other vinylsulfonates were cyclized without further purification.

(4E,6E)-4,6-Octadien-2-yl Vinylsulfonate (**9b**). R_f = 0.47 (petroleum ether/ethyl acetate 4 : 1); ^{1}H NMR δ 1.39 (d, 3 H, *J* = 6.3 Hz, 1'-CH_3), 1.75 (d, 3 H, *J* = 6.9 Hz, 7'-H), 2.42 (m_c, 2 H, 2'-H), 4.64 (m_c, 1 H, 1'-H), 5.38 - 5.48 (m, 1 H), 5.62 - 5.69 (m, 1 H), 5.97 - 6.12 (m, 3 H, 4'-H, 5'-H, 2-H_a), 6.38 (dd, 1 H, *J* = 3.6, 16.7 Hz, 2-H_b), 6.53 (dd, 1 H, *J* = 9.6, 16.7 Hz, 1-H).

Intramolecular Diels-Alder Reaction of Vinylsulfonate **9b** *to Sultones* **10b** *and* **11b**

Vinylsulfonate **9b** (158.1 mg, 0.731 mmol) is heated for 4 h to reflux in toluene (17 ml) as described for **2c** (9 mg BHT). The crude product (**10b** : **11b** = 1.4 : 1 by GC analysis and ^{1}H NMR integration) is recrystallized from hexane and, additionally, the mother liquor is purified by flash chromatography after concentration using petroleum ether/ether 2 : 1 to give a mixture of diastereomers **10b** and **11b** (total yield: 101.5 mg, 64 %) as a white crystalline solid. Analytical samples of the two diastereomers were secured by HPLC using petroleum ether/ether 2 : 1.

(1R,2R*,5R*,2'R*)-5-Methyl-2-propyl-cyclohex-3-ene-1,2'-sultone* (**10b**) *and (1R*,2S*,5S*,2'R*)-5-Methyl-2-propyl-cyclohex-3-ene-1,2'-sultone* (**11b**), *Diastereomeric Mixture.* R_f = 0.27 (petroleum ether/ether 2 : 1); ^{13}C NMR δ 19.0 (q), 20.1 (q), 20.3 (q), 20.4 (q), 25.9 (t), 26.6 (t), 28.1 (d), 29.4 (d), 29.5 (d), 30.5 (t), 36.5 (d), 37.8 (t), 55.4 (d), 56.1 (d), 79.8 (d), 80.7 (d), 125.2 (d), 125.7 (d), 132.7 (d), 134.0 (d); IR (KBr) 2950 (s), 2860 (s), 1680 (m, C=C), 1640 (w, C=C), 1440 (s), 1340 (s, br., SO_2OR), 1160 (s, br., SO_2OR), 1070 (s), 1020 (s), 990 (m), 860 (s) cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3S$: C, 55.53; H, 7.46. Found: C, 55.74; H, 7.39.

(1R,2R*,5R*,2'R*)-5-Methyl-2-propyl-cyclohex-3-ene-1,2'-sultone* (**10b**). ^{1}H NMR δ 1.07 (d, 3 H, *J* = 7.2 Hz, 5-CH_3), 1.43 (d, 3 H, *J* = 6.3 Hz, 3'-H), 1.50 (dd, 1 H, *J* = 2.8, 12.0 Hz, 6-H_a), 1.91 (ddd, 1 H, *J* = 2.4, 3.2, 14.2 Hz, 1'-H_a), 1.99 (ddd, 1 H, *J* = 6.4, 10.9, 12.0 Hz, 6-H_b), 2.11 (m_c, 1 H, 1'-H_b), 2.54 (m_c, 1 H, 5-H), 2.77 (m_c, 1 H, 2-H), 2.85 (ddd, 1 H, *J* = 2.8, 10.9, 10.9 Hz, 1-H), 4.81 (ddq, 1 H, J_d = 2.4, 11.6 Hz, J_q = 6.3 Hz, 2'-H), 5.41 (ddd, 1 H, *J* = 1.7, 1.7, 9.9 Hz, 3'-H), 5.68 (dddd, 1 H, *J* = 1.3, 2.9, 4.1, 9.9 Hz, 4-H); MS (GC/MS) *m/e* (relative intensity): 152 (M^+ - SO_2, 1), 151 (5), 135 (5), 134 (M^+ - H_2SO_3, 37), 133 (8), 119 (M^+ - CH_3 - H_2SO_3, 15), 108 (10), 107 (18), 105 (74), 93 (65), 92 (100), 91 (50), 80 (9), 79 (42), 77 (26), 67 (9), 65 (11), 53 (12), 43 (16), 41 (25), 39 (20); MS (GC/MS, CI-NH_3) *m/e* (relative intensity): 234 ($M \cdot NH_4^+$, 100).

(1R,2S*,5S*,2'R*)-5-Methyl-2-propyl-cyclohex-3-ene-1,2'-sultone* (**11b**). ^{1}H NMR δ 1.08 (d, 3 H, *J* = 6.9 Hz, 5-CH_3), 1.44 - 1.52 (m, 1 H), 1.58 (d, 3 H, *J* = 6.8 Hz, 3'-H), 1.63 (ddd, 1 H, *J* = 1.8, 2.5, 14.5 Hz, 1'-H_a), 2.08 (ddd, 1 H, *J* = 6.6, 12.4, 14.5 Hz, 1'-H_b), 2.21 - 2.28 (m, 1 H), 2.31 - 2.38 (m, 1 H), 3.02 - 3.13 (m, 1 H), 3.44 (ddd, 1 H, *J* = 3.2, 5.5, 12.8 Hz, 1-H), 4.87 (ddq, 1 H, J_d = 1.8, 6.7 Hz, J_q = 6.7 Hz, 2'-H), 5.59 (ddd, 1 H, *J* = 2.3, 4.2, 10.0 Hz, 4-H), 5.65 (m_c, 3-H). MS (GC/MS) *m/e* (relative intensity): 174 (3), 152 (M^+ - SO_2, 0.1), 151 (0.3), 135 (3), 134 (M^+ - H_2SO_3, 5), 133 (1), 119 (M^+ - CH_3 - H_2SO_3, 4), 107 (4), 105 (10), 94 (10), 93 (100), 92 (12), 91 (18), 81 (2), 79 (14), 77 (12), 67 (4), 65 (5), 53 (5), 43 (13), 41 (10), 39 (9); MS (GC/MS, CI-NH_3) *m/e* (relative intensity): 234 ($M \cdot NH_4^+$, 100).

Esterification of Alcohol **8a** *with Vinylsulfonyl Chloride*

(*E*)-3,5-Hexadien-1-ol (**8a**)[16] (948 mg, 9.66 mmol) is dissolved in THF (55 ml) and converted to vinylsulfonate **9a** according to the procedure described for **1a** (triethylamine: 2.69 ml, 19.4 mmol; vinylsulfonyl chloride: 0.96 ml, 10.6 mmol; 5 h 0 °C). The crude vinylsulfonate **9a** (1.581 g, 87 %) is obtained as a pale yellow oil.

(E)-3,5-Hexadien-1-yl Vinylsulfonate (**9a**). R_f = 0.50 (petroleum ether/ethyl acetate 4 : 1); ^{1}H NMR δ 2.52 (m_c, 2 H, 2'-H), 4.15 (t, 2 H, *J* = 6.8 Hz, 1'-H), 5.06 (d, 1 H, *J* = 10.2 Hz, 6'-H_a), 5.16 (d, 1 H, *J* = 16.6 Hz, 6'-H_b), 5.62 (dt, 1 H, J_d = 15.0 Hz, J_t = 7.2 Hz, 3'-H), 6.13 (d, 1 H, *J* = 9.3 Hz, 2-H_a), 6.15 (dd, 1 H, *J* =

10.2, 15.0 Hz, 4'-H), 6.30 (ddd, 1 H, J = 10.2, 10.2, 16.6 Hz, 5'-H), 6.40 (d, 1 H, J = 16.6 Hz, 2-H_b), 6.53 (dd, 1 H, J = 9.3, 16.6 Hz, 1-H).

Intramolecular Diels-Alder Reaction of Vinylsulfonate **9a** *to Sultones* **10a** *and* **11a**

Vinylsulfonate **9a** (196.9 mg, 1.046 mmol) is heated for 2.5 d to reflux in toluene (15 ml) as described for **2c** (10 mg BHT). Flash chromatography of the crude product (**10a** : **11a** = 1 : 1 by GC analysis) using petroleum ether/ethyl acetate 3 : 1 yields a mixture of diastereomers **10a** and **11a** (149.0 mg, 76 %) as a white crystalline solid. Some vinylsulfonate **9a** (22.0 mg, 11 %) was also reisolated.

(1R,2R*)-2-Ethyl-3-cyclohexene-1,2'-sultone* (**10a**) *and (1R*,2S*)-2-Ethyl-3-cyclohexene-1,2'-sultone* (**11a**), *Diastereomeric Mixture.* R_f = 0.35 (petroleum ether/ethyl acetate 3 : 1); ^{1}H NMR δ 1.75 - 1.94 (m, 6 H), 2.18 - 2.40 (m, 6 H), 2.90 - 2.99 (m, 4 H, 1-H and 2-H of both diastereomers), 4.41 - 4.65 (m, 4 H, 2'-H of both diastereomers), 5.48 (d, 1 H, J = 9.9 Hz, 3-H of one diastereomer), 5.72 - 5.76 (m, 3 H, 4-H of one diastereomer, 3-H and 4-H of the other diastereomer); ^{13}C NMR δ 18.3 (t), 20.2 (t), 24.3 (t), 24.5 (t), 27.0 (t), 31.2 (t), 34.0 and 37.6 (d, C-2), 56.6 and 60.9 (d, C-1), 72.0 and 72.5 (t, C-2'), 127.1 and 127.61 and 127.64 and 127.7 (d, C-3, C-4); IR (KBr) 3035 (s), 3004 (s), 2947 (s), 2929 (s), 2900 (s), 2870 (s), 2844 (s), 1653 (m, C=C), 1463 (s), 1434 (s), 1374 (s, br., SO_2OR), 1355 (s, br., SO_2OR), 1339 (s), 1266 (s), 1259 (s), 1208 (s), 1163 (s, br., SO_2OR), 1051 (m), 991 (s), 981 (s), 906 (s), 877 (s), 866 (s), 829 (s), 814 (s), 776 (s), 715 (s), 675 (s), 612 (s), 595 (s), 538 (s), 483 (s) cm^{-1}; Anal. Calcd for $C_8H_{12}O_3S$: C, 51.05; H, 6.43. Found: C, 51.31; H 6.46.

2-Ethyl-3-cyclohexene-1,2'-sultone (first diastereomer). MS (GC/MS) *m/e* (relative intensity): 188 (M^+, 0.1), 124 (M^+ - SO_2, 4), 123 (20), 106 (M^+ - H_2SO_3, 77), 105 (35), 96 (25), 93 (20), 91 ($CH_2CHSO_2^+$, 100), 81 (13), 79 (76), 78 (95), 77 (39), 67 ($C_5H_7^+$, 14), 53 (13), 41 (20), 39 (25).

2-Ethyl-3-cyclohexene-1,2'-sultone (second diastereomer). MS (GC/MS) *m/e* (relative intensity): 189 (M^++1, 0.4), 188 (M^+, 5.5), 124 (M^+ - SO_2, 3), 123 (5), 106 (M^+ - H_2SO_3, 48), 105 (43), 96 (8), 93 (12), 91 ($CH_2CHSO_2^+$, 52), 80 (17), 79 (100), 78 (70), 77 (30), 67 ($C_5H_7^+$, 11), 41 (14), 39 (18).

Esterification of Alcohol **8c** *with Vinylsulfonyl Chloride*

(*E*)-2,2-Dimethyl-6-methyl-5,7-octadien-3-ol (**8c**)[18] (333.8 mg, 1.984 mmol) is dissolved in THF (25 ml) and converted to vinylsulfonate **9c** according to the procedure described for **1a** (triethylamine: 0.55 ml, 3.97 mmol; vinylsulfonyl chloride: 0.18 ml, 1.98 mmol; 2.5 h 0 °C). The crude vinylsulfonate **9c** (401 mg, 78 %) is obtained as a pale yellow oil.

(E)-2,2-Dimethyl-6-methyl-5,7-octadien-3-yl Vinylsulfonate (**9c**). R_f = 0.51 (petroleum ether/ethyl acetate 5 : 1); ^{1}H NMR δ 0.94 [s, 9 H, $(CH_3)_3C$], 1.66 (s, 3 H, 6'-CH_3), 2.01 - 2.18 (m, 1 H, 4'-H), 2.24 - 2.36 (m, 1 H, 4'-H), 4.24 (dd, 1 H, J = 1.9, 11.9 Hz, 3'-H), 4.96 (dd, 1 H, J = 9.1, 10.9 Hz, 8'-H_a), 5.08 (d, 1 H, J = 17.5 Hz, 8'-H_b), 5.44 (dd, 1 H, J = 7.4, 7.4 Hz, 5'-H), 5.87 (d, 1 H, J = 9.7 Hz, 2-H_a), 6.21 (d, 1 H, J = 16.6 Hz, 2-H_b), 6.29 (dd, 1 H, J = 10.9, 17.5 Hz, 7'-H), 6.39 (dd, 1 H, J = 9.7, 16.6 Hz, 1-H).

Intramolecular Diels-Alder Reaction of Vinylsulfonate **9c** *to Sultones* **10c** *and* **11c**

Vinylsulfonate **9c** (391 mg, 1.51 mmol) is heated for 4 h to reflux in toluene (150 ml) as described for **2c** (11 mg BHT). The crude product (**10c** : **11c** = 4.7 : 1 by GC analysis) is separated by flash chromatography using petroleum ether/ether 5 : 1. First, the major diastereomer **10c** (201 mg, 51 %) is eluted followed by a fraction of diastereomer **11c** (38 mg, 10 %) containing a small amount of **10c**. Both diastereomers are obtained as white crystalline solids.

(1R,2R*,2'S*)-2-(3,3-Dimethylbutyl)-3-methyl-3-cyclohexene-1,2'-sultone* (**10c**). mp 142 °C; R_f = 0.28 (petroleum ether/ether 5 : 1); ^{1}H NMR δ 1.01 (s, 9 H, 3'-CH_3), 1.42 (ddd, 1 H, *J* = 12.0, 12.2, 13.9 Hz, 1'-H_a), 1.70 (s, 3 H, 3-CH_3), 1.78 (dddd, 1 H, *J* = 6.8, 12.4 Hz, 12.4 Hz, 12.4 Hz, 6-H_a), 2.12 (ddd, 1 H, *J* = 1.8, 2.8, 13.9 Hz, 1'-H_b), 2.18 (m_c, 2 H, 5-H), 2.35 (m_c, 1 H, 6-H_b), 2.74 (m_c, 1 H, 2-H), 2.90 (ddd, 1 H, *J* = 2.3, 11.1, 12.5 Hz, 1-H), 4.31 (dd, 1 H, *J* = 1.8, 12.0 Hz, 2'-H), 5.49 (m_c, 1 H, 4-H); ^{13}C NMR δ 20.2 (t), 20.6 (q, 3-CH_3), 23.9 (t), 25.5 (q, 3'-CH_3), 28.8 (t), 34.3 (s, C-3'), 39.9 (d, C-2), 60.2 (d, C-1), 91.9 (d, C-2'), 123.0 (d, C-4), 132.2 (s, C-3); IR (KBr) 3028 (w), 2973 (s), 2943 (s), 2912 (m), 2868 (m), 2844 (w), 1484 (w), 1433 (w), 1371 (w), 1358 (s, SO_2OR), 1321 (s), 1215 (w), 1164 (s, SO_2OR), 1068 (w), 967 (m), 938 (m), 925 (s), 887 (s), 865 (m), 833 (w), 797 (w), 616 (m), 566 (m), 498 (w) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 259 (M^++1, 1), 258 (M^+, 5), 193 (2), 179 (M^+ - SO_2 - CH_3, 2), 177 (4), 176 (M^+ - H_2SO_3, 25), 175 (4), 161 (M^+ - H_2SO_3 - CH_3, 12), 133 (5), 120 (15), 119 (48), 118 (9), 109 (7), 108 (16), 107 (37), 106 (100), 105 (25), 94 (17), 93 (57), 92 (20), 91 (47), 83 (9), 79 (32), 71 (32), 70 (22), 57 [$(CH_3)_3C^+$, 85], 55 (23), 43 (52), 41 (91). Anal. Calcd for $C_{13}H_{22}O_3S$: C, 60.43; H, 8.58. Found: C, 60.64; H, 8.60.

(1R,2S*,2'S*)-2-(3,3-Dimethylbutyl)-3-methyl-3-cyclohexene-1,2'-sultone* (**11c**). R_f = 0.18 (petroleum ether/ether 5 : 1); ^{1}H NMR δ 0.99 [s, 9 H, $(CH_3)_3C$)], 1.69 (s, 3 H, 3-CH_3), 1.84 (ddd, 1 H, *J* = 5.0, 10.2, 14.9 Hz), 1.99 - 2.09 (m, 1 H), 2.16 (m_c, 2 H), 2.37 - 2.45 (m, 1 H), 2.46 - 2.65 (m, 1 H), 2.89 (m_c, 1 H), 3.47 (ddd, 1 H, *J* = 4.3, 4.3, 4.3 Hz, 1-H), 4.17 (dd, 1 H, *J* = 2.3, 10.5 Hz, 2'-H), 5.65 (s, 1 H, 4-H).

Preparation of Dibromoalkene **13**

Ethyl 3-(*tert*-butyldimethylsilyloxy)butanoate was prepared by silylation of ethyl 3-hydroxybutanoate according to a general method (88 % yield);[35] for spectroscopic data, see ref 36. This silyloxy ester was reduced to aldehyde **12** using di-*iso*-butylaluminum hydride at -90 °C (91 % yield);[37] for spectroscopic data, see ref 19.

A solution of tetrabromomethane (13.058 g, 39.37 mmol) in dichloromethane (50 ml) is added at 0 °C to a solution of triphenylphosphine (20.655 g, 78.75 mmol) in dichloromethane (100 ml) giving rise to a dark red solution. Aldehyde **12** (3.984 g, 19.69 mmol) is added dropwise to this solution at 0 °C, and the mixture is stirred for further 3.5 h at the same temperature. Triphenylphosphinoxide is precipitated by addition of petroleum ether (500 ml) and removed by suction using a D3 glass frit filter filled with a small amount of silica gel. The filter cake is suspended in petroleum ether (250 ml), filtered again, and washed with petroleum ether (125 ml). After evaporation of the combined filtrates *in vacuo*, flash chromatography using petroleum ether/ether 10 : 1 gives dibromoalkene **13** as a pale yellow oil (5.770 g, 82 %; better yields of up to 91 % were achieved starting from 2.2 mmol **12**). Since **13** decomposes on storage at -20 °C, it has to be used directly after preparation.

5,5-Dibromo-2-(tert-butyldimethylsiloxy)-4-pentene (**13**). R_f = 0.69 (petroleum ether/ether 10 : 1); ^{1}H NMR δ 0.058 [s, 3 H, $(CH_3)_2Si$], 0.060 [s, 3 H, $(CH_3)_2Si$], 0.89 [s, 9 H, $(CH_3)_3CSi$], 1.15 (d, 3 H, *J* = 6.1 Hz, 1-H), 2.17 - 2.30 (m, 2 H), 3.93 (m_c, 1 H, 2-H), 6.47 (dd, 1 H, *J* = 7.3 Hz, 4-H); IR 2956 (s), 2929 (s), 2911 (m), 2860 (s), 1615 (m, C=C), 1472 (m), 1463 (m), 1378 (m), 1362 (m), 1256 (s), 1216 (w), 1132 (s), 1086 (s), 1041 (m), 1004 (m), 972 (m), 836 (s), 808 (m), 777 (s) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 358 (M^+, 0.5), 343 (M^+ - CH_3, 1), 303 [M^+ - $(CH_3)_3C$, 16], 301 [M^+ - $(CH_3)_3C$, 30], 299 [M^+ - $(CH_3)_3C$, 17], 259 (15), 257 (30), 255 (16), 227 (M^+ - TBDMSO, 2), 205 (11), 203 (19), 201 (13), 159 (TBDMSO=$CHCH_3^+$, 15), 139 (22), 137 (19), 103 (30), 83 (100), 75 [$(CH_3)_2Si$=OH^+, 39], 73 (72), 65 (22), 55 (22), 45 (27), 41 (40), 39 (41).

Preparation of Trimethylsilylalkyne **14**

To a solution of dibromoalkene **13** (5.745 g, 16.04 mmol) in THF (115 ml) cooled to -78 °C *n*-BuLi (1.6 M in hexane, 21.05 ml, 33.68 mmol) is added dropwise. The mixture is stirred for 1 h at -78 °C, 2 h at room temperature, and cooled again to -78 °C. After dropwise addition of trimethylsilylchloride (2.83 ml, 22.5

mmol) at -78 °C, the mixture is allowed to slowly warm to room temperature overnight with stirring. The mixure is poured into sat. aqueous Na_2CO_3 (30 ml), and the layers are separated. After extraction of the aqueous layer with ether (3 x 80 ml), the combined organic layers are dried over $MgSO_4$, and the solvent is removed *in vacuo*. Flash chromatography using petroleum ether/ether 30 : 1 yields trimethylsilylalkyne **14** (4.161 g, 96 %) as a colorless liquid.

2-(tert-Butyldimethylsiloxy)-5-trimethylsilyl-4-pentyne (**14**). R_f = 0.60 (petroleum ether/ether 30 : 1); ^{1}H NMR δ 0.07 (s, 3 H, TBDMS-CH_3), 0.08 (s, 3 H, TBDMS-CH_3), 0.14 [s, 9 H, $(CH_3)_3$Si], 0.89 [s, 9 H, $(CH_3)_3$CSi], 1.21 (d, 3 H, J = 6.0 Hz, 1-H), 2.26 (dd, 1 H, J = 6.7, 16.7 Hz, 3-H_a), 2.38 (dd, 1 H, J = 6.1, 16.7 Hz, 3-H_b), 3.95 (m_c, 1 H, 2-H); ^{13}C NMR δ -4.7 (q, TBDMS-CH_3), -4.6 (q, TBDMS-CH_3), 0.1 (q, $(CH_3)_3$Si), 18.1 (s, $(CH_3)_3C$), 23.5 (q, C-1), 25.9 (q, $(CH_3)_3$C), 30.9 (t, C-3), 85.8 (s, C-4), 104.8 (s, C-5); IR 2958 (s), 2930 (s), 2900 (s), 2858 (s), 2179 (s, C≡C), 1473 (m), 1463 (m), 1377 (m), 1362 (w), 1251 (s), 1133 (s), 1102 (s), 1083 (m), 1043 (m), 1034 (m), 1001 (m, br.), 841 (s, br.), 809 (m), 776 (s), 760 (m), 644 (m) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 255 (M^+ - CH_3, 3), 215 (8), 214 (16), 213 [M^+ - $(CH_3)_3$C, 56], 171 (14), 170 (16), 169 (72), 159 (TBDMSO=$CHCH_3^+$, 54), 155 (10), 147 (28), 141 (12), 115 (TBDMS$^+$, 12), 103 (18), 99 (10), 85 (8), 83 (12), 75 [$(CH_3)_2$Si=OH^+, 20], 73 [$(CH_3)_3Si^+$, 100], 59 (14), 55 (12), 45 (17), 43 (12), 41 (8); Anal. Calcd for $C_{14}H_{30}OSi_2$: C, 62.15; H, 11.18. Found: C, 62.26; H, 11.01.

Hydrozirconation/Iodination of Alkyne **14** *to Iodoalkene* **15**

A three-necked flask equipped with a reflux condenser is charged with Cp_2ZrCl_2 (1.831 g, 6.265 mmol) and ether (10 ml). The suspension is cooled to -78 °C, and *tert*-BuLi (1.7 M in ether, 3.69 ml, 6.27 mmol) is added dropwise. The cooling bath is removed, flask and condenser are wrapped in aluminum foil, and the reaction mixture is allowed to warm to room temperature. Toluene (25 ml) is added, and the mixture is heated to 60 °C for 1 h. Alkyne **14** (1.695 g, 6.265 mmol) dissolved in ether (5 ml) is added to the red suspension, and the resultant mixture is heated at 60 °C. After 5 h, the conversion was determined by hydrolyzing an aliquot of the reaction mixture. Since GC analysis of the ether extract showed only 30 % conversion, a second equivalent of the hydrozirconation agent was prepared as described above and added to the reaction mixture through a double-tipped needle. After heating for further 5 h at 60 °C, conversion was found to be 91 %. The mixture is then cooled to -30 °C, treated with a solution of iodine (4.770 g, 18.80 mmol) in THF (20 ml), and stirred for 30 min at -30 °C and overnight at room temperature. Following hydrolysis by addition of sat. aqueous NH_4Cl (10 ml), a few crystals of 2,5-di-*tert*-butyl-4-methylphenol are added, the layers are separated, and the aqueous layer is extracted with ether (3 x 20 ml). The combined organic layers are washed with sat. aqueous Na_2SO_3 (15 ml), filtered to remove precipitated ZrO_2, and the filtrate is washed with sat. aqueous $NaHCO_3$ (15 ml) and brine (15 ml). After drying over $MgSO_4$ and removal of the solvents *in vacuo*, flash chromatography using petroleum ether/ether 30 : 1 yields **15** (1.399 g, 54 %) as a colorless liquid still containing some impurities.

(E)-2-(tert-Butyldimethylsiloxy)-5-iodo-5-trimethylsilyl-4-pentene (**15**). R_f = 0.71 (petroleum ether/ether 30 : 1); MS (GC/MS) *m/e* (relative intensity): 383 (M^+ - CH_3, 0.2), 342 (M^+ - C_4H_8, 2), 341 (M^+ - C_4H_9, 8), 267 (M^+ - TBDMSO, 1), 259 (3), 253 (6), 185 (7), 159 (TBDMSO=$CHCH_3^+$, 38), 147 (20), 141 (11), 125 (4), 115 (TBDMS$^+$, 14), 103 (12), 97 (13), 75 [$(CH_3)_2SiOH^+$,18], 73 [$(CH_3)_3Si^+$, 100], 59 (8), 45 (8).

Cross-Coupling of **15** *with Tri(n-butyl)vinylstannane to Diene* **16** *and Deprotection to Alcohol* **8d**

To dichlorobis(benzonitrile)palladium(II) (25.8 mg, 0.0672 mmol) is added under argon at room temperature a solution of iodoalkene **15** (1.399 g, 3.36 mmol) in DMF (15 ml) followed by dropwise addition of tri(*n*-butyl)vinylstannane (1.18 ml, 4.03 mmol). The resultant mixture is stirred overnight and turns black from colloidal palladium. A 10 % aqueous solution of KF (25 ml) is added and after stirring for several minutes, the mixture is filtered through a glass frit filter filled with some silica gel to remove the precipitate.

The filter is rinsed with ether, the organic layer of the filtrate is separated, and the aqueous layer is extracted with ether (3 x 30 ml). After washing the combined organic layers with brine and drying over $MgSO_4$, the solvents are removed *in vacuo*, and flash chromatography using petroleum ether/ether 30 : 1 gives a mixture of **16** and tri(*n*-butyl)vinylstannane (1.985 g).

This mixture (1.985 g) is dissolved in THF (20 ml), and tetra(*n*-butyl)ammonium fluoride (1 M in THF, 10.1 ml, 10.1 mmol) is added. After stirring at room temperature for 12 h, sat. aqueous $NaHCO_3$ (20 ml) is added. The mixture is extracted with ether (4 x 20 ml), and the combined organic layers are washed with water (15 ml) and dried over $MgSO_4$. Removal of the solvent *in vacuo* and flash chromatography using petroleum ether/ether 3 : 1 give dienol **8d** (108 mg, 9.4 % overall yield from trimethylsilylalkyne **14**) as a colorless liquid.

(Z)-2-(tert-Butyldimethylsiloxy)-5-trimethylsilyl-4,6-heptadiene (**16**). R_f = 0.86 (petroleum ether/ether 30 : 1); MS (GC/MS) *m/e* (relative intensity): 283 (M^+ - CH_3, 0.1), 242 (M^+ - C_4H_8, 0.8), 241 (M^+ - C_4H_9, 3), 167 (4), 160 (10), 159 (TBDMSO=$CHCH_3^+$, 66), 153 (14), 147 (31), 133 (4), 115 (TBDMS$^+$, 24), 103 (22), 75 [$(CH_3)_2SiOH^+$, 13], 73 [$(CH_3)_3Si^+$, 100], 59 (10), 45 (8).

(Z)-5-Trimethylsilyl-4,6-heptadien-2-ol (**8d**). R_f = 0.20 (petroleum ether/ether 3 : 1); ^1H NMR δ 0.20 [s, 9 H, $(CH_3)_3Si$], 1.22 (d, 3 H, *J* = 6.4 Hz, 1-H), 2.35 (m_c, 2 H, 3-H), 3.88 (m_c, 1 H, 2-H), 4.87 (dd, 1 H, *J* = 1.9, 10.6 Hz, 7-H_a), 5.08 (dd, 1 H, *J* = 1.9, 17.3 Hz, 7-H_b), 6.22 (dt, 1 H, J_d = 1.5 Hz, J_t = 7.5 Hz, 4-H), 6.37 (ddd, 1 H, *J* = 1.5, 10.6, 17.3 Hz, 6-H); ^{13}C NMR δ 0.6 [q, $(CH_3)_3Si$], 23.0 (q, C-1), 41.3 (t, C-3), 67.9 (d, C-2), 112.7 (t, C-7), 139.8 (d), 142.5 (d); IR 3365 (s, br., O-H), 3080 (m), 2965 (s), 2928 (s), 2898 (s), 1612 (m, C=C), 1595 (m, C=C), 1457 (m), 1419 (m), 1408 (m), 1375 (m), 1250 (s), 1115 (m), 1077 (m), 1033 (w), 904 (m), 838 (s, br.), 759 (w) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 169 (M^+ - CH_3, 14), 155 (2), 153 (1), 139 (M^+ - C_2H_5O, 5), 125 [$CH_2CHC(TMS)CH^+$, 19], 109 (4), 95 (13), 93 (13), 85 (4), 79 (7), 75 [$(CH_3)_2SiOH^+$, 49], 74 (11), 73 [$(CH_3)_3Si^+$, 100], 67 (5), 59 (5), 53 (4), 45 (CH_3CHOH^+, 36), 43 (12), 39 (7). HRMS Calcd for $C_{10}H_{20}OSi$ (M^+ - CH_3): 169.1049. Found: 169.1050.

Esterification of Alcohol **8d** *with Vinylsulfonyl Chloride and Intramolecular Diels-Alder Reaction to Sultone* **10d**

Dienol **8d** (73.0 mg, 0.396 mmol) is dissolved in THF (5 ml) and converted to vinylsulfonate **9d** according to the procedure described for **1a** (triethylamine: 0.11 ml, 0.79 mmol; vinylsulfonyl chloride: 0.043 ml, 0.48 mmol; 3.5 h 0 °C). The crude vinylsulfonate **9d** (93 mg, 86 %) obtained as a pale yellow oil was cyclized immediately.

Vinylsulfonate **9d** (66.4 mg, 0.242 mmol) is heated for 5 h to reflux in toluene (25 ml) as described for **2c** (5 mg BHT). The crude product (**10d** : **11d** > 99 : 1 by GC analysis) is purified by flash chromatography using petroleum ether/ether 4 : 1 to give **10d** (25.6 mg, 39 %) as a highly viscous colorless oil.

(1R,2R*,2'R*)-2-Propyl-3-trimethylsilyl-3-cyclohexene-1,2'-sultone* (**10d**). R_f = 0.42 (petroleum ether/ether 4 : 1); ^1H NMR δ 0.12 [s, 9 H, $(CH_3)_3Si$], 1.41 (d, 3 H, *J* = 6.4 Hz, 3'-H), 1.46 - 1.54 (m, 1 H, 1'-H_a), 1.76 (dddd, 1 H, *J* = 6.8, 12.1, 12.1, 12.1 Hz, 6-H), 2.11 (ddd, 1 H, *J* = 1.9, 2.3, 13.9 Hz, 1'-H_b), 2.17 - 2.31 (m, 1 H), 2.32 - 2.40 (m, 2 H), 2.87 (ddd, 1 H, *J* = 2.3, 10.6, 12.1 Hz, 1-H), 2.95 (ddd, 1 H, *J* = 2.3, 10.6, 10.6 Hz, 2-H), 4.77 (ddq, 1 H, J_d = 1.9, 11.7 Hz, J_q = 6.4 Hz, 2'-H), 6.05 (m_c, 1 H, 4-H). ^{13}C NMR δ -0.1 [q, $(CH_3)_3Si$], 20.0 (t), 21.2 (q, C-3'), 26.2 (t), 39.3 (t), 39.8 (d, C-2), 60.2 (d, C-1), 80.8 (d, C-2'), 137.5 (d, C-4), 138.5 (s, C-3); IR 3014 (m), 2954 (s), 2910 (m), 2862 (m), 1604 (w, C=C), 1457 (w, C=C), 1432 (w), 1363 (s, SO_2OR), 1329 (m), 1251 (m), 1201 (w), 1173 (s, SO_2OR), 1125 (m), 1090 (w), 1007 (w), 938 (m), 875 (s), 836 (s), 809 (m), 744 (w) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 259 (M^+ - CH_3, 27), 211 (8), 209 (4), 193 (11), 177 (M^+ - H_2SO_3 - CH_3, 5), 161 (10), 149 (7), 135 (9), 123 (25), 121 (24), 119 [M^+ - H_2SO_3 - $(CH_3)_3Si$, 19], 105 (12), 93 (35), 91 (59), 79 (24), 75 [$(CH_3)_2SiOH^+$, 32], 73 [$(CH_3)_3Si^+$, 100], 59 (18), 53 (7), 45 (31), 43 (35), 39 (19). HRMS Calcd for $C_{11}H_{19}O_3SSi$ (M^+ - CH_3): 259.0824. Found: 259.0820.

Oxidative Desulfurization of Sultone **3c** *to Hydroxy Ketone* **18c**

A solution of sultone **3c** (205.5 mg, 0.900 mmol) in THF (12 ml) is cooled to -78 °C, and *n*-BuLi (1.6 M in hexane, 0.79 ml, 1.26 mmol) is added dropwise with stirring. After stirring the resultant bright yellow solution for 1 h 50 min at -78 °C, 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[30] (0.25 ml, 1.44 mmol) is added dropwise, and the mixture is allowed to warm to -50 °C. For complete conversion, more borylation agent (0.06 ml, 0.36 mmol) is added after 1 h at -50 °C, and stirring is continued for further 1.5 h at this temperature. The resultant boronic ester (cf. isolation of **19a**) is oxidized by rapidly transferring the above solution through a double-tipped needle to a suspension of *m*-chloroperbenzoic acid (555 mg, 84 % MCPBA containing 16 % *m*-chlorobenzoic acid, 2.70 mmol) and Na_2CO_3 (9.00 mmol) in ether (10 ml) cooled to -78 °C. The reaction mixture is allowed to warm up to 0 °C, stirred for 3 h 15 min at this temperature, treated with water (10 ml), and extracted with ether (4 x 30 ml). The combined extracts are washed with sat. aqueous Na_2SO_3 (15 ml), 2 N NaOH (25 ml), sat. aqueous Na_2CO_3 (15 ml), and dried over $MgSO_4$. After evaporation of the solvent *in vacuo*, flash chromatography using dichloromethane/acetone 6 : 1 gives **18c** (139 mg, 86 %) as a colorless liquid.

(1R,4S*,2'S*)-1-(2-Hydroxypropyl)-bicyclo[2.2.2]oct-5-en-2-one* (**18c**). R_f = 0.41 (dichloromethane/acetone 5 : 1) ^{1}H NMR δ 1.25 (d, 3 H, J = 6.3 Hz, 3'-H), 1.35 - 1.51 (m, 1 H), 1.56 - 1.76 (m, 3 H), 1.63 (dd, 1 H, J = 2.0, 15.2 Hz, 1'-H_a), 1.98 (ddd, 1 H, J = 0.6, 8.8, 15.2 Hz, 1'-H_b), 2.09 - 2.12 (m, 2 H), 2.98 (m_c, 1 H, 4-H), 3.68 (s, br., 1 H, OH), 4.01 (ddq, 1 H, J_d = 2.0, 8.8 Hz, J_q = 6.3 Hz, 2'-H), 6.07 (dd, 1 H, J = 1.6, 8.2 Hz, 6-H), 6.53 (dd, 1 H, J = 6.5, 8.2 Hz, 5-H); ^{13}C NMR δ 25.2 (q, C-3'), 25.6 (t), 30.2 (t), 32.1 (d, C-4), 40.9 (t), 41.8 (t), 53.0 (s, C-1), 64.9 (d, C-2'), 130.8 (d), 137.0 (d), 216.6 (s, C-2); IR 3420 (s, br., O-H), 3048 (m), 2963 (s), 2943 (s), 2910 (s), 2875 (s), 1716 (s, C=O), 1453 (m), 1406 (m), 1373 (m), 1342 (w), 1280 (w), 1129 (m), 1090 (s), 1056 (m), 994 (w), 948 (w), 820 (w), 711 (s) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 181 (M^++1, 3), 180 (M^+, 8), 165 (M^+ - CH_3, 4), 163 (M^+ - OH, 15), 137 (12), 135 (M^+ - CH_3CHOH, 10), 134 (14), 121 (8), 120 (M^+ - CH_2CO - H_2O, 40), 119 (21), 108 (10), 107 (10), 105 (M^+ - CH_2CO - H_2O - CH_3, 16), 94 (63), 93 (27), 92 (21), 91 (96), 79 (100), 78 (45), 77 (37), 65 (16), 51 (18), 45 (CH_3CHOH^+, 59), 43 (30), 39 (43); Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.25; H, 9.02.

Oxidative Desulfurization of Sultone **3a** *to Hydroxy Ketone* **18a**

Sultone **3a** (150 mg, 0.700 mmol) is converted to **18a** as described for the preparation of **18c** (lithiation: 2.36 M *n*-BuLi in hexane, 0.36 ml, 0.84 mmol, 1 h 20 min -78 °C; borylation: 0.20 ml, 1.19 mmol borylating reagent added dropwise in one portion, 3 h -50 °C; oxidation: 4 h 0 °C). Flash chromatography using dichloromethane/acetone 2 : 1 gives hydroxy ketone **18a** (77.2 mg, 66 %) as a colorless liquid.

(1R,4S*,2'R*)-1-(2-Hydroxypropyl)-5-norbornen-2-one* (**18a**). R_f = 0.53 (dichloromethane/acetone 2 : 1) ^{1}H NMR δ 1.25 (d, 3 H, J = 6.3 Hz, 3'-H), 1.86 (dd, 1 H, J = 3.2, 15.0 Hz, 1'-H), 2.00 (dd, 1 H, J = 9.3, 15.0 Hz, 1'-H), 2.00 - 2.13 (m, 3 H, 3-H_a, 3-H_b, 7-H_a), 2.25 (ddd, 1 H, J = 2.4, 4.1, 9.1 Hz, 7-H_b), 3.15 (s, br., 1 H, 4-H), 3.88 (ddq, 1 H, J_d = 3.2, 9.3 Hz, J_q = 6.2 Hz, 2'-H), 5.83 (dd, 1 H, J = 0.7, 5.5 Hz, 6-H), 6.56 (dd, 1 H, J = 2.9, 5.5 Hz, 5-H); ^{13}C NMR δ 24.9 (q, C-3'), 36.0 (t, C-1'), 38.6 (d, C-4), 38.7 (t, C-3), 53.7 (t, C-7), 62.9 (s, C-1), 66.0 (d, C-2'), 134.3 (d), 143.5 (d), 217.7 (s, C-2); IR 3450 (s, br., O-H), 3060 (m), 2970 (s), 2920 (s), 1725 (s, br., C=O), 1630 (m), 1450 (m), 1410 (m), 1325 (s, br.), 1070 (s, br.), 920 (m), 860 (m), 700 (m) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 166 (M^+, 4), 151 (M^+ - CH_3, 29), 125 (4), 124 (M^+ - CH_2CO, 42), 122 (3), 107 (6), 106 (M^+ - CH_2CO - H_2O, 4), 105 (5), 93 (6), 91 (M^+ - CH_3 - CH_2CO - H_2O, 25), 80 (M^+ - CH_2CO - CH_3CHO, 100), 79 ($C_6H_7^+$, 69), 78 (15), 77 (45), 65 (6), 53 (8), 51 (9), 45 (CH_3CHOH^+, 56), 43 (18), 41 (9), 39 (18). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.04; H, 8.41.

Oxidative Desulfurization of Sultone **3b** *to Hydroxy Ketone* **18b**

Sultone **3b** (797 mg, 3.29 mmol) is converted to **18b** as described for the preparation of **18c** (lithiation: 1.6 M *n*-BuLi in hexane, 2.88 ml, 4.61 mmol, 1 h 30 min -78 °C; borylation: 0.89 ml, 5.3 mmol borylating reagent added dropwise in one portion, 3 h -50 °C; oxidation: 3 h 50 min 0 °C). Flash chromatography using dichloromethane/acetone 8 : 1 gives hydroxy ketone **18b** (384 mg, 60 %) as a colorless liquid. Some sultone **3b** (106 mg, 13 %) was recovered by flash chromatography of the first fractions obtained above using petroleum ether/ethyl acetate 4 : 1.

(1R,4S,2'S)-1-(2-Hydroxy-3-methylbutyl)-5-norbornen-2-one (**18b**). R_f = 0.26 (petroleum ether/ethyl acetate 3 : 1); $[\alpha]_D^{20}$ = -571.8 (c = 1 in $CHCl_3$); ^{1}H NMR δ 0.93 (d, 3 H, *J* = 6.9 Hz, 3'-CH_3), 0.94 (d, 3 H, *J* = 6.9 Hz, 3'-CH_3), 1.68 (d of sept, 1 H, J_d = 5.0 Hz, J_{sept} = 6.9 Hz, 3'-H), 1.81 (s, br., 1 H, OH, removed by D_2O-exchange), 1.85 (dd, 1 H, *J* = 2.9, 15.0 Hz, 1'-H_a), 1.94 (dd, 1 H, *J* = 9.7, 15.0 Hz, 1'-H_b), 1.99 (dd, 1 H, *J* = 4.4, 16.6 Hz, 3-H_a), 2.06 (d, 1 H, *J* = 9.2 Hz, 7-H_a), 2.10 (ddd, 1 H, *J* = 0.8, 2.3, 16.6 Hz, 3-H_b), 2.24 (ddd, 1 H, *J* = 2.3, 4.3, 9.2 Hz, 7-H_b), 3.15 (s, br., 1 H, 4-H), 3.42 (m_c, 1 H, 2'-H), 5.81 (dd, 1 H, *J* = 0.7, 5.5 Hz, 6-H), 6.57 (dd, 1 H, *J* = 2.9, 5.5 Hz, 5-H); ^{13}C NMR δ 17.2 (q), 18.4 (q), 30.8 (t, C-1'), 34.5 (d, C-3'), 38.6 (d, C-4), 38.8 (t, C-3), 53.6 (t, C-7), 63.1 (s, C-1), 74.3 (d, C-2'), 134.3 (d), 143.6 (d), 218.1 (s, C-2); IR 3470 (s, br., O-H), 3062 (w), 2961 (s), 2934 (s), 2875 (s), 1737 (s, C=O), 1468 (m), 1415 (m), 1387 (m), 1332 (m), 1296 (m), 1094 (m), 1071 (m), 1033 (m), 1011 (m), 993 (s), 967 (w), 865 (w), 739 (m), 614 (s) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 195 (M^++1, 0.1), 194 (M^+, 0.6), 176 (M^+ - H_2O, 0.2), 153 (3), 152 (M^+ - CH_2CO, 18), 151 (M^+ - C_3H_7, 14), 134 (M^+ - CH_2CO - H_2O, 2), 119 (3), 109 (M^+ - CH_2CO - C_3H_7, 3), 107 (3), 105 (5), 94 (4), 91 (M^+ - CH_2CO - H_2O - C_3H_7, 6), 81 (12), 80 [M^+ - CH_2CO - $(CH_3)_2CHCHO$, 100], 79 ($C_6H_7^+$, 25), 77 (10), 73 (18), 57 (3), 55 (13), 43 (7), 41 (6), 39 (5). HRMS Calcd for $C_{12}H_{18}O_2S$ (M^+): 194.1307. Found: 194.1304.

Isolation of Boronic Ester **19a**

After lithiation and borylation of sultone **3a** (150 mg, 0.700 mmol) as described above, sat. aqueous ammonium chloride (10 ml) is added. The layers are separated, the aqueous layer is extracted with ether (3 x 25 ml), the combined organic layers are dried over $MgSO_4$, and the solvent is evaporated *in vacuo*. Flash chromatography using petroleum ether/ethyl acetate 6 : 1 yields **19a** (195 mg, 82 %) as a white crystalline solid.

(1R,2R*,4S*,2'R*)-1-Propyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-norbornene-2,2'-sultone* (**19a**). mp 135 °C; R_f = 0.41 (petroleum ether/ethyl acetate 6 : 1); ^{1}H NMR δ 1.18 (m_c, 13 H, CH_3, 7-H_a), 1.47 (d, 3 H, *J* = 6.2 Hz, 3'-H), 1.90 (dd, 1 H, *J* = 1.9, 14.4 Hz, 1'-H_a), 1.97 (dd, 1 H, *J* = 2.3, 12.2 Hz, 3-H_a), 2.35 (d, 1 H, *J* = 8.6 Hz, 7-H_b), 2.46 (dd, 1 H, *J* = 3.7, 12.2 Hz, 3-H_b), 2.59 (dd, 1 H, *J* = 12.3, 14.4 Hz, 1'-H_b), 2.98 (m_c, 1 H, 4-H), 4.79 (ddq, J_d = 1.9, 12.3 Hz, J_q = 6.2 Hz, 2'-H), 5.81 (d, 1 H, *J* = 5.5 Hz, 6-H), 6.28 (dd, 1 H, *J* = 3.1, 5.5 Hz, 5-H); ^{13}C NMR δ 21.1 (q, C-3'), 24.3 (q), 24.4 (q), 32.4 (t), 34.4 (t), 42.3 (d, C-4), 48.5 (t, C-7), 58.7 (s, C-1), 78.6 (d, C-2'), 84.6 (s), 138.1 (d), 140.6 (d); IR (KBr) 3074 (w), 3020 (w), 2982 (s), 2948 (m), 2881 (w), 1448 (w), 1383 (s), 1373 (s), 1344 (s, SO_2OR), 1274 (m), 1176 (s), 1162 (s, SO_2OR), 1138 (s), 1083 (s), 1031 (s), 965 (w), 927 (m), 878 (s), 796 (m), 713 (m), 647 (m), 595 (s), 564 (m) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 340 (M^+, 0.3), 325 (M^+ - CH_3, 1.1), 282 [M+ - $(CH_3)_2CO$, 0.6], 276 (M^+ - SO_2, 0.4), 261 ($C_{10}H_{18}BO_5S^+$, 0.5), 218 (6), 217 ($C_8H_{14}BO_4S^+$, 11), 216 (2), 175 (5), 159 (5), 132 (15), 119 (15), 118 (14), 107 (26), 106 ($C_8H_{10}^+$, 100), 101 (15), 91 ($C_7H_7^+$, 78), 83 (20), 79 ($C_6H_7^+$, 18), 78 (12), 67 (8), 55 (10), 43 (11), 41 (12). Anal. Calcd for $C_{16}H_{25}BO_5S$: C, 56.48; H, 7.41. Found: C, 56.54; H, 7.35.

Preparation of α*-Chlorinated Sultone* **17a**

After lithiation of sultone **3a** (258 mg, 1.20 mmol) as described above, the solution of the α-lithio derivative is transferred through a double-tipped needle into a flask containing hexachloroethane (314 mg, 1.44 mmol) cooled to -78 °C, and the resultant mixture is stirred for 45 min at -78 °C. Work-up as described

for **19a** and flash chromatography using petroleum ether/dichloromethane 2 : 1 yield **17a** as a colorless crystalline solid (235 mg, 79 %).

(1R,2S*,4S*,2'R*)-2-Chloro-1-propyl-5-norbornene-2,2'-sultone* (**17a**). mp 108 °C; R_f = 0.30 (petroleum ether/dichloromethane 2 : 1); ^{1}H NMR δ 1.50 (d, 3 H, *J* = 6.2 Hz, 3'-H), 1.50 (m_c, 1 H, 7-H_a), 1.79 (dd, 1 H, *J* = 3.4, 13.7 Hz, 3-H_a), 1.97 (dd, 1 H, *J* = 1.9, 15.1 Hz, 1'-H_a), 2.40 (dd, 1 H, *J* = 12.2, 15.1 Hz, 1'-H_b), 2.63 (d, 1 H, *J* = 9.2 Hz, 7-H_b), 2.97 (dd, 1 H, *J* = 3.7, 13.7 Hz, 3-H_b), 3.10 (s, br., 1 H, 4-H), 4.91 (ddq, 1 H, J_d = 1.9, 12.2 Hz, J_q = 6.2 Hz, 2'-H), 5.89 (d, 1 H, *J* = 5.5 Hz, 6-H), 6.46 (dd, 1 H, *J* = 3.1, 5.5 Hz, 5-H); ^{13}C NMR δ 20.7 (q, C-3'), 32.2 (t, C-1'), 40.4 (t, C-3), 42.5 (d, C-4), 49.3 (t, C-7), 62.0 (s, C-1), 80.4 (d, C-2'), 83.9 (s, C-2), 138.5 (d), 140.1 (d); IR (KBr) 3150 (w), 3060 (m), 3000 (s), 2980 (s), 2950 (s), 2930 (s), 2870 (m), 2510 (w), 1640 (w, C=C), 1580 (w), 1435 (s), 1340 (s, br., SO_2OR), 1290 (m), 1280 (m), 1255 (m), 1160 (s, br., SO_2OR), 1055 (s, br., C-O), 1005 (s), 980 (m), 915 (s), 870 (s, br.), 830 (s), 805 (m), 780 (s), 750 (s), 715 (s) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 248 (M^+, 0.05), 171 and 169 [$CH_3CHOSO_2C(Cl)CH_2^+$, 0.05 and 0.25], 149 (M^+ - SO_2 - Cl, 0.05), 125 [$CH_2C(Cl)SO_2^+$, 1], 107 (10), 106 [M^+ - $CH_2C(Cl)SO_3H$, 100], 105 (10), 103 (3), 100 (7), 92 (4), 91 [M^+ - CH_3 - $CH_2C(Cl)SO_3H$, 52], 79 ($C_6H_7^+$, 32), 78 (12), 77 (15), 65 ($C_5H_5^+$, 8), 64 (4), 53 ($C_4H_5^+$, 3), 45 (13), 43 (16), 41 (7), 40 (10), 39 ($C_3H_3^+$, 11). Anal. Calcd for $C_{10}H_{13}ClO_3S$: C, 48.29; H, 5.27. Found: C, 48.04; H, 5.20.

Preparation of α*-Methylthio Sultone* **17c**

After lithiation of sultone **3a** (400 mg, 1.87 mmol) as described above, dimethyldisulfide (0.219 ml, 2.43 mmol) is added dropwise at -78 °C. The cooling bath is removed and after stirring the reaction mixture for 4 h, an aqueous NaH_2PO_4/Na_2HPO_4 buffer (ca. 2 N, 15 ml) is added followed by 2 N HCl (10 ml). The layers are separated, and the aqueous layer is extracted with ethyl acetate (3 x 30 ml). After drying over $MgSO_4$ and evaporation of the solvent *in vacuo*, flash chromatography using petroleum ether/ethyl acetate 4 : 1 gives **17c** (392 mg, 81 %) as a white crystalline solid.

(1R,2R*,4S*,2'R*)-2-Methylthio-1-propyl-5-norbornene-2,2'-sultone* (**17c**). mp 89 °C; R_f = 0.40 (petroleum ether/ethyl acetate 4 : 1); ^{1}H NMR δ 1.42 (ddd, 1 H, *J* = 2.2, 2.7, 8.8 Hz, 7-H_a), 1.48 (d, 3 H, *J* = 6.2 Hz, 3'-H), 1.70 (dd, 1 H, *J* = 2.7, 13.1 Hz, 3-H_a), 1.95 (dd, 1 H, *J* = 2.1, 15.0 Hz, 1'-H_a), 2.31 (dd, 1 H, *J* = 12.1, 15.0 Hz, 1'-H_b), 2.35 (s, 3 H, SCH_3), 2.65 (dd, 1 H, *J* = 3.7, 13.1 Hz, 3-H_b), 2.81 (d, 1 H, *J* = 8.8 Hz, 7-H_b), 3.10 (s, br., 4-H), 4.88 (ddq, 1 H, J_d = 2.1, 12.1 Hz, J_q = 6.2 Hz, 2'-H), 5.93 (d, *J* = 5.5 Hz, 1 H, 6-H), 6.34 (dd, *J* = 3.1, 5.5 Hz, 1 H, 5-H); ^{13}C NMR δ 14.7 (q, SCH_3), 20.8 (q, C-3'), 33.3 (t), 33.6 (t), 42.2 (d, C-4), 49.8 (t, C-7), 61.8 (s, C-1), 75.1 (s, C-2), 79.1 (d, C-2'), 138.4 (d), 139.3 (d); IR (KBr) 3050 (w), 2970 (s), 2950 (m), 2930 (m), 2900 (m), 2870 (w), 1580 (w), 1445 (m), 1425 (m), 1380 (m), 1320 (s, br., SO_2OR), 1250 (w), 1200 (w), 1155 (s, br., SO_2OR), 1075 (m), 1060 (s), 1010 (m), 960 (w), 920 (s), 870 (s), 825 (m), 785 (m), 740 (w), 710 (m) cm^{-1}; MS (GC/MS) *m/e* (relative intensity): 261 (M^++1, 0.8), 260 (M^+, 6.6), 196 (M^+ - SO_2, 6), 181 [$CH_3CHOSO_2C(SCH_3)CH_2^+$, 1], 149 ($M^+$ - SO_2 - SCH_3, 70), 137 [$CH_2C(SCH_3)SO_2^+$, 5], 133 (1), 131 (2), 121 (4), 120 (5), 107 (88), 106 [M^+ - $CH_2C(SCH_3)SO_3H$, 100], 105 (26), 91 [M^+ - CH_3 - $CH_2C(SCH_3)SO_3H$, 78], 79 ($C_6H_7^+$, 50), 78 (20), 77 (29), 73 (15), 65 ($C_5H_5^+$, 15), 64 (50), 53 ($C_4H_5^+$, 11), 51 (12), 48 (25), 47 (CH_3S^+, 9), 45 (13), 43 (14), 39 ($C_3H_3^+$, 20). Anal. Calcd for $C_{11}H_{16}O_3S_2$: C, 50.74; H, 6.19. Found: C, 50.54; H, 6.10.

Intermolecular Diels-Alder Reaction of Cyclopentadiene **1a** *with 2-Acetoxyacrylonitrile*

A mixture of **1a** (3.001 g, 24.17 mmol) and 2-acetoxyacrylonitrile (5.07 ml, 48.34 mmol) is stirred for 1 h at 80 °C and for 1 h at 100 °C. After further stirring at room temperature overnight, excess 2-acetoxyacrylonitrile is removed by distillation (65 - 66 °C/12 Torr) to leave crude **20** (6.6 g) as a highly viscous reddish oil. A sample of this crude product was analyzed by GC / MS after silylation of the hydroxyl function with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA). Eleven isomers of gross structure **20** with nearly identical mass spectra were detected.

To crude **20** (2.75 g) dissolved in THF (30 ml) is added water (25 ml) followed by a solution of potassium hydroxide (1.42 g, 25.1 mmol) in water (23 ml). After stirring the resultant mixture for 3 d at room temperature, water (20 ml) is added, and the solution is extracted with ether (3 x 50 ml). The combined organic layers are washed with brine (25 ml), dried over $MgSO_4$, and the solvent is removed *in vacuo*. Filtration of the residue through a short column filled with silica gel using petroleum ether/ethyl acetate 1 : 1 as eluent gives a mixture of the hydroxy ketones (1.903 g). A sample of this mixture was largely separated by HPLC to give eleven fractions corresponding to twelve distinct peaks. ^1H NMR spectra of these fractions recorded after evaporation of the eluent were consistent with the formation of **18a** and at least eleven regio- and stereoisomers.

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8. Crystals of **3a** were obtained by recrystallization from diisopropyl ether, and a crystal with the dimensions 0.06 x 0.15 x 0.21 mm^3 was used. *Crystal data*: $C_{10}H_{14}O_3S$, monoclinic, space group $P2_1/n$ with $a = 9.183(2)$, $b = 9.895(2)$, $c = 11.355(3)$ Å, $\beta = 93.11(2)°$, $V = 1030.3$ $Å^3$, and $Z = 4$. *Data collection and reduction*: 2565 reflections (hk-1 - hkl) up to $2\theta_{max} = 54°$ were measured on a CAD4 diffractometer ($Mo_{K\alpha}$-radiation, graphite monochromator, $\omega/2\theta$-scan mode, scan velocity

1.6 - 5.3°/min, depending on intensity) at room temperature. Averaging symmetry equivalents gave 2243 reflections (R_{merge} = 0.8 %), of which 1712 with $I > 2\sigma(I)$ were considered as observed. *Structure elucidation and refinement*: The structure was determined by direct methods. All calculations were performed with the software package SHELXTL-PLUS (Sheldrick, 1988) on a VAX-cluster. The coordinates of the hydrogen atoms were obtained from difference Fourier syntheses. Anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the hydrogen atoms using full matrix refinement led to R = 4.8 % and R_w = 3.0 % with w = $1/\sigma^2$ (for all 2243 reflections R = 6.6 % and R_w = 3.1 %). Crystallographic details were deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (depository number CSD-56917).

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