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

# Peter Metz,\* Michael Fleischer, and Roland Fröhlich#

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, D-48149 Münster, Germany

Abstract: Vinylsulfonates prepared from hydroxyalkyl substituted cycloalka-1,3-dienes and acyclic 1,3dienes by esterification with vinylsulfonyl chloride cycloadd to  $\delta$ -sultones at temperatures ranging from 0 °C to reflux in toluene. High diastereoselectivity is observed for substrates 2 featuring a cyclic 1,3diene moiety, whereas a substituent R<sup>2</sup> 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.<sup>1</sup> During our studies on intramolecular Diels-Alder cycloadditions of vinylsulfonates, initiated to eventually control side-chain chirality,<sup>2</sup> 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.<sup>2b,c</sup>

Intramolecular Diels-Alder reaction of a vinylsulfonate, readily available by esterification of the corresponding alcohol with vinylsulfonyl chloride,<sup>2a</sup> 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.<sup>3</sup> 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.<sup>4</sup>

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  $\delta$ -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,<sup>5</sup> allows for rather mild cycloaddition conditions. Thus, esterification of alcohols **1a**,**b** as equilibrium mixtures of diene isomers with vinylsulfonyl chloride<sup>6</sup> 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.<sup>7</sup> 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 <sup>1</sup>H, <sup>1</sup>H 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  $\delta$ -sultone for all major products, a chairlike 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 1,2epoxypropane according to a published procedure.<sup>10</sup> In an analogous manner, enantiomerically pure **1b** was obtained through alkylation of sodium cyclopentadienide with (2R)-1,2-epoxy-3-methylbutane which in turn is available from (S)-valine by a known three step sequence.<sup>11</sup> Racemic alcohol **1c** was synthesized from sulfone **4** using a methodology developed by *Bäckvall* (Scheme 3).<sup>12</sup> Temporary blocking of the secondary alcohol ( $5 \rightarrow 6$ ) 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<sup>8,9</sup>



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<sub>2</sub>Cl<sub>2</sub>, 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.<sup>13</sup>



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 <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield 9 [%] <sup>a</sup>	10 : 11 <sup>b</sup>	Yield 10+11 [%] <sup>c</sup>
8	Н	Н	н	87	1:1	76
b	Me	Н	Me	82	1.4 : 1	64
С	t-Bu	Me	Н	78	4.7 : 1	61
ď	Me	SiMe <sub>3</sub>	Н	86	>99:1	39

<sup>a</sup> Yields of crude products. <sup>b</sup> Diastereomeric ratios determined by capillary GC analysis of the crude products. <sup>c</sup> 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 <sup>1</sup>H, <sup>1</sup>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.<sup>14</sup> 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.<sup>14,15</sup>



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



Scheme 5. Preparation of alcohol 8d. a: Ph<sub>3</sub>P, CBr<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 82 - 91 %; b: (i) *n*-BuLi, THF, -78 °C to 20 °C, (ii) Me<sub>3</sub>SiCl, -78 °C, 96 %; c: (i) *i*-BuCp<sub>2</sub>ZrCl, ether, toluene, 60 °C, (ii) I<sub>2</sub>, THF, -30 °C to 20 °C; d: CH<sub>2</sub>=CHSn(*n*-Bu)<sub>3</sub>, DMF, 2 mol % PdCl<sub>2</sub>(PhCN)<sub>2</sub>, 20 °C; e: *n*-Bu<sub>4</sub>NF, 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<sup>20</sup> was followed by a non-optimized sequence consisting of hydrozirconation/iodination<sup>21</sup> of 14 to iodoalkene 15 and subsequent palladium-catalyzed cross-coupling<sup>22</sup> 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.<sup>23</sup> In a first series of experiments, lithiation of 3a with *n*-BuLi<sup>24</sup> 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,<sup>25</sup> this method was not efficient for 3a.<sup>26</sup> Next, we investigated the two-step process depicted in Scheme 6.



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	Е	17	Yield 17 [%]
Cl <sub>3</sub> C-CCl <sub>3</sub>	Cl	а	79 <sup>a</sup>
BrCl <sub>2</sub> C-CCl <sub>2</sub> Br	Br	b	70 <sup>b</sup> (17b : 17a = 1.8 : 1) <sup>b</sup>
	Cl	a	
MeS-SMe	SMe	с	81 <sup>a</sup>
	E-X Cl <sub>3</sub> C-CCl <sub>3</sub> BrCl <sub>2</sub> C-CCl <sub>2</sub> Br MeS-SMe	E-X E Cl <sub>3</sub> C-CCl <sub>3</sub> Cl BrCl <sub>2</sub> C-CCl <sub>2</sub> Br Br Cl MeS-SMe SMe	E-XE17 $Cl_3C-CCl_3$ $Cl$ a $BrCl_2C-CCl_2Br$ $Br$ b $Cl$ aMeS-SMeSMec

<sup>a</sup> Yield of pure product after flash chromatography. <sup>b</sup> 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).<sup>28</sup> NOE difference spectra of 17c allowed for elucidation of both the relative configuration at the electrophilically substituted carbon atom and the conformation of the  $\delta$ -sultone (Figure 3). However, attempted hydrolyses<sup>28</sup> of halogenated compounds 17a,b or methylthio sultone 17c to 18a proceeded unsatisfactorily.<sup>29</sup>

Eventually, an efficient oxidative desulfurization of 3a-c to hydroxy ketones 18a-c was accomplished by borylation of the  $\alpha$ -lithiated sultones with 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane<sup>30</sup> and subsequent chemoselective oxidation of the resulting boronates 19a-c using *m*-chloroperbenzoic acid in the presence of sodium carbonate<sup>31</sup> (Scheme 7). Gratifyingly, GC/MS and <sup>1</sup>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  $\alpha$ -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<sup>32</sup> (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.<sup>33</sup>



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<sub>2</sub>. 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. <sup>1</sup>H NMR spectra (300 MHz, CDCl<sub>3</sub>), NOE difference spectra (300 MHz, CDCl<sub>3</sub>), and  $^{13}$ C NMR spectra (75.47 MHz, CDCl<sub>3</sub>) were obtained on a Bruker WM 300 - m<sub>c</sub> = multiplet centered at, br. = broad. <sup>13</sup>C multiplicities were determined using INEPT or DEPT pulse sequences. IR spectra (CHCl<sub>3</sub>) 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<sup>6</sup> (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<sub>3</sub> (25 ml), and dried over MgSO<sub>4</sub>. 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<sub>f</sub> = 0.27 (petroleum ether/ethyl acetate 6 : 1); <sup>1</sup>H NMR  $\delta$  1.28 (ddd, 1 H, J = 1.7, 2.4, 8.6 Hz, 7-H<sub>a</sub>), 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<sub>a</sub>), 2.07 (dd, 1 H, J = 2.8, 14.9 Hz, 1'-H<sub>a</sub>), 2.16 (dd, 1 H, J = 11.3 Hz, 14.9 Hz, 1'-H<sub>b</sub>), 2.24 (d, 1 H, J = 8.6 Hz, 7-H<sub>b</sub>), 2.28 (ddd, 1 H, J = 4.0, 4.2, 12.5 Hz, 3-H<sub>b</sub>), 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 = 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); <sup>13</sup>C NMR  $\delta$  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<sub>2</sub>OR), 1325 (s), 1310 (s), 1250 (m), 1160 (s, SO<sub>2</sub>OR), 1140 (m), 1120 (m), 1065 (m), 1055 (m), 1000 (w), 920 (s), 875 (s), 860 (s) cm<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 214 (M<sup>+</sup>, 2), 135 (CH<sub>3</sub>CHOSO<sub>2</sub>CHCH<sub>2</sub><sup>+</sup>, 2), 107 (11), 106 (M<sup>+</sup> - CH<sub>2</sub>CHSO<sub>3</sub>H, 100), 105 (8), 92 (5), 91 (M<sup>+</sup> - CH<sub>2</sub>CHSO<sub>3</sub>H - CH<sub>3</sub>, CH<sub>2</sub>CHSO<sub>2</sub><sup>+</sup>, 51), 79 (C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 22), 78 (10), 77 (9), 66 (6), 65 (3), 53 (2), 45 (2), 43 (5), 41 (2), 39 (3). Anal. Calcd for C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>S: 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,<sup>34</sup> 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<sub>f</sub> = 0.27 (petroleum ether/ether 4 : 1);  $[\alpha]_D^{20} = -24.0$  (c = 1.0 in CHCl<sub>3</sub>); <sup>1</sup>H NMR  $\delta$  1.02 (d, 3 H, J = 6.8 Hz, 3'-CH<sub>3</sub>), 1.06 (d, 3 H, J = 6.7 Hz, 3'-CH<sub>3</sub>), 1.26 (dd, 1 H, J = 2.5, 8.6 Hz, 7-H<sub>a</sub>), 1.66 (ddd, 1 H, J = 2.5, 8.5, 12.6 Hz, 3-H<sub>a</sub>), 1.95 (m<sub>c</sub>, 1 H, 3'-H), 2.05 (dd, 1 H, J = 2.4, 14.7 Hz, 1'-H<sub>a</sub>), 2.17 (dd, 1 H, J = 11.8, 14.7 Hz, 1'-H<sub>b</sub>), 2.24 (d, 1 H, J = 8.6 Hz, 7-H<sub>b</sub>), 2.29 (ddd, 1 H, J = 3.9, 4.2, 12.6 Hz, 3-H<sub>b</sub>), 2.85 (ddd, 1 H, J = 1.5, 4.2, 8.5 Hz, 2-H), 3.04 (m<sub>c</sub>, 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); <sup>13</sup>C NMR  $\delta$  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<sub>2</sub>OR), 1332 (s), 1302 (m), 1256 (m), 1169 (s, SO<sub>2</sub>OR), 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<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 163 (M<sup>+</sup> - C<sub>6</sub>H<sub>7</sub>, 2), 135 (14), 134 (M<sup>+</sup> - CH<sub>2</sub>CHSO<sub>3</sub>H - O<sub>3</sub>H<sub>7</sub>, 22), 79 (C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 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<sub>12</sub>H<sub>18</sub>O<sub>3</sub>S: 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<sub>4</sub>, 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.

l-[3-(Phenylsulfonyl)cyclohexen-3-yl]-2-propanol (5), Diastereomeric Mixture. R<sub>f</sub> = 0.36 (petroleum ether/ethyl acetate 1 : 1); <sup>1</sup>H NMR  $\delta$  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<sub>c</sub>, 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<sub>c</sub>, 4 H, 1'-H), 7.54 (m<sub>c</sub>, 4 H), 7.64 (m<sub>c</sub>, 2 H), 7.87 (m<sub>c</sub>, 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<sub>2</sub>R), 1124 (s, br., SO<sub>2</sub>R), 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<sup>-1</sup>; MS *m/e* (relative intensity): 281 (M<sup>+</sup>+1, 0.8), 236 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>O, 1.8), 223 (2), 187 (8), 149 (10), 139 (M<sup>+</sup> - C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>, 18), 95 (100), 94 (46), 93 (33), 91 (33), 81 (C<sub>6</sub>H<sub>9</sub><sup>+</sup>, 16), 80 (24), 79 (64), 78 (33), 77 (46), 67 (40), 57 (18), 55 (28). Anal. Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>3</sub>S: 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 pyridiniumtoluenesulfonate (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 <sup>1</sup>H 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<sub>4</sub>. 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.

 $\begin{array}{l} 1-(1,3-Cyclohexadienyl)propan-2-yl Tetrahydropyran-2-yl Ether (7), 1:1 Mixture of 2 Diastereomers.\\ R_{\rm f}=0.45 (petroleum ether/ether 6:1); ^{1}H NMR \delta 1.11 (d, 3 H, J = 6.1 Hz), 1.23 (d, 3 H, J = 6.3 Hz), 1.48 - 1.60 (m, 8 H), 1.66 - 1.74 and 1.78 - 1.83 (m, 4 H), 2.07 - 2.21 (m, 10 H), 2.35 (dd, 1 H, J = 6.4, 13.7 Hz), 2.45 (dd, 1 H, J = 6.3, 13.5 Hz), 3.46 - 3.51 (m, 2 H), 3.86 - 3.99 (m, 4 H), 4.68 (dd, 1 H, J = 2.9, 2.9 Hz), 4.74 (dd, 1 H, J = 3.4, 3.4 Hz), 5.67 - 5.73 (m, 4 H), 5.85 - 5.89 (m, 2 H); IR 3038 (m), 2938 (s), 2871 (s), 2850 (m), 2825 (m), 1648 (w, C=C), 1590 (w, C=C), 1453 (m), 1440 (m), 1372 (m), 1352 (m), 1339 (m), 1322 (w), 1200 (s), 1122 (s), 1077 (s), 1032 (s), 1021 (s), 996 (s), 942 (w), 904 (w), 871 (m), 813 (m), 747 (w), 692 (m) cm^{-1}; MS (GC/MS, nearly identical spectra for both diastereomers)$ *m/e* $(relative intensity): 222 (M<sup>+</sup>, 1.3), 179 (2), 178 (12), 138 (M<sup>+</sup> - C<sub>5</sub>H<sub>8</sub>O, 8), 131 (6), 129 (M<sup>+</sup> - C<sub>7</sub>H<sub>9</sub>, 2), 121 (M<sup>+</sup> - C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>, 17), 120 (M<sup>+</sup> - C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>, 23), 105 (11), 101 (C<sub>5</sub>H<sub>9</sub>O<sub>2</sub><sup>+</sup>, 11), 93 (C<sub>7</sub>H<sub>9</sub><sup>+</sup>, 21), 92 (18), 91 (C<sub>7</sub>H<sub>7</sub><sup>+</sup>, 55), 86 (15), 85 (C<sub>5</sub>H<sub>9</sub>O<sup>+</sup>, 100), 84 (12), 79 (C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 61), 78 (30), 77 (25), 67 (42), 57 (38), 55 (30), 45 (22), 43 (61), 41 (47), 39 (18). HRMS Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub> (M<sup>+</sup>): 222.1620. Found: 222.1616. \\ \end{array}$ 

# 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 pyridiniump-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); <sup>1</sup>H NMR  $\delta$  1.23 (d, 3 H, J = 6.3 Hz, 3-H), 1.70 (s, 1 H, OH, removed by D<sub>2</sub>O-exchange), 2.05 - 2.22 (m, 6 H, 1-H, 5'-H, 6'-H), 3.93 (m<sub>c</sub>, 1 H, J = 6.3 Hz, 2-H), 5.74 (m<sub>c</sub>, 2 H, 2'-H, 4'-H), 5.90 (m<sub>c</sub>, 1 H, 3'-H); <sup>13</sup>C NMR  $\delta$  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<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 139 (M<sup>+</sup>+1, 4), 138 (M<sup>+</sup>, 37), 120 (M<sup>+</sup> - H<sub>2</sub>O, 8), 105 (M<sup>+</sup> - H<sub>2</sub>O - CH<sub>3</sub>, 10), 95 (7), 94 (58), 93 (30), 92 (15), 91 (C<sub>7</sub>H<sub>7</sub><sup>+</sup>, 77), 80 (13), 79 (C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 100), 78 (40), 77 (48), 66 (7), 65 (C<sub>5</sub>H<sub>5</sub><sup>+</sup>, 15), 51 (11), 45 (CH<sub>3</sub>CHOH<sup>+</sup>, 96), 43 (20), 41 (15), 39 (25). HRMS Calcd for C<sub>9</sub>H<sub>14</sub>O (M<sup>+</sup>): 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.

l - (1,3-Cyclohexadienyl)-propan-2-yl Vinylsulfonate (2c). R<sub>f</sub> = 0.43 (petroleum ether/ethyl acetate 3 : 1); <sup>1</sup>H NMR  $\delta$  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<sub>a</sub>), 2.41 (dd, 1 H, J = 7.2, 13.9 Hz, 1'-H<sub>b</sub>), 4.67 (m<sub>c</sub>, 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<sub>a</sub>), 6.31 (d, 1 H, J = 16.6 Hz, 2-H<sub>b</sub>), 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); <sup>1</sup>H NMR  $\delta$  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<sub>a</sub>), 1.76 (dddd, 1 H, *J* = 2.7, 2.7, 5.9, 13.4 Hz, 3-H<sub>a</sub>), 1.93 (dd, 1 H, *J* = 1.8, 14.5 Hz, 1'-H<sub>b</sub>), 2.08 (ddd, 1 H, *J* = 2.8, 9.8, 13.4 Hz, 3-H<sub>b</sub>), 2.75 (m<sub>c</sub>, 1 H, 4-H), 3.13 (dd, 1 H, *J* = 5.9, 9.8 Hz, 2-H), 4.93 (ddq, 1 H, *J*<sub>d</sub> = 1.8, 11.7 Hz, *J*<sub>q</sub> = 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); <sup>13</sup>C NMR  $\delta$  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<sub>2</sub>OR), 1338 (s), 1326 (s), 1296 (m), 1197 (m), 1172 (s, SO<sub>2</sub>OR), 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<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 229 (M<sup>+</sup>+1, 2), 228 (M<sup>+</sup>, 15), 200 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>, 12), 146 (M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub>, 5), 135 (CH<sub>3</sub>CHOSO<sub>2</sub>CHCH<sub>2</sub><sup>+</sup>, 2), 131 (3), 121 (7), 120 (M<sup>+</sup> - CH<sub>2</sub>CHSO<sub>3</sub>H, 22), 119 (19), 118 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub> - H<sub>2</sub>SO<sub>3</sub>, 42), 117 (5), 105 (M<sup>+</sup> - CH<sub>2</sub>CHSO<sub>3</sub>H - CH<sub>3</sub>, 11), 103 (4), 93 (12), 92 (88), 91 (CH<sub>2</sub>CHSO<sub>2</sub><sup>+</sup>, 100), 79 (13), 78 (15), 77 (11), 65 (8), 45 (14), 43 (11), 41 (12), 39 (9); Anal. Calcd for C<sub>11</sub>H<sub>16</sub>O<sub>3</sub>S: 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<sub>f</sub> = 0.47 (petroleum ether/ethyl acetate 4 : 1); <sup>1</sup>H NMR  $\delta$  1.39 (d, 3 H, J = 6.3 Hz, 1'-CH<sub>3</sub>), 1.75 (d, 3 H, J = 6.9 Hz, 7'-H), 2.42 (m<sub>c</sub>, 2 H, 2'-H), 4.64 (m<sub>c</sub>, 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<sub>a</sub>), 6.38 (dd, 1 H, J = 3.6, 16.7 Hz, 2-H<sub>b</sub>), 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 <sup>1</sup>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); <sup>13</sup>C NMR  $\delta$  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<sub>2</sub>OR), 1160 (s, br., SO<sub>2</sub>OR), 1070 (s), 1020 (s), 990 (m), 860 (s) cm<sup>-1</sup>. 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). <sup>1</sup>H NMR  $\delta$  1.07 (d, 3 H, J = 7.2 Hz, 5-CH<sub>3</sub>), 1.43 (d, 3 H, J = 6.3 Hz, 3'-H), 1.50 (dd, 1 H, J = 2.8, 12.0 Hz, 6-H<sub>a</sub>), 1.91 (ddd, 1 H, J = 2.4, 3.2, 14.2 Hz, 1'-H<sub>a</sub>), 1.99 (ddd, 1 H, J = 6.4, 10.9, 12.0 Hz, 6-H<sub>b</sub>), 2.11 (m<sub>c</sub>, 1 H, 1'-H<sub>b</sub>), 2.54 (m<sub>c</sub>, 1 H, 5-H), 2.77 (m<sub>c</sub>, 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<sub>d</sub> = 2.4, 11.6 Hz, J<sub>q</sub> = 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<sup>+</sup> - SO<sub>2</sub>, 1), 151 (5), 135 (5), 134 (M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub>, 37), 133 (8), 119 (M<sup>+</sup> - CH<sub>3</sub> - H<sub>2</sub>SO<sub>3</sub>, 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<sub>3</sub>) m/e (relative intensity): 234 (M · NH<sub>4</sub><sup>+</sup>, 100).

 $(1R^*, 2S^*, 5S^*, 2'R^*)$ -5-Methyl-2-propyl-cyclohex-3-ene-1,2'-sultone (11b). <sup>1</sup>H NMR  $\delta$  1.08 (d, 3 H, J = 6.9 Hz, 5-CH<sub>3</sub>), 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<sub>a</sub>), 2.08 (ddd, 1 H, J = 6.6, 12.4, 14.5 Hz, 1'-H<sub>b</sub>), 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<sub>d</sub> = 1.8, 6.7 Hz, J<sub>q</sub> = 6.7 Hz, 2'-H), 5.59 (ddd, 1 H, J = 2.3, 4.2, 10.0 Hz, 4-H), 5.65 (m<sub>c</sub>, 3-H). MS (GC/MS) *m/e* (relative intensity): 174 (3), 152 (M<sup>+</sup> - SO<sub>2</sub>, 0.1), 151 (0.3), 135 (3), 134 (M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub>, 5), 133 (1), 119 (M<sup>+</sup> - CH<sub>3</sub> - H<sub>2</sub>SO<sub>3</sub>, 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<sub>3</sub>) *m/e* (relative intensity): 234 (M · NH<sub>4</sub><sup>+</sup>, 100).

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

(*E*)-3,5-Hexadien-1-ol (8a)<sup>16</sup> (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); <sup>1</sup>H NMR  $\delta$  2.52 (m<sub>c</sub>, 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<sub>a</sub>), 5.16 (d, 1 H, J = 16.6 Hz, 6'-H<sub>b</sub>), 5.62 (dt, 1 H, J<sub>d</sub> = 15.0 Hz, J<sub>t</sub> = 7.2 Hz, 3'-H), 6.13 (d, 1 H, J = 9.3 Hz, 2-H<sub>a</sub>), 6.15 (dd, 1 H, J = 16.6 Hz, 6'-H<sub>b</sub>), 5.62 (dt, 1 H, J<sub>d</sub> = 15.0 Hz, J<sub>t</sub> = 7.2 Hz, 3'-H), 6.13 (d, 1 H, J = 9.3 Hz, 2-H<sub>a</sub>), 6.15 (dd, 1 H, J = 16.6 Hz, 6'-H<sub>b</sub>), 5.62 (dt, 1 H, J<sub>d</sub> = 15.0 Hz, J<sub>t</sub> = 7.2 Hz, 3'-H), 6.13 (d, 1 H, J = 9.3 Hz, 2-H<sub>a</sub>), 6.15 (dd, 1 H, J = 16.6 Hz, 6'-H<sub>b</sub>), 5.62 (dt, 1 H, J<sub>d</sub> = 15.0 Hz, J<sub>t</sub> = 7.2 Hz, 3'-H), 6.13 (dt, 1 H, J = 9.3 Hz, 2-H<sub>a</sub>), 6.15 (dd, 1 H, J = 16.6 Hz, 6'-H<sub>b</sub>), 5.62 (dt, 1 H, J<sub>d</sub> = 15.0 Hz, J<sub>t</sub> = 7.2 Hz, 3'-H), 6.13 (dt, 1 H, J = 9.3 Hz, 2-H<sub>a</sub>), 6.15 (dd, 1 H, J = 16.6 Hz, 6'-H<sub>b</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H<sub>a</sub>), 6.15 (dt, 1 H, J = 10.2 Hz, 6'-H\_a), 6'-H<sub>a</sub>), 6'-H<sub>a</sub>), 6'-H<sub>a</sub>), 6'-H<sub></sub>

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<sub>b</sub>), 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<sub>f</sub> = 0.35 (petroleum ether/ethyl acetate 3 : 1); <sup>1</sup>H NMR  $\delta$  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); <sup>13</sup>C NMR  $\delta$  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<sub>2</sub>OR), 1355 (s, br., SO<sub>2</sub>OR), 1339 (s), 1266 (s), 1259 (s), 1208 (s), 1163 (s, br., SO<sub>2</sub>OR), 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<sup>-1</sup>; Anal. Calcd for C<sub>8</sub>H<sub>12</sub>O<sub>3</sub>S: 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<sup>+</sup>, 0.1), 124 (M<sup>+</sup> - SO<sub>2</sub>, 4), 123 (20), 106 (M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub>, 77), 105 (35), 96 (25), 93 (20), 91 (CH<sub>2</sub>CHSO<sub>2</sub><sup>+</sup>, 100), 81 (13), 79 (76), 78 (95), 77 (39), 67 (C<sub>5</sub>H<sub>7</sub><sup>+</sup>, 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<sup>+</sup>+1, 0.4), 188 (M<sup>+</sup>, 5.5), 124 (M<sup>+</sup> - SO<sub>2</sub>, 3), 123 (5), 106 (M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub>, 48), 105 (43), 96 (8), 93 (12), 91 (CH<sub>2</sub>CHSO<sub>2</sub><sup>+</sup>, 52), 80 (17), 79 (100), 78 (70), 77 (30), 67 (C<sub>5</sub>H<sub>7</sub><sup>+</sup>, 11), 41 (14), 39 (18).

# Esterification of Alcohol 8c with Vinylsulfonyl Chloride

(*E*)-2,2-Dimethyl-6-methyl-5,7-octadien-3-ol (8c)<sup>18</sup> (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); <sup>1</sup>H NMR  $\delta 0.94$  [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>C], 1.66 (s, 3 H, 6'-CH<sub>3</sub>), 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<sub>a</sub>), 5.08 (d, 1 H, J = 17.5 Hz, 8'-H<sub>b</sub>), 5.44 (dd, 1 H, J = 7.4, 7.4 Hz, 5'-H), 5.87 (d, 1 H, J = 9.7 Hz, 2-H<sub>a</sub>), 6.21 (d, 1 H, J = 16.6 Hz, 2-H<sub>b</sub>), 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); <sup>1</sup>H NMR  $\delta$  1.01 (s, 9 H, 3'-CH<sub>3</sub>), 1.42 (ddd, 1 H, J = 12.0, 12.2, 13.9 Hz, 1'-H<sub>a</sub>), 1.70 (s, 3 H, 3-CH<sub>3</sub>), 1.78 (dddd, 1 H, J = 6.8, 12.4 Hz, 12.4 Hz, 12.4 Hz, 6-H<sub>a</sub>), 2.12 (ddd, 1 H, J = 1.8, 2.8, 13.9 Hz, 1'-H<sub>b</sub>), 2.18 (m<sub>c</sub>, 2 H, 5-H), 2.35 (m<sub>c</sub>, 1 H, 6-H<sub>b</sub>), 2.74 (m<sub>c</sub>, 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<sub>c</sub>, 1 H, 4-H); <sup>13</sup>C NMR  $\delta$  20.2 (t), 20.6 (q, 3-CH<sub>3</sub>), 23.9 (t), 25.5 (q, 3'-CH<sub>3</sub>), 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<sub>2</sub>OR), 1321 (s), 1215 (w), 1164 (s, SO<sub>2</sub>OR), 1068 (w), 967 (m), 938 (m), 925 (s), 887 (s), 865 (m), 833 (w), 797 (w), 616 (m), 566 (m), 498 (w) cm<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 259 (M<sup>+</sup>+1, 1), 258 (M<sup>+</sup>, 5), 193 (2), 179 (M<sup>+</sup> - SO<sub>2</sub> - CH<sub>3</sub>, 2), 177 (4), 176 (M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub>, 25), 175 (4), 161 (M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub> - CH<sub>3</sub>, 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<sub>3</sub>)<sub>3</sub>C<sup>+</sup>, 85], 55 (23), 43 (52), 41 (91). Anal. Calcd for C<sub>13</sub>H<sub>22</sub>O<sub>3</sub>S: 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<sub>f</sub> = 0.18 (petroleum ether/ether 5 : 1); <sup>1</sup>H NMR  $\delta$  0.99 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>C)], 1.69 (s, 3 H, 3-CH<sub>3</sub>), 1.84 (ddd, 1 H, J = 5.0, 10.2, 14.9 Hz), 1.99 - 2.09 (m, 1 H), 2.16 (m<sub>c</sub>, 2 H), 2.37 - 2.45 (m, 1 H), 2.46 - 2.65 (m, 1 H), 2.89 (m<sub>c</sub>, 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);<sup>35</sup> for spectroscopic data, see ref 36. This silyloxy ester was reduced to aldehyde **12** using di-*iso*-butylaluminum hydride at -90 °C (91 % yield);<sup>37</sup> 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); <sup>1</sup>H NMR  $\delta$  0.058 [s, 3 H, (CH<sub>3</sub>)<sub>2</sub>Si], 0.060 [s, 3 H, (CH<sub>3</sub>)<sub>2</sub>Si], 0.89 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>CSi], 1.15 (d, 3 H, J = 6.1 Hz, 1-H), 2.17 - 2.30 (m, 2 H), 3.93 (m<sub>c</sub>, 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<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 358 (M<sup>+</sup>, 0.5), 343 (M<sup>+</sup> - CH<sub>3</sub>, 1), 303 [M<sup>+</sup> - (CH<sub>3</sub>)<sub>3</sub>C, 16], 301 [M<sup>+</sup> - (CH<sub>3</sub>)<sub>3</sub>C, 30], 299 [M<sup>+</sup> - (CH<sub>3</sub>)<sub>3</sub>C, 17], 259 (15), 257 (30), 255 (16), 227 (M<sup>+</sup> - TBDMSO, 2), 205 (11), 203 (19), 201 (13), 159 (TBDMSO=CHCH<sub>3</sub><sup>+</sup>, 15), 139 (22), 137 (19), 103 (30), 83 (100), 75 [(CH<sub>3</sub>)<sub>2</sub>Si=OH<sup>+</sup>, 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 mixture is poured into sat. aqueous Na<sub>2</sub>CO<sub>3</sub> (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<sub>4</sub>, 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); <sup>1</sup>H NMR  $\delta$  0.07 (s, 3 H, TBDMS-CH<sub>3</sub>), 0.08 (s, 3 H, TBDMS-CH<sub>3</sub>), 0.14 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>Si], 0.89 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>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<sub>a</sub>), 2.38 (dd, 1 H, J = 6.1, 16.7 Hz, 3-H<sub>b</sub>), 3.95 (m<sub>c</sub>, 1 H, 2-H); <sup>13</sup>C NMR  $\delta$  -4.7 (q, TBDMS-CH<sub>3</sub>), -4.6 (q, TBDMS-CH<sub>3</sub>), 0.1 (q, (CH<sub>3</sub>)<sub>3</sub>Si), 18.1 (s, (CH<sub>3</sub>)<sub>3</sub>C), 23.5 (q, C-1), 25.9 (q, (CH<sub>3</sub>)<sub>3</sub>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<sup>-1</sup>; MS (GC/MS) m/e (relative intensity): 255 (M<sup>+</sup> - CH<sub>3</sub>, 3), 215 (8), 214 (16), 213 [M<sup>+</sup> - (CH<sub>3</sub>)<sub>3</sub>C, 56], 171 (14), 170 (16), 169 (72), 159 (TBDMSO=CHCH<sub>3</sub><sup>+</sup>, 54), 155 (10), 147 (28), 141 (12), 115 (TBDMS<sup>+</sup>, 12), 103 (18), 99 (10), 85 (8), 83 (12), 75 [(CH<sub>3</sub>)<sub>2</sub>Si=OH<sup>+</sup>, 20], 73 [(CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>, 100], 59 (14), 55 (12), 45 (17), 43 (12), 41 (8); Anal. Calcd for C<sub>14</sub>H<sub>30</sub>OSi<sub>2</sub>: 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<sub>2</sub>ZrCl<sub>2</sub> (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<sub>4</sub>Cl (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<sub>2</sub>SO<sub>3</sub> (15 ml), filtered to remove precipitated ZrO<sub>2</sub>, and the filtrate is washed with sat. aqueous NaHCO3 (15 ml) and brine (15 ml). After drying over MgSO4 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<sup>+</sup> - CH<sub>3</sub>, 0.2), 342 (M<sup>+</sup> - C<sub>4</sub>H<sub>8</sub>, 2), 341 (M<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>, 8), 267 (M<sup>+</sup> - TBDMSO, 1), 259 (3), 253 (6), 185 (7), 159 (TBDMSO=CHCH<sub>3</sub><sup>+</sup>, 38), 147 (20), 141 (11), 125 (4), 115 (TBDMS<sup>+</sup>, 14), 103 (12), 97 (13), 75 [(CH<sub>3</sub>)<sub>2</sub>SiOH<sup>+</sup>,18], 73 [(CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>, 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<sub>4</sub>, 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<sub>3</sub> (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<sub>4</sub>. 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<sup>+</sup> - CH<sub>3</sub>, 0.1), 242 (M<sup>+</sup> - C<sub>4</sub>H<sub>8</sub>, 0.8), 241 (M<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>, 3), 167 (4), 160 (10), 159 (TBDMSO=CHCH<sub>3</sub><sup>+</sup>, 66), 153 (14), 147 (31), 133 (4), 115 (TBDMS<sup>+</sup>, 24), 103 (22), 75 [(CH<sub>3</sub>)<sub>2</sub>SiOH<sup>+</sup>, 13], 73 [(CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>, 100], 59 (10), 45 (8).

(Z)-5-Trimethylsilyl-4,6-heptadien-2-ol (8d).  $R_f = 0.20$  (petroleum ether/ether 3 : 1); <sup>1</sup>H NMR  $\delta$  0.20 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>Si], 1.22 (d, 3 H, J = 6.4 Hz, 1-H), 2.35 (m<sub>c</sub>, 2 H, 3-H), 3.88 (m<sub>c</sub>, 1 H, 2-H), 4.87 (dd, 1 H, J = 1.9, 10.6 Hz, 7-H<sub>a</sub>), 5.08 (dd, 1 H, J = 1.9, 17.3 Hz, 7-H<sub>b</sub>), 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); <sup>13</sup>C NMR  $\delta$  0.6 [q, (CH<sub>3</sub>)<sub>3</sub>Si], 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<sup>-1</sup>; MS (GC/MS) m/e (relative intensity): 169 (M<sup>+</sup> - CH<sub>3</sub>, 14), 155 (2), 153 (1), 139 (M<sup>+</sup> - C<sub>2</sub>H<sub>5</sub>O, 5), 125 [CH<sub>2</sub>CHC(TMS)CH<sup>+</sup>, 19], 109 (4), 95 (13), 93 (13), 85 (4), 79 (7), 75 [(CH<sub>3</sub>)<sub>2</sub>SiOH<sup>+</sup>, 49], 74 (11), 73 [(CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>, 100], 67 (5), 59 (5), 53 (4), 45 (CH<sub>3</sub>CHOH<sup>+</sup>, 36), 43 (12), 39 (7). HRMS Calcd for C<sub>10</sub>H<sub>20</sub>OSi (M<sup>+</sup> - CH<sub>3</sub>): 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<sub>f</sub> = 0.42 (petroleum ether/ether 4 : 1); <sup>1</sup>H NMR  $\delta$  0.12 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>Si], 1.41 (d, 3 H, J = 6.4 Hz, 3'-H), 1.46 - 1.54 (m, 1 H, 1'-H<sub>a</sub>), 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<sub>b</sub>), 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<sub>c</sub>, 1 H, 4-H). <sup>13</sup>C NMR  $\delta$  -0.1 [q, (CH<sub>3</sub>)<sub>3</sub>Si], 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<sub>2</sub>OR), 1329 (m), 1251 (m), 1201 (w), 1173 (s, SO<sub>2</sub>OR), 1125 (m), 1090 (w), 1007 (w), 938 (m), 875 (s), 836 (s), 809 (m), 744 (w) cm<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 259 (M<sup>+</sup> - CH<sub>3</sub>, 27), 211 (8), 209 (4), 193 (11), 177 (M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub> - CH<sub>3</sub>, 5), 161 (10), 149 (7), 135 (9), 123 (25), 121 (24), 119 [M<sup>+</sup> - H<sub>2</sub>SO<sub>3</sub> - (CH<sub>3</sub>)<sub>3</sub>Si, 19], 105 (12), 93 (35), 91 (59), 79 (24), 75 [(CH<sub>3</sub>)<sub>2</sub>SiOH<sup>+</sup>, 32], 73 [(CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>, 100], 59 (18), 53 (7), 45 (31), 43 (35), 39 (19). HRMS Calcd for C<sub>11</sub>H<sub>19</sub>O<sub>3</sub>SSi (M<sup>+</sup> - CH<sub>3</sub>): 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<sup>30</sup> (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<sub>2</sub>CO<sub>3</sub> (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<sub>2</sub>SO<sub>3</sub> (15 ml), 2 N NaOH (25 ml), sat. aqueous Na<sub>2</sub>CO<sub>3</sub> (15 ml), and dried over MgSO<sub>4</sub>. 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) <sup>1</sup>H NMR  $\delta$  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<sub>a</sub>), 1.98 (ddd, 1 H, J = 0.6, 8.8, 15.2 Hz, 1'-H<sub>b</sub>), 2.09 - 2.12 (m, 2 H), 2.98 (m<sub>c</sub>, 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); <sup>13</sup>C NMR  $\delta$  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<sup>-1</sup>; MS (GC/MS) m/e (relative intensity): 181 (M<sup>+</sup>+1, 3), 180 (M<sup>+</sup>, 8), 165 (M<sup>+</sup> - CH<sub>3</sub>, 4), 163 (M<sup>+</sup> - OH, 15), 137 (12), 135 (M<sup>+</sup> -CH<sub>3</sub>CHOH, 10), 134 (14), 121 (8), 120 (M<sup>+</sup> - CH<sub>2</sub>CO - H<sub>2</sub>O, 40), 119 (21), 108 (10), 107 (10), 105 (M<sup>+</sup> -CH<sub>2</sub>CO - H<sub>2</sub>O - CH<sub>3</sub>, 16), 94 (63), 93 (27), 92 (21), 91 (96), 79 (100), 78 (45), 77 (37), 65 (16), 51 (18), 45 (CH<sub>3</sub>CHOH<sup>+</sup>, 59), 43 (30), 39 (43); Anal. Calcd for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>: 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<sub>f</sub> = 0.53 (dichloromethane/acetone 2 : 1) <sup>1</sup>H NMR  $\delta$  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<sub>a</sub>, 3-H<sub>b</sub>, 7-H<sub>a</sub>), 2.25 (ddd, 1 H, J = 2.4, 4.1, 9.1 Hz, 7-H<sub>b</sub>), 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); <sup>13</sup>C NMR  $\delta$  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<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 166 (M<sup>+</sup>, 4), 151 (M<sup>+</sup> - CH<sub>3</sub>, 29), 125 (4), 124 (M<sup>+</sup> - CH<sub>2</sub>CO, 42), 122 (3), 107 (6), 106 (M<sup>+</sup> - CH<sub>2</sub>CO - H<sub>2</sub>O, 4), 105 (5), 93 (6), 91 (M<sup>+</sup> - CH<sub>3</sub> - CH<sub>2</sub>CO - H<sub>2</sub>O, 25), 80 (M<sup>+</sup> - CH<sub>2</sub>CO - CH<sub>3</sub>CHO, 100), 79 (C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 69), 78 (15), 77 (45), 65 (6), 53 (8), 51 (9), 45 (CH<sub>3</sub>CHOH<sup>+</sup>, 56), 43 (18), 41 (9), 39 (18). Anal. Calcd for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>: 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<sub>f</sub> = 0.26 (petroleum ether/ethyl acetate 3 : 1);  $[\alpha]_D^{20} = -571.8$  (c = 1 in CHCl<sub>3</sub>); <sup>1</sup>H NMR  $\delta$  0.93 (d, 3 H, J = 6.9 Hz, 3'-CH<sub>3</sub>), 0.94 (d, 3 H, J = 6.9 Hz, 3'-CH<sub>3</sub>), 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<sub>2</sub>O-exchange), 1.85 (dd, 1 H, J = 2.9, 15.0 Hz, 1'-H<sub>a</sub>), 1.94 (dd, 1 H, J = 9.7, 15.0 Hz, 1'-H<sub>b</sub>), 1.99 (dd, 1 H, J = 4.4, 16.6 Hz, 3-H<sub>a</sub>), 2.06 (d, 1 H, J = 9.2 Hz, 7-H<sub>a</sub>), 2.10 (ddd, 1 H, J = 0.8, 2.3, 16.6 Hz, 3-H<sub>b</sub>), 2.24 (ddd, 1 H, J = 2.3, 4.3, 9.2 Hz, 7-H<sub>b</sub>), 3.15 (s, br., 1 H, 4-H), 3.42 (m<sub>c</sub>, 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); <sup>13</sup>C NMR  $\delta$  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., 0-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<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 195 (M<sup>+</sup>+1, 0.1), 194 (M<sup>+</sup>, 0.6), 176 (M<sup>+</sup> - H<sub>2</sub>O, 0.2), 153 (3), 152 (M<sup>+</sup> - CH<sub>2</sub>CO, 18), 151 (M<sup>+</sup> - CH<sub>2</sub>CO - H<sub>2</sub>O - C<sub>3</sub>H<sub>7</sub>, 6), 81 (12), 80 [M<sup>+</sup> - CH<sub>2</sub>CO - (CH<sub>3</sub>)<sub>2</sub>CHCHO, 100], 79 (C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 25), 77 (10), 73 (18), 57 (3), 55 (13), 43 (7), 41 (6), 39 (5). HRMS Calcd for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>S (M<sup>+</sup>): 194.1307.

# 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<sub>4</sub>, 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<sub>f</sub> = 0.41 (petroleum ether/ethyl acetate 6 : 1); <sup>1</sup>H NMR  $\delta$  1.18 (m<sub>c</sub>, 13 H, CH<sub>3</sub>, 7-H<sub>a</sub>), 1.47 (d, 3 H, J = 6.2 Hz, 3'-H), 1.90 (dd, 1 H, J = 1.9, 14.4 Hz, 1'-H<sub>a</sub>), 1.97 (dd, 1 H, J = 2.3, 12.2 Hz, 3-H<sub>a</sub>), 2.35 (d, 1 H, J = 8.6 Hz, 7-H<sub>b</sub>), 2.46 (dd, 1 H, J = 3.7, 12.2 Hz, 3-H<sub>b</sub>), 2.59 (dd, 1 H, J = 12.3, 14.4 Hz, 1'-H<sub>b</sub>), 2.98 (m<sub>c</sub>, 1 H, 4-H), 4.79 (ddq, J<sub>d</sub> = 1.9, 12.3 Hz, J<sub>q</sub> = 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); <sup>13</sup>C NMR  $\delta$  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<sub>2</sub>OR), 1274 (m), 1176 (s), 1162 (s, SO<sub>2</sub>OR), 1138 (s), 1083 (s), 1031 (s), 965 (w), 927 (m), 878 (s), 796 (m), 713 (m), 647 (m), 595 (s), 564 (m) cm<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 340 (M<sup>+</sup>, 0.3), 325 (M<sup>+</sup> - CH<sub>3</sub>, 1.1), 282 [M<sup>+</sup> - (CH<sub>3</sub>)<sub>2</sub>CO, 0.6], 276 (M<sup>+</sup> -SO<sub>2</sub>, 0.4), 261 (C<sub>10</sub>H<sub>18</sub>BO<sub>5</sub>S<sup>+</sup>, 0.5), 218 (6), 217 (C<sub>8</sub>H<sub>14</sub>BO<sub>4</sub>S<sup>+</sup>, 11), 216 (2), 175 (5), 159 (5), 132 (15), 119 (15), 118 (14), 107 (26), 106 (C<sub>8</sub>H<sub>10</sub><sup>+</sup>, 100), 101 (15), 91 (C<sub>7</sub>H<sub>7</sub><sup>+</sup>, 78), 83 (20), 79 (C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 18), 78 (12), 67 (8), 55 (10), 43 (11), 41 (12). Anal. Calcd for C<sub>16</sub>H<sub>25</sub>BO<sub>5</sub>S: 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  $\alpha$ -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<sub>f</sub> = 0.30 (petroleum ether/dichloromethane 2 : 1); <sup>1</sup>H NMR  $\delta$  1.50 (d, 3 H, J = 6.2 Hz, 3'-H), 1.50 (m<sub>c</sub>, 1 H, 7-H<sub>a</sub>), 1.79 (dd, 1 H, J = 3.4, 13.7 Hz, 3-H<sub>a</sub>), 1.97 (dd, 1 H, J = 1.9, 15.1 Hz, 1'-H<sub>a</sub>), 2.40 (dd, 1 H, J = 12.2, 15.1 Hz, 1'-H<sub>b</sub>), 2.63 (d, 1 H, J = 9.2 Hz, 7-H<sub>b</sub>), 2.97 (dd, 1 H, J = 3.7, 13.7 Hz, 3-H<sub>b</sub>), 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); <sup>13</sup>C NMR  $\delta$  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<sub>2</sub>OR), 1290 (m), 1280 (m), 1255 (m), 1160 (s, br., SO<sub>2</sub>OR), 1055 (s, br., C-0), 1005 (s), 980 (m), 915 (s), 870 (s, br.), 830 (s), 805 (m), 780 (s), 750 (s), 715 (s) cm<sup>-1</sup>; MS (GC/MS) m/e (relative intensity): 248 (M<sup>+</sup>, 0.05), 171 and 169 [CH<sub>3</sub>CHOSO<sub>2</sub>C(Cl)CH<sub>2</sub><sup>+</sup>, 0.05 and 0.25], 149 (M<sup>+</sup> - SO<sub>2</sub> - Cl, 0.05), 125 [CH<sub>2</sub>C(Cl)SO<sub>2</sub><sup>+</sup>, 1], 107 (10), 106 [M<sup>+</sup> - CH<sub>2</sub>C(Cl)SO<sub>3</sub>H, 100], 105 (10), 103 (3), 100 (7), 92 (4), 91 [M<sup>+</sup> - CH<sub>3</sub> - CH<sub>2</sub>C(Cl)SO<sub>3</sub>H, 52], 79 (C<sub>6</sub>H<sub>7</sub><sup>+</sup>, 32), 78 (12), 77 (15), 65 (C<sub>5</sub>H<sub>5</sub><sup>+</sup>, 8), 64 (4), 53 (C<sub>4</sub>H<sub>5</sub><sup>+</sup>, 3), 45 (13), 43 (16), 41 (7), 40 (10), 39 (C<sub>3</sub>H<sub>3</sub><sup>+</sup>, 11). Anal. Calcd for C<sub>10</sub>H<sub>13</sub>ClO<sub>3</sub>S: 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<sub>4</sub> 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<sub>f</sub> = 0.40 (petroleum ether/ethyl acetate 4 : 1); <sup>1</sup>H NMR  $\delta$  1.42 (ddd, 1 H, J = 2.2, 2.7, 8.8 Hz, 7-H<sub>a</sub>), 1.48 (d, 3 H, J = 6.2 Hz, 3'-H), 1.70 (dd, 1 H, J = 2.7, 13.1 Hz, 3-H<sub>a</sub>), 1.95 (dd, 1 H, J = 2.1, 15.0 Hz, 1'-H<sub>a</sub>), 2.31 (dd, 1 H, J = 12.1, 15.0 Hz, 1'-H<sub>b</sub>), 2.35 (s, 3 H, SCH<sub>3</sub>), 2.65 (dd, 1 H, J = 3.7, 13.1 Hz, 3-H<sub>b</sub>), 2.81 (d, 1 H, J = 8.8 Hz, 7-H<sub>b</sub>), 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); <sup>13</sup>C NMR  $\delta$  14.7 (q, SCH<sub>3</sub>), 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<sub>2</sub>OR), 1250 (w), 1200 (w), 1155 (s, br., SO<sub>2</sub>OR), 1075 (m), 1060 (s), 1010 (m), 960 (w), 920 (s), 870 (s), 825 (m), 785 (m), 740 (w), 710 (m) cm<sup>-1</sup>; MS (GC/MS) *m/e* (relative intensity): 261 (M<sup>+</sup>+1, 0.8), 260 (M<sup>+</sup>, 6.6), 196 (M<sup>+</sup> - SO<sub>2</sub>, 6), 181 [CH<sub>3</sub>CHOSO<sub>2</sub>C(SCH<sub>3</sub>)CH<sub>2</sub>+, 1], 149 (M<sup>+</sup> - SO<sub>2</sub> - SCH<sub>3</sub>, 70), 137 [CH<sub>2</sub>C(SCH<sub>3</sub>)SO<sub>2</sub>+, 5], 133 (1), 131 (2), 121 (4), 120 (5), 107 (88), 106 [M<sup>+</sup> - CH<sub>2</sub>C(SCH<sub>3</sub>)SO<sub>3</sub>H, 100], 105 (26), 91 [M<sup>+</sup> - CH<sub>3</sub> - CH<sub>2</sub>C(SCH<sub>3</sub>)SO<sub>3</sub>H, 78], 79 (C<sub>6</sub>H<sub>7</sub>+, 50), 78 (20), 77 (29), 73 (15), 65 (C<sub>5</sub>H<sub>5</sub>+, 15), 64 (50), 53 (C<sub>4</sub>H<sub>5</sub>+, 11), 51 (12), 48 (25), 47 (CH<sub>3</sub>S<sup>+</sup>, 9), 45 (13), 43 (14), 39 (C<sub>3</sub>H<sub>3</sub><sup>+</sup>, 20). Anal. Calcd for C<sub>11</sub>H<sub>16</sub>O<sub>3</sub>S<sub>2</sub>: C, 50.74; H, 6.19.

#### 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<sub>4</sub>, 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. <sup>1</sup>H 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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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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