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Journal:	<i>Organic & Biomolecular Chemistry</i>
Manuscript ID	OB-ART-11-2024-001781.R1
Article Type:	Paper
Date Submitted by the Author:	18-Dec-2024
Complete List of Authors:	O'Neil, Gregory; Western Washington University, Department of Chemistry Clark, Trevor; Western Washington University, Department of Chemistry Jones, Adam; Western Washington University, Department of Chemistry Wallace, Calvin; Western Washington University, Department of Chemistry Carnahan, D. ; Western Washington University, Department of Chemistry Crockett, Henry; Western Washington University, Department of Chemistry

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Diastereoselective β -Hydroxy Vinylsulfone Isomerizations

G. W. O'Neil,* T. D. Clark, A. P. Jones, C. Wallace, D. M. Carnahan, and H. Crockett

Department of Chemistry, Western Washington University, Bellingham, WA 98225 (USA)

*Corresponding author. Email: oneilg@wwu.edu

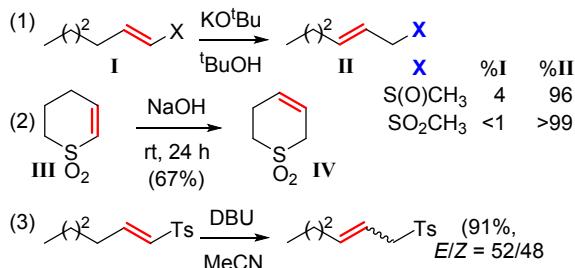
Abstract. Vinylic phenylsulfones containing a β -hydroxyl stereocenter undergo a diastereoselective isomerization to the corresponding allylic isomer upon treatment with 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU). Diastereoselectivity of this reaction increases with increasing size of the group attached to the carbinol carbon (up to >20:1 d.r. with a *tert*-butyl). Isolated yields of the isomerized allylic 1,2-hydroxy phenylsulfone products were comparable among the different vinylsulfones tested (59–66%). The major competing pathway was a C–C bond cleavage process, proposed to occur after the initial isomerization event. The sense of diastereoselection was consistent among all substrates investigated, in favor of the *erythro*-isomer based on NMR analysis.

Introduction

The positional isomerization of carbon–carbon double bonds continues to attract considerable attention as a synthetic tool,¹ owing to the wide availability of olefins as feedstock chemicals and the presence of C–C double bonds in final target structures. Additionally, this transformation benefits from positive atom economy,² in line with green chemistry principles.³ Often, but not always,^{4–6} these processes are driven by thermodynamic considerations, where a less-stable C–C double bond is selectively isomerized to a more stable position. Examples include the isomerization of γ,β -unsaturated esters⁷ and allylbenzenes⁸ to their conjugated isomers. Isomerization can also occur sequentially over longer distances in the presence of metal catalysts such as palladium^{9,10} and ruthenium,^{11,12} favoring formation of the most stable double bond positional isomer. Preventing this thermodynamically controlled chain walking isomerization, for example to select for a monoisomerization product, presents a challenge for these types of processes.¹³

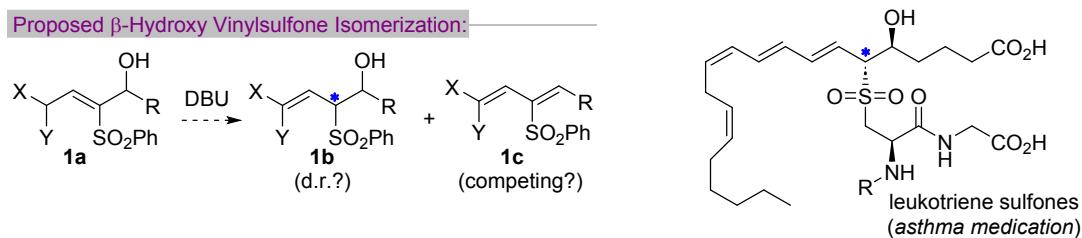
In 1964, O'Connor and Lyness reported a deconjugative monoisomerization of vinyl sulfoxides and sulfones to their allylic isomers upon treatment with potassium *tert*-butoxide (Scheme 1, eq. 1).¹⁴ This was consistent with Fehnel's previous observation that cyclic vinylsulfone **III** readily tautomerizes to **IV** in the presence of sodium hydroxide (eq. 2).¹⁵ Later, Inomata and coworkers showed that a weaker base DBU is similarly capable of vinylic- to allylic sulfone isomerizations, and also studied stereochemical aspects (e.g. *E*:*Z* ratios of the products) of this transformation (eq. 3).^{16–19} Inomata's protocol was subsequently adopted for the total synthesis of the natural products ingenol²⁰ and avermectin B1a,²¹ and has also featured in the synthesis of vinyl azides.²² Theory supports a thermodynamic preference for the allylic isomer in these systems, explained in part by the destabilizing effect of a positively charged sulfur attached to an sp^2 hybridized carbon, presumably due to shorter bond lengths and thus closer proximity to the positively charged carbon nucleus.²³

Scheme 1. Previously reported isomerization of vinylsulfones to their allylic isomer.



Recently our group has been investigating reactions of allylic β -hydroxy phenyl sulfones of type **1b** (Scheme 2).²⁴ Among the different preparative approaches considered for these compounds, one option that surfaced was an isomerization from a vinyl precursor **1a**. This proposal, however, raised several important questions and concerns. Foremost, it was expected that dehydration and formation of the corresponding conjugated diene **1c** would compete. If successful, however, the reaction would produce a new sulfone-containing carbon stereocenter (*). Sulfone stereocenters can be found in a number of medicinally relevant molecules,²⁵ with pertinent examples being the leukotriene sulfones.²⁶ New approaches to their synthesis could therefore be of value to drug discovery programs. Moreover, the presence of an existing hydroxyl stereocenter in **1a** might render the reaction diastereoselective, providing a handle to control the relative (or absolute if **1a** can be prepared enantioenriched) geometry of the final product.

Scheme 2. Proposed isomerization of **1a** for the preparation of allylic β -hydroxy phenylsulfones **1b**.

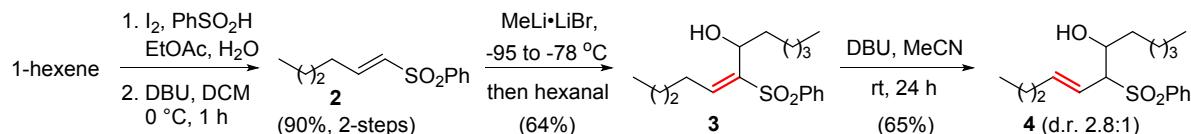


Herein we report results from studies on the diastereoselective isomerization of hydroxy vinylphenylsulfones to *E*-allylic sulfone products. Our results indicate that diastereoselectivity is affected by sterics associated with the group attached to the carbinol carbon ("R" in Scheme 2), and that the sense of diastereoselectivity was the same for all substrates tested in favor of the *erythro*-isomer. Rather than dehydration, the primary competing reaction was a C-C bond cleavage process. Nonetheless, good yields (59-66%) and excellent diastereoselectivity (up to >20:1) of the allylic sulfone product could be obtained.

Results and Discussion

Our studies began with the preparation of β -hydroxy vinylsulfone **3** (Scheme 3). This was accomplished through the union of 1-hexene and hexanal via intermediate vinylsulfone **2** according to the combined procedures of Inomata^{16,17} (for vinylsulfone synthesis) and Eisch and Galle²⁷ (for aldehyde addition). Treatment of **3** with DBU in acetonitrile (MeCN) at room temperature for 24 h resulted in a mixture of products, where the major component was the double-bond isomerized allylic sulfone **4** that was isolated in 65% yield as an inseparable 2.8:1 mixture of diastereomers.

Scheme 3. Synthesis and DBU isomerization of β -hydroxy vinyl phenylsulfone **3**.



The use of COSY NMR allowed for the assignment of signals belonging to major- and minor diastereomers of **4** as well as identification of a single component giving rise to unexpected signals in the alkene region that were coupled to a doublet at 3.72 ppm (Figure 1). Further analysis led to the assignment of these signals belonging to allylic sulfone **5**, which was confirmed by comparison to reported NMR data²⁸ as well as its independent synthesis by the isomerization of **2** with DBU. Interestingly, a ~1:1 *cis:trans* mixture of **5** was obtained from **2** (consistent with Inomata's results¹⁶), whereas formation of **5** from **3** was highly *trans*-selective under the same conditions.²⁹ Similarly, only the *trans*-isomer of **4** was observed from the isomerization of **3** by ¹H NMR analysis ($J_{ab} = 15.5$ Hz).

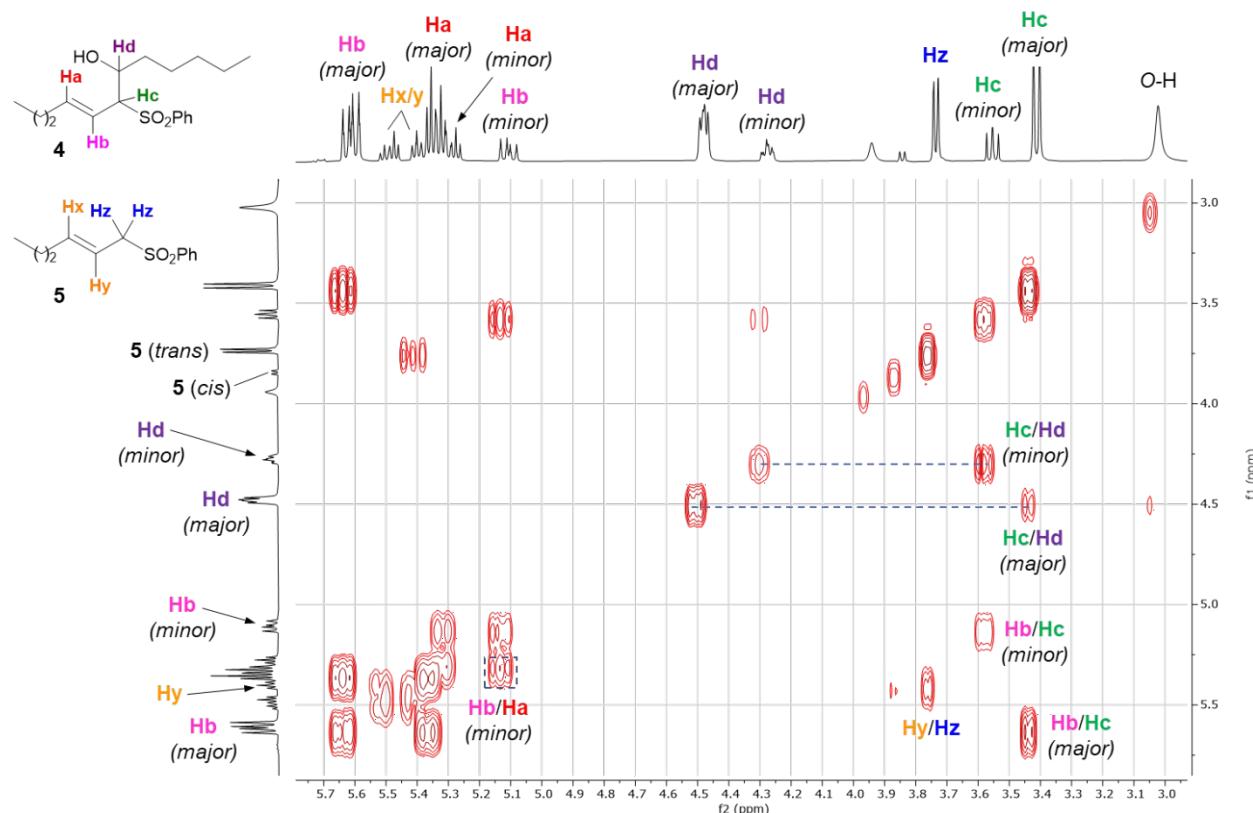
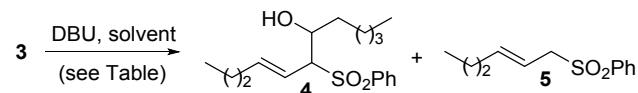


Figure 1. COSY NMR spectrum of the product mixture obtained upon treatment of vinylsulfone **3** with DBU in MeCN at room temperature for 24 h. Cross-peak analysis allowed for the assignment of signals $\text{H}_a\text{-H}_d$ belonging to major- and minor diastereomers of **4** (d.r. 2.8:1) as well as identification of compound **5** as the major side-product.

Other solvents besides MeCN were examined in the DBU isomerization of **3** (Table 1). In general, greater solvent polarity resulted in higher conversions but also increased amounts of side-product **5**. For instance, the reaction in DMSO proceeded with complete conversion but gave a 1.6:1 ratio of **4:5** (Entry 5) Conversely, the use of less polar chloroform (CHCl_3) as solvent under otherwise identical conditions resulted in only 41% conversion, but far greater selectivity for the isomerized product **4** (19.4:1 **4:5**;

Entry 4). An outlier was toluene (PhMe), where lower conversion (31%) was accompanied by significant amounts of **5** (3.6:1 **4:5**; Entry 6), greater than what was obtained with MeCN and methanol (MeOH; 6.7-6.8:1 **4:5**; Entries 1 and 3). Heating the reaction increased conversion as well as compound **5** formation (Entries 7 and 8). Cooling the reaction (e.g. to 0 °C) or reducing the equivalents of DBU resulted in significantly lower conversion (Entries 9 and 10). Balancing conversion with the yield and d.r. of **4**, the use of MeCN and 4.0 equivalents of DBU at room temperature for 20 h was selected as optimal for this transformation.

Table 1. Results from solvent studies on the DBU isomerization of **3**.

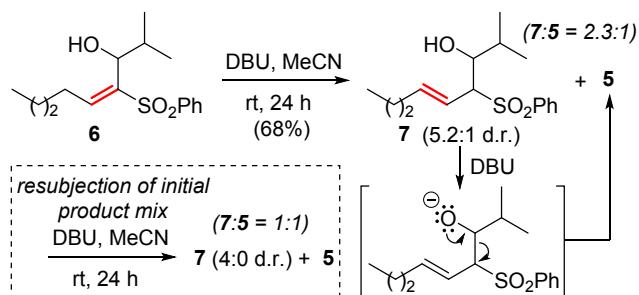


Entry	Solvent ^A	% Conv. ^B	4 d.r. ^C	4 : 5 ^C
1	MeCN	88	2.8 : 1	6.8 : 1
2	THF	57	1.6 : 1	20.0 : 1
3	MeOH	68	2.5 : 1	6.7 : 1
4	CHCl ₃	41	2.1 : 1	19.4 : 1
5	DMSO	100	3.3 : 1	1.6 : 1
6	PhMe	31	2.0 : 1	3.6 : 1
7	THF ^D	91	2.1 : 1	1 : 2.0
8	CHCl ₃ ^D	52	2.1 : 1	7.2 : 1
9	MeCN ^E	11	ND ^F	ND ^F
10	MeCN ^G	32	2.9 : 1	9.0 : 1

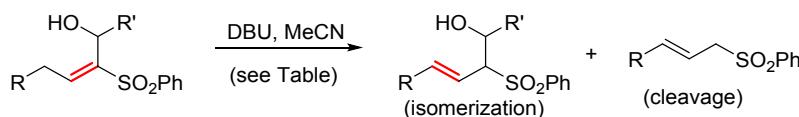
Notes for Table: ^AReactions were performed by adding DBU (4.0 equiv.) to a 0.4 M solution of the vinylsulfone in MeCN and stirring at room temperature for 20 h. ^BCalculated by dividing the product ¹H NMR integration values (major + minor diastereomer) by the sum of product + starting material integrations. ^CFrom ¹H NMR integrations. ^DPerformed at 50 °C. ^EPerformed at 0 °C. ^FNot determined. ^GPerformed with 2.0 equivalents of DBU.

Side-product **5** was also observed in the mixture obtained from isobutyraldehyde-derived hydroxy vinylsulfone **6** upon treatment with DBU in MeCN at rt for 24 h (Scheme 4). The isomerized product **7** was nonetheless the major component, obtained in 68% isolated yield as a 5.2:1 mixture of diastereomers. Formation of **5** from the reaction of **6** (and **3**) is proposed to proceed via a mechanism involving deprotonation of the hydroxyl group followed by a retro-sulfonyl anion aldehyde addition. In support of this mechanism, resubjection of the initially formed 2.3:1 mixture of **7** and **5** with DBU resulted in increased amounts of **5** relative to **7** (now ~1:1), supporting the intermediacy of **7** in the formation of **5**. There was also a slight erosion in the d.r. of **7** (from 5.2:1 to 4.0:1) upon resubjection, perhaps indicating differences in rate for this C-C bond cleavage process between the two diastereomers of **7**.

Scheme 4. Isomerization of **6** and resubjection of the initially formed product mixture. The increased amounts of **5** relative to **7** upon resubjection is consistent with a mechanism involving formation of **7** from **6** followed by the conversion of **7** to **5**.



A series of additional β -hydroxy vinylsulfones were synthesized and examined in their isomerization with DBU to the corresponding allylic isomer (Table 2). A clear trend was observed with larger groups attached to the carbinol carbon resulting in isomerized products with higher d.r. For instance, a methyl group at this position as in compound **8** gave the isomerized hydroxy allylic sulfone with a d.r. of 1.8:1 (Entry 1), whereas an isopropyl resulted in a d.r. of 5.2:1 (Entry 4, *i*-Pr, **6**), and *tert*-butyl produced a single diastereomer by ^1H NMR (Entries 7 and 10, *t*-Bu, **10**). Reducing the reaction time for **6** to 16 h (Entry 5) and 8 h (Entry 6) gave lower conversions (86% and 79% respectively) but higher ratios in favor of the isomerized product over C-C bond cleavage, again consistent with a mechanism involving first isomerization followed by retro-sulfonyl anion aldehyde addition (where the rate of isomerization is greater than cleavage). Comparing results for compounds **6** and **12** (Entries 5 and 9 respectively) and compounds **10** and **13** (Entries 5 and 9 respectively) indicate that the nature of the vinyl substituent had less of an effect on the reaction outcome (i.e. similar yields, d.r., and isomerization:cleavage ratios). However, for reasons that are not yet understood, substituting the terminal CH_3 group in **6** with a phenyl as in compound **14** produced a highly reactive substrate that underwent complete conversion within 8 h (Entry 13). Consistent with our previous results, longer reaction times produced higher amounts of cleavage and a lower d.r. of the product (compare Entries 11-13). Introduction of a phenyl adjacent to the hydroxyl resulted in essentially complete C-C bond cleavage and formation of **5** (Entry 8),²⁹ perhaps as a result of conjugation afforded to the aldehyde coproduct by this group (i.e. benzaldehyde; *ref.* Scheme 4).

Table 2. Results from different β -hydroxy vinyl phenylsulfone reactions with DBU.

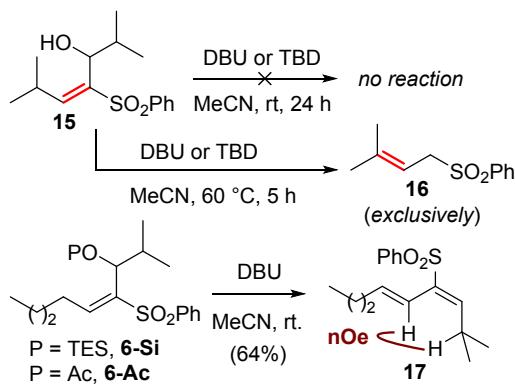
Entry	R	R' (compound #)	% Conversion ^A (% Yield ^B)	d.r. ^C	Isom : Cleav ^C
1	$(\text{CH}_2)_2\text{CH}_3$	Me (8)	92 (59)	1.8 : 1	2.6 : 1
2	$(\text{CH}_2)_2\text{CH}_3$	<i>n</i> -pent (3)	89 (65)	2.8 : 1	6.0 : 1
3	$(\text{CH}_2)_2\text{CH}_3$	<i>i</i> -Bu (9)	89 (61)	2.6 : 1	3.3 : 1
4	$(\text{CH}_2)_2\text{CH}_3$	<i>i</i> -Pr (6)	95 (60)	5.2 : 1	2.3 : 1
5	$(\text{CH}_2)_2\text{CH}_3$	<i>i</i> -Pr (6)	86 ^C	5.8 : 1	5.3 : 1
6	$(\text{CH}_2)_2\text{CH}_3$	<i>i</i> -Pr (6)	79 ^D	4.9 : 1	6.9 : 1
7	$(\text{CH}_2)_2\text{CH}_3$	<i>t</i> -Bu (10)	100 (64)	>20 : 1	3.2 : 1
8	$(\text{CH}_2)_2\text{CH}_3$	Ph (11)	100	--	1:>10
9	$(\text{CH}_2)_3\text{OTIPS}$	<i>i</i> -Pr (12)	94 (61)	6.1 : 1	3.1 : 1
10	$(\text{CH}_2)_3\text{OTIPS}$	<i>t</i> -Bu (13)	100 (66)	>20 : 1	3.2 : 1
11	$(\text{CH}_2)_2\text{Ph}$	<i>i</i> -Pr (14)	100	3.7 : 1	0.7 : 1
12	$(\text{CH}_2)_2\text{Ph}$	<i>i</i> -Pr (14)	100 ^C	4.0 : 1	0.8 : 1
13	$(\text{CH}_2)_2\text{Ph}$	<i>i</i> -Pr (14)	100 ^D (73)	4.6 : 1	2.0 : 1

Notes: ^AReactions were performed by adding DBU (4.0 equiv.) to a 0.4 M solution of the vinylsulfone in MeCN and stirring at room temperature for 24 h. Percent conversions were calculated by dividing the product integration values (major + minor diastereomer) by the product + starting material integrations.

^BIsolated yield after chromatography on silica. ^CDetermined by ¹H NMR. ^DThe reaction was run for 16 h.

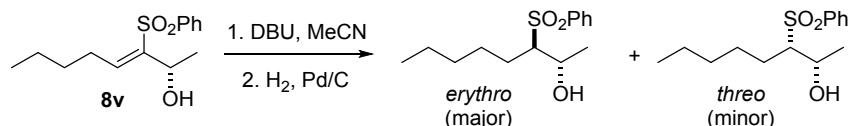
^DThe reaction was run for 8 h.

Attempts to prepare a trisubstituted double bond by isomerization of **15** failed (Scheme 5). Treatment of **15** with DBU or the more basic 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD)³⁰ in MeCN at room temperature for 24 h gave only unreacted starting material. Heating the reaction to 60 °C produced only the cleavage product **16** by ¹H NMR analysis. Attempted isomerization of silyl ether- and ester derivatives **6-Si** and **6-Ac** resulted primarily in elimination and formation of (*E,E*)-**17**.³¹ No evidence for C-C bond cleavage in these reactions was seen by ¹H NMR analysis, consistent with the proposed mechanism for this process involving first deprotonation of the hydroxyl (see Scheme 4).

Scheme 5. Attempted isomerizations of **15**, **6-Si** and **6-Ac**.

Marcantoni and Cingolani noted an upfield shift in the ^{13}C NMR spectrum for the carbinol carbons of β -hydroxy phenylsulfones in the *erythro*-isomer compared with those in the *threo*-isomer.³² For all products listed in Table 2, the major diastereomer consistently displayed an upfield carbinol signal (as well as an upfield sulfonyl carbon signal) in their ^{13}C NMR spectrum. Mase and coworkers noted a trend in coupling constants from the ^1H NMR spectra of beta-hydroxy phenylsulfones that they used for stereochemical assignments.³³ Specifically, the authors state that the *threo*-isomer generally displays a larger coupling constant (~6-8 Hz) between the carbinol hydrogen and the alpha-sulfonyl hydrogen compared to the *erythro*-isomer (1-1.5 Hz). The major isomer we obtained in each case displayed a smaller coupling constant (1-1.5 Hz) between these two protons, consistent with the chemical shift correlations indicating that the *erythro*-isomer is major. To further confirm the *erythro*-isomer as the major stereoisomer from our reactions, the mixture of diastereomers we obtained by isomerization of **8v** was hydrogenated to produce a known compound³³ (Scheme 6). Comparing the ^1H NMR data we obtained to that previously reported for the two diastereomers³³ again indicated that the major stereoisomer is the *erythro*-isomer.

Scheme 6. Hydrogenation of **8a** and comparison of ^1H NMR data obtained to that previously reported.³³



^1H NMR data for the two stereoisomers obtained:

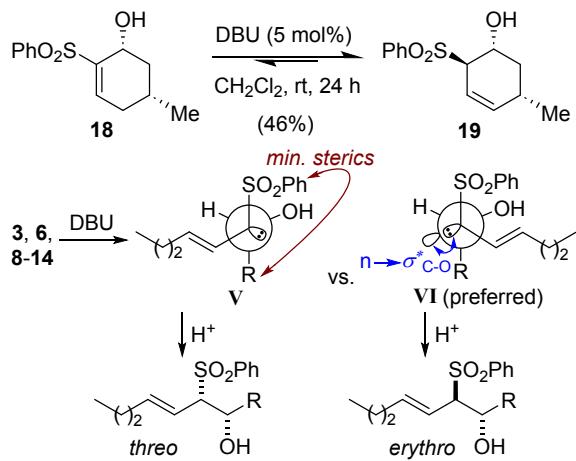
Major				Minor			
δ (ppm)	Splitting	J (Hz)	# Protons	δ (ppm)	Splitting	J (Hz)	# Protons
1.27	d	6.7	3	1.34	d	6.4	3
2.88	dt	1.5, 5.4	1	3.06	ddd	4.8, 6.2, 7.0	1
3.2	d	3.8	1	3.52	d	3.7	1
4.34-				4.26-4.33	m	-	1
4.40	m	-	1				

Previously reported ^1H NMR data for the *erythro* and *threo* isomers:³³

<i>Erythro</i>				<i>Threo</i>			
δ (ppm)	Splitting	J (Hz)	# Protons	δ (ppm)	Splitting	J (Hz)	# Protons
1.27	d	6.6	3	1.34	d	6.3	3
2.88	dt	1.4, 5.4	1	3.03	ddd	4.8, 5.9, 6.7	1
3.2	d	3.8	1	3.51	d	3.6	1
4.20-				4.20-			
4.43	m	-	1	4.43	m	-	1

To our knowledge, only one diastereoselective vinylic to allylic sulfone isomerization has been reported, in this case from cyclic vinylsulfone **18** as part of a synthesis of the C21-C26 segment of apoptolidin

natural products³⁴ (Scheme 7). Treatment of **18** with DBU resulted in a 1:2.5 equilibrium mixture in favor of the allylic isomer from which **19** could be isolated in 46% yield. Compound **19** was described as a single diastereomer, yet in this case the stereochemical outcome is presumably controlled by the cyclohexene ring conformation energetics (i.e. all groups in **19** are equatorial). Other studies indicate that α -phenylsulfonyl carbanions exist largely with the lone-pair of electrons in an sp^3 -hybridized orbital.^{35,36} The structure of the intermediate anion formed upon deprotonation of the β -hydroxy vinylsulfone with DBU might therefore be best represented by the two Newman projections **V** and **VI**. Sterics are minimized between the phenylsulfonyl- and R groups, which becomes increasingly influential as R becomes larger. Dipole-minimization and hyperconjugation³⁷ ($n \rightarrow \sigma^*_{C-O}$) would then favor **VI** from which the *erythro*-isomer would be formed. **Scheme 7.** Previously reported diastereoselective β -hydroxy vinylsulfone isomerization of **18** to **19**³⁴ and proposed model for selective formation of the *erythro*-isomer from acyclic substrates **3**, **6**, and **8-14**.



Conclusion

In summary, β -hydroxy vinyl phenylsulfones undergo diastereoselective isomerization to the corresponding allylic isomer upon treatment with DBU at room temperature. Diastereoselectivity increases with increasing sterics associated with the group attached to the carbinol carbon (e.g. 1.8:1 for Me vs 5.2:1 for *i*-Pr and >20:1 for *tert*-butyl). A competing C-C bond cleavage also occurs during the reaction, which appears to be promoted by higher polarity solvents like DMSO and higher temperature. When performed at room temperature in acetonitrile for 24 h, isolated yields of the isomerized allylic β -hydroxy sulfone products were consistently around 60%. Current efforts are directed at further optimizations and scope studies, as well as investigating strategic applications of the isomerization reaction (and C-C bond cleavage) to the preparation of valuable synthetic targets.

Experimental Section

General Information. All reactions were carried out in vessels under a nitrogen atmosphere unless otherwise specified. Dry solvents were prepared by passing the solvent through a column of activated alumina under nitrogen immediately prior to use. All reagents were purchased and used as received

unless mentioned otherwise. TLC analysis used 0.25 mm silica layer fluorescence UV₂₅₄ plates. Column chromatography: silica gel (230-400 mesh). IR: FT-IR with single-bounce diamond ATR. NMR: Spectra were recorded on a 500 MHz spectrometer in CDCl₃; chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. Solvent signals were used as references (CDCl₃: δ 77.0 ppm; residual CHCl₃ in CDCl₃: δ 7.26 ppm). HRMS: quadrupole time-of-flight LC-MS with electrospray ionization (ESI positive and negative).

General Experimental Procedures.

General Procedure A: Vinyl Phenylsulfone Synthesis.¹⁸ To a solution of sodium benzenesulfinate (1.08 g, 6 mmol) in ethyl acetate (EtOAc, 25 mL) and water (25 mL) open to air was added the 1-alkene (4 mmol) and iodine (1.02 g, 4 mmol) and the mixture was stirred vigorously at room temperature for 2 h. The reaction was quenched with aq. Na₂S₂O₃ (25 mL) and extracted with EtOAc (2 x 25 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The crude product was redissolved in DCM (25 mL) in a flask open to air and cooled to 0 °C. DBU (0.9 mL, 6 mmol) was then added, and the mixture was stirred for 1 h. The reaction was quenched with aq. HCl (1M, 25 mL), and extracted with DCM (2 x 25 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated on a rotary evaporator. Purification of the crude product by chromatography on silica (10:1 to 4:1 hexanes:EtOAc) gave the *E*-vinylsulfone as a colorless oil.

General Procedure B: Vinylsulfone Aldehyde Additions.²⁷ To a solution of (*E*)-(hex-1-en-1-ylsulfonyl)benzene (**2**) or (*E*)-triisopropyl((6-(phenylsulfonyl)hex-5-en-1-yl)oxy)silane in THF (to make a 0.5 M solution) at -95 °C was added a solution of MeLi•LiBr (1.5 M, 1.2 equiv.) and the resulting mixture was warmed to -78 °C and stirred for 30 min. The aldehyde (1.5 equiv.) was then added and the reaction was stirred for 2 h before quenching with aq. NH₄Cl and extracting with EtOAc. The organic phase was dried over MgSO₄, filtered, and concentrated on a rotary evaporator. Purification of the crude product by chromatography on silica (4:1 to 1:1 hexanes:EtOAc) gave the β -hydroxy vinylsulfone as a colorless oil.

General Procedure C: β -Hydroxy Vinylsulfone Isomerizations. To a solution of the β -hydroxy vinylsulfone in MeCN (to make a 0.4 M solution) at room temperature was added DBU (4 equiv.) and the mixture was stirred for 24 h. The reaction was quenched with 1M HCl and extracted with DCM (2x). The combined organic extracts were dried over MgSO₄, filtered, and concentrated on a rotary evaporator. Purification of the crude product by chromatography on silica (4:1 to 1:1 hexanes:EtOAc) gave the β -hydroxy allylic phenylsulfone as a colorless oil.

(*E*)-(Hex-1-en-1-ylsulfonyl)benzene (2**).** Prepared according to procedure A. Compound **2** was obtained as a colorless oil (0.67 g, 75%). *Spectral data matched that previously reported:*³⁸ ¹H NMR (500 MHz, CDCl₃) δ 7.88 – 7.78 (m, 2H), 7.64 – 7.52 (m, 1H), 7.53 – 7.43 (m, 2H), 6.95 (dt, J = 15.1, 6.9 Hz, 1H), 6.28 (dt, J = 15.1, 1.6 Hz, 1H), 2.19 (dtd, J = 8.3, 6.9, 1.6 Hz, 2H), 1.49 – 1.34 (m, 2H), 1.34 – 1.23 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H).

(*E*)-Triisopropyl((6-(phenylsulfonyl)hex-5-en-1-yl)oxy)silane. Prepared according to procedure A. (*E*)-Triisopropyl((6-(phenylsulfonyl)hex-5-en-1-yl)oxy)silane was obtained as a colorless oil (1.2 g, 78%). IR

(ATR): 2972, 2929, 2867, 1470, 1445, 1285, 1183, 1121, 1079, 1045, 1009, 998, 854, 721, 687 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.86 (dd, J = 8.4, 1.4 Hz, 2H), 7.66 – 7.56 (m, 1H), 7.55 – 7.49 (m, 2H), 6.99 (dt, J = 15.1, 6.8 Hz, 1H), 6.31 (dt, J = 15.1, 1.6 Hz, 1H), 3.65 (t, J = 5.9 Hz, 2H), 2.26 (td, J = 6.9, 5.3 Hz, 2H), 1.60 – 1.47 (m, 4H), 1.12 – 0.94 (m, 21H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.1, 140.7, 133.1, 130.4, 129.1, 127.5, 62.7, 32.1, 31.2, 24.0, 17.9, 11.9. HRMS (ESI+) calcd for $\text{C}_{21}\text{H}_{36}\text{NaO}_3\text{SSi}$ ($\text{M}+\text{Na}$): 419.2047. Found 419.2044.

(E)-7-(Phenylsulfonyl)dodec-7-en-6-ol (3). Prepared according to procedure B using vinyl sulfone **2** (0.20 g, 0.89 mmol) and hexanal. Compound **3** was obtained as a colorless oil (0.184 g, 64%). IR (ATR): 3600 – 3400, 2987, 2972, 2867, 1515, 1470, 1293, 1110, 1105, 1085, 1052, 1021, 998, 833, 709, 683 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.90 – 7.81 (m, 2H), 7.62 – 7.56 (m, 1H), 7.56 – 7.42 (m, 2H), 6.94 (t, J = 7.7 Hz, 1H), 4.53 (dd, J = 8.8, 5.5 Hz, 1H), 2.56 (bs, OH), 2.41 – 2.29 (m, 2H), 1.73 (dd, J = 13.4, 9.6, 8.7, 4.8 Hz, 1H), 1.52 – 1.40 (m, 3H), 1.40 – 1.32 (m, 2H), 1.32 – 1.23 (m, 2H), 1.23 – 1.00 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H), 0.81 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.5, 143.0, 141.2, 133.1, 129.1, 127.7, 69.0, 36.7, 31.3, 30.7, 28.2, 25.6, 22.40, 22.38, 13.9, 13.8. HRMS (ESI+) calcd for $\text{C}_{18}\text{H}_{29}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 325.1832. Found 325.1831.

(E)-7-(Phenylsulfonyl)dodec-8-en-6-ol (4). Prepared according to procedure C using β -hydroxy vinyl sulfone **3** (0.13 g, 0.40 mmol). Compound **4** was obtained as a colorless oil (0.085 g, 65%) and 2.8:1 mixture of diastereomers. *Spectral data for the mixture of diastereomers:* IR (ATR): 3600–3300, 2972, 2851, 1468, 1447, 1391, 1373, 1306, 1223, 1125, 1086, 1023, 987 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.85 – 7.78 (m, 4H), 7.65 – 7.60 (m, 2H), 7.55 – 7.50 (m, 4H), 5.61 (ddt, J = 15.5, 9.9, 1.5 Hz, 1H), 5.34 (dt, J = 15.5, 6.8 Hz, 1H), 5.30 – 5.25 (m, 1H), 5.11 (ddt, J = 15.3, 10.1, 1.4 Hz, 1H), 4.48 (ddd, J = 8.4, 5.2, 1.4 Hz, 1H), 4.28 (td, J = 8.3, 2.9 Hz, 1H), 3.94 (s, OH), 3.55 (dd, J = 10.1, 8.7 Hz, 1H), 3.41 (dd, J = 9.9, 1.4 Hz, 1H), 3.02 (s, OH), 1.93 (dd, J = 15.7, 13.9, 6.5, 1.3 Hz, 4H), 1.62 – 1.50 (m, 2H), 1.49 – 1.34 (m, 2H), 1.33 – 1.15 (m, 12H), 0.85 (td, J = 7.0, 3.4 Hz, 3H), 0.76 (dt, J = 9.2, 6.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.6, 141.6, 141.0, 137.5, 133.7, 129.1, 128.90, 128.87, 128.83, 128.77, 128.5, 119.3, 117.0, 116.0, 74.9, 73.0, 68.6, 68.1, 34.7, 34.5, 31.4, 25.0, 22.4, 21.8, 13.9, 13.5. HRMS (ESI+) calcd for $\text{C}_{18}\text{H}_{29}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 325.1832. Found 325.1832.

(E/Z)-(Hex-2-en-1-ylsulfonyl)benzene (5). Prepared according to procedure C using vinylsulfone **2** (0.05 g, 0.22 mmol). Compound **5** was obtained as a colorless oil (0.048 g, 96%) and ~1:1 *cis:trans* mixture. *Spectral data for the mixture matched that previously reported:*²⁸ ^1H NMR (500 MHz, CDCl_3) δ 7.89 (dd, J = 8.3, 1.3 Hz, 2H), 7.87 – 7.84 (m, 2H), 7.70 – 7.61 (m, 2H), 7.54 (dd, J = 8.4, 7.1 Hz, 4H), 5.72 (dtt, J = 10.0, 7.4, 1.3 Hz, 1H), 5.59 – 5.46 (m, 1H), 5.45 – 5.36 (m, 2H), 3.85 (dd, J = 7.9, 1.2 Hz, 2H), 3.74 (dd, J = 7.3, 1.0 Hz, 2H), 2.07 – 1.92 (m, 2H), 1.71 (qd, J = 7.4, 1.7 Hz, 2H), 1.29 (h, J = 7.4 Hz, 2H), 1.15 (h, J = 7.4 Hz, 2H), 0.81 (t, J = 7.4 Hz, 2H), 0.75 (t, J = 7.4 Hz, 3H).

(E)-2-Methyl-4-(phenylsulfonyl)non-4-en-3-ol (6). Prepared according to procedure B using vinyl sulfone **2** (0.20 g, 0.89 mmol) and isobutyraldehyde. Compound **6** was obtained as a colorless oil (0.16 g, 62%).

IR (ATR): 3550-3300, 2989, 2974, 2881, 1510, 1476, 1283, 1181, 1110, 1055, 1032, 1010, 996, 830, 711, 685 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.91 – 7.82 (m, 2H), 7.62 – 7.55 (m, 1H), 7.54 – 7.45 (m, 2H), 6.93 (t, J = 7.6 Hz, 1H), 4.11 (dd, J = 10.1, 4.0 Hz, 1H), 2.75 (d, J = 6.7 Hz, OH), 2.32 (q, J = 7.7 Hz, 2H), 2.01 (dt, J = 9.6, 6.6 Hz, 1H), 1.49 – 1.40 (m, 2H), 1.33 (dq, J = 8.9, 7.2 Hz, 2H), 1.00 (d, J = 6.5 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H), 0.54 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.5, 142.4, 141.3, 133.1, 129.0, 127.7, 74.9, 33.2, 30.5, 28.4, 22.3, 19.4, 18.9, 13.7. HRMS (ESI+) calcd for $\text{C}_{16}\text{H}_{25}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 297.1519. Found 297.1521.

(E)-Triethyl((2-methyl-4-(phenylsulfonyl)non-4-en-3-yl)oxy)silane (6-Si). To a solution of **6** (0.2 g, 0.67 mmol) in DCM (3.4 mL) at 0 °C was added imidazole (0.092 g, 1.34 mmol) followed by chlorotriethylsilane (0.14 mL, 0.81 mmol) and the mixture was stirred and allowed to slowly warm to room temperature over 5 h. The reaction was quenched with aq. NaHCO_3 (10 mL) and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated on a rotary evaporator. Purification by flash column chromatography on silica (10:1 hexanes:ethyl acetate) gave **6-Si** (0.20 g, 73%) as a pale yellow oil. IR (ATR): 2947, 2865, 1520, 1473, 1447, 1303, 1084, 996, 972, 881 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.93 – 7.85 (m, 2H), 7.64 – 7.59 (m, 1H), 7.58 – 7.51 (m, 2H), 7.03 (t, J = 7.5 Hz, 1H), 4.30 (d, J = 5.9 Hz, 1H), 2.56 – 2.45 (m, 2H), 2.20 – 2.05 (m, 1H), 1.52 – 1.44 (m, 2H), 1.40 (ddd, J = 14.3, 7.2, 1.1 Hz, 2H), 0.95 (t, J = 7.1 Hz, 3H), 0.92 (d, J = 6.7 Hz, 3H), 0.81 (t, J = 7.9 Hz, 9H), 0.79 (d, J = 7.0 Hz, 3H), 0.32 (q, J = 7.7 Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.2, 143.0, 133.0, 129.0, 128.5, 74.7, 34.5, 30.9, 29.0, 22.7, 17.8, 13.9, 6.9, 4.5. HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{38}\text{NaO}_3\text{SSi}$ ($\text{M} + \text{Na}$): 433.2209. Found 433.2206.

(E)-2-Methyl-4-(phenylsulfonyl)non-4-en-3-yl acetate (6-Ac). To a solution of **6** (0.2 g, 0.67 mmol) in DCM (3.4 mL) at 0 °C was added *N,N*-dimethylaminopyridine (0.164 g, 1.34 mmol) followed by acetyl chloride (0.07 mL, 1.0 mmol) and the mixture was stirred and allowed to slowly warm to room temperature over 5 h. The reaction was quenched with aq. NaHCO_3 (10 mL) and extracted with DCM (3 x 10 mL). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated on a rotary evaporator. Purification by flash column chromatography on silica (10:1 hexanes:ethyl acetate) gave **6-Ac** (0.13 g, 57%) as a colorless oil. IR (ATR): 2965, 1730, 1507, 1447, 1304, 1225, 1158, 1022, 912 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.90 – 7.83 (m, 2H), 7.63 – 7.56 (m, 1H), 7.53 (ddt, J = 8.2, 6.7, 1.4 Hz, 2H), 7.24 (dd, J = 7.9, 7.0 Hz, 1H), 5.35 (d, J = 10.0 Hz, 1H), 2.60 (ddt, J = 14.1, 7.4, 3.7 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.39 (ddt, J = 15.2, 8.3, 6.7 Hz, 1H), 1.63 – 1.49 (m, 2H), 1.43 (s, 3H), 1.47 – 1.38 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.73, 149.38, 142.16, 137.60, 132.74, 128.92, 127.63, 75.13, 30.97, 30.60, 28.66, 22.52, 19.84, 19.38, 18.75, 13.83, -0.02. HRMS (ESI+) calcd for $\text{C}_{18}\text{H}_{26}\text{NaO}_4\text{S}$ ($\text{M} + \text{Na}$): 361.1449. Found 361.1448.

(E)-2-Methyl-4-(phenylsulfonyl)non-5-en-3-ol (7). Prepared according to procedure C using β -hydroxy vinyl sulfone **6** (0.13 g, 0.44 mmol). Compound **7** was obtained as a colorless oil (0.88 g, 68%) and 5.2:1 mixture of diastereomers. IR (ATR): 3600-3200, 2962, 2897, 2865, 1464, 1444, 1372, 1363, 1306, 1223, 1125, 1085, 1022, 986 cm^{-1} . *Spectral data for the major diastereomer:* ^1H NMR (500 MHz, CDCl_3) δ 7.91 – 7.79 (m, 2H), 7.67 – 7.59 (m, 1H), 7.58 – 7.49 (m, 2H), 5.64 (ddt, J = 15.6, 9.9, 1.5 Hz, 1H), 5.45 – 5.30 (m,

1H), 4.08 (dd, J = 9.0, 1.4 Hz, 1H), 3.60 (dd, J = 9.8, 1.2 Hz, 1H), 2.01 – 1.88 (m, 2H), 1.67 (dp, J = 9.0, 6.7 Hz, 1H), 1.35 – 1.12 (m, 4H), 1.02 (d, J = 6.6 Hz, 3H), 0.80 – 0.74 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.4, 137.4, 133.7, 129.0, 128.8, 117.1, 73.3, 71.3, 34.7, 31.7, 21.8, 19.1, 18.3, 13.5. HRMS (ESI+) calcd for $\text{C}_{16}\text{H}_{25}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 297.1519. Found 297.1519.

(E)-3-(Phenylsulfonyl)oct-3-en-2-ol (8v). Prepared according to procedure B using vinyl sulfone **2** (0.20 g, 0.89 mmol) and acetaldehyde. Compound **8v** was obtained as a colorless oil (0.13 g, 55%). IR (ATR): 3600-3300, 2972, 2928, 2876, 1485, 1443, 1287, 1181, 1152, 1079, 1033, 1011, 998, 832, 754, 691 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.92 – 7.86 (m, 2H), 7.66 – 7.59 (m, 1H), 7.55 (ddt, J = 8.2, 6.7, 1.2 Hz, 2H), 6.95 (t, J = 7.7 Hz, 1H), 4.79 (p, J = 6.7 Hz, 1H), 2.46 (d, J = 6.5 Hz, 1H), 2.41 (qd, J = 7.4, 2.3 Hz, 2H), 1.55 – 1.46 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 (d, J = 6.7 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.9, 143.6, 141.1, 133.2, 129.2, 127.7, 65.0, 30.7, 28.2, 23.2, 22.4, 13.8. HRMS (ESI+) calcd for $\text{C}_{14}\text{H}_{21}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 269.1206. Found 269.1211.

(E)-3-(Phenylsulfonyl)oct-4-en-2-ol (8a). Prepared according to procedure C using β -hydroxy vinyl sulfone **8v** (0.14 g, 0.51 mmol). Compound **8a** was obtained as a colorless oil (0.08 g, 59%) and 1.8:1 mixture of diastereomers. *Spectral data for the mixture of diastereomers:* IR (ATR): 3600-3300, 2967, 2851, 1468, 1447, 1391, 1373, 1306, 1223, 1125, 1086, 1023, 987 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.85 (ddd, J = 8.6, 3.9, 1.3 Hz, 4H), 7.69 – 7.63 (m, 2H), 7.57 (dd, J = 8.5, 7.1 Hz, 4H), 5.65 (ddt, J = 15.5, 10.0, 1.5 Hz, 1H), 5.43-5.32 (m, 2H), 5.13 (ddt, J = 15.4, 10.1, 1.4 Hz, 1H), 4.72 (qd, J = 6.5, 1.5 Hz, 1H), 4.47 (dq, J = 8.6, 6.3 Hz, 1H), 4.03 (bs, OH), 3.53 (dd, J = 10.1, 8.5 Hz, 1H), 3.40 (dd, J = 9.9, 1.5 Hz, 1H), 3.10 (bs, OH), 2.03 – 1.90 (m, 4H), 1.32 – 1.23 (m, 4H), 1.22 (d, J = 6.4 Hz, 6H), 0.88 – 0.76 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.1, 141.2, 137.5, 137.2, 133.9, 133.8, 129.1, 128.90, 128.88, 128.8, 119.3, 116.8, 75.9, 74.0, 34.7, 34.5, 21.84, 21.76, 21.1, 20.6, 13.54, 13.49. HRMS (ESI+) calcd for $\text{C}_{14}\text{H}_{21}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 269.1206. Found 269.1204.

(E)-2-Methyl-5-(phenylsulfonyl)dec-5-en-4-ol (9v). Prepared according to procedure B using vinyl sulfone **2** (0.50 g, 2.2 mmol) and isovaleraldehyde. Compound **9v** was obtained as a colorless oil (0.35 g, 51%). IR (ATR): 3600-3300, 2989, 2932, 2877, 1472, 1431, 1283, 1182, 1145, 1076, 1031, 1012, 994, 852, 709, 683 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.89 – 7.82 (m, 2H), 7.61 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 6.91 (t, J = 7.7 Hz, 1H), 4.61 (dd, J = 10.2, 4.2 Hz, 1H), 2.54 (s, 1H), 2.35 (td, J = 7.4, 3.1 Hz, 2H), 1.72 (ddd, J = 13.9, 9.8, 5.2 Hz, 1H), 1.60 (dpd, J = 8.7, 6.7, 5.2 Hz, 1H), 1.51 – 1.43 (m, 2H), 1.39 – 1.30 (m, 2H), 1.14 (ddd, J = 14.0, 8.6, 4.3 Hz, 1H), 0.91 (t, J = 7.3 Hz, 3H), 0.82 (d, J = 6.7 Hz, 3H), 0.73 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.2, 143.4, 141.2, 133.1, 129.1, 127.8, 67.1, 45.8, 30.7, 28.2, 24.6, 23.2, 22.4, 21.4, 13.8. HRMS (ESI+) calcd for $\text{C}_{17}\text{H}_{27}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 311.1675. Found 311.1675.

(E)-2-Methyl-5-(phenylsulfonyl)dec-6-en-4-ol (9a). Prepared according to procedure C using β -hydroxy vinyl sulfone **9v** (0.10 g, 0.32 mmol). Compound **9a** was obtained as a colorless oil (0.061 g, 61%) and 2.6:1 mixture of diastereomers. IR (ATR): 2967, 2851, 1468, 1447, 1391, 1373, 1306, 1223, 1125, 1086, 1023, 987 cm^{-1} . *Spectral data for the major diastereomer:* ^1H NMR (500 MHz, CDCl_3) δ 7.88 – 7.79 (m,

2H), 7.67 – 7.60 (m, 1H), 7.58 – 7.50 (m, 2H), 5.63 (ddt, J = 15.4, 10.0, 1.5 Hz, 1H), 5.33 (dt, J = 15.4, 6.8 Hz, 1H), 4.61 (ddd, J = 9.0, 4.8, 1.3 Hz, 1H), 3.38 (dd, J = 10.5, 1.2 Hz, 1H), 2.97 (s, 1H), 2.01 – 1.87 (m, 2H), 1.73 (dh, J = 8.4, 6.6 Hz, 1H), 1.51 (ddd, J = 13.7, 9.0, 5.9 Hz, 1H), 1.28 – 1.16 (m, 2H), 1.09 (ddd, J = 13.8, 8.3, 4.8 Hz, 1H), 0.90 (d, J = 6.6 Hz, 3H), 0.88 (d, J = 6.7 Hz, 3H), 0.76 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.7, 137.5, 133.8, 128.93, 128.90, 117.1, 73.3, 66.2, 43.5, 34.7, 24.2, 23.0, 22.0, 21.9, 13.5. HRMS (ESI+) calcd for $\text{C}_{17}\text{H}_{27}\text{O}_3\text{S}$ ($M + \text{H}$): 311.1675. Found 311.1673.

(E)-2,2-Dimethyl-4-(phenylsulfonyl)non-4-en-3-ol (10v). Prepared according to procedure B using vinyl sulfone **2** (0.20 g, 0.89 mmol) and pivaldehyde. Compound **10v** was obtained as a colorless oil (0.16 g, 72%). IR (ATR): 3600–3200, 2989, 2956, 2892, 1473, 1444, 1287, 1183, 1119, 1081, 1039, 1010, 997, 834, 719, 687 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.93 – 7.88 (m, 2H), 7.60 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 6.70 (s, 1H), 4.40 (d, J = 9.1 Hz, 1H), 2.26 (dq, J = 15.4, 8.0 Hz, 2H), 1.40 – 1.29 (m, 2H), 1.21 (h, J = 7.1 Hz, 2H), 1.02 (s, 9H), 0.83 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.8, 143.1, 142.6, 132.9, 129.0, 127.5, 77.6, 37.7, 30.6, 29.7, 26.9, 22.3, 13.7. HRMS (ESI+) calcd for $\text{C}_{17}\text{H}_{27}\text{O}_3\text{S}$ ($M + \text{H}$): 311.1675. Found 311.1672.

(E)-2,2-Dimethyl-4-(phenylsulfonyl)non-5-en-3-ol (10a). Prepared according to procedure C using β -hydroxy vinyl sulfone **10a** (0.07 g, 0.24 mmol). Compound **10v** was obtained as a colorless oil (0.048 g, 64%) and >20:1 mixture of diastereomers. IR (ATR): 3500–3350, 2982, 2856, 1478, 1441, 1323, 1303, 1221, 1145, 1076, 1021, 985 cm^{-1} . *Spectral data for the major diastereomer:* ^1H NMR (500 MHz, CDCl_3) δ 7.84 – 7.77 (m, 2H), 7.68 – 7.59 (m, 1H), 7.56 – 7.49 (m, 2H), 5.69 (ddt, J = 15.7, 9.8, 1.5 Hz, 1H), 5.26 (dt, J = 15.7, 6.9 Hz, 1H), 4.26 (dd, J = 3.4, 0.9 Hz, 1H), 3.71 (dt, J = 9.8, 0.8 Hz, 1H), 2.78 (d, J = 3.3 Hz, 1H), 1.89 (dtdd, J = 8.0, 6.7, 5.6, 1.5 Hz, 2H), 1.25 – 1.15 (m, 2H), 0.91 (s, 9H), 0.77 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.7, 137.0, 133.6, 129.2, 128.8, 118.7, 74.0, 70.6, 35.9, 34.9, 26.6, 21.7, 13.7. HRMS (ESI+) calcd for $\text{C}_{17}\text{H}_{27}\text{O}_3\text{S}$ ($M + \text{H}$): 311.1675. Found 311.1675.

(E)-1-Phenyl-2-(phenylsulfonyl)hept-2-en-1-ol (11v). Prepared according to procedure B using vinyl sulfone **2** (0.20 g, 0.89 mmol) and benzaldehyde. Compound **11v** was obtained as a colorless oil (0.21 g, 73%). IR (ATR): 2982, 2928, 2892, 1473, 1441, 1295, 1164, 1131, 1091, 1041, 1023, 998, 824, 731, 687 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.59 – 7.54 (m, 2H), 7.50 – 7.44 (m, 1H), 7.40 – 7.31 (m, 3H), 7.16 (t, J = 7.7 Hz, 1H), 7.12 (s, 5H), 5.80 (d, J = 5.7 Hz, 1H), 3.47 (d, J = 8.0 Hz, 1H), 2.27 (q, J = 7.6 Hz, 2H), 1.42 (m, 2H), 1.33 – 1.23 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.2, 142.7, 140.7, 139.8, 132.8, 128.9, 128.2, 127.6, 127.3, 125.5, 69.1, 30.4, 28.3, 22.4, 13.7. HRMS (ESI+) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{S}$ ($M + \text{H}$): 331.1362. Found 331.1360.

(E)-2-Methyl-4-(phenylsulfonyl)-9-((triisopropylsilyl)oxy)non-4-en-3-ol (12v). Prepared according to procedure B using triisopropyl((6-(phenylsulfonyl)hex-5-en-1-yl)oxy)silane (0.20 g, 0.50 mmol) and isobutyraldehyde. Compound **12v** was obtained as a colorless oil (0.16 g, 68%). IR (ATR): 2998, 2943, 2876, 1487, 1463, 1285, 1184, 1119, 1081, 1039, 1012, 997, 834, 719, 687 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.90 – 7.84 (m, 2H), 7.61 – 7.55 (m, 1H), 7.55 – 7.47 (m, 2H), 6.94 (t, J = 7.6 Hz, 1H), 4.12 (d, J =

9.7 Hz, 1H), 3.71 – 3.65 (m, 2H), 2.73 (s, 1H), 2.36 (tdd, J = 7.3, 5.1, 2.2 Hz, 2H), 2.02 (dh, J = 9.7, 6.6 Hz, 1H), 1.62 – 1.49 (m, 4H), 1.11 – 1.02 (m, 21H), 1.01 (d, J = 6.5 Hz, 3H), 0.55 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.4, 142.7, 141.4, 133.2, 129.1, 127.8, 75.0, 62.8, 33.4, 32.6, 28.6, 25.1, 19.4, 19.0, 18.0, 12.0. HRMS (ESI+) calcd for $\text{C}_{25}\text{H}_{44}\text{NaO}_4\text{SSi}$ (M + Na): 491.2622. Found 491.2621.

(E)-2-Methyl-4-(phenylsulfonyl)-9-((triisopropylsilyl)oxy)non-5-en-3-ol (12a). Prepared according to procedure C using β -hydroxy vinyl sulfone **12v** (0.08 g, 0.18 mmol). Compound **12a** was obtained as a colorless oil (0.048 g, 61%) and 6.1:1 mixture of diastereomers. IR (ATR): 3550–3300, 2983, 2877, 1505, 1451, 1384, 1372, 1301, 1227, 1145, 1074, 1027, 986 cm^{-1} . *Spectral data for the major diastereomer:* ^1H NMR (500 MHz, CDCl_3) δ 7.89 – 7.77 (m, 2H), 7.66 – 7.59 (m, 1H), 7.53 (ddt, J = 8.4, 6.5, 1.4 Hz, 2H), 5.65 (ddt, J = 15.5, 9.9, 1.5 Hz, 1H), 5.37 (dt, J = 15.6, 6.8 Hz, 1H), 4.07 (dt, J = 9.0, 1.6 Hz, 1H), 3.73 (dd, J = 7.3, 1.0 Hz, 1H), 3.63 – 3.48 (m, 2H), 3.05 (d, J = 2.5 Hz, 1H), 2.12 – 1.95 (m, 2H), 1.66 (dh, J = 9.0, 6.6 Hz, 1H), 1.41 (ddt, J = 13.6, 6.5, 1.9 Hz, 2H), 1.05 – 1.02 (m, 21H), 1.01 (d, J = 3.6 Hz, 3H), 0.77 (d, J = 6.7 Hz, 3H). *Spectral data for the mixture of diastereomers:* ^{13}C NMR (126 MHz, CDCl_3) δ 142.2, 141.5, 138.4, 137.4, 133.7, 133.6, 129.04, 128.95, 128.9, 128.6, 117.1, 116.1, 73.3, 71.3, 62.6, 62.5, 60.2, 32.0, 31.8, 29.2, 29.0, 19.1, 18.4, 18.0, 12.0. HRMS (ESI+) calcd for $\text{C}_{25}\text{H}_{44}\text{NaO}_4\text{SSi}$ (M + Na): 491.2622. Found 491.2625.

(E)-2,2-Dimethyl-4-(phenylsulfonyl)-9-((triisopropylsilyl)oxy)non-4-en-3-ol (13v). Prepared according to procedure B using triisopropyl((6-(phenylsulfonyl)hex-5-en-1-yl)oxy)silane (0.20 g, 0.50 mmol) and pivaldehyde. Compound **13v** was obtained as a colorless oil (0.17 g, 70%). IR (ATR): 3450–3100, 2992, 2928, 2874, 1471, 1423, 1284, 1185, 1181, 1039, 1010, 984, 828, 754, 683 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.93 – 7.86 (m, 2H), 7.59 – 7.54 (m, 1H), 7.53 – 7.47 (m, 2H), 6.71 (s, 1H), 4.40 (d, J = 9.2 Hz, 1H), 3.61 (t, J = 5.8 Hz, 2H), 2.29 (ddd, J = 14.2, 7.9, 6.0 Hz, 1H), 1.52 – 1.37 (m, 4H), 1.11 – 0.97 (m, 30H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.7, 143.2, 142.6, 132.9, 129.0, 127.4, 77.5, 62.8, 37.7, 32.4, 29.8, 27.0, 25.1, 18.0, 12.0. HRMS (ESI+) calcd for $\text{C}_{26}\text{H}_{46}\text{NaO}_4\text{SSi}$ (M + Na): 505.2778. Found 505.2775.

(E)-2,2-Dimethyl-4-(phenylsulfonyl)-9-((triisopropylsilyl)oxy)non-5-en-3-ol (13a). Prepared according to procedure C using β -hydroxy vinyl sulfone **13v** (0.08 g, 0.17 mmol). Compound **13a** was obtained as a colorless oil (0.053 g, 66%) and >20:1 mixture of diastereomers. IR (ATR): 3600–3300, 2972, 2868, 1451, 1437, 1388, 1363, 1301, 1235, 1181, 1084, 1023, 987 cm^{-1} . *Spectral data for the major diastereomer:* ^1H NMR (500 MHz, CDCl_3) δ 7.90 – 7.76 (m, 2H), 7.65 – 7.58 (m, 1H), 7.53 (dt, J = 8.6, 6.9 Hz, 2H), 5.70 (ddt, J = 15.6, 9.7, 1.5 Hz, 1H), 5.27 (dt, J = 15.7, 6.8 Hz, 1H), 4.26 (s, 1H), 3.70 (d, J = 9.7 Hz, 1H), 3.56 (td, J = 6.4, 3.5 Hz, 2H), 2.85 – 2.73 (m, 1H), 1.99 (dddd, J = 14.7, 13.0, 10.6, 6.8 Hz, 2H), 1.44 – 1.34 (m, 2H), 1.12 – 0.97 (m, 21H), 0.91 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.4, 136.9, 133.6, 129.2, 128.7, 118.7, 74.0, 70.6, 62.6, 35.9, 31.8, 29.2, 26.5, 18.0, 11.9. HRMS (ESI+) calcd for $\text{C}_{26}\text{H}_{46}\text{NaO}_4\text{SSi}$ (M + Na): 505.2778. Found 505.2778.

(E)-2-Methyl-7-phenyl-4-(phenylsulfonyl)hept-4-en-3-ol (14v). Prepared according to procedure B using ((4-phenylbut-1-en-1-yl)sulfonyl)benzene²² (0.44 g, 0.16 mmol) and isobutyraldehyde. Compound **14v** was obtained as a colorless oil (0.053 g, 96%). IR (ATR): 2962, 2930, 2872, 1467, 1446, 1285, 1184, 1119,

1081, 1039, 1010, 997, 834, 719, 687 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.84 – 7.77 (m, 2H), 7.66 – 7.57 (m, 1H), 7.56 – 7.46 (m, 2H), 7.28 (tt, J = 6.7, 1.0 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.11 (m, 2H), 6.99 (t, J = 7.5 Hz, 1H), 4.09 (dd, J = 10.1, 3.9 Hz, 1H), 2.83 (t, J = 6.9 Hz, 2H), 2.78 – 2.63 (m, 2H), 2.40 (d, J = 7.2 Hz, OH), 2.04 (ddt, J = 13.3, 9.5, 6.7 Hz, 1H), 1.01 (d, J = 6.5 Hz, 3H), 0.58 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.05, 143.32, 141.12, 140.04, 133.05, 128.97, 128.52, 128.37, 127.76, 126.36, 77.26, 77.00, 76.75, 74.83, 34.49, 33.25, 30.24, 19.19, 18.88. HRMS (ESI+) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 345.1519. Found 345.1519.

(E)-2-Methyl-7-phenyl-4-(phenylsulfonyl)hept-5-en-3-ol (14a). To a solution of the **14v** (0.043 g, 0.13 mmol) in MeCN (0.3 mL) at room temperature was added DBU (0.08 mL, 0.52 mmol) and the mixture was stirred for 8 h. The reaction was quenched with 1M HCl (10 mL) and extracted with DCM (2 x 10 mL). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated on a rotary evaporator. Purification of the crude product by chromatography on silica (4:1 to 1:1 hexanes:EtOAc) gave the **14a** (0.033 mg, 73%) as a colorless oil. IR (ATR): 3550–3400, 2967, 2851, 1468, 1447, 1391, 1373, 1306, 1223, 1125, 1086, 1023, 987 cm^{-1} . *Spectral data for the major diastereomer:* ^1H NMR (500 MHz, CDCl_3) δ 7.83 – 7.79 (m, 2H), 7.63 – 7.58 (m, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.31 – 7.19 (m, 4H), 7.00 – 6.94 (m, 1H), 5.80 (ddt, J = 15.6, 10.1, 1.5 Hz, 1H), 5.52 (dt, J = 15.3, 7.1 Hz, 1H), 4.16 (dd, J = 9.0, 1.3 Hz, 1H), 3.81 (dd, J = 7.4, 1.0 Hz, 1H), 3.68 (dd, J = 9.9, 1.3 Hz, 1H), 3.41 – 3.33 (m, 1H), 3.30 (ddd, J = 15.5, 7.3, 1.5 Hz, 1H), 1.73 (dp, J = 9.3, 6.7 Hz, 1H), 1.07 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H). *Spectral data for the mixture of diastereomers:* ^{13}C NMR (126 MHz, CDCl_3) δ 140.48, 139.91, 138.88, 138.82, 138.17, 137.24, 133.65, 133.55, 128.96, 128.87, 128.50, 128.46, 128.44, 128.35, 126.31, 126.23, 118.57, 117.48, 73.28, 71.02, 59.93, 39.14, 38.82, 31.77, 19.09, 18.38. HRMS (ESI+) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 345.1519. Found 345.1518.

(E)-2,6-Dimethyl-4-(phenylsulfonyl)hept-4-en-3-ol (15). Prepared according to procedure B using (*E*)-((3-methylbut-1-en-1-yl)sulfonyl)benzene³⁹ (0.05 g, 0.29 mmol) and isobutyraldehyde. Compound **14v** was obtained as a colorless oil (0.07 g, 87%). IR (ATR): 3500–3300, 2962, 2930, 2872, 1467, 1446, 1285, 1184, 1119, 1081, 1039, 1010, 997, 834, 719, 687 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.89 – 7.86 (m, 2H), 7.64 – 7.57 (m, 1H), 7.55 – 7.50 (m, 2H), 6.75 (d, J = 10.8 Hz, 1H), 4.13 (d, J = 9.1 Hz, 1H), 2.87 (dp, J = 10.7, 6.6 Hz, 1H), 2.00 (dp, J = 9.7, 6.7 Hz, 1H), 1.07 (d, J = 6.6, 3H), 1.06 (d, J = 6.7 Hz, 3H), 1.02 (d, J = 6.5 Hz, 3H), 0.55 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 152.22, 141.33, 140.32, 133.14, 129.09, 127.77, 75.14, 33.21, 28.10, 21.83, 21.73, 19.44, 19.07. HRMS (ESI+) calcd for $\text{C}_{15}\text{H}_{23}\text{O}_3\text{S}$ ($\text{M} + \text{H}$): 283.1362. Found 283.1362.

((3Z,5E)-2-Methylnona-3,5-dien-4-yl)(phenylperoxy)sulfane (17). Prepared according to procedure C using **6-Ac** (0.15 mmol). Compound **17** was obtained as a pale yellow oil (0.026 g, 64%) IR (ATR): 2962, 1507, 1446, 1304, 1288, 1086, 1070, 967 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.85 – 7.80 (m, 2H), 7.61 – 7.56 (m, 1H), 7.51 (ddt, J = 8.2, 6.7, 1.3 Hz, 2H), 6.77 (d, J = 10.2 Hz, 1H), 5.93 – 5.88 (m, 2H), 2.74 (dp, J = 10.1, 6.6 Hz, 1H), 2.04 (dtd, J = 7.3, 5.3, 2.8 Hz, 2H), 1.33 (q, J = 7.3 Hz, 2H), 1.10 (d, J = 6.7 Hz, 6H), 0.79 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 147.6, 140.4, 137.4, 132.9, 128.8, 127.9, 118.3, 35.4, 28.0, 22.1, 22.0, 13.4. HRMS (ESI+) calcd for $\text{C}_{16}\text{H}_{23}\text{O}_2\text{S}$ ($\text{M} + \text{H}$): 279.1419. Found 279.1418.

Author Contributions

Conceptualization, G. O.; methodology, G.O., T.C.; investigation, G.O., T.C., D.C, H.C., C.W., and A.J.; resources, G.O.; data curation, G.O., T.C., D.C, H.C., C.W., and A.J.; writing—original draft preparation, G. O.; writing—review and editing, G.O., T.C., D.C, H.C., C.W., and A.J.; supervision, G.O.; project administration, G.O.; funding acquisition, G.O

Conflicts of Interest

There are no conflicts of interest to declare.

Data Availability

The data supporting this article have been included as part of the Supplementary Information.

Acknowledgements

Financial support from the National Science Foundation (CHE-2350416) and Alexander von Humboldt Foundation (Fellowship to G. O’Neil) are gratefully acknowledged.

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Data Availability Statement For: Diastereoselective β -Hydroxy Vinylsulfone Isomerizations

The data supporting this article have been included as part of the Supplementary Information.