Use of Samarium Diiodide as an Alternative to Sodium/Mercury Amalgam in the Julia–Lythgoe Olefination†

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Studies into the use of samarium diiodide (SmI_2) in the reductive elimination of 1,2-acetoxy sulfones and the reductive cleavage of vinyl sulfones are reported. Parallel investigations with sodium/mercury amalgam (Na/Hg) revealed over-reduction in several cases in which the desired products were heavily conjugated or conjugated to an aromatic moiety. A mechanistic study revealed some of the intricacies of the SmI_2-promoted Julia–Lythgoe olefination. The classical Na/Hg reductive method was also examined, and an alternative mechanism is proposed. Observations described herein provide important insights into the mechanism and synthetic utility of these methods. The optimum protocol developed utilizes SmI_2 reduction of vinyl sulfones in the presence of DMPU and MeOH and gives generally high yields with good to excellent *E* stereoselectivity.

Introduction

The coupling of two units to form an olefin is a common procedure in organic synthesis and is very often accomplished via either a Wittig–Horner–Emmons[1] or a Julia–Lythgoe[2] olefination. These methods allow for regiospecificity and in some cases provide excellent stereoselectivity. The Julia–Lythgoe coupling procedure has the benefits of utilizing readily available α-sulfonyl carbanions, a tendency to produce predominantly *E* olefins (depending on conditions and substitution),[2e,f] and a long proven history as an important tool in organic synthesis.[3] This procedure is particularly prominent in convergent approaches to complex structures.

During the course of our investigations toward the asymmetric total synthesis of rhizoxin[4] (Figure 1) we found existing Julia olefination procedures to be unsatisfactory for the joining of the three major subunits corresponding to **2**, **3**, and **4**. Unfortunately, it was found that one-electron reductive methods for the reductive elimination of the sulfone either as the hydroxy sulfone or vinyl sulfone were too harsh for the substrate.[2,5] Thus, in a model study, we attempted to couple two subunits similar to **2** and **3** using the Julia olefination as well as variations of the original procedure. We came to the conclusion that a fundamental incompatibility of this method and the desired product (our inability to remove the sulfone in the presence of the triene conjugated to the aromatic heterocycle) would block attempts to use this Julia–Lythgoe olefination in our endeavors (Table 1).

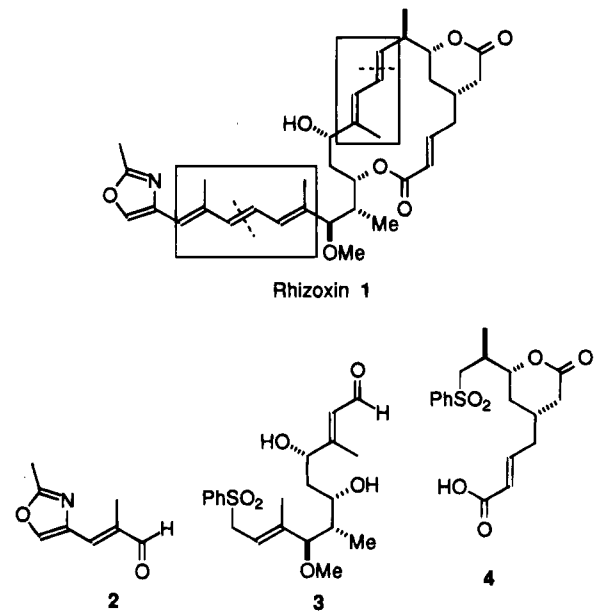

Figure 1.

† Portions of this work have been presented previously: Keck, G. E.; Weglarz M. A.; Savin, K. A. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society, San Diego, CA; American Chemical Society: Washington, DC, 1994; ORGN 400.

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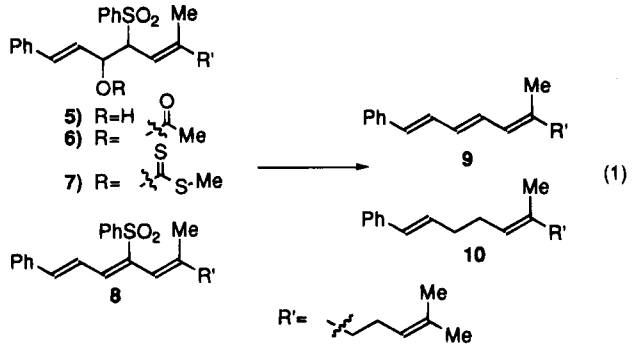
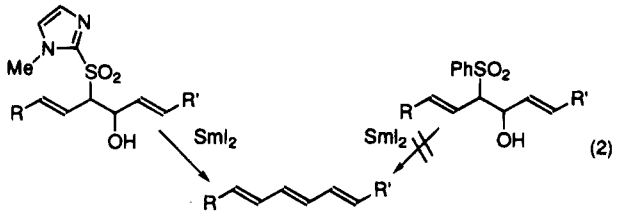
Table 1. Overreduction of Triene Products



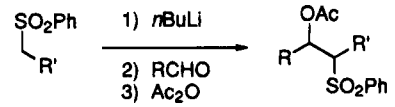
substr	method	additive or condition	time, (h)	recovered starting material (%)	9 (%)	10 (%)
5	Na/Hg	none	12	none	none	60–80
6	Na/Hg	$NaHPO_3$	12	none	none	60–80
6	$Na_2S_2O_4$	heat	12	60	5–10	none
7	Bu_3SnH/ toluene	ACN/heat	3.5	70	none	none
7	Na/Hg	$NaHPO_3$	12	none	none	40
8	Na/Hg	$NaHPO_3$	12	30	none	60–80
8	Bu_3SnH/ toluene	ACN/heat	3.5	70	none	none

The use of samarium diiodide (SmI_2) has become increasingly important in organic synthesis due to its mild properties as a single electron source as well as its facile preparation.[8,9] Recently Kende and co-workers[6] as well as several other groups[7] demonstrated the utility of SmI_2 as a presumed single electron reductant in the place of tri-*n*-butyltin hydride (Bu_3SnH) or Na/Hg for similar purposes. Kende showed that hydroxy imidazolyl sulfones could easily be reduced in one step to the corresponding olefins using SmI_2 (eq 2). The procedure gave good results for many examples and also gave good selectivity for the *E* olefin. One limitation of this method was the failure to reduce β-hydroxy phenyl sulfones.

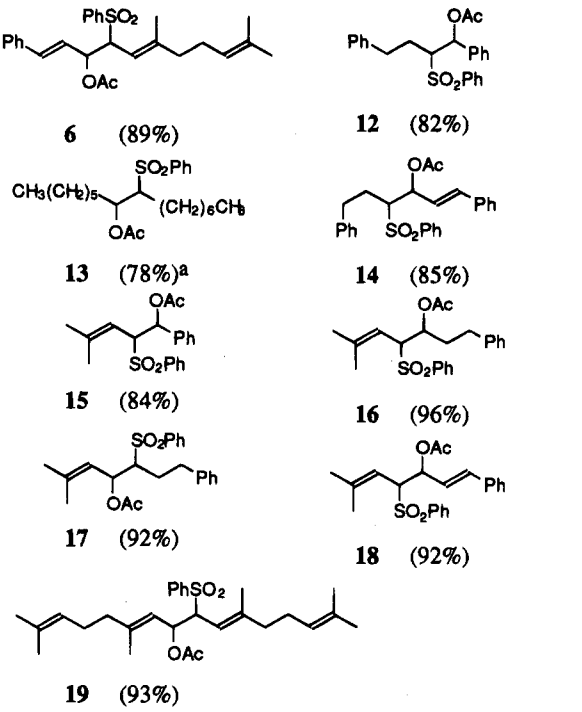


Although the inability to convert the β-hydroxy phenyl sulfones to the product olefin was not encouraging (since we could not easily modify our route to afford an imidazoyl sulfone), we also found several precedents in the literature which showed that β-alkoxy and phenyl vinyl sulfones could be reductively cleaved to the corresponding olefins using SmI_2.[6,7] The issue of product olefin stereochemistry was not present in these previous cases; therefore, we set out to define the parameters controlling the olefin geometry in the SmI_2 reductive cleavage of acetoxy sulfones and vinyl sulfones as well as to further develop this methodology. We describe herein the results of studies using SmI_2 to effect these transformations. In addition, a series of mechanistic studies have given us an improved understanding of not only the SmI_2 reduction of β-acetoxy and vinyl sulfones but also of classical Na/Hg-promoted reductions as well.

Table 2. Preparation of Acetoxy Sulfones



Product (Percent Yield)



[a] The hydroxy sulfone was isolated and then acylated.

Results and Discussion

Preparation of Vinyl Sulfones.[10] The requisite alkyl sulfone starting materials were prepared from the corresponding alkyl bromides in high yields.[11] Deprotonation of the sulfone with *n*-BuLi at −78 °C followed by addition of the appropriate aldehyde led to the corresponding β-hydroxy sulfones. In most cases the reactions were quenched with acetic anhydride (Ac_2O) to give the corresponding β-acetoxy sulfones directly (Table 2).

In some cases the reactions were quenched with H_2O and the hydroxy sulfones were isolated to allow for easy

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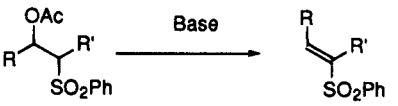
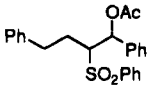
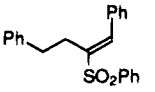
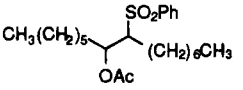
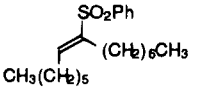
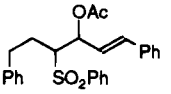
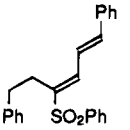
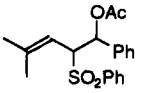
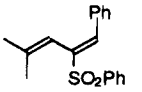
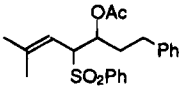
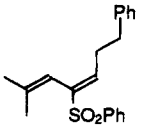
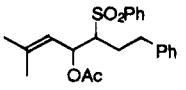
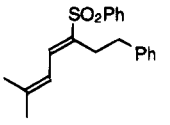
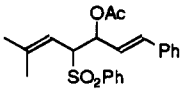
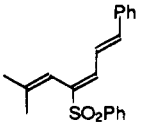
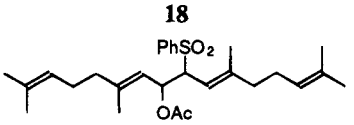
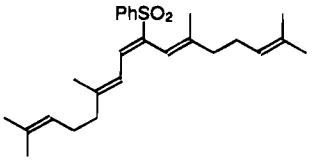
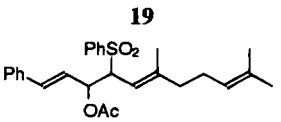
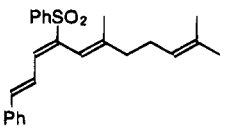
Table 3. Preparation of Vinyl Sulfones



Entry	Acetoxy Sulfone	Yield % (Olefin Ratio)[a]	Product
1		97 (4 : 1)	
2	**12** 	46[33][b, c]	**20** 
3	**13** 	94	**21** 
4	**14** 	98	**22** 
5	**15** 	60 [14][b, c]	**23** 
6	**16** 	86	**24** 
7	**17** 	63	**25** 
8	**18** 	69	**26** 
9	**19** 	81 (4 : 1)	**27** 
	6		**8**

[a] *E*:*Z* geometry was not proven but the major product assumed to be *E*.[2d] [b] Value in brackets denotes recovered starting material. [c] Reaction was run with LDA as the base.

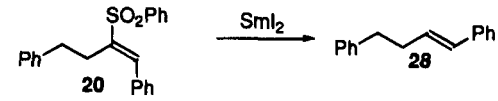
separation of the two diastereomers. The hydroxy sulfones were then acylated to give good yields of the corresponding acetoxy sulfones. Vinyl sulfones were prepared in most cases by elimination of the corresponding acetoxy sulfones with diazobicyclo[5.4.0]undec-7-ene (DBU) (Table 3). In most cases only one geometric isomer was detected. Lithium diisopropylamide (LDA) was used for the elimination in cases where the product olefins could isomerize to give mixtures of both α,β and β,γ unsaturated sulfones (entries 2 and 5, Table 3).[12]

Studies toward the Reductive Elimination of 1,2-Acetoxy Sulfones and Vinyl Sufones. Our first attempts at reducing β-hydroxy phenyl sulfones and β-acetoxy phenyl sulfones began with substrate **12** (and the corresponding hydroxy compound) and were unsuccessful when the compounds were reacted with SmI_2 even after prolonged reaction times (several days). This was also noted in the work by Kende.[6] Although the mechanism of action is not well understood, certain additives are known to give enhanced reaction rates for SmI_2-mediated reactions.[13] The use of *t*-BuOH, H_2O, and MeOH did not enhance the rate of product formation. However, when either hexamethylphosphoramide (HMPA) or 1,3-dimethyl-3, 4, 5, 6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) was added, an increase in reaction rate was observed; in some cases the reactions were complete within 5 min. Unlike the systems studied by Kende, our cases showed a lack of stereoselectivity (vide infra).

Since the direct reduction of 1,2-acetoxy sulfones did not provide the desired results, we next explored the reduction of vinyl sulfones with SmI_2 (Table 4). Again, in the absence of additives, product formation was very slow (50–95% conversion in 5 days), but the yields were good and high selectivity for formation of the *E* olefin was observed (entries 1 and 2, Table 4).

In an attempt to improve upon these initial results with vinyl sulfones, the effect of additives was again investigated. We found the use of *t*-BuOH alone (entry 3, Table 4) gave no positive rate enhancement, but HMPA alone gave a powerful enhancement[13] (from 80% in 5 days to 70–85% [based on molar recovery] in 5 min). However, the HMPA reaction produced a mixture of *E* and *Z* olefins with little selectivity (entry 6, Table 4).

Table 4. SmI_2 Reductive Cleavage of Vinyl Sulfone 20



entry	reaction conditions	*E*:*Z*	yield (%)[a]
1	10 equiv of SmI_2, THF, 5 days	25:1	97
2	8 equiv of SmI_2, THF, 5 days	25:1	95
3	8 equiv of SmI_2, THF, *t*-BuOH, 5 days	25:1	90
4	6 equiv of SmI_2, THF, MeOH, 5 days	1:6.1	60
5	8 equiv of SmI_2, THF, MeOH, 5 days	*E*	90
6	8 equiv of SmI_2, THF, HMPA, 10 min	1.1:1	40 (50)[b]
7	8 equiv of SmI_2, THF, DMPU, 35 min	9.0:1	95
8	8 equiv of SmI_2, THF, DMPU, MeOH, 35 min	*E*	92

[a] All values represent isolated yields. [b] Value in parentheses denotes recovered starting material.

DMPU has also been reported[13] to enhance the rates of many SmI_2-mediated reactions. We found that the desired rate enhancements were observed (95% yield in 35 min, entry 7, Table 4) when DMPU was employed with much less serious degradation in olefin stereoselectivity. The results with DMPU were thus superior to those obtained with HMPA in all respects. The DMPU reactions were rapid and completely consumed starting material (whereas the HMPA reaction proceeded to only *ca.* 50% conversion); the DMPU reaction also gave considerably higher stereoselectivity than was observed using HMPA. Use of MeOH alone as an additive was found to give *E*/*Z* olefin stereoselectivity equal to or even better than that obtained with no additives; however, there was no rate enhancement observed when compared to the additive free reactions (entry 5, Table 4). It was decided that possibly the positive benefits of both additives (MeOH and DMPU) could be combined. The reaction was run with 50 molar equiv of each additive relative to the sulfone, and the results demonstrated both the reaction rate enhancement and good olefin stereoselectivity observed in the single additive cases (entry 8, Table 4). Further studies to optimize the reaction have led to the use of 10 to 20 equiv each of DMPU and MeOH, respectively, which gives reasonable reaction times (5–50 min) and high selectivity for the *E* olefins (4:1 to 99:1) in most cases. Furthermore, only 8 equiv of SmI_2 was found to be required. The use of less SmI_2 or either of the additives led to incomplete reactions, lower stereoselectivity, or both (entry 4, Table 4). This method was applied to a variety of substrates with varying degrees of unsaturation, and the results are summarized in Table 5. The excess SmI_2 is necessary for the completion of the reaction and possibly is required to reduce sulfones to the sulfides; thiophenol and diphenyl disulfide are recovered as byproducts.

The exact role of DMPU and HMPA is not clearly understood. The rate enhancement could be due to a lowering of the oxidation potential of SmI_2. The noticeable color changes from deep blue-green to purple in the presence of these additives may be an indication of the change in electropotential.

Deuterium Labeling Studies: Vinyl Sulfones. In an attempt to determine the role that MeOH is playing in these reactions, we probed the process with deuterated additives. MeOH-d_4 was used as an initial probe into

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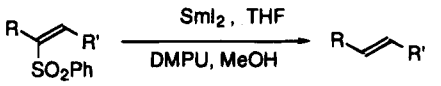
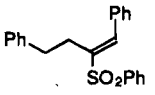
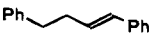
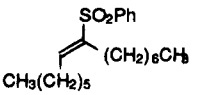
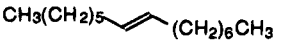
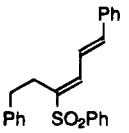
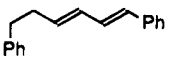
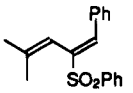
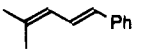
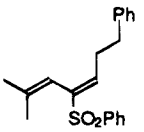
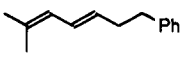
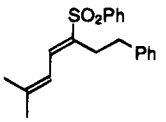
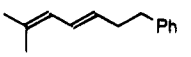
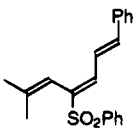
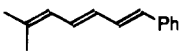
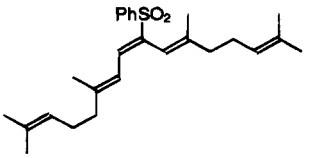
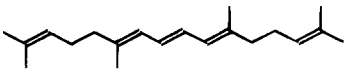
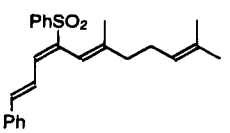
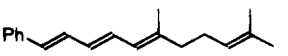
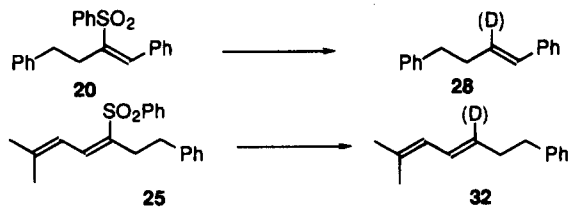
Table 5. SmI_2 Reductive Cleavage of Vinyl Sulfones



Entry	Vinyl Sulfone	Yield % (*E* : *Z* Ratio)	Product
1	 **20**	85 (*E*) [a]	 **28**[14a, b]
2	 **21**	69 (4 : 1)	 **29**[14c]
3	 **22**	94 (*E*) [a]	 **30**[14d]
4	 **23**	95 (*E*) [a]	 **31**[14e, f, g]
5	 **24**	89 (*E*)	 **32**[14h]
6	 **25**	95 (5 : 1)	 **33**[14i]
7	 **26**	94 (5 : 1) [a]	 **34**[14j]
8	 **27**	78 (6 : 1)	 **35**[14j]
9	 **8**	70 (2 : 1) [a]	 **9**

[a] 20 equivalents each of DMPU and MeOH was employed.

Table 6. Deuterium Labeling Studies with Vinyl Sulfones and SmI_2



entry	substr	reaction conditions[a]	E:Z	deuterium incorpn (%)	yield (%)
1	20	A	E		92
2	20	B	E	100	93
3	20	C	E	98	93
4	20	D	E	96	90
5	25	B	6:1	90	91
6	25	D	5:1	90	91
7	25	E	E	90	91
8	20	E	E	88	97

[a] Reaction conditions: A, 8 equiv of SmI_2, THF, DMPU, MeOH, 60 min. B, 8 equiv of SmI_2, THF, DMPU, CD_3OD, 60 min. C, 8 equiv of SmI_2, THF, DMPU, D_2O, 60 min. D, 8 equiv of SmI_2, THF, DMPU, CH_3OD, 60 min. E, 5% Na/Hg, Na_2HPO_4, THF/MeOD (4:1), 0 °C, 60 min.

Table 7. Time Dependency Studies

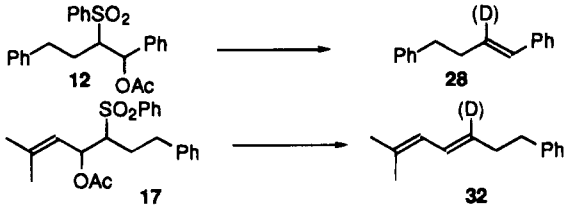
entry	conditions[a]	E:Z	D incorpn (%)	yield (%)
1	t = 0 min[b]	5:1	90	91
2	t = 5 min	2:1	60	90
3	t = 60 min	1.5:1	40	90
4	t = 18 h	1.2:1	30	94

[a] Reaction conditions: 8 equiv of SmI_2, 5 equiv of DMPU, waited a period of time (t), then the 10 equiv of CD_3OD was added. [b] CD_3OD added with the DMPU.

the reaction mechanism of the SmI_2-mediated reduction of vinyl sulfones to the disubstituted olefins. High amounts of deuterium incorporation were observed at the position previously occupied by the sulfone (Table 6). MeOH-d_1 was then used in an attempt to determine if the MeOH was serving as a hydrogen donor via radical abstraction or a proton donor via anionic deprotonation. High levels of deuterium incorporation were again observed when MeOH-d_1 was used (Table 6, entries 4 and 6). Furthermore, since hydrogen was not abstracted from the solvent tetrahydrofuran (THF), it is most probable that the proton is being abstracted by the corresponding vinyl anion. It was also observed that if the MeOH-d_1 initially was withheld from the reaction for varying amounts of time both the deuterium incorporation and the olefin stereoselectivity dropped off as a function of time (Table 7), which means that possibly another proton source is utilized and another reaction pathway followed. In accord with the observations of Curran,[13d] D_2O also performed well as a deuterium source (Table 6, entry 3) but the reaction separated into two phases and began to deposit a precipitate. Due to these technical problems, this modification was not pursued further.

Deuterium Labeling Studies: Acetoxy Sulfones. In our initial attempts to reduce β-acetoxy sulfones with SmI_2, MeOH as well as other additives did not improve olefin stereoselectivity to an observable extent relative to the Na/Hg Julia–Lythgoe reduction conditions. To

Table 8. Deuterium Incorporation in Reductions of Acetoxy Sulfones



entry	substrate	reaction conditions[a]	E:Z	deuterium incorpn (%)	yield (%)
1	12	A	1:1.3		87
2	12	B	1:1.4	0	88
3	17	A	1:1		86
4	17	B	2.3:1	0	80
5	12	D	9.3:1	91	83
6	12	E	9.3:1	47	85
7	17	C	2.5:1		58
8	17	D	4:1	70	66

[a] Reaction conditions: A, 8 equiv of SmI_2, THF, DMPU, MeOH, 60 min. B, 8 equiv of SmI_2, THF, DMPU, CD_3OD, 60 min. C, 5% Na/Hg, Na_2HPO_4, THF/MeOH (4:1), 0 °C, 60 min. D, 5% Na/Hg, Na_2HPO_4, THF/CD_3OD (4:1), 0 °C, 60 min. E, 5% Na/Hg, Na_2HPO_4, THF, 0 °C, 5 min, then CD_3OD, 60 min.

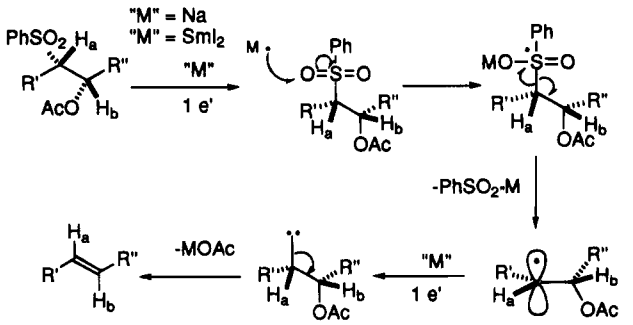


Figure 2. Originally proposed mechanism for the Julia–Lythgoe reduction.

probe the effect of MeOH on the SmI_2 reaction of 1,2-acetoxy sulfones under reductive conditions, MeOH-d_4 was again used to check for deuterium incorporation. As expected, considering previous studies and the accepted mechanism of the Julia–Lythgoe reduction,[2a,e,f] no deuterium incorporation was found (Table 8).

The E:Z ratios derived from these SmI_2-promoted reductions of acetoxy sulfones were considerably different than those using the Na/Hg Julia–Lythgoe procedure; the SmI_2 process is, in general, less E selective. We then decided to probe the classic reduction of an acetoxy sulfone with Na/Hg in THF, a buffer (Na_2HSO_4), and MeOH-d_4. Interesting observations were made differing from what one would expect considering the originally proposed reduction mechanism (Figure 2).[2a,e,f]

The first observation was the appearance of a faint intermediate spot by thin layer chromatography (TLC) which upon completion of the reaction was no longer observed. Quenching the reaction prematurely and isolating the intermediate spot revealed it to be the corresponding vinyl sulfone (>55% yield of the vinyl sulfone isolated when the reaction was quenched after 10 min). Surprisingly, reactions run with deuterated MeOH were found to give almost complete deuterium incorporation (Table 8). This result conflicts with the originally proposed mechanism in which both hydrogens of the alkene are derived from the starting material (Figure 2).[2a,e,f]

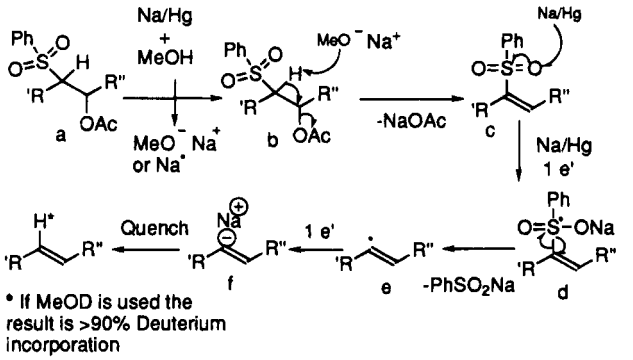


Figure 3. Alternative mechanism for the Na/Hg reductive cleavage of acetoxy sulfones.

Furthermore, it was found that reductions of vinyl sulfones with Na/Hg under the same conditions as used for the acetoxy sulfones gave high selectivity for the *E* olefin. When the Na/Hg reactions were run in the presence of MeOH-d_1, the vinyl sulfones gave the same amount of deuterium incorporation as did the acetoxy sulfones (Table 6). From these deuterium studies, we propose the following mechanism for the Julia–Lythgoe reaction (Figure 3).

The first step is deprotonation of the acetoxy sulfone by NaOMe (a), which leads to the vinyl sulfone (b). The vinyl sulfone is then reduced to the vinyl radical (e) via the predicted pathway, and this intermediate is further reduced to a vinyl anion with sodium as a counterion (f). The ionic species is then quenched to provide the olefin. The mechanism allows for the incorporation of a deuterium as well as the observed olefin stereoselectivity via equilibration of the vinyl radical (e).

In the case of reduction of acetoxy sulfones with SmI_2, a different pathway is most probably followed. The sulfone is reduced to produce an alkyl radical that is further reduced to the alkyl anion (Figure 2). The anion then collapses to produce acetate and the corresponding olefin. The elimination step does not provide for any equilibration and thus leads to the poor olefin stereoselectivity observed in some of these cases. The mechanism is supported by the fact that deuterium incorporation does not occur (Table 8). These pathways (Figures 2 and 3) represent independent limiting possibilities; thus the outcome of a given reduction using Na(Hg) may reflect contributions from both direct reduction of the acetoxy sulfone and adventitious reduction of the corresponding vinyl sulfone.

Concluding Remarks

The SmI_2 variation on the Julia–Lythgoe reaction has shown significant potential. Our probes into the reaction have exposed the utility of this tool in the coupling of conjugated alkene systems with mechanistically predictable results. The Na/Hg reduction of acetoxy sulfones probably does not follow the originally proposed pathway exclusively. The corresponding SmI_2 reduction mechanism most likely follows a different pathway from that of the Na/Hg reductions and for that reason leads to different product mixtures than the classic Julia–Lythgoe reductions. The reason for the difference is presumably the result of an opportunistic reaction that occurs in the Na/Hg reductions and not in the SmI_2-promoted reactions due to a fundamental difference in the properties of these two reductants. Furthermore, the complexity of these processes is further compounded by the results observed when DMPU and MeOH are included and shows the significant effects additives can have on the course and rates of the SmI_2-promoted reductions of 1,2-alkoxy sulfones and vinyl sulfones. Our studies into the use of SmI_2 for reductive elimination of vinyl sulfones and the synthetic utility of this method continue. Further developments will be described in due course.

Experimental Section

General Methods. Solvents were purified according to the guidelines in *Purification of Common Laboratory Chemicals* (Perrin, Armarego, and Perrin, Pergamon Press. Ltd.: Oxford, 1966). Reagent grade *t*-BuOH, MeOH, benzenesulfinic acid sodium salt, and DMPU were purchased and used without further purification. HMPA was distilled from CaH_2 and stored over 4 Å molecular sieves. Hydrocinnamaldehyde, benzaldehyde, cinnamaldehyde, heptaldehyde, and Ac_2O were purchased and distilled prior to use. Thin layer chromatography was performed on Merk kiesegel 60 F_{254} plates eluting with the indicated solvents, visualized by a 254 nm UV lamp, and stained with an ethanolic 12-molybdophosphoric acid solution (Dragendorff's reagent). Flash column chromatography was performed using Davisil 62 silica gel dry packed in glass columns eluting with freshly distilled EtOAc and hexane mixtures as described by Still.[15] Preparative chromatography was also carried out using a Chromatotron using glass plates coated with silica gel (P.F. 254 60) of 1, 2, and 4 mm thickness. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired at 300 MHz with chemical shifts reported in parts per million downfield from TMS (internal reference) for ^{1}H. The abbreviations s, d, t, q, p, and sex stand for the resonance multiplicities singlet, doublet, triplet, quartet, pentuplet, and sextuplet, respectively. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were acquired at 75 MHz with chemical shifts reported in parts per million downfield relative to the center line of the triplet of $CDCl_3$ at 77.0 ppm. Exact masses were calculated with an internal standard whose mass was within 10% of the sample. Analytical C and H combustion analyses were performed by Atlantic Microlab, Inc., Norcross, GA. All reactions were performed in flame- or oven-dried flasks under a positive pressure of nitrogen unless otherwise indicated. Liquid reagents and solvents were introduced by oven-dried syringes through septa-sealed flasks. SmI_2 was prepared by the method of Imamoto[16] in the reaction flask as a 1.0 M solution. Sodium/mercury amalgam was prepared and titrated using a literature proceedure.[17]

General Procedure for Producing Alkyl Sulfones. Preparation of 1-(Phenylsulfonyl)-3-phenylpropane (11). To a stirring solution of 1-(bromophenyl)propane (4.82 g, 24.23 mmol) in DMF (55 mL) was added benzenesulfinic acid sodium salt (5.57 g, 33.94 mmol). The reaction went cloudy white and began to coagulate. The slurry was stirred for 20 h and then diluted with ether (80 mL). After being washed with saturated NH_4Cl (2 × 50 mL), the aqueous layer was reextracted with ether (50 mL) and washed again with saturated NH_4Cl (2 × 20 mL). The combined organics were dried ($MgSO_4$) and then filtered through Celite (1 cm) and silica (4 cm), concentrated, and recrystallized from 5:4:1 CH_2Cl_2/pentanes/ether to yield **11** as clear colorless cubes (mp 68–72 °C) and thick needles (mp 66–71 °C) (3.43 g (first crop), 2.05 g (second crop) 87%): R_f 0.26 (20% EtOAc/hexane); 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.87–7.92 (m, 2 H), 7.67 (m, 1 H), 7.53–7.60 (m, 2 H), 7.17–7.32 (m, 3 H), 7.08–7.13 (m, 2 H), 3.03 (m, 2 H), 2.70 (t, J = 7.5 Hz, 2 H), 2.06 (m, 2 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 139.8, 139.0, 133.7, 129.3, 128.6, 128.4, 127.8, 126.4, 55.2, 34.0, 24.1; IR ($CHCl_3$ film) 3023, 1308, 1217, 1150, 775, 745, 700,

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669; HRMS(EI) m/z calcd for $C_{15}H_{16}O_2S$ 260.0870; found 260.0865. Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.19; H, 6.20. Found: C, 69.01; H, 6.20.

General Procedure 1a for the Coupling of the Alkyl Sulfone and the Aldehyde To Generate the α-Alkoxy Sulfone. Preparation of 1-Acetoxy-1,4-diphenyl-2-(phenylsulfonyl)butane (12). A solution of alkyl sulfone **11** (1.00 g, 3.85 mmol) in THF (35 mL) was cooled to −78 °C, *n*-BuLi (1.88 mL of 2.25 M in hexanes, 4.24 mmol) was added dropwise, and the bright yellow clear solution was mixed for 30 min. Benzaldehyde (429 mg, 0.411 mL, 4.039 mmol) in 4 mL of THF was added dropwise via cannula, and the solution was washed in with 2 mL of THF. The mixture was kept at −78 °C for 3 h before Ac_2O (786 mg, 0.730 mL, 7.70 mmol) was added dropwise via syringe. The bath was maintained at −78 °C for 1 h before the bath was allowed to expire, bringing the solution to room temperature overnight. The reaction was quenched with saturated NH_4Cl, the solution was extracted with CH_2Cl_2 (1 × 50 mL, 2 × 15 mL) and with ether (1 × 20 mL), and the combined organics were dried over $MgSO_4$, filtered through Celite (0.5 cm) and silica gel (2 cm), and concentrated *in vacuo*. The crude product was purified by RPLC (4 mm plate) loaded with 2 mL of 5% EtOAc/hexanes and eluted with 100 mL of hexanes, 100 mL of 5% EtOAc/hexanes, 100 mL of 10% EtOAc/hexanes, 100 mL of 15% EtOAc/hexanes, 150 mL of 20% EtOAc/hexanes, and 150 mL of 35% EtOAc/hexanes to yield 1.325 g (85%) of **12** as a clear slightly yellow liquid: R_f 0.14 (20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.89 (m, 2 H), 7.54–7.71 (m, 3 H), 6.99–7.36 (m, 8 H), 6.78–6.84 (m, 2 H), 6.42 (d, J = 1.8 Hz, 1 H), 3.22 (ddd, J = 6.3, 4.4, 1.8 Hz, 1 H), 2.10–2.70 (m, 4 H), 1.98 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 169.1, 139.9, 138.1, 137.4, 133.8, 129.2, 128.9, 128.7, 128.5, 128.3, 128.1, 126.1, 125.1, 70.1, 60.3, 33.8, 24.5, 20.9; IR ($CHCl_3$ film) 3028, 1749, 1373, 1307, 1233, 760, 700. Anal. Calcd for $C_{24}H_{24}O_4S$: C, 70.46; H, 5.92. Found: C, 70.00; H, 5.83.

Minor isomer: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.89 (m, 2 H), 7.54–7.71 (m, 3 H), 6.99–7.36 (m, 8 H), 6.78–6.84 (m, 2 H), 6.12 (d, J = 9.1 Hz, 1 H), 3.63 (dt, J = 9.1, 5.1 Hz, 1 H), 2.10–2.70 (m, 4 H), 1.63 (s, 3 H).

General Procedure 1b for the Coupling of the Alkyl Sulfone and the Aldehyde To Generate the α-Alkoxy Sulfone. Preparation of 7-Acetoxy-8-(phenylsulfonyl)-pentadecane (13). A solution of *n*-octyl sulfone (500 mg, 1.97 mmol) in THF (8 mL) was cooled to −78 °C, *n*-BuLi (1.88 mL of 1.25 M in hexanes, 2.36 mmol) was added dropwise, and the bright yellow clear solution was mixed for 30 min. Heptaldehyde (337 mg, 2.96 mmol) in 2 mL of THF was added dropwise via cannula and washed in with 2 mL of THF. The mixture was kept at −78 °C for 3 h before the bath was allowed to expire, bringing the solution to rt overnight. The reaction was quenched with saturated NH_4Cl (10 mL), the solution was extracted with ether (3 × 20 mL), and the combined organics were dried over $MgSO_4$, filtered through Celite (0.5 cm) and silica gel (2 cm), and concentrated *in vacuo*. The crude product was purified by RPLC (4 mm plate) loaded with 2 mL of 5% EtOAc/hexanes and eluted with 100 mL of 5% EtOAc/hexanes, 100 mL of 10% EtOAc/hexanes, 100 mL of 15% EtOAc/hexanes, 150 mL of 20% EtOAc/hexanes, and 150 mL of 35% EtOAc/hexanes to yield 616 mg (84%) of the hydroxy sulfone as a clear slightly yellow liquid. The hydroxy sulfone was dissolved into 5 mL of CH_2Cl_2, and to this were added triethylamine (675 mg, 0.931 mL, 668 mmol), one small crystal of DMAP, and then Ac_2O (342 mg, 0.315 mL, 335 mmol). The reaction was mixed overnight before being quenched by dilution into 20 mL of ether and 10 mL of brine. The aqueous phase was extracted with ether (3 × 10 mL), and the combined organics were dried over $MgSO_4$, filtered through Celite (0.5 cm) and silica gel (2 cm), and concentrated *in vacuo*. The crude product was purified by RPLC (4 mm plate) loaded with 2 mL of 5% EtOAc/hexanes and eluted with 100 mL of hexanes, 100 mL of 5% EtOAc/hexanes, 100 mL of 10% EtOAc/hexanes, 150 mL of 15% EtOAc/hexanes, and 150 mL of 20% EtOAc/hexanes to yield 634 mg (93%) of **13** as a clear colorless liquid: R_f 0.39 (20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.90 (m, 2 H), 7.65 (m, 1 H), 7.57 (m, 2 H), 5.10 (dt, J = 2.9, 10.3 Hz, 1H), 3.33 (ddd, J = 10.3, 7.6, 5.2 Hz, 1H), 1.94 (m, 1 H), 1.91 (s, 3 H), 1.74 (m, 1 H), 1.10–1.50 (m, 18 H), 0.82–0.92 (m, 8 H); 75 MHz ^{13}C NMR ($CDCl_3$) δ 169.8, 139.0, 133.4, 128.8, 128.3, 71.2, 65.7, 31.4, 31.3, 29.5, 28.9, 28.5, 28.4, 27.3, 25.5, 23.8, 22.3, 22.2, 20.5, 13.8, 13.7; IR (neat) 2928, 2859, 1744, 1449, 1375, 1306, 1150, 1024, 959, 754. Anal. Calcd for $C_{23}H_{38}O_4S$: C, 67.28; H, 9.33. Found: C, 67.40; H, 9.34.

3-Acetoxy-1,6-diphenyl-4-(phenylsulfonyl)-1-hexene (14). Compound **11** (800 mg, 3.066 mmol) was treated according to the general procedure 1a with *trans*-cinnamaldehyde (426 mg, 0.406 mL, 3.22 mmol) and Ac_2O (626 mg, 0.579 mL, 6.132 mmol) and purified by RPLC (4 mm plate, gradient elution hexanes to 35% EtOAc/hexanes) to give 1.133 g (85%) of **14** as a clear colorless liquid: R_f 0.18 (20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.87–7.92 (m, 2 H), 7.52–7.69 (m, 3 H), 7.04–7.39 (m, 10 H), 6.65 (dd, J = 15.8, 0.9 Hz, 1 H), 6.19 (dd, J = 16.0, 7.0 Hz, 1 H), 5.79–5.98 (m, 1 H), 3.44 (q, J = 5.7, 1 H), 2.73–2.97 (m, 2 H), 2.06–2.50 (m, 2 H), 1.82 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 171.1, 140.1, 139.2, 135.6, 134.7, 133.7, 133.6, 129.2, 128.9, 128.7, 128.6, 128.5, 128.4, 126.8, 126.7, 71.7, 65.3, 33.2, 21.0, 14.1; IR ($CHCl_3$) 3030, 1742, 1449, 1373, 1308, 1233, 1148, 968, 693. Anal. Calcd for $C_{26}H_{26}O_4S$: C, 71.86; H, 6.03. Found: C, 71.59; H, 5.96.

1-Acetoxy-4-methyl-2-(phenylsulfonyl)-1-phenyl-3-pentene (15). Prenyl phenyl sulfone[14k] (1.00 g, 4.762 mmol), was treated according to the general procedure 1a with benzaldehyde (531 mg, 0.508 mL, 5.00 mmol) and Ac_2O (972 mg, 0.900 mL, 9.524 mmol) and purified by RPLC (4 mm plate, gradient elution hexanes to 35% EtOAc/hexanes) to give 1.249 g (84%) of **15** as a clear colorless solid (mp 101–106 °C): R_f 0.08 (20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.84–7.90 (m, 2 H), 7.59–7.68 (m, 1 H), 7.49–7.57 (m, 2 H), 7.17–7.30 (m, 5 H), 6.27 (d, J = 8.9 Hz, 1 H), 4.79 (m, 1 H), 4.42 (dd, J = 11.0, 8.9 Hz, 1 H), 1.91 (s, 3 H), 1.45 (d, J = 1.3 Hz, 3 H), 1.15 (d, J = 1.3 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 169.3, 144.5, 143.1, 139.2, 138.3, 137.1, 133.4, 128.9,. 128.8, 128.2, 127.5, 73.2, 68.0, 54.9, 20.9, 16.6; IR ($CDCl_3$ film) 3023, 1744, 1373, 1306, 1233, 1146, 1026, 755. Anal. Calcd for $C_{20}H_{22}O_4S$: C, 67.01; H, 6.19. Found: C, 66.89; H, 6.23.

Minor isomer: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.84–7.90 (m, 2 H), 7.59–7.68 (m, 1 H), 7.49–7.57 (m, 2 H), 7.17–7.30 (m, 5 H), 6.63 (d, J = 1.76 Hz, 1 H), 5.44 (m, 1 H), 3.94 (dd, J = 10.7, 1.9 Hz, 1 H), 2.00 (s, 3 H), 1.72 (d, J = 1.3 Hz, 3 H), 0.96 (d, J = 1.3 Hz, 3 H).

3-Acetoxy-6-methyl-4-(phenylsulfonyl)-1-phenyl-5-heptene (16). Prenyl phenyl sulfone[14k] (1.00 g, 4.762 mmol) was treated according to the general procedure 1a with hydrocinnamaldehyde (702 mg, 0.692 mL, 5.24 mmol) and Ac_2O (972 mg, 0.900 mL, 9.524 mmol) and purified by RPLC (4 mm plate, gradient elution hexanes to 20% EtOAc/hexanes) to give 1.766 g (96%) of **16** as a clear colorless glass: R_f 0.14 (20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.76–7.82 (m, 2 H), 7.61 (m, 1 H), 7.46–7.55 (m, 2 H), 7.09–7.31 (m, 5 H), 5.42 (ddd, J = 9.4, 6.3, 2.8 Hz, 1 H), 5.09 (m, 1 H), 4.20 (dd, J = 11.0, 6.3 Hz, 1 H), 2.54–2.66 (m, 4 H), 1.99 (s, 3 H), 1.71 (d, J = 1.3 Hz, 3 H), 1.26 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 170.3, 144.3, 141.0, 138.5, 133.5, 128.9, 128.8, 128.5, 128.4, 128.3, 126.0, 112.7, 70.8, 66.3, 31.4, 26.0, 20.9, 17.9; IR ($CDCl_3$ film) 3027, 1738, 1449, 1306, 1235, 1148, 745, 592. Anal. Calcd for $C_{22}H_{26}O_4S$: C, 68.36; H, 6.61. Found: C, 68.40; H, 6.79.

Minor isomer: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.76–7.82 (m, 2 H), 7.61 (m, 1 H), 7.46–7.55 (m, 2 H), 7.09–7.31 (m, 5 H), 5.73 (ddd, J = 7.9, 5.7, 2.2 Hz, 1 H), 5.36 (m, 1 H), 3.84 (dd, J = 10.6, 2.2 Hz, 1H), 2.54–2.66 (m, 4 H), 1.98 (s, 3 H), 1.78 (d, J = 1.3 Hz, 3 H), 1.26 (s, 3 H).

4-Acetoxy-6-methyl-3-(phenylsulfonyl)-1-phenyl-5-heptene (17). Compound **11** (950 mg, 3.65 mmol) was treated according to the general procedure 1a with 2-methyl-2-butenal (460 mg, 5.48 mmol) and Ac_2O (1.86 g, 1.72 mL, 18.25 mmol) and purified by RPLC (4 mm plate, gradient elution hexanes to 30% EtOAc/hexanes) to give 1.295 g (92%) of **17** as a white solid (mp 101–103 °C): major isomer, R_f 0.18 (20% EtOAc/hexane); 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.15–7.90 (m, 10 H), 5.93 (dd, J = 2.2, 8.5 Hz, 1 H), 5.04 (m, 1 H), 3.07 (m, 1 H),

2.91 (m, 2 H), 2.42 (m, 1 H), 2.18 (m, 1 H), 1.79 (s, 3 H), 1.59 (d, J = 1.2 Hz, 3 H), 1.44 (d, J = 1.2 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 169.1, 140.1, 138.3, 138.1, 133.4, 128.8, 128.5, 128.3, 128.2, 125.9, 120.0, 67.7, 66.2, 33.7, 25.4, 25.3, 20.4, 17.7; IR (neat) 3027, 1740, 1447, 1373, 1308, 1235, 1308, 1235, 1148, 1024, 754 cm^{-1}. Anal. Calcd for $C_{22}H_{26}O_4S$: C, 68.36; H, 6.78. Found: C, 68.47; H, 6.72.

Minor isomer: R_f 0.18 (20% EtOAc/hexane); 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.05–7.90 (m, 10 H), 5.87 (dd, J = 6.4, 9.8 Hz, 1 H), 5.08 (m, 1 H), 3.37 (m, 1 H), 2.80 (m, 2 H), 2.32 (m, 1 H), 2.04 (m, 1 H), 1.75 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 169.0, 140.7, 140.1, 139.7, 133.3, 128.8, 128.3, 128.2, 128.1, 126.1, 118.8, 68.8, 65.3, 33.2, 26.6, 25.8, 20.6, 18.5; IR (neat) 3025, 1738, 1449, 1371, 1306, 1233, 1144, 1018, 754 cm^{-1}. Anal. Calcd for $C_{22}H_{26}O_4S$: C, 68.36; H, 6.78. Found: C, 68.16; H, 6.83.

3-Acetoxy-6-methyl-4-(phenylsulfonyl)-1-phenyl-1,5-heptadiene (18). Prenyl phenyl sulfone[14k] (500 mg, 2.381 mmol) was treated according to the general procedure 1a with *trans*-cinnamaldehyde (331 mg, 0.315 mL, 2.500 mmol) and Ac_2O (486 mg, 0.450 mL, 4.762 mmol) and purified by RPLC (4 mm plate, gradient elution 10% EtOAc/hexanes to 50% EtOAc/hexanes) to give 841 mg (92%) of **18** as a clear yellow solid (mp 119–128 °C): R_f 0.09 (20% EtOAc/hexane); 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.86 (m, 2 H), 7.61 (m, 1 H), 7.47–7.55 (m, 2 H), 7.20–7.38 (m, 5 H), 6.68 (d, J = 15.7 Hz, 1 H), 6.16 (m, 1 H), 6.02 (dd, J = 6.9, 6.9 Hz, 1 H), 5.07 (dd, J = 10.8, 1.0 Hz, 1 H), 4.35 (ddd, J = 10.7, 6.5, 1.2 Hz, 1 H), 2.01 (d, J = 1.3 Hz, 3 H), 1.68 (s, 3 H), 1.31 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 169.1, 143.5, 138.5, 135.6, 134.3, 133.3, 128.6, 128.5, 128.2, 127.9, 126.4, 123.1, 112.4, 71.5, 66.6, 25.6, 20.6, 17.8; IR ($CDCl_3$ film) 3027, 2978, 1740, 1449, 1373, 1237, 1148, 966, 691; HRMS(EI) m/z calcd for $C_{22}H_{24}O_4S$ 384.1394, found 384.1384.

8-Acetoxy-9-(phenylsulfonyl)-2,6,11,15-tetramethylhexadeca-2,6,10,14-tetraene (19). Geranyl phenyl sulfone[14l] (1.34 g, 4.81 mmol) was treated according to the general procedure 1a with geranial (805 mg, 5.29 mmol) and Ac_2O (2.46 g, 2.27 mL, 24.03 mmol) and purified by RPLC (4 mm plate in two passes, gradient elution 10% EtOAc/hexanes to 50% EtOAc/hexanes) to give 2.106 g (93%) of **19** as a clear colorless liquid which contained an inseparable mixture of (syn/anti) isomers: R_f 0.30 (20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.88–7.81 (m, 2 H), 7.61 (m, 1 H), 7.56–7.48 (m, 2 H), 6.05 (dd, J = 9.7, 7.5 Hz, 1 H), 5.03 (m , 3 H), 4.95 (d, J = 9.7, 7.5 Hz, 1 H), 4.25 (dd, J = 10.8, 7.5 Hz, 1 H), 2.15–1.85 (m, 8 H), 1.92 (s, 3 H), 1.77 (d, J = 1.2 Hz, 3 H), 1.70–1.61 (m, 6 H), 1.59–1.55(m, 6 H), 1.35 (d, J = 1.3 Hz, 3 H).

Minor isomer: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.88–7.81 (m, 2 H), 7.61 (m, 1 H), 7.60–7.47 (m, 2 H), 6.23 (dd, J = 9.4, 2.4 Hz, 1 H), 5.35 (d, J = 10.6 Hz, 1 H), 5.06 (m, 3 H), 3.85 (dd, J = 10.6, 2.4 Hz, 1 H), 2.15–1.80 (m, 8 H), 1.90 (s, 3 H), 1.75 (d, J = 1.2 Hz, 3 H), 1.70–1.62 (m, 6 H), 1.58(m, 6 H), 1.39 (d, J = 1.3 Hz, 3 H)

3-Acetoxy-6,10-dimethyl-4-(phenylsulfonyl)-1-phenyldodeca-1,5,9-triene (6). Geranyl phenyl sulfone[14l] (250 mg, 0.898 mmol) was treated according to the general procedure 1a with *trans*-cinnamaldehyde (131 mg, 0.990 mmol) and Ac_2O (458 mg, 0.425 mL, 4.490 mmol) and purified by RPLC (4 mm plate, gradient elution 5% EtOAc/hexanes to 50% EtOAc/hexanes) to give 326 mg (89%) of **6** as a clear colorless liquid: R_f 0.17(20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.88–7.78 (m, 2 H), 6.64 (m, 1H), 7.57–7.44 (m, 2H), 7.33–7.14 (m, 5H), 6.69 (dd, J = 15.8, 0.6 Hz, 1H), 6.19 (dd, J = 7.9, 1.9 Hz, 1H), 5.99 (dd, J = 15.8, 7.9 Hz, 1H), 5.41 (dd, J = 10.7, 1.2 Hz, 1H), 5.08 (m, 1H), 4.02 (dd, J = 10.6, 2.5 Hz, 1H), 2.10 (bs, 4H), 1.96 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H), 1.35 (d, J = 1.5 Hz, 3H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 169.3, 147.6, 138.6, 135.6, 134.6, 133.5, 132.0, 129.0, 128.7, 128.5, 127.7, 126.6, 123.7, 123.4, 111.8, 71.2, 67.4, 39.8, 26.1, 25.6, 20.9, 17.6, 16.5; IR (neat) 2969, 2919, 1746, 1449, 1373, 1306, 1229, 1148, 912, 735, 691.

Minor isomer: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.89–7.85 (m, 2 H), 7.62 (m, 1H), 7.56–7.48 (m, 2H), 7.37–7.21 (m, 5H), 6.67 (d, J = 15.7 Hz, 1H), 6.12 (dd, J = 15.7, 7.5 Hz, 1H), 5.99 (m, 1H), 5.04 (dd, J = 10.9, 1.2 Hz, 1H), 4.98 (m, 1H), 4.34 (dd, J = 10.9, 6.9 Hz, 1H), 1.99 (s, 3H), 1.95 (bs, 4H), 1.62 (s, 3H), 1.52 (d, J = 0.7, 3H), 1.35 (d, J = 1.5 Hz, 3H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 169.5, 147.0, 138.8, 135.8, 134.6, 133.5, 132.0, 129.1, 128.8, 128.5, 128.2, 126.7, 123.3, 123.2, 112.7, 71.9, 66.7, 39.7, 26.1, 25.5, 21.0, 17.5, 16.6; IR (neat) 3028, 2969, 2926, 2857, 1744, 1661, 1449, 1306, 1231, 1148, 1022, 912, 735, 691. Anal. Calcd for $C_{27}H_{32}O_4S$: C, 71.65; H, 7.13. Found: C, 71.50; H, 7.11.

General Procedure 2a for the Conversion of Acetoxy Sulfones to Vinyl Sulfones with 1,8-Diazobicyclo[5.4.0]-undec-7-ene. Preparation of 1,4-Diphenyl-2-(phenylsulfonyl)-1-butene (20). To a solution of acetoxy sulfone **12** (1.47 g, 3.607 mmol) in THF (50 mL) was added DBU (3.30 g, 3.24 mL, 21.65 mmol) dropwise via syringe. After 18 h, the reaction was judged complete by TLC and quenched by dilution with ether (20 mL) and brine (10 mL). The aqueous phase was re-extracted with methylene chloride (3 × 60 mL). The combined organics were extracted with brine (10 mL), dried over $MgSO_4$, filtered through Celite (0.5 cm) and silica gel (2.0 cm), and concentrated *in vacuo*. The crude product was purified by RPLC on a 4 mm plate in two passes loaded with 5% EtOAc/hexanes and eluted with 50 mL of hexanes, 75 mL of 5% EtOAc/hexanes, 100 mL of 10% EtOAc/hexanes, 150 mL of 15% EtOAc/hexanes, and 150 mL of 20% EtOAc/hexanes to yield 1.26 g (97%) of the product **20** as a clear colorless solid (mp 87–90 °C): R_f 0.38 (20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 8.05 (m, 1 H), 8.03 (m, 1 H), 7.96 (s, 1 H), 7.58–7.71 (m, 3 H), 7.42–7.50 (m, 5 H), 7.19–7.34 (m, 3 H), 7.10–7.15 (m, 2 H), 2.83 (s, 4 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 140.8, 140.4, 139.5, 138.7, 133.4, 133.3, 129.5, 129.3, 129.2, 128.8, 128.5, 128.2, 128.1, 126.3, 34.2, 29.2; IR ($CHCl_3$) 3070, 1520, 1475, 1290, 1105, 1080, 705, 600. Anal. Calcd for $C_{22}H_{18}O_2S$: C, 75.83; H, 5.79. Found: C, 75.75; H, 5.84.

General Procedure 2b for the Conversion of an Acetoxy Sulfone to a Vinyl Sulfone with LDA. Preparation of 8-(Phenylsulfonyl)pentadec-8-ene (21). A solution of diisopropylamine (DIA) (20 mg, 28 μL, 0.202 mmol) in THF (2.0 mL) was cooled to 0 °C, and n-BuLi (90 μL of 2.25 M in hexanes, 0.202 μL) was added dropwise to the mixture. After 30 min the mixture was further cooled to −78 °C and the acetoxy sulfone **13** (79 mg, 0.192 mmol) was added dropwise via cannula as a solution in 1 mL of THF and washed in with 0.5 mL of THF. The reaction became bright yellow and slowly went bright orange over a 1 h period. After 2 h the reaction was warmed to −23 °C, stirred for 6 h, and then quenched at −23 °C with 15 mL of saturated aqueous NH_4Cl. The mixture was extracted once with ether (20 mL) and methylene chloride (3 × 10 mL), dried over $MgSO_4$, filtered through Celite (0.5 cm) and silica gel (2 cm), and concentrated *in vacuo*. The crude material was further purified by column chromatography loaded with 1 mL of 10% EtOAc/hexanes and run with 15 mL of hexanes, 15 mL of 10% EtOAc/hexanes, 15 mL of 15% EtOAc/hexanes, 15 mL of 20% EtOAc/hexanes, and 15 mL of 35% EtOAc/hexanes to yield 4.0 mg (6%) of hydroxy sulfone, 26.0 mg (33%) of recovered acetoxy sufone **13,** and 31.0 mg (46%) of vinyl sulfone **21** as a clear colorless liquid: R_f 0.48 (20% EtOAc/hexane); 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.87–7.83 (m, 2 H), 7.59 (m, 1H), 7.55–7.48 (m, 2H), 6.91 (t, J = 7.33 Hz, 1H), 2.23–2.14 (m, 3H), 1.47 (m, 2H), 1.29 (m, 8H), 1.17 (s, 7H), 0.90–0.82 (m, 7H); 75 MHz ^{13}C NMR ($CDCl_3$) δ 142.2, 140.9, 140.1, 132.9, 128.9, 127.9, 31.5, 31.4, 29.3, 28.9, 28.6, 28.4, 28.3, 26.4, 22.5, 22.4, 14.0, 13.9; IR ($CDCl_3$ film) 2928, 2857, 1466, 1304, 1154, 1138, 1086, 725, 691. Anal. Calcd for $C_{21}H_{34}O_2S$: C, 71.95; H, 9.78. Found: C, 72.16; H, 9.80.

1,6-Diphenyl-4-(phenylsulfonyl)-1,3-hexadiene (22). Acetoxy sulfone **14** (600 mg, 1.38 mmol) was treated according to the general procedure 2a with DBU (1.261 g, 1.24 mL, 8.28 mmol) and purified by RPLC (4 mm plate, gradient elution hexanes to 50% EtOAc/hexanes) to give 486 mg (94%) of **22** as a clear colorless liquid: R_f 0.25 (20% EtOAc/hexane); major isomer, 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.91–7.97 (m, 2 H), 7.46–7.62 (m, 3 H), 7.41 (dd, J = 11.4, 0.6 Hz, 1 H), 7.18–7.36 (m, 8 H), 7.11–7.60 (m, 2 H), 6.90 (dd, J = 15.4, 0.6 Hz, 1 H), 6.52 (dd, J = 15.4, 11.4 Hz, 1 H), 2.52–2.56 (m, 4 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 154.3, 140.6, 140.1, 138.6, 138.5, 135.7, 133.4,

131.5, 129.2, 128.5, 128.3, 128.2, 128.1, 127.3, 121.3, 35.9, 29.2; IR ($CDCl_3$ film) 3020, 1650, 1590, 1480, 1290, 1090; HRMS(EI) m/z calcd for $C_{24}H_{22}O_2S$ 374.13405, found 374.13256. Anal. Calcd for $C_{24}H_{22}O_2S$: C, 76.90; H, 5.92. Found: C, 77.10; H, 5.99.

Minor isomer: 300-MHz ^1H NMR ($CDCl_3$) δ 8.14 (dd, J = 15.5, 11.6 Hz, 1 H), 7.91–7.97 (m, 2 H), 7.49–7.62 (m, 5 H), 7.09–7.40 (m, 8 H), 6.68 (d, J = 15.7 Hz, 1 H), 6.51 (dt, J = 11.4, 1.9 Hz, 1 H), 2.77 (m, 4 H).

4-Methyl-2-(phenylsulfonyl)-1-phenyl-1,3-pentadiene (23). Acetoxy sulfone **15** (508 mg, 1.568 mmol) was treated according to the general procedure 2a with DBU (1.43 g, 1.37 mL, 9.407 mmol) and purified by RPLC (4 mm plate, gradient elution hexanes to 35% EtOAc/hexanes) to give 456 mg (98%) of **23** as a white solid (mp 89–95 °C): R_f 0.40 (20% EtOAc/hexane); major isomer, 300-MHz ^1H NMR ($CDCl_3$) δ 7.85–7.90 (m, 2 H), 7.73 (d, J = 1.2 Hz, 1 H), 7.46–7.61 (m, 5 H), 7.30–7.36 (m, 3 H), 5.84 (m, 1 H), 1.74 (d, J = 1.2 Hz, 3 H), 0.93 (d, J = 1.17 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 144.9, 139.2, 138.3, 137.0, 133.7, 133.0, 129.8, 129.8, 128.7, 128.6, 128.4, 114.1, 25.2, 18.9; IR ($CDCl_3$ film) 3022, 2361, 1304, 1217, 1148, 774, 747, 689, 669, Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08. Found: C, 72.43; H, 6.11.

6-Methyl-4-(phenylsulfonyl)-1-phenyl-3,5-heptadiene (24). Acetoxy sulfone **16** (636 mg, 1.646 mmol) was treated according to the general procedure 2b with LDA (from n-BuLi (0.864 mL of a 2.00 M solution in hexanes, 1.728 mmol) and DIA (183 mg, 0.254 mL, 1.811 mmol)), but the reaction was quenched after 2 h at −78 °C and the solution was purified by RPLC (4 mm plate, gradient elution 5% EtOAc/hexanes to 20% EtOAc/hexanes) to yield 119.1 mg (21%) hydroxy sulfone, 91 mg (14%) recovered acetoxy sufone **16,** and 321.0 mg (60%) of vinyl sulfone **24** as a clear colorless liquid: R_f 0.27 (20% EtOAc/hexane); major isomer, 300-MHz ^1H NMR ($CDCl_3$) δ 7.72–7.77 (m, 2 H), 7.52–7.58 (m, 1 H), 7.42–7.49 (m, 2 H), 7.11–7.31 (m, 5 H), 6.94 (dt, J = 7.3, 1.0 Hz, 1 H), 5.47 (m, 1 H), 2.76 (t, J = 7.3, 1 H), 2.36 (dq, J = 8.0, 1.0 Hz, 1 H), 1.71 (d, J = 1.5 Hz, 3 H), 1.06 (d, J = 1.2 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 144.4, 140.5, 140.0, 139.3, 132.8, 132.2, 128.7, 128.5, 128.3, 128.2, 126.2, 113.5, 34.2, 31.0, 28.4, 18.9; IR ($CDCl_3$ film) 3025, 1445, 1302, 1146, 1084, 909, 802; HRMS(EI) m/z calcd for $C_{20}H_{22}O_2S$ 326.13405, found 326.13668. Anal. Calcd for $C_{20}H_{22}O_2S$: C, 73.58; H, 6.79. Found: C, 73.30; H, 6.77.

6-Methyl-3-(phenylsulfonyl)-1-phenyl-3,5-heptadiene (25). Acetoxy sulfone **17** (530 mg, 1.37 mmol) was treated according to the general procedure 2a with DBU (2.09 g, 1.02 mL, 13.70 mmol) and purified by RPLC (4 mm plate, gradient elution 5% EtOAc/hexanes to 30% EtOAc/hexanes) to give 384 mg (86%) of **25** as a clear colorless liquid: R_f 0.27 (20% EtOAc/hexane); major isomer, 300-MHz ^1H NMR ($CDCl_3$) δ 7.05–7.95 (m, 11 H), 5.82 (m, 1 H), 2.60 (m, 4 H), 1.93 (d, J = 0.9 Hz, 3 H), 1.87 (d, J = 0.9 Hz, 3 H); 75 MHz ^{13}C NMR ($CDCl_3$) δ 148.3, 140.6, 140.1, 135.7, 134.3, 132.8, 128.9, 128.2, 127.8, 126.0, 118.6, 23.1, 28.6, 26.8, 18.9; IR (neat) 3028, 2932, 1736, 1485, 1447, 1302, 1142, 1090, 910, 851. Anal. Calcd for $C_{20}H_{22}O_2S$: C, 73.58; H,6.79. Found: C, 73.50; H, 6.74.

6-Methyl-4-(phenyl sulfonyl)-1-phenyl-1,3,5-heptatriene (26). Acetoxy sulfone **18** (716 mg, 1.865 mmol) was treated according to the general procedure 2a with DBU (1.70 g, 1.67 mL, 11.19 mmol) and purified by RPLC (4 mm plate, gradient elution hexanes to 20% EtOAc/hexanes) to give 496 mg (83%) of **26** as a clear colorless solid (mp 48–53 °C): R_f 0.39 (20% EtOAc/hexane); major isomer, 300-MHz ^1H NMR ($CDCl_3$) δ 7.82–7.88 (m, 2 H), 7.61–7.40 (m, 6 H), 7.28–7.38 (m, 3 H), 7.01 (d, J = 15.7 Hz, 1 H), 6.62 (dd, J = 15.7, 11.1 Hz , 1 H), 5.75 (bs, 1 H), 1.86 (d, J = 1.5 Hz, 3 H), 1.20 (d, J = 1.3 Hz, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 145.0, 139.7, 138.6, 137.1, 137.1, 136.1, 132.9, 131.5, 129.2, 128.8, 128.8, 128.1, 127.2, 123.4, 31.6, 22.6; IR ($CDCl_3$ film) 2983, 1621, 1447, 1304, 1144, 1088, 995, 721, 604; HRMS(EI) m/z calcd for $C_{20}H_{20}O_2S$ 324.1183, found 324.1187. Anal. Calcd for $C_{20}H_{20}O_2S$: C, 74.04; H, 6.21. Found: C, 73.51; H, 6.20.

Minor isomer: 300-MHz ^1H NMR ($CDCl_3$) δ 8.19 (dd, J = 15.4, 11.7 Hz, 1 H), 7.88 (m, 2 H), 7.29–7.60 (m, 8 H), 6.76 (d, J = 15.7 Hz, 1 H), 6.51 (d, J = 11.7 Hz, 1 H), 5.95 (m, 1 H), 1.79 (d, J = 1.3 Hz, 3 H), 1.46 (d, J = 1.3 Hz, 3 H).

8-(Phenylsulfonyl)-2,6,11,15-tetramethylhexadeca-2,6,8,10,14-pentaene (27). Acetoxy sulfone **19** (416 mg, 0.880 mmol) was treated according to the general procedure 2a with DBU (1.34 g, 1.32 mL, 8.80 mmol) and purified by RPLC (2 mm plate, gradient elution 5% EtOAc/hexanes to 20% EtOAc/hexanes) to give 251 mg (69%) of **27** as a clear pale yellow liquid: R_f 0.41 (20% EtOAc/hexane); major isomer, 300-MHz ^1H NMR ($CDCl_3$) δ 7.83–7.76 (m, 2 H), 7.53 (m, 1 H), 7.48–7.40 (m, 2 H), 5.70 (dd, J = 11.7, 0.9 Hz, 1 H), 5.66 (s , 1 H), 5.12–4.98 (m, 2 H), 2.16–2.08 (m, 5 H), 2.04–2.02 (m, 4 H), 1.95 (d, J = 0.9 Hz, 3 H), 1.69 (s, 3 H), 1.65 (s, 3 H), 1.59 (s, 3 H), 1.58 (d, J = 0.6 Hz, 3 H), 1.10 (d, J = 1.2, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 155.6, 151.2, 147.6, 139.7, 135.7, 132.9, 131.7, 128.4, 127.8, 123.3, 123.1, 122.9, 120.2, 114.0, 113.9, 40.3, 39.0, 28.3, 26.1, 25.4, 17.5, 14.4, 17.1; IR (neat) 2916, 2857, 1674, 1632, 1377, 1304, 1148, 914, 735; HRMS(EI) m/z calcd for $C_{26}H_{36}O_2S$ 412.2434, found 412.2445.

6,10-Dimethyl-4-(phenylsulfonyl)-1-phenyldodeca-1,3,5,9-tetraene (8). Acetoxy sulfone **6** (820 mg, 1.81 mmol) was treated according to the general procedure 2a with DBU (1.65 g, 1.63 mL, 10.87 mmol) and purified by RPLC (4 mm plate, gradient elution 5% EtOAc/hexanes to 50% EtOAc/hexanes) to give 571 mg (81%) of **8** as a clear colorless liquid: R_f 0.36 (20% EtOAc/hexane); major isomer, 300-MHz ^1H NMR ($CDCl_3$) δ 7.83–7.88 (m, 2 H), 7.57 (m, 1H), 7.29–7.52 (m, 8H), 7.02 (d, J = 15.7 Hz, 1H), 6.62 (dd, J = 15.7, 11.1 Hz, 1H), 5.78 (s, 1H), 5.09 (m, 1H), 2.13 (bs, 4H), 1.72 (s, 3H), 1.63 (s, 3H), 1.16 (d, J = 1.3 Hz, 3H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 148.5, 141.6, 139.7, 138.5, 136.9, 136.0, 132.9, 132.2, 129.2, 128.8, 128.7, 128.2, 127.1, 123.5, 123.2, 114.2, 39.2, 26.2, 25.6, 17.7, 17.3; IR (neat) 2915, 1620, 1304, 1144, 978, 752, 721, 689. Anal. Calcd for $C_{25}H_{28}O_2S$: C, 76.49; H, 7.19. Found: C, 76.20; H, 7.22.

Minor isomer: 300-MHz ^1H NMR ($CDCl_3$) δ 8.22 (dd, J = 15.5, 11.7 Hz, 1H), 7.85–7.92 (m, 2 H), 7.45–7.60 (m, 5H), 7.29–7.43 (m, 3H), 6.77 (d, J = 15.4 Hz, 1H), 6.50 (d, J = 11.7 Hz, 1H), 5.96 (s, 1H), 5.06 (m, 1H), 2.08 (bs, 4H), 1.70 (s, 3H), 1.61 (d, J = 0.7 Hz, 3H), 1.45 (d, J = 1.3 Hz, 3H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 145.7, 141.4, 140.9, 136.2, 135.6, 133.0, 132.0, 129.1, 128.9, 128.8, 127.5, 127.4, 123.4, 122.9, 119.4, 39.7, 26.3, 25.6, 17.6, 17.2; IR (neat) 2917, 1615, 1317, 1294, 1134, 978, 752, 689.

General Procedure 3 for the Reductive Cleavage of a Vinyl Sulfone To Afford the Olefin. Preparation of 2-Methyl-7-phenyl-2,4-heptadiene (32). To a suspension of samarium (249 mg, 1.660 mmol) in THF (15 mL) was added iodine (373 mg, 1.470 mmol) in one portion. The mixture was then heated at 65 °C (bath temperature) for 90 min over which time the reaction went from a cloudy brick red color to yellow and then blue green in color characteristic of SmI_2. The mixture was cooled to rt, and the vinyl sulfone **24** (60.0 mg, 0.184 mmol), DMPU (236 mg, 223 μL, 1.84 mmol), and MeOH (61.0 mg, 77 μL, 1.84 mmol) in 2 mL of THF were added dropwise via cannula and washed in with 1 mL of THF. The mixture went purple over the course of the addition. After 30 min, the reaction was judged complete by TLC and quenched with saturated aqueous Na_2SO_3, mixed for 30 min, and then extracted with ether (1 × 20 mL). The organic phase was washed once with 10 mL of brine, and the aqueous phase was then re-extracted once with 10 mL of pentane. The combined organic phase was dried over $MgSO_4$, filtered through Celite (0.5 cm) and silica gel (1.0 cm), concentrated *in vacuo*, and purified via RPLC on a 2 mm plate loaded with 2 mL of 5% EtOAc/hexanes and run with 150 mL of hexanes, 150 mL of 5% EtOAc/hexanes, and 150 mL of 10% EtOAc/hexanes to yield the product **32** as a clear colorless liquid (31 mg, 89%): R_f 0.70 (20% EtOAc/hexane); major isomer, 300-MHz ^1H NMR ($CDCl_3$) δ 7.15–7.35 (m, 5 H), 6.27 (dd, J = 11.0, 15.1 Hz, 1 H), 5.79 (d, J = 11.2 Hz, 1 H), 5.59 (dt, J = 7.8, 15.1 Hz, 1 H), 2.70 (m, 2 H), 2.41 (m, 2 H), 1.75 (s, 3 H), 1.73 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 142.0, 133.3, 130.7, 128.4, 128.3, 127.2, 125.7, 124.9, 36.1, 34.8, 25.9, 18.2; IR (neat) 3027, 2969, 1605, 1497, 1377, 986, 959, 745 cm^{-1}.

6,10-Dimethyl-1-phenyldodeca-1,3,5,9-tetraene (9). Vinyl sulfone **8** (126 mg, 0.321 mmol) was treated according to the general procedure 3 with SmI_2 (2.57 mmol), DMPU (411 mg, 0.388 mL, 3.21 mmol), and MeOH (103 mg, 0.130 mL, 3.21 mmol) and purified by RPLC (2 mm plate, gradient elution 5% EtOAc/hexanes to 30% EtOAc/hexanes) to give 58 mg (70%) of **9** as a clear colorless liquid: R_f 0.73 (20% EtOAc/hexane); 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.46–7.16 (m, 6 H), 6.84 (dd, J = 15.5, 10.7 Hz, 1 H), 6.50 (d, J = 15.5 Hz, 1 H), 6.31 (dd, J = 14.8, 10.7 Hz, 1 H), 5.95 (d, J = 11.1 Hz, 1 H), 5.11 (m, 1 H), 2.10 (s, 4 H), 1.75 (s, 3 H), 1.62 (s, 3 H), 1.55 (s, 3 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 130.9, 130.2, 129.7, 128.9, 128.6, 127.5, 127.1, 126.1, 125.9, 125.1, 123.9, 40.1, 32.7, 26.9, 25.7, 17.7, 16.9; IR (neat) 2967, 2924, 1682, 1377, 985, 747, 691; HRMS(EI) m/z calcd for $C_{19}H_{24}$ 252.1877, found 252.1890.

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Supplementary Material Available: Copies of NMR spectra of five compounds characterized by a high-resolution mass spectrometry: ^{1}H NMR and ^{13}C NMR spectra for **18** and **27** as well as ^{1}H NMR for **9**, **29**, and a mixture of diastereomers of **19**. Also included are ^{1}H NMR spectra for both protonated and deuterated **28** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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