methylchlorosilane and methanol and distilled from sodium methoxide. Tetramethoxysilane (Silar) was used as received. Aqueous buffers were prepared with distilled water which was first passed through an ion-exchange resin and then through a series of Millipore filters. The pH of the prepared buffers was measured with a Leeds-Northrup pH meter equipped with a Beckman combination glass electrode. Calibration was done by bracketting each value with standard solutions. Both sodium and potassium salts were used in the experiments and, within experimental error, no difference was detected. Ionic strength of the solutions was obtained either by the buffer system itself or, in the experiments at lower buffer concentrations, was adjusted to the desired value by the addition of sodium perchlorate or, in a few cases, potassium chloride. No difference was noted by the substitution of perchlorate with chloride.

Analysis of the organic layer was performed on a Shimadzu GC-9A with C-R1B data analyzer. Noting the difficulties in reproducibility of FID methods with silicon compounds, we employed TC detection in conjunction with either a 6 ft 3% OV-101 or a 6 ft Porapak Q column. The latter facilitated monitoring water, methanol, and silicon species. Internal standards were decane (Aldrich, 99%) or octane (Aldrich, 99%) with which response factors were determined.

Temperatures were maintained to ±0.2° in a circulating water bath (27 L volume) equipped with a B. Braun Thermomix heater/circulator. Ice-water baths were used for 0 °C temperature.

Two-Phase Experiment. A 100.0-mL solution of 0.10–0.15 M alkoxysilane and 40 mM octane in pentane and a 100.0-mL buffer solution were separately equilibrated to the desired temperature. The solutions were combined in a round-bottomed flask equipped with a mechanical stirrer and septum for removing sample aliquots. The sealed system was mixed vigorously for timed intervals with sampling periods interpersed. During sampling the mixing was stopped and the phases were allowed to separate. Typically this process took 5–10 s. In experiments with MTMS or $(CH_3O)_4Si$ in base, persistent emulsions formed and aliquots were removed without complete segregation of the phases. The samples were analyzed by GC analysis.

Registry No. $(CH_3)_3Si(OCH_3)$, 1825-61-2; $(CH_3)_2Si(OCH_3)_2$, 1112-39-6; $CH_3Si(OCH_3)_3$, 1185-55-3.

Supplementary Material Available: Table of observed rates as a function of pH and substrate, figure of volume change vs. time for MTMS, and figure of disappearance of MTMS vs. time (5 pages). Ordering information is given on any current masthead page.

Mechanistic Aspects and Profiles of the Double Elimination Reaction of β-Substituted Sulfones

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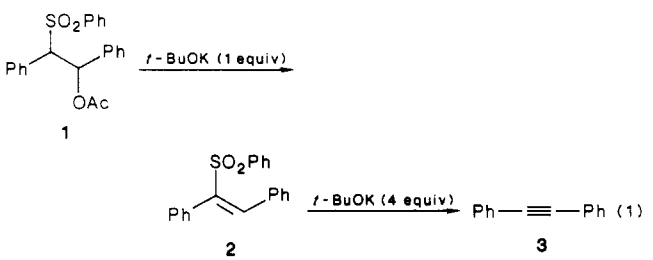
The double elimination reaction of β-acetoxy or β-alkoxy sulfones was investigated in detail by employing some representative reactions. Successful isolation of reaction intermediates revealed the reaction path: the first step is elimination of the acetoxy or alkoxy group to afford a vinyl sulfone. The subsequent elimination of a phenylsulfonyl group from the vinyl sulfone gives acetylenes, while polyenes are formed in cases where isomerization of the vinyl sulfone to an allyl sulfone is possible prior to the second elimination. Besides these mechanistic considerations, general features are discussed in order to make clear the scope and limitations of this synthetically useful reaction.

Previously, we reported a novel double elimination reaction of β-acetoxy or β-alkoxy sulfones which afforded a convenient method for synthesizing enynes and polyenes (Scheme I).[1] Acetylenes are formed when R_2 are phenyl, phenylethynyl, furyl, thienyl, and β-(triorganosilyl)vinyl or -ethynyl groups. By contrast, other (substituted) alkyl and alkenyl aldehydes provide polyene compounds. The utility of this reaction was exemplified by the successful synthesis of *d,l*-muscone and methyl retinoate. More recently, we have demonstrated that this method could be applied to the novel synthesis of vitamin A[2] and (2*E*,4*E*)-dienamides and -dienoates[3] of greater than 90% stereochemical purity. It seems of importance, therefore, to draw out the profile of this reaction. Of particular interest is to disclose what factors determine the reaction path to give either the acetylenic or polyenic compounds. In the hope of obtaining better understanding of these problems, we were attracted to an investigation of some representative reactions in detail. Actually, we have succeeded in isolating the reaction intermediates. In this paper, we describe the mechanistic aspects as well as make some general remarks on the double elimination reaction to make clear the scope and limitations.

Results

Acetylene Formation. When the β-acetoxy sulfone **1** was treated with 1 equiv of *t*-BuOK in *t*-BuOH at room temperature, the vinyl sulfone **2** was formed immediately in 94% yield (eq 1). This is quite reasonable since the



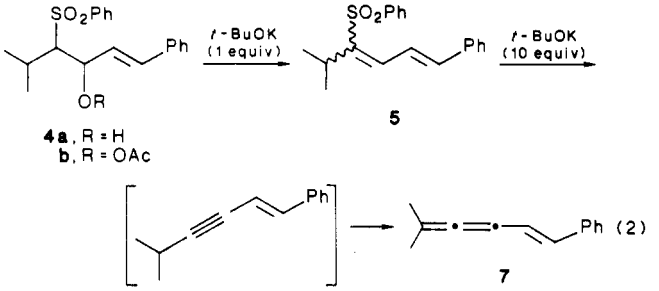
hydrogen α to the phenylsulfonyl group is more acidic than the one α to the acetoxy group. The analogous vinyl sulfone formation from the corresponding tosylates and

(1) Mandai, T.; Yanagi, T.; Araki, K.; Morisaki, Y.; Kawada, M.; Otera, J. *J. Am. Chem. Soc.* **1984**, *106*, 3670.
(2) (a) Otera, J.; Misawa, H.; Mandai, T.; Onishi, T.; Suzuki, S.; Fujita, Y. *Chem lett.* **1985**, 1883. (b) Otera, J.; Misawa, H.; Onishi, T.; Suzuki, S.; Fujita, Y. *J. Org. Chem.*, following paper in this issue.
(3) Mandai, T.; Moriyama, T.; Tsujimoto, K.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1986**, *27*, 603.

0022-3263/86/1951-3830$01.50/0

acetates has been reported by Julia et al.[4] Then, **2** and *t*-BuOK (4 equiv) in THF were heated at reflux to give diphenylacetylene (**3**) in 92% yield.

Another example of the acetylene formation is shown in eq 2. The dienyl sulfone **5** (1*E*,3*Z*/1*E*,3*E* = 9:1) was

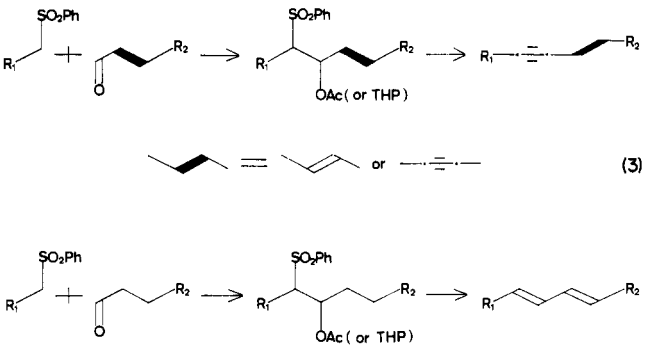


formed on treatment of **4b** with 1 equiv of *t*-BuOK in 84% yield. However, the subsequent reaction of **5** with *t*-BuOK (10 equiv) in refluxing *t*-BuOH yielded the allene **7** (65%) instead of the acetylene **6** probably due to facile isomerization of **6** promoted by *t*-BuOK. As a result, the double elimination reaction leading to acetylenes has proved to proceed via initial elimination of an acetoxy group follwed by desulfonylation.

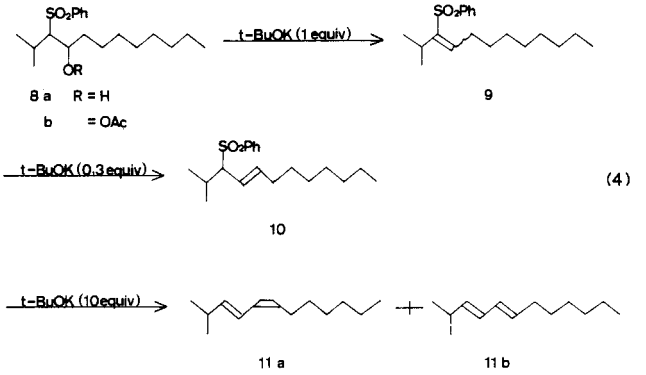
Polyene Formation. When the β-acetoxy sulfone **8b** (anti/syn = 7:3) prepared from isobutyl phenyl sulfone and nonanal was exposed to 1 equiv of *t*-BuOK for 3 h, the vinyl sulfone **9** (*Z*/*E* = 6:4) was formed quantitatively (Scheme II). Treatment of **8b** with 1.3 equiv of *t*-BuOK for 10 h afforded the allylic sulfone **10** which also was obtained quantitatively by treating **9** with 0.3 equiv of *t*-BuOK at room temperature for 5 h. This is consistent with the previous result that vinyl sulfones are readily isomerized to allylic sulfones in the presence of a base.[5] It should be noted that elimination of the phenylsulfonyl group from **10** never occurred at room temperature even though excess *t*-BuOK was employed. However, the reaction of either of the isomers, **9** or **10**, with 10 equiv of *t*-BuOK in refluxing *t*-BuOH was completed within 7 h to give **11** in 85% yield: **11a** (3*E*, 5*Z*):**11b** (3*E*, 5*E*) = 81:19. Consequently, the diene formation proved to be caused by the facile isomerization of a vinyl sulfone to an allylic sulfone followed by 1,4-elimination of benzenesulfinic acid.

Next, reaction of the allylic sulfone **13** was investigated (Scheme III). In this case, an acetoxy group is not suitable for the elimination since the retro-aldol reaction predominates. A tetrahydropyranyloxy group serves as a good eliminating group to give the vinyl sulfone **14** (75%) exclusively on treatment of **13** with 1 equiv of *t*-BuOK. Even excess *t*-BuOK failed to effect the isomerization of **14** to the corresponding allylic sulfone at room temperature, a quite reasonable result since the isomerization should induce the deconjugation of the 2,4-dienic moiety. The reaction of **14** with 10 equiv of *t*-BuOK in refluxing *t*-BuOH afforded a low yield of the triene **15**[6] and unreacted **14** as shown in Table I. The results indicate that the conversion of **14** to the corresponding allylic sulfone was slow as compared with the transformation of this compound to **15** so that the labile triene **15** once formed decomposed during the prolonged reaction period.

Scheme I



Scheme II



Scheme III

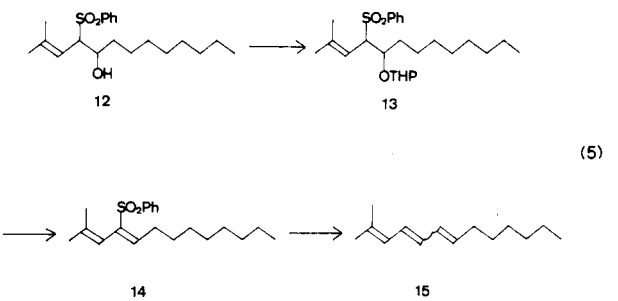


Table I. Reaction of 14 with Excess *t*-BuOK[a]

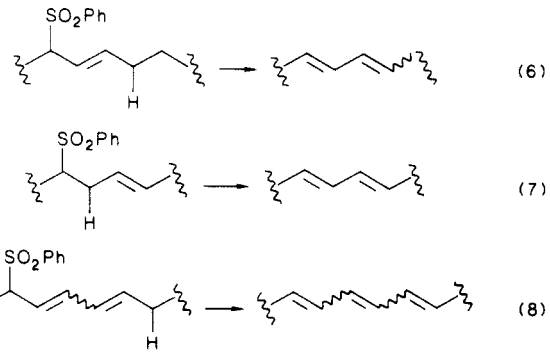
entry	reactn time, h	yield of 15,[b] %	14 recovered,[b] %
1	7	35 (50)[c]	29
2	8	38 (47)[c]	18
3	10	28	
4	48	17	

[a] Reaction conditions: *t*-BuOK/14 = 10, *t*-BuOH, reflux. [b] Isolated by means of column chromatography. [c] Yield based on 14 consumed.

Discussion

With the above results in hand, we can summarize the double elimination reaction as follows. The first step is the elimination of an acetoxy or alkoxy group. If the resultant vinyl sulfone possesses no allylic hydrogen, treatment of excess *t*-BuOK induces the elimination of the phenylsulfonyl group to give acetylenes. On the other hand, the presence of an allylic hydrogen in the vinyl sulfone causes *t*-BuOK-catalyzed isomerization to a thermodynamically favored allyl sulfone. The newly formed allylic hydrogen in the allyl sulfone is responsible for the second elimination. This is the first example of the 1,4-elimination of benzenesulfinic acid (eq 6), although the 1,2-elimination from homoallyl sulfones (eq 7) is known.[7]

(4) Julia, M.; Launay, M.; Stacino, J.-P.; Verpeaux, J.-N. *Tetrahedron Lett.* **1982**, *23*, 2465.
(5) O'Connor, D. E.; Lyness, W. I. *J. Am. Chem. Soc.* **1964**, *86*, 3840.
(6) GLC analysis of **15** thus obtained showed four peaks indicative of poor stereoselectivity in this case.

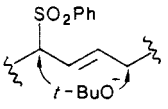


Our previous study[1] suggests that the 1,6-elimination (eq 8) takes place as well. It is concluded, therefore, that the allylic hydrogen plays a key role in controlling the reaction path on account of its facile cleavage by the nucleophilic attack of *t*-BuOK.

Besides the above mechanistic novelty, the following general features are noteworthy. In this study, the acetylenes and polyenes were synthesized by the stepwise reactions. Of course, one-pot synthesis from β-acetoxy or β-alkoxy sulfones is possible, but the stepwise method, in general, proved to afford a little better yield. It may be said that the presence of potassium acetate or tetrahydropyranyl oxide that is formed by the first elimination induces side reactions to some extent. Isolation of the intermediary vinyl or allyl sulfone removes the potassium salts.

As for the first eliminating group, the acetoxy group is most readily employable. However, this group causes a retro-aldol reaction rather than the elimination in the case where β-acetoxy sulfones are derived from allylic sulfones and thus should be substituted for by a THP group.

As described already, THF is a suitable solvent for the acetylene formation, but in the polyene synthesis, complex reaction products are obtained in this solvent. To this end, *t*-BuOH proved to be a good solvent. The analogous effect has been observed and explained by Olson et al.[7d] Unless any steric hindrance were present, the nucleophilic attack of the *tert*-butoxy anion takes place at the α-carbon of both the sulfonyl group and the allylic carbon. Reprotonation by *t*-BuOH suppresses side reactions derived from the α-sulfonyl anion and increases the selectivity of the 1,4-elimination.



Experimental Section

All reactions were carried out under a nitrogen or argon atmosphere. Potassium alkoxides were sublimed before use. Solvents were purified by standard methods. Column chromatography was performed on silica gel (Wako gel C-200). ^{1}H NMR spectra were recorded on Hitachi R-24B (60 MHz), JEOL FX-100 (100 MHz), and JEOLCO GX-500 (500 MHz) spectrometers. Mass spectra were obtained by using a JEOLCO JMS D-300 spectrometer. GLC analyses were carried out on a Hitachi 163 gas chromatograph with 3 mm × 3 m column packed with Silicone OV-17. Melting points were uncorrected.

1-Acetoxy-2-(phenylsulfonyl)-1,2-diphenylethane (1).[8] To a THF solution (40 mL) of benzyl phenyl sulfide (2.0 g, 10 mmol) was added dropwise *n*-BuLi (1.5 N hexane solution, 8.0 mL, 12 mmol) at −78 °C. The solution was stirred for 1 h and then benzaldehyde (1.27 g, 12 mmol) was added to this solution at this temperature. After being stirred for 2 h, the mixture was combined with water and extracted with benzene. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. Column chromatography (15:1 hexane–ethyl acetate) of a crude oil gave 1-hydroxy-2-(phenylthio)-1,2-diphenylethane (2.85 g, 93%). This compound was acetylated in 92% yield by treating with acetic anhydride (10 mL) and pyridine (10 mL) in the presence of a catalytic amount of 4-(dimethylamino)pyridine at room temperature for 5 h. The acetate (2.30 g, 6.61 mmol) thus obtained and *m*-CPBA (85% pure, 3.02 g, 7.93 mmol) in dichloromethane (30 mL) were stirred at room temperature for 5 h. The solution was shaken with $NaHCO_3$ and $Na_2S_2O_3$ solutions successively. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. The crude product was recrystallized from benzene–hexane to give pure **1** (1.48 g, 59%): ^{1}H NMR (60 MHz) (CCl_4) δ 1.80, 1.95 (s, 3 H, diastereomeric), 4.25 (d, 0.67 H, J = 4 Hz, diastereomeric), 4.68 (d, 0.33 H, J = 10 Hz, diastereomeric), 6.65–7.80 (m, 16 H). Anal. Calcd for $C_{19}H_{20}O_4S$: C, 69.45; H, 5.30. Found: C, 69.26; H, 5.26.

Reactions of 1 with *t*-BuOK. A *t*-BuOH solution (25 mL) of **1** (1.40 g, 3.68 mmol) and *t*-BuOK (413 mg, 3.68 mmol) was stirred at room temperature for 1 h and then heated at 50 °C for 1 h. The reaction mixture was extracted with benzene. Usual workup and recrystallization of the crude product from benzene–hexane gave pure **2** (1.11 g, 94%) as white crystals: mp 185–188 °C; HRMS, m/e (M^+) calcd 320.0870, obsd 320.0879.

To a THF solution (25 mL) of **2** (1.10 g, 3.44 mmol) was added *t*-BuOK (1.54 g, 13.75 mmol) in THF (5 mL) at room temperature. The mixture was stirred for 1 h at room temperature and then heated under reflux for 2 h. The mixture was extracted with hexane. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. Column chromatography (hexane) gave diphenylacetylene (**3**) (563 mg, 92%): mp 59–60 °C (undepressed mmp with an authentic sample).

3-Acetoxy-5-methyl-1-phenyl-4-(phenylsulfonyl)hex-1-ene (4b). To a THF solution (20 mL) of isobutyl phenyl sulfone (991 mg, 5 mmol) was added *n*-BuLi (5.5 mmol) at −78 °C, and the solution was stirred at −40 °C for 1 h. *trans*-Cinnamaldehyde (726 mg, 5.5 mmol) in THF (5 mL) was added to this solution at −78 °C. After being stirred at −40 °C for 2 h, the reaction mixture was quenched with water and extracted with benzene. Usual workup and column chromatography (5:1 hexane–ethyl acetate) gave **4a** (1.57 g, 95%, anti/syn = 7:3); ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.05–1.35 (m, 6 H), 2.40–2.50 (m, 0.3 H), 2.50–2.60 (m, 0.7 H), 3.17 (dd, 0.3 H, J = 3.1 and 5.5 Hz), 3.23 (dd, 0.7 H, J = 3.1 and 6.1 Hz), 3.63 (br s, 1 H), 4.76–4.81 (m, 0.3 H), 4.81–4.87 (m, 0.7 H), 6.00 (dd, 0.7 H, J = 6.7 and 15.9 Hz), 6.15 (dd, 0.3 H, J = 5.5 and 15.9 Hz), 6.50–6.67 (m, 1 H), 7.18–7.40 (m, 5 H), 7.42–7.70 (m, 3 H), 7.88 (d, 1.4 H, J = 8.1 Hz), 7.93 (d, 0.6 H, J = 8.1 Hz). Anal. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71. Found: C, 69.09; H, 6.59.

Acetylation of **4a** with Ac_2O-pyridine followed by column chromatography (5:1 hexane–ethyl acetate) afforded **4b** in 81% yield: ^{1}H NMR (60 MHz) (CCl_4) δ 1.20 (br t, 6 H, J = 7 Hz), 1.70, 1.80 (s, 3 H), 2.10–2.75 (m, 1 H), 3.15–3.55 (m, 1 H), 5.50–6.75 (m, 3 H), 6.80–7.90 (m, 15 H).

Reaction of 4b and 5 with *t*-BuOK. A *t*-BuOH solution (15 mL) of **4b** (430 mg, 1.16 mmol) and *t*-BuOK (130 mg, 1.16 mmol) was stirred at room temperature for 3 h. The reaction mixture was extracted with hexane. Usual workup and column chromatography (10:1 hexane–ethyl acetate) gave 5-methyl-1-phenyl-4-(phenylsulfonyl)hexa-1,3-diene (**5**) (303 mg, 84%, 1*E*,3*Z*/1*E*,3*E* = 9:1) as white crystals: mp 136–137 °C; ^{1}H NMR (500 MHz) (CCl_4) δ 1.09 (d, 5.4 H, J = 6 Hz), 1.16 (d, 0.6 H, J = 6 Hz), 2.85 (sept, 0.9 H, J = 6 Hz), 2.93 (sept, 0.1 H, J = 6 Hz), 6.69 (d, 1 H, J = 10 Hz), 6.76 (d, 0.9 H, J = 15 Hz), 6.93 (d, 0.1 H, J = 15 Hz), 7.08 (dd, 0.1 H, J = 10 and 15 Hz), 7.26–7.64 (m, 8 H), 7.85–7.96 (m, 2 H), 8.15 (dd, 0.9 H, J = 10 and 15 Hz). Anal. Calcd

(7) (a) Julia, M.; Arnould, D. *Bull. Soc. Chim. Fr.* **1973**, 746. (b) Manchard, P. S.; Rosenberger, M.; Saucy, G.; Wehri, P. A.; Wong, H.; Chambers, L.; Ferro, M. P.; Jackson, W. *Helv. Chim. Acta* **1976**, *59*, 387. (c) Fischli, A.; Mayer, H.; Simon, W.; Stoller, H.-J. *Helv. Chim. Acta* **1976**, *59*, 397. (d) Olson, G. L.; Cheung, H.-C.; Morgan, K. D.; Neukom, C.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3287. (e) Chabordes, P.; Decor, J. P.; Varagnat, J. *Tetrahedron* **1977**, *33*, 2799. (f) Nicolaou, K. C.; Claremon, D. A.; Papahatjis, D. D.; Magolda, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 6969. (g) Hamann, P. R.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 914.

(8) The reaction of the lithium salt of benzyl phenyl sulfone with benzaldehyde failed to afford the desired aldol adduct.

for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45. Found: C, 72.91; H, 6.44.

A *t*-BuOH solution (15 mL) of **5** (200 mg, 0.64 mmol) and *t*-BuOK (719 mg, 6.41 mmol) was stirred at room temperature and then heated under reflux for 8 h, during which time the reaction flask should be wrapped by aluminum foil due to the light sensitivity of the product. The reaction mixture was extracted with hexane. Workup as described for **3** and column chromatography (hexane) gave **7** (71 mg, 65%): ^{1}H NMR (100 MHz) ($CDCl_3$) δ 1.70 (s, 3 H), 1.76 (s, 3 H), 5.60–6.00 (m, 1 H), 6.40–6.63 (m, 2 H), 7.05–7.62 (m, 5 H); HRMS, *m/e* (M^+) calcd for $C_{13}H_{14}$ 170.1096, obsd 170.1095.

4-Acetoxy-2-methyl-3-(phenylsulfonyl)dodecane (8b). This compound was prepared by the analogous method for **4b** in 85% overall yield based on isobutyl phenyl sulfone after column chromatographic purification (5:1 hexane–ethyl acetate) (anti/syn = 7:3): ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.66–0.98 (br t, 3 H), 0.66–1.48 (m, 20 H), 1.94 (s, 3 H), 2.26–2.68 (m, 1 H), 2.96 (m, 0.3 H), 3.05 (m, 0.7 H), 4.98–5.40 (m, 1 H), 7.38–7.74 (m, 3 H), 7.74–8.06 (m, 2 H).

Careful column chromatography of the parent alcohol **8a** resulted in successful isolation of stereoisomers: the syn isomer (25:1 hexane–ethyl acetate) [^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.85 (br t, 3 H, *J* = 6.0 Hz), 0.96–1.94 (m, 20 H), 2.22–2.50 (m, 1 H), 3.00 (dd, 1 H, *J* = 2.9 and 1.8 Hz), 3.30–3.40 (br s, 1 H), 3.86–4.10 (m, 1 H), 7.42–7.76 (m, 3 H), 7.80–7.96 (m, 2 H). Anal. Calcd for $C_{19}H_{32}O_3S$: C, 67.04; H, 9.47. Found: C, 67.03; H, 9.52.] and the anti isomer (20:1 hexane–ethyl acetate) [^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.85 (br t, 3 H, *J* = 6.0 Hz), 0.96–1.38 (m, 18 H), 1.34–1.74 (m, 2 H), 2.22–2.50 (m, 1 H), 3.00 (dd, 1 H, *J* = 2.1 and 4.5 Hz), 3.36–3.50 (br s, 1 H), 3.88–4.19 (m, 1 H), 7.38–7.63 (m, 3 H), 7.80–7.96 (m, 2 H). Anal. Calcd for $C_{19}H_{32}O_3S$: C, 67.04; H, 9.47. Found: C, 67.30; H, 9.81.

Reaction of 8b and 10 with *t*-BuOK. A *t*-BuOH solution (15 mL) of **8b** (200 mg, 0.52 mmol) and *t*-BuOK (59 mg, 0.52 mmol) was stirred at room temperature for 3 h. The reaction mixture was extracted with benzene. Usual workup and column chromatography (20:1 hexane–ethyl acetate) gave **9** (161 mg, 95%, *Z*:*E* = 6:4): ^{1}H NMR (60 MHz) (CCl_4) δ 0.60–1.68 (m, 21 H), 2.00–3.00 (m, 3 H), 5.90 (t, 0.4 H, *J* = 8 Hz), 6.66 (t, 0.6 H, *J* = 8 Hz), 7.20–7.50 (m, 3 H), 7.50–7.80 (m, 2 H). Anal. Calcd for $C_{19}H_{30}O_2S$: C, 70.76; H, 9.38. Found: C, 70.81; H, 9.68.

The analogous reaction employing **8b** and 1.3 equiv of *t*-BuOK afforded **10** (54%, the *E* isomer only).

A *t*-BuOH solution (15 mL) of **9** (392 mg, 1.22 mmol) and *t*-BuOK (41 mg, 0.37 mmol) was stirred at room temperature for 7 h. Usual workup and column chromatography (20:1 hexane–ethyl acetate) gave **10** (360 mg, 92%, the *E* isomer only): ^{1}H NMR (500 MHz) ($CDCl_3$) δ 0.82 (t, 3 H, *J* = 8 Hz), 0.92 (d, 3 H, *J* = 8 Hz), 1.05 (d, 3 H, *J* = 8 Hz), 0.70–1.31 (m, 10 H), 1.85 (m, 2 H), 2.55–2.68 (m, 1 H), 3.22 (dd, 1 H, *J* = 10.9 and 3.8 Hz), 5.14 (dt, 1 H, *J* = 15 and 6.7 Hz), 5.37 (dd, 1 H, *J* = 15 and 10.9 Hz), 7.36–7.46 (m, 2 H), 7.46–7.56 (m, 1 H), 7.69–7.79 (m, 1 H). Anal. Calcd for $C_{19}H_{30}O_2S$: C, 70.76; H, 9.38. Found: 70.58; H, 9.59.

A *t*-BuOH solution (15 mL) of **10** (278 mg, 0.86 mmol) and *t*-BuOK (968 mg, 8.63 mmol) was stirred at room temperature for 1 h and then heated under reflux for 7 h, during which time the reaction flask was shielded from the light. Extraction of the reaction mixture with hexane followed by usual workup and column chromatography (hexane) gave **11** (132 mg, 85%): GLC analysis (120 °C) exhibited two peaks at t_R 8.3 and 9.6 min, respectively. Comparison with authentic samples separately prepared by the Wittig reaction revealed that the former one (t_R 8.3 min) is attributable to **11a** and the latter to **11b**. The *all-E* configuration of **11b** was also confirmed by the formation of the TCNE adduct.

2-Methyl-4-(phenylsulfonyl)-5-[(tetrahydropyranyl)oxy]tridec-2-ene (13). Prenyl phenyl sulfone and nonanal were coupled according to the analgous method for **8a**. Column chromatography (20:1 hexane–ethyl acetate) afforded **12** in 86% yield (anti/syn = 6:4): ^{1}H NMR (60 MHz) (CCl_4) δ 0.85 (br t, 3 H, *J* = 6 Hz), 1.00–1.50 (m, 17 H), 1.60 (br s, 3 H), 2.98–4.03 (m, 3 H), 4.70 (d, 0.6 H, *J* = 10 Hz), 5.30 (d, 0.4 H, *J* = 10 Hz), 7.15–7.55 (m, 3 H), 7.55–7.81 (m, 2 H). Anal. Calcd for $C_{20}H_{32}O_3S$: C, 67.41; H, 8.96. Found: C, 67.13; H, 8.97.

A dichloromethane solution (20 mL) of **12** (1.57 g, 4.46 mmol), dihydropyran (1.13 g, 13.4 mmol), and a catalytic amount of *p*-toluenesulfonic acid was stirred at room temperature for 3 h. The solution was shaken with $NaHCO_3$ with water, dried ($MgSO_4$), and evaporated. Column chromatography of the residue furnished **13** (1.71 g, 88%): ^{1}H NMR (60 MHz) (CCl_4) δ 0.50–2.05 (m, 29 H), 2.90–5.37 (m, 6 H), 7.03–7.46 (m, 3 H), 7.46–7.76 (m, 2 H).

Reaction of 13 and 14 with *t*-BuOK. A *t*-BuOH solution (15 mL) of **13** (200 mg, 0.46 mmol) and *t*-BuOK (51 mg, 0.46 mmol) was stirred at room temperature for 3 h. Workup and column chromatography (20:1 hexane–ethyl acetate) gave 2-methyl-4-(phenylsulfonyl)trideca-2(*E*),4(*Z*)-diene (**14**) (114 mg, 75%): ^{1}H NMR (100 MHz) ($CDCl_3$) δ 0.88 (br t, 3 H, *J* = 6 Hz), 1.09 (br s, 3 H), 1.13–1.60 (m, 12 H), 1.73 (br s, 3 H), 1.89–2.17 (m, 2 H), 5.56 (br s, 1 H), 6.92 (t, 1 H, *J* = 7.1 Hz), 7.30–7.61 (m, 3 H), 7.71–7.89 (m, 2 H). Anal. Calcd for $C_{20}H_{30}O_2S$: C, 71.81; H, 9.04. Found: C, 71.54; H, 9.29.

A *t*-BuOH solution (25 mL) of **14** (360 mg, 1.08 mmol) and *t*-BuOK (1.21 g, 10.8 mmol) was stirred at room temperature for 1 h and then heated under reflux for 7 h, during which time the reaction flask was shielded from the light. Workup and column chromatography (hexane) gave **15** (72 mg, 35%) and unreacted **14** (106 mg, 29%). The GLC analysis of **15** exhibited four peaks, but assignment of the isomers has not been successful yet. HRMS: *m/e* (M^+) calcd for $C_{14}H_{24}$ 192.1878, obsd 192.1874.

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Registry No. 1, 90083-21-9; **2**, 65645-46-7; **3**, 501-65-5; **4a**, 103904-53-6; **4b**, 103904-54-7; (*E*,*E*)-**5**, 103904-55-8; (*E*,*Z*)-**5**, 103932-86-1; **7**, 84253-63-4; **8a** (isomer 1), 103904-56-9; **8a** (isomer 2), 103904-57-0; **8b** (isomer 1), 103904-58-1; **8b** (isomer 2), 103904-59-2; (*E*)-**9**, 103904-61-6; (*Z*)-**9**, 103904-60-5; **10**, 103904-62-7; **11a**, 90083-36-6; **11b**, 90083-37-7; 12 (isomer 1), 103904-63-8; 12 (isomer 2), 103904-64-9; 13 (isomer 1), 103904-65-0; **13** (isomer 2), 104010-57-3; **14**, 103904-66-1; **15**, 103904-67-2; benzyl phenyl sulfide, 831-91-4; benzaldehyde, 100-52-7; 1-hydroxy-2-(phenylthio)-1,2-diphenylethane, 54130-67-5; 1-acetoxy-2-(phenylthio)-1,2-diphenylethane, 103904-52-5; isobutyl phenyl sulfone, 4170-72-3; *trans*-cinnamaldehyde, 14371-10-9; nonanal, 124-19-6; prenyl phenyl sulfone, 15874-80-3; dihydropyran, 110-87-2.