[Chem. Pharm. Bull. 32(5)1829—1839(1984)]

A New Synthesis of Olefins *via* the Elimination Reaction of β-Tributylstannyl Organosulfur Compounds[1)]

MASAHITO OCHIAI,[a] TATSUZO UKITA,[a] EIICHI FUJITA,*[,a]
and SHIN-ICHI TADA[b]

Institute for Chemical Research, Kyoto University,[a] Uji, Kyoto 611, Japan
and Research Laboratories, Nippon Shinyaku Co., Ltd.,[b]
Minami-ku, Kyoto 601, Japan

(Received September 16, 1983)

Organosulfur compounds on treatment with butyllithium in tetrahydrofuran followed by tributylstannylmethyl iodide **1** afforded olefins. The reaction was found to proceed *via* the destannylsulfurization of the initially formed β-stannyl organosulfur compounds. Thus, allyl 2-pyridyl sulfides **2** or allyl phenyl sulfones **12** were converted into 1,3-dienes **4**. Compounds **13** and **15** were converted into the olefins **14** and **17**. Furthermore, the reaction was applied to the synthesis of α-substituted vinyl sulfides **24** and allene **27**. The stereochemistry of the double bond is discussed.

Keywords——destannylsulfurization; allyl 2-pyridyl sulfide; allyl phenyl sulfone; synthesis of olefin; 1,3-diene; vinyl sulfide; β-tributylstannyl organosulfur compound

Deoxystannylation of β-stannyl alcohols has been studied in detail, and the elimination reaction was found to proceed on heating at 110—180 °C or in strongly acidic media at room temperature.[2)] It was successfully applied to a carbonyl olefination reaction utilizing (triphenylstannyl)methyllithium as an alternative to the Wittig reaction.[2c,d)] Destannylsulfurization of β-stannyl organosulfur compounds, however, has received little attention. Taylor and Wardell reported two distinct types of reactions of $(C_6H_5)_3SnCH_2CH_2SAr$ with electrophiles: iodine or mercuric chloride cleaved the phenyl-tin bond, while the reactions with bromine, methyl iodide, or ArSCl afforded ethylene.[3)]

In this paper we wish to report the synthesis of a variety of olefins by destannylsulfurization of β-stannyl organosulfur compounds, which were prepared by the reaction of the α-anion of the organosulfur compounds with (tributylstannyl)methyl iodide.

Results and Discussion

Synthesis of 1,3-Dienes

1,3-Dienes have been shown to be versatile intermediates for organic synthesis, especially in Diels–Alder reaction. They are also important structural units of some biologically active natural products.[4)] We planned to synthesize 1,3-dienes by utilizing readily available allyl organosulfur compounds. The whole reaction sequence for the synthesis of 1,3-dienes is shown in Chart 1; allyl organosulfur compounds are converted to β-stannyl organosulfur compounds by stannylmethylation with (tributylstannyl)methyl iodide (**1**) and then to 1,3-dienes by destannylsulfurization.

Allyl 2-pyridyl sulfides **2** were expected to be suitable materials for this diene synthesis, because of the high regioselectivity in the α-alkylation of the ambient allyl anion[5)] and of the superiority of the pyridine-2-thio group as a leaving group. Furthermore, availability was an important factor: allyl 2-pyridyl sulfides **2** were easily prepared from the corresponding allyl

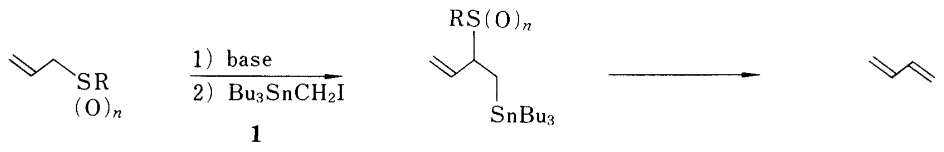
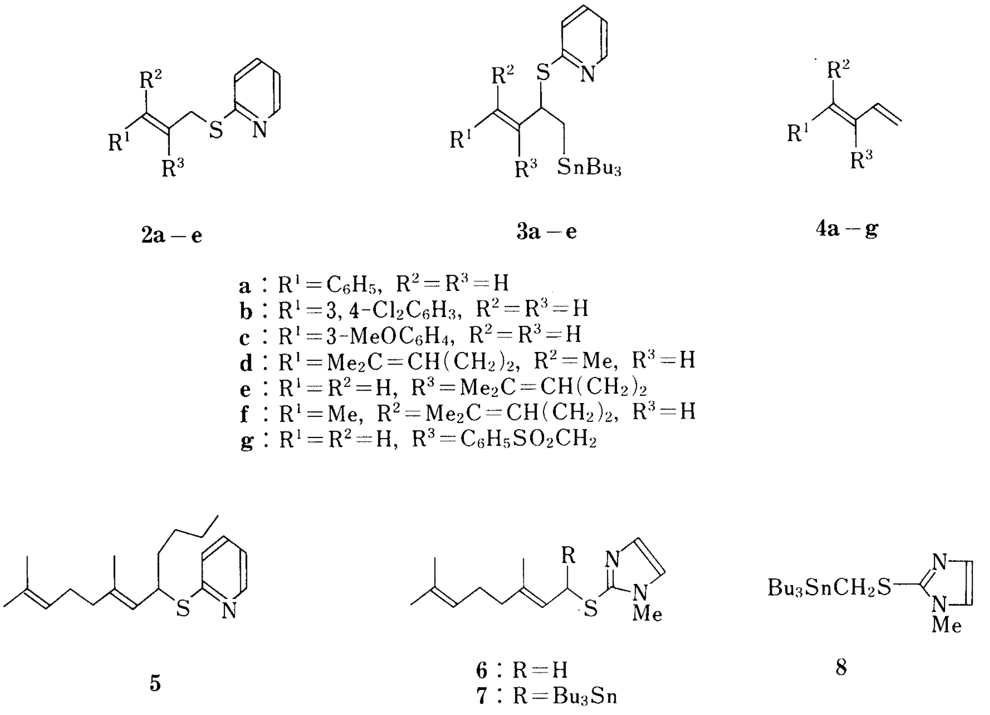


Chart 1

chlorides or bromides by treatment with the sodium salt of 2-mercaptopyridine.[6] When the allyl anion of sulfide **2a** (prepared by the reaction with butyllithium at $-78\,^\circ\mathrm{C}$ in tetrahydrofuran) was treated with the iodide **1** and the resulting reaction mixture was quenched with aqueous ammonium chloride solution, the conjugated 1,3-diene **4a** was obtained directly in 73% yield. The reaction seemed to proceed *via* the initial formation of the β-tributylstannyl sulfide **3a** followed by its ready destannylsulfurization. Actually, the intermediate **3a** was recognized when the reaction mixture was quenched with brine at $-78\,^\circ\mathrm{C}$ instead of aqueous ammonium chloride solution; the major product in the crude reaction mixture was shown to be the sulfide **3a**. Simultaneously the presence of the diene **4a** was also observed in a trace amount. The structure of **3a** was deduced from the diagnostic proton nuclear magnetic resonance (^{1}H-NMR) signals of the proton adjacent to the carbon atom bearing the 2-pyridylthio group; these signals appeared at δ 4.76 (1H, ddd, $J=10$, 8, 6 Hz). The sulfide **3a** was a highly unstable compound and was converted smoothly into the diene **4a** on standing in CDCl$_3$ at room temperature for 3 days.



2a–**e** **3a**–**e** **4a**–**g**

a : R^1=C$_6$H$_5$, R^2=R^3=H
b : R^1=3,4-Cl$_2$C$_6$H$_3$, R^2=R^3=H
c : R^1=3-MeOC$_6$H$_4$, R^2=R^3=H
d : R^1=Me$_2$C=CH(CH$_2$)$_2$, R^2=Me, R^3=H
e : R^1=R^2=H, R^3=Me$_2$C=CH(CH$_2$)$_2$
f : R^1=Me, R^2=Me$_2$C=CH(CH$_2$)$_2$, R^3=H
g : R^1=R^2=H, R^3=C$_6$H$_5$SO$_2$CH$_2$

5

6 : R=H
7 : R=Bu$_3$Sn

8

Chart 2

The results of diene synthesis from a variety of allyl 2-pyridyl sulfides **2** are summarized in Table I. Allyl sulfides **2a**—**c** conjugated with an aromatic ring at the γ-position afforded the desired 1,3-dienes in good yields (Table I, Runs 1—3), while the sulfides **2d** and **2e** gave poor results; even in ether or hexane–THF, the yield of the diene **4d** was not increased (Table I, Runs 5 and 6). The use of excess amounts of butyllithium let to a side reaction: when geranyl 2-pyridyl sulfide **2d** was treated with 2 equivalents of butyllithium followed by the iodide **1**, the major product was shown to be the sufide **5** (62% yield) and the diene **4d** was obtained only in a trace amount. The structure of **5** was identified by comparison with an authentic sample prepared by the reaction of the lithium salt of **2d** with butyl iodide. Compound **5** may be produced from **2d** by alkylation with butyl iodide, which must be produced *in situ* by a rapid reaction of excess butyllithium with the iodide **1**. Such a lithium–halogen exchange reaction of (triphenylstannyl)methyl iodide with butyllithium has been reported.[2c]

The higher selectivity toward α-alkylation of allyl *N*-methyl-2-imidazolyl sulfides in comparison with that of allyl 2-pyridyl sulfides has been reported.[5c] Therefore the reaction of the anion of geranyl *N*-methyl-2-imidazolyl sulfide (**6**) with the iodide **1** was carried out in the hope of getting a better yield of the diene **4d**, but no improvement of the yield of **4d** (45%) was obtained. Considerable amounts of α-tributylstannylation product **7** (31% yield) and (tributylstannyl)methyl *N*-methyl-2-imidazolyl sulfide (**8**) (43% yield) were produced, with the recovery of **6** (14% yield). The structures of **7** and **8** were confirmed by comparison with authentic samples (see Experimental). The formation of these undesirable products can be reasonably explained by considering the following reaction sequence, as shown in Chart 3. The normal α-(tributylstannyl)methylation of **9** produces the β-stannyl sulfide **10**. If the anion **9** is sufficiently reactive, the tin atom of the sulfide **10** can be attacked nucleophilically by another molecule of the anion **9**, with concomitant loss of lithium sulfide **11**, yielding the diene **4d** and the α-stannyl sulfide **7**. Compound **11** further reacts with the iodide **1** to give the stannylmethyl sulfide **8**. In the reactions of **2a**—**2c**, the corresponding anions do not seem to

TABLE I. Synthesis of 1,3-Dienes **4** from Allyl 2-Pyridyl Sulfides **2**

Run	2	Solvent	Reaction conditions	Product	Yield[a] (%)
1	**2a**	THF	−78 °C (10 min) then 0 °C (1.5 h)	**4a**	73 (89)
2	**2b**	THF	−78 °C (1 h)	**4b**	71
3	**2c**	THF	−78 °C (1 h)	**4c**	86
4	**2d**	THF	−78 °C (30 min) then 0 °C (10 min)	**4d**	47 (58)
5	**2d**[b]	Et_2O[c]	−20 °C (20 min) then 0 °C (1 h)	**4d**	(42)
6	**2d**	Hexane–THF	−78 °C (20 min) then 0 °C (10 min)	**4d**	(50)
7	**2d**[d]	THF	−78 °C (40 min) then 0 °C (1.5 h)	**4d**[e]	(7)
8	**2e**	THF	−78 °C (20 min) then 0 °C (1 h)	**4e**	(42)

a) Isolated yield (GC yield).
b) Allyl anion was prepared at −20 °C for 30 min.
c) 5 eq of hexamethylphosphoramide (HMPA) were used.
d) 2 eq of butyllithium were used.
e) Sulfide **5** was obtained in 62% yield.

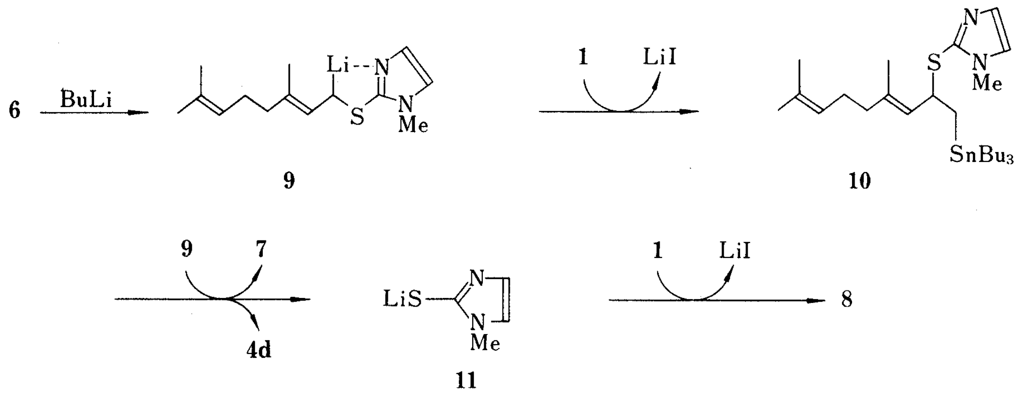


Chart 3

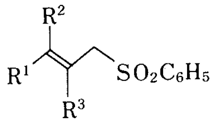
be reactive enough to attack the tin atoms of **3a**—**3c**, because they are considerably stabilized by conjugation with the aromatic rings at the γ-position.

On the basis of the above argument, allyl sulfones seem to be much better compounds for the synthesis of 1,3-dienes than allyl sulfides, because on treatment with butyllithium they produce sufficiently stabilized allyl anions; they are reactive enough, however, towards alkyl halides.[7] We expected that such a stabilized anion of allyl sulfone would not attack the tin atom of the intermediate, β-stannyl sulfone, and the formation of side products would be suppressed. Thus, geranyl phenyl sulfone (**12a**) on treatment with butyllithium at −78 °C followed by the iodide **1** resulted in the formation of **4d** in 78% yield. Neryl phenyl sulfone (**12b**) afforded the (*Z*)-isomer **4f** (Table II), but the sulfones **12c** and **12d** gave poor results. These allyl phenyl sulfones **12** were prepared from the allyl chlorides by treatment with sodium benzenesulfinate dihydrate and tetrabutylammonium bromide according to a slight modification of the procedure of Vennstra and Zwanenburg.[8] The method was applied to the highly stereoselective synthesis of (*E*)- and (*Z*)-9,11-dodecadien-1-yl acetates, sex pheromones of the red bollworm moth.[9]

TABLE II. Synthesis of 1,3-Dienes **4** from Allyl Phenyl Sulphones **12**

Run	12	Reaction conditions	Product	Yield[a] (%)
9	**12a**	−78 °C (1.25 h)	**4d**	78 (94)
10	**12b**	−78 °C (1 h)	**4f**	75
11	**12c**	−78 °C (2.5 h)	**4e**[b]	(46)
12	**12d**	−78 °C (1.5 h) then 0 °C (12 h)	**4g**[c]	26

a) Isolated yield (GC yield).
b) 19% Yield of **12c** was recovered.
c) 44% Yield of **12d** was recovered.



12a: $R^1 = Me_2C=CH(CH_2)_2$, $R^2 = Me$, $R^3 = H$
12b: $R^1 = Me$, $R^2 = Me_2C=CH(CH_2)_2$, $R^3 = H$
12c: $R^1 = R^2 = H$, $R^3 = Me_2C=CH(CH_2)_2$
12d: $R^1 = R^2 = H$, $R^3 = C_6H_5SO_2CH_2$

Chart 4

Synthesis of Olefins

Thus, the stannylmethylation of allyl organosulfur compounds followed by destannylsulfurization was proved to be highly effective for the synthesis of 1,3-dienes. Then we turned our attention to the synthesis of simple olefins. The reaction was found to be applicable to the synthesis of styrene derivaives. Both piperonyl 2-pyridyl sulfide (**13a**) and piperonyl phenyl sulfone (**13b**) produced the styrene derivative **14** in 84 and 80% yields, respectively. When the reaction mixture of the α-anion of the 2-pyridyl sulfone **15** and the iodide **1** was quenched with water at −78 °C, the β-stannyl sulfone **16** was isolated by flash column chromatography[10] in 77% yield. Its destannylsulfonation was carried out in two different ways. Compound **16** on treatment with silica gel in dichloromethane at room temperature afforded the olefin **17** in 53% yield. Thermal destannylsulfonation was also observed, but **16** was shown to be much more stable than the sulfide **3a** : **16** on heating at 80 °C for 50 h in d_6-benzene in a sealed tube gave rise to **17** quantitatively. The thermal destannylsulfonation seems to proceed *via* the cyclic transition state **18** or **19**, in which the initial intramolecular coordination from oxygen of the sulfonyl group or nitrogen of the pyridine ring to tin may play an important role. In the phenyl-tin bond cleavage reaction of the sulfone **20** with iodine in carbon tetrachloride, the coordination of oxygen of the sulfonyl group to tin has been proposed.[11] The inter- or intramolecular coordination from nitrogen to tin has been studied in detail.[12]

Substituted α-iodostannanes are now obtainable by the method developed by Torisawa, Shibasaki, and Ikegami.[13] Thus, our attention was focused on the stereochemistry of the double bond newly formed by the reaction with substituted α-iodostannanes. The reaction of the α-anion of **13b** with 3-phenyl-1-(tributylstannyl)propyl iodide (**21**)[13] did not occur at −78 °C but afforded the disubstituted olefin **22** at 0 °C in 36% yield with the recovery of **13b** (18%). The lower reactivity of the iodide **21** in comparison with that of **1** may be attributable to its steric bulkiness. The reaction showed remarkably high stereoselectivity for (*Z*)-olefin and the ratio of (*E*)- to (*Z*)-isomers of **22** was found to be 1 : 36 by gas chromatography. Their stereochemistry was determined by comparison of the products with authentic samples

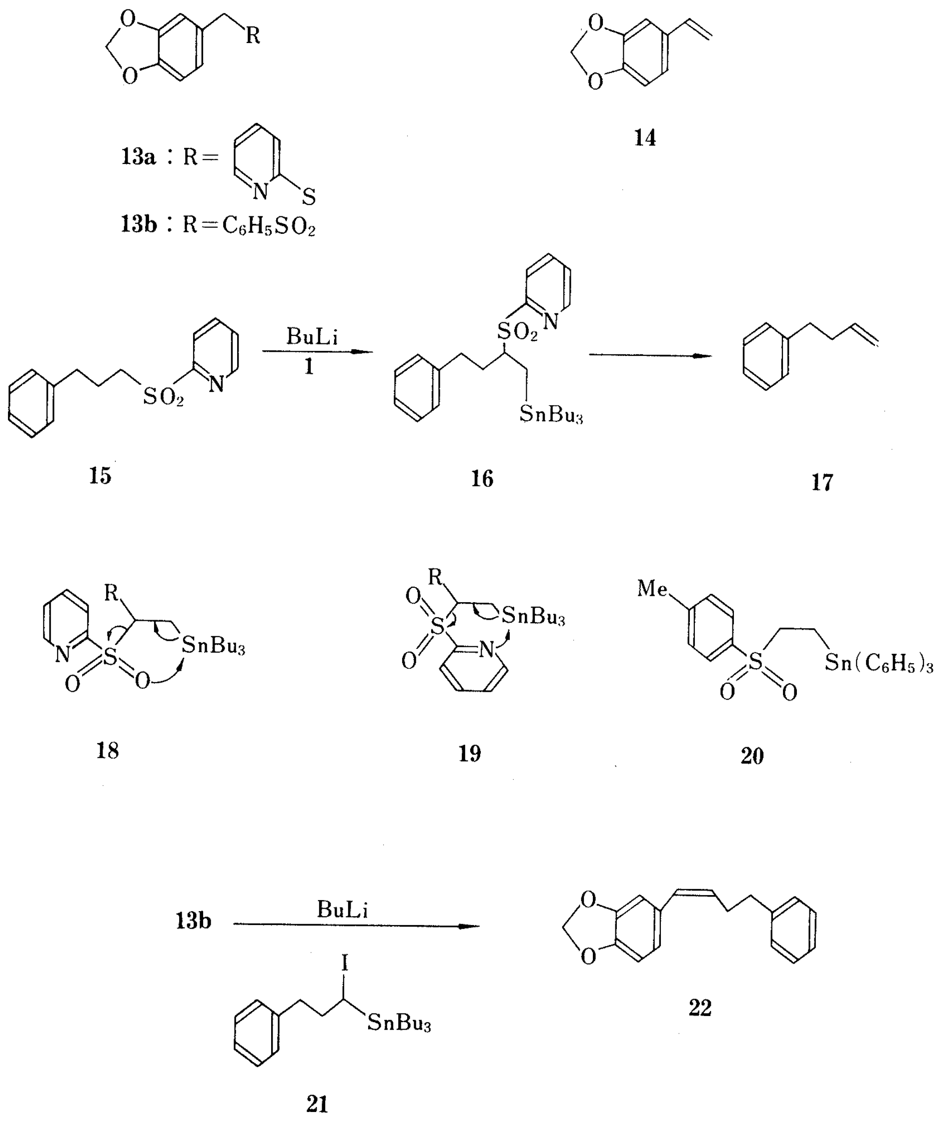


Chart 5

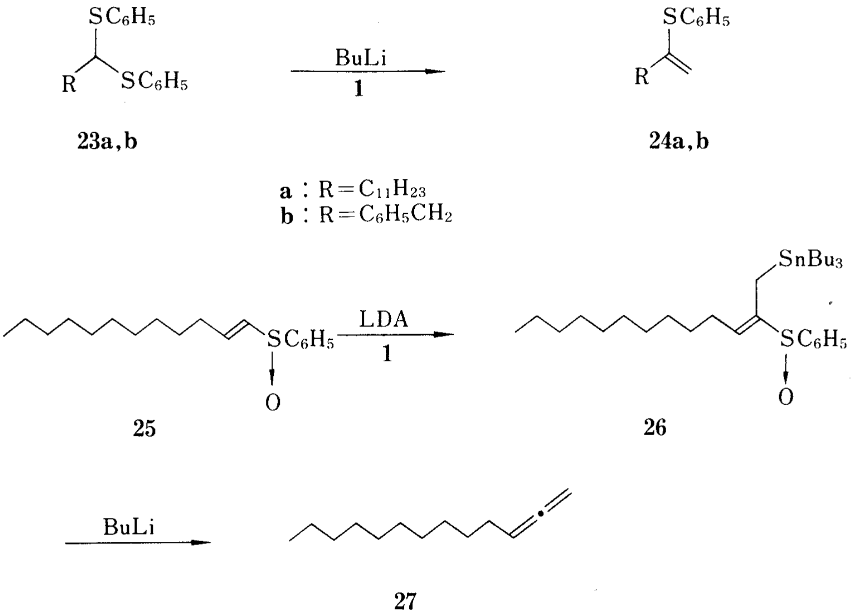


Chart 6

prepared by the Wittig reaction of piperonal with 3-phenylpropyltriphenylphosphonium bromide.

Synthesis of Substituted Olefins

The regioselective synthesis of substituted vinyl sulfides is becoming very important.[14] Thus, the reaction was applied to the regioselective synthesis of α-substituted vinyl sulfides. Dithioacetals **23a** and **23b** on treatment with butyllithium and iodide **1** followed by destannylsulfurization afforded the vinyl sulfides **24a** and **24b** in 65 and 47% yields, respectively, with some recovery of dithioacetals.

Dodecen-1-yl phenyl sulfoxide (**25**) was transformed into the allene **27** *via* the β-stannyl sulfoxide **26**. Compound **25** (a mixture of stereoisomers) was prepared from the dithioacetal **23a** by the following reaction sequence: i) oxidation with *m*-chloroperbenzoic acid (*m*-CPBA), ii) thermal sulfoxide elimination, and iii) oxidation with *m*-CPBA. When the α-anion of the vinyl sulfoxide **25**, produced by the reaction with lithium diisopropylamide (LDA) in THF,[15] was treated with the iodide **1** at −78 °C, the β-stannyl sulfoxide **26** was obtained in 51% yield. The stannane **26** gave rise to the allene **27** on reaction with butyllithium at −78 °C in 57% yield.

Thus, we developed a new general method for the synthesis of a variety of olefins including 1,3-dienes and vinyl sulfides.

Experimental

Infrared (IR) spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer. ^{1}H-NMR spectra were obtained with a JEOL JNM-FX100 or a JEOL JNM-PMX60 spectrometer. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were taken on a JEOL JNM-FX100 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra (MS) were determined on a JEOL JMS-0ISG double-focusing mass spectrometer. Analytical gas chromatography (GC) was performed on a Shimadzu GC-4CM gas chromatograph with a column of 20% Silicone DC-200 on Celite 545 (1 ml). Preparative GC was performed on a Varian Aerograph model 920 gas chromatograph with a column of 10% Silicone DC-200 on Chromosorb WX (1 m). Kieselgel 60 (Merck) was used for the destannylsulfonation of **16** and silica gel column chromatography. Preparative thin layer chromatography (TLC) was carried out on Kieselgel 60 F254 (Merck). All of the compounds whose melting points are not given are oils.

Materials——(Tributylstannyl)methyl iodide (**1**) was prepared by the reaction of ICH$_2$ZnI with tributyltin chloride.[16] 3-Phenyl-1-(tributylstannyl)propyl iodide (**21**) was prepared from the corresponding α-stannyl carbinol.[13]

Synthesis of Allyl 2-Pyridyl Sulfides 2——The sulfides **2** were prepared from the corresponding allyl chlorides or bromides by treatment with the sodium salt of 2-mecaptopyridine in methyl ethyl ketone according to the procedure of Tarbell and McColl.[6]

1-Phenyl-3-(2-pyridylthio)-1-propene (**2a**)[17]: mp 42—42.5 °C (from methanol–chloroform). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1580, 1415, 1130, 965. MS *m/e*: 227 (M$^+$), 194, 117. ^{1}H-NMR (CDCl$_3$) δ: 3.99 (2H, d, J=6 Hz), 6.20 (1H, dt, J=16, 6 Hz), 6.63 (1H, d, J=6 Hz), 6.7—7.7 (8H), 8.3—8.5 (1H, m).

1-(3,4-Dichlorophenyl)-3-(2-pyridylthio)-1-propene (**2b**): IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640, 1580, 1130, 965. MS *m/e*: 295 (M$^+$), 262, 150, 115 (base peak). High resolution MS: Found 295.0036. Calcd for C$_{14}$H$_{11}$Cl$_2$NS (M$^+$) 294.9990. ^{1}H-NMR (CDCl$_3$) δ: 3.95 (2H, d, J=6 Hz), 5.9—6.7 (2H), 6.7—7.6 (6H), 8.3—8.5 (1H).

1-(3-Methoxyphenyl)-3-(2-pyridylthio)-1-propene (**2c**): mp 80—81 °C (from ethyl acetate). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1610, 1520, 1250, 970. MS *m/e*: 257 (M$^+$), 242, 224, 147 (base peak). High resolution MS: Found 257.0832. Calcd for C$_{15}$H$_{15}$NOS (M$^+$) 257.0873. ^{1}H-NMR (CDCl$_3$) δ: 3.71 (3H, s), 3.93 (2H, d, J=6 Hz), 6.06 (1H, dt, J=15, 6 Hz), 6.50 (1H, d, J=15 Hz), 6.6—7.5 (7H), 8.2—8.4 (1H, m). *Anal.* Calcd for C$_{15}$H$_{15}$NOS: C, 70.00; H, 5.88; N, 5.44. Found: C, 70.23; H, 5.80; N, 5.52.

3,7-Dimethyl-1-(2-pyridylthio)-2,6-octadiene (**2d**): IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1680, 1615, 1580, 1450, 1125. MS *m/e*: 247 (M$^+$), 178, 112, 41 (base peak). High resolution MS: Found 247.1431. Calcd for C$_{15}$H$_{21}$NS (M$^+$) 247.1395. ^{1}H-NMR (CDCl$_3$) δ: 1.57, 1.64, 1.72 (each 3H, s), 3.79 (2H, d, J=7.5 Hz), 4.9—5.5 (2H, m), 6.7—7.6 (3H, m), 8.3—8.5 (1H, m).

6-Methyl-2-(2-pyridylthio)methyl-1,5-heptadiene (**2e**): IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640, 1585, 1420, 1130, 905. MS *m/e*: 233 (M$^+$), 218, 200, 164, 150, 112. High resolution MS: Found 233.1252. Calcd for C$_{14}$H$_{19}$NS (M$^+$) 233.1238. ^{1}H-NMR (CDCl$_3$) δ: 1.59, 1.67 (each 3H, s), 2.0—2.4 (4H, m), 3.84 (2H, s), 4.75—5.3 (3H), 6.7—7.6 (3H, m), 8.2—8.5 (1H, m).

General Procedure for Synthesis of 1,3-Dienes 4 from Allyl 2-Pyridyl Sulfides 2——Butyllithium (1.05 eq) in hexane was added to a solution of a sulfide **2** in THF at −78 °C under nitrogen and the solution was stirred for 30 min. A solution of the iodide **1** (1 eq) in THF was added very slowly to the resulting red solution of allyl anion of **2** at −78 °C. The color of the solution changed to pale yellow. The solution was stirred under the conditions described in Table I. The reaction mixture was quenched with aqueous ammonium chloride solution and extracted with pentane–ether. The extract was washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure to give an oil, which on preparative TLC afforded the corresponding 1,3-diene **4**. The yields are given in Table I. The rate of addition of **1** must be very slow, otherwise the yield of the diene **4** drops markedly. In some experiments, the yields of the products were analyzed by GC using an appropriate internal standard.

1-Phenyl-1,3-butadiene (4a)[18]——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1630, 1600, 1005, 950, 905, 690. MS *m/e*: 130 (M$^+$). ^{1}H-NMR (CDCl$_3$) δ: 5.1—5.4 (2H, m), 6.3—6.9 (3H, m), 7.1—7.5 (5H, m).

1-(3,4-Dichlorophenyl)-1,3-butadiene (4b)——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1680, 1465, 1130, 965. MS *m/e*: 198 (M$^+$). High resolution MS: Found 197.9969. Calcd for C$_{10}$H$_8$Cl$_2$ (M$^+$) 198.0003. ^{1}H-NMR (CDCl$_3$) δ: 5.1—5.5 (2H, m), 6.2—6.9 (3H, m), 7.1—7.5 (3H, m).

1-(4-Methoxyphenyl)-1,3-butadiene (4c)[19]——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1600, 1520, 1250, 1040, 1005. MS *m/e*: 160 (M$^+$), 144, 129, 85 (base peak). ^{1}H-NMR (CDCl$_3$) δ: 3.82 (3H, s), 5.0—5.4 (2H, m), 6.3—6.7 (3H, m), 6.8—7.0 (2H), 7.3—7.5 (2H).

4,8-Dimethyl-1,3,7-nonatriene (4d)[20]——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1645, 985, 900. ^{1}H-NMR (CDCl$_3$) δ: 1.60, 1.67, 1.75 (each 3H, s), 1.9—2.2 (4H), 4.85—5.2 (3H, m), 5.81 (1H, d, J=11 Hz), 6.54 (1H, dt, J=17, 11 Hz).

7-Methyl-3-methylene-1,6-octadiene (Myrcene) (4e)——^{1}H-NMR (CDCl$_3$) δ: 1.50, 1.57 (each 3H, s), 2.17 (4H, s), 4.8—5.4 (5H), 7.27 (1H, dd, J=17, 10 Hz).

1-Phenyl-3-(2-pyridylthio)-4-(tributylstannyl)-1-butene (3a)——The reaction of the sulfide **2a** with butyllithium and the iodide **1** in THF was carried out according to the general procedure for 1,3-diene synthesis, except that the reaction mixture was quenched with brine at −78 °C. The ^{1}H-NMR spectrum of the crude reaction mixture showed the presence of the β-stannyl sulfide **3a** as a major product and a trace amount of the 1,3-diene **4a**. **3a**: ^{1}H-NMR (CDCl$_3$) δ: 4.76 (1H, ddd, J=10, 8, 6 Hz, C$\underline{\mathrm{H}}$S), 6.16 (1H, dd, J=16, 8 Hz, C=C$\underline{\mathrm{H}}$CH), 6.44 (1H, d, J=16 Hz, C$_6$H$_5$C$\underline{\mathrm{H}}$=C). Compound **3a** was found to be very unstable. When the crude reaction mixture in CDCl$_3$ was left to stand at room temperature for 3 days, the signals due to the stannane **3a** disappeared completely in the ^{1}H-NMR spectrum and the formation of the 1,3-diene **4a** was observed.

Synthesis of 2,6-Dimethyl-8-(2-pyridylthio)-2,6-dodecadiene 5——A hexane solution of butyllithium (1.55 M solution, 0.224 ml, 0.347 mmol) was added to a stirred solution of the sulfide **2d** (82 mg, 0.33 mmol) in THF (3.3 ml) at −78 °C under nitrogen and the mixture was stirred for 30 min. After the addtion of butyl iodide (64 mg, 0.347 mmol) at −78 °C, the reaction mixture was stirred at −78 °C for 30 min and at room temperature for 1 h. The mixture was poured into aqueous ammonium chloride solution, extracted with dichloromethane, and dried over Na$_2$SO$_4$. After the removal of the solvent, preparative TLC (hexane–ethyl acetate (8 : 2)) of the crude mixture afforded the sulfide **5** (50 mg, 50%). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1655, 1580, 1450, 1125. MS *m/e*: 303 (M$^+$), 288, 248, 234, 69 (base peak). High resolution MS: Found 303.1985. Calcd for $C_{19}H_{29}NS$ (M^+) 303.2020. ^{1}H-NMR ($CDCl_3$) δ: 1.55, 1.62 (each 3H, s), 1.65 (3H, d, $J=1$ Hz), 4.35—4.7 (1H, m), 4.8—5.2 (2H, m), 6.75—7.5 (3H, m), 8.2—8.4 (1H, m). ^{13}C-NMR ($CDCl_3$) δ: 159.7 (s), 149.4 (d), 137.8 (s), 135.7 (d), 131.3 (s), 125.9, 124.1, 123.6, 119.5, 43.6 (each d), 39.6, 35.8, 29.5, 26.6 (each t), 25.6 (q), 22.6 (t), 17.6, 16.7, 14.0 (each q). The compound was shown to be identical with the sulfide **5** obtained in the reaction of Table I, Run 7.

Synthesis of 3,7-Dimethyl-1-(*N*-methyl-2-imidazolylthio)-2,6-octadiene (6)——The sulfide **6** was prepared from geranyl chloride by treatment with the sodium salt of 2-mercapto-1-methylimidazole in methyl ethyl ketone according to the procedure of Tarbell and McColl.[6] **6**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660, 1455, 1280, 910. MS *m/e*: 250 (M^+), 217, 181, 114. High resolution MS: Found 250.1478. Calcd for $C_{14}H_{22}N_2S$ (M^+) 250.1503. ^{1}H-NMR ($CDCl_3$) δ: 1.54, 1.59, 1.67 (each 3H, s), 1.9—2.2 (4H), 3.62 (3H, s), 3.66 (2H, d, $J=8$ Hz), 5.08 (1H, m), 5.34 (1H, t, $J=8$ Hz), 6.96 (1H, d, $J=1$ Hz), 7.10 (1H, d, $J=1$ Hz).

Synthesis of the Diene 4d from the Sulfide 6——Butyllithium (1.55 M solution, 0.147 ml, 0.228 mmol) in hexane was added to a stirred solution of **6** (54 mg, 0.216 mmol) in THF (1.2 ml) at -78 °C under nitrogen and the mixture was stirred for 2 h. A solution of the iodide **1** (93 mg, 0.216 mmol) in THF (3 ml) was added very slowly at -78 °C and the mixture was stirred at -78 °C for 1 h and at 0 °C for 12 h. The reaction mixture was quenched with aqueous ammonium chloride solution. The usual work-up afforded a yellow oil. The yield of the diene **4d** was determined by GC using decane as an internal standard to be 45%. Preparative TLC (hexane–ethyl acetate (6:4)) of the crude reaction mixture gave the other products, the α-stannyl sulfides **7** (35.6 mg, 31%) and **8** (39 mg, 43%), and the sulfide **6** (7.4 mg, 14%). **7**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665, 1640, 1455, 910. ^{1}H-NMR ($CDCl_3$) δ: 1.32 (3H, d, $J=1$ Hz), 1.55, 1.65 (each 3H, s), 3.60 (3H, s), 3.85 (1H, d, $J=11$ Hz), 4.98 (1H, m), 5.23 (1H, d, $J=11$ Hz), 6.81, 6.97 (each 1H, d, $J=1$ Hz). **8**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1460, 1280, 1125, 1080. MS *m/e*: 361 [$(M-Bu)^+$], 247. High resolution MS: Found 361.0748. Calcd for $C_{13}H_{25}N_2S$ ^{120}Sn [$(M-Bu)^+$] 361.0760. ^{1}H-NMR ($CDCl_3$) δ: 0.7—1.8 (27H), 2.43 (2H, s), 3.54 (3H, s), 6.82, 6.98 (each 1H, d, $J=1$ Hz). The structure of **7** was determined by comparison with an authentic sample prepared by the reaction of the allyl anion of **6** with tributyltin chloride (74% yield). The structure of **8** was confirmed by comparison with an authentic sample prepared by the reaction of the sodium salt of 2-mercapto-1-methylimidazole with tributylstannylmethyl iodide (**1**) in methyl ethyl ketone (80% yield).

Synthesis of Allyl Phenyl Sulfones 12——A Typical Example: 3,7-Dimethyl-1-phenylsulfonyl-2,6-octadiene (**12a**):[21] A mixture of geranyl chloride (1.01 g, 5.85 mmol), sodium benzenesulfinate dihydrate (2.07 g, 10 mmol), and tetrabutylammonium bromide (3.22 g, 10 mmol) in THF (30 ml) was stirred at room temperature for 17 h under nitrogen. After the addition of water, the mixture was extracted with ether. The extract was washed with water and brine, dried over Na_2SO_4, and evaporated to leave a yellow oil (1.676 g). Preparative TLC (hexane–ethyl acetate (7:3)) afforded the sulfone **12a** (1.3 g, 80%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1310, 1270, 1155. ^{1}H-NMR ($CDCl_3$) δ: 1.33, 1.58, 1.68 (each 3H, s), 1.9—2.2 (4H), 3.77 (2H, d, $J=8$ Hz), 4.8—5.35 (2H), 7.2—8.0 (5H, m).

3,7-Dimethyl-1-phenylsulfonyl-2,6-octadiene (**12b**):[21] IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1655, 1310, 1150. ^{1}H-NMR ($CDCl_3$) δ: 1.54, 1.64 (each 3H, s), 1.75 (3H, d, $J=1$ Hz). 3.78 (2H, d, $J=8$ Hz), 4.93 (1H, m), 5.15 (1H, t, $J=8$ Hz), 7.4—7.9 (5H, m).

6-Methyl-2-phenylsulfonylmethyl-1,5-heptadiene (**12c**): MS *m/e*: 264 (M^+), 177, 43 (base peak). High resolution MS: Found 264.1139. Calcd for $C_{15}H_{20}O_2S$ (M^+) 264.1183. ^{1}H-NMR ($CDCl_3$) δ: 1.56, 1.65 (each 3H, s), 1.9—2.3 (4H), 3.74 (2H, s), 4.7—5.2 (3H), 7.4—7.9 (5H, m).

1,3-Bis(phenylsulfonylmethyl)-2-methylenepropane (**12d**): mp 127—128 °C (from methanol–chloroform). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1320, 1160, 935, 630, 540. MS *m/e*: 336 (M^+), 195, 131, 91, 77 (base peak). High resolution MS: Found 336.0484. Calcd for $C_{16}H_{16}O_4S_2$ (M^+) 336.0489. ^{1}H-NMR ($CDCl_3$) δ: 3.99 (4H, s), 5.12 (2H, s), 7.3—7.9 (10H, m). *Anal.* Calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.79. Found: C, 56.85; H, 4.87.

General Procedure for Synthesis of 1,3-Dienes 4 from Allyl Phenyl Sulfones 12——Butyllithium (1.05 eq) in hexane was added to a solution of a sulfone **12** in THF at -78 °C under nitrogen and the mixture was stirred for 40 min. A solution of the iodide **1** (1 eq) in THF was added very slowly at -78 °C. The solution was stirred under the conditions described in Table II. The reaction mixture was quenched with aqueous ammonium chloride solution and extracted with pentane–ether. The extract was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to give an oil, which on preparative TLC afforded the 1,3-diene **4**. The yields are given in Table II. In some experiments, the yields of the products were analyzed by GC using an appropriate internal standard.

4,8-Dimethyl-1,3,7-nonatriene (4f)[22]——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680, 1200, MS *m/e*: 150 (M^+), 69 (base peak). ^{1}H-NMR ($CDCl_3$) δ: 1.59, 1.66, 1.76 (each 3H, s), 1.9—2.3 (4H), 4.8—5.2 (3H, m), 5.79 (1H, d, $J=11$ Hz), 6.51 (1H, dt, $J=17$, 11 Hz).

2-Phenylsulfonylmethyl-1,3-butadiene (4g)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1590, 1310, 1155, 910. MS *m/e*: 208 (M^+), 144, 129, 67 (base peak). High resolution MS: Found 208.0551. Calcd for $C_{11}H_{12}O_2S$ (M^+) 208.0557. ^{1}H-NMR ($CDCl_3$) δ: 3.96 (2H, s), 4.9—5.4 (4H), 6.23 (1H, dd, $J=18$, 11 Hz), 7.3—7.9 (5H, m).

1,2-Methylenedioxy-4-(2-pyridylthio)methylbenzene (13a)——Compound **13a** was prepared from piperonyl chloride by treatment with the sodium salt of 2-mercaptopyridine in 89% yield according to the procedure of Tarbell and McColl.[6] **13a**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1585, 1495, 1250, 1130, 1045. MS *m/e*: 245 (M^+), 212, 135 (base peak). High resolution MS: Found 245.0506. Calcd for $C_{13}H_{11}NO_2S$ (M^+) 245.0510. ^{1}H-NMR ($CDCl_3$) δ: 4.31 (2H, s), 5.82 (2H, s), 6.5—7.55 (6H), 8.25—8.45 (1H, m).

1,2-Methylenedioxy-4-(phenylsulfonylmethyl)benzene (13b)——The sulfone **13b** was prepared from piperonyl chloride in a manner similar to that described for the synthesis of **12a**. **13b**: mp 124—125 °C (from ether–dichloromethane). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1490, 1440, 1305, 1150, 1040. MS *m/e*: 276 (M^+), 135, 77 (base peak), 51. ^{1}H-NMR ($CDCl_3$) δ: 4.24 (2H, s), 5.99 (2H, s), 6.4—6.8 (3H, m), 7.4—7.8 (5H, m). *Anal.* Calcd for $C_{14}H_{12}O_4S$: C, 60.85; H, 4.38. Found: C, 60.67; H, 4.25.

Synthesis of 3,4-Methylenedioxyphenylethylene 14 from Sulfide 13a——A hexane solution of butyllithium (1.55 M solution, 0.156 ml, 0.242 mmol) was added to a solution of **13a** (56.4 mg, 0.23 mmol) in THF (1.3 ml) at −78 °C under nitrogen and the solution was stirred for 1 h. A solution of iodide **1** (99 mg, 0.23 mmol) in THF (3.4 ml) was added slowly at −78 °C and the mixture was stirred at −78 °C for 30 min. The reaction mixture was quenched with aqueous ammonium chloride solution. The usual work-up gave a yellow oil. Preparative TLC (hexane–ethyl acetate (19 : 1)) afforded the olefin **14** (28.6 mg, 84%).[23] IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1610, 1495, 1245, 1210, 1040, 910, 865. MS *m/e*: 148 (M^+), 147, 89. ^{1}H-NMR ($CDCl_3$) δ: 5.09 (1H, d, J=10 Hz), 5.53 (1H, d, J=17 Hz), 5.89 (2H, s), 6.59 (1H, dd, J=17, 10 Hz), 6.6—7.2 (3H).

Synthesis of Olefin 14 from Sulfone 13b——The sulfone **13b** (84 mg, 0.304 mmol) was treated with butyllithium (1.55 M hexane solution, 0.206 ml, 0.319 mmol) followed by iodide **1** (131.8 mg, 0.305 mmol) as in the case of the sulfide **13a** to afford the olefin **14** (36.1 mg, 80%).

3-Phenyl-1-(2-pyridylsulfonyl)propane 15——1-Bromo-3-phenylpropane (1.64 g, 8.27 mmol) on treatment with the sodium salt of 2-mercaptopyridine (1.23 g, 11.1 mmol) in methyl ethyl ketone (11 ml) afforded 3-phenyl-1-(2-pyridylthio)propane (1.809 g, 95%). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1580, 1455, 1130. ^{1}H-NMR ($CDCl_3$) δ: 1.99 (2H, quintet, J=7 Hz), 2.74 (2H, t, J=7 Hz), 3.15 (2H, t, J=7 Hz), 6.6—7.5 (8H), 8.15—8.4 (1H, m). The sulfide (523 mg, 2.28 mmol) was dissolved in dichloromethane (23 ml) and a solution of *m*-CPBA (75% purity, 1.05 g, 4.56 mmol) in dichloromethane (40 ml) was added at −78 °C. The mixture was stirred for 12 h at 0 °C and washed with aqueous sodium thiosulfate solution, saturated aqueous sodium bicarbonate solution, and brine. It was then dried over Na_2SO_4, and the solvent was evaporated off. Preparative TLC (hexane–ethyl acetate (1 : 1)) afforded the sulfone **15** (474 mg, 80%). mp 52.5—53.5 °C (from methanol–chloroform). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1580, 1310, 1165, 1115, 910. MS *m/e*: 262 [$(M+1)^+$], 169, 117, 91 (base peak). High resolution MS: Found 262.0931. Calcd for $C_{14}H_{16}NO_2S$ [$(M+1)^+$] 262.0902. ^{1}H-NMR ($CDCl_3$) δ: 1.75—2.35 (2H), 2.72 (2H, t, J=8 Hz), 3.2—3.55 (2H), 6.9—8.15 (8H, m), 8.5—8.7 (1H, m). *Anal.* Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: C, 64.08; H, 5.72; N, 5.30.

4-Phenyl-2-(2-pyridylsulfonyl)-1-(tributylstannyl)butane (16)——A hexane solution of butyllithium (1.55 M solution, 0.313 ml, 0.486 mmol) was added to a solution of **15** (110.4 mg, 0.422 mmol) in THF (2.3 ml) at −78 °C under nitrogen and the mixture was stirred for 1 h. A solution of the iodide **1** (200 mg, 0.464 mmol) in THF (7 ml) was added slowly at −78 °C and the mixture was stirred at −78 °C for 1.5 h. After quenching with water, the mixture was extracted with dichloromethane. Washing with brine, drying, and evaporation gave an oil, which was purified by flash column chromatography using hexane–ethyl acetate (8 : 2) to give the stannane **16** (184.6 mg, 77%). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1580, 1310, 1115, 995. MS *m/e*: 508 [$(M-Bu)^+$], 376 (base peak), 198, 132. High resolution MS: Found 508.1340. Calcd for $C_{23}H_{34}NO_2S^{120}Sn$ [$(M-Bu)^+$] 508.1332. ^{1}H-NMR ($CDCl_3$) δ: 0.6—1.7 (29H), 1.7—2.4 (2H, m), 2.6—3.0 (2H, m), 3.6—4.1 (1H, m), 7.0—7.4 (5H, m), 7.56 (1H, ddd, J=7, 4, 1.5 Hz), 7.98 (1H, dt, J=1.5, 7 Hz), 8.17 (1H, br d, J=7 Hz), 8.78 (1H, br d, J=4 Hz).

Destannylsulfonation of the Sulfone 16——Method A: A mixture of **16** (47.4 mg, 0.084 mmol) and silica gel (1 g) in dichloromethane (4 ml) was stirred at room temperature for 2 h. After the filtration of the mixture, the filtrate was concentrated to give an oil. Preparative TLC (pentane) afforded the olefin **17** (5.9 mg, 53%). IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1640, 995, 915, 700. ^{1}H-NMR ($CDCl_3$) δ: 2.2—2.5 (2H, m), 2.5—2.7 (2H, m), 4.8—5.2 (2H, m), 5.6—6.1 (1H, m), 7.0—7.4 (5H, m). The structure was confirmed by comparison of the product with an authentic sample prepared from allylmagnesium chloride and benzyl chloride.

Method B: A solution of **16** (9.5 mg, 0.017 mmol) in d_6-benzene (0.4 ml) was heated at 80 °C in a sealed tube for 50 h. The quantitative conversion of **16** into the olefin **17** was confirmed by ^{1}H-NMR spectroscopy.

4-Phenyl-1-(3,4-methylenedioxyphenyl)-1-butene (22)——The anion of the sulfone **13b** (53.8 mg, 0.195 mmol) in THF (1.1 ml) was prepared by the reaction with butyllithium (1.55 M hexane solution, 0.132 ml, 0.205 mmol) at −20 °C for 1 h under nitrogen. A solution of iodide **21** (104 mg, 0.195 mmol) in THF (2.8 ml) was added slowly at 0 °C. The mixture was stirred at 0 °C for 1.3 h, then aqueous ammonium chloride solution was added. The usual work-up afforded an oil, which on preparative TLC (hexane–ethyl acetate (9 : 1)) gave a mixture of stereoisomers of the olefin **22** (17.6 mg, 36%) and the sulfone **13b** (9.7 mg). The ratio of (*E*)- to (*Z*)-isomers of **22** was determined to be 1 : 36 by GC. Their stereochemistry was determined by comparison with authentic samples prepared by the Wittig reaction of piperonal with 3-phenylpropyltriphenylphosphonium bromide in ether. (*E*)-**22**: IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1605, 1495, 1250, 1040, 965. MS *m/e*: 252 (M^+), 161 (base peak). High resolution MS: Found 252.1148. Calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150. ^{1}H-NMR ($CDCl_3$) δ: 2.3—2.65 (2H, m), 2.7—2.9 (2H, m,), 5.92 (2H, s), 6.08 (1H, dt, J=16, 6 Hz), 6.36 (1H, d, J=16 Hz), 6.6—7.5 (8H). (*Z*)- **22**: IR $\nu_{\max}^{CHCl_3}$ cm^{-1}: 1605, 1495, 1210, 1040, 940. MS *m/e*: 252 (M^+), 161, 131 (base peak), 103. High resolution MS: Found 252.1187. Calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150. ^{1}H-NMR ($CDCl_3$)

δ: 2.4—2.9 (4H, m), 5.56 (1H, dt, J=11.5, 7 Hz), 5.88 (2H, s), 6.29 (1H, d, J=11.5 Hz), 6.55—6.85 (3H), 7.0—7.35 (5H, m).

Synthesis of Vinyl Sulfides 24——2-Phenylthio-1-tridecene (**24a**): A hexane solution of butyllithium (1.55 M solution, 0.151 ml, 0.234 mmol) was added to a solution of dithioacetal **23a** (70 mg, 0.18 mmol) in THF (2 ml) at -20 °C under nitrogen and the mixture was stirred at -20 °C for 40 min. A solution of the iodide **1** (85.3 mg, 0.198 mmol) in THF (4 ml) was added slowly at -78 °C. After being stirred for 30 min at -78 °C, the mixture was quenched with water and extracted with ether. The usual work-up gave an oil, which on preparative TLC (hexane) afforded the sulfide **24a** (34 mg, 65%) and the dithioacetal **23a** (12 mg). **24a**: IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1610, 1465, 905, 860. MS *m/e*: 290 (M$^+$), 180, 150 (base peak). High resolution MS: Found 290.2063. Calcd for $C_{19}H_{30}S$ (M$^+$) 290.2068. ^{1}H-NMR (CDCl$_3$) δ: 0.8—1.0 (3H), 2.24 (2H, t, J=7H), 4.88 (1H, s), 5.16 (1H), 7.3—7.6 (5H).

3-Phenyl-2-phenylthio-1-propene (**24b**): The dithioacetal **23b** (59.6 mg, 0.185 mmol) was converted to the vinyl sulfide **24b** (19.4 mg, 47%) in a manner similar to that described for the preparation of **24a**. **24b**: IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1610, 1480, 1025, 695. MS *m/e*: 226 (M$^+$), 135 (base peak), 115, 91. High resolution MS: Found 226.0793. Calcd for $C_{15}H_{14}S$ (M$^+$) 226.0815. ^{1}H-NMR (CDCl$_3$) δ: 3.53 (2H, s), 5.02 (1H, s), 5.13 (1H, t, J=1 Hz), 7.1—7.6 (10H, m).

1-Phenylsulfinyl-1-dodecene (25)——The dithioacetal **23a** (5.9 g, 15.3 mmol) was oxidized to the corresponding sulfoxide by the reaction with 1 eq of *m*-CPBA in dichloromethane (110 ml) at -78 °C for 30 min. The crude product was dissolved in dimethoxyethane (100 ml) and refluxed for 3 h. After evaporation of the solvent, the crude mixture was subjected to silica gel column chromatography using hexane–ethyl acetate (9 : 1) as an eluent to give a mixture of stereoisomers of 1-phenylthio-1-dodecene (3.7 g, 88%). IR $\nu_{\max}^{\mathrm{film}}$ cm^{-1}: 950, 740. MS *m/e*: 276 (M$^+$), 149 (base peak), 110. ^{1}H-NMR (CDCl$_3$) δ: 0.7—1.05 (3H), 1.05—1.8 (16H), 2.0—2.5 (2H, m), 5.55—6.35 (2H, m), 7.0—7.5 (5H). The vinyl sulfide (760 mg, 2.75 mmol) on treatment with 1 eq of *m*-CPBA in dichloromethane (25 ml) at -78 °C for 1 h afforded the sulfoxide **25** (775 mg, 97%). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1445, 1030, MS *m/e*: 292 (M$^+$), 276, 149, 104. ^{1}H-NMR (CDCl$_3$) δ: 0.7—1.0 (3H), 1.1—1.7 (16H), 2.1—2.8 (2H, m), 6.1—6.8 (2H), 7.4—7.7 (5H).

2-Phenylsulfinyl-1-(tributylstannyl)-2-tridecene (26)——A solution of the sulfoxide **25** (499 mg, 1.71 mmol) in THF (5 ml) was added to a solution of LDA [prepared from butyllithium (1.55 M hexane solution, 1.21 ml, 1.88 mmol) and diisopropylamine (190 mg, 1.88 mmol) in THF (10 ml)] at -78 °C under nitrogen and the mixture was stirred for 20 min. A solution of the iodide **1** (737 mg 1.71 mmol) in THF (20 ml) was added and the mixture was stirred for 40 min. The temperature was kept at -78 °C throughout the procedure. The mixture was quenched with water, and the usual work-up gave an oil which on preparative TLC (hexane–ethyl acetate (8 : 2)) afforded the stannane **26** (515 mg, 51%). IR $\nu_{\max}^{\mathrm{film}}$ cm^{-1}: 1460, 1040. MS *m/e*: 539 [(M$-$Bu)$^+$], 291 (base peak). ^{1}H-NMR (CDCl$_3$) δ: 1.95—2.25 (2H, m), 6.17 (1H, t, J=7.5 Hz), 7.4—7.7 (5H, m).

1,2-Tridecadiene (27)$^{24)}$——A hexane solution of butyllithium (1.55 M solution, 0.047 ml, 0.074 mmol) was added to a solution of the stannane **26** (20 mg, 0.0336 mmol) in THF (1 ml) at -78 °C under nitrogen and the mixture was stirred for 30 min at -78 °C. The reaction mixture was analyzed by GC using undecane as an internal standard; the result indicated the formation of the 1,2-diene **27** in 90% yield. Preparative GC afforded the pure diene **27** (3.7 mg, 57%). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1960, 1460, 845. ^{1}H-NMR (CDCl$_3$) δ: 0.8—1.0 (3H), 1.1—1.6 (16H), 1.8—2.2 (2H, m), 4.6—4.75 (2H, m), 5.12 (1H, quintet, J=7 Hz).

References and Notes

1) A part of this work has been reported in a preliminary form: M. Ochiai, S. Tada, K. Sumi, and E. Fujita, *Tetrahedron Lett.*, **23**, 2205 (1982).
2) *a*) D. D. Davis and C. E. Gray, *J. Organomet. Chem.*, **18**, 1 (1969); *b*) *Idem*, *J. Org. Chem.*, **35**, 1303 (1970); *c*) T. Kauffmann, R. Kriegesmann, and A. Woltermann, *Angew. Chem. Int. Ed. Engl.*, **16**, 862 (1977); *d*) T. Kauffmann, H. Ahlers, R. Joussen, R. Kriegesmann, A. Vahrenhorst, and A. Woltermann, *Tetrahedron Lett.*, **1978**, 4399.
3) *a*) R. D. Taylor and J. L. Wardell, *J. Organomet. Chem.*, **94**, 15 (1975); *b*) J. L. Wardell and S. Ahmed, *ibid.*, **78**, 395 (1974); *c*) R. D. Taylor and J. L. Wardell, *ibid.*, **77**, 311 (1974).
4) For example, many insect pheromones contain a 1,3-diene system in the molecules: K. Mori, "The Total Synthesis of Natural Products," Vol 4, ed. by J. ApSimon, John Wiley & Sons, New York, 1981, p. 1.
5) *a*) T. Mukaiyama, K. Narasaka, K. Maekawa, and M. Furusato, *Bull. Chem. Soc., Jpn.*, **44**, 2285 (1971); *b*) K. Narasaka, M. Hayashi, and T. Mukaiyama, *Chem. Lett.*, **1972**, 259; *c*) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
6) D. S. Tarbell and M. A. McColl, *J. Am. Chem. Soc.*, **74**, 48 (1952).
7) D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 123.
8) G. E. Vennstra and B. Zwanenburg, *Synthesis*, **1975**, 519.
9) M. Ochiai, T. Ukita, and E. Fujita, *Chem. Pharm. Bull.*, **31**, 1641 (1983).
10) W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).
11) J. L. Wardell and J. McM. Wigzell, *J. Organomet. Chem.*, **205**, C24 (1981).
12) *a*) R. C. Poller, "The Chemistry of Organotin Compounds, " Logos Press Limited, London, 1970, p. 199; *b*) T.

F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 5730 (1966); *c*) M. J. Janssen, J. G. A. Luijten, and G. J. M. van Der Kerk, *J. Organomet. Chem.*, **1**, 286 (1964).
13) Y. Torisawa, M. Shibasaki, and S. Ikegami, *Tetrahedron Lett.*, **22**, 2397 (1981).
14) For example, see B. M. Trost and Y. Tanigawa, *J. Am. Chem. Soc.*, **101**, 4743 (1979).
15) G. H. Posner, P.-W. Tang, and J. P. Mallamo, *Tetrahedron Lett.*, **1978**, 3995.
16) *a*) W. C. Still, *J. Am. Chem. Soc.*, **100**, 1481 (1978); *b*) D. Seyferth and S. B. Andrews, *J. Organomet. Chem.*, **30**, 151 (1971).
17) M. Kocevar, B. Stanovnik, and M. Tisler, *Croat. Chem. Acta*, **45**, 457 (1973) [*Chem. Abstr.*, **80**, 37043*u* (1974)].
18) O. Grummitt and E. J. Christoph, *J. Am. Chem. Soc.*, **73**, 3479 (1951).
19) W. H. Pirkle and P. L. Gravel, *J. Org. Chem.*, **42**, 296 (1977).
20) P. S. Mariano and D. Watson, *J. Org. Chem.*, **39**, 2774 (1974).
21) M. Julia and D. Uguen, *Bull. Soc. Chim. Fr.*, **1976**, 513.
22) L. Barlow and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 1029.
23) P. E. Shaw, J. H. Tatum, D. H. Miyashita, and K. Ohinata, *J. Agric. Food Chem.*, **24**, 1186 (1976).
24) T. H. Chan and W. Mychajlowskij, *Tetrahedron Lett.*, **1974**, 171.